Appendix 2B-2: STA-2 Mercury Special Studies Project Report[1]

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[1] Submitted to the Florida Department of Environmental Protection, dated September 30, 2004.

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SUMMARY

Stormwater Treatment Area 2 (STA-2) Cells 2 and 3 met their permit-mandated mercury start-up criteria in September and November 2000, respectively, while Cell 1 experienced progressively worsening anomalous mercury events in the fall 2000 and 2001 and the summer 2002. The recurrence of first-flush mercury anomalies of increasing magnitude after each dryout and rewetting event had become problematic. The permit issued to the South Florida Water Management District (District or SFWMD) for the operation of STA-2 provides for an adaptive response to such problems. If the first-flush MeHg anomalies in STA-2 Cell 1 could not be brought under control, then one option being considered by resource managers was to decommission Cell 1 and rebuild on adjacent lands less susceptible to a persistent, first-flush methylmercury problem. This would have resulted in a substantial cost penalty.

The form of mercury of concern is methylmercury (MeHg), a highly toxic compound that magnifies its concentration with each step in the aquatic food chain. It is produced inadvertently from the inorganic mercury in runoff, rain, and soils by naturally occurring sulfate-reducing bacteria (SRB) in sediments substantially devoid of oxygen. The general aquatic mercury cycle is depicted in **Figure E-1**. MeHg biomagnification in the Everglades aquatic food chain has impaired the sport fishery and may threaten some highly exposed fish-eating wildlife species foraging in the most contaminated areas. Similar concerns were raised for fish-eating wildlife foraging preferentially in STA-2 Cell 1.

The August 2001 decision by the Florida Department of Environmental Protection (FDEP) to authorize flow-through operation of Cell 1 without it first meeting its mercury start-up criteria was based on three predicted beneficial effects. First, after raising the outflow culverts, it would prevent unintended dryout. Second, it would flush out the excess MeHg from where it could do the most harm to where it could do less harm. Third, it would eventually deplete the pool of whatever was fostering excess MeHg production. In addition, although more in the realm of educated speculation, exposure of Cell 1 soils to the excess sulfate in the inflow water might be sufficient to allow the buildup of a pool of sulfide in soils to levels capable of inhibiting MeHg production.

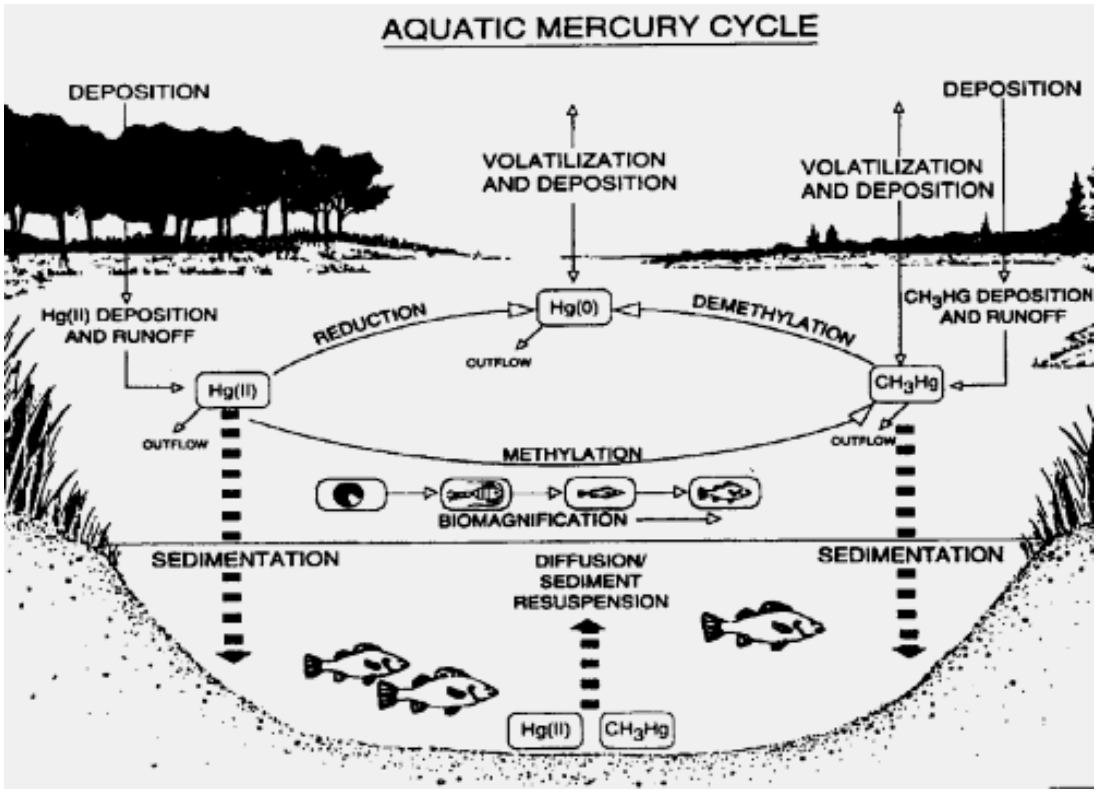

Figure E-1. The generalized mercury cycle in aquatic ecosystems. (Refer to **Figure 7**.)

In July 2002, the Cell 1 outflow weirs were raised to reduce the likelihood of dryout. Cell 1 has not dried out since. Based on the results of the studies described below, it has had the predicted beneficial effect of allowing STA-2 Cell 1 to stabilize from the standpoint of excess MeHg production.

To better understand the cause of these Cell 1 MeHg anomalies, the District began a series of Mercury Special Studies in STA-2. The objectives of these studies were to (1) characterize the total mercury (THg) and methylmercury (MeHg) concentration trajectories in water, soil, vegetation, and mosquitofish over time, (2) quantify THg and MeHg mass budgets for each cell, and to evaluate the physical, chemical, and biological factors that influence the magnitude of MeHg export and bioaccumulation. The requirement to conduct this study was also subsequently codified in a Memorandum of Agreement (MOA) approved by the District's Governing Board in February 2003 (C-13812). To offset some of the costs of this more extensive and intensive monitoring effort, Section 319 grant funds were redirected from evaluating the mercury removal efficiencies of Advanced Treatment Technologies in the ENR Project Test Cells to this study (C-11900-A03/A04). The modified permit, the Section 319 Grant, and the MOA all require annual reports of study progress. This interim report is intended to fulfill those requirements.

Following the first-flush MeHg anomaly in August 2002, surface water and soil MeHg concentrations declined progressively, while mosquitofish THg first increased and then decreased progressively in response to the first-flush MeHg pulse. These time trends are illustrated in **Figures E-2** through **E-4**, respectively.

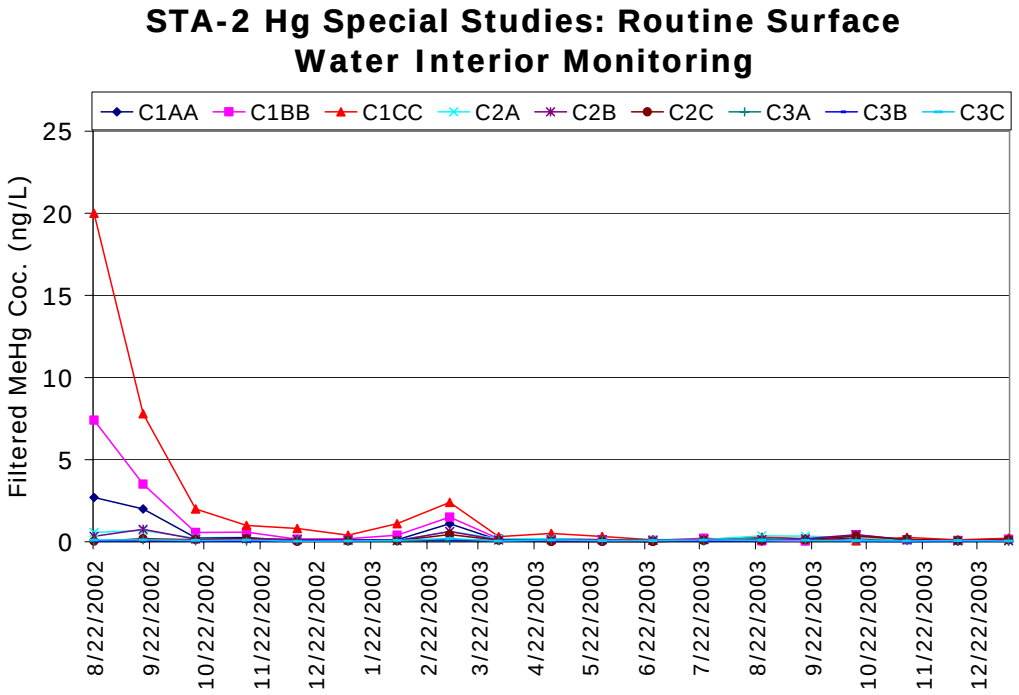

Figure E-2. Concentrations of MeHg (ng/L) in filtered surface water from individual treatment cell interior sites. (Refer to **Figure 17**.)

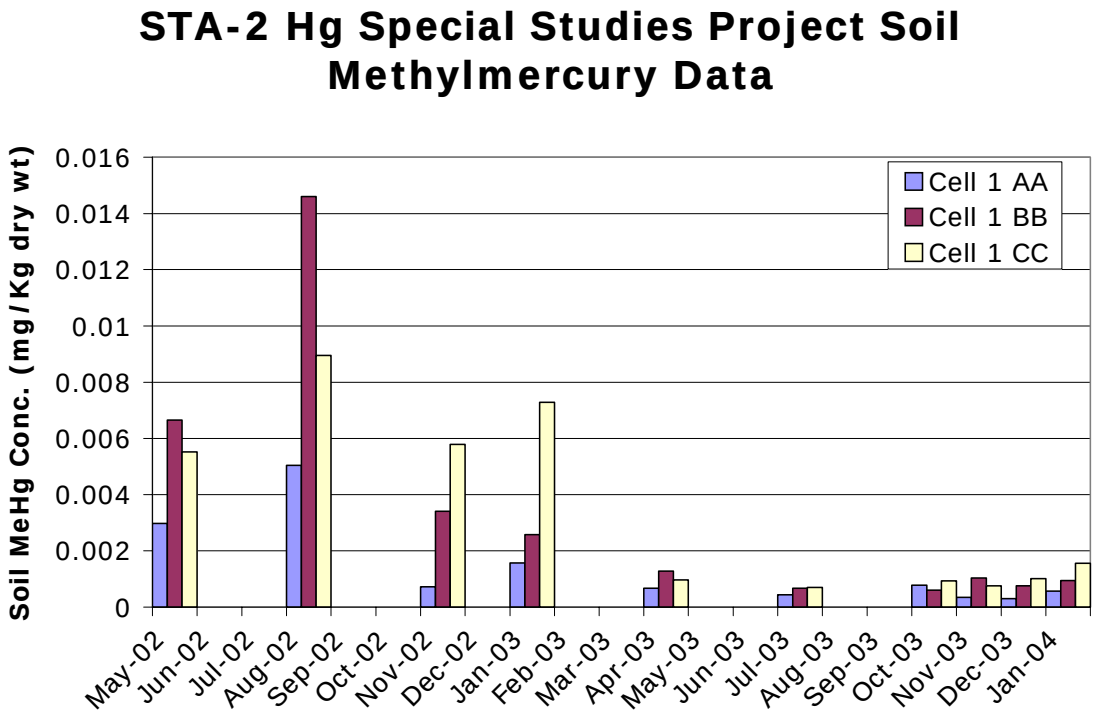

Figure E-3. Concentrations of methylmercury (MeHg) in surficial soil (0-4 cm) from Cell 1 interior sites for the baseline condition in May 2002 through the final sampling event in December 2003–January 2004. (Refer to **Figure 32**.)

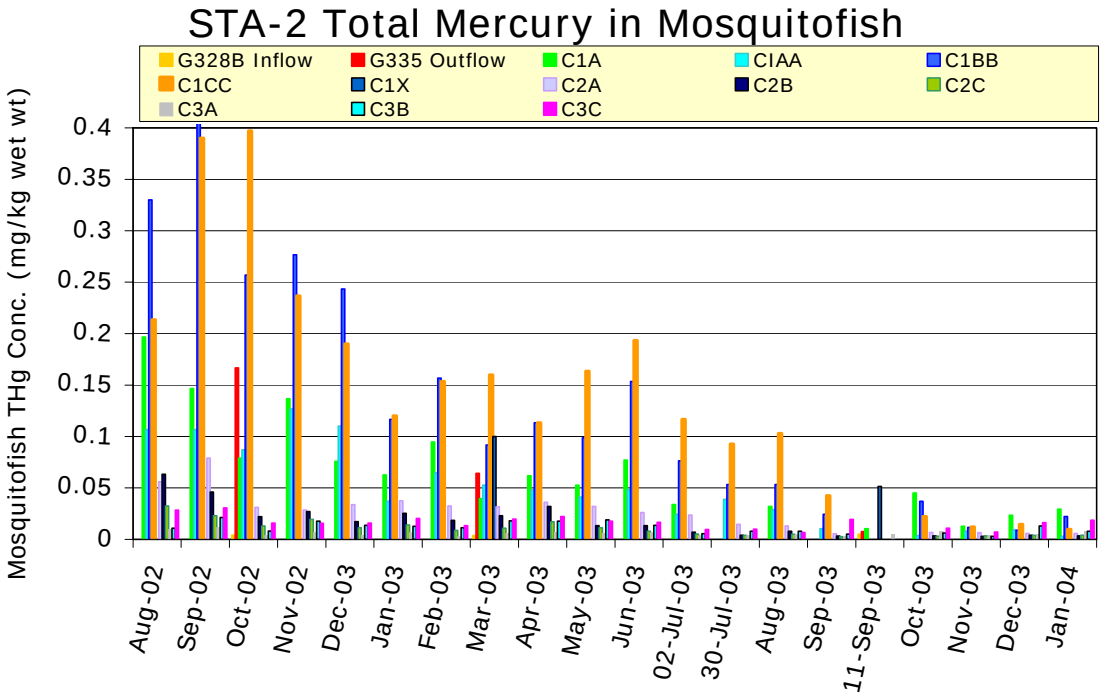

Figure E-4. Concentrations of methylmercury (MeHg) as total mercury (THg) in mosquitofish from treatment cell, inflows, outflows, and interior sites for the period from August 2002 through the final sampling event in January 2004. (Refer to **Figure 33**.)

Using a water budget supplied by others and concentration data obtained in this study, the unprecedented THg and MeHg concentrations in Cell 1 surface water following the last, first-flush anomaly in August 2002 resulted in the calculated net export of about 110 g and 85 g of THg and MeHg mass, respectively, during the first full quarter of operation following reflooding. Concurrently, Cell 1 was a substantial net importer of sulfate and a net exporter of dissolved organic carbon masses. These are two of the three basic ingredients, bioavailable inorganic mercury, Hg(II), being the third, which are required for excess MeHg production. During that same period, the net export of THg and MeHg mass from Cell 2 were calculated to be about 50 g and 2 g, respectively, while Cell 3 was calculated to be a net exporter of about 65 g THg and 2 g MeHg mass.

Between the pre-flood baseline condition in May 2002 and the post-flood condition in August 2002, the change in the masses of THg and MeHg stored in the top 4 cm of soil were calculated to be about -1,000 g and 200 g, respectively. In the following quarter, the changes were reversed, with on the order of 720 g of THg being reabsorbed and 275 g MeHg being lost by the Cell 1 surficial soil. Over the 18-month study, there was a calculated net loss of 1500 g THg and 215 g MeHg from the top 4 cm of soil relative to pre-flood baseline conditions, while there was net export of about 10 g of THg and net export of about 140 g of MeHg based on water budget calculations.

Exploratory calculations suggest that on the order of 280 g of THg and 110 g of MeHg masses were temporarily stored in standing crop plant biomass following the last, first-flush MeHg anomaly in Cell 1 in August 2002. However, the calculation is highly uncertain because the coverage and biomass density measurements did not occur at the same time as the mercury concentration measurements and, therefore, these results should be considered of exploratory value only. Nevertheless, it is highly unlikely that plant storage can account for all of the discrepancies between the changes in the soil mass budget and the net export of THg from STA-2 Cell 1. However, this may not be true of MeHg because the discrepancies are much smaller.

Some of these discrepancies between the soil and surface water mass budgets for THg might be explained by leaching of soil inorganic mercury, Hg(II), into the underlying soil horizon below the 4-cm sampling depth. This would not be inconsistent with the high seepage rate out of Cell 1. Some or all of the remaining discrepancy might be attributable to plant root mining of Hg(II) from surficial soil as elemental mercury, Hg(0), with subsequent evasion to the overlying air via the openings (stomata) on the leaves of emergent plants. This phenomenon was documented at the ENR Project, where roughly 1,000 g were calculated to have been lost by this process over 3,815 acres with a cattail coverage averaging about 50 percent. Based on the aerial photographs taken in November 2003, the emergent plant coverage in STA-2 Cell 1 was likely to have been higher than 50 percent in August 2002. However, it is also possible that the discrepancy is an artifact of the uncertainty in the surficial soil concentration propagated into the calculation of surficial soil mass storage.

The pool of MeHg temporarily stored in plant biomass did not appear to have been recycled back into the aquatic food chain as efficiently as in the first, first-flush anomaly. Perhaps this is because of changes in operational hydrology, standing-crop plant species biomass dynamics, or soil chemistry that occurred since then.

Further, the first-flush effect dissipated more rapidly in the last event than the first two, resulting in lower peak MeHg concentrations in mosquitofish, sunfish, and largemouth bass. This is most likely attributable to the operation of Cell 1 in flow-through mode immediately following reflooding, although beneficial changes in soil chemistry or food chain structure cannot be ruled out with the available information.

Finally, there is some evidence that the decline in the soil MeHg concentrations was accompanied by a concomitant buildup of soil sulfide in the form of acid volatile sulfide. However, the exploratory data analysis indicates that the expected moderate to strong inverse correlation between soil sulfide as acid volatile sulfide and soil MeHg levels occurred only for Cell 3, weakened for Cell 2, and was virtually absent for Cell 1. This may be a consequence of the differences in the pre-construction soil chemistry and the number of consecutive days each cell has remained wet since construction. Remember, unlike Cells 1 and 2, Cell 3 was never farmed, was used to hold dewatering water from the construction of the other two cells, and, due to its higher elevation, dried out frequently prior to the raising of the outflow culverts.

Regarding pore water sampling technology transfer, the modified "sipper" design appears to allow the collection of more of a representative, valid, depth-integrated pore water sample over a depth of 0 to 4 - 6 cm without surface water breakthrough than the original USGS sipper design. This is necessary for projects using commercial laboratories for quantitative chemical analyses rather than research laboratories with micro-analytical capability. However, the method is not suited to projects requiring the discrimination of vertical concentration gradients with the resolution of 1-2 cm, and the depth of sample withdrawal appears to vary somewhat between sites and sample collection times, so the method is more suited to qualification rather than quantification of environmental conditions (e.g., compliance with a pore water sulfide standard to protect sensitive aquatic plant or animal species vis-à-vis calibration of a mass transport model of sediment-water exchange). Nevertheless, the results of the pore water chemistry study tend to support the results of the soil chemistry study, which implicates manganese as having an important role to play in mediating the influence of the iron and sulfur cycles on MeHg production in surficial soil.

This report presents an in-depth discussion of the patterns of correlation observed and their possible mechanistic explanations. However, only well-designed, controlled experiments can discriminate between the possible and actual explanations. In particular, there is as yet no way to discriminate between the hypothesis that progressive decline in soil MeHg was caused by the progressive buildup of inhibitory levels of soil sulfide and the hypothesis that it was caused by the progressive depletion of the pool of the critical limiting factor required for excess MeHg production. Follow-up research by the U.S. Geological Survey and the Smithsonian Institution in the District's STAs should further our understanding of the underlying cause of the statistically, ecologically, and administratively significant observed reductions in MeHg concentrations in STA-2 Cell 1 soil, water, and fish over the course of the study.

Whatever the cause, the results of the STA-2 Mercury Special Studies demonstrate that the desired effect has been achieved. The design and operational corrective actions have proved successful in reducing the adverse impacts of the MeHg anomaly within STA-2 Cell 1 and downstream. Had the first-flush MeHg anomalies in STA-2 Cell 1 proved irreversible, persistent, and of unacceptable magnitude, one option would have been to decommission Cell 1 and rebuild on adjacent lands less susceptible to a persistent, first-flush MeHg problem. That this was not necessary bodes well for similar projects planned for South Florida over the next several decades.

The report provides the background, methods, results, and discussion necessary to support the key findings, conclusions, and recommendations summarized above. The appendices detail the plans and methods used to implement the STA-2 Mercury Special Studies Project and present the raw concentration data for rain, surface water, pore water, soil, plants, and mosquitofish generated by the study.

INTRODUCTION

Cell 1 of Stormwater Treatment Area 2 (STA-2) experienced progressively worsening mercury anomalies in the fall 2000 and 2001 and the summer of 2002 following flooding after extended periods of dryout. The problematic form of mercury in STA-2, the Everglades, and across the planet is methylmercury (hereinafter MeHg, but also known as monomethylmercury, or MMHg). It is a highly toxic compound that increases in concentration as it moves up the aquatic food chain -- a process referred to as biomagnification. MeHg biomagnification in the Everglades aquatic food chain has impaired the Everglades sport fishery, as evidenced by the issuance of sport fish consumption advisories by the Department of Health. The high levels of MeHg in prey fish may threaten some highly exposed fish-eating wildlife species foraging preferentially in the most contaminated areas. Similar concerns were raised for fish-eating wildlife foraging preferentially in STA-2 Cell 1 following each of the anomalous MeHg events.

MeHg is produced inadvertently from the inorganic mercury in runoff, rain, and sediments or flooded soils by naturally occurring sulfate-reducing bacteria (SRB). This generally occurs in the top few centimeters of wet soil or sediment under conditions that are substantially devoid of oxygen. When dry peat soil or sediment is reflooded, it releases stored nutrients, dissolved organic carbon, and trace metals for short periods of time in what is referred to as a "first-flush effect." In some aquatic systems these conditions are also optimum for excess MeHg production. If this phenomenon is short-lived, this is referred to as a mercury first-flush effect. Conversely, if the excessive MeHg production continues and/or the first-flush MeHg in the aquatic food web is efficiently recycled, the problem can persist for years, and this is referred to as a reservoir effect. The reservoir effect has emerged as a world-wide problem based on three decades of experience in hydroelectric reservoir creation in Canada, Sweden, the United States, and elsewhere. Unfortunately, we do not yet fully understand all of the processes that control the production, bioaccumulation, and persistence of MeHg in wetlands, reservoirs, or lakes or the factors that moderate these processes. This limits our ability to respond appropriately to the MeHg anomalies in STA-2 Cell 1.

To better understand the causes of these STA-2 Cell 1 MeHg anomalies, the District designed and implemented a series of increasingly intensive and extensive special studies in and downstream of STA-2 in consultation with the Florida Department of Environmental Protection (FDEP). The studies were also intended to provide information on the effectiveness of various mitigation options, should such become necessary. The most recent set of these special studies began in May 2002 prior to the third reflooding of Cell 1 and was completed in January 2004 after nearly 18 months of continuous operation of Cell 1 without dryout.

The requirement to conduct the mercury special studies in STA-2 Cell 1 is contained in a Memorandum of Agreement between the District and FDEP (C-13812; MOA072) and a Section 319 Grant Cooperative Agreement (C-11900-A03/A04 or SP524). This final report fulfills the requirements for a final report contained in the MOA (MOA072) and the Section 319 Grant Cooperative Agreement (C-11900-A03/A04 or SP524).

The final report first presents relevant background information to provide the reader with needed context. Subsequent sections set forth the methods and procedures used to collect and analyze the data and the results of the statistical, mass budget, and modeling analyses. These are followed by a section discussing the results, including sources of uncertainty and alternative explanations for the observations. The findings, conclusions, and recommendations comprise the last three sections of the report, with an emphasis on potentially effective options for adaptive

responses to avoid or mitigate such first-flush MeHg anomalies in the future. Tables and figures in the "Results" and "Discussion" sections of this document follow the "Literature Cited" section at the end of the document so as not to interfere with the flow of the text. The appendices contain a copy of the Mercury Special Studies Work Plan, the Standard Operating Procedures for sample collection and data quality review, and the raw data, as well as a more detailed discussion of the modified sipper method of pore water collection.

The rain, surface water, soil, fish, and vegetation data collected under these mercury special studies in STA-2 were used to construct mass budgets and evaluate the magnitudes of the influence of various factors on MeHg production and bioaccumulation via appropriate nonparametric univariate and parametric multivariate analysis techniques. Further modifications to the Everglades Mercury Cycling Model, E-MCM(II) (SFWMD, 2004) and its subsequent application to the post-reflooding MeHg anomalies in STA-2 will be paid for by the FDEP within the framework of the MOA (C-13812 or MOA072) between the two agencies. The data collected in this study can be used to calibrate the model for that purpose.

BACKGROUND

SITE DESCRIPTION

As depicted in **Figure 1**, Stormwater Treatment Area 2 (STA-2) is located in western Palm Beach County, adjacent to Water Conservation Area 2A (WCA-2A), with the L-6 levee forming its eastern boundary. Remaining agricultural properties comprise its other boundaries. STA-2 is divided into three, parallel, north-south treatment cells. Cell 1, the eastern most treatment cell, is 1,990 acres, while Cells 2 and 3, the middle and westernmost treatment cells, respectively, are 2,220 acres each. As-built land elevation sequentially decreases as follows: Cell 1 (3.6 m; 11.81 ft NGVD), Cell 2 (3.15 m; 10.33 ft NGVD), and Cell 3 (2.93; 9.61 ft NGVD). Subsurface groundwater flow is thought to be generally to the southwest in response to the hydraulic head in the L-6 canal on the eastern boundary of STA-2 and the active and passive dewatering of the remaining farmlands to its south and west.

Prior to land purchase, with the exception of a small strip of land on its east side, all of Cell 3 was farmed, while only about one-fourth of the northwest corner of Cell 2 was farmed. Cell 1 was never developed, being used instead as the Browns Farm Wildlife Management Area. Prior to construction, Cell 1 vegetation consisted primarily of scrub brush and water-tolerant grasses and scattered small trees growing on elevated hummocks, with a few large trees. Portions of STA-2 were still being farmed immediately prior to construction. Cell 3 had about 30 percent in sugarcane and 45 percent in sod production. Cell 2 had about 10 percent in sod production (in the northwest corner). For additional information about pre-construction site topography, geology, hydrology, hydrogeology, and land use, see SFWMD (1999a).

With the exception of the pre-existing L-6 levee, the perimeter and interior levees were constructed with a mixture of limerock and gravel obtained primarily during dredging of the supply and inflow distribution canals and the outflow collection and distribution canals. Construction activities for STA-2 began in January 1998 and were completed in December 1999. The only site preparation occurred in Cell 3, where a portion of the cell was disked to remove remnant cane (N. Larson, personal communication). Thereafter, limerock was distributed over about 10 acres in the lower third of Cell 3 and submerged macrophytes were encouraged to colonize the area via active management of hydrology and undesirable vegetation. This modification to the original design was made to evaluate the total phosphorus (TP) removal

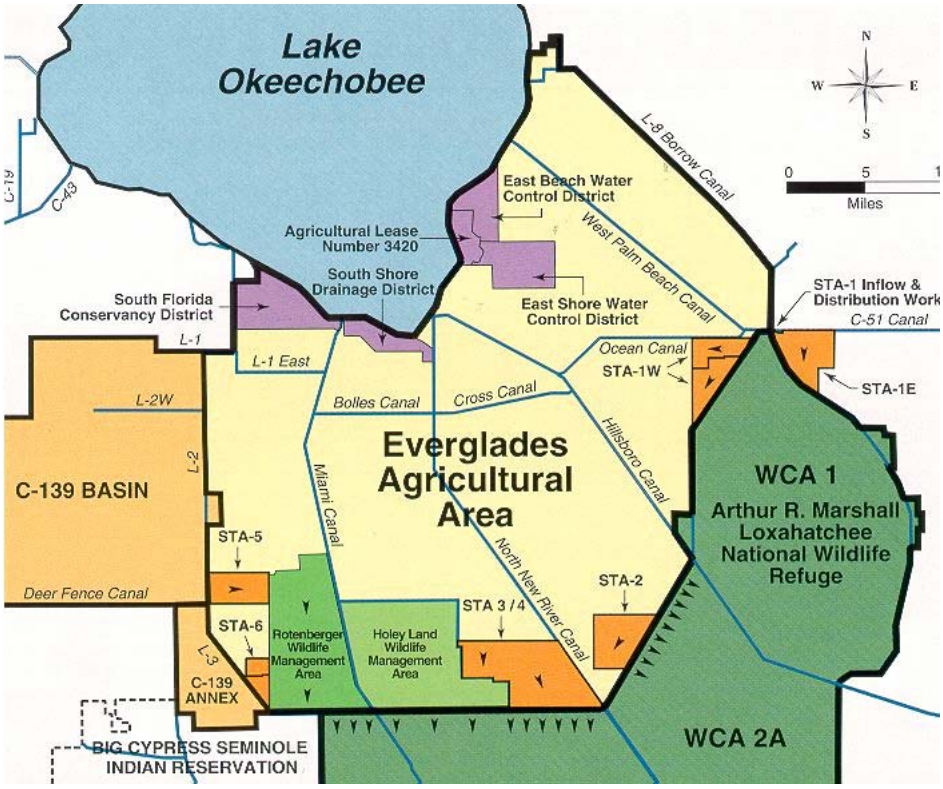

Figure 1. Geographic location and boundaries of STA-2.

efficiency of this advanced treatment technology in the low TP concentration range (< 50 ppb TP).

OPERATIONAL DESIGN

STA-2 was developed to provide a total effective treatment area of 6,430 acres. STA-2 is designed to treat discharges from the S-6/S-2 basin, the G-328 basin, East Shore Water Control District, 715 Farms, portions of the S-5A basin, and Lake Okeechobee via pump station S-6. S-6 and G-328 serve as the primary inflow pumping stations (see **Figure 2**). G-328 serves an approximated 9,980 acres of adjacent agricultural lands. Pumped surface water and subsurface infiltration from S-6 and G-328 enter the supply canal and are conveyed southward to the inflow canal, which extends across the northern perimeter of STA-2. A series of inflow culverts conveys flows from the Inflow Canal to the respective treatment cells (G-329 A–D into Cell 1, G-331 A–G into Cell 2, and G-333 A–E into Cell 3). Flows travel southward through the treatment cells and eventually discharge into the discharge canal via culverts or gated spillways (culverts G-330 A–E from Cell 1, gated spillway G-332 from Cell 2, gated spillway G-334 from Cell 3). Surface flows then travel eastward in the discharge canal to the STA-2 outflow pump station, G-335, which in turn conveys water to a short stub canal leading to the L-6 borrow canal. These structures and flow paths are illustrated in **Figure 2**. The construction of the supply and discharge collection canals, the active management of water levels in the canals and cells, and the operation of the outflow pumps now influence the direction of magnitude of subsurface flows.

Water in the L-6 borrow canal travels north and then east into WCA-2A through six box culverts (each with a capacity of 300 cfs, and an invert of 12 ft NGVD) that are located south of G-339 between 0.5 and 3 miles south of S-6. The area to receive discharge was previously identified as a nutrient-impacted area. Under high-flow conditions, when stage in the L-6 borrow canal exceeds 14.25 ft, treated discharges in the L-6 borrow canal will spill into five 72-inch culverts and travel south toward S-7. Approximately 0.75 miles north of S-7 the eastern levee has been degraded to ground elevation (approximately 12 ft) that will allow water to sheetflow into WCA-2A. Again, the area to receive discharge was previously identified as a nutrient-impacted area.

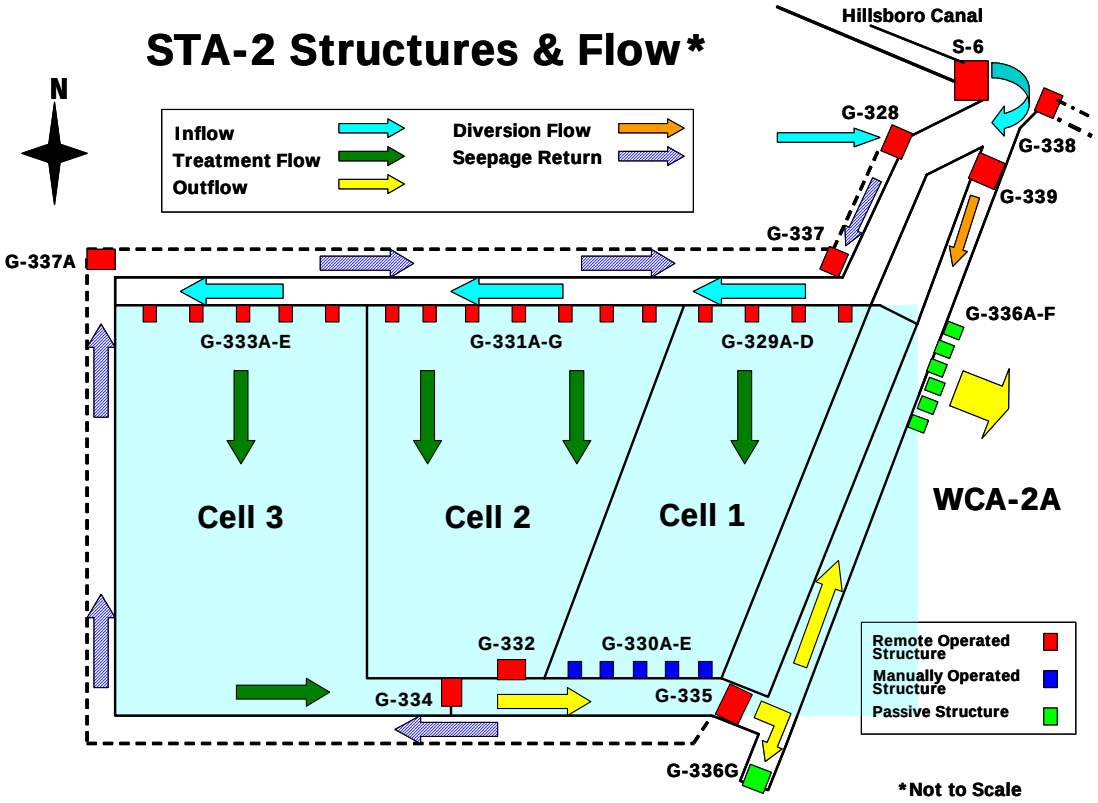

Figure 2. STA-2 levees, culverts, pumps, and flow paths.

OPERATIONAL HISTORY OF STA-2

The treatment cells received differing amounts of water during construction and through the present time. Dewatering was required for construction and installation of spillways and culverts. Cell 1 received most of the water from dewatering operations, except for a short period during Cell 1 construction, at which time Cell 2 received dewatering volumes. Construction of the interior works was completed in June 1999. At that time, inflow gates to Cells 1 and 2 were opened for a brief period and then were closed because the primary operational objective was to raise water depths in Cell 3 to approximately 1 m to prevent growth of emergent vegetation. Cell 3 inflow gates remained open for several months, which included Hurricane Irene (October 15, 1999). The inflow gates to Cells 1 and 2 were reopened briefly in December 1999–January 2000. However, the cells may have partially dried out during the dry season of 1999–2000.

The final operational testing of the outflow pump station, G-335, was completed in October 2000 and a small amount of water was discharged at that time. In addition to rainfall, source water for the treatment cells through early 2001 originated from G-328 and G-337, i.e., the seepage pump. During the severe drought of 2000–2001, STA-2 Cell 1 went dry in April 2001 and Cell 2 went dry in May 2001. Supplemental water deliveries were made during April and May 2001 to Cell 3 to prevent dryout of the submerged aquatic vegetation (SAV). Following local rains, Cell 2 was reflooded about June 1. Cell 1 was reflooded in August 2001, drawn down beginning in November 2001 in response to a second MeHg anomaly, and dried out by the end of December 2001, although some subsurface drainage continued through February 2002. The work of raising the Cell 1 culverts by about 0.3 m (about 1 ft) occurred between June and July 2002. Cell 1 was reflooded in early August 2002. None of the three treatment cells dried out thereafter during the course of the study, which was completed in January 2004. However, water levels did fluctuate throughout the study period. Beginning on September 10, 2002, 30 days after average water levels were above grade for the first time since the preceding winter, maximum, mean, and minimum water levels for Cells 1, 2, and 3 were 0.61, 0.42, and 0.27 m; 1.09, 0.48, and 0.65 m; and 1.12, 0.71, and 0.26 m, respectively.

MERCURY REQUIREMENTS IN EVERGLADES FOREVER ACT PERMITS

The Everglades Forever Act of 1994 (EFA), Section 373.4592, Florida Statutes (F.S.), mandates that the South Florida Water Management District (District or SFWMD) construct and operate the Everglades Construction Project (ECP). The District applied for and received an EFA and a National Pollution Discharge Elimination System (NPDES) permit on September 29, 2000, for STA-2. Exhibit D of the EFA permit describes the mercury monitoring that was originally required for STA-2. These monitoring requirements include (1) establishing a soil baseline for mercury, (2) avoiding first flush discharges, (3) operational monitoring, (4) receiving waters monitoring, (5) annual mercury monitoring reporting, (6) adaptive management, and (7) monitoring and Quality Assurance Plan. Start-up monitoring to detect and respond appropriately to a first-flush phenomenon, including the reporting of anomalously high MeHg concentrations, requires biweekly monitoring of unfiltered water samples at the inflow and a representative interior site. When the interior site is not statistically significantly greater than the inflow for both unfiltered THg and MeHg (one-tailed t test, $p < 0.05$), the start-up mercury criteria are met. If the phosphorus start-up criterion has also been met, discharge under routine operation may commence, available water permitting.

THE STA-2 MERCURY PROBLEM

STA-2 construction was completed in the fall 1999, but sufficient water for start-up flooding did not become available until July 2000. Cell 3 met its start-up mercury criteria in September 2000, followed by Cell 2 in November 2000. By contrast, in late September 2000, the interior concentration of Cell 1 reached a then unprecedented unfiltered MeHg concentration of 4.8 nanograms per liter (ng/L). This MeHg concentration was about 16 times the average inflow concentration at G-328B and about 80 times the average interior MeHg concentration (about 0.06 ng/L) in the Everglades Nutrient Removal (ENR) Project between March 1995 and March 1999, when it ceased operation as a distinct facility and was subsumed by Stormwater Treatment Area 1 West (STA-1W) in April 1999. The District reported this anomalously high MeHg concentration to the FDEP in early October 2000 following quality assurance validation of the data (Rumbold et al., 2001).

ADAPTIVE MANAGEMENT RESPONSE TO THE FIRST MEHG ANOMALY

Beginning in late October 2000, the start-up mercury-monitoring program was expanded to include three sites in Cells 1 and 2 for monthly sampling of filtered water and mosquitofish and one time sediment sampling. The expanded water sampling ended 90 days later in late January 2001, while monthly mosquitofish monitoring in Cell 1 continued until March 2001, when low water levels precluded further sampling. The follow-up study locations, media, and frequencies are depicted and summarized in **Figure 3** and discussed in greater detail in Rumbold and Fink (2003). Splitting samples between contract analytical laboratories confirmed the high MeHg results. The simultaneous collection of filtered and unfiltered samples demonstrated that the high MeHg concentrations could not be attributed solely to high suspended solids concentrations in the water. Significant fluctuations in unfiltered and filtered MeHg concentrations within and between Cells 1 and 2 were observed during the follow-up study. These spatial and temporal fluctuations may have been a result of differences in soil chemistry, water chemistry, or vegetation coverage, the internal recirculation of water via the seepage canal, rapid uptake and release by microscopic plants and animals, or analytical artifacts. By the end of the study, unfiltered MeHg concentrations in Cell 1 surface water had declined to about 5 percent of the September 26, 2000, peak of 4.8 ng/L but still exceeded the inflow concentration, while those in Cell 2 had declined to about 3 percent of the August 3, 2000 peak of 1.9 ng/L. However, following a significant rainfall event in March 2001, concentrations of both THg and MeHg increased dramatically in Cell 1 to near peak levels. These relationships are summarized in **Figure 4**.

As anticipated, the average concentration of THg in mosquitofish increased rapidly from October through December 2000, reaching about the same average concentration as at WCA-3A-15, the mercury "hot spot." From December 2000 through February 2001, the concentrations appeared to have nearly plateaued, but subsequently increased again in March 2001. The time course of THg concentration in STA-2 mosquitofish is depicted in **Figure 5**. Anomalously high MeHg concentrations were also inferred to have been building up in fish species at the next step up in the food chain. Such species include sunfish, which are typically consumed by fish-eating wildlife, including migratory diving and wading birds. The District concluded that the inferred magnitude of sunfish MeHg contamination in STA-2 Cell 1 was likely to represent an unacceptable risk of toxic effects to highly exposed, highly sensitive members of fish-eating wildlife populations foraging there preferentially (Rumbold, 2000).

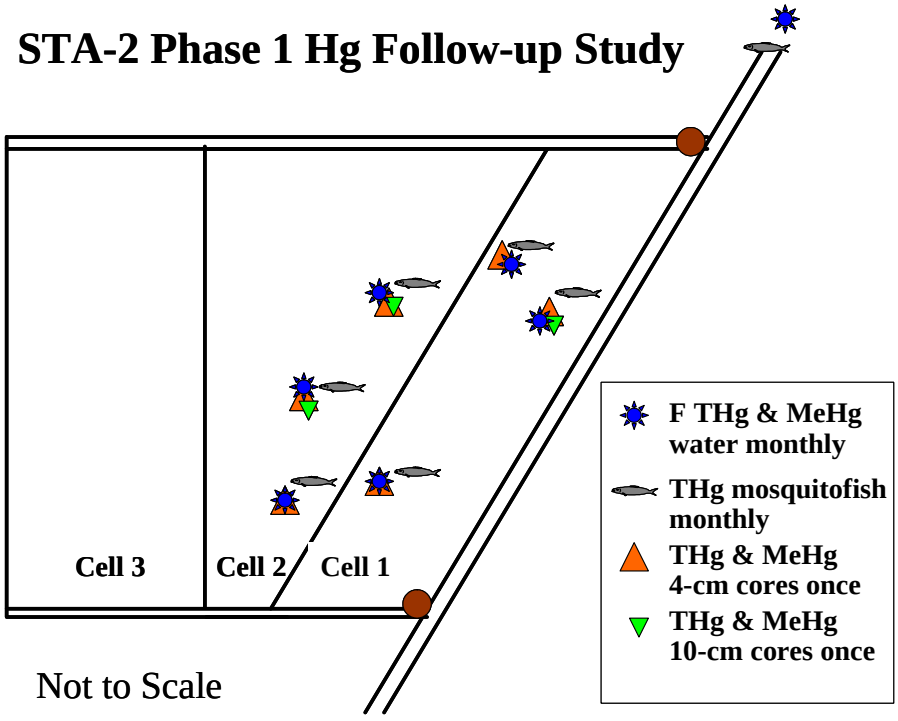

Figure 3. Follow-up adaptive mercury monitoring in response to first STA-2 Cell 1 MeHg anomaly on September 20, 2000.

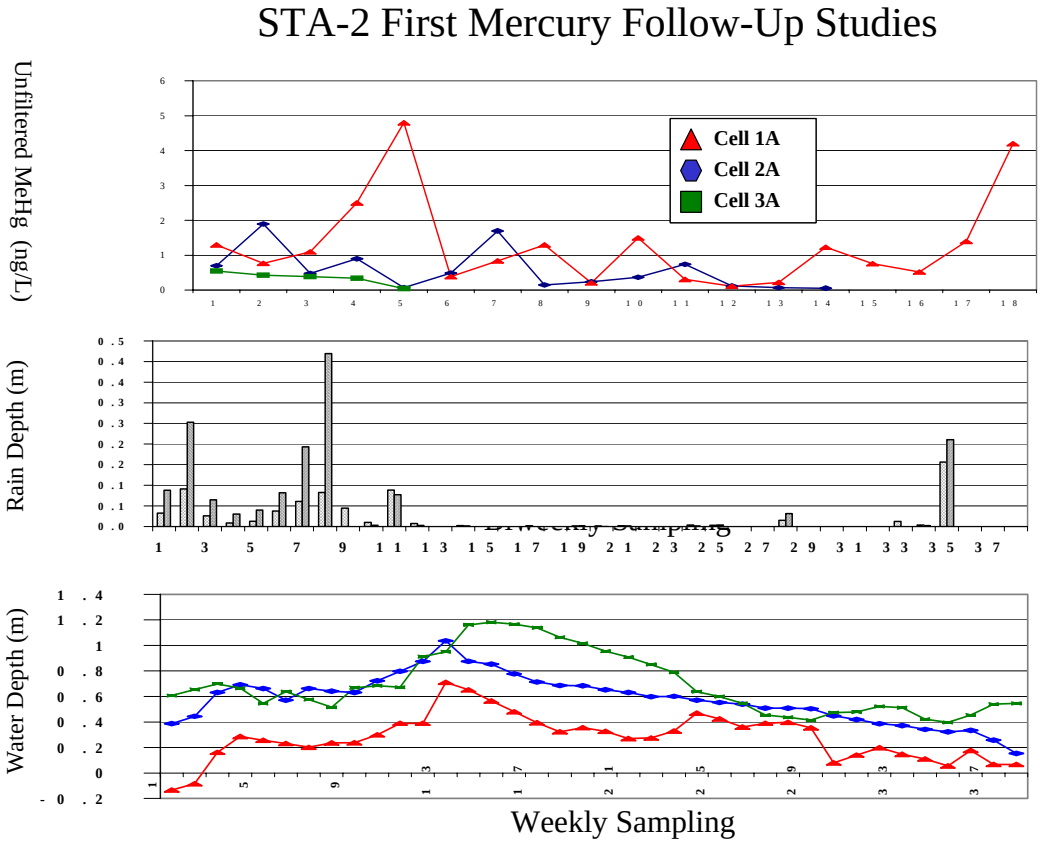

Figure 4. Results of follow-up expanded mercury monitoring after the first STA-2 Cell 1 MeHg anomaly on September 20, 2000.

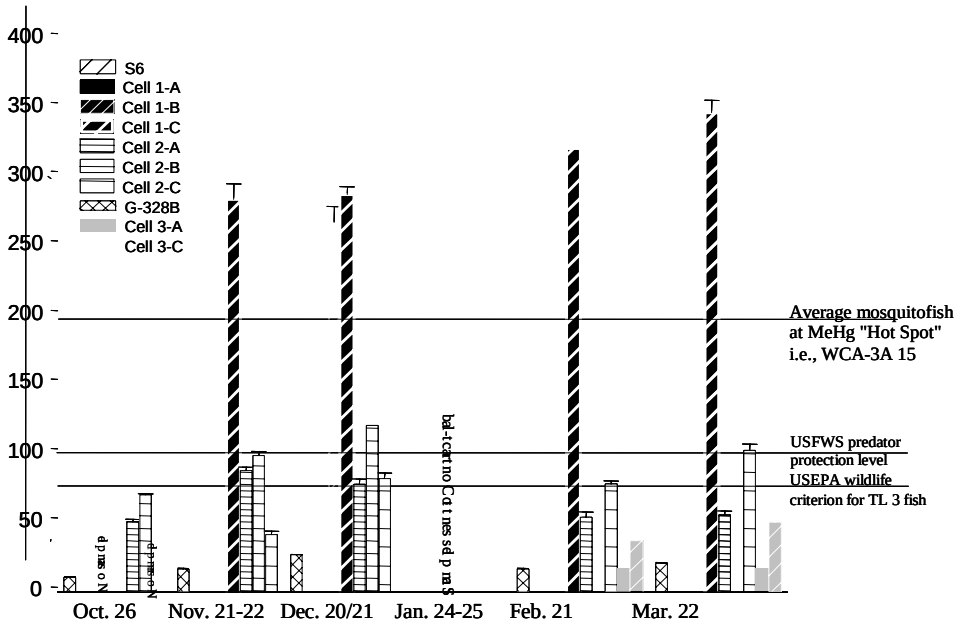

Figure 5. Results of follow-up expanded mosquitofish mercury monitoring after the first STA-2 Cell 1 MeHg anomaly on September 20, 2000.

During initial flooding of Cell 1, water levels were maintained at the STA-2 Operational Plan target elevation of 12 inches. The drought of 2001 necessitated operational changes to STA-2. The Cell 1 ground elevation made inflow to Cell 1 impossible, and the cell dried out in mid April 2001. A concerted effort was made during the drought to use all available water to keep a minimum of 6 inches in Cell 3, which was being maintained to support submerged aquatic vegetation. Cell 1 dried out in mid April 2001 in response to an extended drought. Cell 2 dried out a month later.

PERMIT MODIFICATION FOR FLOW-THROUGH OPERATION

In July 2001, the District petitioned for and in August 2001, the FDEP granted the District permission to initiate flow-through operation of Cell 1. The proposed modified permit requires 12 months of expanded monitoring to better define the mercury status of Cell 1 over time, after which an ecological risk assessment of the MeHg exposures to fish-eating wading birds was required. However, immediate notification and an early risk assessment were required if the THg concentrations in both mosquitofish and sunfish collected from the Cell 1 interior or downstream exceeded two standard deviations of the Everglades average mosquitofish and sunfish THg concentrations.

The modified Cell 1 operations for the 2001 wet season included (1) flowing as much water through Cell 1 as possible, and (2) maintaining a target average depth in Cell 1 of one foot, and a target minimum depth of 6 inches, subject to rainfall and other operational constraints; (3) blending discharges from Cell 1 with other cells in order to minimize mercury export from STA-2; and (4) moving water from Cell 1 to other cells as an option to meet these objectives. For purposes of implementing the second operational provision, the average depth in Cell 1 was to be calculated as the average of depths at the inlet and outlet structures.

In October 2001, as water levels in Cell 1 fell during the dry season, an anomalously high MeHg concentration was detected in STA-2 Cell 1 outflow water, but the concentration of THg in Cell 1 mosquitofish collected that same month had not yet reached anomalously high concentrations. In accordance with the adaptive management provision of the permit, the District requested and was granted permission to dry out Cell 1 in November 2001 before the anomalous MeHg pulse propagated up the food chain and presented an unacceptable risk to fish-eating wildlife, including the endangered wood stork. Dryout was essentially complete in December 2001, although some below-grade drainage continued into February 2002. Mosquitofish and sunfish (**Figure 6**) collected from site C1X in the interior of Cell 1 just above the G-330A outflow culvert in the spring 2002 exhibited anomalously high concentrations of THg.

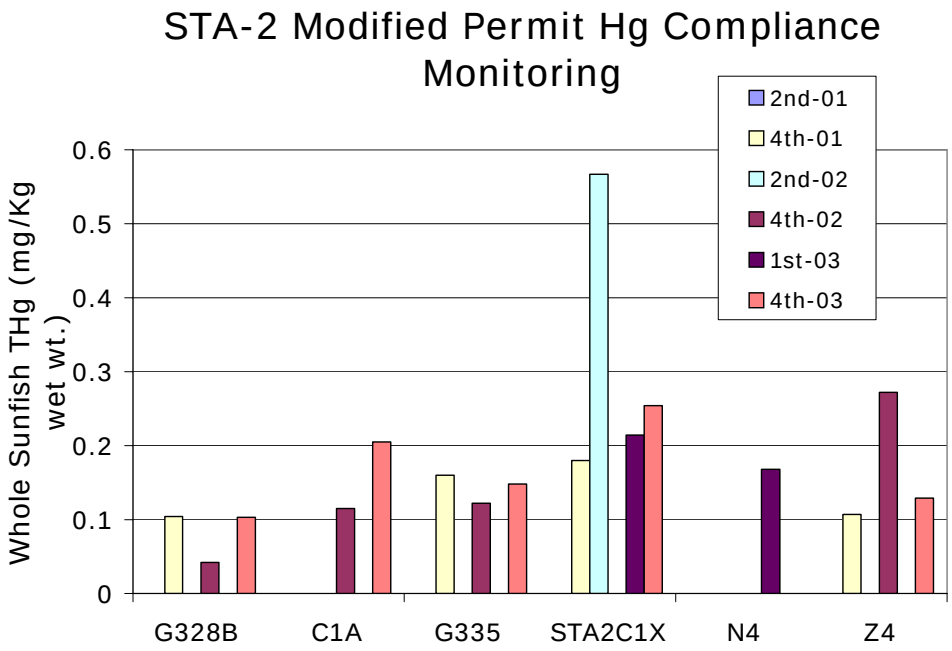

Figure 6. The results of modified permit-mandated sunfish monitoring within and downstream of STA-2 Cell 1 following the second and third methylmercury anomalies in STA-2 Cell 1.

MEMORANDUM OF AGREEMENT

As the modified permit mercury monitoring went into effect, the District and the FDEP developed a broader plan of action to better understand and, if possible, correct the cause of the anomalous MeHg behavior of STA-2 Cell 1. The proposed plan included provisions for more extensive and intensive monitoring of surface water, soil, pore water, and vegetation by the District and more process-level research into cause-effect funded by the FDEP. The monitoring and research data would then be integrated and synthesized by a predictive mathematical model of the transport, fate, and bioaccumulation of MeHg. That model, which has been adapted to the Everglades and upgraded for management-relevant application under another Cooperative Agreement between the District and the FDEP (C-9693), is the Everglades Mercury Cycling Model version II, or E-MCM (II). The final report detailing the development and application of E-MCM(II) is presented in Appendix 2B-2 of the 2004 Everglades Consolidated Report (Atkeson and Axelrod, 2004). The total cost of these studies in Fiscal Years 2002, 2003, and 2004 (FY2002, FY2003, and FY2004) was about $1M for each agency. Co-funding and in-kind service commitments from the FDEP were about $200K, including the redirection of about $107K in Section 319 matching grant funds to the District under C-11900-A03 or SP524. These commitments were codified in a Memorandum of Agreement (MOA) between the two agencies. The MOA (C-13812 or MOA072) was approved by the District's Governing Board at its February 2003 meeting. It remains in effect through February 2006. This report fulfills the requirements to submit a final report under MOA072 and SP524.

WETLAND MERCURY BIOGEOCHEMISTRY

The generalized mercury cycle in aquatic ecosystems is depicted in **Figure 7**. Inorganic mercury, $Hg(II)^{+2}$, is supplied to the Everglades by wet and dry atmospheric deposition, surface flow, and peat soils. Inorganic mercury then distributes itself amongst the dissolved ($Hg(II)_{aq}$), complexed (L- $Hg(II)^{+2}$), and sorbed (S- $Hg(II)^{+2}_{aq}$) phases in the water column. The $Hg(II)^{+2}$ can complex with dissolved organic carbon (DOC) (Wallace et al., 1982; Zhang et al., 1996; Ravichadran et al., 1998; Benoit et al., 2001b; Haitzer et al., 2002 and 2003) or sorb to inorganic colloids (e.g., iron oxyhydoxides: Babiarz et al., 2001) or organic colloids (Wallace et al., 1982; Guentzel et al., 1996), bacteria microfilms (Hintelmann et al., 1993), bacteria (Kelly et al., 2003), algae and periphyton (D'Itri, 1971; Hakanson, 1980; Cope and Rada, 1992; Hurley et al., 1998; SFWMD 1995–1999; Krabbenhoft et al., 2000; Krabbenhoft and Fink, 2001; Miles et al. 2001), or floating and rooted macrophytes (Wolverton and MacDonald, 1978; Rodgers, Jr., et al., 1978; SFWMD, 1995–1999; Hurley et al., 1998; Fink and Rawlik, 2000; Riddle et al., 2002; Fink, 2003). In the Everglades, due to the high concentration of DOC and particles of plant origin (biotic particles), most of the $Hg(II)^{+2}$ is in the complexed or sorbed phases, and only a small fraction is in the truly dissolved phase. However, because DOC-complexed $Hg(II)^{+2}$ will pass through a 0.45 micron filter, one must distinguish between the apparently dissolved (unfiltered minus filtered) and the truly dissolved phases.

Truly dissolved or DOC-complexed $Hg(II)^{+2}$ can then be transformed (reduced) to dissolved elemental mercury, $Hg(0)_{aq}$ in response to the action of sunlight (Saouter et al., 1995; Amyot et al., 1997), and the reaction generally proceeds faster for the DOC-complexed $Hg(II)^{+2}$, but in the Everglades neither reaction occurs especially rapidly and both are probably limited to the top few centimeters of the water column, due to the high concentrations of light-absorbing DOC present (Krabbenhoft et al., 1998; Zhang and Lindberg, 2000). Some of the $Hg(0)_{aq}$ produced in this way can be converted (oxidized) back to $Hg(II)^{+2}_{aq}$ either by direct reaction with dissolved oxidants produced by the action of sunlight on water (Xiao et al., 1994) or on DOC complexes (Xiao et al., 1995; Zhang and Lindberg, 2000). Where the concentration of $Hg(0)_{aq}$ exceeds that required for

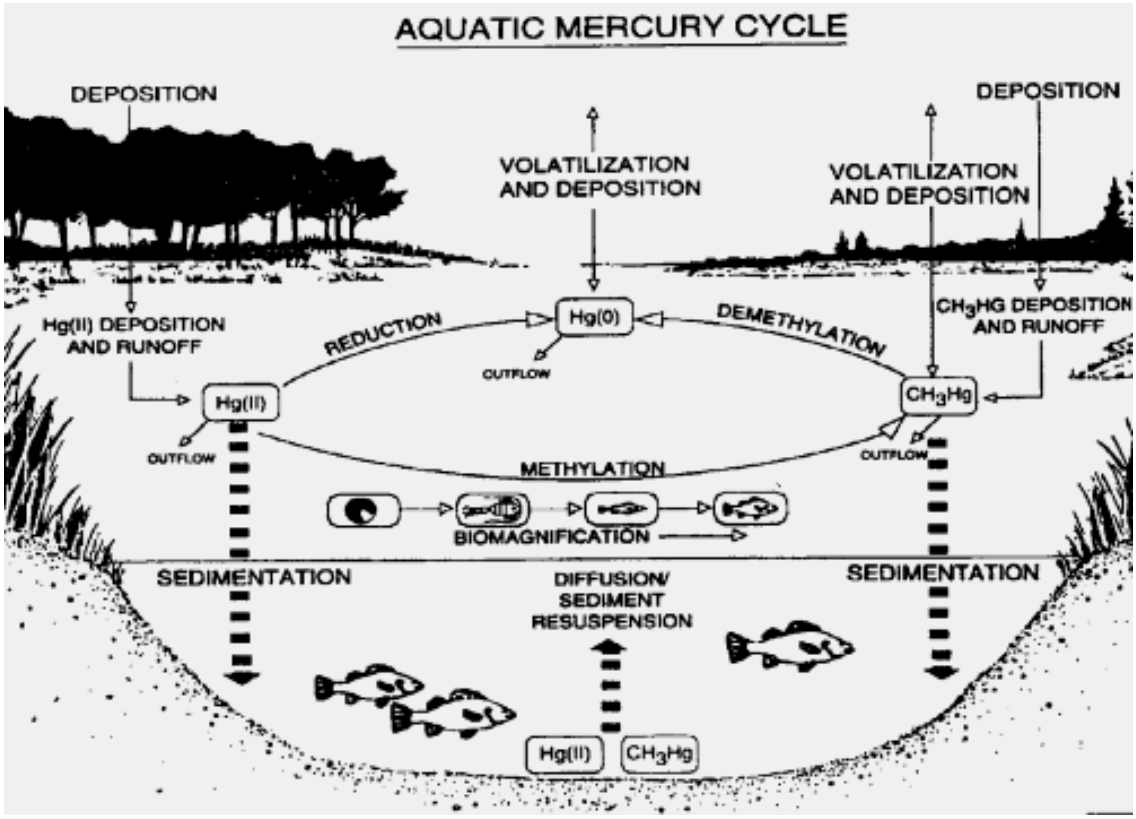

Figure 7. The generalized mercury cycle in aquatic ecosystems.

equilibrium with the concentration in the overlying air, it can also be transferred from water to air (evasion)(Vandal et al., 1991; Vandal et al., 1995; Lindberg et al., 1999; Lindberg and Zhang, 2000), mediated by temperature and wind speed. At night, when sunlight-driven production ceases, the concentration of Hg(0) in the gas phase in overlying air can exceed that required for equilibrium with the concentration of $Hg(0)_{(aq)}$ remaining in water, and there can be net transfer from the air to water (Lindberg et al., 1999). Where rooted macrophytes are present, Hg(0) produced in the soil or sediment can be taken up by the roots and transpired into the overlying air via leaf stomata (Lindberg et al., 2002; Dong et al., 2004). These processes must be distinguished from that which transfers reactive gaseous mercury (RGM) from the air to dry or dew-covered leaves, with subsequent reemission in response to the next morning's sunrise (Rea et al., 2000; Malcolm and Keeler, 2002).

$Hg(II)^{+2}$ reaches the surficial sediment primarily in association with settling particles (Wallace et al., 1982; Watras et al., 1995; Hakanson, 1980; Vaithiyanathan et al., 1996; Ambrose and Araujo, 1998) and, all other factors being equal, the $Hg(II)^{+2}$ settling rate is high where the particle settling rate is high, such as eutrophic areas, and vice versa. However, by competing with particles for $Hg(II)^{+2}{}_{aq}$, DOC can weaken this link and reduce the magnitude of this proportionality. Movement of dissolved and colloid- or DOC-bound $Hg(II)^{+2}$ can also occur from the overlying water to the surficial sediment when the concentrations of the former are greater than the latter (Reddy et al., 1999; Drexel et al., 2002; Haitzer et al., 2002). Once deposited to the surficial sediment, the $Hg(II)^{+2}$ can remain in the form in which it was received or redistribute itself in response to the changing physical, chemical, and microbiological conditions it encounters, the latter being more likely. In the surficial sediment $Hg(II)^{+2}$ can sorb to or complex with soil particle surfaces, either to the organic fraction (Gilmour et al., 1998b, 1999; Xia et al., 1999) or the iron (or manganese) oxyhydroxide fraction (Lockwood and Chen, 1974; Yin et al., 1997), be present in soil pore water in true solution, or, more typically, in association with dissolved organic carbon (Ravichadran et al., 1998; Lu and Jaffe, 2001) or sulfide complexes (Dyrssen, D. and M. Wedborg, 1991; Ravichadran, 1999; Ravichadran et al., 1998; Benoit et al., 1999b; 2001; Jay et al., 2000). The Everglades DOC originates with both external (allocthonous) and internal (autochthonous) sources with differing physicochemical characteristics (Lu et al.,. 2003) and affinities for Hg(II) (Haitzer et al., 2002). The $Hg(II)^{+2}$ in the organic matter fraction of the soil is most likely associated with reduced sulfur (primarily sulfhydryl) groups on the organic molecules that comprise that fraction (Xia et al., 1999; Karlsson and Skyllberg, 2003). However, in a comparatives study of sequential extraction versus x-ray absorption fine structure spectroscopy (XAFS), Kim et al. (2003) found that most of the naturally occurring $Hg(II)^{+2}$ was precipitated as mercuric sulfides or selenides, but the soils tested were not of muck origin, as is the case in the Everglades.

Of the fraction of $Hg(II)^{+2}$ that is bioavailable, some can be converted by soil microbes to $Hg(0)_{aq}$ (M. Gustin, UNLV, personal communication), then taken up by rooted macrophytes and lost to evasion from leaf surfaces (Lindberg et al., 2002; 2004). The rate of soil production is theoretically sufficient to support the measured Hg(0) flux above the macrophyte canopy (S. Lindberg, ORNL, personal communication), but the definitive tracer studies required to confirm this inference have not yet been conducted. The first flush of Hg(0) at first light most likely follows the same lacunal gas transport pathway as methane (Chanton, 1998), while the continuing flux of Hg(0) as the day progresses is more likely associated with the transpiration pathway (Dong et al., 2004). The evasion of Hg(0) shuts down with nightfall and decreases with increasing cloud cover (Lindberg et al., 1999). The production of Hg(0) in surface water is similarly responsive (Lindberg et al., 1999). Hg(II) is also taken up directly by rooted macrophytes, but direct uptake via the water column is believed to predominate for most species and conditions tested to date (Ribeyere and Boudou, 1994). Uptake by the submerged leaves is

mediated by water chemistry, including pH and chloride (Ribeyre and Boudou, 1994) and dissolved organic carbon (REF).

Neutral or charged complexes of $Hg(II)^{+2}$ and sulfide ion ($S^{=2}$) ($[Hg(II)_xS_y]^{-n}$) may also co-precipitate with the more prevalent iron sulfide complexes ($[Fe(II)_xS_y]^{-n}$) (Stumm and Morgan, 1996; Ravichadran et al., 1998; Ravichadran, 1999; Jay et al., 2000) especially as the very stable ore, cinnabar, but cinnabar precipitation in saturated solutions can be slowed or inhibited by the presence of Everglades DOC isolates (Ravichadran et al., 1998; Ravichadran, 1999). Pore water Hg(II), whether in the truly dissolved or DOC-complexed phase, can be transported back to the overlying water by physically mediated processes (i.e., groundwater exfiltration, dispersion, and diffusion: Thibodeaux, 1996; Choi and Harvey, 2000; King, 2000) or biologically mediated processes (i.e., bioturbation, biopumping, or biotransport: D. Krabbenhoft, USGS, personal communication). Because DOC and inorganic colloids compete with stationary particle surfaces for $Hg(II)^{+2}$, their high concentrations in pore water facilitate transport out of surficial soils, irrespective of the mechanism. In the Everglades, pore water DOC concentrations generally exceed that in the overlying water column by a factor of two or three, so diffusive exchange favors loss to the overlying water. However, mass budget calculations indicate that the rate of efflux from the surficial soils exceeds that predicted by DOC-enhanced diffusive exchange, suggesting that one or more of the preceding biologically facilitated transport processes must be at work (TetraTech, Inc., 2002). Reflooding after extended periods of drawdown and dryout can result in a first-flush release of $Hg(II)^{+2}$ (Rumbold and Fink, 2003; Fink, 2004 a, b).

MeHg is produced under anaerobic conditions by a variety of natural bacteria (Wood et al., 1968; Jensen and Jernelov, 1969; Olson and Cooper, 1976; Beijer and Jernelov, 1979; Berman and Bartha, 1986; Regnell, 1994; Gilmour et al., 1996; Gilmour et al., 2001) but primarily the SRB (Gilmour and Henry, 1991; Gilmour et al., 1992; 1998a,b; Benoit et al., 2001) from a bioavailable pool of $Hg(II)^{+2}$ accessible to the SRB. However, $Hg(II)^{+2}$ methylation was observed to be suppressed under iron-reducing conditions in sediments from a river basin (Warner et al., 2003). MeHg production can also be suppressed by Group VI anions (Chen et al., 1997). In the Everglades, MeHg production has been observed primarily in the top 4 cm of surficial soil or sediment but not in the water column (Gilmour et al., 1998b; 1999). The exception to this generalization occurs at highly eutrophic WCA-2A-F1, where a MeHg mass flux gap can only be closed by inferring water column MeHg production (D. Krabbenhoft, USGS, personal communication; R. Harris, Tetra Tech, Inc., personal communication). In addition, some MeHg production has been observed in periphyton mats (Cleckner et al., 1999) and the roots of floating macrophytes (Hurley et al., 1999; Mauro and Guimaraes, 1999; Mauro et al., 2001). In the Everglades, this occurs primarily in highly eutrophic, highly sulfidic areas (i.e., WCA-2A-F1; ENR). However, based on mass balance considerations, most of the MeHg must be originating with the surficial sediment or, in the case of WCA-2A-F1, the water column.

It has been hypothesized that MeHg is produced from the $Hg(II)^{+2}$ concentrated at soil or periphyton mat surfaces but not so strongly bound that it is unavailable to SRB (Gilmour et al., 1998b; Gilmour et al., 1999). However, defining this bioavailable fraction, either functionally (W. Landing, UF, personal communication) or mechanistically (Benoit et al., 1999a, b; 2001; Jay et al., 2000) has proved experimentally challenging. It is not yet known even whether the uptake of bioavailable $Hg(II)^{+2}$ occurs by an active (Golding et al., 2002; Kelly et al., 2003) or passive (Benoit et al., 1999a, b; 2001) mechanism of transport across the bacterial membrane. Interestingly, iron is readily corroded by SRB in marine environments, and this rapid corrosion process has been traced to an extracellular exudate that readily leaches and actively transports to SRB (Chan et al., 2002). Whether Hg(II) is leached from soil particle surface complexes and actively transported to SRB by a similar extracellular exudate will require further study.

Whatever the mechanism of uptake, sulfur cycle species appear to moderate the fraction of soil $Hg(II)^{+2}$ bioavailable to SRB.

Regarding potential nitrogen cycle influences on MeHg production, the occasionally observed inverse relationship between inflow NOx concentration and outflow MeHg might suggest that anaerobic nitrate-reducing bacteria can outcompete sulfate-reducing bacteria for carbon substrate when NOx is in excess, reducing SRB metabolic activity and the inadvertent production of MeHg from bioavailable $Hg(II)^{+2}$. The ability of some anaerobic dentrifiers (e.g., *Thiobacillus denitrificans* and *Thiomicrospira denitrificans*) to strip sulfur from surficial soil in the presence of an inorganic source of carbon has been quantified with the following stoichiometric relationship (Bezbaruah and Zhang, 2003):

$$55S + 20\ CO_2 + 50\ NO^{3-} + 38H_20 + 4\ NH^{4+} \rightarrow 25N_2 + 4C5H7O_2N + 55\ SO_4^{2-} - + 64H^+$$

In low-sulfate systems, the production of bioavailable sulfate from soil sulfur via this process could first stimulate MeHg production up to the point of maximum metabolic activity, then slow MeHg production as sulfide concentrations in pore water build up to inhibitory levels. In high sulfate systems, purple sulfur bacteria in the periphyton mats (Cleckner et al., 1999) and the roots of some floating macrophytes (Hurley et al., 1999; Guimares, et al., 2000) reduce sulfate to sulfur photosynthetically. This coupling of the nitrogen and sulfur cycles in these ways and the interaction of the sulfur cycle with the mercury cycle (Dyrssen and Wedborg, 1991; Gilmour and Henry, 1991; Gilmour et al., 1992) add to the complexity and uncertainty of a proper mechanistic interpretation of the observed positive and inverse correlations between MeHg production and nitrogen and sulfur cycle chemical species concentrations in water and soil.

Once produced, the fate of MeHg is also complex. Some of the MeHg produced from the bioavailable Hg(II) is demethylated by a variety of natural bacteria under anaerobic conditions at the sediment/water interface. At high MeHg concentrations, demethylation proceeds by a pathway associated with a detoxification mechanism (Robinson and Tuovinen, 1984), while at low MeHg concentrations, this pathway is not activated, and demethylation proceeds by various oxidative pathways with the concomitant production of methane or carbon dioxide (Oremland et al., 1991; Marvin-DiPasquale and Oremland, 1998; Pak and Bartha, 1998; Marvin-DiPasquale et al., 2000; Marvin-DiPasquale et al., 2001).

The net flux of MeHg out of surficial soil into the overlying soil or underlying horizons is determined primarily by net production (production by all routes minus decomposition by all routes). Once produced, MeHg can sorb to soil particles (Yin et al., 1997; Gilmour et al., 1998b; Xia et al., 1999), move into pore water, where it distributes itself between the dissolved and colloid-bound or complexed phases, primarily with dissolved organic carbon (Hintelmann et al., 1997; Amirbahman et al., 2002). From pore water, it can migrate back into the overlying surface water by physically mediated processes (i.e., groundwater exfiltration, dispersion, or diffusion: King, 2000) or biologically mediated by benthic organisms or their predators (bioturbation, biopumping, or biotransport: Krabbenhoft et al., 2001). As with $Hg(II)^{+2}$, a fraction of the sediment MeHg is so strongly sorbed to particles that it cannot be transferred either to pore water or the microorganisms and macroorganisms living in or on the sediment. The remaining fraction is thought to be physically, chemically, and biologically available for reaction, transport, or redistribution to other media. As with $Hg(II)^{+2}$, MeHg can be transported into the underlying soil horizon by downward seepage at a rate that more than counteracts the diffusive and dispersive processes (King, 2000). Many STAs have high seepage rates, especially around levees adjacent to seepage collection canals (Harvey et al., 2002). MeHg can also be taken up by rooted plants directly from the surficial sediment (Ribeyre, 1993; Ribeyre and Boudou, 1982; 1994; Fink,

2003). Uptake by the submerged leaves is mediated by water chemistry, including pH and chloride (Ribeyre and Boudou, 1994) and dissolved organic carbon (REF).

Once present in surface water, MeHg sorbs and settles in a similar fashion to $Hg(II)^{+2}$ (see above discussion). MeHg has a high affinity for algae cells (Ribeyre and Boudou, 1982; Pickhardt et al., 2002) and filamentous algae (Cleckner et al., 1998; 1999; SFWMD, 1999a), and the rate of accumulation tends to increase with increasing temperature and decreasing pH (Ribeyre and Boudou, 1982). The equilibrium partitioning of MeHg to algae species present in the Everglades has been studied rigorously using sterile laboratory cultures by Miles et al. (2001), while the uptake kinetics of this process have been quantified by Moye et al. (2002) using the same laboratory cultures. The latter authors conclude that the preponderance of the evidence supports an active uptake mechanism for green and blue-green algae species rather than passive diffusion. MeHg is also taken up by floating macrophytes (SFWMD, 1999a; Fink and Rawlik, 2000). The fraction of MeHg that is not sorbed to nonliving and living particles or actively bioaccumulated by aquatic plants and animals can be decomposed to $Hg(II)^{+2}$ or elemental mercury, $Hg(0)^{0}$, by sunlight (Sellers et al., 1996; Krabbenhoft et al., 1998; Krabbenhoft et al., 2001; Orem et al., 2002). MeHg that sorbs to settling particles or epibenthic periphyton can be reincorporated into the surficial sediments, where all of the physical, chemical, and microbial processes mediating transport, transformation, and bioavailability are again applicable, as discussed above.

WETLANDS MERCURY BIOACCUMULATION

Bioavailable mercury species can enter the food chain by one of three pathways. The first pathway is that of direct transfer to worms and insects (macroinvertebrates) living on or in the soil/sediment (zoobenthos). The second pathway is direct transfer to the plant eaters (herbivores) and meat eaters (carnivores) that ingest sediment particles in the process of foraging for food in the surficial sediment (bottom feeders). The third pathway is indirect and involves transfer to the water column, sorption to or uptake by microscopic plants and animals living in the water column, and then to the herbivores and carnivores that feed on them. The efficiency of transfer from water through the gills or skin surface or from the gut across the intestinal wall is determined by the thickness of the membrane and the differences in the concentration of the mercury specie in the external medium and the blood perfusing the gill or intestinal membrane, and the relative affinities of the mercury specie for the external medium and the blood.

As discussed above, Hg(II) and MeHg are strongly absorbed or adsorbed to living and dead floating, settled, or compacted organic particles, which are then ingested by herbivorous or detritivorous filter feeders living primarily on or in the sediment (zoobenthos) or free-floating in the water column (zooplankton). Hg(II) and MeHg can be taken up readily via body surface or gut by a variety of zoobenthos (Durkerschein et al., 1992; Lawrence et al., 1999; Lawrence and Mason, 2001) or zooplankton (e.g., D. magna) (Monson and Brezonik, 1999; Pickhardt et al., 2002; Tsui and Wang, 2004). High pH and DOC (Monson and Brezonik, 1999) can reduce the Hg(II) uptake efficiency to such organisms by the surface transfer pathways. In larger aquatic animals, Hg(II) can be taken up by all three pathways (Schopfer, 1974), but because it is inefficiently absorbed via the gut (Newman and Doubet, 1989), gill and dermal uptake predominate (Newman and Doubet, 1989), with the bioavailability of Hg(II) being mediated by a number of factors, including pH (Tsai et al., 1976). In mosquitofish, the Hg(II) uptake rate is inversely related to organism size, but the elimination rate showed no size dependence (Newman and Doubet, 1989). Although Hg(0) has been demonstrated to be taken up by fish in excess of the concentration of the surrounding water (Schopfer, 1974), Hg(0) is readily converted to Hg(II), eventually excreted to the gut, and inefficiently reabsorbed via the gut, so, as with Hg(II), there is a minimal tendency to bioaccumulate in fish. By contrast, MeHg (85 percent in yellow perch:

Norstrom et al., 1976; 29 percent in channel catfish: McCloskey et al., 1998) is much more efficiently absorbed from the gut of large fish than Hg(II) (Julsham et al., 1982).

Unlike Hg(0) and Hg(II), MeHg is readily taken up but only slowly eliminated by aquatic organisms (Norstrom et al., 1976; Rodgers, 1994), probably because of its high affinity for sulfur-rich proteins in blood and muscle tissue, its efficient recycling from the gut after being deposited there via the liver and gall bladder in bile, and, most importantly, its slow rate of conversion to Hg(II) by fish, as opposed to birds and mammals (WHO, 1976). Net MeHg production rates and macroinvertebrate and fish metabolic rates increase with increasing temperature, as do the corresponding rates of growth, food consumption, and gill ventilation to oxidize the food (Norstrom et al., 1976). This results in an increase in MeHg bioaccumulation with increasing temperature at all trophic levels (Shin and Krenkel, 1976; Boudou and Ribeyere, 1981). The high average annual temperatures in the subtropical Everglades may contribute to the high bioaccumulation factors in the Everglades, despite what might otherwise be considered short food chains (Loftus et al., 1998). Under typical concentrations of dissolved MeHg in surface water, even small fish tend to take up MeHg primarily from food. However, when the food consumption rate is low, as might occur during the winter months in northern temperate and subarctic lakes, direct uptake from the water may predominate, even for large-bodied fish (Post et al., 1996). Moreover, following a first-flush MeHg anomaly, the surface water concentrations may be 10 to 100 times the typical concentrations, such that gill uptake could predominates for small-bodied fish.

In the Everglades, the biological energy that sustains the structure and function of the aquatic ecosystem is believed to originate predominately with benthic detritus, and most of the MeHg in predatory fish is likely to originate with benthic detritivores. However, neither gut content studies (Loftus et al., 1998; P. Garrison, WDNR, personal communication, 1998; Lange et al., 1998; 1999; Hurley et al., 1999; T. Lange, FFWCC, personal communication, 2003) nor carbon and nitrogen isotope fractionation studies (Kendall et al., 2002) are definitive in this regard, suggesting that foraging habits, especially for the opportunistic omnivores (e.g., mosquitofish), are spatially and temporally dynamic (P. Rawlik, SFWMD, personal communication). Nevertheless, some contribution to MeHg bioaccumulation can be attributed to uptake by primary producers and transfer to grazing macroinvertebrates and fish and thence to their predators.

Where this contribution is significant, as in deep lakes, an inverse relationship can exist between the rate of primary production and the concentration of MeHg at each step in the lake food chain (D'Itri, 1971; Hakanson, 1980; Lange et al., 1993; Pickhardt et al., 2002). This phenomenon was termed "biodilution" by Hakanson (1980). This inverse relationship is less evident in wetlands (Fink, 2003) where (1) MeHg production is controlled by the limiting nutrient (e.g., phosphorus), either directly or indirectly via an intermediary factor or process (e.g., increase in sediment biochemical oxygen demand with a concomitant reduction in overlying water dissolved oxygen concentration and an associated increase in SRB activity or, where sulfate is also in excess, the associated buildup of inhibitory levels of pore water sulfide); (2) direct transfer of MeHg is occurring from the sediment to the detritus-based food chain, essentially short-circuiting the limnetic food chain and the biodilution effect in the water column; or (3) dense stands of emergent macrophytes shade out the algae (Grimshaw et al., 1997) that mediate the biodilution effect in deep lakes.

Most wetlands are net exporters of MeHg (Zillioux et al., 1993; St. Louis et al., 1994; 1996; Driscoll et al., 1995; Paterson et al., 1998; Sellers et al., 2001) but some export more per unit area than others. In tropical, subtropical, and temperate climates, one factor that affects the rate of MeHg production is the flux of sulfate from external sources, including acid rain (Branfireun et al., 1999). High arctic wetlands have also been demonstrated to be net exporters of MeHg, but the

primary methylators may not be sulfate-reducing bacteria (Loseto et al., 2004). The magnitude of the efflux of DOC from upland wetlands may also be a predictor of the amount of MeHg carried in runoff and seepage, stream flow, as well as in the receiving water (Mierle and Ingram, 1991). Anthropogenic upland disturbances can also influence the magnitude, timing, and duration of excess MeHg production, transport, and bioaccumulation (Garcia and Carignan, 2000).

THE FIRST-FLUSH AND RESERVOIR EFFECTS

Following soil dryout, it can be confidently predicted that labile carbon, sulfur, and iron species in surficial soils are oxidized, albeit to different degrees and at different rates (Dmitriw et al., 1995; Yin et al., 1997; Lamers et al., 1998; Gun et al., 2001; Taillifert et al., 2000; W. Orem, USGS, personal communication, 2000; Fink, 2002; 2003). Reinundation of oxidized soils is usually accompanied by a "first-flush" release of nutrients (Newman and Pietro, 2001) and trace metals, including inorganic mercury (Dmytriw et al., 1995; Rawlik, 2001b). Following the first-flush release of $Hg(II)^{+2}$, some of it is either converted to dissolved elemental mercury, Hg(0), and then lost to the overlying air via evasion (Vandal et al., 1995; Saouter et al., 1995; Krabbenhoft et al., 1998; Lindberg and Zhang, 2000; Zhang and Lindberg, 2000), or reabsorbed by bacteria microfilms (Hintelman et al., 1993), algae (Hurley et al., 1998; Miles et al., 2001; Moye et al., 2002) and floating and rooted macrophytes (SFWMD, 1995–1999; Hurley et al., 1998; Fink and Rawlik, 2000), as well as the surficial peat soil (Ambrose and Araujo, 1998). Thereafter, it has been hypothesized that the presence of high concentrations of these oxidized species in a readily bioavailable form accelerates MeHg production until they are reduced by biotic or abiotic processes (Krabbenhoft and Fink, 2001; Krabbenhoft et al., 2000). Following the pulse production of this excess MeHg, it redistributes, sorbs, and settles or is decomposed by sunlight to $Hg(II)^{+2}$ or Hg(0) or is demethylated by a variety of bacteria. If the duration of accelerated MeHg production is short, because the soil pools of labile, bioavailable sulfate, carbon, and inorganic mercury are small and rapidly consumed, then the total mass of MeHg produced will be small and the magnitude and duration of subsequent excessive bioaccumulation of MeHg in top-predator fish and their predators will be short-lived. This is the so-called "first flush effect." In a related phenomenon, seasonally elevated MeHg concentrations and associated mass loads have been observed in a stream receiving organic matter input in the form of fall leaf fall (Balogh et al., 2002).

On the other hand, if limiting pools are large or there is an external source of the limiting factor capable of sustaining a high, first-flush MeHg production rate for a long time, then the first-flush mass of MeHg produced will be large. It will then result in excessive bioaccumulation at the top of the food chain, and it will clear slowly from the ecosystem. This results in the so-called "reservoir effect," first observed in hydroelectric reservoirs created by flooding forested glacial till soils in northern temperate regions (Bodaly et al., 1984; Morrison and Therein, 1994; Scruton et al., 1994; Rodgers et al., 1995) but also observed in natural, created, or expanded wetlands (St. Louis et al., 1994; St. Louis et al., 1996; Kelly et al., 1997; Paterson et al., 1998). This has also resulted in the increase in MeHg body burdens in insect-eating birds (Gerrard and St. Louis, 2001) and fish-eating birds and mammals foraging in these water bodies (Wolfe et al., 1994).

However, if labile, bioavailable sulfate is present in substantial excess, surficial sediments remain anaerobic, and no other factor limits microbial metabolism or affects sulfur speciation, then sulfide, a byproduct of the life processes of sulfate-reducing bacteria, can accumulate to concentrations that actually inhibit MeHg production (Craig and Bartlett, 1978; Compeau and Bartha, 1985; Berman and Bartha, 1986; Gilmour et al., 1998b; Benoit, 1999a, b; Jay et al., 2000; Benoit et al., 2001; Marvin-DiPasquale et al., 2001). It has been hypothesized with moderate

confidence (Gilmour et al., 1998b) that sulfide inhibition is causing eutrophic Everglades regions with conditions otherwise deemed ideal for MeHg production (e.g., ENR Project and WCA-2A-F1) to exhibit low MeHg production and correspondingly low concentrations in fish at all trophic levels (Cleckner et al., 1998; Lange et al., 1998, 1999; Loftus et al., 1998; Rumbold, 2000; Rawlik, 2001a; Rumbold et al., 2001; Rumbold et al., 2002; Rumbold, 2005). Conversely, unimpacted or virtually pristine areas in the Everglades exhibit much higher MeHg production rates (e.g., WCA-2A-U3 and WCA-3A-15) and correspondingly higher concentrations in fish at all trophic levels.

In wetlands, depth and hydroperiod play a significant role in determining the concentration of MeHg in fish (Snodgrass et al., 2000). The first flooding of STA-1W resulted in excess MeHg production and mosquitofish bioaccumulation in the summer 1999 (Rawlik, 2001a). Following reflooding of dried out or burned areas of the Everglades in June 1999, MeHg concentrations in soil or pore water increased as much as thirty-fivefold over historical averages, and in mosquitofish 10-fold, while sites that remained wet throughout the winter increased by no more than 50 percent over historical averages during the summer and fall (Krabbenhoft et al., 2000; Krabbenhoft and Fink, 2001; Fink, 2002; 2003). More recently, net export of MeHg has been observed following first-flush MeHg anomalies in STA-6 (Fink, 2004a), as well as STA-2 Cell 1 (Rumbold and Fink, 2003; Fink, 2004b).

Saouter et al. (1995) have developed and field-validated a laboratory microcosm to simulate key elements of the mercury cycle in a contaminated pond under southern temperate conditions. Morrison and Therein (1994) have also simulated the northern temperate first-flush effect in laboratory micrcosms, as well as attempting to computer-model it and its influences on MeHg production and bioaccumulation to better understand the cause and dynamics of the reservoir effect. To determine whether the STA-2 first-flush effect could be similarly reproduced and studied under controlled conditions in the laboratory, the District and FDEP sponsored a scoping-level microcosm study of rewetted soil cores collected in February 2002 from STA-2 Cell 1 Site C1C and, for comparison, the traditional Everglades hot spot at WCA-3A-15. One set of replicate cores was dried out for 40 days prior to rewetting, while a second set of cores was dried for 299 days prior to rewetting. After the canal water was added to the set of dried cores, water and soil samples were collected at progressively longer intervals to track the first-flush response in the most cost-effective manner (exponential sampling frequency). Because the rate of rehydration of the dried cores was much slower than anticipated, the study duration had to be extended for both sets of soil cores. The results of these laboratory experiments are detailed in Appendix 2B-2 of the 2004 Everglades Consolidated Report (Atkeson and Axelrod, 2004). In summary, the scoping study confirmed that rewetting of STA-2 Cell 1 soils after dryout produce a first-flush MeHg anomaly associated with a first-flush release of the factor limiting the rate of MeHg production and that Cell 1 soils were more responsive than those collected at WCA-3A-15. In general, there is good reproducibility between the results of the 40-day and 299-day dryout experiments and general agreement between what was observed in vitro and *in situ*. A second set of more refined dryout-rewetting studies is now planned to further evaluate the predictive value of this approach.

This report focuses on the description and interpretation of the results of the extensive and intensive studies of progressively worsening MeHg anomalies in STA-2 Cell 1 following rewetting after extended periods of drawdown and dryout. The study design described in the following section was based on the conceptual model of MeHg production, transport-fate, and bioaccumulation, as discussed above.

STUDY DESIGN

As noted in the "Introduction" section, the recurrence of first-flush MeHg anomalies of progressively increasing magnitude after each dryout and rewetting event in STA-2 Cell 1 became problematic. To mitigate or eliminate this problem and to learn how to avoid or mitigate such problems in the future, it was necessary to understand the underlying cause(s) in a more rigorous way in the context of our conceptual model of the aquatic mercury cycle set forth in the preceding section. To do this, a series of special studies was needed in STA-2. The primary objectives of these studies were to:

1. Quantify the mercury and sulfur biogeochemical trajectories and mercury bioaccumulation trajectories of each treatment cell over time and evaluate the influences of the various external conditions and internal factors on those trajectories and their interrelationships within and between cells;

2. Compare the biogeochemical trajectories of Cell 1 and the post-reflooding trajectories of the soil microcosms in the laboratory wet-dry study for study inter-validation;

3. Quantify the dynamics of net import or export of inorganic mercury and MeHg by constructing a mass budget for each cell and evaluate the influences of various external and internal conditions and factors on those mass dynamics within and between cells; and

4. Calibrate a mathematical model of the biogeochemical dynamics of MeHg production and bioaccumulation developed elsewhere to Cell 1 conditions and evaluate model performance by hindcasting the biogeochemical trajectory of STA-2 Cell 1 during the first anomalous mercury event;

5. Quantify the risks of MeHg toxic effects to a highly exposed, highly sensitive avian, mammalian, and amphibian indicator species based on the observed MeHg bioaccumulation trajectory in Cell 1 mosquitofish and the corresponding modeled bioaccumulation trajectories in secondary and tertiary predator fish;

6. Predict the changes in the risks of MeHg toxic effects to those indicator species in response to various changes to start-up and operating regimens.

The secondary objectives of the study were to:

1. Quantify differences in the absolute and relative contributions of various pathways to the THg and MeHg mass budgets between seasons within a cell and between cells within a season;

2. Quantify the influence of various external and internal conditions and factors on the magnitude and duration of the post-reflooding MeHg production and bioaccumulation pulses within a cell between seasons and between cells within a season;

3. Quantify the influences of various external and internal factors on the loci and magnitudes of storage; and

4. Quantify the influences of various external conditions and internal factors on the differences in THg and MeHg mass budgets within a cell between seasons and between cells within a season.

It is unlikely that these secondary objectives could have been fulfilled without at least three, and preferably, five years of continuous, intensive monitoring.

To achieve the primary objectives, unfiltered THg and MeHg monitoring of the inflow at G-328B and outflow at G-335 was increased from quarterly to biweekly, the same constituents and frequencies of outflow monitoring were added for Cells 1, 2, and 3 at sites G-330A, G-332, and G-334, respectively. In addition, to the list of constituents routinely monitored at the common inflow at G-328, the list was increased to include chloride (Cl^-), sulfate ($SO_4^{=2}$), total suspended solids (TSS), and dissolved organic carbon (DOC). These same constituents were also added to routine outflow monitoring of Cells 1, 2, and 3 at G-330A, G-332, and G-334, respectively. At three interior sites in each cell, the study also added filtered THg and MeHg in surface water and THg in mosquitofish every four weeks; THg, MeHg, and other potentially influential constituents in surficial soils and pore water every 12 weeks; and THg and MeHg in plants semiannually. Additionally, every four weeks, filtered samples were collected at the common inflow and outflow and unfiltered samples were collected at the three interior sites in one of the three treatment cells on a rotating basis, such that each cell interior is collected every 12 weeks.

Prior to initiation of the study, no weekly rainfall samples were collected routinely onsite for ultra-trace THg analysis using the equipment and protocols of the National Atmospheric Deposition Program's Mercury Deposition Network (NADP/MDN) and the short-term nature of the Mercury Special Studies at STA-2 precluded formally adding an MDN site at STA-2. Instead, the contractor administering the MDN program and conducting the analyses for the NADP agreed to allow the District to install and use the equipment and protocols for NADP/MDN rain collection at STA-2 (FL99) and to analyze the samples collected in this way for THg, as if the site was an MDN site. This was intended to ensure comparability with other MDN sites. This precluded the need to approximate the rainfall contribution by extrapolating the values from NADP/MDN sites operating at Andytown (FL04 at the junction of U.S. 27 and I-75) and the ENR Project (FL34 at the junction of I-80 and S.R. 84). The rainfall collector was installed atop a concrete shed near the G-335 pump station at a height of about 10 feet (3 m) in August 2002 and came online in September 2003.

Appendix A reproduces the detailed Work Plan for the project. The expanded monitoring constituent lists are detailed for each medium in **Table 1,** and the sites, media, and frequencies of monitoring are depicted in **Figure 8**. Appendix H contains the data from the sipper method validation pre-study.

Based on samples collected from the top 4 cm by ANSERC primarily from one site in WCA-1, two sites in WCA-2A, one site in WCA-2B, and three sites in WCA-3A during the period from 1995–1998 (Gilmour et al., 1999), pore water sulfide correlates strongly with the concentration of MeHg in soil ($r = -0.78$). However, acid volatile sulfide (AVS) is considered a rough surrogate for pore water sulfide, but its correlations with soil MeHg ($r = -0.46$) and pore water sulfide ($r = 0.47$) are weak to moderate. Thus, the development of a pore water sulfide sampling capability for ultra-trace THg and MeHg and sulfide was considered a priority for this project. Unfortunately, despite initiatives to contract with or effect technology transfer from Texas A&M University-Galveston in winter 2001 and the USGS-Middleton and USGS-Reston in spring 2002, at project start-up in May 2002 the District did not yet have access to a method of pore water collection that produced a representative, valid sample for both redox-sensitive constituents and ultra-trace THg and MeHg.

Subsequently, the District modified a USGS *in situ* sipper design in June 2003, constructed it in July 2003, field-tested it in August 2003, and implemented it in September 2003. The study was extended five months from August 2003 through January 2004 to complete at least six separate pore water sampling trips. However, the frequency was reduced from every 12 weeks to every 4 weeks, as was the associated soil sampling. Unavoidably, this intensive sampling occurred after the first-flush MeHg anomaly had dissipated from the Cell 1 soil, surface water, and aquatic food chain.

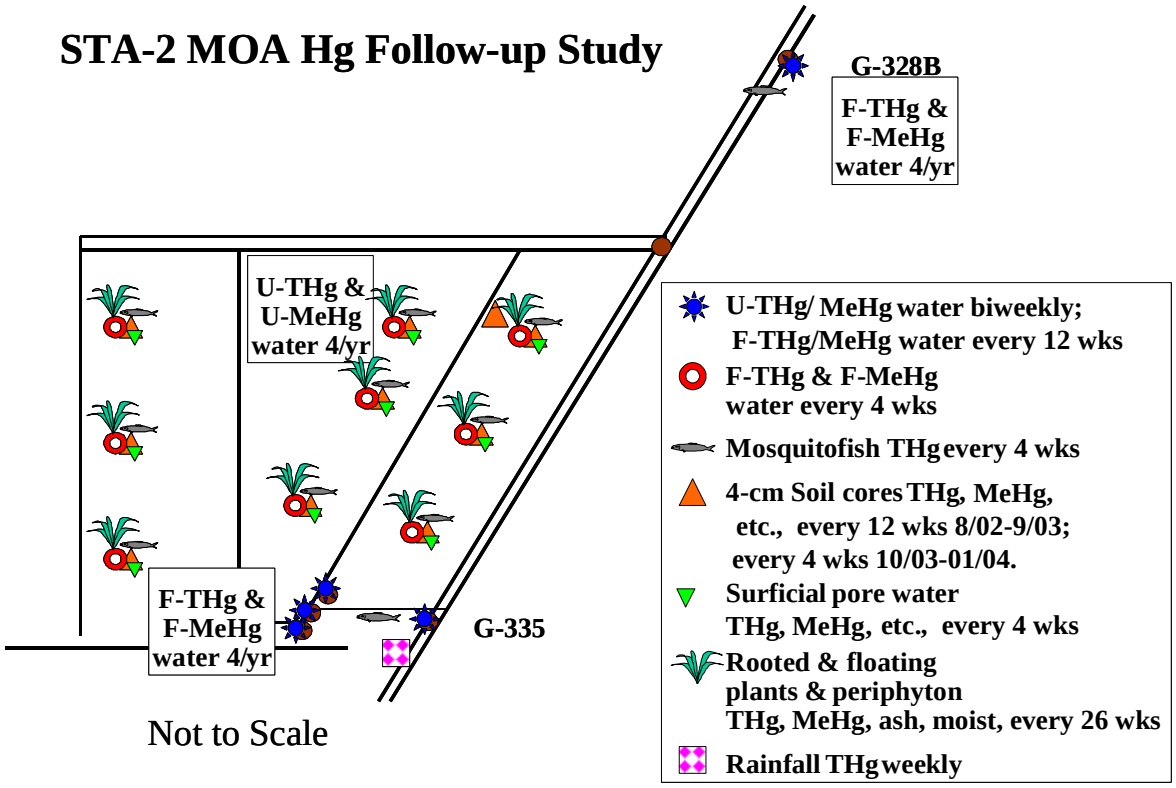

Figure 8. The STA-2 Mercury Special Studies sampling sites and proposed sampling scheme.

Table 1. Plan for expanded monitoring in STA-2.

STA-2	Matrix	Sites	Frequency[1]	Types	Reps	QC	Analytes
	Rain	1	52	1	1	0	U-THg
(1) QC needs met by coordinating with other sampling	STA-2 Inflow STA-2 Inflow Cell Outflow Cell Outflow	1 1 3 3	26 26 26 26	1 1 1 1	1 1 1 1	3 0(1) 0 0(1)	U-THg, U-MeHg(2) TSS, DOC U-THg, U-MeHg(2) TSS, DOC, U-$SO_4^=$ Hydrolab
	STA-2 Inflow Cell Outflow Special	1 1	13 13	1 1	1 1	1 0	F-THg, F-MeHg(2) F-THg, F-MeHg(2)
(2) Ship to FDEP; other analytes to contract labs	Interior Water - Routine	9	13	1	1	3	F-THg, F-MeHg(2), TSS, DOC, F-$SO_4^=$, F-Cl, F-Fe, F-Mn, F-Ca, F-Mg, Alk, Hydrolab
	Interior Water - Special	3	13	1	1	0(1)	U-THg, U-MeHg(2)
(3) Ship to FGS; others to DB labs or equivalent	Pore Water Tier 1	1	5 (7, 14, 28, 56, and 112 days)	1	1 (1 stratum)	1(1)	F-THg, F-MeHg(3) DOC, F-$SO_4^=$, F-Cl, F-$S^=$, F-TFe, Fe^{+2}, F-TMn, Mn^{+2}, F-TCa, F-TMg, Alk, pH, Redox, Conductivity, Prep
	Pore Water Tier 2	1	6 (pre-flood baseline; at start-up; quarterly thereafter)	1	3 (1 stratum)	1(1)	See Tier 1 Pore Water
	Soils Tier 1	1	5 (see Tier 1 pore water)	1	3 (1 stratum)	0	THg, MeHg(3), TS, TFe, TMn, TCa, TMg, AVS, Ash, Bulk Density, Moisture, Prep.
	Soils Tier 2	9	6	1	1 (1 stratum)	0	See Tier 1 Soils
	Plants	9	2	3	1	0	THg, MeHg(3), Ash, Moisture, Prep
	Mosquitofish	9	13	1	3	0	THg(2), Moisture

[1] Frequency is in weeks unless noted otherwise.

METHODS AND PROCEDURES

ROUTINE SAMPLE COLLECTION AND ANALYSIS

Rain

Rain water was collected as a weekly integrated sample using a modified Aerochemetrics® rainfall collector at the top of a 10-ft concrete blockhouse adjacent to a nexus of treatment cell discharge culverts using the equipment and following the sample preservation and ultra-trace THg analysis protocols of the National Atmospheric Deposition Program's Mercury Deposition Network (R. Brunette, Frontier Geosciences, personal communication). This site was registered as FL99. However, because FL99 was associated with a short-term study, it was not considered part of the NADP/MDN. The samples were then shipped to Frontier Geosciences (FGS) of Seattle, WA, for replicate (n = 2) ultra-trace THg analysis using modified methods equivalent to promulgated U.S. Environmental Protection Agency (USEPA) Method 1631. FL99 became operational the last week in August 2002 and the first weekly sample was submitted for analysis for the week ending September 3, 2002. The last sample was submitted for analysis for the week ending January 27, 2004.

Surface Water

At the inflow and outflow canals and cell outflow culverts, for analytes other than THg and MeHg, all surface water samples were collected as grab samples manually at 0.5 m depth. Surface water samples were collected at the interior cell sites following the same protocol but at one-half the water depth. When the wetland water depth fell below 10 cm, surface water sampling was suspended. For ultra-trace THg and MeHg analyses, the samples were collected unpreserved. For analytes other than THg and MeHg, samples were then preserved in the field according to standard methods and procedures. All common anions and cations were obtained as filtered samples, while TOC, TP, and TKN were obtained as unfiltered samples. Ultra-clean samples of surface water for unfiltered and filtered ultra-trace THg and MeHg analysis were collected using "clean hands-dirty hands" technique at the same depths as for the other analytes but unpreserved in 500 ml amber glass bottles with pre-cleaned teflon-lined caps using a peristaltic pump with acid-precleaned Masterflex tubing connected to 3 m of an acid-precleaned Teflon tube with a 6-mm inner diameter. Filtered THg and MeHg samples were collected when required for this project using Meissner ® filters that are certified for ultra-trace metals sampling. Initially the filters were not acid-precleaned, contrary to the procedures followed by the U.S. Geological Survey (USGS), Middleton, Wisconsin. However, the frequency of reversals (filtered MeHg > unfiltered MeHg) proved unacceptable (see also "Flagged Data" section), so filters were acid-precleaned beginning with the October 16, 2003, sampling event. Samples were kept on ice for transport to the analytical laboratory. The standard operating procedures (SOP) for water sample collection, preservation, and processing and is contained in Appendix B-1.

For analytes other than THg and MeHg, surface water analyses were conducted by the District's analytical chemistry laboratory on field-preserved samples using standard methods. For ultra-trace THg and MeHg analyses, samples were acid-preserved at the laboratory within 48 hours of collection at 0.4 percent (0.4 ml per 100 ml sample) with 12 N HCl and then analyzed by FDEP's mercury clean laboratory using cryogenic preconcentration and an ultraviolet fluorescence detector. Ultra-trace THg analysis was performed per a USEPA-approved

modification of the manual method specified in Method 1631 Revision E using an automated instrument vended by Tekran, Inc., of Toronto, Ontario, Canada. Ultra-trace MeHg analysis was performed by FDEP following well-documented modifications of draft USEPA Method 1630 (FDEP CompQAP). The most important deviation from Method 1630 is the direct ethylation of the acidified sample rather than distillation followed by ethylation of the acidified distillate. However, with the withdrawal of draft Method 1630 by USEPA, variances from that method are no longer being reviewed and approved by USEPA. As a consequence, FDEP has yet to resolve issues regarding the effect of the high DOC concentrations present in most Everglades samples on the potential for artifact production of MeHg, ethylation efficiency as a function of post-preservation holding time, and the appropriate sample holding time prior to analysis to avoid an unacceptable loss of ethylation efficiency.

Pore Water

At the time of study implementation, there were no standard or accepted methods for routine pore water collection using an apparatus capable of obtaining a representative sample of pore water that (1) preserved conditions of low redox potential; (2) was appropriate for ultra-clean sample collection for ultra-trace mercury analysis; and (3) was of sufficient volume to allow multi-analytes replicate analyses by a public or commercial analytical laboratory. Subsequently, USGS approved an *in situ* "sipper" method for pore water collection by its National Water Quality Monitoring Program that is valid for ultra-trace mercury sample collection. That method is contained in Appendix D. However, this method could not meet project performance sample volume requirements, so a modification to this method was designed, constructed, tested, validated, and deployed by the District with the assistance of Tetra Tech, Inc. The development and implementation of the modified *in situ* sipper method is discussed in a following subsection by that title. The modified design and its strengths and weaknesses are discussed in Appendix E. The SOP for the modified *in situ* sipper for pore water collection is Appendix F.

Soil/Sediment

To collect 4-cm soil cores, a 15–20 cm clean clear butyrate tube was inserted into the stainless steel corer. The corer was then driven into the sediment to the required depth using the corer's hammer. The butyrate tube was then capped and extracted from the corer. Water above the sediment layer was carefully decanted off. Large plant debris (e.g., roots, sticks, etc.) both living and dead, was removed from the top of the core using gloved hands. Any excess sediment, representing material deeper than desired cm depth, was removed and discarded. The core was then placed into a labeled zip-type storage bag, which is then inserted into a second zip type bag to avoid cross-contamination. Samples were kept on ice for transport to the processing lab. Before and after each use, all sampling utensils were rinsed a minimum of three times with *in situ* water. All soil chemical analyses for constituents other than THg and MeHg were carried out by DB Labs of Gainesville, FL. All soil chemical analyses for THg and MeHg were carried out by FGS using modified Methods 1631 and 1630, respectively. Soil samples received by the laboratory remained frozen until ready for preparation and analysis. When prepared for THg analysis, the thawed homogenate was acid-digested (0.5 to 1 g of wet sample in 10 ml of hot refluxing 70%HNO_3/30%H_2SO_4) and the digestate analyzed for THg following the protocol for THg in surface water. For MeHg analysis in soil, 0.5 to 1 g aliquot of thawed soil was distilled with 24.5 ml of de-ionized (DI) water to which 0.5 ml of 9 M H_2SO_4 and 0.2 ml of 20 percent KCl have been added. The SOP for soil sample collection, preservation, and processing and that for solid sample archiving are contained in Appendices B-2 and B-5, respectively.

Fish

At each sampling site, between 75 and 250 mosquitofish (*Gambusia holbrooki*) were collected using a long-handled, ¼-inch nylon mesh net. The individual fish were stored on ice, refrigerated for no more than 48 hours, and then composited and homogenized using a Polytron® apparatus. Thereafter, the homogenate was frozen prior to shipment on blue ice or double-bagged wet ice to the FDEP mercury clean laboratory. The thawed homogenate was acid-digested (0.5 to 1 g of wet sample in 10 ml of hot refluxing 70%HNO_3/30%H_2SO_4) and the digestate analyzed for THg using an instrument vended by Merlin, Inc. The effective method detection limit (MDL) was 0.005 mg/kg wet wt. Although not a part of this study, semi-annually 20 sunfish (Lepomis spp.) and annually 20 largemouth bass (*Micropterus salmoides*) were collected by staff of the Florida Fish and Wildlife Conservation Commission under contract to the District using an electroshocker powered by a ¾ hp, 750W generator following the protocol of Lange et al. (1993). The lengths of sunfish and largemouth bass were measured in the field. The whole sunfish were placed individually in resealable plastic bags and transferred to District staff in the field. The largemouth bass were then weighed in the laboratory and otoliths removed for aging by FFWCC staff. One half of the bass fillet was retained by the FFWCC and the other half transferred to the District. A cube of muscle was then removed for subsequent analysis. The thawed whole sunfish were homogenized individually in a blender with stainless steel blades. Fifty grams of sunfish homogenate and the largemouth bass muscle cube were then frozen prior to shipment to the FDEP mercury clean laboratory on blue ice or double-bagged wet ice for analysis. The unused portion of the sunfish homogenate and the remaining bass fillet were refrozen and stored for up to five years in archive per the relevant SOP. An aliquot of sunfish and the largemouth bass cube were then acid-digested as per mosquitofish and the digestate analyzed for THg using standard cold vapor atomic absorption analysis. The effective MDL for THg analysis in large-bodied fish samples was 0.020 mg/kg wet wt. The SOP for fish sample collection, preservation, and processing and that for solid sample archiving are contained in Appendices B-3 and B-5, respectively.

Vegetation

Semiannually from September 2002 through September 2003, two species each of rooted emergent macrophytes, rooted submerged macrophytes, and green and blue-green periphyton species were collected based on predominance and accessibility at each of the three sampling sites in each of the three STA-2 treatment cells. For rooted emergent macrophytes, this was tantamount to collecting sawgrass (*Cladium jamaicense*) and cattail (*Typha spp.*). The submerged rooted macrophytes generally included red ludwigia (*Ludwigia repens*), water lily (*Nymphaea odorata*), bladderwort (*Utricularia fibrosa*), torpedo grass (*Panicum repens*), Illinois pondweed (*Potamogeton illinoensis*), Southern naiad (*Najas guadlupensis*). The periphyton species generally consisted of filamentous green algae (e.g., *Spirogyra*) and calcareous blue-green algae (e.g., *Schizothrix calcicola*). Rooted and submerged macrophytes were sampled above ground only. Representative portions of rooted emergent and submerged macrophytes were cut into pieces using a machete, placed in resealable plastic bags, labeled, and placed on ice in coolers for transshipment back to the laboratory for storage frozen until ready for processing. Periphyton samples were collected using gloved hands, drained, and placed in resealable plastic bags, then handled in the same way as the macrophyte samples. In the laboratory, thawed samples were chopped into processable subsamples using a machete, the subsamples composited and mixed in a resealable plastic bag, and an aliquot withdrawn for homogenization in a stainless steel blender. About 50 g of wet, homogenized composite sample of each species was then placed in an individual 125 ml plastic bottle, labeled, placed inside a resealable plastic bag, and frozen prior to shipment to the analytical laboratory. The unused portion of the sample was frozen in a 125 ml

glass bottle and archived for future reference. The SOP for plant sample collection, preservation, and processing and that for solid sample archiving are contained in Appendices B-4 and B-5, respectively. Once received by the analytical laboratory, the samples remained frozen until ready for processing and analysis. The THg and MeHg sample preparation and ultra-trace analyses used by FGS for vegetation are the same as those for soils.

ARCHIVING

The archiving of frozen solid samples for future reanalysis is considered a standard professional practice in environmental studies to address issues regarding ambiguous, inconsistent, or disputed results. As planned, the study design required retention of all remaining unprocessed or processed frozen solid sample for two years, followed by retention of 20 percent of those samples for another five years. The six-month holding times for solid samples applicable to permit compliance samples did not apply to uses unrelated to permit compliance, such as STA operational optimization and corrective action verification.

SAMPLING METHODS DEVELOPMENT

For all but pore water sample collection, standard or mercury ultra-clean sampling, preservation, and storage methods were employed. Since this project had to rely on the District and commercial laboratories for the required quantitative chemical analyses, the pore water collection method adopted for this application would have to be able to generate at least one-half liter of representative pore water sample. In January 2002 it was determined that the FIU engineering laboratory, which was under contract to the District, did not have the required expertise and experience to develop a new or modify an existing method for the collection of a representative, ultra-clean sample of pore water for ultra-trace mercury analysis, and the work was terminated. In February 2002, USGS-Middleton, under contract to FDEP, collected samples of pore water at STA-2 C1C using a pre-cleaned, hollow Teflon cylinder with two sets of two parallel sampling slits 0.2 cm wide and 1.5 cm long cut into opposite sides of the cylinder roughly 3 cm above the bottom of the cylinder. A 2-cm Teflon nose cone, milled to fit inside the cylinder, facilitates entry of the probe into the subsurface soil environment to the desired depth. The USGS-Middleton *in situ* sipper method is described in Appendix D. However, the volume of sample collected by this method was on the order of 50 ml, not the 500 ml required for District or commercial laboratory use.

In March 2002, the District tested a hand-pumped *in situ* sipper, which was used by USEPA in its REMAP II study. Based on its performance, it was rejected for this application, because it was unable to penetrate the compacted soil in Cell 3 and was unable to withdraw sufficient pore water sample volume from the other two cells. The District purchased two complete, pre-cleaned sippers manufactured for USGS-Middleton to its specifications in March 2002. After receipt in mid-May 2002, field-testing of the apparatus in early June 2002 resulted in its rejection for this application, because surface water breakthrough occurred when more than 100 ml was collected continuously from one location, even at the lowest withdrawal rate achievable with the peristaltic pump. In mid June 2002 the District enlisted the assistance of William Orem, Ph.D., of USGS-Reston. A technician supplied by Dr. Orem's laboratory brought the equipment and supplies required to set up and implement the piston "squeezer" method of pore water collection. Unfortunately, field testing revealed that withdrawal of more than 75 ml from a 2-cm horizon of a 10-cm diameter core resulted in breakthrough from either overlying surface water, which had been retained to seal off the surficial sediments from the air, or from pore water from deeper soil strata. While the withdrawal of smaller sample volumes from multiple cores could circumvent

this problem, this could be achieved only at the cost of a substantial increase in the time required to collect and process the cores. This was beyond the capability of a two-person crew budgeted for this project.

In July 2002, the District informed the FDEP that it would not be possible to initiate pore water sampling with a validated method upon reflooding of STA-2 Cell 1 for the reasons set forth above. With the FDEP's approval, the initiation of pore water sampling was postponed until the required technology transfer could be affected. At the beginning of the new fiscal year in October 2002, Gary Gill of Texas A&M University in Galveston expressed general interest in collecting pore water samples for the STA-2 Mercury Special Studies Project using his squeezer method, which substituted nitrogen gas pressure for Dr. Orem's piston. However, before he could commit to the work, he requested a more detailed description of the proposed sampling scheme. In November 2002 a proposed sampling scheme was forwarded to Dr. Gill. In December 2002, follow-up communications were not returned. In January 2003, Dr. Gill indicated that he had insufficient graduate student support to take on this work. In February 2003, Dr. William Landing of Florida State University indicated that he did not posses the required capability. In that same month, Nicholas Bloom of Frontier Geosciences laboratory in Seattle, Washington, was contacted about using his centrifugation pore water extraction method for this purpose. In March 2002, Mr. Bloom expressed general interest but wanted more specifics. In April, Mr. Bloom was unavailable. In May 2003, Mr. Bloom agreed in principle to the work and submitted a preliminary proposal.

In May 2003, it was decided to modify the USGS sipper method, rather than rely on the centrifugation method, which was extremely labor intensive, time-consuming, and, thus, both expensive and impracticable. Because of its Teflon construction, the sipper was appropriate for ultra-clean collection of pore water for ultra-trace mercury analysis, as well as for redox-sensitive analytes such as $Fe(II)^{+2}$ and S^{-2}. In June 2003, a draft Statement of Work was developed for a pre-study to validate the modified sipper method as compared to the centrifugation method and then implementing the validated method for this application. That SOW is Appendix F.

Clearly, the modification of the USGS sipper method had to allow for the collection of a larger volume of pore water, while virtually eliminating surface water breakthrough. If an impermeable barrier could be introduced at the interface of the surface water and underlying surficial sediment, these seemingly mutually exclusive performance criteria might be met simultaneously. The addition of a large disk between the surface water and the surficial sediment appeared to meet these operational requirements.

The prototype of the modified sipper method of pore water collection required the manufacture of a 0.5 m diameter disk 1.25 cm thick with a hole at its center through which the sampling cylinder was inserted and fixed to the desired depth with three plastic screws mounted in a plastic brace affixed to the disk with plastic screws. Handles were added for ease of insertion. Weights were affixed to the handles to ensure that a uniform force per unit area (pressure) was applied by the disk to the surficial sediments sufficient to seal off the surface water from the ground water environments without unduly compacting the underlying sediments. The performance of the prototype was evaluated in the field by continuously monitoring the conductivity of the pore water over time. Table salt was distributed on the surface and at the edges of the disk to ensure that the conductivity demarcation between the two distinct media was unambiguous.

While the first prototype configuration showed promise, there was some indication of breakthrough during the latter stages of withdrawal of 1 L of water, as evidenced by an unmistakable jump in conductivity. The size of the disk was then increased to 0.75 m diameter,

and the larger disk was affixed to the smaller by nylon screws. In addition to reducing the likelihood of surface water breakthrough, this configuration afforded greater stiffness to the apparatus, while allowing reversion to the smaller disk design in the field should that become necessary. The weights were increased in proportion to the area of the disk to ensure that the same pressure would be achieved. Finally, a pre-cleaned plastic cell was interposed between the peristaltic pump and the collection port for continuous monitoring of redox potential as a real-time check on the effectiveness of the seal between the surface water and pore water and continuous verification of the absence of surface water breakthrough around the edges of the disk.

Further field-testing of the refined design indicated that it was meeting its performance specifications, while replicate blank samples tested for THg and MeHg did not indicate that the materials from which the apparatus was constructed were causing excessive THg or MeHg contamination. Field filtration of the pore water samples, which was effected by interposing a Meissner filter in the sampling line between the peristaltic pump and the collection port using a pre-cleaned Teflon connector, was added following the first routine sampling event, after laboratory centrifugation of the unfiltered samples was unable to reduce within-sample analytical variability to acceptable levels. Pre-cleaning of the Meissner filters was initiated after the second sampling event, when it became apparent from a review of the first nine months of study data that the magnitude and frequency of reversals of surface water filtered MeHg (F-MeHg) > unfiltered MeHg (U-MeHg) were outside of what would be expected based on sampling and analytical variability alone.

The first modified design was discussed with the Director of the District's Analytical Chemistry Laboratory in late May and early June 2003, the prototype pieces were fabricated by a local contractor and assembled by the Laboratory Director in mid June 2003, further modified in mid July 2003, and pre-tested in late July and early August 2003 by contractor staff. Concurrently, a method for quantitative analysis of Fe(II) was resurrected and a method for sulfide, in the latter stages of final testing, was green-lighted for this research application. The modified *in situ* sipper apparatus was authorized for routine use by the Project Manager in the last week in August 2003.

A more detailed discussion of the construction and design of the modified *in situ* sipper apparatus is contained in Appendix E. The SOP for the pore water collection method adopted for this project is contained in Appendix F.

QUALITY CONTROL

In addition to the standard blanks, replicates, and spikes for validating each analytical laboratory sample run per standard methods or Methods 1630 and 1631 for ultra-trace THg and MeHg, the quality assurance protocol requires the collection of a field kit blank, a field equipment blank prior to sampling, two field replicates every quarter, and a field cleaning equipment blank at the end of each sampling trip (see **Table 2**). The field kit blank is used as a diagnostic for contamination introduced in the DI water or bottles unrelated to field sampling but not to fatally flag the results of the samples collected using that field kit. If the THg or MeHg equipment or field cleaning equipment blank exceeds 0.5 or 0.05 ng/L, or the field replicate RSD is > 20 percent, the entire set of samples is fatally flagged. If a MeHg result is > 130 percent of a THg result, that data pair is fatally flagged. In addition, an equipment blank is collected from the rinsate of the butyrate soil coring tube at the beginning of each sampling trip and the same for the homogenizers used for fish processing on a quarterly basis. However, due to the much higher concentrations of THg and MeHg in solid media relative to ambient water, a contaminated blank does not result in a fatal flag for any solid sample but is used as a diagnostic for evaluating the

Table 2. QA criteria for total and methyl mercury data review of QC samples.

FQC	Acceptance Criteria	Corrective Action
Field Kit Prep Blank (FKPB)	>0.5ng/Lfor Total Mercury** >0.05 ng/L for Methyl Mercury**	Flag FKPB if > Acceptance Criteria Flag FKPB if > 90 day storage limit with non fatal flag (PMR). No flags for the data
Equipment Blank (EB)	>0.5ng/Lfor Total Mercury** >0.05 ng/L for Methyl Mercury**	Flag EB if >Acceptance Criteria a. Flag sample collected directly after the contaminated blank, if that value is <3x the contaminated blank. Do not flag if value is >3x contaminated blank. b. Flag entire set if both EB and FCEB is >acceptance criteria.
Filtered Equipment Blank (F-EB)	>0.5ng/Lfor Total Mercury** >0.05 ng/L for Methyl Mercury**	Flag F-EB if >Acceptance Criteria a. Flag all filtered samples associated with F-EB if <3x contaminated blank regardless of time sequencing of all filtered samples. Do not flag if value is >3x contaminated blank.
Field Cleaned EB (FCEB)	>0.5ng/Lfor Total Mercury** >0.05 ng/L for Methyl Mercury**	Flag FCEB if >Acceptance Criteria a. Flag all affected samples (samples with concentration < 3x contaminated FCEB value). Do not flag if value is >3x contaminated blank. b. Flag entire set if both EB and FCEB is > acceptance criteria.
*Trip Blank (TB)	>2xMDL	Flag TB if > Acceptance Criteria Flag associated samples if: a. At least one other blank (FB or EB) and the TB > acceptance criteria b. Sample concentration are >criteria and <3x the contaminated blank value to that site.
Split Sample (SS)	Contract Lab's internal Precision criteria	Diagnostic tool for evaluating routinely achievable intra and inter lab precision and should not be used as a field acceptance criteria for routine data review.
Replicate Sample (RS)	RSD or RPD criteria >20% for replicas >PQL. No action is taken when concentrations are below PQL.	Flag entire set if >Acceptance Criteria If the mean value is >PQL and RSD or RPD is >20% then flag the entire set . (See also Field Duplicates).
Reversals 1: MeHg > THg	Unfiltered or filtered (dissolved) MeHg > unfiltered or filtered (dissolved) THg and	If the acceptance criteria are met, flag the sample, if: a. Both values > PQL; b. difference between samples > 20%; and c. difference between samples > 2 x MDL
Reversals 2: Filtered > Unfiltered	Filtered THg > unfiltered THg or Filtered MeHg > unfiltered MeHg and	If the acceptance criteria are met, flag the sample if: a. Both values > PQL; b. difference between samples > 20%; and c. difference between samples > 2 x MDL
*Field Duplicate (FD)	RPD criteria: 40% for duplicates >PQL. No action if observed concentrations are below PQL.	Flag entire set if >Acceptance Criteria

** EPA Method 1631 Revision E; *EB1 renamed EB February 2002; *EB2 renamed FCEB February 2002; ***FD replaced February 2002 with RS.

adequacy of equipment cleaning. In addition, due to the high natural heterogeneity of THg and MeHg concentrations in solid media, the field replicate results were used to quantify sample variability but not to flag sampling trip results.

Prior to initiation of sampling of surface water or pore water, an equipment blank was collected, and at the end of each sampling trip a field cleaning equipment blank was collected. Both were analyzed for the constituents of interest. Replicate (n = 3) pore water samples were collected at Site C1C for each sampling trip. Initially, filtered surface water and pore water samples were collected through a Meissner® filter that had not been acid-precleaned. However, as the study proceeded, it became apparent that the magnitude and frequency of reversals (filtered > unfiltered) for MeHg exceeded what would be expected based on sampling and analytical variability. In response, acid-precleaning of the Meissner® filters was initiated via Frontier Geosciences, Inc., of Seattle, Washington. Subsequently, the magnitude and frequency of MeHg reversals decreased to acceptable levels. One equipment blank was also collected from a representative soil/sediment coring tube prior to each quarterly or monthly sampling event, and an equipment blank was collected from the apparatus used for homogenizing soil and fish samples on a quarterly basis.

For analytes other than ultra-trace THg and MeHg, standard holding times were in effect for water, soil, and vegetation samples. For purposes of implementing this plan, holding times for ultra-trace THg and MeHg analysis of water, pore water, frozen soil/sediment, frozen vegetation, and frozen fish adopted for this project were 28 days, 28 days, six months, six months, and six months, respectively. However, with the publication of Method 1631 Revision E in August 2002, the USEPA-approved holding time for ultra-trace THg analysis of frozen fish and frozen soil/sediment increased to one year. The ultra-trace MeHg analysis method, Method 1630, was withdrawn by USEPA and has not been revised and republished in draft or final form subsequently. Since the FDEP-approved study plan for this project was written and implemented prior to the publication of the final Method 1631 Revision E, this project continued to use the six-month holding times for ultra-trace THg and MeHg in frozen fish, vegetation, and soil/sediment.

Appendix B contains the set of SOPs used for the collection of representative and valid samples of surface water, soil, sediment, fish, and vegetation. Appendix B-6 is the SOP that sets forth the criteria for rejecting a surface water sample based on equipment blank contamination, ultra-trace THg versus MeHg reversals, filtered versus unfiltered reversals, replicate precision, and holding times. The ambient water blank sample rejection criteria also apply to the processing equipment blanks. The SOP also sets forth the criteria for rejecting frozen soil, vegetation, and fish samples based on replicate precision or holding times.

WATER BUDGET CALCULATIONS

As illustrated in **Figure 9**, the water budget for each STA-2 treatment cell consists of a total inflow and outflow, rainfall and evapotranspiration (ET), total net seepage, and net change in storage. These data are generated from measured values for the flows, rainfall, and stage on a daily basis using the data and following the calculation procedure outlined in Appendix J. For ET, the flux per unit area is calculated using measured sunlight intensity and humidity data and a mechanistic equation developed by the District's Wossenu Abtew (Abtew, 1996). For seepage, the flux is calculated using measured head differences, a seepage rate coefficient per linear meter of levee or berm, and an equation based on D'Arcy's Law.

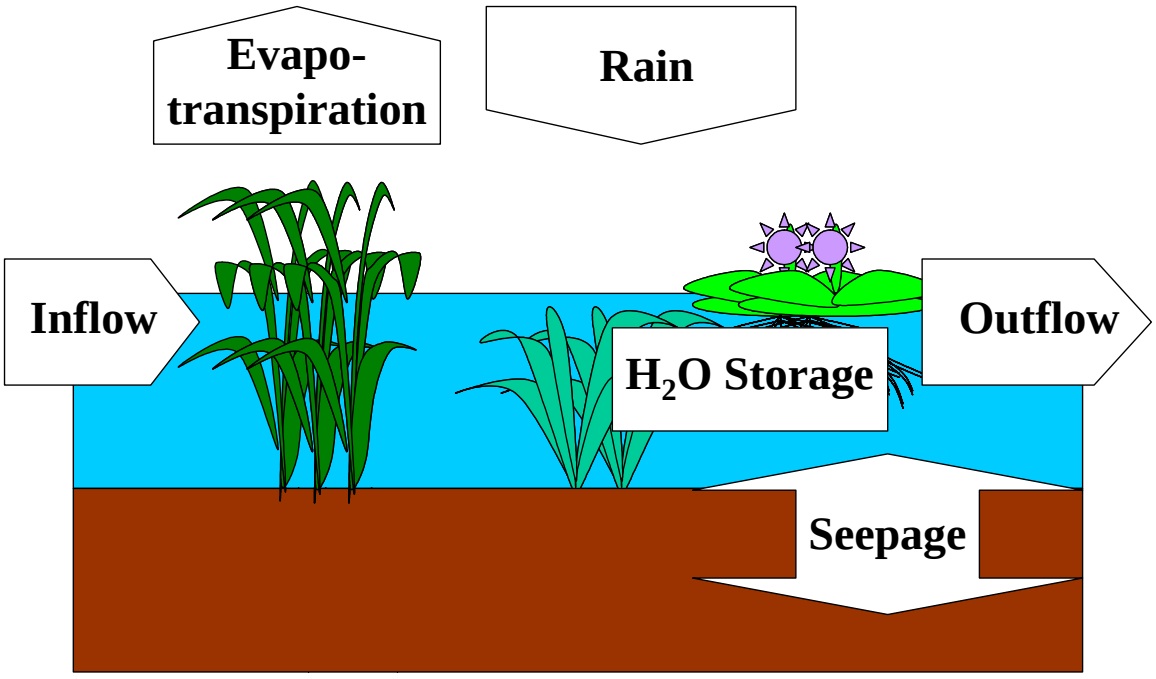

Figure 9. Generalized representation of a water volume budget for a natural or constructed wetland.

Initial Water Budget

The uncertainty in the water budget increases in the order inflow and outflow pumps, stage, calculated flows from gauged inflow and outflow culverts, evapotranspiration, linear seepage under the berms and levees, and aerial seepage down and out (discharge) and up and into (recharge) the treatment cells. **Table 3** summarizes the initial water budget results for each of the three treatment cells and in combination for the six operational 12-week periods. That same table compares these results to the flows from the S-6 pump station, which is the predominant source of water passing through STA-2, and those for the G-335 pump station, through which flows the collective discharges from all three treatment cells. As can be readily ascertained by a scrutiny of these results, there is generally good agreement between the sum of the inflow volumes for the individual treatment cells and the volume of water pumped through S-6 for the same period. However, at the same time, there exists a substantial discrepancy between (1) the inflow and outflow volume of each treatment cell for each 12-week period, which is reflected in the substantial residuals in the initial water budget and (2) the sum of the individual treatment cell inflow volumes or outflow volumes and the corresponding discharge flow volume through the G-335 pump station.

Initial Chloride Budget

Chloride is considered an inert tracer of water movement. Chloride was monitored biweekly at S-6, G-328 just above the point of confluence with the farm runoff culvert, the Cell 1, 2, and 3 outflow culverts at G-330A, G-332, and G-334, and the G-335 outflow pump station. The chloride mass budget was calculated in the same way as the mercury mass budget. **Table 4** summarizes the results of the initial chloride mass budget calculations for each of the six, 12-week operational periods for the study period. The initial chloride budget did not support the water budget, amplifying rather than reducing the magnitude of the substantial discrepancies in the initial water budget.

This suggests one of three things: (1) the chloride concentrations measured at G-328 in the inflow supply canal are unrepresentatively higher than the actual chloride concentrations at the inflow culverts several kilometers downstream; (2) the chloride concentrations measured at the discharge culverts in each of the individual treatment cells are unrepresentatively lower than the actual concentrations discharged through all of the culverts; and/or (3) the chloride tracer is being removed by a transport process unaccounted for in the water or chloride mass budgets.

Regarding the first hypothesis, two things must be taken into consideration. First, because the chloride monitoring occurs upstream of the confluence with a major farm runoff culvert, it is likely that the inflow chloride concentrations are actually higher, not lower than the concentrations being used for the inflow chloride mass transport calculations. This is supported by the observation that the ratio of total inflow chloride budget for the three treatment cells is 145 percent of the chloride discharged through S-6 for the study period. Second, if the inflow chloride concentrations were somehow lower, this would require that the inflow supply canal water be diluted between the G-328 monitoring station and the point of discharge into the three treatment cells. This could occur if there were substantial seepage of subsurface water into the supply canal with a much lower chloride concentrations on average than those that occur in the receiving canal. Based on the work of Harvey et al. (2002), while substantial seepage into the supply canal can occur, it is highly unlikely that the chloride concentrations in the subsurface water were substantially lower than those in the surface water being carried in the canals.

Table 3. Initial STA-2 water budget.

Water Budget Calculations for STA-2

	Flow In [m^3]	Wet [m^3]	Flow Out [m^3]	ET [m^3]	Seep [m^3]	Change Store [m^3]	Residual [m^3]	Residual/ Total Inputs [%]	Residual/ Total Outputs [%]	Inflow/ Out+Seep [%]
Cell 1										
8/14/2002-11/6/2002	1.30E+07	1.97E+06	8.12E+06	2.42E+06	-5.52E+05	6.12E+03	3.84E+06	26	35	150
11/6/2002-1/29/2002	1.85E+07	1.08E+06	1.07E+07	1.75E+06	-5.01E+05	5.58E+03	6.68E+06	34	52	166
1/29/2003-4/23/2003	2.30E+07	1.62E+06	2.01E+07	2.54E+06	-5.68E+05	5.19E+03	1.35E+06	5	6	111
4/23/2003-7/16/2003	2.02E+07	4.34E+06	1.66E+07	2.83E+06	-6.54E+05	5.58E+03	4.42E+06	18	22	117
7/16/2003-10/6/2003	3.99E+07	3.26E+06	3.54E+07	2.46E+06	-6.31E+05	5.50E+03	4.64E+06	11	12	111
10/6/2003-12/29/2003	8.67E+06	9.42E+05	4.09E+06	1.81E+06	-7.59E+05	6.26E+03	2.94E+06	31	44	179
1-YR	8.90E+07	1.04E+07	6.79E+07	1.03E+07	-2.48E+06	1.08E+04	1.86E+07	19	23	126
Study POR	1.23E+08	1.32E+07	9.50E+07	1.38E+07	-3.66E+06	9.38E+03	2.39E+07	18	21	125
Cell 2										
8/14/2002-11/6/2002	8.57E+06	2.20E+06	1.16E+07	2.71E+06	-6.11E+05	4.15E+03	-4.17E+06	-39	-28	70
11/6/2002-1/29/2002	1.11E+07	1.20E+06	9.35E+06	1.96E+06	-5.79E+05	6.41E+03	3.66E+05	3	3	111
1/29/2003-4/23/2003	2.31E+07	1.81E+06	2.53E+07	2.83E+06	-7.14E+05	4.79E+03	-3.92E+06	-16	-14	89
4/23/2003-7/16/2003	3.45E+07	4.84E+06	3.70E+07	3.16E+06	-4.64E+05	1.02E+03	-1.30E+06	-3	-3	92
7/16/2003-10/6/2003	4.59E+07	3.64E+06	5.29E+07	2.74E+06	2.86E+05	3.17E+03	-5.78E+06	-12	-10	87
10/6/2003-12/29/2003	3.86E+06	1.05E+06	3.24E+06	2.02E+06	-8.11E+05	2.14E+03	-1.17E+06	-24	-19	95
1-YR	9.57E+07	1.16E+07	1.03E+08	1.15E+07	-2.19E+06	8.20E+03	-9.06E+06	-8	-8	91
Study POR	1.27E+08	1.47E+07	1.39E+08	1.54E+07	-2.89E+06	4.41E+03	-1.59E+07	-11	-10	89
Cell 3										
8/14/2002-11/6/2002	1.46E+07	2.20E+06	1.56E+07	2.71E+06	-1.84E+06	4.83E+05	-3.80E+06	-23	-18	84
11/6/2002-1/29/2002	1.68E+07	1.20E+06	1.65E+07	1.96E+06	-1.86E+06	8.63E+04	-2.34E+06	-13	-11	92
1/29/2003-4/23/2003	2.53E+07	1.81E+06	2.32E+07	2.83E+06	-1.83E+06	######	-5.53E+05	-2	-2	101
4/23/2003-7/16/2003	4.27E+07	4.84E+06	4.14E+07	3.16E+06	-1.95E+06	######	2.66E+06	6	6	98
7/16/2003-10/6/2003	5.78E+07	3.64E+06	5.47E+07	2.74E+06	-2.04E+06	8.74E+05	1.12E+06	2	2	102
10/6/2003-12/29/2003	9.48E+06	1.05E+06	6.03E+06	2.02E+06	-1.87E+06	1.13E+06	-5.07E+05	-5	-5	120
1-YR	1.22E+08	1.16E+07	1.18E+08	1.15E+07	-8.07E+06	######	-2.47E+06	-2	-2	96
Study POR	1.67E+08	1.47E+07	1.57E+08	1.54E+07	-1.14E+07	6.56E+05	-3.42E+06	-2	-2	99

Table 3. Continued.

Water Budget Calculations for STA-2

	Flow In [m^3]	Wet [m^3]	Flow Out [m^3]	ET [m^3]	Seep [m^3]	Change Store [m^3]	Residual [m^3]	Residual/ Total Inputs [%]	Residual/ Total Outputs [%]	Inflow/ Out+Seep [%]
All Cells Combined										
8/14/2002-11/6/2002	3.62E+07	6.37E+06	3.53E+07	7.83E+06	-3.00E+06	4.94E+05	-4.13E+06	-10	-9	94
11/6/2002-1/29/2002	4.64E+07	3.49E+06	3.65E+07	5.66E+06	-2.94E+06	9.83E+04	4.71E+06	9	10	118
1/29/2003-4/23/2003	7.14E+07	5.25E+06	6.86E+07	8.21E+06	-3.11E+06	######	-3.12E+06	-4	-4	100
4/23/2003-7/16/2003	9.73E+07	1.40E+07	9.51E+07	9.15E+06	-3.07E+06	######	5.79E+06	5	5	99
7/16/2003-10/6/2003	1.44E+08	1.05E+07	1.43E+08	7.94E+06	-2.39E+06	8.82E+05	-2.62E+04	0	0	99
10/6/2003-12/29/2003	2.20E+07	3.04E+06	1.34E+07	5.85E+06	-3.44E+06	1.13E+06	1.27E+06	5	5	131
1-YR	3.07E+08	3.35E+07	2.89E+08	3.34E+07	-1.27E+07	######	7.11E+06	2	2	102
Study POR	4.17E+08	4.27E+07	3.92E+08	4.46E+07	-1.79E+07	6.70E+05	4.53E+06	1	1	102

	Cell Inflow as % of Total Inflow			Cell Outflow as % of Total Outflow		
	Cell 1	Cell 2	Cell 3	Cell 1	Cell 2	Cell 3
8/14/2002-11/6/2002	3.59E+01	2.37E+01	4.04E+01	2.30E+01	3.29E+01	4.41E+01
11/6/2002-1/29/2002	3.99E+01	2.38E+01	3.63E+01	2.92E+01	2.56E+01	4.52E+01
1/29/2003-4/23/2003	3.22E+01	3.24E+01	3.54E+01	2.93E+01	3.69E+01	3.38E+01
4/23/2003-7/16/2003	2.07E+01	3.54E+01	4.38E+01	1.75E+01	3.89E+01	4.36E+01
7/16/2003-10/6/2003	2.78E+01	3.20E+01	4.03E+01	2.48E+01	3.70E+01	3.83E+01
10/6/2003-12/29/2003	3.94E+01	1.75E+01	4.31E+01	3.06E+01	2.43E+01	4.51E+01
1-YR	2.90E+01	3.12E+01	3.98E+01	2.35E+01	3.55E+01	4.10E+01
Study POR	2.95E+01	3.05E+01	4.00E+01	2.42E+01	3.56E+01	4.02E+01

Water Budget Calculations for STA-2

	S-6 [m^3]	G-335 [m^3]	Tot. In/ S-6 [%]	Tot. Out/ S-6 [%]	Tot. In/ G-335 [%]	Tot. Out/ G-335 [%]	Tot. Resid./ G-335 [%]	Outf+Seep+ Resid./G-335 [%]
8/14/2002-11/6/2002	4.69E+07	4.96E+07	7.71E+01	7.54E+01	7.30E+01	7.13E+01	-8.81E+00	6.55E+01
11/6/2002-1/29/2002	5.09E+07	5.19E+07	9.11E+01	7.16E+01	8.94E+01	7.03E+01	9.25E+00	8.07E+01
1/29/2003-4/23/2003	7.31E+07	8.59E+07	9.76E+01	9.38E+01	8.31E+01	7.99E+01	-4.27E+00	8.98E+01
4/23/2003-7/16/2003	9.81E+07	1.20E+08	9.92E+01	9.69E+01	8.14E+01	7.95E+01	5.90E+00	1.05E+02
7/16/2003-10/6/2003	1.42E+08	1.65E+08	1.01E+02	1.01E+02	8.70E+01	8.66E+01	-1.85E-02	1.00E+02
10/6/2003-12/29/2003	2.07E+07	1.76E+07	1.06E+02	6.45E+01	1.25E+02	7.58E+01	6.14E+00	6.51E+01
1-YR	3.23E+08	3.68E+08	9.50E+01	8.96E+01	8.33E+01	1.14E+02	2.20E+00	9.24E+01
Study POR	4.32E+08	4.90E+08	9.65E+01	9.07E+01	8.51E+01	1.13E+02	1.05E+00	9.16E+01

Table 4. Initial STA-2 chloride mass budget.

CL Mass Budget Calculations for STA-2

	In [g]	Rain [g]	Out [g]	Seep [g]	Change Store [g]	Residual	Resid./ Tot. Inputs [%]	Resid./ Tot. Outputs [%]	Inflow/ Out+Seep [%]
Cell 1									
8/14/2002-11/6/2002	2.42E+09	3.90E+06	1.44E+09	-1.06E+08	3.49E+08	5.33E+08	22	28	157
11/6/2002-1/29/2002	3.53E+09	2.13E+06	1.74E+09	-8.71E+07	-3.03E+07	1.74E+09	49	97	193
1/29/2003-4/23/2003	5.70E+09	3.21E+06	3.25E+09	-9.12E+07	-5.70E+07	2.42E+09	42	74	171
4/23/2003-7/16/2003	4.77E+09	8.57E+06	2.40E+09	-1.02E+08	2.83E+08	1.99E+09	42	71	190
7/16/2003-10/6/2003	1.18E+10	6.44E+06	6.25E+09	-1.30E+08	2.89E+07	5.35E+09	45	83	184
10/6/2003-12/29/2003	2.22E+09	1.86E+06	8.64E+08	-1.69E+08	-1.16E+08	1.31E+09	59	142	215
1-YR	1.99E+10	2.05E+07	1.09E+10	-4.24E+08	7.44E+08	7.86E+09	39	65	176
Study POR	3.04E+10	2.61E+07	1.60E+10	-6.85E+08	4.57E+08	1.33E+10	44	78	183
Cell 2									
8/14/2002-11/6/2002	1.44E+09	4.35E+06	4.70E+08	-1.15E+08	4.17E+08	4.39E+08	30	44	246
11/6/2002-1/29/2002	1.86E+09	2.38E+06	3.45E+08	-1.08E+08	-5.53E+08	1.97E+09	105	-2009	411
1/29/2003-4/23/2003	5.57E+09	3.58E+06	3.50E+08	-1.13E+08	-9.13E+07	5.20E+09	93	1386	1203
4/23/2003-7/16/2003	7.84E+09	9.56E+06	4.35E+08	-6.96E+07	5.97E+08	6.74E+09	86	607	1552
7/16/2003-10/6/2003	1.32E+10	7.18E+06	4.81E+08	5.49E+07	3.01E+08	1.25E+10	95	1705	3105
10/6/2003-12/29/2003	9.99E+08	2.08E+06	4.12E+08	-1.80E+08	-1.64E+08	5.73E+08	57	133	169
1-YR	2.12E+10	2.29E+07	1.75E+09	-3.71E+08	5.35E+08	1.85E+10	87	692	999
Study POR	3.09E+10	2.91E+07	2.49E+09	-5.30E+08	5.06E+08	2.74E+10	89	771	1023
Cell 3									
8/14/2002-11/6/2002	2.59E+09	4.35E+06	5.02E+08	-3.59E+08	1.52E+08	1.58E+09	61	156	301
11/6/2002-1/29/2002	2.98E+09	2.38E+06	3.85E+08	-3.55E+08	-4.79E+08	2.73E+09	91	1037	403
1/29/2003-4/23/2003	6.08E+09	3.58E+06	4.32E+08	-2.88E+08	1.96E+07	5.34E+09	88	719	844
4/23/2003-7/16/2003	9.74E+09	9.56E+06	4.32E+08	-3.08E+08	2.38E+07	8.99E+09	92	1162	1317
7/16/2003-10/6/2003	1.68E+10	7.18E+06	4.94E+08	-4.40E+08	4.03E+08	1.54E+10	92	1148	1795
10/6/2003-12/29/2003	2.50E+09	2.08E+06	4.31E+08	-4.14E+08	1.17E+08	1.54E+09	62	160	296
1-YR	2.69E+10	2.29E+07	1.91E+09	-1.43E+09	-3.32E+08	2.39E+10	89	789	806
Study POR	4.07E+10	2.91E+07	2.68E+09	-2.16E+09	2.36E+08	3.56E+10	88	698	840

Table 4. Continued.

CL Mass Budget Calculations for STA-2

	In [g]	Rain [g]	Out [g]	Seep [g]	Change Store [g]	Residual	Resid./ Tot. Inputs [%]	Resid./ Tot. Outputs [%]
Combined								
8/14/2002-11/6/2002	6.45E+09	1.26E+07	2.41E+09	-5.81E+08	9.17E+08	2.56E+09	40	65
11/6/2002-1/29/2002	8.38E+09	6.89E+06	2.47E+09	-5.50E+08	-1.06E+09	6.43E+09	77	327
1/29/2003-4/23/2003	1.73E+10	1.04E+07	4.03E+09	-4.92E+08	-1.29E+08	1.30E+10	75	294
4/23/2003-7/16/2003	2.23E+10	2.77E+07	3.27E+09	-4.80E+08	9.03E+08	1.77E+10	79	379
7/16/2003-10/6/2003	4.17E+10	2.08E+07	7.23E+09	-5.14E+08	7.33E+08	3.33E+10	80	392
10/6/2003-12/29/2003	5.72E+09	6.01E+06	1.71E+09	-7.63E+08	-1.63E+08	3.42E+09	60	148
1-YR	6.80E+10	6.62E+07	1.46E+10	-2.23E+09	9.47E+08	5.03E+10	74	282
Study POR	1.02E+11	8.44E+07	2.11E+10	-3.38E+09	1.20E+09	7.64E+10	75	296

	Cell Inflow as % of Total Inflow			Cell Outflow as % of Total Outflow		
	Cell 1	Cell 2	Cell 3	Cell 1	Cell 2	Cell 3
8/14/2002-11/6/2002	3.76E+01	2.23E+01	4.02E+01	5.97E+01	1.95E+01	21
11/6/2002-1/29/2002	4.22E+01	2.22E+01	3.56E+01	7.04E+01	1.40E+01	16
1/29/2003-4/23/2003	3.29E+01	3.21E+01	3.50E+01	8.06E+01	8.68E+00	11
4/23/2003-7/16/2003	2.13E+01	3.51E+01	4.36E+01	7.35E+01	1.33E+01	13
7/16/2003-10/6/2003	2.82E+01	3.17E+01	4.01E+01	8.65E+01	6.66E+00	7
10/6/2003-12/29/2003	3.88E+01	1.75E+01	4.37E+01	5.06E+01	2.41E+01	25
1 YR	2.93E+01	3.11E+01	3.95E+01	7.49E+01	1.20E+01	13
POR	2.98E+01	3.03E+01	3.99E+01	7.55E+01	1.18E+01	13

CL Mass Budget Calculations for STA-2

	S-6	G-335	Total In/ S-6 [%]	Total Out/ S-6 [%]	Total In/ G-335 [%]	Total Out/ G-335 [%]	Tot. Resid G-335 [%]	Out+Resid., G-335 [%]	Out+Seep+ Resid./G-335 [%]
8/14/2002-11/6/2002	7.17E+09	8.53E+09	8.99E+01	3.36E+01	7.57E+01	2.83E+01	3.56E+01	58	65
11/6/2002-1/29/2002	7.03E+09	9.26E+09	1.19E+02	3.52E+01	9.04E+01	2.67E+01	9.15E+01	96	102
1/29/2003-4/23/2003	9.95E+09	1.30E+10	1.74E+02	4.05E+01	1.33E+02	3.09E+01	1.30E+02	130	134
4/23/2003-7/16/2003	1.32E+10	1.69E+10	1.70E+02	2.48E+01	1.32E+02	1.93E+01	1.35E+02	124	127
7/16/2003-10/6/2003	2.91E+10	2.94E+10	1.44E+02	2.49E+01	1.42E+02	2.46E+01	1.14E+02	138	139
10/6/2003-12/29/2003	4.00E+09	3.63E+09	1.43E+02	4.27E+01	1.58E+02	4.71E+01	8.55E+01	141	162
1 YR	4.74E+10	5.85E+10	1.43E+02	3.08E+01	1.16E+02	1.23E+02	1.06E+02	111	115
POR	7.04E+10	8.08E+10	1.45E+02	3.00E+01	1.26E+02	1.15E+02	1.09E+02	121	125

Regarding the second hypothesis, if rain exceeded ET by more than allowed for in the water budget, then the interior and outflow concentrations would be more diluted than the inflow concentrations, but the net flow of water out of each of the treatment cells would have to be correspondingly higher, unless the seepage is also correspondingly higher. Due to the way ET is calculated, however, the effect would have to be uniform across all three treatment cells, but this does not appear to be the case. To complicate the interpretation, based on the differences in topography and water levels, the seepage discrepancy is unlikely to be uniform across cells, so until the correction is made for the differential discrepancy in the seepage term, it is not possible to evaluate whether the effect of rainfall dilution is being systematically underestimated.

The second hypothesis could also be valid if rain water were ponding in low areas, then overflowing and being routed preferentially to the outflows or ponding near the outflows themselves without completely mixing with the interior surface water prior to discharge. Under such circumstances, the outflow chloride concentrations in each cell would be unrepresentatively low, as would the estimate of the discharged chloride loads based on those concentrations.

As indicated in **Tables 5A** through **5D**, there is a weak inverse correlation between the chloride concentration at the outflow culverts lagged for zero, fourteen, twenty-eight, or forty-two days and the sum antecedent rain depth for seven ($r = -0.437$), fourteen ($r = -0.215$), twenty-eight days ($r = -0.074$), and forty-two days ($r = 0.221$). This same pattern is followed with average antecedent water depth ($r = -0.430$, -0.346, -0.277, and -0.156), but the strength of the correlations diminish at a slower rate with lag time than with the sum of the antecedent rain depth.

Regarding the third hypothesis, this would require that a substantial pathway of water transport was not being accounted for in the water budget. This hypothesis is supported by the large residual for each 12-week period for each treatment cell. Since seepage is the most uncertain of all of the terms in the water budget, the most likely explanation is the substantial underestimate of seepage in each of the three cells. The assumption that the residual in the water budget is the seepage term is also the standard convention when ET has been measured or estimated with acceptable uncertainty (W. Abtew, SFWMD, personal communication).

Revised Water Budget

Based on the above-identified substantial discrepancies in the initial water volume and chloride mass budgets for the individual treatment cells in STA-2, the decision was made to add the residual term to the most uncertain term in the water budget, the seepage term, to determine if this would result in a substantial reduction in these discrepancies. This became the revised water budget for STA-2. **Table 6** summarizes the revised water budget results for the six, 12-week operational periods. A brief review of the results suggests that a substantial reduction has occurred in the above discrepancies for all three cells, as evidenced by the reduction in the ratio of inflow to the sum of the outflow and revised seepage terms. The greatest discrepancy was in Cell 1, and the ratio in the revised water budget has decreased from roughly 125 percent for the study period to roughly 105 percent. This suggests that there is substantial underseepage unrelated to levee underseepage, either directly into the discharge collection canal or indirectly via the seepage collection canal on the western boundary of the project. This would be consistent with the way the discharge canal is operated, with periods of extended drawdown during pumping, maximizing the head difference between the individual treatment cells and the discharge collection canal, albeit only for the period of time required to refill with all water sources. Unfortunately, the volume of seepage collected by the seepage collection canal on the western boundary of STA-2 is not monitored independently, so there is no way to determine the

Table 5A. Intra-correlation analysis with inflow, interior, and outflow chloride concentrations and inter-correlation analysis with hydraulic parameters: antecedent seven-day average rain and water depths with 0 days lag.

LAG-0 DAYS	RAIN DEPTH	CELL 1 DEPTH	G-328B	C1AA	C1BB	C1CC	G-330A	G-335
RAIN DEPTH	1.000	0.079	-0.012	-0.489	-0.480	-0.659	-0.447	-0.439
CELL 1 DEPTH	0.079	1.000	0.205	-0.178	-0.279	-0.468	-0.483	-0.480
G-328B	-0.012	0.205	1.000	0.441	0.480	0.080	-0.047	0.031
C1AA	-0.489	-0.178	0.441	1.000	0.842	0.654	0.457	0.672
C1BB	-0.480	-0.279	0.480	0.842	1.000	0.754	0.683	0.831
C1CC	-0.659	-0.468	0.080	0.654	0.754	1.000	0.908	0.874
G-330A	-0.447	-0.483	-0.047	0.457	0.683	0.908	1.000	0.837
G-335	-0.439	-0.480	0.031	0.672	0.831	0.874	0.837	1.000

Table 5B. Intra-correlation analysis with inflow, interior, and outflow chloride concentrations and inter-correlation analysis with hydraulic parameters: antecedent 14-day average rain and water depths with 14 days lag.

LAG-14 DAYS	RAIN DEPTH	CELL 1 DEPTH	G-328B	C1AA	C1BB	C1CC	G-330A	G-335
RAIN DEPTH	0.050	0.033	0.059	0.201	0.137	-0.103	-0.215	-0.334
CELL 1 DEPTH	0.053	0.965	0.259	0.082	0.007	-0.147	-0.307	-0.476
G-328B	-0.312	0.136	0.572	0.687	0.462	0.282	0.186	0.292
C1AA	-0.598	-0.390	-0.001	#DIV/0!	#DIV/0!	#DIV/0!	0.899	0.895
C1BB	-0.448	-0.298	0.192	#DIV/0!	#DIV/0!	#DIV/0!	0.603	0.898
C1CC	-0.559	-0.445	-0.241	#DIV/0!	#DIV/0!	#DIV/0!	0.475	0.628
G-330A	-0.217	-0.367	-0.198	0.187	0.488	0.744	0.541	0.582
G-335	-0.213	-0.528	-0.110	0.478	0.608	0.867	0.615	0.735

Table 5C. Intra-correlation analysis with inflow, interior, and outflow chloride concentrations and inter-correlation analysis with hydraulic parameters: antecedent 28-day average rain and water depths with 28 days lag.

LAG-28 DAYS	RAIN DEPTH	CELL 1 DEPTH	G-328B	C1AA	C1BB	C1CC	G-330A	G-335
RAIN DEPTH	0.361	0.062	0.027	-0.137	-0.091	-0.384	-0.074	-0.268
CELL 1 DEPTH	-0.072	0.939	0.280	-0.005	-0.080	-0.153	-0.260	-0.449
G-328B	-0.373	0.039	0.302	0.588	0.590	0.630	0.579	0.375
C1AA	-0.687	-0.644	-0.134	0.407	0.538	0.837	0.806	0.659
C1BB	-0.527	-0.516	-0.041	0.604	0.533	0.762	0.541	0.557
C1CC	-0.495	-0.668	-0.285	0.199	0.247	0.365	0.212	0.269
G-330A	-0.172	-0.350	-0.252	0.082	0.019	0.221	0.076	0.259
G-335	-0.191	-0.549	-0.247	0.214	0.118	0.415	0.294	0.470

Table 5D. Intra-correlation analysis with inflow, interior, and outflow chloride concentrations and inter-correlation analysis with hydraulic parameters: antecedent 42-day average rain and water depths with 42 days lag.

LAG-42 DAYS	RAIN DEPTH	CELL 1 DEPTH	G-328B	C1AA	C1BB	C1CC	G-330A	G-335
RAIN DEPTH	0.248	0.117	-0.059	0.087	-0.028	0.181	0.221	-0.108
CELL 1 DEPTH	-0.124	0.908	0.266	0.005	-0.087	-0.089	-0.159	-0.381
G-328B	-0.379	-0.019	0.158	0.096	0.239	0.516	0.471	0.268
C1AA	-0.624	-0.282	-0.244	#DIV/0!	#DIV/0!	#DIV/0!	0.260	0.429
C1BB	-0.598	-0.383	-0.244	#DIV/0!	#DIV/0!	#DIV/0!	0.545	0.551
C1CC	-0.380	-0.070	0.097	#DIV/0!	#DIV/0!	#DIV/0!	0.165	0.209
G-330A	-0.189	-0.315	-0.038	0.070	0.099	-0.013	0.026	0.098
G-335	-0.061	-0.573	-0.275	0.244	0.261	0.185	0.222	0.268

Table 6. Revised STA-2 water budget based on the assumption that all of the residual is seepage.

Water Budget Calculations for STA-2

	Flow In [m^3]	Wet [m^3]	Flow Out [m^3]	ET [m^3]	Seep [m^3]	Change Store [m^3]	Residual [m^3]	Resid./ Tot. Inputs [%]	Resid./ Tot. Outputs [%]	Inflow/ Out+See [%]
Cell 1										
8/14/2002-11/6/2002	1.30E+07	1.97E+06	8.12E+06	2.42E+06	-2.37E+06	2.03E+06	6.05E-09	0	0	124
11/6/2002-1/29/2002	1.85E+07	1.08E+06	1.07E+07	1.75E+06	-6.55E+06	6.36E+05	-2.33E-09	0	0	108
1/29/2003-4/23/2003	2.30E+07	1.62E+06	2.01E+07	2.54E+06	-2.45E+06	-5.35E+05	5.12E-09	0	0	102
4/23/2003-7/16/2003	2.02E+07	4.34E+06	1.66E+07	2.83E+06	-3.94E+06	1.15E+06	0.00E+00	0	0	98
7/16/2003-10/6/2003	3.99E+07	3.26E+06	3.54E+07	2.46E+06	-6.02E+06	-7.39E+05	2.65E-08	0	0	96
10/6/2003-12/29/2003	8.67E+06	9.42E+05	4.09E+06	1.81E+06	-4.05E+06	-3.44E+05	-4.66E-10	0	0	106
1-YR	8.90E+07	1.04E+07	6.79E+07	1.03E+07	-1.72E+07	3.95E+06	2.61E-08	0	0	105
Study POR	1.23E+08	1.32E+07	9.50E+07	1.38E+07	-2.54E+07	2.20E+06	-2.37E-08	0	0	102
Cell 2										
8/14/2002-11/6/2002	8.57E+06	2.20E+06	1.16E+07	2.71E+06	5.69E+06	2.14E+06	-6.05E-09	0	0	145
11/6/2002-1/29/2002	1.11E+07	1.20E+06	9.35E+06	1.96E+06	-1.57E+06	-6.23E+05	3.03E-09	0	0	101
1/29/2003-4/23/2003	2.31E+07	1.81E+06	2.53E+07	2.83E+06	2.31E+06	-8.84E+05	6.05E-09	0	0	101
4/23/2003-7/16/2003	3.45E+07	4.84E+06	3.70E+07	3.16E+06	3.12E+06	2.29E+06	0.00E+00	0	0	102
7/16/2003-10/6/2003	4.59E+07	3.64E+06	5.29E+07	2.74E+06	5.71E+06	-3.58E+05	-4.66E-09	0	0	97
10/6/2003-12/29/2003	3.86E+06	1.05E+06	3.24E+06	2.02E+06	-1.57E+05	-5.08E+05	1.75E-09	0	0	114
1-YR	9.57E+07	1.16E+07	1.03E+08	1.15E+07	9.86E+06	2.99E+06	1.77E-08	0	0	103
Study POR	1.27E+08	1.47E+07	1.39E+08	1.54E+07	1.51E+07	2.05E+06	-3.17E-08	0	0	102
Cell 3										
8/14/2002-11/6/2002	1.46E+07	2.20E+06	1.56E+07	2.71E+06	1.97E+06	4.83E+05	3.03E-09	0	0	107
11/6/2002-1/29/2002	1.68E+07	1.20E+06	1.65E+07	1.96E+06	4.79E+05	8.63E+04	-4.42E-09	0	0	105
1/29/2003-4/23/2003	2.53E+07	1.81E+06	2.32E+07	2.83E+06	-1.27E+06	-1.85E+05	-1.28E-08	0	0	103
4/23/2003-7/16/2003	4.27E+07	4.84E+06	4.14E+07	3.16E+06	-4.61E+06	-1.73E+06	2.10E-08	0	0	93
7/16/2003-10/6/2003	5.78E+07	3.64E+06	5.47E+07	2.74E+06	-3.16E+06	8.74E+05	1.30E-08	0	0	100
10/6/2003-12/29/2003	9.48E+06	1.05E+06	6.03E+06	2.02E+06	-1.36E+06	1.13E+06	4.19E-09	0	0	128
1-YR	1.22E+08	1.16E+07	1.18E+08	1.15E+07	-5.61E+06	-2.06E+06	-1.21E-08	0	0	98
Study POR	1.67E+08	1.47E+07	1.57E+08	1.54E+07	-7.96E+06	6.56E+05	7.36E-08	0	0	101

volume of direct underseepage by comparing the sum of the individual cell outflow volumes to the G-335 pump flow less the seepage return flow. Nevertheless, the revised water budget's substantial reduction in the discrepancy between the G-335 outflow volume and the sum of the individual treatment cell outflow volumes plus the sum of the revised seepage terms suggests that the uncertainties in the calculated inflow and outflow volumes are acceptable.

When the water depth and flows are averaged over 28-day periods and the zero-flow conditions are omitted, the effective hydraulic retention time (HRT) for STA-2 Cell 1, calculated as the effective water volume divided by the outflow ranges between 14 and 56 days. Whether these calculated values are representative of Cell 1 conditions must be evaluated independently via the chloride budget analysis.

Revised Chloride Budget

Table 7 summarizes the revised chloride budget. For Cell 1, the chloride budget discrepancy is also decreased using the revised water budget, with the ratio of inflow to the sum of the pump flow and the revised seepage flow decreasing from 185 percent to 145 percent. However, unlike the revised water budget, the revised chloride budget exacerbates the Cell 2 discrepancies for the study period by an order of magnitude and those of the individual 12-week periods by several orders of magnitude, while increasing those in Cell 3 for the study period from 840 percent to 960 percent. For the three treatment cells combined, there is virtually no change. Now the self-consistency of the revised water budget can be improved by assuming that the residual term is the seepage term, but substantial discrepancies can remain in the chloride mass budget if the chloride concentrations being applied to the revised seepage term are incorrect.

Table 7. Revised STA-2 chloride mass budget based on revised water budget.

CL Mass Budget Calculations for STA-2

	In [g]	Rain [g]	Out [g]	Seep [g]	Change Store [g]	Residual	Resid./ Tot. Inputs [%]	Resid./ Tot. Outputs [%]	Inflow/ Out+Seep [%]
Cell 1									
8/14/2002-11/6/2002	2.42E+09	3.90E+06	1.44E+09	-4.64E+08	3.49E+08	1.76E+08	7	8	127
11/6/2002-1/29/2002	3.53E+09	2.13E+06	1.74E+09	-1.17E+09	-3.03E+07	6.60E+08	19	23	122
1/29/2003-4/23/2003	5.70E+09	3.21E+06	3.25E+09	-3.81E+08	-5.70E+07	2.13E+09	37	60	157
4/23/2003-7/16/2003	4.77E+09	8.57E+06	2.40E+09	-6.33E+08	2.83E+08	1.46E+09	31	44	157
7/16/2003-10/6/2003	1.18E+10	6.44E+06	6.25E+09	-1.23E+09	2.89E+07	4.24E+09	36	56	157
10/6/2003-12/29/2003	2.22E+09	1.86E+06	8.64E+08	-8.94E+08	-1.16E+08	5.82E+08	26	35	126
1-YR	1.99E+10	2.05E+07	1.09E+10	-2.99E+09	7.44E+08	5.30E+09	27	36	143
Study POR	3.04E+10	2.61E+07	1.60E+10	-4.77E+09	4.57E+08	9.25E+09	30	44	147
Cell 2									
8/14/2002-11/6/2002	1.44E+09	4.35E+06	4.70E+08	1.04E+09	4.17E+08	1.59E+09	110	-1104	-254
11/6/2002-1/29/2002	1.86E+09	2.38E+06	3.45E+08	-2.74E+08	-5.53E+08	1.80E+09	96	2628	301
1/29/2003-4/23/2003	5.57E+09	3.58E+06	3.50E+08	2.95E+08	-9.13E+07	5.61E+09	101	-17190	10093
4/23/2003-7/16/2003	7.84E+09	9.56E+06	4.35E+08	5.24E+08	5.97E+08	7.34E+09	94	1417	-8850
7/16/2003-10/6/2003	1.32E+10	7.18E+06	4.81E+08	1.20E+09	3.01E+08	1.37E+10	103	-3357	-1852
10/6/2003-12/29/2003	9.99E+08	2.08E+06	4.12E+08	-5.34E+07	-1.64E+08	6.99E+08	70	230	215
1-YR	2.12E+10	2.29E+07	1.75E+09	1.66E+09	5.35E+08	2.06E+10	97	3160	22666
Study POR	3.09E+10	2.91E+07	2.49E+09	2.72E+09	5.06E+08	3.07E+10	99	10006	-13527
Cell 3									
8/14/2002-11/6/2002	2.59E+09	4.35E+06	5.02E+08	3.25E+08	1.52E+08	2.27E+09	87	682	1470
11/6/2002-1/29/2002	2.98E+09	2.38E+06	3.85E+08	7.57E+07	-4.79E+08	3.16E+09	106	-1880	965
1/29/2003-4/23/2003	6.08E+09	3.58E+06	4.32E+08	-2.70E+08	1.96E+07	5.36E+09	88	739	866
4/23/2003-7/16/2003	9.74E+09	9.56E+06	4.32E+08	-7.48E+08	2.38E+07	8.55E+09	88	704	825
7/16/2003-10/6/2003	1.68E+10	7.18E+06	4.94E+08	-6.40E+08	4.03E+08	1.52E+10	91	986	1478
10/6/2003-12/29/2003	2.50E+09	2.08E+06	4.31E+08	-2.97E+08	1.17E+08	1.66E+09	66	196	343
1-YR	2.69E+10	2.29E+07	1.91E+09	-1.05E+09	-3.32E+08	2.43E+10	90	920	911
Study POR	4.07E+10	2.91E+07	2.68E+09	-1.55E+09	2.36E+08	3.62E+10	89	806	961

Table 7. Continued.

CL Mass Budget Calculations for STA-2

	In [g]	Rain [g]	Out [g]	Seep [g]	Change Store [g]	Residual	Resid./ Tot. Inputs [%]	Resid./ Tot. Outputs [%]	Inflow/ Out+Seep [%]
Combined									
8/14/2002-11/6/2002	6.45E+09	1.26E+07	2.41E+09	8.97E+08	9.17E+08	4.03E+09	62	165	426
11/6/2002-1/29/2002	8.38E+09	6.89E+06	2.47E+09	-1.36E+09	-1.06E+09	5.62E+09	67	202	219
1/29/2003-4/23/2003	1.73E+10	1.04E+07	4.03E+09	-3.57E+08	-1.29E+08	1.31E+10	75	307	395
4/23/2003-7/16/2003	2.23E+10	2.77E+07	3.27E+09	-8.57E+08	9.03E+08	1.73E+10	78	343	541
7/16/2003-10/6/2003	4.17E+10	2.08E+07	7.23E+09	-6.77E+08	7.33E+08	3.31E+10	79	383	528
10/6/2003-12/29/2003	5.72E+09	6.01E+06	1.71E+09	-1.24E+09	-1.63E+08	2.94E+09	51	105	194
1-YR	6.80E+10	6.62E+07	1.46E+10	-2.37E+09	9.47E+08	5.02E+10	74	279	401
Study POR	1.02E+11	8.44E+07	2.11E+10	-3.60E+09	1.20E+09	7.62E+10	75	293	413

	Cell Inflow as % of Total Inflow			Cell Outflow as % of Total Outflow		
	Cell 1	Cell 2	Cell 3	Cell 1	Cell 2	Cell 3
8/14/2002-11/6/2002	3.76E+01	2.23E+01	4.02E+01	5.97E+01	1.95E+01	21
11/6/2002-1/29/2002	4.22E+01	2.22E+01	3.56E+01	7.04E+01	1.40E+01	16
1/29/2003-4/23/2003	3.29E+01	3.21E+01	3.50E+01	8.06E+01	8.68E+00	11
4/23/2003-7/16/2003	2.13E+01	3.51E+01	4.36E+01	7.35E+01	1.33E+01	13
7/16/2003-10/6/2003	2.82E+01	3.17E+01	4.01E+01	8.65E+01	6.66E+00	7
10/6/2003-12/29/2003	3.88E+01	1.75E+01	4.37E+01	5.06E+01	2.41E+01	25
	2.93E+01	3.11E+01	3.95E+01	7.49E+01	1.20E+01	13
1 YR	2.98E+01	3.03E+01	3.99E+01	7.55E+01	1.18E+01	13
POR						

CL Mass Budget Calculations for STA-2

	S-6	G-335	S-6/ G-335 [%]	Total In/ S-6 [%]	Total Out/ S-6 [%]	Total In/ G-335 [%]	Total Out/ G-335 [%]	Tot. Resid. G-335 [%]	Out+Resid./ G-335 [%]
8/14/2002-11/6/2002	7.17E+09	8.53E+09	8.41E+01	8.99E+01	3.36E+01	7.57E+01	2.83E+01	4.73E+01	76
11/6/2002-1/29/2002	7.03E+09	9.26E+09	7.58E+01	1.19E+02	3.52E+01	9.04E+01	2.67E+01	6.06E+01	87
1/29/2003-4/23/2003	9.95E+09	1.30E+10	7.62E+01	1.74E+02	4.05E+01	1.33E+02	3.09E+01	1.00E+02	131
4/23/2003-7/16/2003	1.32E+10	1.69E+10	7.79E+01	1.70E+02	2.48E+01	1.32E+02	1.93E+01	1.03E+02	122
7/16/2003-10/6/2003	2.91E+10	2.94E+10	9.88E+01	1.44E+02	2.49E+01	1.42E+02	2.46E+01	1.13E+02	137
10/6/2003-12/29/2003	4.00E+09	3.63E+09	1.10E+02	1.43E+02	4.27E+01	1.58E+02	4.71E+01	8.10E+01	128
1 YR	4.74E+10	5.85E+10	8.11E+01	1.43E+02	3.08E+01	1.16E+02	1.23E+02	8.58E+01	111
POR	7.04E+10	8.08E+10	8.71E+01	1.45E+02	3.00E+01	1.26E+02	1.15E+02	9.43E+01	120

POLLUTANT MASS BUDGET CALCULATIONS

The procedures followed here paralleled those applied to the THg and MeHg mass budgets for the ENR Project (Miles and Fink, 1998; SFWMD, 1999b). The mass budget calculations outlined below assume an accurate water budget for the system of interest supplied by others. The water budget for STA-2 is discussed in the preceding section. **Figure 10** illustrates a generalized pollutant mass budget calculation scheme for a natural or constructed aquatic ecosystem

Rain

Because the rain concentration is a weekly integrated average value, the daily rain concentration for each week was assumed to be equal to the weekly value. Wet deposition flux of THg was calculated by multiplying the inferred integrated average daily rainfall THg concentration by the daily rain depth for the same day. The daily rain depth was obtained from the water budget developed by the District for STA-2 using the average values for the gauges at the S-6 and S-7 Pump Stations and S-335. Dry deposition of THg was assumed to be 50 percent (USEPA, 1997; Atkeson et al., 2002) of the average annual wet deposition flux of 22 $\mu g/m^2$-yr (Guentzel et al., 2001) or 11 $\mu g/m^2$-yr. The daily value was calculated by dividing that annual average value by 365.

While THg was analyzed in weekly integrated rain samples collected at STA-2 (FL99), this was not the case for MeHg. However, MeHg was measured in four-week composites of weekly integrated samples at Andytown (FL04) and STA-1W (FL34). An analysis of the available overlapping data indicated that the THg concentration observed at FL99 was about 80 percent of the average of the observed values at FL04 and FL34. Absent better information, the MeHg concentration for FL99 was inferred to be 80 percent of the average of the four-week composite values at FL04 and FL34.

As was the case for MeHg, other constituents of potential interest were not measured in rain collected at FL99. Default concentrations had to be substituted for measured concentrations for these other constituents. To fill the data gaps in the THg and MeHg concentrations in rain for the period prior to the start-up of FL99, it was decided to use the average of the THg and MeHg concentrations measured in weekly and monthly integrated rain samples collected at the District's Everglades Nutrient Removal Project (FL34) at the junction of I-80 and S.R. 12 and the Andytown substation (FL04) of Florida Power and Light at the junction of U.S. 27 and I-75. Prior to switchover to the MDN, monthly integrated samples of rain were collected at the top of the same 48-ft towers and analyzed for a suite of constituents other than THg for two years (1995-1996) as part of the Florida Atmospheric Monitoring Study (FAMS). The average of these values for the two sites for the two-year period was averaged as default values for this application. However, due to the absence of reliable data on dry deposition, dry deposition was assumed insignificant relative to rainfall and inflow contributions. Whether this is an appropriate assumption in the context of the burning of sugar cane fields and enhanced ultra-giant particle (ash) deposition must be addressed elsewhere. The temporally and spatially averaged rain concentration values of the other constituents of interest are set forth in Table 1B in Appendix G.

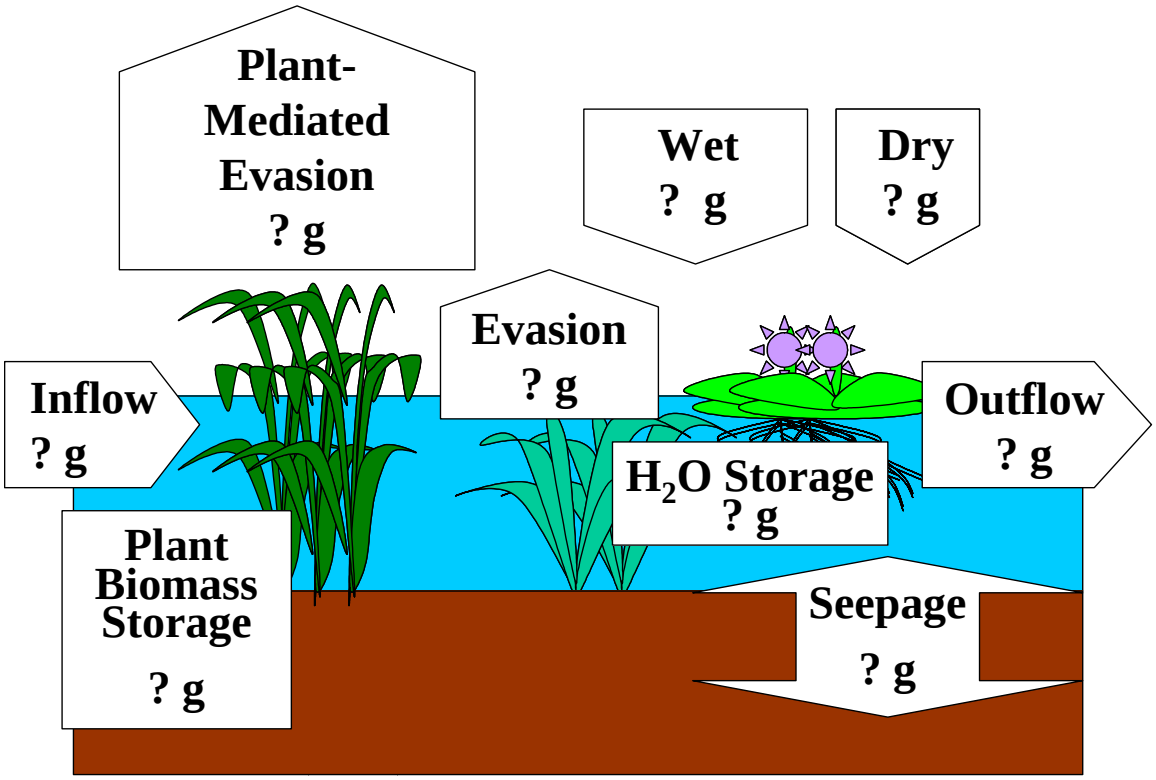

Figure 10. Generalized representation of a pollutant mass budget for a natural or constructed wetland.

Surface Water

Inflow and outflow loads were calculated by multiplying the instantaneous unfiltered THg or MeHg grab sample value for each biweekly period by the total flow volume for that period. Cell 3 change in surface water storage was calculated in three steps. Seepage load was calculated by multiplying the seepage volume by the spatially averaged surface water concentration calculated in the same way as for change in storage. The STA-2 annual evasion flux of elemental mercury Hg(0) was assumed to be approximately the same as that estimated for the ENR Project based on floating chamber measurements conducted by Lindberg and co-workers of the Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN (Lindberg et al. 1999; Lindberg and Zhang, 2000; Lindberg et al., 2002) in the period from 1996–1998. The annual value was then divided by the average interior unfiltered THg concentration of 1.1 ng/L and then 365 to approximate the average daily value. The evasion flux was then calculated by multiplying the daily evasion flux coefficient by the same interior average THg concentration as for the change in storage. More sophisticated approaches involving the two-layer Whitman model of gas diffusion and the calculation of the layer thicknesses from wind velocity, water and air temperatures, and water depth, while perhaps more intellectually satisfying, proved inaccurate in the ENR Project, because the surface water flux was underestimated by about a factor of five for the ENR Project, and, in any case, put a disproportionate effort into quantifying a second-order loss process (SFWMD, 1999b; Lindberg et al., 1999; Lindberg and Zhang, 2000).

