Peer Review Report on the Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands
June 21-22, 2011, South Florida Water Management District, West Palm Beach, Florida

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Introduction:

The Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands was held June 21-22, 2011. The designated peer reviewer, Dr. William M. Landing, participated in the workshop and helped moderate the discussion session on Day 2, as required under Task 1 of the peer review contract.

Fifteen talks were presented at the workshop, covering many aspects of the research on mercury and sulfur in South Florida wetlands. The presentations are available at: http://sfwmd.websitetoolbox.com/?forum=187005. It is necessary to register a free account to access this web site. Talks by USGS personnel (Orem, Krabbenhoft, and Aiken) are not included due to USGS agency restrictions on release of preliminary data.

Part 1 of this report represents a review of the SFWMD Sulfur Action Plan (2009), as required under Task 2(1) of the peer review contract. All of the presentations are reviewed in Part 2 of this report. Recommendations for Future Research are also summarized in Part 2, as required under Task 2(2) of the peer review contract.

The agenda for the meeting is attached as Appendix I. The attendees are listed in Appendix II. The Statement of Work for the peer review of this workshop by Dr. William M. Landing is attached as Appendix III. Responses to the comments from SFWMD staff on the draft peer review report are attached as Appendix IV.

Part 1: Report on the SFWMD Sulfur Action Plan (dated 4/20/09):

The Project Charter for the SFWMD Sulfur Action Plan was signed in April 2009 and identified four specific projects.

Project 1. Internal Eutrophication Study. The following data gaps and management questions were identified in
https://my.sfwmd.gov/portal/page/portal/common/pdf/sd_modeling_scientific.pdf

STA/WCA Internal Eutrophication Study

1. Determine effects of elevated water column sulfate levels on microbial respiration and phosphorous release, using soils collected from un-impacted and impacted wetlands (with respect to both phosphorus and sulfur in South Florida.
2. Evaluate plant toxicity and phosphorus cycling effects for various water, vegetation, and soil types.
3. Assess spatial and temporal variations in sediment pore water phosphorus and sulfur chemistry, and effects on wetland vegetation.

In the 2008 document: DETAILED PROJECT PLAN: AN EVALUATION OF THE ROLE OF SULFATE IN SOUTH FLORIDA WETLANDS. Prepared by: DB Environmental, Inc., the Project Approach states:

To elucidate the role of sulfur in P release, organic matter decomposition and phytotoxicity, we propose to conduct:

1. Laboratory screening trials to determine effects of elevated water column sulfate levels on microbial respiration and P release, using soils collected from un-impacted and impacted wetlands (with respect to both P and S) in south Florida.
2. Mesocosm studies to evaluate plant toxicity and P cycling effects for a number of water, vegetation and soil types.
3. Field monitoring to assess spatial and temporal variations in surface water and sediment pore water P and S chemistry, and effects on wetland vegetation.

This study is described in greater detail in Gabriel et al. (2010) and results from the first set of laboratory incubation experiments with sulfate-amended soil slurries conducted in 2009 are discussed. Results from 2010 are described by Axelrad et al. (2011).

Two presentations were made at the Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands (June 21-22, 2011) by Forest Dierberg and Tom DeBusk of DB Environmental related to this project. In the conclusions from his presentation “Dryout-Reflood Impacts on Spatial Gradients and Temporal Variations in Surface and Pore Water Chemistry in a South Florida (USA) Stormwater Treatment Area”, Dierberg stated that “Strong spatial surface water, pore water, and soil P concentration gradients exist in STA-2 Cell 1. Based on field pore water concentrations and sulfate amended intact lab core incubations, there appears to be no direct causal relationship between sulfide concentration/production and SRP concentration/mobilization. Prior to a prolonged dryout in 2009, STA-2 Cell 1 attained annual outflow TP concentrations of 11 µg/L for 7 years even though sulfate inflow concentrations were > 57 mg/L each of those years. Despite high PW sulfide levels in the outflow region of STA-2 Cell 1, surface and PW SRP levels are low; we would expect a comparable response in the downstream marsh (western WCA-2A) waters and soils.”

In the conclusions from his presentation on “Effects of Sulfate Dosing on Phosphorus Mobilization and Vegetation in WCA-3A Enclosures”, DeBusk concluded that, ”We have established two approaches for addressing potential impairment by sulfate of marsh biogeochemical function and biodiversity. In enclosed surface waters of WCA-3A with sulfate dosing (12 – 48 mg/L), dosing has caused gradual increases in [sulfide], and reductions in dissolved [iron]. For pore waters, 24 and 48 mg/L doses of sulfate have increased [sulfate] and [sulfide], and decreased ORP and diss. [iron]. After 7 months of sulfate dosing, no increase in SW or PW [nutrients] was observed. Research will be continued for additional wet seasons. Regarding sawgrass leaf elongation monitoring in the field, initial field data demonstrates sawgrass growth not impacted by high sulfide environments – oxidized rhizosphere probably results in lower [sulfide] adjacent to roots than predicted by nearby PW sulfide measurements.”

