

# **Appendix 2B-1: Influence of Drying and Rewetting on Mercury and Sulfur Cycling in Everglades and STA Soils**

**AQUATIC CYCLING OF MERCURY  
IN THE EVERGLADES (ACME) GROUP  
PRELIMINARY DRY/REWET EXPERIMENTS  
(2/02-1/03)**

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## **Aquatic Cycling of Mercury in the Everglades (ACME) Group**

Report on Everglades Investigations  
**Influence of Drying and Rewetting on Hg and S Cycling in Everglades and STA Soils**  
Preliminary Dry/Rewet Experiments (2/02-1/03)  
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### 1. Executive Summary

Some Everglades soils produce high levels of toxic methylmercury (MeHg) when rewet following periods of dryness. Field data collected in the northern Water Conservation Areas (WCA) of the Everglades by the Aquatic Cycling of Mercury in the Everglades (ACME) group when the ecosystem rewet after the 1999 drought showed very high MeHg production in soils in northern WCA 3A (burned), and to a lesser extent in WCA 2A (dried out), in the weeks following rewetting. The high levels of MeHg production coincided with high levels of sulfate in the surface water and sediment porewater in these burned and dried areas following rewetting. Data suggested that the sulfate originated from oxidation of soil sulfur (reduced forms) as a result of the drought and fire. Since MeHg is produced in Everglades' sediments primarily by the activity of sulfate reducing bacteria, it was hypothesized that the release of sulfate from the soils (as well as release of sediment-bound mercury) stimulated MeHg production to the exceptionally high levels observed following the drought and fire.

MeHg production is also high in some newly constructed Storm Treatment Areas STA's, upon initial wetting and/or upon wetting after a dry period. However, reasons for the high levels of MeHg in some of the new STA's are unclear, and it is also unknown whether STA's planned or currently under construction will have similar MeHg problems.

This report presents the results of a laboratory experiment designed to examine the impacts of drying and rewetting of Everglades' and STA soils on the recycling of chemical species and the production of MeHg. The experiment involved the collection of small cores from the central Everglades and an STA, drying these cores under controlled laboratory conditions, rewetting of these cores with site water, and the analysis of chemical species and MeHg production in the

overlying water, porewater, and sediments of the rewetted cores. The study was designed to help elucidate why some STAs produce high levels of MeHg upon rewetting, while other do not. More generally, the study was designed to help understand the biogeochemical processes controlling pulses of MeHg produced following rewetting of dried or burned soils in the Everglades ecosystem.

Results from this experiment confirm the observations from field studies that drying and rewetting of Everglades' soils produces large pulses of MeHg. Significant increases in MeHg in sediments and surface water were observed in dried and rewet cores from both the central Everglades and STA sites, relative to *in situ* concentrations. Sulfate concentrations also increased dramatically in the overlying water following rewetting of the dried cores from both sites. This increase in sulfate was similar to what had been observed in field studies following the 1999 drought and burn in the northern Everglades. This result supports the hypothesis that MeHg production is stimulated in rewet soils by oxidation of organic matter and reduced sulfur pools in sediments during drying periods. This observation agrees with the data collected during the natural drought and rewetting of 1999. In the field in 1999, sulfate, sulfide, and MeHg were the only parameters that showed dramatically different concentrations (beyond normal variability during 4 years of monitoring) before and after the drying and rewetting event. The drying and rewetting appears to provide fuel for Hg methylation and microbial sulfate reduction and MeHg production primarily through oxidation of reduced S to sulfate. Release of Hg from soils, and degradation of organic matter during dryout appear to be less important. Build-up of sulfide (sulfide has been shown to inhibit MeHg production) and/or depletion of labile organic matter may end the pulse of MeHg production that follows rewetting of soils. In our experimental dry/rewet cores, sulfide never reached levels high enough to inhibit MeHg production, possibly partly due to the brittle nature of the peaty soil after drying that limited buildup of sulfide in interstitial solution in the sediments. It should be noted, however, that very high levels of sulfide were present in the native Everglades after the 1999 drought, far beyond what is predicted to be inhibitory to mercury methylation, and yet substantial methylation rates were measured under these high sulfide conditions. Other chemical species were also remobilized into overlying water following drying and rewetting of the soils, such as nitrogen species (ammonium and nitrate, phosphate, and chloride). However, sulfate remobilization appears greatest causal factor leading to the stimulation sulfate reduction and MeHg production. The MeHg produced in the plumes following dry/rewet may quickly enter the food chain, and contribute to higher levels of MeHg in fish and higher trophic level wildlife in the ecosystem.

Minimization of drying events in the STAs is a management tool that can be used in STAs that are prone to MeHg production. STAs most prone to MeHg production appear to be those that have not been previously used for agriculture. Very high levels of reduced S in STAs constructed on former agricultural soils, like the former ENR, inhibit MeHg production through the formation of sulfide and Hg-sulfide species that are not available to microorganisms for uptake and methylation. However, iron, cations, organic matter, and other soil chemistry affect the relationships between sulfate reduction, sulfide accumulation, and methylation. Further examination of soils chemistry across the STAs, and the development of a numerical, diagenetic simulation of methylation, is needed to adequately predict the effects of drying and rewetting on MeHg production in these systems.

## 2. Introduction

Drought and fire have historically been forces impacting the Everglades ecosystem. Indeed, drought and fire can be positive forces that help maintain the ecosystem by periodically eradicating invading flora not adapted to living with this normal aspect of Everglades' ecology. Flora native to the Everglades is well adapted to withstand all but the most severe drought and fire conditions, and the recycling of nutrients following drought or fire can actually rejuvenate plant growth.

Construction of water control structures (canals, pumping stations, levees) around Lake Okeechobee and within the Everglades beginning around 1900 and continuing through the 1970's greatly altered the hydrology of the ecosystem. Water management practices routinely routed water toward agriculture and urban areas, and away from the Everglades during periods of low rainfall. This inevitably led to more severe drought and fire within the ecosystem compared to historical trends. One major goal of Everglades' restoration is to restore more natural flow of good quality water into the ecosystem to alleviate some of the extreme drought and fire conditions witnessed during the past several decades.