These same procedures were followed for the constituents other than THg and MeHg. However, since the formation of volatile forms of these other constituents does not occur to any observable extent under ambient aquatic conditions, the evasion loss pathway was ignored. The exception to this generalization is hydrogen sulfide, which could represent a substantial loss pathway for soil total sulfur or pore water sulfide

Soil/Sediment

Change in surficial sediment storage was calculated by multiplying 0.04 m by the measured bulk density and the observed concentration of THg or MeHg at time t+1 and subtracting from that result the same product at time t. The same procedure was followed for constituents other than THg or MeHg. The pore water contribution to constituent mass storage or change in storage was ignored, because the soil concentrations are generally three to six orders of magnitude higher than the corresponding pore water concentrations.

Vegetation

Vegetation storage of THg or MeHg was calculated for each treatment cell by multiplying the fraction of coverage of each plant species sampled (unitless) by its average density (kg/m^2) and the average wet-weight concentration of THg or MeHg for each plant species collected at the three interior sites. The coverage estimates were made from high-altitude aerial photogrammetry based on a false-color infrared picture taken in November 2003. The coverages were broken down into categories of open water (with and without SAV), open water plus hydrilla and potomogeton, mixed open water and emergents (50/50), emergents, floating macrophytes, and other. Absent a further breakdown by plant species, based on observations by others that sawgrass was the predominant emergent species in STA-2 (W. Larson, SFWMD, personal communication), it was assumed that 50 percent of the emergents was sawgrass, 25 percent was cattail, and 25 percent was various grasses. Because periphyton coverages were not reported, periphyton was assumed to cover 0 percent of the open water, 33 percent of the SAV coverage,

and half of that for the areas covered by 50/50 open water and emergents and the open water/hydrilla and potomogeton complex.

The plant densities were based on random stratified sampling of quadrats laid out at each of the sampling stations. For emergents, 0.25 m^2 quadrats were used, while for the submerged and floating plant species, 0.5 m^2 quadrats were used. All density data were reported on a dry-weight basis. Missing density values from a particular cell were estimated by averaging the values from the other two cells. Since the density of periphyton was not measured during the July 2003 sampling event, it was estimated from the annual average interior TP concentration of 20 µg/L and an exponential empirical relationship between surface water TP concentration and periphyton density derived from data collected along the WCA-2A nutrient gradient (Tetra Tech, 2002; 2003). Missing THg or MeHg concentrations were filled by averaging the concentrations from the other two cells. Since no grasses or floating macrophytes were sampled and analyzed for THg and MeHg during the three, semi-annual sampling events, the grass concentrations were estimated as the average of the cattail and sawgrass concentrations for the same cell and the floating macrophytes were estimated as the average of the SAV and periphyton concentrations. Since the measured THg and MeHg concentrations were reported as wet weight only, the concentrations had to be converted to the equivalent dry weight by dividing the wet weight values by (1-%MOIST/100), where the %MOIST for each plant tissue was supplied by DB Laboratory of Gainesville, Florida.

Fish

The storage of MeHg in fish could not be calculated, because no measurements were taken of standing crop densities of fish by species at any time during the study period, despite the fact that there are proposals for opening STAs for sport fishing. However, an exploratory data analyses conducted for the ENR Project suggest that fish biomass generally accounts for < 5 percent of the storage (SFWMD, 1999b), assuming that the fish densities in the canals are equivalent to the fish densities in the marsh, which should constitute an overestimate rather than an underestimate of the marsh fish densities. This generalization must be caveated with the observation that the ENR Project never experienced a first-flush MeHg anomaly during the period of the fish density study (SFWMD, 1999b), so the concentrations of MeHg in the fish were the low, steady-state concentrations typical of the ENR Project. Because the surface water and soil generally purge themselves of anomalously high THg and MeHg concentrations more rapidly than do large-bodied fish at trophic levels 3 and 4, it is possible that MeHg in fish biomass could be the largest single storage reservoir for several months to several years following a substantial first-flush event. Some have hypothesized that the efficient recycling of first-flush MeHg initially captured and stored in fish biomass is the cause of the persistence of a first-flush effect in some recently created reservoirs – the so-called reservoir effect. Interestingly, a persistent MeHg bioaccumulation problem has not been observed in any of the treatment wetlands constructed in South Florida to date, even in systems that experience substantial first-flush MeHg anomalies, such as STA-2 Cell 1. Perhaps this is because the shallow marshes cannot support either the high fish densities or long food chains required for the capture and storage of a substantial fraction of the first-flush MeHg mass in fish biomass or its efficient recycling thereafter.

CALCULATION OF BIOCONCENTRATION FACTORS

For purposes of this report, the bioconcentration factor is defined as the ratio of the concentration of the pollutant of interest in the bacterium, alga, or macrophyte to its concentration in the medium in which the organism resides. In water, the filtered concentration is often

preferred to the unfiltered concentration, since the pollutant on filterable particles is not considered to be bioavailable for direct bioconcentration across external cell membranes. Uptake by these one-celled organisms can be passive (e.g., adsorption or absorption followed by Fickian diffusion along concentration gradients) and/or active (e.g., transfer mediated by exogenous and/or endogenous transport proteins via cell surface channels established and maintained with free energy supplied by the cell).

The bioaccumulation factor is defined as the ratio of the concentration of the pollutant of interest in herbivores or carnivores to the ratio of its concentration in the medium of interest, taking into account pollutant uptake by all routes. In aquatic organisms bioaccumulation occurs primarily via contact transfer from the medium of interest across external body membranes (e.g., skin, gill) and via contact transfer across the gut membrane from ingested forage species living in that medium and/or contaminated medium ingested incidental to foraging. For filter feeders, it is both the filtered and unfiltered fractions of the pollutant in water that are of interest, so the use of concentrations based on unfiltered samples is by no mean precluded in such calculations. It is only necessary to specify which way the water bioaccumulation factor (BAF) will be calculated. In this study, because filtered water samples predominate for interior water sampling, water BAFs will be calculated based on the filtered water concentration of THg, MeHg or Hg(II), the last of which is calculated by subtracting the MeHg concentration from the THg concentration.

For complex food webs and diverse foraging strategies, the bioaccumulation factor represents the diet fraction weighted average exposure, integrated over the cycling time of the pollutant within the organism. For small, rapidly growing organisms and/or for pollutants that are rapidly excreted, the pollutant body burden represents the weighted average of recent exposure, and the increase or decrease in the pollutant concentration in the organism closely tracks that in the source medium or media. For large, slowly growing organisms and pollutants with long retention times, the accumulated body burden represents the weighted average exposure over a much longer period, and the concentration in the organism at time t is virtually independent of the pollutant concentration of the source medium or media at time t. Instead, one must evaluate the concentration at various antecedent sampling events that represent lag times that are multiples of the media sampling frequencies. So, for example, if surface water is sampled every four weeks and mosquitofish sampled every four weeks one week later, Lag-1 week represents the near-instantaneous bioaccumulation condition, Lag-5 weeks represents the influence of the water concentration collected five weeks ago, etc. Since we do not know *a priori* what the MeHg response and averaging times are for the mosquitofish relative to the concentrations of MeHg in water, soil, or plants, the fish/water BAF, fish/soil SBAF, and the fish/plant PBAF will be calculated for lags, averages, and lag-averages up to six months previously, which is the longest expected life time for a mosquitofish or the turnover time of the population.

The biomagnification factor is the ratio of the concentration of the pollutant of interest in an organism at trophic level T+1 to the concentration in its prey at trophic level T. For complex food webs and diverse foraging strategies, the biomagnification factor represents the diet fraction weighted average exposure, integrated over the cycling time of the pollutant within the organism. When such detailed information about foraging behavior is unavailable or uncertain, one can carry out the required calculation as the ratio of the pollutant concentration in a representative organism at trophic level T to the concentration of the pollutant in a representative organism at trophic level T-1. to Since carbon assimilation efficiency between prey and predator is generally in the range of 10 to 25 percent and the assimilation efficiency of the pollutant between gut membrane and predator is in the range of 75 to 95 percent, the range of pollutant biomagnification factors is generally between 2 to 10 times, with 3 to 5 times per trophic step being typical.

Interior treatment cell plant sampling occurred in September 2002, February 2003, and September 2003. For purposes of calculating the plant bioconcentration factors relative to water (BCF) or soil (SBCF), the concentration of the plant species collected at site X at time t was divided by the concentration in water or soil at time t-t*, where t* is the lag time between the immediately preceding medium sampling event and the plant sampling event. For interior water sampling, the theoretical lag time was no more than three weeks and for interior soil sampling, the theoretical lag was no more than 11 weeks. In practice, the soil sampling lag times for the first, second, and third plant sampling events was 4 weeks, 3 weeks, and 8 weeks, respectively.

Interior mosquitofish sampling occurred every four weeks beginning in August 2002 through January 2004. The water sampling always preceded the mosquitofish sampling by one week and soil sampling by two weeks. The water BAFs will be calculated based on Lag-1, -5, -9 weeks, etc., back 26+1 weeks, the average of the preceding 1+2, 1+2+3, 1+2+3+4, 1+2+3+4+5, and 1+2+3+4+5+6 weeks, and the lag-1 through lag-5 of the average of antecedent weeks 1+2, lag-1 through lag-4 for the antecedent weeks 1+2+3, and so on. The same approach was carried out for soil and vegetation, albeit with appropriately longer lag times and averaging periods, as the monitoring frequencies and sampling start dates allowed.

Unlike mosquitofish, neither sunfish nor bass were collected as part of this study. However, under the routine permit issued for the operation of STA-2, an annual collection of mosquitofish, sunfish, and largemouth bass is required at the common inflow, a representative site in the interior of each independently operated treatment train, and the common outflow. Therefore, the BAF, SBAF, and PBAF, the sunfish/mosquitofish, largemouth bass/mosquitofish, and largemouth bass/sunfish biomagnification factors (BMFs) could be calculated based on lags, averages, and lag-averages, as was the case with the mosquitofish BAFs, SBAFs, and PBAFs. However, because the sunfish typically lives about 2 to 3 years, and bass 3 to 7 years, the sunfish/mosquitofish lags, averages, and lag averages would have to be evaluated up to one year antecedent conditions and the bass up to three year antecedent conditions. For sunfish, this does not create a problem, because the study sampling period extended for more than one year, but for bass this is problematic, because the data would have to be used only from the annual collections that occurred in the fall 2000, 2002, and 2003. Unfortunately, the collection in the fall 2000 followed the first Cell 1 MeHg anomaly in September 2000, and the collection in the fall 2001 occurred about the same time as the second Cell 1 MeHg anomaly, so it would not be clear what the bass were responding to in carrying out the lag, average, and lag-average calculations. Therefore, for the purpose of this report, the bass bioaccumulation and biomagnification factor analyses will be dropped from further consideration.

EXPLORATORY DATA ANALYSIS

There were no hypotheses to test for this study, so there were no data quality objectives for the study in terms of the ability to resolve true differences or trends in media chemistry between sites at the same time or between times at the same site with a specified resolving power and acceptability of Type I and Type II error. Even sample replication was limited to one site in Cell 1 for soil and pore water only, based on the observed excellent precision (< +/- 30 percent) routinely achievable in ultra-trace analyses for THg and MeHg in field replicates of surface water and for THg in field replicates of mosquitofish composite homogenate. Instead, the intent of the study was an objective exploratory analysis of the data to identify factors with an apparent influence on MeHg production and/or bioaccumulation that could explain: (1) the differences in the mercury behaviors of Cells 1, 2, and 3; or (2) the mitigative effect of flow-through operation in allowing Cell 1 to stabilize over time or could lead to the development of even more effective mitigative measures in the future. Ultimately, however, correlation is not causation, and the

cause-effect and operational optimization hypotheses that emerged from these exploratory analyses must then be tested under controlled laboratory conditions in microcosm and semi-controlled field conditions in mesocosm with randomized replication of test apparatus and test conditions and replicate chemical analyses of the test media. That said, there are patterns in the data that deserve the attention of the reader. In what follows we describe and rationalize the selection of the methods and procedures used to extract those patterns from these complex data sets.

For this exercise, the dependent variables of interest were the concentrations of THg as MeHg in mosquitofish, THg and MeHg in surface water, pore water, soil, and vegetation, the percent MeHg in the those media, and the fraction of filtered THg or MeHg in water. Because only filtered pore water was collected for the study, it is not possible to evaluate the fraction dissolved THg or MeHg as a dependent variables for pore water. The independent variables of interest included hydrologic variables (e.g., rain depth, inflow rate, water depth), chemistry variables (e.g., the concentrations of common cations and anions, nutrients, pH, DO, DOC, and TSS) and mass variables (e.g., the rain, inflow, outflow loads and change in soil loads). The potential influences were evaluated as to spatial robustness by aggregating or pooling the data at the STA-2 level as a whole, at the individual cell level, and at the individual station level within each cell using all data collected over the course of the study. Temporal robustness of the influences was evaluated by parsing the data at each spatial scale into wet and dry seasons and then to individual quarters within those seasons. However, the increased spatial and temporal resolution is necessarily purchased at the price of fewer and fewer data in the various subcategories to be analyzed. This necessarily weakens the confidence one has that the apparent influence is real and not the product of a real but unrepresentative combination of parameter values attributable to the small sample size.

Beyond the issue of temporal and spatial scales and aggregation and disaggregation schemes, one must also consider how the structure, function, and throughputs of the system translate a perturbation into a measurable response. Even in a static system that has reached steady state with its perturbing influences, the value of the dependent variable at time t and location s in medium j is likely a response to conditions that existed days, weeks, months, or years ago, depending on the rates and routes of the transport, biogeochemical, and ecological processes and pathways that link the effect, the parameter value at time t and location s in medium j, to the cause, the physical condition, chemical concentration, or chemical mass load, at time t-x and location s-y in medium j-z. For example, hydrologic influences, such as water flow or depth, may have an almost instantaneous effect on the concentration of the limiting nutrient in water via volume dilution, but the response of algae, floating plants, and rooted plants to the change in the limiting nutrient concentration in surface water will be delayed by hours, days, and weeks, respectively, based on the inherent differences in anatomy and physiology and the nutrient transport and biogeochemical process routes and rates in the medium from which nutrients are primarily drawn. Further, the MeHg that bioaccumulates in mosquitofish may have been imported via the treatment cell inflow or produced internally, may have been produced in surficial sediment or in the periphyton mats, and may have been passed from prey to predator via the food chain based in the sediment, which is primarily detritivorous, or via the food chain based in the periphyton mats, which is primarily herbivorous. The cycling, integration, and response times of the ecosystem are different for each of the combinations of these components, processes, and pathways, so the strength of the correlation between the concentration of MeHg in soil paired with the THg in mosquitofish at time t may be weak or negative, while the pairing of the mosquitofish THg concentration with the soil or periphyton MeHg concentration from samples collected four, eight, or sixteen weeks previously may be strong. Moreover, the mosquitofish may be responding to the average and not the instantaneous concentration in the medium of interest four, eight, or sixteen weeks previously.

In systems that have been perturbed far from steady state conditions, as is the case when a treatment cell is dried out for extended periods and then reflooded, the hydrologic, biogeochemical, and ecological dynamics of the reflooded system introduce multiple dimensions of differential cycling, integration, and response times to the already complex milieu of intra-media and inter-media relationships in the steady state system. That being the case, the strength and confidence level in the potential physical, chemical, and ecological influences on MeHg production and bioaccumulation must be taken into consideration by evaluating all possible lag, average and lag-average combinations over a reasonable antecedent period.

This exploratory data analysis was carried out in two phases. In the first phase, univariate linear nonparametric correlation analysis was used to explore the intra-relationships among all variables within each medium and the inter-relationships between all possible combinations of media. In the second phase, multivariate linear parametric regression analysis was carried out on the same paired data sets for the lags, averages, and lag-averages appropriate to the system component and monitoring element. For phases of the exploratory analysis, the strength of the apparent influence of the independent variable(s) on the dependent variable was inferred from the magnitude of the correlation coefficient between the dependent variable and the set of independent variables.

As defined by the Pearson Correlation univariate method of analysis, the strength of association between total and methylmercury concentrations and other measured water quality variables was determined based on the correlation coefficient and P-value results obtained using the Pearson Correlation statistical method. A correlation coefficient near +1 indicates there is a strong positive relationship between the two variables, with both always increasing together. In brief, the correlation coefficient r quantifies the strength of the association between the variables. A correlation coefficient near -1 indicates there is a strong negative relationship between the two variables, with one always decreasing as the other increases. A correlation coefficient of 0 indicates no relationship between the two variables. The P value is the probability of being wrong in concluding that there is a true association between the variables (i.e., the probability of falsely rejecting the null hypothesis, or committing a Type I error). The smaller the P value, the greater the probability that the variables are correlated. For the purposes of this analysis, values of $P < 0.05$ suggested that a statistically significant relationship exists between the various water quality parameters and the total mercury and methylmercury species. To ensure consistency in describing the strength of the correlations, the terminology set forth in **Table 8** will be used.

Table 8. Correlation coefficient characterization – definition of terms.

	Range				
None	0	<	r	<	0.05
Virtually Nonexistent	0.05	<	r	<	0.15
Extremely Weak	0.15	<	r	<	0.25
Very Weak	0.25	<	r	<	0.35
Weak	0.35	<	r	<	0.45
Weak-to-Moderate	0.45	<	r	<	0.55
Moderate	0.55	<	r	<	0.65
Moderate-to Strong	0.65	<	r	<	0.75
Strong	0.75	<	r	<	0.85
Very Strong	0.85	<	r	<	0.95
Extremely Strong	0.95	<	r	<	1

The following subsections describe the methods and procedures used in the exploratory analysis of the data for phases 1 and 2 using appropriate nonparametric and parametric analysis techniques.

Univariate Linear Correlation Analysis

Non-parametric Pearson intra-correlation coefficients, r, and confidence levels, P, were calculated for untransformed and then log-transformed data paired by site and sampling time for water using the Spearman method. The analysis was repeated for pooled sites within each treatment cell and then all three treatment cells. The intra-correlation analysis was then extended to the soil, pore water, and vegetation media. Correlation matrices were constructed to summarize the relationships. The approach was then applied to the inter-correlations between surface water and pore water, soil and pore water, surface water and mosquitofish THg, pore water and mosquitofish THg, soil and mosquitofish THg, and vegetation and mosquitofish THg. The univariate nonparametric analysis of the data described in the preceding were then repeated for various lag, average, and lag-averages of the data for THg, MeHg, %MeHg, or the fraction dissolved MeHg as the dependent variables.

For purposes of pairing the data for the intra- and inter-media correlation analyses, the data were organized such that the date the samples were collected appeared in sequential rows with the various water quality parameters listed in columns. To simplify both the algorithms and the interpretation of the intra-media relationships, data collected on different days for the same medium were shifted such that all of the appeared on the first sampling date for that sampling event. This same approach was applied to the inter-media analyses, such that, for example, the lag-0 mosquitofish THg values collected at week t were paired with surface water data collected at week t-1 and soils at week t-2 and vegetation collected at week t-3, even though the actual time lags were one, two, and three weeks, respectively. To extract information about the effect of delays between perturbing influences and dependent variable responses, the lag-0 analysis was then repeated with successive lag times based on the monitoring frequency of medium of interest. So, for example, in surface water, with a monitoring frequency of four weeks, the lag analysis was carried out for lags -4, -8, -16, weeks and so on up to 52 weeks, while for soils, which were monitored with a 12-week frequency, lags -12, -24, and -48, -60, -72, and -84 weeks were evaluated. The general lag-pairing scheme is illustrated in **Figures 11** and **12**. To extract information about the effect of differences in parameter cycling times and mixing volumes, this approach was then repeated with averaging periods of t and t-1, t-1 + t-2, t-2 + t-3, t-3 + t-4, t-4 + t-5, and t-5 + t-6; t + t-1 + t-2, t-1 + t-2 + t-3, t-2 + t-3 + t-4, t-4 + t-5 + t-6, and so on up to t + t-1 + t-2 + t-3 + t-4 + t-5 + t-6. To extract information about the combined effects of differences in cycling times, mixing volumes, and response delays, the process was repeated for lag-averages. The process was then repeated *in toto* for the log-transformed data.

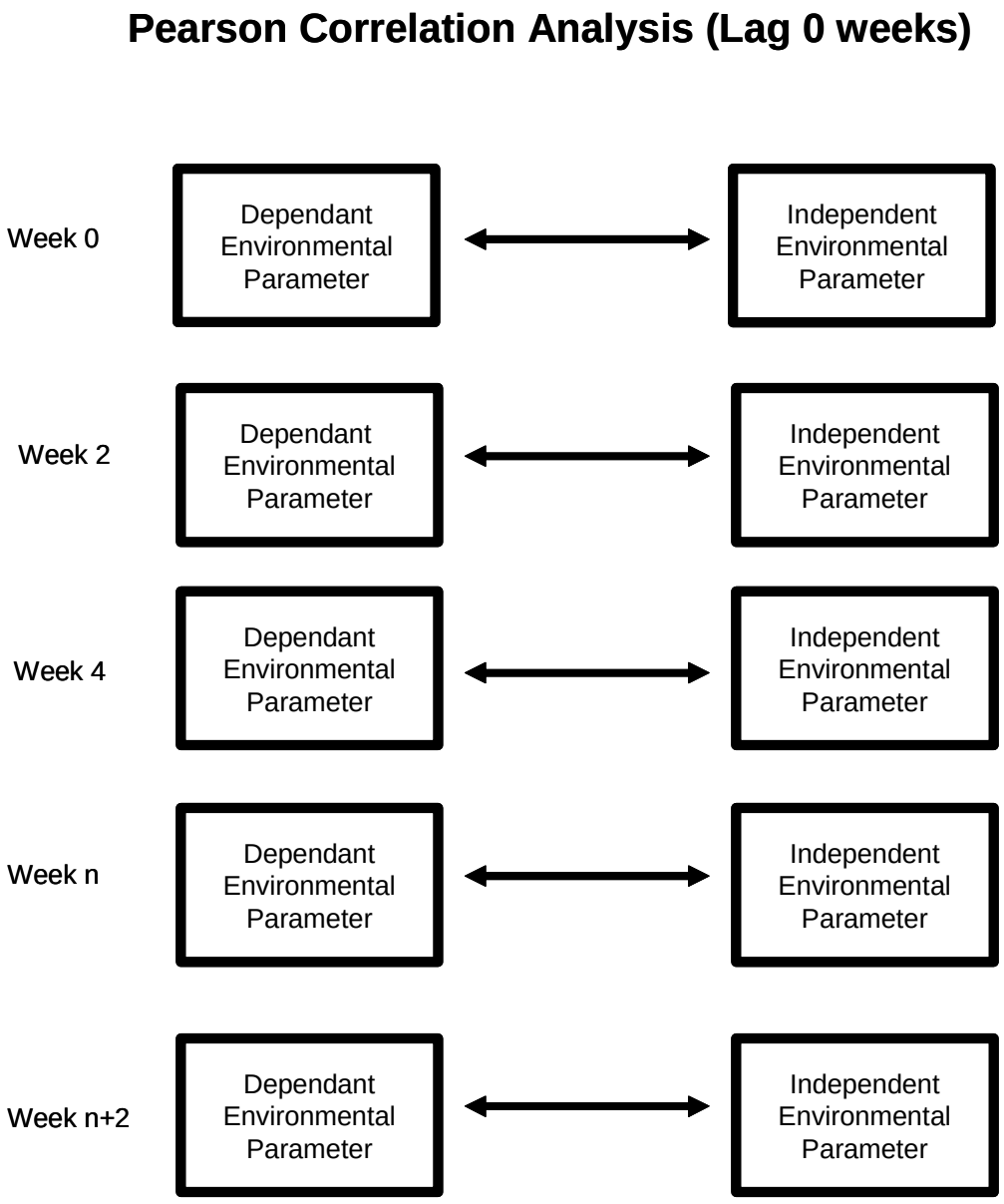

Figure 11. Generalized representation of the data pairing scheme for the lag-correlation statistical analyses for Lag-0.

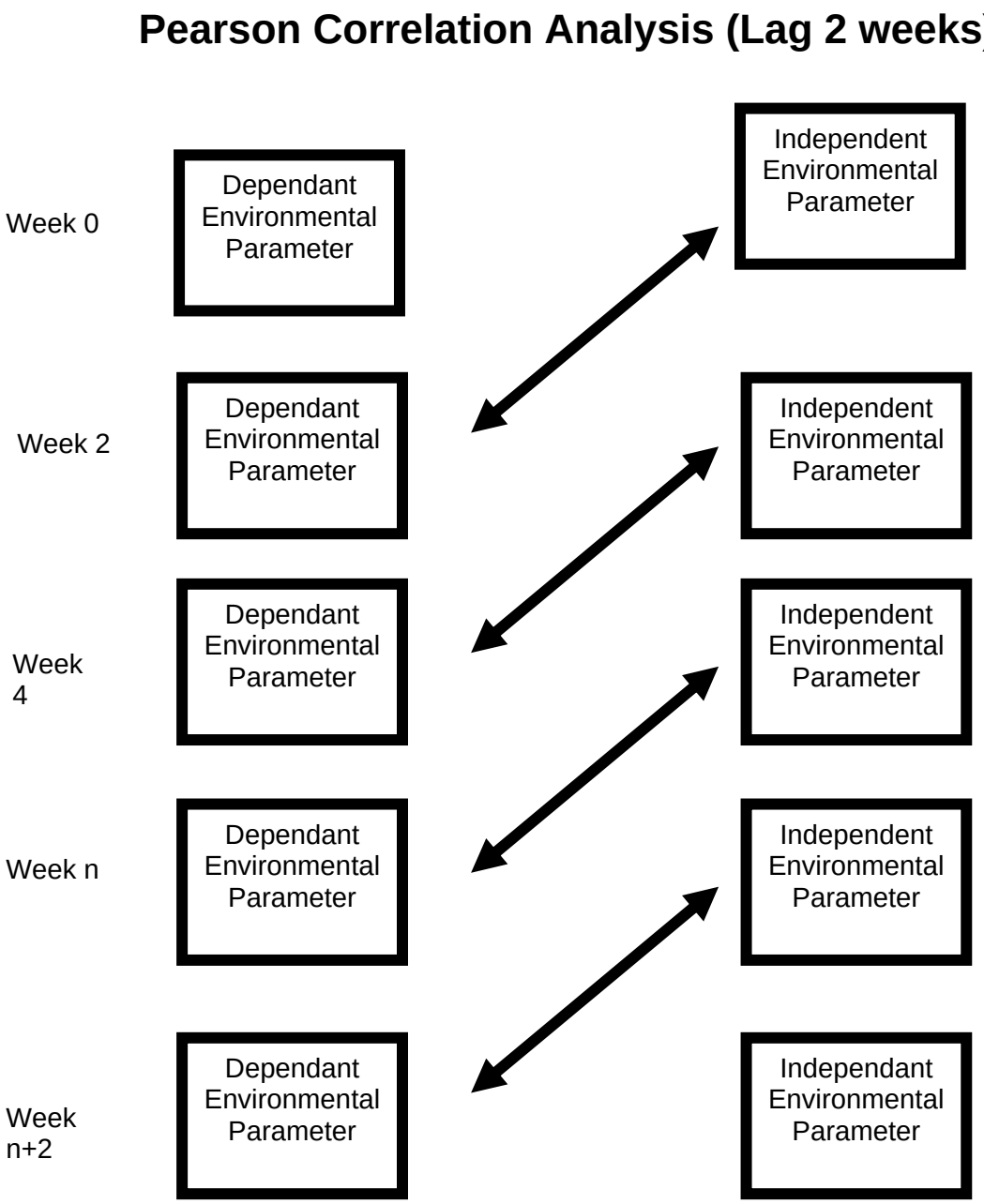

Figure 12. Generalized representation of the data pairing scheme for the lag-correlation statistical analyses for Lag-2 weeks as an example.

Multivariate Linear Regression Analysis

Standard parametric multivariate linear regression analysis was performed on the same data sets used for the univariate analysis using SAS for one dependent variable at a time. As such, the need for an analysis of multiple dependent variables was avoided. However, when MeHg or dissolved fraction MeHg was the dependent variable, THg or dissolved fraction THg was included as an independent variable, but not for %MeHg, because %MeHg is calculated by dividing the MeHg concentration by the THg concentration, whether in water, soil, or vegetation. In addition, the order of analysis was reversed such that the data pooled for all three treatment cells were analyzed first, then the data pooled for each cell, then the data pooled for each station within each cell.

As the limited number and characteristics of the data allowed (e.g., quarterly soil data, monthly water data), lag, average, and lag-average regression analyses were performed over varying time lags as described in the preceding section. Successive elimination of the independent variables that exhibit significant covariance was guided by the magnitudes of the variance inflation factors, correlation coefficients, and P values for each iteration of the linear model. The process was repeated until no further improvement in model performance could be achieved. Where the model equations were undetermined at the outset due to the small size of the data sets, the results from the next level up of spatial or temporal aggregation was used to guide the systematic deletion of the independent variables with the least predictive value rather than to rely on best professional judgment as captured in the conceptual model of mercury transport, biogeochemistry, and bioaccumulation set forth in the “Background” section of this document.

It should be recognized that the parametric multivariate regression analysis was applied to data sets that did not meet the acceptance criteria for normality and homoscedasticity required for the appropriate application of such methods (S. Hill, SFWMD, personal communication). However, the nonparametric alternatives to parametric multivariate regression analysis are not in general use (S. Ward, Janicki and Associates, personal communication, 2004) and are of limited value when the user is interested in quantitative estimates of the dependent variable value as a linear function of the independent variables (S. Hill, SFWMD, personal communication). Therefore, the parametric multivariate linear regression analysis approach was adopted for this exercise.

MISSING DATA

UNREPRESENTATIVE SAMPLING

Surface Water

SITE C1A

Start-up biweekly monitoring of the common inflow (G-328B) and interior Site C1A for unfiltered THg and MeHg in Cell 1 was mandated by Exhibit D of the original operational permit and Exhibit E of the revised operational permit and was performed continuously as conditions allowed (water depth > 10 cm) from start-up in mid July 2000 through mid October 2003. However, it was decided not to use the C1A data for either the exploratory data analyses or the mass budget studies, because (1) site C1A samples were not filtered, as were the other interior sites, so the data would only be comparable every twelve weeks when the unfiltered samples were collected concurrently with the filtered samples; and (2) C1A appeared to be under the disproportional influence of the inflow water quality, possibly due to hydraulic short-circuiting along the levee dividing Cells 1 and 2.

MISSAMPLING

Surface Water

THG AND MEHG

Start-up biweekly monitoring of G-328B inflow and interior Site C1A for unfiltered THg and MeHg in Cell 1 occurred continuously from start-up in mid-July 2000 through mid October 2003, following a year of monitoring after the mercury start-up criteria were met in November 2002. However, it was decided not to use the C1A data for either the exploratory data analyses or the mass budget studies, because (1) site C1A samples were not filtered, and (2) C1A appeared to be under the disproportional influence of the inflow water quality, possibly due to hydraulic short-circuiting along the levee dividing Cells 1 and 2. Biweekly unfiltered sample collection at G-335 began in August 2001 following receipt of FDEP authorization to operate Cell 1 in flow-through mode without first meeting its mercury start-up criteria. Thereafter, unfiltered sample collection at G-328B and G-335 continued on a biweekly basis under the Mercury Special Studies Project. Permit-mandated, routine unfiltered sample collection of the inflow at G-328 and outflow at G-335 continued on a quarterly basis through January 2004. Within this sampling framework, there were no missing THg and MeHg data.

OTHER CONSTITUENTS

For the duration of the project, biweekly grab samples were analyzed for total phosphorus (TP), total dissolved phosphorus (TDP), orthophosphate (o-P), total Kjeldahl nitrogen (TKN), ammonia (NH_3), nitrate-N, nitrite-N, nitrate plus nitrite (NOx), hardness, alkalinity (ALK), pH, temperature, dissolved oxygen (DO), conductivity, and turbidity was conducted at the common inflow at G-328, each of the individual cell outflows, and G-335 common outflow under the

requirements of the original operational permit or the general EFA requirement to monitor for STA operational optimization. The Project added biweekly analyses for dissolved organic carbon, calcium, magnesium, sulfate, chloride, total dissolved iron, total dissolved manganese, and total suspended solids (TSS) at the common inflow and outflow monitoring sites beginning in July 2002 and the interior cell sites and outflows beginning in August 2002. However, calcium was inadvertently omitted from the sample analysis of G-328B samples until March 2003. Analysis of interior samples for chlorophyll *a*, corrected *a*, and *c* began in mid October 2002 and for carotene and phaeophyton in mid November 2002.

Pore Water

Routine pore water sampling at the three interior sampling sites in each of the treatment cells did not begin until August 2003. There were no missing pore water data for the routine samples collected at the nine interior sites. However, due to a misunderstanding by the Tetra Tech sampling crew, replicate (n = 3) pore water sampling of Site C1C in Cell 1 did not occur until October 2003.

Soil/Sediment

The plan did not call for the collection of a pre-flood baseline soil sample at replicate Site C1C in May 2002. Thereafter, samples were supposed to be collected with two weeks of reflooding, then two weeks later, four weeks after that, eight weeks after that, and twelve weeks after that. Due to a misunderstanding by District staff, sampling occurred upon reflooding, two weeks later, and four weeks later, but sampling thereafter was on a four-week basis through July 2003. During the first, post-flood sampling event in August 2002, due to a misunderstanding by the District sampling crew, only one rather than the three samples required by the Plan were collected at Site C1C. Thereafter, triplicate samples were collected by the District sampling crew through July 2003. Due to a misunderstanding, only one sample was collected at Site C1C in October 2003 by the Tetra Tech sampling crew. Thereafter, triplicate samples were again collected through the end of the study in late December 2003. There were no THg or MeHg concentrations in soil below the MDL.

Fish

There were no missing mosquitofish data due to missampling. MeHg was not analyzed in fish tissue, because the predominant form of THg that bioconcentrates, bioaccumulates, and biomagnifies in surface water was assumed to be MeHg. However, for benthic macroinvertebrates, a significant fraction of the THg in tissues is Hg(II), because Hg(II) is generally present in concentrations two or three orders of magnitude greater than MeHg, so even if Hg(II) is only absorbed with one-tenth to one-hundredth the efficiency of MeHg, substantial bioaccumulation can still occur (REFs). Because of the uptake efficiency differential between Hg(II) and MeHg, with each successive trophic level, the percentage of THg that is MeHg generally increases to > 85 percent at T2, > 95 percent at T3 and > 99 percent at T4, unless T2 fish are preying disproportionately on benthic macroinvertebrates, in which case percentage MeHg can be as low as 25 percent, as was observed in mosquitofish collected along the WCA-2A nutrient gradient (unpublished District data).

Vegetation

There were no missing vegetation data due to missampling.

MISANALYSES

Surface Water

There were no misanalyses (inadvertent omission of quantitative chemical analysis of a listed analytes for the medium) of THg, MeHg, or other constituents in surface water.

Pore Water

There were no misanalyses of THg, MeHg, or other constituents in pore water.

Soil/Sediment

There were no misanalyses of THg or MeHg in soil during routine sampling. However, FGS failed to analyze the Site C3C soil strata for 6 to 8 cm and 8 to 10 cm for the side-by-side validation pre-study for MeHg. For constituents other than THg and MeHg, DB Laboratory failed to analyze the first set of routine soil samples collected on 5/21/02 at Site C2B for calcium, magnesium, iron, and manganese.

Vegetation

There were no misanalyses of THg, MeHg, or other constituents in vegetation.

Fish

There were no misanalyses of THg in fish.

DATA LESS THAN THE METHOD DETECTION LIMIT

Surface Water

THG AND MEHG

There were no THg or MeHg concentrations in surface water less than the MDL.

OTHER CONSTITUENTS

For constituents other than TSS, only nitrite-N concentrations were routinely encountered below the MDL in surface water at the cell interior and outflow sampling sites. While TSS was monitored at the common inflow, the interior sites, each cell outflow, and the common outflow, the MDL was 3 mg/L. Based on District experience with the Everglades Nutrient Removal (ENR) Project (Miles and Fink, 1998; SFWMD, 1999b), the particle settling efficiency of constructed

wetlands was such that a TSS MDL of 3 mg/L frequently resulted in < MDL values at the cell interior and outflow monitoring sites. The use of a TSS method with an MDL of 0.3 mg/L ("trace" TSS method) was intended to apply only to the individual cell outflows, due to much longer filtering time required for this method and the limited District laboratory staff resources that could be devoted to this study. Thus, all but the start-up, interior-cell TSS results are < MDL, with but a few exceptions, probably associated with resuspension events caused by low water levels. Despite the use of a TSS method with a MDL of 0.3 mg/L from August 2002, G-330A TSS concentrations were less than the trace MDL on 12/23/03 and 1/13/04, and 1/27/04. Due to a miscommunication with the District laboratory, the trace TSS method was not initiated for the Cell 2 and 3 outflows at G-332 or G-334 samples until mid July 2003.

Pore Water

No pore water THg concentration was less than the MDL, but pore water samples contained concentrations less than the MeHg MDL at Site C2C on 10/06/03, Site C3A on 11/04/03, and Site C3B on 9/8/03, 10/06/03, and 11/04/03. For constituents other than THg and MeHg, TFe, Fe(II) and Fe(III) were frequently less than the MDL.

Sediment/Soil

There were no THg or other constituent concentrations less than their corresponding MDLs in soil/sediment throughout the study. The concentration of MeHg was less than the MDL in a baseline soil sample collected at Site C3A on 5/16/02, prior to the reflooding of Cell 1.

Fish

There were no THg concentrations less than the corresponding MDL in mosquitofish.

Vegetation

The THg concentration in southern naiad (*Najas guadalupensis*) was less than the MDL (0.0073 mg/kg wet wt) at Site C3B on 9/16/02 and less than the MDL (0.0028) in sawgrass (*Cladium jamaicense*) at Site C1AA on 9/18/02. Subsequent sampling events produced no missing values due to concentrations less than the detection limit.

FLAGGED DATA

Surface Water

THG AND MEHG

Table 9 is a summary of all flagged surface water data by sampling date(s), station, sample type and analyte. For a detailed description of each flagged datum, the reader is referred to Appendix I. In the column labeled "number of flagged sample type," the trips highlighted in bold: 11/14/02, 1/8/03, and 5/1/03 had unusually high incidences of flagged data due to method blank contamination (flag V). For the sampling trip on 8/22/03, the high incidence of flagged data was due to analysis outside the holding time (48 hours) for an unpreserved or improperly preserved sample (flag Y).

Table 9. Summary of flagged mercury data by quarters.

Calendar Quarter	Sample Date	Station ID	Total # SW Samples	Total # SW Samples Flagged	% SW Flagged	Analyte
2nd 02	4/4/2002	G335, G332, G334	84	4	4.76	U-MeHg
3rd 02	8/22/2002	G335, C1AA G328B, 330A, G334, G332, C1A,				U-MeHg, F-MeHg
	9/19/2002	G335, C3A, C3B, C3C	146	12	8.22	F-MeHg
4th 02	10/16/2002	CIBB, C2A, C2B, C2C				F-MeHg
	10/17/2002	G334, G328B				U-MeHg,F-MeHg
	11/14/2002	C2A, C2B, C2C, C3A, C3B, C3C,	181	14	7.53	F-MeHg
1st 03	1/8/2003	C1AA, C1BB, C1CC, C2A, C2B, C2C				F-THg
	1/9/2003	C3A, C3B, C3C				U-THg, F-THg
	2/6/2003	C3A, C3B, C3C,	190	15	7.89	F-THg
2nd 03	4/2/2003	G335, G334				F-THg
	5/1/2003	C1AA, C1BB, C1CC, C2A, C2B, C2C, C3A				U-THg, F-THg
	5/28/2003	C3A, C3B, C3C				F-MeHg
	5/29/2003	C2B				F-MeHg
	6/26/2003	G334	214	15	7.01	F-MeHg
3rd 03	8/22/2003	C3A, C3B,C3C	169	6	3.55	F-MeHg,F-THg
4th 03	10/15/2003	C1BB	162	2	1.23	U-MeHg,F-MeHg
1st 04			52	0	0	

FILTERED VERSUS UNFILTERED SURFACE WATER SAMPLES

The observed magnitude and frequency of filtered > unfiltered MeHg (reversals) exceeded those expected from analytical variability for concentrations less than the practical quantitation limit (PQL). In addition, the magnitude of observed filtered MeHg reversals was not strongly inversely correlated with the magnitude of the concentration of MeHg, which one would expect if the problem were unavoidable analytical variability in the low concentration range. Nor was it positively correlated with the magnitude of THg reversals, which one might expect if the reversals were related to uncharacteristic environmental conditions or occasional poor clean-hands technique. Based on these observations, the decision was made to acid-preclean all of the Meissner filters rather than use them as is. This is the protocol followed by USGS-Middleton and the protocol recommended by Frontier Geosciences, Inc, based on many years of experience with spurious contamination of filters.

The first set of acid-precleaned Meissner filters came into use the second week in October 2003. With the advent of acid-precleaning of the Meissner filters, the magnitude and frequency of MeHg reversals decreased noticeably, albeit not statistically significantly so. While all filtered MeHg data collected using the raw filters prior to the institution of precleaned filters are suspect, the importance of being able to analyze the influence of filtered MeHg concentrations in water on MeHg bioaccumulation overrode the need to purge the data sets of suspect data. Nevertheless, the Project Manager is obliged to bring this decision to the reader's attention explicitly in order to put the results and the inferences deriving them into proper perspective.

OTHER CONSTITUENTS

There were no other flagged data for surface water constituents other than THg and MeHg.

Pore Water

THG AND MEHG

There was only one flagged set of concentration data for THg or MeHg in the routine pore water sample collected on November 11, 2003, at Site C3B due to a reversal (i.e., [MeHg] > 1.3 x [THg]). The first sets of pore water samples collected in August and September 2003 were not filtered, and centrifugation of the September 2003 sample set in the laboratory proved inadequate to address the variability in the analytical results due to the fine particulate remaining in the samples. A Meissner filter was added to the sampling train for the October 2003 sampling event, but the filters were not acid-precleaned until the November 2003 sampling event. Based on the preceding, the August and September 2003 data have been omitted from the exploratory data analysis, but the October 2003 data have been retained. Pore water results have not been used in the mass budget calculations.

OTHER CONSTITUENTS

For constituents other than THg and MeHg in the routine pore water samples, no data were flagged. The concentration of Fe(II) was greater than the corresponding TFe concentration for Site C3B collected on 1/6/04 but the difference was less than 20 percent of the TFe value.

Sediment/Soil

THG AND MEHG

There were no flagged data for routine interior or replicate site results for THg or MeHg in surficial soil samples. The Project Manager has chosen to treat as valid the quantitative analytical concentration results for THg and MeHg in soil/sediment for soil samples collected, stored frozen, processed and analyzed within the Program's and Project's holding time of six months for both analytes and Method 1631 Revision E of one year for THg in soil/sediment but outside the FDEP's 28-day holding time for THg analysis in solid and hazardous waste soil samples. This is because the solid/hazardous waste regulations are (a) inapplicable to this environmental monitoring, research, and modeling project, because volatile elemental mercury from anthropogenic sources is not present in the soil; and (b) the stability of THg and MeHg in frozen soil samples for up to one year has been demonstrated to the USEPA's and the Project Manager's satisfaction by Frontier Geosciences (N. Bloom, FGS, personal communication), the contract laboratory performing the soil THg and MeHg analyses for this Project.

OTHER CONSTITUENTS

There were no flagged data for routine interior or replicate site results for constituents other than THg and MeHg in surficial soil samples. However, the total sulfur analyses for soil were carried out by a subcontractor laboratory to DB Laboratory whose NELAP certification expired during the course of the study. Nevertheless, since the method, instrument, and analyst did not change, this had no substantive effect on the quality of the soil total sulfur quantitative analytical results. That being the case, the Project Manager has determined that the concentration data for total sulfur are valid for both the exploratory data analyses and mass budget calculations. Unfortunately, an order-of-magnitude decimal point error in a soil sulfur concentration datum supplied by the contract laboratory for the surficial soil sample collected at Site C1AA on 1/29/03 was not corrected in the DBHYDRO database before the data set was distributed and used for the mass budget calculation and the exploratory data analyses.

While the soil total sulfur analytical results have been determined to be valid for this study, the Project Manager has taken note of the substantial variability in the AVS data generated on replicate samples at Site C1C for each sampling event and between sampling events. These are not true splits but true field replicates, and it is possible that AVS exhibits a higher degree of field heterogeneity over the scale of 1 m^2 than other constituents that are not redox-sensitive. Nevertheless, until the requisite split sample replicate analyses are conducted on a wide range of soils and sediments, the AVS concentration data generated by or for DB Laboratory should be considered semi-quantitative at this juncture.

Fish

There were no flagged data for routine interior or replicate site results for THg in inflow, interior, or outflow mosquitofish samples.

Vegetation

THG AND MEHG

There were no flagged data for routine interior site results for THg or MeHg in vegetation samples.

OTHER CONSTITUENTS

There were no flagged data for routine interior or replicate site results for ash or moisture content in vegetation samples. However, as summarized in **Table 10**, the standard error for field replication for AVS is much higher on average than the other constituents. This may be attributable to the higher within-site variability associated with redox-sensitive constituents of soil. The average standard error for redox potential and pore water sulfide in replicate pore water samples from the same site are also roughly an order of magnitude greater than the inert chloride ion. Nevertheless, until the required studies are conducted to verify this hypothesis, the AVS must be considered semiquantitative for purposes of this study. The Project Manager has chosen to use these data for the soil mass budget and exploratory data analyses with the aforementioned caveat withstanding.

Table 10. The Site C1C standard errors calculated for each constituent analyzed in field replicate (n = 3) surficial (4-cm) soil cores.

SITE C1C SOIL FIELD REPLICATE STANDARD ERROR

	G/CC	ASH	MOISTURE	TP	TN	Ca	Mg	TS	AVS	Fe	Mn	THg	MeHg
08/28/02	0.177	0.091	0.008	0.111	0.028	0.092	0.067	0.143	0.623	0.133	0.119	0.052	0.292
09/11/02	0.100	0.019	0.020	0.061	0.018	0.032	0.052	0.044	1.120	0.107	0.088	0.106	0.447
10/09/02	0.035	0.067	0.010	0.145	0.064	0.095	0.056	0.210	0.895	0.108	0.156	0.133	0.322
12/04/02	0.071	0.027	0.021	0.090	0.032	0.015	0.045	0.274	0.341	0.136	0.088	0.039	0.059
03/26/03	0.030	0.032	0.010	0.040	0.008	0.036	0.074	0.311	0.395	0.049	0.100	0.125	0.241
11/11/03	0.287	0.063	0.046	0.075	0.085	0.121	0.138	0.189	0.223	0.228	0.087	0.399	0.245
12/02/03	0.383	0.101	0.040	0.067	0.087	0.133	0.053	0.098	0.207	0.069	0.046	0.082	0.198
12/30/03	0.143	0.130	0.028	0.099	0.162	0.156	0.091	0.441	0.357	0.098	0.125	0.146	0.735
AVERAGE	0.153	0.066	0.023	0.086	0.060	0.085	0.072	0.214	0.520	0.116	0.101	0.135	0.317

DATA CENSORSHIP, INTERPOLATION, AND REDUCTION

DATA LESS THAN THE METHOD DETECTION LIMIT

Data less than the method detection limit (MDL) were not used in the exploratory data analyses but were used in the mass budget calculations by substituting the MDL for the < MDL value.

FLAGGED DATA

Flagged data were not used in the exploratory data analyses but were not summarily excluded from the mass budget calculations, unless the data bore no relationship to data collected at adjacent sites at time t or at the same site at time t-1 and time t+1.

DATA INTERPOLATION AND EXTRAPOLATION TO FILL MISSING DATA GAPS FOR THE MASS BUDGET ANALYSIS

Data gaps created by missing data were not filled by linear interpolation or extrapolation for the exploratory data analysis but were filled for the mass budget analysis.

Rain

The rain monitoring station FL99 did not come online until late August 2002, so missing data from January 2002 to the end of August 2002 were filled by multiplying the average of the Andytown (FL04) and ENR Project (FL34) rain monitoring stations by 80 percent, which is the average value of the proportion observed between FL99 and the average of the ENR project and Andytown sites after FL99 came online. Missing inflow, interior, and outflow data were filled by averaging the bracketing preceding and succeeding measured values.

Surface Water

Data gaps were filled by averaging the immediately preceding and succeeding (bracketing) results. Linear interpolation was then used to infer the daily concentration value between measured every other week (biweekly) or every four weeks.

Soil/Sediment

There were no data gaps in the routine soil/sediment analyses, so it was not necessary to fill data gaps by averaging the immediately preceding and succeeding (bracketing) results. The changes in soil storage were only calculated for each sampling event, which occurred every 12 weeks, so it was not necessary to infer the concentration value between measured values using linear interpolation.

Vegetation

There were no data gaps in the routine vegetation analyses, so it was not necessary to fill data gaps by averaging the immediately preceding and succeeding (bracketing) results. However, there were insufficient data with which to calculate the change in vegetation biomass storage of THg and MeHg with the desired quantitative rigor.

Fish

There were no data gaps in the routine fish analyses, so it was not necessary to fill data gaps by averaging the immediately preceding and succeeding (bracketing) results. However, there were insufficient data with which to calculate the change in fish biomass storage of THg and MeHg.

RESULTS

CONCENTRATIONS

Rain

The complete set of rain THg concentration data collected for this study is contained in Appendix G, Table 1A. The data are plotted in **Figure 13**. From January through August 2002, the plotted weekly integrated THg concentrations in rain at FL99 were estimated by multiplying the weekly integrated average concentration at the ENR Project (FL34) and Andytown (FL04) by a factor of 0.8. From September 2002 and January 2004, **Figure 13** depicts the actual weekly integrated rain THg concentration data collected at the temporary site at STA-2, FL99. As expected, the THg concentration in rain at FL99 reaches its zenith and nadir in the summer/early fall and late fall/early winter, respectively. Appendix G, Table 1B summarizes the rain concentration data from the Florida Atmospheric Mercury Study (FAMS) used to calculate the average rain concentrations for the other constituents of interest for the mass budget calculations presented in a later section of this report.

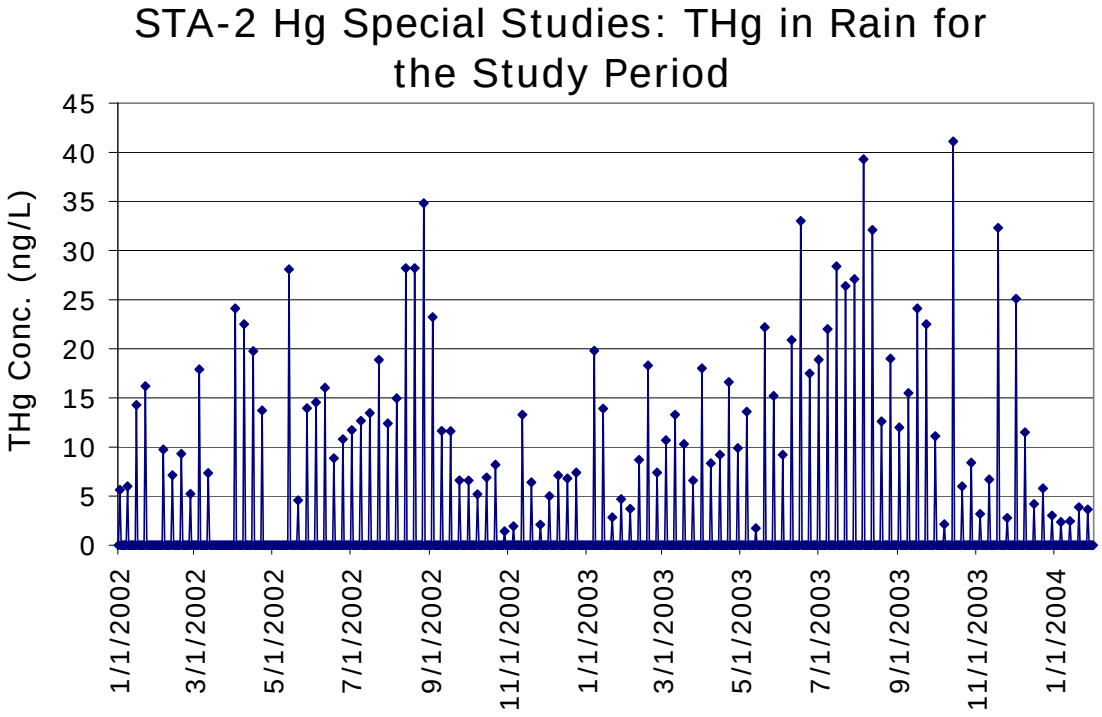

Figure 13. THg concentration of THg (ng/L) in unfiltered rain at FL99.

Surface Water

The complete sets of surface water concentration data for THg and MeHg collected for this study are contained in Appendix G, Tables 2A through 2C. The inflow and outflow THg and MeHg data for STA-2 and the individual treatment cells are plotted in **Figures 14** through **17**. The other constituent concentrations can be accessed via the District's DBHYDRO database.

Clearly, an unprecedented first-flush MeHg anomaly occurred following reflooding of Cell 1 in August 2002 after being dried out in December 2001 through May 2002, when the baseline soil samples were collected. Thereafter, the wet season rains began, rewetting the soil prior to reflooding. Cell 1 was reflooded only when sufficient water could be assured to allow a rapid increase in the water depth and subsequent flow-through to dilute and flush out the first-flush excess Hg(II) and MeHg as quickly as possible. That this operational stratagem was successful is evident in the rapid decline in the concentrations of THg and MeHg at the Cell 1 outflow and the combined outflow at G-335.

Interestingly, first-flush releases of other redox-sensitive species, i.e., iron was also observed in Cell 1 (**Figure 18**). There was also an apparent first-flush release of DOC (**Figure 19**), and net release for all but a few sampling periods thereafter. In contrast, there was a decrease in the sulfate concentration along the longitudinal gradient in Cell 1 from G-328 to C1CC in the August 2002 interior sampling event, but the slope of the gradient decreased (flattened out) in the third sampling event (**Figure 20**). DOC and sulfate are two of the three primary ingredients required for MeHg production, $Hg(II)^{+2}$ being the third. The excess of each of these three primary ingredients must have originated with release from surficial soil and first appeared in excess in surficial soil pore water, because neither inflow nor rainfall concentrations or mass contributions approach the corresponding concentrations or stored masses in Cell 1 interior surface water, and, in the Everglades, MeHg production occurs almost exclusively in the surficial soil. It was these excess concentrations of DOC, sulfate, and $Hg(II)^{+2}$ that likely fed the unprecedented excess MeHg production in Cell 1. Unfortunately, as discussed in the subsection on "Methods Development" in the "Methods" section, the District did not yet possess a reliable method for the simultaneous collection of pore water for sulfide and ultra-trace THg and MeHg analyses at the time of Cell 1 reflooding, so there were no direct measurements of pore water concentrations to corroborate this inference. Nevertheless, the mass budget support for this inference is compelling. The supporting mass budget calculations are set forth in a later subsection of this section.

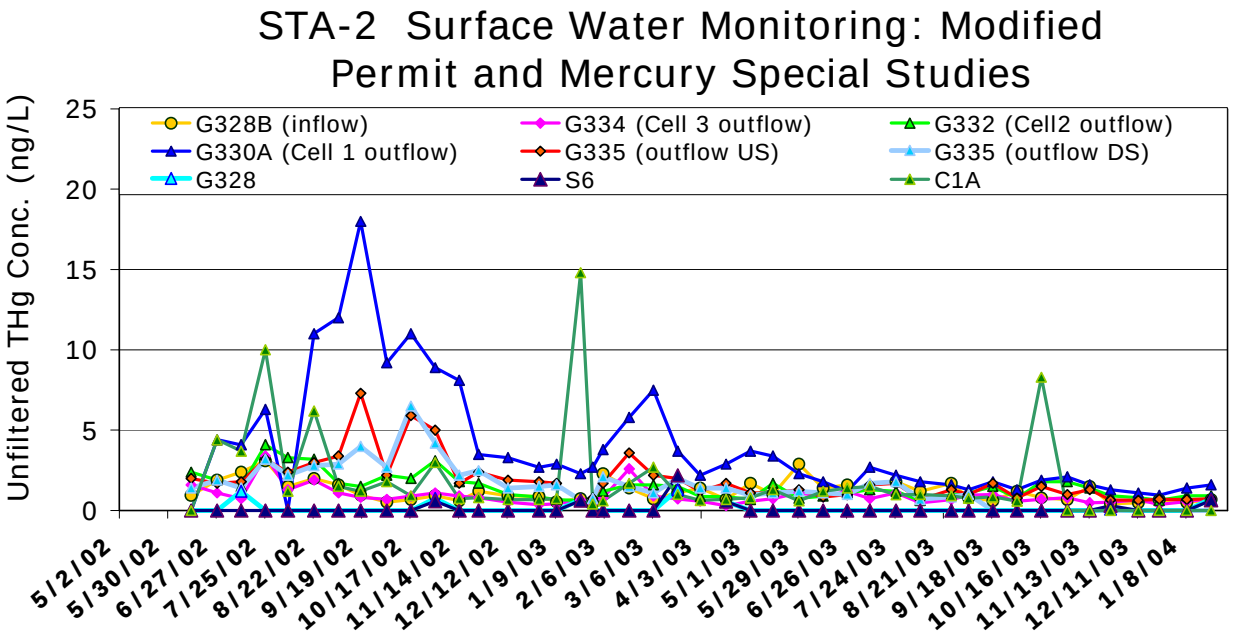

Figure 14. THg concentration of THg (ng/L) in unfiltered surface water in STA-2 and individual treatment cell inflows and outflows.

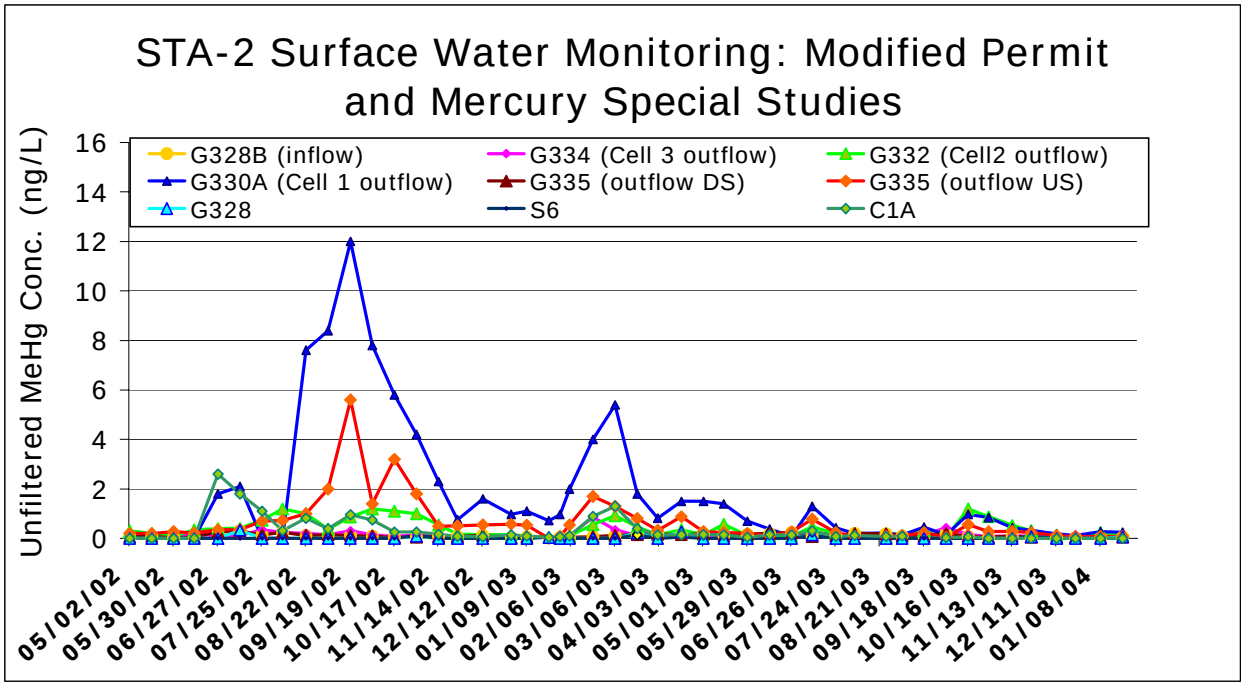

Figure 15. MeHg concentration of THg (ng/L) in unfiltered surface water in STA-2 and individual treatment cell inflows and outflows.

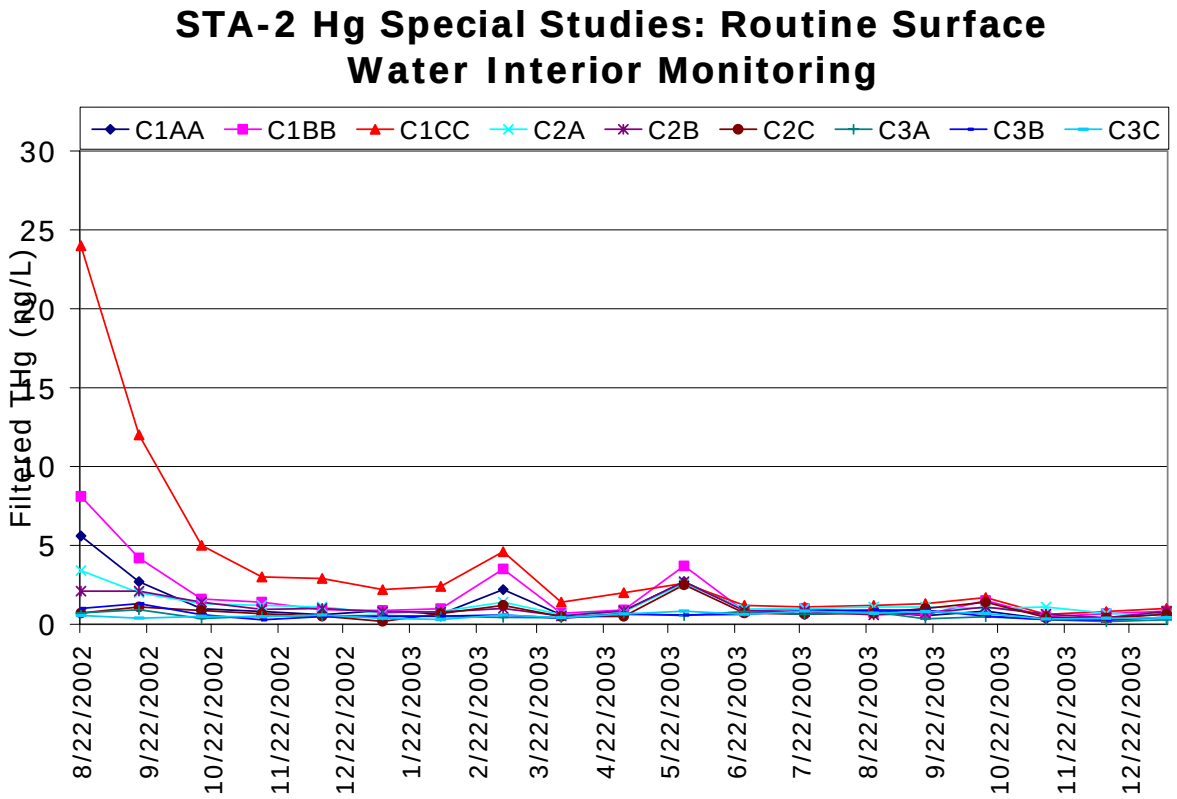

Figure 16. Concentrations of THg (ng/L) in filtered surface water from individual treatment cell interior sites.

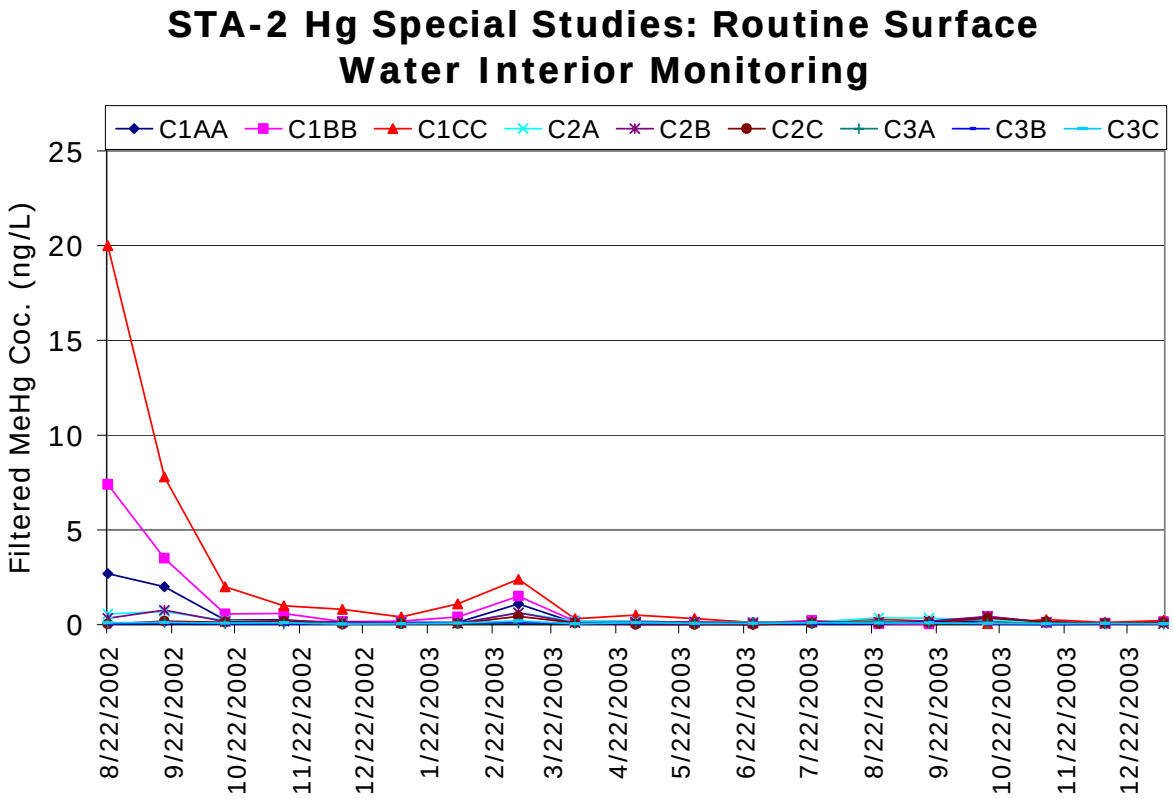

Figure 17. Concentrations of MeHg (ng/L) in filtered surface water from individual treatment cell interior sites.

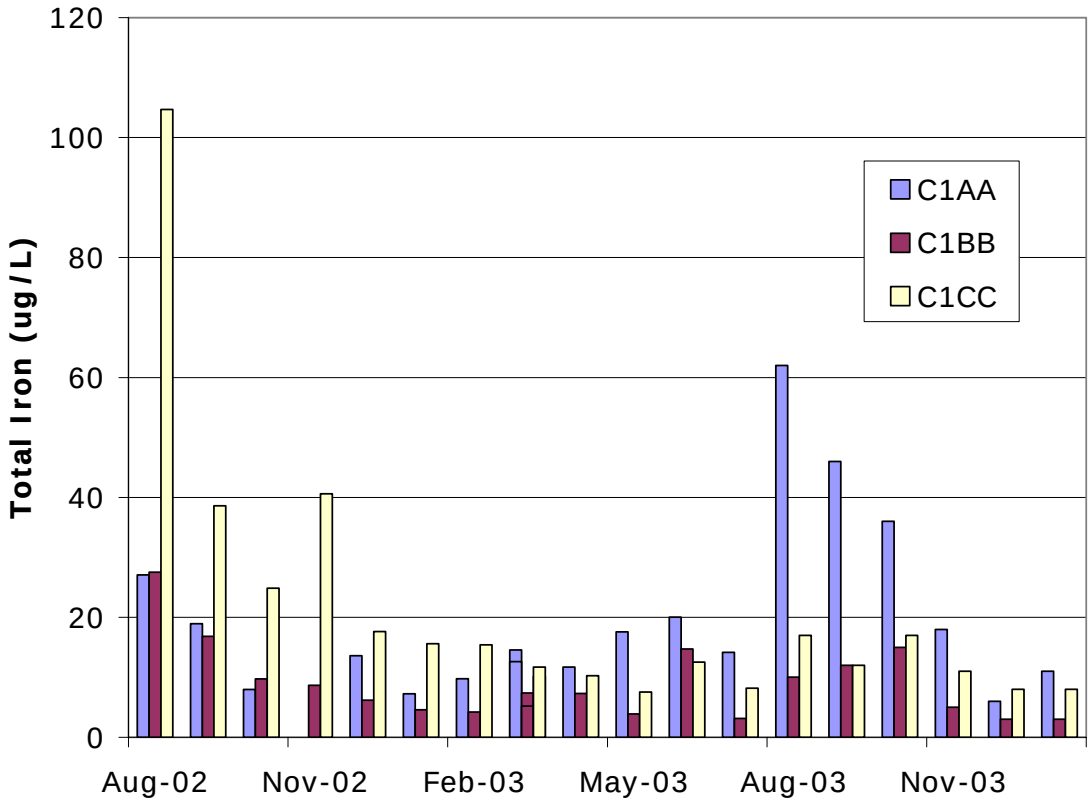

Figure 18. Concentrations of filtered total iron (µg/L) in filtered surface water from individual treatment cell interior sites.

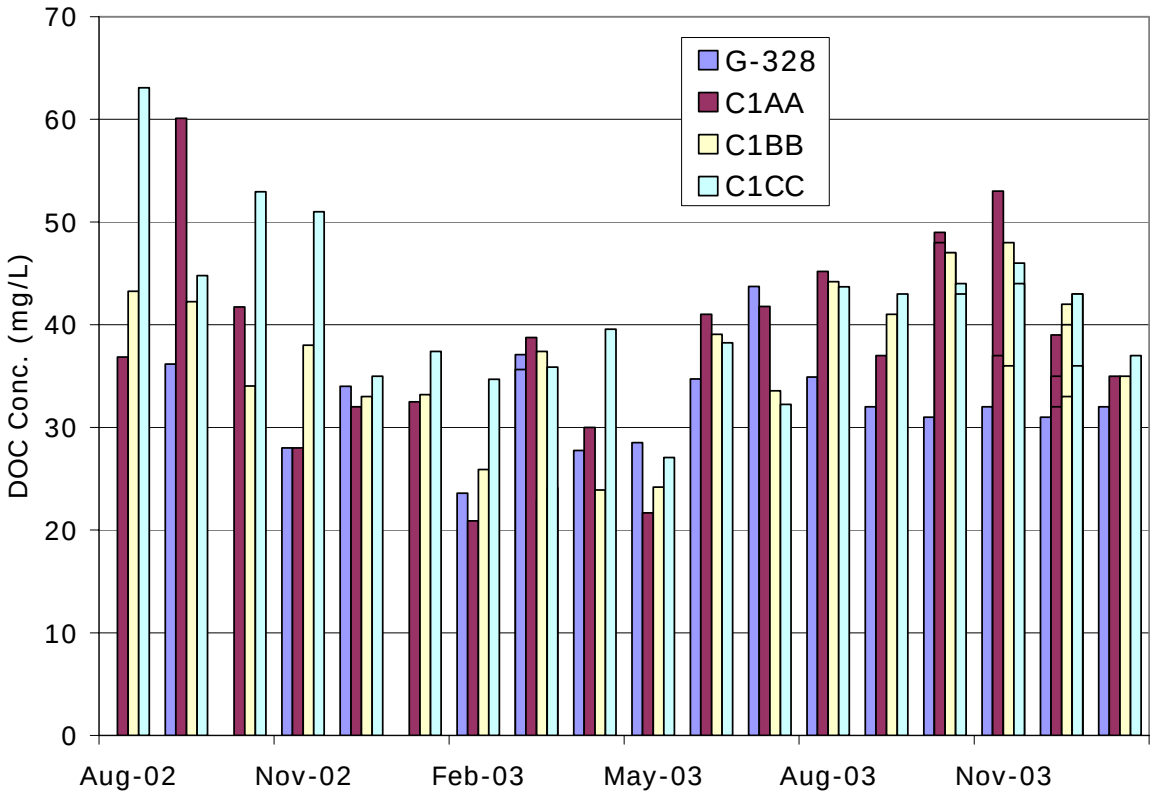

Figure 19. Concentrations of dissolved organic carbon (DOC) (mg/L) in filtered surface water from the common inflow (G-328) and the individual treatment cell interior sites.

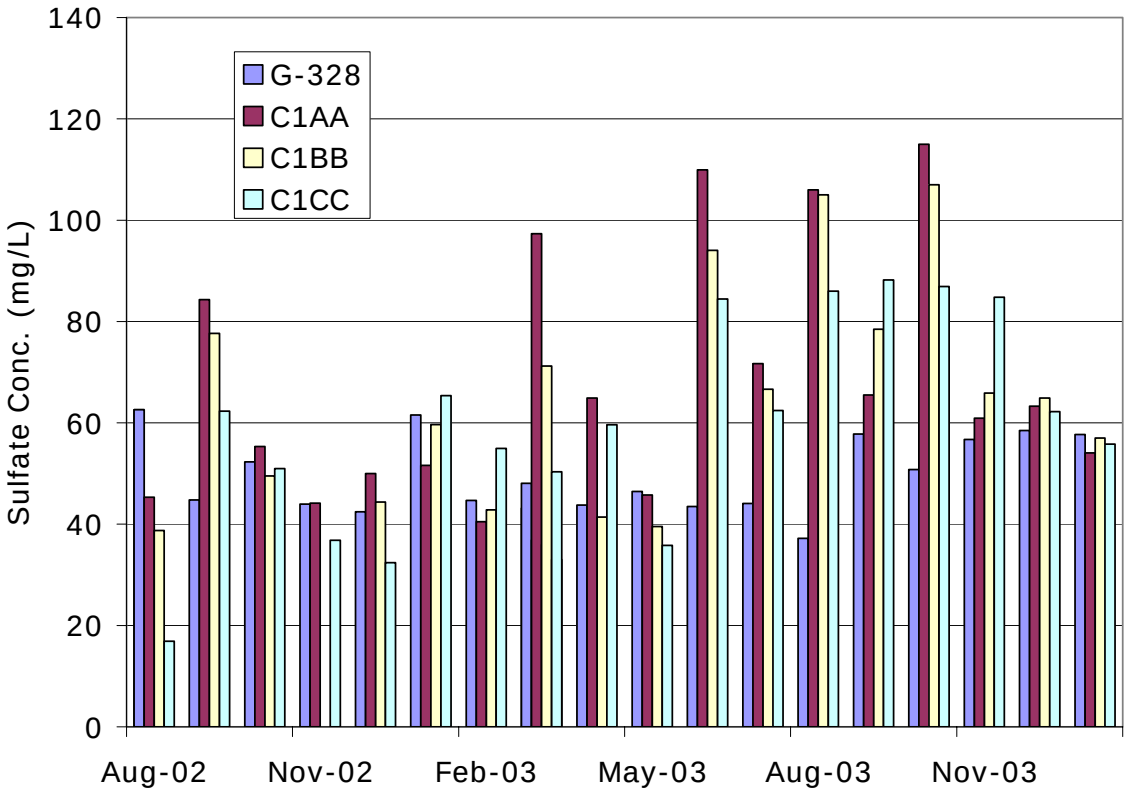

Figure 20. Concentrations of sulfate (SO_4^{-2}) (mg/L) in filtered surface water from individual treatment cell interior sites.

Pore Water

The concentration time trends for pore water sulfate and sulfide versus THg and MeHg for each of the four valid sampling events are depicted in **Figures 21** through **24,** respectively. **Figure 25** depicts the juxtaposition of results for all four sampling trips for Cell 1 Sites C1AA, BB, and CC. The complete set of results of the pore water analyses performed on samples collected via the modified "sipper" method are reproduced in Appendix G, Table 5. In general, for each of the four sampling trips (1) pore water sulfide concentrations tended to increase and MeHg concentrations tended to decrease across cells from Cell 1 to Cell 2 and Cell 2 to Cell 3; (2) no clear relationship was observed between the magnitude of pore water sulfide and MeHg concentrations at the same site and time within each treatment cell, although extremely high sulfide concentrations appeared to be associated with extremely low or non-detectable MeHg concentrations; and (3) within cells, both sulfide and MeHg concentrations tended to peak at the middle station. However, as with many environmental monitoring results, there are exceptions to these generalizations. Nevertheless, where and when it occurs, the third generalization suggests that the central portion of each treatment cell may be isolated to varying degrees at certain times from the influence of inflow water volume and/or chemistry, as might occur due to hydraulic short-circuiting that favors the perimeter of the treatment cell as opposed to sheetflow.

Table 11 below summarizes the routinely achievable precision (expressed as the standard deviation divided by the site average to eliminate the influence of differences in magnitude or in units) in field replicate samples (n = 3) collected at Site C1C. Conductivity was measured consistently only in surface water. Fe(II) and Fe(III) concentrations were frequently less than the MDL, so standard errors could not be calculated for any of the four routine sampling trips. Less than MDL values were encountered for MeHg in the first and third trips, so those calculations are absent, as well. It should be noted that for the November 2003 and January 2004 sampling trips, the SE for MeHg is less than that for THg, suggesting some random contribution from low-level contamination with Hg(II) and/or Hg(0). The source could be either the environment or the filters.

Table 11. The Site C1C site standard deviation normalized to the site average for each constituent analyzed in field replicate (n = 3) surficial (4-cm) pore water collected using the modified sipper method.

Replicate Site C1C Pore Water Standard Deviation Normalized to Site Average

	pH	Redox	DOC	MG	CA	TOTFE	TMN	CL	SO4	S2-	Fe(II)	Fe(III)	Hg	MeHg
Average	0.0035	-0.0445	0.0068	0.0061	0.0056		0.0150	0.0048	0.0128	0.0314			0.26075	0.08479
Oct-03	0.0021	-0.0220	0.0135	0.0096	0.0056		0.0123	0.0000	0.0066	0.0675			0.4039	0.0000
Nov-03	0.0068	-0.0048	0.0139	0.0071	0.0057		0.0086	0.0097	0.0080	0.0112			0.2134	0.1313
Dec-03	0.0032	-0.0169	0.0000	0.0038	0.0041		0.0311	0.0000	0.0057	0.0197			0.2497	
Jan-04	0.0020	-0.1343	0.0000	0.0041	0.0070		0.0081	0.0096	0.0310	0.0270			0.1760	0.1230

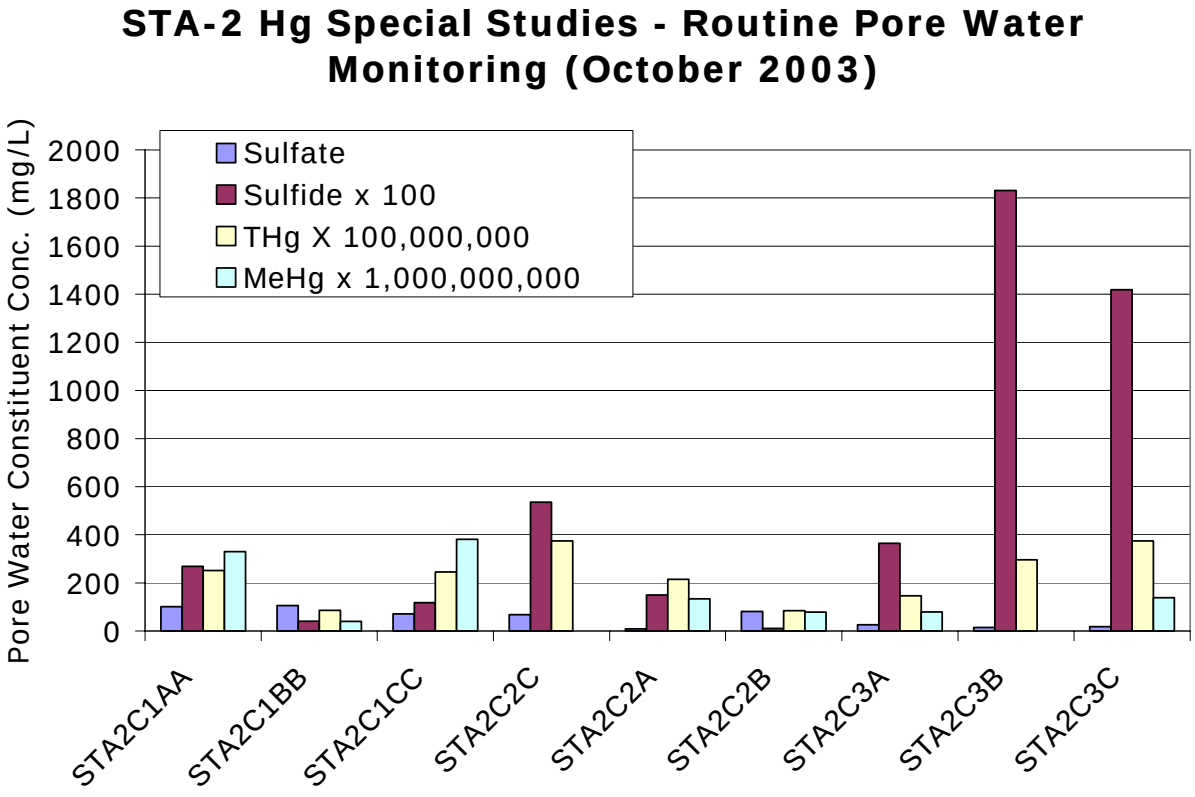

Figure 21. Concentrations of sulfate (SO_4^{-2}), sulfide (S^{-2}), THg, and MeHg in filtered pore water from individual treatment cell interior sites for the first filtered sampling event in October 2003.

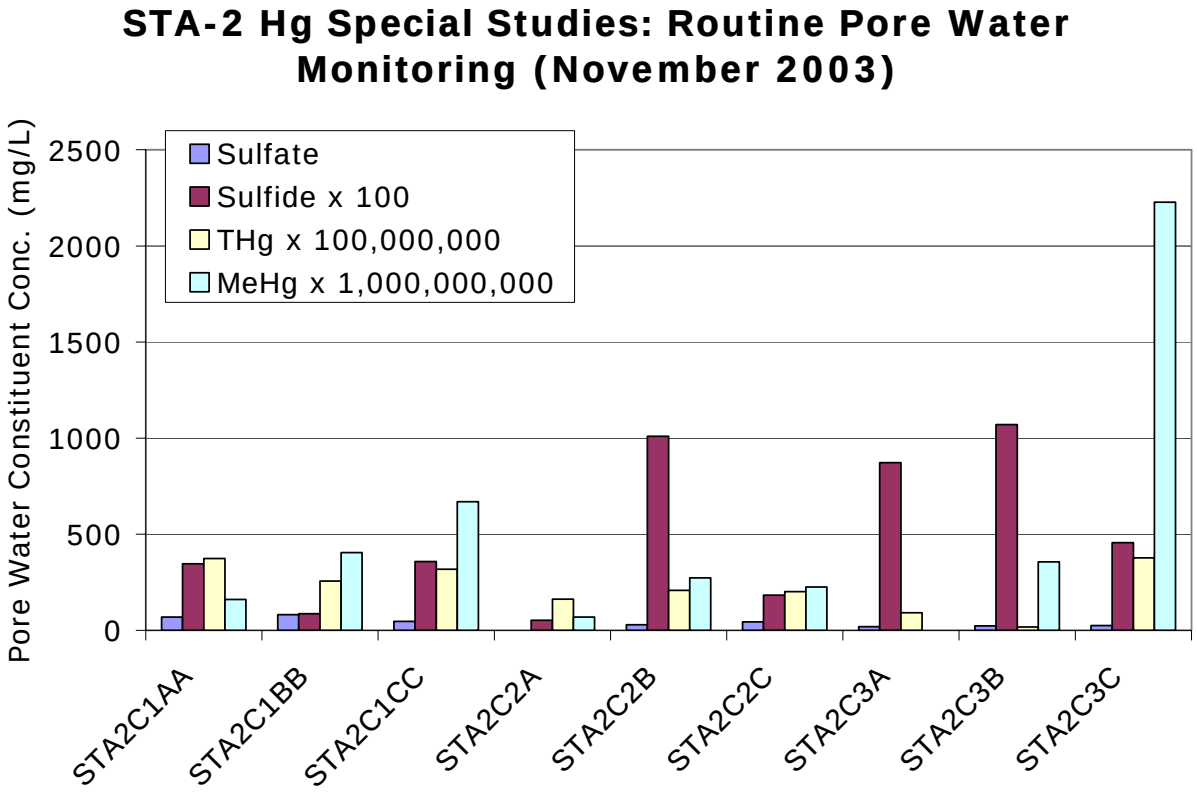

Figure 22. Concentrations of sulfate (SO_4^{-2}), sulfide (S^{-2}), THg, and MeHg in filtered pore water from individual treatment cell interior sites for the second filtered sampling event in November 2003.

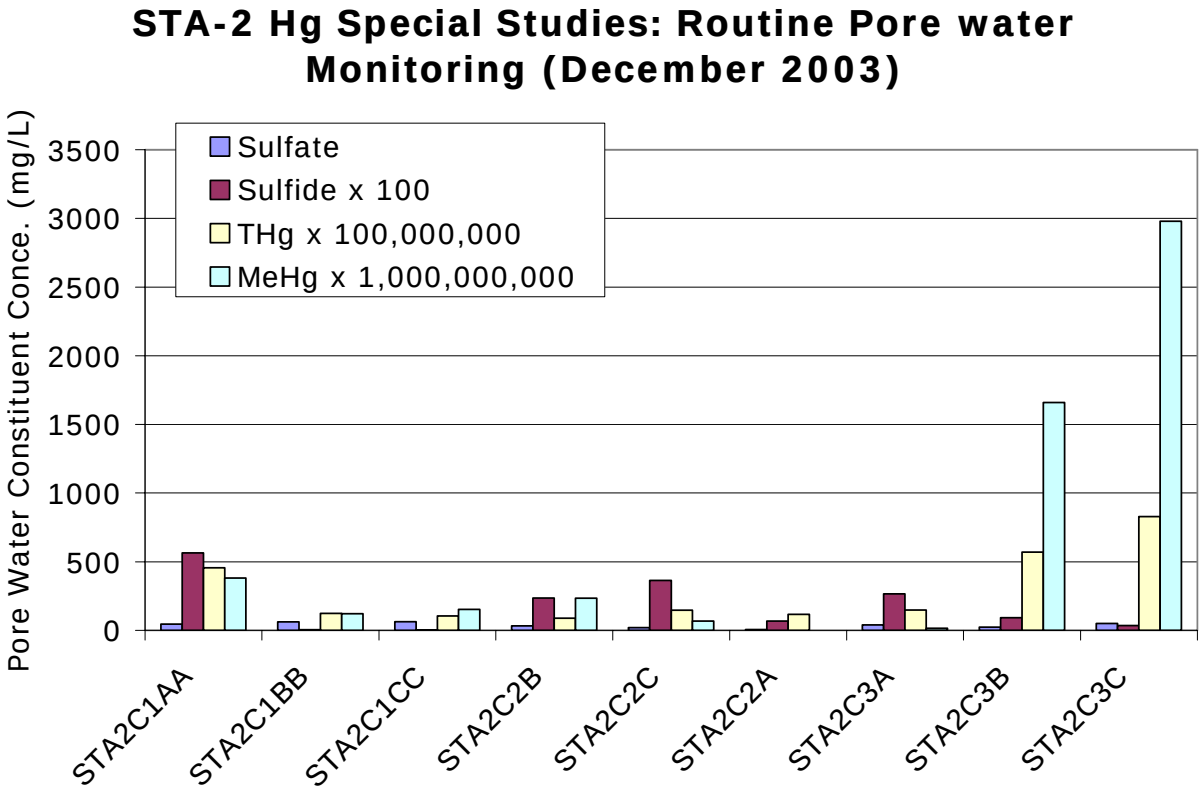

Figure 23. Concentrations of sulfate (SO_4^{-2}), sulfide (S^{-2}), THg, and MeHg in filtered pore water from individual treatment cell interior sites for the third filtered sampling event in December 2003.

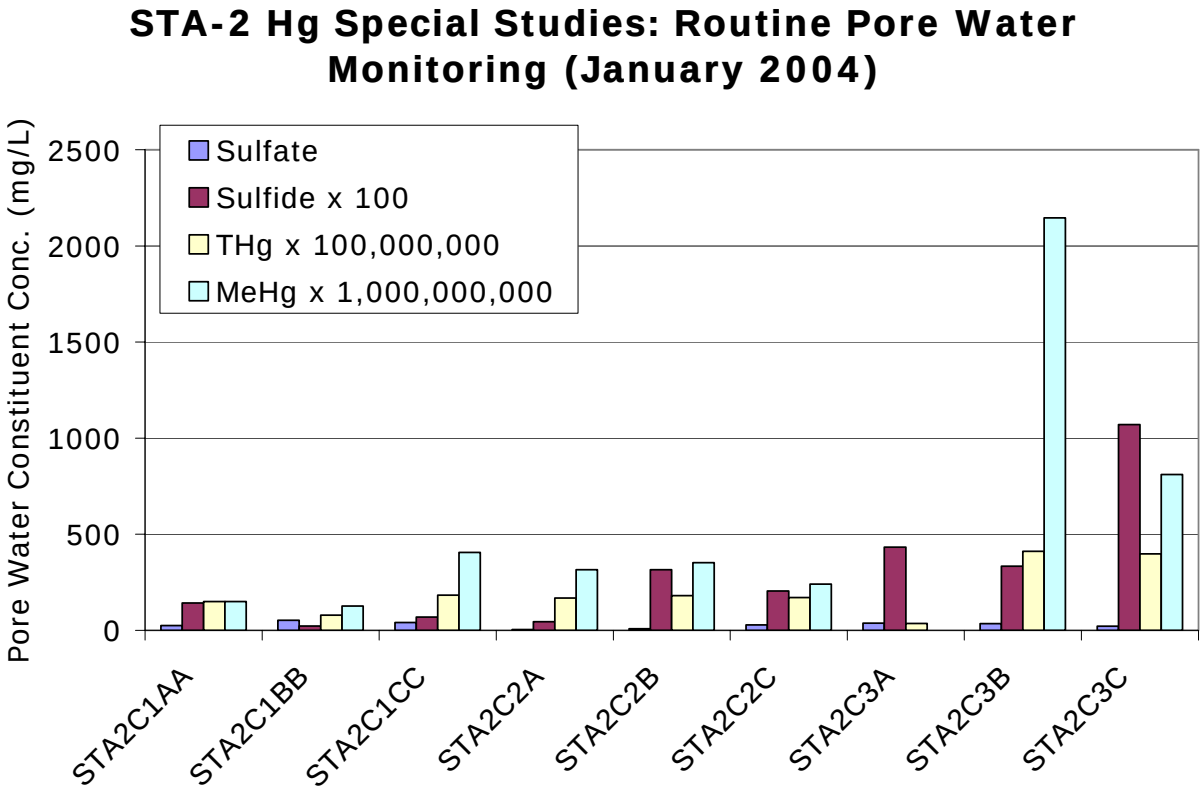

Figure 24. Concentrations of sulfate (SO_4^{-2}), sulfide (S^{-2}), THg, and MeHg in filtered pore water from individual treatment cell interior sites for the last filtered sampling event in January 2004.

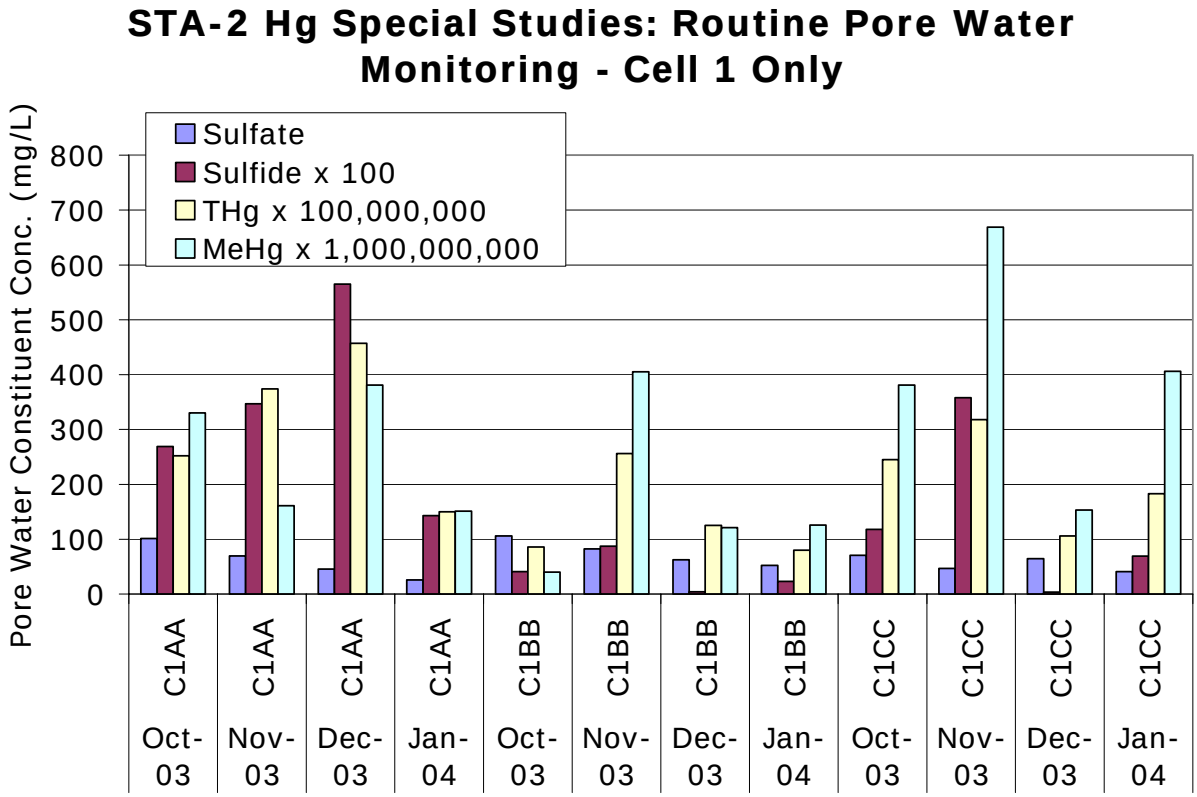

Figure 25. Concentrations of sulfate (SO_4^{-2}), sulfide (S^{-2}), THg, and MeHg in filtered pore water from Cell 1 interior sites for the four filtered sampling events every four weeks from October 2003 through January 2004.

Soil/Sediment

The results of the routine and replicate site soil analyses are reproduced in Appendix G, Table 3. **Table 12** reproduces the standard errors (standard deviation/average) for analytical results for the three field replicate analyses at quality assurance Site C1C discussed in the preceding section on flagged data.

The time trends in the concentrations of THg, MeHg, %MeHg, AVS, TFe, and TS are depicted in **Figures 26** through **31**. **Figure 32** focuses on the soil MeHg time trend. Consistent with the observed surface water MeHg concentrations, the surficial soil MeHg concentrations decreased progressively over time, although there appears to be a slight upturn for the last sampling event. Such fluctuations are expected and should be considered typical.

Fish

Routine fish mercury monitoring at STA-2 includes semiannual collection of a mosquitofish composite and annual collection of twenty each sunfish and largemouth bass at the common inflow at G-328, a representative interior site in each treatment cell, and the common outflow just upstream of the G-335 pump station. In addition, permit modifications were issued for operation of STA-2 Cell 1 without meeting mercury start-up requirements (i.e., interior U-THg and U-MeHg at a representative interior site not statistically significantly greater than corresponding values at the common inflow). Among other things, these modifications required the District to collect mosquitofish quarterly and sunfish semiannually at the common inflow, Cell 1 interior Site C1X at the bottom of Cell 1, and two downstream sites in the transition zones in WCA-2A: N4 and Z4, as well as mosquitofish monthly at representative interior site C1A. Beyond the routine and modified fish monitoring requirements, the STA-2 Mercury Special Studies Project added mosquitofish collection every four weeks at three, more centrally located and more equally spatially distributed interior sites in Cell 1 and the three established interior monitoring sites in each of Cells 2 and 3.

The time trends of the results of the STA-2 inflow, interior, and outflow mosquitofish monitoring and the interior mosquitofish monitoring are plotted in **Figure 33**, while **Figure 34** focus on the mosquitofish THg concentration time trends for interior Cell 1. Two important observations emerge form these graphs. First, the Cell 1 outflow mosquitofish collected in the last two quarters of the study contain less THg as MeHg than the mosquitofish collected at the common inflow. Second, the interior and outflow mosquitofish THg concentrations decreased progressively over time since about the time Cell 1 met its mercury start-up criteria in late November 2002. It is also clear that the THg as MeHg concentration declines in Cell 1 interior surficial soil/sediment MeHg concentrations are mirrored in the declines in mosquitofish THg as MeHg collected at those same interior sites. However, as the interior and outflow concentrations have declined to near background levels, one must interpret the results in the context of the natural background variability associated with intra-seasonal, inter-seasonal, and inter-annual differences in environmental and operational conditions and the natural variability in fish concentrations due to local differences in foraging preferences, growth rates, and the small-scale heterogeneity in MeHg background concentrations in surficial soil/sediment. Nevertheless, absent a dryout event, the expectation is that the concentrations of THg as MeHg in mosquitofish, sunfish, and largemouth bass in Cell 1, the STA-2 common outflow, and the two downstream monitoring sites will fall within the ranges typical of those environments. To ensure that this is the case, the District will continue to monitor those downstream sites annually as part of its so-called non-ECP permit (to operate canal structures upstream and downstream of the STAs and outside of the Everglades Construction Project, or ECP).

Table 12. The Site C1C site standard deviation normalized to the site average calculated for each constituent analyzed in field replicate (n = 3) surficial (0-4 cm) soil collected via core.

Replicate Site C1C Trip Soil Standard Deviation Normalized to Trip Mean

	BD	ASH	MOIST	TN	CA	MG	TS	AVS	FE	MN	THg	MeHg
8/28/2002	0.1768	0.0907	0.0078	0.0276	0.0925	0.0666	0.1434	0.6233	0.1332	0.1195	0.0521	0.2920
9/11/2002	0.1000	0.0186	0.0196	0.0177	0.0323	0.0516	0.0437	1.1197	0.1066	0.0883	0.1058	0.4474
10/9/2002	0.0345	0.0671	0.0100	0.0635	0.0955	0.0563	0.2101	0.8946	0.1077	0.1555	0.1327	0.3218
12/4/2002	0.0714	0.0272	0.0209	0.0320	0.0149	0.0446	0.2745	0.3407	0.1358	0.0881	0.0388	0.0589
3/26/2003	0.0299	0.0324	0.0098	0.0078	0.0361	0.0737	0.3106	0.3950	0.0488	0.1000	0.1247	0.2408
11/11/2003	0.2875	0.0631	0.0457	0.0850	0.1214	0.1377	0.1895	0.2228	0.2280	0.0866	0.3994	0.2454
12/2/2003	0.8440	0.0159	0.0797	0.0579	0.1632	0.2977	0.3385	0.3356	0.2682	0.0558	0.3810	0.2924
12/30/2003	0.1429	0.1305	0.0281	0.1620	0.1556	0.0909	0.4406	0.3571	0.0984	0.1249	0.1462	0.7349

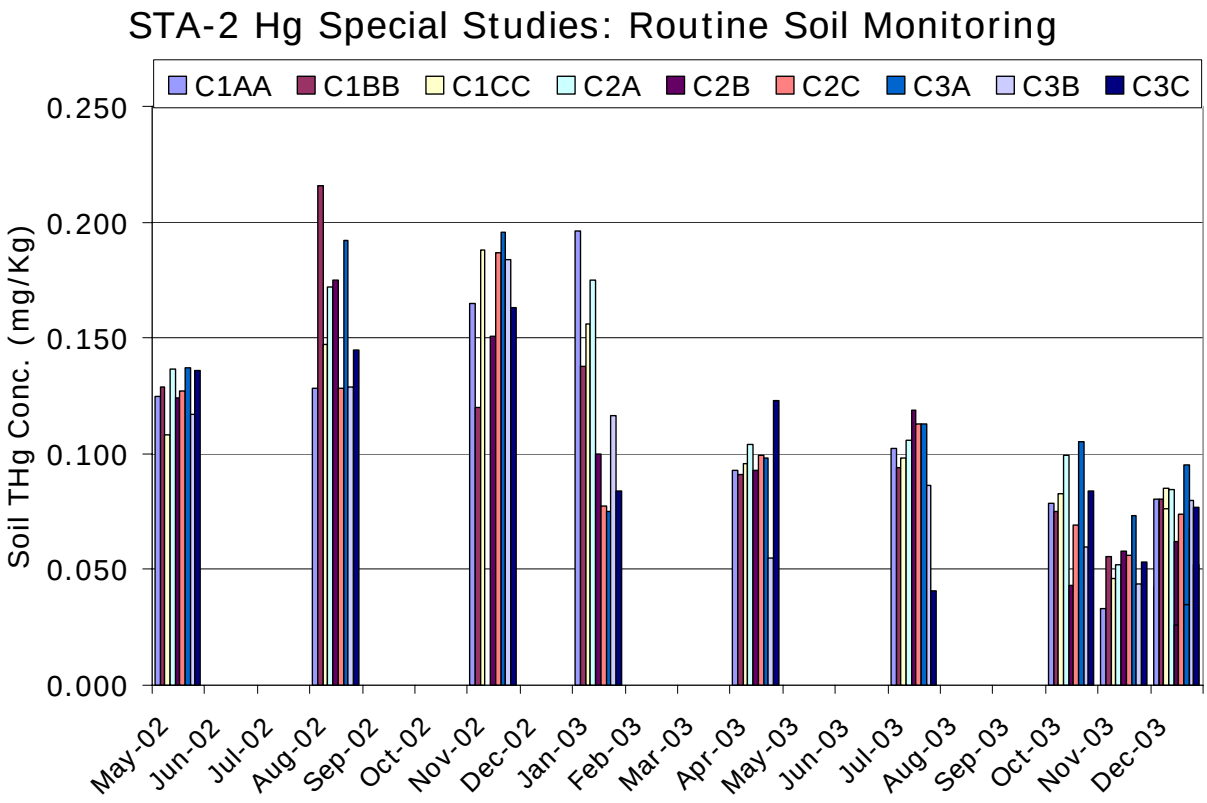

Figure 26. Concentrations of THg in surficial soil (0-4 cm) from treatment cell interior sites for the baseline condition in May 2002 through the final sampling event in December 2003–January 2004.

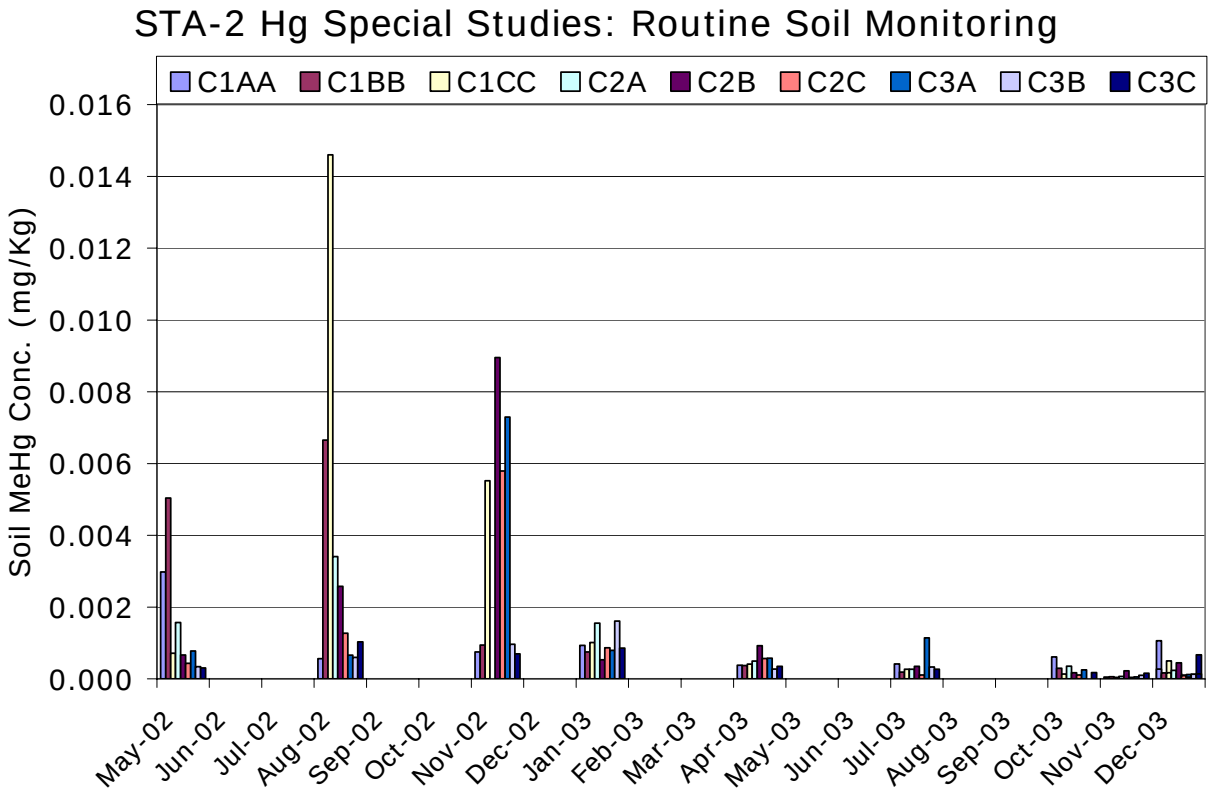

Figure 27. Concentrations of MeHg in surficial soil (0-4 cm) from treatment cell interior sites for the baseline condition in May 2002 through the final sampling event in December 2003–January 2004.

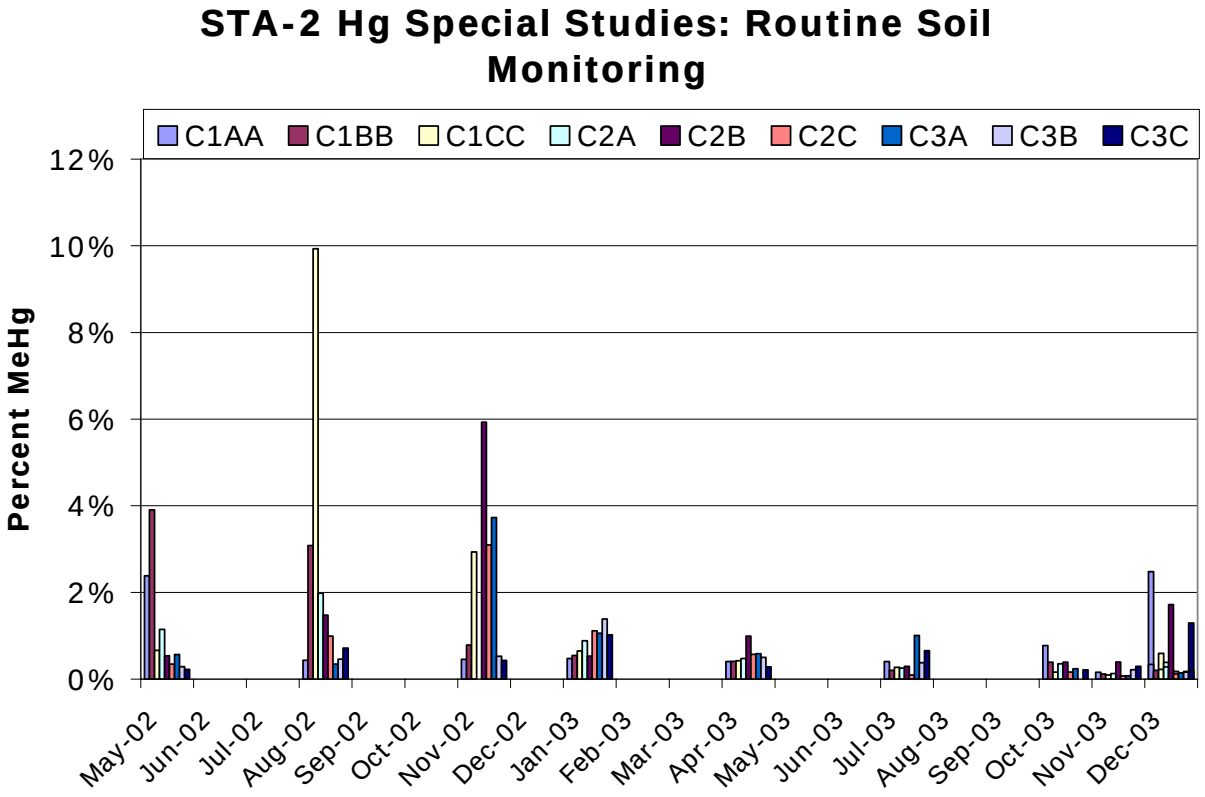

Figure 28. Percent MeHg (100 x [MeHg]/[THg]) in surficial soil (0-4 cm) from treatment cell interior sites for the baseline condition in May 2002 through the final sampling event in December 2003–January 2004.

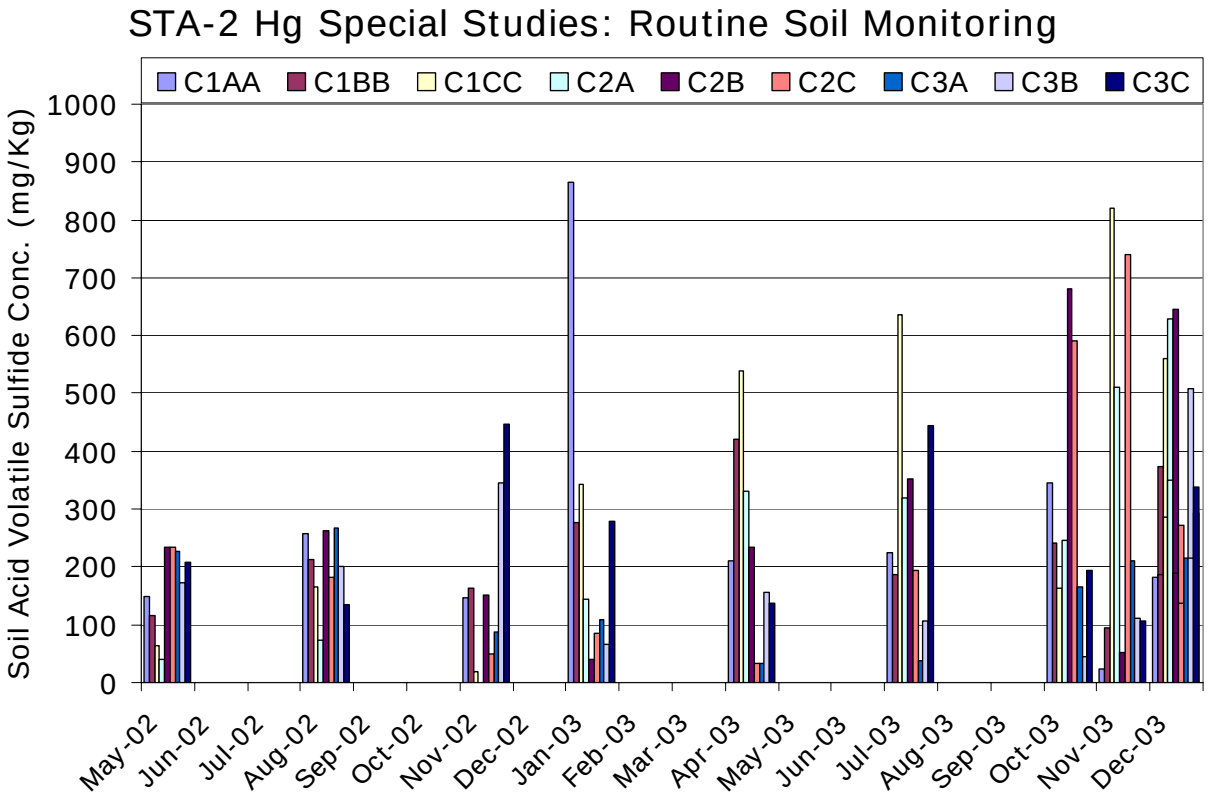

Figure 29. Concentrations of acid volatile sulfide (AVS) in surficial soil (0-4 cm) from treatment cell interior sites for the baseline condition in May 2002 through the final sampling event in December 2003–January 2004.

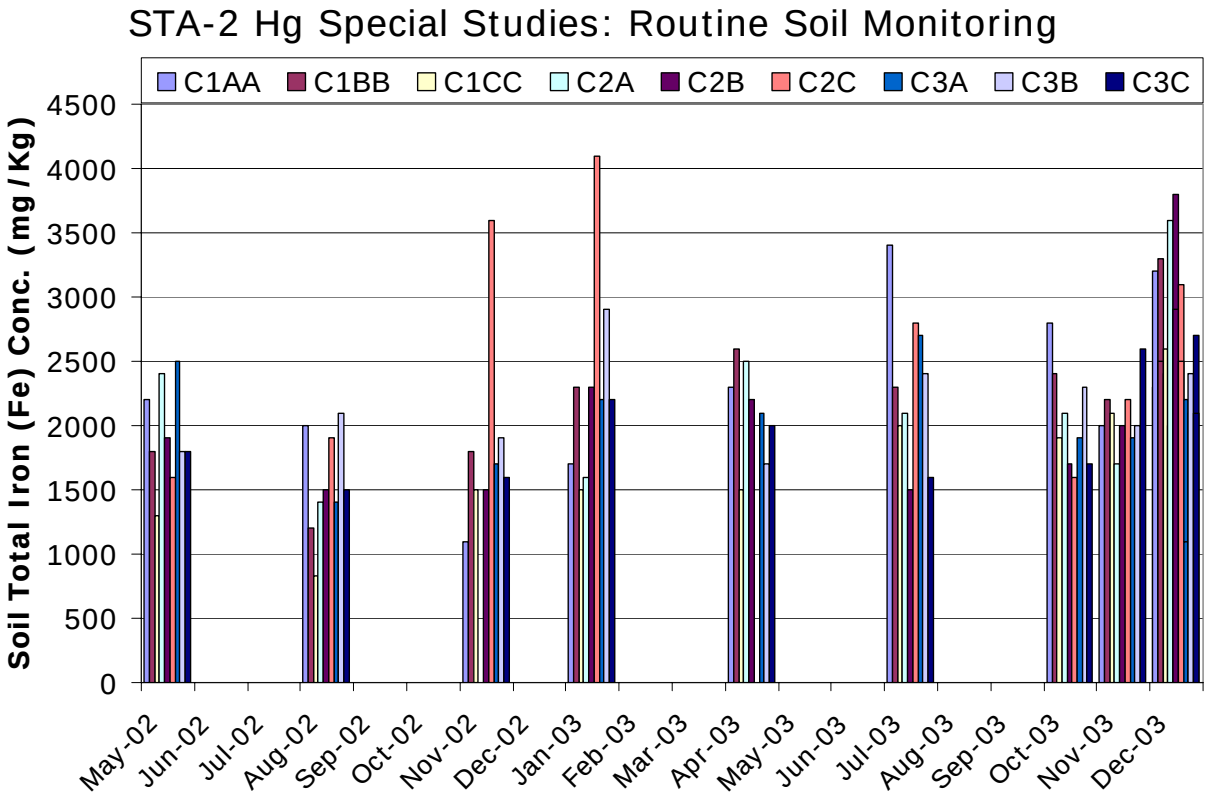

Figure 30. Concentrations of total iron (TFe) in surficial soil (0-4 cm) from treatment cell interior sites for the baseline condition in May 2002 through the final sampling event in December 2003–January 2004.

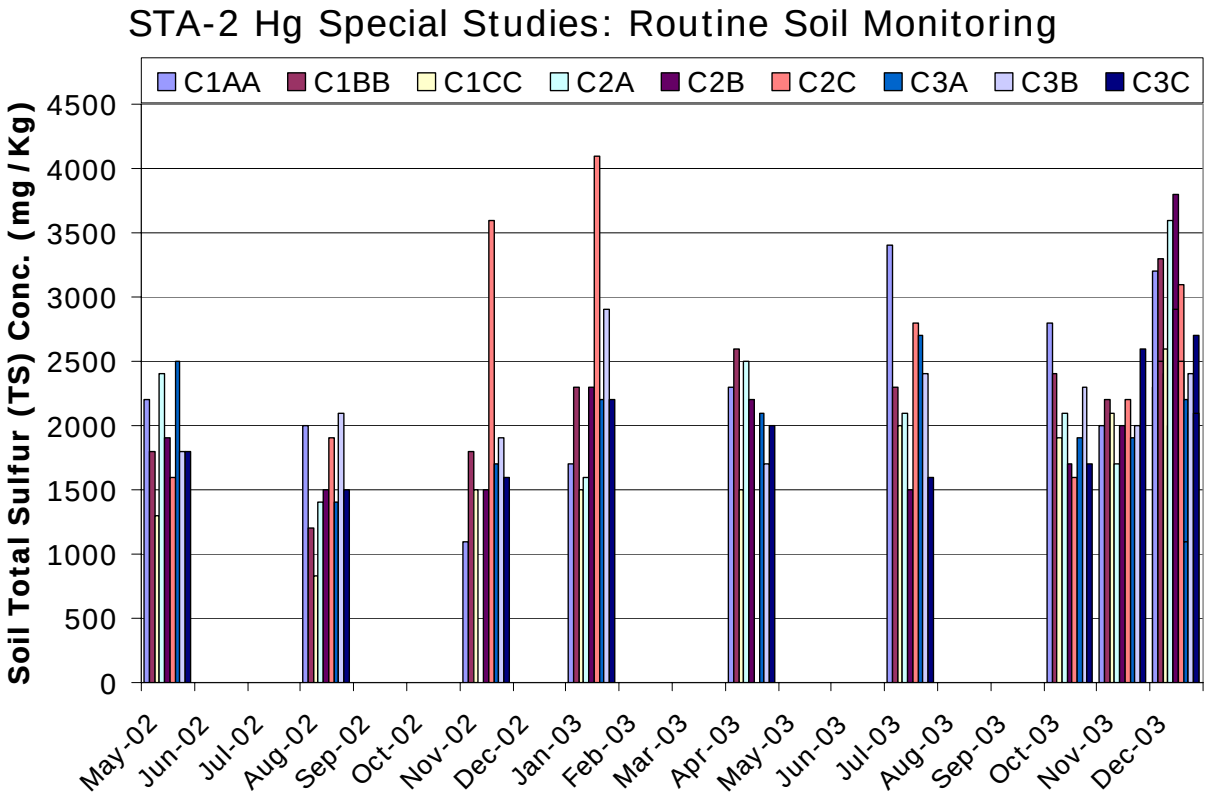

Figure 31. Concentrations of total sulfur (TS) in surficial soil (0-4 cm) from treatment cell interior sites for the baseline condition in May 2002 through the final sampling event in December 2003–January 2004.

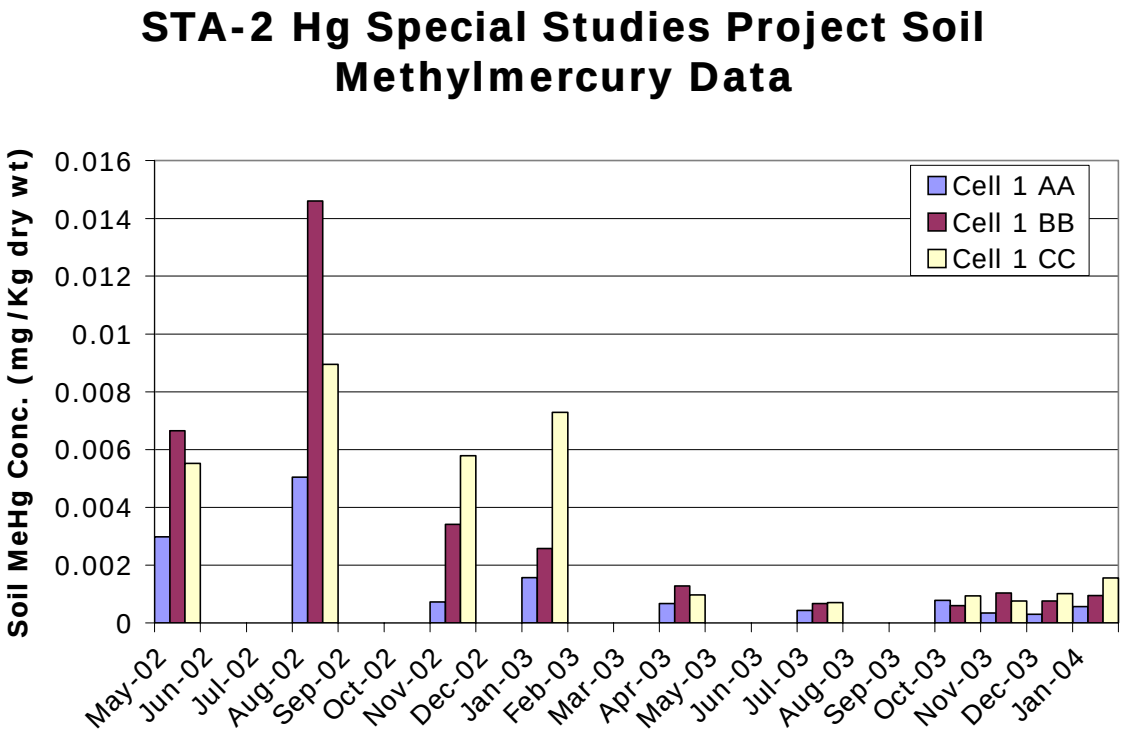

Figure 32. Concentrations of methylmercury (MeHg) in surficial soil (0-4 cm) from Cell 1 interior sites for the baseline condition in May 2002 through the final sampling event in December 2003–January 2004.

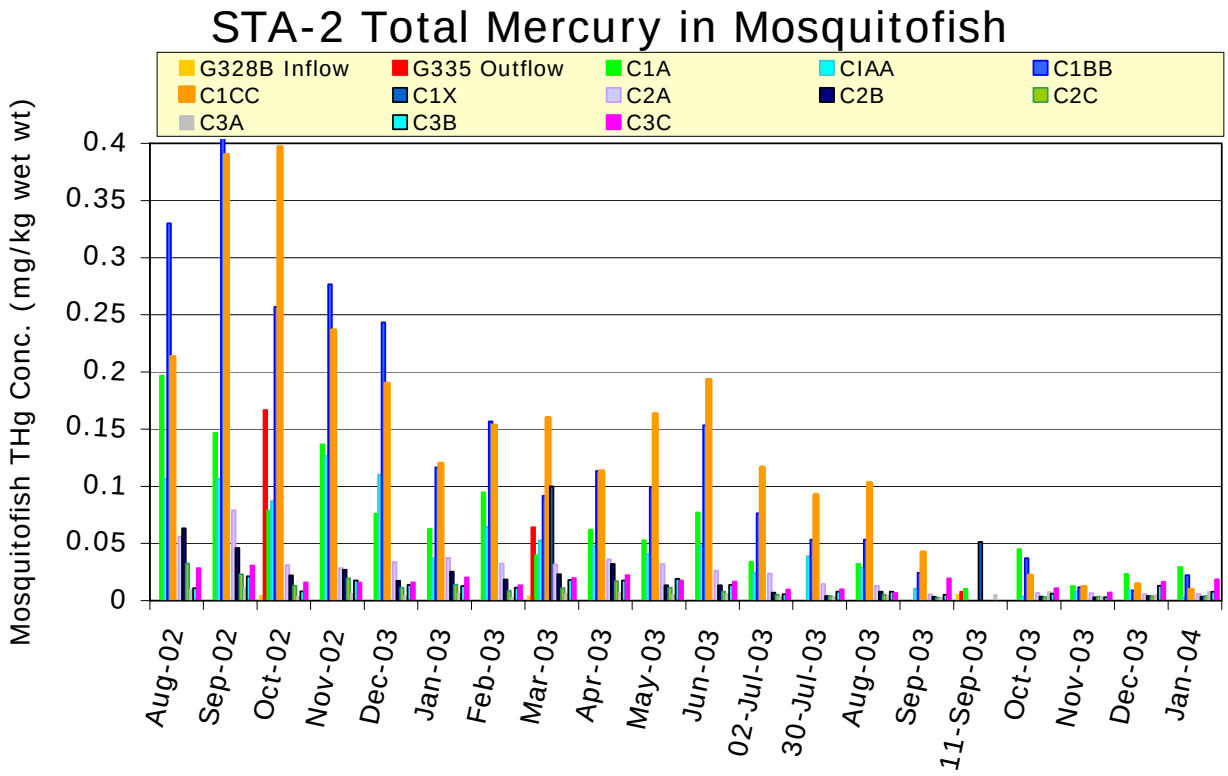

Figure 33. Concentrations of methylmercury (MeHg) as total mercury (THg) in mosquitofish from treatment cell, inflows, outflows, and interior sites for the period August 2002 through the final sampling event in January 2004.

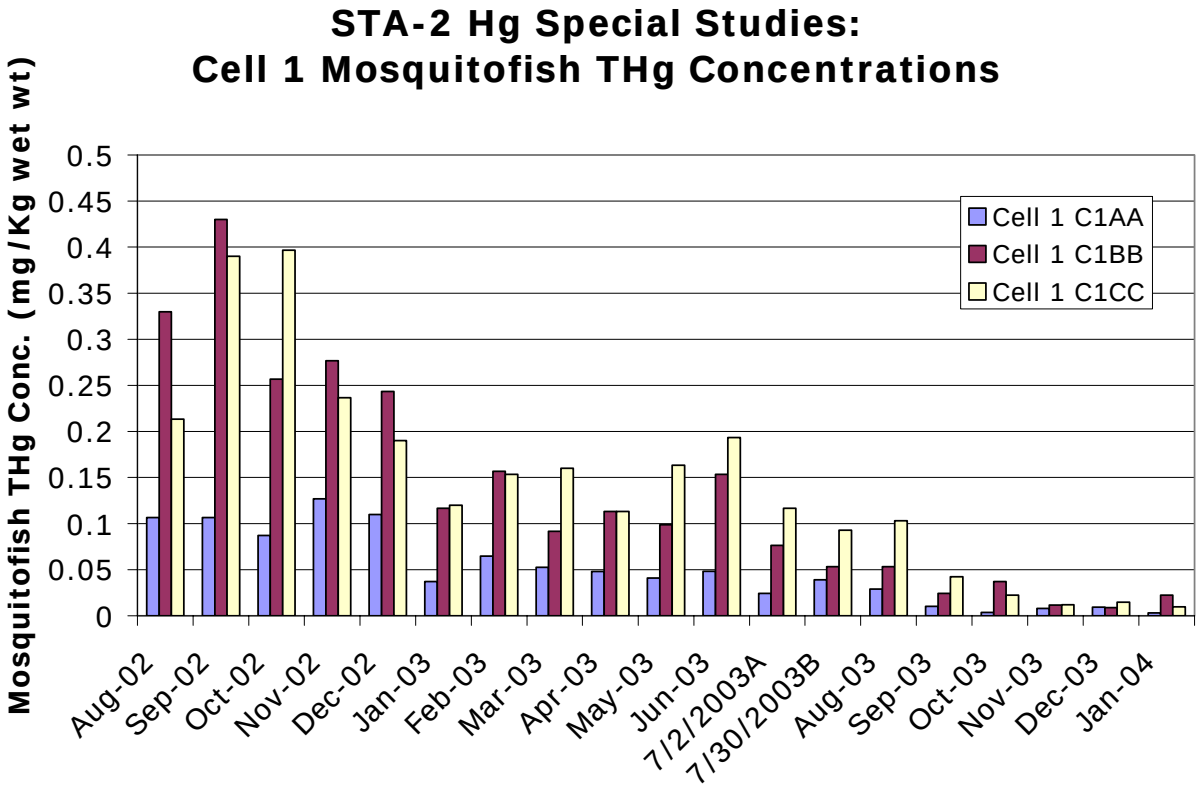

Figure 34. Concentrations of methylmercury (MeHg) as total mercury (THg) in mosquitofish from Cell 1 interior sites for the period August 2002 through the final sampling event in January 2004.

BIOCONCENTRATION, BIOACCUMULATION, AND BIOMAGNIFICATION FACTORS

Mosquitofish / Water

The mosquitofish THg at each of the interior sampling sites (Appendix G, Table 4) were paired with the spatially corresponding, immediately preceding surface water filtered MeHg value one week earlier (Lag-1 week) (Appendix G, Table 2) and the ratio of the former to the latter calculated. This process was repeated for mosquitofish measurements made in the preceding four weeks (Lag-5 weeks), etc. The results are plotted in **Figures 35** through **41**. Two observations are noteworthy.

First, the mosquitofish/surface water BAFs varied with lag time and sampling site, suggesting that the system had not yet reached a steady state with the original first-flush MeHg pulse, that there were also "aftershock" pulses of excess MeHg production from the recycling of first-flush excess Hg(II) with which the aquatic ecosystem had also not yet reached a steady state, that contributions were occurring from other compartments and pathways with different turnover and transport times in response to the original first-flush pulse of excess MeHg production or the "aftershock" pulses, or that trophic relationships continued to change as the aquatic ecosystem matured following reflooding. The other potentially contributing compartments and pathways are discussed in subsequent subsections.

Second, because of the phenomenon discussed in the preceding paragraph, it is not possible to determine from the magnitude of the BAF alone what are the minimum, average, and maximum response time envelopes of the mosquitofish population to changes in the surface water filtered MeHg concentration, other than to note that the BAFs appear to peak at Lag-5 weeks. The ability to further resolve the response time to a possible two, three, or four weeks is precluded by the four-week frequency of mosquitofish sampling and the one-week stagger between surface water sampling and mosquitofish sampling. Some insight into the response time of the mosquitofish population to a change in the surface water MeHg concentration for lag times greater than five weeks may be gained by evaluating the strength of the correlation between the mosquitofish THg concentration and the appropriately lagged surface water unfiltered MeHg concentration. This is discussed further in the "Exploratory Data Analysis" section of this document.

Mosquitofish / Soil

Next, the mosquitofish THg concentration at each of the interior sampling sites (Appendix G, Table 4) was paired with the spatially corresponding, immediately preceding surficial soil MeHg value two weeks earlier (Lag-2 weeks) (Appendix G, Table 3) and the ratio of the former to the latter calculated. This process was repeated for mosquitofish measurements made in the preceding four weeks (Lag-6 weeks), etc. The results are plotted in **Figures 42** through **48**. Based on the magnitudes of the correlations between mosquitofish THg and soil MeHg, the detrital food web could have been making a substantial contribution to the bioaccumulation of MeHg in the Cell 1 aquatic food chain, albeit with a lag time not inconsistent with the time required for MeHg to move from the surficial soil compartment to the trophic level(s) where mosquitofish was (were) foraging, on average. However, support for this inference must await the summary of the results of the exploratory data analysis.

Mosquitofish / Pore Water

The mosquitofish THg concentration at each of the interior sampling sites (Appendix G, Table 4) was then paired with the spatially corresponding, immediately preceding pore water filtered MeHg value two weeks earlier (Lag-2 weeks) (Appendix G, Table 5) and the ratio of the former to the latter calculated. This process was repeated for mosquitofish measurements made in the preceding four weeks (Lag-6 weeks), etc. The results are plotted in **Figures 49** through **52**. The results indicate that, as with surface water, the mosquitofish population appeared to respond with a delay of greater than two weeks. Further parsing of the results must await the exploratory data analysis.

Mosquitofish / Vegetation

Next, the mosquitofish THg concentration at each of the interior sampling sites (Appendix G, Table 4) was paired with the spatially corresponding, immediately preceding average MeHg value for each plant species (e.g., cattail) or category of species (e.g., SAV) two or three weeks earlier (Lag-2 or Lag-3 weeks) (Appendix G, Table 6) and the ratio of the former to the latter calculated. This process was repeated for mosquitofish measurements made in the preceding four weeks (Lag-6 or -7 weeks), etc. The results are plotted for cattail, sawgrass, SAV, and periphyton in **Figures 53** through **56**. The same patterns are extant as for surface water, pore water, and soil, albeit based on only three sampling events. As with the other media, only magnitudes of the correlations between mosquitofish THg and vegetation MeHg will allow one to infer that the autotrophic food web could have been making a substantial contribution to the bioaccumulation of MeHg in the Cell 1 aquatic food chain, albeit with a lag time consistent with the time required for the development of an autotrophic food chain at least to the trophic level(s) where mosquitofish was (were) foraging, on average.

Mosquitofish / Sunfish

Figures 57 and **58** graph the ratio of sunfish THg to mosquitofish THg (biomagnification factor or BMF) for sunfish (Appendix 4-4 of the 2005 South Florida Environmental Report) and mosquitofish samples (Appendix G, Table 4) collected within the same month (Lag-0 months) and for sunfish samples paired with mosquitofish samples collected in the preceding six months (Lag-6 months). These fish samples were collected at the common inflow (G-328), Cell 1 interior sites C1A and C1X, the common outflow at G-335, and two downstream stations in the transition zones of the receiving water body, Water Conservation Area 2A (WCA-2A). These samples were collected on an as available basis, so some sunfish data were missing. Interestingly, when the sunfish THg concentrations are paired with the corresponding mosquitofish THg concentrations from the preceding semi-annual collection, the sunfish/mosquitofish BMFs appear to be substantially lower, less variable, and much more consistent with what would be expected based on studies on aquatic food chain bioaccumulation conducted elsewhere (USEPA, 1997) and based on bioenergetics grounds (Norstrom et al., 1976; Rodgers, 1994). This result would be consistent with the growth and depuration rates of sunfish size-age categories typically collected via electroshocking in the District's canals and marshes (Lange et al., 1998; 1999), which are believed to integrate and average exposures over at least the previous six months, as opposed to the mosquitofish, which, based on this and previous studies of MeHg anomalies, respond to changes in MeHg concentrations in the aquatic environment over a matter of several weeks to several months. This disconnect between the integration and averaging times of the two species can only be reconciled if the data are properly paired temporally as well as spatially. The substantial differences between the Lag-0 and Lag-6 months sunfish/mosquitofish BMFs

upstream, within, and downstream of STA-2 Cell 1 underscore the importance of systematic lag and lag-average analysis of the environmental data.

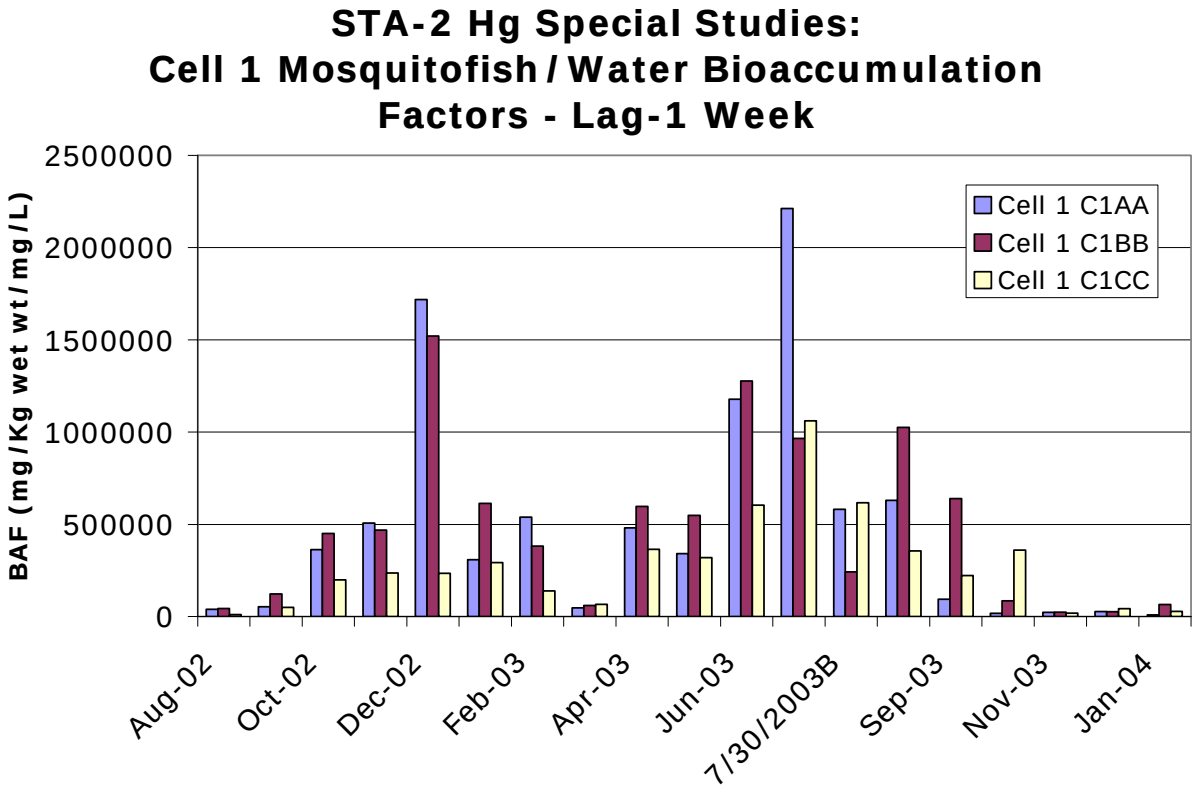

Figure 35. Ratio of THg as MeHg in mosquitofish to concentration of filtered MeHg in surface water from interior Cell 1 collected one week earlier (Lag–1 week) for the period from August 2002 through the final sampling event in January 2004.

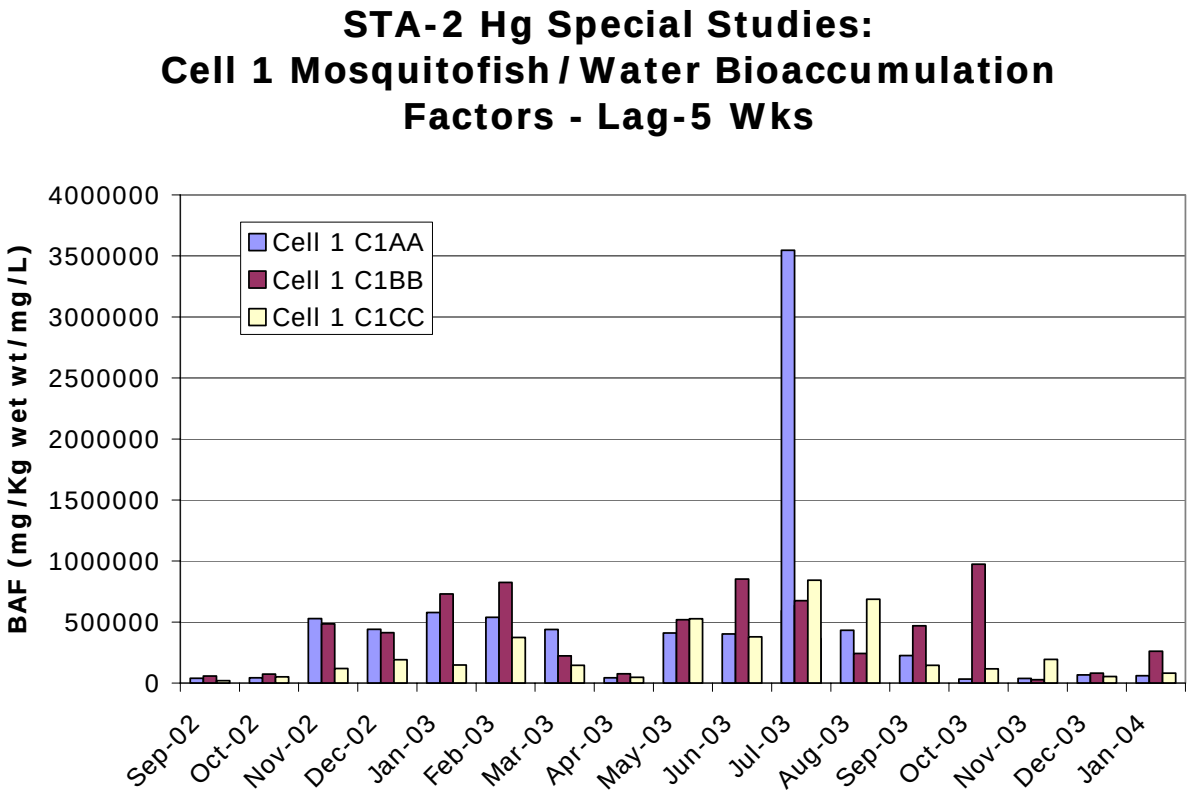

Figure 36. Ratio of THg as MeHg in mosquitofish to concentration of filtered MeHg in surface water from interior Cell 1 collected five weeks earlier (Lag–5 weeks) for the period from August 2002 through the final sampling event in January 2004.

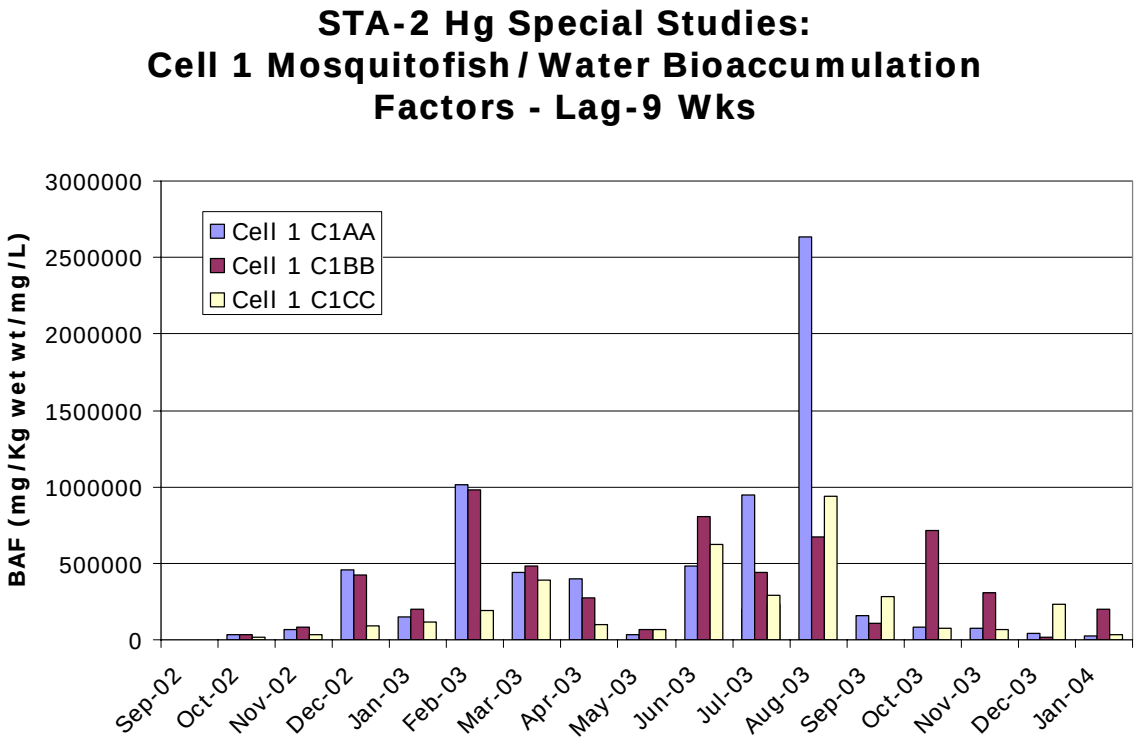

Figure 37. Ratio of THg as MeHg in mosquitofish to concentration of filtered MeHg in surface water from interior Cell 1 collected nine weeks earlier (Lag–9 weeks) for the period from August 2002 through the final sampling event in January 2004.

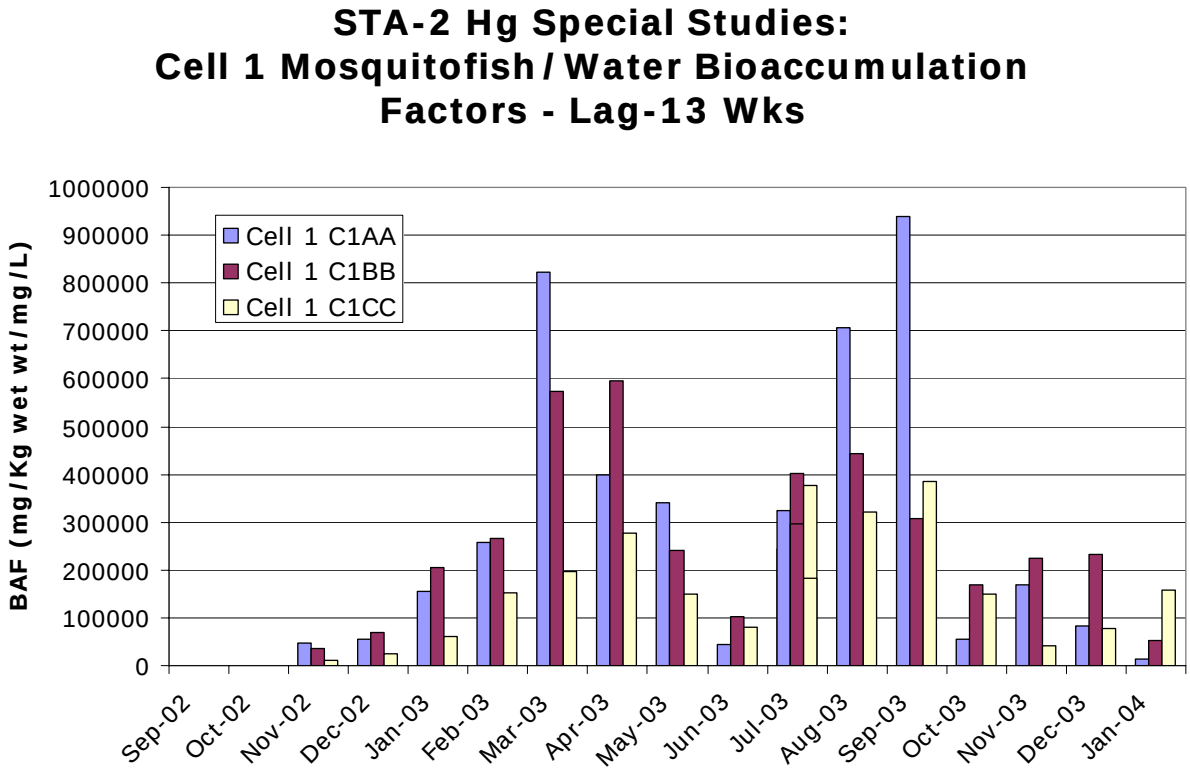

Figure 38. Ratio of THg as MeHg in mosquitofish to concentration of filtered MeHg in surface water from interior Cell 1 collected thirteen weeks earlier (Lag–13 weeks) for the period from August 2002 through the final sampling event in January 2004.

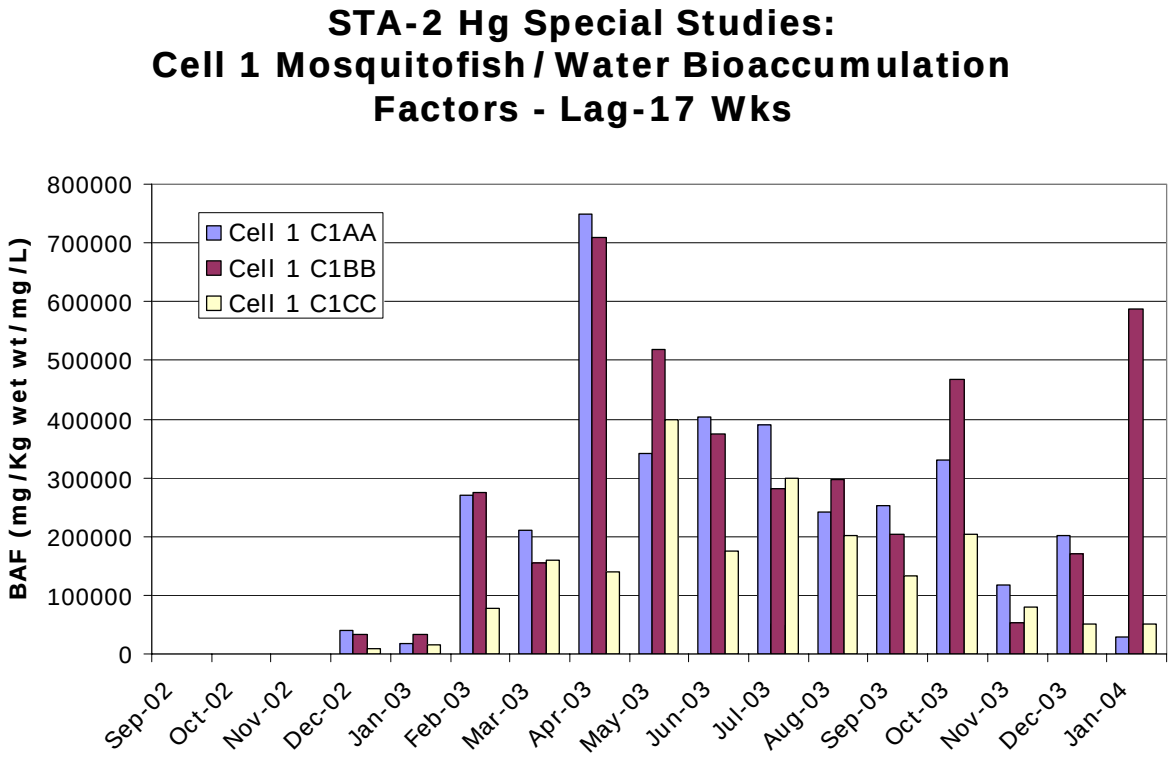

Figure 39. Ratio of THg as MeHg in mosquitofish to concentration of filtered MeHg in surface water from interior Cell 1 collected seventeen weeks earlier (Lag–17 weeks) for the period from August 2002 through the final sampling event in January 2004.

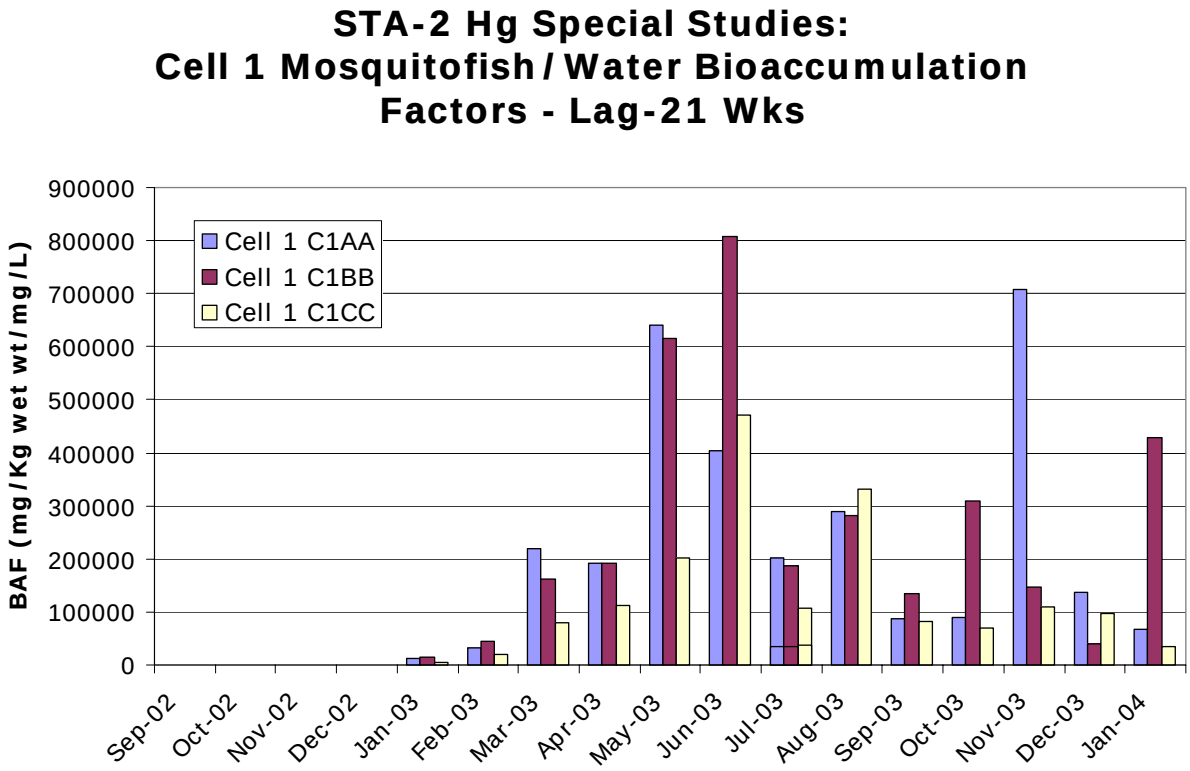

Figure 40. Ratio of THg as MeHg in mosquitofish to concentration of filtered MeHg in surface water from interior Cell 1 collected twenty-one weeks earlier (Lag–21 weeks) for the period from August 2002 through the final sampling event in January 2004.

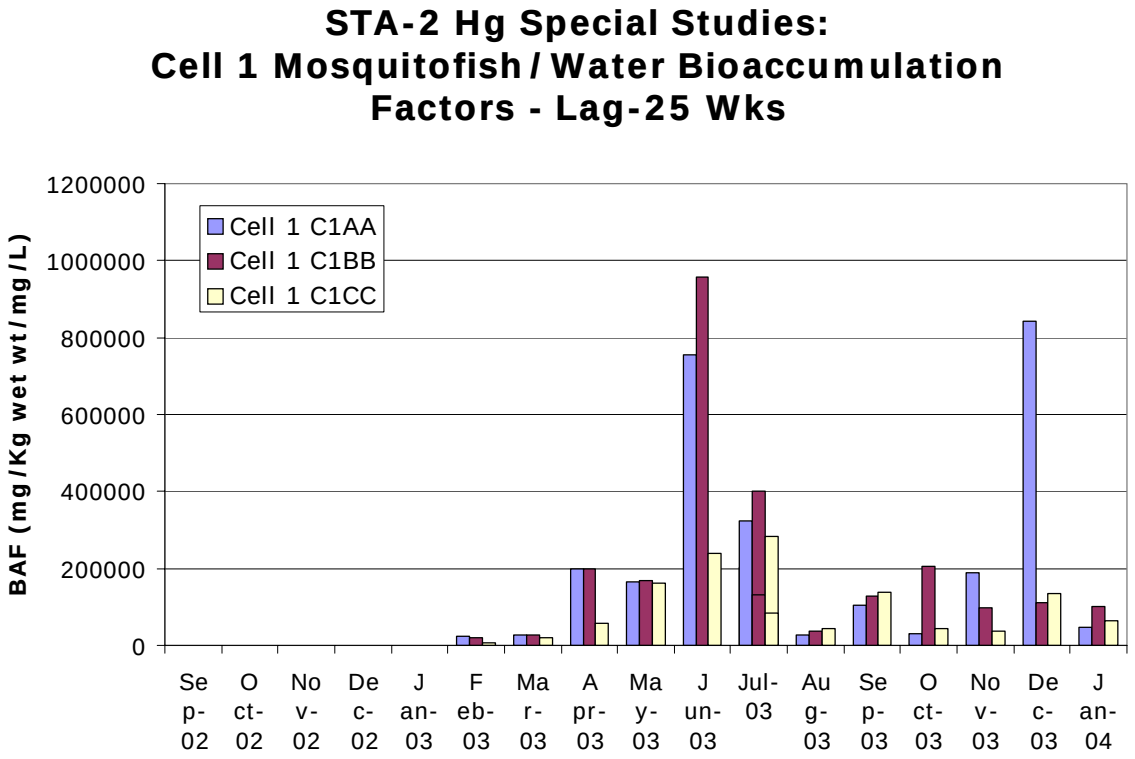

Figure 41. Ratio of THg as MeHg in mosquitofish to concentration of filtered MeHg in surface water from interior Cell 1 collected twenty-five weeks earlier (Lag–25 weeks) for the period from August 2002 through the final sampling event in January 2004.

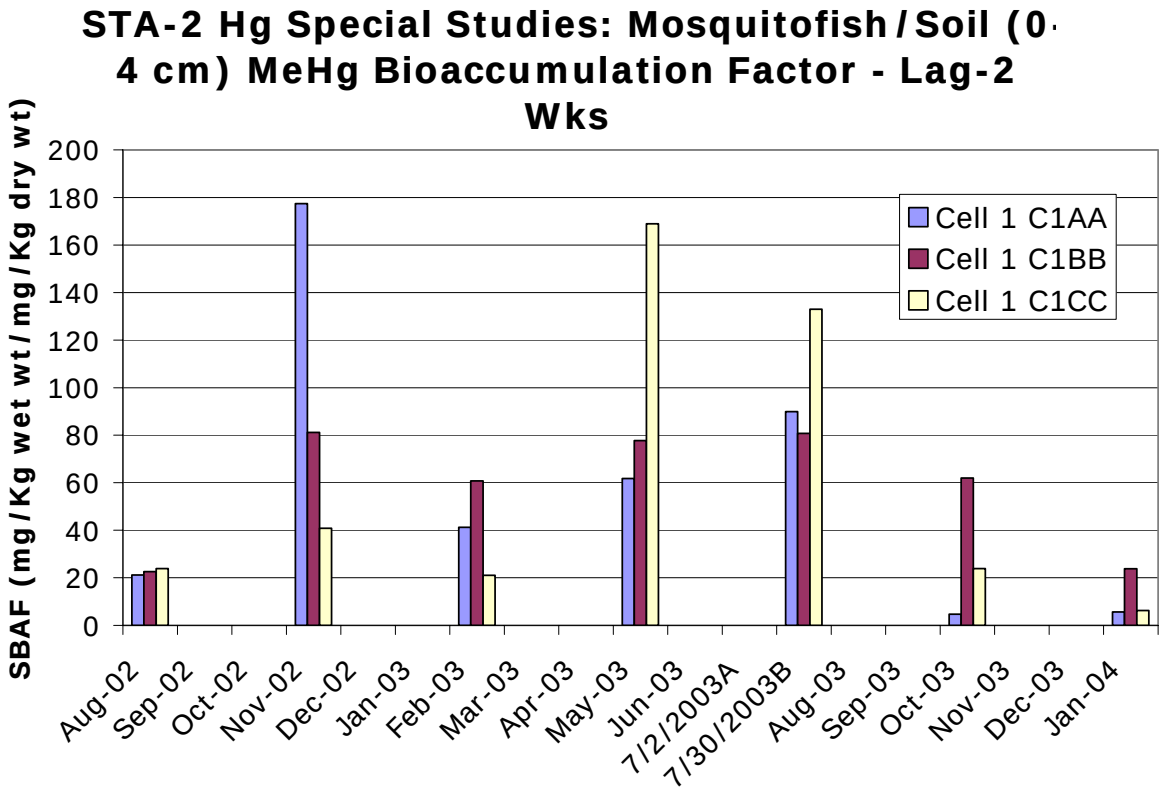

Figure 42. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in surficial sediment (0-4 cm) from interior Cell 1 collected two weeks earlier (Lag–2 weeks) for the period from August 2002 through the final sampling event in January 2004.

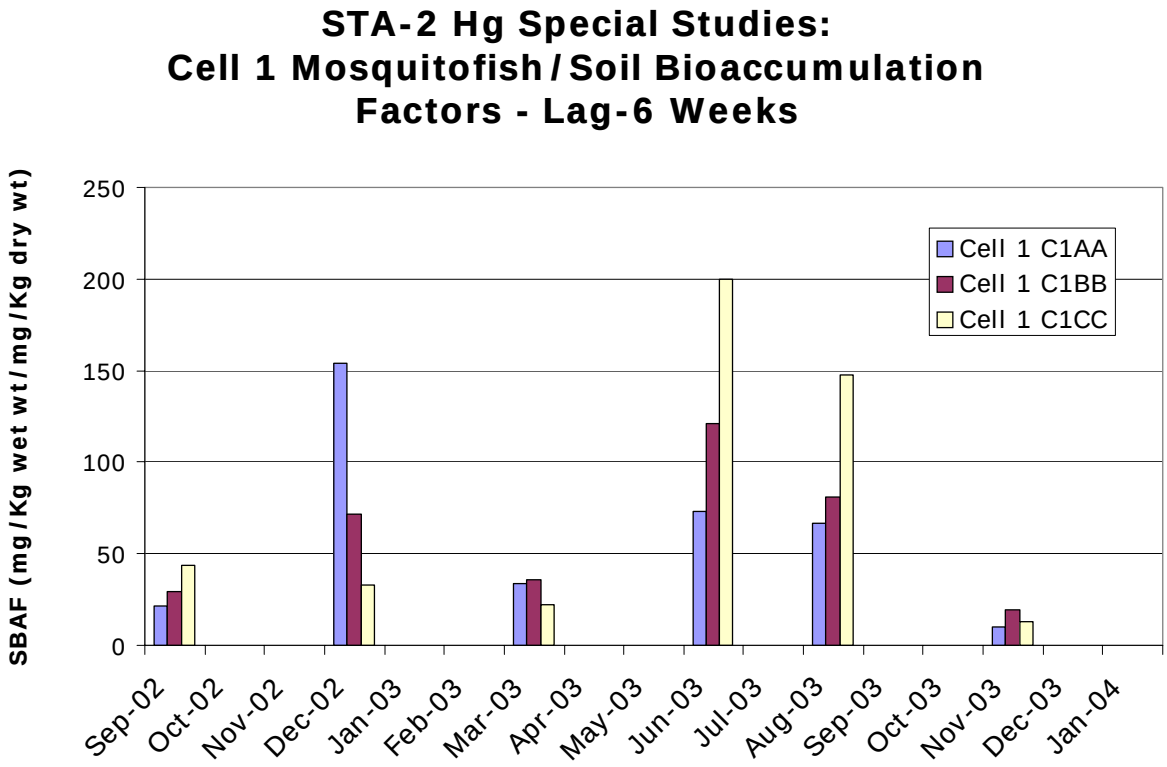

Figure 43. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in surficial sediment (0-4 cm) from interior Cell 1 collected six weeks earlier (Lag–6 weeks) for the period from August 2002 through the final sampling event in January 2004.

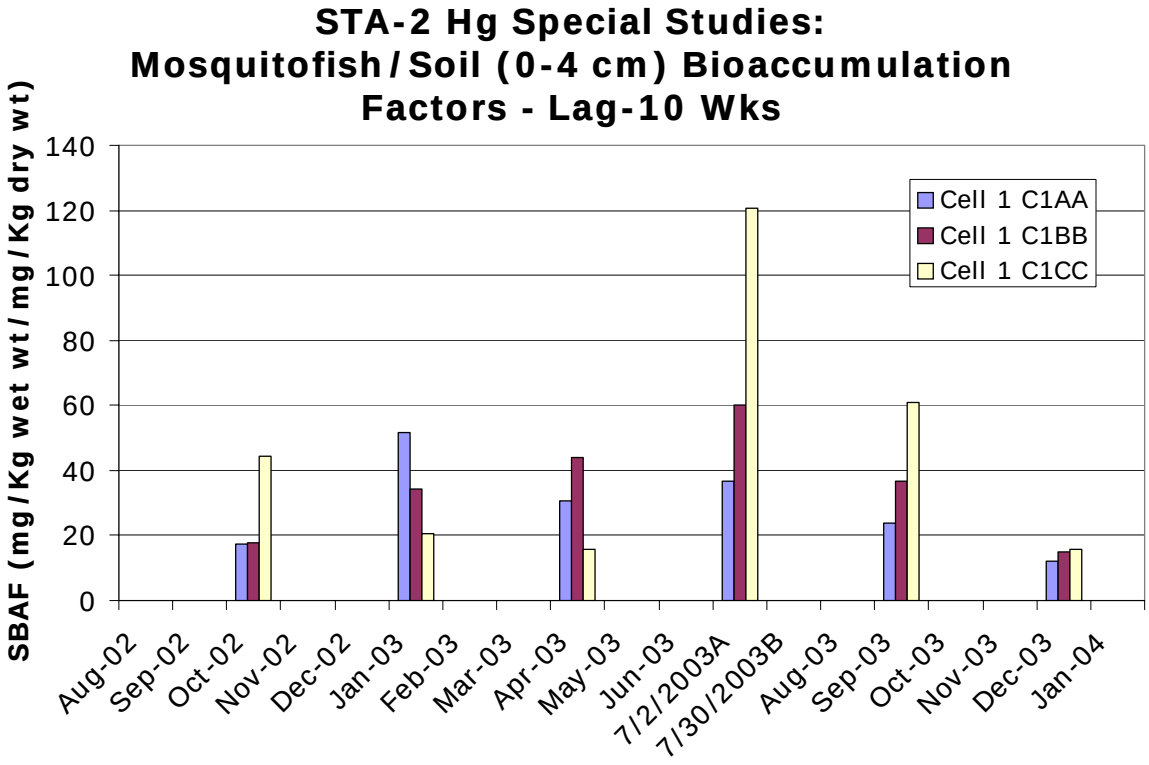

Figure 44. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in surficial sediment (0-4 cm) from interior Cell 1 collected ten weeks earlier (Lag–10 weeks) for the period from August 2002 through the final sampling event in January 2004.

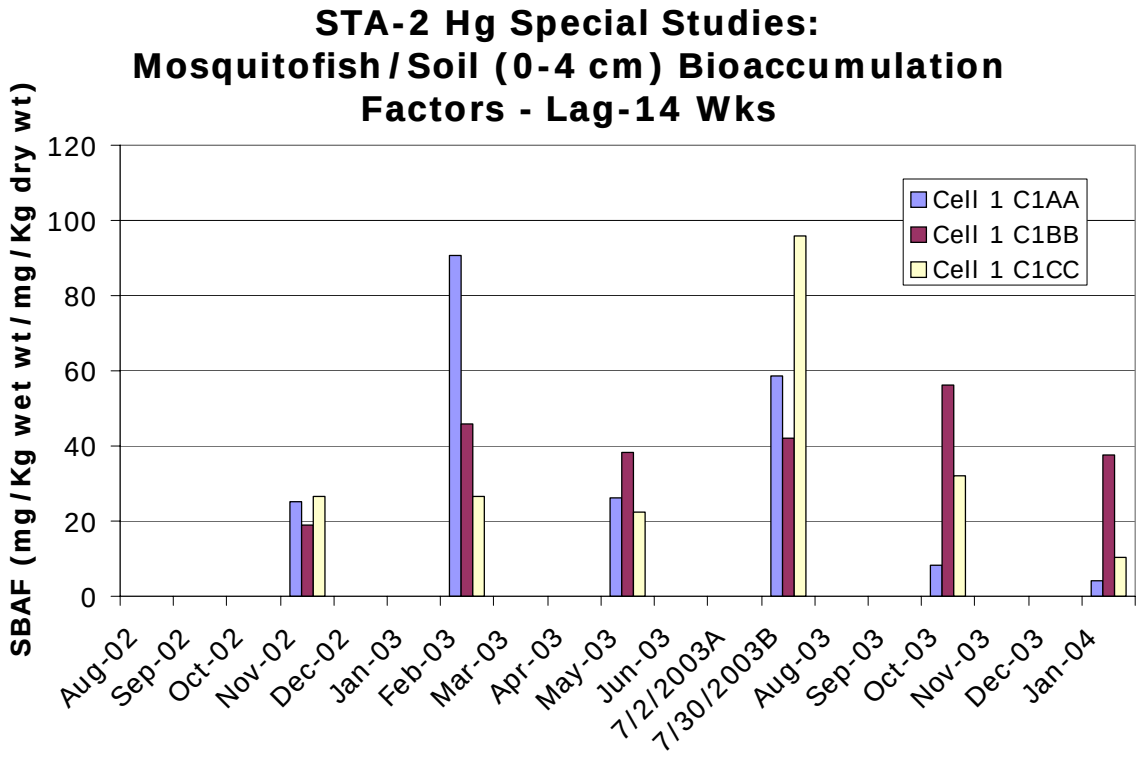

Figure 45. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in surficial sediment (0-4 cm) from interior Cell 1 collected fourteen weeks earlier (Lag–14 weeks) for the period from August 2002 through the final sampling event in January 2004.

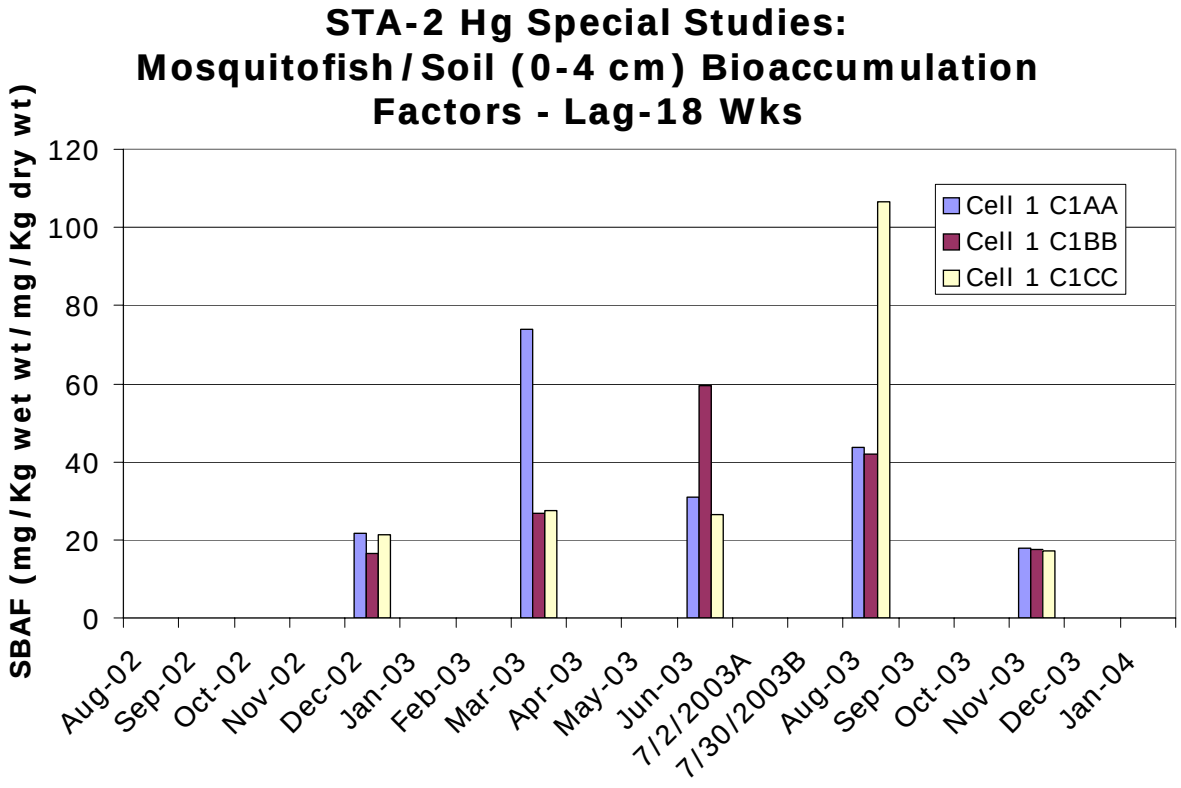

Figure 46. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in surficial sediment (0-4 cm) from interior Cell 1 collected eighteen weeks earlier (Lag–18 weeks) for the period from August 2002 through the final sampling event in January 2004.

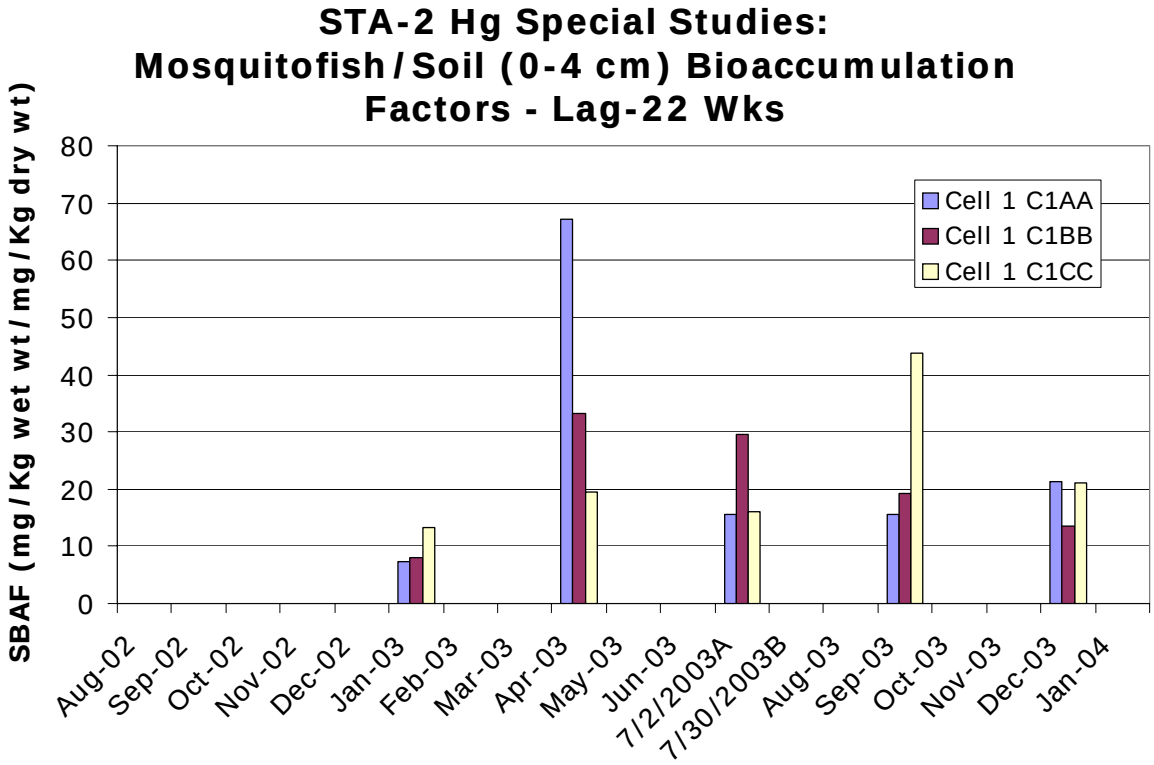

Figure 47. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in surficial sediment (0-4 cm) from interior Cell 1 collected twenty-two weeks earlier (Lag–22 weeks) for the period from August 2002 through the final sampling event in January 2004.

