Appendix 7-14: Stormwater Treatment Area 1 West: Results of Start-Up Mercury Monitoring

Pete Rawlik

INTRODUCTION

Stormwater Treatment Area 1 (STA-1W), located in western Palm Beach County (**Figure A7-14-1**), is one of the six marshes being constructed that will use natural physical, chemical, and biological processes to remove excess nutrients, including total phosphorus (TP), from stormwater runoff prior to discharge into the Everglades. STA-1W is an expanded and modified version of the Everglades Nutrient Removal Project (ENR Project), the prototype STA constructed to demonstrate that large treatment marshes could remove nutrients on a regional watershed scale (For an overview of the ENR Project see Chimney and Moustafa, 1999). The original ENR Project was a 1545-hectare constructed wetland, divided into two treatment trains of two cells each. The revised structure of STA-1W includes the ENR project and adds Cell 5 at 1155.4 hectares. Source water to STA-1W will be from the C-51 canal and controlled by the S-5A pump station. Outflow waters will be discharged to the L-7 Canal located in Water Conservation Area-1, a Class III fresh water, an Outstanding Florida Water, and a national wildlife refuge.

Prior to construction of the ENR Project, concerns were raised that the flooding of former farmland could release inorganic mercury stored in the peat soil. This "first flush" could also result in a net export of substantial quantities of inorganic mercury and an increase in methylmercury production and bioaccumulation both within and downstream of the project resulting in a so-called "reservoir effect". The reservoir effect (Cox et al., 1979) recognizes that there is the potential for mercury to mobilize from newly flooded sediments and standing biomass into the water column and thus increase mercury concentrations and mercury methylation. In addition, because a wide variety of wildlife may be attracted to the newly flooded areas, the increase in methylmercury bioaccumulation could translate into increased exposure and risks to wading birds, including the endangered wood stork.

