Appendix 4A-7: Quarterly Reports on Modified Permit Monitoring at STA-2

Larry Fink
Status Report on STA-2 Start-Up and Routine Mercury Monitoring and Mercury Special Studies
07/01/02-08/22/02

Introduction

This letter report summarizes the most recent results of start-up, routine, and special studies mercury monitoring in STA-2. It includes data collected on 8/22/02 that have not completed internal quality control review. As such, the data must be considered provisional and any interpretations drawn from them preliminary. Accompanying this report are two EXCEL spreadsheet files that summarize the most recent results of mercury sampling in STA-2 for July and August 2002. In addition, we have included a copy of a draft report on the results of the drying and rewetting study conducted for the Florida Department of Environmental Protection (FDEP) and the South Florida Water Management District (District) under District Cooperative Agreement C-13860.

Background

After completion of the levees but prior to flooding, the permit requires that the District collect six representative 10-cm cores for total mercury (THg) and methylmercury (MeHg) analysis. At present, those analyses are being carried out by Frontier Geosciences in Seattle, WA.

Start-up mercury monitoring requirements for initiation of routine operation of STA-2 include biweekly collection of unfiltered surface water samples at the common inflow (G328B) and a representative interior treatment marsh site in Cell 1 (STA2C1A), 2 (STA2C2A), and 3 (STA2C3A) for ultra-trace analysis of THg and MeHg. At present, these and all other ultra-trace mercury water analyses for permit compliance are being carried out by the Florida Department of Environmental Protection (FDEP). When the interior site concentrations of THg and MeHg are not significantly greater than the inflow concentrations, flow-through operation can commence. Cells 3 and 2 met their mercury start-up criteria in September and November of 2000, respectively. Cell 1 still has not as of this writing.

Thereafter, mercury monitoring requirements for routine operation of STA-2 include collection of unfiltered surface water samples at the common inflow (G328) and outflow (G335) quarterly for THg and MeHg analysis. The additional operational mercury monitoring in the proposed modifications to the STA-2 operating permit includes biweekly collection of unfiltered surface water samples of the common inflow (G328B) and outflow (G335), as well as one representative interior site in Cell 1 (STA1A); (b) at site C1A, monthly collection of a mosquitofish (n = 75 – 250 fish; composite homogenate; subsampled n = 3 times) for THg analysis; (c) at Site C1X, semi-annual collection of sunfish (whole fish; homogenized individual; subsampled n = 1) for THg analysis; and (c) downstream sampling of mosquitofish quarterly and n = 20 sunfish
semi-annually at sites WCA-2A-N4 and WCA-2A-Z4. The additional or expanded operational monitoring was initiated by the District in August 2001 following submittal of the application for the permit modification.

The first phase of the special studies began in November 2001 following the second Cell 1 anomalous mercury event. In Phase 1, on a biweekly basis, unfiltered surface water samples are collected at G328B, G335, and the Cell 1 (G330A), Cell 2 (G332), and Cell 3 (G334) outflows and analyzed for THg and MeHg. In Phase 2, a suite of influential constituents will also be analyzed at those sites, as well as filtered surface water samples at G328B and the outflow to one treatment cell every other biweekly period, rotating the cell to be sampled in this manner such that the cycle repeats itself every fourth biweekly period. In addition, every other biweekly period (every 28 days), filtered samples of surface water are collected at three interior sites each in Cells 1, 2, and 3 and analyzed for THg and MeHg, along with a suite of potentially influential constituents. On a rotating basis, unfiltered surface water samples will be collected at each of three interior sites in a treatment cell according to a schedule that repeats every fourth biweekly period. Further, every 28 days mosquitofish will be collected at those same nine interior sites and analyzed for THg, whereas soils will be collected quarterly and vegetation semi-annually for THg and MeHg analysis, as well as a suite of constituents known or reasonably expected to influence the mercury cycle.

In anticipation of issuance of the modified permit, inflow to Cell 1 began the week of August 12, 2002. However, there was no discharge from Cell 1, because water stage at the bottom of Cell 1 had not yet crested the weir, so the sample collected at G330A was for a standing water condition. Phase 2 sampling began 7 to 10 days later on August 22, 2002. Sampling of Cell 1 and one interior site in STA-2 Cell 2 was completed on that date. However, due to inclement weather, sampling could not be completed. The remaining samples were collected a week later. Those results are not yet available from the FDEP laboratory.

Results and Discussion

The attached Excel worksheets summarize the results of the July and August 2002 sampling events at STA-2.

During the July 2002 biweekly permit modification sampling event, the concentrations of THg and MeHg at the inflow and outflow sampling stations were not especially noteworthy, and the interior sample could not be collected due to low water levels at Site C1A (< 10 cm). With the initiation of inflow, this situation changed substantially. The discharge from G335 did not contain anomalously high concentrations of unfiltered or filtered THg (3 ng/L) or MeHg (1 ng/L). However, concentrations of unfiltered and filtered THg and MeHg at the new interior site AA in Cell 1 showed 7.6 and 5.6 ng/L THg and 2.6 ng/L and 2.7 ng/L MeHg; 16 ng/L and 8.1 ng/L THg and 8.6 ng/L and 7.4 ng/L MeHg at C1BB; and 32 ng/L and 24 ng/L THg and 20 ng/L and 20 ng/L MeHg at C1CC.
The water in Cell 1 at the time the interior samples were collected were shallow, and some of the unprecedentedly high levels of THg and MeHg there can be attributed to limited dilution and inadvertent resuspension of sediment during sampling. However, as demonstrated by the results of filtered sampling, not all of the anomalously high concentrations can be caused by sediment resuspension.

Clearly, as anticipated, the initiation of sampling within 7-10 days of initiation of inflow caught the peak of the “first-flush” event. We further anticipate that the next monthly sampling event will reveal substantially lower concentrations of THg and MeHg for four reasons: (1) the external contribution to the Hg(II) concentration in surface water from wet and dry atmospheric deposition and internal contribution from the first-flush release of Hg(II) from oxidized soils will be further diluted by the continuing inflow, which was running 2 ng/L and 0.62 ng/L THg as of the 8/22/02 sampling event, reducing the driving force for excess MeHg production; (2) the excess MeHg produced from the internal and external sources of excess Hg(II) will also be diluted by the continuing inflow water, which was running 0.12 and 0.13 ng/L MeHg as of the 8/22/02 sampling event; (3) the first-flush pool of excess Hg(II) will be substantially depleted; and (4) the rapid regrowth of phytoplankton and periphyton standing crop will rapidly sorb the excess Hg(II) and MeHg, storing it temporarily until the biomass begins to decompose.

However, the prediction of the post-rewetting biogeochemical trajectory of Cell 1 is complicated by several factors. First, with some subsequent release of THg and MeHg from decomposing plants back to the overlying water and underlying surficial sediments, this could feed substantial “aftershock” pulses through the fall, even in the absence of rainfall or inflow, as was observed during the first anomalous mercury event in the summer, fall, and winter of 2000-2001. Second, the build-up of soil sulfate in response to the loads delivered in July through October 2000 and August through November 2001 could have increased the quantity of labile sulfate mobilized following rewetting, resulting in an increase in the peak amplitude of the “first-flush” pulse of excess MeHg production. Third, based on the results of the joint USGS/SFWMD post-burn study, the depletion of the excess sulfate pool and the build-up of the pore water sulfide pool generally presage a reduction in the rate of MeHg production (see draft Appendix 2B-1 in this year’s ECR 2003), but, based on the results of the dry/wet laboratory microcosm study (C-13860), STA-2 Cell 1 soils are quicker to produce excess MeHg, slower to deplete the pool of first-flush pore water sulfate, and slower to build up pore water sulfide relative to WCA-3A-15, the Everglades “hot spot” site. (See attached draft report for reference). This is likely to increase the duration of the “first-flush” pulse of excess MeHg production. Why Cell 1 soils behave so differently relative to WCA-3A-15 soils is not yet known. The proposed Cell 1 mesocosm study should provide some of the answers.

Whatever the cause, the effect of excess MeHg production is not limited to anomalously high concentrations of MeHg in the water column. As has occurred in the preceding two anomalous mercury events in Cell 1, the initial pulse of excess of MeHg production will be transferred to mosquitofish, either directly or via autotrophic or saprotrophic food chains. Interruption of the development of the Cell 1 food chains via drawdown and
dryout in the winters of 2000-2001 and 2001-2002 prevented substantial transfer to sunfish or largemouth bass following the two previous mercury anomalies, however. By contrast, having raised the outflow weirs in Cell 1, we anticipate being able to maintain deeper average water levels for longer periods of time, which could allow the development of indigenous sunfish and largemouth bass populations. If the excess MeHg pulse is not sustained, as was the case in STA1W Cell 5, individual mosquitofish will bioaccumulate this excess MeHg pulse over the next 14 to 28 days and then begin to dilute the residue from this MeHg pulse through growth, while the population will clear the pulse via the die-off of highly contaminated older fish over the next 120-210 days. Individual sunfish and largemouth bass will dilute some of the MeHg from this pulse through growth, but these populations will be slower to clear the MeHg residue from this pulse, because they are longer-lived than mosquitofish. If the “first-flush” pulse of excess MeHg production is sustained or the “aftershock” pulses are substantial, as was the case following the first anomalous mercury event in Cell 1, the build-up of high MeHg concentrations in mosquitofish and then sunfish species or equivalent trophic level 3 fish species could represent an unacceptable risk of toxic effects from MeHg exposure to sensitive members of fish-eating wildlife subpopulations feeding in STA-2 Cell 1 preferentially.
EXCEL SPREADSHEET FILES

Modified Permit Compliance Mercury Monitoring Data Collected to Date

[Available Upon Request]
Executive Summary

STA-2 Cells 2 and 3 met their mercury start-up criteria in September and November 2000, while Cell 1 experienced anomalous mercury events in the fall of 2000 and 2001. The first event, which occurred in late September 2000 after first flooding in mid July 2000, resulted in anomalously high total mercury (THg) and methylmercury (MeHg) concentrations in water and mosquitofish. Due to the drought, Cell 1 dried out in April 2001. Subsequently, the District applied for a permit modification that would allow flow-through operation to commence without meeting mercury start-up criteria, in the belief that exposure to and/or export of MeHg could be reduced in the following ways: the flowing water would (1) dilute the fresh supply of inorganic mercury in atmospheric deposition, (2) dilute the MeHg produced internally, and (3) increase the sulfate load to the point that sulfide inhibition of MeHg production would occur. The application was submitted in July 2001 and, by letter dated August 19, 2001, FDEP notified the District that it had approved the modification.