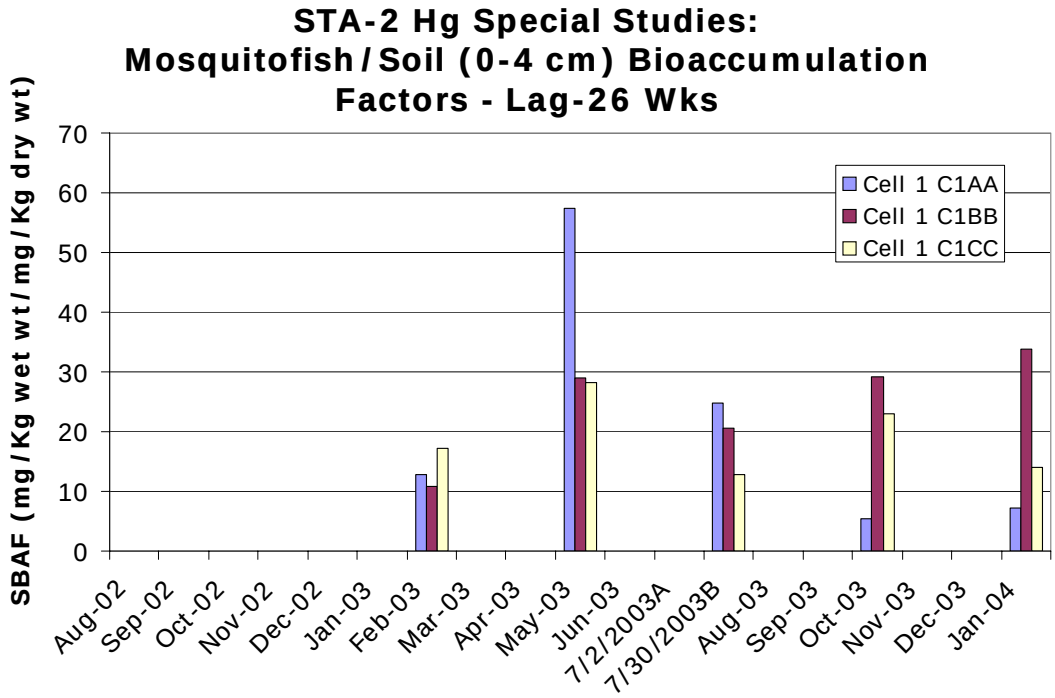

Figure 48. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in surficial sediment (0-4 cm) from interior Cell 1 collected twenty-six weeks earlier (Lag–26 weeks) for the period from August 2002 through the final sampling event in January 2004.

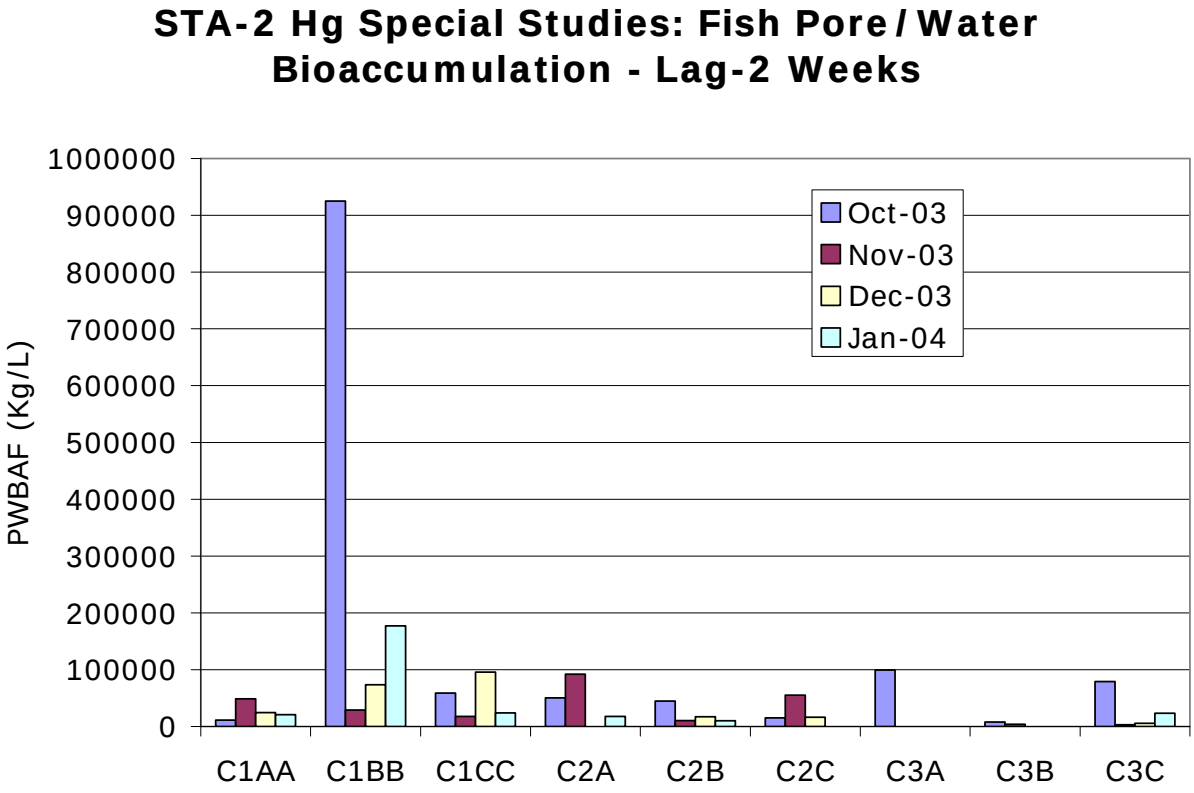

Figure 49. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in pore water (0-4 cm) from interior Cell 1 collected two weeks earlier (Lag–2 weeks) for the period August 2002 from through the final sampling event in January 2004.

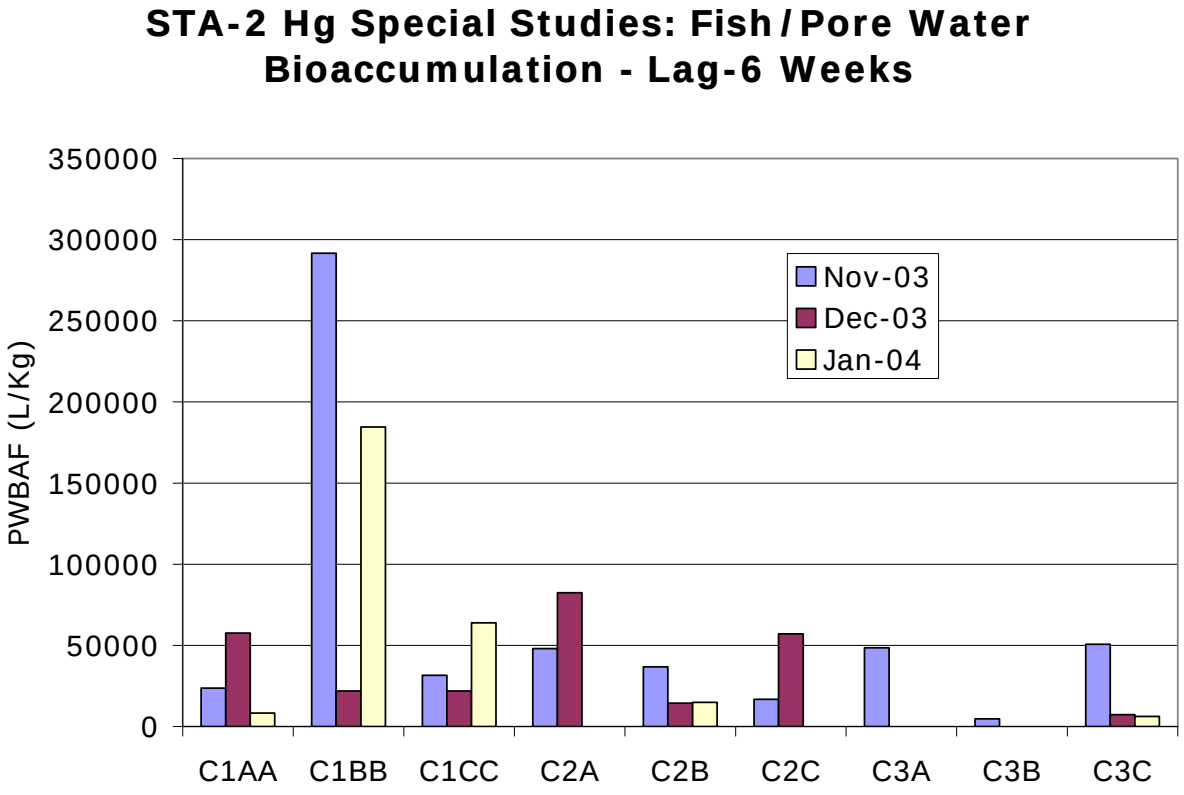

Figure 50. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in pore water (0-4 cm) from interior Cell 1 collected two weeks earlier (Lag–6 weeks) for the period from August 2002 through the final sampling event in January 2004.

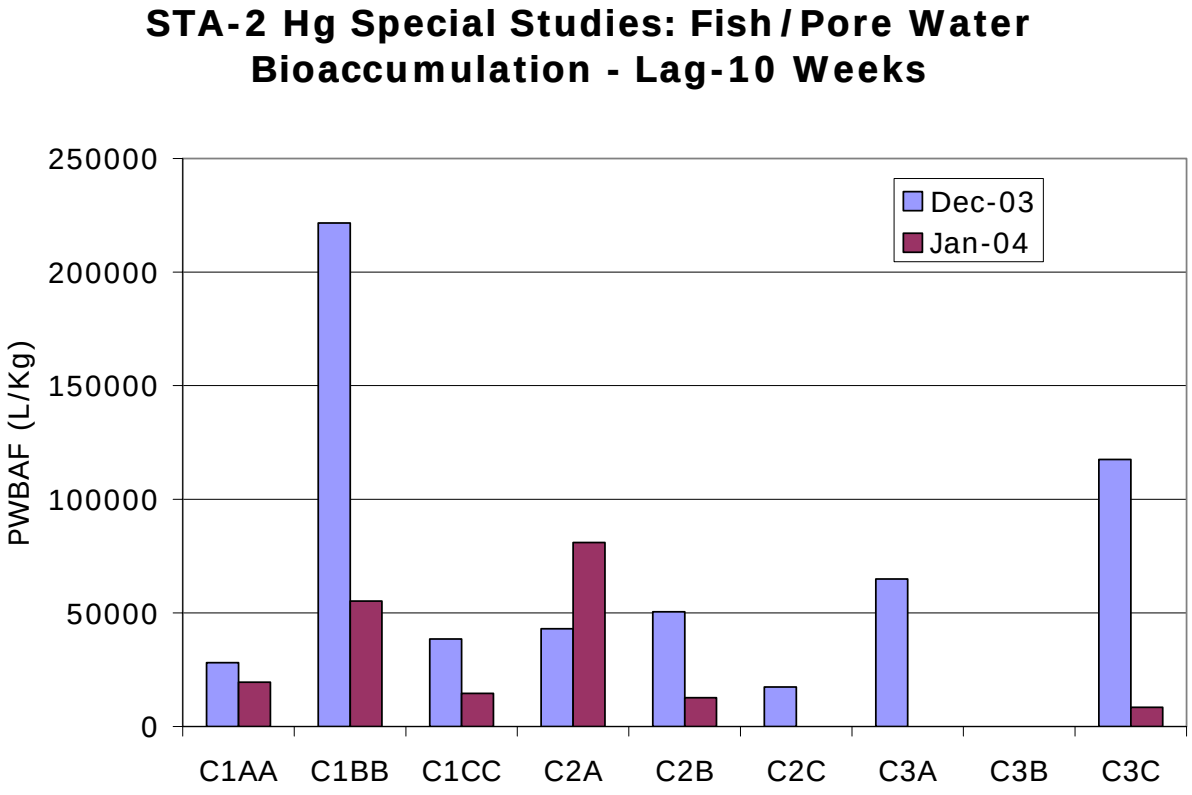

Figure 51. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in pore water (0-4 cm) from interior Cell 1 collected two weeks earlier (Lag–10 weeks) for the period from August 2002 through the final sampling event in January 2004.

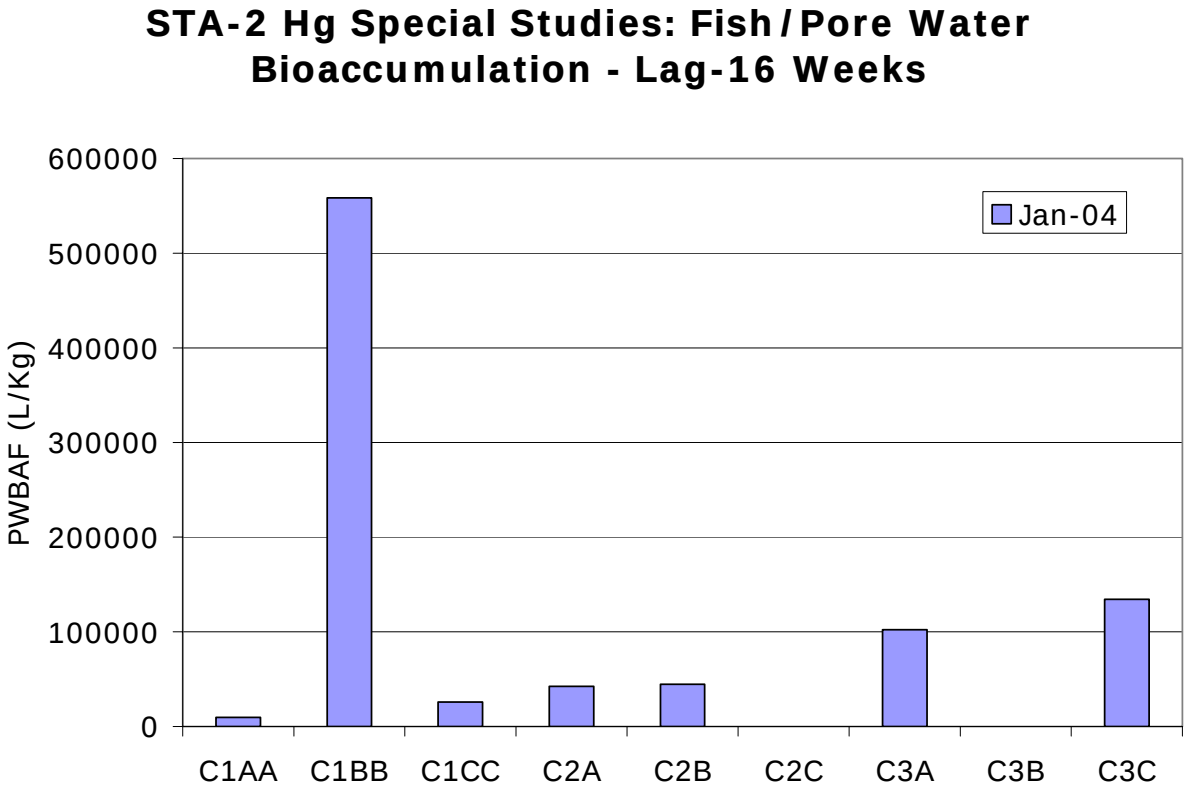

Figure 52. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in pore water (0-4 cm) from interior Cell 1 collected two weeks earlier (Lag–16 weeks) for the period from August 2002 through the final sampling event in January 2004.

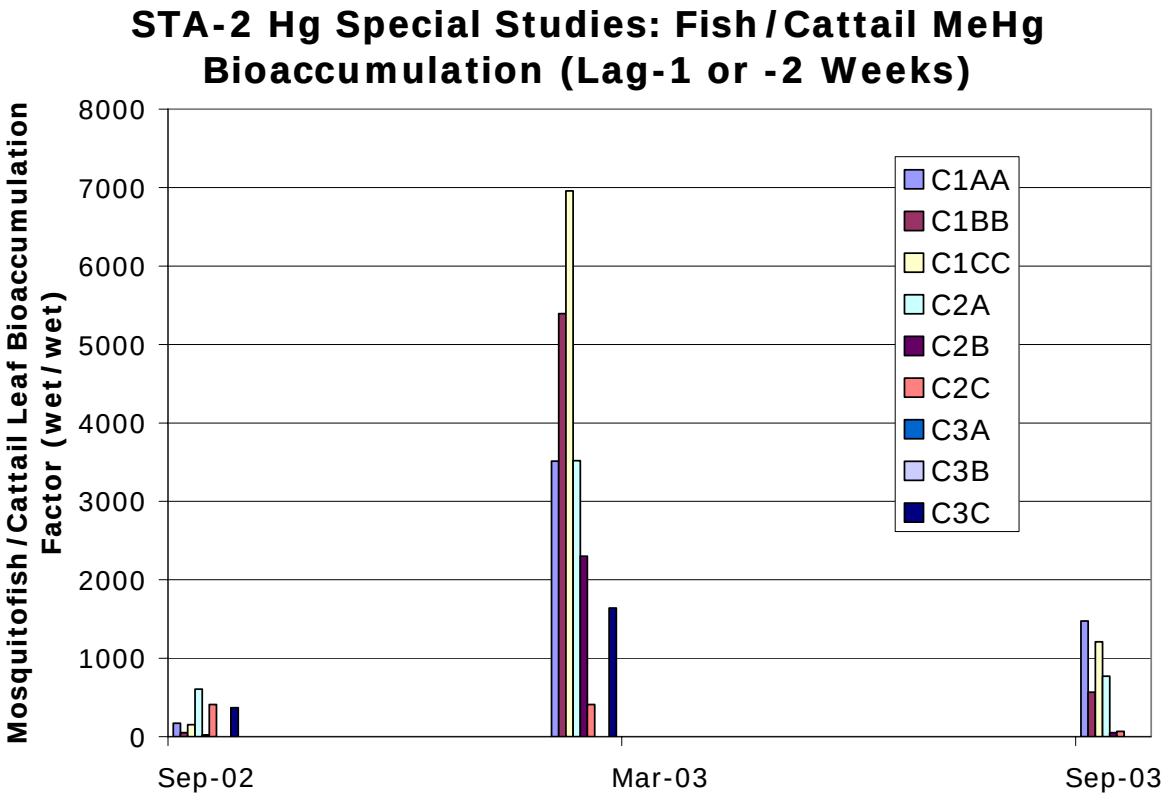

Figure 53. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in cattail leaves from interior treatment cells collected one or two weeks earlier (Lag–1 or -2 weeks) for the period from August 2002 through the final sampling event in September 2003.

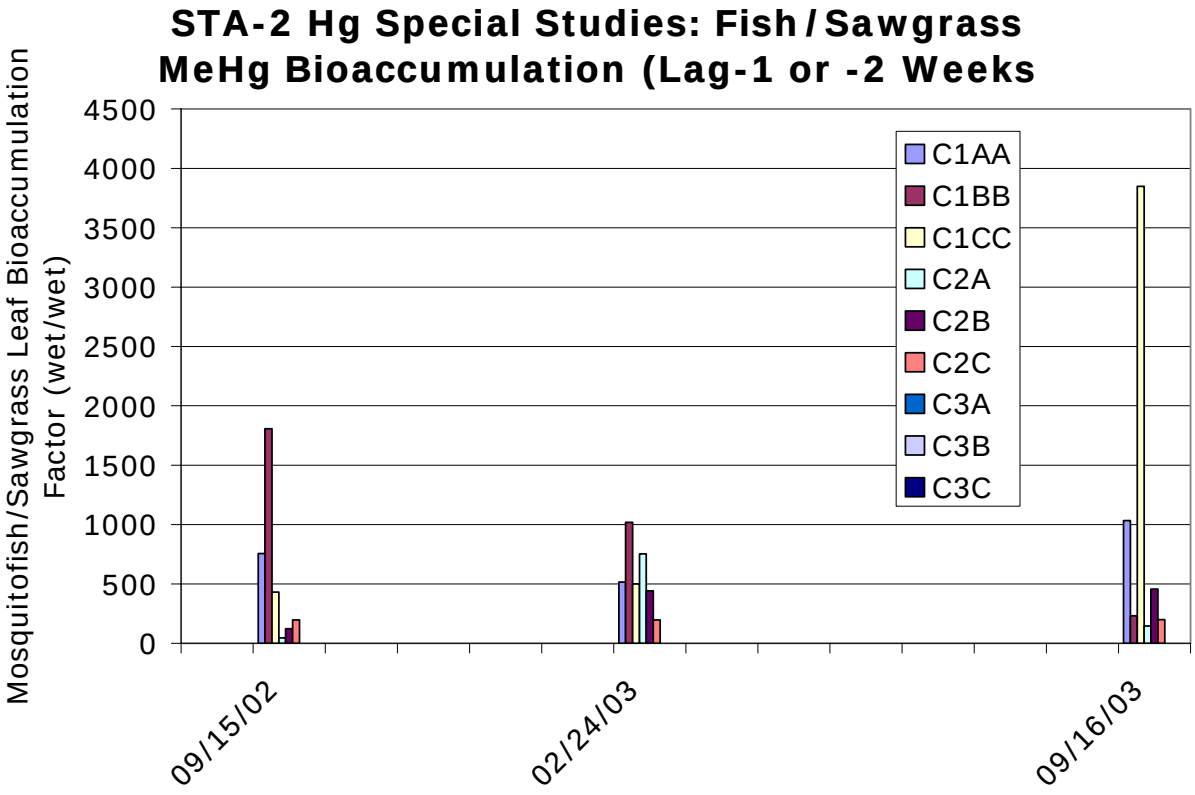

Figure 54. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in sawgrass leaves from interior treatment cells collected one or two weeks earlier (Lag–1 or -2 weeks) for the period from August 2002 through the final sampling event in September 2003.

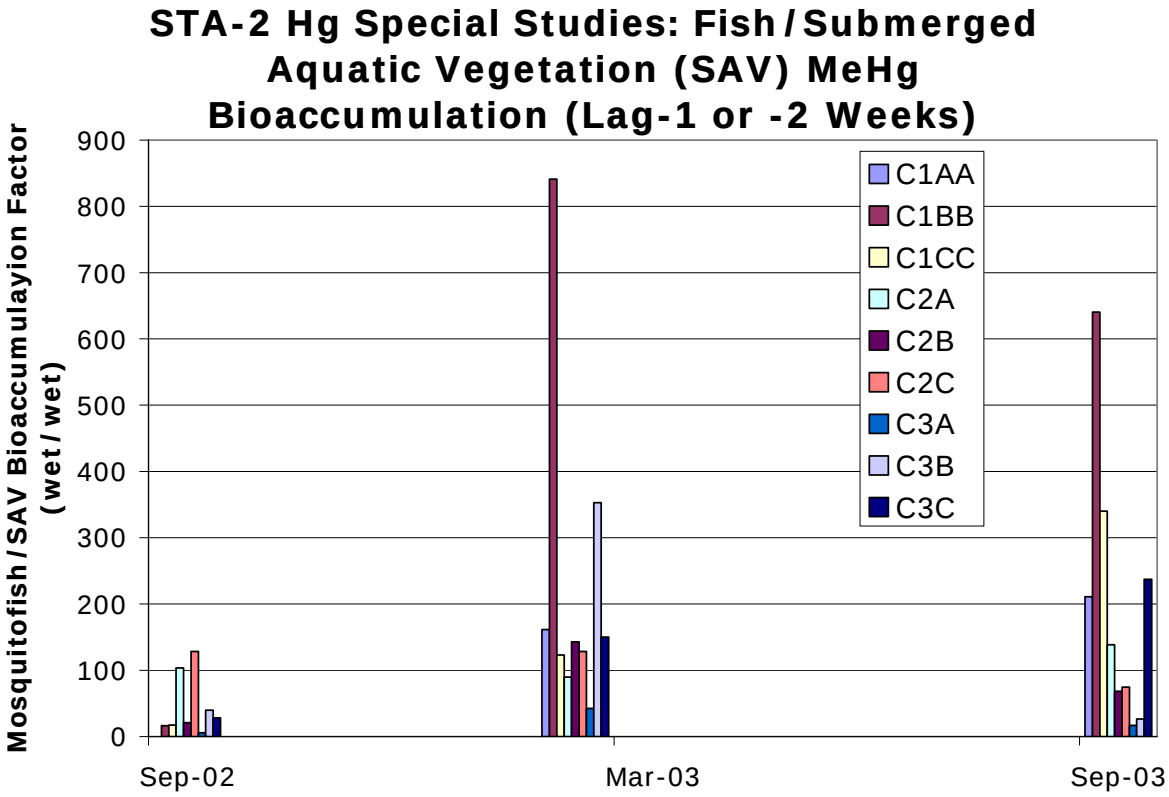

Figure 55. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in submerged aquatic vegetation leaves from interior treatment cells collected one or two weeks earlier (Lag–1 or -2 weeks) for the period from August 2002 through the final sampling event in September 2003.

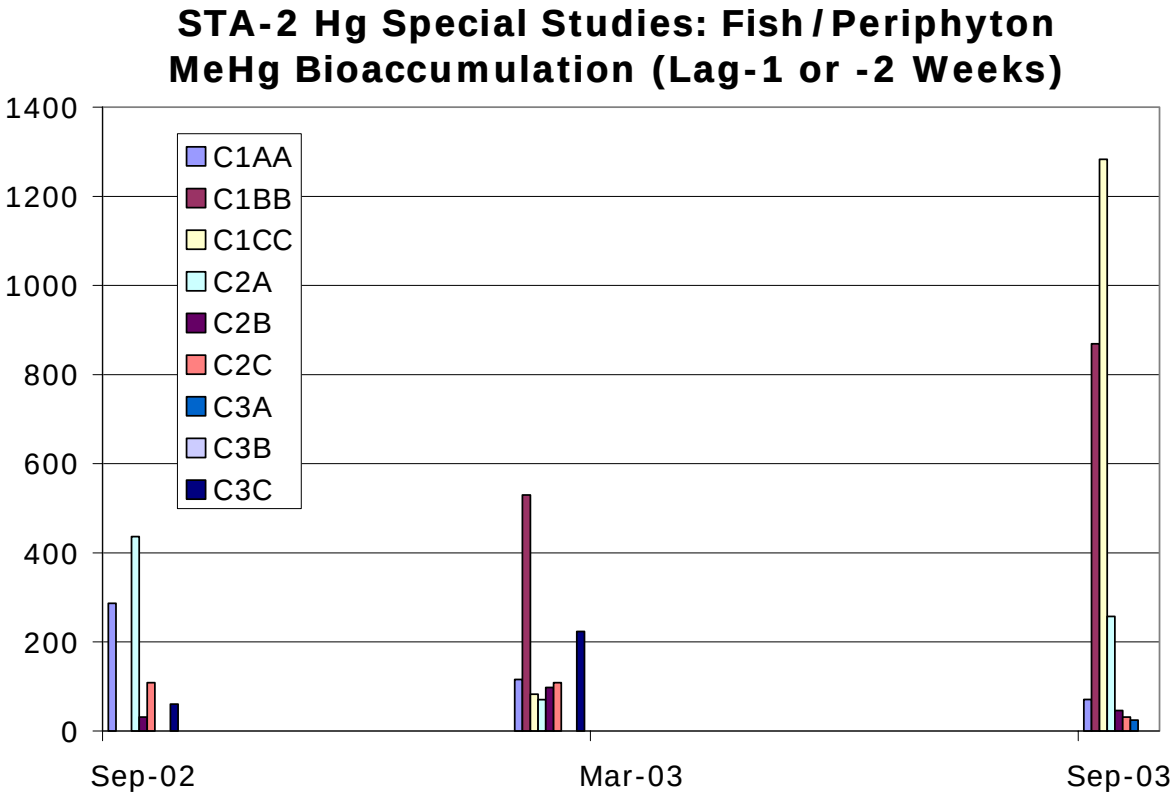

Figure 56. Ratio of THg as MeHg in mosquitofish to concentration of MeHg in green and blue-green algae mats (periphyton) from interior treatment cells collected one or two weeks earlier (Lag–1 or -2 weeks) for the period from August 2002 through the final sampling event in September 2003.

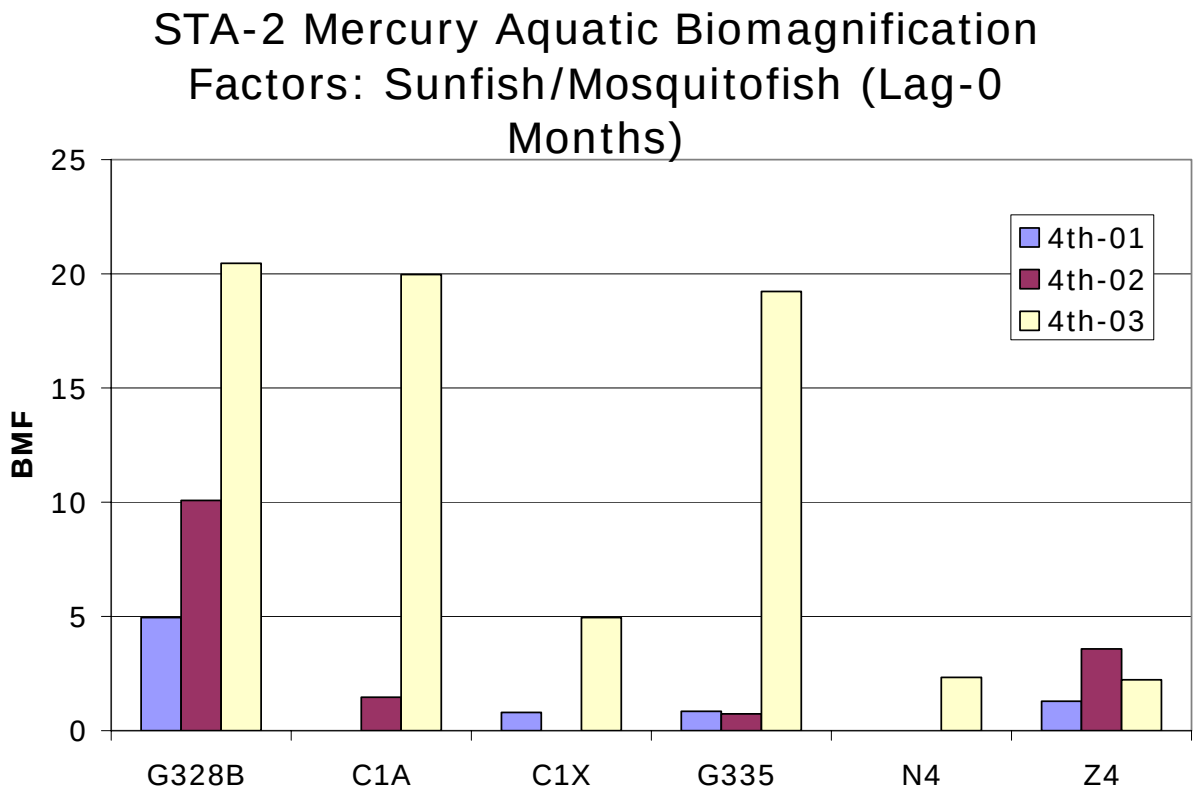

Figure 57. Ratio of THg as MeHg in sunfish to mosquitofish collected at the same time from the inflow, Cell 1 interior, Cell 1 outflow, and downstream transition zone sites for the fourth quarter (September–October) of calendar years 2001, 2002, and 2003.

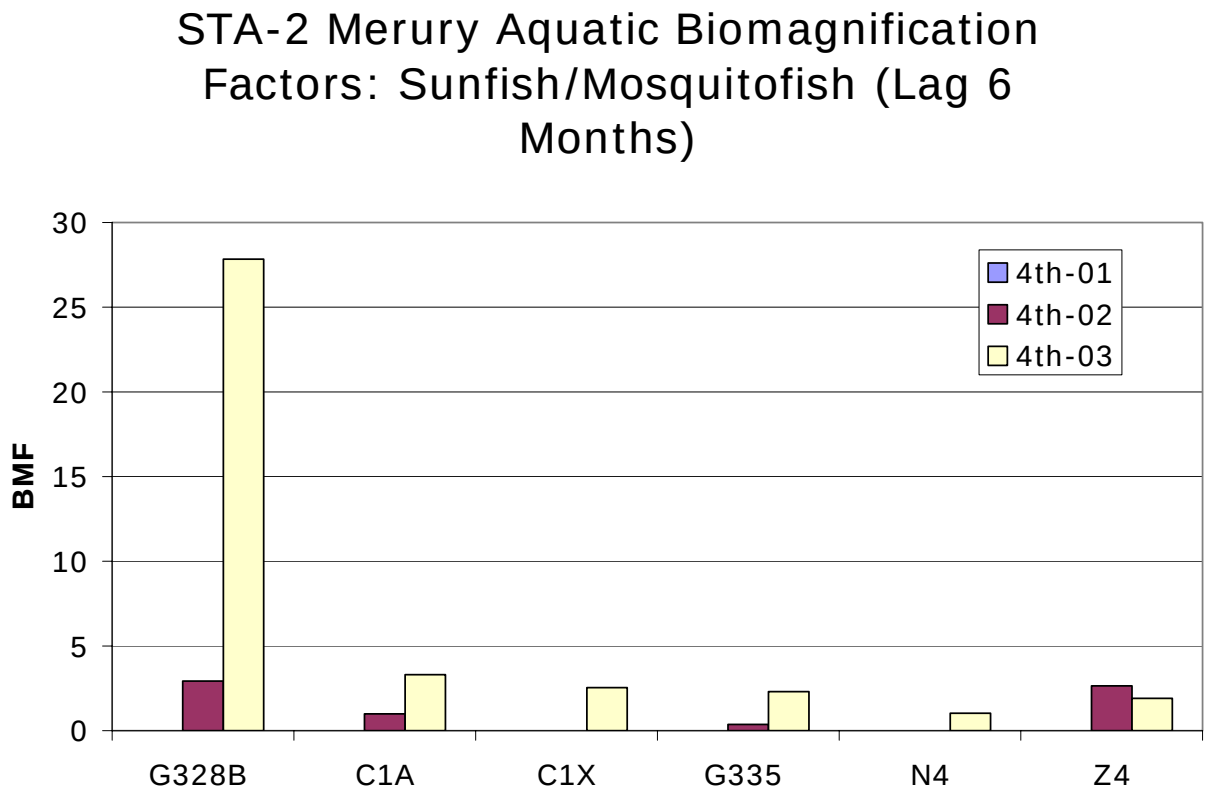

Figure 58. Ratio of THg as MeHg in sunfish to mosquitofish collected six months previously from the inflow, Cell 1 interior, Cell 1 outflow, and downstream transition zone sites in Water Conservation Area 2A for the fourth quarter (September–October) of calendar years 2001, 2002, and 2003.

PARTITION COEFFICIENTS

The particle-water partition coefficients for Hg(II) and MeHg were calculated using the following formula:

KPX = [XP]/([XF]*[TSS]) = (fXp x [XT])/(fXd x [XT] x [TSS])

= (1-fXd)/(fXd x [TSS])

XP = concentration of the mercury species X on particles

XF = concentration of the mercury species X in the filtrate

XT = concentration of the mercury species X in the unfiltered (total) sample

TSS = concentration of total suspended solids (kg/L)

fXd = fraction of mercury species X in apparently dissolved (filtered) fraction

fXp = fraction of mercury species X on particles

= 1-fXd

As discussed previously, because the concentrations of TSS in the treatment cell outflows were generally less than the MDL of 3 mg/L, trace analysis of TSS had to be instituted. Unfortunately, this did not occur until July 2003. This resulted in very few complete sets of unfiltered and filtered THg and MeHg concentrations paired with measurable TSS concentrations. To increase the number of complete data sets, TSS concentration data gaps were filled for 9/16/03 by averaging bracketing measured values in the supply canal at G-328B on 8/19/03 and 9/30/03. The value on 8/16/03 was set equal to that same average value. This approach is supported by the fact that the canal TSS concentration during that period was changing very slowly, from 5 mg/L on 8/19/03 to 6 mg/L on 9/30/03. When the enhanced data sets for the G-328B inflow canal site are combined with the data from G-330A, G-332 and G-334, only twelve and eight complete sets of data were available for the calculation of KP for Hg(II) and MeHg, respectively. There were fewer complete MeHg data sets because of the four instances of filtered MeHg > unfiltered MeHg.

The results of the calculations are summarized in **Table 13**. **Figure 59** depicts the proportions of MeHg on particles in the common inflow and cell interiors and outflows.

Table 13. Particle-water partition coefficients for STA-2.

Site	Count	Average KP Hg(II) [l/kg]	Count	Average KP MeHg [l/kg]
G-328B	5	3.61E5	2	3.3E4
Cell 1 Outflow	3	6.76E5	3	2.60E5
Cell 2 Outflow	3	6.94E5	2	1.43E5
Cell 3 Outflow	1	9.82E5	1	2E5
All Sites Combined	12	5.75E5	8	1.66E5

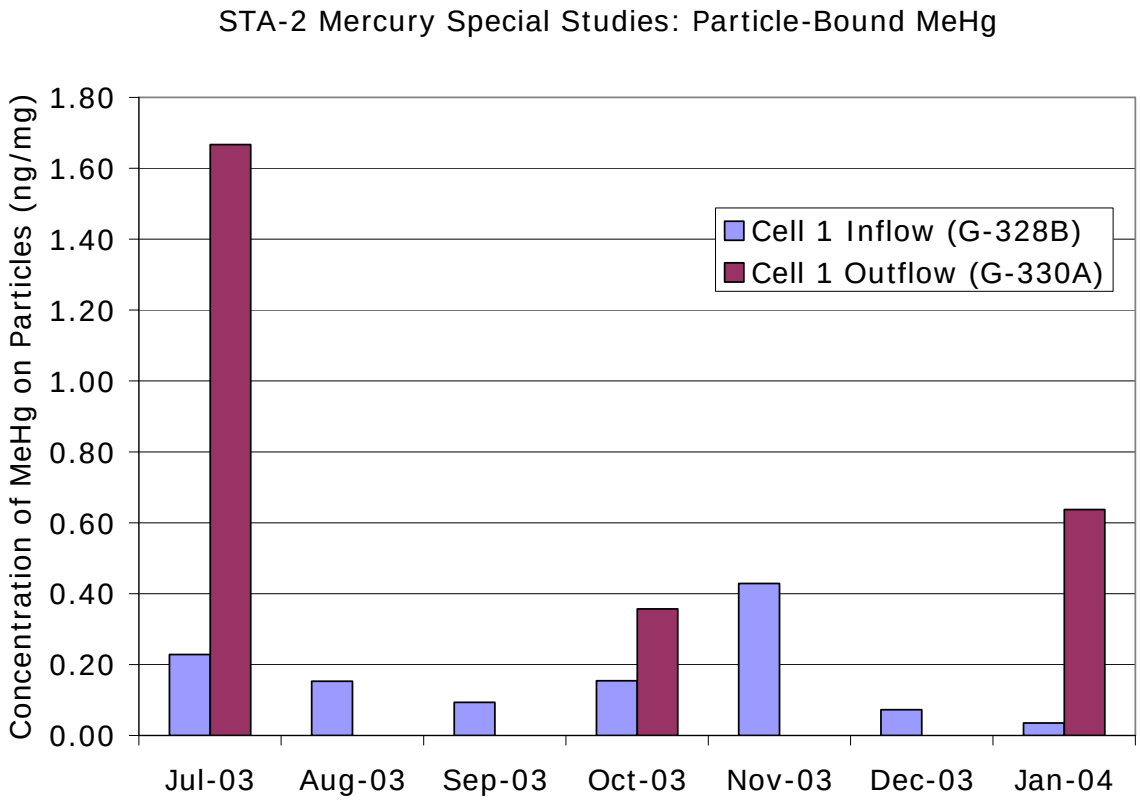

Figure 59. Ratio of MeHg on particles ([unfiltered] – [filtered])/[TSS]) to the corresponding filtered concentrations in surface water for samples collected every four weeks at the common inflow (G-328B) and for the Cell 1 outflow collected every 12 weeks for the period from July 2003, when trace TSS monitoring began, through the final sampling event in January 2004.

MASS BUDGET ANALYSIS

Surface Water

The results of the surface water mass budget calculations for THg, MeHg, Hg(II), TSS, and particle-bound THg, MeHg, and Hg(II) are summarized in **Tables 14** through **18** and for DOC, TP, TKN, NH_3, NO_X, TCA, and SO_4 in **Tables 19** through **25**, respectively. The chloride budget has been discussed in great detail above in the context of water budget validation and therefore is not reiterated in this section. Magnesium (Mg) was not routinely monitored at the individual cell outflows, so it is not possible to calculate a surface water mass budget and evaluate its relationship to the soil/sediment mass budget for Mg, which was analyzed in that medium. For TSS, due to the data limitations described earlier in the document, a TSS mass budget could only be developed for Cell 1 and only for the fifth and sixth quarters of the study. The spreadsheets containing the detailed calculations are available upon request.

MERCURY SPECIES

An inspection of **Tables 14**, **15**, and **16** indicates that the majority of the export of THg, MeHg, and Hg(II) from Cell 1 was primarily confined to the first three quarters following the first-flush MeHg anomaly, which peaked on August 22, 2002, at an unprecedented MeHg concentration of 20 ng/L in filtered surface water at Cell 1 Site C1CC. Following reflooding, the Cell 1 outflow load of THg decreased from more than seven times the inflow load in the first quarter to less than the inflow load in the sixth quarter. However, when all input and output pathways are taken into account, Cell 1 was a net exporter of THg in all six quarterly periods. For Cells 2 and 3, the THg removal efficiency was between 55 and 95 percent for each of the six study quarters, with an average of about 90 percent over the course of the project, which is much greater than the approximately 60 percent achieved by the ENR Project in the period from 1995–1998 (Miles and Fink, 1998; SFWMD, 1999b).

Interestingly, net seepage was positive (into) for Cell 2 for all but the second and sixth quarters. Based on the differences between Cell 1 and Cell 2 heads, one should not be surprised by net positive seepage and mass loads of THg, MeHg, and Hg(II) via this pathway. Unfortunately, the seepage load is calculated by multiplying the seepage flux by the total surface area and the average water column filtered THg concentration, but when seepage is net in rather than net out, the source of THg is not the water column but the interstitial or pore water at the point of efflux. Without measurements of interstitial water concentrations of THg at the point of efflux, it is not possible to accurately quantify the seepage contribution to the THg mass budget. The preceding caveat notwithstanding, when the positive seepage term is treated as an input in the calculation of the removal efficiency, the apparent Cell 1 THg removal efficiency decreases from 82 to 68 percent in the first quarter. Thereafter the effect was less dramatic, with decreases ranging from 2 to 5 percent. Overall, the apparent THg removal efficiency for Cell 2 decreased from 89 to 86 percent when the seepage contribution was reassigned as input for the four quarters in question.

Following reflooding in August 2002, STA-2 Cell 1 was a net exporter of MeHg for every quarter of the study, although the percent removal efficiency became progressively less negative in the fourth, fifth, and sixth quarters, suggesting that the system was stabilizing with respect to excess MeHg production. In the first quarter of the study following reflooding, the outflow MeHg load was more than 50 times (X) the inflow load. Unlike the THg load, however, the MeHg load did not decrease monotonically throughout the study period. Instead, there was a rapid decline to

approximately 9X the inflow load in the second quarter, about 13X, 2.8X and 1.4X in the third, fourth, and fifth quarters, respectively, and back up to about 2.4X in the sixth. Similar oscillations in MeHg concentrations and loads were observed during the first, first-flush MeHg anomaly in Cell 1 in the period from September 2000 through April 2001, when Cell 1 dried out (Fink, 2004b). Based on superpositions of water depth, THg inflow loads, and THg rainfall fluxes on the surface water concentration profile versus time, these oscillations could not be attributed to changes in these forcing functions (Fink, 2004b). One might speculate that these upturns are caused by the release of sorbed MeHg from submerged plant biomass with the onset of plant senescence and increased deadfall decomposition. This generally begins in the late fall of each year, which corresponds to the second and sixth quarters of the study. However, the decrease in primary production during this period, together with increasing flow contributions from Lake Okeechobee water to make up the water supply shortfall, could result in changes in pH and alkalinity that have been shown to affect MeHg sorption to submerged plant biomass (King et al., 2002).

For Cell 2, overall MeHg removal efficiency was initially calculated to be 96 percent for the study period, but Cell 2 MeHg removal efficiencies in the second and sixth quarters exceeded 100 percent relative to the inflow, wet and dry deposition inputs. When seepage is treated as an input rather than an output for the quarters when seepage is net into Cell 2, the removal efficiencies are reduced substantially in the first, third, fourth, and fifth quarters, and the overall MeHg removal efficiency for the study period is reduced from an apparent 96 to 81 percent. This is still higher than the approximately 70 percent removal efficiency achieved by the ENR Project in the period from 1995–1998, albeit with a lower flow-weighted average inflow MeHg concentration (0.16 versus 0.28 ng/L unfiltered) (Miles and Fink, 1998; SFWMD, 1999b). In the quarters with removal efficiencies greater than 100 percent, the seepage is negative, so treating seepage as an input actually increases rather than decreases the percentage removal. This means that one must invoke an unquantified sink for MeHg that is large relative to the inputs and outputs for those quarters. In this case, the sink is the large negative change in water column storage relative to inputs and outputs.

One might speculate that this phenomenon is caused by the replacement of plant standing crop biomass with a low capacity for MeHg uptake from the water column with plant standing crop biomass with a high capacity for MeHg uptake from the water column. This could occur, for example, when periphyton, submerged rooted macrophytes, and floating macrophytes standing crop biomasses expand as the rooted emergent macrophytes senesce and dead leaves fall into the water, increasing the exposure of the water's surface to sunlight (Grimshaw et al., 1997; McCormick et al., 1999). Whether the phenomenon of senescence can simultaneously explain the enhanced export of MeHg in Cell 1, which experienced a first-flush MeHg anomaly, and the enhanced storage of MeHg in Cell 2, which did not, can only be evaluated in the context of a mass budget that includes such plant biomass dynamics. Cell 1 and Cell 2 had very different plant species, densities, and coverages at project start-up in July 2000 (W. Larson, SFWMD, personal communication), but whether these differences were great enough and sufficiently persistent to influence the storage dynamics of the third, first-flush MeHg anomaly in Cell 1 cannot be ascertained with the available data. Unfortunately, without at least quarterly monitoring of standing crop biomass coverages, densities, and THg and MeHg concentrations, there is no way to perform the required mass budget calculations with the required temporal resolution and accuracy. Nevertheless, whatever its cause, this effect militates for evaluating overall treatment system performance on an annual average basis rather than on a biweekly, monthly or quarterly basis. However, this is not the case for risk assessment because of seasonal differences in reproductive status and foraging behavior.

Cell 3, which never experienced quarters of net positive seepage, was also a net importer of MeHg throughout the study period, with quarterly removal efficiencies between 75 and 95 percent, and an overall removal efficiency of 88 percent for the study period, which is higher than the approximately 70 percent achieved by the ENR Project in the period from 1995–1998 based on biweekly inflow and outflow monitoring (Miles and Fink, 1998; SFWMD, 1999b).

THE INFLUENCE OF PARTICLE TRANSPORT ON MERCURY SPECIES REMOVAL EFFICIENCIES

The concentration of TSS in the treatment cell outflows was generally less than the routine method MDL of 3 mg/L. Due to a miscommunication with the District's laboratory, trace analysis of TSS in the treatment cell outflows was not instituted until July 2003, so the data were only sufficient to calculate TSS budgets for the last two quarters of the study. Filtered sampling of the treatment cell outflows occurred every twelve weeks, so the data available for calculating Hg(II) and MeHg removal via particle trapping were even more limited than the data for calculating particle trapping efficiencies. Because Cell 1 was sampled first for filtered outflow samples, it has the most data for calculating Hg(II) and MeHg removal via particle trapping. **Table 17** contains the Cell 1, 2, and 3 particle inflow, outflow, change in storage, net import, and removal efficiency calculations. **Table 18** contains the estimate of the masses of particle-bound THg, MeHg, and Hg(II) transported into and out of the Cell 1. These latter values were calculated by subtracting the unfiltered from the filtered mercury species concentration, dividing by the associated concentration of TSS, and then multiplying that value by the mass of particles transported at that point in space and time. Further, since MeHg contamination of the filters was not corrected until October 2003, all but one of the inflow samples is associated with a sample where the filtered fraction is higher than the unfiltered sample, which results in a negative fraction in the particulate phase. Because the outflow MeHg concentrations are higher than the inflow concentrations for most of the study period, the effect of the filter contamination is somewhat muted, but the outflow values for fraction on particulate must still be considered suspect, so the exploratory particulate mass budget calculation for MeHg is for the sake of completeness only. This propagates into the calculation of Hg(II) removal by particle settling, since the concentration is calculated by subtracting the MeHg concentration from the THg concentration.

An inspection of **Table 18** indicates that, despite the fact that Cell 1 retained almost 80 percent of its inflow particle load in the fifth quarter, there was net export of particle-bound THg. This could be due to the higher average fraction of THg on particles at the outflow than the inflow, which is would indicate a higher affinity of outflow particles for Hg(II) and MeHg than inflow particles. This is supported by the higher average concentrations of THg calculated to be on particles at the outflow than the inflow (See **Figure 57**. This is also reflected in the apparent average Kp values for THg at the outflow, which, for fifth and sixth quarters, were roughly twice the average of the inflow values. This apparent higher affinity of outflow particles for inflow particles could be related to the replacement of particles of primarily allochthonous origin with particles of primarily autochthonous origin between the inflow and outflow, with an attendant increase in the organic matter content of the particles. Alternatively, this could be an apparent phenomenon related to the decrease in allochthonous DOC and an increase in autochthonous DOC, the latter of which, in the Everglades, has a lower affinity for Hg(II) and MeHg than the former (Lu et al., 2001; 2003; Haitzer et al., 2002), which would have the effect of increasing the fraction of Hg(II) and MeHg sorbed to particles and decreasing the fraction associated with DOC. Or both forces could be at work simultaneously. In the sixth quarter, the Cell 1 particle removal efficiency increased to about 96 percent, and there was net removal of particle-bound THg.

A comparison of the THg particle-bound mass loads with the corresponding total mass loads transported into and out of Cell 1 during the fifth and sixth quarters suggests that a significant fraction of each of THg was being transported into, within, or out of Cell 1 in association with particles. Specifically, in the fifth and sixth quarters of the study, 56 and 91 percent of the THg in the total inflow load and 45 and 18 percent of the THg in the outflow load was associated with particle transport. This strongly suggests that treatment systems with design features and operational regimens that enhance particle settling and retention will enjoy a collateral benefit of substantial THg removal. In systems that remain wet year around to avoid first-flush MeHg anomalies, this benefit can be extended to MeHg, as well, although MeHg's generally higher affinity for DOC weakens its association with settling particles, reducing the benefit of particle removal for MeHg removal proportionally.

OTHER CONSTITUENTS

Tables 19 through **25** through present the summaries of the results of the mass budget calculations for DOC, Ca, TP, TN, NH_3, NOX, Fe, and SO_4. Interestingly, Cell 1 was a next importer of SO_4 and a net exporter of DOC during the first quarter following reflooding. If DOC and Hg(II) were in excess following the first-flush release, and the metabolic activity of sulfate reduction was limited only by the sulfate flux to the sediments, then the rate of MeHg production was dictated by the conversion efficiency of the allochthonous sulfate to sulfide and the conversion efficiency of Hg(II) to MeHg. Thereafter, while Cell 1 remained a net exporter of DOC throughout the study, sulfate net import declined progressively, until it switched to net export in the fourth and fifth quarters and then back to a net importer in the sixth quarter. The progressive decrease in sulfate mass import in Cell 1 over time may correspond to the progressive depletion of the pool of bioavailable nutriment limiting SRB activity in Cell 1 following first flush release. By contrast, Cells 2 and 3 were net importers of DOC and SO_4 throughput the study period and increased net sulfate import during the two quarters when Cell 1 became a net exporter. All three cells were net importers of the remaining other constituents, albeit with differing efficiencies.

Table 14. Surface water THg mass budget calculation for STA-2 Cells 1, 2, and 3.

THg Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [g]	Out [g]	Evade [g]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [%]
Cell 1									
1st QTR	1.56E+01	3.74E+01	2.06E+01	1.15E+02	5.15E+01	-1.38E+01	5.76E+00	-1.12E+02	-1.80E+02
2nd QTR	1.55E+01	8.35E+00	2.06E+01	3.55E+01	1.63E+01	-1.31E+01	-2.77E+00	-1.76E+01	-8.53E+01
3rd QTR	2.98E+01	1.75E+01	2.06E+01	8.20E+01	2.03E+01	-7.04E+00	-5.81E-01	-4.08E+01	-9.00E+01
4th QTR	3.84E+01	7.41E+01	2.06E+01	3.37E+01	1.65E+01	-7.48E+00	4.42E-01	7.49E+01	4.10E+01
5th QTR	4.89E+01	7.43E+01	2.06E+01	5.84E+01	1.04E+01	-6.77E+00	-9.91E-01	6.93E+01	3.40E+01
6th QTR	6.56E+00	5.87E+00	1.94E+01	5.46E+00	7.60E+00	-3.23E+00	-1.85E+00	1.74E+01	-5.59E+00
1-yr	1.19E+02	1.83E+02	8.86E+01	2.90E+02	1.08E+02	-4.36E+01	3.04E+00	-5.30E+01	-3.61E+01
Study POR	1.55E+02	2.18E+02	1.23E+02	3.30E+02	1.23E+02	-5.14E+01	1.68E-02	-9.12E+00	-2.66E+01
Cell 2									
1st QTR	9.43E+00	3.69E+01	1.85E+01	5.31E+00	1.23E+01	1.37E+01	7.62E+00	5.32E+01	5.37E+01
2nd QTR	9.24E+00	9.31E+00	4.66E+00	2.18E+00	7.37E+00	-1.31E+00	-3.01E+00	1.54E+01	4.61E+01
3rd QTR	3.24E+01	1.96E+01	9.78E+00	3.42E+00	8.75E+00	2.58E+00	7.95E-02	5.21E+01	6.85E+01
4th QTR	6.31E+01	8.26E+01	4.13E+01	3.50E+00	1.18E+01	2.89E+00	2.69E+00	1.72E+02	6.98E+01
5th QTR	6.12E+01	8.29E+01	4.15E+01	2.93E+00	8.36E+00	5.50E+00	5.82E-01	1.79E+02	7.47E+01
6th QTR	3.00E+00	6.55E+00	3.27E+00	2.50E+00	6.56E+00	-5.37E-01	-3.86E+00	7.08E+00	2.97E+01
1-yr	1.39E+02	2.00E+02	9.98E+01	1.52E+01	4.26E+01	1.80E+01	6.49E+00	3.92E+02	6.67E+01
Study POR	1.78E+02	2.38E+02	1.19E+02	1.99E+01	5.52E+01	2.28E+01	4.10E+00	4.79E+02	6.73E+01
Cell 3									
1st QTR	1.75E+01	3.69E+01	1.85E+01	2.49E+00	6.00E+00	4.20E+00	4.41E+00	6.41E+01	6.27E+01
2nd QTR	1.38E+01	9.31E+00	4.66E+00	1.18E+00	5.35E+00	9.48E-02	-4.27E-02	2.13E+01	6.02E+01
3rd QTR	3.41E+01	1.96E+01	9.78E+00	2.59E+00	6.26E+00	-1.12E+00	5.04E-01	5.29E+01	6.80E+01
4th QTR	7.74E+01	8.26E+01	4.13E+01	2.82E+00	7.72E+00	-4.58E+00	-6.81E-02	1.86E+02	7.20E+01
5th QTR	7.66E+01	8.29E+01	4.15E+01	2.10E+00	6.71E+00	-2.97E+00	-1.04E+00	1.90E+02	7.45E+01
6th QTR	7.79E+00	6.55E+00	3.27E+00	1.21E+00	3.65E+00	-5.03E-01	-7.36E-01	1.30E+01	5.51E+01
1-yr	1.73E+02	2.00E+02	9.98E+01	9.73E+00	2.75E+01	-3.40E+00	3.72E+00	4.28E+02	6.95E+01
Study POR	2.27E+02	2.38E+02	1.19E+02	1.24E+01	3.57E+01	-4.88E+00	3.02E+00	5.28E+02	7.00E+01
Combined									
1st QTR	4.25E+01	1.11E+02	5.75E+01	1.23E+02	6.98E+01	4.06E+00	1.78E+01	5.04E+00	2.38E+00
2nd QTR	3.85E+01	2.70E+01	2.99E+01	3.88E+01	2.90E+01	-1.43E+01	-5.82E+00	1.91E+01	2.00E+01
3rd QTR	9.63E+01	5.67E+01	4.02E+01	8.80E+01	3.53E+01	-5.59E+00	2.26E-03	6.42E+01	3.33E+01
4th QTR	1.79E+02	2.39E+02	1.03E+02	4.00E+01	3.61E+01	-9.18E+00	3.07E+00	4.33E+02	8.31E+01
5th QTR	1.87E+02	2.40E+02	1.04E+02	6.34E+01	2.54E+01	-4.24E+00	-1.45E+00	4.39E+02	8.27E+01
6th QTR	1.73E+01	1.90E+01	2.60E+01	9.18E+00	1.78E+01	-4.27E+00	-6.44E+00	3.74E+01	6.01E+01
1-yr	4.31E+02	5.83E+02	2.88E+02	3.15E+02	1.78E+02	-2.89E+01	1.32E+01	7.67E+02	5.89E+01
Study POR	5.60E+02	6.93E+02	3.60E+02	3.62E+02	2.13E+02	-3.35E+01	7.15E+00	9.98E+02	6.18E+01

Percent Removal Efficiency by Treatment Cell

	Cell 1	Cell 2	Cell 3
1st QTR	-2.23E+03	1.06E+03	1.27E+03
2nd QTR	-9.20E+01	8.04E+01	1.12E+02
3rd QTR	-6.35E+01	8.11E+01	8.24E+01
4th QTR	1.73E+01	3.97E+01	4.30E+01
5th QTR	1.58E+01	4.08E+01	4.34E+01
6th QTR	4.64E+01	1.89E+01	3.46E+01
1-yr	-6.91E+00	5.11E+01	5.58E+01
Study POR	-9.14E-01	4.80E+01	5.29E+01

Table 15. Surface water MeHg mass budget calculation for STA-2 Cells 1, 2, and 3.

MeHg Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [NA]	Out [g]	Evade [NA]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [%]
Cell 1									
1st QTR	1.51E+00	6.47E-01		8.13E+01		-2.74E+00	2.88E+00	-8.47E+01	-1.80E+02
2nd QTR	1.48E+00	7.64E-02		1.33E+01		-3.72E+00	-9.95E-01	-1.45E+01	-8.53E+01
3rd QTR	2.92E+00	4.67E-02		3.93E+01		-2.56E+00	-4.75E-01	-3.84E+01	-9.00E+01
4th QTR	3.86E+00	1.10E-01		9.09E+00		-8.29E-01	-4.94E-01	-5.46E+00	4.10E+01
5th QTR	6.58E+00	1.85E-01		9.25E+00		-1.08E+00	4.95E-01	-4.06E+00	3.40E+01
6th QTR	4.84E-01	4.21E-01		1.37E+00		-7.37E-01	-9.71E-01	-2.34E-01	-5.59E+00
1-yr	1.24E+01	9.61E-01		1.46E+02		-1.02E+01	7.51E-01	-1.44E+02	-3.61E+01
Study POR	1.68E+01	1.49E+00		1.54E+02		-1.17E+01	4.35E-01	-1.47E+02	-2.66E+01
Cell 2									
1st QTR	8.67E-01	6.72E-01		2.24E+00		2.22E+00	2.93E-02	1.50E+00	5.37E+01
2nd QTR	8.90E-01	8.53E-02		3.77E-01		-1.45E-01	-1.33E+00	1.79E+00	4.61E+01
3rd QTR	2.86E+00	5.21E-02		1.16E+00		6.34E-01	3.40E-01	2.05E+00	6.85E+01
4th QTR	6.94E+00	1.22E-01		8.11E-01		4.96E-01	3.34E-01	6.41E+00	6.98E+01
5th QTR	8.44E+00	2.06E-01		5.34E-01		1.07E+00	1.85E+00	7.34E+00	7.47E+01
6th QTR	2.07E-01	4.69E-01		1.05E+00		-1.27E-02	-2.33E+00	1.95E+00	2.97E+01
1-yr	1.52E+01	1.02E+00		4.67E+00		3.27E+00	-5.47E-01	1.54E+01	6.67E+01
Study POR	2.02E+01	1.61E+00		6.16E+00		4.27E+00	-1.11E+00	2.10E+01	6.73E+01
Cell 3									
1st QTR	1.56E+00	6.72E-01		4.24E-01		3.62E-01	4.62E-01	1.71E+00	6.27E+01
2nd QTR	1.27E+00	8.53E-02		1.45E-01		5.10E-03	-3.40E-02	1.25E+00	6.02E+01
3rd QTR	3.24E+00	5.21E-02		7.01E-01		-1.35E-01	2.69E-01	2.18E+00	6.80E+01
4th QTR	8.54E+00	1.22E-01		4.08E-01		-4.91E-01	-1.93E-01	7.96E+00	7.20E+01
5th QTR	1.06E+01	2.06E-01		2.78E-01		-3.81E-01	-8.79E-03	1.02E+01	7.45E+01
6th QTR	5.47E-01	4.69E-01		2.02E-01		-7.31E-02	-1.35E-01	8.77E-01	5.51E+01
1-yr	1.90E+01	1.02E+00		1.76E+00		-4.89E-01	5.11E-01	1.73E+01	6.95E+01
Study POR	2.58E+01	1.61E+00		2.16E+00		-7.13E-01	3.60E-01	2.41E+01	7.00E+01
Combined									
1st QTR	3.93E+00	1.99E+00		8.39E+01		-1.58E-01	3.37E+00	-8.15E+01	-1.38E+03
2nd QTR	3.64E+00	2.47E-01		1.39E+01		-3.86E+00	-2.36E+00	-1.15E+01	-2.95E+02
3rd QTR	9.01E+00	1.51E-01		4.12E+01		-2.07E+00	1.34E-01	-3.42E+01	-3.73E+02
4th QTR	1.93E+01	3.54E-01		1.03E+01		-8.24E-01	-3.53E-01	8.91E+00	4.52E+01
5th QTR	2.56E+01	5.97E-01		1.01E+01		-3.82E-01	2.33E+00	1.35E+01	5.13E+01
6th QTR	1.24E+00	1.36E+00		2.62E+00		-8.22E-01	-3.44E+00	2.59E+00	9.98E+01
1-yr	4.66E+01	3.01E+00		1.53E+02		-7.38E+00	7.16E-01	-1.11E+02	-2.24E+02
Study POR	6.28E+01	4.70E+00		1.62E+02		-8.11E+00	-3.17E-01	-1.02E+02	-1.52E+02

Percent Removal by Treatment Cell

	Cell 1	Cell 2	Cell 3
1st QTR	1.04E+02	-1.84E+00	-2.09E+00
2nd QTR	1.26E+02	-1.56E+01	-1.09E+01
3rd QTR	1.12E+02	-5.99E+00	-6.38E+00
4th QTR	-6.13E+01	7.20E+01	8.93E+01
5th QTR	-3.01E+01	5.45E+01	7.56E+01
6th QTR	-9.00E+00	7.52E+01	3.38E+01
1-yr	1.29E+02	-1.38E+01	-1.55E+01
Study POR	1.44E+02	-2.06E+01	-2.36E+01

Table 16. Surface water Hg(II) mass budget calculation for STA-2 Cells 1, 2, and 3.

Hg(II) Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [g]	Out [g]	Evade [g]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [%]
Cell 1									
1st QTR	1.41E+01	3.68E+01	2.06E+01	3.36E+01	5.15E+01	-1.11E+01	2.89E+00	-2.76E+01	-3.86E+01
2nd QTR	1.40E+01	8.27E+00	2.06E+01	2.21E+01	1.63E+01	-9.34E+00	-1.77E+00	-3.07E+00	-7.16E+00
3rd QTR	2.69E+01	1.75E+01	2.06E+01	4.27E+01	2.03E+01	-4.48E+00	-1.06E-01	-2.34E+00	-3.60E+00
4th QTR	3.45E+01	7.40E+01	2.06E+01	2.46E+01	1.65E+01	-6.65E+00	9.36E-01	8.04E+01	6.22E+01
5th QTR	4.23E+01	7.41E+01	2.06E+01	4.92E+01	1.04E+01	-5.70E+00	-1.49E+00	7.33E+01	5.35E+01
6th QTR	6.08E+00	5.45E+00	1.94E+01	4.09E+00	7.60E+00	-2.50E+00	-8.74E-01	1.76E+01	5.70E+01
1-yr	1.07E+02	1.82E+02	8.86E+01	1.43E+02	1.08E+02	-3.34E+01	2.29E+00	9.10E+01	2.41E+01
Study POR	1.38E+02	2.16E+02	1.23E+02	1.76E+02	1.23E+02	-3.98E+01	-4.19E-01	1.38E+02	2.90E+01
Cell 2									
1st QTR	8.56E+00	3.62E+01	1.85E+01	3.08E+00	1.23E+01	1.15E+01	7.59E+00	5.17E+01	8.18E+01
2nd QTR	8.35E+00	9.23E+00	4.66E+00	1.80E+00	7.37E+00	-1.16E+00	-1.68E+00	1.36E+01	6.11E+01
3rd QTR	3.24E+01	1.96E+01	9.78E+00	3.42E+00	8.75E+00	2.58E+00	7.95E-02	5.21E+01	6.85E+01
4th QTR	6.31E+01	8.26E+01	4.13E+01	3.50E+00	1.18E+01	2.89E+00	2.69E+00	1.72E+02	6.98E+01
5th QTR	6.12E+01	8.29E+01	4.15E+01	2.93E+00	8.36E+00	5.50E+00	5.82E-01	1.79E+02	7.47E+01
6th QTR	3.00E+00	6.55E+00	3.27E+00	2.50E+00	6.56E+00	-5.37E-01	-3.86E+00	7.08E+00	2.97E+01
1-yr	1.39E+02	2.00E+02	9.98E+01	1.52E+01	4.26E+01	1.80E+01	6.49E+00	3.92E+02	6.67E+01
Study POR	1.78E+02	2.38E+02	1.19E+02	1.99E+01	5.52E+01	2.28E+01	4.10E+00	4.79E+02	6.73E+01
Cell 3									
1st QTR	1.59E+01	3.62E+01	1.85E+01	2.07E+00	6.00E+00	3.84E+00	3.95E+00	6.24E+01	8.84E+01
2nd QTR	1.25E+01	9.23E+00	4.66E+00	1.03E+00	5.35E+00	8.97E-02	-8.68E-03	2.01E+01	7.62E+01
3rd QTR	3.08E+01	1.95E+01	9.78E+00	1.89E+00	6.26E+00	-9.89E-01	2.35E-01	5.08E+01	8.44E+01
4th QTR	6.88E+01	8.25E+01	4.13E+01	2.41E+00	7.72E+00	-4.09E+00	1.25E-01	1.78E+02	9.26E+01
5th QTR	6.60E+01	8.27E+01	4.15E+01	1.82E+00	6.71E+00	-2.59E+00	-1.03E+00	1.80E+02	9.47E+01
6th QTR	7.24E+00	6.08E+00	3.27E+00	1.01E+00	3.65E+00	-4.30E-01	-6.01E-01	1.21E+01	7.29E+01
1-yr	1.73E+02	2.00E+02	9.98E+01	9.73E+00	2.75E+01	-3.40E+00	3.72E+00	4.28E+02	6.95E+01
Study POR	2.27E+02	2.38E+02	1.19E+02	1.24E+01	3.57E+01	-4.88E+00	3.02E+00	5.28E+02	7.00E+01
Combined									
1st QTR	3.86E+01	1.09E+02	5.75E+01	3.88E+01	6.98E+01	4.21E+00	1.44E+01	8.66E+01	4.22E+01
2nd QTR	3.49E+01	2.67E+01	2.99E+01	2.50E+01	2.90E+01	-1.04E+01	-3.46E+00	3.06E+01	3.34E+01
3rd QTR	8.73E+01	5.65E+01	4.02E+01	4.68E+01	3.53E+01	-3.52E+00	-1.32E-01	9.84E+01	5.35E+01
4th QTR	1.60E+02	2.39E+02	1.03E+02	2.97E+01	3.61E+01	-8.35E+00	3.42E+00	4.24E+02	8.45E+01
5th QTR	1.61E+02	2.40E+02	1.04E+02	5.34E+01	2.54E+01	-3.85E+00	-3.79E+00	4.25E+02	8.44E+01
6th QTR	1.61E+01	1.76E+01	2.60E+01	6.56E+00	1.78E+01	-3.45E+00	-3.01E+00	3.49E+01	5.84E+01
1-yr	4.19E+02	5.82E+02	2.88E+02	1.68E+02	1.78E+02	-1.88E+01	1.25E+01	9.11E+02	7.07E+01
Study POR	5.43E+02	6.92E+02	3.60E+02	2.09E+02	2.13E+02	-2.18E+01	6.71E+00	1.15E+03	7.18E+01

Percent Removal Efficiency by Treatment Cell

	Cell 1	Cell 2	Cell 3
1st QTR	-3.19E+01	5.98E+01	7.21E+01
2nd QTR	-1.00E+01	4.44E+01	6.57E+01
3rd QTR	-2.38E+00	5.29E+01	5.16E+01
4th QTR	1.89E+01	4.05E+01	4.20E+01
5th QTR	1.72E+01	4.21E+01	4.24E+01
6th QTR	5.06E+01	2.03E+01	3.47E+01
1-yr	9.99E+00	4.30E+01	4.70E+01
Study POR	1.21E+01	4.18E+01	4.61E+01

Table 17. Surface water TSS mass budget calculation for STA-2 Cells 1, 2, and 3.

THg Mass Budget Calculations for STA-2

	In [g]	Out [g]	Change Store [g]	Net Import [g]	Percent Removal Efficiency
Cell 1					
5th QTR	1.61E+08	2.62E+07	7.05E+06	1.42E+08	7.94E+01
6th QTR	3.43E+07	1.99E+06	-6.75E+05	3.16E+07	9.62E+01
Study POR	1.95E+08	2.82E+07	6.37E+06	1.73E+08	8.23E+01
Cell 2					
5th QTR	1.97E+08	3.84E+07	7.05E+06	1.66E+08	7.70E+01
6th QTR	1.27E+07	1.59E+06	-6.75E+05	1.04E+07	9.28E+01
Study POR	2.10E+08	4.00E+07	6.37E+06	1.76E+08	7.79E+01
Cell 3					
5th QTR	2.50E+08	6.07E+07	7.05E+06	1.96E+08	7.29E+01
6th QTR	3.71E+07	3.37E+06	-6.75E+05	3.30E+07	9.27E+01
Study POR	2.87E+08	6.41E+07	6.37E+06	2.29E+08	7.55E+01

Table 18. Surface water mass budget calculation for STA-2 Cells 1, 2, and 3 for THg, MeHg, and Hg(II) associated with inorganic and organic total suspended solids (TSS).

TSS vs THg Species Mass Budget Calculations for STA-2

Cell 1	IN				OUT				CHANGE STORE			
		THg	MeHg	Hg(II)		THg	MeHg	Hg(II)		THg	MeHg	Hg(II)
	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]	[g]
5th QTR	1.61E+08	2.53E+01	1.42E+00	2.39E+01	2.62E+07	2.65E+01	2.99E+00	2.35E+01	7.05E+06	4.12E+00	4.34E-01	3.69E+00
6th QTR	3.43E+07	5.92E+00	3.02E-01	5.62E+00	1.99E+06	9.89E-01	7.82E-02	9.11E-01	-6.75E+05	-2.26E-01	-1.62E-02	-2.10E-01
Study POR	1.95E+08	3.12E+01	1.72E+00	2.95E+01	2.82E+07	2.75E+01	3.07E+00	2.44E+01	6.37E+06	3.89E+00	4.18E-01	3.48E+00

	NET IMPORT				TSS REMOVAL EFFICIENCY				DEPOSITION FLUX			
		THg	MeHg	Hg(II)		THg	MeHg	Hg(II)		THg	MeHg	Hg(II)
	[Kg]	[g]	[g]	[g]	%	%	%	%	[g/m2-d]	[g/m2-d]	[g/m2-d]	[g/m2-d]
5th QTR	1.28E+08	-5.32E+00	-2.01E+00	-3.31E+00	7.94E+01	-2.10E+01	-1.42E+02	-1.39E+01	1.76E-01	-7.34E-09	-2.77E-09	-4.57E-09
6th QTR	3.30E+07	5.16E+00	2.40E-01	4.92E+00	9.62E+01	8.71E+01	7.95E+01	8.75E+01	4.55E-02	7.11E-09	3.31E-10	6.78E-09
Study POR	1.61E+08	-1.60E-01	-1.77E+00	1.61E+00	8.23E+01	-5.13E-01	-1.03E+02	5.45E+00	1.11E-01	-1.10E-10	-1.22E-09	1.11E-09

Table 19. Surface water dissolved organic carbon (DOC) mass budget calculation for STA-2 Cells 1, 2, and 3.

DOC Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [NA]	Out [g]	Evade [NA]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [%]
Cell 1									
1st QTR	4.34E+08	1.97E+06		4.06E+08		-8.81E+07	5.40E+07	-1.13E+08	-2.58E+01
2nd QTR	5.43E+08	1.08E+06		4.16E+08		-2.33E+08	-1.01E+07	-9.48E+07	-1.74E+01
3rd QTR	7.05E+08	1.62E+06		6.51E+08		-7.44E+07	-5.34E+06	-1.33E+07	-1.89E+00
4th QTR	6.99E+08	4.34E+06		6.21E+08		-1.33E+08	5.49E+07	-1.06E+08	-1.51E+01
5th QTR	1.44E+09	3.26E+06		1.38E+09		-2.45E+08	-1.17E+07	-1.67E+08	-1.16E+01
6th QTR	2.74E+08	9.42E+05		1.72E+08		-1.60E+08	-3.65E+07	-2.09E+07	-7.62E+00
1-yr	2.94E+09	1.04E+07		2.53E+09		-6.01E+08	1.33E+08	-3.13E+08	-1.06E+01
Study POR	4.10E+09	1.32E+07		3.65E+09		-9.34E+08	4.53E+07	-5.15E+08	-1.25E+01
Cell 2									
1st QTR	2.84E+08	2.20E+06		1.09E+08		2.28E+08	7.27E+07	3.33E+08	1.16E+02
2nd QTR	3.14E+08	1.20E+06		7.30E+07		-5.36E+07	-1.11E+08	2.99E+08	9.49E+01
3rd QTR	6.85E+08	1.81E+06		8.61E+07		6.40E+07	-3.14E+07	6.96E+08	1.01E+02
4th QTR	1.15E+09	4.84E+06		1.06E+08		1.16E+08	1.32E+08	1.03E+09	8.94E+01
5th QTR	1.66E+09	3.64E+06		1.12E+08		2.42E+08	1.84E+07	1.78E+09	1.07E+02
6th QTR	1.21E+08	1.05E+06		8.23E+07		-8.24E+06	-4.59E+07	7.72E+07	6.33E+01
1-yr	3.13E+09	1.16E+07		4.08E+08		3.71E+08	9.78E+07	3.01E+09	9.57E+01
Study POR	4.21E+09	1.47E+07		5.68E+08		5.89E+08	3.53E+07	4.21E+09	9.96E+01
Cell 3									
1st QTR	4.97E+08	2.20E+06		1.07E+08		7.71E+07	-4.45E+06	4.73E+08	9.49E+01
2nd QTR	4.74E+08	1.20E+06		6.71E+07		8.62E+06	-6.56E+07	4.83E+08	1.02E+02
3rd QTR	7.58E+08	1.81E+06		8.33E+07		-3.54E+07	1.96E+07	6.22E+08	8.18E+01
4th QTR	1.42E+09	4.84E+06		9.97E+07		-1.55E+08	8.68E+06	1.16E+09	8.16E+01
5th QTR	2.09E+09	3.64E+06		1.12E+08		-1.28E+08	5.03E+07	1.81E+09	8.61E+01
6th QTR	3.00E+08	1.05E+06		7.47E+07		-5.31E+07	-2.83E+07	2.02E+08	6.70E+01
1-yr	4.01E+09	1.16E+07		3.92E+08		-1.92E+08	-6.62E+07	3.50E+09	8.71E+01
Study POR	5.54E+09	1.47E+07		5.44E+08		-2.86E+08	-1.99E+07	4.75E+09	8.54E+01
Combined									
1st QTR	1.21E+09	6.37E+06		6.22E+08		2.17E+08	1.22E+08	6.94E+08	5.68E+01
2nd QTR	1.33E+09	3.49E+06		5.56E+08		-2.78E+08	-1.86E+08	6.87E+08	5.15E+01
3rd QTR	2.15E+09	5.25E+06		8.20E+08		-4.58E+07	-1.71E+07	1.30E+09	6.06E+01
4th QTR	3.27E+09	1.40E+07		8.27E+08		-1.71E+08	1.96E+08	2.09E+09	6.36E+01
5th QTR	5.20E+09	1.05E+07		1.61E+09		-1.31E+08	5.70E+07	3.42E+09	6.56E+01
6th QTR	6.95E+08	3.04E+06		3.29E+08		-2.22E+08	-1.11E+08	2.58E+08	3.69E+01
1-yr	1.01E+10	3.35E+07		3.33E+09		-4.22E+08	1.64E+08	6.20E+09	6.13E+01
Study POR	1.39E+10	4.27E+07		4.76E+09		-6.31E+08	6.08E+07	8.45E+09	6.08E+01

Percent Removal Efficiency by Treatment Cell

	Cell 1	Cell 2	Cell 3
1st QTR	-1.62E+01	4.80E+01	6.82E+01
2nd QTR	-1.38E+01	4.35E+01	7.03E+01
3rd QTR	-1.02E+00	5.34E+01	4.77E+01
4th QTR	-5.09E+00	4.93E+01	5.58E+01
5th QTR	-4.89E+00	5.21E+01	5.28E+01
6th QTR	-8.12E+00	2.99E+01	7.82E+01
1-yr	-5.05E+00	4.85E+01	5.65E+01
Study POR	-6.10E+00	4.99E+01	5.62E+01

Table 20. Surface water total dissolved calcium (Ca) mass budget calculation for STA-2 Cells 1, 2, and 3.

CA Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [NA]	Out [g]	Evade [NA]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [%]
Cell 1									
1st QTR	9.39E+08	5.31E+08		5.77E+08		-2.04E+08	1.45E+08	5.43E+08	3.70E+01
2nd QTR	1.39E+09	2.91E+08		8.16E+08		-5.29E+08	3.81E+07	2.98E+08	1.77E+01
3rd QTR	2.24E+09	4.38E+08		1.51E+09		-1.87E+08	-4.75E+07	1.03E+09	3.83E+01
4th QTR	1.89E+09	1.17E+09		1.26E+09		-3.28E+08	1.41E+08	1.33E+09	4.36E+01
5th QTR	4.20E+09	8.77E+08		3.17E+09		-6.05E+08	-2.06E+07	1.33E+09	2.61E+01
6th QTR	7.94E+08	2.54E+08		3.52E+08		-3.68E+08	-7.73E+07	4.05E+08	3.86E+01
1-yr	7.96E+09	2.79E+09		5.17E+09		-1.43E+09	3.82E+08	3.77E+09	3.51E+01
Study POR	1.15E+10	3.56E+09		7.68E+09		-2.22E+09	1.79E+08	4.93E+09	3.29E+01
Cell 2									
1st QTR	6.69E+08	5.76E+08		2.29E+08		4.28E+08	1.30E+08	1.31E+09	1.06E+02
2nd QTR	8.57E+08	3.24E+08		1.63E+08		-1.31E+08	-7.24E+07	9.60E+08	8.12E+01
3rd QTR	2.24E+09	4.88E+08		2.12E+08		1.81E+08	-9.75E+07	2.79E+09	1.02E+02
4th QTR	3.10E+09	1.30E+09		2.71E+08		2.86E+08	2.36E+08	4.18E+09	9.50E+01
5th QTR	4.89E+09	9.79E+08		2.77E+08		6.10E+08	1.35E+08	6.07E+09	1.03E+02
6th QTR	3.52E+08	2.83E+08		1.99E+08		1.03E+07	-1.30E+08	5.76E+08	9.08E+01
1-yr	8.79E+09	3.10E+09		9.59E+08		8.13E+08	3.55E+08	1.14E+10	9.58E+01
Study POR	1.21E+10	3.95E+09		1.35E+09		1.38E+09	2.02E+08	1.59E+10	9.89E+01
Cell 3									
1st QTR	1.14E+09	5.76E+08		1.53E+08		2.15E+08	-2.63E+08	2.04E+09	1.19E+02
2nd QTR	1.31E+09	3.24E+08		1.18E+08		7.20E+07	1.02E+08	1.49E+09	9.09E+01
3rd QTR	2.42E+09	4.88E+08		1.58E+08		-9.70E+07	-2.10E+07	2.68E+09	9.20E+01
4th QTR	3.88E+09	1.30E+09		1.96E+08		-3.20E+08	-1.32E+08	4.79E+09	9.26E+01
5th QTR	6.16E+09	9.79E+08		2.35E+08		-2.55E+08	1.86E+08	6.47E+09	9.05E+01
6th QTR	8.71E+08	2.83E+08		1.20E+08		-8.93E+07	-2.91E+06	9.48E+08	8.21E+01
1-yr	1.11E+10	3.10E+09		6.92E+08		-2.82E+08	-1.87E+08	1.34E+10	9.45E+01
Study POR	1.58E+10	3.95E+09		9.79E+08		-4.75E+08	-1.30E+08	1.84E+10	9.33E+01
Combined									
1st QTR	2.74E+09	1.68E+09		9.58E+08		4.39E+08	1.29E+07	3.89E+09	8.80E+01
2nd QTR	3.56E+09	9.40E+08		1.10E+09		-5.88E+08	6.79E+07	2.75E+09	6.11E+01
3rd QTR	6.90E+09	1.41E+09		1.88E+09		-1.03E+08	-1.66E+08	6.49E+09	7.81E+01
4th QTR	8.86E+09	3.77E+09		1.72E+09		-3.62E+08	2.45E+08	1.03E+10	8.16E+01
5th QTR	1.53E+10	2.84E+09		3.68E+09		-2.51E+08	3.01E+08	1.39E+10	7.66E+01
6th QTR	2.02E+09	8.20E+08		6.71E+08		-4.47E+08	-2.10E+08	1.93E+09	6.80E+01
1-yr	2.78E+10	8.99E+09		6.82E+09		-8.94E+08	5.50E+08	2.86E+10	7.76E+01
Study POR	3.93E+10	1.15E+10		1.00E+10		-1.31E+09	2.51E+08	3.92E+10	7.72E+01

Percent Removal Efficiency by Treatment Cell

	Cell 1	Cell 2	Cell 3
1st QTR	1.40E+01	3.37E+01	5.23E+01
2nd QTR	1.09E+01	3.49E+01	5.42E+01
3rd QTR	1.58E+01	4.30E+01	4.12E+01
4th QTR	1.29E+01	4.05E+01	4.65E+01
5th QTR	9.58E+00	4.38E+01	4.66E+01
6th QTR	2.10E+01	2.99E+01	4.92E+01
1-yr	1.32E+01	3.98E+01	4.70E+01
Study POR	1.26E+01	4.05E+01	4.69E+01

Table 21. Surface water total phosphorus (TP) mass budget calculation for STA-2 Cells 1, 2, and 3.

TP Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [NA]	Out [g]	Evade [NA]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [%]
Cell 1									
1st QTR	3.52E+05	5.91E+03		1.87E+05		-4.22E+04	1.87E+04	1.10E+05	3.07E+01
2nd QTR	3.70E+05	3.24E+03		1.24E+05		-9.03E+04	7.18E+03	1.52E+05	4.06E+01
3rd QTR	8.21E+05	4.87E+03		2.36E+05		-4.61E+04	6.85E+03	5.37E+05	6.50E+01
4th QTR	6.41E+05	1.30E+04		2.46E+05		-7.22E+04	9.60E+03	3.26E+05	4.98E+01
5th QTR	1.46E+06	9.78E+03		4.78E+05		-1.59E+05	-1.29E+04	8.47E+05	5.76E+01
6th QTR	2.13E+05	2.83E+03		4.40E+04		-6.67E+04	-1.18E+04	1.17E+05	5.41E+01
1-yr	2.91E+06	3.11E+04		9.40E+05		-3.05E+05	1.12E+05	1.58E+06	5.38E+01
Study POR	3.86E+06	3.96E+04		1.32E+06		-4.76E+05	1.77E+04	2.09E+06	5.36E+01
Cell 2									
1st QTR	2.01E+05	6.60E+03		5.37E+04		1.91E+05	6.68E+03	3.38E+05	1.63E+02
2nd QTR	2.43E+05	3.61E+03		2.51E+04		-2.47E+04	-3.76E+04	2.35E+05	9.51E+01
3rd QTR	9.32E+05	5.44E+03		5.46E+04		4.74E+04	1.81E+04	9.12E+05	9.73E+01
4th QTR	1.10E+06	1.45E+04		5.95E+04		7.14E+04	3.99E+04	1.09E+06	9.75E+01
5th QTR	1.89E+06	1.09E+04		4.73E+04		1.37E+05	2.24E+04	1.96E+06	1.04E+02
6th QTR	9.89E+04	3.15E+03		2.97E+04		-5.82E+03	-8.55E+04	1.52E+05	1.49E+02
1-yr	3.48E+06	3.47E+04		2.06E+05		2.91E+05	4.64E+04	3.55E+06	1.01E+02
Study POR	4.47E+06	4.42E+04		2.70E+05		4.16E+05	-3.61E+04	4.69E+06	1.04E+02
Cell 3									
1st QTR	4.02E+05	6.60E+03		3.93E+04		8.07E+04	9.80E+04	3.52E+05	8.61E+01
2nd QTR	3.57E+05	3.61E+03		2.80E+04		-1.03E+02	1.69E+04	3.15E+05	8.75E+01
3rd QTR	9.90E+05	5.44E+03		4.25E+04		-2.73E+04	3.36E+04	8.92E+05	8.96E+01
4th QTR	1.45E+06	1.45E+04		4.72E+04		-9.06E+04	-5.82E+04	1.39E+06	9.46E+01
5th QTR	2.33E+06	1.09E+04		4.33E+04		-1.02E+05	-7.03E+03	2.20E+06	9.41E+01
6th QTR	2.36E+05	3.15E+03		2.61E+04		-2.38E+04	-1.16E+04	2.01E+05	8.40E+01
1-yr	4.40E+06	3.47E+04		1.71E+05		-9.97E+04	1.22E+05	4.04E+06	9.12E+01
Study POR	5.76E+06	4.42E+04		2.26E+05		-1.63E+05	7.16E+04	5.34E+06	9.21E+01
Combined									
1st QTR	9.55E+05	1.91E+04		2.80E+05		2.29E+05	1.23E+05	8.00E+05	8.21E+01
2nd QTR	9.70E+05	1.05E+04		1.77E+05		-1.15E+05	-1.36E+04	7.02E+05	7.16E+01
3rd QTR	2.74E+06	1.58E+04		3.33E+05		-2.60E+04	5.85E+04	2.34E+06	8.49E+01
4th QTR	3.20E+06	4.20E+04		3.53E+05		-9.14E+04	-8.78E+03	2.80E+06	8.65E+01
5th QTR	5.67E+06	3.16E+04		5.68E+05		-1.24E+05	2.48E+03	5.01E+06	8.78E+01
6th QTR	5.47E+05	9.13E+03		9.97E+04		-9.63E+04	-1.09E+05	4.69E+05	8.43E+01
1-yr	1.08E+07	1.01E+05		1.32E+06		-1.14E+05	2.80E+05	9.17E+06	8.43E+01
Study POR	1.41E+07	1.28E+05		1.81E+06		-2.23E+05	5.32E+04	1.21E+07	8.53E+01

Percent Removal Efficiency by Treatment Cell

	Cell 1	Cell 2	Cell 3
1st QTR	1.37E+01	4.23E+01	4.40E+01
2nd QTR	2.16E+01	3.35E+01	4.49E+01
3rd QTR	2.30E+01	3.90E+01	3.81E+01
4th QTR	1.16E+01	3.89E+01	4.94E+01
5th QTR	1.69E+01	3.92E+01	4.39E+01
6th QTR	2.49E+01	3.24E+01	4.27E+01
1-yr	1.72E+01	3.87E+01	4.41E+01
Study POR	1.72E+01	3.87E+01	4.41E+01

Table 22. Surface water total Kjeldahl nitrogen (TKN) mass budget calculation for STA-2 Cells 1, 2, and 3.

TKN Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [NA]	Out [g]	Evade [NA]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [g]
Cell 1									
1st QTR	2.58E+07	1.06E+06		2.04E+07		-4.87E+06	3.51E+06	-1.91E+06	-7.10E+00
2nd QTR	3.39E+07	5.79E+05		2.11E+07		-1.29E+07	-6.76E+05	1.20E+06	3.47E+00
3rd QTR	4.85E+07	8.71E+05		3.44E+07		-4.30E+06	-3.09E+05	1.10E+07	2.22E+01
4th QTR	4.87E+07	2.33E+06		3.49E+07		-8.13E+06	4.09E+06	3.97E+06	7.77E+00
5th QTR	1.11E+08	1.75E+06		8.20E+07		-1.50E+07	-8.76E+05	1.65E+07	1.46E+01
6th QTR	1.96E+07	5.05E+05		9.89E+06		-9.45E+06	-2.11E+06	2.90E+06	1.44E+01
1-yr	2.00E+08	5.56E+06		1.37E+08		-3.47E+07	9.26E+06	2.46E+07	1.20E+01
Study POR	2.87E+08	7.09E+06		2.03E+08		-5.46E+07	3.63E+06	3.36E+07	1.14E+01
Cell 2									
1st QTR	1.62E+07	1.18E+06		5.58E+06		1.27E+07	5.60E+06	1.89E+07	1.09E+02
2nd QTR	1.92E+07	6.46E+05		3.95E+06		-3.09E+06	-6.94E+06	1.97E+07	9.95E+01
3rd QTR	4.74E+07	9.72E+05		4.65E+06		3.66E+06	-1.79E+06	4.92E+07	1.02E+02
4th QTR	7.78E+07	2.59E+06		6.13E+06		7.25E+06	9.38E+06	7.22E+07	8.97E+01
5th QTR	1.28E+08	1.95E+06		6.43E+06		1.47E+07	7.40E+05	1.38E+08	1.06E+02
6th QTR	8.71E+06	5.64E+05		4.89E+06		-6.36E+05	-3.37E+06	7.11E+06	7.67E+01
1-yr	2.15E+08	6.20E+06		2.23E+07		2.15E+07	7.98E+06	2.12E+08	9.60E+01
Study POR	2.98E+08	7.90E+06		3.16E+07		3.46E+07	3.61E+06	3.05E+08	9.98E+01
Cell 3									
1st QTR	2.81E+07	1.18E+06		5.93E+06		3.98E+06	1.64E+06	2.57E+07	8.77E+01
2nd QTR	2.95E+07	6.46E+05		3.91E+06		4.92E+05	-4.23E+06	3.10E+07	1.03E+02
3rd QTR	5.22E+07	9.72E+05		4.67E+06		-2.16E+06	1.80E+06	4.45E+07	8.38E+01
4th QTR	9.72E+07	2.59E+06		5.94E+06		-9.76E+06	1.01E+06	8.31E+07	8.33E+01
5th QTR	1.62E+08	1.95E+06		6.63E+06		-8.23E+06	2.49E+06	1.47E+08	8.94E+01
6th QTR	2.17E+07	5.64E+05		4.71E+06		-3.18E+06	-3.94E+06	1.83E+07	8.22E+01
1-yr	2.73E+08	6.20E+06		2.26E+07		-1.31E+07	-1.42E+06	2.45E+08	8.77E+01
Study POR	3.91E+08	7.90E+06		3.18E+07		-1.89E+07	-1.23E+06	3.49E+08	8.76E+01
Combined									
1st QTR	7.01E+07	3.42E+06		3.19E+07		1.18E+07	1.07E+07	4.27E+07	5.80E+01
2nd QTR	8.26E+07	1.87E+06		2.90E+07		-1.54E+07	-1.18E+07	5.19E+07	6.15E+01
3rd QTR	1.48E+08	2.82E+06		4.37E+07		-2.80E+06	-3.02E+05	1.05E+08	6.94E+01
4th QTR	2.24E+08	7.51E+06		4.69E+07		-1.06E+07	1.45E+07	1.59E+08	6.88E+01
5th QTR	4.01E+08	5.65E+06		9.51E+07		-8.56E+06	2.35E+06	3.01E+08	7.39E+01
6th QTR	5.00E+07	1.63E+06		1.95E+07		-1.33E+07	-9.41E+06	2.83E+07	5.48E+01
1-yr	6.88E+08	1.80E+07		1.82E+08		-2.63E+07	1.58E+07	4.82E+08	6.83E+01
Study POR	9.76E+08	2.29E+07		2.66E+08		-3.89E+07	6.02E+06	6.88E+08	6.89E+01

Percent Removal Efficiency by Treatment Cell

	Cell 1	Cell 2	Cell 3
1st QTR	-4.47E+00	4.43E+01	6.01E+01
2nd QTR	2.31E+00	3.80E+01	5.97E+01
3rd QTR	1.05E+01	4.70E+01	4.25E+01
4th QTR	2.49E+00	4.53E+01	5.22E+01
5th QTR	5.48E+00	4.58E+01	4.87E+01
6th QTR	1.02E+01	2.51E+01	6.46E+01
1-yr	5.11E+00	4.40E+01	5.09E+01
Study POR	4.89E+00	4.43E+01	5.08E+01

Table 23. Surface water ammonia (NH_3) mass budget calculation for STA-2 Cells 1, 2, and 3.

NH3 Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [NA]	Out [g]	Evade [NA]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [g]
Cell 1									
1st QTR	2.54E+06	1.51E+05		1.28E+05		-1.08E+05	9.22E+04	2.37E+06	8.78E+01
2nd QTR	3.90E+06	8.28E+04		2.12E+05		-3.79E+05	-6.21E+04	3.46E+06	8.67E+01
3rd QTR	9.62E+06	1.25E+05		3.55E+05		-2.40E+05	1.82E+05	8.97E+06	9.20E+01
4th QTR	9.37E+06	3.33E+05		3.97E+05		-4.73E+05	2.15E+05	8.62E+06	8.88E+01
5th QTR	2.57E+07	2.50E+05		1.66E+06		-1.05E+06	1.24E+05	2.31E+07	8.91E+01
6th QTR	3.30E+06	7.23E+04		1.61E+05		-4.12E+05	-2.99E+05	3.09E+06	9.19E+01
1-yr	3.36E+07	7.96E+05		1.50E+06		-1.49E+06	7.51E+05	3.07E+07	8.91E+01
Study POR	5.44E+07	1.01E+06		2.91E+06		-2.66E+06	2.53E+05	4.96E+07	8.95E+01
Cell 2									
1st QTR	1.27E+06	1.69E+05		1.20E+05		5.49E+05	1.73E+05	1.70E+06	1.18E+02
2nd QTR	1.88E+06	9.24E+04		9.95E+04		-9.86E+04	-2.08E+05	1.98E+06	1.01E+02
3rd QTR	9.17E+06	1.39E+05		1.01E+05		1.25E+05	2.31E+05	9.11E+06	9.78E+01
4th QTR	1.52E+07	3.71E+05		1.22E+05		3.53E+05	5.29E+05	1.53E+07	9.81E+01
5th QTR	2.94E+07	2.79E+05		1.53E+05		1.03E+06	3.02E+05	3.03E+07	1.02E+02
6th QTR	1.52E+06	8.06E+04		1.60E+05		-8.35E+04	-6.51E+05	2.01E+06	1.25E+02
1-yr	3.82E+07	8.87E+05		4.89E+05		1.00E+06	1.02E+06	3.86E+07	9.87E+01
Study POR	5.85E+07	1.13E+06		7.56E+05		1.88E+06	3.75E+05	6.04E+07	1.01E+02
Cell 3									
1st QTR	3.08E+06	1.69E+05		6.03E+04		2.75E+05	-7.29E+04	3.54E+06	1.09E+02
2nd QTR	3.18E+06	9.24E+04		5.02E+04		3.86E+04	-1.26E+05	3.39E+06	1.04E+02
3rd QTR	1.04E+07	1.39E+05		5.55E+04		-1.05E+05	3.72E+05	9.99E+06	9.49E+01
4th QTR	1.90E+07	3.71E+05		9.31E+04		-4.21E+05	3.38E+03	1.89E+07	9.73E+01
5th QTR	3.74E+07	2.79E+05		9.59E+04		-5.36E+05	3.45E+05	3.67E+07	9.74E+01
6th QTR	3.72E+06	8.06E+04		4.66E+04		-1.01E+05	-3.44E+05	4.00E+06	1.05E+02
1-yr	4.88E+07	8.87E+05		2.92E+05		-5.45E+05	4.11E+05	4.84E+07	9.75E+01
Study POR	7.68E+07	1.13E+06		4.02E+05		-8.49E+05	1.77E+05	7.65E+07	9.82E+01
Combined									
1st QTR	6.89E+06	4.89E+05		3.09E+05		7.17E+05	1.92E+05	7.60E+06	1.03E+02
2nd QTR	8.96E+06	2.68E+05		3.62E+05		-4.39E+05	-3.97E+05	8.83E+06	9.56E+01
3rd QTR	2.92E+07	4.03E+05		5.12E+05		-2.20E+05	7.85E+05	2.81E+07	9.49E+01
4th QTR	4.36E+07	1.07E+06		6.12E+05		-5.41E+05	7.48E+05	4.28E+07	9.58E+01
5th QTR	9.25E+07	8.08E+05		1.91E+06		-5.53E+05	7.71E+05	9.01E+07	9.65E+01
6th QTR	8.54E+06	2.33E+05		3.67E+05		-5.97E+05	-1.29E+06	9.11E+06	1.04E+02
1-yr	1.21E+08	2.57E+06		2.28E+06		-1.03E+06	2.18E+06	1.18E+08	9.55E+01
Study POR	1.90E+08	3.27E+06		4.07E+06		-1.63E+06	8.05E+05	1.87E+08	9.66E+01

Percent Removal Efficiency by Treatment Cell

	Cell 1	Cell 2	Cell 3
1st QTR	3.11E+01	2.23E+01	4.65E+01
2nd QTR	3.92E+01	2.25E+01	3.84E+01
3rd QTR	3.20E+01	3.24E+01	3.56E+01
4th QTR	2.01E+01	3.57E+01	4.41E+01
5th QTR	2.57E+01	3.36E+01	4.08E+01
6th QTR	3.40E+01	2.21E+01	4.39E+01
1-yr	2.61E+01	3.28E+01	4.11E+01
Study POR	2.66E+01	3.24E+01	4.10E+01

Table 24. Surface water nitrate plus nitrite (NOx) mass budget calculation for STA-2 Cells 1, 2, and 3.

NOX Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [NA]	Out [g]	Evade [NA]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [g]
Cell 1									
1st QTR	9.35E+06	6.06E+05		5.20E+04		-2.38E+05	1.02E+05	9.56E+06	9.61E+01
2nd QTR	6.98E+06	3.32E+05		1.07E+05		-7.56E+05	-9.43E+03	6.46E+06	8.83E+01
3rd QTR	1.01E+07	5.00E+05		1.66E+05		-4.82E+05	3.83E+05	9.61E+06	9.03E+01
4th QTR	1.10E+07	1.33E+06		2.32E+05		-8.83E+05	-3.15E+05	1.15E+07	9.35E+01
5th QTR	1.33E+07	1.00E+06		5.47E+05		-4.76E+05	-1.06E+05	1.33E+07	9.36E+01
6th QTR	3.61E+06	2.90E+05		1.23E+05		-3.72E+05	1.57E+05	3.25E+06	8.33E+01
1-yr	4.39E+07	3.19E+06		7.00E+05		-2.60E+06	3.11E+05	4.35E+07	9.23E+01
Study POR	5.43E+07	4.06E+06		1.23E+06		-3.21E+06	2.11E+05	5.37E+07	9.20E+01
Cell 2									
1st QTR	7.11E+06	6.76E+05		5.83E+04		1.11E+06	2.60E+05	8.57E+06	1.10E+02
2nd QTR	4.21E+06	3.70E+05		1.33E+05		-1.79E+05	-1.97E+05	4.46E+06	9.75E+01
3rd QTR	9.21E+06	5.57E+05		9.47E+04		2.01E+05	9.94E+04	9.78E+06	1.00E+02
4th QTR	1.80E+07	1.49E+06		8.44E+05		5.81E+05	5.48E+05	1.87E+07	9.58E+01
5th QTR	1.69E+07	1.12E+06		1.39E+05		3.25E+05	-7.34E+05	1.90E+07	1.05E+02
6th QTR	1.67E+06	3.23E+05		9.37E+04		2.37E+04	3.88E+05	1.53E+06	7.70E+01
1-yr	4.80E+07	3.56E+06		1.19E+06		1.73E+06	5.33E+05	5.15E+07	1.00E+02
Study POR	5.72E+07	4.53E+06		1.36E+06		2.06E+06	3.65E+05	6.21E+07	1.01E+02
Cell 3									
1st QTR	1.09E+07	6.76E+05		7.35E+04		1.36E+06	-1.40E+06	1.42E+07	1.23E+02
2nd QTR	6.15E+06	3.70E+05		1.68E+05		2.04E+05	5.04E+04	6.51E+06	9.98E+01
3rd QTR	9.68E+06	5.57E+05		1.03E+05		-5.14E+05	2.38E+06	7.24E+06	7.07E+01
4th QTR	2.26E+07	1.49E+06		5.96E+05		-2.18E+06	-1.31E+06	2.27E+07	9.39E+01
5th QTR	2.15E+07	1.12E+06		2.37E+05		-1.01E+06	-1.40E+06	2.27E+07	1.01E+02
6th QTR	3.91E+06	3.23E+05		6.99E+04		-1.78E+05	9.52E+05	3.03E+06	7.16E+01
1-yr	6.06E+07	3.56E+06		1.03E+06		-1.95E+06	-7.39E+05	6.19E+07	9.65E+01
Study POR	7.47E+07	4.53E+06		1.25E+06		-2.31E+06	-7.37E+05	7.64E+07	9.64E+01
Combined									
1st QTR	2.73E+07	1.96E+06		1.84E+05		2.23E+06	-1.03E+06	3.24E+07	1.11E+02
2nd QTR	1.73E+07	1.07E+06		4.08E+05		-7.31E+05	-1.56E+05	1.74E+07	9.47E+01
3rd QTR	2.90E+07	1.61E+06		3.64E+05		-7.95E+05	2.86E+06	2.66E+07	8.69E+01
4th QTR	5.17E+07	4.31E+06		1.67E+06		-2.48E+06	-1.08E+06	5.29E+07	9.45E+01
5th QTR	5.17E+07	3.24E+06		9.24E+05		-1.16E+06	-2.25E+06	5.51E+07	1.00E+02
6th QTR	9.18E+06	9.36E+05		2.86E+05		-5.26E+05	1.50E+06	7.81E+06	7.72E+01
1-yr	1.53E+08	1.03E+07		2.92E+06		-2.82E+06	1.05E+05	1.57E+08	9.64E+01
Study POR	1.86E+08	1.31E+07		3.84E+06		-3.46E+06	-1.61E+05	1.92E+08	9.64E+01

Percent Removal Efficiency by Treatment Cell

	Cell 1	Cell 2	Cell 3
1st QTR	2.95E+01	2.65E+01	4.40E+01
2nd QTR	3.71E+01	2.56E+01	3.73E+01
3rd QTR	3.61E+01	3.67E+01	2.72E+01
4th QTR	2.18E+01	3.54E+01	4.28E+01
5th QTR	2.42E+01	3.45E+01	4.13E+01
6th QTR	4.16E+01	1.97E+01	3.88E+01
1-yr	2.77E+01	3.28E+01	3.95E+01
Study POR	2.80E+01	3.23E+01	3.98E+01

Table 25. Surface water sulfate (SO_4^{-2}) mass budget calculation for STA-2 Cells 1, 2, and 3.

SO4 Mass Budget Calculations for STA-2

	In [g]	Wet [g]	Dry [NA]	Out [g]	Evade [NA]	Seep [g]	Change Store [g]	Net Import [g]	Removal Efficiency [g]
Cell 1									
1st QTR	7.18E+08	7.07E+05		3.24E+08		-1.40E+08	9.11E+07	1.63E+08	2.27E+01
2nd QTR	8.76E+08	3.87E+05		4.85E+08		-2.99E+08	4.18E+07	5.10E+07	5.82E+00
3rd QTR	1.04E+09	5.82E+05		9.15E+08		-1.12E+08	-1.96E+07	3.07E+07	2.96E+00
4th QTR	9.02E+08	1.55E+06		9.96E+08		-2.40E+08	1.21E+08	-4.53E+08	-5.01E+01
5th QTR	1.66E+09	1.17E+06		2.79E+09		-4.78E+08	2.40E+07	-1.62E+09	-9.76E+01
6th QTR	5.18E+08	3.38E+05		2.78E+08		-2.76E+08	-1.24E+08	8.92E+07	1.72E+01
1-yr	4.12E+09	3.72E+06		3.68E+09		-9.31E+08	3.37E+08	-8.24E+08	-2.00E+01
Study POR	5.71E+09	4.74E+06		5.78E+09		-1.54E+09	1.33E+08	-1.74E+09	-3.05E+01
Cell 2									
1st QTR	5.30E+08	7.88E+05		1.53E+08		3.71E+08	-4.18E+07	7.91E+08	1.49E+02
2nd QTR	4.95E+08	4.32E+05		9.09E+07		-6.77E+07	-7.38E+07	4.11E+08	8.29E+01
3rd QTR	1.05E+09	6.50E+05		1.16E+08		8.39E+07	1.20E+07	1.00E+09	9.57E+01
4th QTR	1.49E+09	1.73E+06		2.06E+08		2.30E+08	2.43E+08	1.28E+09	8.53E+01
5th QTR	1.81E+09	1.30E+06		2.43E+08		5.11E+08	1.06E+08	1.98E+09	1.09E+02
6th QTR	2.29E+08	3.77E+05		1.51E+08		-2.59E+07	-2.66E+08	3.19E+08	1.39E+02
1-yr	4.29E+09	4.15E+06		6.38E+08		6.61E+08	2.84E+08	4.04E+09	9.39E+01
Study POR	5.61E+09	5.28E+06		9.61E+08		1.10E+09	-2.06E+07	5.78E+09	1.03E+02
Cell 3									
1st QTR	9.03E+08	7.88E+05		2.07E+08		1.71E+08	-7.98E+07	9.47E+08	1.05E+02
2nd QTR	7.80E+08	4.32E+05		1.16E+08		3.87E+07	-9.65E+07	8.00E+08	1.02E+02
3rd QTR	1.15E+09	6.50E+05		1.46E+08		-6.09E+07	6.59E+07	8.76E+08	7.63E+01
4th QTR	1.85E+09	1.73E+06		2.28E+08		-3.61E+08	1.27E+08	1.14E+09	6.13E+01
5th QTR	2.28E+09	1.30E+06		2.71E+08		-3.22E+08	1.20E+08	1.57E+09	6.88E+01
6th QTR	5.65E+08	3.77E+05		1.76E+08		-1.17E+08	-2.10E+08	4.83E+08	8.55E+01
1-yr	5.58E+09	4.15E+06		7.78E+08		-4.33E+08	-4.66E+07	4.42E+09	7.91E+01
Study POR	7.53E+09	5.28E+06		1.14E+09		-6.52E+08	-7.36E+07	5.81E+09	7.71E+01
Combined									
1st QTR	2.15E+09	2.28E+06		6.85E+08		4.02E+08	-3.05E+07	1.90E+09	8.83E+01
2nd QTR	2.15E+09	1.25E+06		6.92E+08		-3.28E+08	-1.28E+08	1.26E+09	5.86E+01
3rd QTR	3.23E+09	1.88E+06		1.18E+09		-8.85E+07	5.83E+07	1.91E+09	5.91E+01
4th QTR	4.25E+09	5.02E+06		1.43E+09		-3.71E+08	4.91E+08	1.96E+09	4.61E+01
5th QTR	5.76E+09	3.77E+06		3.30E+09		-2.89E+08	2.49E+08	1.92E+09	3.34E+01
6th QTR	1.31E+09	1.09E+06		6.05E+08		-4.18E+08	-6.01E+08	8.91E+08	6.79E+01
1-yr	1.40E+10	1.20E+07		5.09E+09		-7.03E+08	5.75E+08	7.63E+09	5.45E+01
Study POR	1.89E+10	1.53E+07		7.89E+09		-1.09E+09	3.93E+07	9.85E+09	5.22E+01

Soil/Sediment

The results of the soil/sediment mass budget calculations for THg, MeHg, TP, TKN, TCa, TMg, TS, AVS, TFe, and TMn are summarized in **Tables 26** through **29**, respectively. The spreadsheets containing the detailed calculations are available upon request. **Figures 60** through **62** depict the percent change in surficial soil storage of THg, MeHg, and other influential constituents relative to the pre-flood baseline established in May 2002. As with THg and MeHg, the change in storage of other constituents in the soil reservoir oscillated by quarter, and, as with THg and MeHg, some or perhaps all of these oscillations could be attributed solely to the propagated uncertainties in bulk density and constituent concentration measurements. However, it is also possible that the changes were associated with the uptake and subsurface sequestration of growing and senescing rooted macrophytes as a function of changing environmental conditions associated with changing season. Overall, the first flush-related increase in MeHg storage in surficial soil, which occurred in the first quarter of operation immediately following reflooding, was followed by a concomitant loss of that excess MeHg mass in the second post-reflooding quarter, such that the start-up criterion for MeHg (interior concentration not significantly greater than inflow concentration) was met in late November 2002.

Table 26. Surficial soil mass budgets for THg and MeHg.

Soil Mass Budget

	THg		Percent Change Relative to Baseline	MeHg		Percent Change Relative to Baseline
	Cell 1 Storage [g]	Change [g]	Storage [%]	Cell 1 Storage [g]	Change [g]	Storage [%]
5/16/2002	8.23E+03			2.39E+02		
8/14/2002	7.19E+03	-1.04E+03	-1.26E+01	4.57E+02	2.18E+02	9.12E+01
11/26/2002	7.91E+03	7.17E+02	8.72E+00	1.79E+02	-2.78E+02	-1.16E+02
1/29/2003	8.80E+03	8.89E+02	1.08E+01	2.08E+02	2.84E+01	1.19E+01
4/23/2003	6.48E+03	-2.32E+03	-2.81E+01	4.26E+01	-1.65E+02	-6.91E+01
7/16/2003	6.73E+03	2.47E+02	3.00E+00	2.50E+01	-1.76E+01	-7.35E+00
10/6/2003	4.03E+03	-2.70E+03	-3.28E+01	2.01E+01	-4.92E+00	-2.06E+00
12/30/2003	5.87E+03	1.84E+03	2.23E+01	4.41E+01	2.40E+01	1.01E+01

	THg		Percent Change Relative to Baseline	MeHg		Percent Change Relative to Baseline
	Cell 2 Storage [g]	Change [g]	Storage [%]	Cell 2 Storage [g]	Change [g]	Storage [%]
5/16/2002	8.32E+03			6.05E+01		
8/14/2002	5.56E+03	-2.77E+03	-3.32E+01	3.90E+01	-2.15E+01	-3.56E+01
11/26/2002	2.74E+03	-2.82E+03	-3.39E+01	2.18E+01	-1.72E+01	-2.84E+01
1/29/2003	6.28E+03	3.54E+03	4.26E+01	5.07E+01	2.89E+01	4.77E+01
4/23/2003	4.99E+03	-1.29E+03	-1.55E+01	2.74E+01	-2.33E+01	-3.85E+01
7/16/2003	6.28E+03	1.28E+03	1.54E+01	1.54E+01	-1.20E+01	-1.99E+01
10/6/2003	4.36E+03	-1.92E+03	-2.31E+01	1.50E+01	-4.18E-01	-6.92E-01
12/30/2003	4.71E+03	3.52E+02	4.23E+00	1.99E+01	4.89E+00	8.09E+00

	THg		Percent Change Relative to Baseline	MeHg		Percent Change Relative to Baseline
	Cell 3 Storage [g]	Change [g]	Storage [%]	Cell 3 Storage [g]	Change [g]	Storage [%]
5/16/2002	6.01E+03			1.58E+01		
8/14/2002	4.97E+03	-1.04E+03	-1.73E+01	2.78E+01	1.20E+01	7.59E+01
11/26/2002	4.86E+03	-1.09E+02	-1.82E+00	8.79E+00	-1.90E+01	-1.20E+02
1/29/2003	6.00E+03	1.13E+03	1.89E+01	2.01E+01	1.13E+01	7.16E+01
4/23/2003	2.14E+03	-3.85E+03	-6.41E+01	1.43E+01	-5.79E+00	-3.67E+01
7/16/2003	4.36E+03	2.22E+03	3.69E+01	7.04E+00	-7.28E+00	-4.61E+01
10/6/2003	2.86E+03	-1.50E+03	-2.49E+01	7.29E+00	2.52E-01	1.60E+00
12/30/2003	3.81E+03	9.53E+02	1.58E+01	2.12E+01	1.39E+01	8.80E+01

Table 27. Surficial soil mass budgets for TP and TN.

Soil Mass Budget

	TP			TN		
	Cell 1 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]	Cell 1 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]
5/16/2002	2.17E+07			1.47E+09		
8/14/2002	2.03E+07	-1.39E+06	-6.40E+00	1.62E+09	1.51E+08	1.03E+01
11/26/2002	2.70E+07	6.70E+06	3.09E+01	1.44E+09	-1.78E+08	-1.21E+01
1/29/2003	3.00E+07	3.02E+06	1.39E+01	1.67E+09	2.30E+08	1.57E+01
4/23/2003	2.53E+07	-4.71E+06	-2.17E+01	1.42E+09	-2.51E+08	-1.71E+01
7/16/2003	2.46E+07	-7.12E+05	-3.28E+00	1.30E+09	-1.24E+08	-8.46E+00
10/6/2003	2.10E+07	-3.59E+06	-1.65E+01	8.37E+08	-4.59E+08	-3.13E+01
12/30/2003	2.79E+07	6.90E+06	3.18E+01	1.27E+09	4.36E+08	2.97E+01

	TP			TN		
	Cell 2 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]	Cell 2 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]
5/16/2002	4.32E+07			2.46E+09		
8/14/2002	3.37E+07	-9.42E+06	-2.18E+01	1.81E+09	-6.47E+08	-2.63E+01
11/26/2002	3.78E+07	4.03E+06	9.33E+00	1.35E+09	-4.61E+08	-1.87E+01
1/29/2003	3.75E+07	-2.68E+05	-6.22E-01	1.83E+09	4.83E+08	1.96E+01
4/23/2003	3.43E+07	-3.15E+06	-7.30E+00	1.72E+09	-1.17E+08	-4.76E+00
7/16/2003	3.00E+07	-4.33E+06	-1.00E+01	2.06E+09	3.45E+08	1.40E+01
10/6/2003	2.69E+07	-3.13E+06	-7.25E+00	1.43E+09	-6.35E+08	-2.58E+01
12/30/2003	2.17E+07	-5.18E+06	-1.20E+01	1.37E+09	-5.75E+07	-2.34E+00

	TP			TN		
	Cell 3 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]	Cell 3 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]
5/16/2002	4.46E+07			2.68E+09		
8/14/2002	3.24E+07	-1.22E+07	-2.73E+01	1.86E+09	-8.25E+08	-3.08E+01
11/26/2002	4.64E+07	1.40E+07	3.15E+01	1.87E+09	9.58E+06	3.57E-01
1/29/2003	5.24E+07	6.02E+06	1.35E+01	1.98E+09	1.18E+08	4.39E+00
4/23/2003	3.23E+07	-2.01E+07	-4.51E+01	1.46E+09	-5.24E+08	-1.95E+01
7/16/2003	3.63E+07	3.96E+06	8.89E+00	1.59E+09	1.25E+08	4.65E+00
10/6/2003	3.12E+07	-5.12E+06	-1.15E+01	9.39E+08	-6.46E+08	-2.41E+01
12/30/2003	5.03E+07	1.91E+07	4.30E+01	1.82E+09	8.80E+08	3.28E+01

Table 28. Surficial soil mass budgets for Ca and Mg.

STA-2 Soil Mass Budget

	Ca			Mg		
	Cell 1 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]	Cell 1 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]
5/16/2002	1.38E+09			1.83E+08		
8/14/2002	1.52E+09	1.38E+08	1.00E+01	1.85E+08	2.34E+06	1.28E+00
11/26/2002	1.43E+09	-9.13E+07	-6.60E+00	1.91E+08	5.48E+06	3.00E+00
1/29/2003	1.56E+09	1.26E+08	9.08E+00	1.97E+08	6.87E+06	3.76E+00
4/23/2003	1.30E+09	-2.51E+08	-1.82E+01	1.67E+08	-3.04E+07	-1.66E+01
7/16/2003	1.24E+09	-6.23E+07	-4.50E+00	1.48E+08	-1.91E+07	-1.05E+01
10/6/2003	1.17E+09	-7.17E+07	-5.19E+00	1.11E+08	-3.69E+07	-2.02E+01
12/30/2003	1.64E+09	4.72E+08	3.41E+01	1.68E+08	5.67E+07	3.10E+01

	Ca			Mg		
	Cell 2 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]	Cell 2 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]
5/16/2002	2.27E+09			2.23E+08		
8/14/2002	2.54E+09	2.70E+08	1.19E+01	2.36E+08	1.28E+07	5.73E+00
11/26/2002	2.31E+09	-2.29E+08	-1.01E+01	2.00E+08	-3.55E+07	-1.59E+01
1/29/2003	2.53E+09	2.20E+08	9.70E+00	2.31E+08	3.07E+07	1.38E+01
4/23/2003	2.19E+09	-3.43E+08	-1.51E+01	2.23E+08	-7.55E+06	-3.38E+00
7/16/2003	2.78E+09	5.88E+08	2.59E+01	2.56E+08	3.31E+07	1.48E+01
10/6/2003	1.78E+09	-1.01E+09	-4.42E+01	1.79E+08	-7.75E+07	-3.48E+01
12/30/2003	1.87E+09	9.94E+07	4.37E+00	1.83E+08	4.43E+06	1.99E+00

	Ca			Mg		
	Cell 3 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]	Cell 3 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]
5/16/2002	3.51E+09			4.73E+08		
8/14/2002	3.25E+09	-2.65E+08	-7.53E+00	4.35E+08	-3.79E+07	-8.02E+00
11/26/2002	4.78E+09	1.53E+09	4.35E+01	5.23E+08	8.78E+07	1.86E+01
1/29/2003	5.70E+09	9.22E+08	2.63E+01	5.26E+08	3.47E+06	7.35E-01
4/23/2003	4.04E+09	-1.66E+09	-4.73E+01	3.95E+08	-1.31E+08	-2.78E+01
7/16/2003	4.25E+09	2.16E+08	6.14E+00	4.00E+08	5.03E+06	1.06E+00
10/6/2003	5.28E+09	1.03E+09	2.92E+01	3.75E+08	-2.50E+07	-5.29E+00
12/30/2003	8.66E+09	3.38E+09	9.62E+01	4.96E+08	1.21E+08	2.57E+01

Table 29. Surficial soil mass budgets for Fe and Mn.

STA-2 Soil Mass Budget

	Fe			Mn		
	Cell 1 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]	Cell 1 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]
5/16/2002	7.02E+07			4.55E+06		
8/14/2002	7.22E+07	2.01E+06	2.86E+00	4.56E+06	6.87E+03	1.51E-01
11/26/2002	1.13E+08	4.04E+07	5.76E+01	6.10E+06	1.54E+06	3.39E+01
1/29/2003	9.57E+07	-1.70E+07	-2.42E+01	5.06E+06	-1.04E+06	-2.28E+01
4/23/2003	8.36E+07	-1.20E+07	-1.71E+01	4.60E+06	-4.59E+05	-1.01E+01
7/16/2003	6.42E+07	-1.94E+07	-2.77E+01	3.81E+06	-7.88E+05	-1.73E+01
10/6/2003	5.77E+07	-6.52E+06	-9.28E+00	3.66E+06	-1.46E+05	-3.21E+00
12/30/2003	7.24E+07	1.47E+07	2.09E+01	4.77E+06	1.10E+06	2.42E+01

	Fe			Mn		
	Cell 2 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]	Cell 2 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]
5/16/2002	1.36E+08			9.55E+06		
8/14/2002	1.84E+08	4.75E+07	3.48E+01	1.55E+07	5.95E+06	6.23E+01
11/26/2002	8.82E+07	-9.57E+07	-7.02E+01	8.91E+06	-6.59E+06	-6.90E+01
1/29/2003	1.54E+08	6.61E+07	4.85E+01	1.35E+07	4.58E+06	4.79E+01
4/23/2003	1.55E+08	1.20E+06	8.78E-01	1.02E+07	-3.28E+06	-3.44E+01
7/16/2003	1.51E+08	-4.31E+06	-3.16E+00	1.17E+07	1.51E+06	1.58E+01
10/6/2003	1.02E+08	-4.89E+07	-3.58E+01	8.36E+06	-3.35E+06	-3.51E+01
12/30/2003	1.04E+08	1.80E+06	1.32E+00	5.05E+06	-3.31E+06	-3.47E+01

	Fe			Mn		
	Cell 3 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]	Cell 3 Storage [g]	Change [g]	Percent Change Relative to Baseline Storage [%]
5/16/2002	2.49E+08			1.25E+07		
8/14/2002	1.54E+08	-9.57E+07	-3.83E+01	5.70E+06	-6.84E+06	-5.45E+01
11/26/2002	2.00E+08	4.62E+07	1.85E+01	7.23E+06	1.52E+06	1.21E+01
1/29/2003	2.27E+08	2.66E+07	1.07E+01	9.31E+06	2.09E+06	1.66E+01
4/23/2003	1.43E+08	-8.36E+07	-3.35E+01	4.33E+06	-4.98E+06	-3.97E+01
7/16/2003	1.87E+08	4.43E+07	1.78E+01	5.29E+06	9.54E+05	7.60E+00
10/6/2003	1.22E+08	-6.57E+07	-2.63E+01	5.90E+06	6.19E+05	4.93E+00
12/30/2003	1.78E+08	5.68E+07	2.28E+01	7.42E+06	1.52E+06	1.21E+01

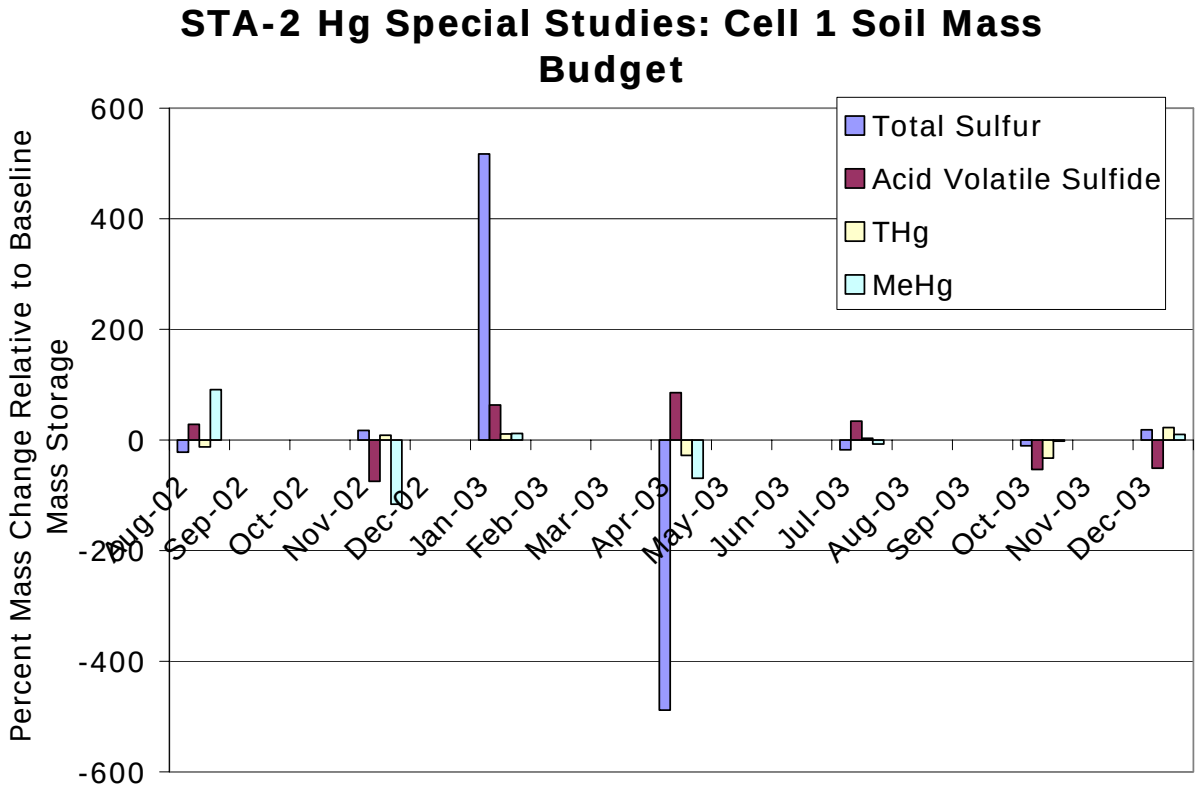

Figure 60. Percent change in TS, AVS, THg, and MeHg masses stored in surficial soil relative to the baseline value established in May 2002**.**

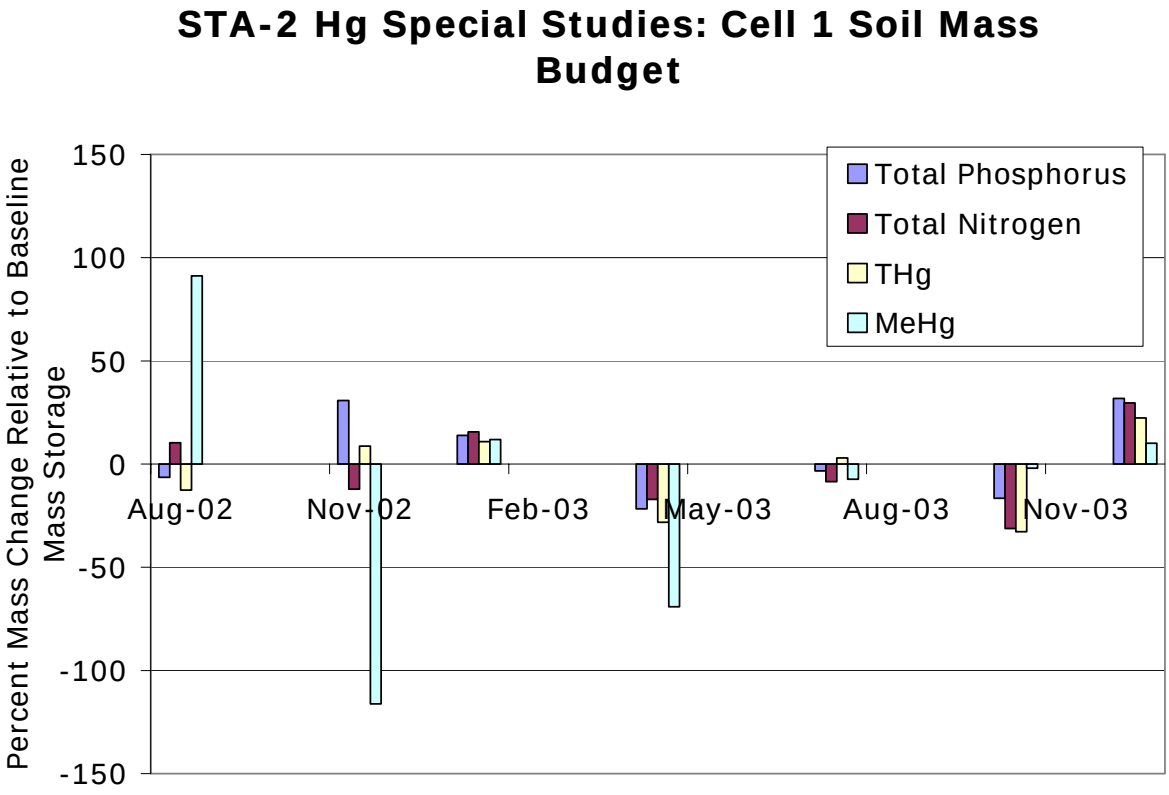

Figure 61. Percent change in TP, TN, THg, and MeHg masses stored in surficial soil relative to the baseline value established in May 2002.

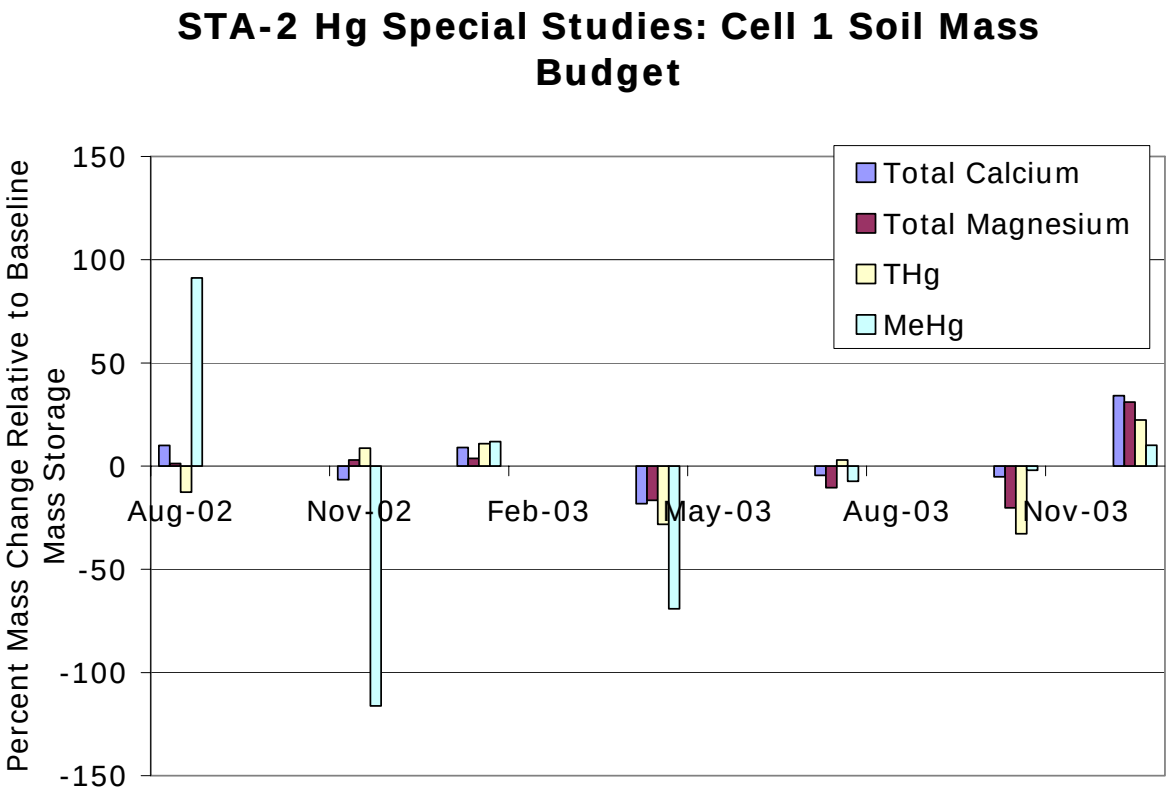

Figure 62. Percent change in TCa, TMg, THg, and MeHg masses stored in surficial soil relative to the baseline value established in May 2002.

Vegetation

The results of the exploratory estimates of the THg, MeHg, and Hg(II) masses stored in above-ground standing crop plant biomass in September 2002, February 2003, and September 2003 are presented in **Tables 30**, **31**, and **32**, respectively. Clearly, cattail, sawgrass, and other emergent macrophytes were likely to be making the largest contributions of THg and MeHg masses stored in plant standing crop biomass in Cells 1 and 2, although the average THg and MeHg concentrations in aboveground leaves tended to be between one-third to one-tenth the corresponding concentrations in floating macrophytes and periphyton. By contrast, water lilies, water lettuce, and other floating macrophytes made the largest contribution to Cell 3 THg and MeHg plant biomass storage.

During the project, there was only one high-altitude aerial photograph of STA-2 from which the open water and vegetation coverages were estimated. This occurred in November 2003, while the measurement of plant densities occurred in July 2003, and the sampling for THg and MeHg analyses occurred in September 2003. Thus, the combinations of these found data can only be used for exploratory analysis to assess the potential significance of plant storage of THg or MeHg and not for the calculation of changes in storage for accurate mass budgets or model initialization or calibration. Furthermore, the coverage estimates were not available for eight months following the monitoring event. As long as the District uses only high-altitude aerial photographs for calculating vegetation coverage in South Florida, the overflights will be limited to the fall and winter. For rapidly colonizing systems following first flooding in the spring or summer, the meteorological requirements for the use of this method are inconsistent with those extant in South Florida, and the authors strongly suggest that low-level aerial photography be substituted for high-altitude aerial photography to accommodate these meteorological realities vis-à-vis the value of such information for adaptive management decision making.

Table 30. Mercury species above-ground storage in STA-2 plant standing crop biomass for samples collected in September 2002.

STA-2 Plant Storage of Mercury Species: September 2002*

COVERAGES

	Open	Open + Hydrilla + Potomo	Emergent + Water [50/50]	Emergent	Floating
	%	%	%	%	%
Cell 1	2.63	0.04	11.04	85.9	0.39
Cell 2	1.61	19.97	5.77	72.29	0.35
Cell 3	3.35	72.63	5.95	17.99	0.07

PLANT ABOVE-GROUND STORAGE

	THg [g]	MeHg [g]	Hg(II) [g]
Cell 1	277.5791	108.254	169.3251
Cell 2	225.3163	15.83379	209.4826
Cell 3	163.1932	33.23349	129.9597

CONTRIBUTION TO STORAGE BY PLANT SPECIES

	THg Emergents %	THg SAV %	THg Floaters %	THg Periphyton %
Cell 1	77.85%	16.42%	0.51%	5.22%
Cell 2	62.24%	6.98%	12.85%	17.94%
Cell 3	18.41%	1.60%	70.34%	9.65%

	MeHg Emergents %	MeHg SAV %	MeHg Floaters %	MeHg Periphyton %
Cell 1	74.68%	24.13%	0.60%	0.59%
Cell 2	69.70%	7.56%	11.10%	11.63%
Cell 3	3.91%	1.07%	90.97%	4.06%

	Hg(II) Emergents %	Hg(II) SAV %	Hg(II) Floaters %	Hg(II) Periphyton %
Cell 1	79.87%	11.49%	0.46%	8.18%
Cell 2	61.67%	6.93%	12.98%	18.41%
Cell 3	22.11%	1.74%	65.07%	11.08%

*** based on mercury analyses from September 2002, plant density measurements from July 2003, and high-altitude aerial photogrammetry in November 2003**

Table 31. Mercury species above-ground storage in STA-2 plant standing crop biomass for samples collected in February 2003.

STA-2 Plant Storage of Mercury Species: February 2003*

COVERAGES

	Open %	Open + Hydrilla + Potomo %	Emergent + Water [50/50] %	Emergent %	Floating %
Cell 1	2.63	0.04	11.04	85.9	0.39
Cell 2	1.61	19.97	5.77	72.29	0.35
Cell 3	3.35	72.63	5.95	17.99	0.07

PLANT ABOVE-GROUND STORAGE

	THg [g]	MeHg [g]	Hg(II) [g]
Cell 1	48.83314	4.587105	44.24604
Cell 2	47.42639	2.302057	45.12433
Cell 3	43.02251	3.993714	39.02879

CONTRIBUTION TO STORAGE BY PLANT SPECIES

	THg Emergents %	THg SAV %	THg Floaters %	THg Periphyton %
Cell 1	62.17%	4.52%	0.83%	32.48%
Cell 2	61.72%	2.08%	11.00%	25.20%
Cell 3	31.27%	0.57%	62.21%	5.96%

	MeHg Emergents %	MeHg SAV %	MeHg Floaters %	MeHg Periphyton %
Cell 1	38.03%	10.00%	1.36%	50.61%
Cell 2	36.62%	7.27%	19.77%	36.34%
Cell 3	5.50%	1.15%	86.61%	6.73%

	Hg(II) Emergents %	Hg(II) SAV %	Hg(II) Floaters %	Hg(II) Periphyton %
Cell 1	64.67%	3.95%	0.77%	30.60%
Cell 2	63.00%	1.81%	10.56%	24.63%
Cell 3	33.90%	0.51%	59.71%	5.88%

*** based on mercury analyses from February 2003, plant density measurements from July 2003, and high-altitude aerial photogrammetry in November 2003**

Table 32. Mercury species above-ground storage in STA-2 plant standing crop biomass for samples collected in September 2003.

STA-2 Plant Storage of Mercury Species: September 2003*

COVERAGES

	Open %	Open + Hydrilla + Potomo %	Emergent + Water [50/50] %	Emergent %	Floating %
Cell 1	2.63	0.04	11.04	85.9	0.39
Cell 2	1.61	19.97	5.77	72.29	0.35
Cell 3	3.35	72.63	5.95	17.99	0.07

PLANT ABOVE-GROUND STORAGE

	THg [g]	MeHg [g]	Hg(II) [g]
Cell 1	33.74762	0.91131	32.83631
Cell 2	25.1648	0.545887	24.61891
Cell 3	14.01984	0.609019	13.41082

CONTRIBUTION TO STORAGE BY PLANT SPECIES

	THg Emergents %	THg SAV %	THg Floaters %	THg Periphyton %
Cell 1	83.90%	8.83%	0.37%	6.90%
Cell 2	80.62%	4.17%	6.83%	8.38%
Cell 3	14.11%	2.31%	60.15%	23.43%

	MeHg Emergents %	MeHg SAV %	MeHg Floaters %	MeHg Periphyton %
Cell 1	75.05%	9.90%	0.56%	14.48%
Cell 2	68.22%	5.90%	10.82%	15.05%
Cell 3	11.39%	12.38%	53.38%	22.85%

	Hg(II) Emergents %	Hg(II) SAV %	Hg(II) Floaters %	Hg(II) Periphyton %
Cell 1	84.15%	8.80%	0.36%	6.69%
Cell 2	80.89%	4.13%	6.74%	8.24%
Cell 3	14.23%	1.85%	60.46%	23.46%

*** based on mercury analyses from September 2003, plant density measurements from July 2003, and high-altitude aerial photogrammetry in November 2003**

COMBINED MERCURY MASS BUDGET

Tables 33, **34**, and **35** summarize the combined THg, MeHg, and Hg(II) mass budgets for Cell 1, 2, and 3 surface water net import and soil and vegetation change in storage by quarter. Clearly the soil was the most substantial storage compartment for THg throughout the study, with thousands of grams apparently being lost in the first quarter, reabsorbed in the second quarter, and oscillating irregularly thereafter. However, the sum of the change in plant storage and net export for THg between the first and second quarters of post-reflood operation are almost equal to the THg mass calculated to have been stored in plant biomass for the preceding quarter. Compare this to the situation for MeHg, in which the sum of net export of MeHg from Cell 1 and the plant canopy storage of MeHg in Cell 1 in the first quarter following reflooding are of the same order as the soil loss for that quarter. The "Discussion" section that follows takes up the question of the potential causes of the apparent consistencies and inconsistencies in the multi-compartment MeHg and THg mass budgets, respectively.

Table 33. Combined THg mass budgets for Cells 1, 2, and 3.

STA-2 Combined Mass Budget

	THg Cell 1 Soil Storage [g]	Change [g]	Average Water Storage [g]	Cell 1 Water Net Import [g]	Cell 1 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	8230													
8/14/2002	7191	-1039			278									
11/26/2002	7909	717	17	-112	163	-114	8089	491	98	0	2	146	-23	-23
1/29/2003	8798	889	6	-18	49	-114	8853	757	99	0	1	117	-2	-15
4/23/2003	6481	-2317	8	-41	44	-5	6533	-2362	99	0	1	98	2	0
7/16/2003	6728	247	6	75	39	-5	6773	317	99	0	1	78	24	-2
10/6/2003	4033	-2696	5	69	34	-5	4071	-2631	99	0	1	102	-3	0
12/30/2003	5868	1835	3	17	34	0	5905	1853	99	0	1	99	1	0
Total		-1323		-9		-244		-1576						

	THg Cell 2 Soil Storage [g]	Change [g]	Average Water Storage [g]	Cell 2 Water Net Import [g]	Cell 2 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	8322													
8/14/2002	5556	-2765			225									
11/26/2002	2736	-2820	9	53	136	-89	2881	-2856	95	0	5	99	-2	3
1/29/2003	6278	3542	5	15	47	-89	6331	3468	99	0	1	102	0	-3
4/23/2003	4992	-1286	7	52	40	-7	5039	-1242	99	0	1	104	-4	1
7/16/2003	6276	1284	8	172	33	-7	6316	1449	99	0	1	89	12	-1
10/6/2003	4356	-1920	6	179	25	-7	4387	-1748	99	0	1	110	-10	0
12/30/2003	4708	352	5	7	25	0	4738	359	99	0	1	98	2	0
Total		-849		478		-200		-570						

	THg Cell 3 Storage [g]	Change [g]	Average Water Storage [g]	Cell 3 Water Net Import [g]	Cell 3 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	6013													
8/14/2002	4970	-1042			163									
11/26/2002	4861	-109	5	64	103	-60	4970	-105	98	0	2	104	-61	57
1/29/2003	5996	1135	4	21	43	-60	6043	1096	99	0	1	104	2	-5
4/23/2003	2142	-3854	5	53	33	-10	2181	-3811	98	0	2	101	-1	0
7/16/2003	4360	2219	6	186	24	-10	4390	2395	99	0	1	93	8	0
10/6/2003	2861	-1499	4	190	14	-10	2879	-1319	99	0	0	114	-14	1
12/30/2003	3814	953	3	13	14	0	3831	966	100	0	0	99	1	0
Total		-1156		528		-149		-777						

Table 33. Continued.

STA-2 Combined Mass Budget Omitting Soil Compartment

	THg Average Water Storage [g]	Cell 1 Water Net Import [g]	Cell 1 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Water	% Storage Plant	% Change Water	% Change Plant
5/16/2002										
8/14/2002			278							
11/26/2002	17	-112	163	-114	180	-227	9	91	50	50
1/29/2003	6	-18	49	-114	55	-132	11	89	13	87
4/23/2003	8	-41	44	-5	52	-46	16	84	89	11
7/16/2003	6	75	39	-5	45	70	14	86	107	-7
10/6/2003	5	69	34	-5	38	64	12	88	108	-8
12/30/2003	3	17	34	0	36	17	7	93	100	0
Total		-9		-244		-253				

	THg Average Water Storage [g]	Cell 2 Water Net Import [g]	Cell 2 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Water	% Storage Plant	% Change Water	% Change Plant
5/16/2002										
8/14/2002			225							
11/26/2002	9	53	136	-89	145	-36	6	94	-147	247
1/29/2003	5	15	47	-89	53	-74	10	90	-21	121
4/23/2003	7	52	40	-7	47	45	15	85	117	-17
7/16/2003	8	172	33	-7	41	165	20	80	105	-5
10/6/2003	6	179	25	-7	32	172	20	80	104	-4
12/30/2003	5	7	25	0	30	7	17	83	100	0
Total		478		-200		278				

	THg Average Water Storage [g]	Cell 3 Water Net Import [g]	Cell 3 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Water	% Storage Plant	% Change Water	% Change Plant
5/16/2002										
8/14/2002			163							
11/26/2002	5	64	103	-60	108	4	5	95	1590	-1490
1/29/2003	4	21	43	-60	47	-39	9	91	-55	155
4/23/2003	5	53	33	-10	39	43	14	86	122	-22
7/16/2003	6	186	24	-10	30	177	20	80	105	-5
10/6/2003	4	190	14	-10	18	181	20	80	105	-5
12/30/2003	3	13	14	0	17	13	17	83	100	0
Total		528		-149		379				

*** includes linearly interpolated values between semi-annually measured values**

Table 34. Combined MeHg mass budgets for Cells 1, 2, and 3.

STA-2 Combined Mass Budget

	MeHg Cell 1 Soil Storage [g]	Change [g]	Average Water Storage [g]	Cell 1 Water Net Import [g]	Cell 1 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	239													
8/14/2002	457	218			108									
11/26/2002	179	-278	3	-85	56	-52	239	-415	75	1	24	67	20	13
1/29/2003	208	28	-1	-15	5	-52	211	-38	98	0	2	-75	38	137
4/23/2003	43	-165	0	-38	3	-1	45	-205	94	-1	7	81	19	1
7/16/2003	25	-18	0	-5	2	-1	27	-24	94	-2	8	72	23	5
10/6/2003	20	-5	0	-4	1	-1	21	-10	93	2	4	48	40	12
12/30/2003	44	24	-1	0	1	0	44	24	100	-2	2	101	-1	0
Total		-413		-147		-107		-668						

	MeHg Cell 2 Soil Storage [g]	Change [g]	Average Water Storage [g]	Cell 2 Water Net Import [g]	Cell 2 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	60													
8/14/2002	39	-22			16									
11/26/2002	22	-17	0	2	9	-7	31	-22	71	0	29	77	-7	30
1/29/2003	51	29	-1	2	2	-7	52	24	98	-3	4	121	7	-28
4/23/2003	27	-23	0	2	2	-1	29	-22	93	1	6	107	-9	3
7/16/2003	15	-12	0	6	1	-1	17	-6	91	2	7	194	-104	9
10/6/2003	15	0	2	7	1	-1	17	6	86	11	3	-7	116	-9
12/30/2003	20	5	-2	2	1	0	18	7	110	-13	3	72	28	0
Total		-19		21		-15		-13						

	MeHg Cell 3 Storage [g]	Change [g]	Average Water Storage [g]	Cell 3 Water Net Import [g]	Cell 3 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	16													
8/14/2002	28	12			33									
11/26/2002	9	-19	0	2	19	-15	28	-32	32	2	67	60	-5	46
1/29/2003	20	11	0	1	4	-15	24	-2	84	0	17	-553	-61	714
4/23/2003	14	-6	0	2	3	-1	17	-5	82	2	16	122	-46	24
7/16/2003	7	-7	0	8	2	-1	9	0	82	-2	20	1611	-1760	249
10/6/2003	7	0	0	10	1	-1	8	9	92	0	8	3	109	-12
12/30/2003	21	14	0	1	1	0	22	15	98	-1	3	94	6	0
Total		-7		24		-33								

*** includes linearly interpolated values between semi-annually measured values**

Table 34. Continued.

STA-2 Combined Mass Budget Omitting Soil Compartment

	MeHg Average Water Storage [g]	Cell 1 Water Net Import [g]	Cell 1 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Water	% Storage Plant	% Change Water	% Change Plant
5/16/2002										
8/14/2002			108							
11/26/2002	3	-85	56	-52	59	-137	5	95	62	38
1/29/2003	-1	-15	5	-52	4	-66	-28	128	22	78
4/23/2003	0	-38	3	-1	3	-40	-16	116	97	3
7/16/2003	0	-5	2	-1	2	-7	-30	130	82	18
10/6/2003	0	-4	1	-1	1	-5	35	65	77	23
12/30/2003	-1	0	1	0	0	0	1620	-1520	100	0
Total		-147		-107		-255				

	MeHg Average Water Storage [g]	Cell 2 Water Net Import [g]	Cell 2 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Water	% Storage Plant	% Change Water	% Change Plant
5/16/2002										
8/14/2002			16							
11/26/2002	0	2	9	-7	9	-5	0	100	-30	130
1/29/2003	-1	2	2	-7	1	-5	-138	238	-36	136
4/23/2003	0	2	2	-1	2	1	17	83	140	-40
7/16/2003	0	6	1	-1	1	6	23	77	110	-10
10/6/2003	2	7	1	-1	2	7	77	23	109	-9
12/30/2003	-2	2	1	0	-2	2	131	-31	100	0
Total		21		-15		6				

	MeHg Average Water Storage [g]	Cell 3 Water Net Import [g]	Cell 3 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Water	% Storage Plant	% Change Water	% Change Plant
5/16/2002										
8/14/2002			33							
11/26/2002	0	2	19	-15	19	-13	2	98	-13	113
1/29/2003	0	1	4	-15	4	-13	-1	101	-9	109
4/23/2003	0	2	3	-1	3	1	9	91	208	-108
7/16/2003	0	8	2	-1	2	7	-13	113	116	-16
10/6/2003	0	10	1	-1	1	9	-1	101	112	-12
12/30/2003	0	1	1	0	0	1	-29	129	100	0
Total		24		-33						

*** includes linearly interpolated values between semi-annually measured values**

Table 35. Combined Hg(II) mass budgets for Cells 1, 2, and 3.

STA-2 Combined Mass Budget Omitting Soil Compartment

	Hg(II) Cell 1 Soil Storage [g]	Change [g]	Average Water Storage [g]	Cell 1 Water Net Import [g]	Cell 1 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	7991													
8/14/2002	6734	-1257			169									
11/26/2002	7729	995	14	-28	107	-63	7850	905	98	0	1	110	-3	-7
1/29/2003	8590	861	7	-3	44	-63	8641	795	99	0	1	108	0	-8
4/23/2003	6439	-2151	9	-2	40	-4	6488	-2158	99	0	1	100	0	0
7/16/2003	6703	265	7	80	37	-4	6747	341	99	0	1	78	24	-1
10/6/2003	4013	-2691	4	73	33	-4	4050	-2621	99	0	1	103	-3	0
12/30/2003	5824	1811	4	18	33	0	5861	1829	99	0	1	99	1	0
Total		-910		138		-136		-908						

	Hg(II) Cell 2 Soil Storage [g]	Change [g]	Average Water Storage [g]	Cell 2 Water Net Import [g]	Cell 2 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	8261													
8/14/2002	5517	-2744			209									
11/26/2002	2714	-2803	9	51	127	-82	2850	-2834	95	0	4	99	-2	3
1/29/2003	6227	3513	7	14	45	-82	6279	3444	99	0	1	102	0	-2
4/23/2003	4964	-1263	7	50	38	-7	5009	-1220	99	0	1	104	-4	1
7/16/2003	6260	1296	8	166	31	-7	6300	1455	99	0	0	89	11	0
10/6/2003	4341	-1920	4	172	25	-7	4370	-1755	99	0	1	109	-10	0
12/30/2003	4688	347	8	5	25	0	4720	352	99	0	1	99	1	0
Total		-829		457		-185		-557						

	Hg(II) Cell 3 Storage [g]	Change [g]	Average Water Storage [g]	Cell 3 Water Net Import [g]	Cell 3 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	5997													
8/14/2002	4943	-1054			130									
11/26/2002	4852	-90	5	62	84	-45	4942	-73	98	0	2	123	-85	62
1/29/2003	5976	1124	4	20	39	-45	6019	1098	99	0	1	102	2	-4
4/23/2003	2128	-3848	5	51	30	-9	2163	-3806	98	0	1	101	-1	0
7/16/2003	4353	2226	6	178	22	-9	4381	2396	99	0	1	93	7	0
10/6/2003	2854	-1499	4	180	13	-9	2871	-1328	99	0	0	113	-14	1
12/30/2003	3793	939	3	12	13	0	3809	951	100	0	0	99	1	0
Total		-1150		504		-117								

*** includes linearly interpolated values between semi-annually measured values**

Table 35. Continued.

STA-2 Combined Mass Budget Omitting Soil Compartment

	Hg(II) Cell 1 Soil Storage [g]	Change [g]	Average Water Storage [g]	Cell 1 Water Net Import [g]	Cell 1 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	7991													
8/14/2002	6734	-1257			169									
11/26/2002	7729	995	14	-28	107	-63	7850	905	98	0	1	110	-3	-7
1/29/2003	8590	861	7	-3	44	-63	8641	795	99	0	1	108	0	-8
4/23/2003	6439	-2151	9	-2	40	-4	6488	-2158	99	0	1	100	0	0
7/16/2003	6703	265	7	80	37	-4	6747	341	99	0	1	78	24	-1
10/6/2003	4013	-2691	4	73	33	-4	4050	-2621	99	0	1	103	-3	0
12/30/2003	5824	1811	4	18	33	0	5861	1829	99	0	1	99	1	0
Total		-910		138		-136		-908						

	Hg(II) Cell 2 Soil Storage [g]	Change [g]	Average Water Storage [g]	Cell 2 Water Net Import [g]	Cell 2 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	8261													
8/14/2002	5517	-2744			209									
11/26/2002	2714	-2803	9	51	127	-82	2850	-2834	95	0	4	99	-2	3
1/29/2003	6227	3513	7	14	45	-82	6279	3444	99	0	1	102	0	-2
4/23/2003	4964	-1263	7	50	38	-7	5009	-1220	99	0	1	104	-4	1
7/16/2003	6260	1296	8	166	31	-7	6300	1455	99	0	0	89	11	0
10/6/2003	4341	-1920	4	172	25	-7	4370	-1755	99	0	1	109	-10	0
12/30/2003	4688	347	8	5	25	0	4720	352	99	0	1	99	1	0
Total		-829		457		-185		-557						

	Hg(II) Cell 3 Storage [g]	Change [g]	Average Water Storage [g]	Cell 3 Water Net Import [g]	Cell 3 Plant* Storage [g]	Change [g]	Sum Storage [g]	Sum Change [g]	% Storage Soil	% Storage Water	% Storage Plant	% Change Soil	% Change Water	% Change Plant
5/16/2002	5997													
8/14/2002	4943	-1054			130									
11/26/2002	4852	-90	5	62	84	-45	4942	-73	98	0	2	123	-85	62
1/29/2003	5976	1124	4	20	39	-45	6019	1098	99	0	1	102	2	-4
4/23/2003	2128	-3848	5	51	30	-9	2163	-3806	98	0	1	101	-1	0
7/16/2003	4353	2226	6	178	22	-9	4381	2396	99	0	1	93	7	0
10/6/2003	2854	-1499	4	180	13	-9	2871	-1328	99	0	0	113	-14	1
12/30/2003	3793	939	3	12	13	0	3809	951	100	0	0	99	1	0
Total		-1150		504		-117								

*** includes linearly interpolated values between semi-annually measured values**

EXPLORATORY DATA ANALYSIS

This subsection summarizes the key results of the nonparametric (Spearman) linear correlation analysis and the parametric linear regression analysis of the untransformed and the log-transformed data within media (intra-correlation analysis) and between media (inter-correlation analysis). The results of the intra-correlations for all combinations of concentrations, loads, media, and station aggregations are presented in Appendix K. First, the results of the univariate linear correlation analysis will be presented, followed by the results of the parametric linear regression analysis. Second, within each class of analysis, the concentration x concentration results will be presented, followed by the concentration x load results. Third, within each category of analysis, the intra-correlations will presented in the order of surface water, pore water, and soil for all applicable sites, followed by the inter-correlations in the order of surface water x pore water, surface water x soil, pore water x soil, fish x surface water, fish x pore water, and fish x soil. Within each subcategory, first the data to be analyzed will be aggregated at the STA-2 level (all cells pooled), at the cell level (all stations within a cell pooled), and at the station level (each station within a cell individually). For data that did not meet the normality requirement of the Shapiro-Wilks test at $p < 0.01$, the data were log-transformed and rescaled by adding 1 to the logarithm value.

The apparent strong, statistically significant correlations between U-THg and U-MeHg or F-THg and F-MeHg with U-Hg(II) and F-Hg(II), respectively, were not further evaluated because the concentration of Hg(II) was calculated by subtracting the U-MeHg or F-MeHg from the U-THg or F-THg value, so the strong correlations were an artifact of the method of calculation. This is also the case for the ratios and percentages of unfiltered and filtered THg, MeHg, and Hg(II). Because MeHg is a substantial component of THg, the strong correlations between THg and MeHg were also not further evaluated. The correlations with color, nitrate-N plus nitrite-N, salinity, total dissolved solids (TDS), ortho reactive phosphorus (ORP), pheophytin, and turbidity were also not further evaluated because they were only monitored at the common inflow (G-328). The apparent strong correlations where the number of observations was greater than 14 also were not further evaluated because the data set cannot be considered representative of the system under study. Where the p value of the correlation is not presented, the correlation relationship has a p value less than 0.05.

UNIVARIATE PARAMETRIC AND NONPARAMETRIC LINEAR CORRELATION ANALYSIS

Intra-Correlations

Concentrations x Concentrations

SURFACE WATER X SURFACE WATER

All STA-2 Sites

No Lag/No Average Correlation Analysis

The strongest valid (not spurious), robust, statistically significant ($p < 0.001$) univariate linear positive correlations were between filtered iron (F-TFe) or total phosphate (TP) and U-THg ($r = 0.56$ or 0.60), U-MeHg ($r = 0.58$ or 0.68), U-Hg(II) ($r = 0.69$ or 0.53), F-THg ($r = 0.36$ or 0.44), and F-MeHg ($r = 0.40$ or 0.54) with dissolved (filtered) iron. Salinity and ortho-phosphate have roughly the same pattern and magnitudes of influence on the water mercury species variables as F-TFe and TP, respectively. [Note: specific conductivity follows a pattern inverse to that of salinity, while they should be strictly equivalent, so the results from the contractor (Janicki Environmental Inc., under contract to BFA) must be considered strictly suspect.] The strongest valid (not spurious), robust, statistically significant ($p < 0.001$) univariate linear inverse correlations were between field pH and U-THg ($r = -0.79$), U-MeHg ($r = -0.75$), U-Hg(II) ($r = -0.72$), F-THg ($r = -0.64$), F-MeHg ($r = -0.63$), F-Hg(II) ($r = -0.61$), and F-%MeHg ($r = -0.33$). Field pH may mediate the sorption of Hg(II) and MeHg to particles and DOC or dissolved iron colloid that have also been implicated in the sorption and transport of dissolved mercury species (Babiarz et al., 2001). There were also very weak to moderate, statistically significant inverse correlations between water depth and U-THg (-0.36; $p < 0.01$), U-MeHg ($r = -0.52$; $p < 0.001$), U-Hg(II)($r = 0.31$; $p < 0.05$), U-%MeHg ($r = -0.57$; $p < 0.001$), F-THg ($r = -0.30$; $p < 0.001$), F-MeHg ($r = -0.43$; $p < 0.001$), and F-%MeHg (-0.44; $p < 0.001$). Water depth may be a surrogate for water flow and the dilution it provides for dissolved and particulate constituents of soil origin. However, it may also be a surrogate for the inverse influence of water depth on negative redox potential and the speciation and transport of redox-sensitive species from surficial soil pore water into the overlying water column. The inverse correlations between sulfate and measured or calculated MeHg values were generally very weak ($r < -0.46$), albeit statistically significant. However, this should not be surprising because it takes time for surface water sulfate to diffuse into the surficial soil and stimulate sulfide production and inhibit MeHg production. Whether the strength of this inverse relationship increases with the time lag between MeHg and sulfate sampling bears further scrutiny. The lag correlation analyses for the individual monitoring stations are summarized in the next section.

Figures 63 and **64** graph the scatter plots of surface water F-THg versus U-THg and F-MeHg and U-MeHg for all inflow, interior, and outflow monitoring study sites. There was excellent agreement for both sets of paired data, providing further evidence for the self-consistency of the results, even at the ultra-trace concentration level with and without filtering. However, the number of valid pairs of F-MeHg versus U-MeHg data was reduced relative to the corresponding U-THg versus F-THg values because of filter contamination discussed previously. **Figures 65** and **66** display the scatter plots of F-MeHg versus alkalinity and pH, respectively. Note that the correlations are extremely weak to virtually nonexistent, suggesting that surface

water parameters usually moderately to strongly correlated with the levels of THg as MeHg in fish from generally deep, northern temperate and subarctic lakes are not mediating MeHg bioaccumulation by directly influencing surface water MeHg concentrations. DOC was expected to have a positive influence on the concentrations of MeHg in surface water by enhancing pore water-to-surface water transport and competing with settling solid particles for MeHg molecules in solution, "hanging up" MeHg molecules in solution longer than would otherwise be expected in the presence of settling solids. The weak positive correlation between F-MeHg and DOC depicted in **Figure 67** supports this expectation. However, iron and manganese were not expected to have more of an influence on surface water MeHg concentrations than DOC, contrary to what is obvious from an inspection of the scatter plots graphed in **Figures 68** and **69**, respectively. As discussed above, it might be inferred from these unexpected findings that iron colloids are also competing with suspended and settled solids for truly dissolved Hg(II) and MeHg complexes, and that manganese may mediate the kinetics of iron colloid speciation, fractionation, complexation, and precipitation by facilitating the uptake and loss of electrons via redox shuttle between pore water and surface water. Although sulfate was not expected to have a direct influence on MeHg transport and fractionation, it was expected to exert an inverse influence via mediating the production of sulfide in the surficial sediment and interstitial pore water. In fact, the influence of surface water sulfate is undetectable in the scatter plots depicted in **Figure 70**. Whether the absence of the expected influence persists into the pore water medium must await the presentation of the results of the exploratory data analysis in the next subsection. The scatter plots in **Figures 71** through **74** demonstrate that the influences of DOC, Fe, Mn, and sulfate strengthen somewhat when U-MeHg is substituted for F-MeHg.