Although fire and drought can have beneficial effects on the ecosystem as mentioned, the full effects of these forces on the ecosystem have not been studied in detail. In particular, the biogeochemical impacts of fire and drought on the recycling of chemical species within the ecosystem have not been investigated in detail. Following an extended drought in the Everglades in 1998-1999, and extensive fires in spring 1999 in northern Water Conservation Area (WCA) 3A, the Aquatic Cycling of Mercury in the Everglades (ACME) team set out to examine biogeochemical impacts, at the behest of Aaron Higer (at the time Program Director of USGS South Florida Ecosystems studies). Extensive field sampling was conducted at both fire- and drought-impacted sites in northern WCA 3A (north of Alligator Alley) and portions of WCA 2A in June and July 1999 following the rewetting of these areas immediately after the fire and drought. Sampling included the collection of sediment, surface water, and porewater samples, and the analysis of these samples for nutrients, anions, cations, sulfur species, mercury species, organic carbon, and general chemical parameters. Periodic sampling of the affected areas continued into the fall of 1999, and a follow-up survey of the biogeochemistry of the affected areas was conducted 14 months after the initial rewetting of the areas.

The results of these studies were extremely exciting. Massive remobilization of some chemical species, most notably sulfate, was observed following fire/drought and rewet. Sediment and water studies showed that sulfur species stored in the sediments (principally acid volatile sulfide and organic sulfur) was oxidized to sulfate by the effects of fire and drought, and remobilized into the surface water following rewetting. At some sites, sulfate levels 50 to 100 fold higher than pre-fire/drought levels were observed in surface water. More exciting still, was the observation of extreme levels of methylmercury in surface water and sediments following drought/fire and rewetting. Remobilization of mercury from the sediments and increases in dissolved mercury in surface water was also observed. These results led to the formulation of the following conclusions regarding the biogeochemical impacts of fire/drought on mercury and sulfur geochemistry in the ecosystem:

- (1) Fire/drought oxidizes reduced sulfur species in sediments (acid volatile sulfides and organic sulfur) into sulfate, which is remobilized into surface water and sediment porewater following rewetting of the fire/drought-impacted area.

- (2) Fire/drought also remobilizes mercury from sediments into dissolved mercury in surface water and sediment porewater following rewetting, providing a vast pool of “new” mercury available for methylation.
- (3) After rewetting of drought/fire-impacted soils, anoxic conditions are slowly reestablished, permitting anaerobic microbial metabolism to again flourish. With a reservoir of newly recycled sulfate and “new” mercury available, microbial sulfate reduction and mercury methylation (mercury is methylated by sulfate reducing bacteria) is rapidly reestablished.
- (4) Immediately after rewetting (and for a significant time afterward) sulfide levels in sediment porewater have not increased to levels inhibitory to mercury methylation, this process can proceed unimpeded to produce some of the highest levels of methylmercury that have been reported in the literature.
- (5) High levels of methylmercury persist for significant periods (perhaps as much as 3-6 months) following rewet after the burn/drought, but methylmercury and sulfate concentrations returned to normal levels within a year of the rewet, as sulfate reduction depleted sulfate and sulfide concentrations (inhibitory to methylmercury production) gradually increased in porewater.
- (6) The high levels of methylmercury produced during the drought/fire and rewet events are likely bioaccumulated. Control of fire/drought and rewet represents an important management issue to minimize methylmercury impacts in the Everglades and the stormwater treatment areas or STA’s.

Although field studies in 1999 provided much insight on how drought/fire and rewet events influence biogeochemical processes and especially toxic methylmercury production and bioaccumulation, many details of the process remained unclear. Furthermore, the observations of the field studies needed to be confirmed using an experimental approach. To address these issues, an experiment designed to further test the impact of fire/drought on biogeochemical processes and methylmercury production was proposed. This experiment and its outcome are described in detail in this report. Results from this experiment will be prepared for publication in peer-reviewed journals during the coming year. The results of the experiment confirm the observations from our field studies in 1999, specifically that drought (or artificial drydown) of Everglades peat and STA soils, followed by rewetting of these soils results in the release of large amounts of sulfate and free mercury, which stimulates sulfate reduction and massive methylmercury production in the affected sediments. Further experimental studies like this one are planned for future years, employing lessons learned from this preliminary study and designed to unravel details of the biogeochemical processes accompanying dry/rewet cycles in the Everglades.

### 3. Background

The experiment was designed to examine the effects of drying of Everglades sediments and subsequent rewetting of these sediments with ambient surface water on: (1) remobilization of chemical substances into the water, and (2) the effects of these remobilized substances on methylmercury production. The overall study is thus referred to as a dry/rewet experiment. Two very different sites were selected for the dry/rewet experiment: a site in the center of Water

Conservation Area 3A (site 3A-15), and a site in Storm Treatment Area 2 (STA-2) cell 1 (Fig. 1). The 3A-15 site is a typical oligotrophic, peat-forming environment in the central Everglades representative of large portions of the ecosystem. This site has been a focal point of ACME studies since 1996 due to the high rates of MeHg production in sediments, and high concentrations of MeHg in fish here. Although this site has not routinely dried out in recent decades, it may experience dry down during extended drought.

The STA-2 site is a recently constructed buffer wetland area designed to help remove excess phosphorus from canal water destined for discharge into the Everglades. STA-2 has three treatment cells that can be operated concurrently and independently. Cell 3, the westernmost treatment cell, was originally a sod farm, Cell 2, the middle cell, was about one-third sod farm and two-thirds undeveloped wildlife preserve, while Cell 1, the easternmost cell and adjacent to the L-6 levee, was entirely undeveloped wildlife preserve. The bottom portion of Cell 3 has been supplemented with limerock and submerged macrophytes, which is presently considered to be the most promising Advanced Treatment Technology (ATT) for routinely achieving 10 ppb total phosphorus at the point of discharge. Cells 2 and 3 do not have a methylmercury problem, but Cell 1 has experienced anomalously high concentrations following reflooding after periods of dryout in the fall of 2000 and 2001. Cell 1 has a higher average elevation than Cells 2 and 3, and consequently, Cell 1 dries out more frequently and for longer periods of time than Cells 2 and 3. A study conducted by the U.S. Geological Survey (USGS) in 1999 demonstrated that reflooding of the northern Everglades following dryout and burn produced a pulse of methylmercury production (see Introduction), but it was of shorter duration than the one experienced in Cell 1.