One journal article has been published from this research (Dierberg et al., 2011) and another article has been submitted. In the published paper, they concluded, “For the soils examined here, alkalinization due to the hydrogen ion consuming reaction of SO4 reduction was not a prominent mechanism. We found that pH decreased in the incubation vessels, and that increases in alkalinity were more likely attributable to calcium carbonate dissolution than SO4 reduction. Moreover, all the soils exhibited near circum-neutral pH levels, with moderate to high concentrations of native alkalinity. Second, formation of iron sulfide (FeSx) compounds has been shown to mobilize iron (Fe)-associated P. Soils from only one of the study sites had Fe concentrations that would be expected to be high enough to influence P mobility. Relatively high pore water Fe:soluble reactive P (SRP) ratios (>83:1) were observed at this site, which suggests that Fe could theoretically exert control over the release of P from the soil. However, soil P levels at this site were too low to measure any substantial influence of Fe on net P mobilization. Finally, availability of electron acceptors such as SO4 is a major determinant of decomposition rate, and thus rate of organic P release. Amending the soils with SO4 did not result in either more heterotrophic microbial respiration as measured by carbon dioxide (CO2) and methane (CH4) production, or increased net P mobilization. In two of the SO4-amended soils where post-incubation total sulfide concentrations were as high as 23.4 mg per liter, SO4 addition reduced production of respiratory carbon end products, suggesting hydrogen sulfide inhibition. Moreover, limitations imposed by substrate quality and low P contributed to the lack of meaningful enhanced decomposition of organic matter with the addition of 32 or 96 mg SO4 per liter to the oligotrophic wetland soils. Even though P release did occur under anaerobic conditions for the more enriched site, addition of SO4 did not enhance P release. The lack of a soil P mobilization response with SO4 enrichment during anaerobic incubations is due to a combination of biogeochemical factors present in the northern Everglades marsh and STA soils. These include high alkalinity, P-limited and C-limited substrates, low Fe-associated P pools, sulfide inhibition, and dissolution of an inorganic substrate (CaCO3) associated with P. Results from the laboratory incubations are consistent with the historical record collected at SO4-enriched WCA-2A U3. While further investigations on SO4 impacts using controlled field mesocosms are underway, our laboratory findings demonstrate that SO4 enrichment neither enhances the mobilization of soil P in northern Everglades soils, nor impairs soil P retention of the STA."

The results of these experiments, as represented by the authors, indicate that the "internal eutrophication" phenomenon whereby addition of sulfate to soils or sediments leads to release of phosphate is not significant in the STA or WCA they studied. Sulfide toxicity effects on the macrophyte community (favoring cattails over sawgrass) were also not conclusively demonstrated.

Project 2. Regional Sulfur Mass Balance:

For the Regional Sulfur Mass Balance Study, the following data gaps and management questions were identified in:
(https://my.sfwmd.gov/portal/page/portal/common/pdf/sd_modeling_scientific.pdf)

1. Determine the mass exchange of total sulfur between the four main land-use areas (Everglades Agricultural Area, Lake Okeechobee, Water Conservation Areas, the eastern shore urban area in South Florida) and how exchanges vary annually by dry and wet season.
2. Determine the approximate percent sulfur loss/gain from physical and biogeochemical processes.
3. Evaluate the sulfur retention/source characteristics of the STAs.
4. Evaluate how exchanges vary over three separate years 2004 (a high precipitation year), 2007 (a low precipitation year), and 2006 (an intermediate scenario).

5. Investigate potential influence of all sulfur sources; for example, cattle grazing areas, suburban, and urban areas that practice fertilizer application, and areas with intense animal operations.

Results from this project were reported by Mark Gabriel on June 12, 2009 at the 2nd Annual Workshop on Mercury and Sulfur in South Florida Wetlands:
http://my.**sfwmd**.gov/portal/page/...**sfwmd**.../gabriel_hgsworkshop.ppt
The results are also summarized in the Gabriel et al. (2010) South Florida Environmental Report:
http://www.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_sfer/tab2236037/2010%20report/v1/chapters/v1_ch3B.pdf.

The status of sulfur inputs and cycling in the greater Everglades (including the EAA) was recently reviewed by Orem et al. (2011). Additional findings from research on this project are discussed in Axelrad et al. (2011). However, as will be discussed below under Future Research Needs, efforts to construct sulfur mass balances for Lake Okeechobee, the EAA, the STAs, and the WCAs have met with limited success. There are significant gaps in our ability to accurately predict how reductions in sulfate loading to the EAA from Lake Okeechobee, or from the release of sulfate from soil oxidation in the EAA, or from applications of agricultural sulfur in the EAA will reduce sulfate input to the downstream WCAs and the ENP. There are still significant policy questions (with respect to agricultural practices and water management practices) to be addressed, although it is clear that the vast majority of the sulfate reaching the WCAs and the ENP passes through the EAA and the STAs. Despite the many uncertainties that remain, it is safe to conclude that reductions in sulfur loading to the EAA ought to result in less sulfate reaching the WCAs and the ENP.

No information was presented at the workshop regarding sulfur mass balance research for Lake Okeechobee, the WCAs, or the eastern shore urban area in South Florida, although such data are presented by Gabriel et al. (2010), Orem et al (2011), and Corrales et al. (2011). Canal outflow of sulfate is the dominant loss term from the EAA to the WCAs and from the WCAs to the ENP, while atmospheric deposition and biogenic emissions (output) are the smallest terms (Gabriel et al., 2010; Axelrad et al., 2011). Sulfate reduction and retention as sedimentary sulfide and organic sulfides are the dominant internal removal mechanisms in these areas.

Regarding item (2), the sulfur mass balance in the EAA presented in Corrales et al. (2011), and reviewed by Orem et al. at the workshop, suggests that a biogeochemical process (soil oxidation) is one of the dominant factors in mobilizing sulfur from the EAA to the downstream areas (30,646-54,127 metric tons per year). However, the sulfur isotopic composition of sulfate in canals draining the EAA and from sulfur in the upper 10 cm of EAA soils is consistent with the sulfur isotopic composition of agricultural sulfur (Orem et al., 2011), suggesting that much of the sulfate released from soil oxidation is “legacy” sulfur from agricultural applications in the past. Prior to development as agricultural land, the areas south of Lake Okeechobee were accumulating peat soil with presumably relatively low sulfur content.