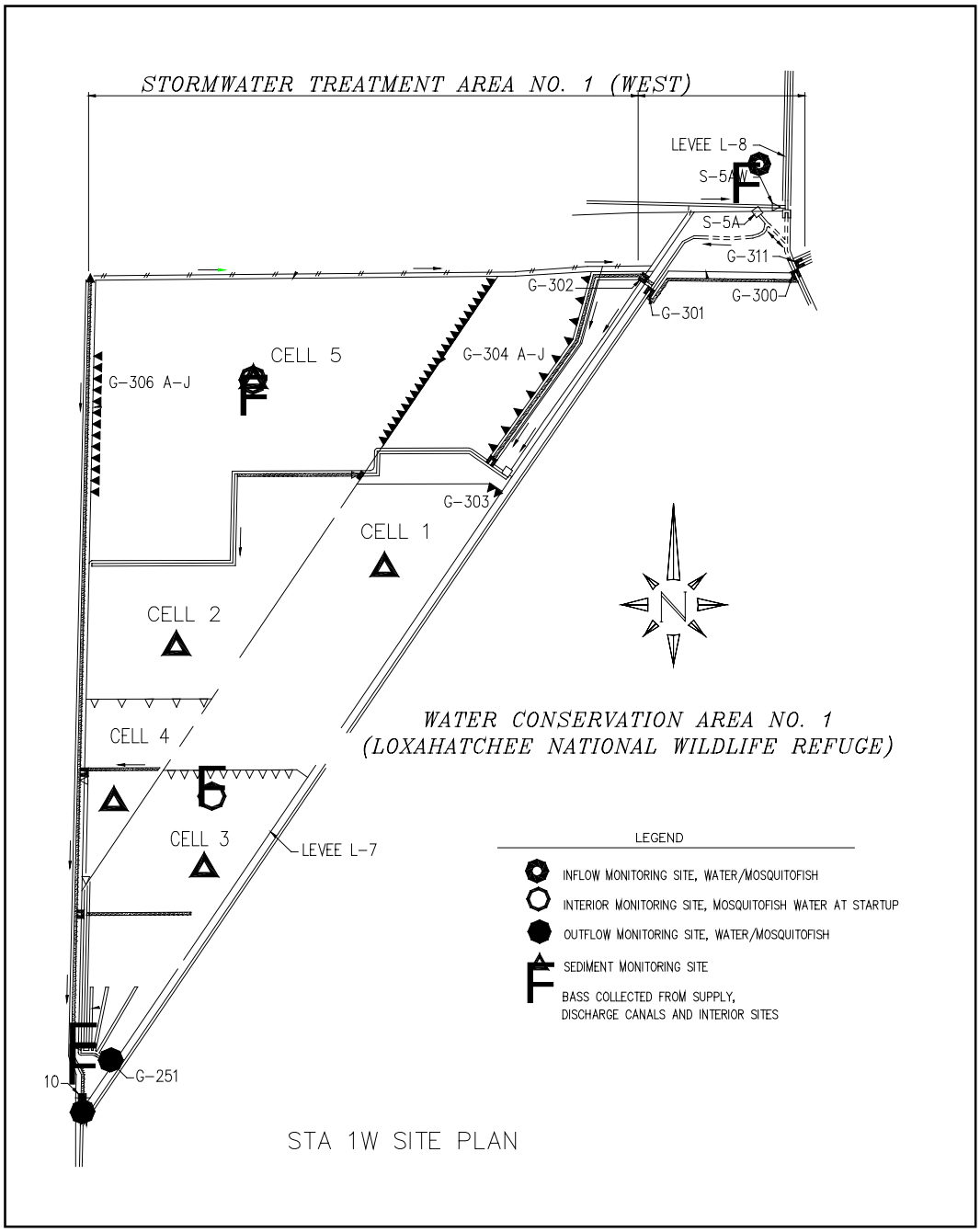

Figure A7-14-1. Map of STA 1 West.

Monitoring to track "first flush" and "reservoir effect" phenomenon in new STAs was mandated in the Florida state construction and operation permit. To meet permit criteria during the start-up period, the District collect unfiltered surface water samples for ultra-trace analysis of total mercury and methylmercury at the inflow and at the midpoint of the STA. For the purposes of STA-1W start-up it was determined that the original ENR Project was already operating as a treatment wetland, and in compliance with operational criteria. Consequently, it would only be necessary for Cell 5 to go through start-up. Under start-up criteria water was considered unacceptable for discharge as long as midpoint concentrations of mercury and phosphorus were significantly greater than inflow concentrations.

Cell 5 was flooded in March 1999 and start-up monitoring began in May 1999. Biweekly monitoring of unfiltered mercury sampling revealed high concentrations of both total mercury and methylmercury at the midpoint of Cell 5. Fearing that mercury concentrations could violate state water quality standards or increase risks to wildlife monitoring was expanded to include filtered water samples and a monthly collection of mosquitofish (*Gambusia affinis*) at the interior site. The collection of mosquitofish was supplemented by the semi-annual collection of fish carried out by the Florida Fish and Wildlife Service which also collected samples of largemouth bass (*Micropterus salmoides*) and sunfish (*Lepomis* spp.).

MATERIALS AND METHODS

SAMPLING SITE

Samples for Cell 5 were collected at one site in the western portion of the cell. This site represented the midpoint as required by the terms of the Florida State permit. While it can be argued that this site cannot possibly represent the entirety of the 1154.5 ha cell, for purposes of permit defined start-up criteria this single interior site serves exactly that purpose.

SOIL CORES

Prior to flooding of STA-1W Cell 5, soil cores were collected from STA-1W in January and February of 1999. Cores, greater than 10 cm in depth, were extracted by hand using polycarbonate tubes. Seven cores from six sites were collected. Five sites were within the area of STA-1W previously designated as the ENR Project. The remaining site the interior site of Cell 5. Two cores were collected from this site in order to provide information on spatial variability. Following collection, the top 10 cm of material was extracted and homogenized using a commercial blender. Homogenized samples were then frozen, placed in a cooler on ice, and shipped over night to the analytical laboratory for total mercury and methylmercury analysis.

SURFACE WATER

Initial surface water samples for comparing total mercury and methylmercury concentrations at the interior site of Cell 5 to the inflow site at S-5A were collected in May 1999. Routine biweekly monitoring of both sites was initiated in June 1999. However, due to logistical challenges associated with the project, including several hurricanes and tropical storms, some consecutive samples were as far apart

as 28 days or as close as 8 days. Only unfiltered samples were required to meet start-up permit requirements but beginning in July 1999 filtered samples were also collected.