Although STA-2 and STA-6 are at different stages of maturation, the anomalous mercury events in STA-2 Cell 1 and the occasional outflow greater than inflow events in STA-6 may share the same cause: a dryout and rewetting cycle that liberates one or more constituents from a soil pool that otherwise limit methylmercury production. Potential limiting factors for methylmercury production include inorganic mercury, easily degradable organic matter, and sulfate. Inorganic mercury is the substrate from which methylmercury is synthesized by natural bacteria in the hydrated soil. Sulfate-reducing bacteria are important methylators in most ecosystems, including the Everglades, and their activity can be limited by either organic matter availability or by the concentration of the electron acceptor used by these anaerobic organisms, sulfate. Sulfate-reducers respire sulfate to produce sulfide. However, sulfide, at concentrations above roughly 10 micromolar in soil interstitial waters, can limit methylation. Sulfide inhibition occurs through the formation of charged mercury-sulfide complexes that are not readily taken up by bacteria. ACME field data collected from 1995-1998 from the WCAs, LNWR and ENP allow prediction of long-term methylmercury production based on the sulfide content of surficial sediment pore waters.

ACME field studies of mercury and sulfur cycling in WCAs 2 and 3 following the 1999 drought and rewetting strongly suggest that sulfur in sediments is oxidized during drying and burning of peat, and that the sulfate formed stimulates microbial sulfate reduction and mercury methylation upon rewetting. However, control of this methylation pulse is not well understood. In particular, the relationship between the amount of sulfur stored in sediments (or available in flooding waters) and the total amount of methylmercury produced upon rewetting is unclear. Since sulfate stimulates methylation, but sulfide inhibits methylation, methylation at high sulfur sites may shut down quickly after rewetting as sulfide accumulates. We need to know more clearly how sulfur levels control the magnitude and duration of the methylation pulse. The relative role of organic matter and mercury release during oxidation in the post-rewetting

methylation pulse is also not known. However, field data from 1999 suggest that sulfur oxidation is the main factor leading to enhanced methylation after rewetting.

Methylmercury production in the “test” STA (ENR) has been low throughout its history. ENR soils are agricultural soils with very high reduced-sulfur content, and inflow waters to STA-1 are high in sulfate (30-60 mg/L). ENR has never undergone a substantial drying period. The net result is a constant, high sulfide concentration in ENR soils that limits Hg uptake by bacteria, and therefore limits methylmercury production. STA-2 soils are likely very different than ENR soils, since some have not been cropped and some have been in turf. The history of sulfur use in these areas, and the concentration of reduced sulfur in STA-2 soils are unknown. Therefore it is difficult to predict either the amount of methylmercury production upon rewetting or the long-term methylmercury production of these cells.

How can Cell 1 be opened to minimize the magnitude and duration of the “first-flush” methylmercury pulse? The three most reasonable hypotheses for why Cell 1 is producing high concentrations of methylmercury are:

1. Sulfate and sulfide concentrations are optimal for Hg methylation. While there is enough sulfate from S6 canal water to fuel sulfate reduction after flooding, reduced-sulfur in Cell 1 soils may be much lower than in the ENR, and dissolved sulfide concentrations do not build up quickly. In the best case, sulfur chemistry may be optimal for only a short time after rewetting, and sulfide build-up will limit methylation after weeks to months.
2. Decomposition of organic matter left over from initial flooding of Cell 1 may be fueling increased microbial activity that is driving excess methylation. It may take months to years to use up this organic matter.
3. Mercury is released from soils during drying, and this fuels a methylation pulse. This release may be related to vegetation flooded during the construction of STA-2. Data collected in WCAs 2 and 3 after the 1999 drought, suggest, however, that Hg is not released from soils for an extended period following drydown.

#### 4. Scope of Study

The basic dry/rewet experiment design involved collecting cores from the two study sites, drying these cores for a selected period of time under simulated natural lighting conditions and temperatures of 25°C in the laboratory, and then rewetting the cores with water collected from the sites (simulating natural rewetting conditions). After rewetting, surface water, sediment porewater, and sediment from the cores was analyzed for various chemical substances of interest, especially sulfur and mercury species to determine the impact of dry/rewet cycles on the remobilization of chemical species and methylmercury production.

The purpose of the experiment was to examine S and Hg cycling in Everglades soils that have dried and then rewet, and to collect detailed information on the link between the S and Hg cycles after rewetting. The study was intended to confirm the 1999 drought/burn field data with controlled, process-level studies, and to examine the magnitude and timing of the post-rewetting MeHg pulse across sites with a range of ambient chemistries, particularly soil S concentrations. There was particular interest in examining mercury cycling in STA-2 Cell 1 soils following drying and rewetting. STA-2 Cell 1 has produced very high concentration of MeHg upon rewetting in each of the last two years. We intended to examine the magnitude and timing of the

peak of MeHg production in STA-2 following rewetting, and to compare results to those from site 3A-15 (a site with low to intermediate sulfur concentrations and very high MeHg production). We hypothesized that differences in soil S concentration and/or chemistry between STA-2 Cell 1 (a site which has not been recently used for agriculture) and most of the other STAs (which were constructed on agricultural soils) account for differences in MeHg production. Results from this study would be used to help understand and manage the process of MeHg production during drying and rewetting cycles, particularly in the STAs.



## 4. Methods and Procedures

### 4a. Background (Ambient) Sampling

Surface water, porewater, and sediment samples were collected at each site for the determination of background (ambient) conditions at each site (STA-2 and WCA 3A-15). Surface water grab samples were carefully collected to minimize resuspension of soil particulate matter or interstitial waters into the sample. Porewater was collected at each site using a micropiezometer approach. The porewater samples represented a depth-integrated sample with an average depth of approximately 5 cm. The sipper is constructed from Teflon and was properly cleaned and stored for ultra-trace mercury and sulfur species analysis. Surface water and porewater was collected at the same sites and times as the soil cores.

Sediment cores from each site for background biogeochemistry were also collected at the same site and time as the water samples for measurement of: total and methylmercury, total sulfur, AVS, CRS, OS, and mercury methylation/demethylation rates. The sediment cores were collected in duplicate in 0-4 cm soils at the time of core collection for the dry/rewet experiment. Methylation and demethylation rates were estimated using Hg stable isotopes. Soil cores were collected using appropriate equipment that was appropriately cleaned and stored prior to use. Soil cores were collected in a manner to preserve the undisturbed physical, chemical, and microbiological community structure of the soil to the maximum practicable extent.

### 4b. Dry/Rewet Experiment Sampling

For this experiment approximately 40 cores were collected in 10 cm teflon and 7 cm PVC core barrels at each of the two sites: on February 6, 2002 at WCA 3A-15 and on February 7, 2002 at STA-2 Cell 1 at Site C. Teflon core barrels were used for cores from which surface water was sampled, and the PVC core barrels were used for sediment analyses. In addition to cores collected for laboratory experiments, additional samples were taken at each site to assess ambient mercury and sulfur biogeochemistry, as described above. The cores were collected to a depth of about 10 cm, which filled the core barrels about halfway. The cores were then topped off with site water and capped to prevent sloshing of the sediment and disturbance during shipment to laboratory facilities. Cores were tightly packed in an upright position in coolers to further protect against disturbance.

