

Appendix 1-3: Comments on the Draft *2010 South Florida Environmental Report – Volume I* from Outside Persons and Organizations

In September 2009, these comments were provided publicly on the District's SFER WebBoard 2 (www.sfwmd.gov/webboards). With the exception of reformatting some information for better readability, this appendix was not edited or spellchecked by the SFER production staff and appears verbatim as posted on the WebBoard.

COMMENTS ON THE DRAFT 2010 SFER – VOLUME I, CHAPTER 1

Reviewer: Florida Department of Environmental Protection

Subject: FDEP Comments on Draft Chapter 1

Posted: 13 Oct 2009 07:29 AM

Florida Department of Environmental Protection¹
October 12, 2009

Chapter 1:

Line 224: Replace 34 with 35

¹ Florida Department of Environmental Protection, Division of Environmental Assessment and Restoration, Restoration Planning and Permitting Program, Tallahassee, FL

COMMENTS ON THE DRAFT 2010 SFER – VOLUME I, CHAPTER 3A

Reviewer: Florida Department of Environmental Protection

Subject: FDEP Comments on Draft Chapter 3, Appendix 3A-8

Posted: 13 Oct 2009 07:38 AM

Florida Department of Environmental Protection¹
October 12, 2009

Appendix 3A-8:

From App. 3A-8 Header inconsistencies...should be “2010 SFER” instead of “2009”. Reporting inconsistencies (compared to the C-111 EO monitoring table) in this version. DO excursions increased for WY2009. In WY2009, about 73% of the DO concentrations were below the 5 mg/L standard, compared to around 60% in WY2008 and CY2007. Please provide an explanation.

COMMENTS ON THE DRAFT 2010 SFER – VOLUME I, CHAPTER 3B

Reviewer: Tom DeBusk, DB Environmental, Inc.

Subject: Comments on Chapter 3B

Posted: 23 Sep 2009 02:36 PM

Comments on SFER Chapter 3B: Mercury and Sulfur Monitoring, Research and Environmental Assessment in South Florida

Tom DeBusk

DB Environmental, Inc.

September 23, 2009

DB Environmental, Inc. (DBE) has just completed its first year of work on a three-year research program designed to evaluate the potential effects of sulfate on phosphorus (P) cycling and plant toxicity in Everglades marshes and in the Stormwater Treatment Areas (STAs). This project is being jointly funded by the South Florida Water Management District (SFWMD) and the Everglades Agricultural Area Environmental Protection District (EAA-EPD). We have just completed the Final Report for Task 2, in which we characterized sulfate amendment effects on the release of P from laboratory-incubated soils collected from Water Conservation Areas (WCAs) 2 and 3, as well as from STAs 2 and 5. The report should be available to the Review Panel members upon request (Mark Gabriel of the SFWMD is the Project Manager). For convenience, I have attached the report's Executive Summary (Item A, below) as part of my comments.

While a description of our initial research also is provided in the current SFER under Appendix 3B-2, (*An Evaluation of the Role of Sulfur in South Florida Wetland – Laboratory Incubation Findings*, by Woody Dierberg), I believe it would be useful for a synopsis of results to be provided in the summary of the main 3B chapter, under the heading of **New Findings**, since the results call into question the previously-accepted hypothesis that elevated sulfate levels will stimulate P release from WCA and STA soils.

Additionally, I am unclear as to why the cover of Appendix 3B-2 has a disclaimer stating that our project results do not reflect the views of the state agencies (SFWMD and FDEP). Our research project has been reviewed exhaustively from both a QA/QC and technical standpoint (numerous internal SFWMD reviews, one outside academic review and one international expert review); project updates are provided to sponsors on a continuous basis (monthly or bi-monthly meetings during the past year); and a manuscript is in preparation, with a SFWMD staff member as a co-author. In summary, our research methodology and findings have been transparent and extensively peer-reviewed.

One potential concern recently expressed to me is that our results contradict some of the findings of the ACME research team's mesocosm studies in WCA-3A. Our methods and results are available to public scrutiny at any time. It would be most helpful if the ACME investigators would similarly agree to allow public review of their methodologies and results, since I believe such an effort would resolve the discrepancies in findings between the two research teams. I would like to note that in the interest of better understanding sulfate effects on P cycling in south Florida wetlands, we previously have requested access to detailed ACME findings, as outlined in my comments on Chapter 3B of the 2009 SFER (Item B, below). To date, however, no additional information has been provided.

Item A: Executive Summary from Task 2 of DBE's Initial (Task 2) Research

This report presents the results of laboratory incubations (Task 2) designed to test the potential effects of elevated water column sulfate levels on microbial respiration and P release for soils collected from unimpacted and impacted wetlands in south Florida. Soils from four separate sites (WCA-3A, WCA-2A site U3, STA-2 and STA-5), ranging from low P and low sulfate to high P and high sulfate environments, were examined. The soils were subjected to anaerobic laboratory incubations to evaluate P release and organic matter decomposition in response to sulfate amendments (0.33 mM [0.32 mg/L] or 1.0 mM [96 mg/L]).

Three processes have been invoked in the literature as to why sulfate enrichment can lead to P release from soils under anaerobic conditions:

- Alkalinization (leads to more favorable pH environment for decomposition)
- Higher electron acceptor concentrations (leads to higher rates of decomposition)
- Formation of FeS_x compounds (mobilizes Fe-associated P)

For the wetland soils examined, alkalinization due to the hydrogen ion-consuming reaction of sulfate reduction was not an overriding process. We found that pH decreased in the incubation vessels, and that increases in alkalinity were more attributable to CaCO_3 dissolution than sulfate reduction. Moreover, all the soils exhibited near circum-neutral pH levels, with moderate to high concentrations of native alkalinity.