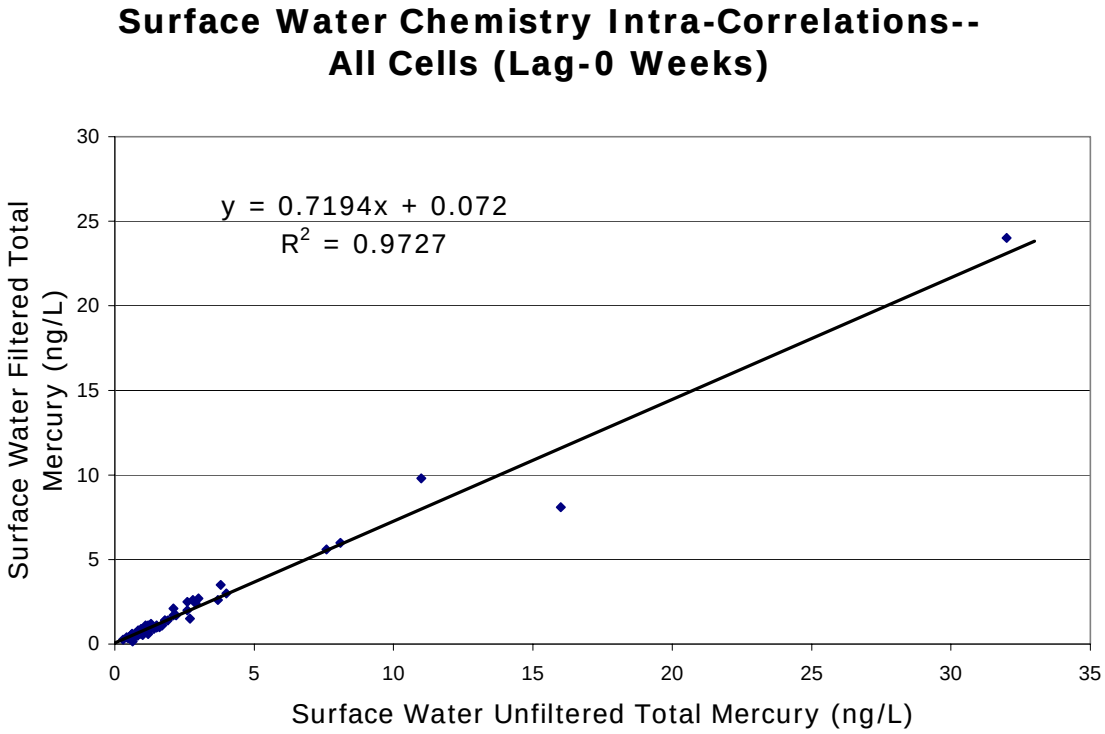

Figure 63. Scatter plot of filtered total mercury (F-THg) concentration versus unfiltered total mercury (U-THg) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

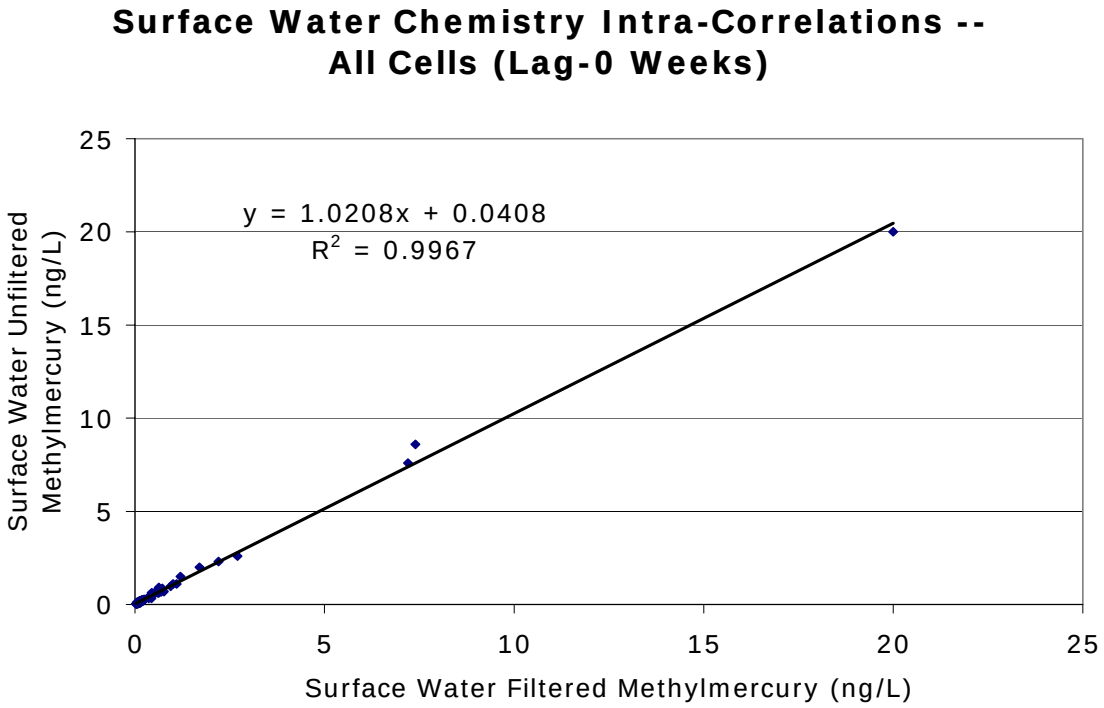

Figure 64. Scatter plot of filtered methylmercury (F-MeHg) concentration versus unfiltered methylmercury (U-MeHg) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

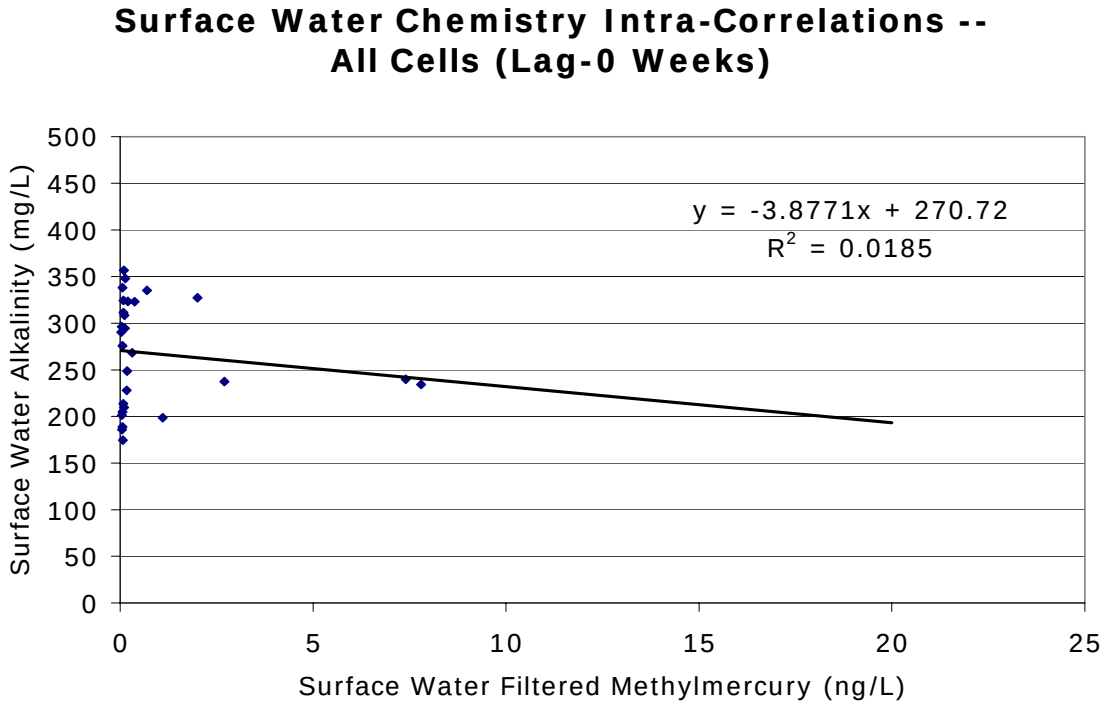

Figure 65. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus alkalinity concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

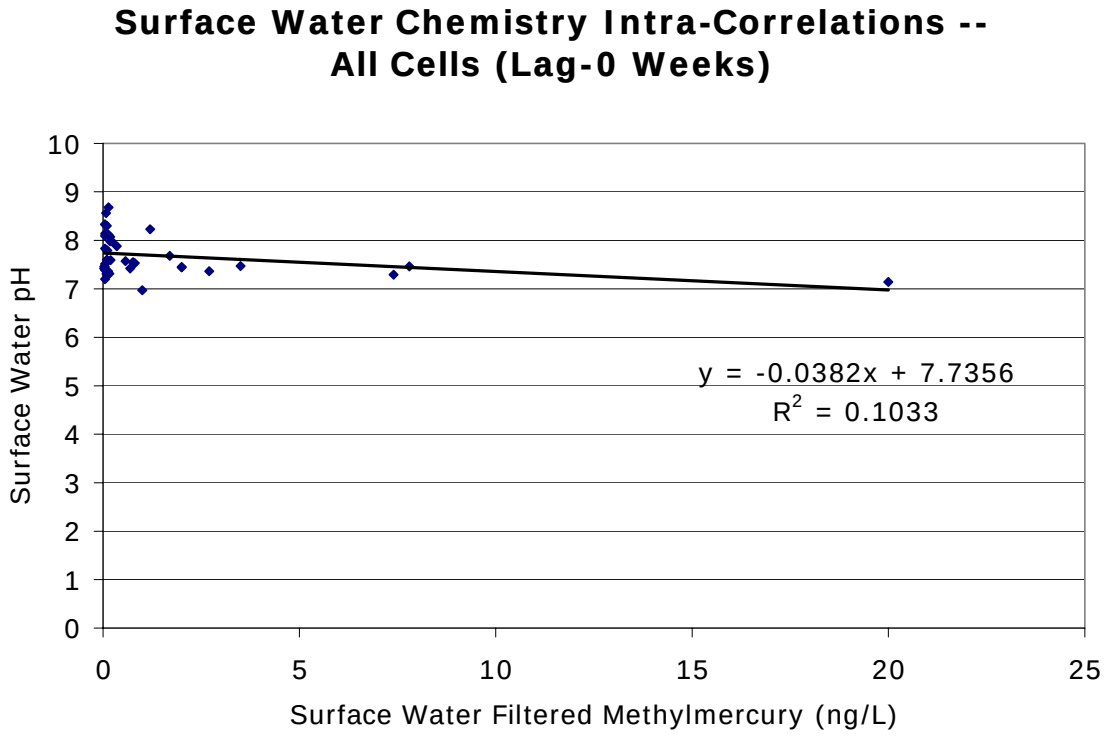

Figure 66. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus pH for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

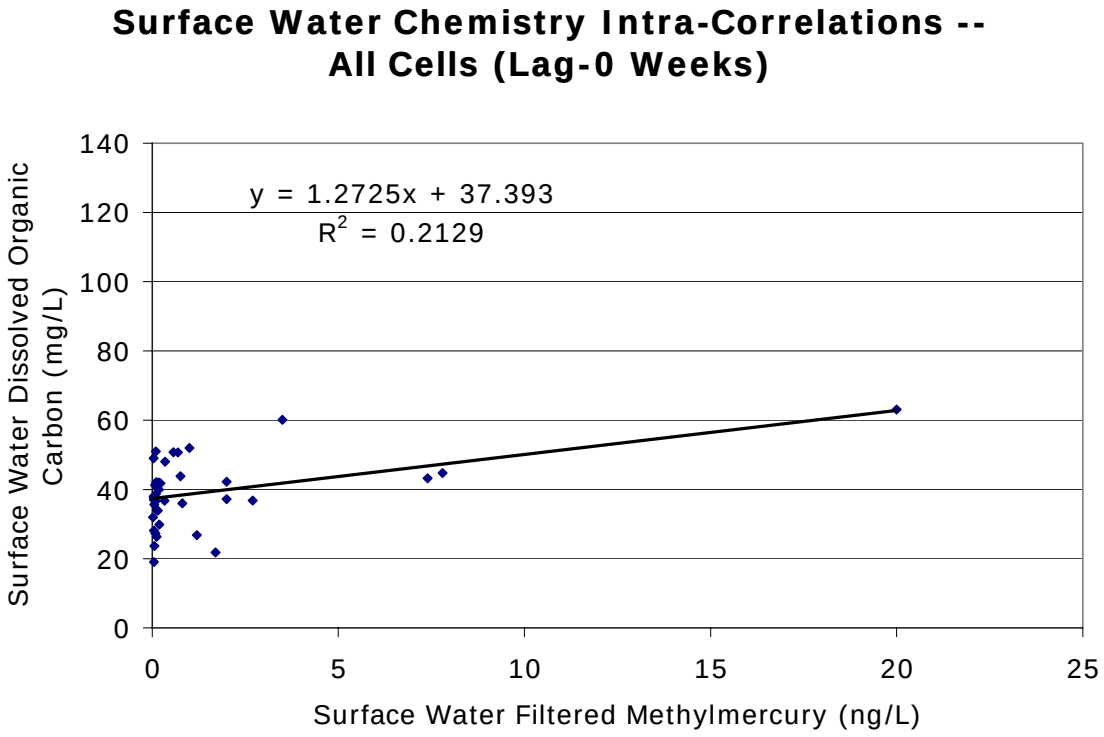

Figure 67. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus dissolved organic carbon (DOC) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

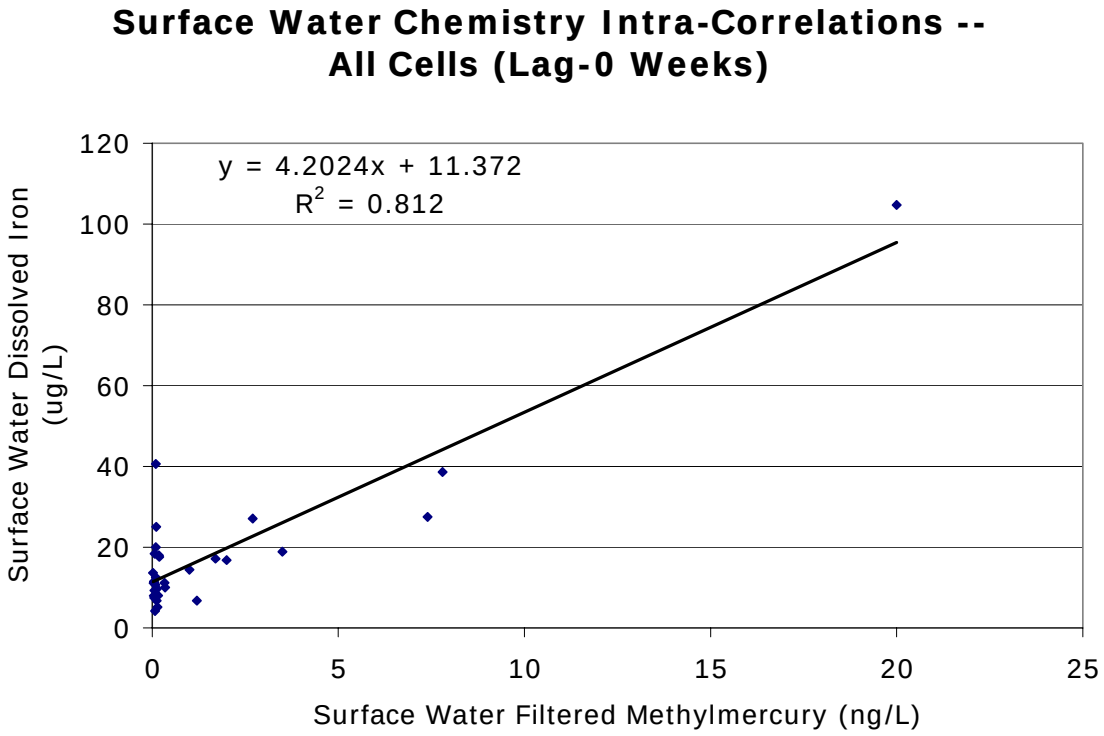

Figure 68. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus dissolved total iron (F-TFe) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

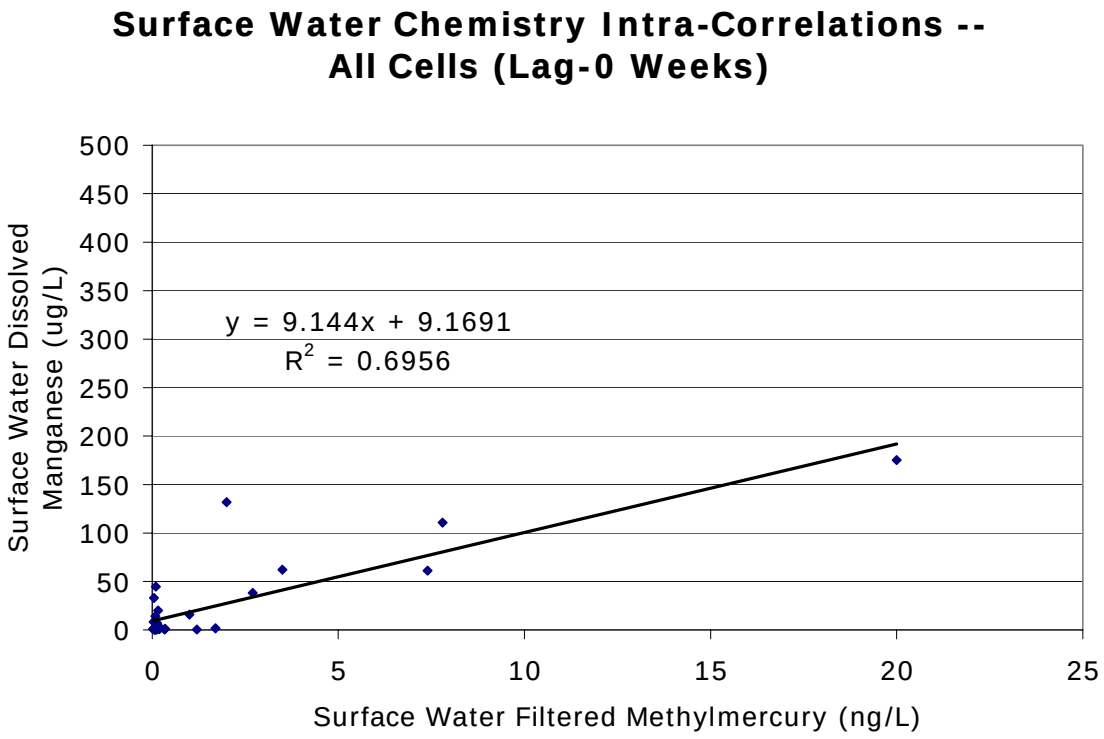

Figure 69. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus dissolved total manganese (F-TMn) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

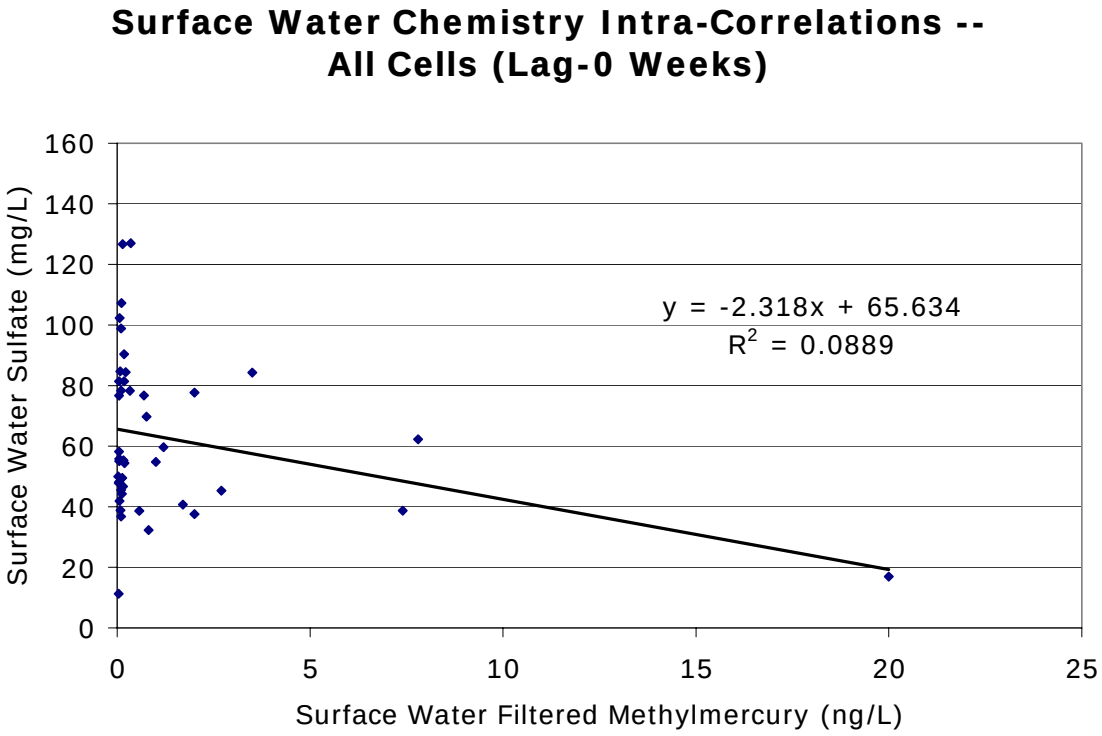

Figure 70. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus sulfate (SO42-) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

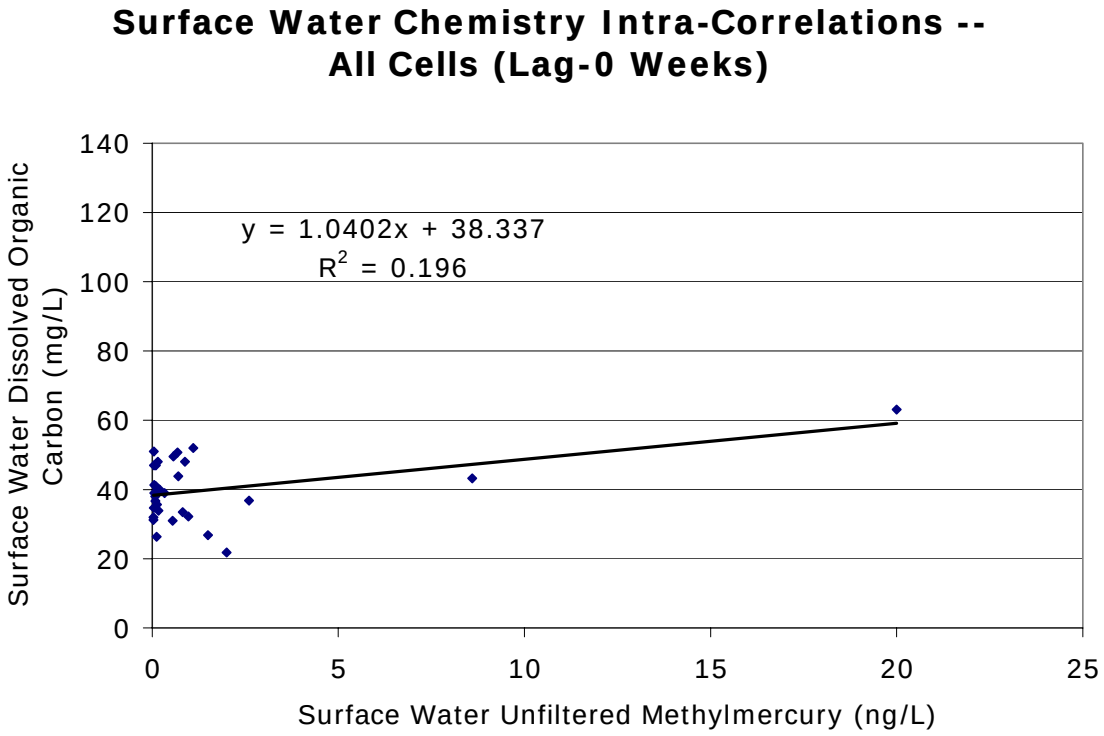

Figure 71. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus dissolved organic carbon (DOC) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

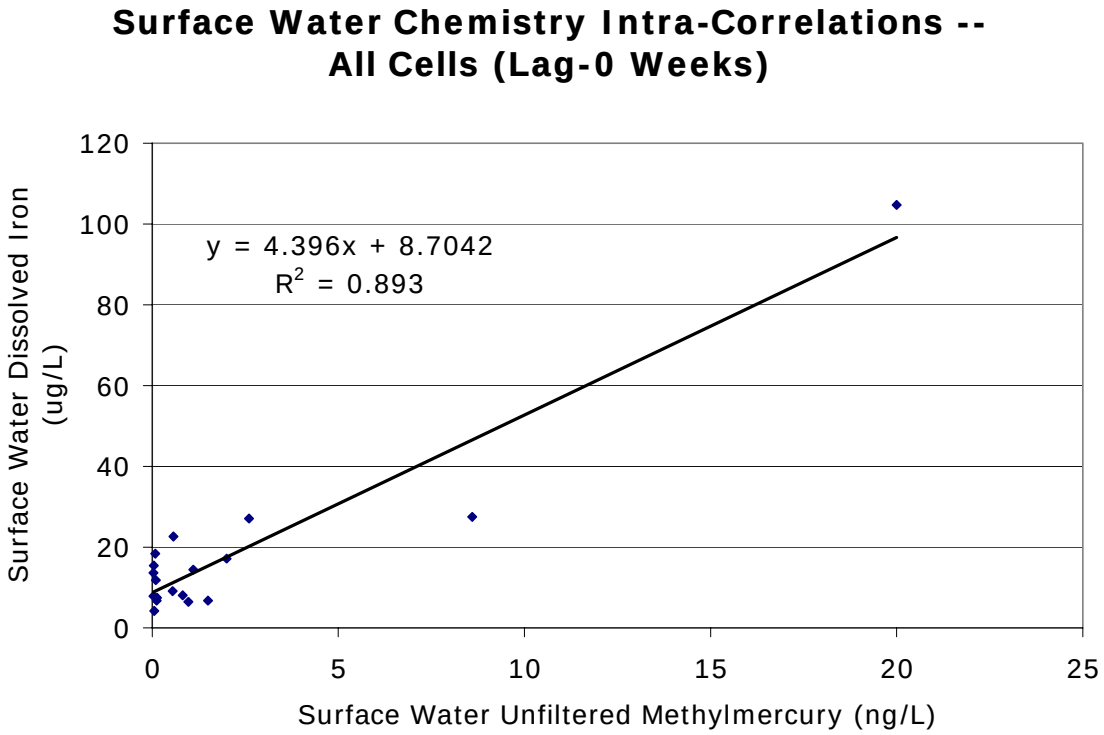

Figure 72. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus dissolved total iron (F-TFe) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

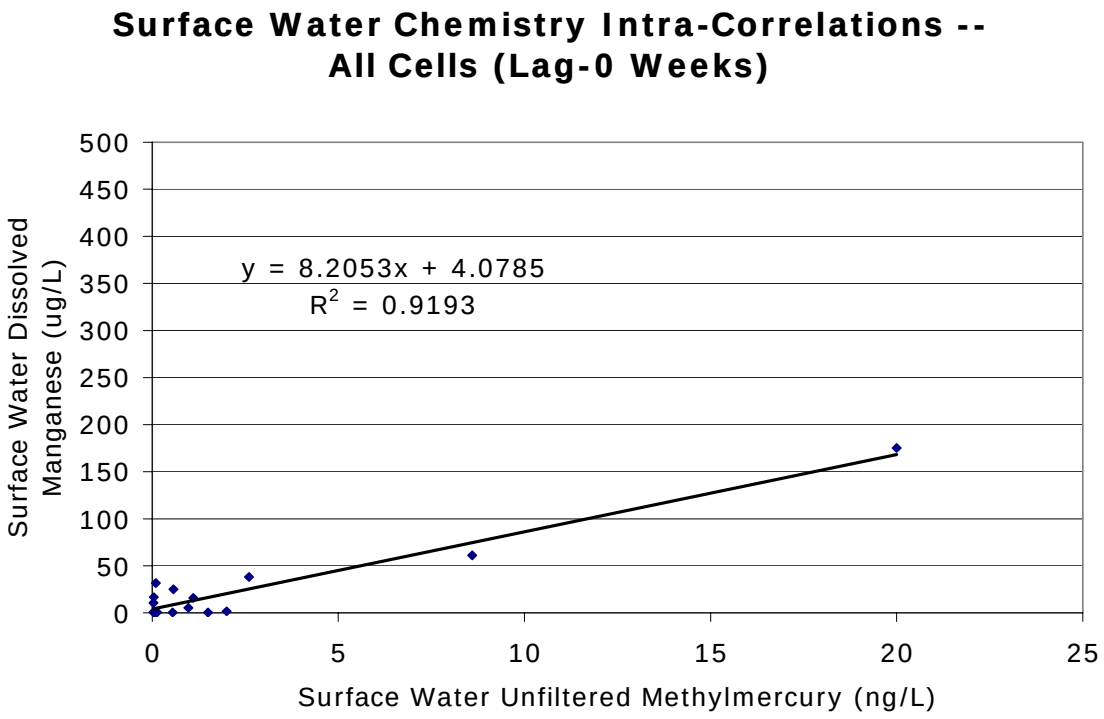

Figure 73. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus dissolved total manganese (F-TMn) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

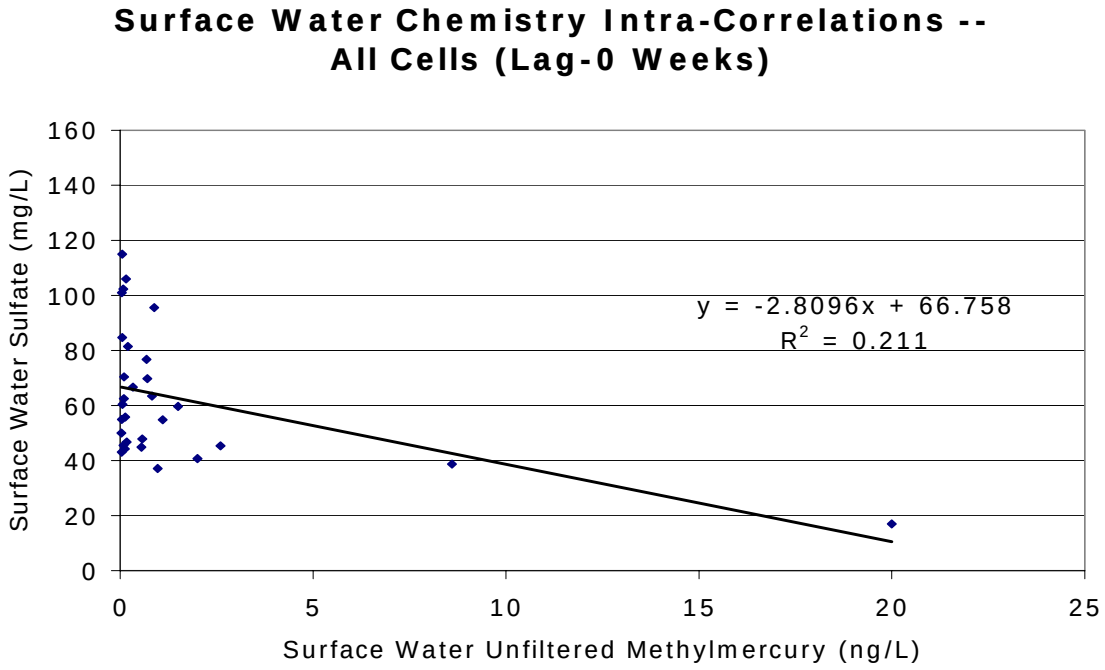

Figure 74. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus sulfate (SO42-) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

G-328B

No Lag/No Average Correlation Analysis

The common STA-2 inflow was monitored weekly or biweekly at G-328 for a variety of constituents and parameters of interest other than ultra-trace U-THg, U-MeHg, F-THg, and F-MeHg. G-328B, which was located several hundred meters downstream of G-328 and immediately downstream of the confluence with a major farm culvert, was monitored for ultra-trace U-THg and U-MeHg biweekly and F-THg and F-MeHg every four weeks. The inflow canal at G-328/B is a distinctly different hydrological, biogeochemical, and ecological environment from the cell interior and outflow constructed wetland sites, so it is appropriate to parse the combined data sets into an inflow canal data set and an interior and outflow sites data set.

As depicted in **Figures 75** and **76**, respectively, F-THg and F-MeHg were moderately to strongly intra-correlated, while U-THg and U-MeHg were not. U-MeHg was moderately positively correlated with NH_3 (r = 0.548) but not U-Hg(II). U-%MeHg but not U-MeHg, F-MeHg, or F-%MeHg was moderately positively correlated with DOC (r = 0.569) (see **Figure 77**). Further, the moderate to strong inverse correlations between Hg(II) or MeHg species and dissolved iron or manganese that were observed when evaluating all of the STA-2 sites combined weakened substantially when G-328B was evaluated individually. Without further study, it cannot be determined whether these shifts were due to differences in the relative affinities of Hg(II) and MeHg for canal particles due to distinctly different sources of particle-bound Hg(II) and MeHg (e.g., stormwater runoff and suspended transport versus internal release or production with subsequent partitioning), changes in sorption, complexation, or partitioning behavior due to changes in the biogeochemical environment, or some other cause.

There was a moderate inverse correlation between DO and F-THg (r = -0.558) but not U-THg and a moderate inverse correlation with U-MeHg (r = -0.645) and a moderate to strong inverse correlation with F-MeHg (r = -0.722). Unfortunately, with the information available it cannot be ascertained whether this effect is due to (1) a real, direct influence of DO on redox potential and MeHg production or affinity for redox-sensitive complexes on particles and colloids (e.g., iron oxyhyroxide or polysulfide complexes); (2) an acausal (not cause-effect) relationship between the flux of MeHg and the flux of biochemical oxygen demand (BOD); or (3) an acausal relationship reflecting DO's co-correlations with alkalinity, pH, and organic particle concentration via its direct influence on primary production. There was a moderate inverse correlation between pH and U-MeHg (r = -0.586) (see **Figure 78**) but not U-THg and a weak to moderate inverse correlation between pH and F-THg (r = -0.503) and a strong inverse correlation between pH and F-MeHg (r = -0.804) (see **Figure 79**). This provides support for the hypothesis that the observed inverse correlations between MeHg and DO were not cause-effect.

There was a moderate inverse relationship between TDP and U-MeHg (r = -0.555) but not U-THg or U-Hg(II) and between TDP and F-THg (r = -0.588), F-MeHg (r = -0.535), and F-Hg(II) (r = -0.55). Because Hg(II) and MeHg both have high affinities for particles, if TDP-mediated primary production and biodilution were the primary cause, the inverse relationship between TDP and U-MeHg would also have been observable for U-Hg(II). That this is not the case suggests that, if TDP is exerting a cause-effect influence, it is indirect via its influences on pH, alkalinity, and/or DO. Nevertheless, due to the complexities of sometimes competing and sometimes reinforcing effects of TDP on the sulfur and mercury cycles via the carbon and oxygen cycles, only controlled experiments in microcosm and mesocosm can be determine the ultimate validity of this hypothesis.

There was a weak to moderate inverse correlation between sulfate and U-MeHg (see **Figure 80**) but not F-MeHg, suggesting co-correlation between a sulfate source and particle bound MeHg, as opposed to sulfate's influence on internal production of MeHg. However, further studies would be required to test this hypothesis.

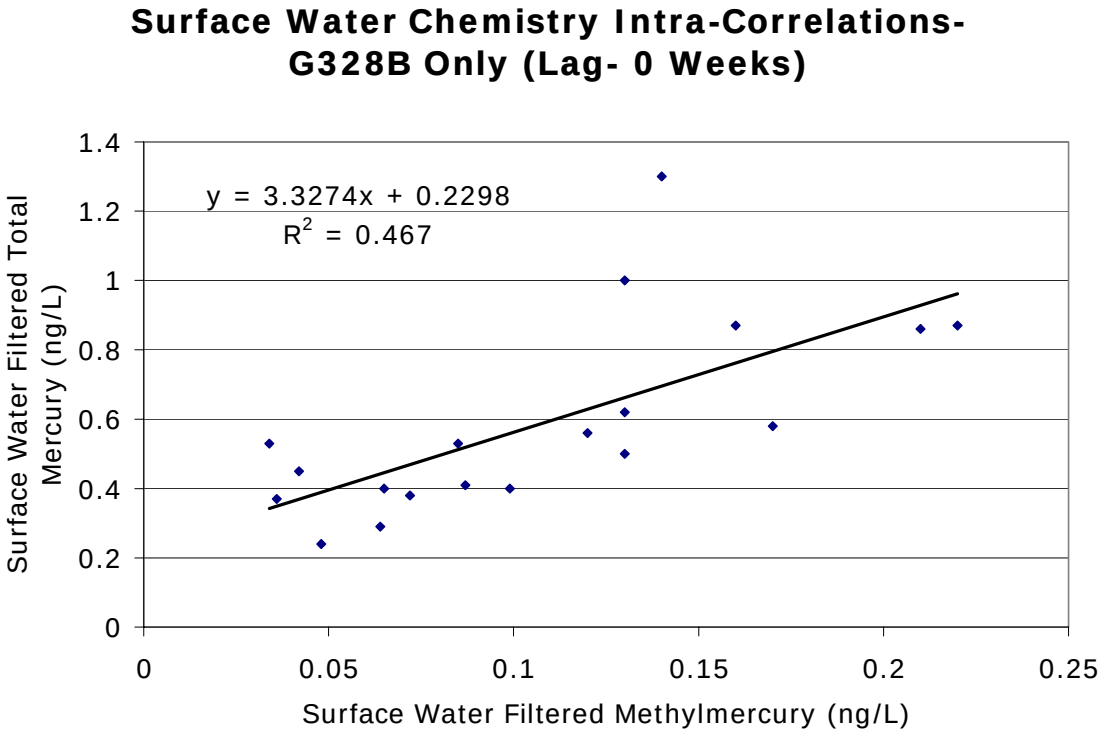

Figure 75. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus filtered total mercury (F-THg) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

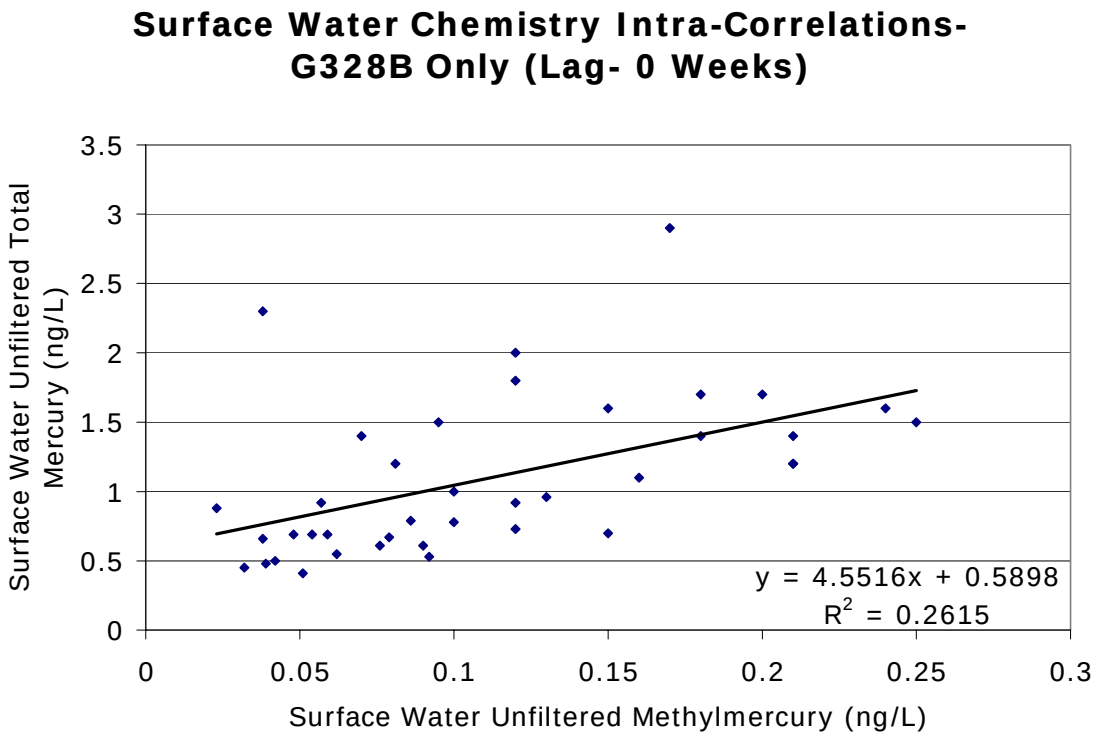

Figure 76. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus unfiltered total mercury (U-THg) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

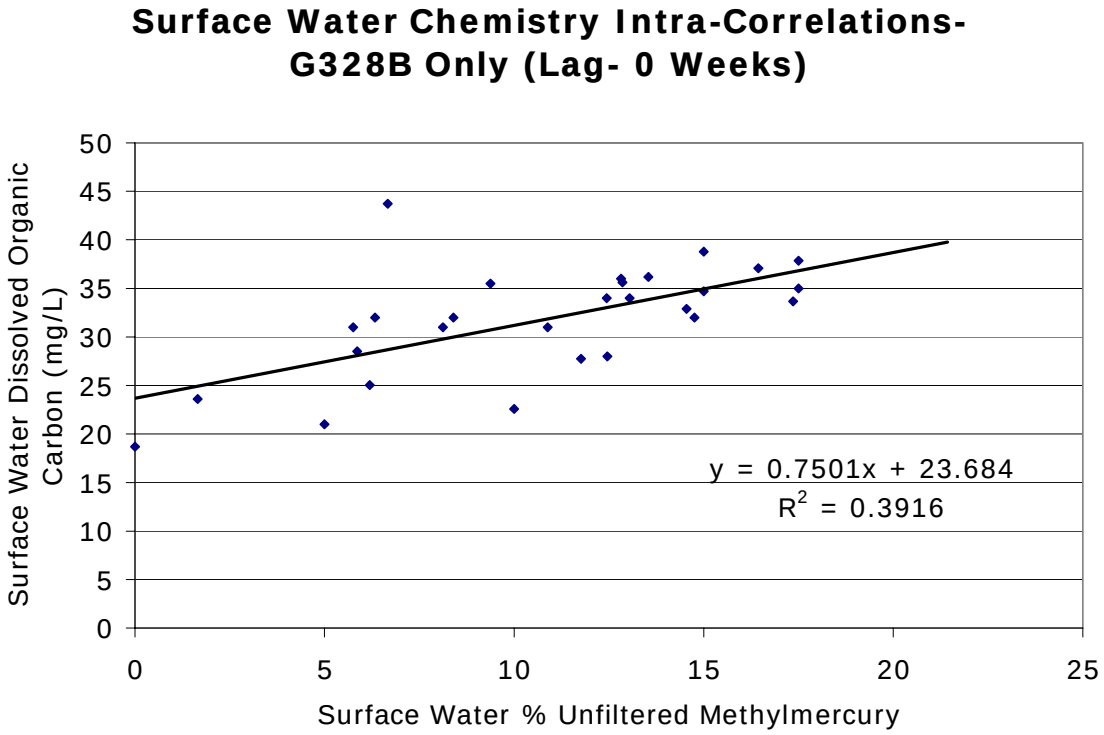

Figure 77. Scatter plot of surface water percent unfiltered methylmercury (U-%MeHg) concentration versus dissolved organic carbon (DOC) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

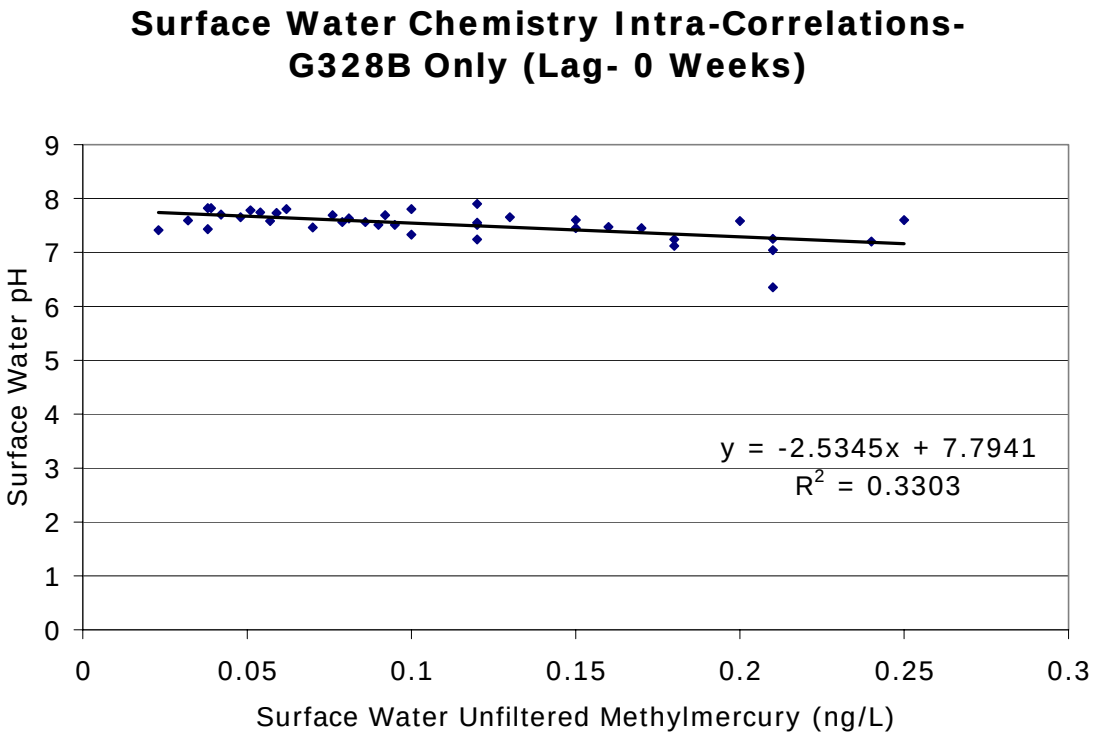

Figure 78. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus pH for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

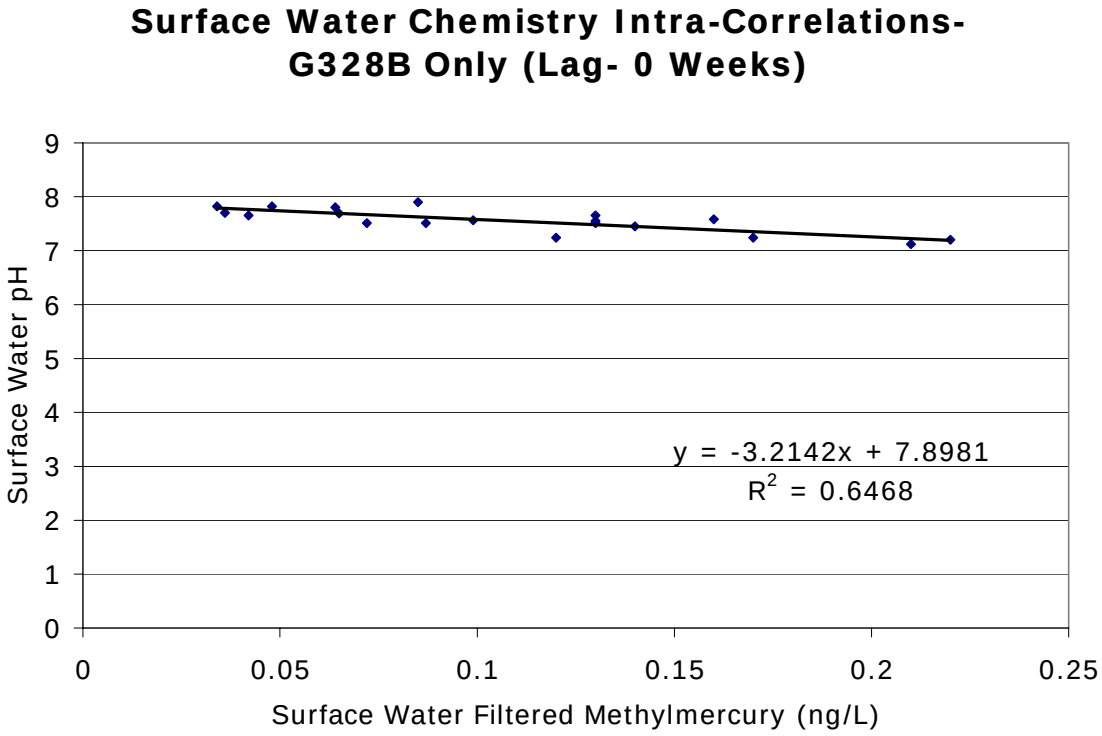

Figure 79. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus pH for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

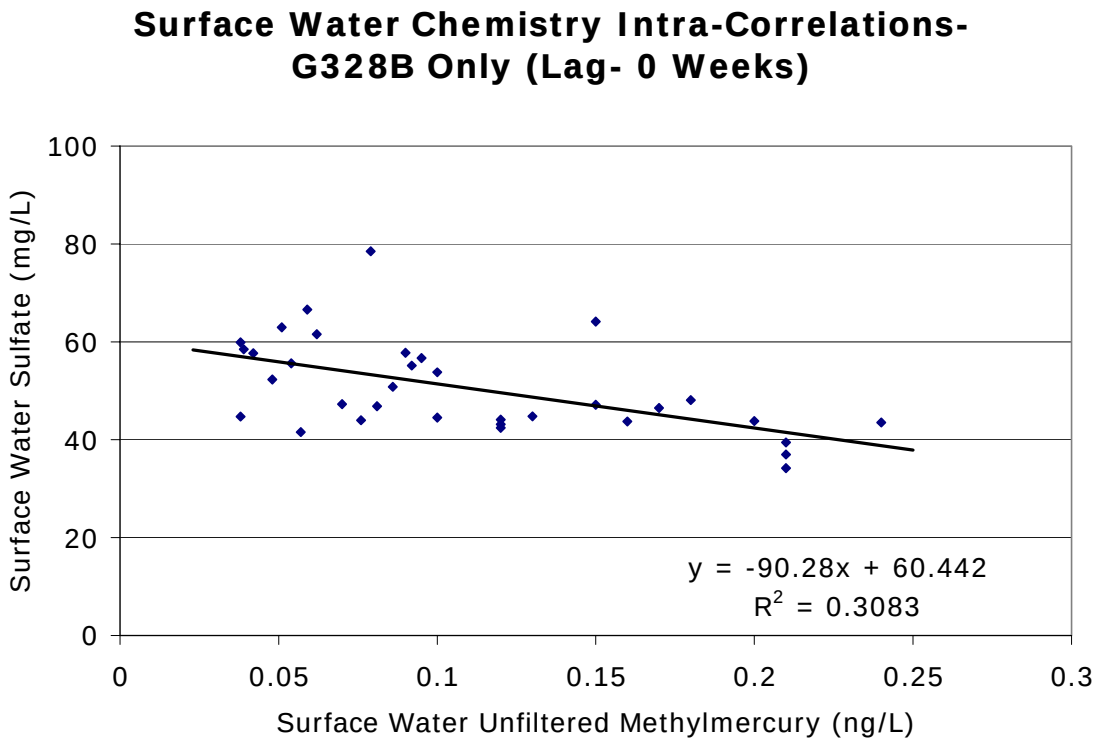

Figure 80. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus dissolved organic carbon (DOC) concentration for all for the combined STA-2 monitoring stations: common inflow, nine interior cell stations, and three cell outflow stations with Lag-0 weeks for the period from August 2002 through January 2004.

STA-2 Interior Sites Only

No Lag/No Average Correlation Analysis

There was a weak to moderate correlation between DOC and U-THg (r = 0.505) or U-MeHg (r = 0.536). DOC competes with living, dying, and dead organic biomass and settling particles for both Hg(II) and MeHg, decreasing the rate of their removal from the water column. Hardness is weakly to moderately positively correlated with the ratio of F-MeHg to U-MeHg (r = 0.512). Hardness (as Ca and Mg) may mediate the influence of DOC on Hg(II) and MeHg settling rates by decreasing the affinity of Hg(II) and MeHg for DOC via an increase in the repulsive surface charge on the DOC molecule (G. Aiken, USGS, personal communication).

As with STA-2 as a whole, the strongest, statistically significant correlations were between dissolved iron and U-THg (r = 0.884) and U-MeHg (r = 0.884) and F-THg (r = 0.672) and F-MeHg (r = 0.705). There was also a weak to moderate inverse correlation with the ratio of F-Hg(II) to U-Hg(II), but not its constituent components. This means that dissolved iron was increasing the apparently dissolved fraction relative to the sorbed, filterable fraction. This may be as a result of the ability of Fe(II), a moderately soft ion, to delay Hg(II) from accessing the weak and strong binding sites on particle surfaces kinetically, even though the binding of Hg(II) is thermochemically favored, or the ability of colloidal iron, which may include polysulfide complexes, to compete with the weak and strong binding sites on particle surfaces for Hg(II).

Dissolved total manganese (F-Mn) was moderately positively correlated with U-THg (r = 0.589), U-MeHg (r = 0.571), U-Hg(II) (r = 0.605), F-THg (r = 0.589), F-MeHg (r = 0.61) but not F-Hg(II), and exhibited a positive weak to moderate positive correlation with the ratio of F-MeHg to U-MeHg (r = 0.588) but a weak to moderate inverse correlation with the ratio of F-Hg(II) to U-Hg(II) (r = -0.548). That an increase in the surface water Mn concentration is associated with a corresponding increase in surface water Hg(II) and MeHg concentrations may reflect only passive co-transport with Hg(II) and MeHg from the surficial soil or active mediation of the speciation, lability, and mobility of the Hg(II) and MeHg species sorbed to soil solids, complexed with pore water DOC and/or iron oxyhydroxide and/or polysulfide colloids, or truly dissolved in pore water. Support for the latter possibility comes from the observation that Mn tends to be more labile and redox-responsive than Fe in a low-redox, high sulfide environment, as evidenced by the greater amplitude in the diel fluctuation of Mn relative to Fe in interior marsh surface waters from the northern Everglades (T. Bechtel, SFWMD, personal communication) and, thus, as it shuttled across the water/soil interface, Mn could have facilitated the oxidation and reduction of iron, sulfur, and iron-oxyhydroxide and iron-sulfur complex species that mediated Hg(II) bioavailability for MeHg production.

Cell 1 Interior Sites Only

No Lag/No Average Correlation Analysis

For the interior and outflow sites, there were much stronger no lag co-correlations between U-THg and U-MeHg (**Figure 81**) and F-THg and F-MeHg (**Figure 82**) than for the common inflow canal at G-328B. This probably reflects the differences in the origins and transport properties of the organic particles to which the sorbed fraction of U-THg and U-MeHg are bound (stormwater runoff in the canals versus internal primary production and resuspension of particles deriving from decaying plant biomass in the constructed wetlands) and the differences in the equilibration times in the two environments (hours to days in the canal versus days to weeks in the constructed wetlands). However, further study would be required to determine whether this is likely to have been the case. As illustrated in **Figures 83**, **84**, and **85**, the moderate to strong positive correlations between DOC, F-TFe, or F-TMn and F-MeHg that disappeared when G-328B was evaluated individually returned when the Cell 1 interior sites were evaluated individually, albeit with weak to moderate correlations. When these same constituents were paired with U-MeHg, the correlation coefficient increased somewhat for DOC (**Figure 86**) but substantially for F-TFe (**Figure 87**) or F-Mn (**Figure 88**). This provides further support for the conjecture that Mn is mediating the sorption, complexation, and/or partitioning of MeHg on, with, or into dissolved iron oxyhydroxide and/or polysulfide complexes and fluxes to/from surfical pore water rather than directly influencing net MeHg production. However, only further controlled laboratory microcosm and field mesocosm studies will provide the data necessary to evaluate the validity of this hypothesis rigorously.

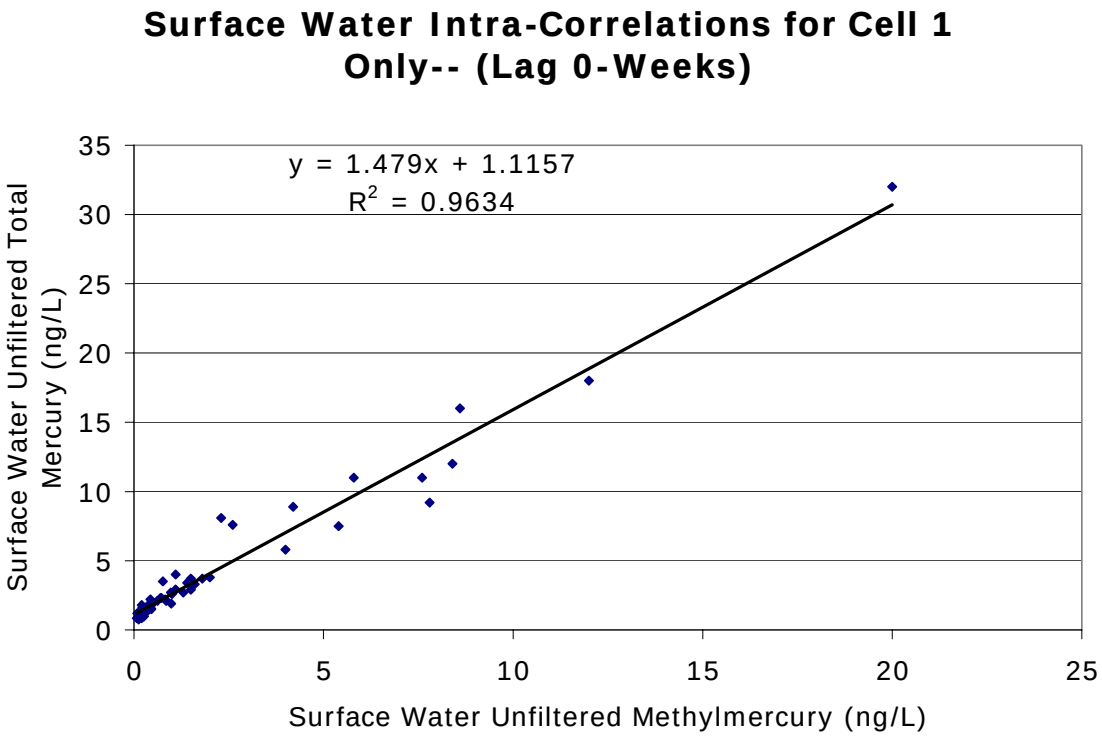

Figure 81. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus unfiltered total mercury (U-THg) concentration for all for Cell 1 stations only: three interior stations and one cell outflow station with | Lag-0 weeks for the period from August 2002 through January 2004.

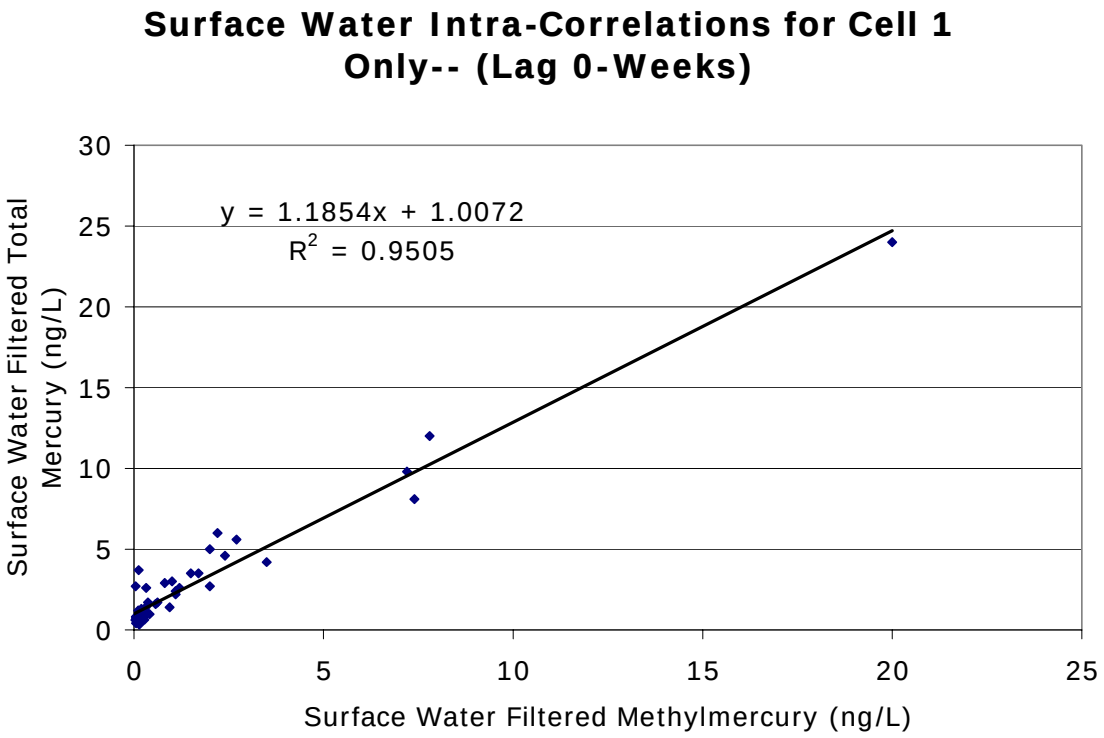

Figure 82. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus filtered total mercury (F-THg) concentration for all for Cell 1 stations only: three interior stations and one cell outflow station with Lag-0 weeks for the period from August 2002 through January 2004.

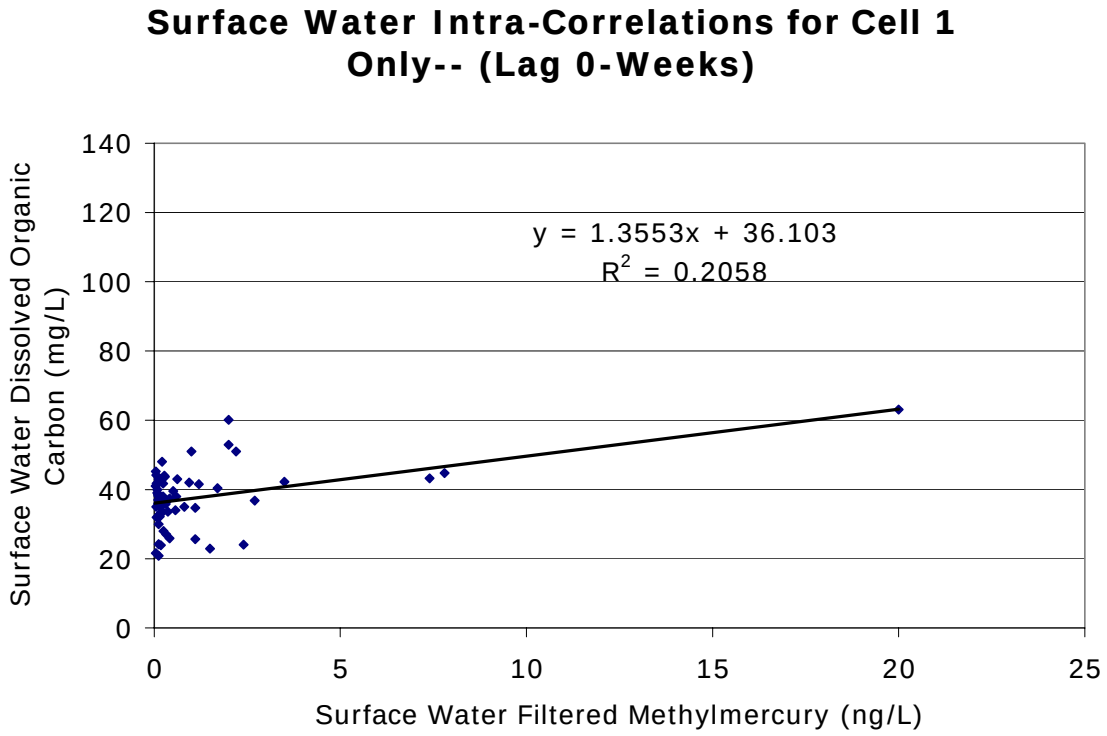

Figure 83. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus dissolved organic carbon (DOC) concentration for all for Cell 1 stations only: three interior stations and one cell outflow station with Lag-0 weeks for the period from August 2002 through January 2004.

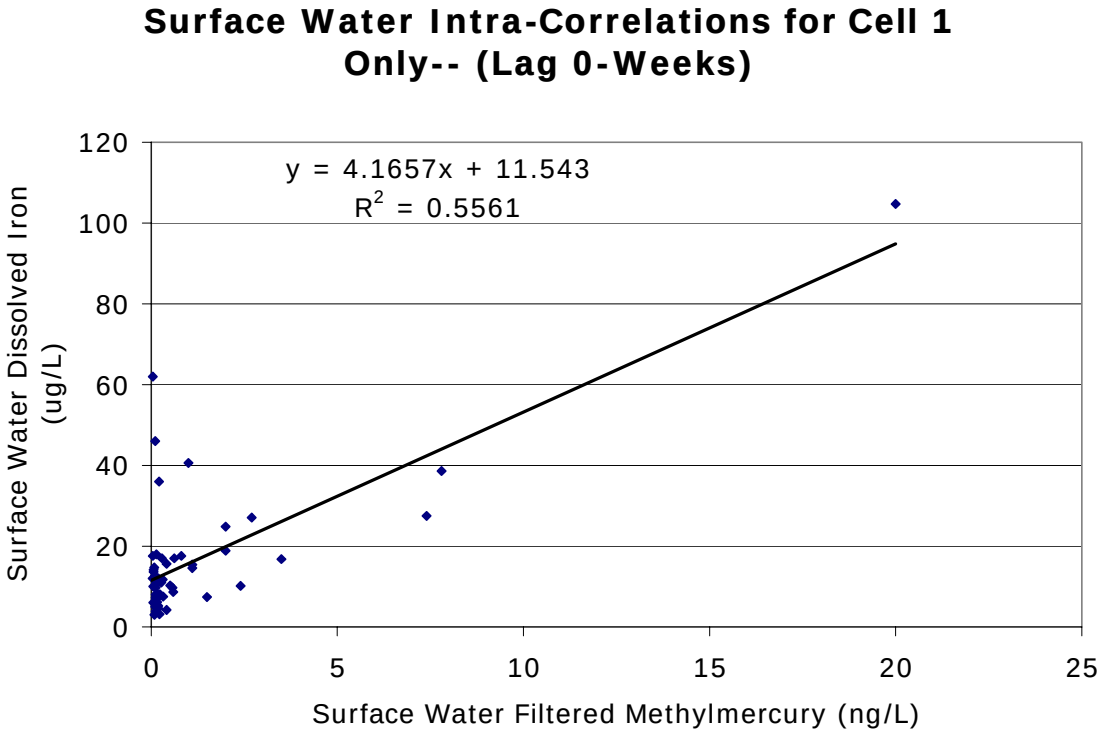

Figure 84. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus dissolved total iron (F-TFe) concentration for all for Cell 1 stations only: three interior stations and one cell outflow station with Lag-0 weeks for the period from August 2002 through January 2004.

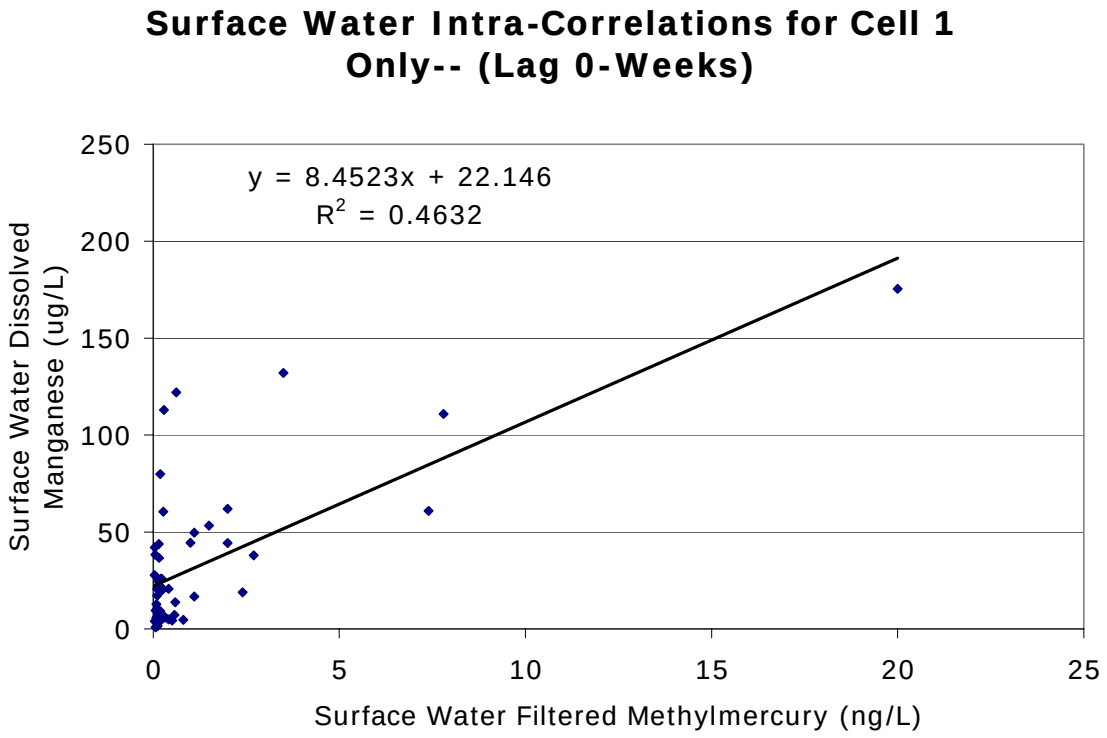

Figure 85. Scatter plot of surface water filtered methylmercury (F-MeHg) concentration versus dissolved total manganese (F-TMn) concentration for all for Cell 1 stations only: three interior stations and one cell outflow station with Lag-0 weeks for the period from August 2002 through January 2004.

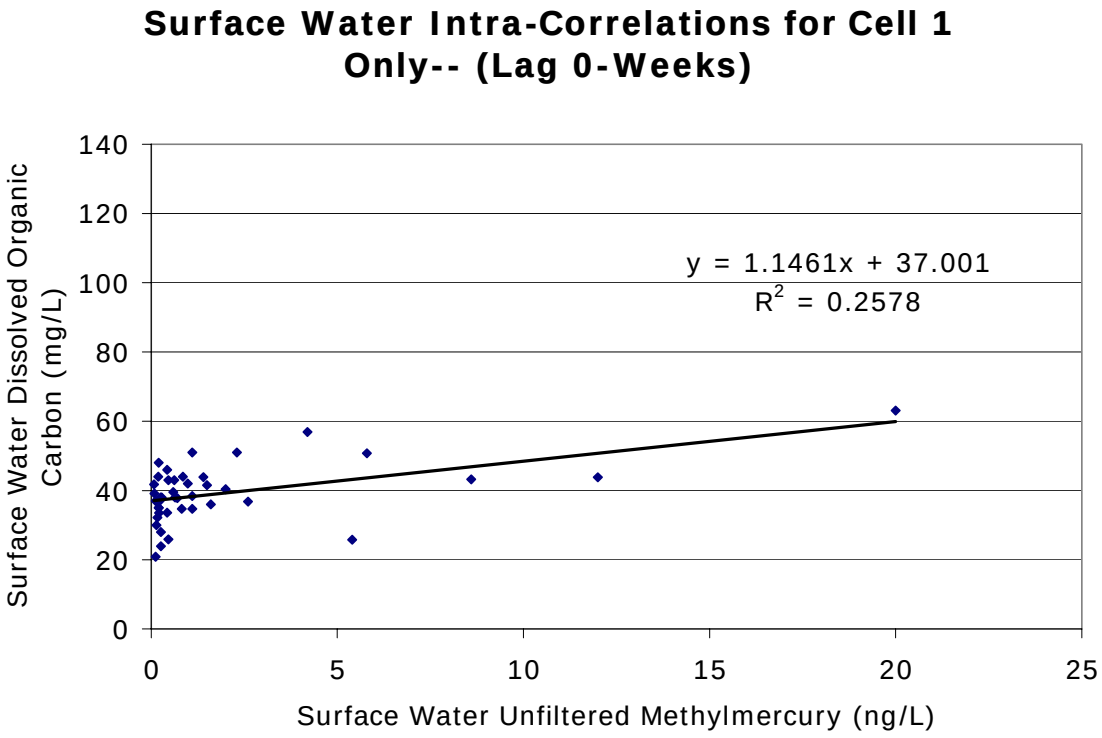

Figure 86. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus dissolved organic carbon (DOC) concentration for all for Cell 1 stations only: three interior stations and one cell outflow station with Lag-0 weeks for the period from August 2002 through January 2004.

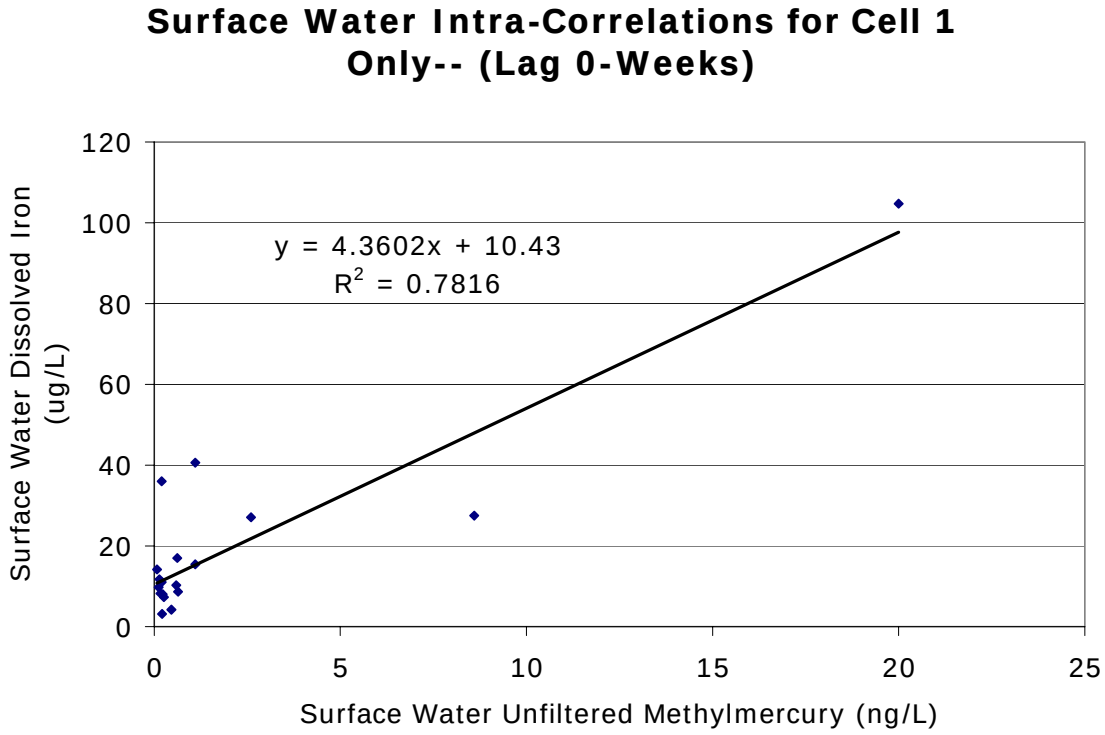

Figure 87. Scatter plot of surface water unfiltered methylmercury (U-MeHg) concentration versus dissolved total iron (F-TFe) for all for Cell 1 stations only: three interior stations and one cell outflow station with Lag-0 weeks for the period from August 2002 through January 2004.

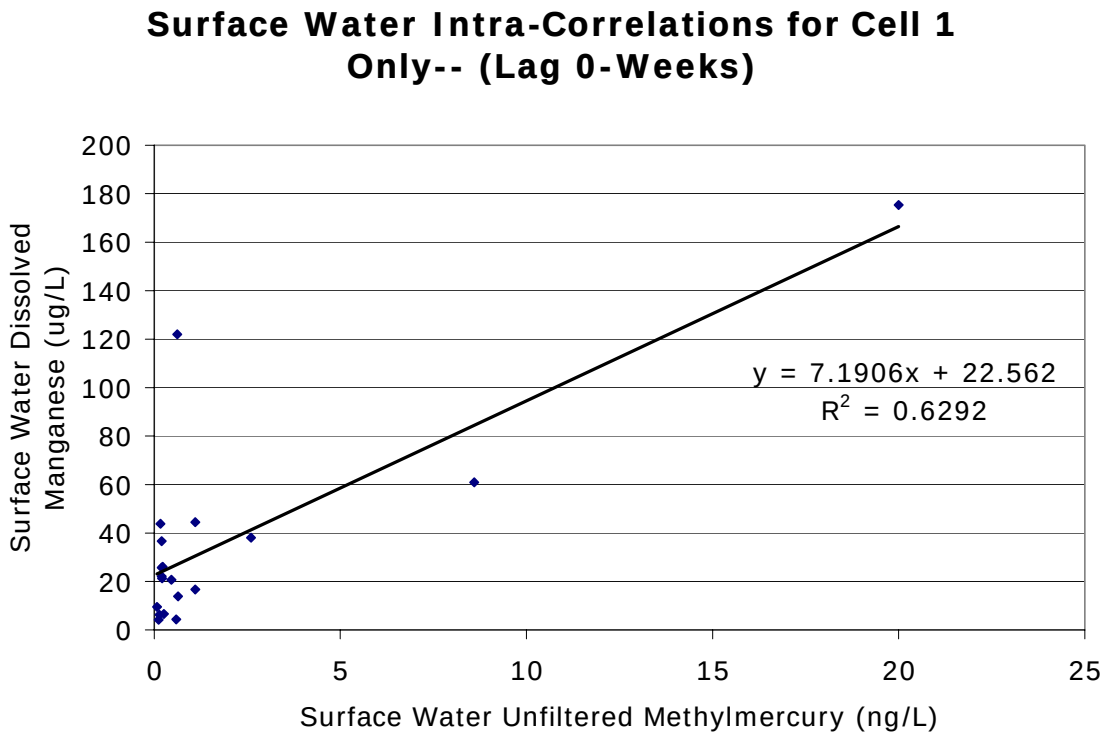

Figure 88. Scatter Plot of surface water unfiltered methylmercury (U-MeHg) concentration versus dissolved total manganese (F-TMn) concentration for all for Cell 1 stations only: three interior stations and one cell outflow station with Lag-0 weeks for the period from August 2002 through January 2004.

C1AA

No Lag/No Average Correlation Analysis

F-MeHg was moderately inversely correlated with water depth (r = -0.61). This was also the case for U-MeHg, albeit with too few samples to be considered a robust observation (n = 7). ALK is weakly to moderately inversely correlated with F-Hg(II) (r = -0.538) but not F-THg or F-MeHg and not with any of the unfiltered mercury species. Mg was weakly to moderately inversely correlated with F-Hg(II) (r = -0.5) but not F-THg or F-MeHg and not with any unfiltered mercury species. There were no statistically significant positive or inverse correlations between any mercury species and sulfate.

Lag Correlation Analyses

Lag-4 Weeks:

For filtered Hg(II), there were no strong positive correlation, while the strongest inverse correlation was with alkalinity (r = -0.65). For MeHg, there were no strong positive correlations, and the strongest inverse correlations were with carotenoids (r = -0.76). The correlations between sulfate were very to weakly inverse with Hg(II) (r = -0.207; p = 0.425) and MeHg (r = -0.357; p = 0.16).

Lag-8 Weeks:

For THg, there was a strong positive correlation with dissolved oxygen (r = 0.519), and the strongest inverse correlation was with temperature (r = -0.807). For F-MeHg, there was a strong positive correlation with dissolved oxygen (r = 0.619), and the strongest inverse correlation was with temperature (r = -0.691). The correlation between sulfate was weakly inverse with MeHg (r = -0.256; p = 0.339) and very weakly positive with Hg(II).

Lag-12 Weeks:

F-MeHg was moderately to strongly positively correlated with dissolved oxygen (r = 0.71). Hg(II) was moderately inversely correlated with pH (r = -0.552). The correlation between sulfate was very weakly inverse with MeHg (r = -0.215; p = 0.442) and weakly inverse with Hg(II) (r = -0.420; p = 0.119).

Lag-16 Weeks:

THg and Hg(II) were moderately inversely correlated with total Kjeldahl nitrogen (r = -0.534 and -0.578, respectively). There was a moderate inverse correlation between Hg(II) and alkalinity (r = -0.559). The correlation between sulfate was very weakly inverse with MeHg (r = -0.211; p = 0.468) and weakly inverse with Hg(II) (r = -0.413; p = 0.142).

Lag-20 through Lag-52 Weeks:

The sample size (n) is less than 14.

C1BB

No Lag/No Average Correlation Analysis

F-MeHg was weakly to moderately inversely correlated with water depth (r = -0.508). This was also the Case for U-MeHg, albeit with too few samples to be considered a robust observation (n = 7). Dissolved iron was weakly to moderately correlated with F-THg (r = 0.621) and F-MeHg (r = 0.711) but not F-Hg(II). TDP was weakly to moderately positively correlated with %MeHg (r = 0.555). There were very weak inverse correlations between MeHg species and sulfate.

Lag Correlation Analyses

Lag-4 Weeks:

At Site C1BB, there was a nearly statistically significant positive correlation between rain THg as Hg(II) and surface water F-THg (r = 0.585; p = 0.0589) but not Hg(II) (r = 0.0533; p = 0.834). There were very strong positive correlation between dissolved iron or total phosphorus and F-THg (r = 0.87, 0.783, respectively) but not F-MeHg or F-Hg(II). There were nonexistent to extremely weak inverse correlations between sulfate and MeHg and Hg(II).

Lag-8 Weeks:

F-MeHg and F-Hg(II) were strongly positively correlated with total dissolved phosphorus (r = 0.511 and 0.651) but not F-THg. F-MeHg and F-Hg(II) were moderately inversely correlated with alkalinity (r = -0.503, r = -0.617, respectively) and Hg(II) with calcium (r = -0.532), magnesium (r = -0.599), manganese (r = -0.586). There was an extremely weakly inverse relationship between sulfate and MeHg (r = -142; p = 0.601) and a weak inverse relationship between sulfate and Hg(II) (r = -0.359; p = 0.172).

Lag-12 Weeks:

F-THg and F-Hg(II) and ortho-phosphate (r = -0.758 and -0.677, respectively) but not MeHg. F-THg and ammonia (r = -0.74). F-MeHg and alkalinity (r = -0.541), dissolved organic carbon (r = -0.519), and specific conductivity (r = -0.549) and a nearly statistically significant inverse correlation with chloride (r = -0.496; p = -0.0603). There was a statistically significant inverse correlation between rain THg as Hg(II) and surface water F-THg (r = -0.669) and a nearly statistically significant inverse correlation with F-Hg(II) (r = -0.465; p = 0.0692). F-Hg(II) with dissolved oxygen (r = 0.596). F-Hg(II) and salinity (r = -0.591). Sulfate had weak inverse correlations (r = -0.31; p = 0.262 and r = -0.384; p = 0.158) with F-MeHg and F-Hg(II), respectively.

Lag-16 Weeks:

There was a strong positive correlation between F-MeHg and magnesium (r = 0.784). There were moderate to strong inverse correlations between F-MeHg or F-Hg(II) and ortho-phosphate (r = -0.731, r = -0.684, respectively). The correlations between F-Hg(II) and F-MeHg and sulfate were nonexistent.

Lag-20 through -52 Weeks:

The sample size (n) is less than 14.

C1CC

No Lag/No Average Correlation Analysis

There was a moderate inverse correlation between water depth at Site C1CC and F-THg (r = -0.536) and F-MeHg (r = -0.589). There was a strong positive correlation between dissolved iron and F-THg (r = 0.772) and F-MeH (r = 0.77). There is a weak positive correlation between TDP and F-THg (r = 0.489) or F-MeHg (r = 0.478), but a very strong positive correlation between TP with F-THg (r = 0.805) and F-MeHg (r = 0.802). The weak relationship with TDP may reflect simultaneous first-flush or subsequent release of dissolved P with dissolved Hg(II) and dissolved MeHg from the surficial soil, while the strong correlation with TP may reflect a co-correlation with colloidal iron.

Lag Correlation Analyses

Lag-4 Weeks:

There were no strong, statistically significant positive or inverse correlations between F-THg, F-MeHg or F-Hg(II) and any other surface water constituent. There were nonexistent to virtually nonexistent inverse correlations between sulfate and F-MeHg or F-Hg(II).

Lag-8 Weeks:

There was a moderate inverse correlation between F-Hg(II) and chlorophyll-a (r = -0.567), and a moderate to strong positive correlation with dissolved total phosphorus (r = 0.673). F-MeHg exhibited a moderate positive correlation with dissolved total phosphorus (r = 0.567). There was a statistically insignificant, virtually nonexistent inverse correlation between sulfate and F-MeHg and a weak inverse relationship with F-Hg(II) (r = -0.36; p = 0.11).

Lag-12 Weeks:

There were moderate to strong positive or inverse correlations between F-Hg(II) and dissolved oxygen (r = 0.594) or ortho-phosphate (r = -0.597). There were very weak to weak inverse correlations between sulfate and F-MeHg (r = -0.249) or F-Hg(II) (r = -0.397).

Lag-16 Weeks:

There were no statistically significant, moderate or strong positive or inverse correlations between F-THg, F-MeHg, or F-Hg(II) and any other surface water constituents. There were nonexistent to virtually nonexistent inverse correlations between sulfate and F-MeHg or F-Hg(II).

Lag-20 through -52 Weeks:

The sample size (n) is less than 14.

G-330A

No Lag/No Average Correlation Analysis

TKN was weakly to moderately inversely correlated with U-MeHg (r = -0.523), while Nitrate-N + Nitrate-N was moderately inversely correlated with %MeHg (r = -0.615). Total phosphorus was weakly to moderately positively correlated with U-THg (r = 0.527) and moderately positively correlated with U-MeHg (r = 0.568), but not Hg(II). U-THg and U-MeHg were very weakly to weakly inversely correlated with sulfate, albeit not statistically significantly.

PORE WATER X PORE WATER

This subsection summarizes the results of the analysis of the intra-correlations between pore water F-THg and F-MeHg and other pore water constituents or parameters. Due to the small sample size (n = 4), the results of the intra-correlations at the individual station level of disaggregation and the spatial average across all stations for each of the four sampling trips will not be presented.

No Lag/No Average Correlation Analysis

All Cells

The results of the parametric univariate intra-correlation analysis are summarized in **Table 36**. For F-THg, there were no moderate to strong positive correlations other than with F-MeHg (r = 0.81) and related variables. The strongest inverse correlations were with LN F-Mn (r = -0.54) and LN F-Fe. For F-MeHg in pore water, the only weak to moderate positive correlation was with surface water depth (r = 0.49), followed by a very weak to weak positive correlation with pH (r= 0.36), while the strongest inverse correlations were with LN Ca (r = -0.55), LN F-Mn (r = -0.53), and LN KPHg(II) (r =-0.42). These correlations weaken slightly with LN F-MeHg. The positive correlation between pore water F-MeHg with surface water depth may reflect the positive relationship between surface water depth and pore water negative redox potential, and between negative redox potential and MeHg production by sulfate-reducing bacteria under negative redox conditions. However, the correlation between pore water F-MeHg and redox potential was extremely weakly positive (r = 0.17) and LN redox was extremely weakly negative (r = -0.10), as was the inverse correlation with sulfate (r = -0.14). Thus, the positive relationship between water depth and the concentration of pore water MeHg may reflect the reduction in the influence of shallow water on surficial sediment turbation and the associated increased flux and depletion of pore water F-MeHg via advection, dispersion, and diffusion. However, F-THg exhibits an even weaker positive correlation with LN water depth (r = 0.35). Perhaps more disconcerting, there was no relationship between pore water sulfide and pore water MeHg (r = 0.00).

All of these interpretations must be caveated with the recognition that in Cell 1 there is gross seepage into the surficial sediment from the L-7 levee and simultaneous seepage out into Cell 2 and from Cell 2 into Cell 3 and from Cell 3 into the seepage collection canal on the west side of Cell 3 operated by the adjacent canal with the potential for recirculation to the headworks and redischarge into the inflow distribution canal. These differences in flux magnitude and chemistries could result in substantial and significant pore water concentration dynamics driven by vertical pore water concentration gradients undetectable by the use of the sipper method of surficial pore water collection, which integrates the pore water chemistry to a depth of at least 0 to 4 cm. Interestingly, pore water DOC and F-Ca or F-Mg are strongly positively correlated

(r =0.71 or r = 0.57), while the corresponding correlations with LN-transformed DOC increased moderately. LN F-Fe(III) and LN F-MN were more strongly positively intra-correlated (r = 0.72) than LN Fe(II) (r = 0.63). Pore water F-TMn was weakly to moderately intra-correlated with F-Ca (r = 0.80) or F-Mg (r = 0.50), suggesting that the ability to weaken the affinity of dissolved or particulate organic matter of these species for organic matter sorption of divalent ions, including F-TMn, was substantial and of biogeochemical significance. Several of the most interesting of these intra-correlations or absence thereof are plotted in **Figures 89** through **93** for F-Hg(II) versus F-MeHg, S2-/(S^{2-} + SO_4^{2-}) versus F-MeHg, SO_4^{2-} versus F-MeHg, F-TMn versus F-TFe, and F-MeHg versus change in pore water sulfide between event t and t-1, respectively. Perhaps the most interesting is the absence of a strong correlation between F-MeHg and Lag-0 weeks sulfide, mole fraction sulfide, or change in sulfide, and the parabolic relationship between F-Fe and F-Mn. Whether this is caused by a change from Mn(II) to Mn(III) or vice versa cannot be determined with the data collected, because, unlike Fe, only TMn was determined analytically. The speciation of Mn and Fe in pore water together should be a priority for follow-up pore water chemistry studies. This is underscored by the apparent parabolic relationship depicted in Figure 92 between TMn and TFe in pore water, which could reflect the effect of changing Mn and Fe redox states on Fe and Mn speciation, complexation, precipitation, lability, and mobility.

Regarding the results of the nonparametric (Spearman) linear univariate correlation analysis, for pore water F-THg, the strongest, statistically significant, positive nonparametric correlation was with sulfide ($r = 0.36$; $p < 0.01$). There were no strong, statistically significant positive correlation between pore water F-MeHg and any other pore water constituent. However, Hg(II) was omitted by the contractor (Janicki Environmental Inc., under contract to BFA) for this intra-correlation analysis, so it is not possible to determine the apparent influence of pore water Hg(II) on the production of MeHg from Hg(II). The strongest, statistically significant inverse correlations for F-THg were with F-TFe ($r = -0.36$; $p < 0.05$) and F-TMn ($r = -0.36$; $p < 0.05$), while that for F-MeHg was with calcium ($r = -0.40$; $p < 0.05$). Since Mn speciation as a function of redox potential was not accessible to this study design, the positive correlation between surface water F-TMn and surface water F-THg documented above and the inverse correlation between pore water F-TMn and pore water F-THg documented here may not be inconsistent. The apparent inconsistent linear influences of Mn on THg may be explained, in part, by the apparent parabolic relationship between pore water F-TMn and pore water F-TFe (**Figure 92**).

Table 36. Pearson correlation coefficients for pore water chemistry parametric intra-correlation exploratory data analysis.

	DEPTH	LN	THg	LN	MeHg	LN	%MeHg	LN	CA	LN	TMG	LN
Depth	1.00	0.94	0.21	0.05	0.49	0.26	0.26	0.11	-0.17	-0.22	-0.03	-0.04
LN Depth	0.94	1.00	0.35	0.22	0.44	0.36	0.31	0.20	-0.19	-0.25	0.05	0.04
F-THg	0.43	0.35	1.00	0.92	0.81	0.77	0.47	0.38	-0.36	-0.43	0.02	0.05
LN THg	0.29	0.22	0.92	1.00	0.70	0.77	0.43	0.34	-0.21	-0.24	0.11	0.15
F-MeHg	0.58	0.44	0.81	0.70	1.00	0.88	0.86	0.73	-0.46	-0.55	-0.12	-0.10
LN F-MeHg	0.44	0.36	0.77	0.77	0.88	1.00	0.85	0.86	-0.43	-0.50	-0.13	-0.12
%MeHg	0.38	0.31	0.47	0.43	0.86	0.85	1.00	0.91	-0.33	-0.38	-0.07	-0.08
LN % MeHg	0.21	0.20	0.38	0.34	0.73	0.86	0.91	1.00	-0.34	-0.39	-0.14	-0.15
F-CA	-0.31	-0.19	-0.36	-0.21	-0.46	-0.43	-0.33	-0.34	1.00	0.99	0.77	0.75
LN F-CA	-0.38	-0.25	-0.43	-0.24	-0.55	-0.50	-0.38	-0.39	0.99	1.00	0.74	0.72
F-MG	0.00	0.05	0.02	0.11	-0.12	-0.13	-0.07	-0.14	0.77	0.74	1.00	1.00
LN F-MG	0.00	0.04	0.05	0.15	-0.10	-0.12	-0.08	-0.15	0.75	0.72	1.00	1.00
DOC	-0.24	-0.13	-0.01	0.09	-0.29	-0.19	-0.28	-0.28	0.71	0.69	0.57	0.55
LN DOC	-0.32	-0.20	-0.06	0.08	-0.35	-0.24	-0.32	-0.31	0.78	0.77	0.65	0.63
CL	-0.21	-0.17	-0.07	-0.09	-0.04	0.02	0.09	0.16	0.22	0.19	0.34	0.32
LN CL	-0.21	-0.18	-0.05	-0.07	-0.03	0.03	0.09	0.16	0.19	0.16	0.31	0.28
F-FE	-0.09	0.00	-0.23	-0.18	-0.25	-0.32	-0.30	-0.35	0.60	0.54	0.27	0.23
LN F-FE	-0.42	-0.29	-0.42	-0.34	-0.43	-0.39	-0.36	-0.32	0.65	0.64	0.19	0.16
F-Fe(II)	0.09	0.14	-0.16	-0.09	-0.22	-0.28	-0.28	-0.36	0.49	0.45	0.16	0.12
LN F-Fe(II)	-0.09	-0.02	-0.13	-0.03	-0.22	-0.16	-0.26	-0.27	0.46	0.44	0.08	0.05
F-Fe(III)	0.25	0.27	-0.08	0.02	-0.32	-0.30	-0.39	-0.41	0.64	0.60	0.41	0.38
LN F-Fe(III)	0.11	0.15	-0.14	0.00	-0.17	-0.12	-0.15	-0.19	0.64	0.62	0.41	0.39
F-MN	-0.28	-0.15	-0.34	-0.24	-0.34	-0.28	-0.26	-0.19	0.80	0.77	0.50	0.48
LN F-MN	-0.43	-0.31	-0.54	-0.44	-0.53	-0.45	-0.39	-0.27	0.72	0.74	0.35	0.33
REDOX	-0.11	-0.13	-0.07	-0.17	0.17	0.19	0.23	0.37	-0.03	-0.07	-0.25	-0.27
LN REDOX	-0.09	-0.05	-0.13	-0.14	-0.10	-0.16	-0.11	-0.10	0.30	0.28	0.09	0.09
[H+]	-0.11	-0.07	-0.14	0.01	-0.28	-0.34	-0.32	-0.47	0.62	0.62	0.57	0.58
pH	0.18	0.15	0.20	0.03	0.36	0.36	0.35	0.46	-0.58	-0.62	-0.55	-0.58
F-SULFATE	-0.22	-0.11	-0.02	-0.06	-0.14	-0.23	-0.20	-0.17	-0.21	-0.17	-0.25	-0.22
LN F-SULFATE	-0.16	-0.10	0.06	0.00	-0.03	-0.11	-0.10	-0.08	-0.44	-0.39	-0.39	-0.37
SULFIDE	0.38	0.33	0.18	0.26	0.00	0.11	-0.04	-0.14	-0.14	-0.11	0.18	0.19
LN SULFIDE	0.34	0.27	0.22	0.33	0.09	0.25	0.10	-0.01	0.00	0.02	0.14	0.14
S=/(SO4+S=)	0.37	0.30	0.07	0.17	-0.02	0.08	-0.01	-0.12	0.16	0.16	0.37	0.37
LN X	0.31	0.24	0.15	0.26	0.09	0.25	0.12	0.02	0.25	0.24	0.29	0.28
KP Hg(II)	-0.43	-0.30	-0.67	-0.76	-0.42	-0.45	-0.14	0.00	0.09	0.11	-0.11	-0.14
LN KP Hg(II)	-0.51	-0.37	-0.77	-0.80	-0.48	-0.47	-0.16	-0.02	0.22	0.26	-0.12	-0.15
KP MeHg	-0.24	-0.12	-0.54	-0.66	-0.42	-0.63	-0.39	-0.40	0.11	0.13	-0.10	-0.10
LN KP MeHg	-0.60	-0.42	-0.80	-0.79	-0.79	-0.81	-0.65	-0.56	0.33	0.39	-0.06	-0.08

Table 36. Continued.

	DOC	LN	CL	LN	TFE	LN	FE(II)	LN	FE(III)	LN	TMN	LN	REDOX	LN
Depth	-0.16	-0.23	-0.20	-0.21	0.01	-0.27	0.14	-0.02	0.25	0.11	-0.11	-0.17	-0.08	-0.04
LN Depth	-0.13	-0.20	-0.17	-0.18	0.00	-0.29	0.14	-0.02	0.27	0.15	-0.15	-0.31	-0.13	-0.05
F-THg	-0.01	-0.06	-0.07	-0.05	-0.23	-0.42	-0.16	-0.13	-0.08	-0.14	-0.34	-0.54	-0.07	-0.13
LN THg	0.09	0.08	-0.09	-0.07	-0.18	-0.34	-0.09	-0.03	0.02	0.00	-0.24	-0.44	-0.17	-0.14
F-MeHg	-0.29	-0.35	-0.04	-0.03	-0.25	-0.43	-0.22	-0.22	-0.32	-0.17	-0.34	-0.53	0.17	-0.10
LN F-MeHg	-0.19	-0.24	0.02	0.03	-0.32	-0.39	-0.28	-0.16	-0.30	-0.12	-0.28	-0.45	0.19	-0.16
%MeHg	-0.28	-0.32	0.09	0.09	-0.30	-0.36	-0.28	-0.26	-0.39	-0.15	-0.26	-0.39	0.23	-0.11
LN % MeHg	-0.28	-0.31	0.16	0.16	-0.35	-0.32	-0.36	-0.27	-0.41	-0.19	-0.19	-0.27	0.37	-0.10
F-CA	0.71	0.78	0.22	0.19	0.60	0.65	0.49	0.46	0.64	0.64	0.80	0.72	-0.03	0.30
LN F-CA	0.69	0.77	0.19	0.16	0.54	0.64	0.45	0.44	0.60	0.62	0.77	0.74	-0.07	0.28
F-MG	0.57	0.65	0.34	0.31	0.27	0.19	0.16	0.08	0.41	0.41	0.50	0.35	-0.25	0.09
LN F-MG	0.55	0.63	0.32	0.28	0.23	0.16	0.12	0.05	0.38	0.39	0.48	0.33	-0.27	0.09
DOC	1.00	0.98	0.30	0.28	0.41	0.35	0.28	0.16	0.40	0.25	0.52	0.43	-0.10	0.18
LN DOC	0.98	1.00	0.30	0.28	0.40	0.39	0.27	0.19	0.41	0.29	0.58	0.50	-0.13	0.19
CL	0.30	0.30	1.00	1.00	-0.09	-0.07	-0.08	-0.17	-0.18	-0.15	0.03	0.10	0.05	-0.25
LN CL	0.28	0.28	1.00	1.00	-0.10	-0.08	-0.08	-0.17	-0.19	-0.17	0.00	0.07	0.06	-0.27
F-FE	0.41	0.40	-0.09	-0.10	1.00	0.84	0.97	0.81	0.98	0.89	0.62	0.51	0.01	0.37
LN F-FE	0.35	0.39	-0.07	-0.08	0.84	1.00	0.88	0.98	0.79	0.94	0.73	0.71	0.24	0.41
F-Fe(II)	0.28	0.27	-0.08	-0.08	0.97	0.88	1.00	0.86	0.90	0.88	0.52	0.48	0.00	0.24
LN F-Fe(II)	0.16	0.19	-0.17	-0.17	0.81	0.98	0.86	1.00	0.72	0.89	0.63	0.63	0.26	0.36
F-Fe(III)	0.40	0.41	-0.18	-0.19	0.98	0.79	0.90	0.72	1.00	0.87	0.65	0.57	-0.17	0.39
LN F-Fe(III)	0.25	0.29	-0.15	-0.17	0.89	0.94	0.88	0.89	0.87	1.00	0.72	0.70	-0.02	0.32
F-MN	0.52	0.58	0.03	0.00	0.62	0.73	0.52	0.63	0.65	0.72	1.00	0.89	0.33	0.53
LN F-MN	0.43	0.50	0.10	0.07	0.51	0.71	0.48	0.63	0.57	0.70	0.89	1.00	0.23	0.39
REDOX	-0.10	-0.13	0.05	0.06	0.01	0.24	0.00	0.26	-0.17	-0.02	0.33	0.23	1.00	0.74
LN REDOX	0.18	0.19	-0.25	-0.27	0.37	0.41	0.24	0.36	0.39	0.32	0.53	0.39	0.74	1.00
[H+]	0.48	0.55	-0.01	-0.02	0.52	0.39	0.40	0.32	0.70	0.48	0.49	0.47	-0.43	0.29
pH	-0.44	-0.53	-0.03	-0.02	-0.25	-0.24	-0.14	-0.16	-0.39	-0.26	-0.42	-0.47	0.39	-0.18
F-SULFATE	-0.16	-0.15	0.03	0.05	-0.31	-0.17	-0.34	-0.29	-0.49	-0.58	-0.27	-0.06	0.23	0.04
.N F-SULFATI	-0.24	-0.26	0.15	0.18	-0.42	-0.35	-0.40	-0.40	-0.55	-0.68	-0.51	-0.26	0.19	-0.07
SULFIDE	-0.01	0.01	-0.12	-0.13	-0.27	-0.41	-0.25	-0.32	-0.22	-0.28	-0.34	-0.47	-0.45	-0.25
LN SULFIDE	0.12	0.14	-0.05	-0.06	-0.20	-0.29	-0.12	-0.11	-0.02	-0.02	-0.20	-0.27	-0.45	-0.28
;=/(SO4+S=	0.18	0.20	-0.07	-0.08	-0.03	-0.19	-0.01	-0.06	0.36	0.39	-0.01	-0.23	-0.38	-0.15
LN X	0.27	0.28	-0.07	-0.09	0.11	0.00	0.16	0.17	0.34	0.40	0.10	-0.05	-0.41	-0.21
KP Hg(II)	-0.09	-0.08	0.32	0.30	0.02	0.18	-0.08	-0.15	-0.28	-0.25	0.11	0.29	0.30	0.10
LN KP Hg(II)	0.01	0.03	0.27	0.26	0.15	0.38	0.03	0.02	-0.23	-0.15	0.28	0.48	0.31	0.15
KP MeHg	-0.09	-0.09	-0.06	-0.05	0.18	0.15	0.09	-0.09	0.03	-0.12	0.05	0.20	-0.01	0.02
LN KP MeHg	0.12	0.16	-0.07	-0.08	0.33	0.48	0.26	0.17	0.18	0.04	0.27	0.51	-0.02	0.15

Table 36. Continued.

	[H+]		SULFATE	LN	SULFIDE	LN	X	LN X	KP Hg(II)	LN	KP MeHg	LN
Depth	-0.04	0.11	-0.16	-0.13	0.30	0.31	0.30	0.30	-0.30	-0.34	-0.05	-0.34
LN Depth	-0.07	0.15	-0.11	-0.10	0.33	0.27	0.30	0.24	-0.30	-0.37	-0.12	-0.42
F-THg	-0.14	0.20	-0.02	0.06	0.18	0.22	0.07	0.15	-0.67	-0.77	-0.54	-0.80
LN THg	0.01	0.03	-0.06	0.00	0.26	0.33	0.17	0.26	-0.76	-0.80	-0.66	-0.79
F-MeHg	-0.28	0.36	-0.14	-0.03	0.00	0.09	-0.02	0.09	-0.42	-0.48	-0.42	-0.79
LN F-MeHg	-0.34	0.36	-0.23	-0.11	0.11	0.25	0.08	0.25	-0.45	-0.47	-0.63	-0.81
%MeHg	-0.32	0.35	-0.20	-0.10	-0.04	0.10	-0.01	0.12	-0.14	-0.16	-0.39	-0.65
LN % MeHg	-0.47	0.46	-0.17	-0.08	-0.14	-0.01	-0.12	0.02	0.00	-0.02	-0.40	-0.56
F-CA	0.62	-0.58	-0.21	-0.44	-0.14	0.00	0.16	0.25	0.09	0.22	0.11	0.33
LN F-CA	0.62	-0.62	-0.17	-0.39	-0.11	0.02	0.16	0.24	0.11	0.26	0.13	0.39
F-MG	0.57	-0.55	-0.25	-0.39	0.18	0.14	0.37	0.29	-0.11	-0.12	-0.10	-0.06
LN F-MG	0.58	-0.58	-0.22	-0.37	0.19	0.14	0.37	0.28	-0.14	-0.15	-0.10	-0.08
DOC	0.48	-0.44	-0.16	-0.24	-0.01	0.12	0.18	0.27	-0.09	0.01	-0.09	0.12
LN DOC	0.55	-0.53	-0.15	-0.26	0.01	0.14	0.20	0.28	-0.08	0.03	-0.09	0.16
CL	-0.01	-0.03	0.03	0.15	-0.12	-0.05	-0.07	-0.07	0.32	0.27	-0.06	-0.07
LN CL	-0.02	-0.02	0.05	0.18	-0.13	-0.06	-0.08	-0.09	0.30	0.26	-0.05	-0.08
F-FE	0.52	-0.25	-0.31	-0.42	-0.27	-0.20	-0.03	0.11	0.02	0.15	0.18	0.33
LN F-FE	0.39	-0.24	-0.17	-0.35	-0.41	-0.29	-0.19	0.00	0.18	0.38	0.15	0.48
F-Fe(II)	0.40	-0.14	-0.34	-0.40	-0.25	-0.12	-0.01	0.16	-0.08	0.03	0.09	0.26
LN F-Fe(II)	0.32	-0.16	-0.29	-0.40	-0.32	-0.11	-0.06	0.17	-0.15	0.02	-0.09	0.17
F-Fe(III)	0.70	-0.39	-0.49	-0.55	-0.22	-0.02	0.36	0.34	-0.28	-0.23	0.03	0.18
LN F-Fe(III)	0.48	-0.26	-0.58	-0.68	-0.28	-0.02	0.39	0.40	-0.25	-0.15	-0.12	0.04
F-MN	0.49	-0.42	-0.27	-0.51	-0.34	-0.20	-0.01	0.10	0.11	0.28	0.05	0.27
LN F-MN	0.47	-0.47	-0.06	-0.26	-0.47	-0.27	-0.23	-0.05	0.29	0.48	0.20	0.51
REDOX	-0.43	0.39	0.23	0.19	-0.45	-0.45	-0.38	-0.41	0.30	0.31	-0.01	-0.02
LN REDOX	0.29	-0.18	0.04	-0.07	-0.25	-0.28	-0.15	-0.21	0.10	0.15	0.02	0.15
[H+]	1.00	-0.91	-0.09	-0.13	0.16	0.23	0.30	0.33	-0.26	-0.13	0.01	0.20
pH	-0.91	1.00	-0.02	0.07	-0.22	-0.31	-0.29	-0.32	0.22	0.07	-0.01	-0.21
F-SULFATE	-0.09	-0.02	1.00	0.92	-0.37	-0.41	-0.66	-0.69	0.34	0.30	0.55	0.45
LN F-SULFAT	-0.13	0.07	0.92	1.00	-0.26	-0.29	-0.60	-0.62	0.28	0.21	0.40	0.31
SULFIDE	0.16	-0.22	-0.37	-0.26	1.00	0.78	0.90	0.64	-0.48	-0.55	-0.44	-0.43
LN SULFIDE	0.23	-0.31	-0.41	-0.29	0.78	1.00	0.78	0.92	-0.64	-0.57	-0.60	-0.49
=/(SO4+S	0.30	-0.29	-0.66	-0.60	0.90	0.78	1.00	0.79	-0.49	-0.49	-0.49	-0.46
LN X	0.33	-0.32	-0.69	-0.62	0.64	0.92	0.79	1.00	-0.64	-0.52	-0.64	-0.49
KP Hg(II)	-0.26	0.22	0.34	0.28	-0.48	-0.64	-0.49	-0.64	1.00	0.93	0.69	0.67
LN KP Hg(II	-0.13	0.07	0.30	0.21	-0.55	-0.57	-0.49	-0.52	0.93	1.00	0.63	0.74
KP MeHg	0.01	-0.01	0.55	0.40	-0.44	-0.60	-0.49	-0.64	0.69	0.63	1.00	0.76
LN KP MeHg	0.20	-0.21	0.45	0.31	-0.43	-0.49	-0.46	-0.49	0.67	0.74	0.76	1.00

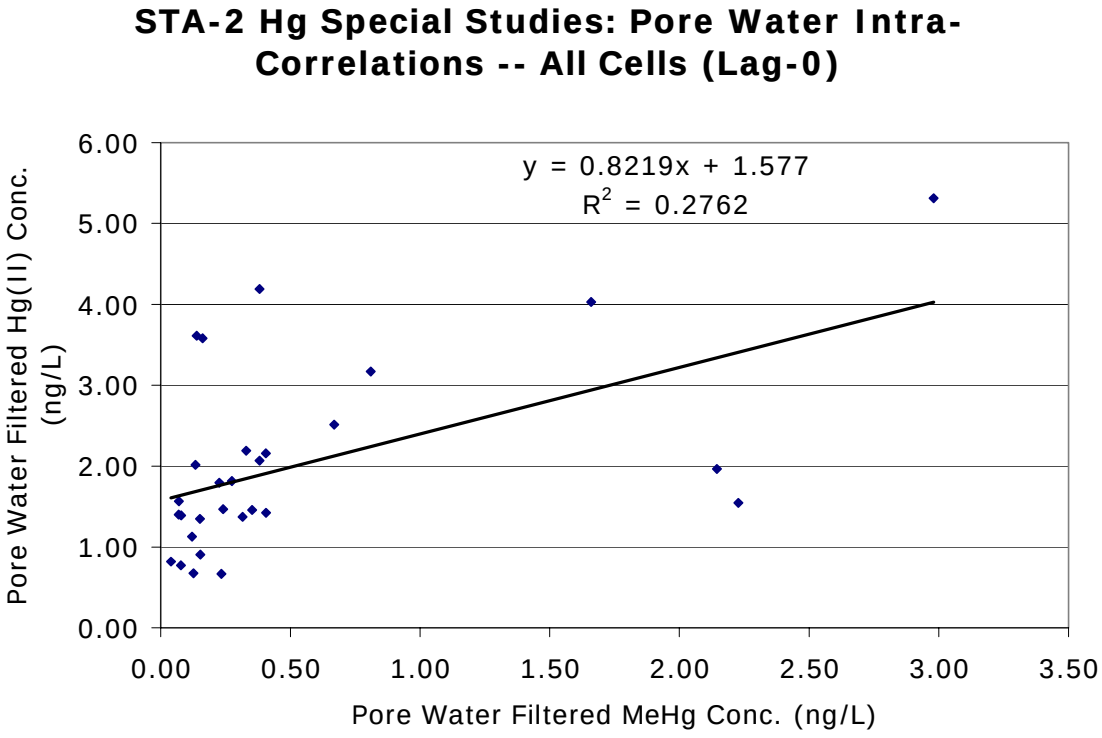

Figure 89. Scatter plot of pore water filtered methylmercury (F-MeHg) concentration versus filtered inorganic mercury (F-Hg(II)) concentration for nine interior stations with Lag-0 weeks for the period from August 2002 through January 2004.

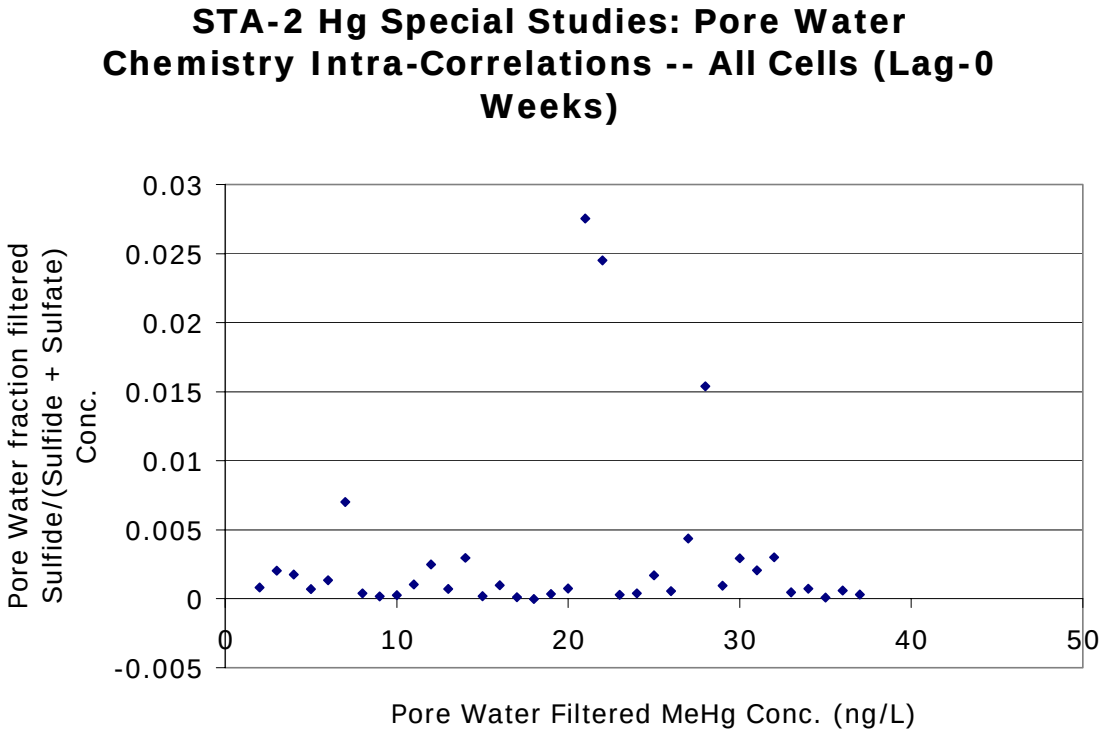

Figure 90. Scatter plot of pore water filtered methylmercury (F-MeHg) concentration versus the molar ratio of sulfide to the sum of sulfate plus sulfide for nine interior stations with Lag-0 weeks for the period from August 2002 through January 2004.

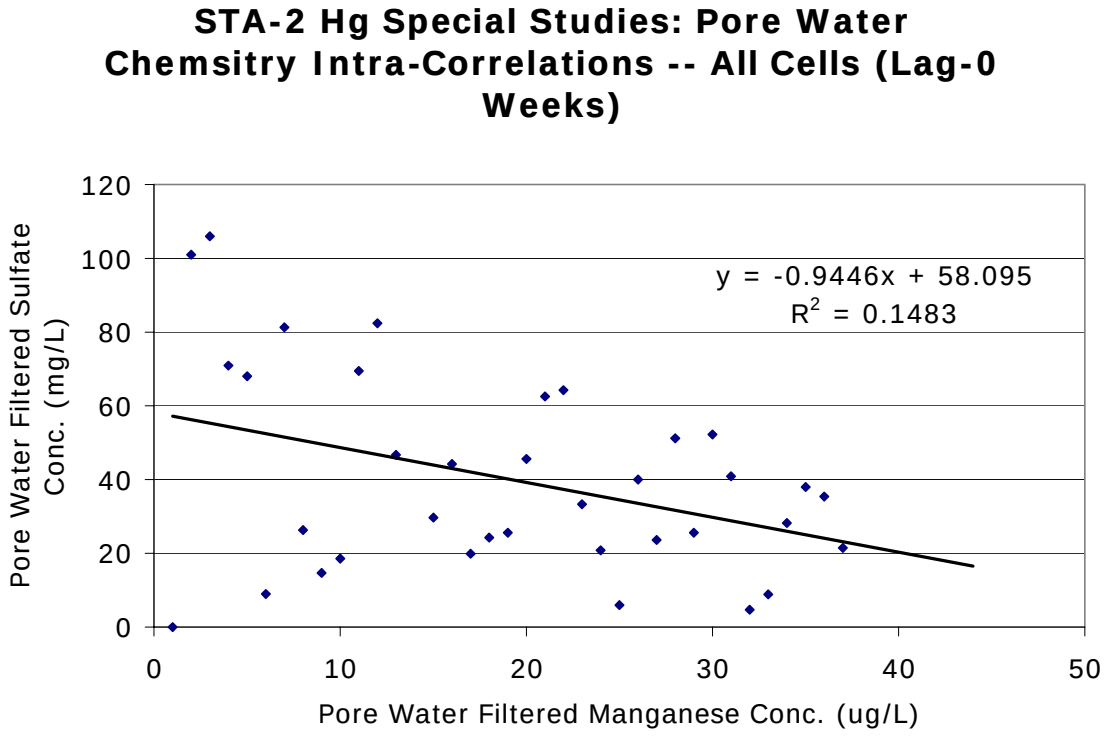

Figure 91. Scatter plot of pore water filtered manganese (F-Mn) concentration versus sulfate concentration for nine interior stations with Lag-0 weeks for the period from August 2002 through January 2004.

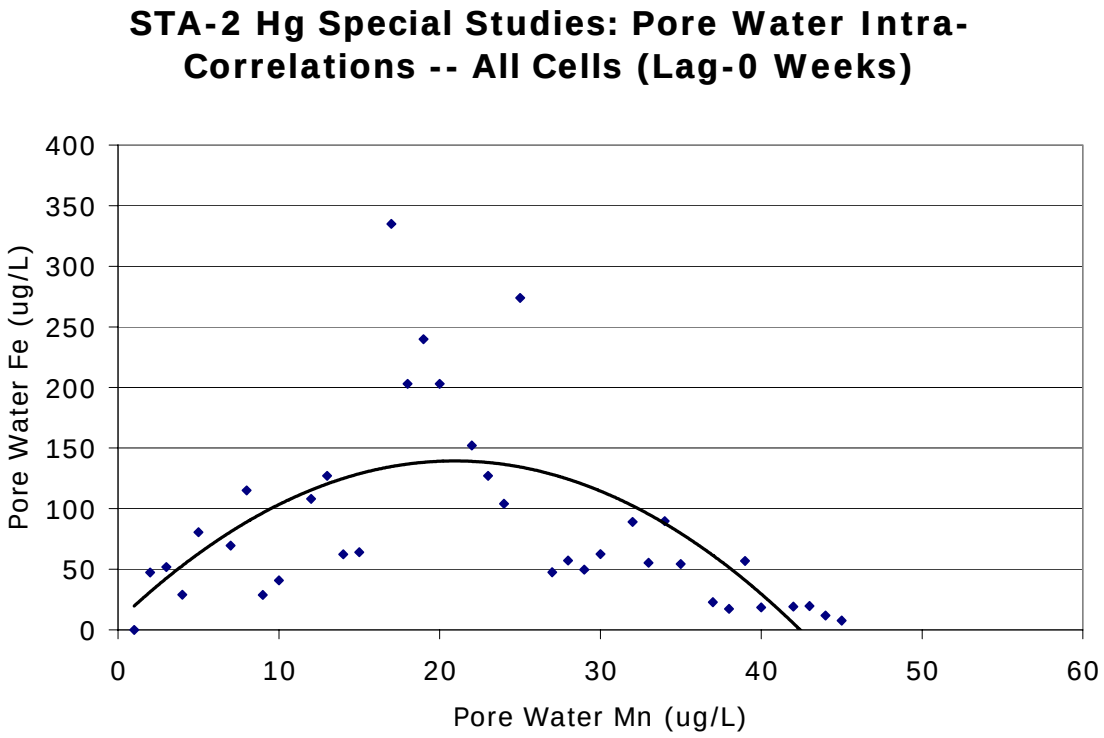

Figure 92. Scatter plot of pore water dissolved total iron (F-TFe) concentration versus dissolved total manganese concentration for nine interior stations with Lag-0 weeks for the period from August 2002 through January 2004.

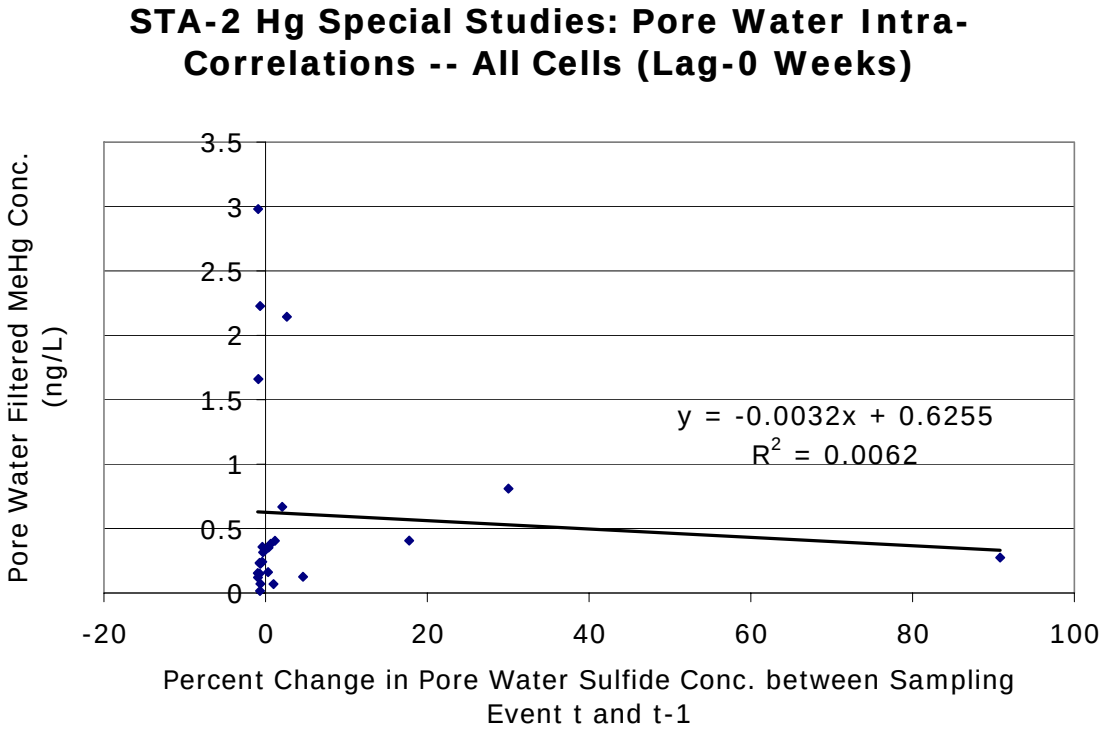

Figure 93. Scatter plot of pore water filtered methylmercury (F-MeHg) concentration versus the percent change in pore water sulfide concentration between sampling event t and t-1 for nine interior stations with Lag-0 weeks for the period from August 2002 through January 2004.

Cell 1 Only

For pore water F-THg, the strongest, statistically significant positive correlation were with DOC ($r = 0.83$; $p < 0.001$) and sulfide ($r = 0.61$; $p < 0.01$). There was a moderate to strong, statistically significant positive correlation between pore water F-MeHg and DOC ($r = 0.69$; $p < 0.05$) and a weak to moderate positive, statistically significant correlation with sulfide ($r = 0.49$; $p < 0.05$). However, Hg(II) was omitted by the contractor (Janicki Environmental Inc., under contract to BFA) for this intra-correlation analysis, so it is not possible to determine the apparent influence of pore water Hg(II) on the production of MeHg from Hg(II). The strongest, statistically significant inverse correlations for F-THg was with redox potential ($r = -0.54$; $p < 0.05$), while those for F-MeHg were with water depth ($r = -0.49$; $p < 0.05$) and redox potential ($r = -0.56$; $p < 0.05$). The weak to moderate inverse relationship between water depth and F-MeHg could reflect the effect of water depth on redox potential and redox potential on a decrease in the concentration or influence of a MeHg production inhibiting factor or on an increase in the concentration or influence of a MeHg production stimulating factor. Water depth and redox potential are inversely correlated, but because the redox potential in surficial pore water is virtually always negative relative to the hydrogen electrode, deeper water corresponds to a more negative redox potential, so the simultaneous inverse correlations of F-MeHg with water depth and redox potential are not inconsistent.

Cell 2 Only

For pore water F-THg, the strong, statistically significant positive correlation with DOC disappeared and with sulfide weakened substantially relative to Cell 1. There moderate to strong, statistically significant positive correlation between pore water F-MeHg and DOC and a weak to moderate positive, statistically significant correlation with sulfide weakened sufficiently to become statistically insignificant. However, Hg(II) was omitted by the contractor (Janicki Environmental Inc., under contract to BFA) for this intra-correlation analysis, so it is not possible to determine the apparent influence of pore water Hg(II) on the production of MeHg from Hg(II). The strongest, statistically significant inverse correlation for F-THg with redox potential observed in Cell 1 disappeared, while that for F-MeHg with water depth strengthened ($r = -0.56$; $p < 0.05$) but that with redox potential weakened substantially.

Cell 3 Only

The strongest positive correlation for F-THg was with F-Fe(II) was weak and not statistically significant, possibly due to the small sample size ($n = 9$). There were strong inverse correlations between F-THg or F-MeHg and F-TFe ($r = 0.70$ or $r = -0.58$, respectively), albeit not statistically significant at $p < 0.05$. By contrast to Cells 1 and 2, for Cell 3 a strong, statistically significant inverse correlation emerged between F-MeHg and calcium ($r = -0.83$; $p < 0.05$), while the weak to moderate, statistically significant inverse correlation with water depth and redox potential switch to strongly ($r = 0.72$; $p < 0.05$) and moderately ($r = 0.59$) positive, respectively. One might infer from this that in Cell 3 shallow water and higher (less negative) redox potential are associated with a decrease in an inhibiting factor for MeHg production, while shallow water and higher redox potential in Cell 1 and Cell 2 are associated with a decrease in a stimulating factor for MeHg production. The switch from a weak to moderate positive correlation between F-MeHg and sulfide in Cells 1 and 2 to a weak inverse correlation in Cell 3 would be consistent with this inference and not inconsistent with the hypothesized parabolic relationship between pore water sulfide concentration and MeHg production (Gilmour et al., 1998b). This difference in the pore water MeHg biogeochemistry between Cell 3 and Cells 1 and 2 may be attributable to differences in antecedent land use (mostly farmed) and operational history (always wet). Whatever the cause, the effect is reflected in the emergence of a moderate to strong, albeit not statistically significant

positive correlation between F-MeHg and sulfate ($r = 0.66$) and inverse, albeit not statistically significant correlations with hardness ($r = -0.68$), F-TFe ($r = -0.58$), F-Mg ($r = -0.49$), F-Mn ($r = -0.54$), and DOC ($r = -0.58$), with the exception of Ca, which was statistically significant ($r = -0.83$; $p < 0.05$).

SOIL X SOIL

The contractor (Janicki Environmental Inc., under contract to BFA) carried out the exploratory data analysis for soil concentration and parameter intra-correlations on all of the soils data sets using a nonparametric univariate Spearman method. The parametric data analysis was carried out on a data set that omitted the November 2003 and December 2003 sampling events, because from October 2003 through January 2004 the soils samples were collected and analyzed on a monthly basis, and this would have given a disproportionate weight to the soil concentrations measured at the end of the study period. The contractor omitted the relationships between soil THg and soil MeHg, so the detection of an influence of soil Hg(II) on soil MeHg is precluded. In addition, the remaining values were averaged spatially. While this may reduce the variability in the data, it also reduces the number of observations, so there is a trade-off in terms of maximizing the correlations between independent variables. So, for example, the number of independent observations was reduced from 9 x 10 at the level of aggregation of STA-2 to 10 observations, and at the level of each individual cell from 3 x 10 to 10. However, this did equalize the number of observations at the STA-2, individual cell, and individual station levels of aggregation, but the analysis did not explicitly take into account the propagated uncertainties of the calculated averages in the correlation results. This problem disappears at the individual station level.

No Lag/No Average Correlation Analysis

All STA-2 Cells

Appendix K contains the results of the nonparametric (Spearman) univariate exploratory data analyses for the inter-media correlation for soil. **Tables 37** through **40** contain the Pearson correlation coefficients for the no lag/no average parametric univariate exploratory data analysis for STA-2 all interior sites for all cells combined, Cell 1 sites only, Cell 2 sites only, and Cell 3 sites only, respectively. Based on the parametric analysis, the strongest positive correlation for soil MeHg was between the natural log-transformed (LN) soil MeHg concentration and the untransformed THg ($r = 0.72$), as depicted in **Figure 94**. The 12-week lag did not change this relationship measurably (see **Figure 95**). Surprisingly, this relationship weakened substantially when the individual cells were treated separately, as depicted in **Figure 96** (Lag-0 Weeks) and **Figure 97** (Lag-12 Weeks) for Cell 1, **Figures 98** and **99** for Cell 2, and **Figures 100** and **101** for Cell 3. Nor did the other combinations of untransformed and log-transformed data increase the strength of these relationships at either Lag-) weeks or Lag-12 weeks. Therefore, the moderate Lag-0 Weeks positive correlation between soil THg and soil MeHg at the level of aggregation of all cells must be considered suspect, because it did not persist when the data were disaggregated to the individual cell level in any cell. The expected inverse relationship between soil MeHg and AVS was not detectable in the scatter plot (Figure 102). Nor did the strength of the relationship improve by pairing the soil MeHg concentration with the AVS concentration observed 12 weeks earlier (See Figure 103).

Focusing on the nonparametric relationships with THg and MeHg, the strongest positive correlations for THg were with soil total nitrogen ($r = 0.60$; $p < 0.001$) and soil total sulfur ($r = 0.52$; $p < 0.001$), and those for MeHg were also with total nitrogen ($r = 0.56$; $p < 0.001$) and total sulfur ($r = 0.37$; $p < 0.001$), albeit not as strong. The strongest inverse correlations for THg

were with calcium ($r = -0.74$; $p < 0.001$), percent ash ($r = -0.67$; $p < 0.001$), and magnesium ($r = -0.61$; $p < 0.001$), and those for MeHg were virtually identical. The inverse relationship between soil acid volatile sulfide and MeHg was weak ($r = -0.30$), albeit statistically significant at $p < 0.01$.

Table 37. Pearson correlation coefficients for soil constituent and parameter parametric intra-correlations for all STA-2 cells combined.

ALL CELLS SOIL X SOIL	BD	LN	%ASH	LN	%MOIST	LN	TP	LN	TN	LN	TCA	LN	TMG	LN
BD	1.00	0.98	0.12	0.20	-0.86	-0.86	-0.14	-0.10	-0.23	-0.18	0.10	0.17	0.36	0.36
LN	0.98	1.00	0.10	0.17	-0.86	-0.85	-0.22	-0.18	-0.20	-0.14	0.05	0.11	0.32	0.32
%ASH	0.12	0.10	1.00	0.97	-0.07	-0.07	0.11	0.11	-0.77	-0.80	0.78	0.82	0.77	0.75
LN	0.20	0.17	0.97	1.00	-0.14	-0.14	0.16	0.16	-0.77	-0.77	0.74	0.84	0.80	0.79
%MOIST	-0.86	-0.86	-0.07	-0.14	1.00	1.00	0.26	0.24	0.27	0.21	-0.07	-0.12	-0.32	-0.32
LN	-0.86	-0.85	-0.07	-0.14	1.00	1.00	0.24	0.22	0.27	0.21	-0.07	-0.12	-0.32	-0.32
TP	-0.14	-0.22	0.11	0.16	0.26	0.24	1.00	0.98	0.04	0.05	0.23	0.26	0.02	0.03
LN	-0.10	-0.18	0.11	0.16	0.24	0.22	0.98	1.00	0.08	0.09	0.24	0.25	0.00	0.01
TN	-0.23	-0.20	-0.77	-0.77	0.27	0.27	0.04	0.08	1.00	0.99	-0.60	-0.68	-0.76	-0.76
LN	-0.18	-0.14	-0.80	-0.77	0.21	0.21	0.05	0.09	0.99	1.00	-0.64	-0.68	-0.75	-0.74
CA	0.10	0.05	0.78	0.74	-0.07	-0.07	0.23	0.24	-0.60	-0.64	1.00	0.94	0.68	0.65
LN	0.17	0.11	0.82	0.84	-0.12	-0.12	0.26	0.25	-0.68	-0.68	0.94	1.00	0.77	0.76
MG	0.36	0.32	0.77	0.80	-0.32	-0.32	0.02	0.00	-0.76	-0.75	0.68	0.77	1.00	1.00
LN	0.36	0.32	0.75	0.79	-0.32	-0.32	0.03	0.01	-0.76	-0.74	0.65	0.76	1.00	1.00
TS	-0.45	-0.46	-0.48	-0.48	0.48	0.48	0.28	0.31	0.58	0.55	-0.46	-0.52	-0.55	-0.53
LN	-0.37	-0.36	-0.59	-0.56	0.40	0.40	0.25	0.28	0.62	0.62	-0.57	-0.60	-0.61	-0.58
AVS	-0.20	-0.25	0.14	0.17	0.25	0.25	-0.04	-0.05	-0.17	-0.16	0.14	0.22	0.24	0.25
LN	-0.19	-0.24	0.05	0.06	0.24	0.23	-0.12	-0.14	-0.09	-0.08	0.06	0.12	0.18	0.19
TFE	0.47	0.46	0.20	0.34	-0.32	-0.32	-0.02	-0.01	-0.12	-0.08	-0.08	0.05	0.21	0.24
LN	0.47	0.46	0.17	0.33	-0.32	-0.32	0.01	0.02	-0.10	-0.05	-0.10	0.06	0.21	0.24
TMN	0.00	0.03	-0.14	-0.09	0.06	0.06	0.28	0.32	0.29	0.29	-0.08	-0.07	-0.37	-0.37
LN	-0.04	-0.03	-0.19	-0.14	0.09	0.09	0.33	0.38	0.38	0.39	-0.10	-0.10	-0.42	-0.42
THg	-0.33	-0.34	-0.57	-0.64	0.30	0.29	-0.03	0.00	0.56	0.55	-0.52	-0.66	-0.64	-0.64
LN	-0.30	-0.31	-0.63	-0.68	0.27	0.27	-0.07	-0.04	0.65	0.64	-0.59	-0.71	-0.70	-0.70
MeHg	-0.07	-0.05	-0.29	-0.38	0.05	0.06	-0.21	-0.22	0.25	0.24	-0.26	-0.38	-0.30	-0.31
LN	-0.23	-0.20	-0.57	-0.64	0.22	0.22	-0.19	-0.18	0.54	0.52	-0.57	-0.69	-0.63	-0.62
%MeHg	-0.02	0.02	-0.27	-0.35	-0.01	-0.01	-0.24	-0.25	0.21	0.20	-0.24	-0.34	-0.24	-0.25
LN	0.14	0.20	-0.32	-0.31	-0.17	-0.16	-0.14	-0.14	0.24	0.24	-0.32	-0.36	-0.18	-0.18

Table 37. Continued.

ALL CELLS SOIL X SOIL	TS	LN	AVS	LN	TFE	LN	TMN	LN	THg	LN	MeHg	LN	%MeHg	LN
BD	-0.45	-0.37	-0.20	-0.19	0.47	0.47	0.00	-0.04	-0.33	-0.30	-0.07	-0.23	-0.02	0.14
LN	-0.46	-0.36	-0.25	-0.24	0.46	0.46	0.03	-0.03	-0.34	-0.31	-0.05	-0.20	0.02	0.20
%ASH	-0.48	-0.59	0.14	0.05	0.20	0.17	-0.14	-0.19	-0.57	-0.63	-0.29	-0.57	-0.27	-0.32
LN	-0.48	-0.56	0.17	0.06	0.34	0.33	-0.09	-0.14	-0.64	-0.68	-0.38	-0.64	-0.35	-0.31
%MOIST	0.48	0.40	0.25	0.24	-0.32	-0.32	0.06	0.09	0.30	0.27	0.05	0.22	-0.01	-0.17
LN	0.48	0.40	0.25	0.23	-0.32	-0.32	0.06	0.09	0.29	0.27	0.06	0.22	-0.01	-0.16
TP	0.28	0.25	-0.04	-0.12	-0.02	0.01	0.28	0.33	-0.03	-0.07	-0.21	-0.19	-0.24	-0.14
LN	0.31	0.28	-0.05	-0.14	-0.01	0.02	0.32	0.38	0.00	-0.04	-0.22	-0.18	-0.25	-0.14
TN	0.58	0.62	-0.17	-0.09	-0.12	-0.10	0.29	0.38	0.56	0.65	0.25	0.54	0.21	0.24
LN	0.55	0.62	-0.16	-0.08	-0.08	-0.05	0.29	0.39	0.55	0.64	0.24	0.52	0.20	0.24
CA	-0.46	-0.57	0.14	0.06	-0.08	-0.10	-0.08	-0.10	-0.52	-0.59	-0.26	-0.57	-0.24	-0.32
LN	-0.52	-0.60	0.22	0.12	0.05	0.06	-0.07	-0.10	-0.66	-0.71	-0.38	-0.69	-0.34	-0.36
MG	-0.55	-0.61	0.24	0.18	0.21	0.21	-0.37	-0.42	-0.64	-0.70	-0.30	-0.63	-0.24	-0.18
LN	-0.53	-0.58	0.25	0.19	0.24	0.24	-0.37	-0.42	-0.64	-0.70	-0.31	-0.62	-0.25	-0.18
TS	1.00	0.96	-0.04	-0.01	-0.12	-0.08	0.08	0.17	0.55	0.55	0.04	0.35	-0.05	-0.11
LN	0.96	1.00	-0.04	-0.02	-0.09	-0.05	0.14	0.24	0.56	0.57	0.08	0.38	0.00	-0.03
AVS	-0.04	-0.04	1.00	0.89	0.04	0.05	-0.19	-0.22	-0.08	-0.11	-0.22	-0.27	-0.23	-0.24
LN	-0.01	-0.02	0.89	1.00	0.03	0.03	-0.28	-0.29	-0.08	-0.08	-0.22	-0.24	-0.23	-0.30
TFE	-0.12	-0.09	0.04	0.03	1.00	0.98	0.19	0.08	-0.28	-0.21	-0.29	-0.20	-0.23	0.01
LN	-0.08	-0.05	0.05	0.03	0.98	1.00	0.19	0.10	-0.31	-0.23	-0.40	-0.26	-0.35	-0.03
TMN	0.08	0.14	-0.19	-0.28	0.19	0.19	1.00	0.96	-0.02	0.05	-0.13	0.01	-0.11	0.08
LN	0.17	0.24	-0.22	-0.29	0.08	0.10	0.96	1.00	0.07	0.14	-0.09	0.05	-0.09	0.08
THg	0.55	0.56	-0.08	-0.08	-0.28	-0.31	-0.02	0.07	1.00	0.96	0.48	0.72	0.31	0.15
LN	0.55	0.57	-0.11	-0.08	-0.21	-0.23	0.05	0.14	0.96	1.00	0.43	0.68	0.26	0.11
MeHg	0.04	0.08	-0.22	-0.22	-0.29	-0.40	-0.13	-0.09	0.48	0.43	1.00	0.76	0.96	0.49
LN	0.35	0.38	-0.27	-0.24	-0.20	-0.26	0.01	0.05	0.72	0.68	0.76	1.00	0.71	0.57
%MeHg	-0.05	0.00	-0.23	-0.23	-0.23	-0.35	-0.11	-0.09	0.31	0.26	0.96	0.71	1.00	0.62
LN	-0.11	-0.03	-0.24	-0.30	0.01	-0.03	0.08	0.08	0.15	0.11	0.49	0.57	0.62	1.00

Table 38. Pearson correlation coefficients for soil constituent and parameter parametric intra-correlations for interior Cell 1 sites only.

Cell 1 Only SOIL X SOIL	BD	LN	%ASH	LN	%MOIST	LN	TP	LN	TN	LN	TCA	LN	TMG	LN
BD	1.00	0.98	-0.21	-0.27	-0.94	-0.94	-0.57	-0.52	0.14	0.15	-0.67	-0.68	-0.27	-0.25
LN	0.98	1.00	-0.31	-0.37	-0.94	-0.94	-0.61	-0.56	0.25	0.26	-0.75	-0.75	-0.38	-0.36
%ASH	-0.21	-0.31	1.00	0.99	0.34	0.32	0.44	0.46	-0.59	-0.61	0.57	0.57	0.72	0.70
LN	-0.27	-0.37	0.99	1.00	0.40	0.39	0.50	0.51	-0.52	-0.55	0.61	0.61	0.73	0.71
%MOIST	-0.94	-0.94	0.34	0.40	1.00	1.00	0.62	0.58	-0.17	-0.18	0.77	0.78	0.45	0.43
LN	-0.94	-0.94	0.32	0.39	1.00	1.00	0.62	0.57	-0.15	-0.16	0.75	0.77	0.43	0.42
TP	-0.57	-0.61	0.44	0.50	0.62	0.62	1.00	0.98	-0.23	-0.22	0.57	0.60	0.52	0.51
LN	-0.52	-0.56	0.46	0.51	0.58	0.57	0.98	1.00	-0.24	-0.24	0.55	0.58	0.49	0.48
TN	0.14	0.25	-0.59	-0.52	-0.17	-0.15	-0.23	-0.24	1.00	1.00	-0.47	-0.41	-0.62	-0.61
LN	0.15	0.26	-0.61	-0.55	-0.18	-0.16	-0.22	-0.24	1.00	1.00	-0.49	-0.43	-0.62	-0.61
CA	-0.67	-0.75	0.57	0.61	0.77	0.75	0.57	0.55	-0.47	-0.49	1.00	0.99	0.66	0.64
LN	-0.68	-0.75	0.57	0.61	0.78	0.77	0.60	0.58	-0.41	-0.43	0.99	1.00	0.67	0.65
MG	-0.27	-0.38	0.72	0.73	0.45	0.43	0.52	0.49	-0.62	-0.62	0.66	0.67	1.00	1.00
LN	-0.25	-0.36	0.70	0.71	0.43	0.42	0.51	0.48	-0.61	-0.61	0.64	0.65	1.00	1.00
TS	-0.41	-0.39	0.14	0.23	0.45	0.46	0.53	0.56	0.32	0.31	0.13	0.19	0.12	0.13
LN	-0.41	-0.37	0.16	0.25	0.43	0.44	0.52	0.57	0.30	0.28	0.14	0.19	0.08	0.08
AVS	-0.62	-0.68	0.26	0.27	0.64	0.63	0.32	0.32	-0.52	-0.54	0.70	0.65	0.36	0.34
LN	-0.60	-0.61	0.01	0.04	0.60	0.60	0.23	0.20	-0.28	-0.28	0.50	0.48	0.24	0.22
TFE	0.15	0.08	0.77	0.77	-0.02	-0.03	0.37	0.39	-0.18	-0.20	0.07	0.10	0.47	0.46
LN	0.10	0.04	0.71	0.74	0.03	0.02	0.44	0.47	-0.08	-0.11	0.13	0.16	0.47	0.47
TMN	-0.15	-0.15	0.21	0.24	0.13	0.13	-0.16	-0.12	-0.09	-0.10	0.11	0.10	0.21	0.21
LN	-0.15	-0.15	0.25	0.28	0.14	0.14	-0.14	-0.11	-0.15	-0.16	0.14	0.14	0.26	0.27
THg	0.22	0.13	0.14	0.07	-0.16	-0.17	-0.01	0.02	-0.59	-0.59	0.07	0.00	0.26	0.26
LN	0.23	0.14	0.12	0.05	-0.16	-0.17	-0.01	0.01	-0.58	-0.57	0.06	-0.01	0.25	0.25
MeHg	0.42	0.37	-0.22	-0.32	-0.38	-0.38	-0.45	-0.51	-0.10	-0.09	-0.28	-0.31	-0.15	-0.15
LN	0.60	0.53	-0.16	-0.26	-0.53	-0.54	-0.47	-0.52	-0.10	-0.10	-0.33	-0.36	-0.08	-0.08
%MeHg	0.40	0.37	-0.27	-0.37	-0.38	-0.39	-0.49	-0.56	-0.02	-0.01	-0.31	-0.34	-0.23	-0.23
LN	0.65	0.62	-0.24	-0.31	-0.62	-0.63	-0.53	-0.55	0.14	0.14	-0.50	-0.54	-0.25	-0.24

Table 38. Continued.

Cell 1 Only SOIL X SOIL	TS	LN	AVS	LN	TFE	LN	TMN	LN	THg	LN	MeHg	LN	%MeHg	LN
BD	-0.41	-0.41	-0.62	-0.60	0.15	0.10	-0.15	-0.15	0.22	0.23	0.42	0.60	0.40	0.65
LN	-0.39	-0.37	-0.68	-0.61	0.08	0.04	-0.15	-0.15	0.13	0.14	0.37	0.53	0.37	0.62
%ASH	0.14	0.16	0.26	0.01	0.77	0.71	0.21	0.25	0.14	0.12	-0.22	-0.16	-0.27	-0.24
LN	0.23	0.25	0.27	0.04	0.77	0.74	0.24	0.28	0.07	0.05	-0.32	-0.26	-0.37	-0.31
%MOIST	0.45	0.43	0.64	0.60	-0.02	0.03	0.13	0.14	-0.16	-0.16	-0.38	-0.53	-0.38	-0.62
LN	0.46	0.44	0.63	0.60	-0.03	0.02	0.13	0.14	-0.17	-0.17	-0.38	-0.54	-0.39	-0.63
TP	0.53	0.52	0.32	0.23	0.37	0.44	-0.16	-0.14	-0.01	-0.01	-0.45	-0.47	-0.49	-0.53
LN	0.56	0.57	0.32	0.20	0.39	0.47	-0.12	-0.11	0.02	0.01	-0.51	-0.52	-0.56	-0.55
TN	0.32	0.30	-0.52	-0.28	-0.18	-0.08	-0.09	-0.15	-0.59	-0.58	-0.10	-0.10	-0.02	0.14
LN	0.31	0.28	-0.54	-0.28	-0.20	-0.11	-0.10	-0.16	-0.59	-0.57	-0.09	-0.10	-0.01	0.14
CA	0.13	0.14	0.70	0.50	0.07	0.13	0.11	0.14	0.07	0.06	-0.28	-0.33	-0.31	-0.50
LN	0.19	0.19	0.65	0.48	0.10	0.16	0.10	0.14	0.00	-0.01	-0.31	-0.36	-0.34	-0.54
MG	0.12	0.08	0.36	0.24	0.47	0.47	0.21	0.26	0.26	0.25	-0.15	-0.08	-0.23	-0.25
LN	0.13	0.08	0.34	0.22	0.46	0.47	0.21	0.27	0.26	0.25	-0.15	-0.08	-0.23	-0.24
TS	1.00	0.98	0.03	0.07	0.35	0.46	0.18	0.15	-0.23	-0.24	-0.58	-0.59	-0.60	-0.53
LN	0.98	1.00	0.06	0.07	0.34	0.45	0.15	0.12	-0.20	-0.21	-0.64	-0.64	-0.66	-0.55
AVS	0.03	0.06	1.00	0.88	-0.15	-0.09	-0.01	0.01	0.34	0.34	-0.29	-0.37	-0.31	-0.50
LN	0.07	0.07	0.88	1.00	-0.29	-0.20	-0.09	-0.08	0.19	0.19	-0.29	-0.44	-0.30	-0.57
TFE	0.35	0.34	-0.15	-0.29	1.00	0.97	0.17	0.19	0.05	0.05	-0.23	-0.08	-0.26	-0.03
LN	0.46	0.45	-0.09	-0.20	0.97	1.00	0.19	0.20	0.01	0.01	-0.40	-0.22	-0.43	-0.13
TMN	0.18	0.15	-0.01	-0.09	0.17	0.19	1.00	0.99	-0.06	-0.06	-0.22	-0.11	-0.23	-0.13
LN	0.15	0.12	0.01	-0.08	0.19	0.20	0.99	1.00	-0.04	-0.03	-0.23	-0.12	-0.24	-0.14
THg	-0.23	-0.20	0.34	0.19	0.05	0.01	-0.06	-0.04	1.00	1.00	0.18	0.31	0.08	0.06
LN	-0.24	-0.21	0.34	0.19	0.05	0.01	-0.06	-0.03	1.00	1.00	0.20	0.33	0.10	0.07
MeHg	-0.58	-0.64	-0.29	-0.29	-0.23	-0.40	-0.22	-0.23	0.18	0.20	1.00	0.92	0.99	0.68
LN	-0.59	-0.64	-0.37	-0.44	-0.08	-0.22	-0.11	-0.12	0.31	0.33	0.92	1.00	0.89	0.80
%MeHg	-0.60	-0.66	-0.31	-0.30	-0.26	-0.43	-0.23	-0.24	0.08	0.10	0.99	0.89	1.00	0.73
LN	-0.53	-0.55	-0.50	-0.57	-0.03	-0.13	-0.13	-0.14	0.06	0.07	0.68	0.80	0.73	1.00

Table 39. Pearson correlation coefficients for soil constituent and parameter parametric intra-correlations for interior Cell 2 sites only.

Cell 2 Only SOIL X SOIL	BD	LN	%ASH	LN	%MOIST	LN	TP	LN	TN	LN	TCA	LN	TMG	LN
BD	1.00	0.99	-0.11	-0.11	-0.77	-0.76	-0.22	-0.18	0.07	0.08	-0.12	-0.10	-0.64	-0.65
LN	0.99	1.00	-0.10	-0.09	-0.77	-0.75	-0.23	-0.18	0.06	0.06	-0.13	-0.11	-0.61	-0.62
%ASH	-0.11	-0.10	1.00	0.99	-0.37	-0.38	0.10	0.11	-0.66	-0.69	0.51	0.50	0.31	0.31
LN	-0.11	-0.09	0.99	1.00	-0.32	-0.33	0.16	0.18	-0.60	-0.63	0.52	0.50	0.36	0.36
%MOIST	-0.77	-0.77	-0.37	-0.32	1.00	1.00	0.33	0.35	0.40	0.41	-0.05	-0.08	0.54	0.55
LN	-0.76	-0.75	-0.38	-0.33	1.00	1.00	0.33	0.35	0.41	0.42	-0.06	-0.09	0.54	0.55
TP	-0.22	-0.23	0.10	0.16	0.33	0.33	1.00	0.97	0.03	0.04	0.25	0.24	0.14	0.14
LN	-0.18	-0.18	0.11	0.18	0.35	0.35	0.97	1.00	0.11	0.12	0.20	0.18	0.16	0.17
TN	0.07	0.06	-0.66	-0.60	0.40	0.41	0.03	0.11	1.00	1.00	-0.58	-0.56	-0.09	-0.09
LN	0.08	0.06	-0.69	-0.63	0.41	0.42	0.04	0.12	1.00	1.00	-0.57	-0.56	-0.10	-0.09
CA	-0.12	-0.13	0.51	0.52	-0.05	-0.06	0.25	0.20	-0.58	-0.57	1.00	1.00	0.32	0.30
LN	-0.10	-0.11	0.50	0.50	-0.08	-0.09	0.24	0.18	-0.56	-0.56	1.00	1.00	0.28	0.26
MG	-0.64	-0.61	0.31	0.36	0.54	0.54	0.14	0.16	-0.09	-0.10	0.32	0.28	1.00	1.00
LN	-0.65	-0.62	0.31	0.36	0.55	0.55	0.14	0.17	-0.09	-0.09	0.30	0.26	1.00	1.00
TS	-0.34	-0.35	-0.23	-0.20	0.58	0.58	0.28	0.37	0.52	0.51	-0.38	-0.40	0.25	0.25
LN	-0.31	-0.32	-0.24	-0.20	0.58	0.58	0.31	0.39	0.52	0.51	-0.36	-0.38	0.27	0.27
AVS	-0.24	-0.23	-0.16	-0.18	0.41	0.40	0.04	0.09	0.16	0.16	0.00	-0.05	0.06	0.04
LN	-0.30	-0.31	-0.10	-0.10	0.47	0.46	0.05	0.07	0.15	0.15	0.01	-0.03	0.16	0.15
TFE	0.30	0.32	0.21	0.24	-0.29	-0.28	-0.02	0.07	0.37	0.34	-0.46	-0.46	-0.12	-0.10
LN	0.30	0.32	0.18	0.21	-0.29	-0.29	-0.09	0.00	0.39	0.36	-0.54	-0.53	-0.15	-0.13
TMN	0.41	0.44	-0.03	0.01	-0.27	-0.26	0.32	0.39	0.35	0.34	-0.27	-0.28	-0.32	-0.32
LN	0.38	0.40	0.00	0.03	-0.23	-0.22	0.33	0.40	0.32	0.31	-0.29	-0.31	-0.26	-0.26
THg	0.03	0.02	-0.30	-0.31	0.00	0.00	-0.35	-0.28	0.37	0.36	-0.52	-0.49	-0.22	-0.21
LN	0.06	0.06	-0.32	-0.34	-0.06	-0.06	-0.40	-0.35	0.39	0.38	-0.60	-0.57	-0.30	-0.28
MeHg	-0.01	0.02	-0.06	-0.04	0.05	0.06	-0.12	-0.10	0.32	0.31	-0.20	-0.18	0.13	0.14
LN	-0.03	0.01	-0.01	0.01	0.03	0.04	-0.13	-0.12	0.28	0.27	-0.13	-0.11	0.03	0.04
%MeHg	0.10	0.14	0.22	0.26	-0.08	-0.07	0.20	0.25	0.00	0.00	0.03	0.02	0.10	0.11
LN	0.11	0.17	0.41	0.45	-0.18	-0.17	0.29	0.32	-0.23	-0.22	0.23	0.23	0.03	0.04

Table 39. Continued.

Cell 2 Only SOIL X SOIL	TS	LN	AVS	LN	TFE	LN	TMN	LN	THg	LN	MeHg	LN	%MeHg	LN
BD	-0.34	-0.31	-0.24	-0.30	0.30	0.30	0.41	0.38	0.03	0.06	-0.01	-0.03	0.10	0.11
LN	-0.35	-0.32	-0.23	-0.31	0.32	0.32	0.44	0.40	0.02	0.06	0.02	0.01	0.14	0.17
%ASH	-0.23	-0.24	-0.16	-0.10	0.21	0.18	-0.03	0.00	-0.30	-0.32	-0.06	-0.01	0.22	0.41
LN	-0.20	-0.20	-0.18	-0.10	0.24	0.21	0.01	0.03	-0.31	-0.34	-0.04	0.01	0.26	0.45
%MOIST	0.58	0.58	0.41	0.47	-0.29	-0.29	-0.27	-0.23	0.00	-0.06	0.05	0.03	-0.08	-0.18
LN	0.58	0.58	0.40	0.46	-0.28	-0.29	-0.26	-0.22	0.00	-0.06	0.06	0.04	-0.07	-0.17
TP	0.28	0.31	0.04	0.05	-0.02	-0.09	0.32	0.33	-0.35	-0.40	-0.12	-0.13	0.20	0.29
LN	0.37	0.39	0.09	0.07	0.07	0.00	0.39	0.40	-0.28	-0.35	-0.10	-0.12	0.25	0.32
TN	0.52	0.52	0.16	0.15	0.37	0.39	0.35	0.32	0.37	0.39	0.32	0.28	0.00	-0.23
LN	0.51	0.51	0.16	0.15	0.34	0.36	0.34	0.31	0.36	0.38	0.31	0.27	0.00	-0.22
CA	-0.38	-0.36	0.00	0.01	-0.46	-0.54	-0.27	-0.29	-0.52	-0.60	-0.20	-0.13	0.03	0.23
LN	-0.40	-0.38	-0.05	-0.03	-0.46	-0.53	-0.28	-0.31	-0.49	-0.57	-0.18	-0.11	0.02	0.23
MG	0.25	0.27	0.06	0.16	-0.12	-0.15	-0.32	-0.26	-0.22	-0.30	0.13	0.03	0.10	0.03
LN	0.25	0.27	0.04	0.15	-0.10	-0.13	-0.32	-0.26	-0.21	-0.28	0.14	0.04	0.11	0.04
TS	1.00	0.99	0.48	0.47	-0.01	0.04	0.03	0.17	0.15	0.14	-0.01	-0.11	-0.10	-0.25
LN	0.99	1.00	0.47	0.49	-0.03	0.02	0.05	0.22	0.09	0.07	0.01	-0.08	-0.06	-0.20
AVS	0.48	0.47	1.00	0.91	-0.23	-0.23	-0.11	-0.02	-0.23	-0.25	-0.30	-0.23	-0.31	-0.29
LN	0.47	0.49	0.91	1.00	-0.22	-0.21	-0.28	-0.19	-0.25	-0.26	-0.39	-0.33	-0.42	-0.37
TFE	-0.01	-0.03	-0.23	-0.22	1.00	0.99	0.57	0.48	0.22	0.27	0.39	0.36	0.37	0.24
LN	0.04	0.02	-0.23	-0.21	0.99	1.00	0.53	0.45	0.30	0.36	0.40	0.37	0.34	0.21
TMN	0.03	0.05	-0.11	-0.28	0.57	0.53	1.00	0.96	0.10	0.08	0.27	0.30	0.43	0.42
LN	0.17	0.22	-0.02	-0.19	0.48	0.45	0.96	1.00	0.02	0.00	0.25	0.28	0.42	0.42
THg	0.15	0.09	-0.23	-0.25	0.22	0.30	0.10	0.02	1.00	0.98	0.15	0.04	-0.25	-0.35
LN	0.14	0.07	-0.25	-0.26	0.27	0.36	0.08	0.00	0.98	1.00	0.16	0.07	-0.26	-0.37
MeHg	-0.01	0.01	-0.30	-0.39	0.39	0.40	0.27	0.25	0.15	0.16	1.00	0.93	0.75	0.53
LN	-0.11	-0.08	-0.23	-0.33	0.36	0.37	0.30	0.28	0.04	0.07	0.93	1.00	0.73	0.63
%MeHg	-0.10	-0.06	-0.31	-0.42	0.37	0.34	0.43	0.42	-0.25	-0.26	0.75	0.73	1.00	0.87
LN	-0.25	-0.20	-0.29	-0.37	0.24	0.21	0.42	0.42	-0.35	-0.37	0.53	0.63	0.87	1.00

Table 40. Pearson correlation coefficients for soil constituent and parameter parametric intra-correlations for interior Cell 3 sites only.

Cell 3 Only SOIL X SOIL	BD	LN	%ASH	LN	%MOIST	LN	TP	LN	TN	LN	TCA	LN	TMG	LN
BD	1.00	0.99	-0.46	-0.40	-0.79	-0.79	0.23	0.23	0.36	0.42	-0.29	-0.31	-0.35	-0.33
LN	0.99	1.00	-0.50	-0.43	-0.78	-0.77	0.17	0.17	0.40	0.47	-0.38	-0.38	-0.39	-0.36
%ASH	-0.46	-0.50	1.00	0.98	0.69	0.67	0.20	0.20	-0.57	-0.62	0.67	0.71	0.62	0.60
LN	-0.40	-0.43	0.98	1.00	0.66	0.65	0.28	0.27	-0.49	-0.52	0.64	0.72	0.56	0.55
%MOIST	-0.79	-0.78	0.69	0.66	1.00	1.00	-0.06	-0.07	-0.42	-0.48	0.38	0.44	0.56	0.55
LN	-0.79	-0.77	0.67	0.65	1.00	1.00	-0.06	-0.08	-0.41	-0.47	0.36	0.43	0.55	0.54
TP	0.23	0.17	0.20	0.28	-0.06	-0.06	1.00	0.99	0.15	0.14	0.44	0.52	0.04	0.02
LN	0.23	0.17	0.20	0.27	-0.07	-0.08	0.99	1.00	0.17	0.16	0.43	0.51	0.04	0.02
TN	0.36	0.40	-0.57	-0.49	-0.42	-0.41	0.15	0.17	1.00	0.99	-0.34	-0.28	-0.27	-0.26
LN	0.42	0.47	-0.62	-0.52	-0.48	-0.47	0.14	0.16	0.99	1.00	-0.41	-0.34	-0.36	-0.34
CA	-0.29	-0.38	0.67	0.64	0.38	0.36	0.44	0.43	-0.34	-0.41	1.00	0.97	0.61	0.58
LN	-0.31	-0.38	0.71	0.72	0.44	0.43	0.52	0.51	-0.28	-0.34	0.97	1.00	0.59	0.57
MG	-0.35	-0.39	0.62	0.56	0.56	0.55	0.04	0.04	-0.27	-0.36	0.61	0.59	1.00	1.00
LN	-0.33	-0.36	0.60	0.55	0.55	0.54	0.02	0.02	-0.26	-0.34	0.58	0.57	1.00	1.00
TS	0.18	0.23	-0.37	-0.27	-0.25	-0.23	0.08	0.07	0.16	0.24	-0.43	-0.36	-0.60	-0.60
LN	0.28	0.35	-0.52	-0.41	-0.37	-0.35	0.08	0.06	0.29	0.39	-0.55	-0.46	-0.66	-0.65
AVS	-0.28	-0.28	-0.03	-0.02	0.30	0.30	-0.38	-0.39	0.16	0.11	-0.07	-0.03	0.11	0.12
LN	-0.18	-0.20	-0.10	-0.13	0.17	0.17	-0.55	-0.53	0.16	0.12	-0.14	-0.16	0.08	0.08
TFE	0.56	0.60	-0.25	-0.17	-0.26	-0.24	-0.27	-0.27	0.28	0.34	-0.52	-0.46	-0.31	-0.29
LN	0.60	0.66	-0.35	-0.25	-0.32	-0.30	-0.24	-0.24	0.38	0.45	-0.61	-0.54	-0.39	-0.36
TMN	0.07	0.06	0.18	0.27	-0.04	-0.04	0.82	0.78	0.13	0.15	0.28	0.39	0.02	0.02
LN	0.15	0.13	0.12	0.21	-0.15	-0.16	0.84	0.82	0.27	0.29	0.27	0.38	-0.01	-0.01
THg	0.44	0.43	-0.41	-0.40	-0.50	-0.50	-0.22	-0.22	0.41	0.43	-0.45	-0.46	-0.23	-0.22
LN	0.40	0.40	-0.35	-0.34	-0.46	-0.46	-0.20	-0.20	0.38	0.41	-0.43	-0.42	-0.20	-0.20
MeHg	-0.06	-0.03	-0.27	-0.30	0.02	0.03	-0.35	-0.32	0.14	0.16	-0.34	-0.37	-0.25	-0.23
LN	0.15	0.19	-0.41	-0.43	-0.14	-0.13	-0.41	-0.39	0.14	0.19	-0.52	-0.56	-0.39	-0.36
%MeHg	-0.10	-0.08	-0.39	-0.43	0.00	0.01	-0.24	-0.22	0.21	0.21	-0.29	-0.35	-0.23	-0.22
LN	0.15	0.18	-0.57	-0.59	-0.16	-0.15	-0.22	-0.23	0.38	0.38	-0.44	-0.48	-0.07	-0.04

Table 40. Continued.

Cell 3 Only SOIL X SOIL	TS	LN	AVS	LN	TFE	LN	TMN	LN	THg	LN	MeHg	LN	%MeHg	LN
BD	0.18	0.28	-0.28	-0.18	0.56	0.60	0.07	0.15	0.44	0.40	-0.06	0.15	-0.10	0.15
LN	0.23	0.35	-0.28	-0.20	0.60	0.66	0.06	0.13	0.43	0.40	-0.03	0.19	-0.08	0.18
%ASH	-0.37	-0.52	-0.03	-0.10	-0.25	-0.35	0.18	0.12	-0.41	-0.35	-0.27	-0.41	-0.39	-0.57
LN	-0.27	-0.41	-0.02	-0.13	-0.17	-0.25	0.27	0.21	-0.40	-0.34	-0.30	-0.43	-0.43	-0.59
%MOIST	-0.25	-0.37	0.30	0.17	-0.26	-0.32	-0.04	-0.15	-0.50	-0.46	0.02	-0.14	0.00	-0.16
LN	-0.23	-0.35	0.30	0.17	-0.24	-0.30	-0.04	-0.16	-0.50	-0.46	0.03	-0.13	0.01	-0.15
TP	0.08	0.08	-0.38	-0.55	-0.27	-0.24	0.82	0.84	-0.22	-0.20	-0.35	-0.41	-0.24	-0.22
LN	0.07	0.06	-0.39	-0.53	-0.27	-0.24	0.78	0.82	-0.22	-0.20	-0.32	-0.39	-0.22	-0.23
TN	0.16	0.29	0.16	0.16	0.28	0.38	0.13	0.27	0.41	0.38	0.14	0.14	0.21	0.38
LN	0.24	0.39	0.11	0.12	0.34	0.45	0.15	0.29	0.43	0.41	0.16	0.19	0.21	0.38
CA	-0.43	-0.55	-0.07	-0.14	-0.52	-0.61	0.28	0.27	-0.45	-0.43	-0.34	-0.52	-0.29	-0.44
LN	-0.36	-0.46	-0.03	-0.16	-0.46	-0.54	0.39	0.38	-0.46	-0.42	-0.37	-0.56	-0.35	-0.48
MG	-0.60	-0.66	0.11	0.08	-0.31	-0.39	0.02	-0.01	-0.23	-0.20	-0.25	-0.39	-0.23	-0.07
LN	-0.60	-0.65	0.12	0.08	-0.29	-0.36	0.02	-0.01	-0.22	-0.20	-0.23	-0.36	-0.22	-0.04
TS	1.00	0.96	-0.08	-0.13	0.33	0.36	0.14	0.12	0.10	0.06	-0.09	0.08	0.11	-0.03
LN	0.96	1.00	-0.08	-0.14	0.39	0.44	0.19	0.18	0.20	0.18	-0.06	0.11	0.12	0.07
AVS	-0.08	-0.08	1.00	0.89	0.20	0.17	-0.30	-0.33	0.08	0.10	-0.06	-0.05	-0.09	0.09
LN	-0.13	-0.14	0.89	1.00	0.29	0.24	-0.51	-0.51	0.24	0.25	0.07	0.12	0.00	0.08
TFE	0.33	0.39	0.20	0.29	1.00	0.98	-0.32	-0.29	0.38	0.36	0.13	0.31	0.07	0.12
LN	0.36	0.44	0.17	0.24	0.98	1.00	-0.26	-0.23	0.38	0.37	0.18	0.36	0.11	0.18
TMN	0.14	0.19	-0.30	-0.51	-0.32	-0.26	1.00	0.97	-0.10	-0.05	-0.26	-0.32	-0.23	-0.13
LN	0.12	0.18	-0.33	-0.51	-0.29	-0.23	0.97	1.00	-0.01	0.02	-0.23	-0.31	-0.19	-0.10
THg	0.10	0.20	0.08	0.24	0.38	0.38	-0.10	-0.01	1.00	0.99	-0.09	0.14	-0.29	0.06
LN	0.06	0.18	0.10	0.25	0.36	0.37	-0.05	0.02	0.99	1.00	-0.10	0.10	-0.35	-0.03
MeHg	-0.09	-0.06	-0.06	0.07	0.13	0.18	-0.26	-0.23	-0.09	-0.10	1.00	0.91	0.79	0.48
LN	0.08	0.11	-0.05	0.12	0.31	0.36	-0.32	-0.31	0.14	0.10	0.91	1.00	0.67	0.49
%MeHg	0.11	0.12	-0.09	0.00	0.07	0.11	-0.23	-0.19	-0.29	-0.35	0.79	0.67	1.00	0.66
LN	-0.03	0.07	0.09	0.08	0.12	0.18	-0.13	-0.10	0.06	-0.03	0.48	0.49	0.66	1.00

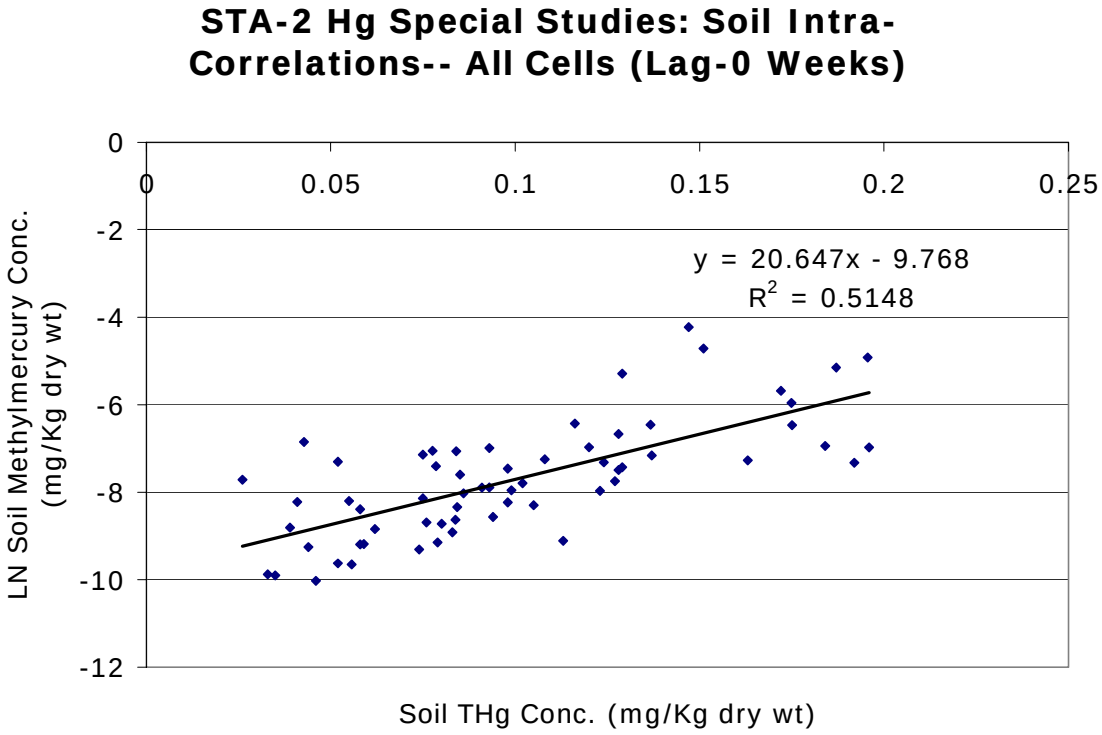

Figure 94. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil total mercury (THg) concentration (mg/kg dry wt) for all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

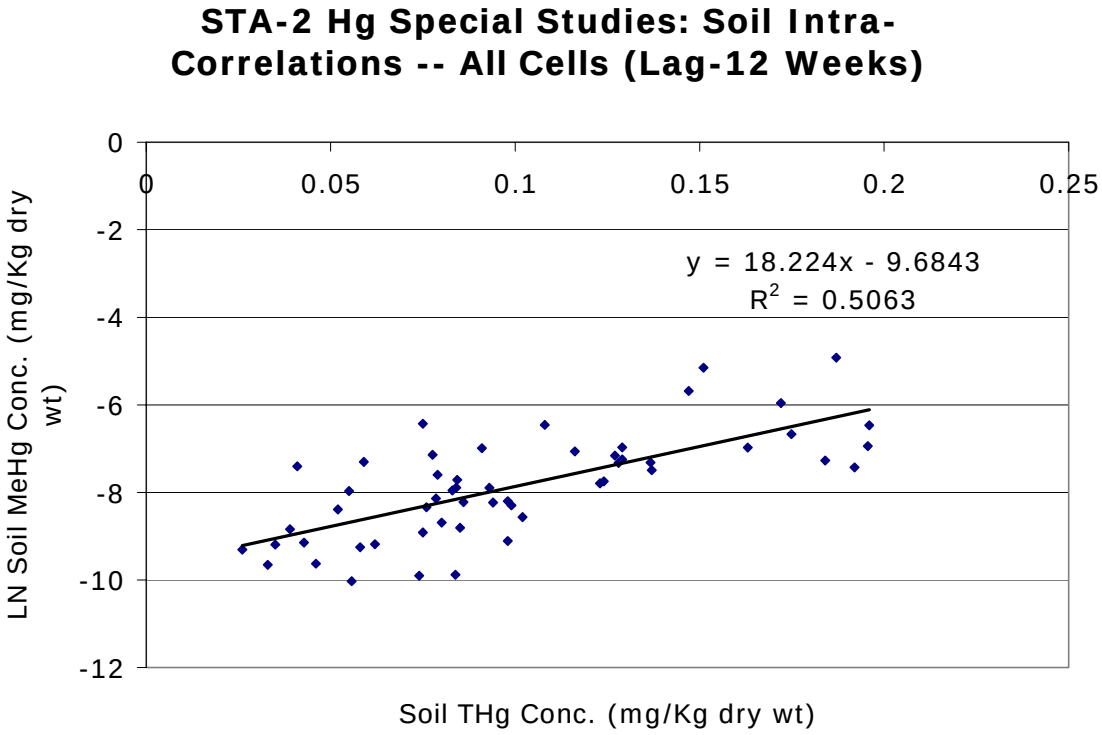

Figure 95. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil total mercury (THg) concentration (mg/kg dry wt) for all cells combined and Lag-12 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

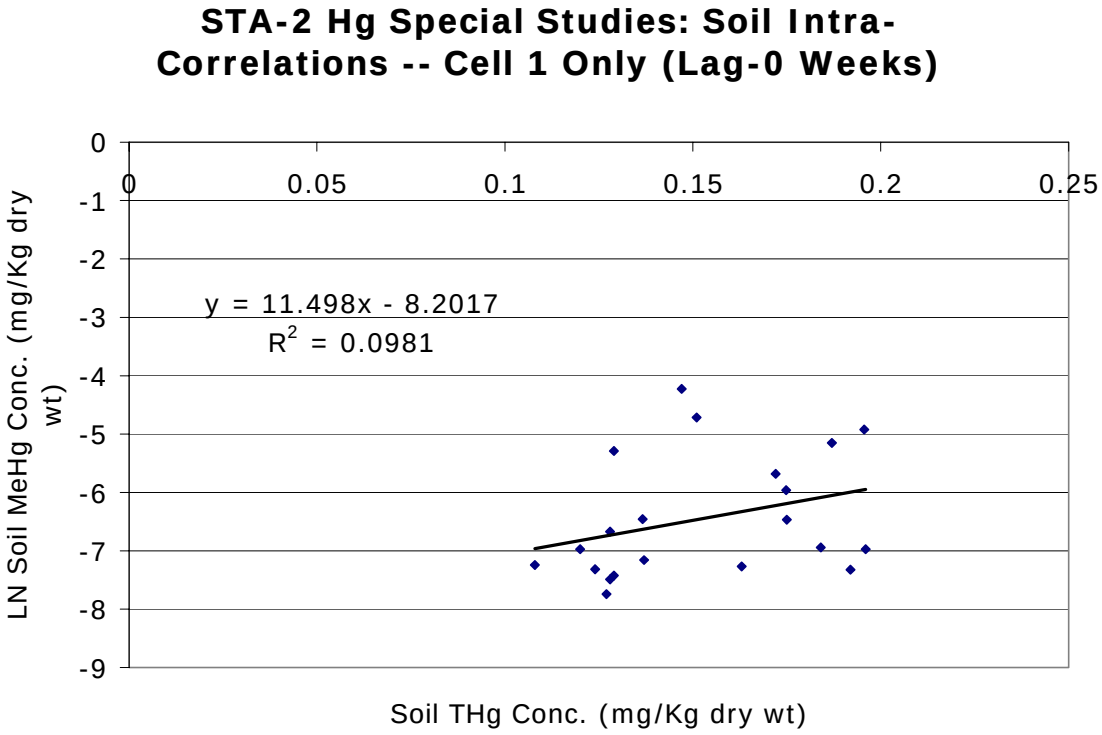

Figure 96. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil total mercury (THg) concentration (mg/kg dry wt) for Cell 1 only and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

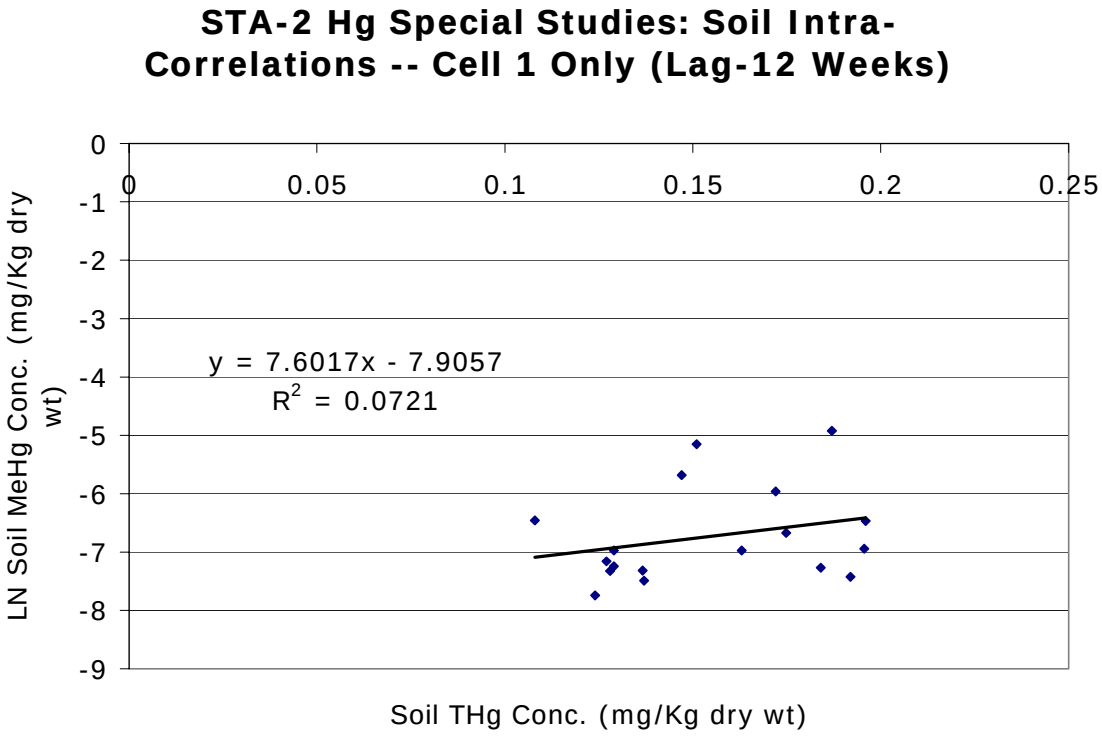

Figure 97. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil total mercury (THg) concentration (mg/kg dry wt) for Cell 1 only and Lag-12 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

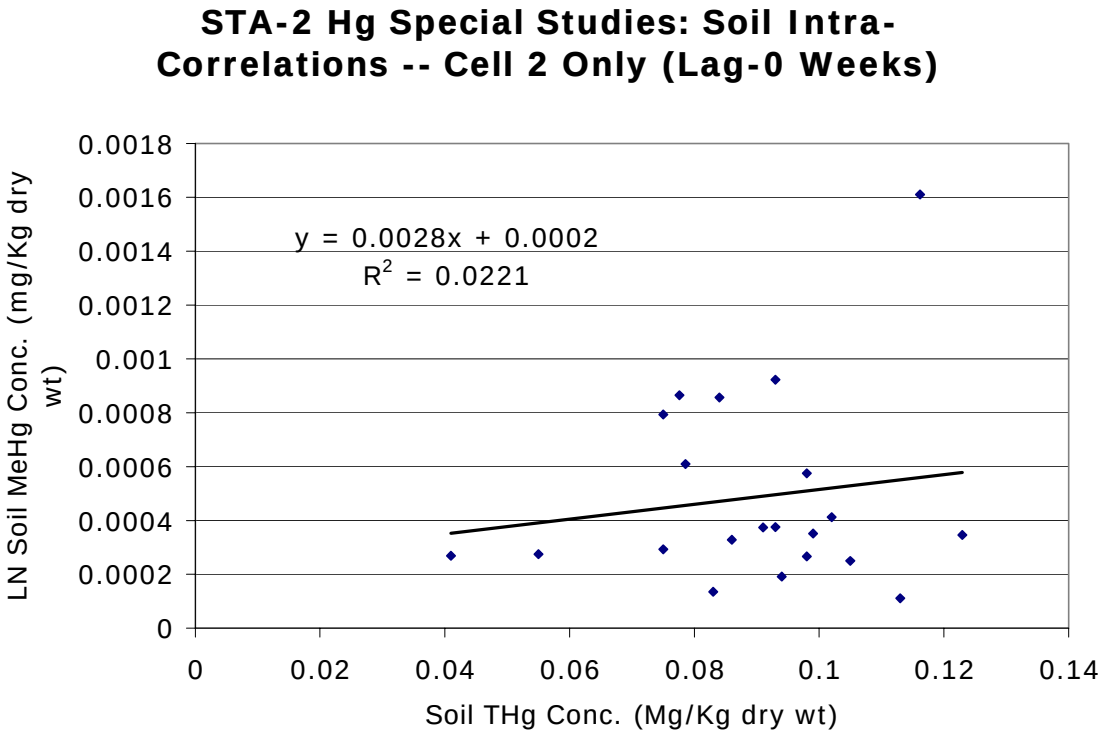

Figure 98. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil total mercury (THg) concentration (mg/kg dry wt) for Cell 2 only and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

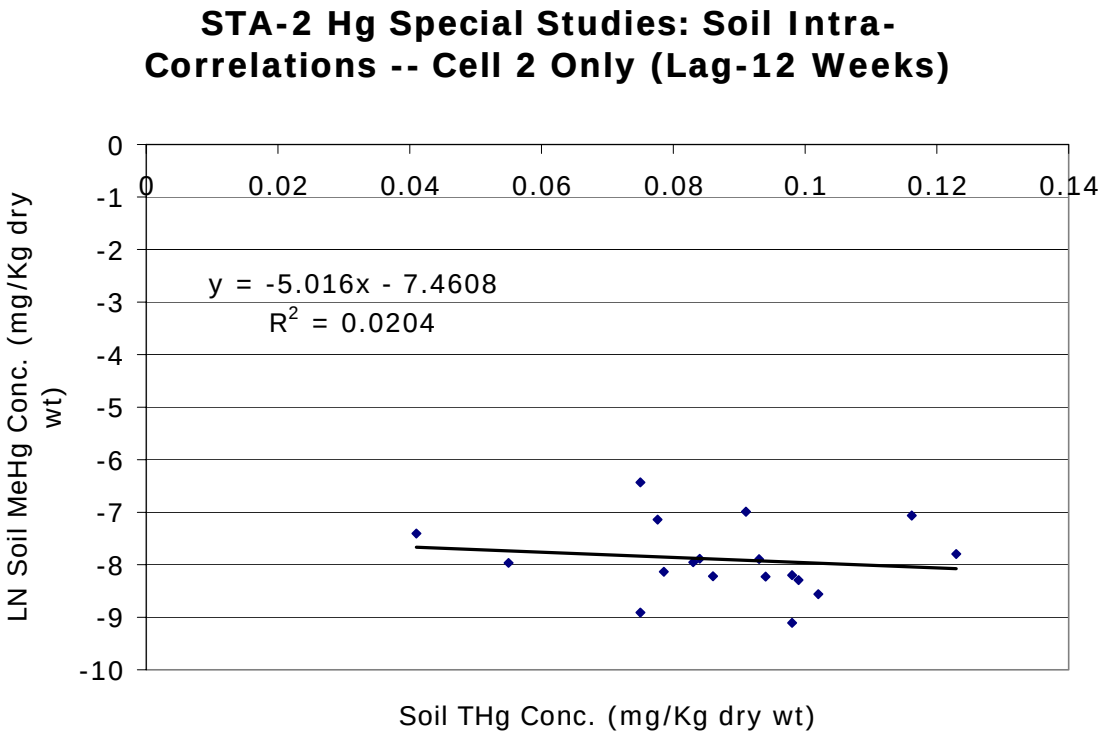

Figure 99. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil total mercury (THg) concentration (mg/kg dry wt) for Cell 2 only and Lag-12 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

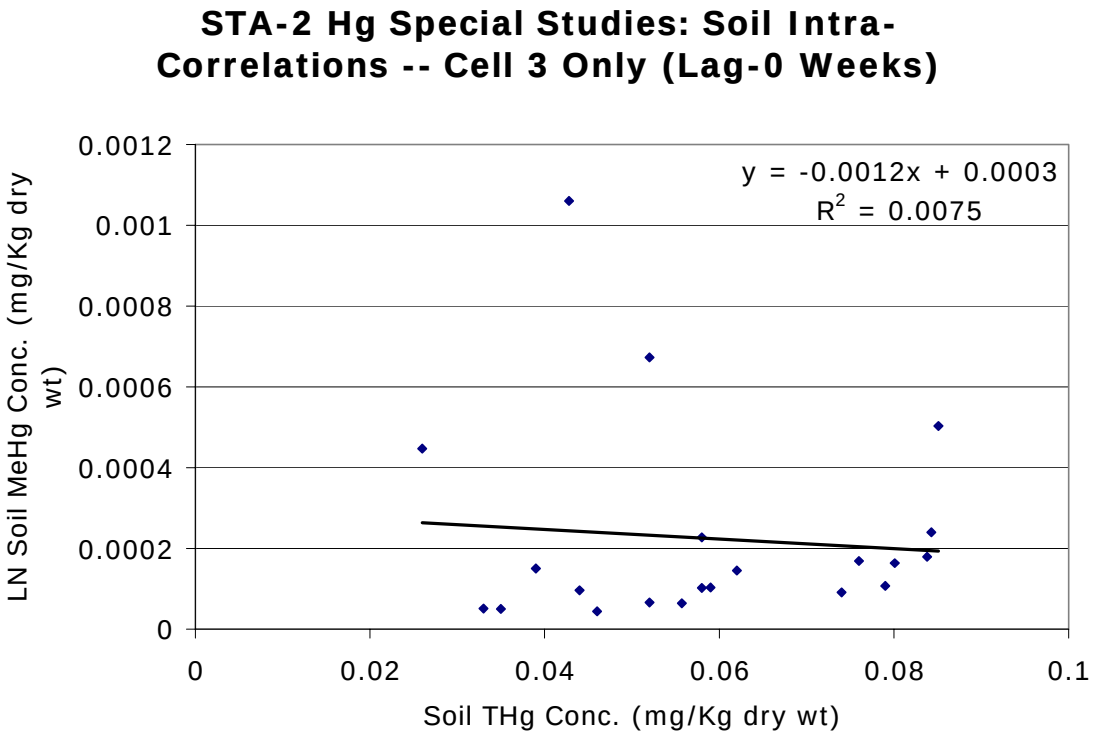

Figure 100. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil total mercury (THg) concentration (mg/kg dry wt) for Cell 3 only and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

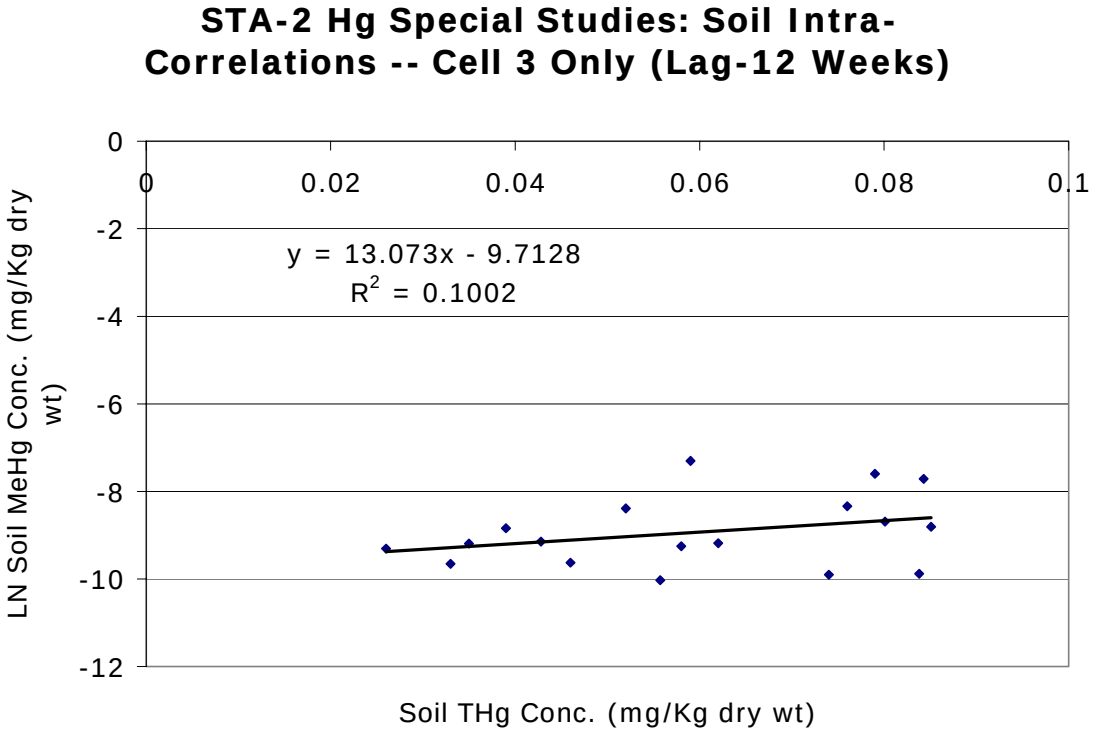

Figure 101. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil total mercury (THg) concentration (mg/kg dry wt) for Cell 3 only and Lag-12 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

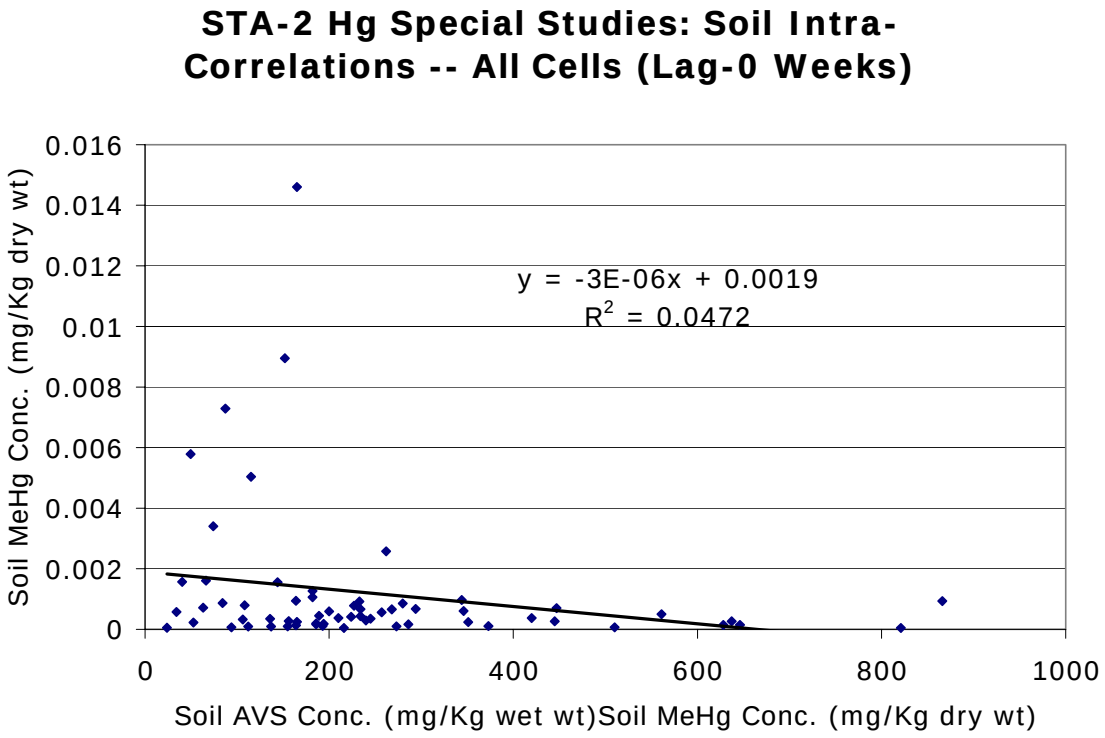

Figure 102. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil acid volatile sulfide (AVS) concentration (mg/kg dry wt) for all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

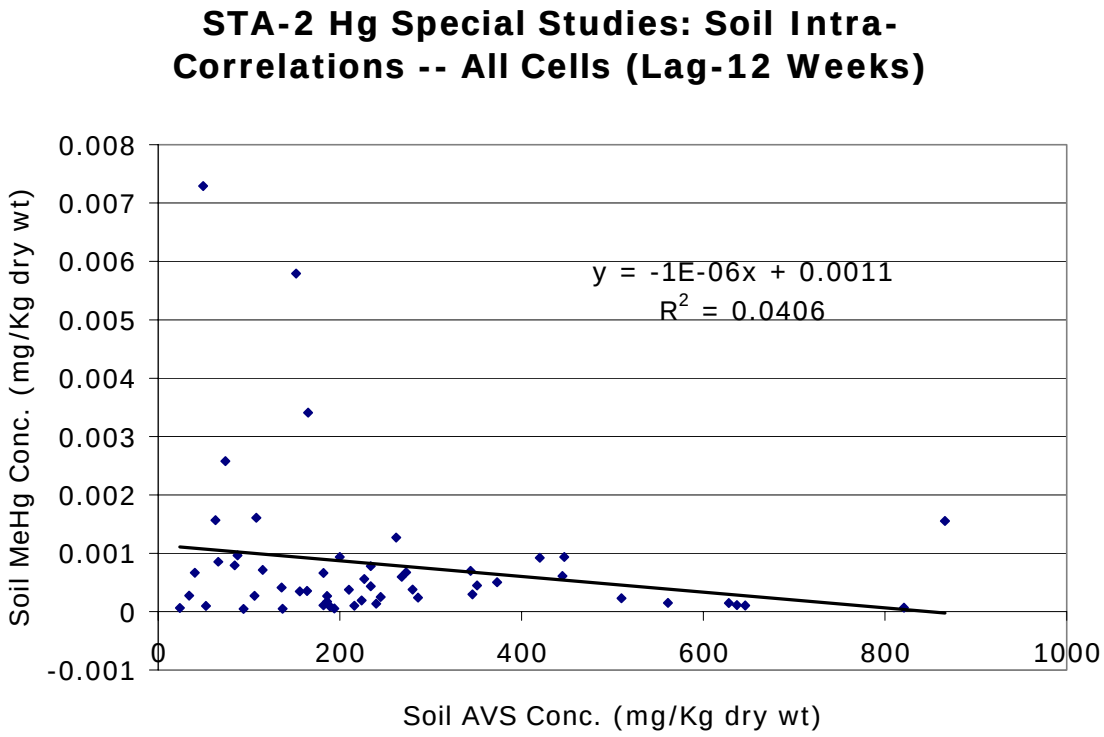

Figure 103. Scatter plot of soil methylmercury (MeHg) concentration (mg/kg dry wt) and soil acid volatile sulfide (AVS) concentration (mg/kg dry wt) for all cells combined and Lag-12 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

No Lag/No Average Correlation Analysis

Cell 1 Only

Soil THg and MeHg were most strongly positively correlated with bulk density ($r = 0.39$; $p < 0.05$ and $r = 0.59$; $p < 0.001$, respectively). Weak to moderate inverse correlations for THg were observed with Ca ($r = -0.38$; $p < 0.05$) and TN ($r = -0.38$; $p < 0.05$), while those for MeHg were with AVS ($r = -0.48$; $p < 0.01$), Ca ($r = -0.49$: $p < 0.01$), percent ash ($r = -0.52$; $p < 0.01$), TP ($r = -0.37$; $p < 0.05$), TS ($r = -0.40$; $p < 0.05$) and percent moisture ($r = -0.63$; $p < 0.001$), but not TFe.