With the onset of summer rain, Cell 1 began refilling in July 2001 and experienced a second occurrence of anomalously high MeHg concentrations in water in November 2001. To avoid the build-up of anomalously high MeHg concentrations in wading bird forage, and with no guarantee that there would be sufficient flow to keep Cell 1 wet throughout the dry season, Cell 1 was intentionally dried out in December 2001. Dryout was essentially complete by February 2002, although some pools of shallow standing water remained through April 2002, primarily on the west side of Cell 1. This also facilitated the raising of the Cell 1 outflow culverts, which was intended to reduce the duration and frequency of dryout events.

During the first biweekly sampling event under the Mercury Special Studies Plan, the concentrations of THg and MeHg at the inflow and outflow sampling stations were not especially noteworthy, and the interior sample could not be collected due to low water levels at Site C1A (< 10 cm). With the initiation of inflow into STA-2 Cell 1, this situation changed substantially. In samples collected on August 22, 2002, the discharge from G335 did not contain anomalously high concentrations of unfiltered or filtered THg (3 ng/L) or MeHg (1 ng/L). However, concentrations of unfiltered and filtered THg and MeHg at the new interior site AA in Cell 1 (C1AA) showed 7.6 and 5.6 ng/L THg and 2.6 ng/L and 2.7 ng/L MeHg; 16 ng/L and 8.1 ng/L THg and 8.6 ng/L and 7.4 ng/L MeHg at C1BB; and 32 ng/L and 24 ng/L THg and 20 ng/L and 20 ng/L MeHg at C1CC. These last results are considered unprecedented. This “first-flush” pulse proceeded through the Cell 1 discharge culverts (G-330A) a month later, peaking at 12 ng/L, then mixed with the higher flows from Cells 2 and 3. The peak concentration of MeHg in the combined outflow at G-335 was 5.8 ng/L on 9/19/02 but never exceeded the Florida Class III Water Quality Criterion of 12 ng/L for THg.
This third anomalous mercury event began to dissipate from the Cell 1 interior water column almost immediately, and this trend has continued through the end of the second quarter of the study. Concentrations of unfiltered MeHg declined from 20 ng/L at Site CC in STA-2 Cell 1 to less than 2 ng/L with the last December 2002 sampling event. Further evidence that the anomalous mercury event has dissipated from STA-2 Cell 1 can be found in the fact that there was no statistically significant difference (one-tail t test; 95th percentile confidence level) between the average concentration of THg or MeHg at the representative interior monitoring site for the last three biweekly sampling events in 2002 and the corresponding long-term average for the period of record for the inflow at G-328B.

The soils data received from Frontier Geosciences (FGS) indicate that the build-up and decline of excess MeHg in water was paralleled by a build-up and decline of excess MeHg in surficial soils in Cell 1, albeit not with the same spatial pattern. The first set of associated chemical analyses for other constituents of interest received from DB Labs suggest that higher total sulfur and lower total iron in Cell 1 vs. lower total sulfur and higher total iron in Cell 3 could explain the differences in MeHg production and bioaccumulation between cells.

The anticipated build-up of the first-flush excess MeHg in mosquitofish in response to the MeHg peak was detected in the following month’s results. Unlike the pattern in the first anomalous event, the build-up appeared to peak in September and October 2002 and declined thereafter in November and December 2002 to roughly half the peak concentrations. While the relatively short-lived mosquitofish could clear this pulse from its Cell 1 population over a three to six month period, the half-life could be extended by the recycling of first-flush Hg(II) from decomposing plants back to the surficial sediment for subsequent methylation and bioaccumulation. There is no evidence of such recycling in the surface water monitoring data, however. For the relatively long-lived sunfish and largemouth bass, the first-flush MeHg pulse is unlikely to clear rapidly from these populations. However, based on data collected in the fall of 2001, sunfish appear to be feeding at the same trophic level on average as the mosquitofish in the shallow, unproductive waters of STA-2 Cell 1, which, if this condition persists, should mitigate the magnitude of the peak in the bioaccumulation of the first-flush excess MeHg in sunfish. This condition could change, however, if the maintenance of deeper water for longer periods of time in STA-2 Cell 1 allows a more mature food web to develop there. Nevertheless, the sunfish samples collected in October 2002 in Cell 1 and the STA-2 discharge canal did not appear to reflect exposure to anomalously high MeHg concentrations in forage. The next semi-annual sunfish sampling is scheduled for March-April 2003.

The District is required to prepare a probabilistic ecological risk assessment (PERA) if the average concentrations of THg as MeHg in mosquitofish and sunfish exceed the respective upper 95th percentile concentration for the Everglades populations. The average mosquitofish concentration has already reached the ecological risk assessment trigger, and but the sunfish collected in the discharge canal in October 2002 have not.
The next scheduled sunfish sampling is in February 2003, and the processing and the analysis of the sunfish will be expedited to the extent practicable.

Based on the steep decline in the water column concentration of MeHg during the last quarter and the corresponding decline in mosquitofish, we recommend that Cell 1 should not be drawn down to eliminate the development of the food web there. Instead, we recommend that the pulse be allowed to build up and decline in the T3 and T4 fish populations, while allowing the soil pore water chemistry to stabilize. During the remainder of the dry season, every effort will be made to keep Cell 1 wet to the extent permitted by available water.
Introduction

This letter report summarizes the most recent results of start-up, routine, and special studies mercury monitoring in STA-2. It includes the results of analyses that completed QC review by 12/31/02. Appended to this report are the EXCEL files of the data for the period of record used to generate the graphs in the report. The data collected this quarter are included in Attachment 1.

Start-up and routine mercury monitoring of the Stormwater Treatment Areas (STAs) are intended to alert the permittee and the permit issuing authority to potential problems that require more intensive follow-up studies. Anomalous mercury events revealed by start-up monitoring in STA-2 Cell 1 in the fall of 2000 and 2001 and the summer of 2002 necessitated the follow-up with special studies in STA-2 intended to better define the problem and probe its cause.

Beyond more fully characterizing the biogeochemical and bioaccumulation trajectories of STA-2 Cell 1 following reflooding, the data collected in the special studies will also support: (1) the construction of THg and MeHg mass budgets to (a) identify all significant sources and sinks of Hg(II) and MeHg production within each cell of STA 2 and (b) more accurately quantify short- and long-term MeHg 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 MeHg production, bioaccumulation, storage, and export; and (3) a probabilistic ecological risk assessment of toxic effects from MeHg exposure to fish-eating wildlife foraging preferentially in STA-2 Cell 1, taking into account the dynamic nature of the build-up and dissipation of MeHg in the preferred preyfish populations.

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 MeHg pulse in Cell 1 following reflooding and to optimize STA-2 operation for the long-term.
Background

The geographic location and aerial photograph of STA-2 are depicted in Figure 1, while Figure 2 illustrates the STA-2 flow management structures.

Pre-Start-Up Monitoring

After completion of the levees but prior to flooding, the permit requires that the District collect six representative 10-cm cores for total mercury (THg) and methylmercury (MeHg) analysis (STA-2 s1-s6). This sampling was carried out in STA-2 in the fall of 1999. Thereafter, this sampling is repeated triennially. At present, the soil ultra-trace mercury analyses are carried out by Frontier Geosciences in Seattle, WA. The pre-start-up soil monitoring sites in STA-2 are shown in Figure 3.

Start-Up Monitoring

Start-up mercury monitoring requirements for initiation of routine operation of STA-2 include biweekly collection of unfiltered surface water samples at the common inflow (G328B) and a representative interior treatment marsh site in Cell 1 (STA2C1A), 2 (STA2C2A), and 3 (STA2C3A) for ultra-trace analysis of THg and MeHg. These sites are depicted in Figure 4. At present, these and all other ultra-trace mercury water analyses for permit compliance are carried out by the Florida Department of Environmental Protection (FDEP). When the interior site concentrations of THg and MeHg are not significantly greater than the inflow concentrations, flow-through operation can commence. Cells 3 and 2 met their mercury start-up criteria in September and November of 2000, respectively. Cell 1 still has not as of this writing.

Routine Operational Monitoring

Thereafter, mercury monitoring requirements for routine operation of STA-2 include collection of (1) unfiltered surface water samples at the common inflow (G328) and outflow (G335) quarterly for THg and MeHg analysis; (2) mosquitofish (n = 75 – 250 fish; composite homogenate; subsampled n = 3 times) semi-annually at those same sites and interior sites C1A, C2A, and C3A for THg analysis; (3) n = 20 sunfish sp. (whole fish; homogenized individual; subsampled n = 1) and n = 20 largemouth bass (whole fish filet; muscle section; subsampled n = 1) at those same sites annually; and (4) soils (1-10 cm cores) at the same six representative interior sites triennially. These sites are shown in Figure 3.

The additional mercury monitoring in the modified STA-2 operating permit includes biweekly collection of unfiltered surface water samples of the common inflow (G328B) and outflow (G335), as well as one representative interior site in Cell 1 Site A (C1A); (b) at site C1A, monthly collection of a mosquitofish (n = 75 – 250 fish; composite homogenate; subsampled n = 3 times) for THg analysis; (c) at Site C1X (near the discharge culverts), semi-annual collection of n = 20 sunfish (whole fish; homogenized...
individual; subsampled n = 1) for THg analysis. Figure 5 illustrates the downstream sites added in the modified permit for the collection of mosquitofish quarterly and n = 20 sunfish semi-annually, WCA-2A-N4 and WCA-2A-Z4. The additional or expanded operational monitoring was initiated by the District in August 2001 following submittal of the application for the permit modification.

*Special Studies*

In response to the third anomalous mercury event in STA-2 Cell 1 in August 2002, the District and the Department worked together to develop a Memorandum of Agreement (MOA) that would address the STA-2 Cell 1 mercury problem. Under that MOA, the District agrees to carry out expanded mercury monitoring in STA-2, while the Department agrees to carry out expanded mercury research and modeling in STA-2. The MOA is recommended for approval by the District’s Governing Board at its regularly scheduled meeting in February 2003. Although the MOA is not yet in effect, the District has proceeded in good faith to carry out its monitoring commitments.