Input of sulfate from Lake Okeechobee is comparable to that released via soil oxidation, although this input term is complicated by the process of runoff and “back-pumping” from the EAA, accounting for perhaps 36% to 50% of the sulfate loading to the lake (Orem et al., 2011). Orem et al. (2011) state that “Since 1985, annual net exports of sulfate from the lake have exceeded imports from the EAA in most years. As a result, during the period of record for water-quality data collection (1974–2006), Lake Okeechobee represents a modest net input of sulfate (approximately 4,500 mt yr^{-1} in surface flows) to the EAA canals…” As will be discussed below, this estimate of net sulfate loading from Lake Okeechobee to the EAA (4,500 metric tons per year) implies that 80-90% of the gross sulfate loading from the lake to the EAA (30,000-40,000 metric tons per year) is due to runoff and back-pumping from the EAA. This seems almost too high to be correct, and I assume that the data (and the expertise) exist at the SFWMD to resolve this apparent discrepancy. It is also important to recognize that essentially 100% of the sulfate in Lake Okeechobee stems from agricultural runoff, whether from activities to the north or the south. Concentrations of sulfate in Lake Okeechobee and the canals leading to and from the EAA are much higher than those in the ENP, thus there is a very large north to south sulfate gradient across the system and the dominant source for that sulfate appears to be from agricultural practices in the Lake Okeechobee watershed and the EAA. An accurate accounting of all of the sources and sinks for sulfate in the lake and the EAA may provide the impetus to reduce sulfate loading to the lake from both upstream and downstream sources.

The use of agricultural sulfur appears to be the third most important input term in the EAA sulfur mass balance (6,286-11,775 metric tons per year), yet it may exceed the net input from Lake Okeechobee (4,500 metric tons per year cited by Orem et al., 2011). If the data are reliable, the export of sulfur in harvested crops more than accounts for the application of agricultural sulfur within the EAA proper. If the majority of the sulfur released during soil oxidation in the EAA is in fact legacy sulfur from past agricultural practices, it implies that the sulfur application rates were much higher in the past than today.

As noted above, it appears that most of the sulfate in the canals leaving the EAA is the result of agricultural practices both upstream of Lake Okeechobee and within the EAA itself. It therefore seems appropriate to develop Best Management Practices to minimize the input of sulfate to rivers and streams entering Lake Okeechobee from upstream and downstream (EAA) sources and to minimize the rate of soil oxidation in the EAA.

Regarding item (3), Dierberg’s report at the workshop showed that sulfate retention in the STAs ranged from 16-33%. The reduction of sulfate to sulfide in pore waters appeared to account for this retention. Regarding item (4), the evaluation of the sulfur mass balance for wet, dry, and intermediate years was reported for the EAA only (see Table 1 below). Regarding item (5), sulfur isotope analysis indicates that agricultural sulfur and legacy agricultural sulfur are the dominant source of the sulfate leaving the EAA in canal flow (Orem et al., 2011).

Project 3. Mercury (Hg)/Sulfur Biogeochemistry Study

A description of the work plan for the Mercury (Hg)/Sulfur Biogeochemical Study (aka the South Florida Mercury Hot Spot Study) was presented in Axelrad et al. (2011). The contract for this research was awarded to Tetra-Tech. Sampling for Year 1 has been completed and further funding is on hold. The following data gaps and management questions were identified in: https://my.sfwmd.gov/portal/page/portal/common/pdf/sd_modeling_scientific.pdf

1. Compare and assess potential differences in surface water and pore water analytes and biological community structure (flora and fauna characteristics) between areas that have high and low fish tissue total mercury levels in an effort to determine the cause of persistent mercury hot spots for fish.
2. Provide investigation into the progressive increase (since the mid-1990s) of total mercury in largemouth bass in the Holey Land Wildlife Management Area by assessing historical trends in important surface water and pore water analytes.

It is important to continue investigations into the loading and cycling of sulfate, DOC, and Hg in these ecosystems in order to develop coupled hydrological/biogeochemical models that can reliably predict how changes in the loadings will affect Hg levels in the biota.

Project 4. Small-Scale Sulfur Mass Balance

The following data gaps and management questions for the Small-Scale Sulfur Mass Balance Study were identified in:
(https://my.sfwmd.gov/portal/page/portal/common/pdf/sd_modeling_scientific.pdf).

1. Determine water column-sediment sulfur fluxes.
2. Determine reaction/process rates of sulfide production, sulfide oxidation, and plant uptake.
3. Determine adsorption-desorption dynamics of sulfur species and what factors impact adsorption.
4. Determine vertical transects levels of sulfur in sediment.
5. Determine hydrogen sulfide air-water surface exchange.

This research has not yet begun. This project is intimately related to Project 3, and it is extremely important to complete both.

Part 2: Review of the conclusions and recommendations from the Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands (2011).

A. Review of the Workshop Presentations:

Leading off the workshop, Bill Orem (USGS) presented a very comprehensive review of the interactions between sulfur and mercury in south Florida wetlands in a talk entitled: “Sulfur Studies in the South Florida Ecosystem: Present Status and Future Research Needs”. He asked, “Why is Sulfur Contamination of the Everglades Important?” He reported that:

1. It drives microbial sulfate reduction and fundamentally changes the biogeochemistry and microbial ecology of the ecosystem.
2. The end-product of microbial sulfate reduction is sulfide, a highly reactive and toxic substance which may affect micronutrient metal bioavailability and impact aquatic flora and fauna.

3. Because of the role it plays in mercury methylation in the Everglades, control of sulfate inflow may represent our best chance to reduce methylmercury contamination in the ecosystem.
4. The influx of an additional electron acceptor into the ecosystem increases overall anaerobic activity with resulting impacts on nutrient recycling and organic soil biodegradation.
5. Entry of sulfate into the Everglades at levels up to 1000x background has led to heavily impacted sites where sulfide levels may exceed EPA standards for surface water."

Orem outlined several Management Questions, noting that, "no USEPA or Florida numeric water quality criteria currently exist for sulfate for ecosystem protection."