Cell 2 Only

Soil THg was not positively correlated with any other soil constituent, while soil MeHg was weakly, albeit statistically significantly positively correlated with TFe ($r = 0.48$; $p <0.01$). The only moderate to strong, statistically significant inverse correlation for THg was with percent ash ($r = -0.50$; $p < 0.01$). MeHg was moderately to strongly inversely correlated with AVS ($r = -0.41$; $p < 0.05$).

Cell 3 Only

For soil THg, the strongest, statistically significant positive and inverse correlations were with soil TN ($r = 0.41$; $p < 0.05$) and percent ash ($r = -0.37$; $p < 0.05$). For MeHg, the strongest statistically significant positive correlation was with TFe ($r = 0.44$; $p < 0.05$), while the strongest inverse correlations were with Ca ($r = -0.69$; $p < 0.001$), Mg ($r = -0.45$; $p < 0.05$), percent ash ($r = -0.55$; $p < 0.01$), and TP ($r = -0.41$; $p < 0.05$).

Cell 1 Individual Sites

C1AA

Soil THg was most strongly positively linearly correlated with soil TFe (r = 0.61), while MeHg was most strongly positively correlated with TN (r = 0.48) but not at the 95th percentile of statistical confidence. The strongest inverse correlation for MeHg was with soil moisture content (r = -0.61) and AVS (r = -0.53), although not statistically significantly so. There were no inverse correlations between soil THg and any other soil constituent.

Lag Correlation Analyses

The strongest Lag-0 positive and inverse correlates with soil MeHg weakened substantially with Lag-12, -24, and -36 weeks. An inverse relationship between soil THg and total nitrogen emerged at lag-12 weeks (r = -0.707; p = 0.07055) and with calcium at lag-24 weeks (r = -0.772; p = 0.105) but switched to strongly positive with calcium at lag-36 weeks (r = 0.996), albeit with only five observations. The weak inverse influence of soil AVS on MeHg did not increase substantially with these lags. The inverse relationship between soil MeHg peaked at lag-24 weeks with calcium (r = -0.663; p = 0.152) and manganese (r = -692; p = 0.128).

C1BB

No Lag/No Average Correlation Analysis

Soil THg was most strongly positively linearly correlated with soil bulk density (r = 0.707). At Site C1BB, MeHg was not strongly positively correlated with any soil constituents. The strongest inverse correlations for THg were with soil moisture content (r = -0.757), ash (r = -0.589), and total iron (r = -0.549), while those for MeHg were percent ash (r = -0.785), total phosphate (r = -0.719), total iron (r = -0.688), and total manganese (r = -0.662). The switch from a moderately positive to moderately inverse correlation between soil THg and iron between Sites C1AA and C1BB may have been related to a change in the average redox potential along the nutrient gradient in Cell 1.

Lag Correlation Analyses

At Lag-12 weeks, the strong positive Lag-0 weeks correlation between soil bulk density and THg disappeared, but a moderate positive correlation with MeHg emerged (r = 0.617; p = 0.14). Moderate to strong inverse correlations also emerged between THg and acid volatile sulfide (r = -0.674; p = 0.0966) and calcium (r = -0.653; p = 0.112). A strong inverse correlation emerged between soil moisture content and MeHg (r = -0.847), but the Lag-0 weeks inverse correlations with ash, phosphorus, iron, and manganese all weakened substantially. The Lag-12 weeks relationship between soil MeHg and acid volatile sulfide was nonexistent.

At Lag-24 weeks, the moderate to strong Lag-12 weeks inverse correlation between THg and acid volatile sulfide switched to weakly positive, while that with calcium became moderately to strongly positive (r = 0.64 ; p = 0.165). The moderate Lag-0 weeks inverse correlations between THg and ash (r = -0.535; p = 0.275) and iron (r = -0.455; p = 0.365) reemerged at Lag-24 weeks, albeit as statistically insignificant relationships. A moderate inverse correlation between THg and manganese also emerged at Lag-24 weeks (r = -0.548; p = 0.26). For MeHg at Lag-24 weeks, the strong Lag-0 weeks inverse relationship with soil ash content reemerged as a moderate inverse relationship (r = -0.695; p = 0.125). The inverse correlation between MeHg and soil moisture

weakened moderately, while a strong inverse correlation with soil iron emerged (r = -0.748; p =0.0875). The Lag-24 weeks relationship between soil MeHg and acid volatile sulfide was virtually nonexistent to extremely weakly negative.

At Lag-36 weeks, a strong positive relationship emerged between THg and soil total nitrogen (r = 0.778; p = 0.122), while a moderate positive, albeit statistically insignificant correlation (re)emerged with manganese (r = 0.52; p = 0.369). A new moderate positive relationship between MeHg and soil total nitrogen emerged (r = 0.522; p = 0.367). A strong inverse relationship between soil moisture and THg reemerged (r = -0.756; p = 0.139) and that with MeHg strengthened (r = -0.72; p = 0.17). The moderate inverse relationship between THg and calcium (r = -0.505; p = 0.385) and acid volatile sulfide (r = -0.566; p = 0.32) remerged, while that with iron weakened substantially. The Lag-24 weeks relationship between soil MeHg and acid volatile sulfide was extremely weakly positive.

C1CC

No Lag/No Average Correlation Analysis

There were no statistically significant positive correlations between THg and any other soil constituent, while MeHg is most strongly positively correlated with bulk density (r = 0.767). The strongest statistically significant inverse correlations for MeHg were with soil moisture content (r = -0.638), acid volatile sulfide (r = -0.623; p = 0.0542); total phosphorus (r = -0.574; p = 0.0826), and total sulfur (r = -0.542; p = 0.105). There were no statistically significant inverse correlations between soil THg and any other soil constituent.

Lag Correlation Analyses

At Lag-12 weeks at Site C1CC, there were no moderate or strong positive correlations between THg or MeHg and any other soil constituent. There were no moderate to strong inverse relationships between soil THg and any other soil constituent. Unlike the other sites, the moderate to strong inverse relationships between soil MeHg and acid volatile sulfide, sulfur, phosphorus, and moisture persisted and strengthened.

Loads x Loads

SURFACE WATER X SURFACE WATER

No Lag/No Average Correlation Analysis

STA-2 All Cells

As summarized in **Table 41**, for MeHg the strongest positive intra-correlation between the quarterly net mass import was with THg (r = 0.72), followed by DOC (r = 0.48) and TKN (r = 0.44), while for THg it was Ca (r = 0.88), followed by TKN (r = 0.84), DOC (r = 0.83) and TP (r = 0.83). The moderate and strong inter-correlations between MeHg or THg net mass import and the other surface water constituents for all STA-2 cells combined are depicted in **Figures 104** through **119**.

Cell 1 Only

An inspection of **Table 42** reveals that, as with STA-2 as a whole, for MeHg the strongest positive intra-correlation between the quarterly net mass import via surface water was with THg ($r = 0.90$), followed by TKN ($r = 0.41$), while for THg it was NH_3 ($r = 0.61$), followed by Ca ($r = 0.59$), and TKN ($r = 0.53$). Unlike STA-2 as a whole, some strong inverse correlations emerge for MeHg with Cl^- ($r = -0.55$) and sulfate ($r = -0.44$), while that for THg was sulfate ($r = -0.69$).

Cell 2 Only

A review of the data summarized in **Table 43** indicates that MeHg and THg net surface water imports were moderately to very strongly correlated to all of the other constituents for which mass budgets could be calculated. The intra-correlation between THg and MeHg was $r = 0.96$, much stronger than for STA-2 as a whole and even stronger than for Cell 1 only.

Cell 3 Only

Based on the results summarized in **Table 44**, all of the correlations for MeHg and THg further strengthened relative to Cell 2, with the exception of chloride, which remained virtually unchanged or weakened marginally.

Tables 41 and **42.**

Intra-correlation between surface water mass budget net import by quarter for STA-2

	TP	TKN	NOX	NH3	TCA	SO4	DOC	CL	THg	MeHg
TP	1.00	0.96	0.84	0.95	0.97	0.57	0.90	0.40	0.83	0.38
TKN	0.96	1.00	0.78	0.86	0.98	0.74	0.98	0.36	0.84	0.44
NOX	0.84	0.78	1.00	0.81	0.86	0.43	0.74	0.57	0.79	0.19
NH3	0.95	0.86	0.81	1.00	0.86	0.31	0.75	0.41	0.77	0.31
CA	0.97	0.98	0.86	0.86	1.00	0.72	0.97	0.44	0.88	0.43
SO4	0.57	0.74	0.43	0.31	0.72	1.00	0.85	0.25	0.53	0.34
DOC	0.90	0.98	0.74	0.75	0.97	0.85	1.00	0.33	0.83	0.48
CL	0.40	0.36	0.57	0.41	0.44	0.25	0.33	1.00	0.39	-0.11
THg	0.83	0.84	0.79	0.77	0.88	0.53	0.83	0.39	1.00	0.72
MeHg	0.38	0.44	0.19	0.31	0.43	0.34	0.48	-0.11	0.72	1.00

Intra-correlation between surface water mass budget net import by quarter for STA-2 Cell 1

	TP	TKN	NOX	NH3	TCA	SO4	DOC	CL	THg	MeHg
TP	1.00	0.97	0.74	0.96	0.79	-0.85	-0.38	-0.19	0.49	0.29
TKN	0.97	1.00	0.56	0.91	0.71	-0.78	-0.20	-0.40	0.53	0.41
NOX	0.74	0.56	1.00	0.74	0.85	-0.71	-0.68	0.51	0.27	-0.12
NH3	0.96	0.91	0.74	1.00	0.78	-0.96	-0.57	-0.11	0.61	0.38
CA	0.79	0.71	0.85	0.78	1.00	-0.72	-0.38	0.26	0.59	0.25
SO4	-0.85	-0.78	-0.71	-0.96	-0.72	1.00	0.71	0.00	-0.69	-0.44
DOC	-0.38	-0.20	-0.68	-0.57	-0.38	0.71	1.00	-0.51	-0.28	0.00
CL	-0.19	-0.40	0.51	-0.11	0.26	0.00	-0.51	1.00	-0.21	-0.55
THg	0.49	0.53	0.27	0.61	0.59	-0.69	-0.28	-0.21	1.00	0.90
MeHg	0.29	0.41	-0.12	0.38	0.25	-0.44	0.00	-0.55	0.90	1.00

Tables 43 and **44.**

Intra-correlation between surface water mass budget net import by quarter for STA-2 Cell 2

	TP	TKN	NOX	NH3	TCA	SO4	DOC	CL	THg	MeHg
TP	1.00	0.99	0.89	0.99	0.99	0.98	0.99	0.50	0.89	0.88
TKN	0.99	1.00	0.88	0.99	0.99	0.97	1.00	0.48	0.89	0.91
NOX	0.89	0.88	1.00	0.86	0.94	0.93	0.91	0.75	0.98	0.90
NH3	0.99	0.99	0.86	1.00	0.98	0.96	0.99	0.48	0.89	0.92
CA	0.99	0.99	0.94	0.98	1.00	0.98	0.99	0.58	0.94	0.93
SO4	0.98	0.97	0.93	0.96	0.98	1.00	0.98	0.63	0.92	0.87
DOC	0.99	1.00	0.91	0.99	0.99	0.98	1.00	0.51	0.91	0.91
CL	0.50	0.48	0.75	0.48	0.58	0.63	0.51	1.00	0.76	0.60
THg	0.89	0.89	0.98	0.89	0.94	0.92	0.91	0.76	1.00	0.96
MeHg	0.88	0.91	0.90	0.92	0.93	0.87	0.91	0.60	0.96	1.00

Intra-correlation between surface water mass budget net import by quarter for STA-2 Cell 3

	TP	TKN	NOX	NH3	TCA	SO4	DOC	CL	THg	MeHg
TP	1.00	0.99	0.82	0.99	0.99	0.92	0.98	0.58	0.91	0.96
TKN	0.99	1.00	0.82	0.99	0.98	0.93	0.99	0.55	0.90	0.96
NOX	0.82	0.82	1.00	0.79	0.90	0.90	0.87	0.50	0.97	0.91
NH3	0.99	0.99	0.79	1.00	0.97	0.91	0.98	0.62	0.88	0.96
CA	0.99	0.98	0.90	0.97	1.00	0.95	0.99	0.57	0.96	0.98
SO4	0.92	0.93	0.90	0.91	0.95	1.00	0.96	0.50	0.89	0.90
DOC	0.98	0.99	0.87	0.98	0.99	0.96	1.00	0.52	0.93	0.97
CL	0.58	0.55	0.50	0.62	0.57	0.50	0.52	1.00	0.54	0.54
THg	0.91	0.90	0.97	0.88	0.96	0.89	0.93	0.54	1.00	0.98
MeHg	0.96	0.96	0.91	0.96	0.98	0.90	0.97	0.54	0.98	1.00

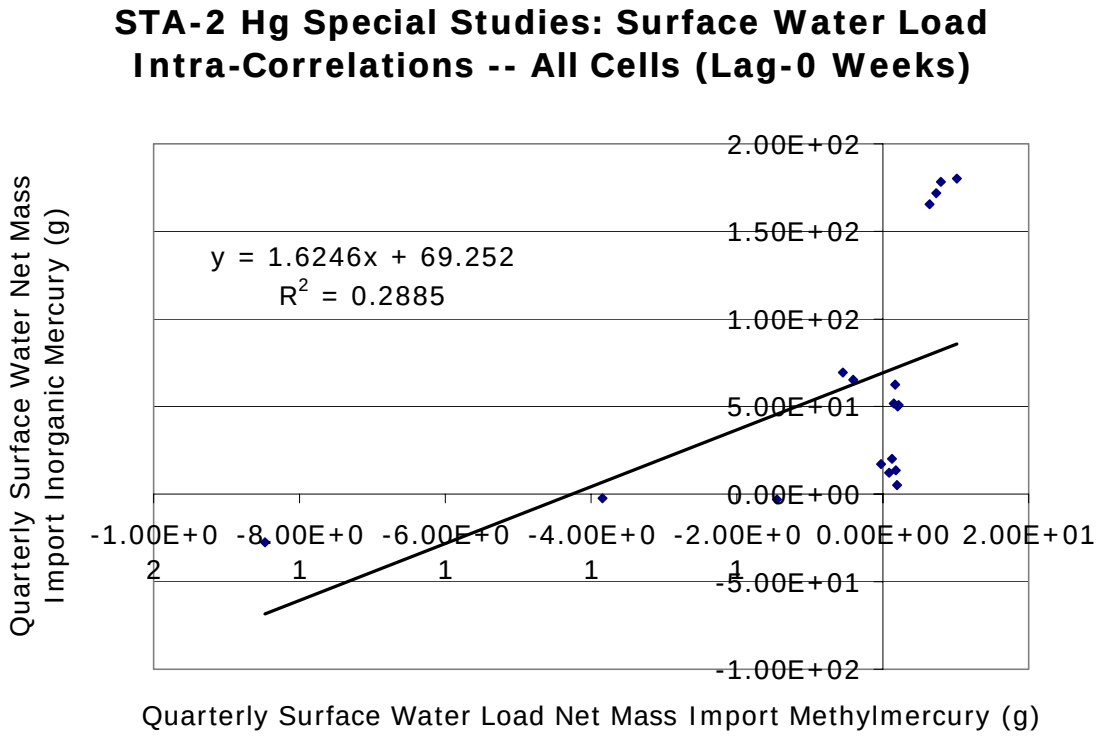

Figure 104. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of methylmercury (MeHg) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

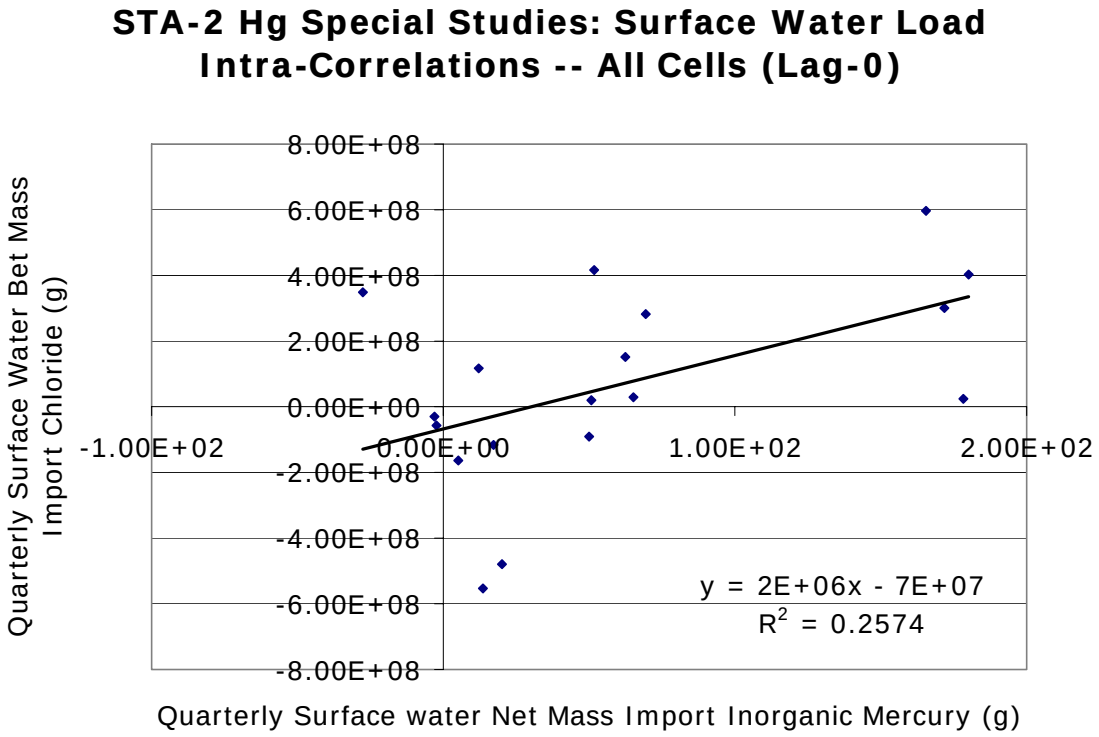

Figure 105. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of chloride (Cl) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

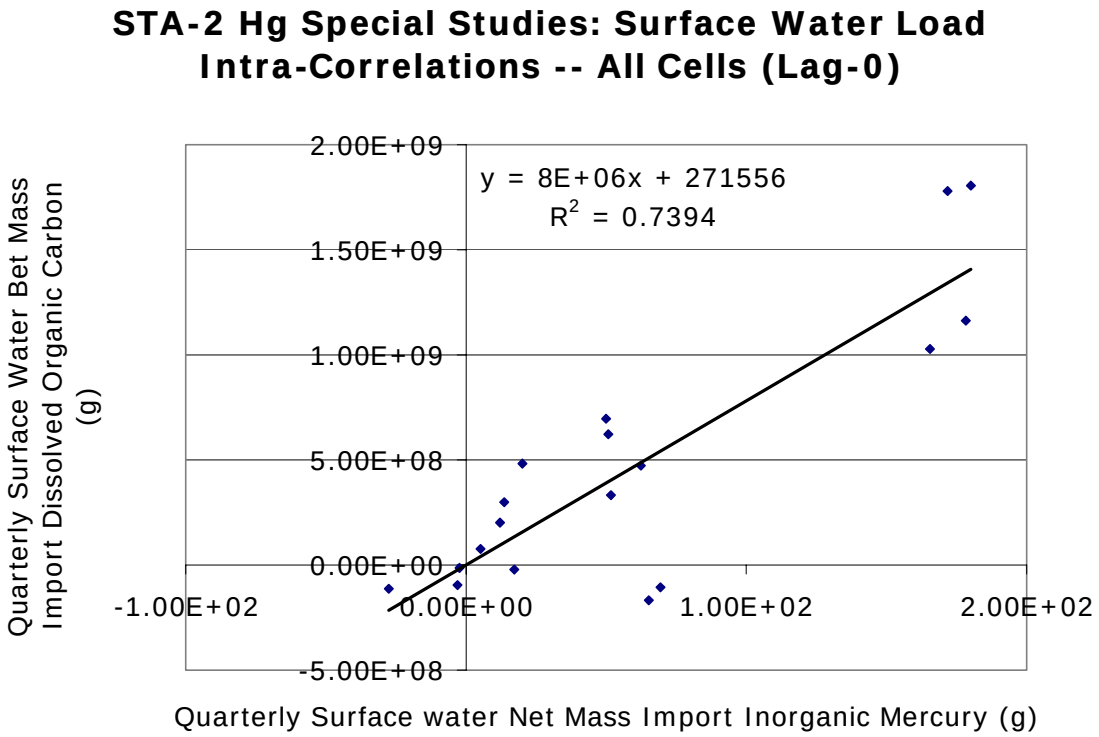

Figure 106. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of dissolved organic carbon (DOC) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

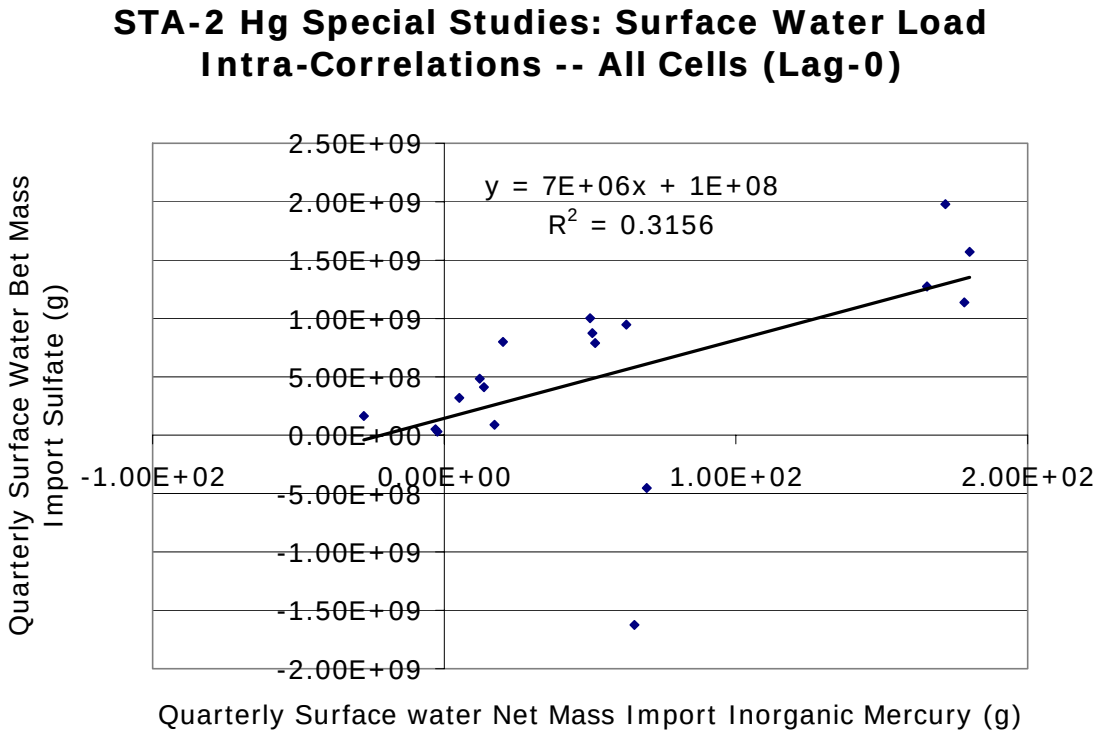

Figure 107. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of sulfate (SO_4^{2-}) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

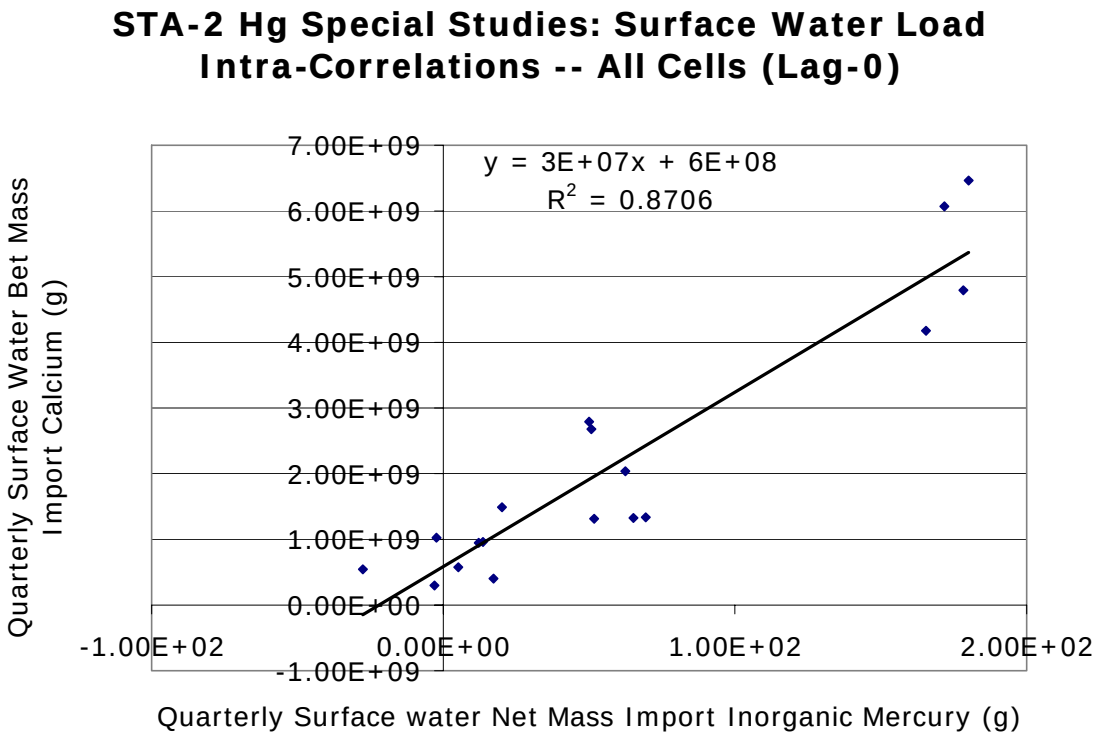

Figure 108. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of calcium (Ca) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

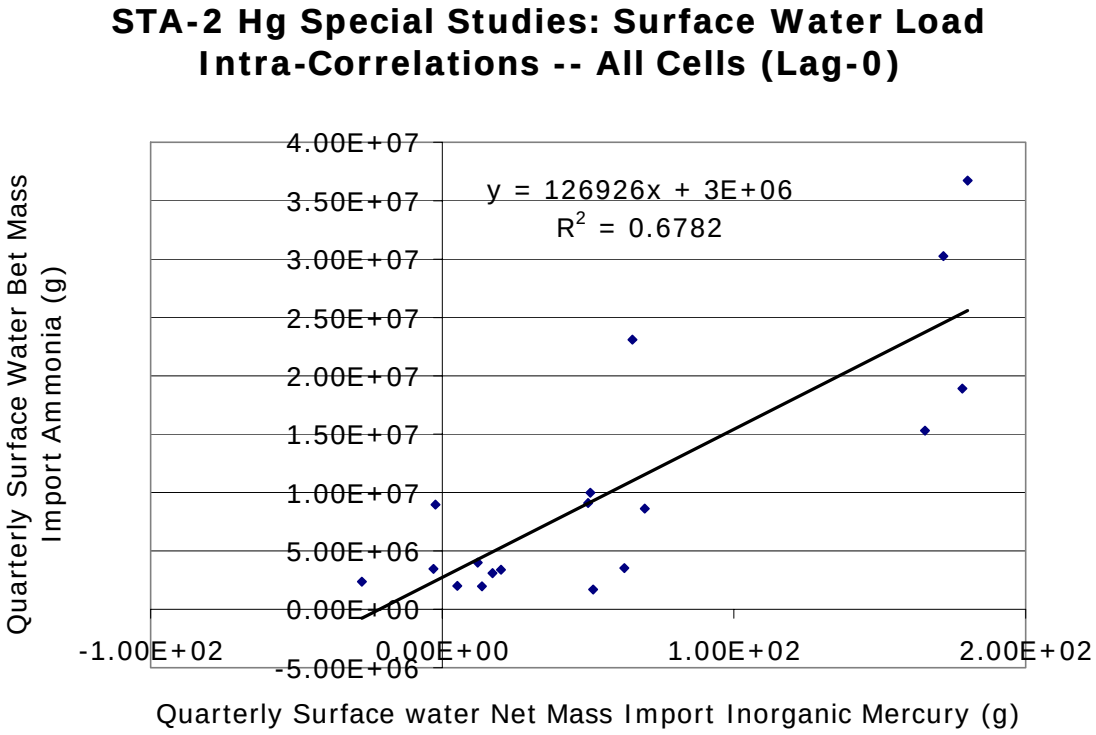

Figure 109. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of ammonia (NH3) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

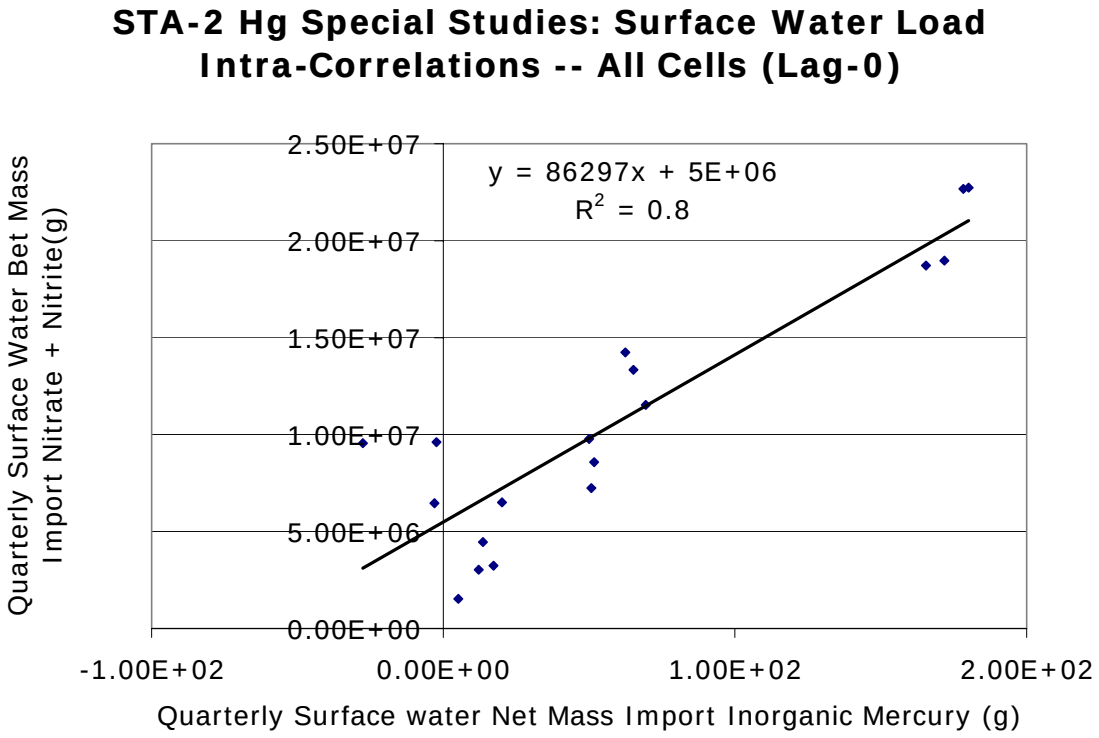

Figure 110. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of nitrate + nitrite (NOx) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

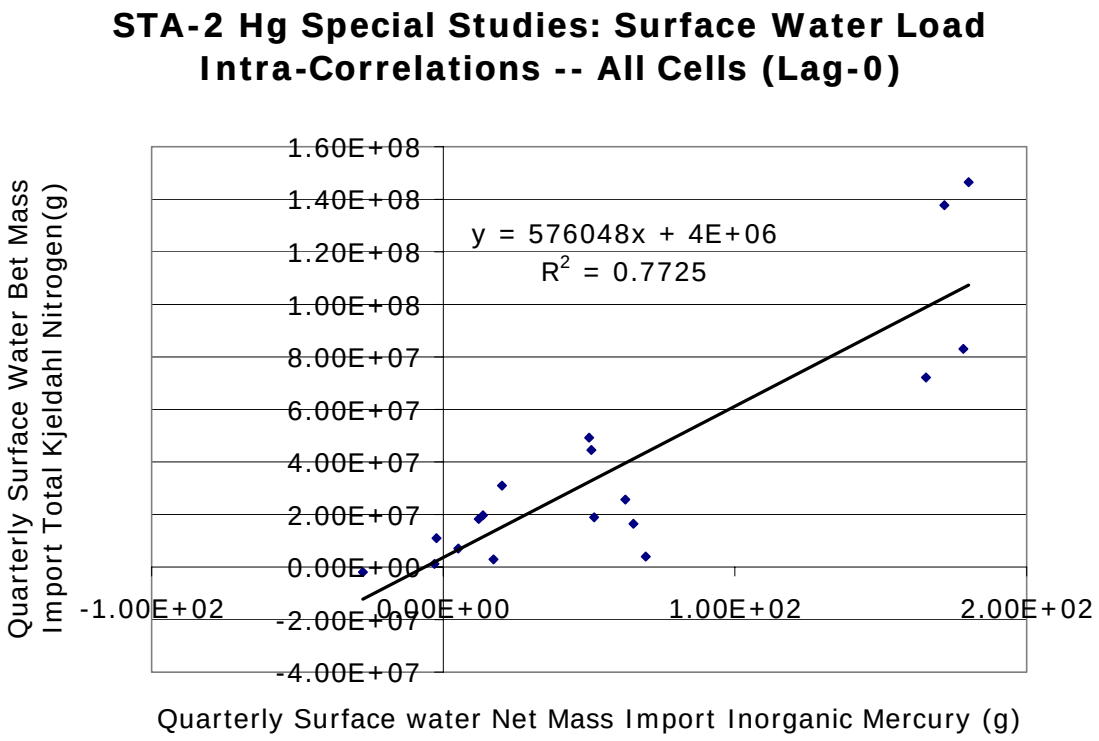

Figure 111. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of total Kjeldahl nitrogen (TKN) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

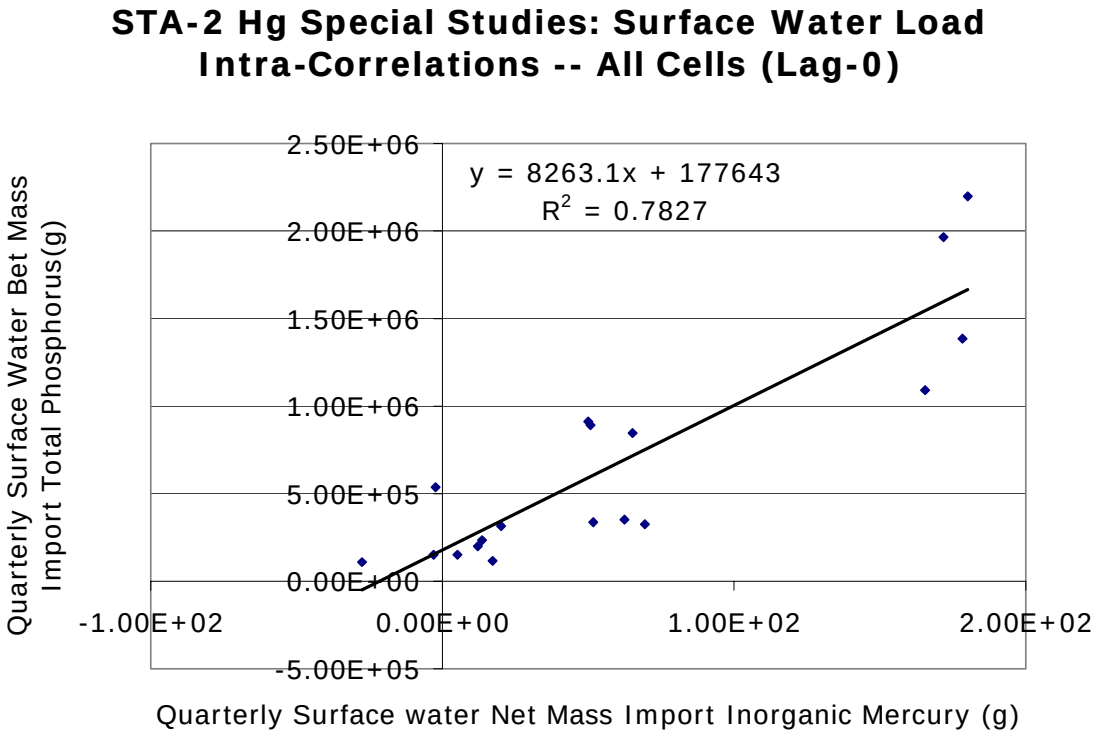

Figure 112. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of total phosphorus (TP and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

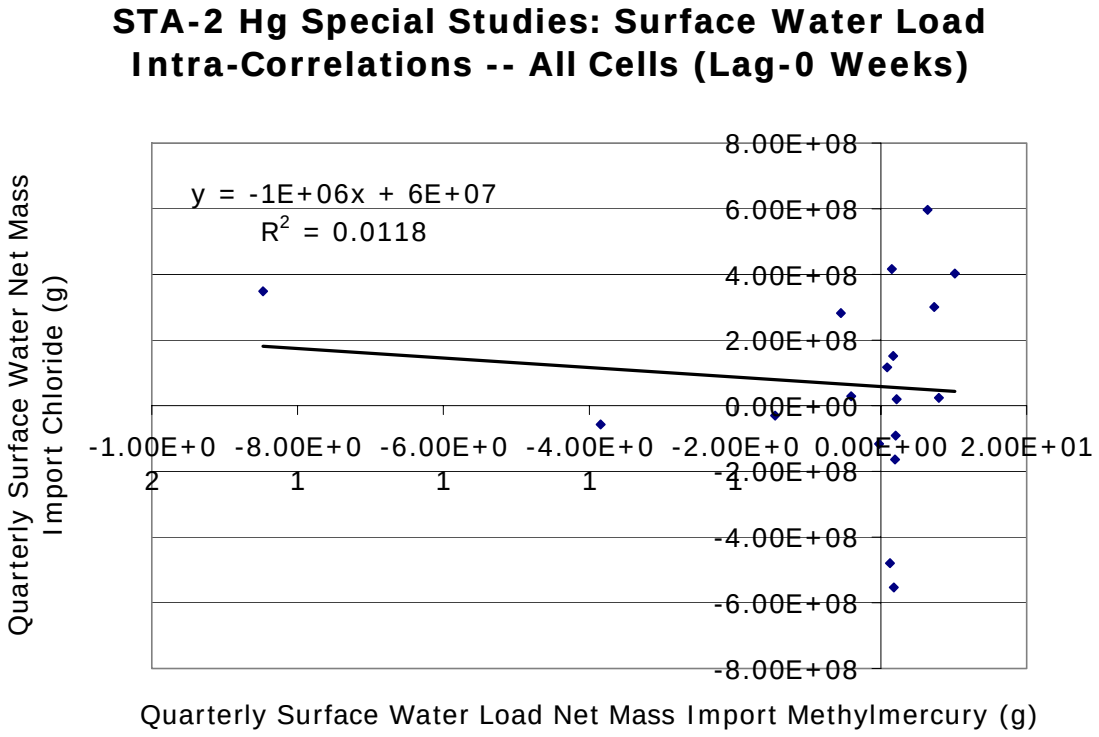

Figure 113. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of chloride (Cl-) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

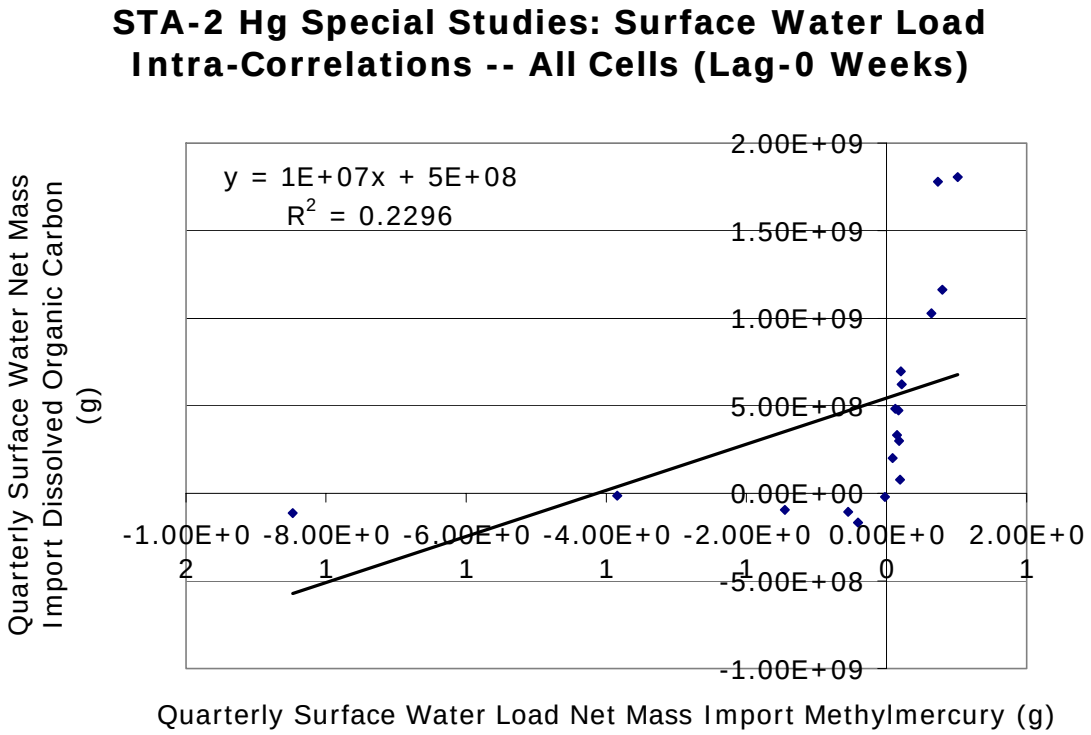

Figure 114. Scatter plot of the quarterly net import of inorganic mercury (Hg(II)) into STA-2 all cells combined and quarterly surface water net mass import of dissolved organic carbon (DOC) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

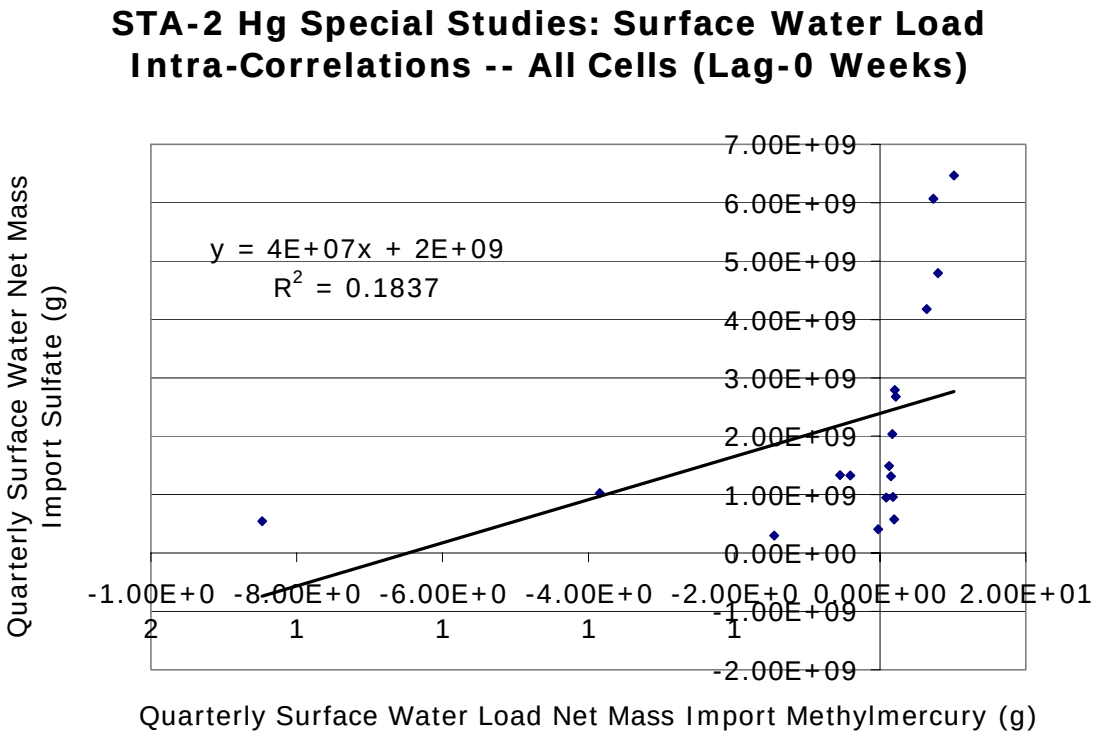

Figure 115. Scatter plot of the quarterly net import of methylmercury (MeHg) into STA-2 all cells combined and quarterly surface water net mass import of sulfate (SO42-) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

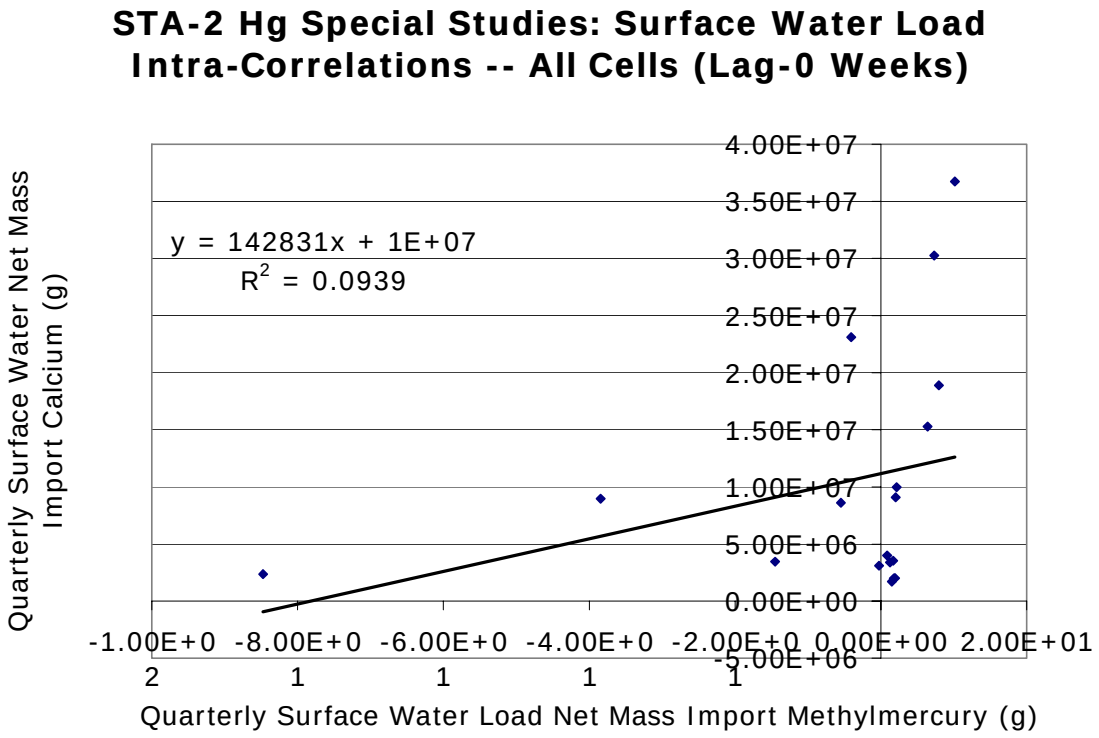

Figure 116. Scatter plot of the quarterly net import of methylmercury (MeHg) into STA-2 all cells combined and quarterly surface water net mass import of calcium (Ca) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

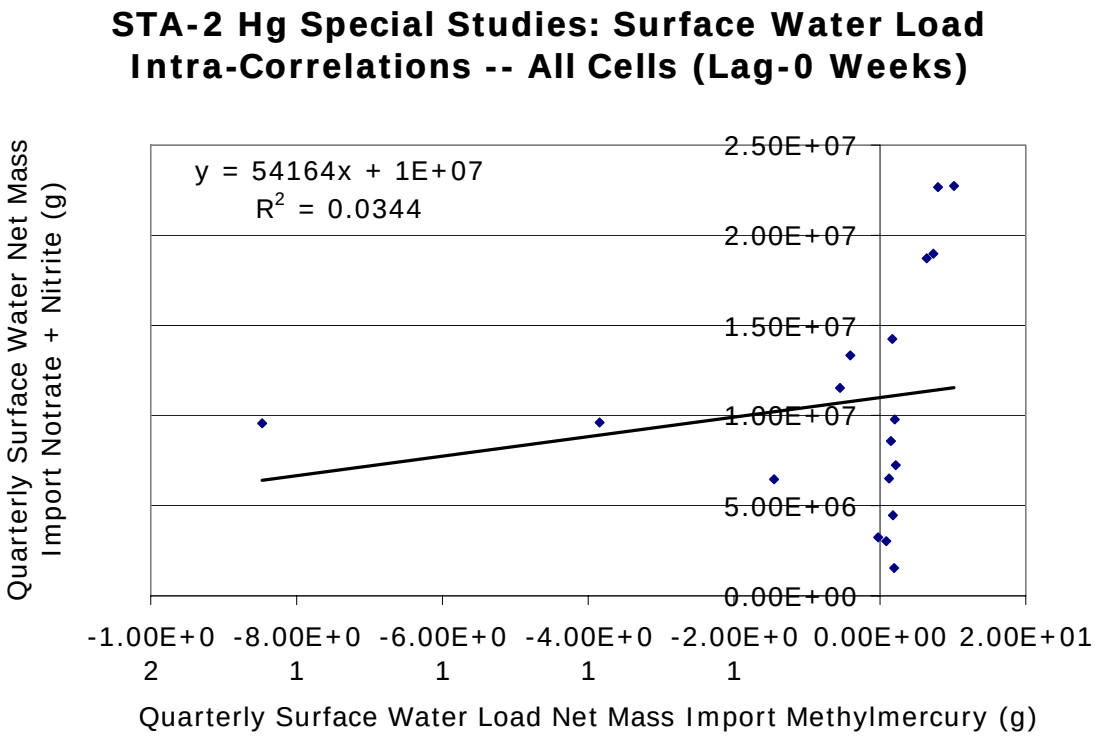

Figure 117. Scatter plot of the quarterly net import of methylmercury (MeHg) into STA-2 all cells combined and quarterly surface water net mass import of Nitrate + Nitrite (NOx) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

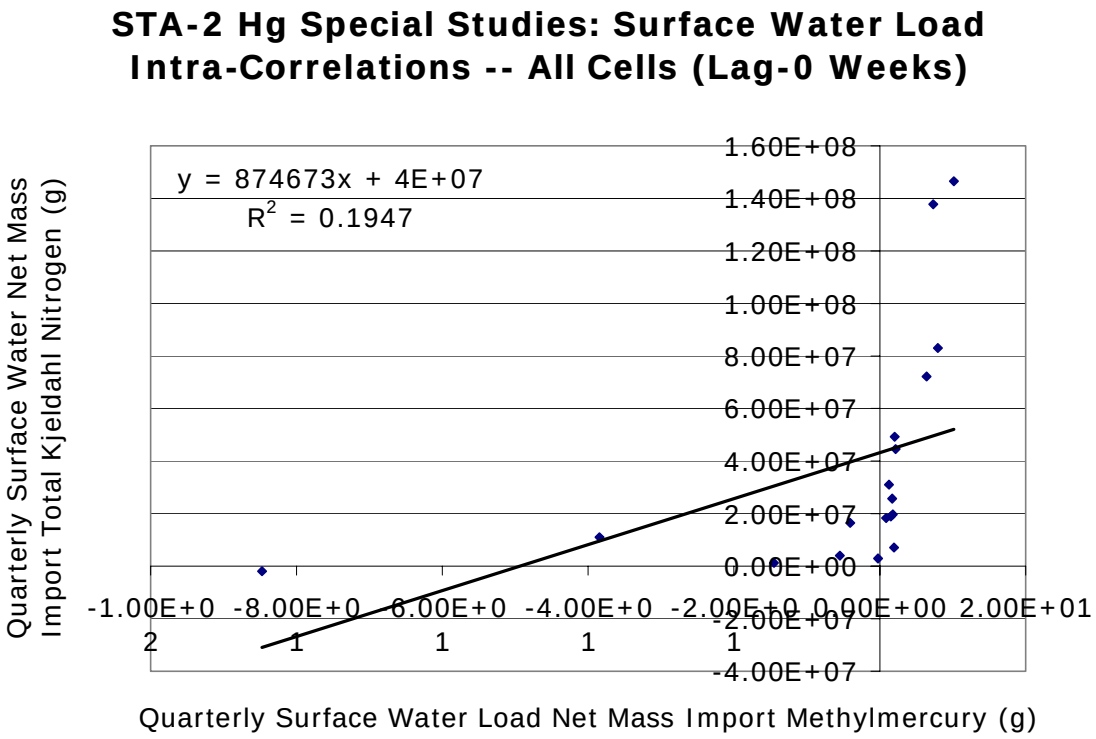

Figure 118. Scatter plot of the quarterly net import of methylmercury (MeHg) into STA-2 all cells combined and quarterly surface water net mass import of total Kjeldahl nitrogen (TKN) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

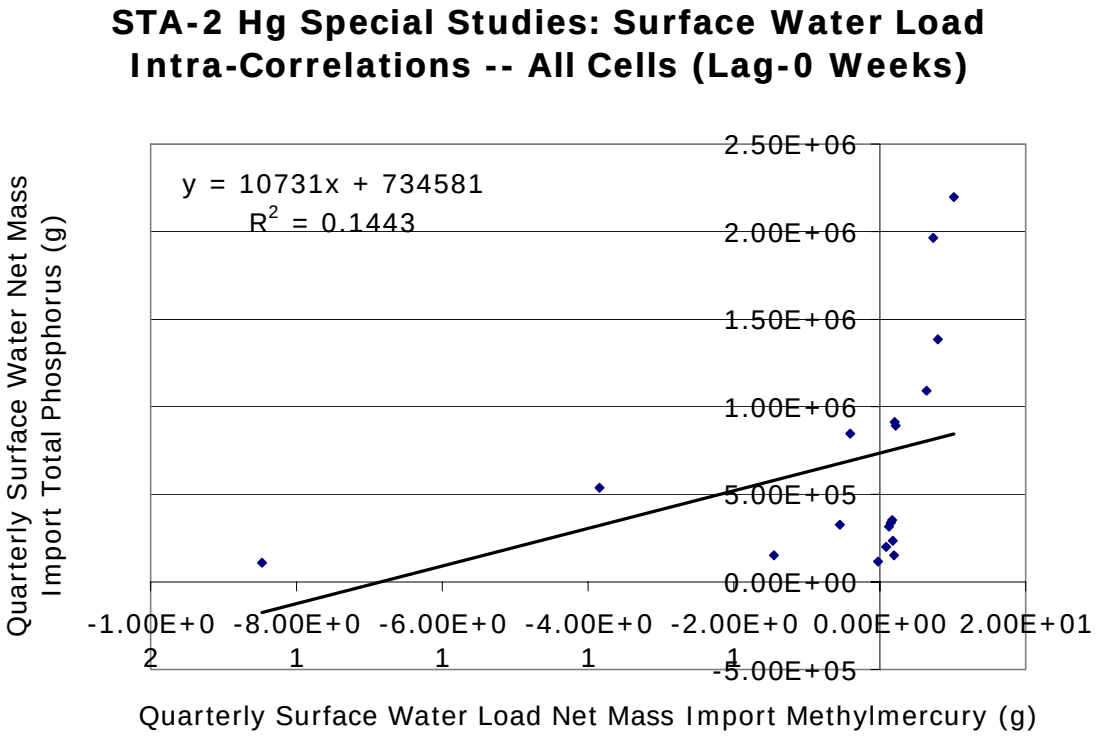

Figure 119. Scatter plot of the quarterly net import of methylmercury (MeHg) into STA-2 all cells combined and quarterly surface water net mass import of total phosphorus (TP) and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

SOIL X SOIL

STA-2 All Cells

As summarized in **Table 45**, the quarterly change in TP soil mass was most strongly positively correlated with the quarterly change in soil Mg or Ca mass (r = 0.84 or 0.79, respectively), TN (r = 0.61; see **Figure 120**) but only weakly to moderately positively correlated with THg (r = 0.61) and not at all with MeHg (r = -0.03). Soil TFe and TMn were strongly intra-correlated (r = 0.79; see **Figure 121**). The quarterly change in soil AVS mass load was weakly to moderately positively correlated with the quarterly change in the soil TS mass load (r = 0.48; see **Figure 122**) but not with TFe (r = -0.03), despite the fact that AVS is believed to be composed primarily of iron sulfide and polysulfide species (C. Gilmour, ANSERC, personal communication).

There were no lag-0 weeks strong positive or inverse parametric intra-correlations with the quarterly change in soil MeHg mass, nor did the correlation increase when inorganic mercury was substituted for THg (**Figure 123**) or lag-12 weeks substituted for lag-0 weeks (**Figure 124**). This was also true of the influence of lag-0 weeks soil AVS (**Figure 125**), which did not increase detectably with a 12 week lag (**Figure 126**). The absence of any substantial correlations may reflect the onset of relatively stable conditions in Cell 1 from a mercury biogeochemistry perspective by November 2002 and the existence of relatively stable conditions in Cells 2 and 3 since mercury start-up criteria were met in September and November 2000, respectively. For THg, the situation was quite different, with the strongest positive correlations in the order TN (r = 0.80), TFe (r = 0.78), TMn (r = 0.75), and TMg or TCa (r = 0.69 or 0.46), and only an extremely weak inverse correlation with AVS (r = -0.17).

Cell 1 Only

Table 46 summarizes the intra-correlations for all possible combinations of the quarterly change in soil constituent mass for Cell 1 only. In contrast to all cells combined, for Cell 1 only MeHg was weakly to moderately positively correlated with TCa (r = 0.58) and TN (r = 0.43) but not THg (r = 0.17) and exhibited moderate to strong inverse relationships with TFe(r = -0.62) and TMn (r = -.050), which were even more strongly intra-correlated (r = 0.97) than for all cells combined, but not with AVS, which was showed an extremely weak positive intra-correlation (r = 0.17). Also unlike all cells combined, THg was most strongly intra-correlated with TP (r = 0.91), followed by TMg or TCa (r = 0.87 or 0.73), which was similar, and TS (r = 0.65), which was absent for all cells combined, while TFe had a moderate to strong influence on all cells combined but was weak for Cell 1 only (r = 0.38).

Cell 2 Only

The intra-correlations for all possible combinations of the quarterly change in soil constituent mass are summarized in **Table 47** for Cell 2 only. In contradistinction to Cell 1, MeHg was moderately to strongly positively rather than inversely correlated with TFe (r = 0.65) and TMn (r = 0.67), while a very weak to weak inverse relationship emerged with AVS (r = -0.33). For THg the positive correlation with TN strengthens (r = 0.93), while that with TP becomes very weakly to weakly inverse (r = -0.29), while a weak to moderate inverse intra-correlation with AVS emerged (r = -0.53). The TFe and TMn intra-correlation strengthened relative to all cells combined and Cell 1 (r = 0.86), as did the inverse relationship between TFe and AVS (r = -0.53). TS and AVS (r = 0.60) was also more strongly intra-correlated than for all cells combined (r = 0.48) and much more so than for Cell 1 only (r = -0.09).

Cell 3 Only

The intra-correlations for Cell 3 only are summarized in **Table 48** for all possible combinations of the quarterly change in soil constituent mass. In general, all positive and inverse correlations with the quarterly change in soil MeHg mass weakened, with the exception of TS ($r = -0.41$), which strengthened substantially. This is in contrast to the weak to moderate positive correlation observed between TS and AVS ($r = 0.54$). This suggests that organic sulfide rather than inorganic sulfide was contributing to the inhibition of MeHg production in Cell 3, while the opposite might be the case for Cell 2. The absence of either a substantial positive or inverse influence of either TS or AVS on Cell 1 the quarterly change MeHg mass stored in surficial soil and the moderate to strong inverse correlations with TFe and TMn suggest that Cell 1 biogeochemistry was distinctly different from Cells 2 and 3. This could be a short-term consequence of the displacement from biogeochemical steady state by the relatively recent oxidation event or a more fundamental and persistent difference in soil chemistry. However, only long-term monitoring, research, and modeling in STA-2 and other STAs will be able to test these hypotheses rigorously.

Table 45.

Intra-correlation between change in soil mass storage for successive quarters for STA-2

	TP	TN	TCA	TMG	TS	AVS	TFE	TMN	THg	MeHg
TP	1.00	0.61	0.79	0.84	0.45	0.18	0.62	0.46	0.51	-0.03
TN	0.61	1.00	0.66	0.83	0.44	0.10	0.75	0.61	0.80	0.24
TCA	0.79	0.66	1.00	0.87	0.06	-0.11	0.56	0.57	0.46	0.18
TMG	0.84	0.83	0.87	1.00	0.32	-0.07	0.76	0.64	0.69	0.10
TS	0.45	0.44	0.06	0.32	1.00	0.48	0.41	0.27	0.41	-0.03
AVS	0.18	0.10	-0.11	-0.07	0.48	1.00	-0.03	-0.20	-0.17	0.04
TFE	0.62	0.75	0.56	0.76	0.41	-0.03	1.00	0.79	0.78	-0.10
TMN	0.46	0.61	0.57	0.64	0.27	-0.20	0.79	1.00	0.75	-0.06
THg	0.51	0.80	0.46	0.69	0.41	-0.17	0.78	0.75	1.00	0.15
MeHg	-0.03	0.24	0.18	0.10	-0.03	0.04	-0.10	-0.06	0.15	1.00

Table 46.

Intra-correlation between change in soil mass storage for successive quarters for STA-2 Cell 1

	TP	TN	TCA	TMG	TS	AVS	TFE	TMN	THg	MeHg
TP	1.00	0.70	0.69	0.88	0.74	-0.52	0.71	0.67	0.91	-0.09
TN	0.70	1.00	0.87	0.91	0.70	0.04	0.10	0.15	0.85	0.43
TCA	0.69	0.87	1.00	0.90	0.55	-0.34	0.20	0.32	0.73	0.58
TMG	0.88	0.91	0.90	1.00	0.69	-0.35	0.48	0.55	0.87	0.20
TS	0.74	0.70	0.55	0.69	1.00	-0.09	0.37	0.27	0.65	0.02
AVS	-0.52	0.04	-0.34	-0.35	-0.09	1.00	-0.78	-0.82	-0.21	0.17
TFE	0.71	0.10	0.20	0.48	0.37	-0.78	1.00	0.97	0.38	-0.62
TMN	0.67	0.15	0.32	0.55	0.27	-0.82	0.97	1.00	0.36	-0.50
THg	0.91	0.85	0.73	0.87	0.65	-0.21	0.38	0.36	1.00	0.15
MeHg	-0.09	0.43	0.58	0.20	0.02	0.17	-0.62	-0.50	0.15	1.00

Table 47.

Intra-correlation between change in soil mass storage for successive quarters for STA-2 Cell 2

	TP	TN	TCA	TMG	TS	AVS	TFE	TMN	THg	MeHg
TP	1.00	-0.23	-0.12	-0.22	0.62	0.58	-0.44	-0.25	-0.29	-0.04
TN	-0.23	1.00	0.87	0.96	0.18	-0.52	0.84	0.87	0.93	0.46
TCA	-0.12	0.87	1.00	0.94	0.03	-0.60	0.49	0.58	0.70	0.19
TMG	-0.22	0.96	0.94	1.00	0.00	-0.62	0.73	0.71	0.82	0.29
TS	0.62	0.18	0.03	0.00	1.00	0.60	0.03	0.45	0.26	0.39
AVS	0.58	-0.52	-0.60	-0.62	0.60	1.00	-0.53	-0.26	-0.53	-0.33
TFE	-0.44	0.84	0.49	0.73	0.03	-0.53	1.00	0.86	0.91	0.65
TMN	-0.25	0.87	0.58	0.71	0.45	-0.26	0.86	1.00	0.95	0.67
THg	-0.29	0.93	0.70	0.82	0.26	-0.53	0.91	0.95	1.00	0.75
MeHg	-0.04	0.46	0.19	0.29	0.39	-0.33	0.65	0.67	0.75	1.00

Table 48.

Intra-correlation between change in soil mass storage for successive quarters for STA-2 Cell 3

	TP	TN	TCA	TMG	TS	AVS	TFE	TMN	THg	MeHg
TP	1.00	0.83	0.90	0.98	0.45	0.26	0.92	0.86	0.78	0.20
TN	0.83	1.00	0.75	0.80	0.55	0.50	0.86	0.55	0.71	0.45
TCA	0.90	0.75	1.00	0.93	0.09	0.02	0.68	0.78	0.58	0.42
TMG	0.98	0.80	0.93	1.00	0.41	0.18	0.86	0.81	0.69	0.15
TS	0.45	0.55	0.09	0.41	1.00	0.54	0.70	0.13	0.47	-0.41
AVS	0.26	0.50	0.02	0.18	0.54	1.00	0.43	-0.05	0.13	0.11
TFE	0.92	0.86	0.68	0.86	0.70	0.43	1.00	0.76	0.89	0.10
TMN	0.86	0.55	0.78	0.81	0.13	-0.05	0.76	1.00	0.85	0.25
THg	0.78	0.71	0.58	0.69	0.47	0.13	0.89	0.85	1.00	0.24
MeHg	0.20	0.45	0.42	0.15	-0.41	0.11	0.10	0.25	0.24	1.00

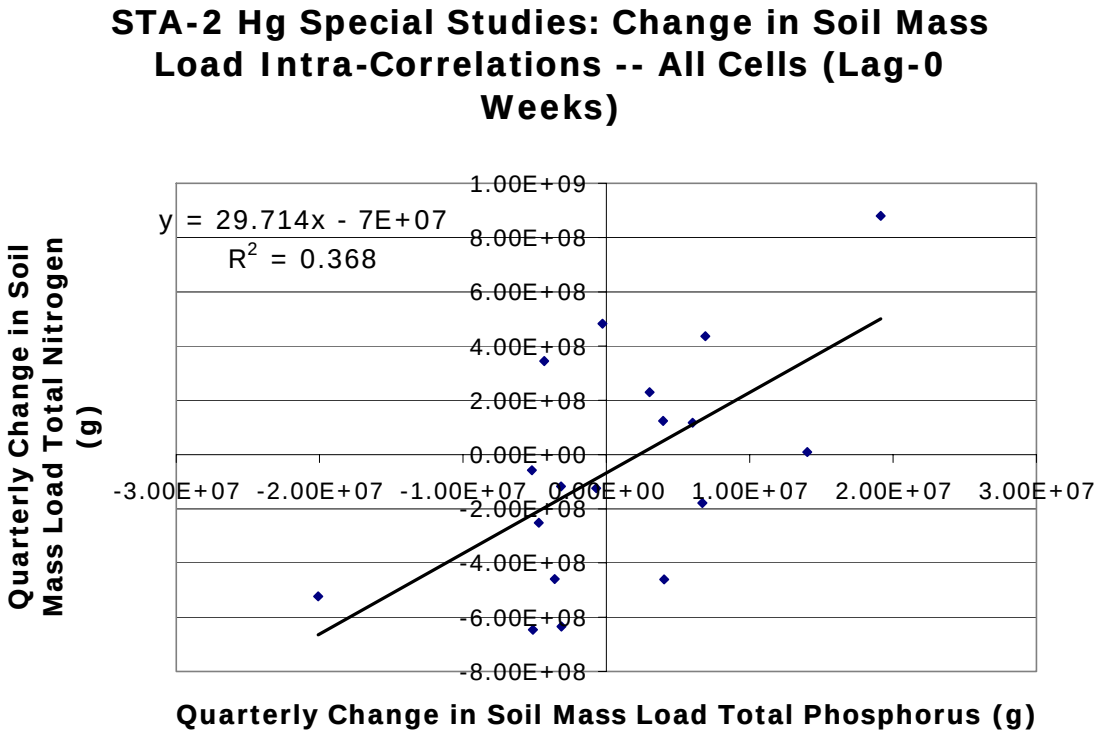

Figure 120. Scatter plot of the quarterly change in soil mass loads for total nitrogen (TN) versus total phosphorus (TP) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

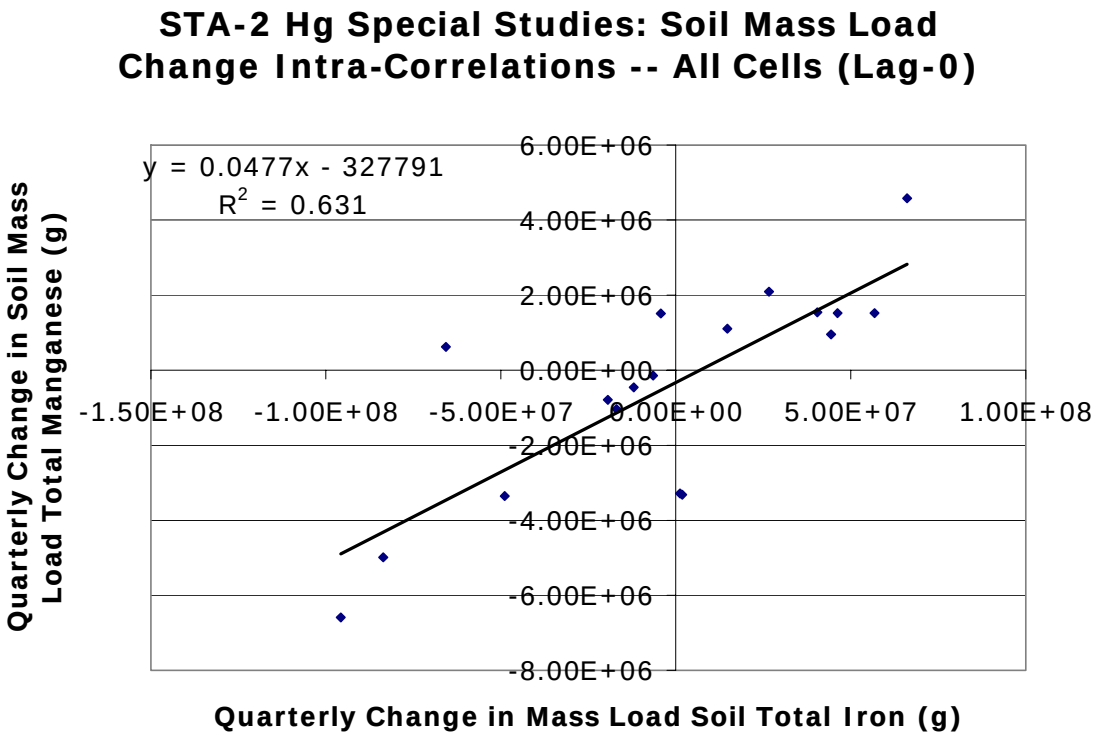

Figure 121. Scatter plot of the quarterly change in soil mass loads for total manganese (TMn) versus total iron (TFe) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

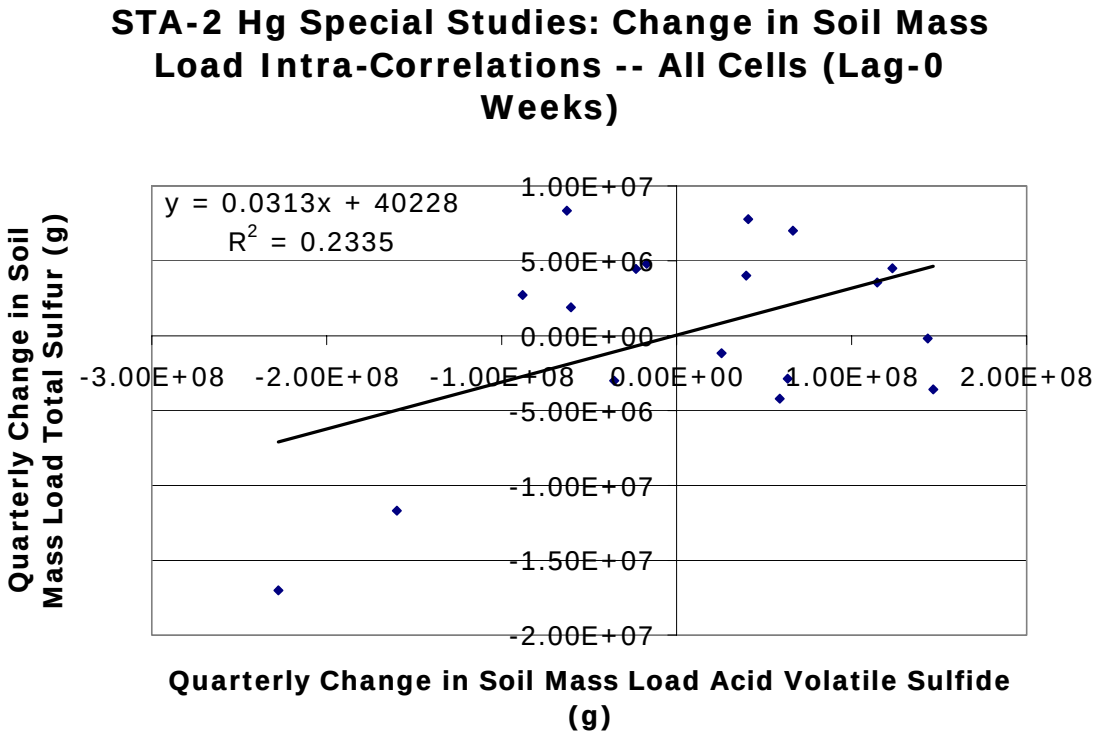

Figure 122. Scatter plot of the quarterly change in soil mass loads for total sulfur (TS) versus acid volatile sulfide (AVS) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

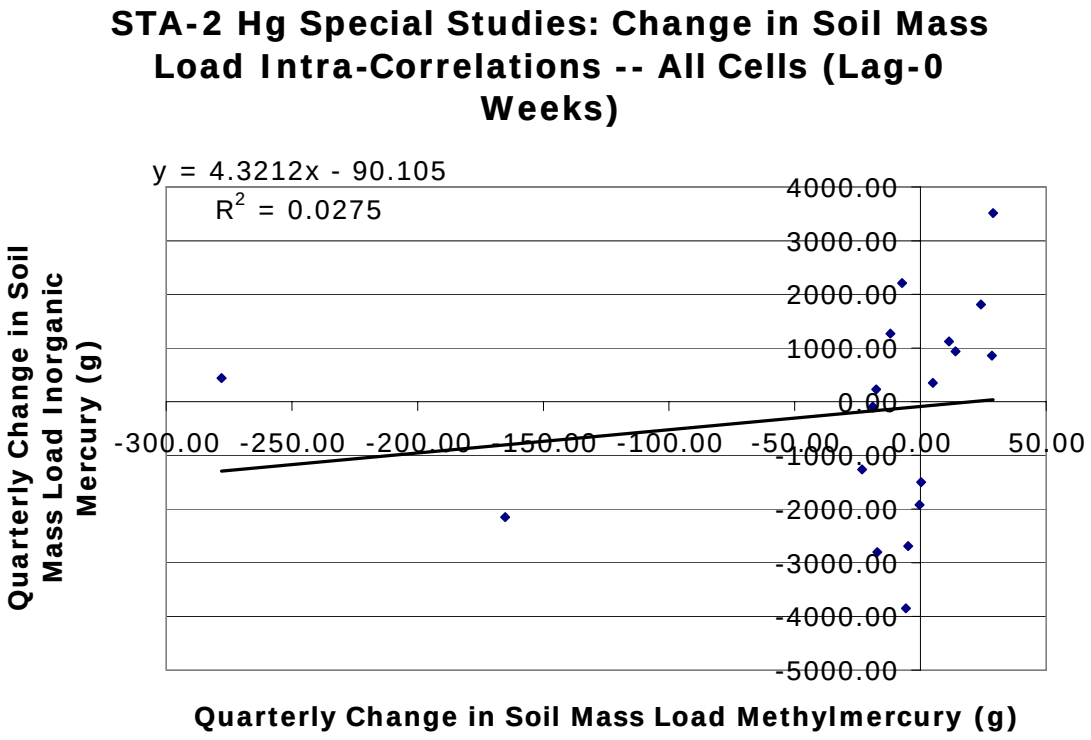

Figure 123. Scatter plot of the quarterly change in soil mass loads for inorganic mercury (Hg(II)) versus methylmercury (MeHg) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

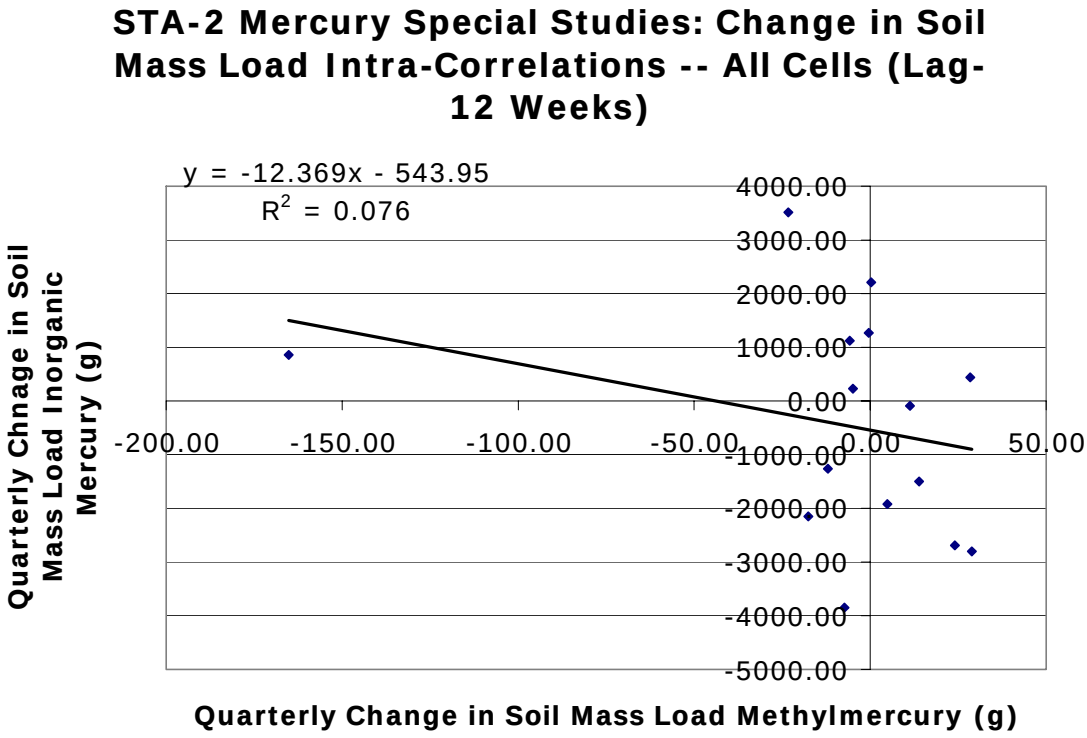

Figure 124. Scatter plot of the quarterly change in soil mass loads for inorganic mercury (Hg(II)) versus methylmercury (MeHg) for STA-2 all cells combined and Lag-12 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

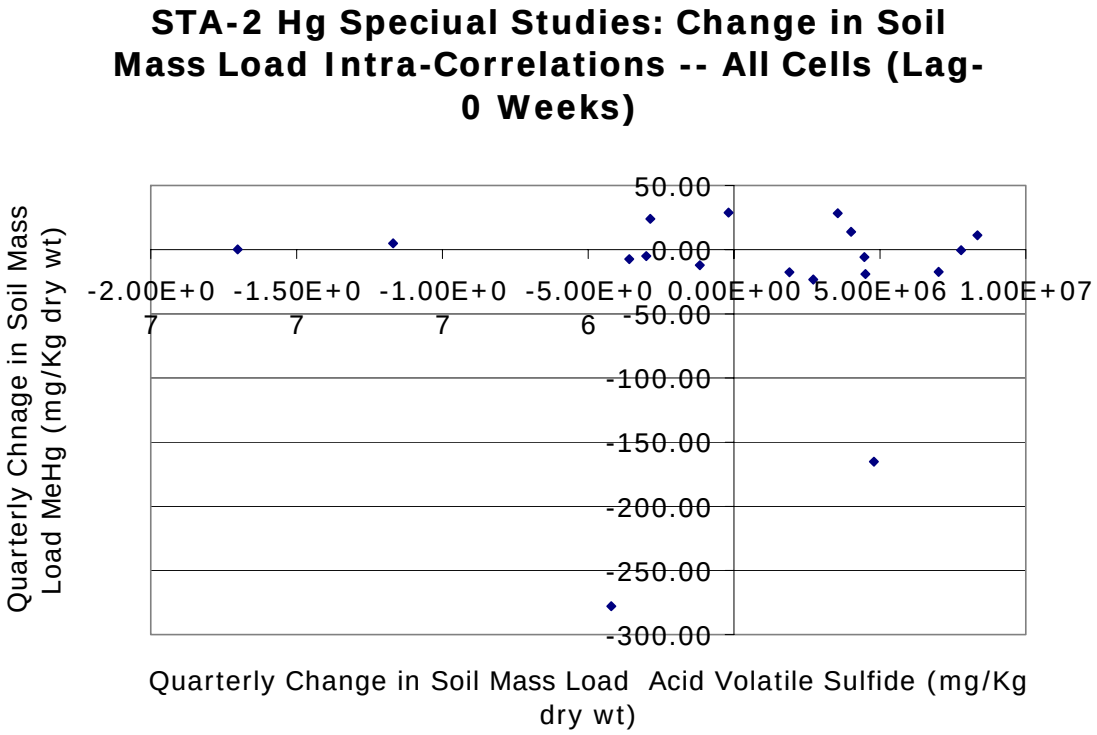

Figure 125. Scatter plot of the quarterly change in soil mass load for methylmercury (MeHg) versus acid volatile sulfide (AVS) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

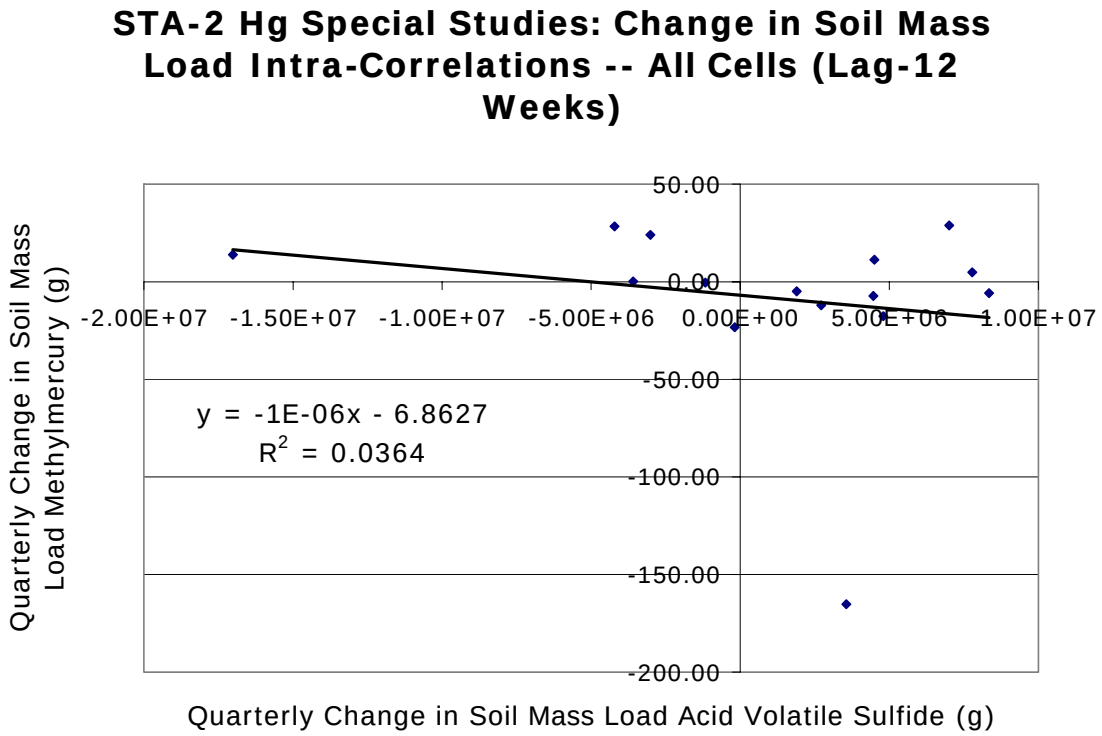

Figure 126. Scatter plot of the quarterly change in soil mass load for methylmercury (MeHg) versus acid volatile sulfide (AVS) for STA-2 all cells combined and Lag-12 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

INTER-CORRELATIONS

Concentrations x Concentrations

SURFACE WATER X PORE WATER

No Lag/No Average Correlation Analysis

The lag-0 weeks inter-correlations between the constituent concentration in surface water versus pore water are depicted in **Figures 127** through **133**, respectively for Cl^-, DOC, sulfate, sulfate versus sulfide, redox, Ca, and F-TFe. The strongest positive correlations are between the conservative anion, Cl^- ($r^2 = 0.298$), and the semi-conservative cation, Ca^{+2} ($r^2 = 0.353$). The former is surprising, because surface water and pore water Cl^- should interchange rapidly and efficiently and thus the concentrations should be virtually identical, as was observed in the side-by-side validation study. The relationship appears to have been biased high for pore water relative to surface water. This might occur as a consequence of the release of organic chloride from decomposing plant biomass in the surficial soil. If precipitation as a relatively insoluble solid would have been occurring, then the pore water would have been biased low relative to surface water. However, Cl^- is considered a conservative tracer because it does not precipitate with any common cation at environmental concentrations. The latter is also somewhat surprising, because one might expect that the precipitation of inorganic Ca^{+2} as the carbonate and/or hydroxide would skew the pore water concentration of Ca^{+2} low, unless the difference would have been made up, in part, by the release of organic Ca^{+2} from decomposing plant biomass. If the latter was the case, then this might explain why the correlation between surface water and pore water Ca^{+2} appeared stronger than Cl^-. Whether one might extract hidden or more accurate inter-correlations by normalizing the other constituent concentrations to the pore water or surface water chloride concentration or their ratio must await a more detailed analysis of the data.

Table 49 presents the Pearson correlation coefficients for the univariate inter-correlation between pore water F-THg, F-MeHg, and F-MeHg/F-THg and all possible concurrently measured surface water constituents or parameters (lag-1 weeks) for the period of concurrent soil and pore water monitoring every four weeks from October 2003 through January 2004. The need to pair pore water F-THg, F-MeHg, and F-%MeHg concentrations with the corresponding surface water concentrations in samples collected a week earlier (lag-1 week) rather than at the same time (lag-0 weeks), as was the case for al of the other constituents, was driven by the high cost of repeating the previous week's routine surface water monitoring of F-THg and F-MeHg at $70 and $200 per sample, respectively. The scatter plots of surface water versus pore water F-THg, F-MeHg, and F-%MeHg are graphed in **Figures 134** through **136**, respectively. For pore water F-MeHg, the strongest positive lag-0 weeks correlations were with surface water hydronium ion concentration ($r = 0.51$) and sulfate ($r = 0.49$). The former could be mediating MeHg sorption or complexation, while the latter could be mediating MeHg production. Continuing the inquiry for pore water F-MeHg, the strongest inverse relationships were with surface water redox ($r = -0.47$), pH ($r = -0.50$), and depth ($r = -0.41$). Redox and water depth tend to be strongly inter-correlated, so these potential influences may be somewhat to substantially redundant, depending on conditions. However, pH is the negative (inverse) logarithm of the hydronium ion concentration, the positive correlation with hydronium ion and the inverse correlation with pH are strictly redundant and are presented here only for the sake of completeness. In general, the LN transformation of pore water F-MeHg increased the strength of the inter-correlations, although not strikingly so. For pore water F-THg, the only weak to moderate positive inter-correlations

were with surface water hydronium ion concentration (r = 0.58) and LN F-Mn (r = 0.45), while the strongest inverse relationships occurred in the order pH (r = -0.60) and surface water depth (r = -0.49). Further parsing of these relationships at the individual cell level of disaggregation would eliminate the effect of differences in antecedent land use and hydrology from the differences in the interactions between surface water and soil pore water chemistries, but there were only four sampling trips and three monitoring stations per cell, so the total number of observations would have fallen below the threshold of n = 14 independent observations, weakening the power and robustness of any observations deriving from that further parsing. The scatter plot of the fraction of MeHg in pore water versus the difference between surface water and pore water sulfate did not track with the expected inverse relationship with pore water sulfide (**Figure 137**), which might be explained by the apparently bimodal relationship between the sulfate difference and pore water sulfide (**Figure 138**) or the apparent trimodal relationship with the manganese difference (**Figure 139**).

Table 49. Parametric inter-correlation Pearson correlation coefficients for surface water versus pore water constituent concentrations.

LAG-0 Parametric R Values

	Surface Water Variables					
Pore Water Variables	THg	LN	MeHg	LN	frac MeHg/THg	LN
SW Depth	-0.49	-0.54	-0.41	-0.58	-0.33	-0.29
LN Depth	-0.38	-0.41	-0.33	-0.48	-0.35	-0.28
F-THg	-0.13	-0.16	-0.17	-0.31	-0.18	-0.27
LN THg	0.05	0.05	-0.02	-0.15	-0.13	-0.24
F-MeHg	-0.29	-0.39	-0.40	-0.56	-0.43	-0.42
LN F-MeHg	-0.17	-0.30	-0.38	-0.57	-0.49	-0.52
%MeHg	-0.22	-0.28	-0.42	-0.52	-0.51	-0.46
LN % MeHg	-0.16	-0.23	-0.41	-0.55	-0.56	-0.54
F-CA	0.27	0.36	0.19	0.29	0.04	0.06
LN F-CA	0.32	0.41	0.23	0.33	0.07	0.07
F-MG	0.27	0.36	0.21	0.22	-0.02	-0.03
LN F-MG	0.30	0.39	0.24	0.23	-0.02	-0.04
DOC	0.18	0.21	0.24	0.33	0.33	0.25
LN DOC	0.29	0.33	0.31	0.39	0.31	0.23
CL	0.17	0.25	0.28	0.54	0.35	0.50
LN CL	0.18	0.26	0.29	0.56	0.36	0.52
F-FE	0.11	0.17	0.02	0.10	-0.09	0.00
LN F-FE	0.23	0.31	0.02	0.15	-0.13	-0.05
F-Fe(II)	0.01	0.06	-0.09	-0.05	-0.19	-0.11
LN F-Fe(II)	0.09	0.13	-0.14	-0.14	-0.32	-0.28
F-Fe(III)	0.02	0.08	0.01	0.02	-0.13	-0.04
LN F-Fe(III)	0.01	0.09	-0.22	-0.23	-0.41	-0.30
F-MN	0.37	0.38	0.15	0.17	-0.11	-0.11
LN F-MN	0.45	0.44	0.29	0.28	0.03	-0.02
REDOX	-0.12	-0.28	-0.47	-0.46	-0.32	-0.35
LN REDOX	0.00	-0.13	-0.39	-0.38	-0.34	-0.39
[H+]	0.58	0.60	0.51	0.50	0.19	0.14
pH	-0.60	-0.63	-0.50	-0.52	-0.22	-0.13
F-SULFATE	0.30	0.24	0.49	0.48	0.43	0.41
LN F-SULFATE	0.14	0.07	0.37	0.35	0.42	0.40
SULFIDE	-0.13	-0.13	-0.01	-0.06	0.07	0.04
LN SULFIDE	-0.06	-0.14	-0.10	-0.15	-0.08	-0.07
S=/(SO4+S=)	-0.17	-0.15	-0.15	-0.15	-0.08	-0.07
LN X	-0.07	-0.11	-0.21	-0.24	-0.24	-0.22
KP Hg(II)	-0.02	0.07	0.01	0.17	0.10	0.16
LN KP Hg(II)	0.08	0.15	0.06	0.24	0.11	0.18
KP MeHg	0.09	0.22	0.17	0.31	0.21	0.24
LN KP MeHg	0.30	0.41	0.35	0.52	0.34	0.36

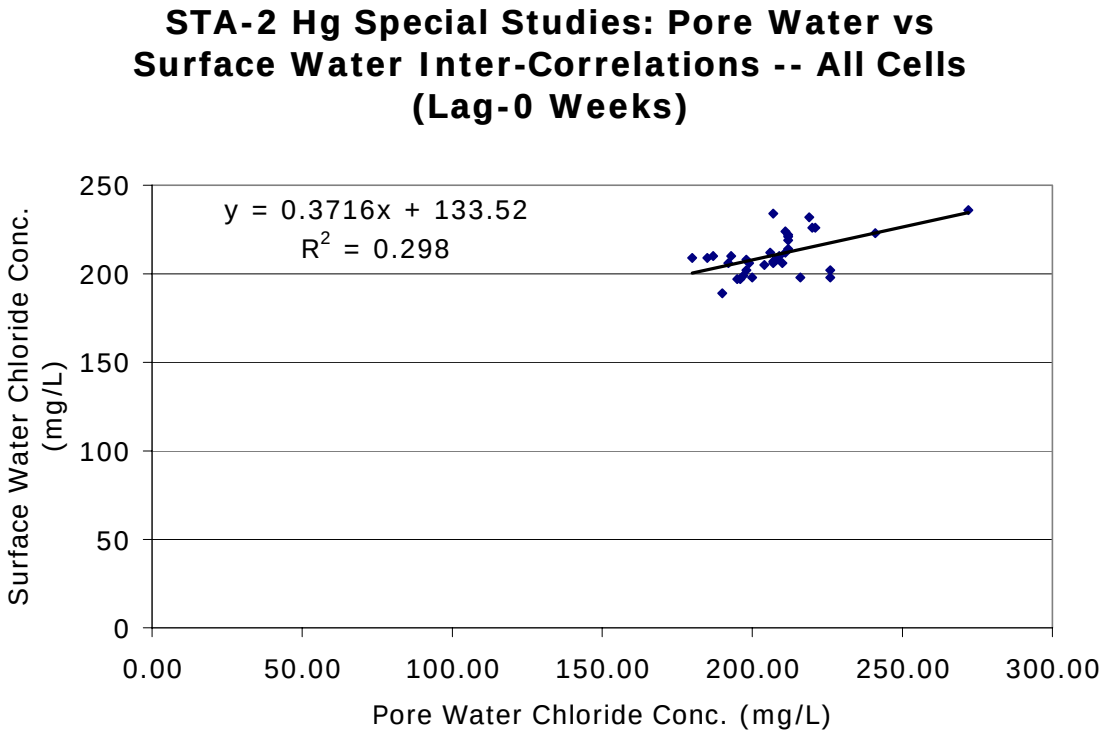

Figure 127. Scatter plot of the concentration of pore water versus surface water chloride (Cl-) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

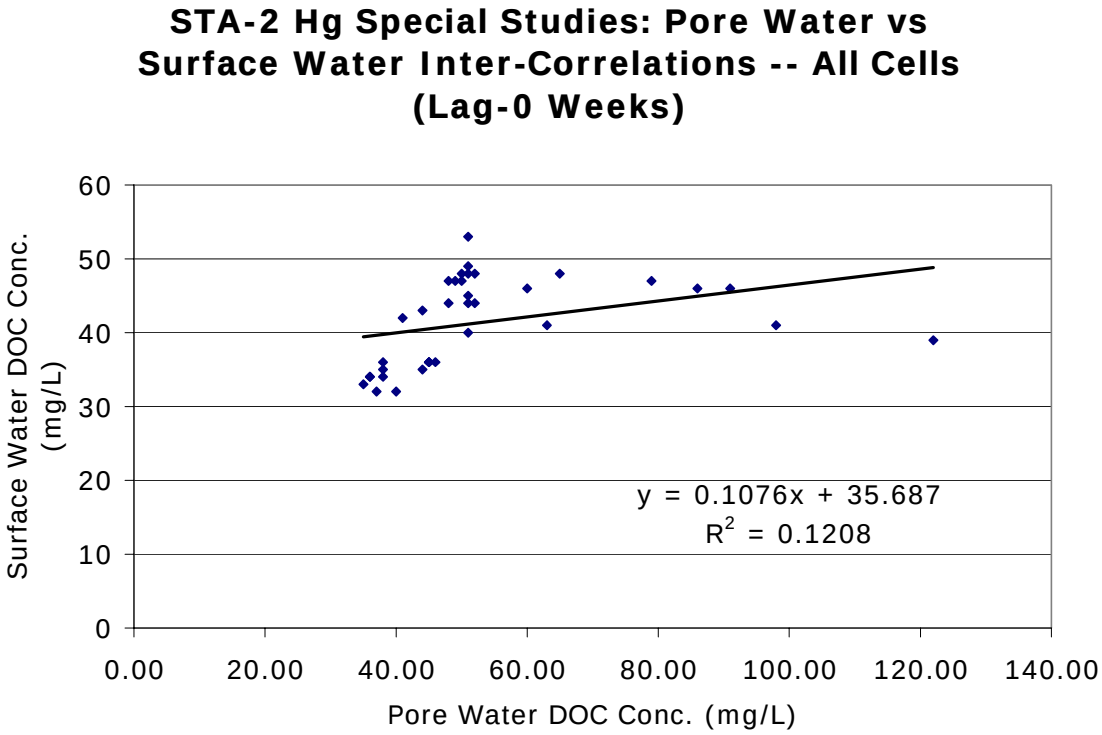

Figure 128. Scatter plot of the concentration of pore water versus dissolved organic carbon (DOC) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

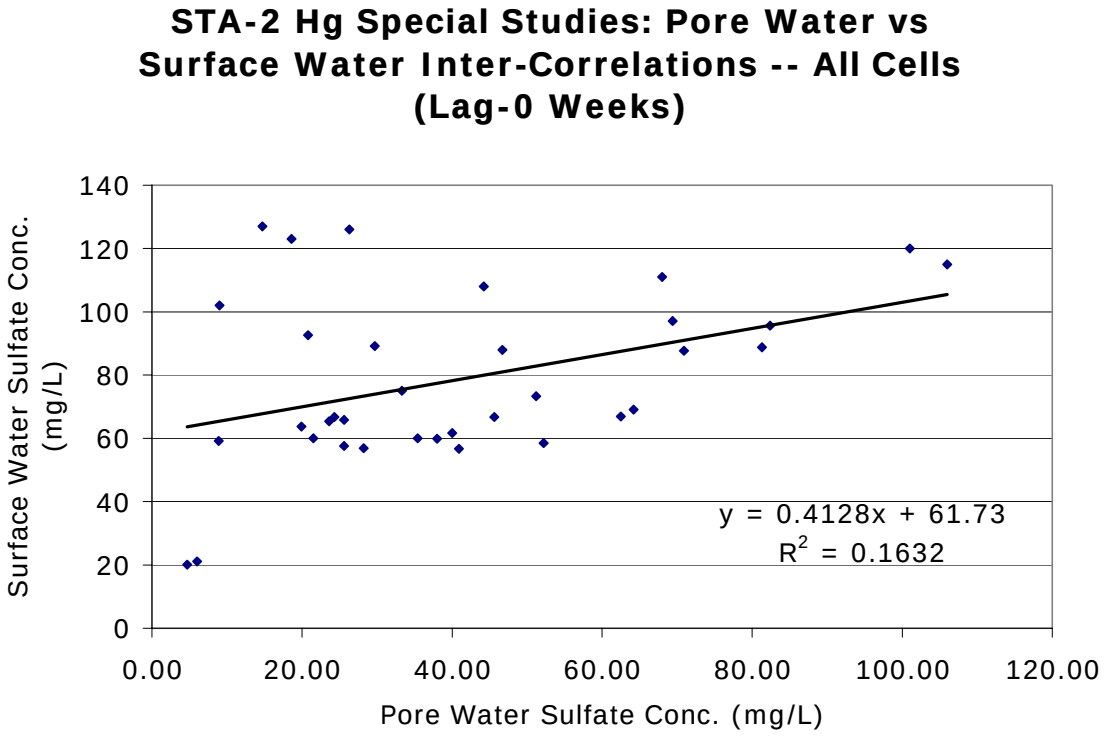

Figure 129. Scatter plot of the concentration of pore water versus surface water sulfate (SO42-) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

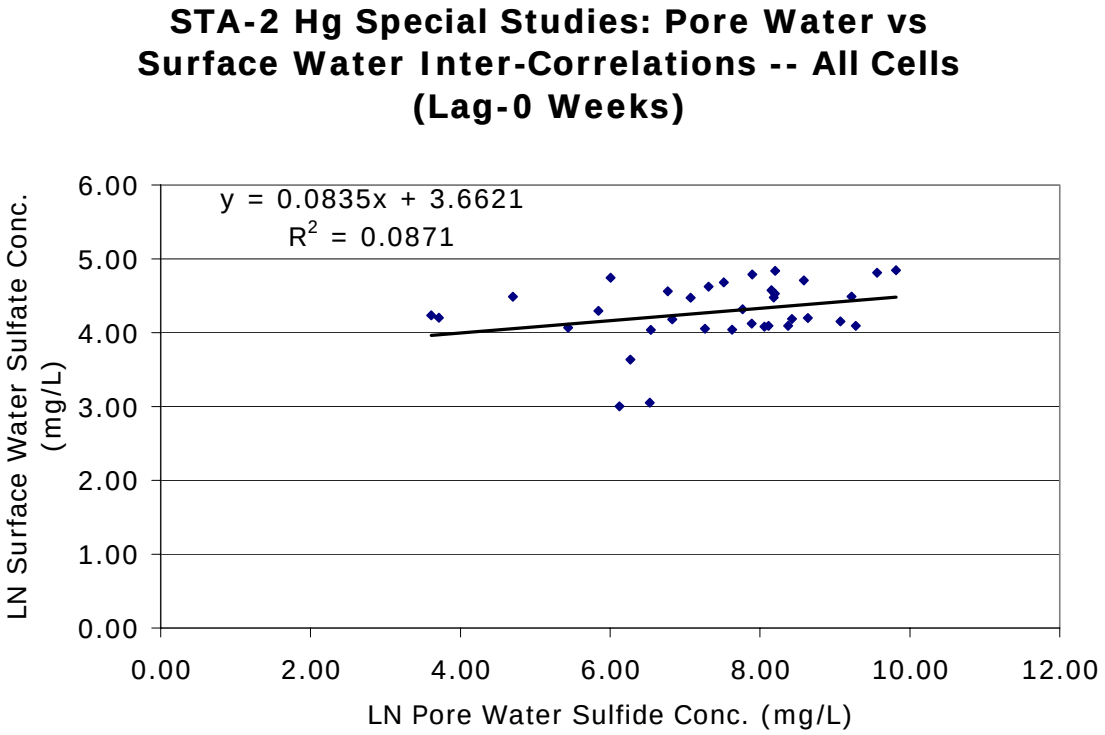

Figure 130. Scatter plot of the concentration of surface water sulfate (SO42-) versus pore water sulfide for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

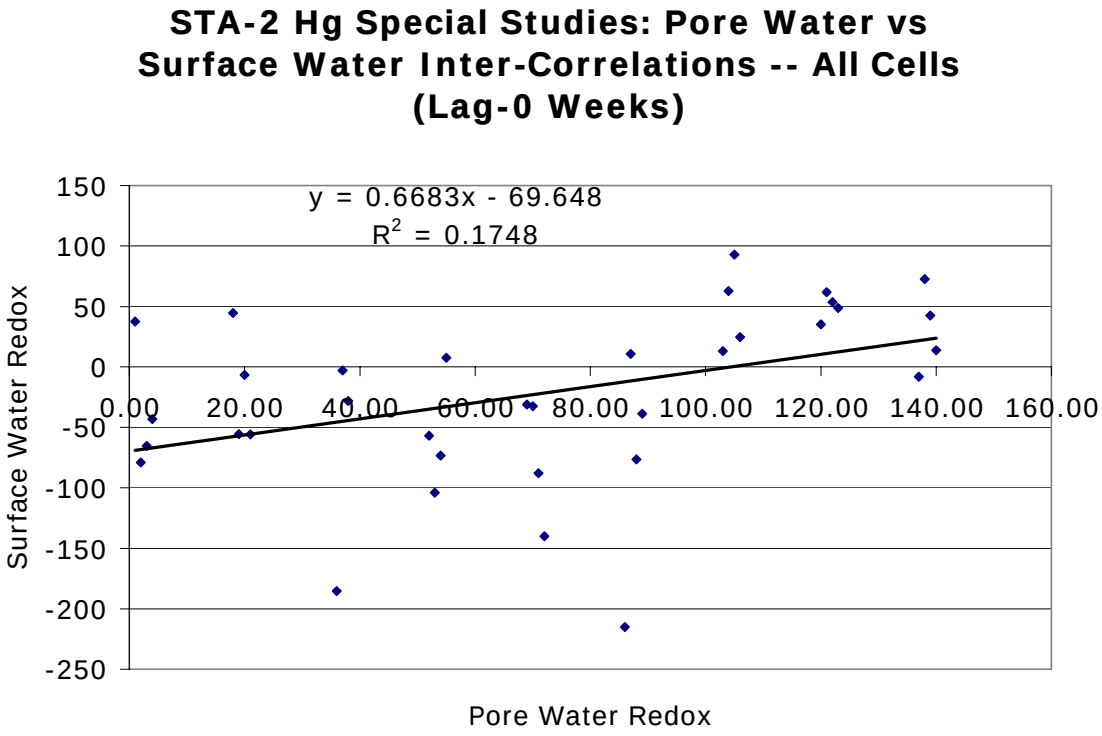

Figure 131. Scatter plot of the surface water versus pore water reduction potential relative to the standardized hydrogen electrode (redox) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

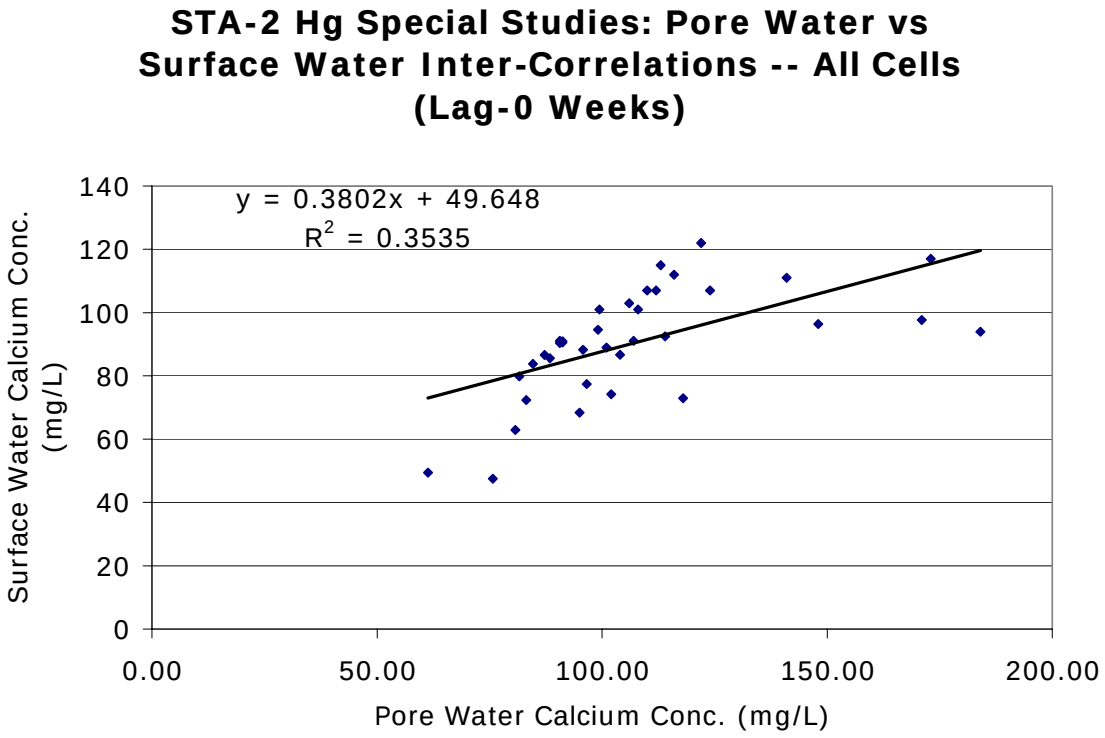

Figure 132. Scatter plot of the surface water versus pore water calcium (Ca) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

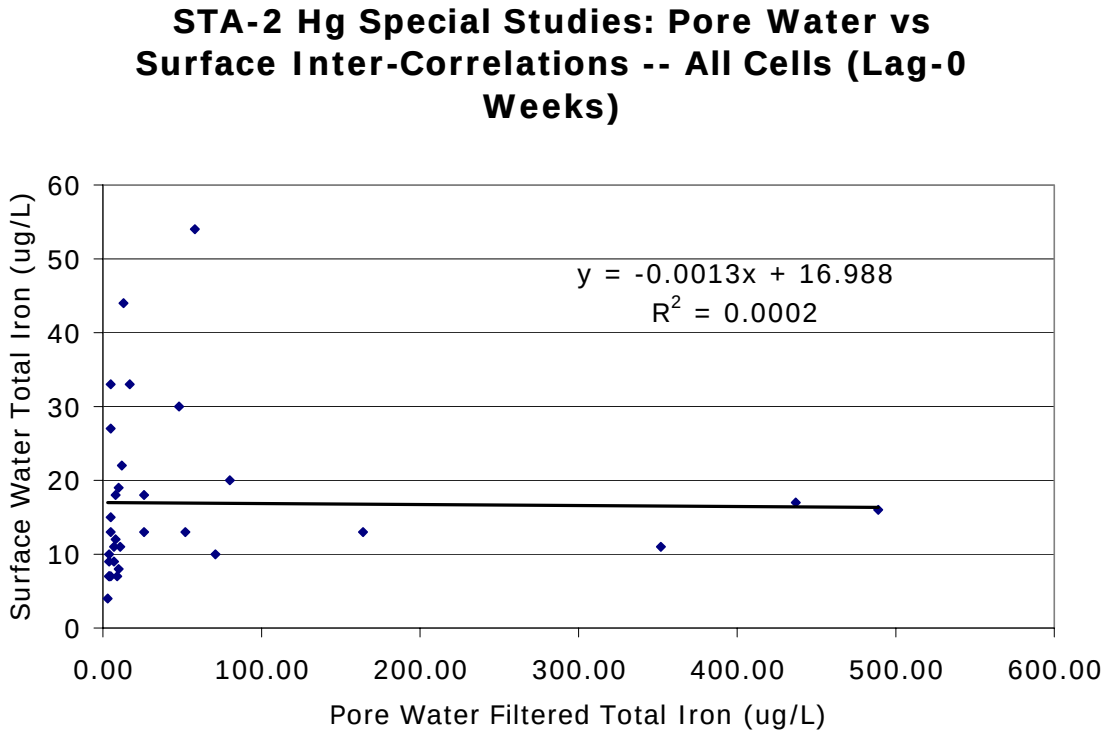

Figure 133. Scatter plot of the surface water versus pore water dissolved total iron (F-TFe) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

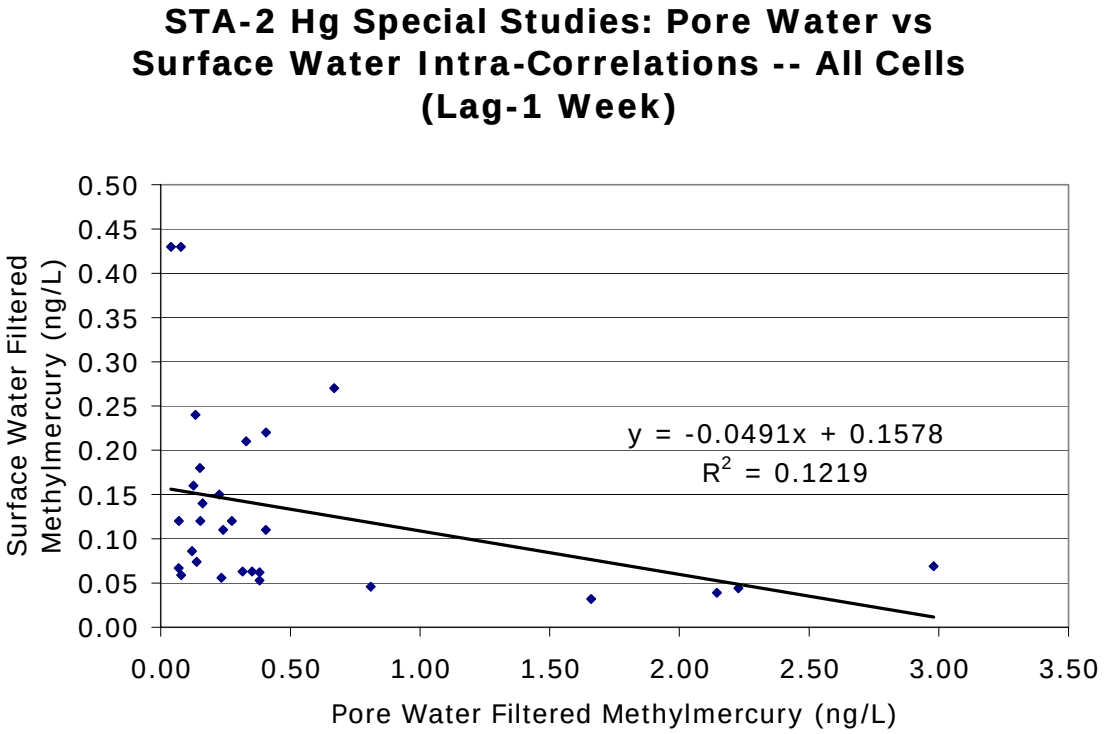

Figure 134. Scatter plot of the surface water versus pore water dissolved methylmercury (F-MeHg) for STA-2 all cells combined and Lag-1 week with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

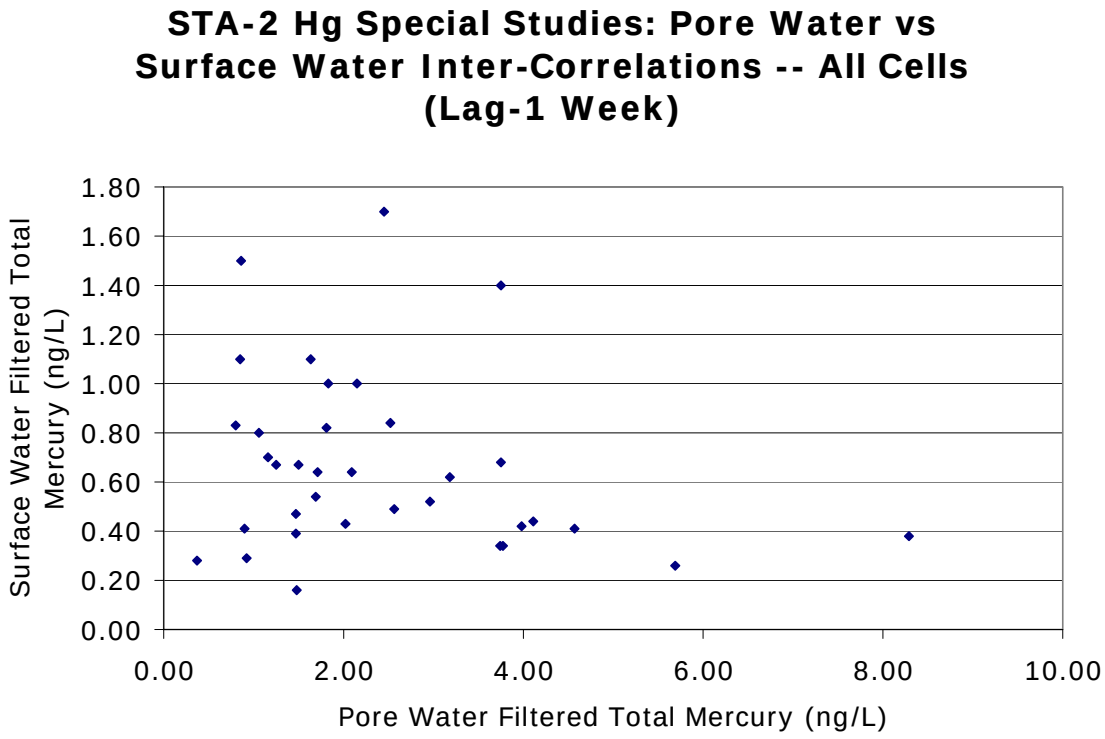

Figure 135. Scatter plot of the surface water versus pore water dissolved total mercury (F-THg) for STA-2 all cells combined and Lag-1 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

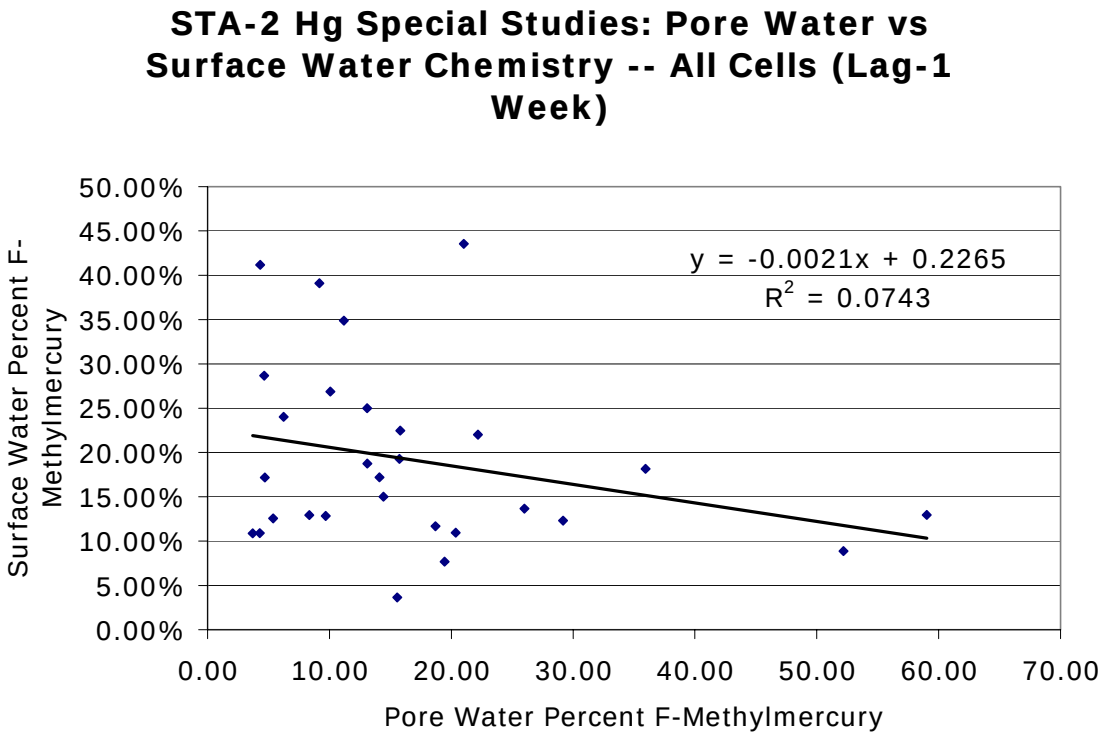

Figure 136. Scatter plot of the surface water versus pore water percent dissolved methylmercury (F-%MeHg) for STA-2 all cells combined and Lag-1 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

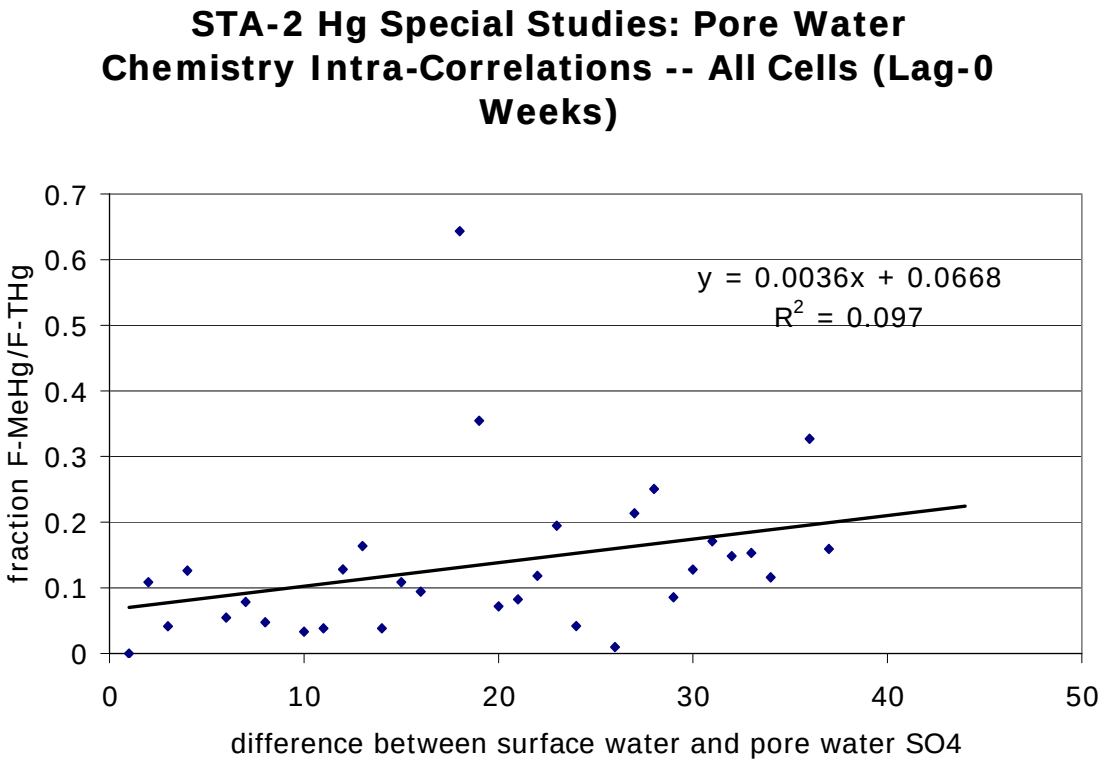

Figure 137. Scatter plot of the difference between surface water and pore water sulfate (SO4) versus the pore water fraction dissolved methylmercury to dissolved total mercury (F-MeHg/F-THg) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

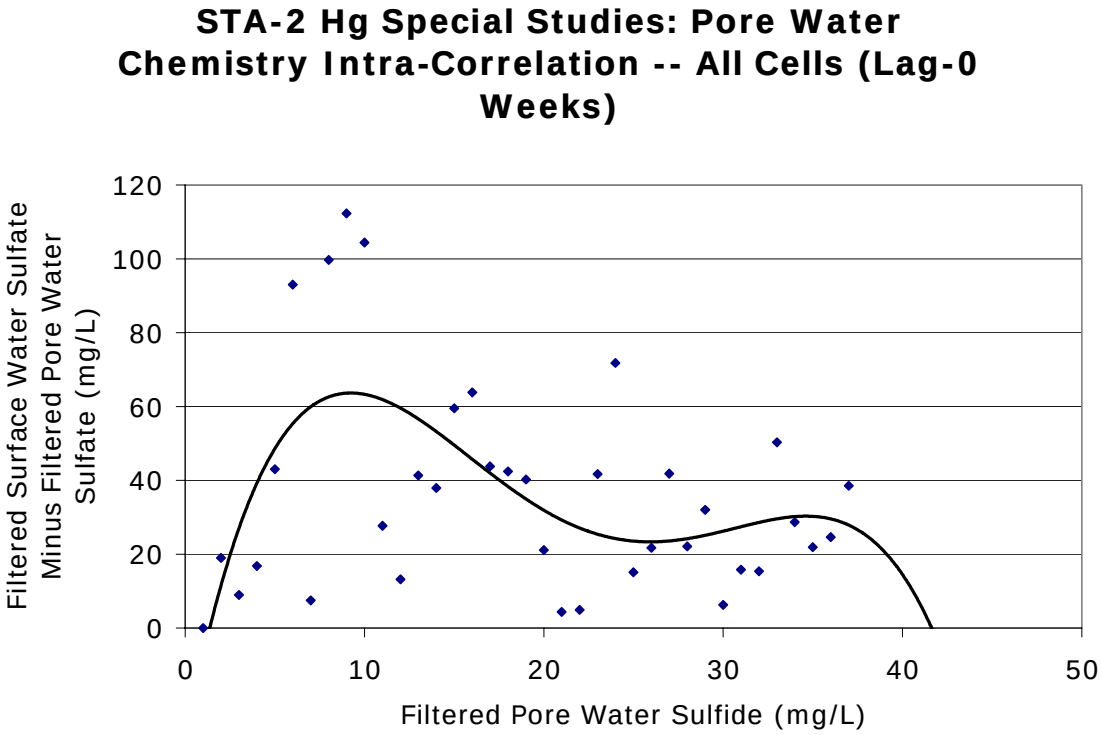

Figure 138. Scatter plot of the pore water concentration of sulfide (S2-) versus the difference of surface water and pore water sulfate for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

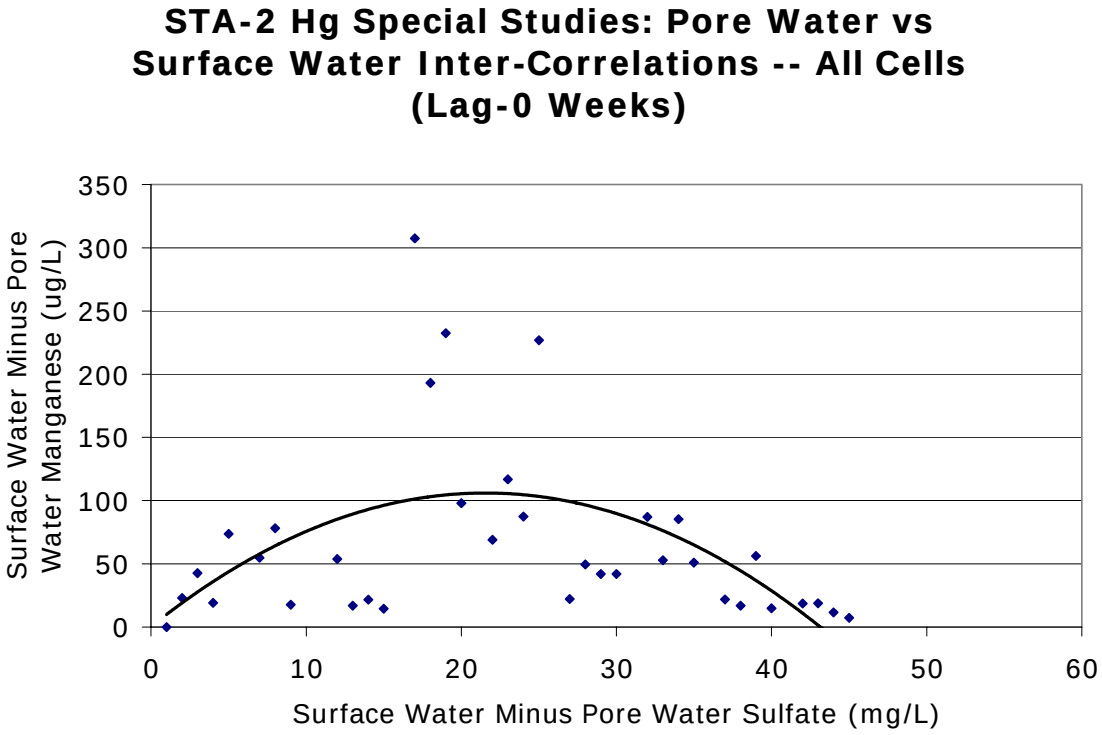

Figure 139. Scatter plot of the difference between the concentrations of surface water and pore water dissolved manganese and the concentration of pore water sulfate for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

SURFACE WATER X PORE WATER

Lag Correlation Analysis

To determine whether there was a delayed influence of pore water sulfide on Hg(II) bioavailability for MeHg production, scatter plots of the pore water F-MeHg concentration versus pore water sulfide at lag-0 weeks (**Figure 140**), lag-4 weeks (**Figure 141**), and lag-8 weeks (**Figure 142**) were graphed. The r^2 values increased progressively and substantially from r^2 = 8E-06 at lag-0 weeks to 0.171 at lag-4 weeks to 0.634 at lag-8 weeks. This suggests that the hypothesized influence of pore water sulfide on Hg(II) bioavailability for MeHg production occurs many weeks prior to the occurrence of that MeHg in pore water. It cannot be ascertained from these data whether this is inconsistent with the observation from controlled mesocosm studies that new Hg(II) is rapidly methylated under similar conditions or consistent with the hypothesis that the Hg(II) being methylated in STA-2 cells originates primarily with surficial soil as opposed to rainfall or inflow. The strength of these correlations did not increase substantially when F-MeHg was replaced by the percent F-MeHg.

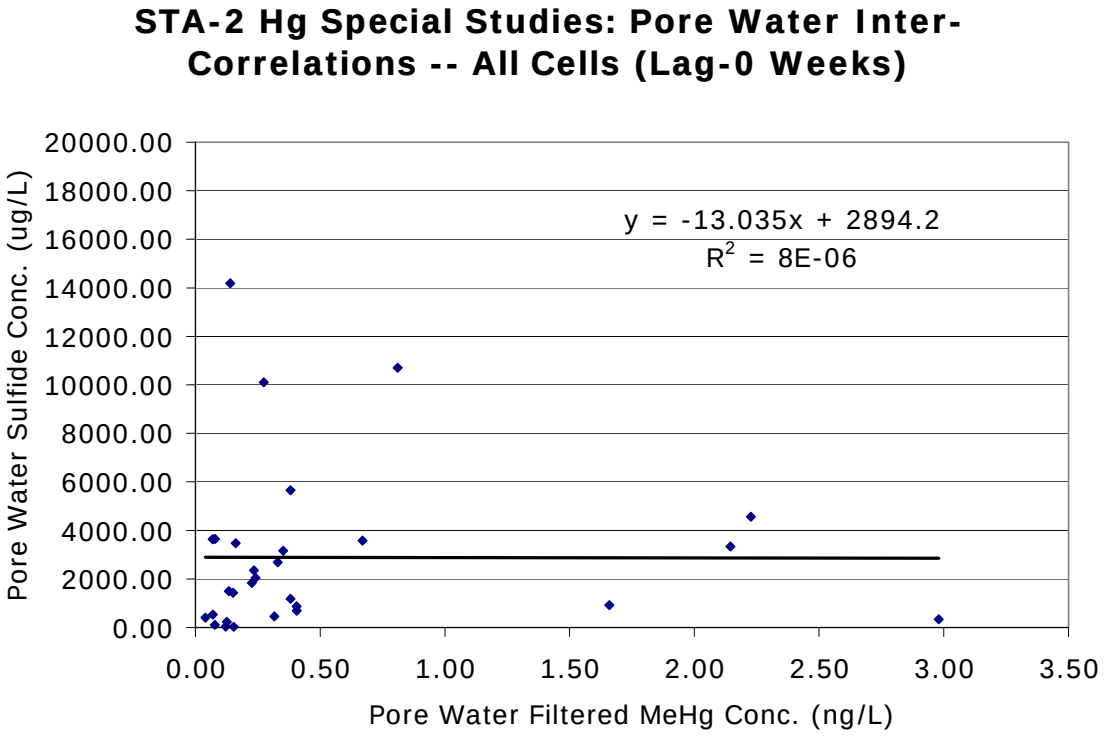

Figure 140. Scatter plot of the pore water concentration of sulfide (S2-) versus the dissolved methylmercury (F-MeHg) for STA-2 all cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

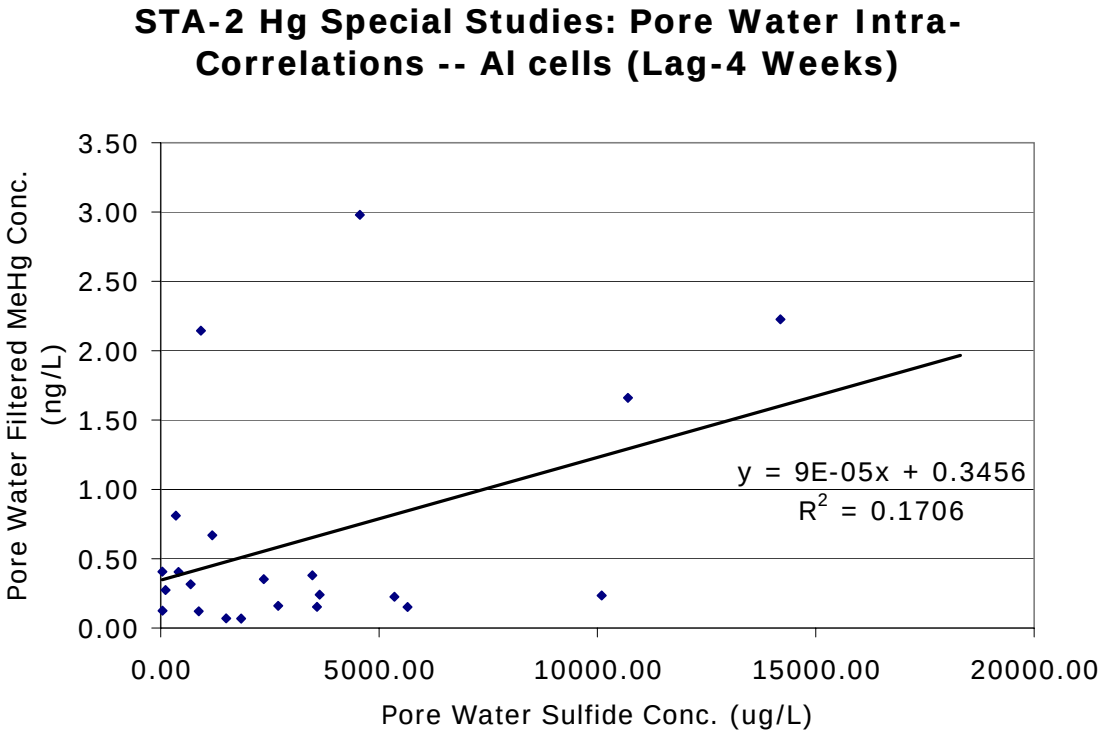

Figure 141. Scatter plot of the pore water concentration of sulfide (S2-) versus the dissolved methylmercury (F-MeHg) for STA-2 all cells combined and Lag-4 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

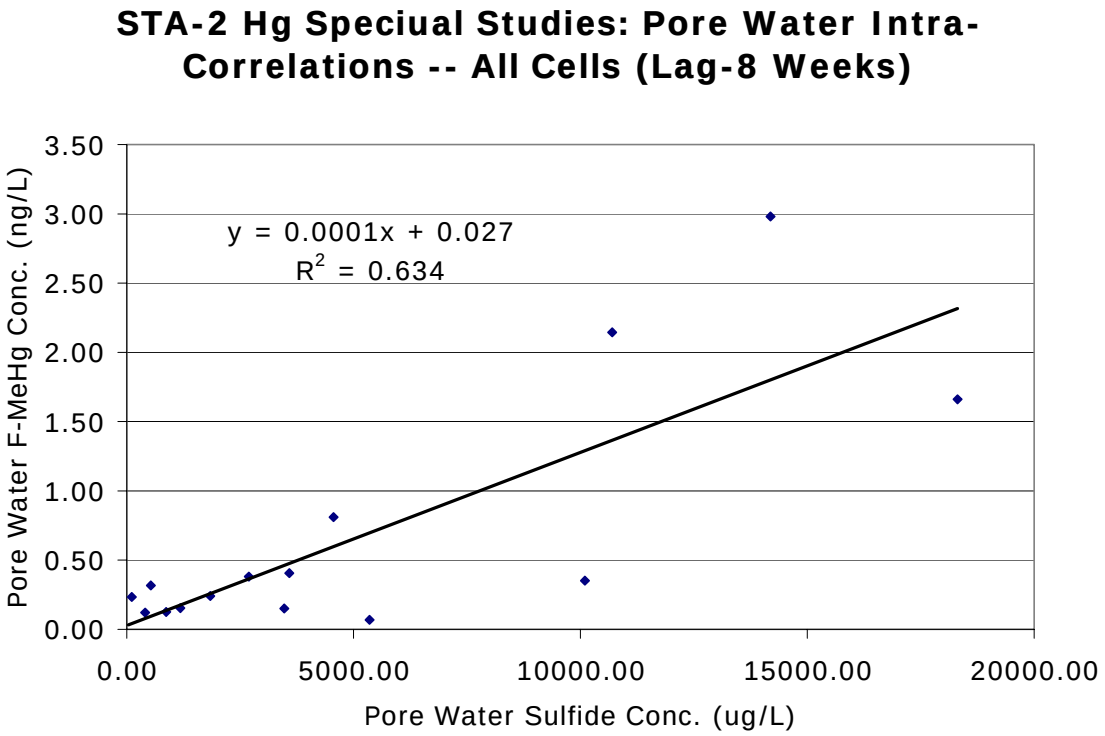

Figure 142. Scatter plot of the pore water concentration of sulfide (S2-) versus the dissolved methylmercury (F-MeHg) for STA-2 all cells combined and Lag-8 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

SURFACE WATER X SOIL

No Lag/No Average Correlation Analysis

All STA-2 Cells

Based on the spatial average of surface water and soil results across all cells for the ten soil sampling events, there was a strong, statistically significant inverse relationship between percent soil moisture and the surface water concentration of Hg(II) ($r = -0.71$; $p < 0.05$) and between surface water F-%MeHg and soil Mn ($r = 0.76$; $p < 0.05$). Although not statistically significant at the 95th percentile confidence level, surface water F-MeHg was moderately positively correlated with soil TMn ($r = 0.62$) and weakly inversely correlated with TCa (-0.42). The inverse correlations between soil AVS and surface water F-THg and F-Hg(II) were moderate ($r = -0.62$ and -0.64), albeit not statistically significantly so, but the inverse correlation with surface water F-MeHg was extremely weak ($r = -0.22$) and not statistically significant.

SOIL X SURFACE WATER

Soil THg was moderately correlated with rain THg ($r = 0.53$), but not statistically significantly so. Soil THg was strongly inversely correlated with surface water pheophytin ($r = -0.75$; $p < 0.05$) and moderately inversely correlated with chlorophyll_a ($r = -0.60$; $p < 0.05$) and chlorophyll_a ($r = -0.62$; $p < 0.05$) corrected, perhaps indicative of the release of Hg(II) and MeHg released from decomposing rooted and floating plant biomass. Conversely, soil MeHg was strongly positively correlated with chlorphyll_c ($r = 0.73$; $p < 0.05$), but moderate to strongly inversely correlated with F-Mn ($r = -0.67$; $p < 0.05$). Other positive and inverse correlations with soil MeHg that were not statistically significant were nitrate + nitrite ($r = 0.52$) and redox ($r = -0.63$), pH (-0.58), sulfate (-0.52), and ammonia (-0.65).

SOIL X PORE WATER

All Cells Combined

No Lag/No Average Correlation Analysis

Table 50 summarizes the Pearson correlation coefficients for all possible pairs of soil and pore water constituents and parameters with lag-0 weeks. Focusing on soil mercury species, the strongest positive correlations for the natural log transformation (LN) of the soil MeHg concentration were with the LN of the Hg(II) soil/pore water partition coefficient (KPHg(II)) ($r = 0.54$) and the LN of the pore water sulfate concentration ($r = 0.46$), while the strongest inverse correlations were with the LN of the mole fraction sulfide/(sulfide + sulfate) ($r = -0.66$) and LN water depth ($r = -0.48$). For the LN %MeHg soil concentration, the strongest positive correlates were LN F-Mn ($r = 0.69$), LN KPHg(II) ($r = 0.71$), and LN Fe ($r = 0.56$), while the strongest inverse correlates were with LN sulfide ($r = -0.61$) and water depth ($r = -0.57$). (The strongest positive and inverse correlates with pore water F-THg, F-MeHg, KPHg(II) and KPMeHg, all of which are interrelated through calculations, so only the KPHg(II) value was highlighted here, because it is likely representative of the bioavailable fraction of Hg(II) for MeHg production.) For soil THg, there were no strong positive pore water constituent correlates, but the strongest inverse correlates were LN F-TFE ($r = 0.36$), LN F-TMn ($r = 0.35$), and Cl^- ($r = 0.30$). The strongest inverse correlates were between soil THg concentration and water depth ($r = -0.53$) and ratio $S^{2-}/(S^{2-} + SO_4^{2-})$ ($r = -0.55$).

Table 50. Pearson correlation coefficients for inter-correlations between surficial soil pore water and surficial soil for the concurrent sampling events in October 2003 through January 2004.

	G/CC	LN	ASH	LN	MOIST	LN	TP	LN	TN	LN	TCA	LN	TMG	LN
Depth	0.70	0.67	0.63	0.64	-0.68	-0.68	-0.13	-0.12	-0.61	-0.61	0.54	0.57	0.70	0.69
LN Depth	0.64	0.67	0.47	0.50	-0.63	-0.62	-0.26	-0.21	-0.53	-0.49	0.41	0.45	0.59	0.58
F-THg	0.17	0.17	0.24	0.29	-0.09	-0.08	-0.17	-0.17	-0.25	-0.23	0.13	0.24	0.34	0.38
LN THg	-0.01	0.01	0.22	0.25	0.08	0.09	-0.18	-0.20	-0.21	-0.21	-0.01	0.10	0.27	0.31
F-MeHg	0.64	0.53	0.24	0.36	-0.56	-0.57	-0.23	-0.23	-0.34	-0.26	0.18	0.36	0.54	0.57
LN F-MeHg	0.58	0.51	0.15	0.26	-0.50	-0.51	-0.25	-0.25	-0.29	-0.20	0.13	0.29	0.47	0.50
%MeHg	0.64	0.56	0.11	0.20	-0.57	-0.58	-0.28	-0.28	-0.27	-0.18	0.03	0.19	0.39	0.41
LN % MeHg	0.59	0.53	-0.11	-0.02	-0.52	-0.52	-0.29	-0.28	-0.10	0.00	-0.14	0.01	0.16	0.18
F-CA	-0.37	-0.31	-0.28	-0.33	0.35	0.35	0.04	0.04	0.31	0.28	-0.32	-0.39	-0.42	-0.43
LN F-CA	-0.42	-0.36	-0.28	-0.35	0.39	0.40	0.06	0.04	0.32	0.29	-0.33	-0.41	-0.45	-0.46
F-MG	-0.15	-0.10	0.02	-0.06	0.17	0.18	-0.13	-0.14	-0.04	-0.07	-0.11	-0.17	-0.06	-0.07
LN F-MG	-0.16	-0.11	0.02	-0.05	0.18	0.19	-0.15	-0.15	-0.04	-0.07	-0.11	-0.17	-0.05	-0.05
DOC	-0.31	-0.25	-0.26	-0.31	0.33	0.34	0.13	0.14	0.27	0.25	-0.26	-0.32	-0.34	-0.33
LN DOC	-0.37	-0.31	-0.27	-0.33	0.40	0.40	0.10	0.10	0.28	0.25	-0.30	-0.36	-0.37	-0.37
CL	-0.01	0.03	-0.38	-0.41	0.03	0.04	0.07	0.13	0.23	0.25	-0.32	-0.37	-0.22	-0.22
LN CL	-0.01	0.03	-0.39	-0.41	0.03	0.04	0.07	0.13	0.24	0.26	-0.32	-0.37	-0.21	-0.21
F-FE	-0.20	-0.14	-0.21	-0.21	0.19	0.19	0.02	0.03	0.27	0.25	-0.16	-0.15	-0.28	-0.28
LN F-FE	-0.35	-0.27	-0.42	-0.44	0.32	0.33	0.01	0.01	0.45	0.43	-0.36	-0.38	-0.56	-0.56
F-Fe(II)	-0.15	-0.08	-0.15	-0.11	0.12	0.13	0.03	0.05	0.20	0.21	-0.01	0.04	-0.18	-0.16
LN F-Fe(II)	-0.17	-0.10	-0.26	-0.21	0.13	0.13	-0.07	-0.06	0.28	0.29	-0.10	-0.04	-0.31	-0.29
F-Fe(III)	-0.04	-0.02	-0.02	0.05	0.05	0.05	-0.06	-0.05	0.14	0.15	0.08	0.12	0.00	0.02
LN F-Fe(III)	-0.04	-0.02	-0.10	-0.03	-0.01	0.00	-0.10	-0.11	0.15	0.17	0.07	0.11	-0.09	-0.06
F-MN	-0.18	-0.11	-0.34	-0.36	0.15	0.16	-0.12	-0.10	0.36	0.35	-0.30	-0.36	-0.43	-0.43
LN F-MN	-0.27	-0.22	-0.43	-0.45	0.23	0.23	0.01	0.03	0.43	0.42	-0.35	-0.43	-0.53	-0.54
REDOX	0.06	0.06	-0.26	-0.25	-0.05	-0.05	-0.06	-0.07	0.23	0.25	-0.12	-0.12	-0.28	-0.29
LN REDOX	0.00	0.04	-0.20	-0.22	0.03	0.03	-0.15	-0.14	0.21	0.20	-0.16	-0.19	-0.30	-0.33
[H+]	-0.19	-0.18	-0.07	-0.06	0.21	0.21	-0.02	0.01	0.07	0.06	-0.19	-0.18	-0.04	-0.03
pH	0.27	0.27	0.11	0.10	-0.28	-0.27	-0.06	-0.07	-0.10	-0.09	0.21	0.19	0.06	0.05
F-SULFATE	-0.30	-0.28	-0.36	-0.38	0.26	0.25	0.17	0.21	0.37	0.35	-0.27	-0.34	-0.40	-0.41
LN F-SULFATE	-0.16	-0.16	-0.25	-0.26	0.14	0.14	0.22	0.28	0.21	0.21	-0.16	-0.21	-0.24	-0.24
SULFIDE	0.26	0.23	0.66	0.62	-0.23	-0.23	-0.11	-0.14	-0.61	-0.63	0.45	0.45	0.65	0.63
LN SULFIDE	0.20	0.13	0.52	0.56	-0.17	-0.18	0.12	0.08	-0.48	-0.47	0.40	0.46	0.58	0.59
S=/(SO4+S=)	0.24	0.21	0.60	0.59	-0.21	-0.21	-0.09	-0.13	-0.55	-0.57	0.42	0.43	0.62	0.61
LN X	0.19	0.13	0.46	0.50	-0.17	-0.18	0.05	0.00	-0.42	-0.40	0.36	0.43	0.51	0.53
KP Hg(II)	-0.10	-0.05	-0.49	-0.56	0.05	0.05	0.03	0.07	0.41	0.41	-0.27	-0.40	-0.55	-0.58
LN KP Hg(II)	-0.14	-0.10	-0.61	-0.64	0.08	0.08	0.11	0.13	0.53	0.54	-0.39	-0.48	-0.62	-0.64
KP MeHg	-0.25	-0.16	-0.32	-0.38	0.14	0.15	-0.07	-0.05	0.41	0.36	-0.31	-0.39	-0.48	-0.50
LN KP MeHg	-0.52	-0.41	-0.40	-0.49	0.44	0.46	0.12	0.11	0.49	0.43	-0.43	-0.55	-0.70	-0.71

Table 50. Continued.

	TS	LN	AVS	LN	TFE	LN	TMN	LN	THg	LN	MeHg	LN	%MeHg	LN
Depth	-0.32	-0.41	-0.14	-0.17	0.43	0.45	0.01	-0.04	-0.53	-0.50	-0.43	-0.48	-0.48	-0.57
LN Depth	-0.26	-0.34	-0.26	-0.26	0.37	0.35	-0.07	-0.13	-0.43	-0.40	-0.38	-0.40	-0.44	-0.55
F-THg	-0.28	-0.32	-0.04	0.05	0.18	0.18	-0.55	-0.59	-0.19	-0.18	-0.22	-0.19	-0.44	-0.66
LN THg	-0.16	-0.23	-0.04	0.06	0.21	0.18	-0.55	-0.59	-0.09	-0.09	-0.13	-0.10	-0.35	-0.57
F-MeHg	-0.37	-0.37	-0.01	0.08	0.40	0.39	-0.44	-0.49	-0.31	-0.29	-0.20	-0.25	-0.50	-0.72
.N F-MeH(	-0.34	-0.33	-0.06	0.03	0.44	0.42	-0.45	-0.48	-0.15	-0.15	-0.05	-0.14	-0.36	-0.62
%MeHg	-0.27	-0.25	-0.08	0.02	0.43	0.41	-0.35	-0.38	-0.17	-0.15	0.00	-0.05	-0.32	-0.55
N % MeH	-0.22	-0.17	-0.06	0.03	0.42	0.42	-0.24	-0.25	0.03	0.05	0.17	0.10	-0.12	-0.37
F-CA	0.37	0.38	0.19	0.22	0.14	0.12	0.40	0.41	0.11	0.18	0.00	0.14	0.24	0.39
LN F-CA	0.41	0.41	0.19	0.22	0.12	0.11	0.42	0.43	0.14	0.21	0.03	0.17	0.28	0.45
F-MG	0.14	0.11	0.13	0.21	0.14	0.08	0.12	0.12	-0.09	-0.04	-0.20	-0.12	-0.07	-0.08
LN F-MG	0.15	0.12	0.14	0.22	0.14	0.07	0.12	0.12	-0.09	-0.04	-0.20	-0.13	-0.07	-0.10
DOC	0.27	0.30	0.10	0.16	0.01	0.00	0.21	0.23	0.18	0.23	-0.06	0.09	0.08	0.26
LN DOC	0.32	0.34	0.14	0.19	0.02	0.01	0.25	0.27	0.20	0.25	-0.03	0.12	0.13	0.30
CL	0.17	0.23	0.02	0.09	-0.27	-0.26	0.05	0.09	0.24	0.29	-0.09	-0.05	-0.14	0.06
LN CL	0.19	0.24	0.02	0.09	-0.28	-0.27	0.04	0.08	0.25	0.30	-0.09	-0.05	-0.15	0.06
F-FE	0.19	0.21	0.18	0.23	0.02	0.02	0.19	0.21	0.07	0.13	0.08	0.21	0.23	0.29
LN F-FE	0.29	0.34	0.18	0.19	0.03	0.05	0.31	0.33	0.31	0.36	0.28	0.41	0.45	0.56
F-Fe(II)	0.07	0.10	0.17	0.23	-0.01	0.01	0.05	0.07	-0.02	0.04	-0.02	0.09	0.12	0.21
.N F-Fe(II	0.03	0.06	0.20	0.25	0.10	0.13	0.12	0.11	0.05	0.11	0.08	0.15	0.21	0.31
F-Fe(III)	0.01	0.06	0.29	0.37	0.19	0.16	0.12	0.14	-0.34	-0.32	-0.19	-0.10	-0.04	0.03
N F-Fe(III	-0.10	-0.04	0.33	0.44	0.31	0.29	0.11	0.13	-0.26	-0.23	-0.12	-0.08	0.01	0.02
F-MN	0.25	0.30	0.18	0.20	0.22	0.22	0.65	0.62	0.15	0.22	0.10	0.20	0.32	0.44
LN F-MN	0.37	0.43	0.24	0.21	0.01	0.04	0.72	0.72	0.29	0.35	0.23	0.32	0.49	0.69
REDOX	-0.07	-0.09	0.14	0.20	0.19	0.21	0.15	0.10	0.13	0.15	0.15	0.21	0.02	0.11
_N REDO›	0.09	0.10	0.29	0.30	0.20	0.20	0.39	0.33	0.02	0.07	0.00	0.11	0.05	0.16
[H+]	0.42	0.46	0.39	0.35	0.04	0.06	0.40	0.40	-0.13	-0.09	-0.19	-0.08	0.03	0.21
pH	-0.46	-0.52	-0.38	-0.33	-0.05	-0.08	-0.42	-0.43	0.07	0.03	0.20	0.12	-0.05	-0.24
F-SULFATI	0.59	0.49	0.01	-0.02	-0.31	-0.27	0.08	0.15	0.51	0.47	0.40	0.46	0.32	0.37
I F-SULFA	0.45	0.37	0.01	-0.05	-0.42	-0.38	-0.05	0.02	0.41	0.36	0.29	0.32	0.14	0.23
SULFIDE	-0.36	-0.42	-0.12	-0.09	0.29	0.22	-0.29	-0.35	-0.46	-0.49	-0.50	-0.59	-0.56	-0.61
N SULFID	-0.23	-0.27	-0.10	-0.11	0.39	0.38	-0.21	-0.26	-0.49	-0.50	-0.55	-0.58	-0.56	-0.45
:/(SO4+S	-0.39	-0.40	-0.06	-0.03	0.41	0.34	-0.15	-0.23	-0.55	-0.55	-0.58	-0.66	-0.57	-0.57
LN X	-0.32	-0.32	-0.06	-0.05	0.46	0.45	-0.14	-0.19	-0.55	-0.52	-0.54	-0.55	-0.46	-0.39
KP Hg(II)	0.32	0.36	-0.06	-0.07	-0.34	-0.32	0.37	0.43	0.56	0.55	0.50	0.49	0.52	0.55
N KP Hg(I	0.45	0.52	-0.03	-0.07	-0.23	-0.20	0.49	0.56	0.61	0.63	0.52	0.54	0.59	0.71
KP MeHg	0.46	0.42	-0.11	-0.12	-0.24	-0.22	0.32	0.38	0.40	0.42	0.43	0.51	0.51	0.49
N KP MeH	0.53	0.53	-0.01	-0.09	-0.38	-0.36	0.47	0.55	0.55	0.54	0.58	0.69	0.75	0.88

FISH X SURFACE WATER

Contrary to SOW specifications, the contractor (Janicki Environmental Inc., under contract to BFA) supplied only the results of the nonparametric Spearman analysis of mosquitofish THg versus surface water constituents other than F-THg, F-MeHg, F-Hg(II), and F-%MeHg. This resulted in a loss of critical information about the influence of surface water MeHg on MeHg bioaccumulation in small fish. Contrary to SOW specifications, the contractor also spatially averaged the individual station data on a monthly and quarterly basis. While reducing the variability in the individual observations, monthly averaging reduced the number of individual observations from 18 x 9 to 18 and quarterly averaging reduced that number to 7. In addition, the uncertainty introduced in the averaging process was not addressed explicitly via propagated error analysis. The results for all cells combined are presented with the preceding caveats. The contractor did not provide the results for the cells analyzed individually.

No Lag/No Average Correlation Analysis

All STA-2 Cells

Monthly Spatial Average

For surface water constituents other than F-THg, F-MeHg, and F-Hg(II), the strongest positive correlation was between mosquitofish THg and chlorophyll_c ($r = 0.49$; $p < 0.05$). The strongest, statistically significant inverse correlations at the $p < 0.01$ level were with pH (-0.67) and ortho-P (-0.60). Whether pH is co-correlated with ortho-P cannot be ascertained, because the contractor (Janicki Environmental Inc., under contract to BFA) did not provide the complete co-correlation table for each intra-correlation analysis by medium. At $p < 0.05$, ammonia (-0.54), U-TFe (-0.50), and TKN (-0.57) predominated. The inverse correlation with sulfate ($r = -0.32$) was not statistically significant at $p < 0.05$.

Quarterly Spatial Average

The only statistically significant positive or inverse correlation between mosquitofish THg and any other surface water constituent other than F-THg, F-MeHg, and F-Hg(II) was an inverse correlation with ortho-P ($r = -0.96$) at $p < 0.001$.

FISH X PORE WATER

No Lag/No Average Correlation Analysis

Table 51 presents the inter-correlations between mosquitofish THg concentrations and the pore water parameters collected two weeks earlier. For the parametric analysis, the strongest correlation between mosquitofish THg concentration and pore water constituents was with the pore water F-MeHg/soil MeHg partition coefficient (KPMeHg) ($r = 0.60$). Interestingly, for the subset of data collected in conjunction with the pore water samples, the Pearson correlation coefficient of mosquitofish THg versus KPMeHg ($r = 0.6$) is much greater than the values for mosquitofish THg versus pore water MeHg ($r = 0.10$) or soil MeHg ($r = 0.32$). To explain this unexpected set of relationships, one might conjecture that the concentration of MeHg on soil particles is more important than the dissolved MeHg in surficial soil pore water for transferring MeHg to the benthic food chain, but that not all MeHg on surficial soil particles is bioavailable to the benthic food chain. Rather, a disproportional fraction of the soil MeHg in equilibrium with pore water dissolved MeHg is bioavailable to the benthic food chain. This is despite the fact that

the KPMeHg value is calculated by dividing the dry-weight soil MeHg concentration by the pore water MeHg concentration. If this conjecture has validity, one might speculate that the correlation would increase substantially if the KPMeHg was calculated using only the labile fraction of soil MeHg in equilibrium with pore water MeHg. If pore water sulfide is mediating the magnitude of the Hg(II) and/or MeHg in pore water solution, one might expect that there would be an inverse relationship between the concentration of Hg(II) and/or MeHg in pore water and a positive relationship with the MeHg in soil. In fact, the opposite obtains, with correlation coefficients between soil THg and MeHg and pore water sulfide of r = -0.49 and r = -0.55, respectively. This is also true of the corresponding KPHg(II) and KPMeHg, with virtually identical inverse correlations with pore water sulfide of -0.64 and -0.60, respectively. This suggests that sulfide complexes of Hg(II) and MeHg are predominately in pore water solution, as opposed to sulfide precipitates on soil particles. However, while there is a weak to moderate positive correlation between pore water sulfate and mosquitofish THg, there is only a very weak inverse relationship between mosquitofish THg and pore water sulfide (r = -0.19).

LAG ANALYSIS

Figures 143 through **145** graph mosquitofish THg as MeHg concentration versus the pore water F-MeHg concentration obtained in the immediately preceding sampling event (lag-2 weeks), the two preceding events (lag-6 weeks), three preceding events (lag-10 weeks), while **Figures 146** through **148** graph the corresponding relationships with pore water sulfide concentration. In summary, all of the correlations are virtually nonexistent, suggesting that something other than pore water MeHg was driving mosquitofish bioaccumulation of MeHg, either directly or indirectly, with or without the influence of pore water sulfide.

Table 51. Pearson correlation coefficients for the inter-correlations between mosquitofish THg and surficial pore water for all STA-2 cells combined for the four sampling events for which surficial soil was collected concurrently from October 2003 through January 2004.