The implementation of the special studies involves three tiers. Tier 1, which is a pore water sampling method development and technology transfer project, was necessitated by the inability of the District to acquire and field-validate a reliable, technician-friendly method of pore water sampling of the surficial soil (0-4 cm) prior to start-up of the project in August 2002. The criteria that such a method must meet are: (1) obtains a sufficient volume of pore water from surficial peat soils (0-4 cm) for numerous analyses; (2) preserves reducing redox conditions; (3) prevents ultra-trace THg and MeHg contamination; (4) avoids inadvertent sampling of surface water while collecting the surficial soil pore water sample; (5) does not require the use of a glove box and centrifuge, neither of which are available to the District at this time and would require extensive laboratory space to implement if purchased and infeasible holding times if not; and (6) is readily mastered by a typical technician. Efforts to secure the services of a recognized expert in ultra-trace mercury pore water sampling using an existing, field-validated reliable method are now under way.

Tier 2 is an intensive study of changes in soil and pore water chemistry at one, well-studied site in STA-2 Cell 1 (C1C). According to the sampling plan, samples of soil and pore water were to be collected in triplicate at start-up and then 7, 14, 28, 56, 112, and 224 days later (exponential sampling) for analysis of ultra-trace THg and MeHg, as well as a suite of potentially influential constituents. The sampling and analysis schemes are summarized in Table 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).

Tier 3 has two phases. Pre-flooding baseline samples of surficial soil and pore water were to be collected at three interior sites in each of the three cells six months prior to reflooding in the spring of 2002. Thereafter, soil samples are collected at these same sites upon reflooding and quarterly thereafter without replication. On a biweekly basis, unfiltered surface water samples are collected at G328B, G335, and the Cell 1 (G330A), Cell 2 (G332), and Cell 3 (G334) outflows and analyzed for THg and MeHg. In Phase 2,
a suite of influential constituents is analyzed at those sites, as well as filtered surface water samples at G328B and the outflow to one treatment cell every other biweekly period, rotating the cell to be sampled in this manner such that the cycle repeats itself every fourth biweekly period. In addition, every other biweekly period (every 28 days), filtered samples of surface water are collected at three interior sites each in Cells 1, 2, and 3 and analyzed for THg and MeHg, along with a suite of potentially influential constituents. On a rotating basis, unfiltered surface water samples will be collected at each of three interior sites in a treatment cell according to a schedule that repeats every fourth biweekly period. Further, every 28 days mosquitofish will be collected at those same nine interior sites and analyzed for THg, whereas soils will be collected quarterly and vegetation semi-annually for THg and MeHg analysis, as well as a suite of constituents known or reasonably expected to influence the mercury cycle. The Tier 3 sampling and analysis schemes are summarized in Table 1. The Tier 1, 2, and 3 sampling sites are depicted in Figure 6.

**Status Update**

To complement the routine start-up mercury monitoring of Cell 1 (Figure 3), unfiltered sampling of the Cell 1, 2, and 3 outflows began in November 2001 following the second Cell 1 anomalous mercury event in October 2001. Those expanded sampling sites are depicted in Figure 5. Baseline soil samples were collected in May 2002 at the sites depicted in Figure 6, but pore water samples could not be collected, because the USEPA-Middleton pore water sampling device could not be demonstrated to collect a valid surficial soil pore water sample under the conditions encountered by District staff. The switch to the squeezer technique used by USGS-Reston and others throughout the world also proved less than successful with respect to ultra-trace mercury analysis due to THg contamination of blanks. Systematic replacement of the various plastic fittings with pre-cleaned teflon and pre-cleaning of the micropore filters was contemplated but could not be completed prior to initiation of the reflooding of Cell 1 in August 2002. At that point, the District concluded with FDEP concurrence that it would require additional expert assistance for adaptation of an existing pore water collection method that met the following criteria: (1) obtains a sufficient volume of pore water from surficial peat soils (0-4 cm) for numerous analyses; (2) preserves reducing redox conditions; (3) prevents ultra-trace THg and MeHg contamination; (4) avoids inadvertent sampling of surface water while collecting the surficial soil pore water sample; (5) does not require the use of a glove box and centrifuge; and (6) is “technician-friendly”.


<table>
<thead>
<tr>
<th>STA – 2</th>
<th>Matrix</th>
<th>Sites</th>
<th>Frequency</th>
<th>Types</th>
<th>Reps</th>
<th>QC</th>
<th>Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rain</td>
<td>1</td>
<td>Weekly (52)</td>
<td>1 (bulk integrated)</td>
<td>1</td>
<td></td>
<td>U-THg(^{(3)})</td>
</tr>
<tr>
<td></td>
<td>STA-2 Inflow</td>
<td>1</td>
<td>Biweekly (26)</td>
<td>1 (grab)</td>
<td>1</td>
<td></td>
<td>U-THg(^{(1)}), U-MeHg(^{(1)})</td>
</tr>
<tr>
<td></td>
<td>STA-2 Inflow</td>
<td>1</td>
<td>Biweekly (26)</td>
<td>1 (grab)</td>
<td>1</td>
<td></td>
<td>TSS, DOC</td>
</tr>
<tr>
<td></td>
<td>Cell Outflow</td>
<td>3</td>
<td>Biweekly (26)</td>
<td>1 (grab)</td>
<td>1</td>
<td></td>
<td>U-THg(^{(1)}), U-MeHg(^{(1)})</td>
</tr>
<tr>
<td></td>
<td>Cell Outflow</td>
<td>3</td>
<td>Biweekly (26)</td>
<td>1 (grab)</td>
<td>1</td>
<td></td>
<td>TSS, DOC, F-SO(_4^–) Hydrolab</td>
</tr>
<tr>
<td>(1)</td>
<td>STA-2 Inflow</td>
<td>1</td>
<td>At start-up and every other biweek thereafter (13)</td>
<td>1 (grab)</td>
<td>1</td>
<td></td>
<td>F-THg(^{(1)}), F-MeHg(^{(1)})</td>
</tr>
<tr>
<td></td>
<td>STA-2 Inflow</td>
<td>1</td>
<td>At start-up and every other biweek thereafter (13)</td>
<td>1 (grab)</td>
<td>1</td>
<td></td>
<td>F-THg(^{(1)}), F-MeHg(^{(1)})</td>
</tr>
<tr>
<td></td>
<td>Cell Outflow</td>
<td>1</td>
<td>At start-up and every other biweek thereafter (13)</td>
<td>1 (grab)</td>
<td>1</td>
<td></td>
<td>F-THg(^{(1)}), F-MeHg(^{(1)})</td>
</tr>
<tr>
<td>(2)</td>
<td>Interior Water</td>
<td>9</td>
<td>At start-up and every other biweek thereafter (13)</td>
<td>1 (grab)</td>
<td>1</td>
<td></td>
<td>F-THg(^{(1)}), F-MeHg(^{(1)})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TSS, DOC, F-SO(_4^–), F-Cl F-Fe, F-Mn, F-Ca, F-Mg nutrients, Chl a, Alk, Hydrolab</td>
</tr>
<tr>
<td>(3)</td>
<td>Interior Water</td>
<td>3</td>
<td>At start-up and every other biweek thereafter (13)</td>
<td>1 (grab)</td>
<td>1</td>
<td></td>
<td>U-THg(^{(1)}), U-MeHg(^{(1)})</td>
</tr>
<tr>
<td></td>
<td>Water-Special</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F-THg(^{(3)}), F-MeHg(^{(3)})</td>
</tr>
<tr>
<td>(4)</td>
<td>Pore Water</td>
<td>1</td>
<td>6 (0, 14, 28, 56, 112, 224 days)</td>
<td>1 stratum</td>
<td>3</td>
<td></td>
<td>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.</td>
</tr>
<tr>
<td></td>
<td>Pore Water Tier 2B</td>
<td>9</td>
<td>13</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>E1 E2 BB</td>
</tr>
<tr>
<td>------------------------------</td>
<td>--------------------</td>
<td>---</td>
<td>----</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>----------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(w/i 1 week start-up and every other biweekly period thereafter)</td>
<td>(0-5 cm by “squeezer” or equivalent)</td>
<td>1 stratum</td>
<td></td>
<td>F-THg$^{(3)}$, F-MeHg$^{(3)}$, DOC, F-SO$_4^{2-}$, F-Cl, F-S$^{(2)}$, F-Fe, Fe$^{2+}$(field), F-Mn, F-Ca, F-Mg, Alk, pH, nutrients, Redox(field), Cond., Prep</td>
</tr>
<tr>
<td>Soils Tier 1 (Baseline)</td>
<td></td>
<td>9</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(dry season; pre-reflood)</td>
<td>(4-cm surface cores)</td>
<td>5</td>
<td>0</td>
<td>THg$^{(4)}$, MeHg$^{(4)}$, TS, TFe, TMn, TCa, TMg, TP, TN, AVS, Ash, Bulk Density Moisture, Prep.</td>
</tr>
<tr>
<td>(1) Ship to DEP; other analytes to District Lab or designated alternate</td>
<td>Soils Tier 2A</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0, 14, 28, 56, 112, 224 days)</td>
<td>(4-cm surface cores)</td>
<td>3 in-tact (1 stratum)</td>
<td>0</td>
<td>THg$^{(4)}$, MeHg$^{(4)}$, TS, TFe, TMn, TCa, TMg, TP, TN, AVS, Ash, Bulk Density Moisture</td>
</tr>
<tr>
<td>(2) Ship to DB; other analytes to District Lab or designated alternate</td>
<td>Soils Tier 2B</td>
<td>9</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(start-up and quarterly thereafter)</td>
<td>(4-cm surface cores)</td>
<td>5</td>
<td>0</td>
<td>THg$^{(4)}$, MeHg$^{(4)}$, TS, TFe, TMn, TCa, TMg, TP, TN, AVS, Ash, Bulk Density Moisture</td>
</tr>
<tr>
<td>(3) ship to FGS; others to District Lab or designated alternate</td>
<td>Plants</td>
<td>9</td>
<td>2</td>
<td>6 species rooted; 2 floating; 2 periphyton</td>
<td>1</td>
<td>0</td>
<td>THg$^{(4)}$, MeHg$^{(4)}$, Ash, Moisture</td>
</tr>
<tr>
<td>(4) ship to FGS; others to DB Labs or designated alternate</td>
<td>Mosquito-Fish (75-250 individual fish)</td>
<td>9</td>
<td>13</td>
<td>1</td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>
The District conveyed these findings, conclusions, and recommendations to DEP’s Thomas Atkeson, the DEP Mercury Coordinator, and Frank Nearhoof, the DEP Permit Coordinator, in August 2002 at the time of the reflooding of STA-2 Cell 1. DEP agreed with the District’s assessment of the situation and the proposed approach to rectify it. Accordingly, a new first tier was added to the expanded study design to accommodate the acquisition of the required pore water sampling technology, training, and field-validation via expert assistance prior to initiation of pore water sampling as part of the mercury special studies monitoring program in STA-2. The Plan submitted under Task 1 of the C-11900-A03 SOW has been modified to reflect the addition of a new Tier 1 study element and resubmitted to Don Axelrad, DEP’s Project Manager. The acquisition of the required expert assistance is under way.