1. The Comprehensive Everglades Restoration Plan (CERP: http://www.evergladesplan.org/) adopted a performance measure for sulfate in surface water of <1 mg/L, and at those levels:
   a. microbial sulfate reduction rates are limited by sulfate availability.
   b. mercury methylation would also be low.
   c. sulfide levels would be low in pore water and < 0.1 ppb in SW.
   d. low sulfide limits sulfide toxicity to aquatic flora and fauna.
   e. low sulfide limits nutrient release from soil by internal eutrophication.
2. Heavily sulfur-impacted marsh sites in the Everglades exceed USEPA water quality criteria for surface water H_2S (2 µg/L).
   a. Sulfur contamination of the Everglades is biogeochemically intertwined with other contaminant issues, notably methylmercury and phosphorus; these linked issues are most effectively addressed in concert.

Orem outlined what we know about sulfur distributions in the Everglades, and how "well" we know it, identifying each issue with a + (not very certain) to +++ (very certain):

1. About 60% of the Everglades has sulfate concentrations in surface water in excess of background (≥ 1 mg/L) +++
2. Average sulfate concentrations at some marsh sites exceed 60 mg/L +++
3. General decrease in sulfate from north to south across the Everglades +++
4. Distributions of sulfide and other reduced sulfur species in soil generally parallel those for surface water sulfate ++
5. The highest sulfate concentrations are observed in canals within the Everglades Agricultural Area (EAA) +++
6. Lake Okeechobee and rivers entering the lake have elevated sulfate levels (10-25 mg/L), but not as high as in EAA canals ++

He outlined what we know about sources of sulfur to the Everglades, using the same scale (+, ++, and +++) for the extent of our understanding:

1. Concentrations of sulfate in surface water show that canal water draining the Everglades Agricultural Area (EAA) is the principal source of sulfate to Everglades' marshes +++
2. Stable isotope results ($\delta^{34}S$) of sulfate in surface water are consistent with sulfur in fertilizers and soil amendments (new and legacy) as a principal source of the sulfate in the canals +++

3. Deep groundwater (below 9 m depth) has high sulfate concentrations, but available geochemical data is not consistent with groundwater as a major source of sulfate to canals or marshes ++
4. Rainwater and dry deposition has generally low sulfate concentrations and is not a major contributor to sulfate contamination in the Everglades, but may be the main source of sulfate in pristine areas +++
5. Drought cycles and burns oxidize reduced sulfur stored in sediments and remobilize this sulfur as sulfate following rewetting ++

He outlined what we know about the biogeochemistry and impacts of sulfur pollution in the Everglades, using the same +, ++, and +++ ratings to reflect the level of our understanding:

1. Sulfate stimulates microbial sulfate reduction and fundamentally alters the microbial community structure in impacted areas +++
2. Sulfate promotes methylation of mercury to its most toxic and bioaccumulative form: methylmercury +++
3. Sulfide is toxic to plants and animals +?
4. Sulfate promotes release of nutrients from sediments (internal eutrophication) +?
5. Sulfide binds metal ions and sequesters them in soils as metal sulfides +?
6. Sulfate enhances biodegradation of organic soils +?

He discussed how fire and drought/rewet cycles affect sulfur and mercury biogeochemistry in the Everglades:

1. Oxidation of organic soil by fire or drought converts reduced sulfur species (organic sulfur and metal sulfides) to sulfate, and releases soil bound mercury and DOC.
2. Large amounts of methylmercury may be produced before sulfate is depleted and/or sulfide levels buildup to levels that inhibit methylation.
3. Effect observed in field studies in the Everglades, in STAs routinely dried down and rewet, and confirmed experimentally in laboratory microcosm experiments.

He concluded that:

1. Sulfate is a serious water quality issue for Everglades Restoration.
   a. levels of sulfate contamination are 100-1000x background levels.
   b. 60% of the ecosystem is impacted by sulfate pollution.
   c. Sulfur has multiple impacts in the Everglades; including being a major driver of MeHg production in the ecosystem
2. Balancing the water quantity needs of the ecosystem with the water quality realities represents one of the most significant challenges for successful restoration of the ecosystem. Failure to successfully address the sulfur-mercury water quality issue leaves wildlife vulnerable and severely limits recreational use of the land for fishing.
3. Reduction of sulfate to background levels will be difficult to achieve – but any significant reduction is likely to provide benefits to the ecosystem as a whole. Success in reducing sulfur loading and impacts will likely require a combination of BMPs, mitigation strategies, and correct water management practices.

He identified the following knowledge gaps:

1. Accounting of all sulfur added within EAA – fertilizers, soil amendments, fungicides, algal control, etc.
2. Release of sulfur from soil oxidation versus new additions.
3. How much can BMPs reduce sulfur loading while minimizing impacts on agriculture?
4. How will differential decreases in sulfate loading impact MeHg production in various scenarios (sheet flow versus canal transport); where will MeHg hotspots develop?
5. Can STAs be reconfigured or operated in a manner to remove sulfate more effectively?
6. How toxic is sulfide to Everglades flora and fauna?
7. What is the role played by sulfate with respect to nutrient recycling and organic soil biodegradation?
8. How does sulfide affect trace metal biogeochemistry?

Mike Waldon (DOI Everglades Program Team) gave a presentation on his research: “Near Zeroth Order Sulfate Disappearance Rate Estimated using Models of the Arthur R. Marshall Loxahatchee National Wildlife Refuge”. He described how the hydrology of the Loxahatchee area (aka WCA1) has been altered from a predominantly sheet-flow system to a riparian wetland, and that the water chemistry had been altered from a rainfall-fed system to one with elevated chloride, sulfate, and total P. He stated that the input of canal water was the primary source of sulfate contamination in the marsh interior. The rate of sulfate disappearance (reduction flux) was relatively constant (~15 g/m2/yr) and was not sulfate limited. The results of their efforts to model sulfate concentrations in the canals and the marsh suggested that a first order model required a 20-fold adjustment in the rate constant (the effective sulfate disappearance rate in m/yr) to fit data from the canals to the marsh interior, while a simple zeroth order model worked well to fit the observations. Future work might extend the model to add simulation of sulfide and Hg. Further work is needed to test whether zeroth order sulfate disappearance is common in other natural & treatment wetlands. The zeroth order model leads to a number of interesting conclusions:

1. It implies that factor(s) limiting the disappearance of sulfate are:
   a. Not the sulfate concentrations
   b. Not the dispersion of sulfate
   c. Not the total phosphorus concentrations
2. Treatment: The percent removal of sulfate would be proportional to treatment area (i.e. linear rather than exponential relationship), so that doubling the size a treatment area would double the removal of sulfate.
3. Source Control – reduction in sulfate concentrations in the inflow to an STA would result in an equal reduction in outflow concentration (NB: it is not clear if this refers to reductions in absolute concentration units or in the percentage of reduction for inflow and outflow).
4. Sediment sources or benthic sulfate release are not significant.
5. With regard to spatial patterns of sulfide and sulfate in the system:
      a. A plot of sulfide vs. surface water sulfate should have sulfide unrelated to sulfate at higher concentrations.
      b. Sulfide should be more constant in areas impacted by sulfate pollution.

There as insufficient time at the workshop to work through the development of Waldon's models, however some comments on the model, as it was presented at the workshop, are included in Appendix IV.

Paul McCormick (SFWMD) gave a talk on: "Spatial Patterns of Sulfur Enrichment within the Loxahatchee National Wildlife Refuge". He noted that despite large canal inflows, the Refuge is relatively insulated from canal-water intrusion. Based on a combination of a synoptic survey of core samples, an east-west transect of core samples across Refuge, and a set of mesocosm sulfate dosing experiments he concluded that:

1. Steep sulfur gradients exist within the Refuge.
2. Sulfur has accumulated in plant tissue as well as soils.
3. Even interior areas appear to have experienced some exposure to canal sulfate loads.
4. Opportunities exist to build on previous data collection.

Alan Wright (IFAS/UF) discussed "Sulfur Use in the Everglades Agricultural Area: Soil Biogeochemical and Crop Responses." He noted that:

1. Subsidence results in historical loss of 1 in/yr and current loss of 0.6 in/year and is related to water table depth.
2. The EAA is naturally P and micronutrient limited.
3. Bedrock limestone gets incorporated into surface soil.
4. dissolved salts are mobilized.
5. soil pH is increasing.
6. Enhanced P and micronutrient retention in forms unavailable to crops is occurring.
7. Farmers are using higher fertilization rates to offset fixation in soil.

Sources of sulfur in fertilizer include:

1. Elemental sulfur (90% granular S).
2. STM5 (granular S with 80% S, 5% Mn).
3. Sulfate fertilizers:
    a. Historic use of copper sulfate to correct sulfate deficiency
    b. Ammonium sulfate
    c. SPM (sulfate of potash magnesia)
    d. Magnesium sulfate
    e. Sulfate forms of micronutrients

Sugarcane crop trials are ongoing to:

1. update and verify sugarcane recommendations, and to establish baseline data for some vegetables.
2. Test different sources and pH amendments.
3. Assess temporal and spatial variability.
4. Test different sites, soil types, years.

In his conclusions, he stated:

1. There was a variable response to S but clearly S is not needed for all fields with pH>6.6.
2. Soil calcium may be a better criteria but we need more data.
3. Previous tests for soils with high calcium carbonate content showed significant responses to elemental S.
4. We will combine the results from those tests with results from various locations to revise the S recommendations.

Those recommendations may include:

1. Modifications of the micronutrient formulations and application procedures.
2. Breeding of flood tolerant varieties of sugarcane.
3. Reduced tillage:
    a. increased aggregation and organic matter content, nutrient supply.
    b. reduced rate of soil subsidence.
    c. minimize pH increases and reduces nutrient fixation.
4. Maintenance of high water tables:
    a. Improves water quantity.
    b. Field flooding reduces soil oxidation.
    c. Crop rotation can enhance productivity.
5. Establish preliminary data for S transformations in soil and fate of S fertilizers

He identified these areas for future sulfur research:

1. Revise IFAS recommendations for sulfur application to sugarcane and vegetables.
2. Complete a mass balance study of S inputs/exports in the EAA.
    a. Identify sources.
    b. Quantify inputs/outputs.
    c. Fertilizer or soil S.
    d. S transformations in soil and water.
    e. Retention mechanisms.
    f. Sulfate reduction.
    g. Mineralization rates.
    h. Leaching/runoff potential.
    i. Fate of mineralized S and fertilizer S.

Presentations by Forest Dierberg and Tom DeBusk (DB Environmental) are discussed above under the heading of the Review of the SFWMD Sulfur Action Plan: Internal Eutrophication Study.

Sue Newman (SFWMD) discussed “Landscape Scale Patterns of Total Sulfur and Total Mercury in Soils of the Greater Everglades Ecosystem.” She discussed the present landscape scale patterns of Everglades soil TS and THg, with a focus on results of soil analyses derived from the Everglades Soil Mapping sampling effort (2003-2004), and an overview of key findings and identification of areas of concern. The rationale for the study was to get a “Big picture” perspective, to identify regional impacts and “hot spots” (areas of concern), to identify trends at the ecosystem scale, and to enable assessment of ecosystem restoration success via comparison to baseline conditions (change detection). She concluded that:

1. TS in soil cores was associated with agricultural inflows (Refuge, WCA-2A, WCA-3A).
2. TS was elevated in areas of significant soil subsidence.
3. THg enrichment was not related to agricultural inflows.
4. Significant enrichment of THg was observed downstream of subsidence hotspots.
5. Me-Hg was elevated in the Refuge and northern WCA-3A, both areas of significant TS enrichment.
6. Neither TS nor THg were elevated in the ENP where fish levels of Me-Hg are highest.

Lena Ma (UF) discussed “Mercury Distribution in Tree Islands and Surrounding Marsh in the Everglades”. She described tree islands as:

1. Patches of high and dry ground dotting Everglades marshes: a prominent feature.
2. Possibly trash piles from human settlements ~ 5,000 years ago (Science Daily).
3. Having higher biomass and diversity than the surrounding marsh.
4. High elevation provides dry habitat for mammals.