Amending the soils with sulfate did not result in either more microbial respiration as measured by CO_2 and CH_4 gas emissions, or increased P mobilization. This implies that an addition of 0.33 or 1.0 mM of sulfate did not translate into meaningful enhanced decomposition of organic matter, likely due to limitations imposed by substrate quality and low P in the oligotrophic WCAs. In the more enriched STA sites, where P release did occur during anaerobic incubation, sulfate enrichment still did not result in more net P release because the source of P was likely due to dissolution of an inorganic substrate (CaCO_3) that was sensitive to soil solution acidity. Neither oxidation-reduction potential (ORP) nor electron acceptor concentrations, as influenced by sulfate additions, would be expected to accelerate CaCO_3 dissolution and associated P release.

Soils from only one of the study sites (WCA-3A) had iron (Fe) concentrations (0.73 – 1.0%) that would be expected to be high enough to be associated with substantial levels of soil P. Porewater Fe:SRP ratios ($> 83:1$ wt/wt) observed at this site suggest that Fe theoretically could be controlling the release of P from the soil. However, the available P pools in the soil at this site were too low to result in a measurable response in this P-limited environment.

The lack of a P response to sulfate amendments observed in the incubation studies are in agreement with findings from long-term field monitoring efforts. For example, after a prolonged history (over 40 years) of sulfate enrichment in WCA-2A, surface water and porewater P concentrations are not elevated at U3, a site which historically has been considered relatively pristine, exhibiting little P enrichment and a balanced biological community.

The results from other research platforms, including field-scale mesocosms and chemical gradient analyses in STAs, which are designed to further explore the effects of elevated sulfate levels on P release from soils and to examine the toxicity of sulfide on plant communities and species, will be presented in future reports.

Item B: Previous Comments (last year) by Tom DeBusk on the 2009 SFER Chapter 3B: Mercury and Sulfur Monitoring, Research and Environmental Assessment in South Florida

Based on several years of monitoring data, it is clear that surface water sulfate concentrations are elevated in certain regions of the northern Everglades Protection Area due to historical discharges of runoff and lake waters. Additionally, as noted on page 3B-19, areas in the northwest portion of WCA-2A that recently have received STA-2 discharges for hydropattern restoration are exhibiting increases in sulfate levels. Areas of WCA-2A that previously exhibited water column sulfate concentrations of 4 – 12 mg/L now display concentrations of 52 – 78 mg/L.

What is not well understood is the impact, if any, of these elevated sulfate concentrations on MeHg production, wetland P retention, and health of aquatic biota. The implication from page 3B-18 is that extremely low surface water sulfate levels are required to minimize potential adverse effects of sulfate. The Chapter 3B authors state: “At the CERP goal of 1 mg/L sulfate in Everglades surface water, data indicate that microbial sulfate reduction and MeHg production rates would be low due to sulfate limitation, and sediment porewater sulfide levels would only be in the tens of µg/L, minimizing both sulfide toxicity to aquatic plants and animals and internal eutrophication – phosphate and ammonia release from sediments (Gilmour et al., 2007 a, b).”

While numerous scientific studies have shown that the presence of sulfate in freshwater marsh waters *can* stimulate MeHg formation, sediment release of ammonium and P, as well as cause toxic effects to biota (all a consequence of sulfide formation), the minimum sulfate concentration (or range of concentrations) that will cause these adverse effects in the Everglades marshes remains unknown.

For example, in their development of the P criterion in the early 2000s, FDEP classified site U3 in the interior of WCA-2A as a “reference” site, since it provides both a desirable assemblage of “balanced” biota (plant communities extremely sensitive to P enrichment, such as calcareous periphyton and bladderworts), and low water column TP concentrations (10 µg/L). It should be noted that site U3 has received water inputs with sulfate levels of 40 – 50 mg/L for decades, but still exhibits the desirable biological and chemical characteristics of a balanced and pristine south Florida freshwater marsh. Therefore, if sulfate indeed causes adverse effects on P cycling and plant toxicity in south Florida marshes, the effects undoubtedly occur at concentrations substantially higher (by more than 50X) than the 1 mg/L concentration suggested on page 3B-18.

Similarly, the chapter authors note the increased sulfate levels in the hydropattern restoration area in the NW of WCA-2A, but provide no additional information related to resulting biological or chemical impacts. The SFWMD is conducting monitoring to evaluate effects of STA-2 discharges on water and soil chemistry and biota in this area. Their most recent report (Garrett and Ivanoff 2008) states: “ In summary, these results indicate that there have been improvements at several previously nutrient impacted sites, i.e., areas with soil TP > 500 mg/kg, and there was generally no negative impact at previously unimpacted sites in WCA-2A resulting from STA-2 discharge. The benefits include increased hydroperiod and improved water quality, as evidenced by decreased surface water TP, steady soil TP concentrations, increased relative abundances of low nutrient periphyton indicator species, decreased relative abundances of high nutrient periphyton indicator species, and decreased nutrient content in periphyton tissues.”

The existing data from WCA-2A northwestern and central interior sites therefore demonstrate that sulfate in the water column at concentrations exceeding 50 mg/L can result in elevated porewater sulfide levels, but adverse impacts to wetland P cycling or to biota have not been demonstrated.