Inflow, outflow, and interior surface water samples were collected at start-up and every other biweekly period thereafter (every 28 days). The enhanced monthly mosquitofish collection required by the modified permit was reinstituted at C1A in July 2002 when water levels began to rise again following intensive wet season rains. Follow-up quarterly monitoring of mosquitofish and soils began in August 2002 at a new set of interior monitoring sites in Cell 1 (C1AA, C1BB, and C1CC vs C1A, C1B, and C1C), and at the original monitoring sites in Cell 2 (C2A, C2B, and C2C) and Cell 3 (C3A, C3B, and C3C). Semi-annual plant sample collection was initiated in September 2002.

The Statement of Work (SOW) for the Work Order for outside contractor support to carry out the expanded mercury monitoring at STA-2 was issued to Foster-Wheeler in October 2002. That WO SOW is Attachment 1. Training of F-W personnel began immediately thereafter. The first water samples were collected by F-W personnel with District oversight the second week in November 2002 and the first soil samples were collected by them with District oversight the following week. The second set of plant samples is not scheduled for collection until February-March 2003.

**Results and Discussion**

The surface water, soils, and vegetation data collected this quarter, which were available as of January 30, 2003, are included as Attachment 1. The results of treatment cell inflow and outflow monitoring of surface water for unfiltered THg and MeHg are summarized in Figures 7 and 8. The interior and downstream mosquitofish THg results are depicted in Figures 9 and 10, while those for sunfish species are depicted in Figures 11 and 12. Unfiltered THg and MeHg concentrations collected from the expanded inflow and outflow monitoring sites from April 2002 through December 2002 are illustrated in Figures 13 and 14. Filtered THg and MeHg concentrations collected from the expanded interior monitoring sites in August, September, October, November, and December 2002 are illustrated in Figures 15 and 16.

As summarized in the Status Update section, the anticipated first-flush event after rewetting following an extended period of dryout resulted in excess MeHg production, which manifested itself in a peak concentration of 20 ng/L in unfiltered and 20 ng/L in filtered surface water at site C1CC on August 22, 2002. These unprecedented results
were confirmed by the FDEP laboratory. The peak then passed through the Cell 1 outflow at G-330A four weeks later, and thence the common outflow at the G-335 Pump Station. As anticipated, the next monthly sampling event revealed substantially lower concentrations of THg and MeHg relative to peak levels at C1CC, and this trend has continued through the remainder of the last quarter. Further evidence that the anomalous mercury event has dissipated from STA-2 Cell 1 can be found in the fact that there was no statistically significant difference (one-tail t test; 95th percentile confidence level) between the average concentration of THg or MeHg at the representative interior monitoring site for the last three biweekly sampling events in 2002 and the corresponding long-term average for the period of record for the inflow at G-328B.

The peak in the soil MeHg concentrations appear to follow this same trajectory, albeit only approximately. There are four potential reasons for this: (1) the external contribution to the Hg(II) concentration in surface water from wet and dry atmospheric deposition and internal contribution from the first-flush release of Hg(II) from oxidized soils will be further diluted by the continuing inflow, which was running 2 ng/L and 0.62 ng/L THg as of the 8/22/02 sampling event, reducing the driving force for excess MeHg production; (2) the excess MeHg produced from the internal and external sources of excess Hg(II) will also be diluted by the continuing inflow water, which was running 0.12 and 0.13 ng/L MeHg as of the 8/22/02 sampling event; (3) the first-flush pool of excess Hg(II) will be substantially depleted; and (4) the rapid regrowth of phytoplankton and periphyton standing crop will rapidly sorb the excess Hg(II) and MeHg, storing it temporarily until the biomass begins to decompose.

Whatever the cause, the effect of excess MeHg production is not limited to anomalously high concentrations of MeHg in the water column. As has occurred in the preceding two anomalous mercury events in Cell 1, the initial pulse of excess of MeHg production is being transferred to mosquitofish, either directly or via autotrophic or saprotrophic food chains. The results to date for mosquitofish THg in STA-2 Cells 1, 2, and 3 are plotted in Figure 17. Sunfish and bass are generally placed at trophic levels 3 and 4, respectively, while mosquitofish, an opportunistic omnivore, is often placed between trophic levels 2 and 3. In the interior Everglades, the biomagnification factor (BMF) between mosquitofish and sunfish is generally between 2 and 3, as is the BMF between sunfish and bass (see annual compliance reports and special reports on STA-2 follow-up mercury studies in the Everglades Consolidated Report 2002 and 2003). However, in STA-2 Cell 1, the sunfish BMF in 2001 is less than 1. This likely has two causes: (1) interruption of the development of the Cell 1 food chains via drawdown and dryout in the winters of 2000-2001 and 2001-2002 limit sunfish foraging to lower trophic levels; and (2) the interior sunfish and bass present in Cell 1 at the time of sampling in September 2000, 2001, and 2002 probably entered via the inflow and had not yet reached steady state with their new environment. Nevertheless, the higher average concentrations of THg as MeHg in sunfish and bass from Cell 1 relative to Cells 2 and 3 reflect the excess bioaccumulation that took place during the average period of contact with the much more contaminated food chain.
By contrast to preceding years, having raised the outflow weirs in Cell 1, we anticipate being able to maintain deeper average water levels for longer periods of time, which could allow the development of longer food chains and indigenous sunfish and largemouth bass populations. If the excess MeHg pulse is not sustained, as now appears to be the case, individual mosquitofish are likely to bioaccumulate this excess MeHg pulse in the first 90-180 days and then begin to dilute this MeHg pulse through growth, while the population will clear the pulse via the die-off of highly contaminated older fish over the following 90-180 days thereafter. Although individual sunfish and largemouth bass will be slower to bioaccumulate the excess MeHg from the first-flush pulse and will dilute some of it through growth, these individuals will be slower to clear the pulse from their bodies, because they have much longer MeHg half-lives than does the mosquitofish (Norstrom et al., 1976; Eisler, 1987). Moreover, the populations will be slower to clear the excess MeHg residue from this pulse, because both species are longer-lived than mosquitofish (Loftus et al., 1998). If the “first-flush” pulse of excess MeHg production is sustained or the “aftershock” pulses are substantial, as was the case following the first anomalous mercury event in Cell 1, the build-up of high MeHg concentrations in mosquitofish and then sunfish species or equivalent trophic level 3 (T3) fish species could represent an unacceptable risk of toxic effects from MeHg exposure to sensitive members of fish-eating wildlife subpopulations feeding in STA-2 Cell 1 preferentially.

However, the prediction of the post-rewetting biogeochemical trajectory of Cell 1 based on the previous experiences is complicated by several factors. First, the flow rate and depth of surface water in Cell 1 affords some dilution of the internally produced MeHg. While a detailed water budget is not yet available for STA-2, based on the significant differences in MeHg concentrations among the treatment cells, it can be inferred that the Cell 1 outflow is being diluted by at least three-to-one at G-335 during routine operation. Further, raising the outflow culvert weir crests by one-half foot has allowed the District to maintain deeper water levels for longer periods of time to preclude surficial soil oxidation, while providing additional dilution of each rainfall event. The stages of Cells 1, 2, and 3 for the period of operation are depicted in Figure 18. Second, the depths and THg concentrations in rainfall received in the summer and fall of 2002 are different than the summer and fall of 2000 and 2001. The rain depth for the period of STA-2 operation is displayed in Figure 18, while the rainfall THg concentrations for September 2002 are summarized in Figure 19A and October, November, and December 2002 in Figure 19B.