The cores were transported in a USGS van on February 8 and 9, 2002 from Florida to southern Maryland (Co-investigator Gilmour's labs at the Academy of Natural Sciences Estuarine Research Center in St. Leonard, MD) where the dry/rewet experiment was conducted. The cores were incubated in a 28 °C water bath under artificial sunlight ("sunlight" bulbs) using a 12 hour day/night cycle. A photograph of the core drying and incubation setup is shown in Fig. 2, and a picture of the cores prior to the beginning of the drying experiment is shown in Fig. 3. Isotopic  $^{201}\text{Hg}$  was spiked into all cores to follow the changes in Hg during methylation. The actual drying experiment was begun on February 14, 2002. One set of cores was dried for a period of 40 days before rewet, while another smaller set of cores was dried for 299 days before rewet. A detailed timeline for the study is presented in Table 1, and details of the study design for the 40-day drying experiment are shown in Fig. 4. Following the 40-day and 299-day drydown, cores from sites 3A-15 and STA-2 were rewet with site water. The initial rewet after the 40-day drydown was on March 27, 2002, and for the 299-day drydown the initial rewet was

on December 11, 2002. After the initial rewet, samples were collected from the rewet cores according to the schedules shown in Tables 2a and b (overlying water sampling), Tables 3a and b (porewater sampling), and Tables 4a and b (sediment sampling).

#### 4c. Analytical Methods

Overlying water samples and porewater samples were analyzed for the following parameters: mercury species (total and MeHg), anions (chloride, fluoride, bromide), nutrients (nitrate, ammonium, and phosphate), sulfur species (sulfate, sulfide, sulfite, and thiosulfate), dissolved organic carbon, pH, major cations (Ca, Mg, Na, K), iron, manganese, conductivity, dissolved oxygen, salinity, total dissolved solids, and redox. Due to poor rewetting of the cores following drying, porewater recovery from the rewet samples was minimal, and few porewater measurements were made. Standard electrochemical methods were used for the analysis of pH, conductivity, salinity, total dissolved solids, dissolved oxygen (solid state microelectrode), sulfide, and redox. Anions, cations, and nitrate concentrations were determined by ion chromatography using standard suppressed IC methods and in-line conductivity and variable wavelength uv/vis spectrometry (nitrate only) for detection. Sulfite and thiosulfate were determined by HPLC using a diode array detection system. Ammonium and phosphate were determined using standard colorimetric methods with fiber optic uv/vis spectrophotometric detection. Dissolved organic carbon was determined using high temperature combustion and nondispersive infrared detection. Mercury species were determined using ICP-MS methods. Appropriate field quality control samples of surface water were collected and analyzed for total mercury and MeHg. In the analytical laboratory, appropriate laboratory blanks, spikes, and replicates were run each day. The data were reviewed routinely to ensure that quality control criteria were met.

Sediments were analyzed for the following parameters: total C, organic C, total N, total S, sulfur speciation (acid-volatile sulfides, chromium-reducible sulfides, organic sulfur, and sulfates), mercury species (total and MeHg), sulfate reduction rates, and mercury methylation rates. Total C, organic C, total N, and total S were analyzed by high temperature combustion using a Leco 932 CNS analyzer. Sulfur species were determined using wet chemical methods, with gravimetric analysis. Mercury species were determined after extraction from sediments by ICP-MS. Sulfate reduction rates and mercury methylation rates were determined using standard addition of radiotracer, incubation, and radiometric analysis of products.

Data entry was done electronically in Excel spreadsheets. Data entries were checked against hardcopy of the data report by a technician and then the Quality Assurance Officer (one of the principal investigators). An electronic copy of the database is included with this report.

Details of analytical methods and QA procedures can be found in the ACME FL DEP RQUAPP.

## 6. Results

### 6a. Ambient conditions at study sites

Results for ambient conditions at both sites 3A-15 and STA-2 are shown in Table 5. Ambient conditions were measured on 2/6/02 at site 3A-15, and on 2/7/02 at STA-2. Figures 5-7 show

comparisons of mercury results from the STA-2 and 3A-15 ambient sampling to long term mercury results from the ACME sites in the Everglades. In general, measurements made at 3A-15 in February of 2002 were comparable to averages from long-term studies (1995-1998) at this site. MeHg concentrations and production rates at STA2 were generally above the running averages for all of the ACME Everglades sites. Sulfate-reduction rates, fueled by high SO<sub>4</sub> inputs from the EAA canals, and probably from oxidation during drying of reduced S stored in sediments, were also at the high end of average for Everglades soils. Concentrations of salts and of suspended solids were higher at STA2 than at 3A15.

#### 6b. Results of Dry/Rewet Experiments

Overlying water results from the dry/rewet 40-day experiment are shown in Tables 6 (all results), and 7 (average values for each date). Porewater results from the 40-day dry/rewet experiment are shown in Tables 8 (all results) and 9 (average values for each date). Sediment results for the 40-day dry/rewet experiment are shown in Tables 10 (all results) and 11 (average values for each date). Results for the 299-day dry/rewet study are shown in Tables 12 (overlying water), 13 (porewater) and 14 (sediments).

### 7. Discussion

#### 7a. Bulk density of wet, dried and rewet soils

Surface soils sampled in February 2002 at STA-2 cell 1 site C were 3-4 times denser than surface flocs at site 3A15. After six weeks of drying, cores from both sites had about the same density (Fig. 8). Soil cores shrank significantly during drying, pulling away from the sides of the core barrels. Soils from both sites rewet very slowly, with rewetting still very incomplete after six weeks. Soils from site 3A15 were slightly easier to rewet. Because of this rewetting issue, little porewater was obtained from the dry/rewet cores.

#### 7b. Oxygen in wet vs. dried/rewet cores

Cores that were dried and then rewet rapidly became anoxic after rewetting. Depth profiles of oxygen, through time, are compared for wet controls vs. cores dried and rewet on 3/27/02, in Fig. 9 (3A15) and Fig. 10 (STA2). Dried cores were fully oxic top to bottom before rewetting. In 3A15 cores, oxygen levels within dried cores began to drop within 24 hours of rewetting, and anoxia was fully developed within 5 days. Oxygen levels in cores that remained wet stayed fairly constant throughout the experiment, with intermittent oxygen in the top 4 cm of sediment. Oxygen levels in dried and rewet STA2 cores dropped dramatically within 24 hours of rewetting, and anoxia was fully developed within 5 days. Oxygen levels in cores that remained wet stayed fairly constant throughout the experiment, with only the top 1 cm containing any oxygen.