In 2008, the SFWMD initiated a three-year research program to address these discrepancies between “theoretical” impacts of sulfate and actual impacts to P cycling and plant toxicity in Stormwater Treatment Areas and Everglades marshes, and a description of this effort (Projects #1

– 3) is provided on pages 3B–25 and 3B-26. Additional data on sulfate effects are likely available from the USGS and Smithsonian scientists that comprise the Aquatic Cycling of Mercury in the Everglades (ACME) project team. These scientists have studied mercury cycling in the Everglades since 1995. In a description of their prior efforts (page 3B-27) it is noted: “.....the second component of the study is a series of field mesocosm experiments designed to test cause and effects hypotheses. Additions to mesocosms have included mercury, sulfate, DOC and phosphate. Mesocosm experiments have been run in WCA-1, WCA-2 and WCA-3, the most detailed sulfate and DOC addition studies were carried out at site 3A-15, WCA-3A.”

We are very interested in the ACME team’s findings from the mesocosms at site 3A-15, but have found the reported results inconclusive. We have submitted repeated requests for the raw data so that we could study the experimental design and findings in more detail. To date, the ACME group has released only a small subset of data, which represents only partial results from selected experiments. Our analysis of these raw data packages has not provided needed answers, but rather has raised several concerns about the experimental design and laboratory procedures used by the ACME (USGS/Smithsonian) research team.

The first package of data contained copies of two contracts (between SFWMD and the Smithsonian, and FDEP and the Smithsonian), a brief report from the USGS (Chemical Results of Laboratory Dry/Rewet Experiments Conducted on Wetland Soils from Two Sites in the Everglades, Florida), and raw laboratory bench sheets and instrument printouts that appear to be from the Dry/Rewet Experiments. We have developed a list of analytes and sample locations from the bench/instrument sheets that were included in the package (**Table 1**).

Table 1. Analytes, sample locations, and dates of analyses pertaining to the Smithsonian/USGS Dry/Rewet Experiments.

Analyte(s)	Sample Location	Date of Analyses
Ammonium & Phosphate	STA-2	Feb-April 2002
Anions (Sulfate)	STA-2; WCA3A15	April-July 2002
Ammonium & Phosphate	STA-2; WCA3A15	June 2002
Phosphate	STA-2; WCA3A15	Feb 2003
Anions (Sulfate)	STA-1W; STA-2; STA $\frac{3}{4}$; STA-6	May 2006
Ammonium & Phosphate	STA-1W; STA-2; STA $\frac{3}{4}$; STA-6	May-June 2006
Anions (Sulfate)	STA-2; WCA3A15	April-Sept 2006
Ammonium & Phosphate	STA-1W; STA-2; STA $\frac{3}{4}$; STA-6	Aug-Sept 2006

Our review of the laboratory bench sheets and instrument printouts suggest that the USGS laboratory(s) failed to adhere to a number of critical QA/QC requirements. One possibility is that USGS excluded QA/QC information from the information request. However, many of the QA/QC protocols (i.e, spikes, duplicates, continuing check standards) typically are embedded in the analytical runs, and therefore should show up in the types of printouts that were provided in the data package. A summary of key QA/QC procedures that USGS apparently did not perform (i.e., not included in the package) is provided below.

THE FOLLOWING NATIONAL ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM (NELAP) - OR FDEP-APPROVED QA/QC COMPONENTS WERE NOT INCLUDED IN THE DATA PACKAGE:

1. Chain-of-custody (COC) was not provided. This is a very significant component of NELAP-approved QA/QC. The COC sheet tracks the route taken by a set of samples from the time of collection to their final destination at the lab. It also lists the persons responsible for each leg of the journey and provides evidence as to the preserved state of the samples when they arrived at the lab (e.g., sample temperature if ice melted; acid preservative added by taking pH of sample). Given the distances from south Florida and the number of labs that the samples were shipped to, proof of timely arrival and proper sample preservation, with no accidental or purposeful tampering during the shipment, is essential.
2. No secondary check standard was performed in any of the analyses. The secondary standard is from a source other than the one that is used for the standard curve. The secondary standard provides a check on the accuracy of the primary standard.
3. No addition of a known analyte to a sample matrix (i.e., spike recovery) was performed on any of the analyses. A spiked sample with a known amount of the analyte indicates whether there are positive or negative chemical interferences present in the sample matrix.
4. No continuing check standards (CCS) were performed on any of the analytical runs with the exception of the sulfate analysis from April-Sept. 2006. The appropriate frequency is a minimum of 5% (1 for every 20 samples) or at least once if sample number is less than 20. The CCS provides assurance that the instrument and chemistry during the complete analytical run have not been compromised.
5. Laboratory blanks (distilled or de-ionized water) were not always run at a minimum frequency of 5% (1 for every 20 samples) or at least once if sample number is less than 20. This ensures that there has not been contamination introduced by the lab water, reagents, or glassware.

Due to the profound management implications of the sulfur and mercury research performed by the ACME group, we recommend that they make raw data available to interested parties, and also facilitate a documentation review by FDEP and SFWMD QA/QC personnel to ensure appropriate quality assurance protocols were followed during their monitoring and experimental efforts in south Florida marshes.

A second information release from USGS raised concerns about the mesocosm design and operational procedures used at site 3A-15. The investigators used a series of mesocosms to spike constituents such as sulfate into the water over a range of concentrations, and chemical and biological constituents in the water column and sediments subsequently were monitored over time to characterize the responses, such as MeHg and sulfide formation.