	MFISH THg	LN	WATER BCF	LN	SOIL BAF	LN	PW BAF	LN
Depth	-0.07	-0.05	0.42	0.32	0.63	0.49	0.05	-0.19
LN Depth	0.06	0.10	0.41	0.33	0.50	0.45	0.03	-0.22
F-THg	0.13	0.26	0.47	0.34	0.40	0.35	-0.28	-0.54
LN THg	0.01	0.14	0.35	0.21	0.27	0.18	-0.39	-0.60
F-MeHg	0.10	0.22	0.51	0.48	0.31	0.37	-0.23	-0.67
LN F-MeHg	-0.03	0.13	0.54	0.47	0.24	0.22	-0.46	-0.83
%MeHg	-0.02	0.08	0.37	0.39	0.07	0.10	-0.27	-0.72
LN % MeHg	-0.02	0.06	0.37	0.32	-0.04	-0.05	-0.37	-0.74
F-CA	-0.27	-0.33	-0.48	-0.42	-0.38	-0.36	0.04	0.16
LN F-CA	-0.29	-0.37	-0.53	-0.47	-0.43	-0.40	0.06	0.20
F-MG	-0.21	-0.22	-0.21	-0.13	-0.03	-0.03	-0.03	-0.04
LN F-MG	-0.20	-0.21	-0.20	-0.12	-0.02	-0.01	-0.02	-0.04
DOC	-0.20	-0.17	-0.27	-0.18	-0.27	-0.20	-0.09	0.03
LN DOC	-0.23	-0.23	-0.35	-0.26	-0.32	-0.27	-0.08	0.04
CL	-0.11	-0.15	-0.14	-0.04	-0.12	-0.06	-0.07	-0.13
LN CL	-0.09	-0.14	-0.13	-0.04	-0.11	-0.04	-0.06	-0.13
F-FE	-0.21	-0.18	-0.32	-0.32	-0.25	-0.31	-0.06	0.16
LN F-FE	-0.30	-0.29	-0.51	-0.51	-0.49	-0.58	-0.13	0.12
F-Fe(II)	-0.22	-0.20	-0.29	-0.28	-0.29	-0.29	-0.10	0.10
LN F-Fe(II)	-0.29	-0.27	-0.35	-0.40	-0.44	-0.42	-0.22	-0.05
F-Fe(III)	-0.27	-0.25	-0.27	-0.28	-0.20	-0.16	-0.10	0.05
LN F-Fe(III)	-0.43	-0.45	-0.31	-0.36	-0.40	-0.39	-0.25	-0.20
F-MN	-0.20	-0.20	-0.35	-0.32	-0.36	-0.33	-0.05	0.08
LN F-MN	-0.20	-0.25	-0.50	-0.45	-0.53	-0.47	0.03	0.20
REDOX	0.14	0.12	0.02	-0.07	-0.11	-0.12	-0.29	-0.24
LN REDOX	-0.09	-0.08	-0.23	-0.37	-0.17	-0.16	-0.04	0.06
[H+]	-0.21	-0.24	-0.36	-0.37	-0.22	-0.10	0.01	0.18
pH	0.20	0.28	0.36	0.36	0.23	0.08	-0.07	-0.21
F-SULFATE	0.44	0.33	-0.14	-0.23	-0.23	-0.23	0.47	0.39
LN F-SULFATE	0.37	0.30	-0.05	-0.15	-0.14	-0.11	0.32	0.29
SULFIDE	-0.19	-0.19	0.20	0.19	0.49	0.44	-0.16	-0.14
LN SULFIDE	-0.32	-0.34	0.12	0.08	0.34	0.34	-0.23	-0.37
S=/(SO4+S=)	-0.31	-0.30	0.15	0.18	0.45	0.43	-0.22	-0.21
LN X	-0.43	-0.41	0.09	0.09	0.27	0.26	-0.32	-0.43
KP Hg(II)	0.30	0.19	-0.22	-0.10	-0.39	-0.35	0.40	0.49
LN KP Hg(II)	0.13	0.01	-0.35	-0.23	-0.58	-0.50	0.31	0.40
KP MeHg	0.60	0.43	-0.23	-0.10	-0.23	-0.16	0.84	0.81
LN KP MeHg	0.14	0.03	-0.53	-0.43	-0.58	-0.59	0.43	0.75

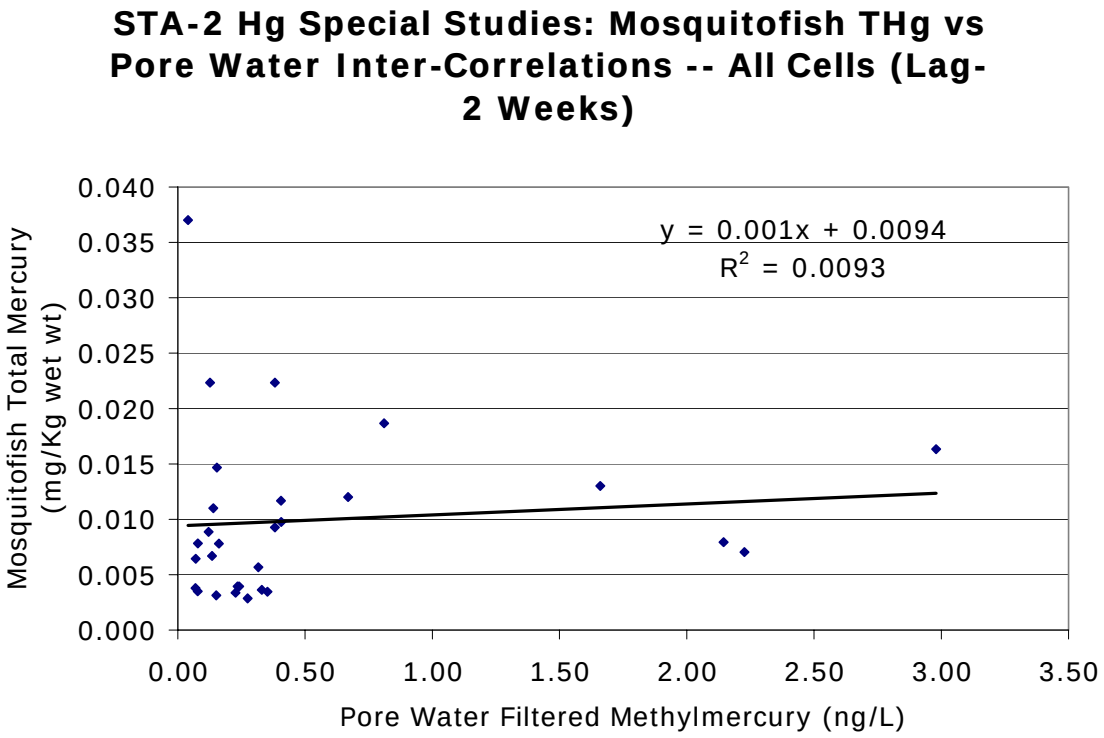

Figure 143. Scatter plot of the mosquitofish THg concentration versus the pore water dissolved methylmercury concentration (F-MeHg) for STA-2 all cells combined and Lag-2 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

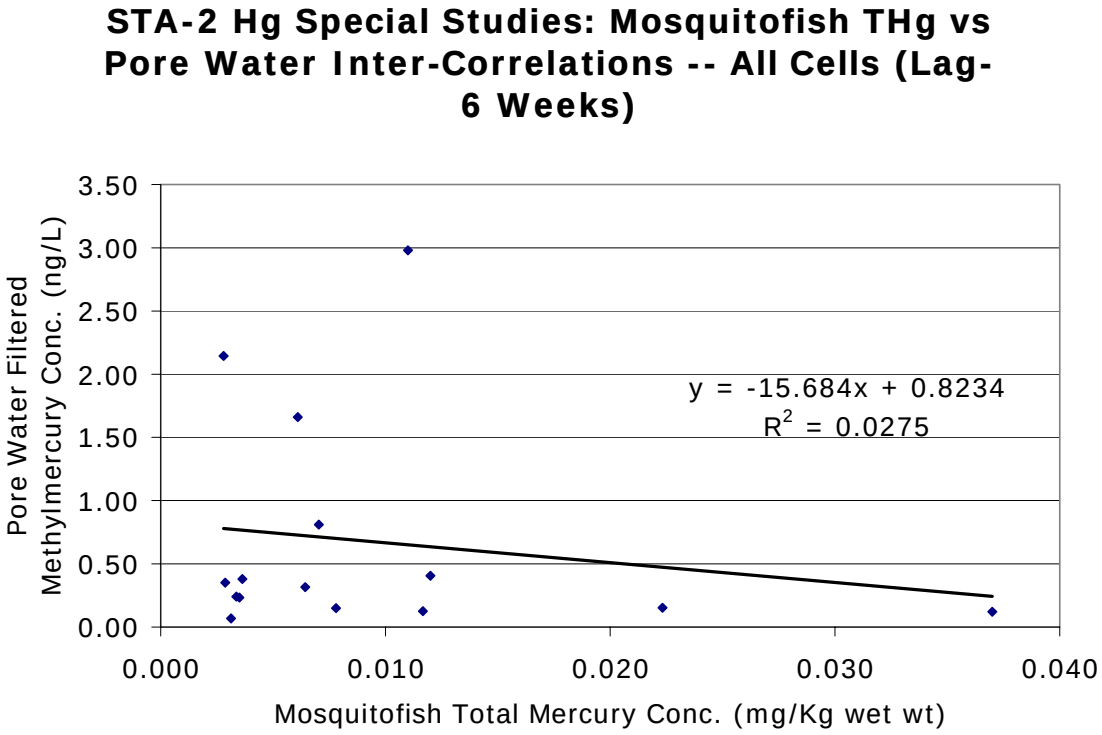

Figure 144. Scatter plot of the mosquitofish THg concentration versus the pore water dissolved methylmercury concentration (F-MeHg) for STA-2 all cells combined and Lag-6 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

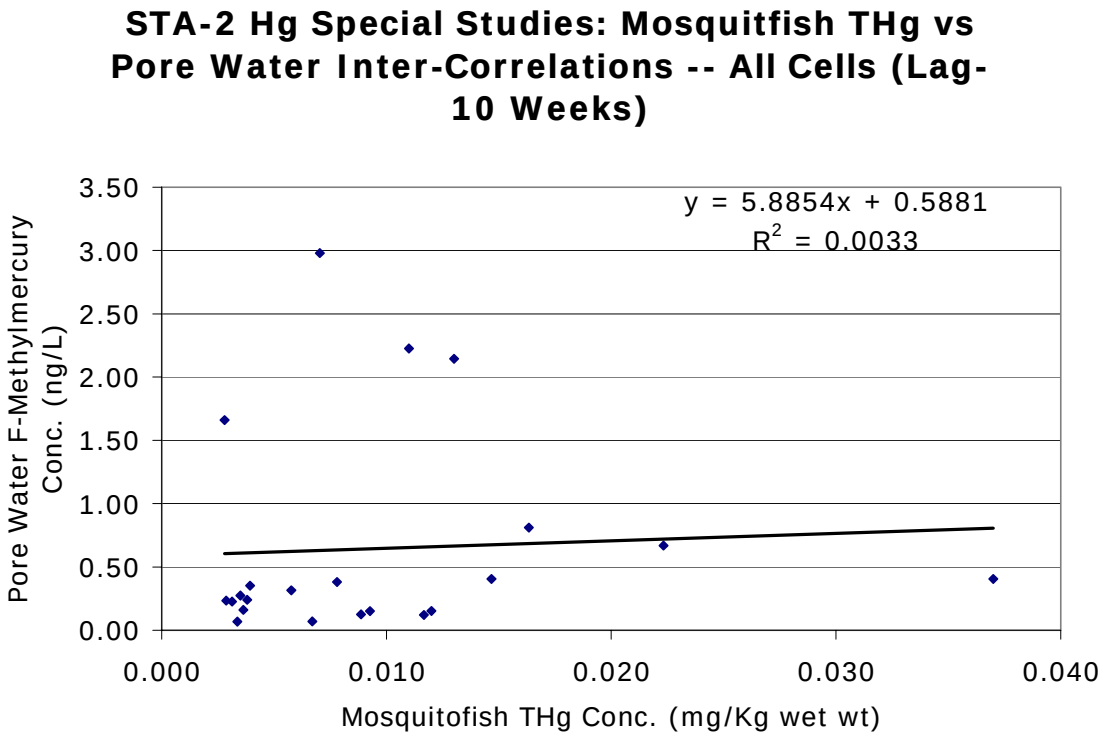

Figure 145. Scatter plot of the mosquitofish THg concentration versus the pore water dissolved methylmercury concentration (F-MeHg) for STA-2 all cells combined and Lag-10 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

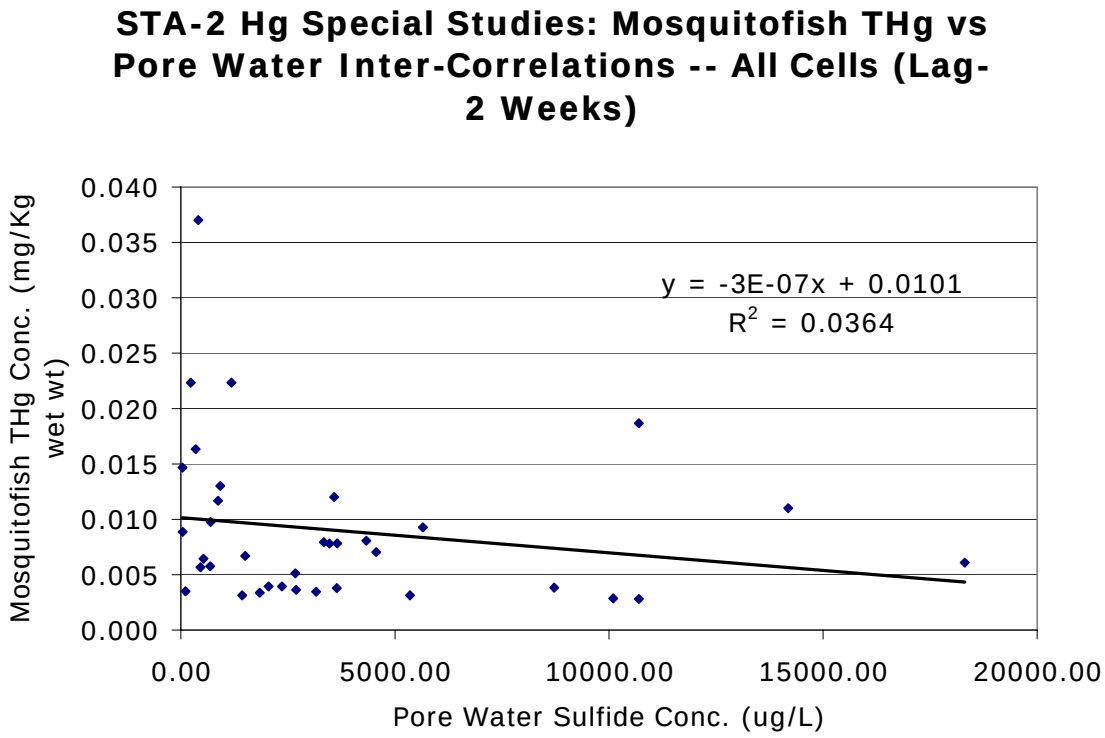

Figure 146. Scatter plot of the mosquitofish THg concentration versus the pore water dissolved sulfide concentration (S2-) for STA-2 all cells combined and Lag-2 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

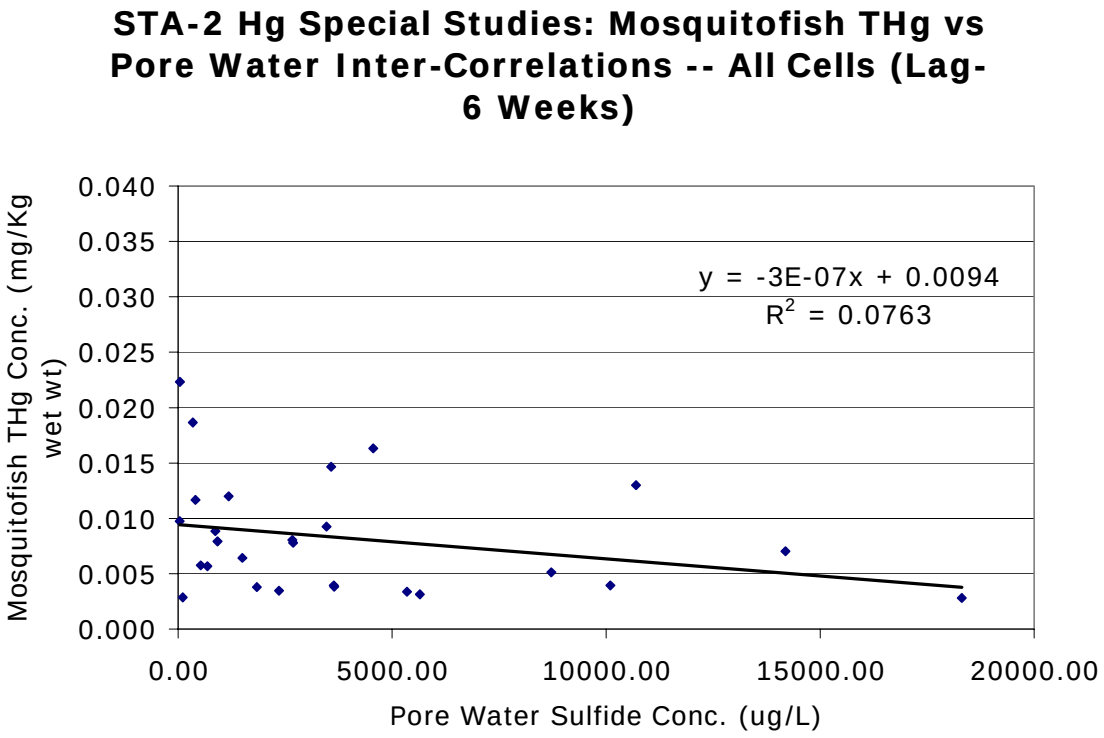

Figure 147. Scatter plot of the mosquitofish THg concentration versus the pore water dissolved sulfide concentration (S2-) for STA-2 all cells combined and Lag-6 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

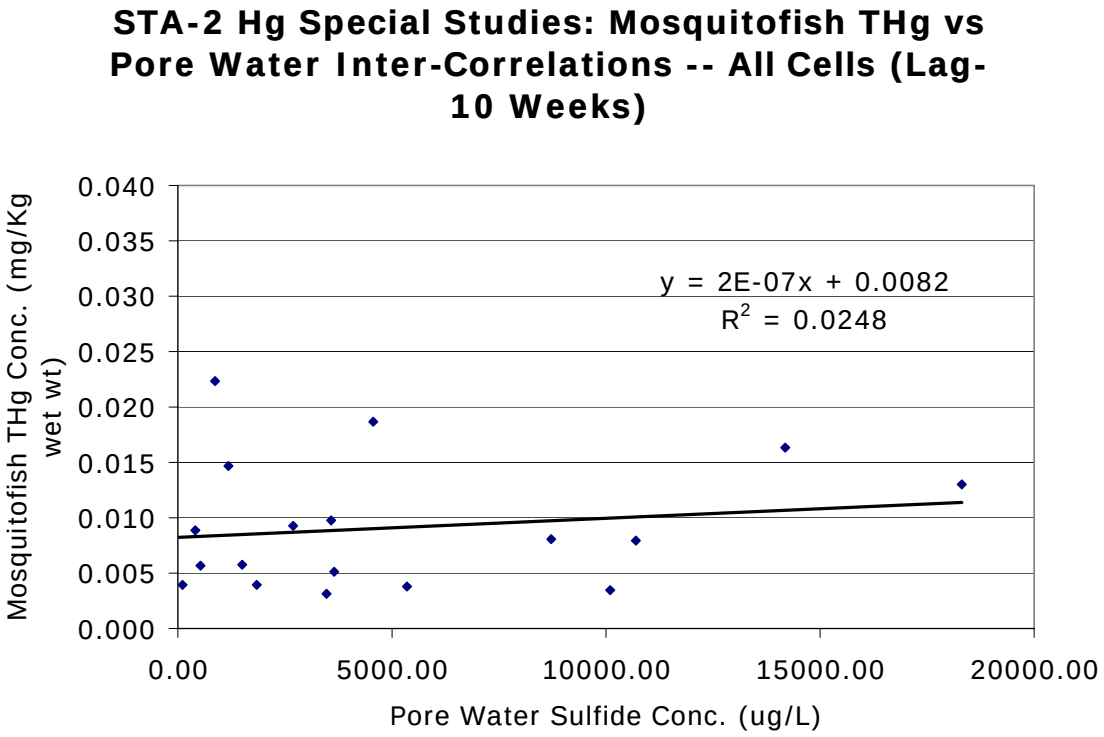

Figure 148. Scatter plot of the mosquitofish THg concentration versus the pore water dissolved sulfide concentration (S2-) for STA-2 all cells combined and Lag-10 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

FISH X SOIL

The contractor (Janicki Environmental Inc., under contract to BFA) omitted soil THg and MeHg as independent variables. Thus, the detection of the likely influence of soil MeHg on mosquitofish MeHg bioaccumulation as THg was precluded. The deficient results are presented below with that Caveat. In addition, the contractor was supplied with a soil data set that contained an erroneous soil total sulfur concentration value that was biased high by an order of magnitude (decimal point transcription error). Because there were only ten soil sampling trips, this decreased the r^2 and increased the p values of the univariate and multivariate regression models of fish versus soil total sulfur. The log-transformed data may have suppressed the influence of this one erroneous datum in the multivariate regression analysis, however. Unfortunately, the contractor did not perform a univariate analysis on the log-transformed data.

STA-2 All Cells

No Lag/No Average Correlation Analysis

No Spatial Average

As iterated in **Table 52** and depicted in **Figure 149**, the strongest apparent influence of surficial soil chemistry paired with the THg as MeHg in mosquitofish collected two weeks later (lag-2 weeks) from the three interior stations in each of Cells 1, 2, and 3 is surficial soil MeHg concentration (r^2 = 0.692). However, when the cells are graphed individually (**Figures 150** through **152**), the r^2 values decrease progressively from 0.62 to 0.21 to 0.041. The fact that none of the disaggregated data sets produces as strong a correlation as the combined data set suggests that the strong positive correlation may be spurious, although it could also be the effect of a reduction in the number of independent observations in each of the disaggregated data sets.

Spatial Average Monthly

For the nonparametric univariate analysis, there was only one statistically significant positive or inverse correlation between mosquitofish THg and any soil constituent other than THg and MeHg: Ca ($r = -0.80$; $p < 0.001$). There were weak to moderate inverse correlation with percent moisture, total Mg, and AVS (r = -0.65, -0.57, and -0.53, respectively).

Spatial Average Quarterly

There were no statistically significant positive or inverse correlations between mosquitofish THg and any soil constituent other than THg and MeHg. There were a weak to moderate inverse correlation with percent moisture, percent ash, Ca, and AVS (r = -0.68, -0.71, -0.64, and -0.64, respectively).

Table 52. Pearson correlation coefficients of untransformed and natural log-transformed mosquitofish THg, surface water bioaccumulation factors, or soil bioaccumulation factors versus untransformed and natural log-transformed soil constituent concentrations.

		Lag-2 Wks		Lag-6 Wks		Lag-10 Wks		Lag-14 Wks	
All	(N = 144 pairs)	SOIL MeHg (N = 144)	LN	SOIL MeHg (N = 144 - 9)	LN	SOIL MeHg (N=144-18)	LN	SOIL MeHg (N = 144-27)	LN
	MFISH THg	0.83	0.75	0.89	0.76	0.86	0.72	0.94	0.80
	LN MFISH THg	0.62	0.73	0.68	0.83	0.70	0.80	0.71	0.80
	MFISH BAF	-0.08	0.11	-0.02	0.19	0.14	0.32	0.31	0.47
	LN MFISH BAF	-0.10	0.07	0.03	0.17	0.30	0.46	0.34	0.45
	MFISH SBAF	-0.23	-0.41					0.16	0.06
	LN MFISH SBAF	-0.20	-0.38					0.18	0.08
Cell 1 Only		(N = 48)		(N = 48 - 3)		(N=48-6)		(N = 48-9)	
	MFISH THg	0.78	0.79	0.85	0.79	0.81	0.80	0.93	0.94
	LN MFISH THg	0.56	0.63	0.65	0.71	0.74	0.85	0.68	0.80
	MFISH BAF	-0.39	-0.34	-0.48	-0.44	-0.46	-0.32	-0.41	-0.24
	LN MFISH BAF	-0.34	-0.26	-0.49	-0.43	-0.51	-0.37	-0.42	-0.27
	MFISH SBAF	-0.34	-0.37					-0.30	-0.28
	LN MFISH SBAF	-0.20	-0.20					-0.13	-0.06
Cell 2 Only		(N = 48)		(N = 48 - 3)		(N=48-6)		(N = 48-9)	
	MFISH THg	0.47	0.54	0.57	0.64	0.71	0.73	0.74	0.75
	LN MFISH THg	0.47	0.55	0.61	0.68	0.64	0.73	0.67	0.73
	MFISH BAF	0.11	0.12	-0.07	-0.05	0.24	0.30	0.28	0.38
	LN MFISH BAF	0.32	0.38	0.10	0.10	0.39	0.45	0.51	0.62
	MFISH SBAF	-0.12	-0.02					0.20	0.29
	LN MFISH SBAF	-0.15	-0.09					0.32	0.41
Cell 3 Only		(N = 48)		(N = 48 - 3)		(N=48-6)		(N = 48-9)	
	MFISH THg	0.17	0.32	0.52	0.63	0.05	0.18	0.50	0.53
	LN MFISH THg	0.25	0.41	0.51	0.63	0.13	0.24	0.47	0.56
	MFISH BAF	0.15	0.21	0.42	0.49	0.22	0.37	0.82	0.76
	LN MFISH BAF	0.09	0.17	0.39	0.45	0.30	0.38	0.56	0.59
	MFISH SBAF	-0.57	-0.62					0.34	0.21
	LN MFISH SBAF	-0.78	-0.76					0.36	0.28

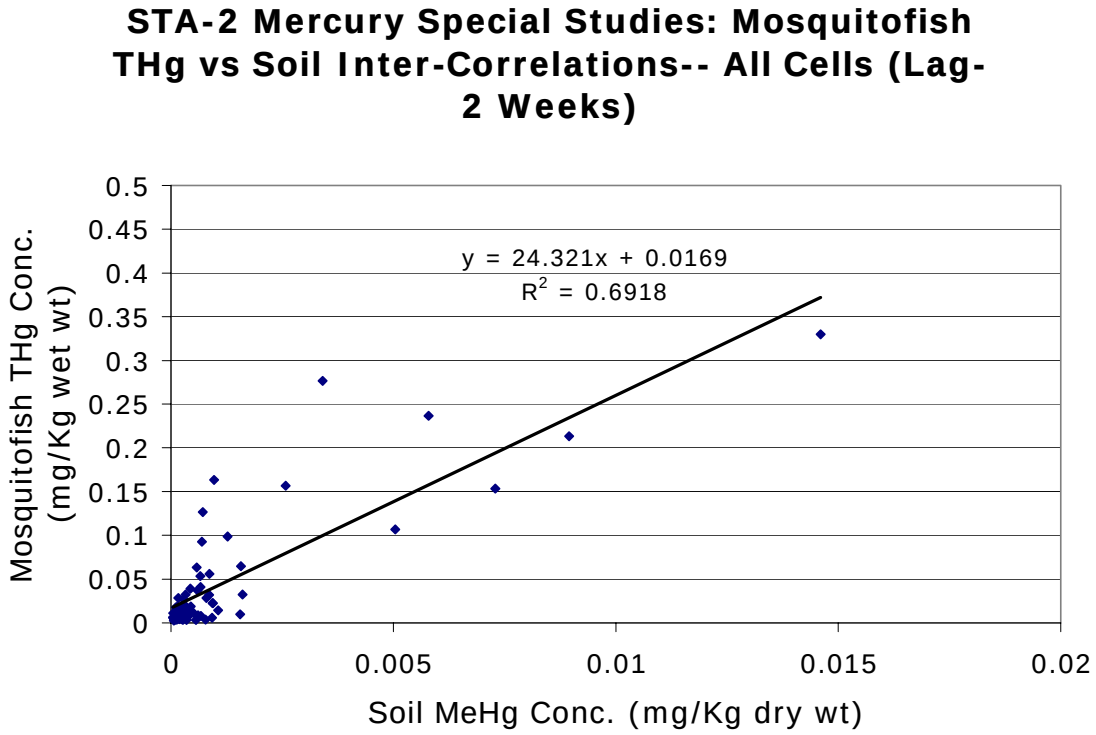

Figure 149. Scatter plot of the mosquitofish THg concentration versus the soil methylmercury (MeHg) concentration for STA-2 all cells combined and Lag-2 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

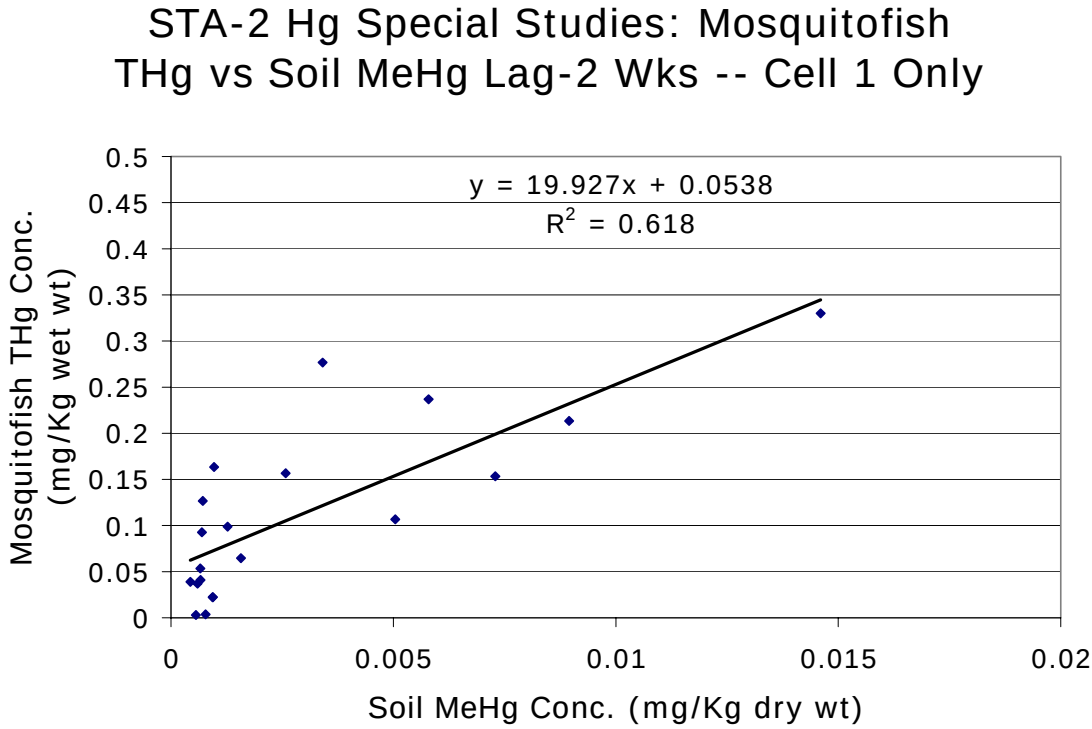

Figure 150. Scatter plot of the mosquitofish THg concentration versus the soil methylmercury (MeHg) concentration for Cell 1 only and Lag-2 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

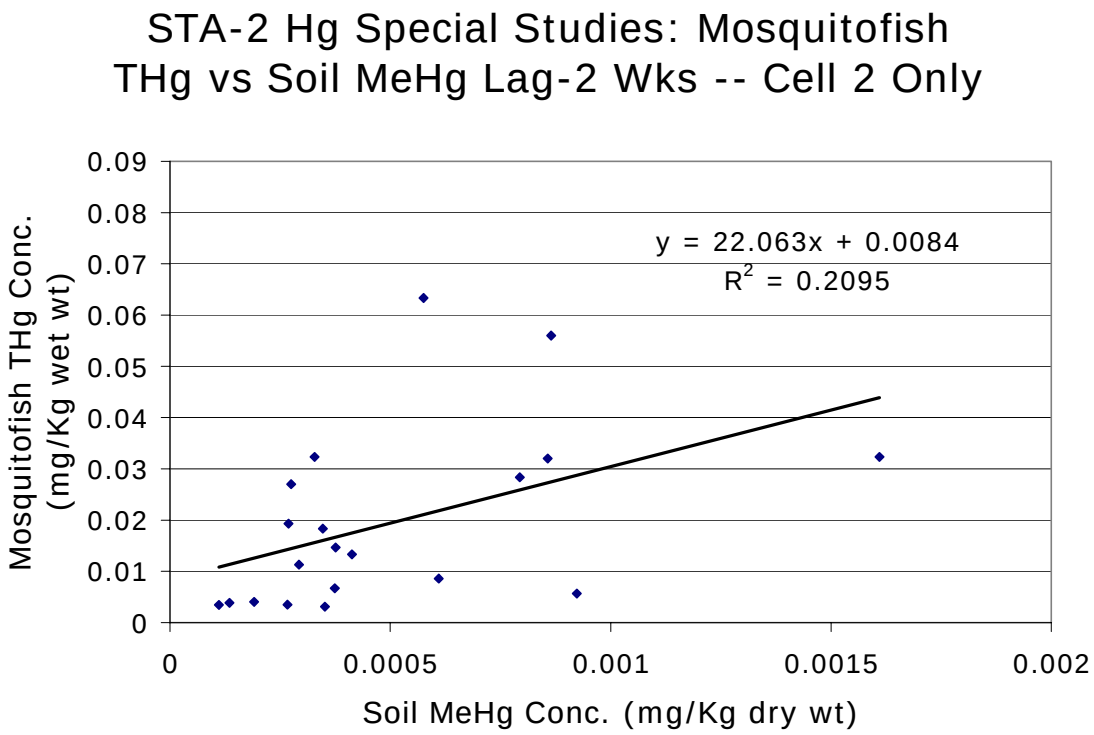

Figure 151. Scatter plot of the mosquitofish THg concentration versus the soil methylmercury (MeHg) concentration for Cell 2 only and Lag-2 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

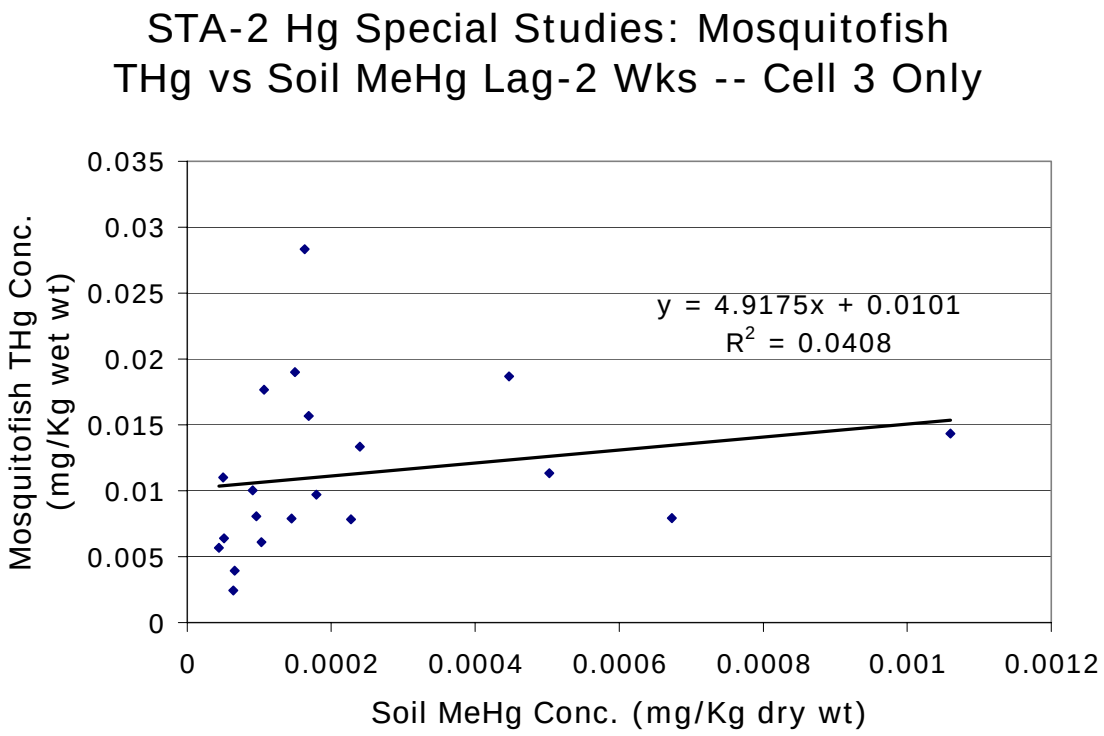

Figure 152. Scatter plot of the mosquitofish THg concentration versus the soil methylmercury (MeHg) concentration for Cell 1 only and Lag-2 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

Lag Analysis

Table 52 iterates the parametric inter-correlations to evaluate the effect of pairing the mosquitofish THg concentrations for all cells combined with the soil MeHg concentration in a sample collected two weeks, six weeks, ten weeks, and fourteen weeks previously. As can be ascertained by inspection of **Table 52**, for all cells combined and Cell 1, the correlations were strong initially and increase from lag-2 to lag-6 weeks, declined slightly at lag-10 weeks, and reached its peak at lag-14 weeks. This pattern is illustrated for Cell 1 in **Figures 153** through **155**. Cell 2 correlations increased progressively through lag-14 weeks, while Cell 3 increased progressively from lag-2 to lag-6 weeks, then decreased to virtually nonexistent at lag-10 weeks, then increased substantially at lag-14 weeks but not quite to the peak correlation at lag-6 weeks. The natural log transformations of the data generally result in a corresponding increase in the magnitudes of the correlation coefficients for all cells combined and each of the individual cells with a few exceptions. As depicted in **Figure 156**, the lag-18 weeks correlation for Cell 1 decreased detectably relative to lag-14 weeks, and this pattern was repeated for all cells combined and Cells 2 and 3, as well. That is why **Table 52** was truncated at lag-14 weeks. Further parsing of the lag-time influences on the strength of the correlation in Cell 1 at the individual station level might allow a discrimination of the influence of trophic dynamics from MeHg production dynamics, and the number of sampling events exceeds the threshold of n = 14, but time did not permit this additional analysis.

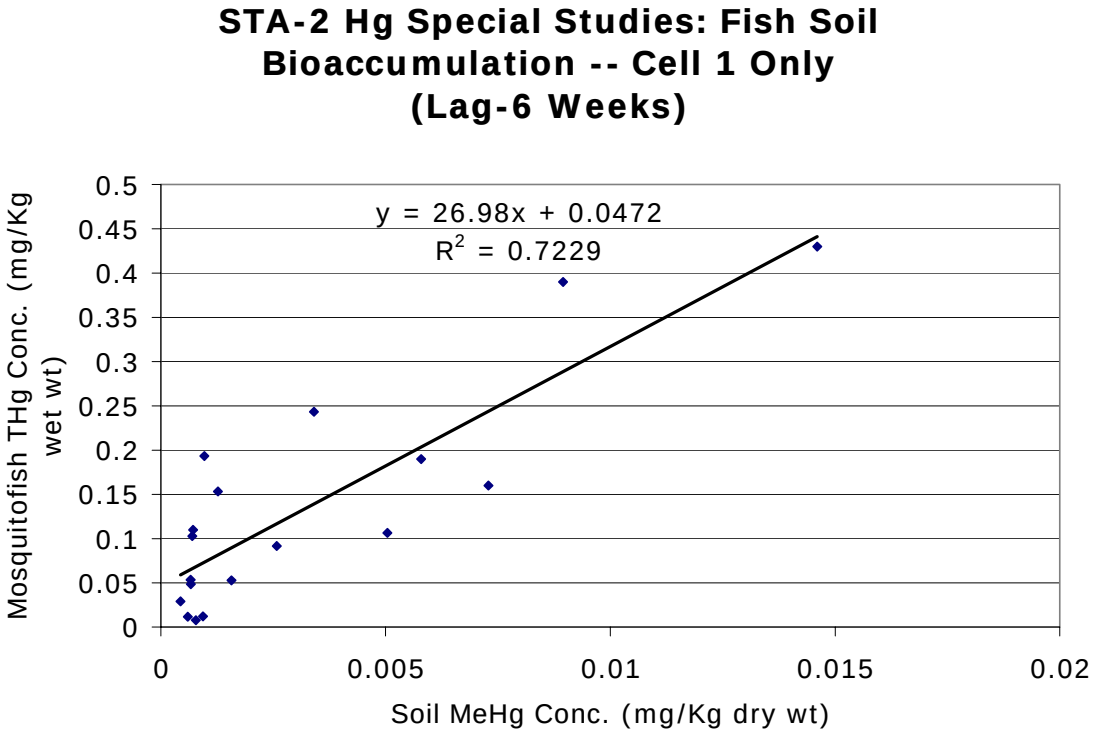

Figure 153. Scatter plot of the mosquitofish THg concentration versus the soil methylmercury (MeHg) concentration for Cell 1 only and Lag-6 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

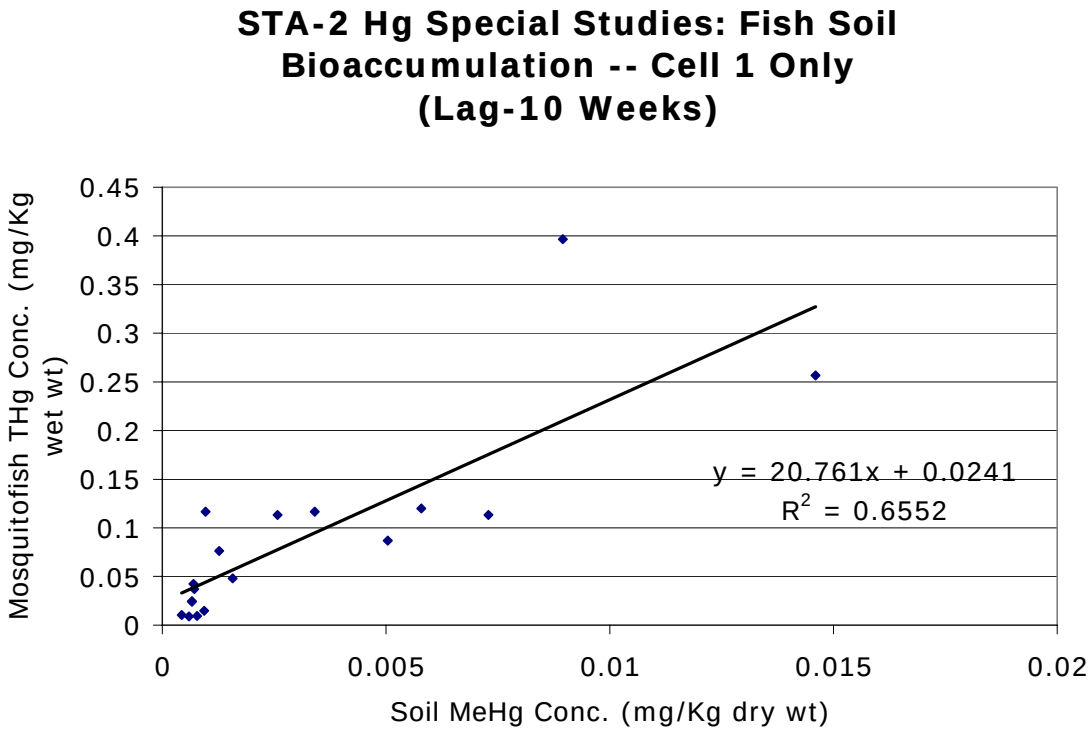

Figure 154. Scatter plot of the mosquitofish THg concentration versus the soil methylmercury (MeHg) concentration for Cell 1 only and Lag-10 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

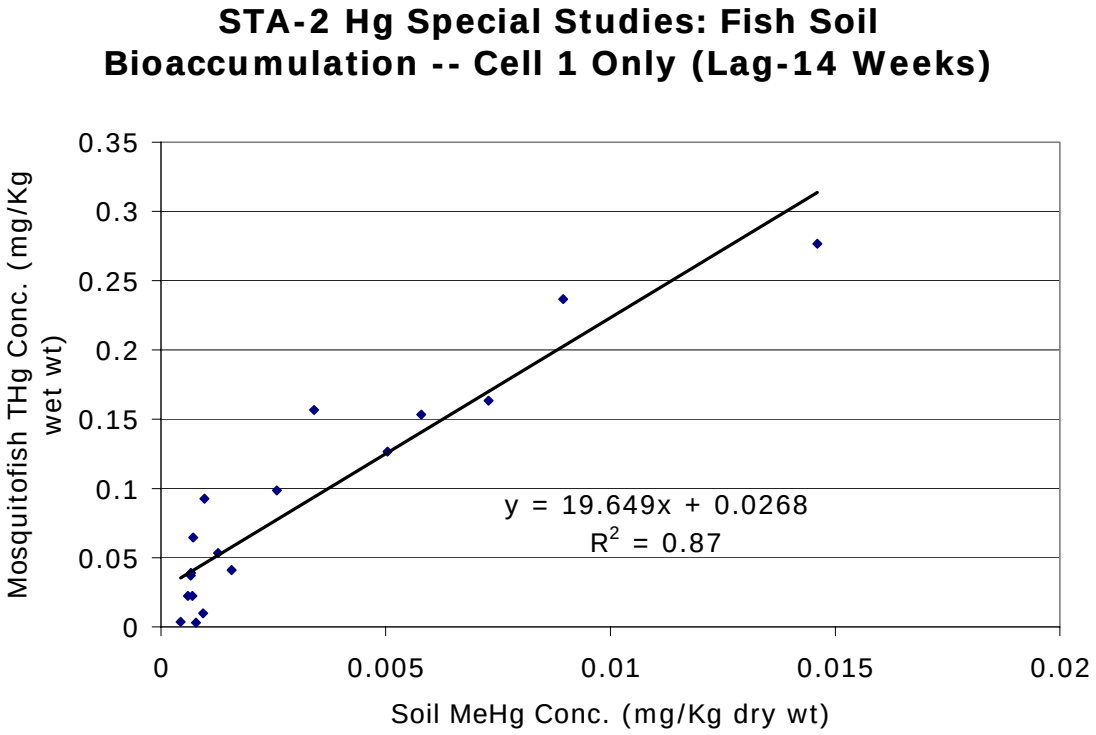

Figure 155. Scatter plot of the mosquitofish THg concentration versus the soil methylmercury (MeHg) concentration for Cell 1 only and Lag-14 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

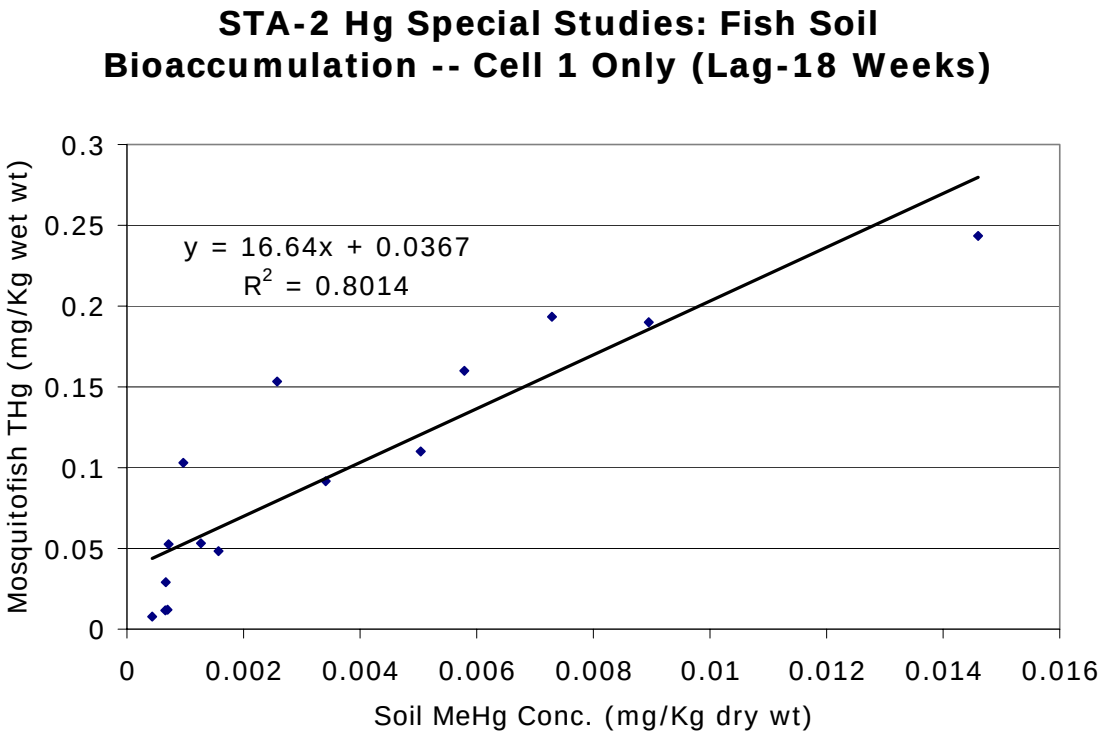

Figure 156. Scatter plot of the mosquitofish THg concentration versus the soil methylmercury (MeHg) concentration for Cell 1 only and Lag-18 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

Cells 1, 2, and 3 Individually

As presented in **Table 52**, the strongest apparent influence of surficial soil chemistry on the concentration of THg as MeHg in mosquitofish from the three interior stations in Cell 1 is surficial soil MeHg concentration. However, the r value decreases substantially and progressively as one moves from Cell 1 ($r^2 = 0.618$) to Cell 2 ($r^2 = 0.2095$) and Cell 2 to Cell 3 ($r^2 = 0.0418$). Interestingly, the combined data sets for Cells 1, 2, and 3 yields an overall r^2 value of 0.698, which is greater than the individual cell data sets of which it s comprised.

Individual Cell 1 Sites

C1AA

No Lag/ No Average Correlation Analysis

The mosquitofish THg concentration exhibited a strong to very strong positive correlation with soil MeHg (r = 0.874), bulk density (r = 0.85), and total nitrogen (r = 0.945) and strong to very strong inverse correlation with soil moisture (r = -0.923) and ash content (r = -0.799). In general, the correlations with the bioconcentration factor weaken somewhat to substantially relative to the mosquitofish THg concentration.

Lag Correlation Analyses

Lag-12 Weeks:

The mosquitofish THg concentration exhibited a strong to very strong inverse correlation with soil moisture (r = -0.884) and ash content (r = -0.833). In general, the correlations with the bioconcentration factor weakened somewhat substantially relative to the mosquitofish THg concentration.

Lag-24 Weeks:

The mosquitofish THg concentration exhibited a strong to very strong inverse correlation with soil moisture (r = -0.961) and ash content (r = -0.833). In general, the correlations with the bioconcentration factor weakened somewhat substantially relative to the mosquitofish THg concentration.

Lag-36 Weeks:

The mosquitofish THg concentration exhibited a strong to very strong inverse correlation with soil moisture (r = 0.975) and ash content (r = -0.994). In general, the correlations with the bioconcentration factor weakened somewhat substantially relative to the mosquitofish THg concentration.

Lag-48 Weeks, etc.:

The total number of observations was less than five.

C1BB

No Lag/No Average Analysis

There were moderate to strong inverse correlations with soil calcium (r = -0.683), magnesium (r = -0.669), percent ash (-0.897) and total sulfur (-0.793). A nearly statistically significant inverse relationship was also observed with soil total phosphorus (r = -0.628; p = 0.0703). In general, the mosquitofish BCF relationships weaken slightly to substantially relative to the mosquitofish THg concentration.

Lag-12 Weeks:

No statistically significant moderate to strong positive or inverse correlations emerged between mosquitofish THg and any soil constituent. Several BCF correlations were statistically significant or nearly so, but the number of observations was only four versus six for mosquitofish THg, so the results were not considered robust.

Lag-36 Weeks:

No statistically significant moderate to strong positive or inverse correlations emerged between mosquitofish THg and any soil constituent. Several BCF correlations were statistically significant or nearly so, but the number of observations was only four versus six for mosquitofish THg, so the results were not considered robust.

Lag-48 Weeks, etc.:

The total number of observations was less than five.

C1CC

Lag-0 Weeks:

There were strong to very strong positive correlations between mosquitofish THg and soil MeHg (r = 0.741) and bulk density (r = 0.715). There was a strong inverse relationship between mosquitofish THg and soil magnesium (r = -0.785). There was a strong positive relationship between the mosquitofish BCF and soil magnesium (r = -0.747). In general, for the remaining relationships, the correlations between mosquitofish BCF and soil constituents were somewhat to substantially weaker than the corresponding correlations with mosquitofish THg.

Lag-12 Weeks:

There were strong to very strong positive correlations between mosquitofish THg and soil MeHg (r = 0.887) and bulk density (r = 0.722; p = 0.0671). There was a strong inverse relationship between mosquitofish THg and soil total phosphorus (r = -0.89) and total sulfur (-0.765). In general, the correlations between mosquitofish BCF and soil constituents were virtually nonexistent.

Lag-24 Weeks:

There were strong to very strong positive correlations between mosquitofish THg and soil MeHg (r = 0.767) and bulk density (r = 0.655; p = 0.11). There was a strong inverse relationship between mosquitofish THg and acid volatile sulfide (r = -0.804), soil total phosphorus (r = -0.794), soil moisture (r = -0.835), and total sulfur (r = -0.676; p = 0.0955). In general, for the remaining relationships, the correlations between mosquitofish BCF and soil constituents were somewhat to substantially weaker than the corresponding correlations with mosquitofish THg.

Lag-36 Weeks:

There was a strong to very strong positive correlations between mosquitofish BCF and soil iron (r = 0.804; p = 0.0539). There was a strong inverse relationship between mosquitofish THg and soil total phosphorus (r = -0.868), soil moisture (r = -0.73; p = 0.099), and total sulfur (r = -0.944). In general, for the remaining relationships, the correlations between mosquitofish BCF and soil constituents were somewhat to substantially weaker than the corresponding correlations with mosquitofish THg.

Lag-48 Weeks, etc.:

The total number of observations was less than five.

Loads x Loads

SURFACE WATER X SOIL

No Lag/No Average Correlation Analysis

Perhaps most instructive were the results of the inter-correlations between the net import of surface water mass or load in each of the six quarters of the study and the change in surficial soil mass or load in that same quarter. The parametric results are presented in **Table 53** for all STA-2

cells combined and **Tables 54** through **56** for Cells 1, 2, and 3, respectively. The influence of water budget parameters on the load inter-correlations are summarized in **Table 57**. The nonparametric results are presented in **Tables 58** through **60** for Cells 1, 2, and 3 individually respectively. **Figure 157** is a plot of the quarterly net import of surface water THg mass versus change in soil THg mass, while **Figure 158** is the equivalent MeHg plot. The inter-relationship of the quarterly surface water and soil mass budgets is extremely weak for THg but extremely strong for MeHg. This supports one of the assumptions upon which the study design was based: that the internal production of MeHg in the surficial soil layer with subsequent transfer to surface water, and not imported MeHg, dominates the surface water mass budget for MeHg. The weaker inter-correlation with THg may be due in part to the focus on the 0-4 cm horizon, where MeHg production from labile Hg(II) is maximized but from which labile Hg(II) may be lost to deeper soil horizons via leaching without being accounted for in the truncated monitoring of the soil horizon. However, this hypothesis is not supported by an inspection of the parametric correlation coefficients for the inter-relationships among water budget parameters and the quarterly changes in soil constituent mass in the top four cm of surficial peat soil in STA-2 (**Table 57**), as the correlations between seepage volume and soil constituents are generally weak and weak for THg and MeHg specifically.

Nor was any other soil or surface water constituent mass budget strongly correlated with the quarterly change in the soil MeHg mass. Moreover, the net import of THg was not strongly correlated with the change in soil MeHg mass at Lag-0 weeks nor did the correlation strengthen when the net import was lagged by 12 weeks. This was also true of the net import of sulfate at Lag-0 and Lag-12 weeks. Those virtually nonexistent inter-correlations between the quarterly change in soil MeHg and the net mass import of THg mass and sulfate mass are illustrated for lag-0 and lag-12 weeks in **Figures 159** through **162**, respectively. However, the soil MeHg concentration, as opposed to the quarterly change in soil mass load, was moderately inversely correlated with soil acid volatile sulfide, for example, so the significance of the absence of strong intra- and inter-correlations in the mass budget realm should not be extended to the concentration realm, except where otherwise specifically noted.

Table 53.

Inter-correlation between surface water mass budget net import by quarter and change in soil mass storage for successive quarters for STA-2

	TP	TKN	NOX	NH3	TCA	SO4	DOC	CL	THg	MeHg
TP	-0.42	-0.29	-0.17	-0.38	-0.31	-0.06	-0.24	-0.02	-0.24	-0.13
TN	-0.54	-0.42	-0.44	-0.55	-0.43	-0.11	-0.34	-0.35	-0.26	0.07
CA	-0.22	-0.10	-0.11	-0.16	-0.13	0.01	-0.07	0.00	-0.03	0.14
MG	-0.45	-0.32	-0.23	-0.41	-0.33	-0.07	-0.26	-0.11	-0.19	0.01
TS	-0.32	-0.26	-0.05	-0.37	-0.23	-0.01	-0.19	-0.08	-0.14	-0.14
AVS	-0.27	-0.23	-0.22	-0.36	-0.22	0.05	-0.16	-0.14	-0.18	0.01
TFE	-0.42	-0.35	-0.21	-0.39	-0.34	-0.19	-0.30	-0.45	-0.31	-0.20
TMN	-0.15	-0.08	0.06	-0.06	-0.09	-0.14	-0.09	-0.29	-0.08	-0.15
THg	-0.35	-0.20	-0.17	-0.36	-0.21	0.01	-0.14	-0.35	-0.10	-0.01
MeHg	0.15	0.22	-0.05	0.13	0.18	0.15	0.25	-0.27	0.51	0.93

Table 54.

Inter-correlation between surface water mass budget net import by quarter and change in soil mass storage for STA-2 Cell 1

	TP	**TKN**	**NOX**	**NH3**	**TCA**	**SO4**	**DOC**	**CL**	**THg**	**MeHg**
TP	-0.87	-0.84	-0.70	-0.74	-0.80	0.58	0.14	0.17	-0.44	-0.28
TN	-0.78	-0.62	-0.95	-0.72	-0.78	0.63	0.54	-0.40	-0.07	0.29
CA	-0.52	-0.37	-0.81	-0.38	-0.61	0.24	0.28	-0.43	0.19	0.47
MG	-0.78	-0.65	-0.92	-0.70	-0.79	0.58	0.46	-0.25	-0.21	0.08
TS	-0.71	-0.64	-0.76	-0.67	-0.98	0.60	0.22	-0.26	-0.56	-0.22
AVS	0.06	0.10	0.00	-0.12	0.10	0.26	0.40	-0.29	0.07	0.20
TFE	-0.43	-0.47	-0.25	-0.38	-0.45	0.33	0.01	0.35	-0.65	-0.68
TMN	-0.36	-0.36	-0.30	-0.31	-0.37	0.26	0.11	0.22	-0.50	-0.52
THg	-0.94	-0.89	-0.75	-0.82	-0.73	0.65	0.25	0.13	-0.21	-0.03
MeHg	0.12	0.23	-0.24	0.24	0.03	-0.35	-0.07	-0.54	0.80	0.96

Table 55.

Inter-correlation between surface water mass budget net import by quarter and change in soil mass storage for succesive quarters for STA-2 Cell 2

	TP	TKN	NOX	NH3	TCA	SO4	DOC	CL	THg	MeHg
TP	-0.32	-0.31	-0.17	-0.38	-0.33	-0.18	-0.27	0.06	-0.26	-0.44
TN	-0.45	-0.43	-0.26	-0.43	-0.37	-0.52	-0.41	-0.41	-0.26	-0.19
CA	-0.59	-0.58	-0.27	-0.57	-0.49	-0.59	-0.56	-0.08	-0.25	-0.24
MG	-0.59	-0.59	-0.36	-0.58	-0.51	-0.64	-0.57	-0.34	-0.36	-0.32
TS	0.10	0.17	0.27	0.10	0.14	0.17	0.20	0.03	0.23	0.16
AVS	0.55	0.54	0.58	0.46	0.53	0.65	0.58	0.39	0.47	0.29
TFE	-0.28	-0.26	-0.35	-0.25	-0.28	-0.43	-0.27	-0.75	-0.34	-0.18
TMN	-0.10	-0.04	0.00	-0.05	-0.04	-0.19	-0.04	-0.42	0.01	0.13
THg	-0.36	-0.30	-0.28	-0.29	-0.31	-0.46	-0.31	-0.56	-0.24	-0.09
MeHg	-0.28	-0.18	-0.40	-0.17	-0.29	-0.37	-0.21	-0.68	-0.31	-0.10

Table 56.

Inter-correlation between surface water mass budget net import by quarter and change in soil mass storage for successive quarters for STA-2 Cell 3

	TP	TKN	NOX	NH3	TCA	SO4	DOC	CL	THg	MeHg
TP	-0.53	-0.42	-0.17	-0.43	-0.45	-0.43	-0.43	-0.08	-0.28	-0.31
TN	-0.69	-0.64	-0.50	-0.61	-0.66	-0.77	-0.67	-0.28	-0.50	-0.52
CA	-0.35	-0.23	-0.21	-0.20	-0.32	-0.34	-0.28	0.15	-0.25	-0.20
MG	-0.47	-0.37	-0.14	-0.36	-0.40	-0.39	-0.39	0.08	-0.25	-0.27
TS	-0.53	-0.59	-0.08	-0.59	-0.43	-0.48	-0.53	-0.18	-0.18	-0.37
AVS	-0.94	-0.96	-0.80	-0.98	-0.93	-0.87	-0.94	-0.73	-0.87	-0.94
TFE	-0.59	-0.53	-0.15	-0.55	-0.49	-0.51	-0.50	-0.30	-0.26	-0.35
TMN	-0.17	-0.03	0.16	-0.07	-0.09	-0.03	-0.03	-0.13	0.04	0.05
THg	-0.25	-0.17	0.13	-0.20	-0.15	-0.21	-0.14	-0.32	0.06	0.02
MeHg	-0.19	-0.11	-0.52	-0.09	-0.28	-0.39	-0.20	-0.37	-0.37	-0.19

Table 57.

Inter-correlation between change in soil mass storage for successive quarters and surface water budget parameters for STA-2

	Flow In [m^3]	Wet [m^3]	Flow Out [m^3]	ET [m^3]	Seep [m^3]	Change Store [m^3]	Residual [m^3]	Resid./ Tot. Input [%]	Resid./ Tot. Output [%]	Inflow/ (Out+Seep) [%]
TP	-0.40	-0.22	-0.40	-0.36	0.00	0.24	0.14	0.25	0.25	0.43
TN	-0.51	-0.32	-0.54	-0.47	-0.19	0.05	-0.03	0.22	0.22	0.13
TCA	-0.20	-0.16	-0.23	-0.31	-0.09	0.26	0.23	0.36	0.36	0.28
TMG	-0.43	-0.24	-0.44	-0.37	-0.08	0.19	0.19	0.41	0.41	0.25
TS	-0.27	-0.05	-0.25	-0.08	0.00	0.00	-0.07	-0.07	-0.07	0.14
AVS	-0.29	-0.20	-0.20	-0.01	0.40	0.05	-0.51	-0.51	-0.51	0.17
TFE	-0.34	-0.21	-0.37	-0.35	-0.26	-0.22	0.35	0.64	0.64	-0.12
TMN	0.00	0.01	-0.08	-0.28	-0.39	-0.03	0.38	0.51	0.51	-0.29
THg	-0.30	-0.08	-0.33	-0.38	-0.25	-0.03	0.10	0.30	0.30	-0.10
MeHg	0.09	0.02	0.12	-0.17	0.04	-0.28	-0.11	-0.24	-0.24	-0.22

Table 58. Spearman correlation coefficients for the constituent surface water net mass import by quarter versus the change in the constituent mass stored in surficial soil between sampling event t and t-1 for STA-2 Cell 1 only.

Data Source: Cell 1 H2O vs. Cell 1 Soil

Cell Contents:
Correlation Coefficient
P Value
Number of Samples

	TKN	NOX	NH3	TCA	SO4	DOC	TCL	THg	MeHg
TP	**0.92**	**0.718**	**0.976**	**0.863**	-0.909	**0.0186**	**0.971**	**0.53**	0.338
	0.01	0.108	**0.00084**	**0.0268**	**0.012**	**0.972**	**0.00121**	0.279	**0.513**
	6	6	6	6	6	6	6	6	6
TKN		0.464	**0.919**	**0.749**	-0.848	0.382	**0.978**	**0.668**	**0.608**
		0.354	**0.00964**	0.0868	**0.033**	0.455	**0.00073**	0.147	0.2
		6	6	6	6	6	6	6	6
NOX			**0.73**	**0.842**	-0.769	-0.566	**0.624**	0.316	-0.0889
			0.0998	**0.0354**	0.0739	0.241	0.185	**0.542**	**0.867**
			6	6	6	6	6	6	6
NH3				**0.894**	-0.975	-0.00794	**0.98**	**0.616**	0.384
				0.0162	**0.00091**	**0.988**	**0.00062**	0.193	0.453
				6	6	6	6	6	6
TCA					-0.915	-0.166	**0.838**	**0.746**	0.429
					0.0107	**0.753**	**0.0374**	0.0886	0.396
					6	6	6	6	6
SO4						0.111	-0.927	-0.66	-0.368
						0.835	**0.00775**	0.154	0.473
						6	6	6	6
DOC							0.18	0.35	**0.731**
							0.733	0.497	0.099
							6	6	6
TCL								**0.635**	0.485
								0.176	0.33
								6	6
THg									**0.889**
									0.0179
									6
MeHg									

The pair(s) of variables with positive correlation coefficients and P values below 0.050 tend to increase together.
For the pairs with negative correlation coefficients and P values below 0.050, one variable tends to decrease while the other increases.
For pairs with P values greater than 0.050, there is no significant relationship between the two variables.

Table 59. Spearman correlation coefficients for the constituent surface water net mass import by quarter versus the change in the constituent mass stored in surficial soil between sampling event t and t-1 for STA-2 Cell 2 only.

Data Source: Cell 2 Surface Water Mass Budget vs. Soil

Cell Contents:
Correlation Coefficient
P Value
Number of Samples

	TKN	NOX	NH3	TCA	SO4	DOC	TCL	THg	MeHg
TP	**0.992**	**0.886**	**0.988**	**0.987**	**0.995**	**0.99**	**0.998**	**0.877**	**0.823**
	1E-04	**0.0188**	**0.00021**	**0.00026**	**4.3E-05**	**0.00015**	**7.6E-06**	**0.0216**	**0.0442**
	6	6	6	6	6	6	6	6	6
TKN		**0.877**	**0.992**	**0.981**	**0.983**	**0.997**	**0.998**	**0.881**	**0.852**
		0.0217	**8.6E-05**	**0.00051**	**0.00044**	**1.2E-05**	**9.3E-06**	**0.0205**	**0.031**
		6	6	6	6	6	6	6	6
NOX			**0.882**	**0.946**	**0.916**	**0.898**	**0.884**	**0.98**	**0.792**
			0.0202	**0.0043**	**0.0104**	**0.0152**	**0.0193**	**0.000592**	**0.0605**
			6	6	6	6	6	6	6
NH3				**0.979**	**0.974**	**0.984**	**0.99**	**0.898**	**0.856**
				0.00065	**0.00104**	**0.00036**	**0.00016**	**0.0151**	**0.0297**
				6	6	6	6	6	6
TCA					**0.992**	**0.988**	**0.987**	**0.94**	**0.859**
					8.9E-05	**0.00021**	**0.00026**	**0.00535**	**0.0286**
					6	6	6	6	6
SO4						**0.988**	**0.992**	**0.893**	**0.81**
						0.00022	**9.5E-05**	**0.0166**	**0.0506**
						6	6	6	6
DOC							**0.997**	**0.895**	**0.861**
							1.7E-05	**0.016**	**0.0276**
							6	6	6
TCL								**0.88**	**0.843**
								0.0207	**0.0351**
								6	6
THg									**0.872**
									0.0234
									6
MeHg									

The pair(s) of variables with positive correlation coefficients and P values below 0.050 tend to increase together.
For the pairs with negative correlation coefficients and P values below 0.050, one variable tends to decrease while the other increases.
For pairs with P values greater than 0.050, there is no significant relationship between the two variables.

Table 60. Spearman correlation coefficients for the constituent surface water net mass import by quarter versus the change in the constituent mass stored in surficial soil between sampling event t and t-1 for STA-2 Cell 3 only.

Data Source: Cell 3 Surface Water Mass Budget vs. Soil

Cell Contents:
Correlation Coefficient
P Value
Number of Samples

	TKN	NOX	NH3	TCA	SO4	DOC	TCL	THg	MeHg
TP	**0.989**	**0.841**	**0.986**	**0.987**	**0.983**	**0.989**	**0.995**	**0.914**	**0.963**
	0.0002	**0.0361**	**0.0003**	**0.0002**	**0.0004**	**0.0002**	**3E-05**	**0.0107**	**0.002**
	6	6	6	6	6	6	6	6	6
TKN		**0.844**	**0.995**	**0.979**	**0.982**	**0.995**	**0.997**	**0.908**	**0.971**
		0.0345	**4E-05**	**0.0007**	**0.0005**	**4E-05**	**1E-05**	**0.0123**	**0.0012**
		6	6	6	6	6	6	6	6
NOX			**0.817**	**0.916**	**0.914**	**0.885**	**0.823**	**0.98**	**0.926**
			0.0471	**0.0104**	**0.0107**	**0.019**	**0.044**	**0.00059**	**0.0079**
			6	6	6	6	6	6	6
NH3				**0.969**	**0.965**	**0.982**	**0.994**	**0.887**	**0.955**
				0.0014	**0.0018**	**0.0005**	**6E-05**	**0.0184**	**0.003**
				6	6	6	6	6	6
TCA					**0.996**	**0.991**	**0.978**	**0.965**	**0.984**
					2E-05	**0.0001**	**0.0007**	**0.00181**	**0.0004**
					6	6	6	6	6
SO4						**0.996**	**0.979**	**0.959**	**0.985**
						3E-05	**0.0006**	**0.00243**	**0.0004**
						6	6	6	6
DOC							**0.991**	**0.938**	**0.982**
							0.0001	**0.00562**	**0.0005**
							6	6	6
TCL								**0.895**	**0.959**
								0.016	**0.0025**
								6	6
THg									**0.974**
									0.001
									6
MeHg									

The pair(s) of variables with positive correlation coefficients and P values below 0.050 tend to increase together.
For the pairs with negative correlation coefficients and P values below 0.050, one variable tends to decrease while the other increases.
For pairs with P values greater than 0.050, there is no significant relationship between the two variables.

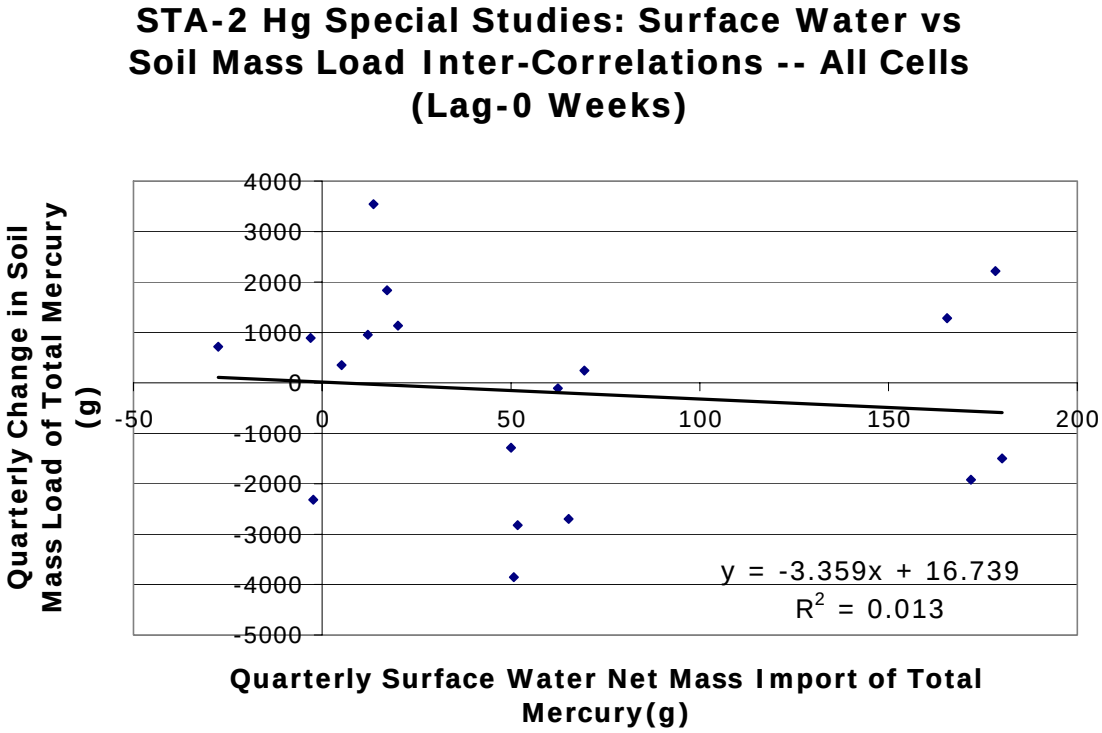

Figure 157. Scatter plot of the quarterly change in the soil mass load of total mercury (THg) versus the quarterly surface water net mass import of total mercury for all STA-2 cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

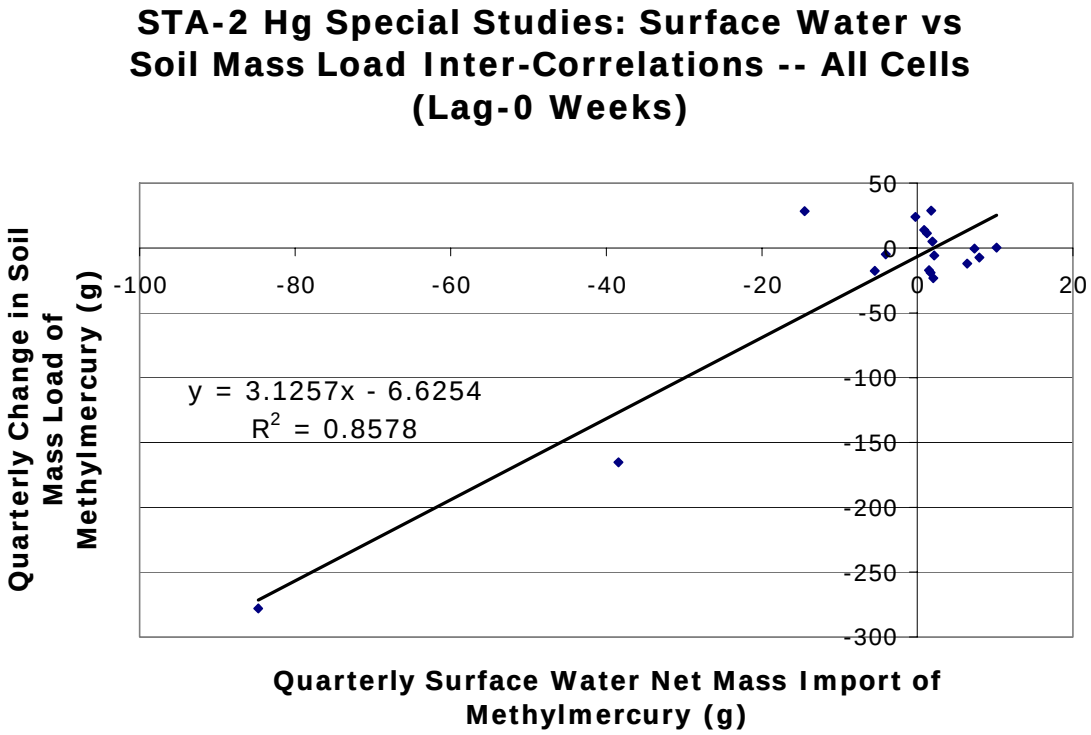

Figure 158. Scatter plot of the quarterly change in the soil mass load of methylmercury (MeHg) versus the quarterly surface water net mass import of methylmercury for all STA-2 cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

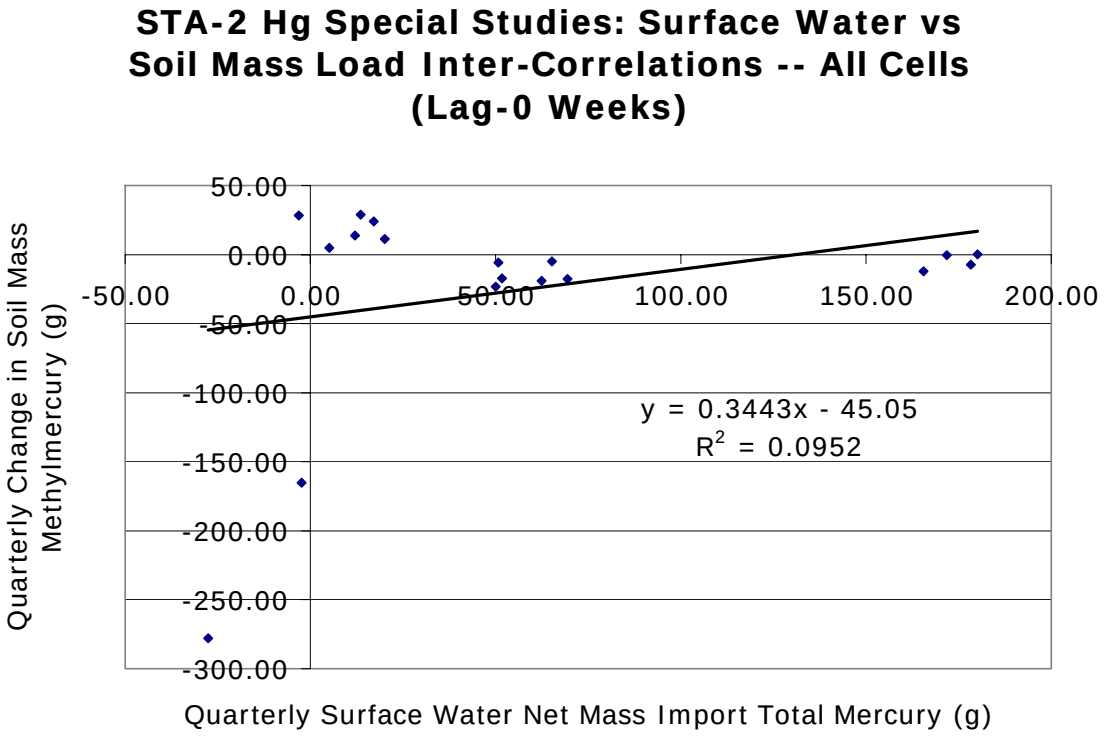

Figure 159. Scatter plot of the quarterly change in the soil mass load of methylmercury (MeHg) versus the quarterly surface water net mass import of total mercury (THg) for all STA-2 cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

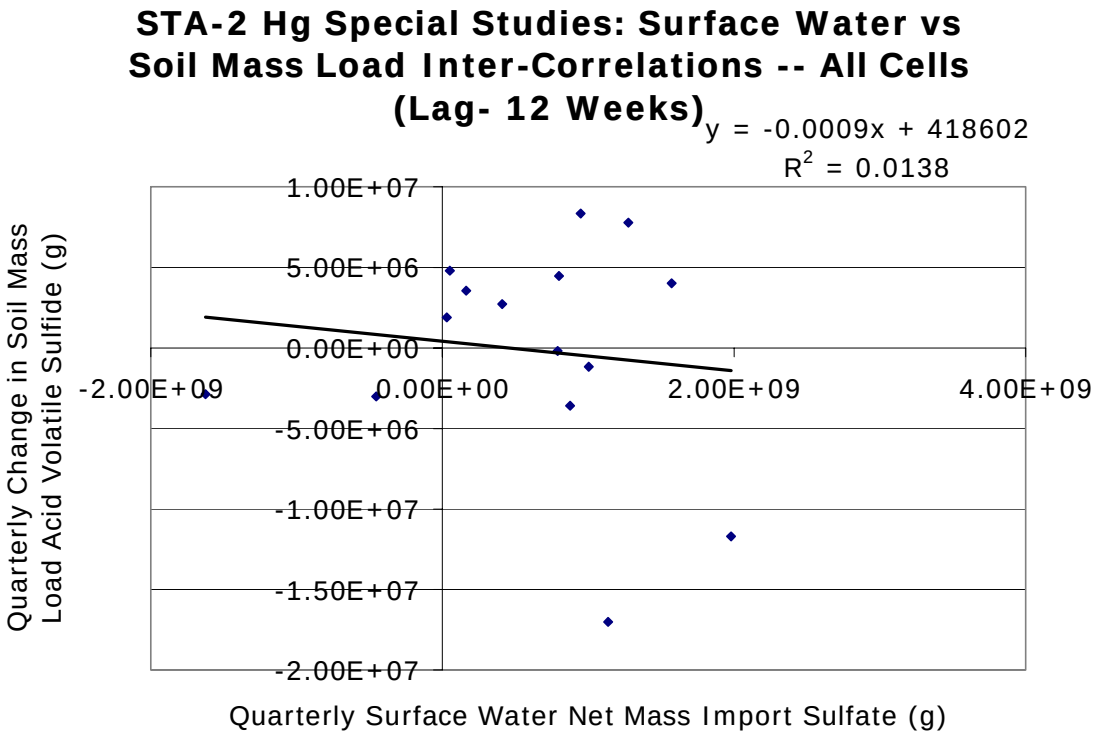

Figure 160. Scatter plot of the quarterly change in the soil mass load of acid volatile sulfide (AVS) versus the quarterly surface water net mass import of sulfate (SO42-) for all STA-2 cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

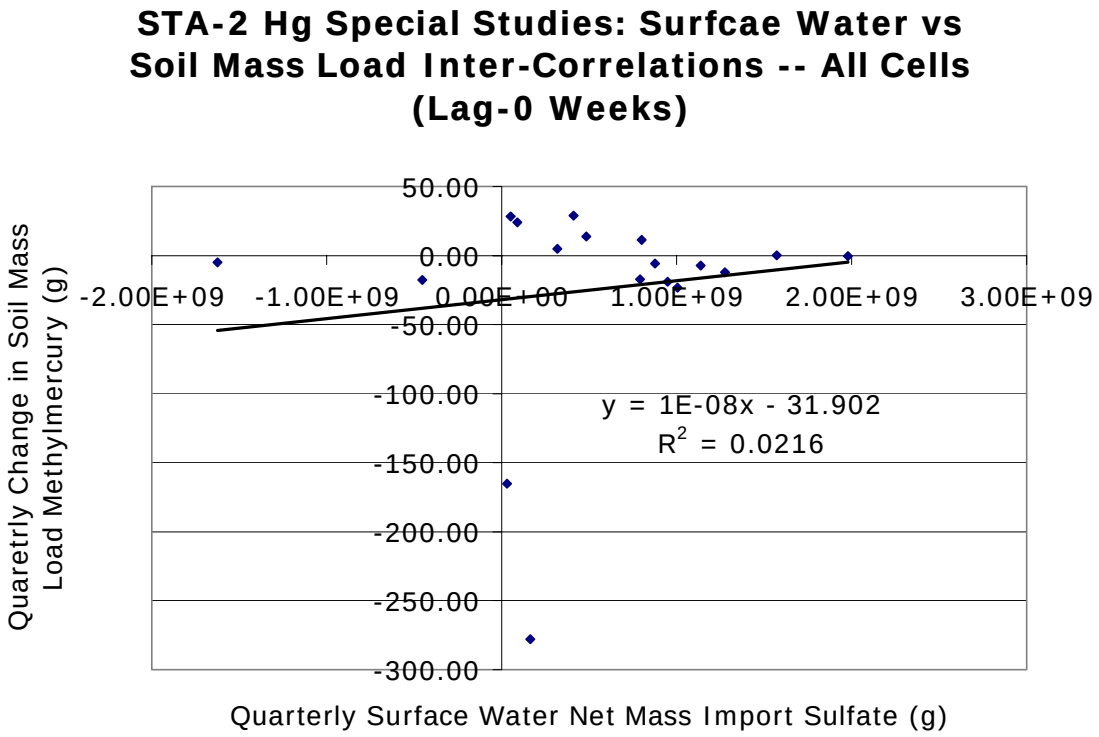

Figure 161. Scatter plot of the quarterly change in the soil mass load of methylmercury (MeHg) versus the quarterly surface water net mass import of sulfate (SO42-) for all STA-2 cells combined and Lag-0 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

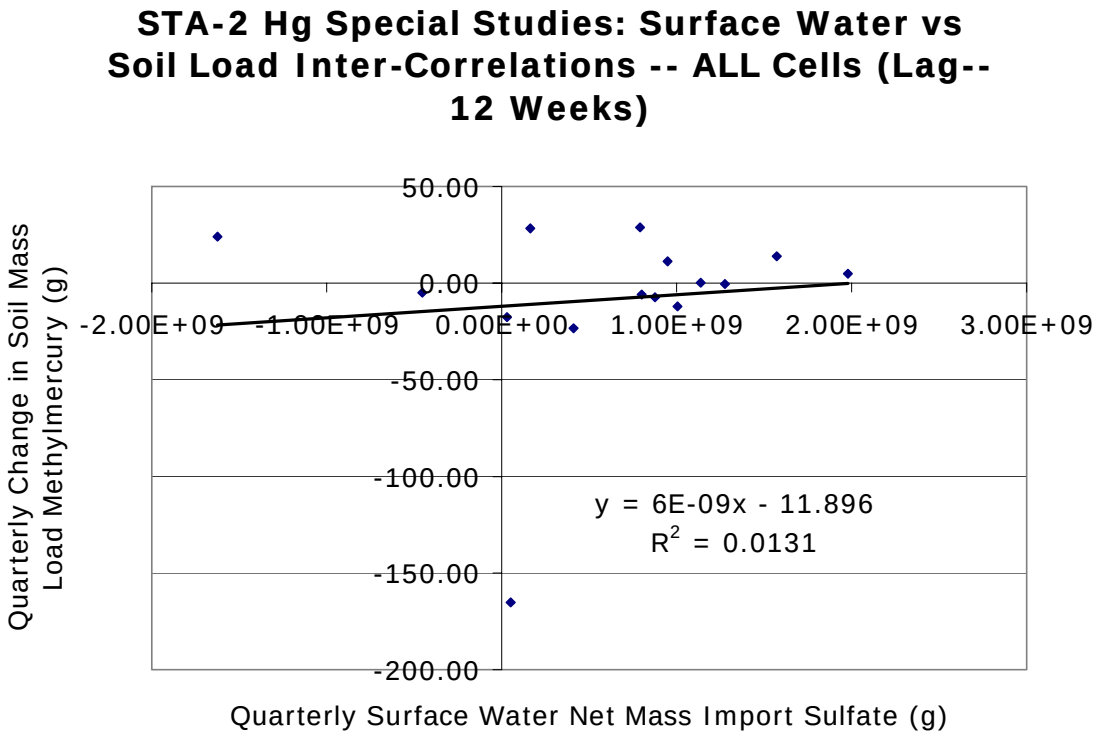

Figure 162. Scatter plot of the quarterly change in the soil mass load of methylmercury (MeHg) versus the quarterly surface water net mass import of sulfate (SO42-) for all STA-2 cells combined and Lag-12 weeks with the linear regression relationship and the square of the Pearson correlation coefficient displayed.

MULTIVARIATE PARAMETRIC LINEAR REGRESSION ANALYSIS

Only concentration and load variables that met the initial significance test at $p < 0.15$ were evaluated for inclusion in the regression model. The first variable for inclusion in the model was the one of the set of all variables that maximized r^2 and minimized model error, as measured by several SAS diagnostics. The two-variable regression model was constructed by testing all of the remaining media concentration or load mass variables, and so-on until the addition of another variable did not meet the $p < 0.15$ criterion or the overall model goodness of fit decreased. However, inexplicably, the contractor (Janicki Environmental Inc., under contract to BFA) arbitrarily cut off the model development at three steps and thus three variables. There is no reason to believe that this procedure was either robust in general or even in terms of producing the strongest three-variable model. Nevertheless, as this was the only regression analysis output available to the District, the results are presented here with the preceding caveat. For the lag-time, moving average, and lag/average regression model development, a mix of untransformed and transformed values were used. The decision to substitute the log-transformed data for the untransformed data was based on whether the data met the Shapiro-Wilks test of normality. The log transformed data were then rescaled by adding 1 to the logarithm such that untransformed and transformed data were of the same numerical scale. However, the transformation criteria, the scaling procedure, and the mixing of untransformed and rescaled log-transformed data by the contractor were not approved by the District. Instead, the regression analyses were supposed to be performed on the untransformed data for all lags, moving averages, and lag/averages pooled at the level of STA-2, then each individual cell, then each individual station. This set of procedures was then to be repeated on the log-transformed data. This would have allowed a direct comparison with which to identify the independent variables that had a predominately exponential influence on the dependent variable and which a predominately linear influence. Nevertheless, as this was the only regression analysis output available to the District, those results are presented with the preceding caveat.

INTRA-CORRELATIONS

Concentrations x Concentrations

SURFACE WATER X SURFACE WATER

STA-2 All Cells

No Lag/No Average Analysis

The strongest linear, multi-variable model for F-THg, with an overall model r^2 of 0.7854 and an overall model $p < 0.001$, occurs in the order: pH (-4.34389), hardness (-0.97916), total phosphorus (9.93636), nitrite-N (1.99770), and sulfate (0.3054) with an intercept of 14.12930.

For F-MeHg, the strongest linear, multi-variable model, with an overall model r^2 of 0.7636 and $p < 0.001$, occurs in the order: manganese (0.04684) and chlorophyll _a (0.03770) with an intercept of -0.06115.

For F-Hg(II), the strongest model, with an overall r^2 of 0.6227 and $p = 0.0003$, consists of pH (-3.72855), hardness (-0.43029), and nitrite-N (2.88024) with an intercept of 10.98394.

For percent F-MeHg, the strongest model, with an overall r^2 of 0.4247 and an overall model p = 0.001, is hardness (1.50036) and chlorophyll _a (0.22432) with an intercept of -6.71481.

PORE WATER X PORE WATER

STA-2 All Cells

No Lag/No Average Analysis

The strongest linear, multi-variable model for F-THg, with an overall model r^2 of 0.6346 and an overall model p = 0.0005, occurs in the order: sulfide (0.14376), chloride (-1.12431), dissolved organic carbon (0.59777), and calcium (-0.85260) with an intercept of 7.67037.

For F-MeHg, the strongest linear, multi-variable model, with an overall model r^2 of 0.1405 and p = 0.078, occurs in the order: manganese (-0.13373) with an intercept of 0.89346.

For F-Hg(II), the strongest model, with an overall r^2 of 0.6227 and p = 0.0003, consists of pH (-3.72855), hardness (-0.43029), and nitrite-N (2.88024) with an intercept of 10.98394.

For percent F-MeHg, the strongest model, with an overall r^2 of 0.4247 and an overall model p = 0.001, is hardness (1.50036) and chlorophyll _a (0.22432) with an intercept of -6.71481.

SOIL X SOIL

STA-2 All Cells

No Lag/No Average Analysis

The strongest linear, multi-variable model for soil THg, with an overall model r^2 of 0.5483 and an overall model p < 0.001, occurs in the order: Calcium (-0.03576), total iron (-0.03721), magnesium (-0.03570), and total sulfur (0.01058) with an intercept of 0.97324.

For soil MeHg, the strongest linear, multi-variable model, with an overall model r^2 of 0.3405 and p < 0.001, occurs in the order: percent ash (-0.00131), total iron (-0.00296), acid volatile sulfide (-0.00060568), total phosphorus (-0.00131), and calcium (-0.00164) with an intercept of 0.05164.

Cell 1 Only

No Lag/No Average Analysis

The strongest linear, multi-variable model for soil THg, with an overall model r^2 of 0.4414 and an overall model p < 0.001, occurs in the order: total nitrogen (-0.24032), soil moisture (-0.00162), and percent ash (-0.03917) with an intercept of 2.87435.

For soil MeHg, the strongest linear, multi-variable model, with an overall model r^2 of 0.4344 and p = 0.0052, occurs in the order: total phosphorus (-0.00693), total manganese (-0.00366), total nitrogen (-0.01427), and acid volatile sulfide (-0.00114) with an intercept of 0.21730.

Cell 2 Only

No Lag/No Average Analysis

The strongest linear, multi-variable model for soil THg, with an overall model r^2 of 0.3526 and an overall model p = 0.0035, occurs in the order: percent ash (-0.06065) and total iron (0.02685) with an intercept of 0.05641.

For soil MeHg, the strongest linear, multi-variable model, with an overall model r^2 of 0.3528 and p = 0.0035, occurs in the order: acid volatile sulfide (-0.00023240) and total nitrogen (0.00151) with an intercept of -0.01387.

Cell 3 Only

No Lag/No Average Analysis

The strongest linear, multi-variable model for soil THg, with an overall model r^2 of 0.2572 and an overall model p = 0.0180, occurs in the order: bulk density (0.18602) and acid volatile sulfide (0.00612) with an intercept of -0.00927.

For soil MeHg, the strongest linear, multi-variable model, with an overall model r^2 of 0.1883 and p = 0.0664, occurs in the order: calcium (-0.00023431) and total sulfur (-0.00014375) with an intercept of 0.00400.

INTER-CORRELATIONS

Concentrations x Concentrations

FISH X SURFACE WATER

STA-2 All Cells

No Lag/No Average Analysis

This analysis was based on the average of all mosquitofish and surface water values for the period of record of the study for the nine interior cell sites. Based on this temporal aggregation scheme, the strongest predictors of mosquitofish THg in surface water with an overall model r^2 of 0.8724 and p = 0.002 were: ortho-phosphate (-0.22375), pheophytin (0.02003), and dissolved iron (-0.01506) with an intercept of 007545.

Loads x Loads

SURFACE WATER CONCENTRATIONS X MASS LOADS

STA-2 All Cells

No Lag/No Average Analysis/No Average Analysis

F-THg: r^2 = 0.8555 at p =< 0.0001 with variables: change in soil MeHg load (-0.00519), change in soil total sulfur load (0.27710), and ammonia water out load (0.10097) with an intercept of -0.57044.

F-MeHg: r^2 = 0.9606 at p < 0.0001 with variables change in soil MeHg load (-0.00604), change in soil total sulfur load (0.25170), and NOx inflow load (-0.00796) with an intercept of 0.20214.

F-THg/U-THg: r^2 = 0.9912 at p < 0.001 with variables chloride load out (0.51148), NOx load out (-0.01398), and change in soil magnesium load (0.00048473) with intercept -9.43778.

F-MeHg/U-MeHg: Insufficient data.

F-%MeHg: r^2 = 0.7355 at p = 0.0002 with variables change in soil MeHg load (-0.00480), total Kjeldahl nitrogen rain load (-0.27856), and change in soil manganese load (-0.06356) with an intercept of 3.10401.

Moving Average Analysis

F-%MeHg: r^2 = 0.8828 at p = 0.0004 with variables total Kjeldahl nitrogen rain load (-0.35963), change in soil total sulfur load (1.33011), and change in soil MeHg load (-0.00681) with an intercept of 3.4116.

Lag/Average Analysis

F-%MeHg: r^2 = 0.9041 at p = 0.0002 with lag-1 sampling period change soil total sulfur load (0.39977), NOx out load (-0.30299), and lag-1/average (t = 0, -1) change in soil Ca load (-0.14421) with intercept = 6.57686.

PORE WATER CONCENTRATIONS X MASS LOADS

STA-2 All Cells

F-THg: r^2 = 0.8925 at p = 0.0353 with variables change in soil calcium (1.17409) and change in soil total sulfur (-2.07741) and an intercept of 2.54550. However, there were only four observations because the spatial average of the nine sites for each of the four sampling trips was used instead of each of the nine sites individually for each of the four trips.

F-MeHg: r^2 = 0.9979 at p < 0.001 with variables Hg(II) Inflow Load (0.25587) and change in soil total phosphorus load (0.77987) and an intercept of -0.15845. However, there were only four observations because the spatial average of the nine sites for each of the four sampling trips was used instead of each of the nine sites individually for each of the four trips.

SOIL CONCENTRATIONS X MASS LOADS

For purposes of carrying out these regression analyses, the soil THg, MeHg, and %MeHg concentrations from samples of surficial soil collected every 12 weeks were paired with the rain, inflow, and outflow loads and the change in surficial soil stored mass loads for that same 12-week period. Unfortunately, the contractor (Janicki Environmental Inc., under contract to BFA) included the change in the soil THg and MeHg loads in the regression analysis of the corresponding soil THg and MeHg concentrations. Since the change in soil load is calculated using the corresponding soil concentration, where the change in soil load appears as one of the three variables in the three-variable regression model, the correlation is spurious and the regression equation is meaningless. Nevertheless, the results are included here with the preceding caveat, recognizing that the other variables in the regression relationship have qualitative if not quantitative meaning. However, if the spurious variable is deleted from the data set, there is no guarantee that the next two variable extracted by the model development process will be the same first and second or second or third variables in the development of the non-spurious regression model. When the corrected results are received, the report will be revised to include the corrected results.

No Lag/No Average Analysis

All STA-2 Cells

Soil THg: $r^2 = 0.8988$ at $p < 0.001$ with variables: Hg(II) outflow load (0.03449), change in soil THg load (0.00671), and NOx inflow load (-0.00146) and an intercept of 0.05432.

Soil MeHg: $r^2 = 0.9482$ at $p < 0.001$ with variables: change in soil MeHg load (-0.02077), change in soil total sulfur load (1.89694), and DOC rainfall load (-0.49012) and an intercept of 7.55307.

Moving Average Analysis

STA-2 All Cells

Soil THg: $r^2 = 0.9875$ at $p < 0.001$ with variables: Ca outflow load (0.04590), change in soil TN load (0.11006), and change in soil TMN load (-0.01185) and an intercept of -0.80505.

Soil MeHg: $r^2 = 0.9627$ at $p < 0.001$ with variables (coefficients): Hg(II) water out load (0.41469), change in soil total sulfur load (0.30298), and sulfate water out load (-0.17888) and an intercept of 3.15409.

Soil %MeHg: $r^2 = 0.8348$ and $p = 0.0003$ with variables (coefficients): Hg(II) inflow load (-0.00728) and change soil THg load (-0.03640) and an intercept value of 0.56303. The effect of adding rain sulfate load was to raise the r^2 to 0.9193. However, the sulfate rain load was synthesized using observed rainfall depth but an unmeasured average rain sulfate values measured in monthly integrated rain samples at the ENR Project and Andytown sites of the Florida Atmospheric Mercury Study (FAMS) in the period 1994-1996. In addition, other models were generated starting with the change in soil MeHg load, which is too closely related to soil %MeHg to be of value, and another based on TP Inflow Load (-0.45254), NOx Rain Load (-0.24290), and calcium Inflow Load (0.28399) with an intercept of -5.13033, resulting in a higher r^2 of 0.9735 at $p < 0.001$. This suggests that the iterative procedure used to generate the linear regression models is not robust for the small sample size ($n = 6$ observations). Therefore, the results must be considered suggestive but not quantitatively complete (i.e., there are a number

of other possible models, some of which might have a higher r^2 and lower overall p value than the models cited above).

FISH VERSUS MASS LOADS

The mosquitofish THg concentrations collected every four weeks were averaged over a 12-week period from project initiation in August 2002 and paired with the rainfall, inflow and outflow mass load calculations and change in soil mass calculations for the same 12-week period. The results were combined for all STA-2 cells, then disaggregated to the individual cell level, and then the individual station level within each cell. Because there were so few data, the confidence in the results at the station level of disaggregation preclude their further consideration for thus particular subcategory of analysis.

No Lag/No Average Analysis

STA-2 All Cells

Mosquitofish THg: $r^2 = 0.9924$ at $p < 0.0001$ with variables Hg(II) outflow load (44.08705), change in soil total sulfur mass (14.08231), and ammonia outflow load (-20.04048) and an intercept of 187.15062.

Lag/Average Analysis

STA-2 All Cells

Mosquitofish THg: $r^2 = 0.9853$ at $p < 0.0001$ with variables lag-1 average ($t = 0, -1$) of the change in soil MeHg load (0.64928), the Hg(II) outflow load (13.69520), and lag-1 average ($t = 0, -1$) sulfate rainfall load (-17.45970) and an intercept of 11.20760.

DISCUSSION

METHODS DEVELOPMENT: PORE WATER SAMPLING VIA THE MODIFIED "SIPPER" METHOD

There are four issues that have emerged in the process of developing, testing, and implementing the modified sipper method of pore water collection that are discussed in this subsection: (1) separation of surface water from surficial pore water; (2) locus of ellipsoid of withdrawal for pore water collection; (3) validity; and (4) reproducibility. In greater detail, Appendix E discusses the strengths and weaknesses of the modified sipper method and its application ramifications.

Separation of Surface Water from Surficial Pore Water

The addition of the disk to provide physical separation between the surface water and surficial soil compartments has made it possible to collect a high-volume pore water sample for multi-constituent commercial analysis without inadvertently collecting surface water from the overlying water column. Support for this conclusion comes from two pieces of evidence. First, in early field testing, when salt was distributed around the disk to raise the ionic strength and specific conductivity of surface water relative to pore water, there was no evidence of conductivity breakthrough when the sample volume was less than 750 ml using the larger diameter disk. Second, there were consistently substantial, albeit not always statistically significant differences in pH, redox, and/or conductivity between the pore water samples and the surface water sample collected concurrently at the same sites during (a) the two-day pre-study and (b) during routine implementation of the modified sipper method (Zuloaga et al., 2004).

Locus of Ellipsoid of Pore Water Withdrawal

Where in the surficial soil or sediment horizon the pore water is extracted by the modified sipper method goes to the question of the representativeness of the sample. The conclusion that surface water is not being collected inadvertently with the large-volume pore water collection required for multi-analyte analysis without micro-analytical technique using the modified sipper method must be tempered by the potential for large-volume sample withdrawal to introduce a new source of uncertainty unrelated to the inadvertent sampling of surface water with surficial pore water. Chloride is considered to be a conservative tracer in surface water and ground water environments. Chloride concentrations were virtually indistinguishable in surface water and pore water collected via the centrifugation method at Sites C1CC, C2C, and C3C based on the results of a methods development pre-study (Zuloaga et al., 2004). This was also true of the samples collected via the modified sipper method at the same location concurrently (Zuloaga et al., 2004). However, during the pre-study only enough sample was collected at each site to allow replicate analysis of filtered ultra-trace THg and MeHg, SO_4^{2-}, S^{2-}, Fe(II), F-Fe(III), TFe, and chloride, which is about half of the volume required for the remaining analyses tested during routine implementation of the modified sipper method. Unfortunately, there is a substantial if not statistically significant difference between the surface water and pore water chloride concentrations in some of the "routine" samples collected by the sipper method in the period October 2003 and January 2004. In general, the chloride concentrations in pore water samples were biased high relative to the surfaced water samples. These chloride discrepancies are also

reflected in the observed weak inter-correlation between surface water and pore water chloride for those same samples.

This suggests that at some sites under some conditions the sipper is sampling a much deeper region of the soil horizon where physical communication between surface water and pore water occurs at a rate much slower than the rate of release of chloride from decomposing organic matter. This allows the buildup of chloride over time to concentrations that exceed those of the overlying surface water. Selective exclusion of chloride by plant roots may enhance this concentration process. The inadvertent sampling of the deeper soil strata may be facilitated by vertical channels created by decomposing macrophyte roots. In fact, if this is occurring and it is not possible to determine at which sites this will occur *a priori* absent a pre-study using depth-dependent tracers, then the method cannot be assumed to yield a reproducible sample from the 0–4 to 0–6 cm surficial soil horizon when the volume of withdrawal is large (i.e., 500–750 ml), as was the case for the routine monitoring when multiple constituents are of interest and micro-analytical technique is unavailable. Under such circumstances the sampling method would have to be considered to produce irreproducible results.

However, where only a few analytes are of interest and each requires only 25–50 ml for replicate analysis, as would be the case with monitoring solely for sulfate and sulfide, for example, there is a greatly reduced likelihood that pore water withdrawal would be occurring from deeper soil strata using the modified sipper method. Until the issue of inadvertent deep-soil pore water sampling of indeterminate magnitude is resolved rigorously and reproducibly, the method must still be considered to produce uncertain results and to be of semi-quantitative utility, at best. Nevertheless, where one is more concerned with whether site pore water quality is changing over time or meeting a pore water quality criterion at any particular time than with mass transfer calculations or exploratory data analyses, the method may still have much to commend itself.

Validity

To assess the validity of the modified sipper method of pore water collection, the concentrations of key constituents in pore water collected via the modified sipper method were compared to the corresponding concentrations in pore water collected by a preferred method. Based on a side-by-side study of pore water sampling for ultra-trace mercury species in surficial sediments conducted elsewhere, centrifugation extraction of pore water from soil cores was deemed most likely to yield representative, accurate, and precise results within a well-defined stratum (Mason et al., 1998). Subsequently, a two-day, side-by-side comparison of the performance of the modified sipper method to the centrifugation method was carried at Site C1C in STA-2 Cell 1. The details of the study design are set forth in Appendix C. In summary, four sets of eight, 0–4 cm soil cores were collected on Day 1, extracted, and the extract composited for subsequent $n = 4$ replicate subsampling. Concurrently, $n = 4$ pore water samples were collected via the modified sipper method from the same location where the soil cores were being collected. Each sample was then analyzed for sulfate, sulfide, TFe, Fe(II) and ultra-trace THg and MeHg. As the bottom line, there were statistically significant differences ($p < 0.05$) between the sipper and centrifugation method results on Day 1 for some constituents and on Day 2 for others.

Reproducibility

WITHIN-TRIP REPRODUCIBILITY

The contractor did not conduct the study as designed, thus compromising its value. Instead of setting aside each of the four, 8-core composites for N = 4 individual analyses, all of the individual core composites collected on Day 1 were mixed and subsampled n = 4 times. This approach eliminated all information on sampling variability while convolving laboratory and compositing variabilities. It also precluded combining the Day 1 and Day 2 results to increase the statistical resolving power of the study. While the laboratory reproducibility was generally very good, with the exception of iron species, this had no bearing on the within-trip sampling reproducibility. Nevertheless, this approach did establish a baseline of compositing and laboratory analysis variability against which to measure within-site sampling reproducibility properly at some future date. Unfortunately, neither time nor the available budget allowed for the correction of this fatal error. To avoid such fatal errors in the future, direct oversight of every non-routine or one-time aspect of the project by the project manager is recommended.

However, the STA-2 Hg Special Studies Project design also built in the requirement to conduct more frequent replicate (n = 3) sampling at Site C1C simultaneously to more accurately characterize the soil and pore water concentration time trajectories of the first-flush effect and to determine the within-site heterogeneity that would contribute to the uncertainty in the applications of the data. **Table 61** expresses the relative precision or intrinsic variability for each constituent and each sampling event as the ratio of the standard deviation to the mean of the three samples for the October 2003 through January 2004 sampling trips. There were too few results greater than the MDL for F-TFe, F-Fe(II) and F-Fe(III) for these constituents to be included in this analysis. Chloride is considered to have the lowest intrinsic natural variability in surface water and pore water, so it should be the standard against which all of the other constituents are judged. In that frame of reference, all of the constituents exhibited excellent field reproducibility with the exception of sulfide, F-THg, and F-MeHg. Sulfide exhibited field variability that ranged from roughly equal to roughly 25 times the intrinsic variability of chloride in the same trip, while MeHg was consistently about an order of magnitude greater. The average intrinsic variability of F-THg was about three times that of F-MeHg for the complete set of replicates.

While the F-THg results may suggest unacceptable field reproducibility, with this approach field reproducibility and analytical reproducibility cannot be deconvolved, and it is important to remember that the F-THg concentration in pore water is generally within a factor of 2 to 10 of its MDL. Moreover, filtration of the pore water sample may introduce spurious F-THg unrelated to the field reproducibility of the sample. However, acid-precleaning of the filters, which began after the October 2003 sampling trip to correct problems with F-MeHg > U-MeHg in surface water, appears to have cut the intrinsic field variability in the remaining trips, and the variability of that variability is low. Furthermore, in the last trip in January 2004, the intrinsic field variabilities of F-MeHg and F-THg are virtually indistinguishable, albeit about 12 and 18 times the corresponding chloride value in a concentration range eight orders of magnitude greater. Therefore, the Project Manager has determined that the pore water F-THg results do not need to be flagged based on observed field imprecision. However, the intrinsic variabilities of the field results need to be normalized to the intrinsic variabilities of a corresponding set of three analytical laboratory replicates to reveal the true field precision routinely achievable for this and other soil contamination studies involving ultra-trace constituents.

Table 61. Constituent relative precision of the field replicate (n = 3) results for pore water samples collected at Site C1C in STA-2 Cell 1.

Replicate Site C1C Pore Water Standard Deviation Normalized to Site Average

	pH	Redox	DOC	MG	CA	TFE	TMN	CL	SO4	S2-	Fe(II)	Fe(III)	Hg	MeHg
Average	0.004	-0.044	0.007	0.006	0.006		0.015	0.005	0.013	0.031			0.261	0.085
10/03/03	0.002	-0.022	0.014	0.010	0.006		0.012	0.000	0.007	0.068			0.404	0.000
11/03/03	0.007	-0.005	0.014	0.007	0.006		0.009	0.010	0.008	0.011			0.213	0.131
12/03/03	0.003	-0.017	0.000	0.004	0.004		0.031	0.000	0.006	0.020			0.250	
01/04/04	0.002	-0.134	0.000	0.004	0.007		0.008	0.010	0.031	0.027			0.176	0.123

SUCCESSIVE TRIP REPRODUCIBILITY

There were also significant differences in the average critical constituent concentrations between Days 1 and 2 of the side-by-side pre-study for the same pore water collection method. For the sipper, these differences were not most likely solely attributable to surface water breakthrough, because there were significant differences between surface water and pore water redox potential via the sipper method on both days and the pore water extracted via centrifugation also exhibited similar variability. However, there were statistically significant differences in the redox potential of pore water extracted via centrifuge and collected via the sipper method, with the sipper method biased high, suggesting some surface water breakthrough.

The same-method differences between Days 1 and 2 could also be attributed to the effect of intromission of the sipper probe and subsequent withdrawal of a large volume of pore water for the four consecutive sets of samples that had to have been made up with water from other sources: pore water from the same soil stratum, pore water from deeper soil strata, and surface water. While sorption, partitioning and complexation equilibria would have been reestablished relatively rapidly, this would not necessarily be the case for kinetically slow processes such as precipitation reactions involving sulfide formation, for example, or for reactions for which reactants are supplied or consumed or reaction conditions mediated by microbial activity in excess of steady state conditions following introduction of a fresh supply of limiting nutrient with the replacement water. Nevertheless, the effect of natural diel fluctuations on redox-sensitive chemical kinetics and microbial activity cannot be ruled out as the explanation for the changes in pore water chemistry at Site C1C between Days 1 and 2, especially since both the test and reference methods exhibited such variability, albeit to differing degrees and with different constituents.

SOURCES OF POTENTIALLY SIGNIFICANT UNCERTAINTY IN MASS BUDGET AND EXPLORATORY DATA ANALYSIS

The ability of the District and contractor sampling crews to collect representative, reproducible surface water samples for ultra-trace unfiltered and filtered THg and MeHg has been established in quarterly replicate surface water sampling that has been well documented in other report and therefore is not reiterated here. This is also true of the accuracy and precision of ultra-trace THg and MeHg analyses of those samples, as established in annual split sample round robins between the District's primary and secondary contract analytical laboratories as well as among several outside laboratories. By contrast, routine soil sampling for permit compliance requires sampling of 0 to 10 cm cores without replication and, to date, there have been no multi-laboratory, soil sample round robin analyses sponsored by or for the District or the FDEP. Nevertheless, in the context of the STA-2 Mercury Special Studies (MSS) Project, the importance of representative, accurate, and precise soil THg and MeHg concentrations for the accuracy of the mass budget calculations and exploratory data analyses involving univariate and multi-variate intra- and inter-correlations of constituent concentrations and mass loads cannot be overstated. As such, it is appropriate to determine whether the soil THg and MeHg analyses conducted on the 0 to 4 cm soil cores collected at three stations in each of the three treatment cells were sufficiently representative and reproducible to justify their use in the STA-2 Mercury Special Studies Project. The following information presented in this section is intended to affirmatively address this question.

Reproducibility

Replicate (n = 3) soil core samples were collected at Site C1C at STA-2 Cell 1 following an exponential sampling scheme (i.e., 14 days, 14 days, 28 days, 56 days, and 112 days) through March 2003 and then every 4 weeks beginning in October 2003 through January 2004. The results are summarized in **Table 62**. With the exception of AVS, TS, and MeHg, and BD, the field precision for the constituents of interest was good to excellent. For TS, BD, and MeHg the field precision was somewhat erratic. For AVS, the Project Manager has determined that the field precision was unacceptable, although the trend was toward improvement over time, suggesting a laboratory rather than a field precision problem. The data have been flagged as semi-quantitative until follow-up studies are conducted to determine whether AVS is naturally more variable than the components of which it is comprised (i.e., TFe and TS) or there is a problem with analytical laboratory imprecision.

Table 62.

Replicate Site C1C Trip Soil Standard Deviation Normalized to Trip Mean

	BD	ASH	MOIST	TN	CA	MG	TS	AVS	FE	MN	THg	MeHg
8/28/2002	0.1768	0.0907	0.0078	0.0276	0.0925	0.0666	0.1434	0.6233	0.1332	0.1195	0.0521	0.2920
9/11/2002	0.1000	0.0186	0.0196	0.0177	0.0323	0.0516	0.0437	1.1197	0.1066	0.0883	0.1058	0.4474
10/9/2002	0.0345	0.0671	0.0100	0.0635	0.0955	0.0563	0.2101	0.8946	0.1077	0.1555	0.1327	0.3218
12/4/2002	0.0714	0.0272	0.0209	0.0320	0.0149	0.0446	0.2745	0.3407	0.1358	0.0881	0.0388	0.0589
3/26/2003	0.0299	0.0324	0.0098	0.0078	0.0361	0.0737	0.3106	0.3950	0.0488	0.1000	0.1247	0.2408
11/11/2003	0.2875	0.0631	0.0457	0.0850	0.1214	0.1377	0.1895	0.2228	0.2280	0.0866	0.3994	0.2454
12/2/2003	0.8440	0.0159	0.0797	0.0579	0.1632	0.2977	0.3385	0.3356	0.2682	0.0558	0.3810	0.2924
12/30/2003	0.1429	0.1305	0.0281	0.1620	0.1556	0.0909	0.4406	0.3571	0.0984	0.1249	0.1462	0.7349

Representativeness

PRE-CONSTRUCTION

Prior to completion of STA-2 construction, 0–10 cm and 10–30 cm soil cores (as compared to 0–4 cm cores for this study) were collected at three interior sites in Cell 1, four in Cell 2, and three in Cell 3 (White and Reddy, 2001). Sites 1-A, 1-B, and 1-C for the pre-constriction study are spatially near corresponding soil sampling Sites C1AA, C1BB, and C1CC for this study. Site 2-D is not too far from C2A, and 2-B is reasonably close to Site C2C. For 2-C, there is no corresponding site for this study. While Sites 3-A, 3-B, and 3-C are on roughly the same latitudes as C3A, C3B, and C3C, the former fall along a north-south line just east of the north-south line bisecting Cell 3, while C3A, C3B, and C3C only about 100 m east of the western levee. Further, while the land uses in the area sampled at 3-A and C3A and 3-C and C3C appear to be the same, those for 3-B and C3B are distinctly different. Thus, for purposes of pre-study comparison, the focus here will be on Cell 1. Soil samples were analyzed for total carbon, total nitrogen, total phosphorus, moisture, ash, and bulk density using standard methods. Microbial biomass was also measured, as was the extractable phosphorus by a standard agricultural soils extraction scheme.

The pre-construction Cell 1 soil sampling results are summarized in **Table 63**, sans the microbial biomass and extractable phosphorus results. For comparison, the corresponding 0–4 cm soil core results for the STA-2 Mercury Special Studies Project are presented in **Table 64** for the May 2002 pre-reflooding, baseline soil sampling event, sans total carbon, which was not routinely analyzed per the STA-2 Mercury Special Studies Project Work Plan.

Table 63. Results of the STA-2 soil pre-study conducted by the University of Florida.

Site	Field ID	Soil Depth	Lab ID	Total Carbon	Total Nitrogen	Total Phosphorus	Moisture Content	Loss on Ignition	Dry Weight Bulk Density
STA-2	1-A	0-10	63	476	35.3	675	87.3	88.99	0.121
	1-A	10-30	64	474	30.62	223	85.3	88.68	0.151
	1-B	0-10	65	476.8	30.68	402	84.0	87.26	0.173
	1-B	10-30	66	514.2	31.25	158	86.4	89.45	0.144
	1-C	0-10	67	474.3	27.91	596	86.3	88.64	0.135
	1-C	10-30	68	494.5	27.95	242	88.6	87.25	0.168

Table 64. Results of the District's baseline mercury monitoring prior to reflooding STA-2 Cell 1 in May 2002.

Site	Field ID	Soil Depth	Lab ID	Total Carbon	Total Nitrogen	Total Phosphorus	Moisture Content	Loss on Ignition	Dry Weight Bulk Density
STA-2	C1AA	0-4	60, 69	NA	33	606	77.66	88.2	0.104
	C1BB	0-4	61, 70	NA	32.5	432	78.55	87.8	0.158
	C1CC	0-4	62, 71	NA	32.6	452	69.21	89.5	0.157

The TN data between these two unrelated studies are remarkably comparable, and those for TP are generally within a factor of 50 percent of one another. The most notable discrepancy in the pre-construction data sets is in the inversion of the expected bulk density relationship at Site 1-B, with the 0–10 cm core having a greater bulk density than the 10–30 cm core. If peat generally expands upon (re)wetting (gel swelling) and the opposite process occurs when the peat dries out, then it may be expected that moisture content and bulk density to be inversely related, as appears to be the case for Site 1-B. This effect may also explain the inversion of the expected bulk density relationship between Site 1-C versus Site C1CC. This is supported by the substantially lower moisture content of the Site C1CC soils from the May 2002 sampling event (69.21 percent) versus the pre-construction sampling event (86.3 percent). While the White and Reddy (2001) samples were collected prior to completion of STA-2, Cell 1 was used to hold construction-related dewatering water from Cells 2 and 3 prior to completion of the levees in December 1999, as noted in the "Background" section of this document, so one should not be nonplused by the higher moisture content of the pre-construction Cell 1 soils relative to the pre-reflood soils in May 2002.

The results of the pre-reflood baseline and post-reflood soils data indicate oscillating concentrations of THg in the surficial soil cores in Cell 1, perhaps associated with the reabsorption of the stored first-flush Hg(II) from the decomposing plant biomass or with subsequent intense summer rains that delivered substantial quantities of Hg(II) to STA-2. However, neither explanation is likely because the change in soil THg mass is on the order of thousands of grams in each quarter, while the change in plant biomass Hg(II) storage and atmospheric deposition-associated Hg(II) mass delivered to Cell 1 are at most, on the order of hundreds of grams, respectively.

In addition to the UF soil pre-study, in July 2003 a soil study was conducted for District staff using a stratified random sampling design to collect 0–10 and 10–30 cm cores at multiple sites in STA-2 Cells 1, 2, and 3 on a scale that resulted in the collection of about 200 samples was conducted nearly concurrently with the STA-2 Mercury Special Studies 0–4 cm core sampling of the nine fixed station sites every 12 weeks. A comparison of the averages, standard deviations, and standard deviations normalized to the sampling mean of the average Cell 1 soil concentrations for THg and MeHg compare reasonably well with the 0–10 cm core sample results generated by the same laboratory used by the District. The comparison is set forth in **Table 65**. This indicates that the spatial average concentrations and stored masses calculated from those concentrations and soil bulk densities at the same site are likely to be reasonably representative of the results obtained using many more samples per cell and 0–10 cm cores. This should provide additional confidence that the soil-related data and derivative calculations are reasonably spatially representative.

Table 65. Comparison of results of 0–4 cm soil cores and 0–10 cm soil cores for THg and MeHg analysis from the near-concurrent July 2003 sampling event.

	0-4 cm cores Fixed Stations THg Ave. n = 3	SD	0-10 cm cores Stratified Random THg Ave.	SD	Sample No.	Percent Difference	(two-tailed t test) Sig. Diff. p < 0.05 ?
Cell 1	0.16	0.20	0.19	0.05	8	13.60	NO
Cell 2	0.09	0.07	0.12	0.36	6	26.18	NO
Cell 3	0.06	0.01	0.09	0.02	6	27.83	NO

	0-4 cm cores Fixed Stations MeHg Ave n = 3	SD	0-10 cm cores Stratified Random MeHg Ave	SD		Percent Difference	Sig. Diff. p < 0.05 ?
Cell 1	0.00060	0.24	0.00107	0.54	8	43.94	NO
Cell 2	0.00023	0.54	0.00027	1.28	6	13.97	NO
Cell 3	0.00010	0.00004	0.00020	0.00015	6	50.33	NO

MASS BUDGETS

Water Budget

REVISED WATER BUDGET CALCULATIONS

The revised water budget, which assumes that the residual is attributable to seepage, resulted in a substantial reduction in the discrepancy between the combined culvert and seepage discharges from the treatment cells and the volume of water discharged through the G-335 pump station for the same period. An analysis of the relationship between the magnitude of this water budget discrepancy and the magnitudes of the differences in the stages of the individual treatment cells, the L-7 canal, and the discharge canal stages is outside the scope of this report. However, it is recommended that such an analysis be undertaken to increase the absolute accuracy of the mass budget calculations upon which the operational optimization of nutrient removal efficiencies is based. Even an extremely accurate water budget will not necessarily produce an accurate chloride budget, unless the chloride concentrations are accurate for all of the important water transport pathways. Since all of these pathways are not currently being monitored, substantial improvements to the chloride budget by further improvements in the accuracy of the water budget cannot be made at this time.

REVISED CHLORIDE BUDGET CALCULATIONS

If the chloride concentrations in the underseepage are higher than those in the overlying surface water, perhaps due to leaching of soluble chlorides from dry soils, then the calculation of the revised chloride mass budget using the revised water budget for each of the three cells would not necessarily decrease the discrepancies in the water budget and could make them greater, as was observed for Cell 2. If Cell 1 accumulated a substantial pool of subsurface soil chloride during the last period of extended dryout, then upon refilling, downward seepage of water into the subsurface environment could leach that chloride pool into Cell 2, but Cell 2 was likely to have been leaching far less subsurface soil soluble chloride into Cell 3 because it never dried out during the preceding several years, as was the case also for Cell 3. If this explanation has merit, then it may be expected that the load of chloride transported through the G-335 pump station will decrease over time relative to the inflow chloride load. An inspection of the revised chloride budget for Cell 1 suggests that this is the case for the inflow load based on chloride concentrations and flows monitored at S-6 and the inflow load based on chloride concentrations monitored at G-328 and the flows monitored at the individual cell inflow culverts. Whether this trend will continue or has already achieved its new steady state can evaluated using the chloride and flow data routinely collected for S-6 and G-335.

CHLORIDE BUDGET INTRA- AND INTER-CORRELATION ANALYSES

As discussed in the "Results" section of this document, an exploratory data analysis was carried out to evaluate the influences of rain, water depth, and inflow chloride concentrations on interior and outflow chloride concentration values as a function of lag-time. The results of the intra- and inter-correlation analyses as Pearson correlation coefficients are summarized in **Tables 5A-D**. These results provide further support for the conjecture that the effective retention time of STA-2 is between 14 and 28 days. This is also supported by a straightforward cells-in-series model of chloride transport and mixing in STA-2, the results of which are discussed in the next section. However, it appears that the inflow from G-328B is being short-circuited around Site C1CC, as evidenced by the virtually nonexistent correlation between the two sites, as compared

with weak to moderate positive correlations between G-328B and Sites C1AA and C1BB. The influence of G-328B on C1CC increases and then decreases as one increases the lag-time from 14 to 42 days by 14 day increments. Conversely, the influence of rain depth decreases in the order C1CC > C1BB > C1AA. This provides further support for the inference that the influence of the inflow on Site C1CC chemistry is being substantially diluted, perhaps due to increasing net rainfall dilution with increasing inflow travel distance, by hydraulic short-circuiting, or both.

Water depth generally increases with increasing flow through G-328B. The inverse influence of water depth on interior chloride concentration, albeit very weak to moderately weak, increases in the order C1AA < C1BB < C1CC, providing further support for the conjecture that C1CC is more hydraulically isolated from the influence of G-328B than sites C1AA and C1BB, and that increasing water depth has a disproportionate diluting effect on the G-328B influence on interior chloride concentrations, suggesting that short-circuiting, rather than net rainfall dilution, is the most likely cause of the observed effect. Only controlled tracer studies can validate this hypothesis directly, however.

Mercury Mass Budget

The rain load was calculated treating the weekly integrated rain THg concentration as the daily average value and daily rain depth measurements interpolated as the average of three weather stations within several miles of the study site. Inflow and outflow concentrations of unfiltered and filtered THg and MeHg were measured in grab samples of surface water collected biweekly at mid-depth whether the culverts were open or not, while daily average surface water flows were estimated using field-calibrated headwater-tailwater equations. Surficial (0–4 cm) soil samples were collected at three interior sites in each cell every 12 weeks.

The sources of uncertainty in the mercury mass budget decrease in the order rain load, inflow and outflow loads, change in water storage load, seepage load, change in vegetation storage load, and change in soil storage load. The uncertainties in the inflow and outflow load estimates could have been reduced somewhat by switching from biweekly grab to weekly flow proportional sampling using an autosampler modified for ultra-trace mercury species collection. Such an apparatus was developed by Frontier Geosciences for the District in the mid 1990s, tested by the District, and found acceptable. However, the increase in the accuracy of the mercury species surface water mass budgets would be purchased at the price of modifying, installing, and maintaining the autosampler and increasing the sampling frequency from biweekly to weekly, since longer holding times increase the risk of autosampler overflow, while simultaneously increasing the risk of spurious mercury contamination.

The seepage load is highly uncertain due to the uncertainties in the net as well as the directions and magnitudes of the gross seepage fluxes, but the seepage load is generally much less than the inflow, outflow, and rainfall loads. Therefore, increasing the accuracy of the estimates of the net and gross seepage loads into and out of STA-2 Cell 1 and Cell 3 should not be considered a priority from the standpoint of reducing the uncertainty in the mercury species surface water mass budgets. However, the seepage out of Cell 1 likely impacts Cell 2, albeit in a way that has yet to be fully characterized. Following the first flush event in Cell 1, seepage from Cell 1 to Cell 2 was likely a major THg and MeHg load source to Cell 2 and might explain why Cell 2 exhibited a MeHg mini-anomaly even though it had not dried out and reflooded immediately prior to August 2002, as was the case with Cell 1. Clearing up such discrepancies in Cell 2 mercury biogeochemical dynamics with more accurate seepage information might also resolve the discrepancies in the chloride budget. Furthermore, obtaining more accurate information on the magnitudes and directions and localized areas of seepage influxes and outfluxes could assist in

refining and selecting from among various hypotheses regarding the role of seepage in accelerating or retarding MeHg production, soil/water exchange, or bioaccumulation.

Exploratory calculations suggest that on the order of 280 g of THg and 110 g of MeHg masses were temporarily stored in standing crop plant biomass following the last, first-flush MeHg anomaly in Cell 1 in August 2002. However, the calculation is highly uncertain because the coverage and biomass density measurements did not occur at the same time as the mercury concentration measurements and, therefore, the results should be considered of exploratory value only. Nevertheless, it is highly unlikely that plant storage can account for all of the discrepancies between the changes in the soil mass budget and the net export of THg from STA-2 Cell 1. However, this may not be true of MeHg because the discrepancies are much smaller.

Some of this discrepancies between the soil and surface water mass budgets for THg might be explained by leaching of soil inorganic mercury, Hg(II), into the underlying soil horizon below the 4-cm sampling depth. This would not be inconsistent with the high seepage rate out of Cell 1. Some or all of the remaining discrepancy might be attributable to plant root mining of Hg(II) from surficial soil as elemental mercury, Hg(0), with subsequent evasion to the overlying air via the openings (stomata) on the leaves of emergent plants. This phenomenon was documented at the Everglades Nutrient Removal (ENR) Project, where roughly 1,000 g were calculated to have been lost by this process over 3,815 acres with a cattail coverage averaging about 50 percent. Based on the aerial photographs taken in November 2003, the emergent plant coverage in STA-2 Cell 1 was likely to have been higher than 50 percent in August 2002. However, it is also possible that the discrepancy is an artifact of the uncertainty in the surficial soil concentration propagated into the calculation of surficial soil mass storage.

Time did not permit nor did the circumstances warrant a rigorous propagated error analysis for this project. However, the surface water mass budget estimates for this study should be considered to have been calculated according to accepted professional practices and therefore be sufficiently accurate to support resource management decision-making and hypothesis development. Despite the demonstrated comparability of results between the results of soil analyses conducted for this study and other soils studies conducted in STA-2 roughly concurrently, the uncertainties in the spatially averaged soil THg and MeHg concentrations are probably on the order of ±50–100 percent, which, when multiplied by 0.04 m and 4047 m^2/acre x 1990 acres yields a significant mass uncertainty in the stored THg mass and the change in stored THg mass. For THg the soil change in storage mass uncertainty overwhelms all other surface water mass inputs, outputs, and storages, but for MeHg the uncertainty in the change in soil mass load is on the same order as the other input, output, and storage pathways, so the latter may also yield a nearly self-consistent mass budget between surface water and soil.

While the surface water mass budget calculations for THg and MeHg are both instructive and useful, the mass budget calculations would have benefited from a probabilistic presentation that incorporated the actual or estimated uncertainties in each term in the mass budget calculation as a probability density function (pdf) and overall pdf that represented the propagated error in the final mass budget result as a pdf rather than a single value. However, limited time and resources did not permit carrying out this additional task.

Taking into consideration the above caveats, based on the mass budget calculations carried out for this study, there was a net export of about 85 g of MeHg in the first quarter following reflooding of Cell 1, while the rainfall contribution of Hg(II) during that same time period was about 40 g and the inflow contribution was about 15 g. Assuming dry deposition averages about 50 percent of wet deposition, this added another 20 g to the inputs, for a total of about 75 g. The loss of Hg(II) via evasion, seepage, and discharge was roughly 100 g, for a net export of about

25 g of Hg(II). The difference was likely made up of net loss from the surficial soil. (The gross loss of soil THg from the top 4 cm of surficial soil between May 2002 when the baseline measurements were made and the September 2002 post-reflood sampling was calculated to be about 1050 g, of which about 275 g was stored in vegetation biomass and all but about 320 g was calculated to have been reabsorbed in the following quarter.) If 100 percent of the inflow, atmospheric, and soil input Hg(II) mass in the first quarter was methylated, then there would be no mass gap between the net export of MeHg mass in the first quarter following reflooding and the quantity of Hg(II) throughput during that same quarter. However, this would require a conversion efficiency of 85 percent, which is virtually unheard of in such circumstances.

On the other hand, if only about 8.5 percent of the Hg(II) calculated to have been lost from surficial soil during the first quarter were methylated, the mass of net MeHg exported could be accounted for. Such a methylation efficiency would not be unreasonable, especially in the presence of excess short-chain dissolved organic carbon molecules and excess sulfate associated with first-flush conditions. If one adds the MeHg calculated to have been stored in standing crop vegetation biomass to the net mass export of MeHg for the first quarter post-reflood, then about 200 g of MeHg would have had to have been produced, and the conversion efficiency of the THg temporarily lost from soil would have to have been about 20 percent. The 20-percent conversion efficiency, while high, is still within the realm of possibility under first-flush conditions. Since the mass of MeHg in surficial soil was calculated to have increased by about 200 g during that same period, then about 400 g of MeHg mass would have had to have been produced from the Hg(II) temporarily lost from surficial soil during the first-flush event. A 40-percent conversion efficiency would be considered very high under any circumstance. However, if one refocuses on the roughly 8000 g of THg calculated to have been stored in the soil prior to reflooding rather than the roughly 1000 g of THg lost temporarily following reflooding, then only about 5 percent of the stored THg, of which all but about 2 percent was Hg(II), would have had to have been converted to MeHg. This is a very reasonable conversion efficiency under these circumstances. However, it does not determine how much of that roughly 8000 g of THg as Hg(II) was bioavailable immediately following reflooding because it is the bioavailable fraction and not the total (acid-digestable) fraction, that can be methylated. This continues to be the focus of microcosm, mesocosm, and macrocosm research in the Everglades and the experimental lakes region of Ontario, Canada, where a different stable mercury isotope tracer was added to an upland watershed, to the lake in that watershed, and to a set of mesocosms in the lake in Year 1 and a new different set of stable isotopes added in Year 2. To date, these studies are still ongoing.

Clearly the roughly 75 g of net inputs of Hg(II) from sources other than soil could not have produced enough MeHg mass to have accounted for the next export of 85 g, the net storage of 115 g in vegetation biomass, and the net increase of 200 g of MeHg in surficial soil, even taking into account the propagated uncertainties in the mass budget calculations. One ignores such mass budget discrepancies at one's own peril.

MERCURY BIOGEOCHEMISTRY

The focus of the discussion here is on the ratio of the particle-bound concentration of Hg(II) or MeHg surface water particle-bound/surface water partition coefficient values and the apparent influences on them, as this is the first time sufficient data have been collected to carry out the required calculations and associated exploratory data analyses. Here KPHg(II) stands for the Hg(II) particle/water partition coefficient, while KPMeHg is the corresponding MeHg partition coefficient.

The first observation is that there is a moderate inverse correlation between the concentration of surface water TSS and the KP values. This must necessarily be the case, because the concentration of TSS appears in the denominator in the equation for the calculation of the KP value. That the correlation is not exactly -1 is in part a result of the analytical variabilities of the concentrations of the species required for the calculation of KP and in part because factors other than the concentration of TSS are influencing the sorption process. The weak and moderate inverse relationships between total phosphorus (TP) and KPHg(II) and KPMeHg, respectively, is probably more a measure of the strength of the co-correlation of TP with organic particle concentration, rather than a measure of the biodilution effect, since the correlations with total dissolved phosphorus (TDP) and reactive orthophosphate (ORP) are only weakly inverse. Unfortunately, the organic carbon content of particles was not determined, because TOC was not measured concurrently with DOC. However, past experience suggests that DOC exceeds TOC with sufficient frequency to undermine one's confidence in such calculations.

If biodilution were operative, an inverse relationship with temperature might be expected because plants grow more rapidly as the water temperature increases up to the point of thermal toxicity. There is a weak inverse relationship with temperature for KPHg(II) but a weaker positive relationship with KPMeHg. If MeHg uptake by living microplankton is active rather than passive (Moye et al., 2001), and if the uptake rate has a steeper temperature dependence than the growth rate, then one should not be disconcerted by a positive influence of temperature on the apparent sorption of MeHg by living biotic particles. However, there are other positively and negatively influential factors and processes with complementary and conflicting temperature dependencies that confound this straightforward interpretation. These factors, processes, and temperature dependencies are discussed below.

The second observation is that the average KPHg(II) value is always greater than the corresponding KPMeHg value at each site and for the combined sites. This might be explained if Hg(II) has a higher affinity for organic particles than MeHg or if MeHg has a higher affinity for DOC than Hg(II). The former explanation has merit because CH3Hg(II)+1 is formed by a covalent bond between the carbon atom of the methyl moiety and the outer orbitals of $Hg(II)^{+2}$ that would otherwise interact with the sulfhydryl moieties on the surfaces of the organic particles or the DOC. By shifting electron density from the methyl group to $Hg(II)^{+2}$, the affinity of the $CH3Hg(II)^{+1}$ for the sulfhydryl moieties is reduced. (Whether the oxidation state of Hg should be formally changed from Hg(II) to Hg(I) when $Hg(II)^{+2}$ is methylated remains open to debate. Most environmental chemists vote "No" on this issue.) The weaker affinity of MeHg for organic particles and DOC is reflected in experimental measurements of $Hg(II)^{+2}$ versus $CH_3Hg(II)^{+1}$ KP and KDOC values, as well as what has been observed in monitoring of Everglades surface water (Hurley et al., 1998). DOC competes with particle surfaces for both Hg(II) and MeHg but passes through a 0.45 micron filter, so the DOC-complexed $Hg(II)^{+2}$ or $CH_3Hg(II)^{+1}$ appears in the filtered sample and therefore is part of the apparently rather than the truly dissolved fraction. However, this phenomenon would require a stronger inverse correlation between the concentration of DOC and KP MeHg than KP Hg(II). In addition, this would require a positive influence of H+ (inverse influence of pH) and Ca^{+2} and a negative influence of ALK on Hg(II) binding because H^{+1} and Ca^{+2} would compete with $Hg(II)^{+2}$ for the weak ligands and the diffuse electrostatic binding sites on the DOC molecules, weakening the affinity of $Hg(II)^{+2}$ for DOC, while ALK would compete with these sites for Ca^{+2}. An increase in H^{+1} and Ca^{+2} relative to ALK would thus cause a net increase the sorption of Hg(II) to particles, while an increase in ALK relative to H^{+1} and Ca^{+2} would cause a net decrease. However, to the extent that the particles are of organic origin, and the ligands and electrostatic binding sites on the particle surfaces are similar to those on the free-floating DOC molecules, it might be expected that the opposing

effects of H^{+1} and Ca^{+2} on $Hg(II)^{+2}$ sorption would effectively cancel, resulting in a weak net positive or inverse correlation.

In fact, the correlation with DOC is moderately positive for KPHg(II) and that for MeHg virtually nonexistent. The apparent positive influence of DOC on Hg(II) sorption might be the result of a real positive co-correlation between the organic content of the particles and the concentration of DOC, as DOC could sorb to the particles, such that the higher the DOC concentration, the higher the sorptive power of the particles, or it could be the result of a spurious co-correlation between the concentration of DOC and the organic content of the particles, as both originate with the production and decomposition of plant biomass. The sorption of DOC to particle surfaces would likely be entropically rather than enthalpically driven. If that were the case, then the DOC sorption would increase rather than decrease with increasing temperature. Conversely, because complexation is an enthalpically driven process, Hg(II) complexation with both Cl^- and the negatively charged organic ligands would decrease rather than increase with increasing temperature. The effective net temperature dependence of this process would be the result of the relative magnitudes of these competing processes in determining the magnitude of $Hg(II)^{+2}$ sorption. The correlation analysis indicates that the net effect is weakly inverse ($r = -0.3$) for $Hg(II)^{+2}$, suggesting that DOC deposition is less important than the chloride complexation and ligand exchange in determining the magnitude of Hg(II) sorption. Further, in this analysis, Ca^{+2} and pH have weak and very weak positive influences, respectively, on KPHg(II), while the influence of ALK is virtually nonexistent. By contrast, the influence of pH on KPMeHg is virtually nonexistent, while the influences of Ca^{+2} and ALK are weakly inverse.

Interestingly, there is a moderate inverse correlation between KPMeHg and chloride. This would be consistent with the measured power of chloride ion to complex with MeHg. However, there is a negligible inverse correlation between chloride and KPHg(II). This might be explained by the complexing power of chloride ion for $Hg(II)^{+2}$ to form $Hg(II)Cl^2$, which would not be repelled by positively charged particle surfaces. The positive charges arises because the negatively charged ligands on the particle's surface bind with positively charged species such as H^{+1} and Ca^{+2}. Once the neutrally charged $Hg(II)^{+2}$ complex penetrates the positive columbic field of the particle surface, it could then exchange with a ligand for which it has a greater affinity than H^{+1} or Ca^{+2}. This requires a close approach to the ligand, which occur much less frequently when $Hg(II)^{+2}$ is uncomplexed or partially complexed. If these competing processes were of roughly equal magnitudes, the influences of chloride on $Hg(II)^{+2}$ sorption would effectively cancel. Why then would chloride not have the same effect on $CH_3Hg(II)^{+1}$? Having formed a covalent bond with the methyl moiety, the affinity of $CH_3Hg(II)^{+1}$ for the ligands in the organic matrix of the particle's surface is orders of magnitude lower than that of $Hg(II)^{+2}$, apparently of the same order as chloride, which is present in high ppm concentrations, rather than fractions of a ppm, as is the case on particle surfaces. For MeHg there is a weak positive temperature dependence, consistent with the expected weakening of the $CH_3Hg(II)Cl$ complex with increasing temperature.

The apparent moderate to strong positive influence of sulfate on KPHg(II) may reflect the co-correlation of sulfate ($SO4^{-2}$) and sulfide (S^{-2}). While S^{-2} binds with $Hg(II)^{+2}$ much more strongly than Cl-, it is possible that the neutrally charged $HgxSy_{(aq)}$ species would then be able to penetrate the columbic barrier and exchange with strong sulhydryl ligands, as was hypothesized for the neutral chloride complex. The ability of Everglades DOC to solubilize or prevent the precipitation of red cinnabar (HgS) under otherwise saturated solution conditions (Ravichadran et al., 1998; Ravichadran, 1999) supports this speculative mechanistic explanation. Since sulfide is present in surface water in low ppb concentrations, and the sulfhydryl moieties on organic particles or DOC are in the low ppm and high ppb concentrations, the sulfhydryl ligands on particles could compete effectively for sulfide-complexed $Hg(II)^{+2}$. It is not clear whether such

partially oxidized sulfur species would have the same influence on MeHg uptake by algae, but the weak positive relationship between sulfate and KPMeHg suggests that facilitated uptake by this mechanism is not occurring to any substantial extent. However, this might also reflect the positive influence of sulfate on sulfide production and the negative influence of sulfide on MeHg bioavailability to living biota in the low sulfide concentration range. Conversely, the high sulfate could cause a high rate of MeHg production relative to the low rate of particle production, resulting in effective supersaturation of the water column with dissolved MeHg, facilitated by DOC, with an apparent inverse influence on the magnitude of the calculated KPMeHg value from the relative fractions of particle-bound and apparently dissolved phases relative to the particle concentration.

The above potential mechanistic explanations of the observed correlation relationships are complex, often convoluted, sometimes conflicting. This underscore the importance of conducting controlled experiments to elucidate the most likely from the potential mechanistic explanations, especially where a factor or set of factors can have competing influences on a process such as sorption to particle surfaces.

METHYLMERCURY BIOACCUMULATION DYNAMICS IN STA-2

The focus of the discussion here is on the MeHg bioaccumulation dynamics of STA-2 Cell 1 in response to the soil and surface water mercury first-flush mercury biogeochemical dynamics that occurred in August 2002 following Cell 1 reflooding after an extended period of dryout. The August 2002 occurrence of peak surface water filtered MeHg concentrations of about 2.5, 7.5, and 20 ng/L at Cell 1 Sites C1AA, BB, and CC (**Figure 17**) was followed by a precipitous decline at Sites C1BB (less than half the preceding concentration) and C1CC (about half the preceding concentration) four weeks later and more than half again at the next sampling event four weeks after that. By contrast, the concentration of MeHg at C1AA declined only slightly between the first and second four-week sampling events but precipitously between the second and third. Based on the mass budget studies, roughly half of the nearly 200 g of MeHg that was exported from Cell 1 for the first year post-reflood was exported in the first quarter post-reflood. There was a mini-anomaly in surface water that peaked at all three interior Cell 1 sites in early March 2003, which then declined to near background levels thereafter. (Interestingly, this mini-anomaly was also observed in the other two treatment cells, suggesting a common external cause. This issue is taken up in the "Discussion" section of the Interim Report (Fink, 2004b) and therefore is not reiterated here.) There were no noticeable MeHg peaks from that time to the end of the study in January 2004.

In general, the surface water MeHg concentrations tracked closely with the soil MeHg concentrations, but there were exceptions. All three sites reached peak surficial soil MeHg concentrations in September 2002 following Cell 1 reflooding in August 2002, but, unlike surface water, the relative magnitudes were in the order C1BB > C1CC > C1AA (Figure 32). Rather than being under the sole or predominant influence of the underlying soil MeHg flux, the filtered MeHg concentration in surface water at Site C1CC seems to have reflected the combined influence of MeHg released from C1BB soils upstream of C1CC and the MeHg released from the surficial soils underlying Site C1CC. Like the water column concentrations, the soil MeHg concentrations at C1AA, C1BB, and C1CC declined in the next quarterly sampling period to about one-tenth, one-third, and one-half the preceding concentrations at C1AA, BB, and CC, respectively, with the order of concentration magnitude now switching to C1CC > C1BB > C1AA. In the third soil sampling event 12 weeks later, Site C1AA soil MeHg roughly doubled, C1BB decreased by about one-fourth, and Site C1CC increased by about one-eighth. The MeHg mini-anomaly that was observed in early March 2003 at all three Cell 1 surface interior water

sites tracked virtually one-to-one with the upturn in the soil MeHg concentrations in the preceding month. Thereafter, the surficial soil appears to have reached a new steady state condition in which the concentrations are between one-third and one-seventh the baseline concentrations measured under pre-reflood conditions in May 2002.

As depicted in **Figure 34**, mosquitofish THg as MeHg concentrations at sites C1AA, BB, and CC peaked at about 0.1, 0.43, and 0.4 mg/kg wet wt in September 2002, while the peak for Site C1CC persisted through October 2002. The mosquitofish population at Site C1AA appeared to be more under the influence of inflow canal conditions than first-flush conditions and the mosquitofish population sampled at C1AA may have been a mixture of imported and resident populations, with high flow conditions weighting the population average to inflow canal origin. Thereafter, the mosquitofish THg concentrations declined progressively to between one-quarter and one-third the peak values in January 20003. Almost a year after the first-flush anomaly in August 2002, a lesser peak roughly half the first occurred in July 2003. This may have been caused in part by seasonal increases in MeHg production associated with concomitant increases in wet deposition Hg(II) load, inflow sulfate and DOC loads, and temperature (Gilmour et al., 1998a, b; 1999) or by seasonal changes in mosquitofish foraging preferences resulting in a higher average trophic level and thus a higher average MeHg bioaccumulation factor. To explain the tenfold higher concentrations of THg as MeHg in mosquitofish collected in Cell 4 versus Cell 3 of the ENR Project, gut content studies conducted for the District by the University of Wisconsin's Hurley and coworkers documented substantial and interesting differences in mosquitofish foraging preferences between Cell 3 and Cell 4. These differences effectively raised the mosquitofish two or three tropic levels. The tenfold difference in mosquitofish THg concentrations between cells disappeared in the winter and spring, from which it was inferred that the differences in mosquitofish foraging preferences between cells disappeared, as well, probably in response to seasonal declines in prey populations at intervening trophic levels.

Based on the exploratory data analysis, the strongest determinant of the concentrations of THg as MeHg in mosquitofish was soil MeHg, the influence of which peaked at about a 14-week lag period. Pore water MeHg concentrations had no detectable influence on mosquitofish THg concentrations at any lag. However, based on an exploratory bioenergetics modeling exercise conducted outside this study, gill uptake of the anomalously high dissolved MeHg concentrations in surface water could have made a substantial, even predominant contribution to mosquitofish MeHg body burdens in the period immediately following the reflooding of Cell 1.

Based on the preceding, it can be hypothesized with reasonable confidence that the MeHg bioaccumulation trajectories observed in the Cell 1 mosquitofish populations were the product of exposure via multiple pathways, the relative contributions of which were changing over time in response to the initial passage and subsequent recycling of a first-flush pulse of excess MeHg and the simultaneous redevelopment of the Cell 1 saprotrophic (detrital) and autotrophic food chains. In addition, there is evidence of a contribution from a MeHg mini-anomaly that occurred in early March 2003, but it cannot be ascertained from the information available whether it was in response to the release of some of the excess first-flush Hg(II) sorbed to standing crop plant biomass in the first few month following reflooding or other hydrological or physicochemical forcing functions. The explanation for the observed lag time between the appearance of the first-flush MeHg pulse and the peak in the mosquitofish THg concentrations is taken up below.

The differences in the observed mosquitofish THg concentrations over time and the observed lag-correlations among the three treatment cells are consistent with the observed MeHg dynamics and inferred trophic dynamics in the three cells over their operational lifetimes. For STA-2 Cell 1, there was an excess MeHg production pulse associated with the first-flush MeHg anomaly superposed on the transport and turnover time relationships in Cell 1. It can be speculated with

reasonable confidence that this excess MeHg pulse has a primary propagation time between its origin in the surficial soil immediately following reflooding (source) and the mosquitofish population (receptor) that depends on the turnover time of each of the intervening compartments through which the MeHg passes as determined by the pathway(s) taken between source and receptor. Once the pulse reaches the mosquitofish, the average MeHg concentration in mosquitofish is determined by the average half-life in the individual mosquitofish and the average turnover time of the mosquitofish population. The average MeHg half-life in an individual mosquitofish is determined by the average mosquitofish depuration and growth rates. Thereafter, the secondary propagation time of the first-flush pulse is determined by (1) the thickness, bulk density, and bioenergetic value of the rewetted detrital layer to rapidly colonizing detritivores; (2) the refractory periods, initial growth rates, and population turnover times of various primary producer biological compartments at the base of the food web, taking into account diel, seasonal and inter-annual variability; (3) the refractory, colonization, and turnover times of various herbivores and carnivore populations in response to the growth, expansion, die-off, and decay of the autotrophic base of the food web; and (4) the uptake efficiencies, depuration rates, and growth rates of the average member of each of the species at each trophic level intervening between source and receptor. There is also a possibility of secondary or after-shock pulses of excess MeHg production fed by the first-flush Hg(II) initially stored in short-term compartments (e.g., plant biomass; surficial soil floc), as appeared to be the case in the first, first-flush MeHg anomaly in STA-2 Cell 1 (Fink, 2004b).

Within the preceding conceptual framework, the most direct pathway linking the first-flush excess MeHg pulse originating in the surficial soil to mosquitofish bioaccumulation of that excess MeHg pulse would most likely have been the rapidly colonizing benthic detritivores (P. Rawlik, SFWMD, personal communication). In areas where the food chain is stunted by adverse conditions associated with eutrophy, including the shading out of the periphyton mat, mosquitofish have been observed to forage disproportionately on benthic detritivores, with a roughly equal amount of soil/sediment in their guts (Cleckner et al., 1998; Hurley et al., 1998; P. Schuster, WDNR, personal communication; T. Lange, FFWCC, personal communication). This could also occur where the hydroperiod is short (P. Rawlik, SFWMD, personal communication). Conversely, in areas where the chemical and hydrological conditions are conducive to the development of long food chains, mosquitofish have been observed to forage disproportionately on periphyton herbivores and their predatory insects, with a roughly equal amount of periphyton in their guts (Cleckner et al., 1998; Hurley et al., 1998; P. Schuster, WDNR, personal communication; T. Lange, FFWCC, personal communication).

The observed peak in the magnitude of the lag-correlation occurred at 14 weeks in Cell 1, and this is roughly the average 90-day turnover time of the mosquitofish population, although some mosquitofish live as long as six months (Loftus et al., 1998). If the turnover time of the periphyton mat is between two and four weeks, depending on the limiting nutrient concentration, sunlight intensity and angle, and ambient temperature (H. Grimshaw, SFWMD, personal communication), then it might be expected that the excess MeHg sorbed by the periphyton mat following the third, first-flush event would have been released at a progressively decreasing (exponential) rate over time, such that the initial concentration would have decreased to between 1.5 and 12.5 percent of the starting concentration over a period of 14 weeks. However, the concentration of MeHg in the periphyton detritus pool upon which the detritivores forage would first have increased and then decreased over time as the periphyton died and began to decay. The MeHg as THg concentration in mosquitofish that foraged exclusively on those detritivores would also have first increased and then decreased over time. At the same time, one might conjecture with reasonable confidence that (1) the autotrophic food chain was developing, and that some mosquitofish began to include in their foraging preferences herbivores that grazed

the periphyton mat; (2) the populations of small predatory insects might also begin to grow with a lag-time appropriate to a predator-prey relationship; and (3) at some point, the mosquitofish could add the predatory insect to its diet. The result would be the observed mosquitofish MeHg bioaccumulation trajectory observed in Cell 1 with the observed lag-time correlation pattern.

While the preceding hypothesis is not inconsistent with the observed mosquitofish MeHg bioaccumulation patterns and lag-correlation patterns, it cannot be verified without a combination of tracer and gut content studies. Samples of STA-2 mosquitofish, plants, and soil have been split with Carol Kendall and co-workers of the U.S. Geological Survey (USGS), Palo Alto. The samples will eventually be analyzed for 14-C and 13-N to discern the average food chain relationships among detritus, primary producers, and mosquitofish. However, the food chain inferences from such results still need to be verified by gut content studies and comparison to observed dynamic MeHg bioaccumulation patterns. The definitive results would have been obtained by introducing stable isotope mercury tracers into STA-2 Cells 1, 2, and 3 about 90 days prior to and at the time of reflooding of Cell 1 in August 2002. Such studies have been conducted successfully at an experimental lake in Ontario, Canada, in a first of its kind study (Gilmour et al., 2001).

ANALYSIS, INTEGRATION, AND SYNTHESIS

The original conceptual model set forth in the "Background" section of this document was a frame of reference upon which to base the design of this study and a framework within which to organize, interpret, and apply the results of this study. The question then arises whether that conceptual model needs to be revised in part or in whole in response to the monitoring results, mass budget calculations, or exploratory correlations. This subsection attempts to answer that question by redefining the roles of inorganic mercury, sulfur, iron, and manganese in methylmercury production and DOC, chloride, iron, and manganese in MeHg bioaccumulation.

THE ROLE OF SOIL DEPTH IN METHYLMERCURY PRODUCTION AND BIOACCUMULATION

The side-by-side pre-study of the modified sipper method vs. the centrifugation method required the collection of multiple soil cores from 0–2, 2–4, 4–6, 6–8, and 8–10 cm strata at Sites C1CC, C2C, and C3C in STA-2 Cells 1, 2, and 3, respectively, for ultra-trace THg and MeHg analysis by Frontier Geosciences. In every case, the maximum soil and pore water MeHg concentrations were observed in the 0–2 or 2–4 cm strata, with a precipitous decline thereafter. Those results are depicted in Figures AE-3, AE-4, and AE-5 in Appendix E. Thus, there is no need to revise the conceptual model with respect to the surficial soil strata in which MeHg production is a maximum based on the results of STA-2 Mercury Special Studies Project.

THE ROLE OF WATER DEPTH IN METHYLMERCURY PRODUCTION AND BIOACCUMULATION

In the original conceptual model, water depth was assumed to influence MeHg production via indirect effects on surficial soil redox potential and on bioaccumulation via its relationship to flow and dilution of the MeHg flux from the soil. In some cases, an inverse relationship between water depth and soil or pore water MeHg was observed, suggesting that redox potential was the controlling factor, and in others there was a positive relationship, suggesting that the buildup of MeHg in surficial soil and pore water was inversely related to surficial soil mechanical

disturbance by wind and wave action, and that the magnitude of such disturbances decreased with increasing water depth. However, where surface water and not soil was supplying one of the limiting nutrients for MeHg production (e.g., sulfate), increased disturbance of the surficial soil could increase the flux of the limiting nutrient from the overlying water to the surficial soil, and thus the MeHg production rate. This might be at the expense of driving the sulfate-reducing bacteria deeper to avoid the toxic oxidation threshold, reducing the MeHg diffusive flux out of the surficial soil layer into the overlying water column. These conflicting effects may explain why the apparent influence of surface water depth on soil or pore water is often ambiguous.

Moreover, the conceptual model also assumed that most of the MeHg in mosquitofish was being bioaccumulated via the detrital food chain, thus short-circuiting the effect of dilution or any other factor on surface water MeHg concentrations and their bioavailability to mosquitofish. However, a bioenergetics modeling analysis carried out by the senior author outside this study suggests that surface water dissolved MeHg can make a substantial contribution to the MeHg body burden in small fish such as the mosquitofish where anomalously high dissolved MeHg concentrations are present surface water, such as were encountered in STA-2 Cell 1 in August 2002. This means that water depth can have a greater influence on the bioaccumulation of first-flush MeHg than previously believed, and, that, as a consequence, raising the water levels quickly under rapidly flowing conditions can more effectively reduce the peak bioaccumulation in T2 fish and in the T3 and T4 fish that prey on them than previously believed.

THE ROLE OF SURFACE WATER, SOIL, PORE WATER, AND RAINFALL INORGANIC MERCURY IN METHYLMERCURY PRODUCTION AND BIOACCUMULATION

It has been hypothesized by others (Krabbenhoft et al., 2001; Gilmour et al., 2002; Orem et al., 2002) that the MeHg in Everglades surface water, soil, and fish is produced primarily by methylating the Hg(II) in wet and dry atmospheric deposition ("new mercury") and only secondarily, if at all, by methylating the Hg(II) already present in surficial soil ("old mercury"). This hypothesis is supported by several years of data collected from studies of semi-controlled mesocosms dosed with stable mercury isotopes in concentration ranges typical of the environments in which the mesocosms are located. However, the mesocosms are so designed that they mimic exactly the hydroperiod of the environments in which they are located, and none of these sites has dried out and rewetted since the mesocosms have been emplaced and dosed. In systems that remain wet year around, this hypothesis is probably reasonable, but in systems that rewet after drying for extended periods of time, as was the case in STA-2 Cell 1 in August 2002, this cannot be the case, because of the mass shortfall of the gross input mass of inflow, wet and dry deposition that occurred in the first quarter following reflooding of Cell 1and the mass of MeHg that would have had to have been produced to account for the MeHg mass that was calculated to have been exported, stored in vegetation, and stored in surficial soil in that same quarter.

The original conceptual model had already been modified to accommodate the existence of strong contrary evidence to the hypothesis that virtually all of the MeHg produced by sulfate-reducing bacteria derives from Hg(II) supplied by wet and dry atmospheric deposition, as opposed to release from the surficial soil reservoir following reflooding after extended periods of dry out. Prior to this study, the strongest compelling contrary evidence was collected by the USGS and the District in a jointly funded study of THg and MeHg concentrations in water, soil, plants, and fish following the dryout of many areas and burn of a few areas of the northern Everglades in the winter and spring of 1999 (Krabbenhoft et al., 2000; Krabbenhoft and Fink, 2001; Fink, 2002; 2003). Among other things, a MeHg concentrations more than 30 times the

baseline concentration value was observed at a well-studied site in one of the most eutrophic areas of the northern Everglades. Unfortunately, the study could not be carried out in such a way as to close the THg and MeHg mass budget for each sampling site. That deficiency has been corrected by the STA-2 Mercury Special Studies Project on a macro-scale. The mass budget results support the conclusion that the soil reservoir, and not wet and dry atmospheric deposition, or any other non-soil source, must make a substantial, likely predominant contribution to the Hg(II) transformed into MeHg by sulfate-reducing bacteria in the first quarter following refolding after an extended period of dryout. The remaining question is not whether soil Hg(II) was involved but what fraction of the theoretically bioavailable Hg(II) was actually converted to MeHg under the first-flush conditions encountered.

THE ROLE OF SOIL, PORE WATER, AND SURFACE WATER CARBON SPECIES

Based on the exploratory data analysis, the inverse influence of DOC on Hg(II) and MeHg sorption to suspended, settled, or consolidated organic particles was weaker than expected, while the positive correlations with percent soil organic matter (100 percent - % ash) were much stronger than expected. If the percent organic matter is a surrogate for the fraction of sulfhydryl binding sites, then this might explain why soil Hg(II) is positively correlated with % ash, but MeHg and %MeHg are negatively correlated with the same parameter, because the bioavailability of Hg(II) for methylation is inversely related to the number of sulfhyrdyl binding sites in soil. Pore water

The magnitude, duration, and frequency of recurrence of a first-flush MeHg anomaly depends on the magnitudes, durations, and frequencies of recurrence of the pools of the factors that limit sulfate-reducing bacteria metabolism as opposed to limiting the bioavailability of Hg(II) to sulfate-reducing bacteria for inadvertent uptake and methylation. Carbon in the form of short-chain carboxylic acids, sulfur in the form of sulfate, and Hg(II) in a form that can be readily taken up actively or passively by sulfate-reducing bacteria (SRB) are required for MeHg production. The primary if not the only internal source of the organic carbon in aquatic ecosystems is plant biomass, while dissolved organic carbon can make a substantial contribution to the carbon load in blackwater swamps, rivers, and lakes. In the Everglades, EAA runoff contains a substantial DOC load that competes with internal production for carbon load dominance in the constructed wetlands during routine operation.

However, pre-operational start-up is another matter altogether. Unlike site preparation at the ENR Project, no standing crop biomass was cleared from STA-2 Cells 1, 2, or 3 prior to first flooding in the summer 2000. It is likely that the initial standing crop of dead biomass associated with last-crop planting and rapidly colonizing ephemeral wetland species that invaded prior to first-flooding of Cell 3 have long-ago decayed, while the more refractory woody plants that were present in Cell 1 may still be decomposing and supplying an excess flux of organic carbon to the sulfur cycle bacteria. This means that in Cell 3 the continuing flux of short-chain organic acids required for SRB metabolism is now being supplied by the decomposition of wetland plant biomass produced in a low-nutrient environment. Where the plant biomass is dominated by relatively refractory rooted and floating wetland plants to the exclusion of the more rapidly decomposed periphyton, as is now increasingly the case in all three STA-2 treatment cells, organic carbon limitation cannot be ruled out as the cause of the low MeHg production in Cell 3 without additional study.

THE ROLE OF SOIL, PORE WATER, AND SURFACE WATER SULFUR SPECIES

The expected strong inverse correlation between pore water sulfide and pore water MeHg or soil MeHg observed in the Everglades by others (Gilmour et al., 1998a, b; 1999) was not observed in this study. DOC in EAA runoff may weaken the influence of pore water sulfide on the bioavailable fraction of Hg(II) by strongly binding Hg(II) via sulfhydryl moieties with extremely high affinities for Hg(II) (Ravichadran et al., 1998a, b; Ravichadran, 1999; Jay et al., 2000; Haitzer et al., 2002). However, a moderate inverse correlation was observed between soil AVS and soil MeHg for a much larger data set that included the soil samples collected immediately following the first-flush event but excluding the pre-flood baseline monitoring event. This moderate inverse relationship was also observed with mosquitofish THg, while that with pore water sulfide was not. It might be inferred from this latter relationship that the MeHg associated with soil solids, and not the MeHg in pore water, is the MeHg that is bioaccumulating in benthic invertebrates that are consumed by primary predators.

THE ROLE OF SOIL, PORE WATER, AND SURFACE WATER IRON

The iron sulfide (pyrite) layer is readily observable in soil cores collected from Everglades sites under eutrophic conditions in the presence of excess sulfate, which is readily converted to sulfide by sulfate-reducing bacteria (C. Gilmour, ANSERC, personal communication). It has been hypothesized by others that iron associated with soil particles and in pore water plays an important role in mediating the precipitation and dissolution of HgS via the formation and dissolution of iron oxyhydroxide (Dmytriw et al., 1995) and iron sulfide-polysulfide complexes (C. Gilmour, ANSERC, personal communication) associated with soil particle surfaces. More recently it has been hypothesized that iron colloids could be mediating Hg(II) and MeHg partitioning (Babiarz et al., 2001), and by extension, the transport and transformation processes that occur on settling or settled organic particles. We did observe moderate to strong positive and inverse correlations with soil and/or pore water iron on Hg(II) and MeHg in pore water and partitioning. Unexpectedly, the apparent influences of iron colloids on these processes appear to be stronger than the corresponding influences of DOC. This is also consistent with the observations of Babiarz et al. (2001). The role of iron sulfide-polysulfide colloids in complexing Hg(II) in a form bioavailable for MeHg production that might otherwise form more thermochemically stable precipitates that are not bioavailable for MeHg production should be a priority for further investigation. In particular, priority should be given to developing a successive Everglades soil extraction scheme for obtaining progressively more loosely bound fractions of Hg(II) associated with soil inorganic and organic sulfide complexes of Hg(II) that can be correlated with the labile, mobile, and/or methylatable soil Hg(II) fractions.

THE ROLE OF SOIL PORE WATER, AND SURFACE WATER MANGANESE

A moderate inverse relationship between soil MeHg and soil TMn was first observed by the senior author when pairing the MeHg concentrations in the 0–10 cm cores collected semi-annually from the Everglades Nutrient Removal Project in the period from 1995–1996 with TMn concentrations in the 0–5 cm soil cores collected at the same sites at approximately the same time in an unrelated study. It has also been observed that dissolved Mn exhibits substantial diel fluctuations in surface water along a well-studied nutrient gradient in the northern Everglades (T. Bechtel, SFWMD, personal communication). Due to its inferred greater lability and mobility than iron in the presence of high pore water sulfide concentrations under ambient Everglades

conditions, it is speculated by some that dissolved Mn may act as a redox shuttle between surface water and surficial pore water, mediating redox-sensitive physicochemical processes involving dissolved, colloidal, sorbed, complexed, and precipitated iron and thus, indirectly, the sulfur cycle. The appearance of moderate to strong positive and inverse correlations between the concentrations of soil, pore water, or surface water manganese and the corresponding Hg(II) and MeHg concentrations within or between those media suggests that the role of Mn in mediating the mercury cycle via the iron and sulfur cycles has been generally underappreciated. The apparent parabolic relationship between pore water dissolved iron and pore water dissolved Mn (**Figure 92**) should also be of general interest. It is thus strongly recommended that research be initiated into the role of Mn in mediating mercury species transport, biogeochemistry, and bioaccumulation via its direct influences on the iron cycle and indirect influences on the sulfur cycle.

THE ROLE OF SOIL PORE WATER, AND SURFACE WATER PHOSPHORUS

There were no moderate to strong correlations between soil, pore water, or surface water total phosphorus (TP) or total dissolved phosphorus (TDP) concentrations and the corresponding MeHg concentrations. There was some evidence of an inverse relationship between surface water TP or TDP and mosquitofish THg as MeHg. The hypothesis that this is due to biodilution is not supported by the positive and inverse correlations with other factors that are known or reasonably anticipated to mediate or moderate the biodilution process. An alternative hypothesis is that there is a progressively increasing concentration gradient in MeHg production and concentrations in surficial soil from treatment cell inflow to outflow that co-correlates with the TP and TDP gradients in surficial soil. It might be speculated that this is a direct cause-effect relationship reflecting the direct influence of TP and/or TDP on anaerobic metabolic rates of sulfate-reducing bacteria. Alternatively, it might be conjectured that TP or TDP is the limiting nutrient for bacteria that decompose plant litter aerobically, that aerobic bacteria draw down the dissolved oxygen in surface water, that the virtual absence of DO is required for obligate anaerobes such as SRB, that sulfate is consumed and sulfide produced under anaerobic conditions and thus that TP or TDP influences soil MeHg production via its direct influence on the carbon cycle and its indirect influence on the oxygen cycle, and, via the oxygen cycle, the sulfur, iron, and mercury cycles. Because the average inflow and outflow concentrations from STA-2 Cells 1, 2, and 3 are virtually indistinguishable, something else must be exerting a primary influence on MeHg production and bioaccumulation in Cells 1, 2, and 3, since the MeHg concentrations in soil, water, and fish are so very different among the three cells. The interest in this hypothesis must be tempered by the observation that over time the differences in MeHg concentrations in water, soil, and fish among cells are decreasing and the concentrations appear to be converging to the same steady state, as long as the cells remain wet. That being the case, further evaluation of the role of TP or TDP in MeHg production and bioaccumulation should be relegate to a secondary priority, if at all.

THE ROLE OF SOIL, PORE WATER, AND SURFACE WATER NITROGEN CYCLE SPECIES

There are several known and potential points of direct or indirect influence of the nitrogen cycle on the mercury cycle to explain the persistent appearance of surface water or pore water ammonia, NOx, or TKN or soil TN as strong positive or inverse correlates with surface water, pore water, or soil THg or MeHg. MeHg production was not stimulated when soil cores spiked with a radioisotope of Hg(II) were dosed with excess nitrate (Gilmour et al., 1998a). Under sulfidic conditions ammonia and phosphate are liberated from soils, increasing the fluxes to the

overlying water column (Lamers et al., 1998). Soil sulfur can be converted to sulfate by nitrate-reducing bacteria in the presence of soil calcium carbonate, and the excess sulfate could than then support accelerated SRB metabolism (Bezbaruah and Zhang, 2003). If the sulfide produced by SRB is oxidized back to sulfur in surficial soil by photosynthetic bacteria, the cycle can start all over again. In addition, under conditions where nitrogen cycle bacteria outcompete SRB for a limited supply of short-chain carboxylic acids, the sulfate-reducing bacteria metabolism could be throttled back, reducing inadvertent MeHg production. The moderate to strong positive correlation between soil TN and THg could be a spurious co-correlation or real. If this is accurate, then it is possible that nitrogen cycle bacteria co-exist with "upstream" aerobic bacteria and "downstream" anaerobic bacteria that prefer/require even lower redox potential for electron transfer to the ultimate acceptor and are directly or indirectly involved in mediating iron or sulfur cycle bacteria activity.

EMERGING HYPOTHESES

- The excess MeHg production that occurred following reflooding of STA-2 Cell 1 in August 2002 was supported primarily by a sudden increase in the bioavailable fraction of soil Hg(II), not external inputs from inflow and wet and dry atmospheric deposition and not the first-flush flux of Hg(II) from the surficial soil to the water column.

- The net loss of Hg(II) from surficial soils over the 18 months of the study was primarily due to rooted plant-mediated evasion, and not seepage-driven leaching into the underlying soil strata or plant uptake and storage in standing crop living, dying, and dead plant biomass above or below ground.

- Surface water MeHg made a substantial contribution to mosquitofish MeHg body burdens during the first quarter of post-reflood operation of STA-2 Cell 1.

- The depletion of the oxidized sulfur pool in surficial soils following reflooding, and not the build-up of inhibitory levels of pore water sulfide, was the short-term cause of the rapid stabilization of STA-2 Cell 1 with respect to MeHg production. The high rate of seepage out of Cell 1 may have expedited this process.

- The buildup of organic sulfides rather than inorganic sulfides in surficial soil was the long-term cause of the approach of STA-2 Cell 1 to Cell 3-like conditions with respect to MeHg production.

- Iron colloids have a greater influence on the magnitude of Hg(II) and MeHg sorption to suspended, settled, and consolidated organic particles than do DOC colloids.

- Due to its lability in the presence of high pore water sulfide concentrations under ambient Everglades conditions, dissolved Mn, not dissolved Fe, acts as a redox shuttle between surface water and surficial pore water, mediating redox-sensitive physicochemical processes involving dissolved, colloidal, sorbed, complexed, and precipitated iron and thus, indirectly, the surficial soil sulfur cycle, and, thence the mercury cycle, while contributing to the greater diel variability in surficial soil pore water chemistry than was anticipated.

FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

- Regarding technology transfer of the modified sipper method, until the cause of the discrepancies between the results of the modified sipper method and centrifugation method of pore water collection is identified, and a determination is made as to whether it is inherent to the test method design or can be reduced to acceptable levels by further modifications of the modified sipper design, one must challenge the generalization that the modified sipper method is collecting pore water from the 0-4 to 0-6 cm surficial soil horizon. Where this can be established on a site-specific basis using appropriate tracers, the assertion of representativeness of the pore water sample for this surficial soil stratum can be defended. Nevertheless, the within-site field reproducibility of the sipper method must be deemed acceptable at this juncture, even for F-THg and F-MeHg.

- Following the first-flush MeHg anomaly in August 2002, surface water and soil MeHg concentrations declined progressively, while mosquitofish THg first increased and then decreased progressively in response to the first-flush MeHg pulse.

- Using a water budget supplied by others and concentration data obtained in this study, the unprecedented THg and MeHg concentrations in Cell 1 surface water following the last, first-flush anomaly in August 2002 resulted in the calculated net export of about 110 g and 85 g of THg and MeHg mass, respectively, during the first full quarter of operation following reflooding. Concurrently, Cell 1 was a substantial net importer of sulfate and a net exporter of dissolved organic carbon masses. These are two of the three basic ingredients, bioavailable inorganic mercury, Hg(II), being the third, that are required for excess MeHg production. During that same period, the net export of THg and MeHg mass from Cell 2 were calculated to be about 50 g and 2 g, respectively, while Cell 3 was calculated to be a net exporter of about 65 g THg and 2 g MeHg mass.

- Between the pre-flood baseline condition in May 2002 and the post-flood condition in August 2002, the change in the masses of THg and MeHg stored in the top 4 cm of soil were calculated to be about -1,000 g and +200 g, respectively. In the following quarter, the changes were reversed, with on the order of 720 g of THg being reabsorbed and 275 g MeHg being lost by the Cell 1 surficial soil. Over the 18 months of the study, there was a calculated net loss of 1500 g THg and 215 g MeHg from the top 4 cm of soil relative to pre-flood baseline conditions, while there was net export of about 10 g of THg and net export of about 140 g of MeHg based on water budget calculations.

- Exploratory calculations suggest that on the order of 280 g of THg and 110 g of MeHg masses were temporarily stored in standing crop plant biomass following the last, first-flush MeHg anomaly in Cell 1 in August 2002. However, the calculation is highly uncertain, because the coverage and biomass density measurements did not occur at the same time as the mercury concentration measurements, so the results should be considered of exploratory value only. Nevertheless, it is highly unlikely that plant storage can account for all of the discrepancies between the changes in the soil mass budget and the net export of THg from STA-2 Cell 1. This may not be true of MeHg, however, because the discrepancies are much smaller.

- The roughly 75 g of net inputs of Hg(II) from sources other than soil could not have produced enough MeHg mass to have accounted for the next export of 85 g, the net storage of 115 g in vegetation biomass, and the net increase of 200 g of MeHg in surficial soil, even taking into account the propagated uncertainties in the mass budget calculations.

- The strong inter-correlation between the quarterly change in surficial soil storage of MeHg and the quarterly next export of MeHg via surface water from all three cells links changes in surficial soil chemistry to the performance of STA-2 with respect to MeHg production and export.

- The pool of MeHg temporarily stored in plant biomass did not appear to have been recycled back into the aquatic food chain as efficiently as in the first, first-flush anomaly. Perhaps this is because of changes in operational hydrology, standing-crop plant species biomass dynamics, or soil chemistry that occurred since then.

- Further, the first-flush effect dissipated more rapidly in the last event than the first two, resulting in lower peak MeHg concentrations in mosquitofish, sunfish, and largemouth bass. This is most likely attributable to the operation of Cell 1 in flow-through mode immediately following reflooding, although beneficial changes in soil chemistry or food chain structure cannot be ruled out with the available information.

- Finally, there is some evidence that the decline in the soil MeHg concentrations was accompanied by a concomitant build-up of soil sulfide in the form of acid volatile sulfide. However, the exploratory data analysis indicates that the expected moderate to strong inverse correlation between soil sulfide as acid volatile sulfide and soil MeHg levels occurred only for Cell 3, weakened for Cell 2, and was virtually absent for Cell 1. This may be a consequence of the differences in the pre-construction soil chemistry and the number of consecutive days each cell has remained wet since construction.

- While the surface water mass budget calculations for THg and MeHg are both instructive and useful as is, the mass budget calculations would have benefited from a probabilistic presentation that incorporated the actual or estimated uncertainties in each term in the mass budget calculation as a probability density function (pdf) and overall pdf that represented the propagated error in the final mass budget result as a pdf rather than a single value. Limited time and resources did not permit carrying out this additional task for this project, however.

- This report presents an in-depth discussion of the patterns of correlation observed and their possible mechanistic explanations. However, only well-designed, controlled experiments can discriminate between the possible and actual explanations (hypotheses). In particular, there is as yet no way to discriminate between (1) the hypothesis that progressive decline in soil MeHg was caused by the progressive build-up of inhibitory levels of soil sulfide and the hypothesis that it was caused by the progressive depletion of the pool of the critical limiting factor required for excess MeHg production; or (2) the hypothesis that the absence of a strong inverse correlation between pore water or soil sulfide and pore water or soil MeHg in STA-2 treatment cells is due to the influence of manganese (Mn) on the iron (Fe) cycle and the hypothesis that this same effect is caused by dissolved organic carbon (DOC). Follow-up research by the U.S. Geological Survey and the Smithsonian Institution in the District's STAs should further our understanding of the underlying cause of the

statistically, ecologically, and administratively significant observed reductions in MeHg concentrations in STA-2 Cell 1 soil, water, and fish over the course of the study.

- Whatever the cause, the results of the STA-2 Mercury Special Studies demonstrate that the desired effect has been achieved. The design and operational corrective actions have proved successful in reducing the adverse impacts of the MeHg anomaly within STA-2 Cell 1 and downstream. Had the first-flush MeHg anomalies in STA-2 Cell 1 proved irreversible, persistent, and of unacceptable magnitude, one option would have been to decommission Cell 1 and rebuild on adjacent lands less susceptible to a persistent, first-flush MeHg problem. That this was not necessary bodes well for similar projects planned for South Florida over the next several decades.

LITERATURE CITED

Abtew, W. 1996. Evapotranspiration measurements and modeling for three wetland systems in South Florida. *Journal of the American Water Resources Association*, 32 (3), 465-473.

Ambrose, Jr., R.B. and R. Araujo. 1998. Applications of the Phase I Everglades mercury cycling model. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA, at the Third Annual Everglades Mercury Workshop, Sheraton West Palm Beach Hotel, West Palm Beach, FL.

Amirbahman, A., A.L. Reid, T.A. Haines, J.S. Kahl and C. Arnold. 2002. Association of MeHg with dissolved humic acids. *Environ. Sci. Technol.*, 36(4): 690-695

Amyot, M., D. Lean and G. Mierle. 1997. Photochemical formation of volatile mercury in high arctic lakes. J. *Environ. Toxicol. Chem.*, 16(10): 2054-2063.

Atkeson, T, D. Axelrad, C. Pollman and J. Keeler. 2002. Integrating atmospheric mercury deposition and aquatic cycling in the Florida Everglades. Integrated Summary. Prepared by the Florida Department of Environmental Protection for the U.S. Environmental Protection Agency Region 4. Tallahasee, FL.

Atkeson, T. and D. Axelrad 2004. Chapter 2B: Mercury Monitoring, Research, and Environmental Assessment. G. Redfield, ed. In: *2004 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.

Babiarz, C.L., J.P. Hurley, S.R. Hoffmann, A.W. Andren, M.M. Shafer and D.E. Armstrong. 2001. Partitioning of THg and MeHg to the colloidal phase in freshwaters. *Environ. Sci. Technol,*. 35(24): 4773-4782.

Beijer, K. and A. Jernelov. 1979. Methylation of mercury in aquatic environments. J. O. Nriagu, ed. In: *The biogeochemistry of mercury in the environment*. Elsevier/North Holland Biomedical Press, New York, NY.

Benoit, J.M., C.C. Gilmour, R.P. Mason and A. Heyes. 1999a. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Env. Sci. Technol.*,33(6): 951-957.

Benoit, J.M., R.P. Mason and C.C. Gilmour. 1999b. Estimation of mercury-sulfide speciation in sediment pore waters using octanol-water partitioning and its implications for availability to methylating bacteria. *J. Env. Toxicol. Chem.*, 8 (10): 2138-2141.

Benoit, J.M., C.C. Gilmour and R.P. Mason. 2001a. The influence of sulfide on solid-phase mercury bioavailability for methylation by pure cultures of *Desulfobulbus propionicus* (1pr3). *Envir. Sci. Technol*., 35(1): 127-132.

Benoit, J.M., R.P. Mason, C.G. Gilmour and G.R. Aiken. 2001b. Constants for mercury binding by dissolved organic matter isolates from the Florida Everglades. *Geochimica et Cosmochimica Acta*., 65: 4445-4451

Bezbaruah, A. N. and T.C. Zhang. 2003. Performance of a constructed wetland with a sulfur/limestone denitrification section for wastewater nitrogen removal. *Environ. Sci. Technol.*, 37(8):1690-1697.

Balogh, S.J., Y. Huang, M.L. Meyer and D.K. Johnson. 2002. Episodes of elevated MeHg concentrations in prairie streams. *Environ. Sci. Technol.*, 36(8): 1665-1670.

Berman, M. and R. Bartha. 1986. Control of the methylation process in a mercury-polluted aquatic sediment. *Environ. Pollution (Series B),* 11: 41-53.

Bodaly, R.A., R.E. Hecky and R.J.P. Fudge. 1984. Increases in fish mercury levels in lakes flooded by the Churchill River diversion, northern Manitoba. *Can. J. Fish. Aquat. Sci.,* 41: 682.

Boudou, A. and F. Ribeyere. 1981. Comparative study of trophic transfer of two mercury compounds, $HgCl^2$ and CH3HgCl, between *Chlorella vulgaris* and *Daphnia magna*. Influences of temperature. *Bull. Environ. Contam. Toxicol.*, 27: 624-629.

Branfireun, B.A., N.T. Roulet, C.A. Kelly and J.W.M. Rudd. 1999. *In situ* sulphate stimulation of mercury methylation in a boreal peatland: toward a link between acid rain and MeHg contamination in remote environments. *Global Biogeochem. Cycle*, 13: 743-750.

Chan, K.Y., L.C. Xu and H.P. Fang. 2002. Anaerobic Electrochemical Corrosion of Mild Steel in the Presence of Ectracellular Polymer Substances Produced by a Culture Enriched in Sulfate-Reducing Bacteria. *Environ. Sci. Technol.*, 36(8): 1720-1727.

Chanton, J. 1998. Methane as a surrogate for plant-mediated mercury vapor exchange—field scoping studies. Department of Oceanography, Florida State University, Tallahasee, FL. Final Report to the South Florida Management District, West Palm Beach, FL. May.

Chen, Y., J.C. Bonzongo, W.B. Lyons and G.C. Miller. 1997. Inhibition of mercury methylation in anoxic freshwater sediment by group VI anions. *J. Environ. Toxicol. Chem.*, 16(8): 1568-1574.

Choi, J. and J.W. Harvey. 2000. Quantifying time-varying ground-water discharge and recharge in wetlands of the northern Florida Everglades. *Wetlands*, 20(3): 500-511.

Cleckner, L.B. P.J. Garrison, J.P. Hurley, M.L. Olson and D.P. Krabbenhoft. 1998. Trophic transfer of methylmercury in the northern Florida Everglades. *Biogeochemistry*, 40: 347-361.

Cleckner, L. B., C. C. Gilmour, J. P. Hurley and D. P. Krabbenhoft. 1999. Mercury methylation in periphyton of the Florida Everglades. *Limno. Oceanogr.*, 44(7): 1815-1825.

Compeau, G. and R. Bartha. 1985. Sulfate-reducing bacteria. Principal methylators of mercury in anoxic estuarine sediments. *Applied Environ. Microbiol.*, 50: 498-502.

Cope, W.G. and R.G. Rada. 1992. Accumulation of Mercury by Aufwuchs in Wisconsin Seepage Lakes: Implications for Monitoring. Arch. *Environ. Contam. Toxicol.*, 23: 172-178.

Craig, P.J. and P.D. Bartlett. 1978. The role of hydrogen sulphide in environmental transport of mercury. *Nature*, 275: 635-637.

Dmytriw, A. Mucci, M. Lucotte and P. Pichet. 1995. The partitioning of mercury in the solid components of dry and flooded forest soils and sediments from a hydroelectric reservoir, Quebec (Canada). *Water, Air and Soil Pollution*, 1099-1103.

D'Itri, F.M., C.S. Annett and A.W. Fast. 1971. Comparison of mercury levels in an oligotrophic and eutrophic Lake. *J. Mar. Technol. Soc.*, 5(6): 10-14.

Dong, W., S.E. Lindberg, J. Chanton, R.G. Qualls and T. Meyers. 2004. A mechanism of biomodal emissions of gaseous mercury from aquatic macrophytes in the Everglades. In Prep.

Drexel, R.T., M. Haitzer, J.N. Ryan, G.R. Aiken and K.L. Nagy. 2002. Mercury (II) sorption to two Florida Everglades peats: evidence for strong and weak binding and competition by dissolved organic matter released from the peat. *Environ. Sci. Technol.* 36(19): 4058-4064.

Driscoll, C.T., V. Blette, C. Yan, C.L.Scofield, R. Munson and J. Holsapple. 1995. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. *Water, Air, and Soil Pollution,* 80: 499-508.

Dyrssen, D. and M. Wedborg. 1991. The sulphur-mercury(II) system in natural waters. *Water Air Soil Poll.*, 56: 745-767.

Fink, L.E. and P. Rawlik. 2000. Chapter 7: The Everglades Mercury Problem. G. Redfield, ed. In: *2000 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL. January.

Fink, L.E. 2002. Appendix 2B-3: The effect of effect of dryout and rewetting on mercury bioaccumulation. G. Redfield, ed. In: *2002 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, Fl.

Fink, L.E. 2003. Appendix 2B-1: The effect of dryout and rewetting on mercury bioaccumulation. G. Redfield, ed. In: *2003 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.