Surface water samples were collected following "a clean hands – dirty hands" protocol, using a peristaltic pump and a sampling train primarily comprised of Teflon tubing with a small section of masterflex tubing for insertion into the peristaltic pump. Sampling trains were pre-cleaned to ultra-trace standards and bagged before use. A 0.45 micron capsule filter was used. All fittings were comprised of Teflon and pre-cleaned with the sampling train. Sample bottles were Teflon, and were also pre-cleaned to ultra-trace standards and double bagged before use.

Quality assurance samples including a field blank, a starting and ending equipment blank, a trip blank, and a field duplicate were routinely collected during each trip. Following collection, samples were placed on ice and shipped overnight for preservation and analysis. Preservation of samples was not carried out in the field because the SFWMD lacks a clean room and is therefore not capable of maintaining the proper storage of ultra-trace grade preservatives.

MOSQUITOFISH

Sampling for mercury concentrations in mosquitofish was initiated in June 1999 and was carried out on a monthly basis until January 2000. Samples were collected at or around the interior site by dipnet. Additional samples at the S-5A inflow structure were collected in October 1999 and March 2000. Mosquitofish were then homogenized using a commercial blender, and a ten-gram subsample was collected and frozen. Frozen homogenate subsamples were shipped overnight on blue ice to the analytical laboratory. Remaining sample was frozen and archived for future use.

SPORTFISH

Largemouth bass and sunfish were collected at the S-5A inflow structure and from the interior of Cell 5 in October of 1999 in cooperation with the Florida Fish and Wildlife Service (Lange, 2000). Since the density of these animals is extremely low, insufficient numbers exist to obtain all of the required samples at the interior site. Consequently, the sportfish samples were collected across the entirety of the cell. Individuals were filleted and frozen for storage and shipping pending sample analysis.

ANALYTICAL METHODS

Samples were analyzed for total mercury and methylmercury by the Florida Department of Environmental Protection (FDEP) using modified EPA methods 1631 and 1630, respectively. Appropriate quality assurance samples and procedures including equipment blanks, standard reference materials and laboratory replicates were analyzed to assure acceptable precision and accuracy. For a full review of the methodology see the SFWMD Comprehensive Quality Assurance Plan and the appropriate FDEP Laboratory Methods.

RESULTS

SOIL CORES

Results for total mercury and methylmercury in the top 10-cm soil cores collected from STA-1W are shown in **Table A7-14-1**. Quality assurance for the samples was generally good but there were some areas of concern. Due to a laboratory error, all samples except for those from Cell 5, were analyzed outside of stated holding times. Additionally, the majority of results for THg were below the practical quantitation limit for the method. Similarly, the majority of results for MeHg were below the method detection limit (0.002 ng/g). Finally, the field duplicate in Cell 5 generated results for MeHg that were outside the quality assurance criteria for reproducibility. This suggests that field variability in the system is relatively high, which is consistent with previous results.

Table A7-14-1. Mercury and methylmercury concentrations in the top 10 cm of sediment cores from STA-1W collected in January 1999.

Site	THg (ng/g)	MeHg (ng/g)
Cell 1	120	<0.002
Cell 2	67	<0.002
Cell 3	96	<0.002
Cell 3	140	0.002
Cell 4	110	<0.002
Cell 5	98	0.523
Cell 5 dup	89	0.341

WATER

Results for mercury monitoring of surface water samples are shown in **Figures A7-14-2** and **A7-14-3**. Following initial flooding, concentrations of total mercury and methylmercury in Cell 5 were ten-fold higher than the concentrations at S-5A. From June 1999, concentrations of both THg and MeHg fluctuated until September 1999.

In September MeHg concentrations at both sites dropped below 0.4 ng/L and appeared to stabilize. In contrast, THg concentrations at S-5A increased to more than 8 ng/L and continued to fluctuate while THg concentrations in Cell 5 decreased rapidly and remained below 4 ng/L. Analysis of filtered samples revealed that on average 50% of the THg in Cell 5 was sorbed to particulate material, with a range of 30 to 78%.