The goals of this research were to:

1. Compare Hg levels in tree islands compared to that in the surrounding marsh.
2. Compare Hg levels in tree islands compared to other parts of Everglades.
3. Determine the major sources of Hg in tree islands.

She concluded that:

1. Total Hg concentrations in soils from selected tree islands were greater than the surrounding marsh.
2. Bio-waste such as wading bird guano displayed higher Hg concentrations than those in biota and soil.
3. Hg accumulation profiles in tree island soil reflected the historic changes in atmospheric deposition.
4. More research is needed to investigate the sources of high Hg concentrations in tree islands soils and their potential contribution to Hg cycling in Everglades.

Discussion on these conclusions focused on her observations that the highest soil Hg concentrations were found at the “head” of the tree islands were the tallest trees were found. It seems likely that guano (with high Hg concentrations) from fish-eating birds could account for this observation since birds tend to perch on the tallest trees in a given area.

Dave Krabbenhoft (USGS) discussed “Mercury and Methylmercury Distributions, Drivers and Trends in Everglades National Park." He reviewed the mercury cycle in the Everglades, described the ENP Sampling Network, and presented results from the 2008-2010 surveys. He concluded that:

1. The delivery of sulfate and DOC from canal water to regions of Everglades National Park has a profound effect on MeHg levels and distribution.
2. Most of the Shark River Slough shows elevated levels of MeHg compared to “background” (areas unaffected by canal water input of sulfate).
3. Lower C111 canal and Rocky Glade areas exhibit possible carbon limitation for MeHg production.
4. Sampling locations nearest the S12 and L67 canal discharge locations appear to show the “high sulfate inhibition effect” first revealed in WCA 2A.
5. Sulfate-DOC stimulation of MeHg production carries into the food web.

Yong Cai (FIU) discussed “Photodegradation of Methylmercury and Its Effects on Mercury Distribution and Cycling in the Florida Everglades.” He stated that while great efforts have been made to investigate the production and bioaccumulation of MeHg in the Everglades, there was a relative lack of knowledge on the degradation of MeHg in Everglades water, and that this represents “missing information” on MeHg cycling in the Everglades. The objectives of his project were to investigate the degradation of MeHg in Everglades water and to assess the role of this process in spatial distribution and cycling of MeHg in the Everglades. He concluded that:

1. Photodegradation of MeHg plays an important role in controlling the distribution of MeHg in Everglades water.
2. Degradation of MeHg in Everglades water is mediated by sunlight, and that UV-A and UV-B radiation are the principal drivers.
3. Photodegradation of MeHg represented 6.1% of the annually produced MeHg.
4. Photodegradation of MeHg removed about 31.4% of the MeHg diffused into the water column.
5. MeHg photodegradation potential (PPD) generally presented an increasing trend from north to south, which was opposite to the spatial distribution of MeHg concentration in Everglades water.
6. Correlation analysis shows that MeHg in Everglades water and PPD were significantly related.

George Aiken (USGS) presented his research on "From Field to Lab – Understanding the Dissolved Organic Matter-Mercury Connection." He noted that Hg-DOM complexation is only part of the story; that there are many other ecosystem DOM reactivity issues:

1. DOM serves as a substrate for microbial activity.
2. DOM concentrations and character controls light penetration into the water column.
3. DOM is involved in the transport of hydrophobic organic compounds and metals (e.g. Cu – Biotic Ligand Model).
4. DOM is photochemically and redox reactive.
5. DOM influences the bioavailability of nutrients, metals, etc.
6. DOM controls geochemical reactions e.g. calcite precipitation and As mobilization.
7. DOM creates problems for water treatment (municipal water supplies)

Using data from field sites and mesocosm experiments he concluded that:

1. Optical measurements serve as excellent proxies for DOM concentrations and composition, with the caveat that each system needs to be 'rated' due to spatial and temporal variability in the DOM composition.
2. Information about DOM sources and reactivity can be extracted from optical data.
3. In many systems, optical measurements can be good proxies for [Hg] and have the following advantages:
   a. Easier, cheaper than analyzing for Hg.
   b. Amenable to frequent sampling, e.g. ISCO automated water samplers and in-situ sensor measurements.
   c. Improved estimates of flux during high flow periods.

Don Axelrad (DEP) described the results of research on "Effects of Methylmercury Contamination on Reproduction and Endocrine Function in White Ibises." He discussed the "Hydrological Restoration Hypothesis" wherein increased flow to estuaries and removal of barriers, and restoration of the natural timing of flows and the natural variability in hydroperiod would lead to increased prey productivity, more "right-sized" fish, and greater availability to birds. This would then be reflected in increased numbers of nesting birds, increased nesting success, and an overall movement back to the estuary. Using a set of captured birds in an aviary, he reported on the effects of methylmercury dosing of bird food in the aviary. They concluded that Everglades levels of MeHg exposure were associated with:

1. 53% loss of productivity in dosed groups.
2. dramatically increased male-male pairing.
3. significant alteration of testosterone and estradiol.
4. reduced male display rates.
5. First animal model of the effects of MeHg on sexual preference?
6. Birds currently are exposed to 0.05 ppm MeHg in diet.
7. Bird numbers have recovered since the late 1990s.
8. Florida's Freshwater Hg TMDL may lead to reductions of MeHg in prey fish.

April Brandon (FGCU) described her research on "Spatial and Temporal Trends in Mercury Concentrations in the Blood and Hair of Florida Panthers (Puma concolor coryi)." Her research objectives were to evaluate the spatial and temporal trends of tissue Hg concentrations in Florida panthers and to examination of influential factors which may affect Hg concentrations found in these cats, including age, sex, and the effects of altered hydroperiod. Panthers in the Everglades region suffer from a number of stressors:

1. Low genetic diversity.
2. Inbreeding depression.
3. Exotic diseases.
4. Parasites.
5. Human interactions.
6. Poor nutrition.
7. Habitat loss and degradation.
8. Environmental Toxicants

She concluded that all panthers had measurable levels of Hg present in blood and hair, although there was considerable variation over time and space. Blood and hair Hg levels were higher in the late 1980s and early 1990s, and the highest concentrations were found in cats from the ENP. There does not appear to be any influence of age or sex. The influence of hydroperiod was unable to be assessed statistically although it appeared to be a factor in Hg exposure.