Fink, L.E. 2004a. Appendix 2B-6: STA-6 Mercury Special Studies Interim Report. G. Redfield, ed. In: *2004 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL. January.

Fink, L.E. 2004b. Appendix 2B-7: STA-2 Mercury Special Studies Interim Report. G. Redfield, ed. In: *2004 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL. January.

Garcia, E. and R. Carignan. 2000. Mercury concentrations in northern pike (*Esox lucius*) from boreal lakes with logged, burned, or undistrubed catchments. *Can J. Fish. Aquatic Sci.*, 57 (Suppl.2): 129-135.

Gerrard, P.M. and V.L. St. Louis. 2001. The effects of experimental reservoir creation on the bioaccumulation of MeHg and reproductive success of tree swallows (Tachycineta bicolor). *Environ. Sci. Technol.,* 35(7): 1329-1338.

Gilmour, C.C. and E.A. Henry. 1991. Mercury methylation in aquatic systems affected by acid deposition. *Environ. Pollut.,* 71: 131.

Gilmour, C.C., E.A. Henry and R. Mitchell. 1992. Sulfate stimulation of mercury methylation in sediments. *Environ. Sci. Technol.,* 26: 2281-2287.

Gilmour, C.C., G.S. Riedel, J.D. Coates and D. Lovley. 1996. Mercury methylation by Iron (III) reducing bacteria. Am. Soc. of Microbiology 96th General Meeting, New Orleans, LA. May 19-23. Abstract (98) O-15: 356.

Gilmour, C.C., G.S. Ridel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill and M.C. Stordal. 1998a. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry,* 40: 327-345.

Gilmour, C.C., A. Heyes, J. Benoit, G. Reidel, J.T. Bell and G.Gill. 1998b. Distribution and biogeochemical control of mercury methylation in the Florida Everglades. Annual Report for 1998. Academy of Natural Sciences, Estuarine Research Center, St. Leonard, MD. Contract C-7690 with the South Florida Water Management District.

Gilmour, C.C., A. Heyes, J. Benoit, G. Reidel, J.T. Bell and G.Gill. 1999. Distribution and biogeochemical control of mercury methylation in the Florida Everglades. Final Report. Academy of Natural Sciences, Estuarine Research Center, St. Leonard, MD. Contract C-7690-A01 with the South Florida Water Management District, West Palm Beach, FL.

Gilmour, C.C, A. Heyes, R.P. Mason and J.W.M. Rudd. 2001. Response of Methylmercury Production and Accumulation to Changes in Hg Loading: A Whole-Ecosystem Mercury Loading Study. Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments. Sheraton, West Palm Beach, Florida. Sponsored by the U.S. Environmental Protection Agency, Washington, D.C. May 8-10, 2001.

Golding, G.R., C.A. Kelly, R. Sparling, P.C. Loewen, J.W.M. Rydd and T. Barkay. 2002. Evidence for Facilitated Uptake of Hg(II) by *Vibrio anguillarum* and *Escherichia coli* under Anaerobic and Aerobic Conditions. *Limnol. Oceanog.*, 47(4): 967-975.

Grimshaw, H. J., R. G. Wetzel, M. Brandenburg, K. Segerblom, L. J. Wenkert, G. A. Marsh, W. Charnetzky, J. E. Haky and C. Carraher 1997. Shading of periphyton communities by wetland emergent macrophytes: Decoupling of algal photosynthesis from microbial nutrient retention. *Arch. Hydrobiol.*, 139 (1): 17-27.

Guentzel, J.L., R.T. Powell, W.M. Landing and R.P. Mason. 1996. Mercury associated with collodial material in estuarine and open-coean environment. Marine Chemistry 55: 177-188.

Guentzel, J.L., W.H. Landing, G.A. Gill and C.D. Pollman. 2001. Processes Influencing Deposition of Mercury in Florida. *Envir. Sci. Technol.*, 35:863-873.

Gun, J., A. Goifman, I. Shkrob, J. Kamyshny, B. Ginzburg, O. Hadas, I. Dor, A.D. Modestov and O. Lev. 2001. Formation of polysulfides in an oxygen rich freshwater lake and their role in the production of volatile sulfur compounds in aquatic systems. *Environ. Sci. Technol.*, 34(22): 4741-4746.

Haitzer, M., G.R. Aiken and J.N. Ryan. 2002. Binding of Mercury(II) to Dissolved Organic Matter: The Role of the Mercury-to-DOM Concentration Ratio. *Environ. Sci. Technol.*, 36(16): 3564-3570

Haitzer, M., G.R. Aiken and J.N. Ryan, J.N. 2003. Binding of mercury(II) to aquatic humic substances: influence of pH and source of humic substances. *Environ. Sci. Technol.*, 37 (11): 2436-2441.

Hakanson, L. 1980. The quantitative impact of pH, bioproduction and Hg-contamination on the Hg- content of fish (pike). *Environ. Pollut. (Series B),* 1: 285-304.

Harvey, J.W., S.L. Krupa, C. Gefvert, R.H. Mooney, J. Choi, S.A. King and J. Giddings. 2002. Interaction between surface water and ground water and effects on mercury transport in the north-central Everglades. Water-Resources Investigations Report 02-4050. U.S. Geological Survey, Department of Interior, Reston, VA.

Hintelmann, H., R. Ebinghaus and R.D. Wilken. 1993. Accumulation of mercury(II) and MeHg by microbial biofilms. *Water Res.,* 27(2): 237-242.

Hintelmann, H., P.M. Wellbourn and D.R. Evans. 1997. Measurement of complexation of methylmercury(II) compounds by fresh water humic substances using equilibrium dialysis. *Environ. Sci. Technol.,* 31: 489-495.

Hurley, J.P., D.P. Krabbenhoft, L.B Cleckner, M.L. Olson, G. Aiken and P.J. Rawlik, Jr. 1998. System controls on aqueous mercury distribution in the northern Everglades, *Biogeochemistry,* 40: 293-311.

Hurley, J.P., L.B. Cleckner, and P. Gorski. 1999. Everglades Nutrient Removal Project Mosquitofish Bioaccumulation Study. Draft Report. Prepared for the South Florida water Management District, West Palm Beach, FL. Contract (PC C-8691-0300). University of Wisconsin Water Chemistry Program, Madison, WI.

Jay, J.A., F.M.M. Morel and H.F. Hemond. 2000. Mercury speciation in the presence of polysulfides. *Environ. Sci. Technol.,* 34(11): 2196-2200.

Jensen, S. and A. Jernelov. 1969. Biological methylation of mercury in aquatic ecosystems. *Nature*, 223: 753-754.

Julsham, K., O. Ringdal, K-E Slinning and O.R. Braekkan. 1982. Mercur concentration in the liver and muscle of cod (*Gadus morhua*) as and evidence of migration between waters with different levels of mercury. *Bull. Environ. Contam. Toxicol.*, 29: 544-549.

Karlsson, T. and U. Skyllberg. 2003. Bonding of ppb levels of methyl mercury to reduced sulfur groups in soil organic matter. *Environ. Sci. Technol.,* 37(21): 4912-4918.

Kelly, C.A., J.W.M Rudd, R.A. Bodaly, N.P. Roulet, V.L. St. Louis, A Heyes, T.R. Moore, S. Schiff, R. Aravena, K.J. Scott, B. Dyck, R. Harris, B. Warner and G. Edwards. 1997. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. *Environ. Sci. Technol.*, 31(5): 1334-1344.

Kelly, C.A., J.W.M. Rudd and M.H. Holoka. 2003. Effect of pH on Mercury Uptake by An Aquatic Bacterium: Implications for Hg Cycling. *Environ. Sci. Technol.,* 37:2941-2946.

Kendall, C., B.E. Bemis, S.D. Wankel, P.S. Rawlik, T.Lange and D.P. Krabbenhoft. 2002. Effects of seasonal and spatial differences in food webs on mercury concentrations in fish in the Everglades. Spring Conference. American Geophysical Union. Washington, D.C. May 28–31., EOS. Trans. AGU, 83(19), Spring Meet. Suppl., Abstract H32D-08, p. S164.

Kim, C.S., N.S. Bloom, J.J. Rytuba and G.E. Brown, Jr. 2003. Mercury speciuation by X-ray absorption fine structure spectroscopy and sequential chemical extractions: a comparison of speciation methods. *Environ. Sci. Technol.,* 37(22):5102-5108.

King, J. K., S.M. Harmon, T.T. Fu and J.B. Gladden. 2002. Mercry Removal, Methylmercury Production, and Sulfate-Reducing Bacteria Profiles in Wetlands Mesocosms. *Chemopshere,* 46: 859-870.

King, S. 2000. Mercury Distribution, Speciation and Transport in the Everglades Nutrient Removal Treatment Wetland. Ph.D. Dissertation. Department of Water Chemistry, University of Wisconsin, Madison, WI.

Krabbenhoft, D.P., J.P. Hurley, M.L. Olson and L.B. Cleckner. 1998. Diel variability of mercury phase and species distributions in the Florida Everglades. *Biogeochemistry,* 40: 311-325.

Krabbenhoft, D.P., L.E. Fink, M.L. Olson and P.S. Rawlik, II. 2000. The Effect of Drydown and Natural Fires on Mercury Methylation in the Florida Everglades. Conf. proc., International Conference on Heavy Metals in the Environment. University of Michigan, Ann Arbor, MI.

Krabbenhoft, D.P. and L.E. Fink. 2001. Appendix 7-8: The effect of drydown and natural fires on mercury methylation in the Florida Everglades.G. Redfield, ed. In: *2001 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.

Krabbenhoft, D.P., C.C. Gilmour, W.H. Orem, G. Aiken, M.L. Olson, J.F. DeWild, S.D. Olund, A. Heyes, G.S. Riedel, J.T. Bell, H. Lerch, J.M. Benoit and S. Newman. 2001. Interfacing Process-Level Research and Ecosystem-Level Management Questions: Aquatic Cycling of Mercury in the Everglades (ACME) Phase II. Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments. Sheraton West Palm Beach, West Plam Beach, Florida. Sponsored by the U.S. Environmental Protection Agency, Washington, D.C. May 8-10, 2001.

Lamers, L.P.M., H.B.M. Tomassen and I. G.M. Roelofs. 1998. Sulfate induced eutrophication and phytotoxicity in freshwater wetlands. *Environ. Sci. Technol.*, 32(2): 199-205.

Lange, T.R., H.E. Royals and L.L. Connor. 1993. Influence of Water Chemistry on Mercury Concentration in Largemouth Bass from Florida Lakes. *Trans. Mer. Fisheries Soc.*, 122: 74-84.

Lange, T.R., D.A. Richard and H.E. Royals. 1998. Trophic relationships of mercury bioaccumulation in fish from the Florida Everglades. FINAL Annual Report. Florida Game and Fresh Water Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.

Lange, T.R., D.A. Richard and H.E. Royals. 1999. Trophic relationships of mercury bioaccumulation in fish from the Florida Everglades. Annual Report. Florida Game and Fresh Water Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.

Lawrence, A.L., K.M. McAloon, R.P. Mason and L.M. Mayer. 1999. Intestinal Solubilization of Particle-Associated Organic and Inorganic Mercury as a Measure of Bioavailability to Benthic Invertebrates. *Environ. Sci. Technol.*, 33: 1871-1876.

Lawrence, A.L. and R.P. Mason. 2001. Factors Controlling the Bioaccumulation of Mercury and Methylmercury by the Estuarine Amphipod, *Leptocheirus plumulosus. Environ. Poll.*, 111: 199-208.

Lindberg, S.E., H. Zhang and Meyers, T.P. 1999. Application of Field Methods and Models to Quantify Mercury Emissions from Wetlands at the Everglades Nutrient Removal Project (ENR). Prepared by Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN and National Oceanic and Atmospheric Administration, ATDD, Oak Ridge, TN. Second Final Report. Everglades Mercury Air/Surface Exchange Study (E-MASE). Prepared for South Florida Water Management District, West Palm Beach, FL (C-6660).

Lindberg, S.E. and H. Zhang. 2000. Air/Water Exchange of Mercury in the Everglades II: Measuring and Modeling Evasion of Mercury from Surface Waters in the Everglades Nutrient Removal Project. *Science of Total Environ.*, 259: 135-143.

Lindberg, S.E., W. Dong and T. Meyers. 2002. Transpiration of gaseous elemental mercury through vegetation in a subtropical wetland in Florida. *Atmospheric Environ.*, 36: 5207-5219.

Lockwood, R.A. and K.Y. Chen. 1974. Adsorption of Hg(II) by Ferric Hydroxide. *Environ. Lett.*, 6(3): 151-166.

Loftus, W. F., J. C. Trexler and R.D. Jones. 1998. Mercury Transfer Through and Everglades Aquatic Food Web. Report to Fl. Dept. of Environmental Protection, Tallahassee, FL.

Losetto, L.L., S.D. Siciliano and D.R.S. Lean. 2004. Methylmercury Production in High Arctic Wetlands. *Env. Tox. Chem.,* 23(1): 17-23.

Lu, X.Q. and R. Jaffe. 2001. Interaction between Hg(II) and Dissolved Organic Matter in Surface Waters of the Florida Everglades: a Fluorescence Spectroscopy Baserd Study. *Water Research,* 35: 1793-1803.

Lu, X.Q., N. Maie, J.V. Hanna, D.L. Childers and R. Jaffe. 2003. Molecular Characterization of Dissolved Organic Matter in Freshwater Wetlands of the Florida Everglades. *Water Research,* 37: 2599-2606.

McCloskey, J.T., I.R. Schulz and M.C. Newman. 1998. Estimating the Oral Bioavailability of Methylmercury to Channel Catfish (*Ictalrurus punctatus*). *Environ. Toxicol. Chem.*, 17(8): 1524-1529.

Malcolm, E.G. and G.J. Keeler. 2002. Measurements of Mercury in Dew: Atmospheric Removal of Mercury Species to a Wetted Surface. *Environ. Sci. Technol.*, 36(13):2815-2821.

Marvin-DiPasquale, M.C. and R.S. Oremland. 1998. Bacterial Methylmercury Degradation in Florida Everglades Peat Sediment. *Environ. Sci. Technol.*, 32(17): 2556-2563.

Marvin-DiPasquale, M.M., J. Agee, R.S. Oremland, M. Thomas, D.P. Krabbenhoft and C.G. Gilmour. 2000. Methylmercury Degradation Pathways: A Comparison Among Three Mercury-Impacted Ecosystems. *Environ. Sci. Technol.*, 34: 4908-4916.

Marvin-DiPasquale, M.M., J. Agee and R.S. Oremland. 2001. Environmental Controls of Methylmercury Production and Degradation by Bacteria in Florida Everglades Sediments. Draft report to the South Florida Water Management District under contract C-11719 by U.S. Geological Survey, Menlo Park, CA.

Mason R. Bloom N. Cappellino S. Gill G. Benoit J. and Dobbs C. 1998. Investigation of Porewater Sampling Methods for Mercury and Methylmercury. *Environ. Sci. Technol.*, 32, 4031-4040.

Mauro, J.B.N. and J.R.D. Guimaraes. 1999. Hg methylation potential in aquatic macrophytes of the Everglades Nutrient Removal Area. Report to the South Florida Water Management District, West Palm Beach, FL.

Mauro, J.B.N., J.R.D. Guimaraes and R. Melamed. 2001. Mercury methylation in macrophyte roots of a tropical lake. *Water, Air, and Soil Pollution,* 127: 271-280

Mierle, G. and Ingram, R. 1991. The Role of Humic Substances in the Mobilization of Mercury from Watersheds. *Wat. Air Soil Pollut.*, 56: 349-358.

Miles, C.J. and L.E. Fink. 1998. Monitoring and Mass Budget for Mercury in the Everglades Nutrient Removal Project. *Archives of Environ. Contam. and Toxicol.*, 35(4): 549-557.

Miles, C.J., H.A. Moye, E.J. Phlips and B. Sargent. 2001. Partitioning of MonoMeHg between Freshwater Algae and Water. *Envir. Sci. Technol*., 35(21):4277-4282.

Monson, B.A. and P.L. Brezonik. 1999. Influence of food, aquatic humus, and alkalinity on methylmercury uptake by *Daphnia magna*. *Environ. Toxicol. Chem.,* 18(30): 560-566.

Morrison, K.A. and N. Therein. 1994. Mercury Release and Transformation from Flooded Vegetation and Soils: Experimenta; Evaluation and Simulation Modeling. In C.J. Watras and J.W. Huckabee, Mercury Pollution Integration and Synthesis, Lewis Publishers, Boca Raton, FL. 355-365.

Moye, H.A., C.J. Miles, E.J. Phips, B. Sargent and K.K. Merritt. 2002. Kinetics and Uptake Mechanisms for Monomethylmercury between Freshwater Algae and Water. *Envir. Sci. Technol*., 36(16):3550-3555.

Newman, M.C. and D.K. Doubet. 1989. Size-Dependence of Mercury (II) Accumulation Kinetics in the Mosquitofish, *Gambusia affinis* (Baird and Girard). *Arch. Environ. Contam. Toxicol.*, 18: 819-825.

Newman, S. and K. Pietro. 2001. Phopshorus storage and release in response to flooding: implications for Everglades stormwater treatment area. *Ecological Engineering,* 18: 22-38

Norstrom, R. J., A.E. McKinnon and A.S.W. DeFreitas. 1976. A bioenergetics-based model for pollutant accumulation by fish. Simulation of PCB and MeHg residue levels in Ottawa River yellow perch (*Perca flavescens*). *J. Fish Res. Board Can.,* 33: 248-267.

Olson, B.H. and R.C. Cooper. 1976. Comparison of aerobic and anaerobic methylation of mercuric chloride by San Francisco Bay sediments. *Water Resources,* 10: 113-116.

Orem, W., D.P. Krabbenhoft and C. Gilmour. 2002. Summary of ACME I and II Results. Presentation to Peer Review Workshop. Everglades Consolidated Report. September 25.

Oremland, R.S., C.W. Culbertson, and M.R. Winfrey. 1991. Methylmercury Decomposition in Sediments and Bacterial Cultures: Involvement of Methanogens and Sulfate Reducers in Oxidative Demethylation. *Appl. Environ. Microbiol.,* 57(1): 130-137.

Pak, K. and R. Bartha. 1998. Products of Mercury Demethylation by Sulfidgens and Methanogens. Bull. Environ. Contam. Toxciol. 61: 690-694.

Paterson, M.J., J.W.M. Rudd and V. St. Louis. 1998. Increases in Total and Methylmercury in Zooplankton following Flooding of a Peatland Reservoir. Env. Sci. Technol. 32(24): 3868-3874.

Pickhardt, P.C., C.L. Folt, C.Y. Chen, B. Klaue and J.D. Blum. 2002. Algal Blooms Reduce the Uptake of Toxic MeHg in Freshwater Food Webs. PNAS Biological Sciences: Ecology 99, 4419-4423.

Post, J.R., R. Vandenbos and D.J. McQueen. 1996. Uptake rates of food-chain and waterborne mercury by fish: field measurements, a mechanistic model, and an assessment of uncertainties. *Can. J. Fish. Aquatic Sci.,* 53: 395-407.

Ravichandran, M., G.R. Aiken, M.M Reddy and J.N. Ryan. 1998. Enhanced Dissolution of Cinnabar (mercuric sulfide) by Dissolved Organic Matter Isolated from the Florida Everglades. Env. Sci. Technol. 32: 3205-3311.

Ravichandran, M. 1999. Interactions between mercury and dissolved organic matter in the Florida Everglades. Ph.D. Thesis. University of Colorado. Spring.

Rawlik, P. 2001a. Appendix 7-15: Mercury concentrations in mosquitofish from treatment wetlands in the northern Everglades. G. Redfield, ed. In: *2001 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, Fl.

Rawlik, P. 2001b. Appendic 7-14: Stormwater Treatment Area 1 West: results of start-up mercury monitoring. G. Redfield, ed. In: 2001 Everglades Consolidated Report. South Florida Water Management District, West Palm Beach, FL.

Rea, A.W., S.E. Lindberg and G.J. Keeler. 2000. Assessment of Dry Deposition and Foliar leaching of Mercury and Selected Trace Elements Based on Washed Foliar and Surrogate Surfaces. *Environ. Sci. Technol.,* 34(12):2418-2425.

Reddy, M.M., G. Aiken, P.F. Schuster. 1999. Hydroperiod-Driven Solute Transport at the Peat-Water Interface in the Florida Everglades: Hydrophobic Acid Diffusion from Peat. Unpublished Mansucript. U.S. Geological Survey, Boulder, CO.

Regnell, O. 1994. The effect of pH and dissolved oxygen levels on methylation and partitioning on mercury in freshwater model systems. *Environ. Pollut.*, 84: 7-13.

Ribeyre, F. 1993. Evolution of Mercury Distribution within an Experimental System "Water-Sediment-Macrophytes (*Elodea densa*). *Environ. Technol.,* 14: 201-214.

Ribeyre, F. and A. Boudou. 1982. Study of the Dynamics of the Accumulation of Two Mercury Compounds – $HgCl_2$ and CH_3HgCl – by *Chlorella Vulgaris*: Effect of Temperature and pH Factor of the Environment. Intern. *J. Environ. Studies,* 20: 35-40.

Ribeyre, F. and A. Boudou. 1994. Experimental study of inorganic and methylmercury bioaccumulation by four species of freshwater rooted macrophytes from water and sediment contamination sources. *Ecotox. and Environ. Safety*, 28: 270-286.

Riddle, S.G., H.H. Tran, J.G. Dewitt, and J.C. Andrews. 2002. Field, laboratory, and X-Ray Absorption Spectroscopic Studies of Mercury Accumulation by Water Hyacinths. *Environ. Sci. Technol.,* 36(9): 1965-1970.

Robinson, J.B., and O.H. Tuovinen. 1984. Mechanisms of microbial resistance and detoxification of mercury and organomercury compounds: physiological, biochemical, and genetic analyses. *Microbiol. Rev.,* 48:95-124.

Rodgers, Jr., J.H., D.S. Cherry, R.K. Guthrie. 1978. Cycling of Elements in Dick Weed (Lemna perpusilla) in Ash Settling Basin and Swamp Drainage System. *Water Res.,* 12: 765-770.

Rodgers, D.W. 1994. You Are What You Eat and a Little Bit More: Bioenergetics-based Models of Methylmercury Accumulation in Fish Revisited. In C.J. Watras and J.W. Huckabee, editors, Mercury Pollution Integration and Synthesis, Lewis Publishers, Boca Raton, FL. 427-439.

Rodgers, D.W., M. Dickman and X. Han. 1995. Stories from Old Reservoirs: Sediment Hg and Hg Methylation in Ontario Hydroelectric Developments. *Water, Air and Soil Pollution,* 80: 829-839.

Rood, B.F., J.F. Gottegens, J.J. Delfino, C.D. Earle, amd T.L. Crisman. 1995. Mercury Accumulation Trends in Florida Everglades and Savannas Marsh Flooded Soils. *Water, Air and Soil Pollution*, 80:981-990.

Rumbold, D.G., S.L. Niemczyk, L.E. Fink, T. Chandrasekhar, B. Harkanson and K.A. Laine. 2001. Mercury in Eggs and Feathers of Great Egrets (*Ardea albus*) from the Florida Everglades. *Arch. Environ. Contam. Toxicol.*, 41:501-507.

Rumbold, D.G., L.E. Fink, K.A. Laine, S.L. Niemczyk, T. Chandrasekhar, S.D. Wankel and C. Kendall. 2002. Levels of Mercury in Alligators (*Alligator mississippiensis*) Collected along a Transect through the Florida Everglades. *Sci. Tot. Environ.*, 297:239-252.

Rumbold, D.G. 2000. Appendix 7.3b: Methylmercury risk to Everglades wading birds: a probabilistic ecological risk assessment. G. Redfield, ed. In *2000 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.

Rumbold, D.G., L. Fink, K. Laine, F. Matson, S. Niemczyk and P. Rawlik. 2001a. Appendix 7-9: Annual permit compliance monitoring report for mercury in Stormwater Treatment Areas and downstream receiving waters of the Everglades Protection Area. G. Redfield, ed. In: *2001 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.

Rumbold, D.G., L. Fink, K. Laine, F. Matson, S. Niemczyk, and P. Rawlik. 2001b. Appendix 7-13: Stormwater Treatment Area 6 follow-up mercury studies. Appendix 7-13 In: *2001 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.

Rumbold, D. and L. Fink. 2003. Appendix 4-2: Report on Expanded Mercury Monitoring at STA-2. G. Redfield, ed. In: *2003 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL

Rumbold, D. 2005. Appendix 2B-1: Annual Permit Compliance Report for Mercury in Downstream Receiving Waters of the Everglades Protection Area. G. Redfield, ed. In: *2005 South Florida Environmental Report*. South Florida Water Management District, West Palm Beach, FL.

SFWMD. 1995. Everglades Nutrient Removal Project: 1994 Monitoring Report. South Florida Water Management, Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.

SFWMD. 1996. Everglades Nutrient Removal Project: 1995 Monitoring Report. South Florida Water Management, Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.

SFWMD. 1997. Everglades Nutrient Removal Project 1996 Monitoring Report. South Florida Water Management District, West Palm Beach, FL.

SFWMD. 1998. Everglades Nutrient Removal Project 1999 Monitoring Report. South Florida Water Management District, West Palm Beach, FL.

SFWMD. 1999a. Everglades Nutrient Removal Project 1998 Monitoring Report. South Florida Water Management District, West Palm Beach, FL.

SFWMD. 1999b. Final Report on the Effect of Best Management Practices on the Loading of Mercury Species to/from the Everglades Nutrient Removal Project: Monitoring Program (Project C-1). Submitted by the South Florida Water Management District, West Palm Beach, Florida, to the Floirda Department of Environmental Protection, Tallahassee, Florida, to fulfill the requirements of a Section 319 Grant (SP335/C-6663/4) from U.S. Environmental Protection Agency Region 4, Atlanta, GA.

St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, N.S. Bloom and R.J. Flett. 1994. The importance of wetlands as sources of methylmercury to boreal forest ecosystems. *Can. J. Fish. Aquatic Sci.*, 51: 1065-1076.

St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, R.J. Flett and N.T. Roulet. 1996. Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. *Environ. Sci. Technol.*, 30(9): 2719-2729.

Saouter, E., M. Gillman, R. Turner and T. Barkay. 1995. Development and field validation of a microcosm to simulate the mercury cycle in a contaminated pond. *Environ. Toxicol. Chem.*, 14(1): 69-77.

Schopfer, N.J. 1974. The Uptake, Biotransformation, and Elimination of Elemental Mercury by Fish. Masters These. University of Georgia. Athens, GA.

Scruton, D.A., E.L. Petticrew, L.J. LeDrew, M.R. Anderson, U.P. Williams, B.A. Bennett and E.L. Hill. 1994. Methylmercury levels in fish tissue from three reservoir systems in insular Newfoundland, Canada. In C.J. Watras and J.W. Huckabee, Mercury Pollution Integration and Synthesis, Lewis Publishers, Boca Raton, FL. 441-455.

Sellers, P., C.A. Kelly, J.W.M. Rudd and A.R. MacHutchon. 1996. Photodegradation of methylmercury in lakes. *Nature*, 380(25): 694-697.

Sellers, P., C.A. Kelly and J.W.M. Rudd. 2001. Fluxes of methylmercury to the water column of a drainage lake: the relative importance of internal and external sources. *Limnol. Oceanogr.*, 46(3): 623-631.

Shin, E.B. and P.A. Krenkel. 1976. Mercury uptake by fish and biomethylation mechanisms.1976. *J. Water Pollution Control Federation*, 48(3):

Snodgrass, J.W., C.H. Jagoe, A.L. Bryan, Jr. and J. Burger. 2000. Effects of trophic status and wetland morphology, hydroperiod, and water chemistry on mercury concentrations in fish. *Can. J. Fish. Aquatic Sci.*, 57: 171-180.

Stumm, W. and J.J. Morgan. 1996. *Aquatic Chemistry*. Wiley, NY. pp 281-305.

Tallifert, M., A.B. Bono and G.W. Luther III. 2000. Reactivity of freshly formed Fe(III) in synthetic solutions and (pore)waters: voltammetric evidence of an aging process. *Environ. Sci. Technol.*, 34(11): 2169-2177

Tetra Tech. 2002. Mercury cycling and bioaccumulation in Everglades marshes Phase I and II. Interim Report. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL, and the South Florida Water Management District, West Palm Beach, FL.

Tetra Tech, Inc. 2003. Modeling mercury cycling and bioaccumulation in Everglades marshes with the Everglades Mercury Cycling Model (E-MCM). Final Report. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL, and the South Florida Water Management District, West Palm Beach, FL.

Thibodeaux, L.J. 1996. *Environmental Chemodynamics*. 2nd Ed. John Wiley and Sons, Inc. pp. 593.

Tsai, S.C., G.M. Boush and F. Matsumura. 1976. Importance of water pH in accumulation of inorganic mercury in fish. *Bull. Environ. Contam. Toxicol.,* 13(2): 188-193.

Tsui, M.T.K., and W.X. Wang. 2004. Uptake and elimination of inorganic mercury and methylmercury in *Daphnia magna*. *Environ. Sci. Technol.,* 38(3): 808-816.

USEPA. 1997. Mercury Study Report to Congress. Volume III: Fate and Transport of Mercury in the Environment. Office of Air Quality Planning and Standards and Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. EPA-452/R-97-005.

Vaithiyanathan, P., C. J. Richardson, R, G. Kavanaugh, C. B. Craft and T. Barkay. 1996. Relationships of eutrophication to the distribution of mercury and the potential for methylmercury production in the peat soils of the Everglades. *Environ. Sci. Technol.,* 30(8): 2591-2597.

Vandal, G.M., R.P. Mason and W.F. Fitzgerald. 1991. Cycling of valoatile mercury in temperate lakes. *Water, Air and Soil Poll.,* 56: 791-803.

Vandal, G.M., W.F. Fitzgerald, K.R. Rolfhus and C.H. Lamborg. 1995. Modeling the elemental mercury cycle in Palette Lake, Wisconsin, USA. *Water, Air and Soil. Pollution*, 80: 529-538.

WHO. 1976. Environmental Health Criteria 1: Mercury. World Health Organization. Geneva.

Wallace, Jr., G.T., D.L. Seibert, S.M. Holzknecht and W.H. Thomas. 1982. The Biogeochemical Fate and Toxicity of Mercury in Controlled Experimental Ecosystems. *Estuarine, Coastal, and Shelf Sci.,* 15: 151-182.

Warner, K.A., E.E. Roden and J.C. Bonzongo. 2003. Microbial Mercury Transformation in Anoxic Freshwater Sediments under Iron-Reducing and Other Electron-Accpeting Conditions. *Environ. Sc. Technol.,* 37(10): 2159-2165.

Watras, C.J., N.S. Bloom, S.A. Claus, K.A. Morrison, C.G. Gilmour, and S.R. Craig. 1995. Methylmercury production in the anoxic hypolimnion of a dimictic seepage lake. *Water, Air and Soil Pollution*, 80: 735-745.

White, J.R. and K. R. Reddy. 2001. Storwater Treatment Areas 2, 5, and 6: Soil Characteristics and Phosphrous Forms. Submitted to the Ecological Technologies Department, South Florida Water Management District, West Palm Beach, FL by the Wetland Biogeochemistry Laboratory, Soil and Water Science Department, University of Florida, Gainesville, FL.

Wolfe, M.F., D.M. Norman, and R. Sulaiman. 1994. Mercury monitoring in wetlands birds and mammals at Clear Lake, CA. Toxicology Task Force, Seattle, WA.

Wolverton, B.C. and R.C. MacDonald. 1978. Water Hyacinth Sorption Rates of Lead, Mercury and Cadmium. ERL Report No. 170. National Atmopsheric and Space Administration. Washington, D.C.

Wood, J.M, F.S. Kennedy and C.G. Rosen. 1968. Synthesis of MeHg compounds by extracts of methanogenic bacterium. *Nature,* 220: 173-174.

Xia, K, U.L. Skyllberg, W.F. Bleam, P.R. Bloom, E.A. Nater and P.A. Helmke. 1999. X-ray absorption spectroscopic evidence for the complexation of Hg(II) by reduced sulfur in soil humic substances. *Env. Sci. and Technol.,* 33(5): 786-795.

Xiao, Z.F., J. Munthe, D. Stromberg and O. Lindqvist. 1994. Photochemical Behavior of Inorgnaic Mercury Compounds in Aquaeous Solution. Pages 581-592 in C.J. Watras and W.J. Huckabee, editors Mercury Pollution: Integration and Synthesis. Lewis Pub., Boca Raton, FL.

Xiao, Z.F., D. Stromberg and O. Lindqvist. 1995. Influence of Humic Substances on Photolysis of Divalent Mercury in Aqueous Solution. Water and Soil Pollution 80: 789-798.

Yin, Y., H.E. Allen, C.P. Huang, D.L. Sparks and P.F. Sanders. 1997. Kinetics of mercury (II) adsorption and desorption on soil. *Environ. Sci. Technol.,* 31: 496-503.

Zhang, Y-J, N.D. Bryan, F.R. Livens and M.N. Jones. 1996. Complexing of Metal Ions by Humic Substances. In J.S. Gaffney, N.A. Marley, and S.B. Clark, Eds. Humic and Fulvic Acids: Isolation, Structure, and Environmental Role. ACS Symposium Series 651. American Chemical Society, Washington, D.C. pp. 194-206.

Zhang, H. and S.E. Lindberg. 2000. Air/water Exchange of Mercury in the Everglades I: the Behavior of Dissolved Gaseous Mercury in the Everglades Nutrient Removal Project. *Science of Total Environ.,* 259: 135-143.

Zillioux, E.J., D.B. Porcella and J.M. Benoit. 1993. Mercury cycling and effects in freshwater wetland ecosystems. *Environ. Toxicol. Chem.,* 12: 2245-2264.

Zuloaga, P., R. Keyser, L. Fink, D. Struve and M. Zhou. A Cost-Effective Method for Extracting Pore Water: Sipper vs Centrifuge. Department of Defense Environmental Monitoring and Data Quality Work Shop. Reno, Nevada. May 10-14, 2004. Tetra Tech, Inc. Stuart, FL and South Florida Water Management District, West Palm Beach, FL.

Appendices

Appendix A. Plan of the Study for STA-2 Mercury Special Studies Project

Appendix B. Standard Operating Procedures for Implementing the STA-2 Mercury Special Studies Project

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Appendix A. Plan of the Study for STA-2 Mercury Special Studies Project

STA-2 Mercury Special Studies Plan
09/18/02

by
Environmental Monitoring and Assessment Department
South Florida Water Management District

1.0 Introduction

This is the Plan of Study for Mercury Special Studies in Stormwater Treatment Area 2 (STA-2). STA-2 is a 6,430-acre constructed wetland in south Florida that treats agricultural stormwater runoff prior to discharge into the northern Everglades. It has experienced several incidents of excess methylmercury production following reflooding after extended periods of drawdown and dryout. Studies conducted elsewhere by the U.S. Geological Survey in Middleton, WI, and the Academy of Natural Sciences in St. Leonard, MD are under way to look at the effect of drying and reflooding on the timing, magnitude, and duration of excess methylmercury production and the surface water, soil, and pore water chemistries associated with that phenomenon. The District and the Department of Environmental Protection (FDEP) are jointly funding that study. The special studies covered by this Plan focus on expanded mercury monitoring in STA-2 to better understand the nature, cause, and effect of excess methylmercury production and bioaccumulation within STA-2.

The implementation of the study will involve two tiers. Tier 1 monitoring will focus on the short-term changes in pore water and soil chemistry following reflooding at one, well-studied site in Cell 1. These data will be compared to the results of a laboratory study of soil cores collected from the same site under another contract (C-13860). In Tier 2, increased monitoring of treatment cell inflows and outflows will continue, while new or more frequent monitoring at three sites in each treatment cell will be initiated. Beyond more fully characterizing the biogeochemical and bioaccumulation trajectories of STA-2 Cell 1 following reflooding, the data collected in this study will also support: (1) the construction of total mercury and methylmercury mass budgets to (a) identify all significant sources and sinks of inorganic mercury and methylmercury production within each cell of STA 2 and (b) more accurately quantify short- and long-term methylmercury storage and export by each treatment cell; (2) an exploratory data analysis using various appropriate parametric and nonparametric statistical methods to identify significant differences, spatial and temporal trends, and intra- and inter-media correlations within and between treatment cells regarding excess methylmercury production, bioaccumulation, storage, and export; and (3) a probabilistic ecological risk assessment of toxic effects from methylmercury exposure to fish-eating wildlife foraging preferentially in STA-2 Cell 1. In addition, together with process rate data gathered

under a related contract, these data will also support the parameterization and calibration of the Everglades Mercury Cycling Model (Version 2) adapted to STA-2 Cell 1 and the downstream environment. The modeling will be carried out under a separate contract. The results of these quantitative assessments will support adaptive management decision-making regarding the development of short-term measures to ameliorate the magnitude and duration of the excess methylmercury pulse in Cell 1 following reflooding and to optimize STA-2 operation for the long-term.

One of the most important and challenging aspects of this Plan is the routine monitoring of surficial soil pore water for redox potential, ultra-trace total mercury and methylmercury, iron species, sulfide and sulfate ions, dissolved organic carbon, and a suite of other anions and cations that are known or can be inferred to influence excess methylmercury production or bioaccumulation. The routine monitoring of pore water is not required in any State of Florida permit to operate or discharge to the waters of the state, and none of the FDEP-approved pore water sampling methods have been validated for ultra-trace total mercury and methylmercury analysis. While such methods are available, they are only used routinely by world-class research scientists and not as part of any routine monitoring program. Therefore, the Plan's inclusion of routine monitoring of ultra-trace total mercury and methylmercury in surficial soil pore water must be considered experimental. As such, there is no guarantee that the methods adopted by the District for implementation of this element of the Plan will produce valid, quantitative results for all constituents at all times. Nevertheless, the District recognizes the importance of pore water monitoring in this context and is committed to making a good faith effort to carry out this Plan element to the extent practicable. Any problems encountered in implementing the pore water monitoring element of this Plan will be brought to FDEP's attention in a timely fashion so that the Plan can be modified as needed within an adaptive management framework.

1.1 Need

Exhibit D of each Everglades Forever Act (EFA) permit for the operation of Stormwater Treatment Areas (STAs) in the Everglades Construction Program (ECP) includes mercury monitoring requirements for start-up and routine operation. Prior to flooding but after completion of construction, six, 10-cm cores are collected at representative sites in each STA and triennially thereafter for total mercury and methylmercury analysis. The start-up of an STA can commence only when the concentrations of unfiltered total mercury and methylmercury at a representative interior marsh site are not significantly greater than the inflow based on biweekly sampling. In STAs with multiple treatment cells that can be operated independently, the District has applied this start-up criterion to each such treatment cell separately.

Once the start-up phosphorus and mercury criteria are met, routine operation and monitoring begin: unfiltered inflow and outflow waters are analyzed for total mercury and methylmercury quarterly; inflow, interior, and outflow mosquitofish (*Gambusia holbrooki*) for total mercury semi-annually; and sunfish (*Lepomis sp.*) and largemouth bass (*Micropterus salmoides*) for total mercury at these same sites annually. In addition,

under the Non-ECP permit for other District structures, unfiltered surface water is collected at 10 sites quarterly for total mercury and methylmercury analysis; mosquitofish, sunfish, and bass are monitored for total mercury annually at 12 representative interior marsh sites, while weekly rainfall samples are collected for total mercury analysis at three representative sites along the eastern edge of the Everglades. The EFA permit also requires reporting anomalous mercury conditions that develop during start-up or subsequent routine operations. The benchmark for normal mercury conditions in the inflows/outflows and interior marshes of an STA are the average conditions in the Everglades canals and interior marshes.

STA-2 consists of the three parallel treatment cells (Figure 1). Cells 2 and 3 met the mercury start-up criteria set forth in the state's EFA permit No. 012764 in September and November 2000, respectively, but Cell 1 still has not as of April 2002. An anomalous methylmercury concentration of 4.8 ng/L was detected in the interior of STA-2 Cell 1 in a September 26, 2000 collection and reported to FDEP on October 13, 2000 following quality assurance confirmation. At FDEP's request, the District initiated a 90-day expanded mercury monitoring program in Cells 1 and 2 to more fully characterize the methylmercury conditions in Cell 1, to identify known or potential causes of the very different start-up trajectories of Cells 1 and 2, and to evaluate options for mitigation should such become necessary. The results verified the results for water while tracking the build-up of methylmercury as total mercury in Cell 1 mosquitofish. In January 2001, the average total mercury concentration in Cell 1 mosquitofish exceeded that at WCA-3A-15, the Everglades "hot spot" of about 200 ug/Kg wet wt. By analogy to similar systems, anomalously high concentrations of methylmercury were also inferred to have been building up in fish species at the next trophic level, including sunfish species, which are typically consumed by fish-eating wildlife (Rumbold et al, 2000a; 2001). Although appearing to peak in February 2001, the total mercury concentration in mosquitofish climbed to 325 ug/Kg wet weight in March 2001. Cell 1 dried out under the influence of the extended drought in mid-April 2001.

In July 2001, the District petitioned for a permit modification that would allow initiation of flow-through operation, even if the mercury start-up criteria had not been met. Following receipt of authorization from DEP in August 2001, the District began flow-through operation and the required expanded mercury monitoring. In mid-October 2001, anomalously high methylmercury concentrations were again encountered in Cell 1 water. The District then initiated a series of adaptive follow-up studies to verify the results and localize the source. In addition to the required biweekly monitoring of the STA-2 inflow, Cell 1 interior, and STA-2 outflow, the District added biweekly monitoring of the Cell 1, 2, and 3 outflows, as well as downstream monitoring of the STA-2 outflow pump station (G335). The Department analyzed these at no additional cost to the District. The adaptive follow-up studies determined that the Cell 1 outflow was the source of the excess MeHg in the STA-2 outflow and that the mercury chemistry at the Cell 1 interior monitoring site was not representative of the outflow mercury chemistry. In response to this second mercury anomaly in STA-2 Cell 1, the District requested and was granted permission by the Department to draw down and dry out Cell 1 rather than allow MeHg concentrations to build up in higher trophic level fish with the concomitant risks to fish-

eating wildlife. Dryout began the first week in December 2001 and was essentially complete two weeks later, although low flow drainage continued throughout the winter.

1.2 Study Objectives

The primary objectives of this study are to:

(1) quantify the mercury and sulfur biogeochemical trajectories and mercury bioaccumulation trajectories of each treatment cell over time and evaluate the influences of the various external conditions and internal factors on those trajectories and their interrelationships within and between cells;
(2) compare the biogeochemical trajectories of Cell 1 and the post-reflooding trajectories of the soil microcosms in the laboratory wet-dry study for study inter-validation;
(3) quantify the dynamics of net import or export of inorganic mercury and methylmercury by constructing a mass budget for each cell and evaluate the influences of various external and internal conditions and factors on those mass dynamics within and between cells;
(4) calibrate a mathematical model of the biogeochemical dynamics of methylmercury production and bioaccumulation developed elsewhere to Cell 1 conditions and evaluate model performance by hindcasting the biogeochemical trajectory of STA-2 Cell 1 during the first anomalous mercury event;
(5) quantify the risks of methylmercury toxic effects to a highly exposed, highly sensitive avian, mammalian, and amphibian indicator species based on the observed methylmercury bioaccumulation trajectory in Cell 1 mosquitofish and the corresponding modeled bioaccumulation trajectories in secondary and tertiary predator fish;
(6) predict the changes in the risks of methylmercury toxic effects to those indicator species in response to various changes to start-up and operating regimens.

The secondary objectives of the study are to:

(7) quantify differences in the absolute and relative contributions of various pathways to the total mercury and methylmercury mass budgets between seasons within a cell and between cells within a season;
(8) quantify the influence of various external and internal conditions and factors on the magnitude and duration of the post-reflooding methylmercury production and bioaccumulation pulses within a cell between seasons and between cells within a season;
(9) quantify the influences of various external and internal factors on the loci and magnitudes of storage;
(10) quantify the influences of various external conditions and internal factors on the differences in total mercury and methylmercury mass budgets within a cell between seasons and between cells within a season.

It is unlikely that these secondary objectives can be fulfilled without at least three, and preferably, five years of continuous, intensive monitoring.

2.0 Site Description and Operational History of STA-2

2.1 Site Description

STA-2 is located in western Palm Beach County near the Browns Farm Wildlife Management Area. STA-2 was developed to provide a total effective treatment area of 6,430 acres (Cell 1 is 1990 acres, Cells 2 and 3 each 2220 acres; for additional details, see SFWMD, 1999a). Portions of STA-2 were still being farmed immediately prior to construction. Cell 3 had about 30% in sugarcane and 45% in sod production. Cell 2 had about 10% in sod production (in the northwest corner). Construction activities for STA-2 began in January 1998 (N. Larson, personal communication). The only site preparation occurred in Cell 3, where a portion of the cell was disked to remove remnant cane.

STA-2 is designed to treat discharges from the S-6/S-2 Basin, the G-328 basin, East Shore Water Control District, 715 Farms, portions of the S-5A Basin, and Lake Okeechobee via pump station S-6. S-6 and G-328 serve as the primary inflow pumping stations (see Figure 1). G-328 serves an approximated 9,980 acres of adjacent agricultural lands. Inflows from S-6 and G-328 enter the Supply Canal and are conveyed southward to the Inflow Canal, which extends across the northern perimeter of STA-2. A series of inflow culverts conveys flows from the Inflow Canal to the respective treatment cells (G-329 A-D into Cell 1, G-331 A-G into Cell 2, G-333 A-E into Cell 3). Flows travel southward through the treatment cells and eventually discharge into the discharge canal via culverts or gated spillways (culverts G-330 A-E from Cell 1, gated spillway G-332 from Cell 2, gated spillway G-334 from Cell 3). Flows then travel eastward in the discharge canal to the STA-2 outflow pump station, G-335, which in turn conveys water to a short stub canal leading to the L-6 Borrow canal.

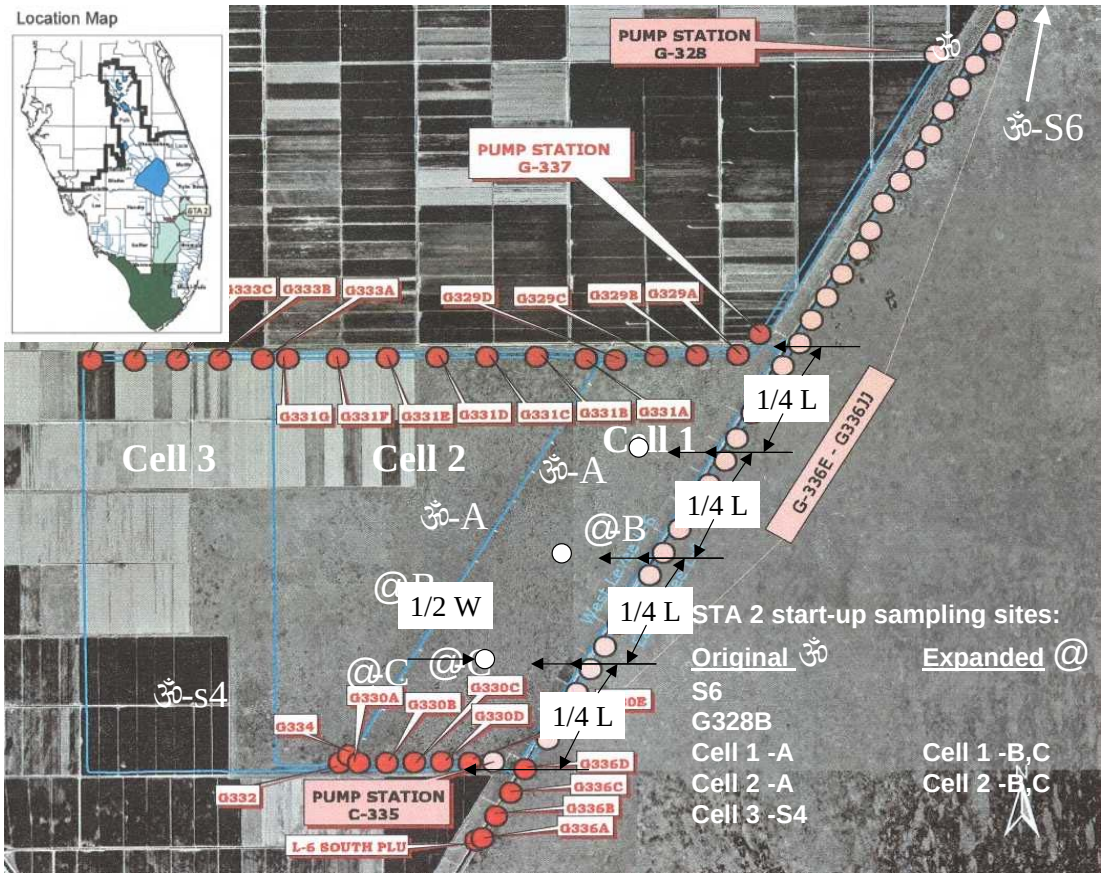

Figure 1. Areal photograph showing STA-2 sampling sites.

Figure 1. Geographic location and boundaries of STA-2

Water in the L-6 borrow canal travels north and then east into WCA-2A through six box culverts (each with a capacity of 300 cfs, and an invert of 12 ft NGVD) that are located south of G-339 between 0.5 and 3 miles south of S-6. The area to receive discharge was previously identified as a nutrient-impacted area. Under high-flow conditions, when stage in the L-6 borrow canal exceeds 14.25 ft, treated discharges in the L-6 borrow canal will spill into five 72-inch culverts and travel south toward S-7. Approximately 0.75 miles north of S-7 the eastern levee has been degraded to ground elevation (approximately 12 ft) that will allow water to sheetflow into WCA-2A. Here again, the area to receive discharge was previously identified as a nutrient-impacted area.

2.2 Operational History of STA-2

The treatment cells received differing amounts of water during construction and through the present time. Dewatering was required for construction and installation of spillways and culverts. Cell 1 received most of the water from dewatering operations, except for a short period during Cell 1 construction, at which time Cell 2 received dewatering volumes. Construction of the interior works was completed in June 1999. At that time inflow gates to Cells 1 and 2 were opened for a brief period then closed because the primary operational objective was to raise water depths in Cell 3 to approximately 1 m to prevent growth of emergent vegetation. Cell 3 inflow gates remained open for several months, which included Hurricane Irene (15 October 1999). The inflow gates to Cells 1 and 2 were reopened briefly in December 1999 – January 2000. However, the cells may have partially dried out during the dry season of 1999-2000. The final operational testing of the outflow pump station, G-335, was completed in October 2000 and a small amount of water was discharged at that time. In addition to rainfall, source water for the treatment cells through early 2001 originated from G-328 and G-337, i.e., the seepage pump. During the severe drought of 2000-2001, STA-2 Cell 1 went dry in April 2001 and Cell 2 went dry about May 10, 2001. Supplemental water deliveries were made during April and May 2001 to Cell 3 to prevent dryout of the submerged aquatic vegetation (SAV). Following local rains, Cell 2 was reflooded about June 1.

3.0 Study Design

3.1 Quantification of Cell Biogeochemical and Bioaccumulation Trajectories

3.1.1 Biogeochemistry

Methylmercury in the Everglades is produced from inorganic mercury present in wet and dry atmospheric deposition, surface flow, and peat soils under anaerobic conditions, generally in the top 4 cm of sediment or peat soil (Gilmour et al., 1991; Gilmour and Henry, 1992; Gilmour, 1996; Gilmour et al., 1998a,b; Krabbenhoft et al., 2000; Krabbenhoft and Fink, 2001). It is a virtual certainty that wet and dry atmospheric deposition to Cells 1, 2, and 3 were roughly equal during start-up (Guentzel, 1997; Fink and Rawlik, 2000; Rumbold et al., 2000, 2001; Guentzel et al., 2001), so the significant differences in the methylmercury concentrations in soil, water, and mosquitofish between

cells must be attributed to some other factor or factors, such as antecedent land use, antecedent stage-duration with and without dryout, differences in the hydraulic loading rates of make-up water, or intrinsic differences in soil chemistry. Based on topographic considerations, Cell 1, with the highest elevation, is likely to dry out first, followed by Cell 2, and then Cell 3. To the extent that frequent dryout and rewetting accelerate methylmercury production, it might be expected that Cell 1 would behave anomalously.

Following soil dryout, it can be confidently predicted that carbon, sulfur, and iron species in surficial soils are oxidized, albeit to different degrees and at different rates (Dmitriw et al., 1995; Yin et al., 1997; Lamers et al., 1998; Gun et al., 2000; Taillfert et al., 2000; W. Orem, USGS, personal communication, 2000; Fink, 2001). Reinundation of oxidized soils is usually accompanied by a "first-flush" release of nutrients (Newman and Pietro, 2000) and trace metals, including inorganic mercury (Dmytrw et al., 1995; Rawlik, 2001b). Following the first-flush release of inorganic mercury, some of it is either converted to dissolved elemental mercury, Hg(0), and then lost to the overlying air via evasion (Vandal et al., 1994; Saouter et al., 1995; Krabbenhoft et al., 1998; Lindberg and Zhang, 2000; Zhang and Lindberg, 2000), or reabsorbed by bacteria microfilms (Hintelman et al., 1993), algae (Hurley et al., 1998; Miles and Moye, 2000) and floating and rooted macrophytes (SFWMD, 1995-1999; Hurley et al., 1998; Fink and Rawlik, 2000), as well as the surficial peat soil (Ambrose and Araujo, 1998). Thereafter, it has been hypothesized that the presence of high concentrations of these oxidized species in a readily bioavailable form accelerates methylmercury production until they are reduced by biotic or abiotic processes (Krabbenhoft and Fink, 2000; Krabbenhoft et al., 2000). Following this production pulse of methylmercury, it absorbs in a similar fashion to inorganic mercury (see above discussion), is decomposed to inorganic mercury or elemental mercury by sunlight (Sellers et al., 1996; Krabbenhoft et al., 1998; D. Krabbenhoft, USGS, personal communication, 2000), or is demethylated by carbon-oxidizing and sulfate-reducing bacteria under anaerobic conditions (Oremland et al., 1991; Marvin-DiPasquale and Oremland, 1998; Pak and Bartha, 1998; Marvin-DiPasquale et al., 2000; Marvin-DiPasquale et al., 2001).

If the duration of accelerated methylmercury production is short, because the soil pools of labile, bioavailable sulfate, carbon, and inorganic mercury are small and rapidly consumed, then the total mass of methylmercury produced will be small and the magnitude and duration of subsequent excessive bioaccumulation of methylmercury in top-predator fish and their predators will be short-lived. This is the so-called "first flush effect." Conversely, if these pools are large or there is an external source of the limiting factor capable of sustaining a high, first-flush methylmercury production rate for a long time, then the first-flush mass of methylmercury produced will be large. It will then result in excessive bioaccumulation at the top of the food chain, and it will clear slowly from the ecosystem. This results in the so-called "reservoir effect," first observed in hydroelectric reservoirs created by flooding forested glacial till soils in northern temperate regions (Bodaly et al, 1984; Scruton et al., 1994; Rodgers et al., 1995) but also observed in natural, created, or expanded wetlands (St. Louis et al., 1994; St. Louis et al., 1996; Kelly et al., 1997; Paterson et al., 1998). This has also resulted in the increase in

methylmercury body burdens in insect-eating birds (Gerrard and St. Louis, 2001) and fish-eating birds and mammals foraging in these water bodies (Wolfe et al., 1994).

However, if labile, bioavailable sulfate is present in substantial excess, surficial sediments remain anaerobic, and no other factor limits microbial metabolism or affects sulfur speciation, then sulfide, a byproduct of the life processes of sulfate-reducing bacteria, can accumulate to concentrations that actually inhibit methylmercury production (Craig and Bartlett, 1978; Compeau and Bartha, 1984; Berman and Bartha, 1986; Gilmour et al., 1998b; Benoit, 1999a,b; Jay et al., 2000; Benoit et al., 2001; Marvin-DiPasquale et al., 2001). It has been hypothesized with moderate confidence (Gilmour et al, 1998b) that sulfide inhibition is causing eutrophic Everglades regions with conditions otherwise deemed ideal for methylmercury production (e.g., ENR Project and WCA-2A-F1) to exhibit low methylmercury production and correspondingly low concentrations in fish at all trophic levels (Cleckner et al., 1998; Lange et al., 1998, 1999; Loftus et al., 1998; Rumbold et al., 2000; Rawlik, 2001a; Rumbold et al., 2001). Conversely, unimpacted or virtually pristine areas in the Everglades exhibit much higher methylmercury production rates (e.g., WCA-2A-U3 and WCA-3A-15) and correspondingly higher concentrations in fish at all trophic levels. Both the fraction of methylmercury in surficial soils and in mosquitofish are strongly inversely correlated with pore water sulfide in surficial soils across the Everglades (Krabbenhoft et al., 2000; Krabbenhoft and Fink, 2001; Fink, 2001).

Results of a joint USGS-District study of an Everglades dryout and burn that occurred in the spring of 1999 suggest that the relatively rapid decline from peak methylmercury concentrations in pore water and soils was brought about by the rapid depletion of the excess sulfate pool created by the oxidation of inorganic and organic sulfides; however, the alternative hypothesis that this was caused by the relatively rapid onset of sulfide inhibition cannot be ruled out (Krabbenhoft and Fink, 2001; Krabbenhoft et al, 2000). The relatively rapid onset of sulfide-inhibition in sulfur-amended agricultural soils could also explain why STA-1W Cell 5, after exhibiting a first-flush effect, retuned to ENR-like conditions within 180 days of start-up (Rawlik, 2000).

Based on the above summary of the relevant biogeochemical processes, it is clear that oxidized and reduced sulfur species, dissolved organic carbon, and iron or manganese redox couples are known to or can reasonably be expected to mediate the production of methylmercury in the surficial sediment, that pore water chemistry will respond most rapidly to changes in environmental conditions that favor methylmercury production, and that the rate of change of pore water chemistry and methylmercury production will be most rapid following reflooding of soil after an extended period of dryout. As a consequence, pore water monitoring will be conducted in two tiers. In the Tier 1 study, pore water will be collected from the same site where the soils were collected for the laboratory dryout and rewetting study, sampled at roughly the same frequency, and analyzed for filtered.total mercury, methylmercury, sulfate, calcium and magnesium, total iron and manganese, Fe^{+2}, sulfate, and sulfide. Surficial soils (0-4 cm) will be sampled at the same frequency and analyzed for THg, MeHg, total sulfur, iron, and manganese, acid volatile sulfide, and mineral content. In the Tier 2 study, pore water and surficial soil

will be collected from three interior sites in each cell and sampled every other biweekly period and quarterly, respectively, for the same constituents as in the Tier 1 study. Surface water chemistry will also be monitored with the same frequency as the underlying pore water.

3.1.2 Bioaccumulation

Methylmercury is rapidly taken up, but only slowly depurated from fish tissue. The uptake and depuration rates via body surfaces (e.g., gills, kidney) decrease with increasing fish size (Norstrom et al., 1976). This results in a tendency to bioaccumulate methymercury at each trophic level and biomagnify the methylmercury as one moves from one trophic level to the next (Rodgers, 1994). The mosquitofish (*Gambusia holbrookii*) has been chosen as the indicator of methylmercury bioavailability and bioaccumulation potential for several reasons. First, it can tolerate a wide range of habitats, *i.e.* it is ubiquitous; second, it is readily collected using a dip net; third, it has a small range, such that it integrates local exposures to methylmercury; fourth, it depurates methylmercury relatively rapidly (t1/2 ~ 7-14 days; Newman et al., 199X), such that the body burden in an individual fish reflects the bioavailble methylmercury that has been produced relatively recently. It is also relatively short-lived (~60 days), so that the population purges itself of the methylmercury within the timeframe of seasonal changes in average ambient temperature and rainfall. The bioaccumulation responsiveness of mosquitofish to methylmercury in its environment makes it an ideal choice for an indicator of bioavailability and bioaccumulation potential.

The reason for monitoring total mercury as a surrogate for methylmercury also has a firm basis in sound science. Virtually all (>85%) of the mercury in mosquitofish tissues from most sites is in the methylated form (SFWMD, unpublished data, 1996). Therefore, the analysis of mosquitofish tissue for THg, which is a more straightforward and less costly procedure than for MeHg, can be interpreted as equivalent to the analysis of MeHg. The only caveat is that for the mosquitofish that consumes a disproportionate fraction of its diet as detritus, a significant fraction of the THg in the mosquitofish is inorganic mercury. However, the variability in the THg and MeHg concentration data for mosquitofish tissue is sufficiently high that the ratio of MeHg to THg cannot be used as a reliable benchmark of its trophic status.

3.2 Quantification of Mercury Mass Budgets

The mass budget of a system is based on the principle of conservation of mass. The calculation of a mass budget for a pollutant ensures that all significant inputs, storages, and outputs are accounted for. In addition, for inputs, storages, or outputs for which there is a great deal of uncertainty in the measurement or that are hard to measure (e.g., seepage losses; net methylation rates), such values can be calculated by difference assuming mass balance. Moreover, mass budget data can be used to initialize and calibrate a mathematical model of the transport, transformation, and bioaccumulation of inorganic mercury and methylmercury.

To carry out the mass budget calculations, rain will be collected on site as a weekly integrated sample and analyzed for THg using the same equipment, methods, schedule, and analytical laboratory as that of the National Atmospheric Deposition Program's Mercury Deposition Network (MDN). However, the site will not be officially part of the MDN, because the District cannot make a long-term commitment to rainfall monitoring

at STA-2. Inflow and outflow monitoring of each cell for unfiltered total mercury and methylmercury will ensure that both dissolved and particle-bound mercury species inputs and outputs are accurately quantified. Monitoring will be conducted biweekly, because the annual average hydraulic retention time (HRT) for each cell is calculated to be about 25 days, and biweekly monitoring proved adequate for the ENR Project where the annual average HRT was about 21 days. Interior surface water will be filtered to minimize the influence of particle resuspension on the representativeness of the monitoring results, even under low water depth and/or high flow-through conditions. This should also allow a more accurate calculation of traditional bioaccumulation factors for interior marsh flora and fauna, which are required for the preceding and succeeding analyses and modeling. The proposed frequency of interior surface water monitoring is every other biweekly period or every 28 days, which approximates the estimated annual average HRT for Cell 1 of 25 days.

Surficial soil (0-4 cm) will be collected quarterly. While the peat accretion rate is on the order of one to two cm per year, uptake and release in response to seasonal changes in overlying water chemistry occur more rapidly. Bulk density may also change in response to dryout and rewetting, and this will affect the mass storage calculations for surficial sediment. Moreover, it is important to distinguish between the influence of soil release and uptake from other seasonally varying inputs and outputs. During initial colonization, rapid growth of plants may store a significant quantity of THg or MeHg relative to inputs from inflow, wet and dry atmospheric deposition, and soil release. During decomposition, the Hg(II) and MeHg stored in plant biomass are released back to the water column or sediments. Six different vegetation species will be collected semi-annually, because the uptake of THg and MeHg are highly species-specific, and rooted macrophytes generally have a semi- annual cycle of production and senescence, whereas floating macrophytes and periphyton turn over more frequently than rooted macrophytes and more rapidly in the summer than the winter. However, seasonal monitoring should be sufficient to interpolate the periphyton and floating macrophyte bioaccumulation factors between sampling events.

3.3 Identification of Significant Differences, Trends and Influential Factors

This is not a hypothesis-driven study design. This is an enhanced study of the timing, magnitude, duration, and frequency of recurrence of excess methylmercury production, bioaccumulation, storage, and export in a constructed wetland that has repeatedly exhibited anomalously methylmercury behavior following reflooding in the wet season after a period of drawdown during the dry season. The data are being collected and analyzed to characterize the differences, spatial and temporal trends, and apparent external and internal influences on the timing, magnitude, duration, and frequency of recurrence of this anomalous phenomenon and its biogeochemical manifestations viz-a-viz the performance of the two adjacent treatment cells. These cells were constructed at the same time and operated in parallel with the problem treatment cell, but exhibited low and moderate rates of methylmercury production, bioaccumulation, storage, and export under the same external influences. The number of sampling events of each medium is dictated by a trade-off between the reduction in the uncertainty achieved and the cost of

achieving that reduction and not by an arbitrary set of data quality objectives for precision, resolving power, and confidence level in discriminating significant differences, trends, or correlations.

Principal component analysis will be used to discriminate potentially significantly influential individual factors or sets of related factors from the set of all candidate factors. Multivariate regression analysis will then be used to quantify the degree to which the variance in the data can be explained by each influential factor or set of related factors. To the extent permitted by the duration of the study, seasonal changes in the direction and magnitude of these influences will also be evaluated. Statistical significance will be assumed at $p \leq 0.05$. However, because correlation is not causation, the hypotheses that emerge from the interpretation of the results of the exploratory data analysis must be tested under rigorous, controlled conditions in laboratory microcosms or field mesocosms based on a rigorous statistical design. Such studies are outside the scope of this effort.

3.4 Predictive Model Development

The flow, concentration, load, stage, and disposition data collected in this study, together with equilibrium and kinetic rate coefficients obtained from other studies at this or related sites in the Everglades, will be used to initialize and calibrate a mechanistic mathematical model of the production, transport, disposition, destruction, and bioaccumulation of methylmercury in each of the three cells. The model will serve three purposes: (1) to organize, integrate, and synthesize the disparate physical, chemical, and biological data into a self-consistent framework; (2) to evaluate the short- and long-term mercury benefits and detriments of various alternatives for operating STA-2 Cells 1, 2, and 3; and (3) to guide the design of follow-up studies intended to reduce the most significant sources of modeling uncertainty based on sensitivity and propagated error analysis.

4.0 Methods and Procedures

4.1 Sampling

Rainfall will be collected at ground level using a modified Aerochemetrics rainfall collector modified according to the specifications and protocols of the National Atmospheric Deposition Program's Mercury Deposition Network. Surface water, sediment, fish, and vegetation samples will be collected according to the methods and procedures outlined in the Standard Operating Procedures appended to this Plan, except as noted in the individual tasks. Surface water samples will not be preserved in the field, and, therefore, must be shipped on blue ice or bagged wet ice in clean coolers within 24 hours of collection to ensure preservation within 48 hours of collection. Pore water sampling will be carried out following methods published by the U.S. Geological Survey (USGS) (Orem et al., 1998). Pore water redox will be measured at the point of collection and pore water sulfide will be fixed in the field at the time of collection prior to analysis. Fe(II) will be analyzed in the field with two hours of collection using a quantitative colorimetric method. The remaining pore water samples will not be preserved in the field, and, therefore, must be shipped on blue ice in clean coolers within 24 hours of

collection to ensure preservation within 48 hours of collection. Sediments not destined for quantification of bulk density and/or moisture content may be frozen prior to processing. Processing will be completed and samples shipped within 7 days. Mosquitofish will be collected by dip net or equivalent, placed in clean plastic bags, and placed on ice without freezing prior to compositing and homogenization. Following processing the mosquitofish may be frozen for a period not to exceed 28 days prior to shipping for analysis. Macrophyte leaves will be cut with a machete and placed in a resealable plastic bag, while periphyton will be collected using a wide-mouth jar. Both may be frozen prior to processing and shipping within 28 days. Solid samples in excess of that required for analysis will be archived. There shall be no deviations from the SOPs, except as indicated in the individual tasks, without the express written approval of the project manager prior to sampling.

It should be noted that the routine monitoring of pore water is not required in any State of Florida permit to operate or discharge to the waters of the state, and none of the FDEP-approved pore water sampling methods have been validated for ultra-trace total mercury and methylmercury analysis. While such methods are available, they are only used routinely by world-class research scientists and not as part of any routine monitoring program. Therefore, the Plan's inclusion of routine monitoring of ultra-trace total mercury and methylmercury in surficial soil pore water must be considered experimental. As such, there is no guarantee that the methods adopted by the District for implementation of this element of the Plan will produce valid, quantitative results for all constituents at all times. Nevertheless, the District recognizes the importance of pore water monitoring in this context and is committed to making a good faith effort to carry out this Plan element to the extent practicable. Any problems encountered in implementing the pore water monitoring element of this Plan will be brought to FDEP's attention in a timely fashion so that the Plan can be modified as needed within an adaptive management framework.

4.2 Chemical Analysis

For analytes other than total mercury and methylmercury, chemical analyses will be carried out in each medium according to standard methods where extant. There shall be no deviations from the standard or specified alternative analytical methods without the express written approval of the project manager prior to sampling. For ultra-trace total mercury and methylmercury, there are no standard methods or finalized USEPA-approved methods. For total mercury, the sample is digested using bromine monochloride, reduced to elemental mercury using stannous chloride, preconcentrated in the vapor phase on a gold column, and detected in the vapor phase using ultraviolet fluorescence following quantitative thermal desorption. For methylmercury, the sample is weakly acidified with HCl to form a neutral, volatile complex, distilled to liberate it from organic complexes, derivatized, eluted through a gas chromatograph, thermally decomposed and reduced to elemental mercury, and then analyzed as for total mercury. Until USEPA-approved methods are finalized, the most recent versions of proposed USEPA Methods 1631 and 1630 (withdrawn), respectively, will be followed. There shall

be no deviations from the standard or specified alternative analytical methods without the express written approval of the project manager prior to sampling.

The volume of pore water produced by squeezing the top 5 cm of a core roughly 8 cm in diameter with a bulk density of 0.15 g/cc and a particle density of 1.5 g/cc is on the order of 250 ml of theoretically available pore water, but only about 50% of that can be routinely extracted in practice. Moreover, one must include a margin of safety during extraction to ensure that the sample is collected from the top 5 cm of the core, as opposed to deeper layers. If the squeezing is stopped at 4 cm of core compression, this means that only 80% of the 50% of the theoretically available pore water is available in practice. Thus, typically one can expect no more than 100 ml of pore water per core. If the ultra-trace analysis of total mercury and methylmercury requires 40 ml per run (L.Hawkins, FGS, personal communication), the volume required for three runs is about 120 ml. If sulfide ion requires 120 ml, redox requires 10 mls, and all of the other anions and cations require 250 ml, this will require the squeezing of 5 cores per site to meet these requirements. The addition of nutrients to the analyte list will increase the required number of cores to six. Each core requires about two hours of squeezing, which includes up to six changes of filters. With a 4-core squeezer, one can generate enough pore water from one suite of analyses for two sites in six hours. The Plan calls for the sampling of one site with an exponentially decreasing sampling frequency and nine sites every other biweekly period. To allow completion of all pore water sampling for a sampling event within the same work week for purposes of synoptic survey, it has been decided that a maximum of six cores will be collected per site, such that two sites per day can be sampled and squeezed.

However, as with the quality of the sample of pore water collected by the proposed "squeezer" method, there is also uncertainty associated with the quantity of the sample volume that can be produced from a core, due to the inherent variability of the soil bulk density within a treatment cell, as well as between treatment cells with different antecedent land use histories. As a consequence, there may be occasions when the volume of pore water sample generated is less than the minimum required for the analysis of all of the analytes with the required margin of safety. In such cases, the margin of safety will be reduced from two samples to one. If there is still insufficient sample volume, the hierarchy of priority for analysis of the available pore water will be in the order: $S^{=}$, $SO_4^{=}$, MeHg, THg, DOC, pH, Fe^{+2}, Fe, Mn, redox, Cl, Ca, Mg, alk, and nutrients.

4.3 Data Analysis

Appropriate parametric and nonparametric tests, models, and methods will be applied to the data in evaluating significant differences, spatial and temporal trends, and intra- and intermedia correlations within and between treatment cells as regards the timing, magnitude, duration, and frequency of recurrence of methylmercury contamination, bioaccumulation, storage, and export (Sokal and Rolf, 1973; Snedecor and Cochran, 1980; Johnson and Wichern, 1988; Berthouex and Brown, 1994; Zar, 1996).

4.4 Modeling

4.4.1 Transport-Fate-Bioaccumulation

For purposes of mechanistic mathematical modeling, this study will adopt the Everglades Mercury Cycling Model (Version 2), developed by TetraTech, Inc. under contract to the Department and the District (C-9693).

4.4.2 Exposure and Risk

The significance of the timing, magnitude, duration, and frequency of recurrence of excess methylmercury production will be characterized using quantitative probabilistic ecological risk assessment (PERA). The sentinel avian and mammalian species to be protected from unacceptable risk of toxic effects from methylmercury exposure via the diet are the endangered wood stork and the Everglades mink. USEPA protocols will be followed in carrying out the data reduction, analysis, integration, synthesis, and interpretation of the results required for the PERA (USEPA, 1998).

5.0 Scope of Work for Expanded Mercury Monitoring in STA-2

The expanded monitoring will be carried out in three tiers. In Tier 1, candidate pore water sampling methods will be identified for application in this study and field-tested for subsequent full-scale implementation in Tiers 2 and 3. In Tier 2, immediately following re-flooding, soil and pore water will be collected in triplicate at STA-2 Cell 1 site C1C on day 7, 14, 28, 56, 112, and 254 to mimic the sampling of the triplicate cores removed from this site for a drying and rewetting experiment under another contract. The lists of Tier 2 analytes to be tested for in soil and pore water are identified in Table 2. In the third tier, prior to re-flooding of Cell 1, a set of surficial soil cores will be collected at each of the sites depicted in Figure 1 at the latitudes and longitudes iterated in Table 1 to establish a biogeochemical baseline. Upon re-flooding of Cell 1, the inflow at G-328B and each cell's outflow will be sampled biweekly, the interior water, soil pore water, and mosquitofish every other bi-weekly period (13 times per year), surficial soil quarterly, and six types of vegetation vegetation semi-annually at three interior sites in each cell at the locations depicted in Figure 1. Quality-assured data from this enhanced monitoring will be stored and available in a centrally accessible electronic database (Microsoft EXCEL or equivalent). The District will provide quarterly status reports under contract C-11900-A03 and a final report under this Cooperative Agreement. The final report will contain a description of the study design, methods, quality assurance procedures, results, discussion based on an integration of those results within the appropriate algebraic, statistical, and mass balance quantitative frameworks, and findings, conclusions, and recommendations based on those quantitative analyses. The significance of the timing, magnitude, duration, and frequency of recurrence of excess methylmercury production in STA-2 Cell 1 will be characterized via probabilistic ecological risk assessment. The electronic database for this study will be transmitted to DEP with the final report.

Table 1. Latitudes and longitudes of each sampling site in STA-2 and STA-6

Site	Latitude		Longitude
STA2C1C	262312.024		803052.921
STA2C1AA	262444.068		802951.640
STA2C1BB	262406.233		803020.828
STA2C1CC	262312.024		803052.921
STA2C2A	262434.145		803035.771
STA2C2B	262422.759		803057.462
STA2C2C	262358.304		803128.933
STA2C3A	262439.800		803308.800
STA2C3B	262350.741		803305.021
STA2C3C	262303.085		803307.879

Table 2. Summary of STA-2 Expanded Hg Monitoring Plan

STA – 2	Matrix	Sites	Frequency	Types	Reps	QC	Analytes
	Rain	**1**	**Weekly (52)**	**1 (bulk integrated)**	**1**	**1**	**U-THg[3]**
[a] Coordinated with other routine or special sampling	**STA-2 Inflow**	**1**	**Biweekly (26)**	**1 (grab)**	**1**	**3**	**U-THg[1], U-MeHg[1]**
	STA-2 Inflow	**1**	**Biweekly (26)**	**1 (grab)**	**1**	**0[a]**	**TSS, DOC**
	Cell Outflow	**3**	**Biweekly (26)**	**1 (grab)**	**1**	**0[a]**	**U-THg[1], U-MeHg[1]**
	Cell Outflow	**3**	**Biweekly (26)**	**1 (grab)**	**1**	**0[a]**	**TSS, DOC, F-$SO_4^=$ Hydrolab**
(1) Ship to DEP; other analytes to District Lab or designated alternate	**STA-2 Inflow Special**	**1**	**At start-up and every other biweek thereafter (13)**	**1 (grab)**	**1**	**1**	**F-THg[1], F-MeHg[1] B. C. D. E. F.**
	Cell Outflow Special	**1**	**At start-up and every other biweek thereafter (13)**	**1 (grab)**	**1**	**0[a]**	**G. F-THg[1], F-MeHg[1]**
(2) Ship to DB; other analytes to District Lab or designated alternate	**Interior Water**	**9**	**At start-up and every other biweek thereafter (13)**	**1 (grab)**	**1**	**3 E1 E2 BB**	**F-THg[1], F-MeHg[1] TSS, DOC, F-$SO_4^=$, F-Cl F-Fe, F-Mn, F-Ca, F-Mg nutrients, Alk, Hydrolab**
(3) ship to FGS; other analytes to District Lab or designated alternate	**Interior Water-Special**	**3**	**At start-up and every other biweek thereafter (13)**	**1 (grab)**	**1**	**2 E1 E2**	**U-THg[1], U-MeHg[1]**
(4) ship to FGS; other analytes to DB Labs or designated alternate	**Pore Water Tier 2A**	**1**	**6 (0, 14, 28, 56, 112, 224 days)**	**1 (0-5 cm by "squeezer" or equivalent)**	**1 1 stratum**	**3 E1 E2 BB**	**F-THg[3], F-MeHg[3] DOC, F-$SO_4^=$, F-Cl, F-$S^{=(2)}$, F-Fe, Fe^{+2}(field), F-Mn, F-Ca, F-Mg, Alk, pH, nutrients, Redox (field), Cond.**

Table 2 (Continued)

STA – 2	Matrix	Sites	Frequency	Types	Reps	QC	Analytes
	Pore Water Tier 2B	**9**	**13 (w/i 1 week start-up and every other biweekly period**	**1 (0-5 cm by "squeezer" or equivalent)**	**1 1 stratum**	**3 E1 E2 BB**	**F-THg[3], F-MeHg[3] DOC, F-$SO_4^{=}$, F-Cl, F-$S^{=(2)}$, F-Fe, Fe^{+2}(field), F-Mn, F-Ca, F-Mg, Alk, pH, nutrients, Redox(field), Cond.,**
	Soils Tier 1 (Baseline)	**9**	**1 (dry season; pre-reflood)**	**1 (4-cm surface cores)**	**5 (2 in tact; 3 homo-genized composite 1 stratum)**	**0**	**THg[4], MeHg[4] TS, TFe, TMn TCa, TMg, AVS, Ash, Bulk Density Moisture, Prep.**
(1) Ship to DEP; other analytes to District Lab or designated alternate	**Soils Tier 2A**	**1**	**6 (0, 14, 28, 56, 112, 224 days)**	**1 (4-cm surface cores)**	**5 (2 in tact; 3 homo-genized composite 1 stratum**	**0**	**THg[4], MeHg[4] TS, TFe, TMn TCa, TMg, AVS, Ash, Bulk Density Moisture, Prep.**
(2) Ship to DB; other analytes to District Lab or designated alternate	**Soils Tier 2B**	**9**	**5 (start-up and quarterly thereafter)**	**1 (4-cm surface cores)**	**5 (2 in tact; 3 homo-genized composite 1 stratum)**	**0**	**THg[4], MeHg[4] TS, TFe, TMn TCa, TMg, AVS, Ash, Bulk Density Moisture, Prep.**
(3) ship to FGS; others to District Lab or designated alternate	**Plants**	**9**	**2 (semi-annually)**	**6 species (2 rooted; 2 floating; 2 peri-phyton)**	**1**	**0**	**THg[4], MeHg[4] Ash, Moisture, Prep**
(4) ship to FGS; others to DB Labs or designated alternate	**Mosquito-Fish (75-250 individual fish)**	**9**	**13 (every other biweekly period)**	**1 (*Gambusia holbrooki*)**	**3 (sub-sample homo-genate)**	**0**	**THg[1], Moisture[1]**

Table 3. Sampling and Shipping Schedule for STA-2

WEEK (1) Same day (2) Within 28 calendar days (3) Within 14 calendar days	**STA 2**	SW UA RT FE AR CE	P S RH OI CP ES S	PW OA RT EE R	P S RH OI CP ES S	S OI L	P S RH OI CP ES S	P LA NT S	P S RH OI CP ES S	MF OI S S QH UI TO	P S RH OI CP ES S	
7/22/02-7/26/02		X	(1)									
7/29/02-8/02/02												
08/05/02-08/08/02		X	(1)	X	(1)					X	(3)	
08/12/02-08/15/02												
08/19/02-08/22/02		X	(1)					X				
08/26/02-08/29/02												
09/02/02-09/05/02		X	(1)	X	(1)					X	(3)	
09/09/02-0912/02												
09/16/02-09/19/02		X	(1)									
09/23/02-09/26/02												
09/30/02-10/03/02		X	(1)	X	(1)	X	(2)			X	(3)	
10/07/02-10/10/02												
10/14/02-10/17/02		X	(1)									
10/21/02-10/24/02												
10/28/02-10/31/02		X	(1)	X	(1)					X	(3)	
11/04/02-11/07/02												
11/11/02-11/14/02		X	(1)									
11/18/02-11/21/02												
11/25/02-11/28/02		X	(1)	X	(1)					X	(3)	
12/02/02-12/05/02												
12/09/02-12/12/02		X	(1)									
12/16/02-12/19/02												
12/23/02-12/26/02		X	(1)	X	(1)	X	(2)			X	(3)	
12/30/02-01/02/03												
01/06/03-01/09/03		X	(1)									
01/13/03-01/16/03												
01/20/03-01/23/03		X	(1)	X	(1)					X	(3)	
01/27/03-01/30/03												
02/03/03-02/06/03		X	(1)					X				
02/10/03-02/13/03												
02/17/03-02/20/03		X	(1)	X	(1)					X	(3)	
02/24/03-02/27/03												
03/03/03-03/06/03		X	(1)									
03/10/03-03/13/03												
03/17/03-03/20/03		X	(1)	X	(1)	X	(2)			X	(3)	
03/24/03-03/27/03												
03/31/03-04/03/03		X	(1)									
04/07/03-04/10/03												
04/14/03-04/17/03		X	(1)	X	(1)					X	(3)	
04/21/03-04/24/03												
04/28/03-05/01/03		X	(1)									
05/05/03-05/08/03												
05/12/03-05/15/03		X	(1)	X	(1)					X	(3)	
05/19/03-05/22/03												
05/26/03-05/29/03		X	(1)									
06/02/03-06/05/03												
06/09/03-06/12/03		X	(1)	X	(1)	X	(2)			X	(3)	
06/16/03-06/19/03												
06/23/03-06/26/03		X	(1)									
06/30/02-07/03/03												
07/07/03-07/10/03		X	(1)	X	(1)					X	(3)	
07/14/03-07/17/03												
07/21/03-07/24/03		X	(1)									
07/28/03-07/31/03												

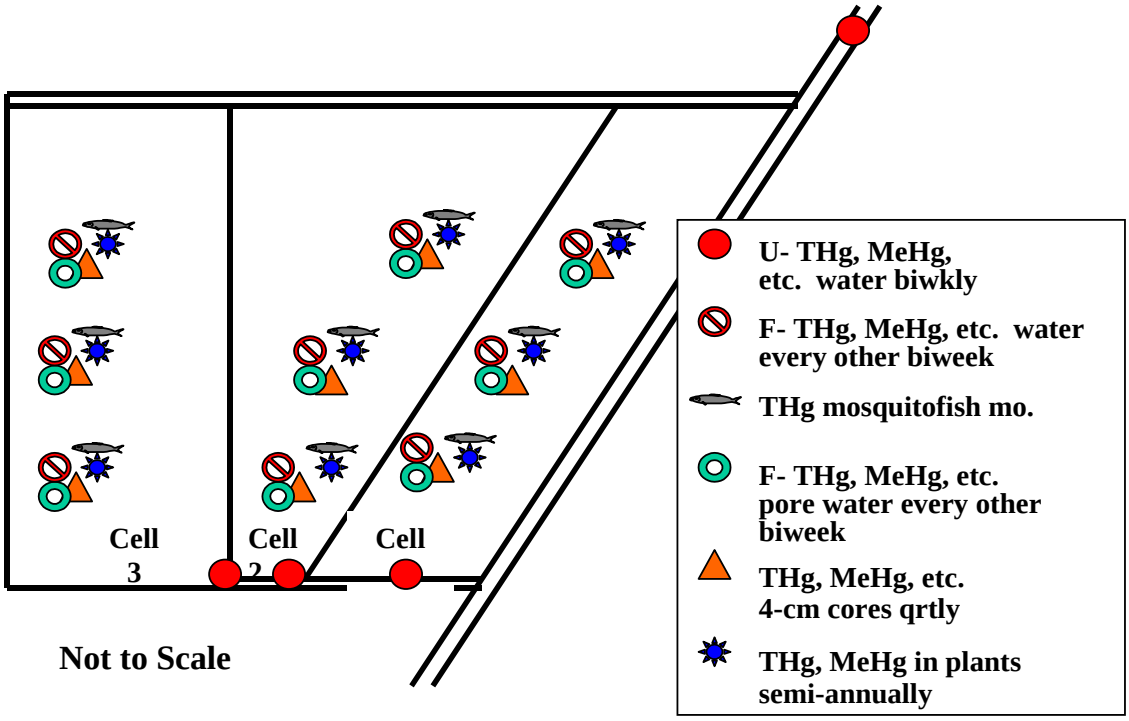

Figure 2. STA-2 sampling locations and frequencies by medium for expanded mercury monitoring.

6.0 Work Breakdown Structure

6.1 Tier 1 Study: Pore Water Method Pilot Study

Prior to implementation of Tiers 2 and 3 of this Plan, the District tested several candidate methods for collection of pore water from surficial sediments. The methods needed to be able to collect a representative, valid sample in such a way that redox is preserved and sufficient volumes of pore water are collected to allow ultra-trace mercury analysis, other trace metals, nutrients, and common anions and cations, as well as sulfide, Fe(II) and Mn(II). Based on the physical, chemical, and biological response times of surficial soils and sediments, the pore water sampling cycle must be completed within ten working days to qualify as synoptic. Unfortunately, the two methods tested to date have not been able to meet all of these performance criteria. As a consequence, the District requested and FDEP agreed to postpone pore water sample collection until such time as the District had acquired the equipment and training required to implement a proven or adequately tested pore water sampling capability. In Tier 1 of this study, a new pore water method is systematically developed or acquired, tested, documented, approved in principle, passed along through training and certification, and implemented following approval in practice.

Task 1. Expert Assistance

Task 1.1 Prepare Work Order SOW for Expert Assistance

See Section 8.6: Appendix 6.

Deliverable: WO
Due Date: September 30, 2002

Task 2.2 Select Expert

Task 2.2.1 Develop Candidate List of Experts

Deliverable: Candidate List
Due Date: September 30, 2002

Task 2.2.2 Develop Selection Criteria

With input from external and internal interested and knowledgeable parties, the Project Manager will develop a set of criteria that an expert must meet to be selected for the ultra-trace mercury pore water sampling technology transfer pilot project.

Deliverable: Selection Criteria
Due Date: September 30, 2002

Task 2.3 Issue Expert WO

The District will make a good faith effort to issue a Work Order for Expert Assistance in October 31, 2002, for acquiring the required pore water sampling capability.

Deliverable: Issue WO
Due Date: by October 31, 2002

Task 2.4 Expert Conducts Field Reconnaissance Trip

After issuance of the WO to the selected Expert, he or she will meet with District staff in the field to evaluate the District's needs, taking into account preservation of redox potential, avoidance of contamination with ultra-trace total mercury or methylmercury, required pore water volumes, soil physical and chemical characteristics, environmental conditions, and application logistics. Based on this field reconnaissance trip, the Expert shall prepare a letter report summarizing what existing equipment or modifications thereto will meet the District's needs.

Deliverable: Expert's Field Recon Letter Report
Due Date: November 15, 2002

Task 2.5. Conference Call

Following the first field recon trip, the Expert shall discuss the contents of his or her Letter Report with the Project Manager and such other external and internal individuals as he deems appropriate, focusing on the recommended existing or modified equipment for the collection of pore water for redox, sulfide, Fe(II)/Fe(III), Mn(II)/Mn(III) and ultra-trace mercury analysis. The Expert shall also discuss his or her plan and schedule for the second field trip for testing the existing or modified equipment appropriate for this application.

Deliverable: Conference Call
Due Date: by November 22, 2002

Task 2.5 Expert Constructs or Modifies Required Equipment

Following discussions with the District in the Conference Call, the Expert shall construct or modify existing pore water sampling equipment capable of collecting a sufficient, representative, valid sample of pore water from surficial soil or sediment so as to preserve redox conditions for subsequent analysis for sulfide, Fe(II)/Fe(III), and with the cleanliness required for ultra-trace mercury sample collection.

Deliverable: Letter Report with Photo of Finished Apparatus
Due Date: December 31, 2002

Task 3. Field Testing

Task 3.1 Prepare Field Test Plan

The Expert shall prepare a draft field test plan to fully evaluate the capability of the pore water sampling apparatus to meet the District's performance specifications. The District will review and comment on the draft test plan. The Expert shall explain the reason for rejecting any of the District's recommendations in a Letter Report accompanying the Final Field Test Plan.

Deliverable: Draft Field Test Plan
Due Date: January 03, 2003

Deliverable: Final Field Test Plan
Due Date: January 10, 2003

Task 3.2 Field Test Plan Implementation

On the second field trip, the Expert shall fully test the candidate pore water collection apparatus at a variety of sites to fully exercise the method. Based on the results of the field test, the Expert shall recommend adopting the method as is, further modifying the method for re-testing, or seeking an alternative method due to unforeseen circumstances.

Deliverable: Letter Report on Field Test Plan Findings, Conclusions, and Recommendations
Due Date: by January 31, 2003

Task 3.3. Apparatus Modifications

Due Date: by February 21, 2003

Task 3.4 Field Testing of Further Modified Apparatus

Deliverable: Letter Report
Due Date: by February 28, 2003

Task 3.5 Obtain District Approval

Deliverable: District Approval
Due Date: by March 14, 2003

Task 3.6 Prepare SOP and Supporting Documentation

Deliverable: SOP and Supporting Documentation
Due Date: March 28, 2003

Task 4. Obtain DEP Approval of Pore Water Sampling Method in Principle

Deliverable: FDEP Approval
Due Date: April 25, 2003

Task 5. Technology Transfer

Task 5.1 Prepare Instruction Manual for Technology Transfer

Task 5.1 Prepare Instruction Manual for Technology Transfer

The Expert shall prepare an instruction manual for teaching District and contractor technicians how to implement the modified pore water sampling method.

Deliverable: Draft Instruction Manual
Due Date: April 10, 2003

Deliverable: Final Instruction Manual
Due Date: by time of teaching session per Task 5.2

Task 5.2 Teach Class

The Expert shall travel to West Palm Beach and train select District staff in the collection of surficial sediment pore water under anaerobic conditions for quantitation of various redox sensitive analytes, as well as ultra-trace THg and MeHg. The Expert shall prepare a training manual and schedule, including a "dry lab" session at the Field Operations Center to familiarize staff with the equipment and its proper cleaning, use, and maintenance and two field days in which to evaluate staff performance under real field conditions. The field study will be carried out at STA-2 in Cells 1 and 2, if possible, to ensure that the device and method are appropriate to the compact soils there. Pore water samples will be collected and analyzed for redox, pH, ultra-trace THg and MeHg, sulfide, DOC, and Fe(II).

Deliverable: Training of District Staff
Due Date: by April 25, 2003

Task 5.3 Test Students for Certification

Deliverable: Training and Certification
Due Date: by April 25, 2003

Task 6. Method Pilot Testing

Following completion of training by the Expert, trained District technicians and trained contractor technicians shall pilot test the method for 21 days (three weekly sampling cycles) by collecting pore water samples biweekly at Sites STA-2 C1A, C2A, and C3A. The District Project Managers will review the data and make any changes he deems

appropriate to the SOP to ensure the collection of a representative, valid sample of sufficient volume for ultra-trace mercury analysis and redox, sulfide, Fe(II)/Fe(III), and Mn(II)/Mn(III) analysis.

Deliverable: Letter Report Transmitting Results and Requesting Approval of Method
Due Date: June 20, 2003

Task 7. DEP Approval of Method Implementation

Following the completion of Tasks 1 through 6, the Project Manager shall submit a Letter Report certifying that the District is ready to fully implement the new pore water sampling method. The FDEP will review the report and either agree or disagree with the District's conclusion. If the former, the District shall implement the method as soon thereafter as is practicable. If the latter, the District shall meet with appropriate FDEP staff to develop alternatives with which to correct deficiencies precluding approval for implementation at this time.

Deliverable: Letter Approving or Disapproving Pore Water Method Implementation
Due Date: June 30, 2003

6.2 Tier 2 Study: High-Frequency Sampling

Task 1: Collect Post-Flooding, High-Frequency Samples

1.1 Pore Water

The implementation of this substask presupposes successful completion of the Tier 1 Pore water Pilot Study resulting in an approved pore water sampling method. Samples of filtered pore water (0-5 cm) will be collected in triplicate at Site STA-2C1C on post-flood days 0, 14, 28, 56, 112, and 224 and analyzed for the constituents set forth in Table 2 to track the rehydrated soil biogeochemistry. This sampling frequency also mimics that for the microcosm study carried out under C-13860. However, redox, pH, conductivity, and Fe(II) will be measured at the point and time of sample collection. Samples will be collected separately for sulfide preservation, iron speciation, and total and methylmercury analysis. Unpreserved and preserved samples will be stored on wet or blue ice and then shipped the same day as collected for processing and analysis within holding times.

However, as with the quality of the sample of pore water collected by the proposed "squeezer" method, there is also uncertainty associated with the quantity of the sample volume that can be produced from a core, due to the inherent variability of the soil bulk density within a treatment cell, as well as between treatment cells with different antecedent land use histories. As a consequence, there may be occasions when the volume of pore water sample generated is less than the minimum required for the analysis of all of the analytes with the required margin of safety. In such cases, the margin of safety will be reduced from two samples to one. If there is still insufficient sample volume, the hierarchy of priority for analysis of the available pore water will be in the

order: $S^{=}$, $SO_4^{=}$, MeHg, THg, DOC, pH, Fe^{+2}, Fe, Mn, redox, Cl, Ca, Mg, alk, and nutrients.

Start Date: Upon initiation of flow-through operation on or about July 1, 2002
Deliverables: Filtered samples in triplicate
Due Dates: On days 7, 14, 28, 56, 112, and 224 from initiation of flow-through operation.

1.2 Soils

Samples of surficial soil (0-4 cm) will be collected in triplicate at Site STA-2C1C on post-flood days 7, 14, 28, 56, 112, and 224 and analyzed for the constituents identified in Table 2 to track the rehydrated soil biogeochemistry. This sampling frequency also mimics that for the microcosm study carried out under C-13860. Samples will be collected separately for physical properties (e.g., bulk density, moisture, and ash content), metals, sulfur and acid volatile sulfide, and total and methylmercury analyses.

Start Date: Upon initiation of flow-through operation on or about July 1, 2002
Deliverables: Wet soil samples in triplicate
Due Dates: On days 0, 14, 28, 56, 112, and 224 from initiation of flow-through operation.

Task 2: Analyze Post-Flooding, High-Frequency Samples for Key Constituents

2.1 Pore Water

The implementation of this substask presupposes successful completion of the Tier 1 Pore water Pilot Study resulting in an approved pore water sampling method. The pore water collected in Tier 1 Task 1 will be analyzed for the constituents and properties set forth in Table 2.

Start Date: Upon initiation of flow-through operation on or about July 1, 2002
Deliverables: Filtered samples in triplicate
Due Dates: Analysis within holding times.
Report within 15 working days of analysis.

2.2 Soils

The soils collected in Tier 1 Task 1 will be analyzed for the constituents and properties set forth in Table 2 according to approved analytical protocols.

Start Date: Upon initiation of flow-through operation on or about July 1, 2002
Deliverables: Wet soil samples in triplicate
Due Dates: Analysis within holding times.
Report within 15 working days of analysis.

Task 3: Quality Assure Post-Flooding, High Frequency Sample Results

See Task 5 of Tier 2 Study.

Task 4: Censor, Reduce, Analyze, Integrate, and Synthesize Data

4.1 Data Censorship

See Task 6.1 of Tier 2 Study.

4.2 Data Reduction and Analysis

See Task 6.2 and 6.3 of Tier 2 Study.

4.3 Data Integration and Synthesis

See Task 6.4 of Tier 2 Study.

Task 5: Prepare Final Report

See Task 7 of Tier 2 Study

5.1 Draft Final Report

Due Date: November 30, 2003

5.2 Final Report

Due Date: January 31, 2004

Task 6: Transfer Electronic Database

Due Date: January 31, 2004

6.3 Tier 3 Study

Task 1: Collect Pre-Flooding Baseline Samples

1.1 Pore Water

NA

1.2 Soils

Samples of soil (0 - 4 cm) will be collected using an appropriate coring device at Sites STA-2 C1AA, BB, and CC, C2A, C2B, and C2C, and C3A, C3B, and C3C prior to the onset of the wet season and reflooding and quarterly thereafter. Replicate samples will be collected as necessary to provide minimum sample volumes and masses for the various analytes listed in Table 2 but not for purposes of quality control. Samples will be stored on wet or blue ice and then refrigerated prior to processing and shipping within holding times. Samples should not be frozen for bulk density or moisture analyses. A minimum of 30 grams and preferably 60 grams of sample will be sent to the laboratory for subsampling and analysis. Wherever possible, a minimum of 50 grams but no less than 30 grams of excess sample will be archived.

Deliverable: Nine soil samples
Due Date: By May 22, 2003

Task 2: Analyze Baseline Samples for Key Constituents

2.1 Pore Water

NA

2.2 Soils

Each of the 9 sets of homogenized soils collected per Tier 2 Task 1 will be processed and analyzed for the constituents and properties set forth in Table 2 following approved analytical protocols. Only necessary deviations from the approved protocols will be documented.

Deliverable: Results for 9 individual samples as per Table 2
Due Date: Analysis Within Holding Times
Preliminary Results Within 20 Working Days of Analysis
Final Results Within 40 Working Days of Analysis

Task 3: Collect Post-Flooding Samples

3.1 Rain

Rain volume will be measured at ground level by a Belfort rain gauge. Rain samples will be collected via Aerochemetric sampler at ground level on a weekly basis and analyzed for total mercury (THg) following the same protocols and using the same analytical laboratory as the Mercury Deposition Network of National Atmospheric Deposition Program.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Weekly average rain concentrations of THg
Due Date: At start and biweekly thereafter

3.2 Surface Water

3.2.1 Inflows and Outflows

3.2.1.1 Routine

Collect unfiltered water samples biweekly using clean hands technique for total mercury and methylmercury and appropriate technique for other constituents at G328B and a representative outflow structure for each of the STA-2 treatment cells.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Biweekly unfiltered samples.
Due Date: At start and biweekly thereafter

3.2.1.2 Special

In conjunction with the sampling in Section 3.2.1.1, collect filtered water samples at the inflow at G328B and outflow at one of the three cells every other biweekly sampling period using clean hands technique for total mercury and methylmercury to permit discriminating between particle-bound and non-filterable (truly dissolved plus colloid-bound) fractions. Each cell will be resampled every eighth biweekly period.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Every other biweekly period for filtered samples.
Due Date: At start and every other biweekly period thereafter

3.2.2 Interior Water

3.2.2.1 Routine

Collect filtered water samples every other biweekly sampling period using clean hands technique for total mercury and methylmercury and appropriate technique for other constituents at sites C1AA, C1BB, and C1CC in Cell 1, C2A, C2B, C2C in Cell 2, and C3A, C3B, and C3C in Cell 3.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Filtered samples every other biweekly period.
Due Date: At start and every other biweekly period thereafter

3.2.2.2 Special

In conjunction with the sampling in Section 3.2.1.2, collect unfiltered water samples at the three interior sites in one of the three cells every other biweekly sampling period using clean hands technique for total mercury and methylmercury to permit discriminating between particle-bound and non-filterable (truly dissolved plus colloid-bound) fractions. Each cell will be resampled every eighth biweekly period.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Every other biweekly period for filtered samples.
Due Date: At start and every other biweekly period thereafter

3.3 Pore Water

NA

3.4 Soils

See Task 1 for locations and procedures.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Quarterly core samples.
Due Date: At start and quarterly thereafter

3.5 Mosquitofish

About 75-250 mosquitofish will be collected at each of three interior marsh sites in STA-2 Cells 1, 2, and 3 every other biweekly period for one year. The mosquitofish will be homogenized and frozen prior to processing. A minimum of 3 grams and preferably 6 grams of sample will be sent to the laboratory for subsampling and analysis. Wherever possible, a minimum of 5 grams but no less than 3 grams of excess sample will be archived.

Start Date: Within 14 days of reflooding and every other biweekly period thereafter for one year.
End Date: One year later
Deliverables: At least 3 grams of mosquitofish homogenate from each sampling location every other biweekly period.
Due Date: At start and every other biweekly period thereafter

3.6 Vegetation

Representative above-ground samples (~ 5 Kg wet or ~ 0.5 Kg semi-dry) of rooted macrophytes (e.g., sawgrass and utricularia), floating macrophytes (e.g., water lettuce and

water hyacinth), and periphyton (green and blue-green) will be collected at each of three interior marsh sites in STA-2 Cells 1, 2, and 3 semi-annually for one year. A minimum of 30 grams and preferably 60 grams of sample will be sent to the laboratory for subsampling and analysis. Wherever possible, a minimum of 50 grams but no less than 30 grams of excess sample will be archived.

Deliverables: At least 0.5 Kg semi-dry plant leaf grindings for six plant species from each sampling location semi-annually.
Due Dates: August 2002 and February 2003

Task 4: Perform Quantitative Chemical Analysis on Environmental Samples

4.1 Surface Water

The surface water samples collected in Tier 2 Task 1 will be analyzed for the constituents and properties set forth in Table 2 according to approved analytical protocols. Only necessary deviations from those protocols will be documented.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Unfiltered surface water samples
Due Dates: Analysis within holding times.
Preliminary report within 20 working days of analysis
Final report within 40 working days of analysis.

4.2 Pore Water

NA

4.3 Soil/Sediments

The wet soil samples collected in Tier 2 Task 1 will be analyzed for the constituents and properties set forth in Table 2 according to approved analytical protocols. Only necessary deviations from those protocols will be documented.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Filtered samples
Due Dates: Analysis within holding times.
Preliminary report within 20 working days of analysis
Final report within 40 working days of analysis.

4.4 Vegetation

The wet vegetation samples collected in Tier 2 Task 1 will be analyzed for the constituents and properties set forth in Table 2 according to approved analytical protocols. Only necessary deviations from those protocols will be documented.

Start Date: August 2002
Deliverables: Filtered samples
Due Dates: Analysis within holding times.
Preliminary report within 20 working days of analysis
Final report within 40 working days of analysis.

4.5 Fish

The wet mosquitofish samples collected in Tier 2 Task 1 will be analyzed for the constituents and properties set forth in Table 2 according to approved analytical protocols. Only necessary deviations from those protocols will be documented.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Filtered samples
Due Dates: Analysis within holding times.
Preliminary report within 20 working days of analysis
Final report within 40 working days of analysis.

Task 5: Quality Assure Results

5.1 Laboratory Quality Control

Only DEP-certified laboratories will be used for the quantitative analysis of the constituents identified for the analysis of Tier 2 samples in Table 2. In addition to the standard suite of blanks, spikes, reference materials, and replicate analyses, a bottle blank will be retained in the laboratory to discriminate field contamination of the equipment blanks from bottle or DI water contamination. If the bottle blank concentration of total mercury or methylmercury is greater than two times the MDL but less than five times the MDL, all results for that analytical run will be non-fatally flagged. If the bottle blank concentration of total mercury or methylmercury is greater than five times the MDL, all results for that trip will be fatally flagged. The District will review and verify laboratory quality assurance reports.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Pore water and wet soil analysis results in triplicate
Due Dates: Report within 40 working days of analysis.

5.2 Field Quality Control

Field sampling staff will be trained and certified in clean-hands sampling technique to ensure the quality of sampling. Samples will be maintained under chain-of-custody protocols from the time of collection through storage, processing, and shipping to the analytical laboratory. A start-of-trip equipment blank and an end-of-trip equipment blank will be collected for each surface water and pore water sampling trip for field quality control. If the starting or ending equipment blank is greater than two times the MDL and the bottle blank is less than two times the MDL, the data will be non-fatally flagged. If the starting or ending equipment blank is greater than five times the MDL and the bottle blank is less than two times the MDL, the data will be fatally flagged. No quality control samples will be taken for soil, vegetation, or fish, but unused portions of solids samples will be stored should discrepancies in the results arise that can only be resolved by reanalysis of the remaining sample. The District will review and verify field quality assurance reports.

Start Date: Upon initiation of flow-through operation
End Date: One year later
Deliverables: Pore water and wet soil analysis results in triplicate
Due Dates: Report within 15 working days of receipt of analytical results from the laboratory

Task 6: Censor, Reduce, Analyze, Integrate, and Synthesize the Quality Assured Data

This task will be carried out after receipt of the last set of quality assured data.

6.1 Data Censorship

The process will start with uncensored sets of data from the study database. The study data set to be used for analysis will be censored to remove data that fail laboratory or field quality control criteria prior to reduction and analysis, if such removal does not preclude or substantially weaken the power and confidence level of a subsequent analysis. Where such is the case, the results of the analysis will be caveated by noting that it could only be carried by including the questionable data, but that the results must be interpreted and applied with caution. Data greater than 3 standard deviations of the mean of the data set will be flagged but not censored. After evaluating the power and confidence level of the difference or trend or univariate or multivariate regression with the flagged data, the flagged data will be removed and the analysis repeated to determine the sensitivity of the results to the presence or absence of the questionable data.

6.2 Data Reduction

The censored data set will be used for all subsequent data reductions. Data reduction will include: (1) expressing all fish and soil results on a wet weight basis to prevent confusion during mass budget calculations; (2) calculating the apparent dissolved concentration of total mercury or methylmercury in water as the difference between the unfiltered and

filtered concentration. (Where that difference is negative, the data pair will be rejected.); (3) calculating the concentration of total mercury or methylmercury on particulate as the difference between the unfiltered and filtered concentration divided the concentration of total suspended solids; (4) calculating the surface water bioaccumulation factor (BAF) as the ratio of the concentration of total mercury in fish to the concentration of filtered methylmercury in water; (5) calculating the sediment bioaccumulation factor (SBAF) as the ratio of the concentration of total mercury as methylmercury in fish to the concentration of methylmercury in surficial soil; (6) calculating the apparent dissolved fraction of total mercury or methylmercury in water as the ratio of the filtered to unfiltered total mercury or methylmercury concentration in water; (7) calculating the apparent particulate fraction of total mercury or methylmercury in water as 1 minus the dissolved fraction of total mercury or methylmercury in water; (8) calculating the standard ultraviolet absorbance (SUVA) of dissolved organic carbon (DOC) as the ratio of the concentration of the dissolved organic carbon to its absorption efficiency at a wavelength of 260 nm.

6.3 Data Analysis

Where appropriate, analysis of covariance (ANCOVA; SAS GLM procedure) will be used to evaluate spatial and temporal differences in mercury concentrations, with age (largemouth bass) or weight (sunfish) as a covariate. However, use of ANCOVA is predicated on several critical assumptions (for review see ZAR, 1996), including (1) that regressions are simple linear functions, (2) that regressions are statistically significant (i.e., non-zero slopes), (3) that the covariate is a random fixed variable, (4) that both the dependent variable and residuals are independent and normally distributed, and (5) that slopes of regressions are homogeneous (parallel). Regressions also require that collected samples exhibit a relatively wide range of covariate, i.e., fish from a given site are not all the same age or weight. Where these assumptions are not met, ANCOVA is inappropriate. Instead, standard ANOVAs or Student's t-tests (SigmaStat, Jandel Corporation, San Rafael, California) will be used; possible covariates will be considered separately, sometimes qualitatively. The assumptions of normality and equal variance will be tested by the Kolmorogov-Smirnov and Levene Median tests, respectively. Data-sets lacking homogeneity of variance or that depart from normal distribution will be natural-log transformed and re-analyzed. If transformed data meet the assumptions, they will be used in ANOVA. If not, raw data sets will be evaluated using non-parametric tests, such as the Kruskal-Wallis ANOVA on ranks or the Mann-Whitney Rank sum test. If the multigroup null hypothesis is rejected, groups will be compared using either Tukey HSD or Dunn's method.

6.4 Data Integration and Synthesis

6.4.1 Mass Budgets

The first-order integration and synthesis tool in this study will be the individual cell mass budgets for total mercury and methylmercury. The procedures followed here will parallel those applied to the total mercury and methylmercury mass budgets for the ENR Project

(Miles and Fink, 1998; SFWMD, 1999). To fill the seepage flux data gap in the water budget, it will be calculated by difference. The total mercury and methylmercury loads and fluxes will be calculated by multiplying the measured concentration for that period by the corresponding water volume or flux. Wet deposition flux of THg will be calculated by multiplying the weekly rain THg concentration by the rain depth for that period. Dry deposition of THg will be assumed to be 50% (USEPA, 1997) of the average annual wet deposition flux of 22 ug/m^2-yr (Guentzel et al, 2001), unless better information becomes available during the course of the study. Inflow and outflow loads will be calculated by multiplying the instantaneous unfiltered THg or MeHg grab sample value for each biweekly period by the total flow volume for that period. Change in water storage will be calculated by multiplying the average of the five spatial values (inflow, three interior, outflow) by the average cell depth for time t and subtracting the same product for time t-1. Seepage will be estimated by difference in the water budget. Seepage load will be calculated by multiplying the seepage flow by the spatially averaged surface water concentration. Change in surficial sediment storage will be calculated by multiplying 0.04 m by the measured bulk density and concentration of THg or MeHg at time t+1 and subtracting from that result the same product at time t. Change in vegetation storage will be calculated by multiplying the coverage (fraction of total area) and wet density (Kg/M^2) of species i by the concentration of THg or MeHg at time t+1 and subtracting from that result the same product at time t, summed over all vegetation species.

6.4.2 Mechanistic Mathematical Models

The primary synthesis tool in this study will be the mechanistic mathematical model.

6.4.2.1 Sorption Model

The sorption of inorganic mercury and methylmercury to living and nonliving particles affects their settling rates, bioaccumulation, and bioavailability to sulfate-reducing bacteria that methylate inorganic mercury and demethylate methylmercury. The inorganic mercury complexed with DOC is reduced to elemental mercury more efficiently than the dissolved ion (Zhang and Lindberg, 2001), while methylmercury complexed with DOC is generally protected from photodecomposition (Krabbenhoft et al., 2001). The apparent solid/water partition coefficient is the ratio of the concentration of the species on the solid divided by the concentration dissolved in water. The concentration on the solid phase is generally calculated by subtracting the filtered from the unfiltered concentration and dividing by the concentration of TSS. However, mercury species are also complexed with DOC, which will pass through a 0.4 micron filter. The actual partition coefficient on TSS for inorganic mercury or methylmercury can only be calculated from observed unfiltered and filtered data if its corresponding partition coefficient for DOC has been measured or vice versa, using the two-phase partition equation of the form:

$$Fd = (1+Kp \times [TSS] + KDOC \times [DOC])^{-1}$$

Where:

Fd = fraction dissolved in surface water
Fd = CD/CT
CD = concentration dissolved = difference between unfiltered and filtered
CT = concentration total = concentration unfiltered
[TSS] = concentration of total suspended solids
[DOC] = concentration of dissolved organic carbon
Kp = particle partition coefficient
KDOC = DOC complexation coefficient

However, the binding of inorganic mercury and methylmercury to the TSS and DOC organic ligands is mediated by the monovalent cation, H^+, the negative logarithm of the concentration of which is pH, divalent cations (eg., Ca^{+2}, Mg^{+2}, Fe^{+2}, Mn^{+2}), monovalent anions (e.g., Cl-, OH-), and divalent anions (e.g., $S^{=}$). A more general model for partitioning that takes such effects into account is of the form:

$$Fd = (1 + KP \times [TSS]/([pH]^a \times [Ca^{+2} + Mg^{+2}]^b \times [Cl^-]^c \times [OH^-]^d \times [Fe^{+2} + Mn^{+2}]^e) + KDOC \times [DOC]/([pH]^v \times [Ca^{+2} + Mg^{+2}]^w \times [Cl^-]^x \times [OH^-]^y \times [Fe^{+2} + Mn^{+2}]^z))^{-1}$$

When a = b = c = d = w = x = y = z = 0, the model reduces to one which is insensitive to the effects of pH, hardness, chloride, sulfide, iron, or manganese on electrostatic and coordinate covalent complexation of the sorption efficiency of particulate and dissolved organic carbon toward inorganic mercury or methylmercury. The actual particle-water partition coefficients for total mercury and methylmercury in surface water will be calculated from a best-fit, recursive analysis of all filtered and unfiltered data pairs to the following multivariate model that minimizes the root mean square error between the observed and modeled dissolved fraction.

6.4.2.2 Transport-Fate Models

A complex, dynamic mechanistic mathematical model, the Everglades Mercury Cycling Model (Version 2) or EMCM-II (TetraTech, 2002) will be applied to the problem of simulating the production, storage, and bioaccumulation of methylmercury in STA-2 Cell 1. The description of EMCM-II can be obtained from the Report: Integrating Atmospheric Mercury Deposition with Aquatic Cycling in the Florida Everglades: A Pilot Study for Conducting a Total Maximum Daily Load analysis for an Atmospherically Derived Pollutant. It will not be repeated here. Major processes involved in the mercury cycle in an Everglades marsh that are represented by the model include surface inflows and outflows, vertical groundwater flow, instantaneous mercury partitioning between some binding sites on abiotic solids and dissolved complexes, slower adsorption/desorption kinetics for Hg(II) on other sites on abiotic solids (see Appendix A), particulate settling, resuspension and burial, macrophyte related fluxes

(throughfall, litter, transpiration), atmospheric deposition, air/water gaseous exchange, in-situ transformations (e.g. methylation, demethylation, methylmercury photodegradation, Hg(II) reduction, Hg(0) oxidation), mercury kinetics in plankton, and methylmercury fluxes in fish populations (uptake via food and water, excretion, egestion, mortality, fishing). The first year of expanded monitoring will be used to initialize and calibrate the model. The calibrated model will be used to predict the effect of various site preparation, start-up, and operational alternatives on the magnitude, duration, and frequency of the first-flush pulse of excess methylmercury production.

6.4.2.3 Bioaccumulation Models

A bioenergetics-based bioaccumulation model is already incorporated into EMCM-II and will be used to ensure that primary production and carbon and energy transfer efficiencies between prey and predator set an upper bound to the maximum turnover rate of each species at each trophic level (TetraTech, 2002).

6.4.2.4 Exposure Models

6.4.3.4.1 Deterministic Formulation

The methylmercury dose rate of protected species i in age class j will be calculated using the following exposure model:

$$DRij = \sum_{ijklm} [(FSij \times CSm \times AESijm + FPij \times CPklm \times AEPijkl) \times FCTijm]$$

DRij = dose rate of protected species i in age class j
FSij = weight of sediment consumed by protected species i in age class j as a fraction of body weight
FPij = weight of prey consumed by protected species i in age class j as a fraction of body weight
FCTijm = contact time between protected species i in age class j and contaminated area m as fraction of a year
FDijklm = fraction of protected species i in age class j diet that is species k in size class l in area m
CSm = concentration of methylmercury in sediment in area m
CPklm = concentration of methylmercury in species k in size class l in area m
AESijm = absorption efficiency of methylmercury by protected species i in size class j from sediment in area m
AEPijkl = absorption efficiency of methylmercury from prey species k in size class l by protected species i in size class j

6.4.3.4.2 Probabilistic Formulation

For the probabilistic formulation of the exposure model, the single values in the above exposure equation will be replaced with a probability density function with a mean equal to the single value used in the deterministic formulation. In the absence of a well-defined pdf for a particular variable, a triangular distribution will be used, where the peak of the triangle is the mean value and the other two vertices occur at minus and plus three standard deviations of the mean value or the minimum or maximum observed value, whichever is greater. The probabilistic formulation of the exposure model will be implemented using Crystal Ball ® software or equivalent.

6.4.2.5 Risk Model

6.4.2.5.1 Deterministic Formulation

The dose rate estimated from the deterministic exposure model set forth in 4.4.2.5.1 will be divided by the measured no observable adverse effect level (NOAEL) dose rate to calculate the hazard coefficient for a particular wildlife species following USEPA protocols (USEPA 2000). Where a NOAEL for a particular receptor species is unavailable, but a lowest observable adverse effect level (LOAEL) is available, the latter will be divided by a factor of three to approximate the NOAEL. If neither a NOAEL nor a LOAEL for a particular receptor species is unavailable, the NOAEL value will be estimated by dividing the NOAEL of a related species in the same genus by a factor of three and another genus in the same family by a factor of six. If the LOAEL for a given species is unavailable, it will be calculated by multiplying the observed or estimated NOAEL by a factor of three. The mean, reasonable minimum, and reasonable maximum dose rates for the receptor species will be divided by the corresponding NOAEL and LOAEL to place the likelihood of biologically significant adverse toxic effect into perspective.

6.4.2.5.2 Probabilistic Formulation

To implement the probabilistic approach, the same protocol will be followed as in 4.2.5.6.1, except that the reasonable minimum, mean, and maximum values will be replaced by the exposure pdf. The loci where the calculated dose exceeds the NOAEL and LOAEL will be identified and the probability of exceeding that dose will be quantified to place the likelihood of biologically significant adverse toxic effect into perspective.

Task 7: Prepare Final Report

7.1 Draft Final Report

The report outline will include:

1. Executive Summary
2. Introduction
3. Background
4. Scope of Work
5. Methods and Procedures
6. Results
7. Discussion
8. Conclusions
9. Recommendations for Improved Mercury Management in STA-2 Cell 1
9. References

The Draft Final Report will be submitted for project manager review and comment within 120 calendar days of receipt of the last laboratory data report following completion of internal peer review and response to comment.

Due Date: November 30, 2003

7.2 Final Report

Due Date: January 31, 2004

Task 8: Transfer Electronic Database

Due Date: January 31, 2004

7.0 References

Ambrose, Jr., R.B. and R. Araujo. 1998. Applications of the Phase I Everglades Mercury Cycling Model. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA, at the Third Annual Everglades Mercury Workshop, Sheraton West Palm Beach Hotel, West Palm Beach, FL. May.

Amirbahman, A., A.L. Reid, T.A. Haines, J.S. Kahl, and C. Arnold. 2002. Association of methylmercury with dissolved humic acids. Environ. Sci. Technol. 36(4): 690-695

Amyot, M., D. Lean, and G. Mierle. 1997. Photochemical formation of volatile mercury in high arctic lakes. J. Environ. Toxicol. Chem. 16(10): 2054-2063.

Babiarz, C.L., J.P. Hurley, S.R. Hoffmann, A.W. Andren, M.M. Shafer, and D.E. Armstrong. 2001. Partitioning of total mercury and methylmercury to the colloidal phase in freshwaters. Environ. Sci. Technol. 35(24): 4773-4782.

Balogh, S.J., Y. Huang, M.L. Meyer, and D.K. Johnson. 2002. Episodes of elevated methylmercury concentrations in prairie streams. Environ. Sci. Technol. 36(8): 1665-1670.

Beijer, K., and A. Jernelov. 1979. Methylation of mercury in aquatic environments. In J. O. Nriagu (ed) The Biogeochemistry of mercury in the Environment. Elsevier/North Holland Biomedical Press, New York.

Benoit, J.M., C.C. Gilmour, R.P. Mason, and A. Heyes. 1999a. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Env. Sci. Technol. 33(6): 951-957.

Benoit, J.M., R.P. Mason and C.C. Gilmour. 1999b. Estimation of mercury-sulfide speciation in sediment pore waters using octanol-water partitioning and its implications for availability to methylating bacteria. J. Env. Toxicol. Chem. 8 (10): 2138-2141.

Benoit, J.M., C.C. Gilmour, and R.P. Mason. 2001. The influence of sulfide on solid-phase mercury bioavailability for methylation by pure cultures of *Desulfobulbus propionicus* (1pr3). Environ. Sci. Technol. 35(1): 127-132.

Berman, M. and R. Bartha. 1986. Control of the methylation process in a mercury-polluted aquatic sediment. Environ. Pollution (Series B) 11: 41-53.

Berthouex, P.M., and L. C. Brown. 1994. Statistics for Environmental Engineers. Lewis Publishers. Boca Raton, FL

Bodaly, R.A., R.E. Hecky and R.J.P. Fudge. 1984. Increases in fish mercury levels in lakes flooded by the Churchill River diversion, northern Manitoba. Can. J. Fish. Aquat. Sci. 41: 682.

Branfireun, B.A., N.T. Roulet, C.A. Kelly, and J.W.M. Rudd. 1999. *In situ* sulphate stimulation of mercury methylation in a boreal peatland: toward a link between acid rain and methylmercury contamination in remote environments. Global Biogeochem. Cycle 13: 743-750.

Chen, Y., J.-C. Bonzongo, W.B. Lyons, G.C. Miller. 1997. Inhibition of mercury methylation in anoxic freshwater sediment by group VI anions. J. Environ. Toxicol. Chem. 16(8): 1568-1574.

Choi, J. and J.W. Harvey. 2000. Quantifying time-varying ground-water discharge and recharge in wetlands of the northern Florida Everglades. Wetlands 20(3): 500-511.

Choi, S.-C., and R. Bartha, 1994. Environmental factors affecting mercury methylation in estuarine sediments. Bull. Environ. Contam. Toxicol. 53: 805-812.

Cleckner, L.B. P.J. Garrison, J.P. Hurley, M.L. Olson and D.P. Krabbenhoft. 1998. Trophic transfer of methylmercury in the northern Florida Everglades. Biogeochemistry 40: 347-361.

Cleckner, L. B., C. C. Gilmour, J. P. Hurley, and D. P. Krabbenhoft. 1999. Mercury methylation in periphyton of the Florida Everglades. Limno. Oceanogr. 44(7): 1815-1825.

Compeau and Bartha. 1985. Sulfate-reducing bacteria. Principal methylators of mercury in anoxic estuarine sediments. Applied Environ. Microbiol. 50: 498-502.

Craig, P.J. and P.D. Bartlett. 1978. The role of hydrogen sulphide in environmental transport of mercury. Nature. 275: 635-637.

D'Itri, F.M., C.S. Annett and A.W. Fast. 1971. Comparison of mercury levels in an oligotrophic and eutrophic Lake. J. Mar. Technol. Soc. 5(6): 10-14.

Dmytriw, A. Mucci, M. Lucotte and P. Pichet. 1995. The partitioning of mercury in the solid components of dry and flooded forest soils and sediments from a hydroelectric reservoir, Quebec (Canada). Water, Air and Soil Pollution: 1099-1103.

Dyrssen, D. and M. Wedborg. 1991. The sulphur-mercury(II) system in natural waters. Water Air Soil Poll. 56: 745-767.

Fink, L.E. 2000. ENR Project Mercury Studies: 1994-1999. Appendix 7-5. Everglades Consolidated Report. South Florida Water Management District, West Palm Beach, FL. January.

Fink, L.E. and P. Rawlik. 2000. Chapter 7: The Everglades Mercury Problem in the Everglades Consolidated Report, The South Florida Water Management District, West Palm Beach, FL. January.

Fink, L.E. 2001. The effect of surface and pore water quality on mercury bioaccumulation. Appendix 7-11 In The Everglades Consolidated Report 2001. South Florida Water Management District, West Palm Beach, Fl.

Fink, L.E. 2002. The effect of effect of dryout and rewetting on mercury bioaccumulation. Appendix 2B-3 In The Everglades Consolidated Report 2002. South Florida Water Management District, West Palm Beach, Fl.

Gerrard, P.M. and V.L. St. Louis. 2001. The effects of experimental reservoir creation on the bioaccumulation of methylmercury and reproductive success of tree swallows (Tachycineta bicolor). Environ. Sci. Technol. 35(7): 1329-1338.

Gilmour, C.C. and E.A. Henry. 1991. Mercury methylation in aquatic systems affected by acid deposition. Environ. Pollut. 71: 131.

Gilmour, C.C., E.A. Henry and R. Mitchell. 1992. Sulfate stimulation of mercury methylation in sediments. Environ. Sci. Technol. 26(11): 2281-2287.

Gilmour, C.C., G.S. Riedel, J.D. Coates, and D. Lovley. 1996. Mercury methylation by Iron (III) reducing bacteria. Am. Soc. Of Microbiology 96th General Meeting, New Orleans, LA. May 19-23. Abstract (98) O-15: 356.

Gilmour, C.C., G.S. Ridel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill and M.C. Stordal. 1998a. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry. 40: 327-345.

Gilmour, C.C., A. Heyes, J. Benoit, G. Reidel, J.T. Bell and G.Gill. 1998b. Distribution and biogeochemical control of mercury methylation in the Florida Everglades. Annual Report for 1998. Academy of Natural Sciences, Estuarine Research Center, St. Leonard, MD. Contract C-7690 with the South Florida Water Management District. June.

Gilmour, C.C., A. Heyes, J. Benoit, G. Reidel, J.T. Bell and G.Gill. 1999. Distribution and biogeochemical control of mercury methylation in the Florida Everglades. Final Report. Academy of Natural Sciences, Estuarine Research Center, St. Leonard, MD. Contract C-7690-A01 with the South Florida Water Management District. November

Hurley, J.P., D.P. Krabbenhoft, L.B Cleckner, M.L. Olson, G. Aiken and P.J. Rawlik, Jr. 1998. System controls on aqueous mercury distribution in the northern Everglades, Biogeochemistry 40: 293-311.

Henry, E.A. 1992. The role of sulfate-reducing bacteria in environmenatl mercury methylation in freshwater sediments. Ph.D. dissertaion. Harvard University. Cambridge, MA.

Guentzel, J. 1997. The atmospheric sources, transport and deposition of mercury in Florida. Ph.D. Thesis, Florida State University, Tallahassee, Florida, USA. 177pp.

Guentzel, J.L., W.H. Landing, G.A. Gill, and C.D. Pollman. 2001. Processes influencing deposition of mercury in Florida. Environ. Sci. Technol. 35: 863-873.

Guentzel, J.L., R.T. Powell, W.M. Landing, and R.P. Mason. 1996. Mercury associated with collodial material in estuarine and open-coean environment. Marine Chemistry 55: 177-188.

Gun, J., A. Goifman, I. Shkrob, J. Kamyshny, B. Ginzburg, O. Hadas, I. Dor, A.D. Modestov, and O. lev. Formation of polysulfides in an oxygen rich freshwater lake and their role in the production of volatile sulfur compounds in aquatic systems. Environ. Sci. Technol. 34(22): 4741-4746.

Hakanson, L. 1980. The quantitative impact of pH, bioproduction and Hg-contamination on the Hg- content of fish (pike). Environ. Pollut. (Series B) 1: 285-304.

Hintelmann, H., R. Ebinghaus, R-D Wilken. 1993. Accumulation of mercury(II) and methylmercury by microbial biofilms. Water Res. 27(2): 237-242.

Howard, D. 1993. Trent Uiniversity. Petersborough, Ontario, Canada. Personal communication. 20 July.

Hurley, J.P., D.P. Krabbenhoft, L.B Cleckner, M.L. Olson, G. Aiken and P.J. Rawlik, Jr. 1998. System controls on aqueous mercury distribution in the northern Everglades, Biogeochemistry 40: 293-311.

Hurley, J.P., L.B. Cleckner, and P. Gorski. 1999. Everglades Nutrient Removal Project Mosquitofish Bioaccumulation Study. Draft Report. Prepared for the South Florida water Management District, West Palm Beach, FL. Contract (PC C-8691-0300). University of Wisconsin Water Chemistry Program, Madison, WI. May.

Jay, J.A., F.M.M. Morel, and H.F. Hemond. 2000. Mercury speciation in the presence of polysulfides. Environ. Sci. Technol. 34(11): 2196-2200.

Jensen, S. and A. Jernelov. 1969. Biological methylation of mercury in aquatic ecosystems. Nature. 223: 753-754.

Johnson, R. A. and D.W. Wichern. 1988. Applied Multivariate Statistcial Analysis. Prentice-hall. Englewood Cliffs, NJ.

Kelly, C.A., J.W.M Rudd, R.A. Bodaly, N.P. Roulet, V.L. St. Louis, A Heyes, T.R. Moore, S. Schiff, R. Aravena, K.J. Scott, B. Dyck, R. Harris, B. Warner, and G. Edwards. 1997. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. Environ. Sci. Technol. 31(5): 1334-1344.

King, S.A. 2000. Mercury distribution, speciation, and transport in the Everglades Nutrient Removal treatment wetland. Ph.D. Thesis. Water Chemistry. University of Wisonsin. Masdison, WI.

Krabbenhoft, D.P., J.P. Hurley, M.L. Olson and L.B. Cleckner. 1998. Diel variability of mercury phase and species distributions in the Florida Everglades. Biogeochemistry 40: 311-325.

Krabbenhoft, D.P., L.E. Fink, M.L. Olson, and P.S. Rawlik, II. 2000. The effect of dry down and natural fires on mercury methylation in the Florida Everglades. Conference Proceedings, International Conference on Heavy Metals in the Environment, University of Michigan, Ann Arbor. August.

Krabbenhoft, D.P., C.C. Gilmour, W.H. Orem, G. Aiken, M.L. Olson, J.F. DeWild, S.D. Olund, A. Heyes, G.S. Riedel, J.T. Vbell, H. Lerch, J.M. Benoit, and S. Newman. 2001. Interfacing Process-Level Research and Ecosystem-Level Management Questions: Aquatic Cycling of Mercury in the Everglades (ACME) Phase II.

Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments. Sheraton West Palm Beach, West Plam Beach, Florida. Sponsored by the U.S. Environmental Protection Agency, Washington, DC. May 8-10, 2001.

Krabbenhoft, D.P. and L.E. Fink. 2001. The effect of dry down and natural fires on mercury methylation in the Florida Everglades. Appendix 7-8 in Everglades Consolidated Report, South Florida Water Management District, West Palm Beach, FL. January.

Lamers, L.P.M., H.B.M. Tomassen, and I. G.M. Roelofs. 1998. Sulfate induced eutrophication and phytotoxicity in freshwater wetlands. Environ. Sci. Technol. 32(2): 199-205.

Lange, T.R., D.A. Richard and H.E. Royals. 1998. Trophic relationships of mercury bioaccumulation in fish from the Florida Everglades. FINAL Annual Report. Florida Game and Fresh Water Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL. April.

Lange, T.R., D.A. Richard and H.E. Royals. 1999. Trophic relationships of mercury bioaccumulation in fish from the Florida Everglades. Annual Report. Florida Game and Fresh Water Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL. April.

Lindberg, S.E., H. Zhang and Meyers, T.P. 1999. Application of field methods and models to quantify mercury emissions from wetlands at the Everglades Nutrient Removal Project (ENR). Prepared by Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN and National Oceanic and Atmospheric Administration, ATDD, Oak Ridge, TN. Second Final Report. Everglades Mercury Air/Surface Exchange Study (E-MASE). Prepared for South Florida Water Management District, West Palm Beach, FL (C-6660). January.

Lindberg, S.E. and H. Zhang. 2000. Air/water exchange of mercury in the Everglades II: measuring and modeling evasion of mercury from surface waters in the Everglades Nutrient Removal Project. Science of Total Environ. 259: 135-143.

Lockwood, R.A. and K.Y. Chen. 1974. Adsorption of Hg(II) by ferric hydroxide. Environ. Lett. 6(3): 151-166.

Loftus, W.F., J.C. Trexler, and R.D. Jones. 1998. Mercury transfer through an aquatic food web. Report submitted by Florida International University, Miami. Florida, to the Florida Department of Environmental Protection, Tallahassee, FL.

Mauro, J. B. N., and J. R. D. Guimaraes. 1999. Hg methylation potential in aquatic macrophytes of the Everglades Nutrient Removal Area. Report to the South Florida Water Management District, W. Palm Beach

Mauro, J. B. N., J. R. D. Guimaraes, and R. Melamed. 1999. Mercury methylation in macrophytes roots in a tropical lake. Water, Air, Soil Pollution 127: 271-280.

Marvin-DiPasquale, M. C. and D.G. Capone. 1998. Benthic sulfate reduction along the Chesapeake Bay central channel. I. Spatial trends and controls. Marine Ecology Progress series. 168: 213-228.

Marvin-DiPasquale, M.C. and R.S. Oremland. 1998. Bacterial methylmercury degradation in Florida Everglades peat sediment. Environ. Sci. Technol. 32(17): 2556-2563.

Marvin-DiPasquale, M.M., J. Agee, R.S. Oremland, M. Thomas, D.P. Krabbenhoft, and C. G. Gilmour. 2000. Methylmercury degradation pathways: a comparison among three mercury-impacted ecosystems. Environ. Sci. Technol. 34: 4908-4916.

Marvin-DiPasquale, M.M., J. Agee and R.S. Oremland. 2001. Environmental controls on methylmercury production and degradation by bacteria in Florida Everglades sediments. Draft report to the South Florida Water Management District under contract C-11719 by U.S. Geological Survey, Menlo Park, CA. April.

Miles, C.J. and L.E. Fink. 1998. Monitoring and mass budget for mercury in the Everglades Nutrient Removal Project. Archives of Environ. Contam. and Toxicol. 35(4): 549-557.

Miles, C.J., H.A. Moye. E.J. Phlips, and B. Sargent. 2001. Partitioning of monomethylmercury between freshwater algae and water. Environ. Sci. Tecnol. 35(21): 4277-4282.

Newman, S. and K. Pietro. 2001. Phopshorus storage and release in response to flooding: implications for Everglades stormwater treatment area. Ecological Engineering. In Press.

Norstrom, R. J., A.E. McKinnon and A.S.W. DeFreitas. 1976. A bioenergetics-based model for pollutant accumulation by fish. Simulation of PCB and methylmercury residue levels in Ottawa River yellow perch (*Perca flavescens*). J. Fish Res. Board Can. 33: 248-267.

Olson, B.H. and R.C. Cooper. 1976. Comparison of aerobic and anaerobic methylation of mercuric chloride by San Francisco Bay sediments. 10: 113-116.

Orem, W.H., H.E. Lerch, and P. Rawlik. 1998. Geochemistry of Surface and Pore water at USGS Coring Sites in Wetlands of South Florida: 1994 and 1995. USGS Open File Report.

Oremland, R.S., C.W. Culbertson, and M.R. Winfrey. 1991. Methylmercury decomposition in sediments and bacterial cultures: involvement of methanogens and sulfate reducers in oxidative demethylation. Appl. Environ. Microbiol. 57(1): 130-137.

Pak, K. and R. Bartha. 1998. Products of mercury demethylation by sulfidgens and methanogens. Bull. Environ. Contam. Toxicol. 61: 690-694.

Paterson, M.J., J.W.M. Rudd, and V. St. Louis. 1998. Increases in total and methylmercury in zooplankton following flooding of a peatland reservoir. Env. Sci. Technol. 32(24): 3868-3874

Pickhardt, P.C., C.L. Folt, C.Y. Chen, B. Klaue, and J.D. Blum. 2002. PNAS 99(7): 4419-4423

Rodgers, D.W. 1994. You are what you eat and a little bit more: bioenergetics-based models of methylmercury accumulation in fish revisited. In C.J. Watras and J.W. Huckabee, Mercury Pollution Integration and Synthesis, Lewis Publishers, Boca Raton: 427-439.

Rodgers, D.W., M. Dickman and X. Han. 1995. Stories from old reservoirs: sediment Hg and Hg methylation in Ontario hydroelectric developments. Water, Air and Soil Pollution 80: 829-839.

Ravichandran, M., G.R. Aiken, M.M Reddy and J.N. Ryan. 1998. Enhanced dissolution of cinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades. Ennv. Sci. Technol. 32: 3205-3311.

Ravichandran, M. 1999. Interactions between mercury and dissolved organic matter in the Florida Everglades. Ph.D. Thesis. University of Colorado. Spring.

Rawlik, P. 2001a. Mercury concentrations in mosquitofish from treatment wetlands in the northern Everglades. Appendix 7-15 In The Everglades Consolidated Report 2001. South Florida Water Management District, West Palm Beach, Fl.

Rawlik, P. 2001b. Stormwater Treatment Area 1 West: results of start-up mercury monitoring. Appendix 7-14 In The Everglades Consolidated Report 2001. South Florida Water Management District, West Palm Beach, Fl.

Reddy, M.M., G. Aiken, P.F. Schuster. 1999. Hydroperiod-Driven Solute Transport at the Peat-Water Interface in the Florida Everglades: Hydrophobic Acid Diffusion from Peat. Unpublished Mansucript. U.S. Geological Survey, Boulder, CO. June.

Riddle, S.G., H.H. Tran, J.G. Dewitt, and J.C. Andrew. 2002. Filed, laboratory, and X-ray absorption spectroscopic studies of mercury accumulation by water hyacinth. Environ. Sci. Technol. 36(9): 1965-1970.

Rumbold, D.G. 2000. Methylmercury risk to Everglades wading birds: a probabilistic ecological risk assessment. Appendix 7.3b In Everglades Consolidated Report 2000. South Florida Water Management District, West Palm Beach, Fl.

Rumbold, D.G., L. Fink, K. Laine, F. Matson, S. Niemczyk, and P. Rawlik. 2001a. Annual permit compliance monitoring report for mercury in Stormwater Treatment Areas and downstream receiving waters of the Everglades Protection Area. Appendix 7-9 In The Everglades Consolidated Report 2001. South Florida Water Management District, West Palm Beach, Fl.

Rumbold, D.G., L. Fink, K. Laine, F. Matson, S. Niemczyk, and P. Rawlik. 2001b. Stormwater Treatment Area 6 follow-up mercury studies. Appendix 7-13 In The Everglades Consolidated Report 2001. South Florida Water Management District, West Palm Beach, Fl.

SFWMD. 1995. Everglades Nutrient Removal Project: 1994 Monitoring Report. South Florida Water Management, Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.

SFWMD. 1996. Everglades Nutrient Removal Project: 1995 Monitoring Report. South Florida Water Management, Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.

SFWMD. 1997. Everglades Nutrient Removal Project 1996 Monitoring Report. South Florida Water Management District, West Palm Beach, FL. March.

SFWMD. 1998. Everglades Nutrient Removal Project 1999 Monitoring Report. South Florida Water Management District, West Palm Beach, FL. March.

SFWMD. 1999a. Everglades Nutrient Removal Project 1998 Monitoring Report. South Florida Water Management District, West Palm Beach, FL. March.

SFWMD. 1999b. Final Report on the Effect of Best Management Practices on the Loading of Mercury Species to/from the Everglades Nutrient Removal Project: Monitoring Program (Project C-1). Submitted by the South Florida Water Management District, West Palm Beach, Florida, to the Floirda Department of Environmental Protection, Tallahassee, Florida, to fulfill the requirements of a Section 319 Grant (SP335/C-6663/4) from U.S. Environmental Protection Agency Region 4, Atlanta, GA.

St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, N.S. Bloom and R.J. Flett. 1994. The importance of wetlands as sources of methylmercury to boreal forest ecosystems. Can. J. Fish. Aquatic Sci. 51: 1065-1076.

St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, R.J. Flett, and N.T. Roulet. 1996. Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. Environ. Sci. Technol. 30(9): 2719-2729.

Saouter, E., M. Gillman, R. Turner, and T. Barkay. Development and field validation of a microcosm to simulate the mercury cycle in a contaminated pond. Environ. Toxicol. Chem. 14(1): 69-77.

Scruton, D.A., E.L. Petticrew, L.J. LeDrew, M.R. Anderson, U.P. Williams, B.A. Bennett and E.L. Hill. 1994. Methylmercury levels in fish tissue from three reservoir systems in insular Newfoundland, Canada. In C.J. Watras and J.W. Huckabee, Mercury Pollution Integration and Synthesis, Lewis Publishers, Boca Raton: 441-455.

Sellers, P., C.A. Kelly, J.W.M. Rudd, A.R. MacHutchon. 1996. Photodegradation of methylmercury in lakes. Nature 380(25): 694-697.

Snedecor, G.W. and W.G. Cochran. 1980. Statistical Methods. 7th Ed. The Iowa State University Press, Ames, IW

Sokal, R.R. and F.J. Rohlf. 1973. Introduction to Biostatistics. W.H. Freeman. San Francisco.

Vaithiyanathan, P., C. J. Richardson, R, G. Kavanaugh, C. B. Craft and T. Barkay, 1996. Relationships of eutrophication to the distribution of mercury and the potential for methylmercury production in the peat soils of the Everglades. Environ. Sci. Technol. 30(8): 2591-2597.

Vandal, G.M., R.P. Mason and W.F. Fitzgerald. 1991. Cycling of Volatile Mercury in Temperate Lakes. Water, Air and Soil Pollution 56:791-803.

Vandal, G.M., W.F. Fitzgerald, K.R. Rolfhus and C.H. Lamborg. 1995. Modeling the elemental mercury cycle in Pallette Lake, Wisconsin, USA. Water, Air and Soil Pollution 80: 529-538.

Wolfe, M.F., D.M. Norman, R. Sulaiman. 1994. Mercury monitoring in wetlands birds and mammals at Clear Lake, CA. Toxicology Task Force, Seattle, WA.

Wood, J.M, F.S. Kennedy, and C.G. Rosen. 1968. Synthesis of methylmercury compouns by extracts of methanogenic bacterium. Nature. 220: 173-174.

Xia, K, U.L. Skyllberg, W.F. Bleam, P.R. Bloom, E.A. Nater and P.A. Helmke. 1999. X-ray absorption spectroscopic evidence for the complexation of Hg(II) by reduced sulfur in soil humic substances. Env. Sci. and Technol. 33(5): 786-795.

Yin, Y. H.E. Allen, and C.P. Huang. Kinetics of mercury (II) adsoprtion and desorption on soil. Environ. Sci. Technol. 31(2): 496-503.

Zhang, H. and S.E. Lindberg. 2000. Air/water exchange of mercury in the Everglades I: the behavior of dissolved gaseous mercury in the Everglades Nutrient Removal Project. Science of Total Environ. 259: 135-143.

8.0 Appendices

- 8.1 SOP for Surface Water Collection [See Appendix B]
- 8.2 SOP for Pore Water Collection [See Appendix B]
- 8.3 SOP for Soil/Sediment Collection [See Appendix B]
- 8.4 SOP for Vegetation Collection [See Appendix B]
- 8.5 SOP for Fish Collection [See Appendix B]
- 8.6 Draft WO for Expert Assistance for Pore Water Method Acquisition

WATER RESOURCES EVALUATION DEPARTMENT
REQUEST FOR EXPERT ASSISTANCE

Tracking Information:

RFA Number:

Requesting Professional: Larry E. Fink

Project Name: Pore Water Sampling Method Development/Adaptation and Technology Transfer for Ultra-Trace Mercury, Sulfur Species, and Redox Analyses

Date: **0901802**

Area of Expertise Requested: Methods Adaptation and Technology Transfer for the Collection of Pore Water from Everglades Surficial Sediments for Ultra-Mercury, Sulfur, and Iron Speciation and Quantitation

Introduction/Background:

Pursuant to the mercury compliance conditions in state and federal permits to operate each Stormwater Treatment Areas (STA), the District has collected soil, water, and fish at designated sites and frequencies. Prior to start-up and triennially thereafter, six, 10-cm cores of peat soil from the interior of each STA. During start-up, unfiltered water samples for ultra-trace analysis of total mercury and methylmercury were collected at the inflow and a representative interior site. If the interior concentrations of THg and MeHg are not significantly greater than the corresponding inflow concentrations, operation may commence. Thereafter, inflow and outflow water samples are collected quarterly and inflow, interior, and outflow mosquitofish, sunfish, and bass are collected semi-annually, annually, and annually, respectively. In addition, if the concentrations of water, soil, or fish are anomalously high relative to the Everglades Nutrient Removal (ENR) Project, the District is required to report this situation to FDEP immediately. Following start-up of STA-2 in July 2000, Cell 1 exhibited anomalous mercury behavior and, as of mid-April 2001, had still not met its mercury start-up criteria. Expanded monitoring of STA-2 Cell 1 beginning in October 2000 and ending in March 2001 demonstrated that, while methylmercury water concentrations had declined to low levels, methylmercury as total mercury in mosquitofish continued to climb to levels higher than the average concentration measured at WCA-3A-15, the Everglades "hot spot." Cell 2 exhibited water concentrations not much different than those in Cell 1, but soil levels rose to a bulk density-weighted average concentration only about one-third to one-fourth that in Cell 1, while mosquitofish concentrations rose to an average of only about 100 ug/Kg. This concentration is only about one-third to one-fourth the average concentration in Cell 1 and about equal to the average concentration in mosquitofish collected at WCA-2A-U3. The District's

probabilistic ecological risk assessment for WCA-2A-U3 (Rumbold et al., 2001) concludes that the risks to fish-eating wildlife are not likely to be unacceptable, while the risks to fish-eating wildlife foraging preferentially at WCA-3A-15 could represent an unacceptable risk to sensitive members of sensitive species populations, including the great egret. This conclusion is supported by site-specific great egret epidemiological studies (Purefoy et al., 1997).

Further study of the biogeochemical evolution of Cell 1 vs Cell 2 is required to understand why these differences exist and persisted and what can be done, if anything, to prevent or minimize the build-up of anomalously high methymercury concentrations in water, soil, and fish in STA-2 Cell 1 and other STAs during start-up from dry soil conditions. Although follow-up expanded monitoring has enhanced our understanding of what was happening, it did not enhance our understanding of why it was happening. Methylmercury production and bioaccumulation has been strongly linked to the sulfur biogeochemical cycle and, more particularly, the concentrations of sulfate and sulfide in surficial peat soil pore water. To better understand why STA-2 Cell 1 is very different from STA-2 Cell 2 in terms of methylmercury production and bioaccumulation, there is a need to monitor surface water chemistry, pore water chemistry, and their interaction and evolution over time following reflooding. Because there are no USEPA-promulgated or FDEP-approved methods for carrying out pore water monitoring for sulfide and ultra-trace mercury analysis, it must necessarily be carried out outside the federal and state permits for operating STA-2. Because the District lacks the resources to carry out such a study, it must be carried out by outside contractors. This can best be carried out using experts with experience in monitoring sulfur and mercury speciation in water, soil, and pore water as a function of environmental conditions and factors. This scoping study will assist in determining whether or how to carry out a full-scale study of mercury and sulfur pore water chemistries in STA-2 Cells 1, Cell 2, and Cell 3.

Scope of Work - Duties and Tasks of Expert

The purpose of this pilot study is to: (1) modify and adapt an existing pore water sampling technology to Everglades conditions for the collection of a representative, valid sample of pore water from the top 5 cm of surficial soil in such a way that redox potential is preserved and in sufficient volumes for the analysis of ultra-trace total mercury and methylmercury, sulfate and sulfide, common anions and cations, Fe(II)/Fe(II), pH, redox, and Mn(II)/Mn(III); (3) field-validate the modified/adapted method; (4) prepare SOP and supporting validation package; and (5) transfer the field-validated technology to District and contractor staff in a timely fashion.

Description of Expert Assistance by Task

Task 1. Field Reconnaissance Trip

Task 1.1 Pre-Trip Conference Call

After issuance of the WO to the selected Expert, he or she will participate in a conference call with the District's Project Manager and such other staff as he shall designate to discuss the scope, schedule, and upcoming field recon trip.

Deliverable: Expert's Participation in Conference Call
Due Date: November 15, 2002

Task 1.2 Field Trip

The Expert shall meet with District staff at the Field operations Center and accompany them into field to evaluate the District's needs, taking into account preservation of redox potential, avoidance of contamination with ultra-trace total mercury (THg) or methylmercury (MeHg), required pore water volumes, soil physical and chemical characteristics, environmental conditions, and method application logistics challenges. Based on this field reconnaissance trip, the Expert shall prepare a letter report summarizing what existing equipment or modifications thereto are most likely to meet the District's needs.

Deliverable: Expert's Field Recon Letter Report
Due Date: November 15, 2002

Task 1.3. Post-Trip Conference Call

Following the first field recon trip, the Expert shall discuss the contents of his or her Letter Report with the Project Manager and such other external and internal individuals as he deems appropriate, focusing on the recommended existing or modified equipment for the collection of pore water for redox, sulfide, Fe(II)/Fe(III), Mn(II)/Mn(III) and ultra-trace mercury analysis. The Expert shall also discuss his or her plan and schedule for the second field trip for testing the existing or modified equipment appropriate for this application.

Deliverable: Expert's Participation in Conference Call
Due Date: by November 22, 2002

Task 2 Expert Constructs or Modifies Required Pore Water Sampling Equipment

Following discussions with the District in the Conference Call, the Expert shall construct or modify existing pore water sampling equipment capable of collecting a sufficient, representative, valid sample of pore water from surficial soil or sediment so as to preserve redox conditions for subsequent analysis for sulfide, Fe(II)/Fe(III), and with the cleanliness required for ultra-trace mercury sample collection.

Deliverable: Letter Report with Photo of Finished Apparatus
Due Date: December 16, 2002

Task 3. Field Testing of Modified Apparatus and Method

Task 3.1 Prepare Field Test Plan

The Expert shall prepare a draft field test plan to fully evaluate the capability of the pore water sampling apparatus to meet the District's performance specifications. The District will review and comment on the draft test plan. The Expert shall explain the reason for rejecting any of the District's recommendations in a Letter Report accompanying the Final Field Test Plan.

Deliverable: Draft Field Test Plan
Due Date: January 03, 2003

Deliverable: Final Field Test Plan
Due Date: January 10, 2003

Task 3.2 Field Test Plan Implementation

On the second field trip, the Expert shall fully test the candidate pore water collection apparatus at a variety of sites to fully exercise the method. Based on the results of the field test, the Expert shall recommend adopting the method as is, further modifying the method for re-testing, or seeking an alternative method due to unforeseen circumstances.

Deliverable: Letter Report on Field Test Plan Findings, Conclusions, and Recommendations
Due Date: by January 31, 2003

Task 3.3. Apparatus Modifications

Due Date: by February 21, 2003

Task 3.4 Field Testing of Further Modified Apparatus

Deliverable: Letter Report
Due Date: by February 28, 2003

Task 3.5 Obtain District Approval

Deliverable: District Approval
Due Date: by March 14, 2003

Task 3.6 Prepare SOP and Supporting Documentation

Deliverable: SOP and Supporting Documentation
Due Date: March 28, 2003

Task 4. Obtain DEP Approval of Pore Water Sampling Method in Principle

Deliverable: FDEP Approval
Due Date: April 25, 2003

Task 5. Technology Transfer

Task 5.1 Prepare Instruction Manual for Technology Transfer

The Expert shall prepare an instruction manual for teaching District and contractor technicians how to implement the modified pore water sampling method.

Task 5.2 Teach Class

The Expert shall travel to West Palm Beach and train select District staff in the collection of surficial sediment pore water under anaerobic conditions for quantitation of various redox sensitive analytes, as well as ultra-trace THg and MeHg. The Expert shall prepare a training manual and schedule, including a "dry lab" session at the Field Operations Center to familiarize staff with the equipment and its proper cleaning, use, and maintenance and two field days in which to evaluate staff performance under real field conditions. The field study will be carried out at STA-2 in Cells 1 and 2, if possible, to ensure that the device and method are appropriate to the compact soils there. Pore water samples will be collected and analyzed for redox, pH, ultra-trace THg and MeHg, sulfide, DOC, and Fe(II).

Deliverable: Training of District Staff
Due Date: By April 15, 2003

Task 5.3 Test Students for Certification

Deliverable: Training and Certification
Due Date: by April 25, 2003

Task 1. First Field Recon Trip

Task 2. Modify an Existing Pore Water Collection Device and Method for Pore Water Collection that Preserves Anaerobic Conditions and Mercury-Free Materials for Ultra-Trace Mercury Quantitation

The Expert shall modify an existing pore water collection apparatus and method for the collection of a representative, valid sample of surficial (0-5 cm) sediment pore water in such a way that redox potential is preserved and in sufficient volume to support ultra-trace analysis of THg and MeHg and trace analysis of other common anions and cations, as well as redox, pH, sulfide, and Fe(II)/Fe(III) and Mn(II)/Mn(III). This equipment shall become the property of the District following completion of the training session in Task 4.

Deliverable: Letter Report 1 Describing Existing Equipment and Method Modification
Due Date: By December 31, 2002

Task 3. Field-validate Modified Method

Task 4. Prepare SOP and Supporting Method Validation Package

The Expert shall prepare a Standard Operating Procedure for the modified pore water sample collection apparatus and method following the District format and an accompanying validation package containing a letter report explaining and justifying the modifications to the equipment and procedures and demonstrating the validity of the method relative to the performance of centrifugation under mercury-free, oxygen-free conditions.

Deliverable: SOP and Supporting Method Validation Package
Due Date: By March 30, 2003

Task 5. Train District Staff in Soil and Pore Water Collection under Anaerobic Conditions for Sulfur Speciation using Modified Equipment and Method

Task 4. Carry Out a Follow-Up Evaluation of District Staff performance

The Expert will return to the District twice thereafter to evaluate District staff performance by carrying out side-by-side sample collection with District staff.

Deliverable: Letter Reports 2 and 3 with Expert's and District's Pore Water and Soils Data and Evaluation of District Staff Performance
Date Due: By October 1, 2001, and November 1, 2001

Task 5. Prepare Final Report

The Expert will summarize the speciation of sulfur under the influence of controlling soil and pore water chemistries in STA-2 Cells 1 and 2 and attempt to explain the cause of the differences in sulfur biogeochemical dynamics between Cells 1 and 2 in terms of a conceptual model of sulfur speciation that accounts for sorption, complexation, precipitation processes in terms of appropriate chemical equilibria and kinetics as a function of redox potential, pH, ionic strength, dissolved and solid organic carbon content, and temperature of the key physical, chemical, and biological processes and sources.

Deliverable: Final Report
Date Due: By December 1, 2001

Responsibilities of Requesting Division:

The Project Manager for this RFA is Larry Fink of the Hydro and Information Resources Department, Environmental Monitoring and Assessment Division. Mr. Fink will be available to answer questions that the Expert may have in order to clarify any areas that Expert does not understand. The Project Manager will provide the Expert with the reports and data listed in Attachment 1 required to complete Tasks 1-5. The District will reimburse the Expert at the standard District rate for labor for training, chemical analysis, and data analysis, integration, synthesis, and presnetation, the cost of three trips to West Palm Beach to fulfill the requirements of Tasks 1-5, and incidental costs for copying and mailing of letter reports.

Evaluation Criteria for Acceptance of Deliverables:

Acceptability of the letter reports will be based on the scientific insight, completeness, and accuracy in the formulation of the problem, the completeness and accuracy of the conceptual model of mercury biogeochemistry in STA-2 Cells and 2 applied to the problem, the appropriateness of methods used in data reduction, analysis, synthesis and integration, the quality of the presentation of the data, and the clarity and conciseness of the Expert's writings on the subject.

Summary of Time Line and Responsibilities

Task	Responsible Party	Due Date
Task 1. Conference Call Deliverable: Participate in Conference Call	Expert and District	By August 9, 2001
Task 2. Modify Equipment and Methods Deliverable: Letter Report 1	Expert	By August 25, 2001
Task 3. Train District Staff in Modified Equipment and Method Deliverable: Letter Report 2	Expert	By September 1, 2001
Task 4. Follow-Up Monitoring Deliverable: Letter Reports 3 and 4	Expert	By October 1, 2001 and November 1, 2001
Task 5. Prepare Final Report Deliverable: Final Report	Expert	December 1, 2001

Attachment I

I. List of Background Materials

1. Everglades Mercury Monitoring Plan
2. Everglades Compliance Quality Assurance Project Plan
3. 1998 Combined Compliance Report
4. 1999 Combined Compliance Report
5. Water Quality Data Excel Spreadsheets
6. Everglades Mercury Baseline Report
7. Compliance Contingency Plan Discussion

Appendix B. Standard Operating Procedures for Implementing the STA-2 Mercury Special Studies Project

Appendix C. Plan of Study for STA-2 Modified *In Situ* Pore Water Collection Method Validation

Statement of Work

TIER 1 PORE WATER SAMPLING METHOD PILOT STUDY
FINAL 082103

INTRODUCTION

This is the Statement of Work (SOW) for the Tier 1 Pore Water Sampling Method Pilot Study set forth in the Plan of Study for Mercury Special Studies in Stormwater Treatment Area 2 (STA-2). The Pilot Study is necessitated by the absence of a practicable, on-site method of valid pore water collection under oxygen-free conditions for subsequent analysis of ultra-trace mercury species and other redox-sensitive analytes. The work will begin as soon as possible but no later than September 22, 2003, and be completed by January 31, 2003. The report on the validation of the alternative method for mercury ultra-clean, oxygen-free pore water sampling (modified sipper) will be submitted by the District to the Florida Department of Environmental Protection (FDEP) for review and approval of the modified sipper method pursuant to the requirements set forth in C-11900-A03 and MOA C-13812.

2. SCOPE OF WORK

The Contractor shall review the results of the soil core characterization study carried out under another contract to determine the number of replicate 4-cm cores that must be collected to generate sufficient pore water volume to support replicate on-site analysis of pH and redox and off-site analysis of THg, MeHg, $S^{=}$, $SO4^{=}$, $Fe(II)^{+2}$, $Fe(III)^{+3}$, TMn, DOC, Ca^{+2}, Mg^{+2} and Cl^{-} in that order and whether any modifications will be required to the standard soil sampling or soil sample centrifugation method for pore water extraction to accommodate site-specific conditions.

The Contractor shall set up the portable laboratory for mercury ultra-clean, oxygen-free extraction of pore water from soil cores collected at STA-2 on-site according to the approved SOP to implement the Preferred Method. The Contractor shall process a sufficient number of 4-cm soil cores at STA-2 Site C1C for n = 11 replicate extractions and analyses to evaluate the validity of the proposed alternative field pore water sampling method (*in situ* sipper method) for the replicate on-site analysis of pH and redox and replicate off-site analysis of THg, MeHg, $S^{=}$, $SO4^{=}$, $Fe(II)^{+2}$, $Fe(III)^{+3}$, TMn, DOC, Ca^{+2}, Mg^{+2} and Cl^{-} in that order. Based on the amount of pore water provided, the analytical laboratory shall analyze the sample once through in constituent priority order, repeat any analyses failing QC, and then repeat the analyses in the same priority order with the remaining sample volume until the sample is exhausted.

The Contractor shall arrange for an objective, acknowledged expert in the field of mercury ultra-clean pore water extraction to review and comment on the SOPs and the results of the validation study for the alternative pore water collection method.

The Contractor shall collect a sufficient number of 4-cm soil cores at each of the n = 9 sites identified in the Plan of Study for STA-2 Mercury Special Studies, extract sufficient pore water volume using mercury ultra-clean, oxygen-free technique, conduct replicate analyses for pH and redox potential on-site and appropriately complex, stabilize, or preserve the remaining samples, and transmit the appropriate sample sets on blue ice to each of the designated off-site analytical laboratories for the analysis of THg, MeHg, $S^{=}$, $SO4^{=}$, $Fe(II)^{+2}$, $Fe(III)^{+3}$, TMn, DOC, Ca^{+2}, Mg^{+2} and Cl^{-} in that order. Based on the amount of pore water provided, the analytical laboratory shall analyze the sample once through in constituent priority order, repeat any analyses failing QC, and then repeat the analyses in the same priority order with the remaining sample volume until the sample is exhausted.

STA-2 is located on the northwestern edge of Water Conservation Area 2A (WCA-2A) and consists of the three parallel treatment cells totaling about 6,100 acres. The Project Manager will supply information regarding the distance from the Ft. Lauderdale airport to the S-6 Pump Station, from the S-6 Pump Station to each sampling entry point in STA-2, travel times to and from sampling sites from sampling entry points, and other access and logistics information required for purposes of estimating the travel and sampling labor costs associated with this SOW. The Contractor will base the labor and time requirements to process soil samples delivered to the mobile laboratory based on past experience. The cost of pore water sample shipping and analysis will be borne by the District under other contracts with the specified overnight carriers and recipient laboratories.

To qualify for this SOW, the Contractor must meet all of the following criteria:
(1) has extensive experience in developing, documenting, and implementing methods for ultra-clean mercury species sampling for ultra-trace analysis adopted by USEPA and/or FDEP (Bloom, 1989; Bloom et al., 1995a,b; 1997; 1999);
(2) has participated in an inter-comparison of the mercury ultra-clean pore water sampling method via oxygen-free centrifugation with the sipper, squeezer, and equilibrator ("peeper") methods (Mason et al., 1998);
(3) has published its pore water extraction method in the peer-reviewed scientific literature (Mason et al., 1998);
(4) has extensive experience in analyzing the unique surface water and peat soil samples typical of the Everglades;
(5) has been recently audited by the District;
(6) offers services for both mercury ultra-clean soil sample collection and sample processing for pore water extraction in an oxygen-free environment;
(7) due to the tight schedule for completing this project, is ready to initiate this study within the next six weeks; and
(8) has the approval of the FDEP Project Manager for C-11900-AO3.

These criteria necessitate that the prime contractor will carry out this work using a subcontractor approvable by the District.

3. WORK BREAKDOWN STRUCTURE

TASK 1 - Prepare SOP for Peat Soil Sampling for Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction

1.1 Adaptation of Soil Sampling Scheme to Meet Ultra-Trace Mercury, Redox, and Pore Water Volume Requirements

The District's Project Manager will supply the Contractor with a table of pore water volume requirements for each of the analysis of each of the specified analytes. The Contractor shall review the results of the soil core characterization study carried out under another contract to determine:

(1) the number of replicate 4-cm cores that must be collected to generate sufficient pore water volume to support replicate analysis of pH, redox, $Fe(II)^{+2}/Fe(III)^{+3}$, $Mn(II)^{+2}/Mn(III)^{+3}$, $SO4^{=}$, $S^{=}$, THg, MeHg, Ca^{+2}, Mg^{+2}, Cl^{-}, and DOC; and

(2) whether any modifications will be required to the standard soil sampling or soil sample centrifugation method for pore water extraction to (a) prevent contamination per ultra-trace mercury analysis; (b) prevent compromising redox conditions in the core; and (c) to accommodate site-specific conditions of bulk density, moisture content, and soil structure (e.g., roots and debris).

1.2 Draft SOP

The Contract shall prepare a Draft SOP for Field Soil Sample Collection for Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction via Soil Centrifugation based on the validated field pore water collection method following as a model the organization, content, detail, person, tense, and tone of the District model SOP in Appendix 1.

1.3 Final SOP

The draft SOP will be reviewed by the District Project Manager and such other District and non-District staff as he shall designate for that purpose. The Contractor shall make the required changes to the draft document in response to the comments transmitted by the District's Project Manager. The Contractor shall deliver the revised SOP as the Final SOP for Field Soil Sample Collection for Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction via Soil Centrifugation. Thereafter, the District staff will conform to this SOP for all soil sampling required to implement this WO SOW.

TASK 2 - Prepare SOP for Set-Up of Portable Lab for Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction via Soil Centrifugation

2.1 Draft SOP

The Contract shall prepare a Draft SOP for Set-Up of Portable Lab for Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction via Soil Centrifugation based on the validated field pore water collection method following as a model the organization, content, detail, person, tense, and tone of the SOP in Appendix 1.

2.2 Final SOP

The draft SOP will be reviewed by the District Project Manager and such other District and non-District staff as he shall designate for that purpose. The Contractor shall make the required changes to the draft document in response to the comments transmitted by the District's Project Manager. The Contractor shall deliver the revised SOP as the Final SOP for Set-Up of Portable Lab for Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction via Soil Centrifugation.

TASK 3 - Prepare SOP for Peat Soil Centrifugation for Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction in Portable Lab Environment

3.1 Draft SOP

The Contract shall prepare a Draft SOP for Peat Soil Centrifugation for Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction in Portable Lab Environment based on the validated laboratory pore water extraction method following as a model the organization, content, detail, person, tense, and tone of the SOP in Appendix 1.

3.2 Final SOP

The draft SOP will be reviewed by the District Project Manager and such other District and non-District staff as he shall designate for that purpose. The Contractor shall make the required changes to the draft document in response to the comments transmitted by the District's Project Manager. The Contractor shall deliver the revised SOP as the Final SOP for Peat Soil Centrifugation for Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction in Portable Lab Environment

TASK 4 - Prepare SOP for Stabilization/Preservation of Redox-Sensitive Analytes in Mercury Ultra-Clean, Oxygen-Free Portable Lab Environment

4.1 Draft SOP

The Contractor shall prepare a Draft SOP for Stabilization/Preservation of Redox-Sensitive Analytes in Mercury Ultra-Clean, Oxygen-Free Portable Lab Environment

based on the validated laboratory pore water extraction method and the procedures outlined in Appendix 2, but following as a model the organization, content, detail, person, tense, and tone of the SOP in Appendix 1.

4.2 Final SOP

The draft SOP will be reviewed by the District Project Manager and such other District and non-District staff as he shall designate for that purpose. The Contractor shall make the required changes to the draft document in response to the comments transmitted by the District's Project Manager. The Contractor shall deliver the revised SOP as the Final SOP for the Stabilization/Preservation of Redox-Sensitive Analytes in Mercury Ultra-Clean, Oxygen-Free Portable Lab Environment.

Task 5 - Purchase Equipment

The Contractor shall purchase the capital equipment and disposable supplies required to implement the centrifugation method of pre water collection in STA-2 soils under this contract. All other reusable equipment, sampling bottles, coring devices, shall be provided by the Contractor at no additional cost to this WO. Following completion of the study but prior to contract WO expiration, the Contractor shall transfer to the District physical control of and title to the capital equipment in a clean condition and in good working order, along with any unused disposable supplies purchased under this contract WO.

TASK 6 - Secure Portable Lab Space

The Contractor shall make arrangements to secure a mobile laboratory or equivalent to accommodate the space, water, sewer, and electrical requirements for the portable laboratory for mercury ultra-clean, oxygen-free pore water extraction from soil using centrifugation. One of the following options is acceptable:

(1) Use an existing air-conditioned, mercury-free mobile laboratory owned by the Contractor or its subcontractor that can accommodate the portable mercury ultra-clean, oxygen-free glove bag, soil core rack, centrifuge, centrifuge tube rack, sample bottle rack, syringe rack, pipette rack, compressed nitrogen gas tank and regulator, and such other equipment and supplies as will be required to perform this method in the required manner with the required outcome; or
(2) Rent an air-conditioned camper with sink, electricity, and benchtop space to accommodate the equipment and its space-filling configuration per the requirements set forth in (1).

TASK 7 - Train Contractor Staff in Adapted/Modified Soil Core Field Sampling to support Mercury Ultra-Clean, Oxygen-Free Portable Lab for Pore Water Extraction via Centrifugation

The Contractor shall provide each of three field sampling crew Trainees with the approved SOP for field sample collection of soil cores for mercury ultra-clean, oxygen-free pore water extraction. The Contractor shall train each of three Trainees to implement the SOP with the required technique.

TASK 8 - Set Up Mercury Ultra-Clean, Oxygen-Free Portable Lab

The Contractor shall set up the portable laboratory for mercury ultra-clean, oxygen-free pore water extraction via centrifugation according to the approved SOP in a mobile laboratory or camper-equivalent. The required information shall be recorded in the appropriate field and laboratory notebooks.

TASK 9 - Collect Test Peat Cores according to Appropriate SOP for Side-by-Side Validation of In Situ Pore Water Sipper Method with Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction via Centrifugation

Task 9.1 Following the Modified Soil Coring SOP for Redox Preservation, Carefully Emplace n = 14 Soil Coring Tubes Randomly within a One (1) Square Meter Area, Cap the Coring Tubes, and Press The Coring Tubes that Fall Within the Footprint of the In Situ Sipper Disk Uniformly Down to the Level of the Soil Horizon.
Task 9.2 Hang/Place the Appropriate Weights on the In Situ Sipper to Achieve a Standardized Force Per Unit Area of 25 Kg/M2
Task 9.3 Collect the Pore Water Volumes for Each Analyte and Preserve as Identified in Appendix 2.
Task 9.4. Following the Completion of the Collection of the Pore Water Using the Sipper Method, Remove the Emplaced Peat Soil Cores
Task 9.5 Collect n = 14 Replicate Peat Soil Cores (4-cm depth) from Site C1C for Validation Study according to the approved SOP within a 1 square meter area
Task 9.6 Combine and Composite the Peat Soil From All Cores in a Mercury Ultra-Clean Environment under Nitrogen in the Glovebox
Task 9.7 Extract the Pore Water from n = 11 Randomly Selected Composite Sub-Samples via Centrifugation in an Mercury Ultra-Clean, Oxygen-Free Environment in the Portable Lab for Validation Study
Task 9.8 Stabilize/Preserve $Fe(II)^{+2}$ and $S^{=}$ On-Site in the Mercury Ultra-Clean, Oxygen-Free Environment in the Portable Lab for Off-Site Chemical Analysis for Validation Study
Task 9.9 Transmit Stabilized/Preserved Samples to Specified Labs under Specified Conditions within Field Holding Time via Overnight Carrier
Task 9.10 Perform QC Review of Analytical Results
Task 9.11 Quantify Bias and Precision of Adapted/Modified Standard Method Using appropriate Parametric and Non-Parametric Statistics
Task 9.12 Document Results, Findings, Conclusions, and Recommendations for Further Modifying/Adapting the Equipment and/or Method

The required information shall be recorded in the appropriate field and laboratory notebooks.

TASK 10 - Collect Peat Cores according to Appropriate SOP for Pore Water Sample Collection by Mercury Ultra-Clean, Oxygen-Free Pore Water Extraction via Centrifugation at 10 STA-2 Interior Sites

Task 10.1 Site C1C Replication Study

At STA-2 Site C1C, the Contractor shall collect three replicates of a sufficient number of 4-cm cores according to the SOP prepared per Task 1 and the training obtained in Task 7 to generate the requisite pore water volumes specified in Appendix 2 for the requisite chemical analyses identified in Table 1. In the portable laboratory set up with the requisite equipment according to the protocols set forth in the SOP prepared per Task 2, the soil cores shall be physically combined, homogenized, and placed into centrifuge tubes and sealed under a positive pressure nitrogen atmosphere in the glove box according to the protocols set forth in the SOP prepared per Task 3. The sealed tubes shall then be centrifuged according to the protocols set forth in the SOP prepared per Task 3. The sealed tubes shall be returned to the glove box under positive pressure nitrogen gas, unsealed, and the pore water filtered through a 0.4 micron filter or smaller according to the protocols set forth in the SOP prepared per Task 3. The requisite volumes of filtered pore water as set forth in Appendix 2 shall then be distributed into appropriate sample containers, appropriately preserved per Appendix 2, sealed, and labeled prior to removal from the glove box under positive nitrogen pressure. The labeled samples shall be transmitted to the appropriate labs identified in Table 1, either directly for those constituents being analyzed by the District's laboratory, or, in the case of ultra-trace THg and MeHg, via an overnight carrier to Frontier Geosciences in Seattle, WA.

The appropriate data and metadata shall be recorded in the appropriate field and laboratory notebooks dedicated to this study.

Task 10.2 One-Time Soil sampling Campaign for Pore water Extraction via Centrifugation

At STA-2 Sites C1AA, C1BB, and C1CC, Sites C2A, C2B, and C2C, and C3A, C3B, and C3C, the Contractor shall collect one set of a sufficient number of 4-cm cores according to the SOP prepared per Task 1 and the training obtained in Task 7 to generate the requisite pore water volumes specified in Appendix 2 for the requisite chemical analyses identified in Table 1. In the portable laboratory set up with the requisite equipment according to the protocols set forth in the SOP prepared per Task 2, the soil cores shall be physically combined, homogenized, and placed into centrifuge tubes and sealed, all under a positive pressure nitrogen atmosphere in the glove box according to the protocols set forth in the SOP prepared per Task 3. The sealed tubes shall then be centrifuged according to the protocols set forth in the SOP prepared per Task 3. The sealed tubes shall be returned to the glove box under positive pressure nitrogen gas, unsealed, and the pore water filtered through a 0.4 micron filter or smaller according to the protocols set forth in the SOP prepared per Task 3. The requisite volumes of filtered pore water as set forth in Appendix 2 shall then be distributed into appropriate sample

containers, appropriately preserved per Appendix 2, sealed, and labeled prior to removal from the glove box under positive nitrogen pressure. The labeled samples shall be transmitted to the appropriate labs identified in Table 1, either directly for those constituents being analyzed by the District's laboratory, or, in the case of ultra-trace THg and MeHg, via an overnight carrier to Frontier Geosciences in Seattle, WA.

The appropriate data and metadata shall be recorded in the appropriate field and laboratory notebooks dedicated to this study.

TASK 11 – Prepare SOP for Mercury Ultra-Clean, Oxygen-Free Field Pore Water Sample Collection using Alternative "Sipper" Method

Task 11.1 Draft SOP

The Contract shall prepare a Draft SOP for Mercury Ultra-Clean, Oxygen-Free Field Pore Water Sample Collection using Alternative "Sipper" Method that incorporates the procedure outlined in **Appendix 2** following the organization, content, detail, person, tense, and tone of the model SOP in **Appendix 1**.

Task 11.2 Final SOP

The draft SOP will be reviewed by the District Project Manager and such other District and non-District staff as he shall designate for that purpose. The Contractor shall make the required changes to the draft document in response to the comments transmitted by the District's Project Manager. The Contractor shall deliver the revised SOP as the Final SOP for Mercury Ultra-Clean, Oxygen-Free Field Pore Water Sample Collection using the Alternative "Sipper" Method.

TASK 12 - Peer Review of Results

The SOPs prepared in Tasks 1, 2, 3, 4, the results of the validation studies conducted pursuant to Task 9, and the results of the monitoring campaign conducted per Task 17 shall be reviewed critically by an independent, objective, recognized expert in mercury ultra-clean, oxygen-free extraction of pore water from soil cores and the mercury ultra-trace analysis of the pore water so extracted (e.g., Robb Mason at U Maryland, or equivalent). The expert shall codify his or her findings, conclusions, and recommendations in a letter report. If the modified sipper method is found not to produce result substantially equivalent to the centrifugation method, the expert shall (1) identify appropriate modifications to the design or operation of the sipper equipment to increase the likelihood of substantial equivalence; and (2) assuming the routinely achievable performance of the sipper cannot be improved to achieve substantial equivalence to the centrifugation method, identify potentially useful applications with appropriate limitations that are not inconsistent with its routinely achievable performance.

4. RESPONSIBILITIES OF PARTIES

The District shall supply (1) background information requested by the Contractor; (2) the results of a soil cores characterization study carried out under another contract. The Contractor shall perform the work with the quantity, quality, and timeliness appropriate to standards of professional conduct and performance for the industry. The Subcontractor shall demonstrate the required scientific, technical, environmental, and analytical expertise required to perform pore water extraction for ultra-trace mercury analysis via centrifugation under oxygen-free conditions as set forth in this SOW via publication of the specified sample collection, processing, and analysis methodologies in the peer-reviewed scientific, engineering, and regulatory literature. The Contractor shall supply all of the personnel, equipment, supplies, laboratory space and services, and transportation required to perform the work set forth in this SOW according to general standards of professional practice to meet the specifications of quantity, quality, and timeliness in this Work Order.