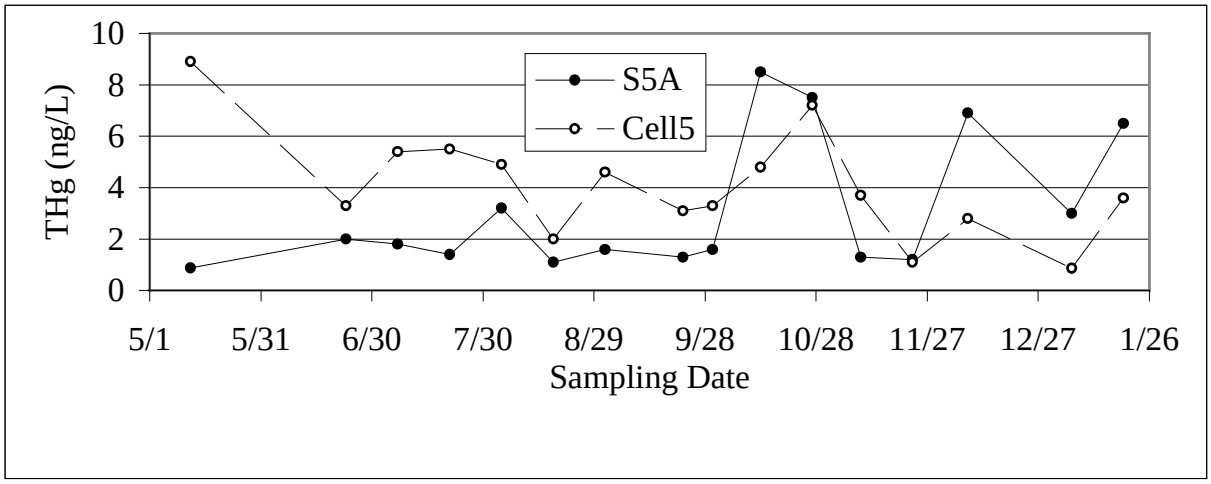

Figure A7-14-2. Unfiltered THg concentrations at S5-A and in Cell 5 during the start-up phase of STA-1W

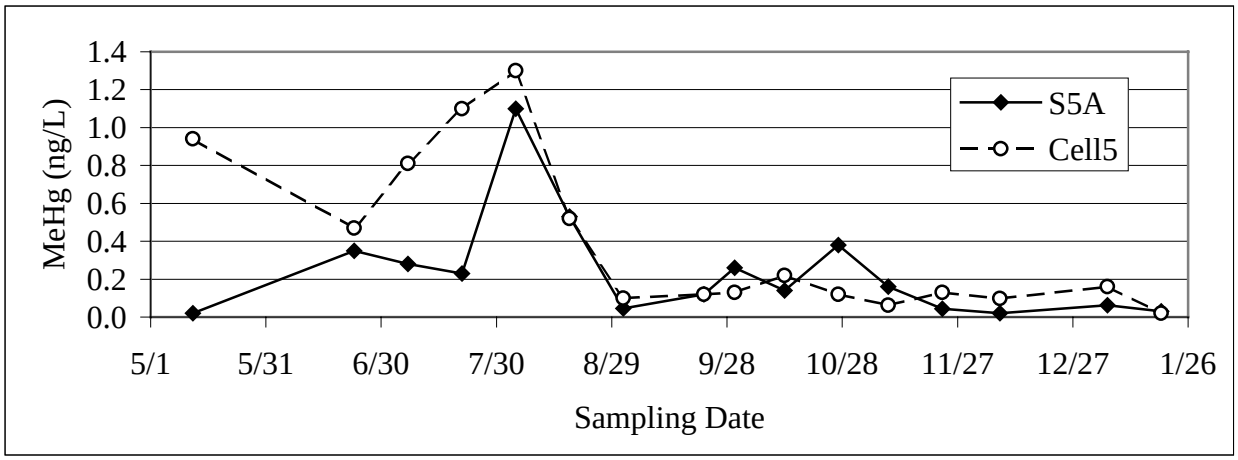

Figure A7-14-3. Unfiltered MeHg concentrations at S-5A and in Cell 5 during the start-up phase of STA-1W.