Based on the information release, each of the mesocosms apparently was totally isolated from the surrounding environment (i.e., there were no planned water exchanges with the outside environment at pre-determined intervals). During prolonged periods of constant water stages in WCA-3A, the mesocosms therefore would remain stagnant, with no exchange of water with the surrounding wetland. During periods of stage increases in WCA-3A (onset of the wet season), however, the elevated water levels outside the mesocosms would cause water to be pushed upward through the sediments into the mesocosm. Similarly, when water stages in WCA-3A were dropped, water would flow out the bottom of the mesocosms through the sediments, so that internal water levels could equilibrate with the surroundings.

For mesocosms to be effective in addressing “cause and effect” hypotheses, considerable care is needed with respect to design and operations to ensure that the small-scale systems accurately mimic conditions in the natural wetland. Because many of the processes of interest (e.g., sulfide formation) occur in the sediments and at the sediment-water interface, the operational approach utilized for the 3A-15 mesocosms appears questionable. A more thorough analysis of these findings, with respect to chemistry changes during prolonged stagnant periods, and during periods of rapid stage changes (and consequently, rapid bulk flow through the sediments), would help clarify the validity and representativeness of their findings.

References

- Garrett, B. and D. Ivanoff. 2008. Hydropattern Restoration in Water Conservation Area 2A. Report in fulfillment of Permit #0126704-001-GL (STA-2). Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.
- Gilmour, C.C, D. Krabbenhoft, W. Orem, G. Aiken and E. Roden. 2007a. Appendix 3B-2. Status Report on ACME Studies on the Control of Mercury Methylation and Bioaccumulation in the Everglades. In: 2007 South Florida Environmental Report – Volume I. South Florida Water Management District, West Palm Beach, FL.
- Gilmour, C.C, W. Orem, D. Krabbenhoft, and I.A. Mendelssohn. 2007b. Appendix 3B-3. Preliminary Assessment of Sulfur Sources, Trends and Effects in the Everglades. In: 2007 South Florida Environmental Report – Volume I. South Florida Water Management District, West Palm Beach, FL.

Reviewer: Victor Bierman, LimnoTech

Subject: LimnoTech Comments on Chapter 3B

Posted: 23 Sep 2009 07:09 PM

This post consists of two attached files. The first file contains LimnoTech comments on Chapter 3B and the second file contains comments on the consensus points and some of the unanswered questions from the Second Annual Workshop on Mercury and Sulfur in South Florida Wetlands, SFWMD, June 11-12, 2009. A brief summary of this workshop appears in Chapter 3B.

September 23, 2009

Comments on

2010 Draft South Florida Environmental Report

Chapter 3B: Mercury and Sulfur Monitoring, Research and Environmental Assessment in South Florida

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CHAPTER 3B SUMMARY

A synopsis of the mercury and sulfur problem in the Everglades is provided in the summary. Chapter 3B builds on the previous SFER reports with emphasis on results from the most recent monitoring and new findings. The ecological problems posed by sulfur (i.e., mercury methylation, internal eutrophication and plant toxicity) in the Everglades are introduced. Considerable research and monitoring has been conducted to better understand mercury-sulfur interactions. It should be noted that the research on S related issues other than mercury, promoted by the South Florida Water Management District (SFWMD) and the Florida Department of Environmental Protection (FDEP), is still in its early stages.

It was stated that fish Hg concentrations in the Water Conservation Areas (WCAs) have declined markedly from the late 1980s to the early 1990s. An important question is whether there had been a substantial decrease in the atmospheric Hg loading during the same time period. Total Hg deposition in South Florida does not appear to show a declining trend (Appendix 3B-1). Other factors that may have caused the decline in fish Hg should be considered and discussed in this report.

Appendix 3B-1 of this chapter reports that the conditions are generally improving with regard to fish Hg in the downstream receiving waters and that the generally-observed spatial gradient in fish Hg increasing from south to north is disappearing. This is an encouraging sign towards recovery. However, fish Hg found in the WCAs still continue to be in excess of the human health criterion of 0.3 mg/kg MeHg. Further south of WCAs, the Everglades National Park (ENP) continues to exhibit high levels of fish Hg. It is interesting to note that the ENP, despite containing sulfate concentrations several-fold lower than the WCAs, shows higher Hg

bioaccumulation in fish. Further evaluation of the various controlling factors for Hg bioaccumulation in the ENP, Shark River Slough in particular, should be conducted. It has been suggested that higher sulfate levels would enhance and lower sulfate levels would reduce, respectively, Hg bioaccumulation in the Everglades. It has also been argued that a reduction in sulfate loads would only result in overall benefit to the ecosystem. However, a linear relationship between Hg bioaccumulation in the Everglades and sulfate loads has not been demonstrated.

Hydro pattern restoration and best management practice (BMP) in the Everglades Agriculture Area (EAA) are suggested as options for mitigating the MeHg problem. In this regard, the FDEP and SFWMD have identified multiple research needs to better understand S sources and overall S processes in the EAA. This is a positive aspect and will also help further the understanding of Hg-S interactions in the Everglades.

NEW FINDINGS

This section provides a summary of the recent findings on Hg in fish in the Everglades

Protection Area (EPA) including the WCAs and regions north of EPA. In the WCAs, it was encouraging to note that system-wide median Hg concentrations in largemouth bass (LMB) have declined 62% since 1988. However, annual median values indicate that the human health fish consumption criterion of 0.3 mg/kg (Environmental Protection Agency) remains to be met for 50% of the all the LMB collected since 1998. The sample size has increased substantially from 1988 (n = 12) to 2008 (n = 241). It would be useful to provide the sample sizes in parentheses with the various years to better interpret Figure 3B-2.