Third, the fractions of cell surface area covered by open water, dead and decaying woody plants and small trees, emergent, submergent, and floating wetlands plants, and periphyton mats have changed over time, as has their potentials to facilitate MeHg production by increasing microbial activity or to store excess MeHg in standing crop biomass. Quantification of present-day coverages in Cell 1 awaits the issuance of the aerial photography contract. However, satellite imagery may also be useful in this regard. Fourth, with some subsequent release of THg and MeHg from decomposing plants back to the overlying water and underlying surficial sediments, this could feed substantial “aftershock” pulses through the fall, even in the absence of rainfall or inflow, as was observed during the first anomalous mercury event in the summer, fall, and winter of 2000-2001.
Fifth, the build-up of soil sulfate in response to the loads delivered in July through October 2000 and August through November 2001 could have increased the quantity of labile sulfate mobilized following rewetting, resulting in an increase in the integrated mass of excess MeHg produced in the “first-flush” pulse. The change in surficial soil (0-4 cm) THg and the corresponding build-up of soil MeHg are depicted in Figures 20 and 21, respectively. Across Cells 1, 2, and 3, the soil MeHg concentration trajectory generally follows that in the overlying water column, albeit not exactly. Although soil sulfate was not measured directly, soil total sulfur (TS) and acid volatile sulfide (AVS) were, along with total nitrogen (TN), total phosphorus (TP), calcium (TCa), magnesium (TMg), iron (TFe), manganese (TMn), which are plotted for the May ’02 and August ’02 sampling events in Figures 22 and 23, respectively, as well as bulk density, percent ash, and percent moisture content. Those results are summarized in Tables 2 and 3 for the May ’02 and August ’02 sampling events, respectively. Sixth, based on the results of the joint USGS/SFWMD post-burn study, the depletion of the excess sulfate pool and the build-up of the pore water sulfide pool generally presage a reduction in the rate of MeHg production (see draft Appendix 2B-1 in this year’s ECR 2003), but, based on the results of the dry/wet laboratory microcosm study (C-13860), STA-2 Cell 1 soils are quicker to produce excess MeHg, slower to deplete the pool of first-flush pore water sulfate, and slower to build up pore water sulfide relative to WCA-3A-15, the Everglades “hot spot” site (Gilmour et al., 2002). This is likely to increase the duration of the “first-flush” pulse of excess MeHg production.
Table 2. Preflooding baseline soil (0-4 cm cores) chemistry data from May ‘02 sampling event

<table>
<thead>
<tr>
<th></th>
<th>C1AA</th>
<th>C1BB</th>
<th>C1CC</th>
<th>C2A</th>
<th>C2B</th>
<th>C2C</th>
<th>C3A</th>
<th>C3B</th>
<th>C3C</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Moisture</td>
<td>77.66</td>
<td>78.55</td>
<td>69.21</td>
<td>76.59</td>
<td>75.26</td>
<td>77.54</td>
<td>67.25</td>
<td>69.86</td>
<td>67.3</td>
</tr>
<tr>
<td>% Ash</td>
<td>11.8</td>
<td>12.2</td>
<td>10.5</td>
<td>14.2</td>
<td>12</td>
<td>13</td>
<td>13.2</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>0.104</td>
<td>0.158</td>
<td>0.157</td>
<td>0.218</td>
<td>0.213</td>
<td>0.236</td>
<td>0.22</td>
<td>0.215</td>
<td>0.318</td>
</tr>
<tr>
<td>TSULFUR</td>
<td>9200</td>
<td>8200</td>
<td>6100</td>
<td>4100</td>
<td>3700</td>
<td>3800</td>
<td>6000</td>
<td>5500</td>
<td>3000</td>
</tr>
<tr>
<td>TFE</td>
<td>2200</td>
<td>1200</td>
<td>1500</td>
<td>2300</td>
<td>2200</td>
<td>2700</td>
<td>2300</td>
<td>2600</td>
<td>3200</td>
</tr>
<tr>
<td>TMN</td>
<td>89</td>
<td>130</td>
<td>80</td>
<td>160</td>
<td>200</td>
<td>190</td>
<td>220</td>
<td>55</td>
<td>140</td>
</tr>
<tr>
<td>TMG</td>
<td>4100</td>
<td>4100</td>
<td>4000</td>
<td>4100</td>
<td>3500</td>
<td>4100</td>
<td>5800</td>
<td>6500</td>
<td>4000</td>
</tr>
<tr>
<td>TCA</td>
<td>33000</td>
<td>30000</td>
<td>30000</td>
<td>47000</td>
<td>43000</td>
<td>37000</td>
<td>35000</td>
<td>37000</td>
<td>43000</td>
</tr>
<tr>
<td>TP</td>
<td>606</td>
<td>432</td>
<td>452</td>
<td>496</td>
<td>634</td>
<td>496</td>
<td>518</td>
<td>366</td>
<td>564</td>
</tr>
<tr>
<td>TN</td>
<td>33000</td>
<td>32500</td>
<td>32600</td>
<td>30500</td>
<td>31900</td>
<td>30000</td>
<td>27800</td>
<td>35300</td>
<td>27300</td>
</tr>
<tr>
<td>AVS</td>
<td>150</td>
<td>213</td>
<td>19.5</td>
<td>40.9</td>
<td>34.1</td>
<td>37.4</td>
<td>43.8</td>
<td>107</td>
<td>54.7</td>
</tr>
</tbody>
</table>

Table 3. Reflooding soil (0-4 cm cores) chemistry from August ’02 sampling event

<table>
<thead>
<tr>
<th></th>
<th>TP</th>
<th>TN</th>
<th>TMg</th>
<th>TCa</th>
<th>TS</th>
<th>TMn</th>
<th>AVS</th>
<th>TFe</th>
<th>BD</th>
<th>ASH</th>
<th>MOISTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1AA</td>
<td>408</td>
<td>35400</td>
<td>3400</td>
<td>1200</td>
<td>0.72</td>
<td>73</td>
<td>115</td>
<td>1800</td>
<td>0.16</td>
<td>13.3</td>
<td>81.19</td>
</tr>
<tr>
<td>C1BB</td>
<td>378</td>
<td>30900</td>
<td>3500</td>
<td>1100</td>
<td>0.49</td>
<td>82</td>
<td>165</td>
<td>830</td>
<td>0.12</td>
<td>10.7</td>
<td>86.21</td>
</tr>
<tr>
<td>C1CC</td>
<td>414</td>
<td>30100</td>
<td>4000</td>
<td>1200</td>
<td>0.4</td>
<td>110</td>
<td>152</td>
<td>1500</td>
<td>0.19</td>
<td>12.2</td>
<td>79.52</td>
</tr>
<tr>
<td>C2A</td>
<td>690</td>
<td>31700</td>
<td>3800</td>
<td>1600</td>
<td>0.38</td>
<td>340</td>
<td>84</td>
<td>4100</td>
<td>0.19</td>
<td>20.3</td>
<td>78.51</td>
</tr>
<tr>
<td>C2B</td>
<td>478</td>
<td>29200</td>
<td>3500</td>
<td>1700</td>
<td>0.31</td>
<td>240</td>
<td>34</td>
<td>2100</td>
<td>0.2</td>
<td>16</td>
<td>78.61</td>
</tr>
<tr>
<td>C2C</td>
<td>392</td>
<td>23300</td>
<td>3900</td>
<td>1400</td>
<td>0.33</td>
<td>120</td>
<td>106</td>
<td>2400</td>
<td>0.14</td>
<td>28.9</td>
<td>74.13</td>
</tr>
<tr>
<td>C3A</td>
<td>366</td>
<td>27200</td>
<td>6700</td>
<td>2000</td>
<td>0.42</td>
<td>82</td>
<td>194</td>
<td>1700</td>
<td>0.17</td>
<td>18.8</td>
<td>74.7</td>
</tr>
<tr>
<td>C3B</td>
<td>420</td>
<td>26400</td>
<td>6200</td>
<td>2000</td>
<td>0.33</td>
<td>72</td>
<td>182</td>
<td>2300</td>
<td>0.15</td>
<td>18</td>
<td>79.66</td>
</tr>
<tr>
<td>C3C</td>
<td>558</td>
<td>26600</td>
<td>6000</td>
<td>1800</td>
<td>0.3</td>
<td>88</td>
<td>186</td>
<td>2500</td>
<td>0.26</td>
<td>18.5</td>
<td>68.99</td>
</tr>
</tbody>
</table>

There is still a great deal of uncertainty as to why this might be the case. The results of correlation analyses between soil baseline MeHg vs THg for the May ’02 and August ’02 sampling events are plotted in Figures 24 and 25, respectively. The correlation analysis results for the soil MeHg vs Total Sulfur in May and August ’02; vs Total Calcium in May and August ’02; Total Iron in May and August ’02; and vs Total Phosphorus in May and August ’02, are plotted in Figures 26 and 27, 28 and 29, and 30 and 31, respectively. The relationship between the fraction MeHg and acid volatile sulfide (AVS) as a surrogate for pore water sulfide is weak in May ’02 (Figure 32) and weaker still in August ’02 (Figure 33), perhaps because of the high variability in the AVS data, as observed in triplicate samples collected at Site C (Figure 34). This correlation is
positive, not negative, as was observed by Gilmour et al. (1999) in Everglades soil across a wide range of habitats in the period 1995-1998.

However, there appears to be a general relationship between relatively higher high soil total mercury and sulfur and lower soil iron in Cell 1 vs. low soil total mercury and sulfur and high soil iron in Cell 3 (Table 2 and Table 3). This soil total mercury pattern may be a consequence of the farming of Cell 3 soils. The act of cultivating the peat may facilitate the production of elemental mercury, Hg(0), from Hg(II) caused by the action of sunlight on soil, with subsequent evasion as Hg(0) gas, as has been observed in the EAA (S. Lindberg, ORNL, personal communication, 1996) and elsewhere. Iron is a common additive in fertilizer and may have been added to Cell 3 soils. The low iron concentration in Cell 1 soils could limit the formation of free sulfide in soil pore water by forming poorly crystallized iron sulfide (FeS) and associated polysulfides (FexSy) (Ravichadran et al., 1998; Jay et al., 2000). High pore water sulfide concentrations in the Everglades are generally associated with inhibition of methylmercury production, while intermediate concentrations are generally associated with maximum methylmercury production (Gilmour et al, 1998; Gilmour et al., 1999; Orem et al., 2002; Fink, 2002, 2003). The delay in the formation of pore water sulfide was observed in STA-2 Cell 1 Site C soils relative to WCA-3A-15 soils where the fish concentration “hot spot” has occurred historically (Gilmour et al., 2002). Unfortunately, as noted above, the collection of a valid pore water sample by District staff or the contractors trained by District staff could not be carried out without the required technology transfer.

Conversely, at higher soil iron concentrations, more of the inorganic mercury, Hg(II)\(^{+2}\), could be stored in oxic soils and released from binding with iron oxyhydroxides in soil upon the return of anaerobic conditions following rewetting. There may be some evidence of the release of soil Hg(II)\(^{+2}\) for subsequent excess methylmercury production from Cell 3 soils in August 2002 during the first substantial summer rainfall, but this was a localized, short-lived effect, as opposed to the response of Cell 1 soils. However, Cell 3 soils have not been allowed to dry out as completely, as have those in Cell 1. With the raising of the outflow culverts in Cell 1, the frequency of recurrence of dryout and rewetting in Cell 1 should be reduced substantially.