Comparison of oxygen levels in different treatments through time in cores from sites 3A-15 and STA-2 are shown in Fig. 11. All dates are after rewetting dried cores on 3/27/02. Oxygen levels in water over all soils were lower than in water-only controls (which approximate saturation) because of sediment oxygen demand. Oxygen levels in water overlying rewet cores may have been slightly lower than in cores that remained wet, especially for the cores from site STA-2. Oxygen levels were somewhat higher in the overlying water of rewet cores held in 10 cm diameter Teflon core barrels than in cores held in 7 cm diameter PVC core barrels. Note that all water-only controls and wet controls were held in Teflon core barrels.

### 7c. Solid-phase Hg and MeHg

Average concentrations for native MeHg and excess Me201Hg (top), and native total Hg and excess labeled 201Hg (bottom) for site 3A-15, are shown in Fig 12 plotted by date. The data shown include *in situ* values for MeHg and total Hg from the site during core collection on 2/6/02, the concentrations of MeHg and Hg in wet cores immediately after return to the lab in Maryland (2/14/02), and concentrations in dried cores after rewetting (dates 4/4/02 and later). Native MeHg increased significantly within 5 days of rewetting dried cores, and stayed roughly the same (or slightly increased) over the next six weeks. Me201Hg also appeared to increase, however, most excess Me201Hg data points are at or below the detection limit (BDL). Note that the detection limit for excess Me201Hg is about 1% of the total MeHg, and that the scales on the native MeHg and excess Me201Hg plots are 100x different. Therefore the degree of confidence in Me201Hg values is low. Detailed plots by date of all data for native MeHg and excess Me201Hg (top), and native total Hg and excess 201Hg (bottom) for site 3A-15 are shown in Fig. 13.

Average concentrations for native MeHg and excess Me201Hg (top), and native total Hg and excess 201Hg (bottom) for cores from site STA-2, plotted by date are shown in Fig. 14. Data include *in situ* values for MeHg and total Hg from the site during core collection (2/7/02), the concentrations of MeHg and total Hg in wet cores immediately after return to the lab in Maryland (2/14/02), and concentrations in dried cores after rewetting (dates 4/4/02 and later). Native MeHg increased significantly within 5 days of rewetting dried cores from STA-2, and remained at that level for the next six weeks (similar to results from site 3A-15). Me201Hg also appeared to increase, however, most excess Me201Hg data points are at or below the detection limit (BDL). Note that the detection limit for excess Me201Hg is about 1% of the total MeHg, and that the scales on the native MeHg and excess Me201Hg plots are 100x different. Therefore the degree of confidence in Me201Hg values is low. Detailed plots by date of all data for native MeHg and excess Me201Hg (top), and native Hg and excess 201Hg (bottom) for site STA-2 are shown in Fig. 15.

*In situ* MeHg concentrations at 3A-15 were somewhat lower (about 4%) than average values over the course of the ACME study for this site. From 1995-1998, site 3A-15 showed some of the highest %MeHg and MeHg production rates within the ACME data set. The % methylation of the 201Hg spike into cores appears much higher than the % methylation of native Hg in cores (Fig. 13), suggesting higher bioavailability of the isotopically labeled “new” mercury added to the cores. However, the degree of confidence in 201Hg values is low, as most data are at or below the DL.

*In situ* MeHg concentrations were somewhat higher in STA-2 soils than in peats from 3A-15 during sampling in February 2002. However, because the total Hg concentration (per g dry weight) is much higher at 3A-15, the % of native total Hg methylated at STA-2 is much higher than at 3A-15 (Figs. 16 and 17). The %MeHg *in situ* at STA-2 in February 2002 (Fig. 17) is about the same as the 4 year average for the ACME sites of highest MeHg production in the Everglades (2BS, 3A15 and TS7). The % MeHg at STA-2 after drying and rewetting soils substantially exceeds the average %MeHg for these sites (Fig. 17). The % methylation of the 201Hg spike into cores appears much higher than the % methylation of native total Hg in cores (Fig. 17), suggesting higher bioavailability of the labeled spike (“new” mercury). Again, however, the degree of confidence in 201Hg values is low, as most data are at or below the DL.

#### 7d. Solid-phase sulfur chemistry

In 3A-15 sediment cores, acid volatile sulfides or AVS (the more reactive inorganic sulfides) decreased with drying, and began to increase again about six weeks after rewetting (Fig. 18). Chromium-reducible sulfides (pyrites and other disulfides) did not change appreciably with either drying or rewetting (Fig. 18). Most of the reduced sulfur in Everglades peats is CRS and organic sulfur. Variability among cores is high at this site (as usual).

In STA-2 sediment cores, AVS decreased to essentially zero with drying (fig. 19), and stayed that way for six weeks after rewetting. Chromium-reducible sulfides did not change appreciably with either drying or rewetting (Fig. 19). Variability among cores is lower at this site than at many open marsh sites.

In situ AVS and CRS concentrations are very comparable at STA-2 and 3A-15, and much lower than in northern WCA 2A or in the former ENR.

#### 7e. MeHg in water over cores

Graphs of all data for native MeHg (top) and excess Me201Hg (bottom) in water overlying experimental (dry/rewet) cores from site 3A-15 are shown in Fig. 20. Average values by treatment through time for native MeHg (top) and excess Me201Hg (bottom) in water overlying experimental cores from site 3A-15 are shown in Fig. 21. In the 3A-15 samples, MeHg concentrations increased in the water above the cores after rewetting, relative to cores that remained wet, and to water-only controls (top panel). The maximum MeHg concentration in water was achieved 3-4 weeks after rewetting the cores. These are raw concentration data from which fluxes can be determined. Water to surface ratios for all cores are not the same, however, so patterns in concentration may not reflect patterns in sediment/water efflux of MeHg. Flux of Me201Hg from soils to the overlying water is difficult to assess (bottom panel) because most values are at or below the detection limit (BDL). Note that the detection limit for excess Me201Hg is about 1% of the total MeHg. Note the differences in the scales on the MeHg and excess Me201Hg plots (Figs. 20 and 21). Most excess Me201Hg data points are BDL. Therefore the degree of confidence in Me201Hg values is low.