A discussion of the factors that contributed to the long-term MeHg decline in LMB in WCAs should be included in this chapter or its appendices. In the region north of EPA, including the Kissimmee basin, Hg impairment due to bioaccumulation in fish has been observed, but to a lesser extent compared to EPA. It is notable that the lowest median LMB concentration of 0.23 mg/kg for the period of record occurred during 2008. In Shark River Slough, higher levels of Hg were found in fish, including mosquitofish, sunfish, and LMB, compared to other locations in the EPA. This raises an important question as discussed earlier: Why are the levels of Hg in fish higher in Shark River Slough than elsewhere in the EPA?

MERCURY IN FISH – CURRENT YEAR SAMPLING

Fish Collection, Analysis and Mercury Concentration Normalization

Average Hg concentrations in LMB were used to evaluate spatial patterns in Hg bioaccumulation across EPA and in regions north of EPA. While this comparative approach provides some useful information, it should be realized that there may be considerable differences in food web structure and feeding ecology of LMBs, and in nutrient dynamics, that can influence Hg bioaccumulation.

Mercury levels in LMB were standardized to an expected age-3 Hg concentration (EHg3) to interpret results. While it is a common practice to normalize Hg concentrations for evaluations of spatial and temporal patterns, the underlying assumptions regarding EHg3 standardization in this study need to be clarified. For example, spatial variability in growth rates and food sources of LMB across EPA can confound interpretation of EHg3 normalized results. Furthermore, three year-old fish can exhibit a range of sizes and lipid content. There should be some discussion of the residual uncertainties in these EHg3 results.

Trends in the Everglades Protection Area

Long-term LMB concentrations were compared for WCAs, the ENP and the region north of EPA. Substantially higher Hg bioaccumulation was observed in the ENP, and 2008 median LMB Hg concentrations were much larger than those in the WCA and the region north of EPA. Of the three regions, only the WCAs have shown a declining trend over the long-term and ENP

exhibited the largest variations in median LMB Hg concentrations. Despite no apparent longterm trend, LMB Hg exposure appears to be relatively lower for the region north of EPA compared to the WCAs.

The observed pattern in Shark River slough provides a case to better understand the processes controlling Hg methylation and bioaccumulation. Some description of hydropattern in ENP would help to better understand the high Hg bioaccumulation pattern. If ENP exhibits natural wetting and drying cycles combined with low sulfate concentrations (i.e., less influenced by canal influx), then the observed trend in this region may provide some indication of how the WCAs might respond to hydropattern restoration in combination with the reduced sulfate loads scenario. It is also possible that the growth rates of LMB in ENP may be slower and thus they may accumulate more Hg per unit body mass over time compared to WCAs. In any case, the factors controlling Hg bioaccumulation in the ENP warrant further investigation.

Site Specific Trends

The site specific long-term plots show that for all WCA sites minimum concentrations of EHg3 in LMB occurred between 1999 and 2009 and maximum concentrations for all WCAs generally occurred during the early 1990s (period of record: early 1990s to 2009). Notably, most recent EHg3 concentrations remained below 0.3 mg/kg (EPA criterion for human health) at site WCA 3A. However, it should be noted that average concentrations instead of the standardized EHg3 concentrations were reported for this site due to lack of a significant relationship.

Page 3B-9, Line 285 – year 2008 should be corrected to 2009. Table 3B-2 indicates that the period of record (POR) for most sites ends in 2008, but the plots indicate POR extending up to 2009 (e.g., Figure 3B-6, 3B-4, 3B-8 and 3B-10). For the HOLEY site, the general upward trend observed in recent years appears to be on the downturn for two consecutive years (2008 and 2009). Data for two sites in ENP, ENPLOT and ENPNP, were reported. Site ENPNP which is located in Shark River Slough continues to follow the historically high EHg3. Both sites continue to exhibit EHg3 levels above 0.5 mg/kg.

The STA site (STA1WC3) has exhibited the lowest LMB EHg3 levels compared to any sites in the EPA. LMB EHg3 never reached the 0.3 mg/kg limit at this site during the entire period of record (1995 - 2008). Also, Appendix 5-6 presents some interesting fish Hg monitoring results in STAs. It appears that STAs that are highly efficient in P removal (including STA2 and STA1W) exhibited the lowest fish Hg levels compared to low performing STAs (e.g., STA5). Phosphorus retention that promotes productivity and biodilution may be controlling Hg exposure in the STAs. This should be further investigated. Page 3B-20 – Figure 3B-15 should be labeled as 3B-13.

SECOND ANNUAL WORKSHOP ON MERCURY AND SULFUR IN SOUTH FLORIDA WETLANDS

Draft Notes from the Second Annual Workshop on Mercury and Sulfur in South Florida Wetlands were prepared by Dr. Mark Gabriel, South Florida Water Management District. These draft notes and all workshop presentations are on the workshop website

(http://my.sfwmd.gov/pls/portal/docs/PAGE/PG_GRP_SFWMD_ERA/PORTLET_REP ORTS/TAB4712183/mercury/index.html).

The draft notes contain a bulletized list of consensus points related to mercury and sulfur in the Everglades and a bulletized list of unanswered questions. In a separate posting on the WebBoard, LimnoTech has provided comments on these consensus points and some of the unanswered questions.