Ted Lange (FFWCC) described results from "Fisheries Research/Monitoring". The goals of that program are to:

1. Assess human and wildlife risks from consumption of mercury-contaminated fish.
2. Describe spatial and temporal trends in mercury bioaccumulation-relevant endpoint at appropriate scale.
3. Support efforts to gain a better understanding of the ecological significance of mercury bioaccumulation in fish and wildlife.
4. Support modeling efforts (E-MCM, FW-TMDL, GOM-TMDL) and work to understand bioaccumulation pathways in panthers, wading birds, and alligators.

He reported that 58% of <14" Large-Mouth Bass (LMB), and 100% of the >14" LMB, exceed the 0.3 ppm EPA guideline for consumption. LMB Hg concentrations in the WCAs and canals have decreased by about a factor of 2-3 since the early 1990s (1.5 ppm vs. 0.5 ppm in late 2000s). LMB in the Shark River Slough system have decreased as well since the early 1990s, although not as much (1.5-2 ppm vs. 1-1.5 ppm in late 2000s). Among the variety of species studied, higher fish Hg levels were positively correlated with trophic position.

With regard to their observations and future research needs:

1. Continue to measure human health/ecological endpoints as measure of system response to management or other changes influencing MeHg availability.
2. Mercury concentrations vary spatially among sites/habitats in response to ambient MeHg concentrations.
3. Shallow marsh system-strong association between sediment MeHg and biota across trophic levels.
4. Variations in growth rate for LMB aren't significant across Everglades.
5. Length/Complexity of Food Webs varies among habitats and can influence MeHg bioaccumulation.
6. Ontogenetic shifts in diet of LMB (older fish accumulate Hg faster as they feed higher in the food web).
7. What are the effects of long-term changes in hydroperiod?
    a. Fish movement between canals/marsh.
    b. Shifts in prey base and availability

Ben Gu (SFWMD) discussed "Trophic Position and Mercury Levels of Largemouth Bass in South Florida Wetlands." He summarized that:

1. The large variations of mercury level in largemouth bass cannot be fully explained by the Goldilocks hypothesis (wherein optimum MeHg production occurs where sulfate levels are "just right").
2. This analysis reveals a close relationship between largemouth bass trophic position and mercury level.
3. High sulfate (sulfide) concentration and low trophic position may be responsible for the some of the low mercury levels in largemouth bass.
4. High trophic position in monitoring sites with high sulfate may be responsible for the high mercury level in largemouth bass.
5. The difference in largemouth bass trophic position among monitoring sites is thought to relate to the type of prey available to fish which is in turn controlled by plant coverage and community structure.

B. Recommendations for Future Research Needs

The five recommendations for future research needs listed immediately below were developed and discussed on the afternoon of Day 2 of the workshop. The order for these recommendations was not discussed with the other participants, but reflects my own sense of which is likely to be the most rewarding from a scientific perspective. The rationale for each recommendation is explained in detail in the following section.

Recommendation 1: Conduct careful water and sulfur mass balance studies for the entire system, from the tributaries to Lake Okeechobee to the outflow from the ENP.

Recommendation 2: Support development of models for the various biogeochemical and physical components of the system focused on mercury, sulfate, DOM.

Recommendation 3: Continue long-term monitoring efforts in order to demonstrate when changes occur and to quantify the rates and extent of change.

Recommendation 4: Continue and expand the quantification and characterization of dissolved organic matter (DOM) in water quality monitoring programs.

Recommendation 5: Continue to conduct field surveys and experiments on the factors and conditions that lead to formation of MeHg in the system.

Recommendation 1: Sulfur Mass Balance Studies.
This issue is also discussed above (pg. 4-5) with regard to the review of Project 2 of the 2009 SFWMD Sulfur Action Plan. There is compelling evidence that elevated levels of sulfate can trigger the production of MeHg by Sulfate Reducing Bacteria (SRB) in Everglades ecosystems (see Axelrad et al., 2011). It has been suggested that this process is the primary cause for high MeHg concentrations in sediments and biota throughout the Everglades Protection Area (EPA). Current estimates for the sulfur budget in the EAA (Table 1) implicate three processes for the majority of the sulfate loading reaching the water conservation areas and the ENP via the canal system: sulfate release from soil oxidation, sulfate input from Lake Okeechobee, and agricultural applications of sulfur. Sulfate loading to the EAA from Lake Okeechobee needs to be carefully evaluated since as much as 36-50% of the sulfate in the lake may be the result of runoff and back-pumping from the EAA (Orem et al., 2011).

Table 1: Estimates of Sulfur inputs to, and outputs from, the EAA.