All data for native MeHg (top) and excess Me201Hg (bottom) in water overlying experimental cores from site STA-2 are shown in Fig. 22. MeHg concentrations in water over STA-2 cores were very high soon after the cores were returned to the lab (this was not true of 3A15 cores). Flux of Me201Hg from soils to the overlying water is difficult to assess (bottom panel) because most values are at or below the detection limit (BDL). Note that the detection limit for excess Me201Hg is about 1% of the total MeHg. Note the different scales for the MeHg and excess Me201Hg plots (Fig. 22). Most excess Me201Hg data points are BDL. Therefore the degree of confidence in Me201Hg values is low. Average values for native MeHg (top) and excess Me201Hg (bottom) in water overlying experimental cores from site STA-2 are shown in Fig. 23. Graphs show averages by treatment and date. In the top plot, the scale has been decreased to better show MeHg concentration after core rewetting. MeHg concentrations increased in water over both rewet cores and cores that remained wet throughout the experiment, relative to water-only controls, although the difference may not be significant. MeHg concentrations continued to increase through six weeks after rewetting. These are raw concentration data from which fluxes may be determined. Water to surface ratios for all cores are not the same, therefore patterns in concentration may not reflect patterns in sediment/water efflux of MeHg.

#### 7f. Dissolved Organic Carbon (DOC) in water overlying experimental cores

Average concentrations for dissolved organic carbon (DOC) in water overlying experimental cores by treatment and date for site 3A-15 are shown in Fig. 24. Some pore water information is also shown for rewet cores in Fig. 24. The DOC concentration of 3A-15 surface waters used to refill cores was 12.6 ppm. Higher DOC concentrations in water overlying cores and in water controls may reflect evaporation and/or efflux from pore waters. DOC concentrations were somewhat higher in porewaters than in overlying water suggesting that efflux contributes to surface water DOC.

Average concentrations for DOC in water overlying experimental cores by treatment and date for site STA-2 are shown in Fig. 25. Some pore water information is also shown for rewet cores in Fig. 25. The DOC concentration of canal water used to refill cores was 27.1 ppm. Higher DOC concentrations in water overlying cores and in water controls may reflect evaporation and/or efflux from pore waters. DOC concentrations were somewhat higher in porewaters than in overlying water suggesting that efflux contributes to surface water DOC.

#### 7g. Chloride in water overlying experimental cores

Chloride data (Fig. 26) in overlying water from experimental cores provide information on the relative ionic strength of waters at both sites, with STA-2 about ten times “saltier” than 3A-15. See the data file for this experiment (Tables 6 and 7) for F1 and Br data. The concentration of conservative ions like chloride also provides information on the amount of evaporation occurring in each treatment throughout the experiment. All cores were open to the air starting 2/14/02, and were held at the same controlled temperature. Cores were refilled with fresh site water as needed to maintain a constant volume of overlying water (except core that were drying). The chloride concentration of dry/rewet cores (after rewetting, in red) and the chloride in cores that remained wet are not too dissimilar, showing roughly equal rates of evaporation.

#### 7h. Nutrients in water overlying experimental cores

Average concentrations for nutrients (nitrate, phosphate, and ammonium) in overlying water from experimental dry/rewet cores by treatment and date for site 3A-15 are shown in Fig 27. Dried 3A-15 soils released nitrate immediately after rewetting, and ammonium in the first few weeks after rewetting, as soils become anoxic again. Nitrate and phosphate increases observed in water overlying cores that remained wet may have been evaporation, or de novo production and efflux from soils.

Average concentrations by treatment and date for nutrients in overlying water of experimental cores from site STA-2 are shown in Fig. 28. Dried STA-2 soils released nitrate and ammonium immediately after rewetting, releasing more nitrate and less ammonium than 3A-15 dry/rewet soils. Phosphate results were exceptionally variable, because one core of the triplicate dry/rewet cores released large amounts of phosphate.

#### 7i. Sulfur species in water overlying experimental cores

Average concentrations by treatment and date for sulfate and sulfide in water overlying experimental cores from site 3A-15 are shown in Fig. 29. Dried 3A-15 soils released large concentrations of sulfate immediately after rewetting. Concentrations generated in these enclosed systems in the week following rewetting were roughly 100X ambient wet period concentrations. The concentration of sulfate in the 3A-15 surface water used to refill these cores was only about 5  $\mu$ M. Therefore, almost all the sulfate generated was derived from oxidation of the reduced

sulfur in sediments during soil drying. Most of the sulfate generated by drying the cores was used up again within about 3 weeks after rewetting the cores. The concentration of sulfate in soil pore waters (Fig. 29) also rose after rewetting, but was lower than sulfate in water over the cores, reflecting active sulfate reduction. Water over all cores, pore waters, and water-only controls contained very low levels of sulfide (Fig. 29). No appreciable sulfide built up in pore waters after rewetting cores.

Average concentrations of sulfate and sulfide by treatment and date in water overlying experimental cores from site STA-2 are shown in Fig. 30. Dried STA-2 soils released sulfate upon rewetting, but the high sulfate canal water used to refill these cores also contributed much of the sulfate in this experiment. The sulfate concentration in the STA2 inflow canal was about 500  $\mu\text{M}$ . Sulfate concentrations in rewet cores were comparable to water only controls, but higher than wet cores. Sulfate in water can increase due to evaporation, or be lost through sulfate reduction in soils. Information on refill volumes is available, and calculation of evaporation can be made from existing data. This information can be used to estimate the relative contribution of sulfate from oxidized STA-2 soils and from canal refill water. Sulfate concentrations in the canal water and especially in cores after rewetting are exceptionally high for freshwater systems. Sulfate in the rewet cores was depleted back to levels found in the wet control cores over the course of about 4 weeks. Sulfide levels in water overlying cores and in water-only controls (Fig. 30) were low and comparable to levels in water overlying 3A-15 cores. However, sulfide built up to about 3.5  $\mu\text{M}$  in the pore water of rewet controls from site STA-2.

Detailed plots of all the porewater sulfide data (Fig. 31) for 3A-15 cores (top) and STA-2 cores (bottom) highlight the somewhat higher sulfide levels in rewet STA-2 cores, and the variability among cores. The plot in Fig. 32 shows sulfide concentrations in porewaters (0-4 cm) through time at 8 ACME sites in the Everglades. Ambient porewater sulfide concentrations at both STA-2 and 3A-15 (less than 1  $\mu\text{M}$ ) were at the low end of the range observed in the ecosystem. Even after rewetting dried cores, porewater concentrations at both sites remained low relative to sulfide in northern WCA 2A or in ENR.