The soils data collected between August 14 and August 28, 2002, within a few weeks of reflooding tell a somewhat different story from the preflooding baseline soils data collected in May ’02. The correlation between soil THg and MeHg concentrations among the nine interior sites has weakened substantially (\(R^2 = 0.94\) to 0.69), but the correlation between MeHg with soil moisture content has increased (\(R^2 = 0.041\) to 0.57). This suggests that the pre-flooding, dry-season soils were producing MeHg primarily from the surficial soil reservoir of bioavailable inorganic mercury (which may have been continuously replenished by dry atmospheric deposition), while the post-flooding, wet-season soils were also producing MeHg from a source of inorganic mercury less strongly linked to the surficial soil pool (i.e., inflow and/or rainfall). In addition, the positive correlation with soil sulfur has decreased substantially (\(R^2 = 0.51\) to 0.21), perhaps because the new supply of labile sulfate from inflow water is more readily bioavailable to the sulfate-reducing bacteria involved in MeHg production than the dry soil sulfate pool.
The inverse correlation with soil total iron has also weakened substantially ($R^2 = 0.86$ to 0.44), perhaps for the same reason as for soil sulfur, while the positive correlation with AVS, which was weak for the May '02 sampling event, is virtually non-existent for the Aug '02 sampling event. This trend between soil MeHg and AVS could continue, with a shift to a weakly, then a moderately, and then a strongly inverse relationship with AVS as the pore water sulfide builds up to concentrations capable of inhibiting MeHg production under the conditions of soil chemistry encountered (Gilmour et al., 1998; 1999; Benoit et al., 1999a,b; 2001). It is also possible that inhibition is already occurring in STA-2 Cell 3 but stimulation is still occurring in STA-2 Cell 1. As more data become available, the data can be parsed by treatment cell to discriminate such differences with greater resolving power and confidence level. Interestingly, the inverse relationship between the soil MeHg concentration and soil TP, which has been observed elsewhere (e.g., WCA-2A transect: Fink, 2001, 2003), was virtually non-existent in May '02 ($R^2 = 0.07$), but increased to an $R^2$ of 0.49 in the August '02 sampling event with a distinctly negative slope. Perhaps this reflects the association between soil TP and aerobic and anaerobic soil microbe activity, including the sulfate-reducing bacteria involved in MeHg production. By comparison, the inverse correlation between soil MeHg concentration and soil total calcium concentration weakens only slightly ($R^2 = 0.68$ to 0.49). (Note: the limited number of data points available in May '02 (n = 7 to 9) and August '02 (n = 9) limit the confidence level for these inferences. As the number of data points increases, so will the power of the analysis to discriminate spatial and temporal trends and correlations between soil MeHg concentrations and potentially influential soil chemistry variables.)

Another, perhaps more plausible and compelling explanation for the weakening of the correlations between MeHg and soil total mercury, total sulfur or total iron with the onset of reflooding is the rapid transition from a system in which the MeHg production rate is slow to one that is fast relative to the rates of chemical equilibration in the surrounding soil microenvironment. If this latter explanation is the correct one, then, as the rate-limiting pool of sulfate, inorganic mercury, or short-chain organic carbon is depleted following rewetting and the rate of MeHg production decreases, the correlations between the soil MeHg concentration and these influential soil factors should begin to increase, albeit perhaps not to their preflooding, dry soil values. Correspondingly, the correlation with soil moisture content should decrease. While the November 2002 sample collection may be too soon to see this reversion, the February 2003 sampling should not be. By this same logic, the correlations between MeHg and these influential soil factors should again decrease with the onset of the wet season and the increase in the deposition flux of a fresh supply of inorganic mercury, which will translate into an increase in the rate of MeHg production in the surficial soil. Among other things, this suggests that the data should be pooled based on season when conducting the multivariate regression analysis.

Although the above discussion is suggestive, it is not yet known why Cell 1 soils behave so differently relative to the soils in Cells 2 and 3 of STA-2 or relative to Everglades “hot spot” soils at WCA-3A-15. The proposed Cell 1 mesocosm study should provide some of the answers. These results will be interpreted in the context of a more complete set of results for the expanded monitoring of THg, MeHg, and associated constituents in surface
water and soil. The mesocosm and monitoring data will be used to calibrate and validate a model of MeHg production and bioaccumulation in STA-2 Cell 1. The model will be used to evaluate the efficacy of various proposed short-term mitigative measures and long-term operational regimens for maximizing phosphorus removal while minimizing the magnitude, duration, and frequency of recurrence of excess MeHg production. The mesocosm and modeling studies are being carried out under separate initiatives.

**Recommendations**

The District is required to prepare a probabilistic ecological risk assessment (PERA) if the average concentrations of THg as MeHg in mosquitofish and sunfish exceed the respective upper 95th percentile concentration for the Everglades populations. The average mosquitofish concentration has already reached the ecological risk assessment trigger, but the sunfish collected in the discharge canal in October 2002 have not. The next scheduled sunfish sampling is in February 2003, and the processing and the analysis of the sunfish will be expedited to the extent practicable.

Based on the steep decline in the water column concentration of MeHg following the August 22, 2002, anomaly, and the accompanying decline in mosquitofish THg that began in November 2002, we recommend that Cell 1 should not be drawn down to eliminate the development of the food web there. Instead, we recommend that the pulse be allowed to build up and decline in the T2, T3, and T4 fish populations, while allowing the soil pore water chemistry to stabilize. During the remainder of the dry season, every effort will be made to keep Cell 1 wet to the extent permitted by available water.
References


Attachment 1. Data Printouts (Not supplied with review draft)
Figure 1. STA-2 geographic location in South Florida and aerial photograph.
Figure 2. STA-2 graphic representation with inflow and outflow structures.
Figure 3. STA-2 routine mercury monitoring sites for original permit compliance.
Figure 4. STA-2 start-up mercury monitoring sites for original permit compliance.
Figure 5. STA-2 start-up mercury monitoring sites for modified permit compliance.
Figure 6. STA-2 expanded mercury monitoring sites for STA-2 Special Mercury Studies (MOA).
Figure 7. Inflow and interior surface water THg results for modified permit compliance monitoring (Exhibit E).
Figure 8. Inflow and interior surface water MeHg results for modified permit compliance monitoring (Exhibit E).
**Figure 9.** Interior mosquitofish THg concentration results for modified permit compliance monitoring (Exhibit E).
Figure 10. Downstream mosquitofish THg concentration results for modified permit compliance monitoring (Exhibit E).
Figure 11. STA-2 sunfish THg monitoring results for modified permit compliance (Exhibit E).
Figure 12. Downstream sunfish THg concentration results for modified permit compliance monitoring at Sites N4 and Z4 (Exhibit E).
STA2 Total Mercury in Surface Water

Figure 13. Surface water THg monitoring results for the STA-2 Mercury Special Studies Project (Exhibit E).
Figure 14. Surface water MeHg monitoring results for the STA-2 Mercury Special Studies Project (Exhibit E).
Figure 15. Interior filtered THg monitoring results for the STA-2 Mercury Special Studies Project (Exhibit E).
Figure 16. Interior filtered MeHg monitoring results for the STA-2 Mercury Special Studies Project (Exhibit E).
Figure 17. Mosquitofish THg concentration monitoring results for the STA-2 Mercury Special Studies Project (MOA).
Figure 18. Average water depth within individual cells of STA-2 and average rainfall. Note, depth estimated from mean stage (G329B_T, G330A_H; G331E_T, G332_H; G33C_T, G334_H) minus average ground elevation (11.82, 10.33, 9.61) for Cells 1, 2, 3, respectively. Rainfall is average recorded at S6 and S7.
Figure 19A. Rain THg concentration monitoring results for the STA-2 Mercury Special Studies Project (MOA) (3rd quarter 2002).
Figure 19B. Rain THg concentration monitoring results for the STA-2 Mercury Special Studies Project (MOA) (4th quarter 2002).
Figure 20. Soil THg concentration (0-4 cm cores) baseline monitoring results for the STA-2 Mercury Special Studies Project (MOA).
Figure 21. Soil MeHg concentration (0-4 cm cores) baseline monitoring results for the STA-2 Mercury Special Studies Project (MOA).
Figure 22. Soil (0-4 cm cores) baseline monitoring results (May '02 sampling) for the STA-2 Mercury Special Studies Project (MOA).
Figure 23. Soil (0-4 cm cores) post-reflooding monitoring results (August ’02 sampling) for the STA-2 Mercury Special Studies Project (MOA).
Figure 24. Baseline soil core (0-4 cm: May 2002) correlation analysis results: MeHg Conc. (mg/Kg dry wt) vs THg Conc. (mg/Kg dry wt) for the STA-2 Mercury Special Studies Project (MOA).
Figure 25. Reflooding soil core (0-4 cm: Aug ‘02) correlation analysis results: MeHg Conc. (mg/Kg dry wt) vs THg Conc. (mg/Kg dry wt) for the STA-2 Mercury Special Studies Project (MOA).
Figure 26. Baseline soil core (0-4 cm: May '02) correlation analysis results: Total Sulfur Conc. vs MeHg Conc. for the STA-2 Mercury Special Studies Project (MOA).
Figure 27. Reflooding soil core (0-4 cm: Aug ‘02) correlation analysis results: Total Sulfur Conc. vs MeHg Conc. for the STA-2 Mercury Special Studies Project (MOA).
STA-2 Expanded Mercury Monitoring Soils Data
Correlation Analysis - May '02 Sampling

\[ y = -3 \times 10^{-7}x + 0.015 \]

\[ R^2 = 0.6815 \]

Figure 28. Baseline soil core (0-4 cm: May '02) correlation analysis results: MeHg Conc vs Total Calcium Conc. for the STA-2 Mercury Special Studies Project (MOA).
Figure 29. Reflooding soil core (0-4 cm: Aug ‘02) correlation analysis results: MeHg Conc vs Total Calcium Conc. for the STA-2 Mercury Special Studies Project (MOA).
Figure 30. Baseline soil core (0-4 cm: May 2002) correlation analysis results: MeHg Conc. (mg/Kg dry wt) vs Total phosphorus Conc. (mg/Kg dry wt) for the STA-2 Mercury Special Studies Project (MOA).
**Figure 31.** Reflooding soil core (0-4 cm: Aug ‘02) correlation analysis results: MeHg Conc. (mg/Kg dry wt) vs Total phosphorus Conc. (mg/Kg dry wt) for the STA-2 Mercury Special Studies Project (MOA).
Figure 32. Baseline soil core (0-4 cm: May ‘02) correlation analysis results: MeHg Conc. (mg/Kg dry wt) vs acid volatile sulfide (AVS) Conc. (mg/Kg dry wt) for the STA-2 Mercury Special Studies Project (MOA).
STA-2 Expanded Mercury Monitoring Soils Data
Correlation Analysis - Aug '02 Sampling