MOSQUITOFISH

Mercury concentrations in mosquitofish collected during the start-up period are shown in **Figure A7-14-4**. Initial concentrations of mercury in mosquitofish exceeded 100 ng/g wet-wt but declined to less than 50 ng/g, wet-wt by August and remained there for the duration of sampling. The total mercury concentration in S-5A mosquitofish for October was 150 ng/g, wet-wt but later in March the concentration declined to 33 ng/g, wet-wt.

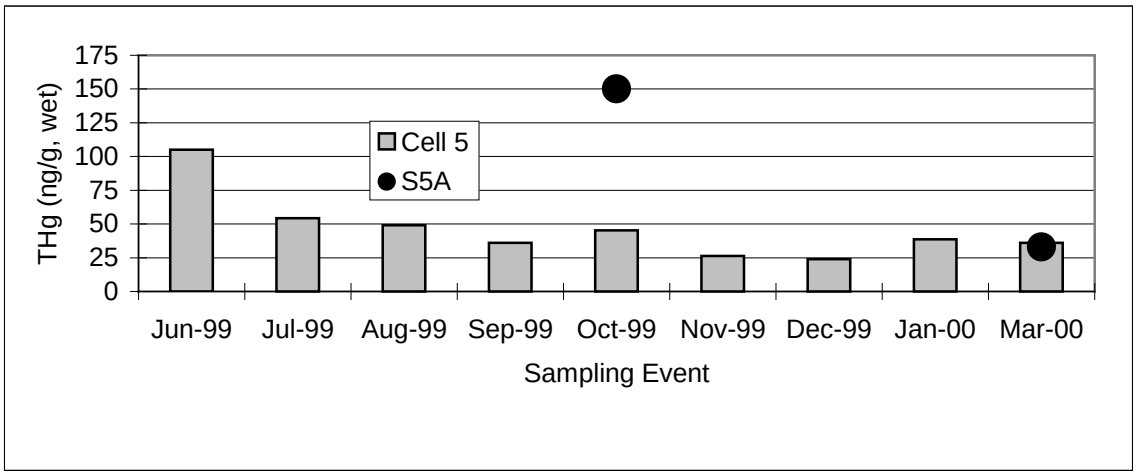

Figure A7-14-4. Mercury in mosquitofish homogenates from Cell 5 and the S5A Inflow Pump.

SPORTFISH

Results for total mercury concentrations in sportfish are shown in **Figure A7-14-5**. Individuals collected in Cell 5 were significantly smaller than those collected at S-5A, and this limits the comparability between the sites. Recognizing this limitation, the bass in Cell 5 had average THg concentrations of 240 mg/Kg, compared to an average of 270 mg/Kg in bass collected at S-5A. Sunfish in Cell 5 had average THg concentrations of 41.6 mg/Kg, compared to an average of 37.2 mg/Kg at S-5A.

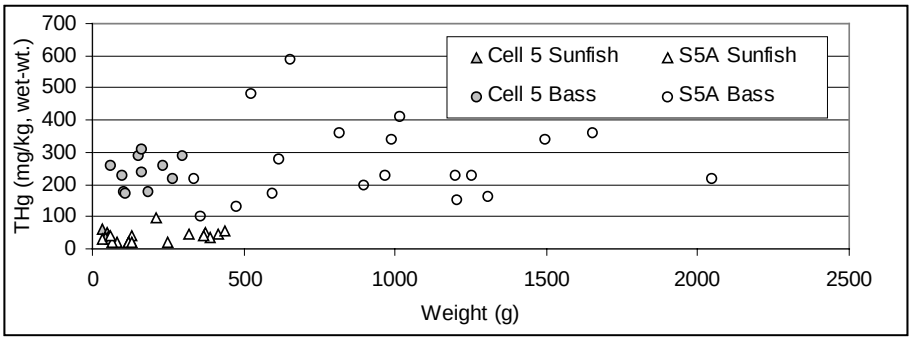

Figure A7-14-5. Total mercury concentrations in sportfish at S-5A and Cell 5.