5. SCHEDULE OF DELIVERABLES

Table 1. Schedule of Deliverables

Task	Responsible Party	Deliverable	Due Date
Task 1 Prepare SOP for Peat Soil Sampling for Pore Water Collection for Ultra-Trace Mercury Analysis	Contractor	Draft SOP	Within 14 calendar days of Contract signing
	District	Review Comments	Within 7 calendar of receipt
	Contractor	Final SOP	Within 7 calendar days of receipt of review comments
Task 2 Prepare SOP for Set-Up of Portable Lab for Conducting Preferred Method of Pore Water Extraction	Contractor	Draft SOP	Within 14 calendar days of Contract signing
	District	Review Comments	Within 7 calendar of receipt
	Contractor	Final SOP	Within 7 calendar days of receipt of review comment

Task 3 Prepare SOP for Preferred Method of Pore Water Extraction	Contractor District Contractor	Draft SOP Review Comments Final SOP	Within 14 calendar days of Contract signing Within 7 calendar of receipt Within 7 calendar days of receipt of review comments
Task 4 Prepare SOP for Stabilization and Preservation of Redox-Sensitive Analytes in Mercury Ultra-Clean, Oxygen-Free Portable Lab Environment	Contractor District Contractor	Draft SOP Review Comments Final SOP	Within 14 calendar days of Contract signing Within 7 calendar of receipt Within 7 calendar days of receipt of review comments
Task 5 Purchase Equipment for Mercury Ultra-Clean, Oxygen-Free Portable Lab	Contractor	Copy of Invoices	Within 21 calendar days of Contract signing. Turn over capital equipment and unused supplies to District at end of study prior to contract WO expiration.
Task 6 Secure Portable Lab Space	Contractor	Copy of Invoices	Within 21 calendar days of Contract signing
Task 7 Train Contractor Staff in Adapted/Modified Soil Core Field Sampling	Contractor	Copy of Invoices	Within 31 calendar days of Contract signing
Task 9 Set Up Mercury Ultra-Clean, Oxygen-Free Portable Lab	Contractor	Copy of Invoices	Within 31 calendar days of Contract signing
Task 10 Field Validation of "Sipper" Method	Contractor	Written Report	Within 45 calendar days of Contract signing

Task 11 Collect Pore Water from 10 Interior Sites using Centrifugation Method	Contractor	Written Report	Within 45 calendar days of Contract signing
Task 12 Peer Review of SOPs, Preferred and Alternative Method Validation Studies	Outside Expert	Final SOPs Results of Validation Studies	Within 60 calendar days of Contract signing Within 120 calendar days of Contract signing

6. SCHEDULE OF PAYMENTS

Table 2. Schedule of Payments

Task	Payment
1 Prepare SOP 1	
2 Prepare SOP 2	
3 Prepare SOP 3	
4 Obtain Access to Mobile Work Space	
5 Purchase Equipment	
6 Secure Rooms and Travel From Site with Hotel and Per Diem	
7 Train Technicians for Soil Core Sampling per SOP	
8 Train Technicians for Lab Set-Up per SOP	
9 Set up Portable Lab	
10 Collect Test Peat Cores	
11 Further Adapt Method	
12 Modify SOP	
13 Train Staff	
14 Validate Staff Performance	
15 Collect and Process Cores for Sipper Validation Study	
16 Conduct Sipper Validation Study	
17 Modify Sipper Method as Needed	
18 Prepare Modified Sipper SOP	
19 Peer Review Work	
Total Cost	

7. REFERENCES

Bloom, N.S., Gill, G.A., Cappellino, S., Dobbs, C., McShea, L., Driscoll, C., Mason, R., and Rudd, J.W.M. 1999. “Speciation and Cycling of Mercury in Lavaca Bay, Texas, Sediments,” *Env. Sci. and Technol.* 33: 7-13.

Bloom, N.S., Coleman, J.A., and Barber, L. 1997. “Artifact Formation of Methyl Mercury During Extraction of Environmental Samples by Distillation.” *Fres. Anal. Chem.* **358**: 371-377.

Bloom N.S. 1995 "Mercury as a Case Study of Ultra-Clean Sample Handling and Storage in Aquatic Trace Metal Research," *Environmental Lab,* **March/April:** 20

Bloom, N.S. and von der Geest, E.J. 1995. "Matrix Modification to Improve Recovery of MMHg from Clear Waters using the Acid/Chloride Distillation Procedure," *Wat Air Soil Pollut* **80:** 1319.

Bloom, N.S 1989. "Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapor Atomic Fluorescence Detection." *Can. J. Fish Aq. Sci.* **46**: 1131-1140.

Mason, R.M., Benoit, J. A., Bloom, N.S., Capellino, S., Driscoll, C.T., Gill, G.A. (1998) “Investigation of Porewater Sampling Methods for Mercury and Methylmercury” *Env. Sci. and Technol.* 32: 4031-4040.

8. APPENDICES

Appendix 1.

Model SOP: Soil Sample Collection for Ultra-Trace Total Mercury and Methylmercury Analysis

(See Appendix B this report)

Appendix 2

Sampling Protocol for Pore Water Collection Using *In Situ* Sipper Method for STA-2 Hg Special Studies
Rev. 08/20/03

Perform Surface Water Collection upon arrival at the site before disturbing the water column.

1. Collect a 250 mL Nalgene pre-cleaned bottle of sample at mid-depth by immersing the bottle and opening.

Porewater will then be collected via the "modified sipper" as follows.

1. After insertion of the probe purge approximately 100 ml of water.
2. Immediately collect two 15 mL centifruge tubes of water, fill one to the top and seal (for Fe(II)) and fill the other, add 2 drops of $Zn(Ac)_2$/NaOH and seal.
3. Next collect the samples for MeHg and THg using the containers from Frontier.
4. Next collect 200 mL of sample into a pre-cleaned 250 Nalgene bottle.

Sample bottles for each site:

1 SW 250 mL bottle for misc. parms

1 PW 15 mL tube (no headspace) for Fe(II)
1 PW 15 mL tube preserved with $Zn(Ac)_2$/NaOH for sulfide
1 PW bottle for THg and MeHg (unpreserved; minimum 100 mls but prefer 200 mls)
1 PW 250 mL bottle for misc. params

Parameters to be analyzed for each site:

PW Sulfide	SW CA
PW Fe(II)	SW CL
PW MeHg	SW DOC
PW THg	SW MG
PW CA	SW SO4
PW CL	SW TOTFE
PW DOC	SW TOTMN
PW MG	

PW SO4
PW TOTFE
PW TOTMN

Sites to be sampled:

STA2C1AA
STA2C1BB
STA2C1CC
STA2C1C
STA2C2A
STA2C2B
STA2C2C
STA2C3A
STA2C3B
STA2C3C

Quality Controls:

1. One EB collected at the beginning of the day and one FCEB at the end of the day.
2. The same probe will be used for sampling all of the sites, with a clean probe in reserve in case of accidental contamination. The probe will be returned to a storage bag at night or when not in use.
3. Site STA2C1C will be sampled in triplicate to verify reproducibility. First will be designated type “SAMP” other two will be type “RS”. When collecting in triplicate, sampling protocol should be followed such that all three replicates are collected together for each sample container. That is, collect three samples for Fe(II), then three for Sulfide, then three for MeHg etc etc. until all of the bottles are filled.

Contract Number C-12452-WO#13A

Statement of Work

I. BACKGROUND

This Statement of Work (SOW) is an amendment to existing work order C-12452-WO13, Pore Water Sampling Pilot Study. An amendment is necessary because the side by side validation study called for in the original work order under Task 9 needs to be redesigned in response to what has been learned to date in performing the other tasks. First, the time allotted was not sufficient to conduct the study. Second, the volume of pore water generated by the centrifugation method of pore water collection produced less than predicted based on the results of an earlier pre-study. Third, the results obtained to date using the centrifugation method of pore water extraction indicate that the chemistry of pore water extracted by centrifugation is a sensitive function of soil depth and bulk density. Fourth, the depth at which the *in situ* sipper method extracts pore water is uncertain. A three day pre-study (Task 9A) is proposed to determine if the optimum number of soil cores, time, and sampling depth for the side-by-side comparison (Task 9B) of the in situ and centrifugation methods of pore water collection. Task 9 under the original WO SOW is replaced by Tasks 9A and 9B.
OBJECTIVE

This information is required to determine the number of sediment cores and length of time needed to conduct the side by side validation study called for under C-12452-WO13 task #9. The three-day pre-study would also allow us to evaluate the optimum depth for coring, as the present method produced results that suggest too much mixing with the surface water.

J. PROJECT LOCATION

Stormwater Treatment Area 2 (STA-2) is located within Sections 25, 26, 27, the eastern ¾ of Sections 28 and 33, and Sections 34, 35, and 36, Township 46 South, Range 38 East and a western portion of Section 30, the far northwestern tip of Section 31, Township 46 South, range 39 east, and the northwest corner of Section 1, Sections 2, 3, 4, Township 47 South, range 38 East and Section Government Lot 5, Township 43.5, range 40 east in Palm Beach County, Florida.

K. SCOPE OF WORK

The objective of this revised Task 9 is to (1) optimize the depth at which the 4-cm soil cores will be collected for the modified side-by-side validation study of the *in situ* sipper *vs.* the centrifugation method based on the change in soil and pore water chemistries with depth at three different sites with different bulk densities; and (2) complete the side-by-side validation study at that optimum depth. The sites where the Task 9A pre-validation study will be carried out are sites STA2C1C, STA2C2C, and STA2C3C. The work will be carried out by two, two-person teams, one of which, the sample processing team, will work a 12-hr day and the other of which, the sample collection team, will work a 6-hr

day. This optimization is to be accomplished by (1) emplacing the *in situ* sipper device at the sampling site; (2) collecting sixteen, 10-cm cores roughly equally distributed in an annulus defined by an inner circle with a radius of 0.75/2 m (the outer circumference of the sipper disk) and an outer circle with a radius of 1.5/2 m (see Diagram 1); (3) using the second, two-person sampling team, transporting the first set of sixteen, 10-cm cores to the portable lab for extrusion into the nitrogen glove box and processing concurrently with the subsequent steps under this task; (4) using the emplaced sipper, document if the pore water volumes required for the analyses of S=, Fe(II), SO4, THg, MeHg, TFe, TMn, Mg, Ca, DOC and Cl can be collected; (5) following the collection of pore water using the emplaced sipper, collecting another set of roughly equally spaced, nineteen, 10-cm cores in the same outer annulus; (6) transporting this second set of soil cores to the field laboratory for processing per steps (3) through (5); (7) reserving three, 10-cm cores for replicate BD and moisture analysis by 2-cm stratum by DB Labs and the remaining sixteen cores for subsequent sectioning, compositing by stratum, and subsampling in triplicate for subsequent analysis by FGS for THg and MeHg analysis and DB Labs for BD, ash, moisture, TS, TFe, and AVS analysis. Thereafter, the pore water chemical analysis results will be reduced, analyzed, and evaluated as to the best match between the chemistry of the pore water in each 2-cm stratum generated using the centrifugation method and the integrated pore water sample collected using the sipper method. This will define the optimum depth at which the 4-cm cores will be collected at Site C1C for the side-by-side validation study detailed in Task 9B of C-12452-WO13A. Task 9B will be conducted only after the optimization analysis is completed and the requisite information regarding the optimum coring depth is supplied by the Project Manager to the Contractor. Task 9B will repeat steps (1) through (6) at STA-2 Cell 1 Site C1C for sixteen cores on Day 1 and sixteen cores on Day 2. Although the study is projected to be completed in five 12-hr days, a 6^{th} day has been added as a contingency to address unforeseen difficulties and the exigencies of inclement weather or equipment failure.

Task 9A. Optimization of Soil Sampling Depth for Task 9B.

On Day 1, the first sixteen, 10-cm cores shall be collected per Diagram 1 at Site C3C, transported to the field laboratory, extruded into the glove box under nitrogen, subsectioned into five, 2-cm cores, and each stratum shall be centrifuged, filtered, composited, and subsampled for subsequent preservation for analysis of S=, Fe(II), SO4, and Cl. Filtration shall be accomplished using four individual pumps and 0.45 micron filters concurrently to ensure that all of the cores are extracted in an eight-hour period for subsequent transport to the District lab prior to closing. The filters will be acid-cleaned in the glove box prior to use according to the procedures set forth in the SOP prepared per Task 3 and used for Task 10. The first set of soil core samples collected at each site shall be processed for pore water extraction under nitrogen each day for three consecutive days. The second set of nineteen, 10-cm cores will be stored on ice without freezing for subsequent transmittal in a timely fashion to DB Labs in tact. Three of the nineteen soil cores will be subsectioned by DB Labs into five, 2-cm cores for analysis of BD and moisture content, while the remaining sixteen, in tact cores will be subsectioned into five, 2-cm cores, composited by stratum per Diagram 2, homogenized, and subsampled n = 3 times for replicate analysis of TS, TFe, and AVS by DB Labs and THg and MeHg by

FGS. To accomplish the latter, DB Labs will ship the appropriate subsamples to FGS using FGS's shipper code for THg and MeHg analysis under the District contract. Record all relevant information in the appropriate field and laboratory notebooks. On Days 2 and 3 this procedure shall be repeated for Sites C2C and C1C.

Task 9B. Side-By-Side Validation Study for In Situ Sipper vs Soil Centrifugation

Once the Task 9A study has been completed and the optimum depth at which the cores will be sectioned determined, new Task 9B of C-12452-WO13A shall be initiated. Using the same two, 2-person teams and scheduling as detailed above, on Day 4 collect the samples per Diagram 1 and process sixteen, 4-cm cores at Site C1C at the optimum depth prior to and sixteen, 4-cm cores following sipper pore water sample collection on Day 1 using the same protocol as detailed above. The extrusion of sediment cores into the glove box under nitrogen shall be progress and be processed as per Task 9A, except that the composite pore water collected each day shall be subsampled n = 4 times, preserved as required, and analyzed for S=, Fe(II), THg, MeHg, SO4, TFe, TMn, DOC, and Cl. Repeat the procedure on Day 5. Record all relevant information in the appropriate field and laboratory notebooks.

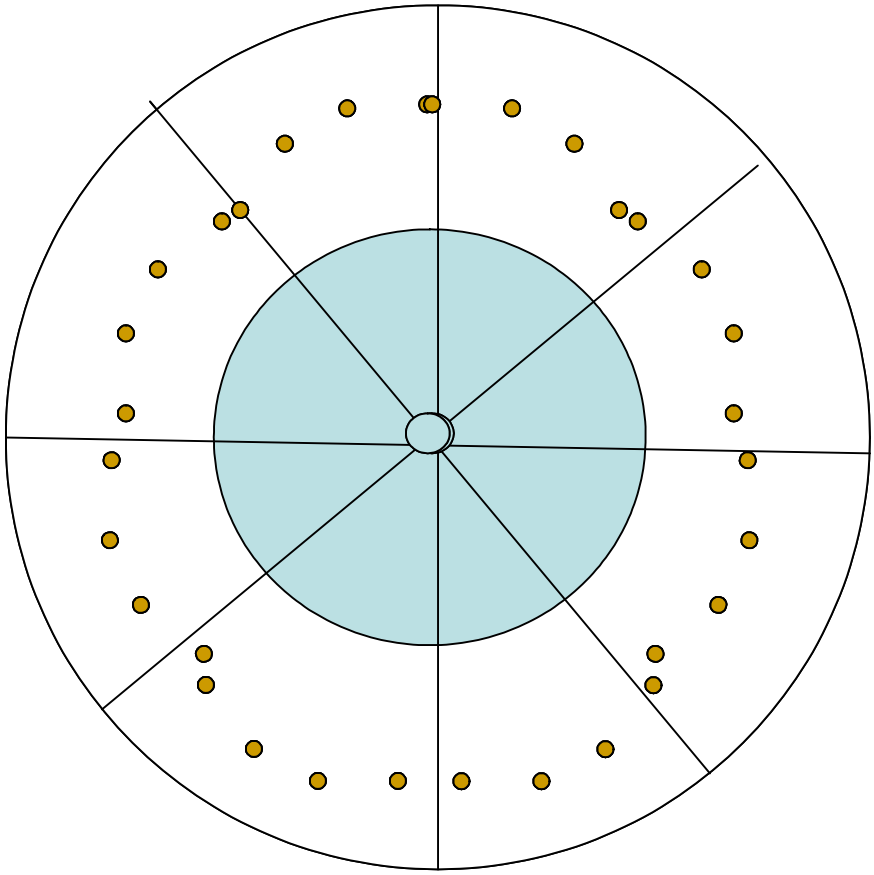

Diagram 1. Placement of Core For Sediment Collection

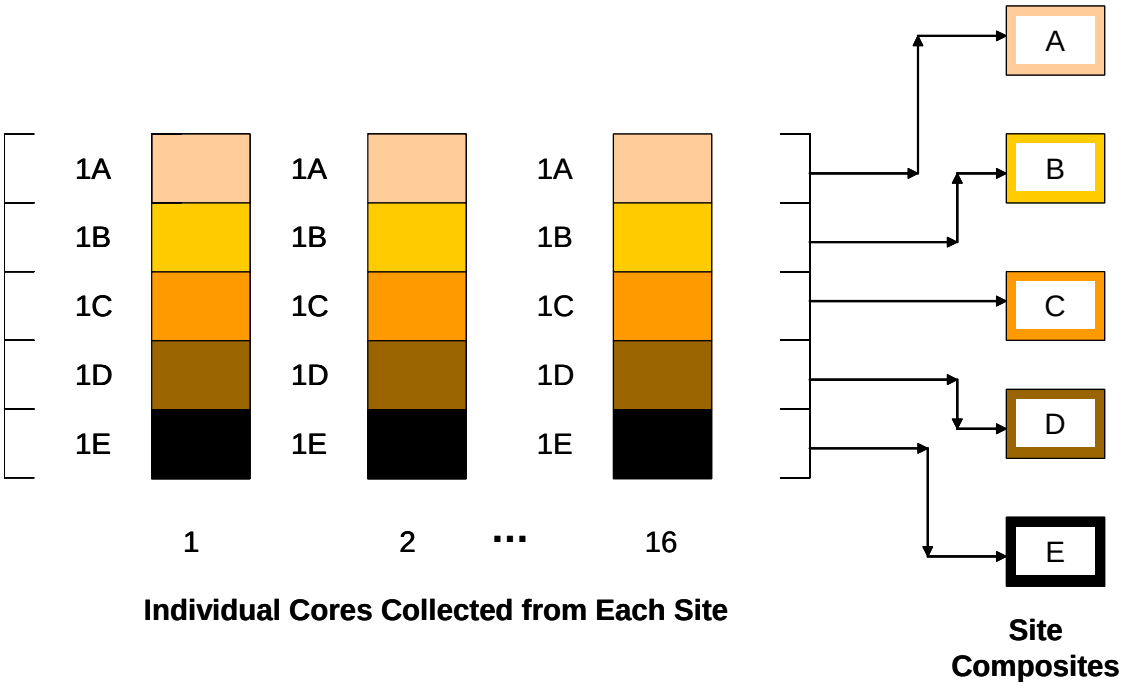

Diagram 2. Soil Compositing Scheme Across Strata at Each Site

COST ESTIMATES

Replace the Task 9 cost estimate with the following:

Cost Estimate - Tier I Pore Water Sampling Add-on

Activity	Hours	Estimated Cost ($)
Labor		
Three day Pre-Study C1CC		
(4 Field Persons)	132	8,380
Side by Side Validation Study		
(4 Field Persons)	98	6,262
Frontier (Equip. Purchase)		1,900
Lab Set-Up w/N Tanks		1340
AirBoat USA (5 days)		2,809
Coordinate & Manage	24	2,384
Sub total	*254*	*23,075*
Travel		358
Directs		500
Sub total		*23,933*
Contingency @ 5%		1196
Lump Sum Total	**254**	**$ 25,129**
Add: Contingency Day		
Labor		
Additional Field Day		
(4 Field Persons)	42	2,671
AirBoat USA (1 day)		562
Sub total	*42*	*3,233*
Travel		72
Directs		100
Sub total		*3,405*
Contingency @ 5%		170
Lump Sum Total	**42**	**$ 3,575**
Grand Total	**296**	**$ 28,704**

Appendix D. Standard Operating Procedure for *In Situ* Sipper Method for the Collection of Pore Water for the Quantitative Analysis of Ultra-Trace Mercury Species and Redox-Sensitive Species Using Micro-Analytical Methods

Porewater Collection Protocols for The NAWQA Mercury Study

By: Dennis Wentz, Mark Brigham, Mark Marvin DiPasquale, Bill Orem, Dave Krabbenhoft, George Aiken, and Margo Corum

I. Introduction

This document outlines the protocols for collection of stream-sediment porewater, subsampling for the various assays, sample preservation, and shipping requirements for the NAWQA Mercury Study. This protocol is written for collection of porewater using a slotted Teflon probe ("sipper") deployed at a sediment depth of 2 cm. The general procedures are readily adaptable to sampling other depths (up to about 10 cm), when desired, using the Teflon probe from the mercury lab. Analyses to be conducted on these samples include: mercury and methylmercury concentration; organic carbon; anions; and field analyses of sulfide and ORP.

II. Sampling Strategy

The schedule for collection of sediment and porewater is outlined in the Sediment Protocol document. Porewater should be collected in a relatively level area of stream sediment, directly adjacent (and in similar sediment) to the stream-bed sediment sampling zone. Choose one location per stream (sediment site with maximum methylation potential determined during initial sampling—either S1, S2, or S3), pending analysis of spatial data by Mark Marvin-DiPasquale.

III. Equipment and Supplies (number needed in parentheses; one unless otherwise noted)

<u>Supplied by Wisconsin District Mercury Laboratory</u>

- Teflon porewater probes (1 or 2 total)—Teflon cylinder with slots and fittings for ¼" Teflon tubing. Rinse between sites w/ 5% HCl and stream water.
- Acrylic plastic discs for porewater probes (2)
- Short Teflon sampling line [1/4 in. OD]
- Short C-flex pump head tubing
- Loaded filter cartridges (47 mm diameter quartz fiber filter; 5 per porewater sediment site)
- 500-mL Teflon sample bottles for porewater Hg/MeHg samples, precoded from WI Mercury Lab (1/site)

Supplied by Orem's laboratory

- Calibrated sulfide probe and meter

Supplied by Hg team

- ORP (redox) probe (Microelectrode)
- ORP standard (ThermoOrion 967961); alternatively follow procedures in NFM chapter 6.5.
- Sulfide antioxidizing buffer (SAOB)
- Minipiezometer (to measure head)
- Orion 250A+ pH/mV/Temperature meter and manual
- Orion pH probe
- Plastic syringe (5 mL, or 12 mL) with luer-lock ends (for ORP)
- C-flex tubing for filling syringe
- Magnetic stir plate
- Stir bars (1/2" long)
- Electrode holder

Supplied by Study Unit (or by WDML, if needed and requested in advance)

- Peristaltic pump fitted with pump head suitable for Masterflex # 15 and #24 tubing
- 12-V batteries (2)
- Plastic scintillation vials (20 mL) for sulfide, ORP, and anions (3/site + extras)
- Floating plastic tub [shallow tub, outfitted with Styrofoam (swimming noodle) floats] to hold pump, filters, bottles, etc.
- USGS Field forms
- Porewater sulfide data sheet (Attachment 1A)
- Plastic scintillation vials for calibrating meters.
- (Suggested deletion—instead use Orion ORP solution, or ZoBell's solution from Ocala, per National Field Manual)
- pH buffer series (4, 7 and 10)
- Small cooler for making pH and redox measurements
- Pipettor or syringe for delivering ~8 mL of SAOB (equivalent volume as sulfide sample)
- Prelabeled 20 mL plastic scintillation vial for porewater sulfate and chloride assay (2 per site, Liquinox cleaned → DI rinsed → dried)
- 40-mL brown DOC bottles (1/site)
- Meter stick (to measure head)

- Hand-operated vacuum pump (to pull water through minipiezometer)

IV. Sampling

General notes

- To minimize infiltration of stream water, carefully insert the probe vertically into the sediments. Sample in relatively horizontal sediments such that the probe is vertical and the disk is horizontal.
- Fast water will tend to slant probe toward downstream. Place small rocks on disc on upstream side (but not so many that the disc sinks into the sediment) or, preferably, have someone hold probe in place.
- Avoid disturbing the probe while it is deployed (disturbance can create channels that allow surface water to infiltrate).
- Pumping depletes pore waters in the desired depth increment, inducing infiltration of both deeper water and stream water to the zone around the probe. To minimize this effect, consider collecting a composite porewater from 3 separate deployments of the Teflon probe for each depth sampled. All deployments should be within a small (<1 m^2) area. (See "Suggested revision" below.)
- Remove filter cartridge from C-flex tubing before each deployment; slowly flush particle slug through pump line before reattaching filter cartridge**. This initial particle slug can clog filters instantly**.
- Calibrate ORP probe using calibration standards provided by the manufacturer, and procedures outlined in the National Field Manual and/or the manufacturer's probe manual.

Sampling Method

- Attach disc to probe at desired sampling depth (generally 2 cm; probe is etched 2 cm above screened interval).
- Insert probe into sediment until disc contacts surface. Disc should lie flat on sediment surface, and probe must be vertical
- Attach Teflon tubing to C-flex tubing with nylon cable tie to prevent blowing off under pressure.
- Pump very slowly to flush slug of dirty water from line before attaching filter cartridge. (Pumping slowly minimizes the formation of a cone of depression and contamination from surface water.)
- When water is fairly clear, and while still pumping slowly, attach the filter cartridge and hold upright to purge air out of filter cartridge.
- Flush filter with **a few** mL of water.
- Pump 150 mL from each of three deployments of the Teflon probe, and composite the water into a clean 1 L PET bottle. After the third aliquot is pumped into the bottle (total volume=450 mL), fill a scintillation vial full for ORP sample.

ORP (aka redox potential)—Measure ORP immediately.

- Microelectrode ORP probe is stored in glass sheath, with DI-moistened sponge in the sheath. Probe is taped to glass sheath to form a seal.
- Remove probe from glass sheath and connect probe to meter. Make sure it is locked in place. Uncover hole on the ORP probe (remove small rubber plug).
- Check calibration using either freshly prepared saturated quinhydrone solutions in pH4 and pH7 buffers. Alternatively, use Orion ORP Standard (Orion 967961, absolute mV reading is 220 mV [+/- 5 mV]). Record mV readings of ORP standards. The meter is not calibrated, as is typically done with pH or dissolved oxygen. If readings are unacceptable, clean and maintain probe per manufacturer's instructions, or replace probe.
- Attach a small piece of tubing to the end of the syringe.
- Draw ~5 mL sample water into syringe, with tubing attached. Take sample immediately from anion vial, or directly from pump line.
- Insert probe into tubing.
- Slowly discharge sample water past the electrode, noting the mV readings on the meter.
- Record ORP reading in mV. Note: ORP mV readings are noisy; record a central value. Some samples are more stable than others. Pay attention to readings as you push the last bit of sample over the probe.
- In between samples, you do not rinse the tube or the electrode.
    - To clean up the electrode between samples, push slowly to clean the tube and electrode with the sample.
- Rinse and blot dry the electrode when sampling is completed. Replace rubber plug in the hole in the electrode, and store electrode in its glass sheath.

Immediately begin splitting the composite sample into sample containers:

1. Pour small amount of sample into PET bottle cap; syringe (or pipette) 8 mL into a scintillation vial that contains 8 mL of SAOB (sulfide anti-oxidizing buffer). [Margo wrote 3 mL sample into 3 mL SAOB—critical to use equal volumes of sample and SAOB.]

   Sulfide is unstable until sample is placed in SAOB.
   See Attachment 1B—sulfide analyses. Sulfide is analyzed by electrode either on site, or in hotel same night of sampling. Keep sample in cool, dark place until analysis.
   At end of week, return sulfide probe and meter to Orem's lab.

2. Rinse 500 mL Teflon Hg bottle twice with ~5 mL aliquots of sample water, then fill bottle at least half full. Preserve with HCl preservative. Ship to Wisconsin District Mercury Lab.

3. 40 mL amber glass vial for DOC. Keep sample on wet ice until delivery to Aiken's lab.

4. Fill plastic vial for anions (chloride/sulfate). Keep samples cool and in dark. Ship to Orem's lab.

V. Head Measurement

To conceptually link porewater geochemistry with the overlying stream water, it is desirable to know if groundwater is discharging from the sediment zones being sampled. Positive groundwater head (elevation of water in minipiezometer > elevation of surface of stream) indicates groundwater discharge. Negative groundwater head (elevation of water in minipiezometer < elevation of stream surface) indicates recharge. At constant groundwater discharge rate, head increases with depth of sediment, and with the "resistance to flow" of the sediment (fine sediment resists flow more than coarse sediment). Groundwater head equals stream-water elevation at the sediment-water interface, and is likely immeasurable in the upper couple cm.

When sediment and porewater sampling is complete, attempt to measure head with the minipiezometer. Minipiezometer consists of steel casing (marked in 10 cm increments); rigid clear plastic tubing; and a drive point attached to the tubing.

Drive minipiezometer to the first 10 cm mark on the steel casing. Remove casing. Measure head (difference between water elevations) to nearest mm, and record in field notes. Pull a slight vacuum on minipiezometer to draw water farther up the tube; remove vacuum and let water re-equilibrate. Water should return to previously measured value. If it differs, there may have been head induced by deployment of the minipiezometer. Repeat procedure for 20 and 30 cm depths, if possible. Record values. Be careful when removing minipiezometer from sediments. If steel drive point breaks off of tubing, retrieve it and mount it on a spare length of tubing.

VI. Quality Control Samples

Replicates: Mercury lab has collected replicates for porewater THg and MHg at all sites; no further replicates are needed for mercury. During remainder of study, each study unit should collect a total of two sets of replicates for the remaining analytes.

Equipment blanks: Once, early in the study, each study unit should collect a blank sample for each analyte at one site. Pump blank water through Teflon probe, pump lines, and filter.

For DOC, use organic blank water and inorganic blank water.

For anions, ORP, and sulfide, use inorganic blank water.

For mercury, use Milli-Q from WDML (must request).

VII. Questions? Contact / Shipping Info:

a) Dave Krabbenhoft - phone: (608) 821-3843, e-mail: dpkrabbe@usgs.gov; Mark Olson - phone: (608) 821-3878, e-mail: mlolson@usgs.gov; John DeWild - phone: (608) 821-3846, e-mail: jfdewild@usgs.gov
USGS / 8505 Research Way / Middleton, WI 53562-3581

b) George Aiken - phone: (303) 541-3036, e-mail: graiken@usgs.gov
USGS / 3215 Marine Street, Suite E-127 / Boulder, CO 80303

c) Bill Orem - phone: 703-648-6273, e-mail: borem@usgs.gov
USGS / 12201 Sunrise Valley Drive / Mailstop 956 / Reston, VA 20192

Attachment 1A—Porewater Sulfide data sheet

Site Name:_____ Site Number:_____

Project Name: _____ Date: _____

Detection Limit of Electrode: -700 mV Electrode Used:_____

Sample ID	Sulfide Reading (mV)

Attachment 1B—Sulfide measurement by Ion Selective Electrode
Protocol from Margo Corum

I. Preparation:

A. Night Before Sampling

Fill the Sulfide electrode with solution A. It is the only filling solution in the black case.

- Unscrew the black top on the filling solution A, remove the red stopper/plug, and replace the white top to fill the electrode. Remove the tape and teflon tape from the electrode, and fill with the filling solution A.
- Place the tape back over the hole on the electrode to store (overnight or when not in use), even if the electrode is soaking in SAOB/ascorbic mix.

Make sure the cap stays on the bottom of the electrode when not in use, shipping, or any other time unless, the electrode is in the SAOB/ascorbic mix

B. First thing in the morning

- Mix one container of pre-weighed ascorbic acid with one container of pre-measured SAOB.
    - Dump the ascorbic acid in the pre-measured SAOB, cap and shake.
    - Rinse the ascorbic acid container with SAOB.
        i. Pour some of the mix back into the container of ascorbic acid, cap and shake.
        ii. Pour back into the SAOB bottle.
    - Let the SAOB mix sit for 10 minutes, before using.
- Soak the sulfide electrode
    - Place ~3 mL SAOB in an extra scintillation vial
    - Place the electrode in the 3 mL SAOB mix.
    - Let the electrode soak in the mix until ready to use.
    - Keep the electrode soaking the entire time, day and night until you need to use.

EACH DAY YOU COLLECT SULFIDE SAMPLES MIX FRESH SAOB MIX

II. Collecting and Storing the Samples

- Pipette out of the big collection bottle 3 mL into the appropriate sulfide scintillation vial, which should already have the SAOB mix in it and cap.
    - Store in dry dark cooler or dark area, until ready to measure.
- . Pour off sample from the big collection bottle into the 60 ml bottle for nutrients.
    - Fill the bottle to the shoulder or almost full. If you are taking out sample for redox see below.
    - Store nutrient sample in labeled bag, with date, site name, and number in a cooler with dry ice to be shipped back frozen.
- Pour off sample from the big collection bottle to the appropriate anion vial.
    - Store anion vials in labeled bag, with date, site name, and number in a cooler to be shipped back. These samples do not need to be frozen, just stored in a cooler.

III. Reading Sulfide

- Connect the sulfide electrode to meter.
    - Make sure BNC connector is locked in place.
- Place little stir bars in each sample you will be reading.
- Remove the sulfide electrode from the buffer.
- Rinse the electrode with DI water and dry with a kimwipe.
- Place the sample with stir bar on the stir plate
    - Turn stir plate on.
        - Just enough to gently stir the sample.
- Lower the electrode into the sample.
    - To prevent the meter from turning itself off, hit “yes” key every few minutes, especially if the sample is below detection limit.
    - If the sample is below detection limit. Keep electrode in sample for ~5-10 minutes.
        - For 5 minutes if it is really low, 10 minutes if it is borderline.
- Record the value in **mV** (millivolts).
    - If the sample is below detection limit, the reading will not stabilize.
    - If the sample is above detection limit, the value of sulfide will become stable faster.
- Between samples, rinse the electrode with DI water and blot dry with a kimwipe.

Appendix E: Summary of the Interim SFWMD Modified Procedure for Pore Water Sample Collection

This is a summary of the interim SFWMD procedure for the collection of pore water using a modification of the *in situ* sipper design developed by the U.S. Geological Survey. The final procedure is being prepared under a separate contract work order.

Modified Apparatus

Figure AE-1 illustrates the original USGS *in situ* minipiezometer or "sipper" design for the ultra-clean collection of ultra-trace mercury species analytes in pore water. The apparatus has been modified to include four new features. These new features are intended to allow for a substantial increase in the pore water sample volume collected without surface water breakthrough at a well-defined, reproducible sediment depth. These new features are depicted in **Figure AE-2**.

The first new feature is the addition of a 0.75 m diameter x 0.025 m thick molded disk composed of "starboard" marine-grade plastic (high-density polyethylene) through which a 0.025 m hole has been drilled through the center to accommodate the Teflon barrel of the sipper probe. A PE circular brace with a 0.025-m diameter hole aligned with a 0.025-m diameter hole in the center of the disk is mounted on the upper side of the disk with four PE plastic screws. An acid-precleaned Teflon "O" ring is rolled over the probe barrel until it is about 2 cm above the sampling slits. The probe with encircling "O" ring is inserted through the brace and disk and pushed to the desired depth. Next the "O" ring is adjusted until a water and air-tight seal is achieved with the disk. The probe with surrounding "O" ring is then fixed at the desired depth by tightening three nylon set screws threaded through the barrel of the brace at 120-degree angles.

The second new feature is a one-meter long, PVC handle added for ease of insertion of the probe into the subsurface soil/sediment layer, even in relatively deep water conditions in the constructed wetland. The handle is affixed to the top of the disk with a series of four mounts with circular braces to accommodate each of the four tubes that comprise the handle. The handle is stiffened with a series of cross bars affixed at 90-degree angles to the handle tubes.

The third new feature is a set of five, equally distributed 12 Kg weights laid across the handle cross-bars. The weights are threaded 0.07 m outer dia x 0.7 m length PE cylinders containing lead shot sealed at both ends with screw caps. The weights are intended to ensure that a uniform pressure is exerted on the sediment to define functionally the sediment/water interface, to seal off the water/sediment interface so defined so as to prevent inadvertent collection of surface water during the collection of the pore water while attaining a depth equivalent to a constant sediment bulk modulus across sampling sites. The high density of the weights minimizes the effect of buoyancy on the uniform application of pressure at sites in deep vs. shallow water.

The fourth new feature is the low volume, flow-through cell with sampling ports interposed between the sample collection tubing on the other side of the peristaltic pump and the sample discharge port to the collection bottle. A two microprobes are inserted into the cell for continuous measurement of redox potential and pH during sampling. This provides for a continuous verification of the absence of surface water breakthrough and thus sample validity.

Operation of the Modified In Situ Sipper Apparatus

Approximately 3 m of 0.5-cm diameter acid-precleaned Teflon tubing connects the sipper probe to a Masterflex® peristaltic pump with EZ-off head. Standard, acid-precleaned C-Flex® tubing is passed through the pump head and joined to the acid-precleaned Teflon tubing by inserting the smaller diameter tubing into the larger for a pressure seal. An acid-precleaned, high-surface area 0.45 micron Meissner®

capsule filter certified for ultra-trace metals analysis is connected to the C-Flex tubing and the acid-precleaned Teflon tubing with an acid-precleaned Teflon connector. A flow-through acid-precleaned sampling cell with sampling ports for the redox and pH probes is connected to the acid-precleaned Teflon tubing with an acid-precleaned Teflon connector. A short (~ 0.5 m) piece of Teflon tubing leads from the last Teflon connector to the sample bottle.

All acid-precleaned equipment, sampling bottles, and supplies are stored in unused, resealable plastic bags into which the equipment, bottles, and supplies have been inserted under clean-room or equivalent conditions and then placed in a second, outer bag labeled with the contents and the date the order was filled. “Dirty Hands” sets up the modified sipper apparatus, opens the coolers, opens and closes the outer bags, and opens the E-Z off head of Masterflex® Pump. “Clean Hands” handles only the inner bags and acid-precleaned equipment and supplies and connects the acid-precleaned tubing according to the configuration and in the order specified in the SOP.

Modified Method Validation

The results of equipment blanks collected at the beginning and end of the sampling trip indicate that contamination of the sample with spurious sources of THg and MeHg are higher than is generally encountered with surface water sampling at the same sites. These higher than expected THg blank concentrations are not considered problematic, however, because the concentrations are generally less than 5% of the typical concentrations measured in the sampled environment.

The vacuum that typically persist through the end of the pore water sample collection process indicates that the seal between surface water and the underlying sediment is acceptable. The low (<-150 mv) redox potentials and high sulfide and Fe(II) concentrations relative to sulfate and Fe(III) indicate that surface water breakthrough is not occurring routinely, althoμgh the effectiveness of the seal can be reduced at sites with high rooted plant densities, even when the plants are trimmed back to the sediment surface plane (Zuloaga et al., 2004).

The representativeness of the pore water samples collected using the modified *in situ* sipper method has been demonstrated in a side-by-side study comparing the chemistry of the pore water collected by the modified *in situ* apparatus to that in pore water collected in the top four cm of surficial sediment using the centrifμgation method (**See Figures AE-3, 4 and 5**). The exception to this generalization is pore water sulfide, which can be lower in the pore water collected by the centrifμgation method, perhaps because of off-gassing of H_2S during centrifμging and/or vacuum filtration of the centrifμged sample. However, lower concentrations in the sipper water have also been encountered. The validity of the sipper method for the collection of pore water sulfide must be considered to be uncertain at present, so the results must be treated as semi-quantitative until the cause of these discrepancies can be identified and corrected, if necessary.

Advantages of the Modified Design

The practical advantages of the *in situ* sipper method over the more cumbersome and time-consuming squeezer or centrifμgation methods are well known and will not be repeated here. The advantages of the modified over the original *in situ* sipper design include hands-free sampling with less susceptibility to inadvertent movement of the probe during sample collection, a more consistent insertion angle, a more reproducible sampling depth at each sampling station, and a much greater pore water sample volume without surface water breakthrough. These design modifications now make routine pore water sampling accessible to a much wider range of entities and for a much wider range of applications.

Many research analytical laboratories and almost all commercial analytical laboratories do not have a microvolume analytical capability, such that the use of the *in situ* pore water piezometers or micro-extractors popular with soil and sediment biogeochemists (REFs) is precluded for all but a few specialists. With our apparatus, following system purging with roμghly 0.03 L of *in situ* pore water, this modified

design allows the subsequent routine collection of roμghly 0.5 L of filtered sample using the acid-precleaned 0.45 micron Meissner capsule filter without surface water breakthrough. Based on a series of field studies described elsewhere (Zuloaga et al., 2004), the sample is likely being collected over an elongated ellipsoid of withdrawal centered beneath the probe tip at an average sediment depth of 0-4 to 0-6 cm (See **Figure AE-6**) in wetland sediments with bulk densities in the range of 50 to 300 Kg/m^3. This is optimal for sampling of ultra-trace MeHg and associated ultra-trace THg and trace sulfide analyses.

The 0.5 L sample volume has proved sufficient for routine replicate (two plus a lab spike) analyses of THg, MeHg, SO_4, S^{-2}, DOC, Cl, Ca, Mg, Fe(II), TFe, and TMn following standard surface water methods. The absence of surface water breakthrough has been verified by monitoring pore water redox potential continuously during collection: redox potentials are in the range of -150 to -300 mv relative to the standard hydrogen electrode and do not approach the redox potentials of the overlying surface water, which are in the range -30 to + 70 mv. The collection of large sample volumes has the additional advantages of overwhelming the short-term, localized effects of probe intromission on mixing of surface water with pore water and the associated change in redox potential and associated chemical speciation, which precludes the need for hours, days, or weeks of re-equilibration, and by averaging out the local microheterogeneities in soil pore water chemistry that could otherwise prove unrepresentative of the pore water at the scale of the system or subsystem of interest.

Disadvantages of the Modified Design

The primary disadvantage of the modified *in situ* sipper design is that in soils or sediments that are perforated by physical (e.g., fissures) or biological (e.g., plant root or burrowing animal) channels or conduits, the path of least resistance of pore water flow may be in the vertical rather than the horizontal, and the larger sample volume accessible to this method maximizes the unrepresentativeness of the sample collected under such circumstances. However, since such channels also increase the physicochemical communication of the upper and lower soil strata in the absence of pore water sampling, the sample may still be representative of the pore water chemistry of the active sediment layer.

A second disadvantage of the modified design is that the sample is collected at a constant sediment bulk modulus rather than a constant sediment depth. However, in water bodies with flocculent and/or unconsolidated sediments, where the water/sediment interface is indistinct and/or ill-defined but the sediment composition and density are relatively uniform, this approach is likely to introduce less variability into the pore water sampling depth than when attempting to insert the probe to a constant depth relative to the perceived water/sediment interface. Moreover, even in water bodies with substantial heterogeneity in sediment composition and bulk density, the depth of mixing of surface water and pore water is a function of the degree of soil or sediment consolidation, and, therefore, proportional to the bulk modulus, so sampling at a depth equal to a constant bulk modulus may result in sampling at a more uniform redox potential between sites than does sampling at a fixed depth. More work is required to validate this hypothesis, however.

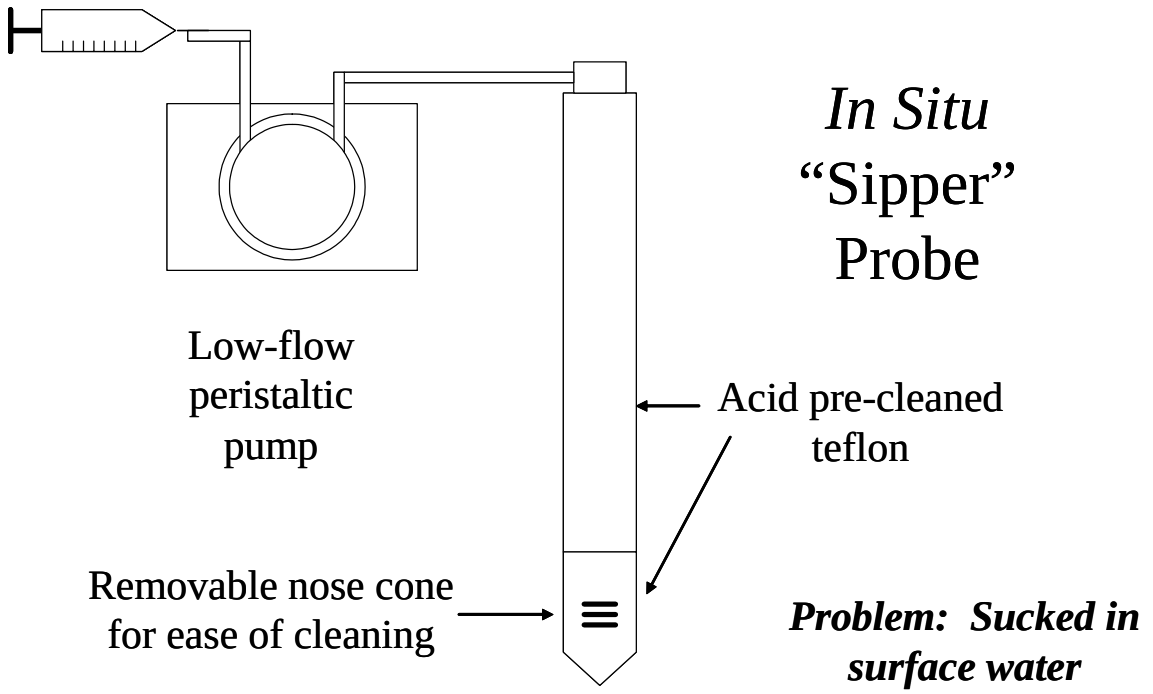

Figure AE-1. Original *in situ* "sipper" design from the U.S. Geological Survey for application to the collection of pore water from surficial sediment for ultra-trace total mercury and methylmercury analysis.

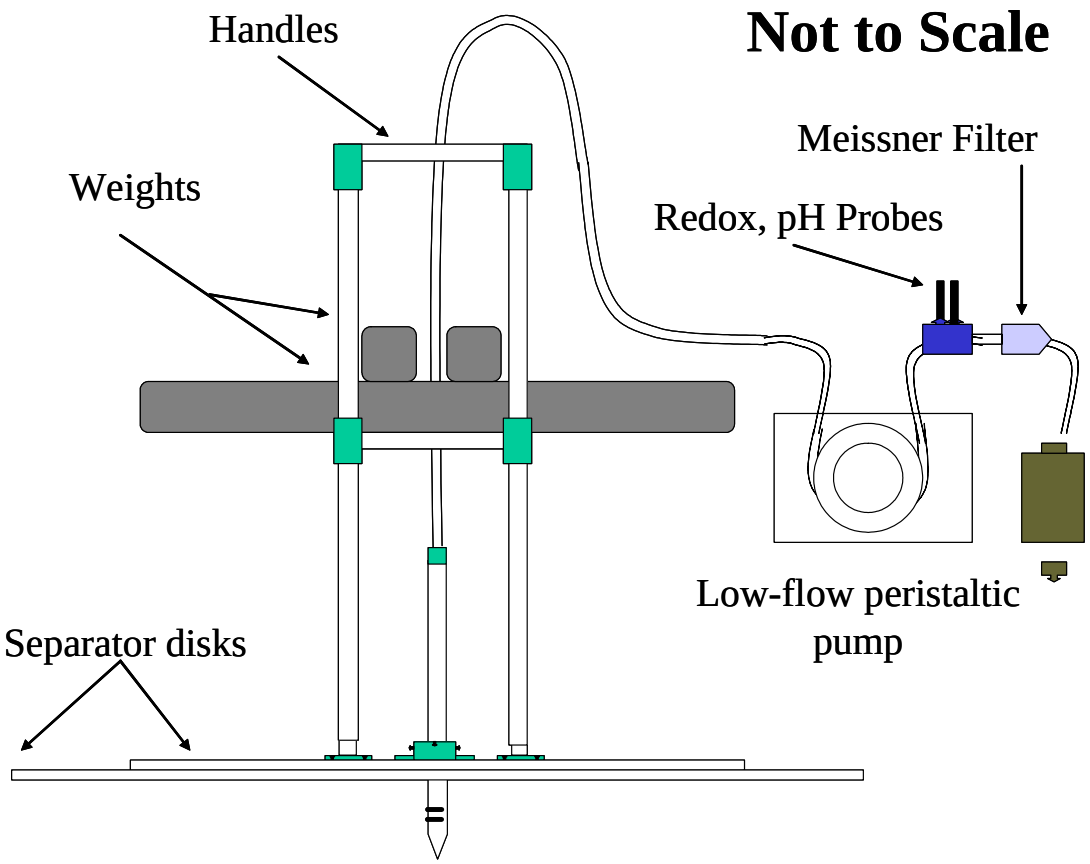

Figure AE-2. Modified *in situ* "sipper" design from the U.S. Geological Survey for application to the collection of pore water from surficial sediment for ultra-trace total mercury and methylmercury analysis.

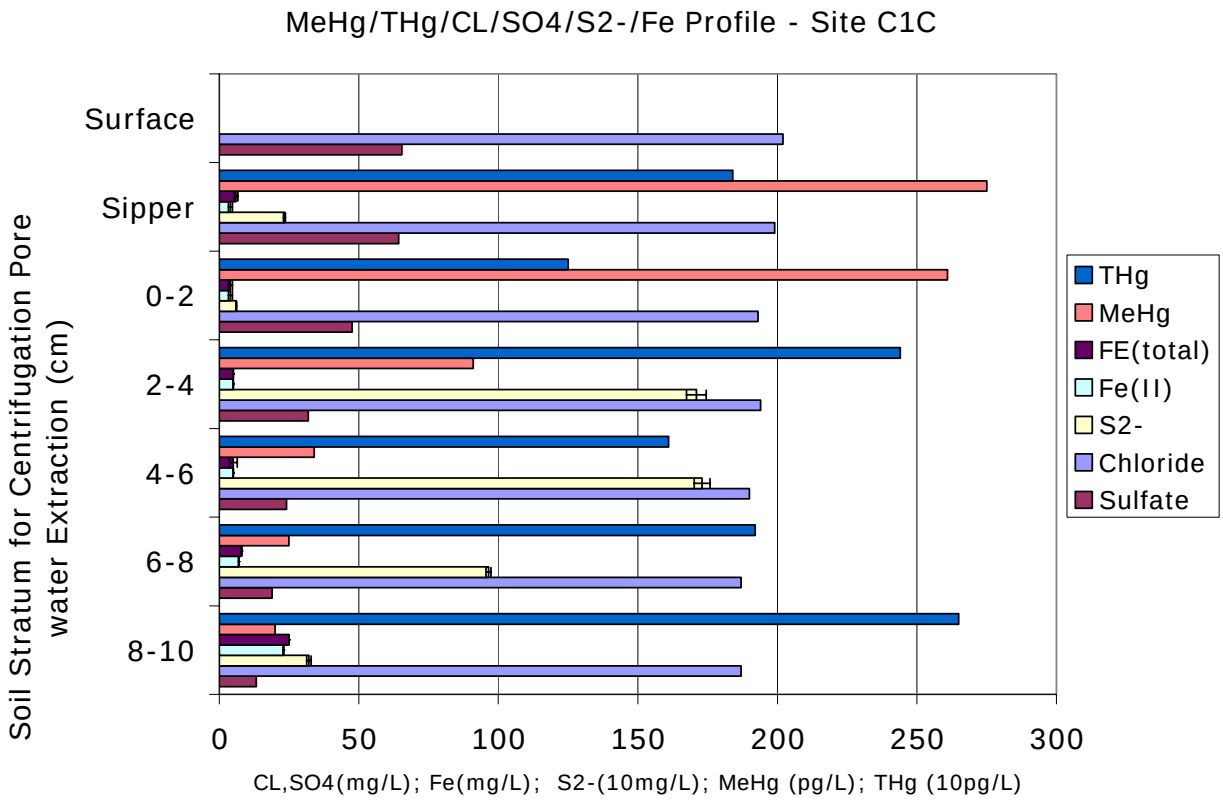

Figure AE-3. Results of side-by-side comparison of centrifiguation method and modified in situ sipper method of pore water collection for Site C1C in STA-2 Cell 1.

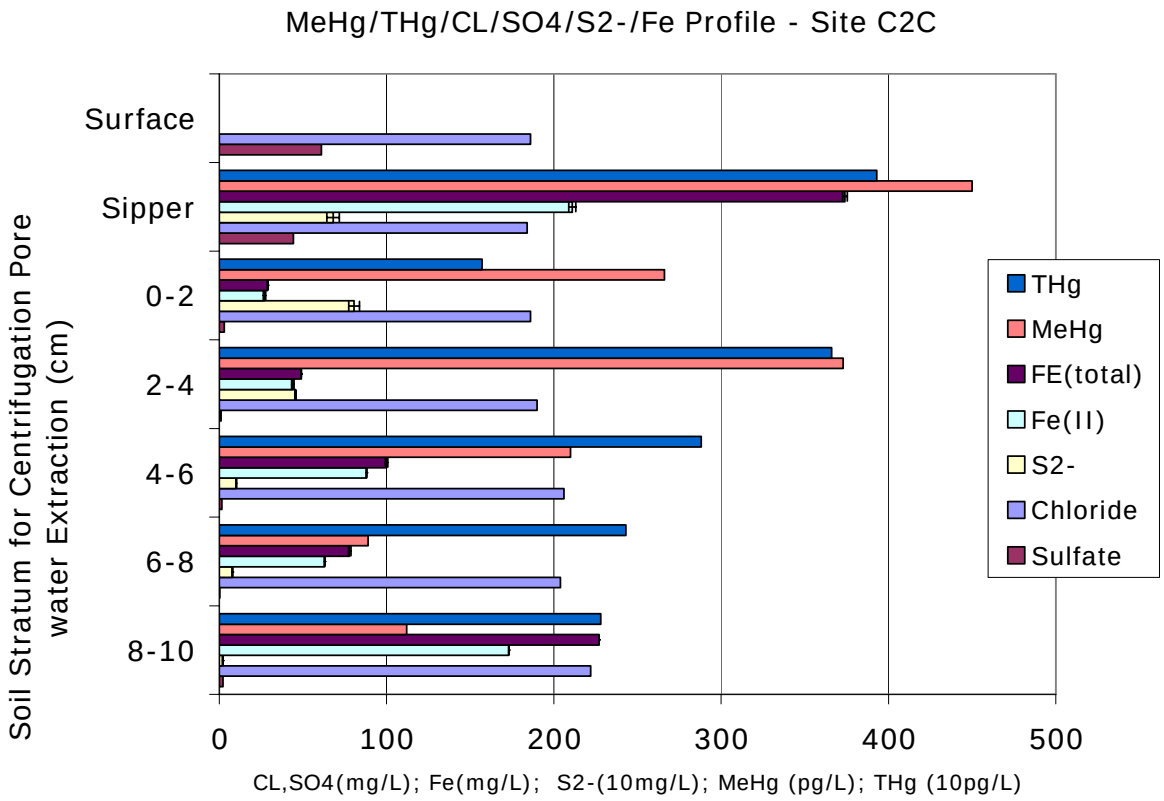

Figure AE-4. Results of side-by-side comparison of centrifiguation method and modified in situ sipper method of pore water collection for Site C2C in STA-2 Cell 2.

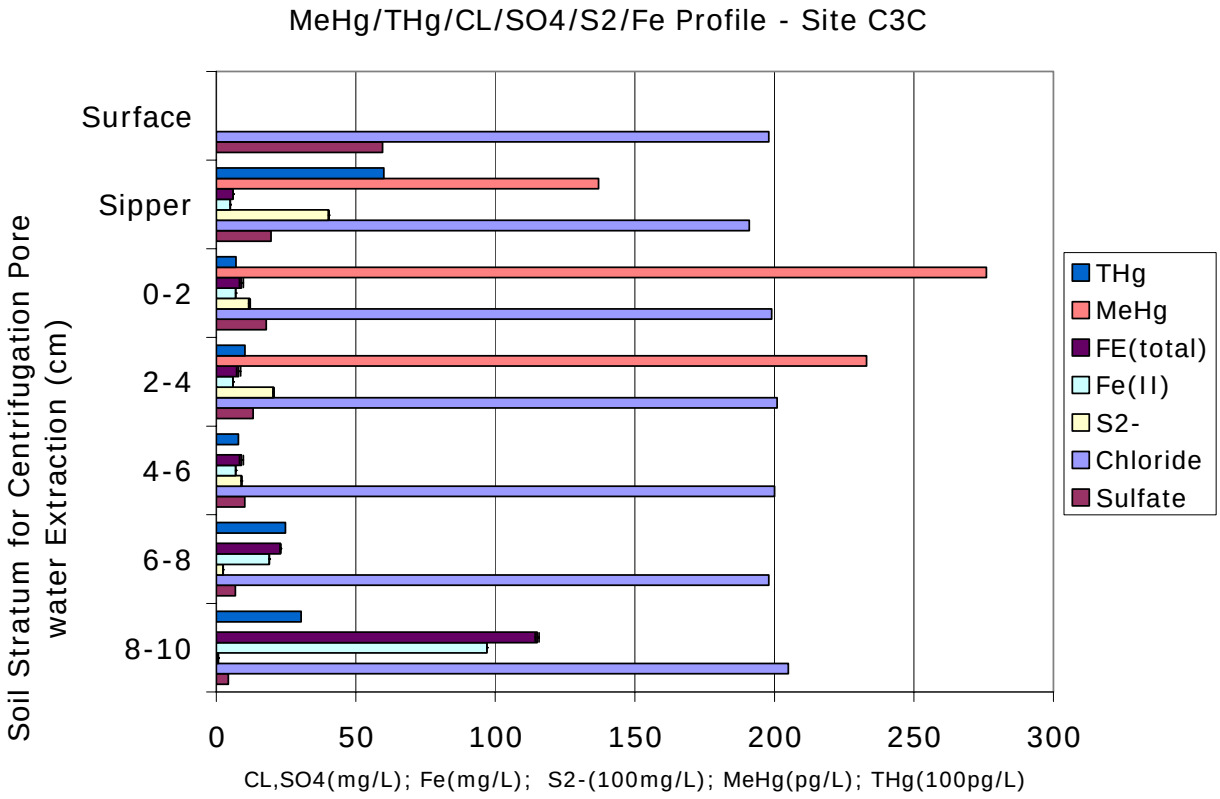

Figure AE-5. Results of side-by-side comparison of centrifiguation method and modified in situ sipper method of pore water collection for Site C3C in STA-2 Cell 3.

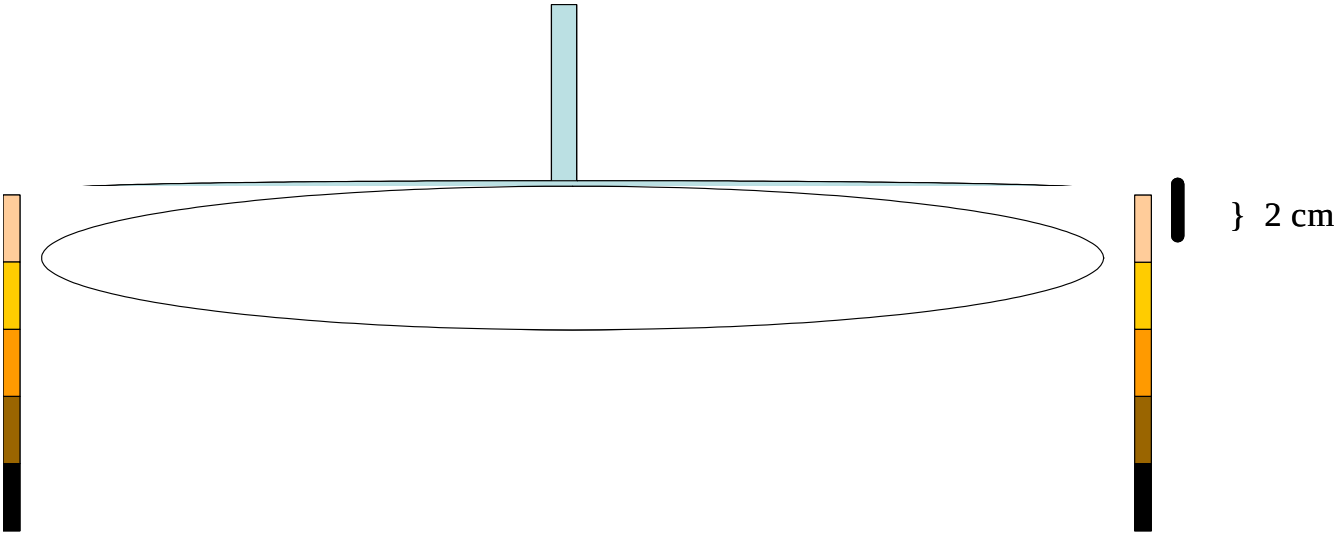

Figure AE-6. Inferred ellipsoid of pore water withdrawal from results of in situ sipper vs. stratified soil centrifugation results.

Appendix F. Standard Operating Procedure for Modified *In Situ* Sipper Method for the Collection of Pore Water for the Quantitative Analysis of Ultra-Trace Mercury Species and Redox-Sensitive Species by Commercial Laboratories

[Tetra Tech Contract Work Product]

STA-2 Mercury Special Studies: Pore Water Methods Development Pre-Study Data Comparing Centrifugation Extraction Method Results for Five Vertical Strata with Modified Sipper Results

	C1C						
Centrifuge Pore Water	CL mg/L	SO4 mg/L	MeHg pg/L	THg ng/L	S2- mg/L	Fe(II) mg/L	FE(total) mg/L
8-10	187	13.3	20	2.65	0.321	23	25
6-8	187	18.9	25	1.92	0.965	7	8
4-6	190	24.1	34	1.61	1.73	5	5
2-4	194	31.9	91	2.44	1.71	5	5
0-2	193	47.6	261	1.25	0.061	4	4
Sipper	199	64.3	275	1.84	0.234	4	6
Surface	202	65.4					
	C2C						
Centrifuge Pore Water	CL mg/L	SO4 mg/L	MeHg pg/L	THg ng/L	S2- mg/L	Fe(II) mg/L	FE(total) mg/L
8-10	222	2.2	112	2.28	0.021	173	227
6-8	204	0.3	89	2.43	0.079	63	78
4-6	206	1.6	210	2.88	0.102	88	100
2-4	190	1.0	373.0	3.66	0.456	44	49
0-2	186	3	266	1.57	0.806	27	29
Sipper	184	44.3	450	3.93	0.681	211	374
Surface	186	61					
	C3C						
Centrifuge Pore Water	CL mg/L	SO4 mg/L	MeHg pg/L	THg ng/L	S2- mg/L	Fe(II) mg/L	FE(total) mg/L
8-10	205	4.3		3.04	0.07	97	115
6-8	198	6.8		2.48	0.246	19	23
4-6	200	10.2		0.79	0.908	7	9
2-4	201	13.2	233	1.03	2.055	6	8
0-2	199	17.9	276	0.71	1.19	7	9
Sipper	191	19.6	137	6.01	4.03	5	6
Surface	198	59.6					

STA-2 Mercury Special Studies: Pore Water methods Development Pre-Study Data Comparing Centrifugation Extraction Method Results for Five Vertical Strata with Modified Sipper Results

SOIL	depth (cm)	Avg BD	Stdev BD	AVS	ash (%)	Fe	Sulfur	MeHg	THg
C3C	0-2	0.078	0.009	368	60.5	1200	2900	0.00035	0.03600
	2-4	0.099	0.005	293	55.6	1500	1700	0.00024	0.02300
	4-6	0.132	0.028	241	37.1	2000	3400	0.00022	0.04700
	6-8	0.247	0.059	281	23.2	2900	7100	0.00020	0.08500
	8-10	0.313	0.023	237	19.2	3300	3100	0.00024	0.08000
C2C	0-2	0.086	0.086	803	21.1	2700	6400	0.00059	0.03800
	2-4	0.127	0.115	601	19.8	2500	7400	0.00015	0.07600
	4-6	0.133	0.097	329	16.9	2900	6100	0.00020	0.07500
	6-8	0.184	0.032	336	16.3	3200	4500	0.00028	0.09300
	8-10	0.195	0.011	240	16.2	2900	4000	0.00028	0.08200
C1C	0-2	0.104	0.006	228	31.2	3300	3300	0.00079	0.08800
	2-4	0.155	0.009	226	27.6	3000	5000	0.00044	0.07600
	4-6	0.165	0.016	309	20.9	2800	7100	0.00020	0.10600
	6-8	0.174	0.027	256	17.3	2600	5700	0.00020	0.13900
	8-10	0.154	0.027	400	16.1	2100	5500	0.00019	0.11900

Sipper vs. Centrifuge Data (n=4 for all except suface where n=1)							
Side-by-Side Pre-Study at STA-2 Site C1C							
Day1:							
		CL	**SO4**	**S2-**	**Fe(II)**	**Fe(T)**	**Redox**
	Surface	212	71.3				-42.1
	Sipper	209±0.6	68.0±0.8	240±27	6±3.1	7±3.7	-135
	Centrifuge	208±1.9	61.7±0.6	461±24	5±0.5	7±1.3	-182
Day2:		**CL**	**SO4**	**S2-**	**Fe(II)**	**Fe(T)**	**Redox**
	Surface	211	71.4				-39.9
	Sipper	208±3.1	62.5±1.0	1317±63	3±0	3±0.5	-186
	Centrifuge	212±2.4	60.4±0.3	576±37	5±0.5	6±1.0	-264

Ultra-Trace THg and MeHg Results from Side-By-Side Sipper vs Centrifuge Pore Water Collection Method Validation Study at Site C1C

PROJECT	SAMPLE_ID	FLAG	VALUE	UNITS	REM	DATE	SAMPLE_T	DEPTH	TEST	TEST_NAME
ST2P	P18898-1	V	0.77	ng/L		04/20/04	EB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18898-2		0.042	ng/L	I	04/20/04	EB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18898-4	V	2	ng/L		04/20/04	SAMP	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18898-5		0.732	ng/L		04/20/04	SAMP	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18898-7	V	2.17	ng/L		04/20/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18898-8		0.844	ng/L		04/20/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18898-10		2.48	ng/L		04/20/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18898-11		0.815	ng/L		04/20/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18898-13	V	2.17	ng/L		04/20/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18898-14		0.803	ng/L		04/20/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18898-19		0.31	ng/L	I	04/20/04	EB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18898-20		0.022	ng/L	I	04/20/04	EB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18898-22		0.37	ng/L	I	04/20/04	FCEB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18898-23		0.044	ng/L	I	04/20/04	FCEB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18899-1		0.46	ng/L		04/20/04	FKPB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18899-2		-0.003	ng/L	U	04/20/04	FKPB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18899-3		-0.03	ng/L	U	04/20/04	EB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18899-4		-0.001	ng/L	U	04/20/04	EB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18899-6		2.04	ng/L		04/20/04	SAMP	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18899-7		1.07	ng/L		04/20/04	SAMP	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18899-9		2.17	ng/L		04/20/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18899-10		1.1	ng/L		04/20/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18899-12		1.83	ng/L		04/20/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18899-13		1.14	ng/L		04/20/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18899-15		-0.06	ng/L	U	04/20/04	FCEB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18899-16		-0.004	ng/L	U	04/20/04	FCEB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18899-18		1.86	ng/L		04/20/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18899-19		1.14	ng/L		04/20/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18988-1		0.39	ng/L	I	04/21/04	EB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18988-2		0.046	ng/L	I	04/21/04	EB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18988-4		2.41	ng/L		04/21/04	SAMP	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18988-5		0.606	ng/L		04/21/04	SAMP	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18988-7		2.24	ng/L		04/21/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18988-8		0.702	ng/L		04/21/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18988-10		2.31	ng/L		04/21/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18988-11		0.625	ng/L		04/21/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18988-13		2.41	ng/L		04/21/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18988-14		0.737	ng/L		04/21/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18988-19		0.29	ng/L	I	04/21/04	EB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18988-20		0.02	ng/L	I	04/21/04	EB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18988-22		0.34	ng/L	I	04/21/04	FCEB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18988-23		0.023	ng/L	I	04/21/04	FCEB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18989-3		0.15	ng/L	I	04/21/04	EB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18989-4		-0.012	ng/L	U	04/21/04	EB	0	203	METH MERCURY, TOT ULTRATR
ST2P	P18989-6		1.11	ng/L		04/21/04	SAMP	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18989-7		0.214	ng/L		04/21/04	SAMP	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18989-9		1.11	ng/L		04/21/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18989-10		0.17	ng/L		04/21/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18989-12		1	ng/L		04/21/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18989-13		0.244	ng/L		04/21/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18989-15		1.14	ng/L		04/21/04	RS	0.04	207	MERCURY, TOT, ULTRATRACE
ST2P	P18989-16		0.261	ng/L		04/21/04	RS	0.04	203	METH MERCURY, TOT ULTRATR
ST2P	P18989-18		0.11	ng/L	I	04/21/04	FCEB	0	207	MERCURY, TOT, ULTRATRACE
ST2P	P18989-19		-0.007	ng/L	U	04/21/04	FCEB	0	203	METH MERCURY, TOT ULTRATR

Appendix G. Data Collected for the STA-2 Mercury Special Studies Project

Table 1A. THg Concentration Data for Weekly Integrated Rain Samples Collected and Analyzed at STA-2 (FL99) According to NADP/MDN Protocols

FL99

Collection End Date	Precip. Hg Conc. (ng/L)
09/03/02	23.23
09/10/02	11.64
09/17/02	11.62
09/24/02	6.61
10/01/02	6.60
10/15/02	6.90
10/22/02	8.20
10/29/02	1.42
11/05/02	1.94
11/12/02	13.30
11/19/02	6.40
11/26/02	2.10
12/03/02	5.00
12/10/02	7.10
12/17/02	6.80
12/23/02	7.40
12/31/02	2.07
01/07/03	19.80
01/14/03	13.90
01/21/03	2.84
01/28/03	4.69
02/04/03	3.70
02/11/03	8.70
02/18/03	18.30
02/25/03	7.40
03/04/03	10.70
03/11/03	13.30
03/18/03	10.30
03/25/03	6.60
04/01/03	18.00
04/08/03	8.34
04/15/03	9.20
04/22/03	16.60
04/29/03	9.90
05/06/03	13.60
05/13/03	1.74
05/20/03	22.20
05/27/03	15.20

FL99

Collection End Date	Precip. Hg Conc. (ng/L)
06/03/03	9.20
06/10/03	20.90
06/17/03	33.00
06/24/03	17.50
07/01/03	18.90
07/08/03	22.00
07/15/03	28.40
07/22/03	26.40
07/29/03	27.10
08/05/03	39.30
08/12/03	32.10
08/19/03	12.60
08/26/03	19.00
09/02/03	12.00
09/09/03	15.50
09/16/03	24.10
09/23/03	22.50
09/30/03	11.10
10/07/03	2.15
10/14/03	41.10
10/21/03	6.00
10/28/03	8.40
11/04/03	3.20
11/12/03	6.70
11/18/03	32.30
11/25/03	2.79
12/02/03	25.10
12/09/03	11.50
12/16/03	4.20
12/23/03	5.80
12/30/03	3.02
01/06/04	2.38
01/13/04	2.45
01/20/04	3.88
01/27/04	3.65

Table 1B. Concentrations of Constituents Other Than Mercury in Monthly Integrated Rain Samples Collected for the Florida Atmospheric Mercury Study at Andytown and ENR Project

Florida Atmospheric Mercury Study Non-Mercury Rain Concentration Data

STATION	START	STOP	NA	K	CA	MG	CL	NO3-N	SO4-S	TN	NH4-N	PH
			[all concentrations in units of microgram per liter, except pH, which is unitless]									
AT	02/06/95	03/08/95	1927	75	439	227	3102		530			
AT	03/08/95	04/05/95	3494	113	402	383	5953		517			4.3
AT	04/05/95	05/02/95	667	38	366	72	862		195			3.9
AT	05/02/95	05/30/95	455	38	621	51	739		527			3.3
AT	05/30/95	06/26/95	434	19	256	43	516		202		33	4.5
AT	06/26/95	07/25/95	349	19	548	51	447		444		26	3.3
AT	07/25/95	08/30/95	434	19	292	43	560		275		17	4.0
AT	08/30/95	09/25/95	371	19	329	36	409		348			3.7
AT	09/25/95	10/24/95	371	0	256	32	424	320	177	405	45	4.2
AT	10/24/95	11/29/95										
AT	11/29/95	01/06/96	316	6	74	48	871		369		46	3.1
AT	01/06/96	01/31/96										
AT	01/31/96	02/26/96										
AT	02/26/96	03/27/96	400	36	43	51	1207		387		121	2.4
AT	03/27/96	05/01/96	279	10	187	44	860		435		23	3.1
AT	05/01/96	05/30/96	137	0	53	21	321	153	215	287	109	4.6
AT	05/30/96	06/26/96	308	13	53	49	659		180		25	5
AT	06/26/96	07/31/96	3337	7	319	47	702	341	292	397	82	4.9
AT	07/31/96	08/28/96					530	159	276	166	49	4.8
AT	08/28/96	10/02/96					339	117	277	117	26	4.5
AT	10/02/96	10/30/96					662	38	93	47	42	4.8
AT	10/30/96	12/04/96					8550	131	545	226	83	4.8
AT	12/04/96	01/08/96					5412	183	512	413	214	4.9
EN	02/05/95	03/08/95	1239	38	621	173	16669		331			4.5
EN	03/08/95	04/05/95	678	0	439	90	879		366			4.3
EN	05/01/95	05/30/95	752	19	548	94	930		391			4.0
EN	05/30/95	06/26/95	593	38	183	61	845	913	333	1178	51	4.1
EN	06/26/95	07/24/95	275	19	292	32	257	1408	277	1634	93	3.8
EN	07/24/95	08/30/95	508	131	402	54	498	439	354	2281	428	6.0
EN	08/30/95	09/24/95	286	19	219	22	276		282			3.6
EN	09/24/95	10/23/95	413	113	183	36	529		257	1849	5	3.4
EN	10/23/95	11/29/95	1090	75	402	144	9994		940			2.5
EN	11/29/95	01/06/96	1101	113	439	155	2431		1099		194	2.0
EN	01/06/96	01/31/96	711	0	27	101	1519		212		35	3.5
EN	01/31/96	02/26/96										
EN	02/26/96	03/27/96	415	0	0	50	3038		185		31	2.6
EN	03/27/96	05/01/96	288	0	21	41	648		315		110	4.3
EN	05/01/96	05/30/96	167	19	102	28	339	225	301	384	158	4.4
EN	05/30/96	06/26/96	215	17	65	31	417	160	171	196	35	4.9
EN	06/26/96	07/31/96	252	21	167	45	227		401	281	75	4.7
EN	07/31/96	08/28/96					128		666	202	43	4.4
EN	08/28/96	10/01/96					264		153	59	47	4
EN	10/01/96	10/30/96					2141	47	180	77	50	4.7
EN	10/30/96	12/04/96					2278	53	160	112	42	4.6
EN	12/04/96	01/08/96					3586	231	528	414	40	4.7
ong-Term Average Concentratior			718	33	269	76	1976	307	358	536	77	4

AT = Andytown
EN = ENR Project

Table 2A. All Inflow and Outflow THg Data (all concentrations in units of ng/L)

THg

	S6	G328	Inflow (G328B)	FILTER INFLOW G328B	RATIO	Cell 1 (G330A)	FILTER G330A	RATIO	G330B C1A	Cell 2 (G332)	FilLTER Cell 2 (G332)	RATIO	Cell 3 (G334)	FILTER cell3 (G334)
10/4/01	0.00	0.7	1.2			-				1.2	-		-	
10/18/01			0.89			-				1.1	-		-	
11/1/01			0.69			-				0.87	-		-	
11/15/01			0.75			5.8				0.9	2		1.2	
11/29/01			0.34			9.5				-	1.6		-	
12/12/01			1.3			7.8				1.3	2.4		2.7	
12/27/01			0.5			-				-	1.8		1	
1/10/02	0.00	0.41	0.5			-				-	1.7		0.59	
1/24/02	-	-	1.4			-				-	3.1		2.1	
2/7/02	-	-	0.88			-				-	1.5		0.81	
2/21/02	-	-	1.7			3.7				1.9	2		2	
3/7/02	-	-	1.4			3.4				-	1.6		0.66	
3/21/02	-	-	1.2			2.6				-	1.9		1.2	
4/4/02		-	0.84			-				-	1.7		1.2	
4/18/02	0.00	0.79	0.73			5.3				-	1.8		1.2	
5/2/02	-	-	0.72			-				-	1.5		1.1	
5/16/02	-	-	0.69			-				-	1.4		1.1	
5/30/02	-	-	0.83			-				-	1.2		0.99	
6/12/02	-	-	0.94			-				-	2.4		1.6	
6/27/02	-	-	1.9			4.4			5.1	4.4	1.9		1.1	
7/11/02	0.00	1.2	2.4			4.1				3.7	1.5		0.74	
7/25/02	-	-	3.1			6.3				10	4.1		3.4	
8/7/02	-	-	1.5			-				1.2	3.3		1.3	
8/22/02	-	-	2	0.62	0.31	11	9.8	0.89		6.2	3.2		1.9	
9/5/02	-	-	1.6			12				1.5	1.7		1.1	
9/18/02	-	-	0.96	0.5	0.52	18				1.2	1.5	1 0.67	0.82	
10/3/02	-	-	0.53			9.2				1.8	2.2		0.7	
10/17/02	-	-	0.69	0.45	0.65	11				0.92	2		0.89	0.6
10/31/02	0.59	0.76	0.92			8.9				3	3.1		1.1	
11/14/02	-	-	0.61	0.4	0.66	8.1	6	0.74		0.74	1.8		0.9	
11/25/02	-	-	1.2			3.5			-	0.81	1.7		0.79	
12/12/02	-	-	0.92	0.53	0.58	3.3				0.68	0.99	0.76 0.77	0.51	
12/30/02	-	-	0.88			2.7				0.69	0.84		0.36	
1/9/03	-	-	0.55	0.29	0.53	2.9				0.74	0.69		0.43	0.41
1/23/03	0.62	0.69	0.74			2.3				14.8	0.61		0.66	
1/30/03	-	-	0.45			2.7				0.42	0.79		0.45	
2/5/03	-	-	2.3	0.53	0.23	3.8	3.5	0.92		0.6	1.2		0.79	
2/20/03	-	-	1.4	-		5.8	-			1.7	1.6	-	2.6	-
3/6/03	-	-	0.73	0.56	0.77	7.5	-			2.7	1.6	1 0.63	0.91	-
3/20/03	2.2	1.3	1.1	-		3.7	-			1	1.5	-	0.72	-
4/2/03			1.4	0.58	0.41	2.2	-			0.64	0.88	-	0.59	0.31
4/17/03	0.56	0.56	0.7	-		2.9	-			0.7	0.87	-	0.31	-
5/1/03	-	-	1.7	0.87	0.51	3.7	2.6	0.70		0.8	0.7	-	0.59	-
5/14/03	-	-	1	-		3.4	-			1.3	1.7	-	0.73	-
5/29/03	-	-	2.9	1.3	0.45	2.3	-			0.6	0.77	0.51 0.66	1.1	-
6/12/03	-	-	1.4	-		1.8	-			1.2	0.9	-	0.86	-
6/26/03	-	-	1.6	0.87	0.54	1.2	-			1.4	1.1	-	1.2	0.77
7/9/03	-	-		-		2.7	-			1.5	1.3	-	0.75	-
7/24/03	-	-	1.8	1	0.56	2.2	1.7	0.77		0.98	1.2	-	1.1	-
8/7/03	-	-	1.2	-		1.8	-			1	0.62	-	0.48	-
8/25/03	-	-	1.7	0.86	0.51	1.6	-			0.92	1	0.52 0.52	0.68	-
9/4/03	-	-	0.78	-		1.3	-			0.76	1.1	-	0.96	-
9/18/03	-	-	0.61	0.41	0.67	1.8	-			0.85	1.5	-	1	0.81
10/2/03	-	-	1.2	-		1.3	-			0.59	0.77	-	0.57	-
10/16/03	-	-	0.79	0.4	0.51	1.9	1.4	0.74		8.3	1.8	-	0.71	-
10/31/03	-	-	0.69	-		2.1	-			discontinued	1.8	-	0.81	-
11/13/03	-	-	1.5	0.38	0.25	1.6	-				1.4	0.97 0.69	0.49	-
11/25/03	0.31	0.07	0.41	-		1.3	-				0.92	-	0.52	-
12/11/03	-	-	0.48	0.24	0.50	1.1	-				0.81	-	0.66	0.43
12/23/03	-	-	0.66	-		0.95	-				0.64	-	0.39	-
1/8/04	-	-	0.5	0.37	0.74	1.4	0.89	0.64			0.92	-	0.56	-
1/22/04	0.63	0.75	0.69	-		1.6					0.92	-	0.75	-

Table 2B. All Inflow and Outflow MeHg Data (all concentrations in units of ng/L)

MeHg	S6	G328	Inflow (G328B)	FILTER INFLOW G328B	RATIO	Cell 1 (G330A)	FILTER G330A	RATIO	G330B C1A	Cell 2 (G332)	FiILTER Cell 2 (G332)	RATIO	Cell 3 (G334)	FILTER cell3 (G334)
10/4/01	-	0.07	0.15			-			0.31	-			-	
10/18/01	-	-	0.13			-			0.37	-			-	
11/1/01	-	-	0.14			-			0.16	-			-	
11/15/01	-	-	0.12			3.5			0.43	0.73			0.32	
11/29/01	-	-	0.084			7.2			0.44	1			0.3	
12/12/01	-	-	0.061			2			0.55	0.7			0.82	
12/27/01	-	-	0.057			-			-	0.34			0.11	
1/10/02	-	0.059	0.035	-		-	-		-	0.24	-		0.032	-
1/24/02	-	-	0.092	-		-	-		-	0.71	-		0.25	-
2/7/02	-	-	0.081	-		-	-		-	0.35	-		0.11	-
2/21/02	-	-	0.13	-		1.4	-		0.59	0.22	-		0.15	-
3/7/02	-	-	0.087	-		1.2	-		-	0.34	-		0.17	-
3/21/02	-	-	0.18	-		1.2	-		-	0.76	-		0.33	-
4/4/02	-	-	0.061	-		F*	-		-	F*	-		F*	-
4/18/02	-	0.9	0.11	-		0.76	-		-	0.41	-		0.33	-
5/2/02	-	-	0.072	-		-	-		-	0.3	-		0.26	-
5/16/02	-	-	0.09	-		-	-		-	0.21	-		0.22	-
5/30/02	-	-	0.03	-		-	-		-	0.089	-		0.065	-
6/12/02	-	-	0.057	-		-	-		-	0.35	-		0.19	-
6/27/02	-	-	0.27	-		1.8	-		2.1 2.6	0.4	-		0.099	-
7/11/02	-	0.33	0.3	-		2.1	-		- 1.8	0.41	-		0.12	-
7/25/02	-	-	0.15	-		-	-		- 1.1	0.74	-		0.36	-
8/7/02	-	-	0.25	-		-	-		- 0.32	1.2	-		0.24	-
8/22/02	-	-	0.12	0.13	**1.08**	7.6	7.2	0.95	0.82	1	-		0.21	-
9/5/02	-	-	0.15	-		8.4	-		0.39	0.38	-		0.14	-
9/19/02	-	-	0.13	0.13	**1.00**	12	-		0.96	0.87	0.72	0.83	0.31	-
10/3/02	-	-	0.092	-		7.8	-		0.75	1.2	-		0.15	-
10/17/02	-	-	0.048	0.042	0.88	5.8	-		0.26	1.1	-		0.08	0.11
10/31/02	0.13	0.086	0.057	-		4.2	-		0.26	1	-		0.15	-
11/14/02	-	-	0.076	0.065	0.86	2.3	2.2	0.96	0.17	0.55	-		0.098	-
11/26/02	-	-	0.081	-		0.76	-		0.088	0.17	-		0.07	-
12/12/02	-	-	0.12	0.085	0.71	1.6	-		0.062	0.16	0.11	0.69	0.087	-
12/30/02	-	-	0.023	-		0.98	-		0.14	0.14	-		0.077	-
1/9/03	-	-	0.062	0.064	**1.03**	1.1	-		0.096	0.092	-		0.067	0.057
1/23/03	0.056	0.039		-		0.72	-		0.05	0.048	-		0.05	-
1/30/03	-	-	0.032	-		0.97	-		0.068	0.035	-		0.041	-
2/5/03	-	-	0.038	0.034	0.89	2	1.7	0.85	0.1	0.11	-		0.11	-
2/20/03	-	-	0.07	-		4	-		0.9	0.56	-		0.86	-
3/6/03	-	-	0.12	0.12	**1.00**	5.4	-		1.3	0.92	0.63	0.68	0.35	-
3/20/03	0.14	0.22	0.16	-		1.8	-		0.4	0.48	-		0.12	-
4/2/03	-	-	0.18	0.17	0.94	0.82	-		0.14	0.14	-		0.081	0.064
4/17/03	0.053	0.27	0.15	-		1.5	-		0.14	0.36	-		0.1	-
5/1/03	-	-	0.2	0.16	0.80	1.5	1.2	0.80	0.16	0.14	-		0.096	-
5/14/03	-	-	0.10	-		1.40	-		0.14	0.58	-		0.12	-
5/29/03	-	-	0.17	0.14	0.82	0.7	-		0.049	0.12	0.093	0.78	0.071	-
6/12/03	-	-	0.21	-		0.38	-		0.15	0.088	-		0.092	-
6/26/03	-	-	0.24	0.22	0.92	0.086	-		0.14	0.096	-		0.16	0.37
7/9/03	0.12	0.14	0.079	-		1.3	-		0.32	0.48	-		0.22	-
7/24/03	-	-	0.12	0.13	**1.08**	0.43	0.37	0.86	0.08	0.2	-		0.17	-
8/5/03	-	-	0.21	-		0.2	-		0.12	0.033	-		0.046	-
8/25/03	-	-	0.18	0.21	**1.17**	0.22	-		0.08	0.054	0.058	**1.07**	0.065	-
9/4/03	-	-	0.1	-		0.14	-		0.096	0.12	-		0.15	-
9/18/03	-	-	0.09	0.087	0.97	0.46	-			0.3	-		0.14	0.14
10/2/03	-	-	0.21	-		0.15	-		0.032	0.05	-		0.43	-
10/16/03	-	-	0.086	0.099	**1.15**	0.98	0.94	0.96	0.07	1.2	-		0.16	-
10/29/03	-	-	0.059	-		0.85	-		discontinued	0.88	-		0.077	-
11/13/03	-	-	0.095	0.072	0.76	0.43	-		-	0.53	0.47	0.89	0.1	-
11/25/03	0.089	0.07	0.051	-		0.33	-		-	0.32	-		0.093	-
12/11/03	-	-	0.039	0.048	**1.23**	0.19	-		-	0.14	-		0.056	0.05
12/23/03	-	-	0.038	-		0.12	-		-	0.056	-		0.14	-
1/8/04	-	-	0.042	0.036	0.86	0.28	0.24	0.86	-	0.24	-		0.059	-
1/22/04	0,075	0.064	0.054	-		0.25	-		-	0.13	-		0.1	-
flagged														
means	0.10	0.23	0.12	0.12		1.97	2.27		0.42	0.42	0.35		0.17	0.15

Table 2C. Interior Cell (Experimental) THg and MeHg Data (all concentrations in units of ng/L)

THg		C1AA	C1AA Filtered	Ratio	STA2 C1BB	C1BB Filtered	Ratio	STA2 C1CC	C1CC Filtered	Rati	STA2 C2A	C2A Filtered	Ratio	STA2 C2B	C2B Filtered		STA2 C2C	C2C filtered	Ratio
	Aug-02	7.6	5.6	0.74	16.00	8.10	0.51	32.00	24	##		3.4			2.1			0.71	
	Sep-02		2.7			4.2			12		2.6	2	0.77	2.1	2.1	1.00	1.5	1.1	0.73
	Oct-02		0.99			1.6			5			1.3			1.4			0.87	
	Nov-02	0.98	0.8	0.82	1.8	1.4	0.78	4	3	##		1.2			0.95			0.67	
	Dec-02		0.61			0.92			2.9		1.2	1.1	0.92	1.2	1	0.83	0.59	0.52	0.88
	Jan-03		0.87			0.88			2.2			0.7			0.78			0.18	
	Feb-03	0.76	0.65	0.86	1.5	0.98	0.65	2.9	2.4	##		0.8			0.78			0.68	
	Mar-03		2.2			3.5			4.6		1.8	1.4	0.78	1.8	1	0.56	1.3	1.2	0.92
	Apr-03		0.6			0.7			1.4			0.61			0.53			0.48	
	May-03	0.86	0.85	0.99	1.1	0.91	0.83	2.1	2	##		0.79			0.85			0.5	
	May-03		2.7			3.7			2.6		2.8	2.6	0.93	3	2.7	0.90	2.6	2.5	0.96
	Jun-03		0.92			0.84			1.2			0.96			0.85			0.71	
	Jul-03	0.85	0.62	0.73	1.1	1	0.91	1.1	1.1	##		1			0.81			0.64	
	Aug-03		0.81			0.74			1.2		1.7	1.1	0.65	1.2	0.6	0.50	0.86	0.69	0.80
	Sep-03		0.54			0.61			1.3			1.1			0.7			1	
	Oct-03	1	0.84	0.84	2.70	1.5	0.56	2.1	1.7	##		1			1.1			1.4	
	Nov-03		0.34			0.49			0.62		1.3	1.1	0.85	0.9	0.64	0.71	0.69	0.43	0.62
	Dec-03		0.41			0.67			0.8			0.7			0.41			0.39	
	Jan-04	0.85	0.67	0.79	1.00	0.83	0.83	1.2	1	##		0.54			0.82			0.64	
		last updated 3/01/04																	
MHG				**Ratio**			**Ratio**			**Ratio**			**Ratio**			**Ratio**			**Ratio**
	Aug-02	2.6	2.7	1.04	8.6	7.4	0.86	20	20	##		0.57			0.33			0.034	
	Sep-02	-	2			3.5			7.8		0.68	0.69	1.01	0.7	0.76	1.09	0.2	0.18	0.90
	Oct-02	-	0.24			0.57			2			0.22			0.16			0.13	
	Nov-02	0.26	0.25	0.96	0.64	0.59	0.92	1.1	1	##		0.17			0.18			0.17	
	Dec-02	-	0.064			0.16			0.81		0.085	0.099	1.16	0.17	0.15	0.88	0.03	0.024	0.80
	Jan-03	-	0.12			0.19			0.41			0.065			0.1			0.051	
	Feb-03	0.12	0.12	1.00	0.46	0.41	0.89	1.1	1.1	##		0.07			0.074			0.058	
	Mar-03		1.1			1.5			2.4		0.83	0.64	0.77	0.86	0.62	0.72	0.64	0.44	0.69
	Apr-03		0.1			0.19			0.31			0.18			0.1			0.091	
	May-03	0.14	0.12	0.86	0.26	0.18	0.69	0.59	0.51	##		0.18			0.13			0.011	
	May-03		0.041			0.12			0.32		0.14	0.12	0.86	0.087	0.14	1.61	0.011	0.011	1.00
	Jun-03		0.011			0.079			0.11			0.13			0.088			0.011	
	Jul-03	0.076	0.067	0.88	0.21	0.22	1.05	0.17	0.15	##		0.13			0.14			0.085	
	Aug-03		0.046			0.052			0.29		0.33	0.36	1.09	0.16	0.14	0.88	0.12	0.071	0.59
	Sep-03		0.11			0.038			0.19			0.35			0.18			0.12	
	Oct-03	0.2	0.21	1.05	0.33	0.43	1.30	0.062	0.062	##		0.24			0.43			0.35	
	Nov-03		0.14			0.11			0.27		0.14	0.12	0.86	0.21	0.12	0.57	0.14	0.15	1.07
	Dec-03		0.053			0.086			0.12			0.047			0.056			0.067	
	Jan-04	0.2	0.18	0.90	0.2	0.16	0.80	0.23	0.22	##		0.063			0.063			0.11	

Table 3. All Soil THg and MeHg Data (all concentrations in mg/Kg dry wt)

STATION_ID	DATE	BD	TCA	TFE	TMG	TMN	THG	MEHG	TN	%ASH	TP	MOIST	TS
STA2S1	4/21/99						0.0408	0.0004					
STA2S2	4/21/99						0.0866	0.0032					
STA2S3	4/21/99						0.0718	0.0002					
STA2S4	4/21/99						0.1034	0.0019					
STA2S5	4/21/99						0.1025	0.0026					
STA2S6	4/21/99						0.1388	0.005					
STA2C1C	12/14/00	0.19										81.73	
STA2C1C	12/14/00			2400						16.4			5200
STA2C1C	12/14/00						0.0971	0.0014					
STA2C1B	12/14/00	0.16										85.55	
STA2C1B	12/14/00			1800						13.1			7000
STA2C1B	12/14/00						0.168	0.0032					
STA2C1A	12/14/00	0.22										79.74	
STA2C1A	12/14/00			1300						18.9			4800
STA2C1A	12/14/00						0.143	0.0094					
STA2C1A	12/14/00	0.2										78.41	
STA2C1A	12/14/00			1300						15.1			4900
STA2C1A	12/14/00						0.116	0.004					
STA2C2A	12/19/00	0.17										81.04	
STA2C2A	12/19/00			2800						16.5			5000
STA2C2A	12/19/00						0.139	0.0011					
STA2C2A	12/19/00	0.18										81.48	
STA2C2A	12/19/00			2500						15.4			3800
STA2C2A	12/19/00						0.131	0.0009					
STA2C2B	12/19/00	0.23										83.56	
STA2C2B	12/19/00			3700						27.3			4000
STA2C2B	12/19/00						0.122	0.0021					
STA2C2C	12/19/00	0.25										76.36	
STA2C2C	12/19/00			2300						15.1			2600
STA2C2C	12/19/00						0.09	0.0014					
STA2S2	12/19/00	0.2										78.89	
STA2S2	12/19/00			3000						16.6			4000
STA2S2	12/19/00						0.106	0.0016					
STA2C1A	4/29/02						0.137	0.0053					
STA2C2A	4/29/02						0.0691	0.0003					
STA2C2C	4/29/02						0.0673	0.0006					
STA2C3A	4/29/02						0.126	0.0005					
STA2C3C	4/29/02						0.113	0.0005					
STA2C3D	4/29/02						0.0336	0.0003					
STA2C1AA	5/16/02						0.125	0.003					
STA2C1AA	5/16/02	0.104	33000	2200	4100	89			33000	11.8	606	77.66	9200
STA2C1AA	5/16/02												
STA2C1BB	5/16/02						0.216	0.0067					
STA2C1BB	5/16/02	0.158	30000	1200	4100	130			32500	12.2	432	78.55	8200
STA2C1BB	5/16/02												
STA2C1CC	5/16/02						0.188	0.0055					
STA2C1CC	5/16/02	0.157	30000	1500	4000	80			32600	10.5	452	69.21	6100
STA2C1CC	5/16/02												
STA2C2C	5/16/02						0.113	0.0011					
STA2C2C	5/16/02	0.236	37000	2700	4100	190			30000	13	496	77.54	3800
STA2C2C	5/16/02												
STA2C2B	5/21/02						0.099	0.0006					
STA2C2B	5/21/02	0.213							31900	12	634	75.26	3700
STA2C2B	5/21/02												
STA2C2A	5/21/02						0.0996	0.0005					
STA2C2A	5/21/02	0.218	47000	2300	4100	160			30500	14.2	496	76.59	4100
STA2C2A	5/21/02												
STA2C3A	5/21/02						0.0599	-5E-05					
STA2C3A	5/21/02	0.22	35000	2300	5800	220			27800	13.2	518	67.25	6000
STA2C3A	5/21/02												
STA2C3B	5/21/02						0.0531	0.0002					
STA2C3B	5/21/02	0.215	37000	2600	6500	55			35300	12	366	69.86	5500
STA2C3B	5/21/02												
STA2C3C	5/21/02						0.0805	0.0003					
STA2C3C	5/21/02	0.318	43000	3200	4000	140			27300	15	564	67.3	3000
STA2C3C	5/21/02												

STATION_ID	DATE	BD	TCA	TFE	TMG	TMN	THG	MEHG	TN	%ASH	TP	MOIST	TS
STA2C1C	8/14/02						0.148	0.0122					
STA2C1C	8/14/02	0.2	39000	1700	4800	120			28900	14.9	362	80.93	4400
STA2C1CC	8/14/02						0.151	0.009					
STA2C1CC	8/14/02	0.19	31000	1500	4000	110			30100	12.2	414	79.52	4000
STA2C1BB	8/14/02						0.147	0.0146					
STA2C1BB	8/14/02	0.12	29000	830	3500	82			30900	10.7	378	86.21	4900
STA2C1AA	8/14/02						0.129	0.005					
STA2C1AA	8/14/02	0.16	30000	1800	3400	73			35400	13.3	408	81.19	7200
STA2C2A	8/14/02	0.19	41000	4100	3800	340			31700	20.3	690	78.51	3800
STA2C2A	8/14/02						0.0776	0.0009					
STA2C2B	8/14/02						0.098	0.0006					
STA2C2B	8/14/02	0.2	42000	2100	3500	240			29200	16	478	78.61	3100
STA2C3A	8/20/02						0.0838	0.0002					
STA2C3A	8/20/02	0.17	49000	1700	6700	82			27200	18.8	366	74.7	4200
STA2C3B	8/20/02						0.0428	0.0011					
STA2C3B	8/20/02	0.15	49000	2300	6200	72			26400	18	420	79.66	3300
STA2C3C	8/20/02						0.0801	0.0002					
STA2C3C	8/20/02	0.26	44000	2500	6000	88			26600	18.5	558	68.99	3000
STA2C1C	8/28/02						0.1	0.0018					
STA2C1C	8/28/02	0.11	36000	1600	4000	180			31500	14.3	426	79.37	5200
STA2C2C	8/28/02						0.086	0.0003					
STA2C2C	8/28/02	0.14	36000	2400	3900	120			23300	28.9	392	74.13	3300
STA2C1C	9/11/02						0.203	0.0096					
STA2C1C	9/11/02	0.18	32000	1300	4200	110			31500	13.8	464	77.82	4700
STA2C1C	10/9/02						0.111	0.0007					
STA2C1C	10/9/02	0.183	40000	2100	4500	220			32100	16.7	410	80.81	3800
STA2C1AA	11/6/02						0.108	0.0007					
STA2C1AA	11/6/02	0.13	31000	1300	3600	89			31000	13.2	578	82.52	7200
STA2C1BB	11/6/02						0.172	0.0034					
STA2C1BB	11/6/02	0.14	27000	1400	3500	160			32000	12.4	512	82.37	6400
STA2C1CC	11/6/02						0.187	0.0058					
STA2C1CC	11/6/02	0.19	29000	3600	4300	120			25900	27.2	552	79.76	6400
STA2C2A	11/6/02						0.075	0.0008					
STA2C2A	11/6/02	0.14	36000	2200	4000	200			29500	16.5	492	85.25	6700
STA2C2B	11/6/02						0.055	0.0003					
STA2C2B	11/6/02	0.12	49000	1700	3900	200			28200	18.2	1250	87.15	6000
STA2C2C	11/6/02						0.041	0.0003					
STA2C2C	11/6/02	0.14	60000	1600	4600	160			26900	22.4	688	86.11	5000
STA2C3A	11/6/02						0.033	5E-05					
STA2C3A	11/6/02	0.2	96000	2000	6600	140			21200	35.9	802	78.95	4300
STA2C3B	11/6/02						0.079	0.0001					
STA2C3B	11/6/02	0.18	47000	3300	6500	51			25300	29	342	81.41	5200
STA2C3C	11/6/02						0.076	0.0002					
STA2C3C	11/6/02	0.26	47000	2600	7200	89			26100	19.9	636	75.26	4700
STA2C1C	12/4/02						0.112	0.0008					
STA2C1C	12/4/02	0.13	39000	1300	4900	170			30200	15.8	440	84.22	5800
STA2C1AA	1/29/03						0.1366	0.0016					
STA2C1AA	1/29/03	0.15	33000	2400	3700	120			34200	15.7	714	85.11	1E+05
STA2C1BB	1/29/03						0.1748	0.0026					
STA2C1BB	1/29/03	0.15	30000	1500	4000	110			31600	12.9	376	84.51	4900
STA2C1CC	1/29/03						0.1956	0.0073					
STA2C1CC	1/29/03	0.18	28000	1700	3800	70			31700	12.4	646	81.3	9200
STA2C2A	1/29/03						0.1162	0.0016					
STA2C2A	1/29/03	0.16	39000	2900	4200	220			31300	17.7	624	84.38	7800
STA2C2B	1/29/03						0.123	0.0003					
STA2C2B	1/29/03	0.16	46000	2000	3800	270			30200	17.9	648	83.66	6100
STA2C2C	1/29/03						0.0786	0.0006					
STA2C2C	1/29/03	0.18	42000	2800	3600	190			30400	18.9	608	83.4	7400
STA2C3A	1/29/03						0.0557	6E-05					
STA2C3A	1/29/03	0.2	93000	2200	7500	180			22800	35.1	762	79.89	3900
STA2C3B	1/29/03						0.0851	0.0005					
STA2C3B	1/29/03	0.17	63000	2400	6600	58			25400	22.6	398	81.55	3600
STA2C3C	1/29/03						0.0843	0.0002					
STA2C3C	1/29/03	0.29	63000	3600	6100	110			26500	23.7	750	74.97	3800

STATION_ID	DATE	BD	TCA	TFE	TMG	TMN	THG	MEHG	TN	%ASH	TP	MOIST	TS
STA2C1C	3/26/03						0.151	0.0004					
STA2C1C	3/26/03	0.19	46000	2500	4400	200			29200	18.8	506	82.13	7800
STA2C1AA	4/23/03						0.124	0.0007					
STA2C1AA	4/23/03	0.13	31000	1900	3900	86			33600	15.3	610	86.47	10500
STA2C1BB	4/23/03						0.128	0.0013					
STA2C1BB	4/23/03	0.13	29000	1900	3800	150			31400	15	530	84.86	9200
STA2C1CC	4/23/03						0.184	0.001					
STA2C1CC	4/23/03	0.15	29000	1900	3700	81			31900	12.7	585	82.78	9300
STA2C2A	4/23/03						0.084	0.0009					
STA2C2A	4/23/03	0.12	38000	2200	4000	150			30000	16.9	460	87.16	5700
STA2C2B	4/23/03						0.102	0.0004					
STA2C2B	4/23/03	0.17	35000	3400	3900	250			29400	19.9	635	82.48	4300
STA2C2C	4/23/03						0.075	0.0003					
STA2C2C	4/23/03	0.19	41000	2400	3800	130			30200	18.4	650	82.19	7400
STA2C3A	4/23/03						0.046	4E-05					
STA2C3A	4/23/03	0.14	120000	2100	7500	140			32400	44.3	740	86.36	2400
STA2C3B	4/23/03						0.039	0.0002					
STA2C3B	4/23/03	0.16	42000	2000	6400	31			16600	17.6	320	81.43	3400
STA2C3C	4/23/03						0.026	0.0004					
STA2C3C	4/23/03	0.2	51000	2900	6100	58			25000	25.3	575	80.41	7100
STA2C1AA	7/16/03						1.2	0.0004					
STA2C1AA	7/16/03	0.13	31000	1600	3300	83			33700	14.8	496	85.48	9600
STA2C1BB	7/16/03						1.26	0.0007					
STA2C1BB	7/16/03	0.13	29000	1400	3800	110			29500	13.4	516	84.01	9100
STA2C1CC	7/16/03						1.08	0.0007					
STA2C1CC	7/16/03	0.13	29000	1600	3500	80			29700	12.3	752	84.35	7400
STA2C2A	7/16/03						0.563	0.0004					
STA2C2A	7/16/03	0.15	36000	2300	3900	170			30500	15.6	412	83.97	6300
STA2C2B	7/16/03						0.5	0.0002					
STA2C2B	7/16/03	0.25	41000	2300	3200	210			30100	15.8	418	74.79	4400
STA2C2C	7/16/03						0.484	0.0001					
STA2C2C	7/16/03	0.18	42000	1900	4200	110			28400	16.6	468	81.19	5500
STA2C3A	7/16/03						0.346	7E-05					
STA2C3A	7/16/03	0.12	88000	1700	5800	140			22100	32.9	672	79.72	5900
STA2C3B	7/16/03						0.28	0.0001					
STA2C3B	7/16/03	0.2	66000	3800	6600	49			22300	34.1	372	79.18	6400
STA2C3C	7/16/03						0.306	9E-05					
STA2C3C	7/16/03	0.24	49000	2500	5500	73			25500	21.7	616	73.03	6400
STA2C1AA	10/6/03						0.137	0.0008					
STA2C1AA	10/6/03	0.079	38000	2500	4300	90			31500	17.8	1100	90.91	14300
STA2C1BB	10/6/03						0.129	0.0006					
STA2C1BB	10/6/03	0.11	34000	2100	3700	170			33900	14.9	524	86.3	12600
STA2C1CC	10/7/03						0.196	0.0009					
STA2C1CC	10/7/03	0.064	65000	1700	4500	130			24700	22.9	802	93.33	8500
STA2C1C	10/7/03						0.097	0.0006					
STA2C1C	10/7/03	0.085	94000	3200	8900	120			23800	35.8	466	91.69	8000
STA2C2A	10/8/03						0.091	0.0004					
STA2C2A	10/8/03	0.14	38000	2600	4100	200			32100	17.8	496	86.33	9000
STA2C2B	10/8/03						0.098	0.0003					
STA2C2B	10/8/03	0.14	35000	2000	3500	220			30700	13.7	620	85.91	8900
STA2C2C	10/9/03						0.099	0.0004					
STA2C2C	10/9/03	0.1	46000	2100	4300	110			31200	19.6	682	89.24	8700
STA2C3A	10/9/03						0.058	0.0002					
STA2C3A	10/9/03	0.16	65000	2000	6200	210			19500	45.8	828	84.28	6100
STA2C3B	10/10/03						0.059	0.0001					
STA2C3B	10/10/03	0.19	65000	3100	7000	56			18400	53.2	376	81.71	2800
STA2C3C	10/10/03						0.035	5E-05					
STA2C3C	10/10/03	0.097	220000	1100	8300	52			12600	68.3	580	89.15	1200

STATION_ID	DATE	BD	TCA	TFE	TMG	TMN	THG	MEHG	TN	%ASH	TP	MOIST	TS
STA2C1AA	11/4/03						0.117	0.0003					
STA2C1AA	11/4/03	0.13	35000	1800	4700	73			32300	16.3	478	86.56	10300
STA2C1BB	11/4/03						0.145	0.001					
STA2C1BB	11/4/03	0.11	37000	1500	4700	150			31800	16	542	89.28	11600
STA2C1CC	11/5/03						0.138	0.0008					
STA2C1CC	11/5/03	0.12	42000	2300	4600	190			31100	17.3	484	88.39	10400
STA2C2A	11/5/03						0.096	0.0004					
STA2C2A	11/5/03	0.1	45000	1500	4600	120			29900	17.4	700	89.3	11000
STA2C2B	11/7/03						0.106	0.0003					
STA2C2B	11/7/03	0.2	22000	2100	4800	210			30300	14.2	514	79.38	9400
STA2C2C	11/7/03						0.043	0.0002					
STA2C2C	11/7/03	0.086	43000	1700	4500	120			28800	18.9	636	91.33	8700
STA2C3A	11/7/03						0.056	4E-05					
STA2C3A	11/7/03	0.16	84000	2200	7900	150			22200	35.3	728	84.58	8400
STA2C3B	11/11/03						0.095	0.0001					
STA2C3B	11/11/03	0.18	82000	2200	6200	68			24700	27.2	366	82.71	5200
STA2C3C	11/11/03						0.08	0.0001					
STA2C3C	11/11/03	0.2	71000	2400	6800	61			25800	23.6	552	80.79	9300
STA2C1C	11/11/03						0.073	0.0004					
STA2C1C	11/11/03	0.095	94000	2400	9100	120			22500	39	508	90.8	5000
STA2C1AA	12/1/03						0.136	0.0003					
STA2C1AA	12/1/03	0.11	45000	1800	4400	84			31400	17	915	89.3	7400
STA2C1BB	12/1/03						0.165	0.0008					
STA2C1BB	12/1/03	0.13	31000	1100	4000	130			31400	13.6	485	86.04	8100
STA2C1CC	12/2/03						0.156	0.001					
STA2C1CC	12/2/03	0.13	31000	1500	4100	89			30700	15.2	660	87.47	5700
STA2C1C	12/2/03						0.089	0.0003					
STA2C1C	12/2/03	0.059	150000	2700	20000	130			20000	44.5	565	93.88	2800
STA2C2B	12/3/03						0.119	0.0003					
STA2C2B	12/3/03	0.14	34000	1500	3800	140			28100	12.4	735	86.23	6100
STA2C2C	12/3/03						0.069	0.0001					
STA2C2C	12/3/03	0.043	54000	1600	5000	78			33000	23.1	1280	95.29	6500
STA2C2A	12/3/03						0.104	0.0005					
STA2C2A	12/3/03	0.13	43000	2500	4400	220			31800	17.4	495	85.94	5800
STA2C3A	12/4/03						0.073	6E-05					
STA2C3A	12/4/03	0.23	75000	1900	6800	160			24100	32	780	74.82	3200
STA2C3B	12/4/03						0.068	0.0001					
STA2C3B	12/4/03	0.19	91000	2100	6600	56			24600	31	420	81.94	2900
STA2C3C	12/4/03						0.077	0.0001					
STA2C3C	12/4/03	0.19	63000	2100	5900	65			26100	24.7	615	81.68	3500
STA2C1AA	12/29/03						0.128	0.0006					
STA2C1AA	12/29/03	0.1	52000	2000	4300	89			30700	20.3	926	89.33	6900
STA2C1BB	12/29/03						0.12	0.0009					
STA2C1BB	12/29/03	0.13	35000	1800	4100	160			32200	15.8	532	86.46	11000
STA2C1CC	12/29/03						0.175	0.0016					
STA2C1CC	12/29/03	0.15	37000	1600	4000	98			30700	14.2	656	83.9	10200
STA2C1C	12/30/03						0.102	0.0007					
STA2C1C	12/30/03	0.16	160000	3500	11000	160			18100	51.4	596	83.55	2400
STA2C2A	1/5/2004 1						0.093	0.0009					
STA2C2A	1/5/2004 1	0.13	43000	2200	4100	110			30900	15.8	348	85.77	4400
STA2C2B	1/5/2004 1						0.113	0.0001					
STA2C2B	1/5/2004 1	0.12	34000	2800	4200	180			30700	17.8	682	87.57	9100
STA2C2C	1/5/2004 1						0.105	0.0003					
STA2C2C	1/5/2004 1	0.13	46000	1900	3800	48			28700	15.4	416	86.37	2900
STA2C3A	1/6/2004 9						0.044	1E-04					
STA2C3A	1/6/2004 1	0.25	190000	2000	6600	160			24500	33.1	832	73.91	3400
STA2C3B	1/6/2004 1						0.052	0.0007					
STA2C3B	1/6/2004 1	0.2	61000	2700	6600	55			21100	43.2	446	81.24	2200
STA2C3C	1/6/2004 1						0.058	0.0001					
STA2C3C	1/6/2004 1	0.18	70000	2500	6500	61			26900	26.5	682	81.53	3700

Table 4. Mosquitofish THg Data for the Period of Record (all concentrations in mg/Kg wet wt)

	G328B inflow	G335 outflow	C1A	C1AA	C1BB	C1CC	C1X	C2A	C2B	C2C	C3A	C3B	C3C
10/15/01	0.021	0.248	0.109				0.312	0.069			0.013		
11/15/01			0.021										
12/12/01			0.018										
2/21/02			0.186										
3/14/02	0.014	0.242	0.172				0.285	0.045			0.018		
4/18/02			0.154										
7/11/02			0.072										
Aug-02			0.197	0.107	0.33	0.213		0.056	0.063	0.032	0.0097	0.011	0.028
Sep-02			0.147	0.107	0.43	0.39		0.079	0.046	0.023	0.012	0.021	0.031
Oct-02	0.004	0.167	0.079	0.087	0.257	0.397		0.031	0.022	0.013	0.004	0.008	0.016
Nov-02			0.137	0.12666667	0.277	0.237		0.028	0.027	0.019	0.006	0.018	0.016
Dec-03			0.076	0.110	0.243	0.190		0.034	0.017	0.011	0.004	0.014	0.016
Jan-03			0.063	0.037	0.117	0.120		0.037	0.025	0.014	0.006	0.013	0.020
Feb-03			0.095	0.065	0.157	0.153		0.032	0.018	0.009	0.002	0.011	0.013
Mar-03	0.0037	0.064	0.040	0.053	0.092	0.16	0.1	0.032	0.023	0.011	0.006	0.018	0.020
Apr-03			0.062	0.048	0.113	0.113		0.036	0.032	0.017	0.007	0.018	0.022
May-03			0.053	0.041	0.099	0.163		0.032	0.013	0.011	0.006	0.019	0.018
Jun-03			0.077	0.048	0.153	0.193		0.026	0.013	0.008	0.006	0.014	0.017
02-Jul-03			0.034	0.024	0.076	0.117		0.024	0.007	0.005	0.004	0.006	0.010
30-Jul-03				0.039	0.053	0.093		0.015	0.004	0.004	0.004	0.008	0.010
Aug-03			0.032	0.029	0.053	0.103		0.013	0.008	0.005	0.004	0.008	0.007
Sep-03				0.010	0.024	0.042		0.0054	0.0032	0.0026	0.0029	0.0052	0.0193
11-Sep-03	0.0050	0.0077	0.0103				0.0513				0.0051		
Oct-03			0.0450	0.004	0.037	0.022		0.007	0.004	0.003	0.0078	0.0061	0.011
Nov-03			0.0127	0.0078	0.012	0.012		0.0064	0.0029	0.0034	0.0038	0.0028	0.0070
Dec-03			0.0233	0.0093	0.0089	0.0147		0.006	0.004	0.0038	0.005133	0.013	0.016333
Jan-04			0.0293	0.003	0.022	0.010		0.006	0.003	0.004	0.008	0.008	0.019

Table 5. Routine Pore Water Sampling Results for Period of Record from 08/03 through 01/04

STATION_ID	DATE	TCA	DOC	CL	DEPTH	DO	HARD	TFE	TMG	TMN	THG	MeHg	pH	SPCON	SULFATE	TEMP
STA2C1AA	09/30/03				0.96						1.95		8.04			
STA2C1AA	09/30/03				0.96								8.04			
STA2C1AA	09/30/03											0.03				
STA2C1BB	09/30/03				0.84								7.49			
STA2C1BB	09/30/03											0.011				
STA2C1BB	09/30/03				0.84						2.13		7.49			
STA2C1CC	09/30/03				0.94						3.46		7.93			
STA2C1CC	09/30/03				0.94							0.088	7.93			
STA2C2A	10/01/03				0.87						2.16		8.07			
STA2C2A	10/01/03				0.87								8.07			
STA2C2A	10/01/03											0.066				
STA2C2B	10/01/03				0.77								8.21			
STA2C2B	10/01/03											0.061				
STA2C2B	10/01/03				0.77						1.68		8.21			
STA2C2C	10/02/03				0.81						2.8		7.84			
STA2C2C	10/02/03				0.81								7.84			
STA2C2C	10/02/03											0.029				
STA2C3A	10/02/03				0.79						1.16		8.09			
STA2C3A	10/02/03				0.79								8.09			
STA2C3A	10/02/03											0.021				
STA2C3B	10/03/03				0.61								7.99			
STA2C3B	10/03/03											0.035				
STA2C3B	10/03/03				0.61						1.63		7.99			
STA2C3C	10/03/03				0.57						3.17		7.71			
STA2C3C	10/03/03				0.57								7.71			
STA2C3C	10/03/03											0.074				

Table 5. Pore Water Sampling Results for Period of Record from 08/03 through 01/04 (continued)

STATION_ID	DATE	TCA	DOC	CL	DEPTH	DO	HARD	TFE	TMG	TMN	THG	MeHg	pH	SPCON	SULFATE	TEMP
STA2C1AA	10/06/03	122	49	202	0.67	0.49	500	33	45.6	24.4			7.37	1529	120	25.9
STA2C1AA	10/06/03										0.34					
STA2C1AA	10/06/03											-0.001				
STA2C1AA	10/06/03		1													
STA2C1AA	10/06/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1AA	10/06/03				0.67						2.52					
STA2C1AA	10/06/03				0.67							0.33				
STA2C1AA	10/06/03	122	51	198	0.67		500	17	45.6	47.4			7.32		101	
STA2C1AA	10/06/03															
STA2C1BB	10/06/03	115	47	212	0.57	2.09	500		44.2	14.7			7.42	1497	115	26.6
STA2C1BB	10/06/03							9								
STA2C1BB	10/06/03				0.87						0.86					
STA2C1BB	10/06/03				0.57											
STA2C1BB	10/06/03											0.04				
STA2C1BB	10/06/03	113	48	206	0.57		400		42.6	69.5			7.28		106	
STA2C1BB	10/06/03							7								
STA2C1BB	10/06/03															
STA2C1BB	10/06/03										0.31					
STA2C1BB	10/06/03											-0.001				
STA2C1BB	10/06/03		1													
STA2C1BB	10/06/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1CC	10/07/03	103	44	197	0.64	0.16	400	13	40.2	54.2			7.36	1419	87.7	26.3
STA2C1CC	10/07/03															
STA2C1CC	10/07/03										-0.123					
STA2C1CC	10/07/03											-0.006				
STA2C1CC	10/07/03		1													
STA2C1CC	10/07/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1CC	10/07/03				0.64						2.45					
STA2C1CC	10/07/03				0.64							0.381				
STA2C1CC	10/07/03	106	52	195	0.64		400	26	39.8	108			7.1		70.9	
STA2C1CC	10/07/03															
STA2C2A	10/08/03	117	46	209	0.57	0.2	500	17	43.6	27.5			7.4	1548	102	24.8
STA2C2A	10/08/03															
STA2C2A	10/08/03										-0.03					
STA2C2A	10/08/03											-0.009				
STA2C2A	10/08/03		2							0.2						
STA2C2A	10/08/03	-0.2					-0.1	-3	-0.1							
STA2C2A	10/08/03			1.2											0.6	
STA2C2A	10/08/03				0.57						2.15					
STA2C2A	10/08/03				0.57							0.134				
STA2C2A	10/08/03	173	91	185			600	437	53.1	335			6.72		9	
STA2C2A	10/08/03															
STA2C2B	10/08/03	107	44	197	0.59	0.31	400	13	40.5	83			7.34	1438	88.8	25.3
STA2C2B	10/08/03															
STA2C2B	10/08/03				0.59						0.85					
STA2C2B	10/08/03				0.59							0.078				
STA2C2B	10/08/03	112	48	196			400	52	39	152			7.21		81.3	
STA2C2B	10/08/03															
STA2C2B	10/08/03										-0.107					
STA2C2B	10/08/03											-0.009				
STA2C2B	10/08/03		1													
STA2C2B	10/08/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C2C	10/09/03	112	48	208	0.67	0.09	500	22	44	25.4			7.43	1533	111	25.3
STA2C2C	10/09/03															
STA2C2C	10/09/03										0.18					
STA2C2C	10/09/03											-0.009				
STA2C2C	10/09/03		2													
STA2C2C	10/09/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C2C	10/09/03				0.67						3.75					
STA2C2C	10/09/03				0.67							0.449				
STA2C2C	10/09/03	116	50	198	0.67		500		43.3	47.6			7.07		68	
STA2C2C	10/09/03							12								
STA2C2C	10/09/03															
STA2C3A	10/09/03	107	47	210	0.85	6.4	500	18	46.9	2			7.85	1544	126	26.8
STA2C3A	10/09/03				0.85						1.47					
STA2C3A	10/09/03				0.85							0.079				
STA2C3A	10/09/03	110	50	193	0.85		400		42.7	89.1			7		26.3	
STA2C3A	10/09/03							8								
STA2C3A	10/09/03															
STA2C3A	10/09/03										0.12					
STA2C3A	10/09/03											0.009				
STA2C3A	10/09/03		1													
STA2C3A	10/09/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C3B	10/10/03	91.1	48	210	0.75	3.82	400	13	47.2	0.9			7.75	1500	127	26.7
STA2C3B	10/10/03										-0.05					
STA2C3B	10/10/03											-0.013				
STA2C3B	10/10/03		2													
STA2C3B	10/10/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C3B	10/10/03				0.75						2.96					
STA2C3B	10/10/03				0.75											
STA2C3B	10/10/03											-0.016				
STA2C3B	10/10/03	107	51	187	0.75		500		51.2	22.8					14.7	
STA2C3B	10/10/03							5								
STA2C3C	10/10/03	77.4	47	206	0.95	6.13	400		45.1				7.91	1402	123	27.2
STA2C3C	10/10/03							10		0.4						
STA2C3C	10/10/03															
STA2C3C	10/10/03				0.95						3.75					
STA2C3C	10/10/03				0.95							0.139				

Table 5. Pore Water Sampling Results for Period of Record from 08/03 through 01/04 (continued)

STATION_ID	DATE	TCA	DOC	CL	DEPTH	DO	HARD	TFE	TMG	TMN	THG	MeHg	pH	SPCON	SULFATE	TEMP
LABQC	11/04/03										0.133					
LABQC	11/04/03											-0.002				
STA2C1AA	11/04/03	101	53	226	0.53	0.52	400		45.4	9.2			7.43	1553	97.1	23.6
STA2C1AA	11/04/03															
STA2C1AA	11/04/03							20								
STA2C1AA	11/04/03										-0.081					
STA2C1AA	11/04/03											-0.01				
STA2C1AA	11/04/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1AA	11/04/03		2													
STA2C1AA	11/04/03				0.53						3.74					
STA2C1AA	11/04/03				0.53							0.161				
STA2C1AA	11/04/03	108	51	221	0.53		400	80	42.8	51.9			7.06		69.4	
STA2C1AA	11/04/03															
STA2C1BB	11/04/03	91	48	208	0.42	0.99	400		42.5	36.8			7.46	1428	95.6	24.2
STA2C1BB	11/04/03															
STA2C1BB	11/04/03							7								
STA2C1BB	11/04/03				0.42						2.563					
STA2C1BB	11/04/03				0.42							0.405				
STA2C1BB	11/04/03	91.2	52	208	0.42		400		41	115			7.31		82.4	
STA2C1BB	11/04/03															
STA2C1BB	11/04/03							9								
STA2C1BB	11/04/03										0.052					
STA2C1BB	11/04/03											-0.007				
STA2C1CC	11/04/03	-0.2		-0.1			-0.1		-0.1	-0.2					-0.1	
STA2C1CC	11/04/03		2					6								
STA2C1CC	11/05/03	86.7	46	214	0.55		400	18	40.3	108			7.27	1411	88	23.3
STA2C1CC	11/05/03					0.18										
STA2C1CC	11/05/03															
STA2C1CC	11/05/03										-0.021					
STA2C1CC	11/05/03											-0.002				
STA2C1CC	11/05/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1CC	11/05/03		2													
STA2C1CC	11/05/03				0.55						3.182					
STA2C1CC	11/05/03				0.55							0.669				
STA2C1CC	11/05/03	104	60	212	0.55		400	26	41.4	127			7		46.7	
STA2C1CC	11/05/03															
STA2C2A	11/05/03	94	41	198	0.62		400	16	39.2	9.9			7.3	1365	37.9	23.9
STA2C2A	11/05/03					0.65										
STA2C2A	11/05/03															
STA2C2A	11/05/03				0.62						1.635					
STA2C2A	11/05/03				0.62											
STA2C2A	11/05/03											0.07				
STA2C2A	11/05/03	184	98	226	0.62		700	489	55.5	203			6.73		1.3	
STA2C2A	11/05/03															
STA2C2A	11/05/03										-0.039					
STA2C2A	11/05/03											-0.007				
STA2C2A	11/05/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C2A	11/05/03		2													
STA2C2B	11/07/03										0.18					
STA2C2B	11/07/03											-0.011				
STA2C2B	11/07/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C2B	11/07/03		1													
STA2C2B	11/07/03	72.9	48	202	0.61	0.77	300		37.2	10.2			7.44	1305	89.2	24.8
STA2C2B	11/07/03							8								
STA2C2B	11/07/03															
STA2C2B	11/07/03				0.61						2.09					
STA2C2B	11/07/03				0.61							0.274				
STA2C2B	11/07/03	118	65	226	0.61		500		46	127			6.88		29.7	
STA2C2B	11/07/03							10								
STA2C2B	11/07/03															
STA2C2C	11/07/03	74.2	45	207	0.7	1.24	400		42.8	7.6			7.43	1376	108	25.2
STA2C2C	11/07/03							12								
STA2C2C	11/07/03				0.7						2.021					
STA2C2C	11/07/03				0.7							0.226				
STA2C2C	11/07/03	102	51	207	0.7		400		42.8	57.2			6.99		44.2	
STA2C2C	11/07/03							8								
STA2C2C	11/07/03															
STA2C3A	11/07/03	94.6	36	198	0.81	5.52	400	18	32.4	2.4			7.77	1333	63.7	27.1
STA2C3A	11/07/03				0.81						0.922					
STA2C3A	11/07/03				0.81											
STA2C3A	11/07/03											-0.019				
STA2C3A	11/07/03	99.1	46	216	0.81		400		40.3	55.3			7		19.9	
STA2C3A	11/07/03							-3								
STA2C3A	11/07/03										0.089					
STA2C3A	11/07/03											-0.004				
STA2C3A	11/07/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C3A	11/07/03		2													
STA2C3B	11/11/03										0.184					
STA2C3B	11/11/03											-0.006				
STA2C3B	11/11/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C3B	11/11/03		2													
STA2C3B	11/11/03	85.6	36	206	0.74	6.65	400		34.5				8.01	1329	66.7	24.7
STA2C3B	11/11/03							7		0.4						
STA2C3B	11/11/03				0.74						3.773					
STA2C3B	11/11/03				0.74							0.357				
STA2C3B	11/11/03	88.4	45	210	0.74		400		41.9	17.3			7.23		24.3	
STA2C3B	11/11/03							4								
STA2C3B	11/11/03															

Table 5. Pore Water Sampling Results for Period of Record from 08/03 through 01/04 (continued)

STATION_ID	DATE	TCA	DOC	CL	DEPTH	DO	HARD	TFE	TMG	TMN	THG	MeHg	pH	SPCON	SULFATE	TEMP
STA2C1AA	12/01/03										0.07					
STA2C1AA	12/01/03											0.064				
STA2C1AA	12/01/03	-0.2					-0.1	-3	-0.1	-0.2						
STA2C1AA	12/01/03		1	0.3											0.2	
STA2C1AA	12/01/03	101	39	219	0.52		400	15	37.7	9.8			7.42	1417	66.7	15.8
STA2C1AA	12/01/03					1.36										
STA2C1AA	12/01/03															
STA2C1AA	12/01/03				0.52						4.57					
STA2C1AA	12/01/03				0.52							0.381				
STA2C1AA	12/01/03	99.4	122	212	0.52		400		37.5	29			7.51		45.6	
STA2C1AA	12/01/03							5								
STA2C1AA	12/01/03															
STA2C1BB	12/01/03	86.6	42	226	0.35		400		40.7	11.1			7.57	1416	66.9	18.3
STA2C1BB	12/01/03							5								
STA2C1BB	12/01/03					3.76										
STA2C1BB	12/01/03															
STA2C1BB	12/01/03				0.35						1.25					
STA2C1BB	12/01/03				0.35							0.121				
STA2C1BB	12/01/03	87.2	41	220	0.35		400		40.4	28.9			8.08		62.5	
STA2C1BB	12/01/03							-3								
STA2C1BB	12/01/03										0.09					
STA2C1BB	12/01/03											-0.011				
STA2C1BB	12/01/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1BB	12/01/03		1													
STA2C1CC	12/02/03										0.18					
STA2C1CC	12/02/03	90.4	43	232	0.45	0.42	400	19	41.1	40.7			7.11	1434	69.1	16.2
STA2C1CC	12/02/03															
STA2C1CC	12/02/03											-0.005				
STA2C1CC	12/02/03	-0.2	-1	-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1CC	12/02/03				0.45						1.06					
STA2C1CC	12/02/03				0.45											
STA2C1CC	12/02/03											0.153				
STA2C1CC	12/02/03	90.6	44	219	0.45		400		40.3	62.4			7.55		64.2	
STA2C1CC	12/02/03							10								
STA2C1CC	12/02/03															
STA2C2B	12/03/03	96.4	47	236	0.36		400		43.9	16.6			7.28	1502	75	16.1
STA2C2B	12/03/03							11								
STA2C2B	12/03/03					1.11										
STA2C2B	12/03/03															
STA2C2B	12/03/03										0.08					
STA2C2B	12/03/03											-0.003				
STA2C2B	12/03/03	-0.2	-1				-0.1	-3	-0.1	-0.2						
STA2C2B	12/03/03			0.3											0.2	
STA2C2B	12/03/03				0.36						0.9					
STA2C2B	12/03/03				0.36							0.234				
STA2C2B	12/03/03	148	79	272	0.36		600		57.4	104			7.28		33.3	
STA2C2B	12/03/03							11								
STA2C2B	12/03/03															
STA2C2C	12/03/03	92.5	44	234	0.52		400	44	47.6	7.7			7.42	1507	92.6	17.3
STA2C2C	12/03/03					3.65										
STA2C2C	12/03/03															
STA2C2C	12/03/03				0.52						1.47					
STA2C2C	12/03/03				0.52											
STA2C2C	12/03/03											0.069				
STA2C2C	12/03/03	114	51	207	0.52		400	13	41.5	49.7			7.19		20.8	
STA2C2C	12/03/03															
STA2C2A	12/03/03	107	40	206	0.37		400	13	43	7.4			7.58	1389	21.1	17
STA2C2A	12/03/03					3.02										
STA2C2A	12/03/03															
STA2C2A	12/03/03				0.37						1.16					
STA2C2A	12/03/03				0.37											
STA2C2A	12/03/03											-0.009				
STA2C2A	12/03/03	124	51	199	0.37		500	164	42.4	240			7.35		6	
STA2C2A	12/03/03															
STA2C2A	12/03/03										0.24					
STA2C2A	12/03/03											-0.02				
STA2C2A	12/03/03	-0.2					-0.1	-3	-0.1	-0.2						
STA2C2A	12/03/03		1	0.3											0.2	
STA2C3A	12/04/03	83.8	34	221	0.96	8.08	400	27	39.9	4.4			8.31	1371	61.7	19.2
STA2C3A	12/04/03										0.07					
STA2C3A	12/04/03											-0.009				
STA2C3A	12/04/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C3A	12/04/03		1													
STA2C3A	12/04/03				0.96						1.48					
STA2C3A	12/04/03				0.96											
STA2C3A	12/04/03											-0.016				
STA2C3A	12/04/03	84.6	36	212	0.96		400		36.8	89.7			7.34		40	
STA2C3A	12/04/03							5								
STA2C3A	12/04/03															
STA2C3B	12/04/03	72.3	35	224	1.1	9.87	300		40.2				8.29	1320	65.4	19.9
STA2C3B	12/04/03							9		0.6						
STA2C3B	12/04/03				1.1						5.69					
STA2C3B	12/04/03				1.1							1.66				
STA2C3B	12/04/03	83.1	38	111	1.1		400		42.9	56.9			7.84		23.6	
STA2C3B	12/04/03							4								
STA2C3B	12/04/03															
STA2C3C	12/04/03	49.4	36	222	1	10.1	300		38.6				8.52	1226	73.3	20.4
STA2C3C	12/04/03							4		0.2						

Table 5. Pore Water Sampling Results for Period of Record from 08/03 through 01/04 (continued)

STATION_ID	DATE	TCA	DOC	CL	DEPTH	DO	HARD	TFE	TMG	TMN	THG	MeHg	pH	SPCON	SULFATE	TEMP
STA2C1AA	12/29/03	90.6	32	198	0.6	3.43	400		32.9	6.9			7.52	1307	57.6	16.4
STA2C1AA	12/29/03							11								
STA2C1AA	12/29/03															
STA2C1AA	12/29/03										-0.02					
STA2C1AA	12/29/03											-0.002				
STA2C1AA	12/29/03	-0.2	-1	-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1AA	12/29/03				0.6						1.5					
STA2C1AA	12/29/03				0.6							0.151				
STA2C1AA	12/29/03	91.2	40	200	0.6		400	352	32.1	80.6			8.02		25.6	
STA2C1AA	12/29/03															
STA2C1BB	12/29/03	91.1	33	205	0.52	3.21	400	33	34.1	45.3			7.53	1344	58.5	18.1
STA2C1BB	12/29/03															
STA2C1BB	12/29/03				0.52											
STA2C1BB	12/29/03										0.8					
STA2C1BB	12/29/03				0.52							0.126				
STA2C1BB	12/29/03	90.6	35	204	0.52		400		34	40.8			7.87		52.2	
STA2C1BB	12/29/03							5								
STA2C1BB	12/29/03															
STA2C1CC	12/29/03	88.3	36	210	0.5	1.52	400		36.2	49.5			7.41	1364	56.7	16.9
STA2C1CC	12/29/03							10								
STA2C1CC	12/29/03															
STA2C1CC	12/29/03				0.5						1.83					
STA2C1CC	12/29/03				0.5							0.406				
STA2C1CC	12/29/03	95.8	45	209	0.5		400	71	37.9	64.1			7.81		40.9	
STA2C1CC	12/29/03															
STA2C1CC	12/29/03										-0.01					
STA2C1CC	12/29/03											-0.007				
STA2C1CC	12/29/03	-0.2	-1	-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C2A	01/05/04	111	41	209	0.55	1.66	400	528	41.4	105			7.66	1442	20.1	17.3
STA2C2A	01/05/04										-0.07					
STA2C2A	01/05/04											-0.008				
STA2C2A	01/05/04		1													
STA2C2A	01/05/04	-0.2					-0.1	-3	-0.1	-0.2					-0.1	
STA2C2A	01/05/04			0.3												
STA2C2A	01/05/04				0.55						1.69					
STA2C2A	01/05/04				0.55							0.316				
STA2C2A	01/05/04	141	63	180	0.55		500	118	47.9	203			7.36		4.7	
STA2C2A	01/05/04															
STA2C2B	01/05/04	97.7	46	223	0.54	1.51	400	30	39.4	47			7.47	1479	59.2	18.1
STA2C2B	01/05/04															
STA2C2B	01/05/04				0.54						1.81					
STA2C2B	01/05/04				0.54							0.352				
STA2C2B	01/05/04	171	86	241	0.54		600	48	54.8	274			7.56		8.9	
STA2C2B	01/05/04															
STA2C2C	01/05/04	89	36	212	0.7	2.52	400	54	37.1	20.6			7.59	1385	56.9	19.3
STA2C2C	01/05/04															
STA2C2C	01/05/04				0.7						1.7					
STA2C2C	01/05/04				0.7							0.241				
STA2C2C	01/05/04	101	45	211	0.7		400	58	35.5	62.6			7.78		28.2	
STA2C2C	01/05/04															
STA2C2C	01/05/04										-0.02					
STA2C2C	01/05/04											-0.011				
STA2C2C	01/05/04	-0.2	-1	-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C3A	01/06/04	79.8	34	189	0.89	5.75	300	13	35	3.3			8.1	1251	59.9	22.1
STA2C3A	01/06/04										0.09					
STA2C3A	01/06/04											-0.001				
STA2C3A	01/06/04	-0.2	-1				-0.1	-3	-0.1	-0.2						
STA2C3A	01/06/04			0.2											0.2	
STA2C3A	01/06/04				0.89						0.37					
STA2C3A	01/06/04				0.89											
STA2C3A	01/06/04											-0.002				
STA2C3A	01/06/04	81.6	36	190	0.89		300		34.2	54.3			7.85		38	
STA2C3A	01/06/04							-3								
STA2C3B	01/06/04	62.9	34	199	0.82	7.11	300		35.6	3.6			8.08	1231	60	23.4
STA2C3B	01/06/04							11								
STA2C3B	01/06/04				0.82						4.11					
STA2C3B	01/06/04				0.82							2.145				
STA2C3B	01/06/04	80.7	38	197	0.82		300		35.2	18.5			8.08		35.4	
STA2C3B	01/06/04							7								
STA2C3B	01/06/04															
STA2C3C	01/06/04	47.5	32	208	0.99	9.12	300		34.5				8.33	1191	60	22.6
STA2C3C	01/06/04							7		0.4						
STA2C3C	01/06/04				0.99						3.98					
STA2C3C	01/06/04				0.99							0.81				
STA2C3C	01/06/04	75.7	37	208	0.99		300		37.9	7.7			7.75		21.5	
STA2C3C	01/06/04							4								
STA2C3C	01/06/04															
STA2C3C	01/06/04										0.13					
STA2C3C	01/06/04											-0.008				
STA2C3C	01/06/04	-0.2	-1				-0.1	-3	-0.1	-0.2						
STA2C3C	01/06/04			0.3											0.2	

Table 5. Pore Water Sampling Results for Period of Record from 08/03 through 01/04: Replicate Site C1C

STATION_ID	DATE	TCA	DOC	CL	DEPTH	DO	HARD	TFE	TMG	TMN	THG	MeHg	pH	SPCON	SULFATE	TEMP
STA2C1C	09/09/03										0.254					
STA2C1C	09/09/03											-0.006				
STA2C1C	09/09/03				0.73						6.598					
STA2C1C	09/09/03										3.732					
STA2C1C	09/09/03										4.181					
STA2C1C	09/09/03				0.73											
STA2C1C	09/09/03											0.04				
STA2C1C	09/09/03											0.026				
STA2C1C	09/09/03											0.025				
STA2C1C	10/07/03	112	44	208	0.69	0.14	400		43	9.2			7.4	1523	106	25.9
STA2C1C	10/07/03							6								
STA2C1C	10/07/03															
STA2C1C	10/07/03	112	44	209	0.69	0.14	400		43.2	9.2			7.4	1523	107	25.9
STA2C1C	10/07/03							6								
STA2C1C	10/07/03															
STA2C1C	10/07/03	111	45	209	0.69	0.14	400		43.2	6.9			7.4	1523	106	25.9
STA2C1C	10/07/03							6								
STA2C1C	10/07/03															
STA2C1C	10/07/03				0.69						4.64					
STA2C1C	10/07/03										2.86					
STA2C1C	10/07/03										2.12					
STA2C1C	10/07/03				0.69											
STA2C1C	10/07/03											0.035				
STA2C1C	10/07/03											0.019				
STA2C1C	10/07/03											-0.008				
STA2C1C	10/07/03	103	42	191	0.69		400		39.9	72.1			7.33		53.6	
STA2C1C	10/07/03							-3								
STA2C1C	10/07/03	103	43	191	0.69		400		39.8	73.7			7.35		53.2	
STA2C1C	10/07/03							-3								
STA2C1C	10/07/03	102	43	191	0.69		400		39.2	73.6			7.36		52.9	
STA2C1C	10/07/03							-3								
STA2C1C	10/07/03										-0.117					
STA2C1C	10/07/03											-0.008				
STA2C1C	10/07/03		1													
STA2C1C	10/07/03	-0.2		-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1C	11/11/03	77.5	36	207	0.75	0.49	400		40.1	3.2			7.42	1351	67.4	24.4
STA2C1C	11/11/03															
STA2C1C	11/11/03							6								
STA2C1C	11/11/03	76.9	36	207	0.75	0.49	400		39.7	3.9			7.42	1351	67.9	24.4
STA2C1C	11/11/03															
STA2C1C	11/11/03							6								
STA2C1C	11/11/03	77.5	37	208	0.75	0.49	400		40	3.7			7.42	1351	67.8	24.4
STA2C1C	11/11/03															
STA2C1C	11/11/03							7								
STA2C1C	11/11/03				0.75						0.916					
STA2C1C	11/11/03										1.191					
STA2C1C	11/11/03										0.788					
STA2C1C	11/11/03				0.75											
STA2C1C	11/11/03											0.034				
STA2C1C	11/11/03											0.039				
STA2C1C	11/11/03											0.03				
STA2C1C	11/11/03	88.3	42	208	0.75		400		37.6	59.1			7.32		64.8	
STA2C1C	11/11/03															
STA2C1C	11/11/03							4								
STA2C1C	11/11/03	88.8	42	206	0.75		400		37.7	59.4			7.23		64.5	
STA2C1C	11/11/03															
STA2C1C	11/11/03							4								
STA2C1C	11/11/03	87.8	41	204	0.75		400		37.2	60.1			7.24		63.8	
STA2C1C	11/11/03															
STA2C1C	11/11/03							4								
STA2C1C	11/11/03										-0.091					
STA2C1C	11/11/03											-0.006				
STA2C1C	11/11/03						0.9									
STA2C1C	11/11/03								-0.1						-0.1	
STA2C1C	11/11/03	0.4	2	0.2				184		0.4						

Table 5. Pore Water Sampling Results for Period of Record from 08/03 through 01/04: Replicate Site C1C (continued)

STATION_ID	DATE	TCA	DOC	CL	DEPTH	DO	HARD	TFE	TMG	TMN	THG	MeHg	pH	SPCON	SULFATE	TEMP
STA2C1C	12/02/03	78.4	34	212	0.54	1.08	400		42	4.4			7.38	1369	68.3	16.2
STA2C1C	12/02/03							7								
STA2C1C	12/02/03	78.3	34	222	0.54	1.08	400		42	3.2			7.38	1369	71.9	16.2
STA2C1C	12/02/03							6								
STA2C1C	12/02/03	78	34	214	0.54	1.08	400		41.9				7.38	1369	68.9	16.2
STA2C1C	12/02/03							5		0.5						
STA2C1C	12/02/03				0.54						1.44					
STA2C1C	12/02/03										1.24					
STA2C1C	12/02/03										0.86					
STA2C1C	12/02/03				0.54											
STA2C1C	12/02/03											0.044				
STA2C1C	12/02/03											-0.015				
STA2C1C	12/02/03											-0.012				
STA2C1C	12/02/03	84.9	35	212	0.54		400		40.3	38.3			7.92		57.1	
STA2C1C	12/02/03							-3								
STA2C1C	12/02/03	84.6	35	212	0.54		400		40.2	37			7.9		57	
STA2C1C	12/02/03							-3								
STA2C1C	12/02/03	85.3	35	212	0.54		400		40.5	36			7.87		56.5	
STA2C1C	12/02/03							3								
STA2C1C	12/02/03															
STA2C1C	12/02/03										0.15					
STA2C1C	12/02/03											-0.005				
STA2C1C	12/02/03	-0.2	-1	-0.1			-0.1	-3	-0.1	-0.2					-0.1	
STA2C1C	12/30/03										-0.07					
STA2C1C	12/30/03											-0.002				
STA2C1C	12/30/03														0.1	
STA2C1C	12/30/03	-0.2	-1				-0.1	-3	-0.1	-0.2						
STA2C1C	12/30/03			0.2												
STA2C1C	12/30/03	86.4	32	208	0.77	1.48	400		35.6	5			7.33	1358	56.1	17.1
STA2C1C	12/30/03															
STA2C1C	12/30/03							5								
STA2C1C	12/30/03	85.9	32	209	0.77	1.48	400		35.5	4.9			7.33	1358	59	17.1
STA2C1C	12/30/03															
STA2C1C	12/30/03							4								
STA2C1C	12/30/03	86.1	32	207	0.77	1.48	400		35.4	4.9			7.33	1358	58.5	17.1
STA2C1C	12/30/03															
STA2C1C	12/30/03							5								
STA2C1C	12/30/03				0.77						3.33					
STA2C1C	12/30/03										2.7					
STA2C1C	12/30/03										2.36					
STA2C1C	12/30/03				0.77							0.409				
STA2C1C	12/30/03											0.462				
STA2C1C	12/30/03											0.361				
STA2C1C	12/30/03	85.8	34	211	0.77		400		37.1	32.6			7.57		42.2	
STA2C1C	12/30/03							-3								
STA2C1C	12/30/03	86.5	34	207	0.77		400		37.2	32.7			7.59		39.7	
STA2C1C	12/30/03							-3								
STA2C1C	12/30/03	87	34	209	0.77		400		37.4	33.1			7.6		40.6	
STA2C1C	12/30/03							-3								
STA2C1C	12/30/03										-0.01					
STA2C1C	12/30/03											-0.007				
STA2C1C	12/30/03														0.1	
STA2C1C	12/30/03	-0.2	-1				-0.1		-0.1	-0.2						
STA2C1C	12/30/03			0.2				4								

Table 6. STA-2 Hg Special Studies Vegetation Data for Project (all concentrations in mg/Kg dry wt)

STATION_ID	DATE_COLLECTE	MERCURY,TOT	METHYL MERC	PERCENT AS	SOIL MOISTU	SPECIES			
STA2C3A	9/16/2002	0.005	0.00206	70.5	88.26	Southern Naiad			
STA2C3A	9/16/2002	0.00593	0.000186	76.1	81.31	Calcareous Periphyton			
STA2C3A	9/16/2002	0.0105	0.000024	6.9	77.65	Cattail			
STA2C3A	9/16/2002	-0.0073	0.000473	15.1	93.46	Duck-Potato			
STA2C3B	9/16/2002	0.00414	0.000599	51.7	82.39	Potamogeton			
STA2C3B	9/16/2002			44.4	89.71	Southern Naiad			
STA2C3C	9/16/2002	0.004	0.000083	10	82	Cattail			
STA2C3C	9/16/2002	0.00481	0.000142	10.1	69.27	Panicum			
STA2C3C	9/16/2002	0.00752	0.00203	66.2	88.96	Southern Naiad			
STA2C3C	9/16/2002	0.00349	0.000574	77.5	84.12	Calcareous Periphyton			
STA2C3C	9/16/2002	0.00804	0.000574	69.3	86.24	Filamentous Algea			
STA2C3A	9/16/2002	0.00698	0.000436			SOUTHERN NAIAD			
STA2C2A	9/17/2002	0.00325	0.00013	9.52	81.31	Typha			
STA2C2A	9/17/2002	0.00833	0.000181	4.49	63.13	Cladium			
STA2C2A	9/17/2002	0.0104	0.000764	66.6	92.82	Calcareous Periphyton			
STA2C2A	9/17/2002	0.0199	0.00218	65.7	95.34	Utricularia			
STA2C2B	9/17/2002	0.00674	0.000371	3.49	62.5	Cladium			
STA2C2B	9/17/2002	0.021	0.00221	23.3	94.03	Ludwigia			
STA2C2B	9/17/2002	0.0279	0.00147	65.5	93.2	Calcareous Periphyton			
STA2C2B	9/17/2002			10.1	86.26	Typha			
STA2C2C	9/17/2002	0.00911	0.000056	14.7	85.24	Typha			
STA2C2C	9/17/2002	0.0035	0.000117	4.2	64.36	Cladium			
STA2C2C	9/17/2002	0.01	0.000179	71.9	92.08	Calcareous Periphyton			
STA2C2C	9/17/2002	0.0151	0.0017	24	94.37	Ludwigia			
STA2C2A	9/17/2002	0.0075	0.000212			TYPHA			
STA2C1AA	9/18/2002	0.00878	0.00063	8.57	84.11	Typha			
STA2C1AA	9/18/2002	0.00845	0.000372	4.21	61.22	Cladium			
STA2C1AA	9/18/2002	0.0185	0.00876	59.8	93.08	Periphyton			
STA2C1BB	9/18/2002	0.0382	0.0267	10.5	89.63	Ludwigia			
STA2C1BB	9/18/2002	0.00607	0.000238	10	83.55	Typha			
STA2C1BB	9/18/2002			4.48	58.67	Cladium			
STA2C1CC	9/18/2002	0.00757	0.00256	12.6	86.75	Typha			
STA2C1CC	9/18/2002	0.0102	0.000902	4.6	56.91	Cladium			
STA2C1CC	9/18/2002	0.048	0.0227	12.8	89.97	Diodia			
STA2C1CC	9/18/2002	-0.0028	0.000141			DIODIA			

Table 6. STA-2 Hg Special Studies Vegetation Data for Project (continued) (all concentrations in mg/Kg dry wt)

STATION_ID	DATE_COLLECTE	MERCURY,TOT	METHYL MERC	PERCENT ASH	SOIL MOISTU	SPECIES
STA2C1AA	2/24/2003	0.001385	0.000017	7.1	79.08	Cattail (Typha domingensis)
STA2C1AA	2/24/2003	0.00354	0.00032			Cattail (Typha domingensis)
STA2C1AA	2/24/2003	0.00499	0.000042	2.9	59.91	Sawgrass (Cladium jamaicense)
STA2C1AA	2/24/2003	0.004666	0.000052			Sawgrass (Cladium jamaicense)
STA2C1AA	2/24/2003	0.002268	0.00011	9.08	86.54	Smartweed (Polygonum hydropiperoides)
STA2C1AA	2/24/2003	0.002845	0.000456	57.2	94.32	Periphyton (Calcareous)
STA2C1BB	2/24/2003			6.29	76.13	Cattail (Typha domingensis)
STA2C1BB	2/24/2003	0.00339	0.00009	3.69	56.95	Sawgrass (Cladium jamaicense)
STA2C1BB	2/24/2003	0.002832	0.000109	12.6	88.84	Red Ludwigia (Ludwigia repens)
STA2C1BB	2/24/2003	0.00323	0.000173	26.4	96.68	Periphyton (filamentous green algae)
STA2C1CC	2/24/2003	0.001888	0.000023	9.08	80.82	Cattail (Typha domingensis)
STA2C1CC	2/24/2003	0.001355	0.000015	3.88	57	Sawgrass (Cladium jamaicense)
STA2C1CC	2/24/2003	0.005303	0.001302	14.3	89	Red Ludwigia (Ludwigia repens)
STA2C1CC	2/24/2003	0.000947	0.00033	10.5	87	Fragrant Water Lily (Nymphaea odorata)
STA2C1CC	2/24/2003	0.011463	0.001938	28.2	95.88	Periphyton (Calcareous)
STA2C2A	2/24/2003	0.001066	0.000009	8.18	78.86	Cattail (Typha domingensis)
STA2C2A	2/24/2003			4.2	58.05	Sawgrass (Cladium jamaicense)
STA2C2A	2/24/2003	0.00118	0.000044	9.6	87.09	Fragrant Water Lily (Nymphaea odorata)
STA2C2A	2/24/2003	0.003089	0.000663	33.3	93.84	Bladderwort (Utricularia fibrosa)
STA2C2A	2/24/2003	0.006128	0.000451	46.6	93.49	Periphyton (Calcareous)
STA2C2B	2/24/2003	0.002651	0.00001	8.78	81.36	Cattail (Typha domingensis)
STA2C2B	2/24/2003	0.002352	0.000102	3.09	58.23	Sawgrass (Cladium jamaicense)
STA2C2B	2/24/2003	0.000691	0.000045	11.9	89.28	Fragrant Water Lily (Nymphaea odorata)
STA2C2B	2/24/2003	0.001166	0.000277	17.6	94.21	Bladderwort (Utricularia fibrosa)
STA2C2B	2/24/2003	0.005224	0.000235	21.8	97.04	Periphyton (filamentous green algae)
STA2C2C	2/24/2003	0.0015	0.000004	8.57	81.34	Cattail (Typha domingensis)
STA2C2C	2/24/2003			4.71	60.67	Sawgrass (Cladium jamaicense)
STA2C2C	2/24/2003	0.000843	0.000053	9.42	85.67	Fragrant Water Lily (Nymphaea odorata)
STA2C2C	2/24/2003	0.002034	0.000446	22.6	93.54	Bladderwort (Utricularia fibrosa)
STA2C2C	2/24/2003	0.000934	0.000174	21.7	93.44	Periphyton (filamentous green algae)
STA2C2C	2/24/2003	0.00087	0.000326			Periphyton (filamentous green algae)
STA2C3A	2/25/2003	0.000839	0.000088	38.4	86.14	Southern Naiad (Najas guadalupensis)
STA2C3A	2/25/2003	0.000448	0.000162	27.2	87.31	Illinois Pondweed (Potamogeton illinoensis)
STA2C3B	2/25/2003	0.000225	0.000032	80.6	86.06	Southern Naiad (Najas guadalupensis)
STA2C3B	2/25/2003	0.00038	0.00007	39.3	84.84	Illinois Pondweed (Potamogeton illinoensis)
STA2C3C	2/25/2003			72.1	86.54	Periphyton (Calcareous)
STA2C3C	2/25/2003	0.000366	0.000108	21.8	91.68	Illinois Pondweed (Potamogeton illinoensis)
STA2C3C	2/25/2003	0.000863	0.000154	9.12	82.17	Torpedograss (Panicum repens)
STA2C3C	2/25/2003	0.001922	0.000012	10	81.41	Cattail (Typha domingensis)
STA2C3C	2/25/2003	0.001136	0.000118			Cattail (Typha domingensis)

Table 6. STA-2 Hg Special Studies Vegetation Data for Project (continued) (all concentrations in mg/Kg dry wt)

STATION_ID	DATE_COLLECTE	MERCURY,TOT	METHYL MERC	PERCENT ASH	SOIL MOISTU	SPECIES
STA2C1AA	9/15/2003	0.002616	0.000007	7.91	84.28	Cattail (Typha domingensis)
STA2C1AA	9/15/2003	0.000845	0.000011			Cattail (Typha domingensis)
STA2C1AA	9/15/2003	0.000545	0.00001	5.71	64.52	Sawgrass (Cladium jamaicense)
STA2C1AA	9/15/2003	0.001533	0.000007			Sawgrass (Cladium jamaicense)
STA2C1AA	9/15/2003	0.002232	0.000049	55.5	94.9	Common Salvinia (Salvinia sp.)
STA2C1AA	9/15/2003	0.000316	0.000119			Common Salvinia (Salvinia sp.)
STA2C1AA	9/15/2003	0.000783	0.000146	63.4	94.9	Periphyton
STA2C1BB	9/15/2003			8.27	86.43	Cattail (Typha domingensis)
STA2C1BB	9/15/2003	0.001932	0.000105	4.4	68.24	Sawgrass (Cladium jamaicense)
STA2C1BB	9/15/2003	0.002316	0.000038	56.5	92.24	Red Ludwigia (Ludwigia repens)
STA2C1BB	9/15/2003	0.000724	0.000018	9.08	89.2	Fragrant Water Lily (Nymphaea oderata)
STA2C1BB	9/15/2003	0.001897	0.000028	59.7	94.53	Periphyton
STA2C1CC	9/15/2003	0.001364	0.000035	8.67	82.27	Cattail (Typha domingensis)
STA2C1CC	9/15/2003	0.003384	0.000185	5.58	67.34	Sawgrass (Cladium jamaicense)
STA2C1CC	9/15/2003	0.00303	0.000064	42	94.45	Bladderwort (Utricularia sp.)
STA2C1CC	9/15/2003	0.000973	0.000033	10.2	86.9	Fragrant Water Lily (Nymphaea oderata)
STA2C1CC	9/15/2003	0.001502	0.000007	68.1	91.96	Periphyton
STA2C2A	9/15/2003			10.8	86.15	Cattail (Typha domingensis)
STA2C2A	9/15/2003	0.002125	0.000037	3.6	64.57	Sawgrass (Cladium jamaicense)
STA2C2A	9/15/2003	0.000591	0.000036	70.6	86.51	Fragrant Water Lily (Nymphaea oderata)
STA2C2A	9/15/2003	0.001105	0.000042	45.2	95.25	Bladderwort (Utricularia sp.)
STA2C2A	9/15/2003	0.001508	0.000021	47.6	90.99	Periphyton
STA2C2B	9/15/2003	0.002456	0.000063	10.7	84.12	Cattail (Typha domingensis)
STA2C2B	9/15/2003	0.003997	0.000047	3.9	61.92	Sawgrass (Cladium jamaicense)
STA2C2B	9/15/2003	0.000803	0.000069	14.1	88.54	Fragrant Water Lily (Nymphaea oderata)
STA2C2B	9/15/2003	0.001786	0.000038	38	91.93	Periphyton
STA2C2C	9/15/2003	0.000645	0.000013	9.78	86.88	Cattail (Typha domingensis)
STA2C2C	9/15/2003			3.39	60.93	Sawgrass (Cladium jamaicense)
STA2C2C	9/15/2003	0.000734	0.000035	9.16	86.46	Fragrant Water Lily (Nymphaea oderata)
STA2C2C	9/15/2003	0.001481	0.000083	20.3	96.66	Filamentors green algae
STA2C3A	9/15/2003	0.001053	0.000206	53.8	86.69	Southern Naiad (Najas guadalupensis)
STA2C3A	9/15/2003	0.00062	0.000144	48.3	84.6	Illinios Pondweed (Potamogeton illinoensis)
STA2C3A	9/15/2003	0.000497	0.000051	24.3	96.67	Common Salvinia (Salvinia sp.)
STA2C3A	9/15/2003	0.00077	0.00037	45.8	90.31	Filamentous Green Algae
STA2C3B	9/15/2003	0.000393	0.000024	26.9	92.42	Southern Naiad (Najas guadalupensis)
STA2C3B	9/15/2003	0.00066	0.000074	36.4	88.15	Illinois Pondweed (Potamogeton illinoensis)
STA2C3C	9/15/2003	0.000592	0.000089	43.3	91.01	Southern Naiad (Najas guadalupensis)
STA2C3C	9/15/2003			51.3	87.28	Illinois Pondweed (Potamogeton illinoensis)
STA2C3C	9/15/2003	0.000804	0.000032	12	84.24	Torpedograss (Panicum repens)
STA2C3C	9/15/2003	0.00085	0.000036	75.7	89.36	Periphyton
STA2C3C	9/15/2003	0.001298	0.000043			Periphton

Appendix H. Data Collected for the Side-by-Side validation of the Modified *In Situ* Sipper Method for the Collection of Pore Water vs. the Centrifugation Method

[TBS]

APPENDIX I. Flagged Data for STA-2 Mercury Special Studies Project

Table 1. Table of all flagged mercury data during 1/1/02 to 1/31/04 for the project ST2M

Sample ID	Station ID	Date	QC Type	FLAG	Remark Code	F-THg	U-THg	F-MeHg	U-MeHg
P11165-16	G332	04/04/02		J	J				0.48
P11165-12	G334	04/04/02	RS	J	J				0.29
P11165-14	G334	04/04/02	RS	J	J				0.37
P11165-18	G334	04/04/02		J	J				0.21
P12528-20	G328B	08/22/02		V					0.12
P12528-22	G328B	08/22/02		V				0.13	
P12528-26	G328B	08/22/02	EB	V	I				0.054
P12773-20	STA2C2B	09/18/02		J3					0.7
P12774-6	STA2C3A	09/19/02		V				0.11	
P12774-9	STA2C3B	09/19/02		V	I			0.067	
P12774-15	STA2C3C	09/19/02	EB	V				0.12	
P12957-6	STA2C1AA	10/16/02		V				0.24	
P12957-15	STA2C2A	10/16/02		V				0.22	
P12957-18	STA2C2B	10/16/02		V				0.16	
P12957-21	STA2C2C	10/16/02		V				0.13	
P12957-24	STA2C2C	10/16/02	EB	V					0.12
P12978-20	G328B	10/17/02		V	I				0.048
P12978-22	G328B	10/17/02		V	I			0.042	
P12978-26	G328B	10/17/02	EB	V	I				0.059
P12978-14	G334	10/17/02		V	I				0.08
P12978-16	G334	10/17/02		V				0.11	
P13391-7	STA2C1BB	11/14/02		V			1.8		
P13391-9	STA2C1BB	11/14/02		V		1.4			
P13391-17	STA2C2A	11/14/02		V		1.2			
P13391-20	STA2C2B	11/14/02		V	A	0.95			
P13391-23	STA2C2C	11/14/02		V		0.67			
P13391-26	STA2C3A	11/14/02		V		0.52			
P13391-29	STA2C3B	11/14/02		V	I	0.28			
P13391-32	STA2C3C	11/14/02		V		0.47			
P13391-35	STA2C3C	11/14/02	EB	V			0.84		
P13875-3	STA2C1AA	01/08/03	EB	V			0.91		
P13875-5	STA2C1AA	01/08/03	EB	V		0.64			
P13875-7	STA2C1AA	01/08/03		V	A	0.87			
P13875-10	STA2C1BB	01/08/03		V		0.88			
P13875-13	STA2C1CC	01/08/03		V		2.2			
P13875-16	STA2C2A	01/08/03		V	A	0.7			
P13875-19	STA2C2B	01/08/03		V		0.78			
P13875-22	STA2C2C	01/08/03		V	I	0.18			
P13875-25	STA2C2C	01/08/03	EB	V			1.2		
P13876-1	STA2C3A	01/09/03	EB	V			0.73		
P13876-3	STA2C3A	01/09/03	EB	V		0.63			

Table 1. Continued

Sample ID	Station ID	Date	QCType	FLAG	Remark Code	F-THg	U-THg	F-MeHg	U-MeHg
P13876-10	STA2C3B	01/09/03		V	A		0.61		
P13876-12	STA2C3B	01/09/03		V		0.49			
P13876-15	STA2C3C	01/09/03		V			0.75		
P13876-17	STA2C3C	01/09/03		V	I	0.37			
P13876-20	STA2C3C	01/09/03	EB	V			0.9		
P14112-5	STA2C3A	02/06/03		V		0.5			
P14112-8	STA2C3B	02/06/03		V	A	0.51			
P14112-11	STA2C3C	02/06/03		V	I	0.3			
P14112-14	STA2C3C	02/06/03	EB	V	I		0.39		
P15035-7	STA2C1AA	05/01/03		V			0.86		
P15035-9	STA2C1AA	05/01/03		V		0.85			
P15035-12	STA2C1BB	05/01/03		V	A		1.1		
P15035-14	STA2C1BB	05/01/03		V		0.91			
P15035-17	STA2C1CC	05/01/03		V			2.1		
P15035-19	STA2C1CC	05/01/03		V		2			
P15035-22	STA2C2A	05/01/03		V	A	0.79			
P15035-25	STA2C2B	05/01/03		V		0.85			
P15035-28	STA2C2C	05/01/03		V		0.5			
P15035-31	STA2C2C	05/01/03	EB	V			0.76		
P15049-4	STA2C3A	05/28/03	EB	V				0.13	
P15049-6	STA2C3A	05/28/03		V	I			0.086	
P15049-9	STA2C3B	05/28/03		V	I			0.051	
P15049-12	STA2C3C	05/28/03		V	I			0.067	
P15450-16	G334	06/26/03		J3					0.16
P15450-18	G334	06/26/03		J3				0.37	
P15176-1	STA2C3A	08/22/03	EB	Y	I		0.2		
P15176-2	STA2C3A	08/22/03	EB	Y	U				-0.022
P15176-3	STA2C3A	08/22/03	EB	Y	I	0.16			
P15176-4	STA2C3A	08/22/03	EB	Y	U			-0.022	
P15176-5	STA2C3A	08/22/03		Y	A	0.78			
P15176-6	STA2C3A	08/22/03		Y				0.2	
P15176-8	STA2C3B	08/22/03		Y		0.91			
P15176-9	STA2C3B	08/22/03		Y	I			0.052	
P15176-11	STA2C3C	08/22/03		Y		0.7			
P15176-12	STA2C3C	08/22/03		Y	I			0.077	
P15176-14	STA2C3C	08/22/03	EB	Y	I		0.15		
P15176-15	STA2C3C	08/22/03	EB	Y	U				-0.022
P15191-13	STA2C1BB	10/15/03		J3					0.33
P15191-15	STA2C1BB	10/15/03		J3				0.43	

Appendix J. DBHYDRO Data and Equations Used in the Calculation of the STA-2 Water Budget

DB Keys

Stage

	Station	DB Key	
Cell 1			
	G329B_T	MT238	(omit)
	G330A_H	MQ893	mean
	G330D_H	MQ894	mean
Cell 2			
	G331B_T	MT241	mean
	G331E_T	MT244	mean
	G332_H	N3458	mean
Cell 3			
	G333C_T	N0751	
	G334_H	N3452	(omit)
Supply Canal			
	S6_T	06685	mean
	G328_T	MQ898	mean
	G337_T	LG728	mean
Inflow Canal			
	G329B_H	MT237	mean
	G331D_H	MT248	mean
	G333C_H	N0750	mean
	G337_T	LG728	mean
Discharge Canal			
	G332_T	N3459	
	G335_H	MR463	(omit)
L6 Canal			
	G335_T	MR464	mean
	G339_T	MS576	mean
Seepage Canal			
	G337_H	LG727	

Flow

STA 2

S6	15034	
G328	J0718	
G335_P	N0659	
G337_P	LG701	
G338_C	MC705	
G339_S	MC706	

Cell 1

G329A_C	N0748	sum inflow
G329B_C	LG703	
G329C_C	LG704	
G329D_C	LG705	
G330A_C	LG706	sum outflow
G330B_C	LG707	
G330C_C	LG708	
G330D_C	LG709	
G330E_C	LG710	

Cell 2

G331A_C	LG711	sum inflow
G331B_C	LG712	
G331C_C	LG713	
G331D_C	LG714	
G331E_C	LG715	
G331F_C	LG716	
G331G_C	LG718	
G332_S	LG719	outflow

Cell 3

G333A_C	LG720	sum inflow
G333B_C	LG721	
G333C_C	LG722	
G333D_C	LG723	
G333E_C	LG724	
G334_S	LG725	outflow

Rainfall

EAA5	JW233	mean
S6_R	15203	
S7_R	15204	

Evapotranspiration

STA1W	KN810

Equations

General

Inflow + Rainfall – Outflow – Evapotranspiration – Seepage – Change in Storage = Error

Note: all units below in acre-feet per day

Cell 1

Inflow

= ((24 x 3600)/43560) x (N0748 + LG703 + LG704 + LG705)

Rainfall

= (1990/(3 x 12)) x (JW233 + 15203 + 15204)

Outflow

= ((24 x 3600)/43560) x (LG706 + LG707 + LG708 + LG709 + LG710)

Evapotranspiration

= (1990/(25.4 x 12)) x (KN810)

Seepage

= ((24 x 3600)/43560) x SF_1* x [1.04 x (((MQ893 + MQ894)/2) – ((LG728 + MT237 + MT248 + N0750)/4)) + 3.41 x (((MQ893 + MQ894)/2) – ((MS576 + MR464)/2)) + 1.06 x (((MQ893 + MQ894)/2) – (N3459))] + ((SF_1 + SF_2)/2) x 3.37 x (((MQ893 + MQ894)/2) – ((MT241 + MT244 + N3458)/3))]

* - user defined (adjusted) seepage factor, SF. (Four, unique for each cell and the entire STA).

Change in Storage

= (IF(((MQ893 + MQ894)/2)$_t$<11.82,(IF(((MQ893 + MQ894)/2)$_t$>(MQ893 + MQ894)/2)$_{t-1}$,(0.59-0.033 x (11.82-((MQ893 + MQ894)/2)$_t$) x 30.48 + 0.00068 x ((11.82-((MQ893 + MQ894)/2)$_t$) x 30.48)^2 - 0.00000483 x ((11.82-((MQ893 + MQ894)/2)$_t$) x 30.48)^3),(0.95-0.275 x (11.82-((MQ893 + MQ894)/2)$_t$) x 30.48 + 0.036 x ((11.82-((MQ893 + MQ894)/2)$_t$) x 30.48)^2 - 0.00237 x ((11.82-((MQ893 + MQ894)/2)$_t$) x 30.48)^3 + 0.000085 x ((11.82-((MQ893 + MQ894)/2)$_t$) x 30.48)^4 - 0.00000169 x ((11.82-((MQ893 + MQ894)/2)$_t$) x 30.48)^5 + 0.00000001743 x ((11.82-((MQ893 + MQ894)/2)$_t$) x 30.48)^6 - 0.00000000007278 x ((11.82-((MQ893 + MQ894)/2)$_t$) x 30.48)^7))),1)) x (((MQ893 + MQ894)/2)$_t$-(MQ893 + MQ894)/2)$_{t-1}$) x 1990

Note: subscripts t and t-1 refer to the current day's value and the vale for the previous day, respectively. This equation accounts for change of storage when water goes below mean ground elevation.

Cell 2

Inflow

= ((24 x 3600)/43560) x (LG711 + LG712 + LG713 + LG714 + LG715 + LG716 + LG718)

Rainfall

= (2220/(3 x 12)) x (JW233 + 15203 + 15204)

Outflow

= ((24 x 3600)/43560) x (LG719)

Evapotranspiration

= (2220/(25.4 x 12)) x (KN810)

Seepage

= ((24 x 3600)/43560) x SF_3* x [2.08 x (((MT241 + MT244 + N3458)/3) – ((LG728 + MT237 + MT248 + N0750)/4)) + ((SF_2 + SF_3)/2) x 2.84 x (((MT241 + MT244 + N3458)/3) – ((N0751 + N3452)/2)) + 0.38 x (((MT241 + MT244 + N3458)/3) – (N3459)) + ((SF_1 + SF_2)/2) x 3.37 x (((MT241 + MT244 + N3458)/3) – ((MQ893 + MQ894)/2))]

* - user defined (adjusted) seepage factor, SF. (Four, unique for each cell and the entire STA).

Change in Storage

= (IF(((MT241 + MT244 + N3458)/3)$_t$<10.33,(IF(((MT241 + MT244 + N3458)/3)$_t$>(MT241 + MT244 + N3458)/3)$_{t-1}$,(0.59-0.033 x (10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48 + 0.00068 x ((10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48)^2 - 0.00000483 x ((10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48)^3),(0.95-0.275 x (10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48 + 0.036 x ((10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48)^2 - 0.00237 x ((10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48)^3 + 0.000085 x ((10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48)^4 - 0.00000169 x ((10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48)^5 + 0.00000001743 x ((10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48)^6 - 0.00000000007278 x ((10.33-((MT241 + MT244 + N3458)/3)$_t$) x 30.48)^7))),1)) x (((MT241 + MT244 + N3458)/3)$_t$-(MT241 + MT244 + N3458)/3)$_{t-1}$) x 2220

Cell 3

Inflow

= ((24 x 3600)/43560) x (LG720 + LG721 + LG722 + LG723 + LG724)

Rainfall

= (2220/(3 x 12)) x (JW233 + 15203 + 15204)

Outflow

= ((24 x 3600)/43560) x (LG725)

Evapotranspiration

= (2220/(25.4 x 12)) x (KN810)

Seepage

= ((24 x 3600)/43560) x SF_2* x [1.21 x (((N0751 + N3452)/2) – ((LG728 + MT237 + MT248 + N0750)/4)) + 2.96 x (((N0751 + N3452)/2) – (LG727)) + 1.21 x (((N0751 + N3452)/2) – (N3459)) + ((SF_2 + SF_3)/2) x 2.84 x (((N0751 + N3452)/2) – ((MT241 + MT244 + N3458)/3))]

* - user defined (adjusted) seepage factor, SF. (Four, unique for each cell and the entire STA).

Change in Storage

= (IF(((N0751 + N3452)/2)$_t$<9.61,(IF(((N0751 + N3452)/2)$_t$>(N0751 + N3452)/2)$_{t-1}$,(0.59-0.033 x (9.61-((N0751 + N3452)/2)$_t$) x 30.48 + 0.00068 x ((9.61-((N0751 + N3452)/2)$_t$) x 30.48)^2 - 0.00000483 x ((9.61-((N0751 + N3452)/2)$_t$) x 30.48)^3),(0.95-0.275 x (9.61-((N0751 + N3452)/2)$_t$) x 30.48 + 0.036 x ((9.61-((N0751 + N3452)/2)$_t$) x 30.48)^2 - 0.00237 x ((9.61-((N0751 + N3452)/2)$_t$) x 30.48)^3 + 0.000085 x ((9.61-((N0751 + N3452)/2)$_t$) x 30.48)^4 - 0.00000169 x ((9.61-((N0751 + N3452)/2)$_t$) x 30.48)^5 + 0.00000001743 x ((9.61-((N0751 + N3452)/2)$_t$) x 30.48)^6 - 0.00000000007278 x ((9.61-((N0751 + N3452)/2)$_t$) x 30.48)^7))),1)) x (((N0751 + N3452)/2)$_t$-(N0751 + N3452)/2)$_{t-1}$) x 2220

STA 2

Inflow

= ((24 x 3600)/43560) x (15034 + J0718 + LG701 – MC705 + MC706)

Rainfall

= (6537/(3 x 12)) x (JW233 + 15203 + 15204)

Outflow

= ((24 x 3600)/43560) x (N0659)

Evapotranspiration

= (6537/(25.4 x 12)) x (KN810)

Seepage

= ((24 x 3600)/43560) x [SF_{STA}* x 4.43 x (((LG728 + MT237+MT248+N0750)/4) – (LG727)) + SF_3 x 2.96 x (((N0751 + N3452)/2) – (LG727)) + SF_{STA} x 2.65 x ((N3459) – ((MR464 + MR576)/2)) + SF_1 x 3.41 x (((MQ893 + MQ894)/2) – ((MS576 + MR464)/2))]

* - user defined (adjusted) seepage factor, SF. (Four, unique for each cell and the entire STA).

Change in Storage

= Change in Store (Cell 1)$_t$ + Change in Storage (Cell 2)$_t$ + Change in Storage (Cell 3)$_t$ + (3000/43560) x [(0.5 x ((06685 + MQ898 + LG728)$_t$/3 + 4) x (114 + 5 x ((06685 + MQ898 + LG728)$_t$/3 + 4))) - (0.5 x ((06685 + MQ898 + LG728)$_{t-1}$/3 + 4) x (114 + 5 x ((06685 + MQ898 + LG728)$_{t-1}$/3 + 4)))] + (23400/43560) x [(0.5 x ((MT237 + MT248 + N0750 + LG728)$_t$/4 + 4) x (40 + 6 x ((MT237 + MT248 + N0750 + LG728)$_t$/4 + 4))) - (0.5 x ((MT237 + MT248 + N0750 + LG728)$_{t-1}$/4 + 4) x (40 + 6 x ((MT237 + MT248 + N0750 + LG728)$_{t-1}$/4 + 4)))] + (6000/43560) x [(0.5 x (N3459)$_t$ + 4) x (116 + 6 x (N3459)$_t$ + 4))) - (0.5 x (N3459)$_{t-1}$ + 4) x (116 + 6 x (N3459)$_{t-1}$/2 + 4)))]

Appendix K. Exploratory Data Analysis Output

Results of the intra- and inter-media univariate, nonparametric linear correlation analyses and multivariate parametric linear regression analyses are too extensive to reproduce in this document and therefore are available electronically upon request.