$y = 2085.5x + 127.97$
$R^2 = 0.0386$

Figure 33. Reflooding soil core (0-4 cm: Aug '02) correlation analysis results: MeHg Conc. (mg/Kg dry wt) vs acid volatile sulfide (AVS) Conc. (mg/Kg dry wt) for the STA-2 Mercury Special Studies Project (MOA).
Figure 34. Baseline soil core (0-4 cm: May 2002) comparison of replicate acid volatile sulfide (AVS) results at site C1C for the STA-2 Mercury Special Studies Project (MOA).
Executive Summary

STA-2 Cells 2 and 3 met their permit-mandated mercury start-up criteria in September and November 2000, respectively, while Cell 1 experienced anomalous mercury events in the fall of 2000 and 2001. Subsequently, the District applied for a permit modification that would allow flow-through operation to commence without meeting mercury start-up criteria. This was done in the belief that exposure to and/or export of MeHg could be reduced by the flowing water, because it would (1) dilute the fresh supply of inorganic mercury in atmospheric deposition, (2) dilute the MeHg produced internally, and (3) increase the sulfate load to the point that sulfide inhibition of MeHg production would occur. The application was submitted in July 2001 and, by letter dated August 9, 2001, FDEP notified the District that it had approved the modification.

The District commenced the expanded mercury monitoring program under the modified permit in August 2001. This was further expanded to include biweekly monitoring of the Cell 1, 2, and 3 outflows after the second anomalous MeHg event occurred in Cell 1 in October 2001. In anticipation that there would be insufficient water during the dry season to keep the water flowing through Cell 1, the District recommended that Cell 1 be dried out until the following wet season, and the Department concurred. This also provided the District with an opportunity to raise the Cell 1 outflow weirs so as to minimize the occurrence of dryouts in the future. Dyout was essentially complete by December 31, 2001, but some drainage continued through February 2002.

With the return of the wet season flows in August 2002, the District began a one-year special study to characterize the THg and MeHg concentration trajectories in water, soil, vegetation, and mosquitofish over time, to 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. To offset some of the costs of this extensive effort, Section 319 grant funds were redirected from evaluating the mercury removal efficiencies of Advanced Treatment Technologies in the ENR Project Test Cells to the this study (C-11900-A03). 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). The modified permit, the Section 319 Grant, and the MOA all require a quarterly report of study progress. This report is intended to fulfill those requirements.

The third anomalous mercury event, which was detected by this study and occurred on August 22, 2003, in STA-2 Cell 1, began to dissipate from the interior water column almost immediately, and this trend continued through the end of the second quarter of the study. The concentration of filtered MeHg declined at interior Site CC in STA-2 Cell 1
from 20 ng/L filtered MeHg to less than 2 ng/L in December 2002, then flattened out in January 2003, began to increase in February 2003, and peaked at about twice the January 2003 concentrations of THg and MeHg in March 2003. While outside the reporting period, the April 2003 concentrations of THg and MeHg declined to January 2003 levels, probably in response to increased water depths and flows and decreased rainfall. The unfiltered MeHg concentrations at the G-330A, the Cell 1 outflow, followed a similar trajectory to Site C1CC, albeit at higher concentrations, suggesting that turbidity in the declining water levels may have played a role. Mosquitofish THg concentrations tracked the water column MeHg concentrations. The build-up and decline of excess MeHg in water paralleled that in surficial soils in Cell 1, but not with the same spatial pattern. The rapid changes in soil chemistry that occurred following Cell 1 reflooding appear to be slowing and stabilizing, with the inverse correlation between acid volatile sulfide as a surrogate for pore water sulfide switching from weakly positive prior to reflooding to moderately negative in the last soil sampling campaign in April 2003.

The District is required to prepare an ecological risk assessment if, at any time, the average concentrations of THg in mosquitofish and sunfish exceed their respective upper 95th percentile concentrations calculated using monitoring data collected at 12 representative interior marsh sites beginning in 1998. The average mosquitofish THg concentration reached the ecological risk assessment trigger concentration of 120 ug/Kg wet wt at Site C1CC in August 2002, fell below the trigger level for the first time in April 2003, then crossed the threshold value again in May 2003. However, the sunfish collected in the discharge canal in October 2002 and the Cell 1 interior in March 2003 did not exceed the trigger level of 235 ug/Kg wet wt. While the sunfish THg concentration at downstream site WCA-2A-Z4 exceeded the risk reporting trigger, this was not the case for the average THg concentration in mosquitofish collected at both sites.

Based on the apparent trend toward stabilization of Cell 1 soil chemistry and a steady decline in the concentration of soil MeHg during the dry season, we recommend that Cell 1 continue to operate in flow-through mode during the wet season to facilitate the build-up of pore water sulfide to inhibitory levels while diluting any excess MeHg production.

**Introduction**

This is the third quarterly report on expanded mercury monitoring in Stormwater Treatment Area 2 (STA-2) under the modified permit FDEP No. 0126704-001-GL, Cooperative Agreement C-11900-A03, and the Memorandum of Agreement (MOA: C-13812) between the Florida Department of Environmental Protection (FDEP) and the South Florida Water Management District (SFWMD). **Attachment 1** contains a set of tables of the data collected to date. **Attachment 2** is the final Work Order (WO) Statement of Work (SOW) for the characterization of peat soil and the quantification of pore water volume via centrifugation. **Attachment 3** is the draft WO SOW for Tier 1 pore water collection using the modified sipper method. **Attachment 4** is the draft WO SOW for side-by-side validation of the modified sipper method with the soil core centrifugation method.
**Tier 1 Status Update**

All three tiers of the study are now under way. In this quarter, the District has made substantial progress in acquiring a viable field pore water sampling capability under Tier 1. **Attachment 2** is a final WO SOW with DB Laboratory in Gainesville to centrifuge STA-2 soil cores for the purpose of quantifying the range of extractable pore volume and the extraction time under oxygen-free conditions in a glove bag under a nitrogen atmosphere. **Attachment 3** is a draft WO SOW with TetraTech (formerly Foster-Wheeler) to implement the Tier 2 pore water sampling using a modified *in situ* “sipper” method originally developed by the U.S. Geological Survey in Middleton, WI. **Attachment 4** is a draft WO SOW with TetraTech (formerly Foster-Wheeler) to conduct a side-by-side field validation study of the modified pore water “sipper” method with the centrifugation method developed by Frontier Geosciences. Because we are now in the last quarter of what was planned as a one-year study, we are proposing to initiate the use of the modified “sipper” in July 2003, but increasing the frequency of sampling of pore water, surrounding soil, and surface water to every four weeks to ensure that a minimum of five samples are collected through the end of December 2003. This will ensure that there are sufficient data to evaluate the strength of correlation of pore water chemistry with soil and water chemistries and mosquitofish methylmercury bioaccumulation within as well as between STA-2 treatment cells. The side-by-side validation study will likely occur in the September-November 2003 timeframe. FDEP approval of this modified plan and schedule is requested.

**Results**

The surface water, soils, and vegetation data collected this quarter, which were available as of May 31, 2003, are included as **Attachment 1**. The results of treatment cell inflow and Cell 1 interior biweekly monitoring of surface water for unfiltered THg and MeHg are summarized in **Figures 7** and **8**. The inflow and interior mosquitofish THg results are depicted in **Figure 9**. The inflow, outflow, and downstream concentrations of THg in mosquitofish and sunfish are depicted in **Figures 10** and **11**, respectively. Although not required to be collected by either the modified permit conditions or the Section 319 Grant Work Plan, the largemouth bass data are presented in **Table 1**. **Figures 12** and **13** illustrate the concentrations of unfiltered THg and MeHg in water samples collected from the expanded inflow and outflow monitoring sites from April 2002 through March 2003. Filtered THg and MeHg concentrations collected from the expanded interior monitoring sites through April 30, 2003, are displayed in **Figures 14** and **15**, while **Figure 16** summarizes the mosquitofish THg concentrations. The stages of Cells 1, 2, and 3 for the period of operation are depicted in **Figure 17**, along with the rain depth for the period of STA-2 operation. The rainfall THg concentrations from September 2002 through March 2003 from the rainfall collector at STA-2 (FL99) are summarized in **Figure 18**, along with data from the Loxahatchee Refuge site (FL34) at the junction of SR-12 and I-80 and the Andytown site (FL07) at the junction of I-75 and US-27. The MeHg concentrations in the top 4 cm of soil at Sites AA, BB, and CC in Cell 1 are displayed in **Figure 19**. **Figure 20** summarizes the univariate Pearson correlation coefficient values between soil MeHg concentration and other soil chemistry parameters for each of the five soil
sampling campaigns completed to date, while Figure 21 refocuses on the correlation between the MeHg/THg fraction and other soil parameters for all five soil campaigns broken out by treatment cell. Figures 22A and 22B illustrate the magnitudes of the THg and MeHg bioconcentration factors (BCFs) for cattail and periphyton, respectively, as the ratio of wet tissue concentrations to filtered water concentration in samples collected from the same site and time period. Table 2 reproduces the Pearson correlation coefficients of the fraction MeHg vs soil constituent concentration for all nine sampling sites and (1) the five sampling campaigns; (2) all the post-flood campaigns, and (3)(a)-(e) each of the campaigns individually.

**Compliance Discussion**

Exhibit E requires the District to file an expedited risk assessment report to the Department if the average THg concentrations in mosquitofish and sunfish collected at the STA-2 Cell 1 interior or downstream monitoring sites exceed their respective 95th percentile upper confidence level concentrations in the Everglades for the period of record. The expanded monitoring requires monitoring of THg in mosquitofish monthly at a representative, centrally located site interior to Cell 1 (i.e., Site C1CC) and quarterly at downstream sites WCA-2A-N4 and WCA-2A-Z4 and in sunfish collected semi-annually at a representative, centrally located interior site in Cell 1 (i.e., C1X) and annually at sites N4 and Z4. For the data collected through October 2002, those mosquitofish and sunfish triggers are:

Grandmean of THg in downstream mosquitofish for POR (1998-02) ± 95%CI: 102 ± 18 ug/Kg wet wt (n = 64), so the 95th percentile upper bound mosquitofish THg concentration is 120 ug/Kg wet wt.