SULFUR LEVELS, SOURCES, AND EFFECTS ON THE EVERGLADES

This section has elaborate details on S dynamics in the Everglades and EAA in particular, compared to the previous 2009 SFER. It is asserted that the predominant pathway of sulfur influx to the WCAs is through canal transport. The sources of high canal sulfate appear to originate in the EAA. Historical sulfur usage in the EAA stems from the fact that S is an important plant nutrient and S application is used as a soil amendment to increase crop yield. Current levels of S application (30 – 100 lb/ac) in the EAA are several-fold less than the recommended application rate (300 – 500 lb/ac). Management of S inputs from the EAA is being considered as an option by the FDEP and SFWMD to mitigate the observed Hg burden in fish across the Everglades.

Sulfate is an important substrate for the production of MeHg through biological processes. However, it is also well known that a number of other factors control the MeHg production including sulfide, pH, organic carbon, temperature and anoxia. It is the complex interaction of these factors that influences the conversion of ionic Hg to MeHg. Organic carbon can favor or hinder methylation by controlling the bioavailability of both Hg and sulfate. Elevated sulfide levels can form cinnabar and charged Hg-S complexes and lead to the inhibition of methylation.

A great deal of knowledge has been gained with regard to Hg, S and organic carbon interactions in the Everglades over the years through controlled experiments and field scale studies. The Everglades is a spatially heterogeneous system and its ecological conditions vary markedly. The complexity of the ecosystem needs to be considered when attempting to upscale the knowledge obtained from field-based and controlled experimental studies to the Everglades as a whole.

Site 3A-15, formerly a MeHg hotspot, is currently showing substantial declines in MeHg and fish Hg levels with a concomitant decline in sulfate concentrations. It was inferred in this report that reducing sulfate load would yield similar results in other parts of the Everglades. The case presented in site 3A-15 may not hold true for elsewhere in the Everglades. To the contrary, sites ENPNP in Shark River Slough and LNWR in interior marshes of Loxahatchee exhibit comparatively low sulfate concentrations but show elevated bioaccumulation in fish.

While sulfate influences the production of MeHg, the bioaccumulation of Hg in fish is strongly influenced by factors that do not necessarily control MeHg production. A recent analysis by Liu et al. (2009) indicates that the spatial variation in soil MeHg and mosquito fish Hg do not overlap. In another assessment of water quality and fish mercury data, Pollman (2008) found that Lakes Tohopekaliga and East Tohopekaliga, located north of EPA, both exhibited nearly similar levels of sulfate concentration. However, LMB Hg levels differed with comparatively higher levels in Lake East Tohopekaliga. Pollman suggested that differences in water quality along with other factors may be contributing to the observed differences in fish Hg. The spatial heterogeneity of MeHg bioaccumulation and Hg and sulfate concentrations in the Everglades needs to be addressed within a conceptual framework that can satisfactorily explain the influence of the various confounding factors.

It was asserted that atmospheric sources of Hg to the Everglades originate predominantly from global sources rather than local. This statement is not well supported. Considerable uncertainty still exists regarding the contribution of local and continental sources.

Apart from Hg issue, concerns regarding other ecological effects of elevated sulfate were implied in this report including liberation of nutrients from soils and higher sulfide levels leading to plant toxicity. Studies conducted in the Everglades do not show clear evidence of sulfate-induced phosphorous liberation in soils. An incubation study (reported in Appendix 3B-2) conducted on different Everglades soils showed no mobilization of P occurred at higher sulfate treatment levels. A preliminary study focusing on sulfide toxicity, presented at the Second

Annual Workshop on Mercury and Sulfur in South Florida Wetlands, showed that the tolerance levels for sulfide toxicity may vary among different plant species in the Everglades.

Annual mass fluxes of sulfur entering and leaving the EAA were provided for three years: a wet year (2004), an intermediate year (2003) and a dry year (2007). Sulfur loads to the EAA included canal inflows from Lake Okeechobee, soil oxidation, atmospheric deposition and agricultural application. Sulfur losses from the EAA included canal outflow and removal from harvesting of crops. Except for the dry year (2007) canal sulfur flux exported from the EAA (into the WCAs) was several times greater than the canal influx to the EAA from Lake Okeechobee. Soil oxidation within EAA appears to be a significant sulfur source (31,000 metric tons) to the WCAs. Current agriculture application (6,000 metric tons) and atmospheric deposition (3,000 metric tons) appear to be relatively minor sources to the EAA.

Canal sources and atmospheric deposition of S can be constrained because they are based on direct measurements. However, other fluxes including soil oxidation were based on indirect estimates or literature values and are therefore much more uncertain. In order to better understand S dynamics in the EAA, several information needs and recommendations are identified in this report. Some highlights of these recommendations include a higher resolution sampling framework, better quantification of current soil oxidation and agricultural application rates of S, quantification of groundwater S inputs, and assessment of cost effectiveness of BMPs for the EAA.

Beyond the proposed recommendations, the details and the different components of the planned BMPs with regard to the S in the EAA should be outlined. Although the EAA seems to be a major source to WCAs, the contribution from current agriculture application is relatively small. Sulfur is a plant macronutrient. If BMPs require optimizing S application, then they should be implemented in a way that satisfies plant requirements while minimizing environmental impacts. Soil oxidation, which is a less manageable source, appears to be releasing substantial amounts of S from the EAA. The components of BMPs in the EAA that would result in reduced S load to the WCAs should be evaluated.

The report states that efforts are underway to compile and synthesize ACME data and provide open public access to these data. We strongly support the effort in bringing these data into the public domain. This will allow external review and evaluations of ACME experimental design and data, and facilitate better-informed inputs to the process of developing restoration and management options for the EPA.