#### 7j. Iron and manganese in water overlying experimental cores

Dissolved Iron and manganese are redox indicators. Average concentrations for iron and manganese in overlying water and porewater from site 3A-15 are shown in Fig. 33. After dried cores were rewet, the concentrations of both iron and manganese increased in porewaters and overlying waters for about 3 weeks, following the development of anoxia in the soils. The dissolved iron concentration in water used to refill 3A-15 cores was 48  $\mu\text{g/L}$ ; the Mn concentration was 1.8  $\mu\text{g/L}$ . High Fe and Mn concentrations in wet cores on 2/14/02 (immediately after return to the lab) may indicate development of anoxia during transport.

Average dissolved iron and manganese concentrations by treatment and date for overlying water and porewater from site STA-2 are shown in Fig. 34. Neither Fe nor Mn concentrations increased in water over STA-2 cores after rewetting, and concentrations of both were low and comparable in all treatments. Porewater Fe and Mn concentrations were much higher than in surface waters, reflecting the anoxic condition of these soil cores. Dissolved Fe concentrations decreased after rewetting dried cores, possibly due to precipitation of iron sulfides formed after sulfate reduction to sulfide. The dissolved iron concentration in water used to refill STA-2 cores was 24  $\mu\text{g/L}$ ; the Mn concentration was <1  $\mu\text{g/L}$ . High Fe and Mn concentrations in wet cores on 2/14/02 (immediately after return to the lab) may indicate development of anoxia during

transport. Dissolved Fe concentrations in porewaters of 3A-15 rewet cores (~500  $\mu\text{M}$ ) were much higher than STA-2 porewaters (~150  $\mu\text{M}$ ).

#### 7k. Sulfur chemistry and MeHg production

Fig. 35 shows MeHg as percent of total Hg, and measured methylation rates constants (bottom) against sulfur chemistry and modeled dissolved Hg complexation (top), for the 1995-1998 ACME data set. Maximal MeHg production occurred at sulfide concentrations around 10  $\mu\text{M}$  and sulfate reduction rates of 250-500  $\mu\text{moles/cc-day}$ . Sulfide concentrations in STA-2 and 3A-15 soils after rewetting appear optimal for MeHg production. Sulfate reduction rates in both soils in wet cores and cores after rewetting were calculated from sulfate depletion.

#### 7l. Comparison MeHg with other sites across the Everglades

Fig. 36 shows Hg, MeHg and %MeHg in ACME site soils (0-4 cm) from 1995-1998. The %MeHg in situ at STA-2 in Feb. 2002 was 2-3%, comparable to the highest site averages for the ACME study. After rewetting, STA2 cores contained 6-8% MeHg, much higher than the highest average values for any of the ACME sites. In situ MeHg concentrations at STA-2 in Feb. 2002 were 2-4 ng/gdw. After rewetting dried cores, MeHg climbed to 6-8 ng/gdw. Total Hg in soils at STA-2 was about 150 ng/gdw, somewhat higher than ENR soils, but much lower than 3A-15 soils. The %MeHg in situ at 3A-15 in Feb. 2002 was 0.5-1%, lower than the running average for 1995-1998 for this site. After rewetting, 3A-15 cores contained about 1.5% MeHg. In situ MeHg concentrations at 3A15 in Feb. 2002 were about 2 ng/gdw. After rewetting dried cores, MeHg climbed to 4-7 ng/gdw. Measured total Hg in 3A15 soils in Feb 2002 were quite variable, as usual at this site, ranging from about 200 to 400 ng/gdw.

#### 7m. Impacts of longer-term drying: 299-day drying experiment.

Some of the cores sampled in Feb. 2002 were held for about 10 months before rewetting. The objectives of this repeated dry/rewet experiment were to examine the potential effects of longer drying periods on reduced S oxidation and MeHg production, and to provide a second test of our hypothesis that dry/rewet cycles fuel Hg methylation through the oxidation of reduced S stored in soils.

Cores for this study were rewet with 3A15 surface water on 12/11/02. This is a change from the first dry/rewet experiment, in which 3A15 cores were rewet with 3A14 surface water, but STA2 cores were rewet with EAA canal water (inflow to STA2). Our objective in using 3A15 water for all cores was to separate the sulfate arising from oxidation of reduced S within cores, from the high background sulfate levels in EAA canal water. Surface water from 3A15 contained only about 10  $\mu\text{M}$  sulfate.

After rewetting, each 7 cm core was spiked with 1.125  $\mu\text{g}$   $^{198}\text{Hg}$  into the overlying water on 12/11/02. Note that for this experiment, the isotopic Hg spike level was increased over the level used in the first dry/rewet experiment, in order to provide a signal farther above background.

Figs. 37 and 38 show the concentrations of native and isotopic Hg and MeHg in the top 4 cm of the sediment cores through time, after rewetting. For cores from both sites, native MeHg increased significantly within a week of rewetting dried cores, and stayed roughly the same over the next six weeks.  $\text{Me}^{198}\text{Hg}$  also increased, following the same pattern as native MeHg production. For cores taken from both sites, MeHg concentrations in cores held for 10 months before rewetting were similar to MeHg in cores held 2 months.



Fig. 39 shows the same data, plotted as %MeHg (MeHg/Hg X 100) for both native and excess  $^{198}\text{Hg}$ . Note the much higher production of both native and isotope spike MeHg at STA2 relative to 3A15. About 7% of the native Hg was methylated in one week in rewet STA2 cores in comparison with about 1% in the 3A15 cores. Also note that the isotope spike is methylation to a much larger extent than the native Hg at both sites. Almost 25% of the  $^{198}\text{Hg}$  spike was methylated during the first week after STA2 cores were rewet.

Native MeHg in the water overlying the cores increased significantly within a week of rewetting dried cores, and declined over the next six weeks (Fig. 40).  $\text{Me}^{198}\text{Hg}$  also increased, following the same pattern as native MeHg production. Concentrations of especially native MeHg were much higher in STA2 cores than in 3A15 cores, the same pattern seen in surface soils, where MeHg is presumably produced. Although MeHg concentrations in surface soils were similar for cores dried for 2 vs. 10 months, MeHg concentrations in water over the cores was much higher in the cores that were dried longer.

Fig. 41 shows sulfate concentrations in water overlying the cores, through time after rewetting. The sulfate concentration in the 3A15 surface water used to rewet cores was only 8.8  $\mu\text{M}$  (0.85 ppm). Therefore, essentially all of the sulfate in the water overlying cores derived from oxidation of reduced S within cores during drying. Note that sulfate was present immediately after rewetting, demonstrating the presence of sulfate in the dried cores before rewetting. After 1 week, sulfate concentrations were similar at both sites. Sulfate was depleted to essentially zero within 6 weeks of rewetting at both sites.