DISCUSSION

It is likely that several factors combined to increase mercury concentrations in the water column of the newly flooded Cell 5. The primary factor is most likely release of inorganic mercury from sediments into the water column. The flooding of peat soils and vegetation releases organic material and nutrients, which are known to increase the rate of mercury methylation (Bisogni, 1979; Hecky et al., 1986). Sediment THg concentrations in Cell 5 were in the same range as concentrations reported for sediment cores prior to start-up of the ENR Project (Miles and Fink, 1998). However, the MeHg concentrations were high in comparison to concentrations reported for sediment cores prior to start-up of the ENR Project (Miles and Fink, 1998). Consequently, the amount of THg as MeHg in the Cell 5 cores was higher than that reported for the ENR Project (0.5% compared to 0.15% respectively). This analysis is complicated by the poor data quality of the Cell 5 samples.

Additionally, it is established that the flooding of acidic soils can reduce water pH, which has been found to influence methylation (Lodenius and Seppanen, 1984). While no soil pH measurements were taken during start-up, this factor cannot be ignored.

A secondary source may have been the standing dead vegetation that most certainly provided an additional source of mercury but also provided a source of readily available carbon and organic material to the water column (Morrison and Therien, 1996). Sulfate-reducing bacteria (SRB), the primary organism in mercury methylation, prefers anaerobic systems (Compeau and Bartha, 1985) and establishment of this community in decaying vegetation may be the source of the rising methylmercury concentrations from June through July.

Finally, a third source of mercury, atmospheric deposition, may have been a factor, particularly during the rainy season of July through September. THg concentrations in rain during the start-up period averaged nearly 18 ng/L (NADP, 2000). This value is more than twice the concentration in surface water inputs through the S-5A structure and thus could account for a significant load to the system.

Unfortunately, the full impact of these factors cannot be determined as mercury concentrations in the upper sediments were not monitored, nor was the amount of standing crop dead biomass determined before flooding. The amount of mercury contributed to the system by surface waters cannot be determined because the volume of water pumped and recirculated into the cell was never quantified. Consequently, the total load of mercury into Cell 5 from surface waters and rainfall cannot be estimated.

Decreases in MeHg concentrations beginning in August may have been driven by the increase in aquatic vegetation and periphyton in Cell 5. While such communities do provide areas for the development of anaerobic communities conducive to mercury methylating SRB (Cleckner et al., 1999), they also provide several benefits that may help to reduce mercury concentrations in the water column. Primary among these benefits is the absorption of mercury into the growing biomass which functionally removes mercury through biodilution (Hakanson, 1980). Additionally, the structure of these communities serves as a natural filter, removing particles from the water column (Tchonbanoglous et al., 1979). Finally, these communities function to reduce the effects of wind and other factors that result in

resuspension of settled particulate matter (Kristensen et al., 1992). Antecedent monitoring of the ENR Project found that the filterable component of THg was in the range of 0% to 17%, as compared to the filterable portion of the THg in Cell 5, which averaged 50%. The Cell 5 interior site values are therefore more comparable to results of antecedent monitoring at the inflow pump station (Miles and Fink, 1998) than in other cells.

Another possibility is sulfide inhibition of mercury methylation. No data on sufate or sulfide were collected during the start-up period but observations in other systems have suggested that the build up of sulfides can inhibit the methylation process and thus reduce methylmercury concentrations (Krabbenhoft and Fink, 2001).

The mean concentrations of total mercury in Cell 5 mosquitofish appear high when compared to results from antecedent monitoring in the adjacent ENR Project, which were normally below 25 ng/g, wet wt (Fink, 2000). However, if the concentration of total mercury in mosquitofish collected in October 1999 at S-5A is representative of fish entering the project, then the trends in the interior fish represent a reduction in concentrations and relative improvement.

Similarly, the results of the THg analysis of sportfish in Cell 5 are not substantially different from the results from samples collected at S-5A. As such, there is no evidence to suggest that residing in Cell 5 has increased THg concentrations in sportfish. However, the exact date when these individuals entered the cell is uncertain, and cannot have a residence time of more than several months. Consequently, these individuals may not have resided in Cell 5 long enough for elevated mercury levels to pass up the food chain. Additionally, all individuals collected in Cell 5 were relatively small compared to individuals at S-5A. Lange et al. (1998) has shown that largemouth bass less than 300 mm in length feed on different prey than larger individuals with the occurrence of small prey such as bluefin killifish, mosquitofish and grass shrimp decreasing with age. As the concentration of mercury in mosquitofish decreased following the initial peak in July 1999, there is no reason to expect to see elevated mercury levels in largemouth bass.