Regional Sulfur Mass Balance Study

In the regional mass balance study, source-sink characteristics are quantified for four major land use areas: WCA1, WCA2, Lake Okeechobee and the EAA. Annual fluxes from different compartments were evaluated for three years with varying precipitation (wet, intermediate and dry year). Canal transport is the largest mass transport pathway for the WCAs and Lake Okeechobee. WCA2 appears to be a sulfur sink during all three precipitation years. WCA1 varied between being a sulfur sink during wet and dry years, and a sulfur source during the intermediate precipitation year. The EAA was predominantly a source of sulfur. These initial mass balance estimates provide a better understanding of source/sink characteristics of different land use areas in the Everglades. However, work should continue to further refine these initial mass balance results.

Sulfur fluxes pertaining to biogenic gas emission and water column oxidation in Lake Okeechobee should also be quantified. Although a challenging task, soil oxidation within the EAA soils should be better quantified by direct measurements rather than relying only on literature values. This could be accomplished by actual measurements of soil oxidation in the EAA during varying moisture conditions. Alternatively, a pilot scale S mass balance study could

be undertaken in one of the STAs where other S flux components could be quantified and soil oxidation flux could be determined by difference. Knowledge gained from such a pilot study could then potentially be applied on larger scales in the Everglades.

It is not clear why soil oxidation in WCAs was not included in the mass balance calculation. If soil oxidation in WCAs had already been known to be not significant, then it should be mentioned in the report. Otherwise, future refinements in sulfur mass balances should consider quantifying soil oxidation in WCAs. There was no explanation offered as to why WCA3 was excluded from the S mass balance. We suggest that efforts be made to include WCA3 in future S mass balance studies. Future refinements in mass balance should consider potential contributions from ground water S inputs to the WCAs and EAA.

September 23, 2009
Comments on
Points of Consensus and Unanswered Questions
from
Second Annual Workshop on Mercury and Sulfur in South Florida Wetlands
June 11-12, 2009, South Florida Water Management District, West Palm Beach, Florida

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INTRODUCTION

Draft Notes from the Second Annual Workshop on Mercury and Sulfur in South Florida Wetlands were prepared by Dr. Mark Gabriel, South Florida Water Management District. These draft notes and all workshop presentations are on the workshop website

(http://my.sfwmd.gov/pls/portal/docs/PAGE/PG_GRP_SFWMD_ERA/PORTLET_REPORTS/TAB4712183/mercury/index.html).

The draft notes contain a bulletized list of consensus points related to mercury and sulfur in the Everglades and a bulletized list of unanswered questions. Below are LimnoTech comments on these consensus points and some of the unanswered questions.

POINTS OF CONSENSUS AMONG WORKSHOP ATTENDEES

○ *Potential sulfur sources in the Everglades include atmospheric deposition, agricultural runoff, groundwater, canals, and other sources.*

Comment: Yes, there was consensus on this point. It should be noted that the contributions from these different sources are not well quantified, but it was recognized that further research is needed on such quantification.

○ *Increased sulfate concentrations in surface water increases the rate of mercury methylation, which can lead to bioaccumulation of mercury in fish to levels that are unsafe for human consumption. Sulfate may also contribute to the release of phosphorus from sediments.*

Comment: Yes, there was consensus that increased sulfate concentrations in surface water increases the rate of mercury methylation. Whether or not sulfate contributes to the release of P from sediments still remains unresolved, and there was no consensus on this item.

○ *Under certain conditions, sulfate can be converted to sulfide, which can be toxic to some aquatic plants. Sulfide also inhibits the production of methylmercury.*

Comment: Hydroponic experiments on cattail and sawgrass indicate that sulfide can be toxic to these species. Sulfide toxicity to other plant species in the Everglades is not known. There was consensus, based on mesocosm studies, that higher sulfide levels can inhibit the production of methylmercury.

○ *Sulfate has been used as an agricultural amendment for centuries to improve crop yields. Current application rates in the Everglades Agricultural Area are much lower than in the past.*

Comment: Yes, there was consensus on this point.

○ *The atmospheric deposition rates of mercury in South Florida are the highest in the country, although rainfall is comparable to other areas of the country. This may be related to larger convective systems (e.g., taller thunderhead clouds) that reach higher elevations in the atmosphere.*

Comment: Yes, there was consensus on this point.

○ *Atmospheric deposition is most likely from international sources; local air emission sources have significantly decreased in the past 10 to 15 years. Therefore, it is more feasible to realize short-term reductions in sulfur inputs to the Everglades by addressing surface water inflows than global air emissions.*

Comment: It is not clear whether these statements on “deposition” and “emission” sources are referring to sulfate or mercury. The reader was led to assume that “atmospheric deposition” and “emission” refers to mercury and that the “surface water” component refers to sulfate. There was no clear evidence presented at the workshop that the source of mercury deposited in South Florida originates from international sources. Emission inventories indicate that local sources have declined over the last decade. Despite declines in local Hg emission, statistical analyses conducted by Dave Krabbenhoft (USGS) indicate that Hg deposition has not been declining in South Florida. Therefore, it can be inferred that international sources may be influencing Hg deposition in the Everglades. But this assertion remains speculative and requires further investigation. The contribution of different sources to atmospheric Hg deposition was not a specific discussion topic at the workshop. There was no basis to conclude there was consensus among workshop attendees that atmospheric Hg deposition to South Florida originates from international sources.

○ *Sulfur is present at much higher levels than phosphorus in the South Florida environment.*

Comment: Yes, there was consensus on this point.