Grandmean of site means of THg in downstream sunfish for POR (1998-02) ± 95%CI: 195 ± 40 ug/Kg wet wt (n = 57), so the sunfish 95th percentile upper bound THg concentration is 235 ug/Kg wet wt.

Although not required in Exhibit E as an expedited risk reporting trigger, for comparison purposes the corresponding largemouth bass values standardized to age class 3 years is:

Grandmean of EHg3 calculated for downstream largemouth bass caught over the POR (1998-02) +/- 95%CI: 591 ± 116 (n = 32), so the largemouth bass 95th percentile upper bound THg concentration is 707 ug/Kg wet wt.

Following issuance of the modified permit in August 2002, at interior Site C1CC only the April 2003 mosquitofish did not exceed the trigger value. Although outside the reporting period, the average THg concentration in mosquitofish collected from this site again exceeded the trigger value in May 2002. Interestingly, for mosquitofish collected in the outflow canal just upstream of the pump station, only the October 2002 fish exceeded the trigger value, suggesting that, as with the water, the mosquitofish population discharged from Cell 1 is mixed with the populations discharged from Cells 2 and 3, “diluting” the average THg concentration in the Cell 1 mosquitofish population with the combined
populations in the discharge collection canal. At site N4, in April 2003 the concentration of THg in mosquitofish exceeded the trigger value (163 vs 120 ug/Kg wet wt), but at site Z4 the trigger value has never been exceeded, and the average concentration of THg in mosquitofish collected at both sites in April 2003 was below the reporting threshold.

After August 2002, for sunfish collected semi-annually at interior Site C1X, the THg concentration approached but did not exceed the trigger value in April 2003 (214 vs 235 ug/Kg wet wt). Sunfish collected annually from the discharge canal in October 2002 were well below the reporting threshold at 120 ug/Kg wet wt. No sunfish could be collected annually in October 2002 at N4, despite a documented good faith effort, because of the degraded conditions of habitat quantity and quality and water quality there that preceded the construction and operation of STA-2 (T. Lange, FGFWFC, personal communication). At Z4, the average concentration of THg in sunfish collected in October 2002 exceeded the reporting trigger value (272 vs 235 ug/Kg wet wt). The October 2002 value is more than 2.5 times that of October 2001. However, as noted above, the corresponding average mosquitofish THg concentrations at site Z4 have been below the trigger value for the period of record. This suggests that the food chain structure at these two sites is very different, consistent with observed differences in habitat quantity and quality and water quality.

Although the largemouth bass data are not used to trigger expedited risk reporting, it is important to note that the EHg3 for LMB at G335 was 1169 ± 233 in 2002 or more than twice the advisory threshold of 0.5 ppm. In addition, the unadjusted average outflow bass THg concentration was more than twice the concentration of the inflow bass. THg concentrations in bass from the discharge canal did not differ significantly between 2001 and 2002 (ANCOVA, df = 1, 37; F = 0.01, P = 0.936). (Note: G335 was the only STA-2 site in 2001 for which the collected bass had an age distribution suitable for establishing an age-concentration relationship, i.e., where an EHg3 was calculated and ANCOVA was run in 2002).

**Recommendations**

Based on the apparent trend toward stabilization of Cell 1 soil chemistry and the steady decline in the concentration of soil MeHg during the dry season, we recommend that Cell 1 continue to operate in flow-through mode during the wet season to facilitate the build-up of pore water sulfide to inhibitory levels while diluting incoming rainfall Hg(II)²⁺ and any excess MeHg production.
Table 1. Descriptive statistics for THg concentrations in largemouth bass collected at the inflow, interior, and outflow sites at STA-2

<table>
<thead>
<tr>
<th>Location</th>
<th>2002 EHg3 LMB THg (ug/Kg wet wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G328B</td>
<td>509 ±184*</td>
</tr>
<tr>
<td>STA2C1A</td>
<td>661 ±196</td>
</tr>
<tr>
<td>STA2C2A</td>
<td>384 ±106*</td>
</tr>
<tr>
<td>STA2C3A</td>
<td>247 ±117*</td>
</tr>
<tr>
<td>G335</td>
<td>1169 ±233</td>
</tr>
<tr>
<td>Z4</td>
<td>NA</td>
</tr>
<tr>
<td>N4</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 2. Pearson Correlation Coefficients of the Ratio of the Soil MeHg Concentration to Soil THg Concentration vs Soil Constituent Concentrations

<table>
<thead>
<tr>
<th></th>
<th>TP</th>
<th>TN</th>
<th>TCA</th>
<th>TS</th>
<th>AVS</th>
<th>TFE</th>
<th>TMN</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALL WET</td>
<td>-0.29</td>
<td>0.27</td>
<td>-0.38</td>
<td>0.00</td>
<td>-0.20</td>
<td>-0.41</td>
<td>-0.21</td>
</tr>
<tr>
<td>Pre-Flood Baseline May-02</td>
<td>-0.14</td>
<td>0.31</td>
<td>-0.86</td>
<td>0.80</td>
<td>0.49</td>
<td>-0.88</td>
<td>-0.24</td>
</tr>
<tr>
<td>Aug-02</td>
<td>-0.37</td>
<td>0.47</td>
<td>-0.77</td>
<td>0.47</td>
<td>0.22</td>
<td>-0.64</td>
<td>-0.32</td>
</tr>
<tr>
<td>Nov-02</td>
<td>-0.24</td>
<td>0.31</td>
<td>-0.59</td>
<td>0.53</td>
<td>-0.44</td>
<td>0.28</td>
<td>0.18</td>
</tr>
<tr>
<td>Jan-03</td>
<td>-0.14</td>
<td>0.54</td>
<td>-0.66</td>
<td>0.06</td>
<td>-0.33</td>
<td>-0.46</td>
<td>-0.42</td>
</tr>
<tr>
<td>Apr-03</td>
<td>-0.25</td>
<td>-0.14</td>
<td>-0.32</td>
<td>0.35</td>
<td>-0.59</td>
<td>0.22</td>
<td>-0.23</td>
</tr>
</tbody>
</table>
Figures
Figure 1. STA-2 geographic location in South Florida and aerial photograph.
Figure 2. STA-2 graphic representation with inflow and outflow structures.
Figure 3. STA-2 routine mercury monitoring sites for original permit compliance.
**Figure 4.** STA-2 start-up mercury monitoring sites for original permit compliance.
Figure 5. STA-2 start-up mercury monitoring sites for modified permit compliance.
STA-2 MOA Hg Follow-up Study

Figure 6. STA-2 expanded mercury monitoring sites for STA-2 Special Mercury Studies (MOA).
Figure 7. Inflow and interior surface water THg results for modified permit compliance monitoring (Exhibit E).
Figure 8. Inflow and interior surface water MeHg results for modified permit compliance monitoring (Exhibit E).
Figure 9. Interior STA-2 mosquitofish THg concentration results for modified permit compliance monitoring (Exhibit E).
Figure 10. STA-2 downstream mosquitofish THg concentration results for modified permit compliance monitoring (Exhibit E).
STA-2 Modified Permit Hg Compliance Monitoring

![Graph showing THg monitoring results for STA-2 sunfish](image)

**Figure 11.** STA-2 sunfish THg monitoring results for modified permit compliance (Exhibit E).
Figure 12. Surface water THg monitoring results for the STA-2 Mercury Special Studies Project (Exhibit E).
Figure 13. Surface water MeHg monitoring results for the STA-2 Mercury Special Studies Project (Exhibit E).
Figure 14. Interior filtered THg monitoring results for the STA-2 Mercury Special Studies Project (Exhibit E).
Figure 15. Interior filtered MeHg monitoring results for the STA-2 Mercury Special Studies Project (Exhibit E).
Figure 16. Mosquitofish THg concentration monitoring results for the STA-2 Mercury Special Studies Project (MOA).
Figure 17. Daily rainfall at STA-2 (average of measurements taken at EAA5, S6, and S7 rain gauges)
Figure 18. Weekly rain THg concentration monitoring results for the STA-2 Mercury Special Studies Project (MOA) for the period of record as compared to the ENR Project and Andytown NADP/MDN site results for the same period.
Figure 19. Soil MeHg concentration (0-4 cm cores) monitoring results to date for the STA-2 Mercury Special Studies Project (MOA).
Figure 20A. Correlation between the methylmercury (MeHg) concentration in top 4 cm of peat soil and the parameter of interest for all nine interior sites for each sampling campaign to date.
**Figure 20B.** Correlation between the methylmercury (MeHg) concentration in top 4 cm of peat soil and the parameter of interest for all nine interior sites for each sampling campaign to date.
**Figure 20C.** Correlation between the methylmercury (MeHg) concentration in top 4 cm of peat soil and the parameter of interest for all nine interior sites for each sampling campaign to date.
Figure 21. Correlation between the fraction of methylmercury (MeHg) in top 4 cm of peat soil ([MeHg]/[THg]) and the parameter of interest for each cell for all sampling campaigns.
Figure 22A. THg and MeHg bioconcentration factors (BCFs) for cattail (*Typha domingensis*), as the ratio of wet tissue concentrations to filtered water concentration in samples collected from the same site and time period. Samples were collected where available.
**Figure 22B.** THg and MeHg bioconcentration factors (BCFs), as the ratio of wet tissue concentrations to filtered water concentration, in samples collected from the same site and time period for green algae (periphyton) at C1AA, C2A, C2C; blue-green periphyton at C3A; and blue-green and green periphyton, respectively, at C3C. Samples were collected where available.
Attachment 1: Water, Rain, Soil, Fish Plant, and Fish Data Collected to Date for this Project

[Available Upon Request]


[Available Upon Request]

Attachment 3: Draft WO SOW for Tier 1 Pore Water Collection using the Modified Sipper Method.

[Available Upon Request]

Attachment 4: Draft WO SOW for Validation of the Modified Sipper Method

[Available Upon Request]