CONCLUSIONS

Based on the surface water data, there is sufficient evidence to suggest that following flooding, large quantities of THg and MeHg were released to the water column. This release elevated THg concentrations in Cell 5 over those at S-5A. The source of this mercury is unknown but could be sediments, vegetation, rainfall, or some combination of the three. Additionally, the increase in interior water MeHg concentrations over those at S-5A in May 1999 suggest that methylation was occurring in Cell 5. Based on the Cell 5 data, it would appear that methylation was elevating the methylmercury concentrations in the water column through July. However, S-5A samples in August through September suggest that MeHg in Cell 5 was similar to MeHg at S-5A. This would seem to indicate that either S-5A was the primary source of MeHg to Cell 5, or similar processes were occurring at both sites. Fish, particularly mosquitofish, did not show elevated mercury concentrations in Cell 5 compared to S-5A. In fact, Cell 5 mosquitofish show a general decreasing trend over time. However, the data at S-5A is limited and may not be comparable to the more extensive data from Cell 5.

LITERATURE CITED

Bisogni, J.j., Jr. 1979. Kinetics of methylmercury formation and decomposition in aquatic environments, In: The Biogeochemistry of Mercury in the Environment, Nriagu, J. O., Ed., Elsevier, North Holland, Amsterdam.

Chimney, M. J., and M. Z. Moustafa. 1999. Effectiveness and Optimization of Stormwater Treatment Areas for Phosphorus Removal, Chapter 6, In: Everglades Interim Report, SFWMD, W. Palm Beach, FL, USA.

Cleckner, L.B., C.C. Gilmour, J.P. Hurley, and D.P. Krabbenhoft. 1999. Mercury methylation in periphyton of the Florida Everglades. Limno. Oceanogr. 44(7).

Compeau, G. and R. Bartha. 1985. Sulfate-reducing bacteria: principle methylators of mercury in anoxic estuarine sediment, Appl. Environ. Microbiol. 50.

Cox, J.A., J. Carnahan, J. Dinunzio, J. McCoy, and J. Meister. 1979. Source of mercury in new impoundments. Bull. Environ. Contam. Toxicol. 23.

Fink, L. 2000. ENR project mercury studies: 1994-1999, Appendix 7-5, In: Everglades Consolidated Report, SFWMD, W. Palm Beach, FL, USA.

Hakanson, L. 1980. The quantitative impact of pH, bioproduction and Hg-contamination on the Hg-content of fish (pike). Environ. Pollut. (Series B) 1.

Hecky, R.E., R.A. Bodaly, D.J. Ramsey, and N.E. Strange. 1986. Enhancement of mercury bioaccumulation in fish by flooded terrestrial materials in experimental ecosystems, Canada-Manitoba Agreement on the Study and monitoring of Mercury in the Churchill River Diversion, Appendix.

Kristensen, P., M. Sondergaard, and E. Jeppesen. 1992. Resuspension in a shallow eutrophic lake, Hydrobiologia, 228.

Lange, T.R., D.A. Richard, and H.E Royals. 1998. Trophic relationships of mercury bioaccumulation in fish from the Florida Everglades. FGFWFC, Eustis, FL, USA.

Lodenius, M., and A. Seppanen. 1984. Binding of mercury to aquatic humus, Vatten, 40.

Miles, C.J., and L.E. Fink. 1998. Monitoring and mass budget for mercury in the Everglades Nutrient Removal Project. Archives of Environ. Contam. and Toxicol. 35(4).

Morrison, K.A., and N. Therien. 1994. Mercury release and transformation from flooded vegetation and soils: experimental evaluation and simulation modeling, In Mercury Pollution: Integration and Synthesis: Watras, C. J. and J. W. Huckabee, Eds, Lewis, Boca Raton, FL, USA.

National Atmospheric Deposition Program (NRSP-3)/Mercury Deposition Network. (2000). NADP Program Office, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820.

Tchonbanoglous, G., R. Stowell, R. Ludwig, J. Colt, and A. Knight. 1979. Aquaculture systems for wastewater treatment: Seminar Proceedings and Engineering Assessment. EPA 430/9-80-006, R.K. Bastian and S.C. Reed, Eds.