○ *Current Stormwater Treatment Areas (STAs) are designed to remove phosphorus from surface water inflows. Typical STA performance is about 70 percent removal of phosphorus and 11 percent removal of sulfur.*

Comment: Yes, there was consensus on this point.

○ *The Everglades is a unique ecosystem with unique environmental issues not seen elsewhere in the United States or other countries. The Netherlands shares some water management and flooding concerns. Mercury and sulfur interactions have been studied at some locations in the United States.*

Comment: Yes, there was consensus on this point. Mercury and sulfur interactions are being investigated in the Everglades. However, other ecological effects of sulfur in the Everglades are not clearly understood. The unique settings of the Everglades present a challenge in understanding ecosystems processes and functioning.

UNANSWERED QUESTIONS

○ *What are the current agricultural sulfur application practices and soil oxidation/subsidence rates? (Parties need to team with the Institute of Food and Agricultural Sciences [IFAS] to quantify the “Everglades Agriculture Area [EAA] black box”).*

○ *How long would it take to flush out existing legacy sulfur in soils and surface water? 10 years? 100 years? 1000 years? (If current agricultural rates account for only 5 to 10 percent of sulfur export from the EAA, it may not be possible to reach a critical input level to the*

Everglades even by eliminating 100 percent of farm runoff. Therefore, funding for corrective measures should consider cost vs. potential benefits. Is it feasible to improve the restoration of the Everglades with a reduction of sulfur inflows?)

Comment: These are important questions that need to be resolved for restoration of the Everglades. Cost-effective restoration measures will depend on knowing the relative contributions of sulfur inputs from current agricultural applications versus those from “flushing out” sulfur from the existing legacy pool in the soils. Another issue is that it may not be possible to identify source waters with sufficiently low sulfate concentrations that can be delivered to the Everglades and meet a critical sulfur input level.

○ *Is there a viable solution for limiting sulfur impacts by implementing best management practices on farms or in canals?*

Comment: This question cannot be answered without a better understanding of the various sources of sulfur.

○ *Is carbon farming in rotation with sugarcane crops a viable alternative to build up wetland soils?*

○ *Is groundwater a significant source of sulfur in the Everglades? How does groundwater move from north to south in the Everglades?*

Comment: Future research should include emphasis on groundwater discharge zones, surface water and shallow groundwater interactions, and contributions from shallow versus deep groundwater sources.

○ *What is the role of limestone in mobilizing sulfur in groundwater?*

○ *What causes different bioaccumulation rates in fish when exposed to methylmercury in sediments versus surface water?*

○ *What is the effect of sulfate on phosphorus mobilization?*

○ *Can STAs be modified to enhance their ability to remove sulfur?*

○ *What is the mechanism for increased mercury methylation when rewetting occurs after dryout of an STA or marsh?*

Comment: Perhaps the mechanism is the oxidation of organic matter and sulfide, resulting in substrate availability, which in turn enhances the production of methylmercury. Other potential mechanisms that may be unique to the Everglades should be investigated.

○ *What are the water column dynamics that influence sulfide release and mercury methylation in the porewater and surface water?*

COMMENTS ON THE DRAFT 2010 SFER – VOLUME I, CHAPTER 4

Reviewer: Florida Department of Environmental Protection

Subject: FDEP Comments on Chapter 4

Posted: 13 Oct 2009 07:31 AM

Florida Department of Environmental Protection¹
October 12, 2009

Chapter 4:

Table 4-1: Six sub watersheds identified within the table show observed measurements above the baseline average. Are the observed measurements above the max for the baseline POR? If so, should there be a discussion as to why these areas are above the baseline average/max? On the flip side, is there discussion as to why the other basins are performing better than the baseline average?

Table 4-2: Is instrumentation proposed at the Boynton basin to capture discharges.

Line 511: There is a discussion of two primary components. FDEP has many components associated with its NPDES program. This should have some sort of context included within it.

Line 523 to 525: This should be revised to state that water bodies that do not meet the associated criteria may be identified as impaired for particular pollutants, should those pollutants not be considered naturally occurring at levels other than the criteria in the water body (i.e., site specific criteria may apply).

Line 570-571: Should be revised to read “The FDEP was scheduled to submit the final numeric nutrient criteria rule package to the USEPA for review and approval by December 2009. However, FDEP has recently suspended formal rulemaking procedures.”

Line 778-779: Please elaborate on the suspected reasons for the differences in the Indian Prairie sub-watershed.

Line 1845-1846: Is there any idea why?

Line 1864-1867: Is there an anticipated date of completion?

COMMENTS ON THE DRAFT 2010 SFER – VOLUME I, CHAPTER 5

Reviewer: Florida Department of Environmental Protection

Subject: FDEP Comments on Draft Chapter 5

Posted: 13 Oct 2009 07:33 AM

Florida Department of Environmental Protection¹
October 12, 2009

Chapter 5:

Line 19-23: Please explain what the additional 20,000 acres (65k -45k) of STA is used for.

Line 35-37: This statement is repeated from the previous line.

Table 5-2: Based on flow calculations, revisions to the STA-6 portion of the table and the chapter text may be warranted.

Table 5-2: Where do we explain the 3 year 50 ppb compliance with associated facilities?

Line 473-542: Revise language where appropriate.

Table 5-31: How is the District proposing to meet the goals identified in the table? Should a similar table and description included for STA-1W and 6 (or maybe 5/6)? If STA-1W is on the way to recovery and no further action is proposed, this should be stated.