Low concentrations of sulfide accumulated in water over cores and in porewaters through time after rewetting (Fig. 42). The cores remained quite dry after rewetting, and never re-expanded horizontally to fill the core barrels. Low volumes (<5ml) of interstitial water could be obtained by siphoning off the overlying water and allowing the interstitial waters to drain out of the peat. These samples were used for sulfide analysis, since sulfide is a key factor in Hg bioavailability and methylation. Roughly 5-15  $\mu\text{M}$  sulfide accumulated in porewaters of the cores in the first week after rewetting, after which sulfide concentrations decrease. Sulfide concentrations in this range are ideal for Hg methylation in Everglades soils.

Overall, the 299-day drying experiment gave similar results as the 40-day drying experiment. High concentrations of sulfate accumulated during drying, fueling high levels of sulfate reduction and Hg methylation upon rewetting. In both experiments, Hg methylation occurred predominantly in the first week after rewetting. The release of sulfate did not appear to be significantly different after the longer drying period. Somewhat higher accumulation of MeHg in water overlying cores that had been dried for the longer time period may reflect other changes in chemistry through time during drying, e.g. DOC chemistry.

## 8. Conclusions and Recommendations for Mitigation

We hypothesized that MeHg production is stimulated in some rewet soils because oxidation of organic matter and of reduced sulfur pools in sediments during drying provides fuel for microbial sulfate reduction once soils are rewet. Preliminary data analysis supports this idea, with very large observed increases in sulfate concentrations in dried and rewet cores from both sites. Soils from both sites rewet very slowly, with rewetting still very incomplete after six weeks. Soils from 3A-15 were slightly easier to rewet. However, anoxia was fully developed in soils from both sites within 5 days of rewetting dried cores.

MeHg increased significantly in soils from both sites within a week of rewetting dried cores, and stayed roughly the same (or crept up slightly) over the next six weeks. Water column MeHg concentrations lagged a bit behind soil, as MeHg in water derived from production in and flux from soils. The pulse of MeHg production following rewetting was rapid, but MeHg concentrations in surface soils remained high for at least six weeks following rewet.

This study confirms that the high MeHg concentrations observed in STA-2 Cell 3 are a result of *in situ* production in surface soils immediately following rewetting. The soil chemistry at STA-2 Cell 1 is ideal for MeHg production, which is further fueled by the addition of high sulfate canal waters to the STA from EAA canal water runoff. *In situ* MeHg concentrations in the STA-2 soils were higher than the 4-year average for the ACME sites of highest MeHg production in the Everglades. The % MeHg in STA-2 cores after drying and rewetting substantially exceeded the average %MeHg for the high MeHg sites in the WCAs.

The most labile fraction of reduced sulfur in soils (AVS) was lost from soils from both sites during the first 40 days of drying. AVS began to build up again in 3A-15 cores about 6 weeks after rewetting, but not in STA-2 cores. Dissolved iron concentrations were somewhat higher in 3A-15 waters than STA-2 waters, which may account for lower dissolved sulfide concentrations and higher accumulation of AVS in rewet cores from 3A-15. Solid phase sulfur concentrations (*in situ* AVS and CRS) were very comparable at STA-2 and 3A-15, and both much lower than in northern WCA 2A or in the former ENR.

Nitrate and ammonium fluxes were observed after rewetting after 40 days of drying, but no significant phosphate flux was observed. In field observations after the drought and fire in June 1999, we observed some recycling of nitrogen species, but phosphate levels in the surface water after rewetting remained low. Thus, phosphorus does not appear to be as readily recycled after a brief drydown and rewet as nitrogen species. The 299-day dry/rewet experiment resulted in extensive remobilization of phosphorus, suggesting longer or more severe drying events are necessary to remobilize the phosphorus from the soils.

A number of steps can be taken to minimize the large MeHg pulses observed after dry/rewet events in the Everglades and STA's. Certainly sulfur appears to play a central role (along with mercury deposition) in generating these MeHg pulses. In the long run, implementation of BMP's for sulfur in the EAA will help to mitigate these kinds of events by reducing some of the large sulfur pools currently available in the ecosystem. In the short run, however, the best approach is to minimize the occurrence of drydown events. STA's, in particular, should be allowed sufficient water during drought periods to remain wet, even if only a few cm of water cover. Further study in STA's is needed in order to determine what STA's are more susceptible to MeHg production plumes during start up (initial wetting). An understanding of the factors involved in producing these MeHg pulses would facilitate the development of approaches to minimize the impact of these events. The ACME group with funding from the USGS and the Florida Department of Environmental Protection is planning on undertaking a study of STA's over the next several years to determine the factors important in producing dry/rewet MeHg plumes.

Table 1. Dry/rewet experiment time line.

<b><u>Date</u></b>	<b><u>Activity</u></b>
2/6/02 – 2/7/02	Sample multiple cores in PVC and Teflon tubes from sites 3A15 and STA2 Collect surface water in PETG bottles.
2/8/02 – 2/9/02	Drive samples to Maryland Sealed cores placed in 28 degree water bath at ANSERC.
2/13/02	Spike all cores with 201Hg Begin drying subset of cores (take off cover on all cores) Cores exposed to 12h light/dark cycle with “sunlight” bulbs.
2/14/02	Sample sediments, water and pore waters in wet controls (baseline) Begin 40 day and 299 day drydown experiments
2/14/02 – 3/27/02	40 day drydown experiment Refill wet cores and water controls weekly to maintain water level
3/27/02	Rewet dry cores from 40 day drydown experiment using site water.
3/27/02 – 5/13/02	Sample sediments, water and pore waters through time in rewet cores, wet controls, and water-only controls from 40 day drydown experiment. Refill cores weekly to maintain water level
6/1/02 – 12/1/02	Chemical analysis of surface water, porewater, and sediments from ambient sample collection (2/7/02) at WCA 3A-15 and STA-2 sites and from 40 day drydown experiment.
2/14/02 – 12/11/02	299 day drydown experiment Refill wet cores and water controls weekly to maintain water level
12/11/02	Rewet dry cores from 299 day drydown experiment using site water
12/11/02 – 1/31/03	Sample sediments, water and pore waters through time in rewet cores, wet controls, and water-only controls from 299 day drydown experiment. Refill cores weekly to maintain water level
2/1/03 – 6/1/03	Chemical analysis of surface water, porewater, and sediments from 299 day drydown experiment.