Estimates of Sulfur Inputs to and Outputs from the EAA					
	Shueneman (2001) Wright et al. (2008)	Corrales et al. (2011)	Gabriel et al. (2010)		
			Moderate Year	Wet Year	Dry Year
			2003	2004	2007
EAA area (acres)	700,000	718,073	693,031	693,031	693,031
soil oxidation rate (cm/yr)	1.30	1.40	1.30	1.30	1.30
Sulfur concentration in soils (percent)	0.96	0.35	0.37	0.37	0.37
Sulfur input to EAA (metric tons per year)					
soil oxidation	54,127	49,169	30,646	30,646	30,646
agricultural applications	10,490a	11,775a	6,286	6,286	6,286
TS in to EAA from Lake Okeechobee[b]	33,968	35,217	31,057	40,626	28,494
levees		5,858			
groundwater		4,055			
atmospheric deposition, wet	1,587-2,540c	4,229	3,864	2,861	3,295
atmospheric deposition, dry			529	487	508
Total: TS inputs to EAA	**92,053-93,006**	**98,528**	**72,382**	**80,906**	**69,229**
Sulfur output from the EAA					
crop harvest		23,182	25,500	25,500	25,500
TS canal output to EPA		116,360	102,214	106,756	24,961
Total: TS outputs from EAA		**139,542**	**127,714**	**132,256**	**50,461**
[a]Based on 37 kg/ha/yr in Wright et al. (2008)					
[b]Net input estimated at 4,500 mt/yr (Orem et al., 2011)					
[c]Updated calculations based on EAA total area.					
Barbara Donner and Don Axelrad, FDEP. DRAFT 2011_05_18					

As one can see, there are large variations in the individual input and output estimates and this creates large imbalances between total sulfur input to, and output from, the EAA. The release of sulfur from soil oxidation in the EAA is one of the largest terms in all of the EAA sulfur budgets, yet it is highly uncertain due to uncertainty in the rate of soil oxidation and the sulfur and water content of the soils. While sulfur isotope analysis indicates that the sulfate in EAA drainage canals is consistent with the sulfur applied agriculturally, it is not possible to distinguish between recent applications and “legacy” sulfur from past applications, or from net sulfate input from Lake Okeechobee. The agricultural application rate used in these calculations also ranges over a factor of ~2. The input from Lake Okeechobee appears to be relatively well constrained, yet it is possible that the majority of this “input” is in fact a circular routing of water and sulfate due to back-pumping. In his recent review paper, Orem et al. (2011) estimated that the net flux of sulfate from the lake to the EAA was only 4,500 metric tons per year (11-16% of the gross flux). Only the budget from Corrales et al. (2011) includes flow over levees and a groundwater flux. It appears that crop harvesting can more than balance the reported application rate of agricultural sulfur (37 kg/ha/yr; Wright et al., 2008).

Because of these uncertainties, it is not currently possible to reliably calculate how changes in any of these input terms might affect the flux of sulfate out of the EAA via the canal system to the EPA. In order to make reliable predictions for the sulfur flux to the canals leaving the EAA under various remediation scenarios, it is necessary to obtain accurate water and sulfur mass balances for Lake Okeechobee and the EAA. For the lake, the input of water and sulfate from back-pumping and the outflow back into the EAA must be explicitly quantified. For the EAA, it is essential to obtain reliable data from the agriculture industry for the agricultural applications of all forms of sulfur and for the export of sulfur via crop harvesting. Also, the rates of sulfur release from soil oxidation must be more accurately quantified across the EAA.

It is anticipated that IFAS is interested in pursuing studies on several important aspects of the EAA sulfur problem. A comprehensive soil survey could be used to quantify the rates of soil oxidation across the EAA while measurements of sulfur speciation in soil cores would reveal which forms of sulfur are most abundant and most likely to be released to canal waters. IFAS can also recommend best management practices (BMPs) to reduce the need for the agricultural application of sulfur in the Lake Okeechobee watershed and the EAA, and to minimize soil oxidation in the EAA.

Recommendation 2: Modeling Studies.
It is accepted that the ability to reliably predict how any system will respond to changes in inputs or outputs or internal cycling rates requires the use of models. The Everglades Mercury Cycling Model (E-MCM) is a dynamic model that includes a wide variety of rate equations covering the important mercury cycling processes in the Everglades (Gabriel et al., 2010). It could be further developed to be applicable to the variety of conditions found throughout the system, from the EAA, the STAs, the water conservation areas, and the ENP. An effort to construct a predictive model for water quality, sulfate, MeHg, and Hg levels in Gambusia is being undertaken by Dr. Curt Pollman (Aqua Lux Lucis) under contract to FDEP, with a report due in Fall 2011. In addition, the ELM model (described at http://my.sfwmd.gov/portal/page/portal/xweb%20-%20release%202/elm) could perhaps be adapted to include sulfur cycling. It is important for some of these models to include a detailed accounting of the current movement of water throughout the system, and this can be provided from the SFWMD. It is important that the modeling efforts provide predictive capability from the local to the landscape scale. It is desirable that multiple modeling efforts be pursued simultaneously since the modeling results are likely to be more reliable when they converge towards consensus with respect to their predictions.

Another suggestion/recommendation which was not discussed during the workshop is to conduct metadata analysis using the historic water quality data (sulfate, DOC, color etc). This analysis, using water quality data from the EPA and SFWMD monitoring networks, would be to document the historic trends of sulfate concentration and the relationships between sulfate, DOC and total mercury in fish. Such analyses are also extremely useful to modeling efforts in a hind-casting sense.

Recommendation 3: Monitoring.
Long-term monitoring in various media have provided an extremely useful database to help us examine trends and to understand a wide variety of processes. These efforts should be continued, and include:

Recommendation 3(a): MDN sites (monitoring of wet deposition of rainfall Hg).
Rainfall Hg deposition has been relatively constant over the region since 1994. It has been hypothesized that rainfall Hg deposition would have been perhaps twice as high prior to the

early 1990s when municipal solid waste and medical waste incinerators were operating in southeastern Florida. Those local sources have been dramatically lowered since the late 1980s, and it appears that the majority of the rainfall Hg results from long-range transport from distant sources (i.e. outside of Florida). Further reductions in the rainfall Hg load to the region may be required to lower fish Hg concentrations to acceptable levels, so it is essential that the monitoring program be continued in order to quantify the impacts on rainfall Hg deposition from source reductions. The report from the FDEP-sponsored Florida Freshwater TMDL study is due this Fall 2011, and it is anticipated that this report will include recommendations on whether it is necessary to pursue further reductions in local source atmospheric emissions of Hg. This report should be used to guide the state (FDEP) and the district in developing plans to reduce atmospheric Hg loading to the system.

Recommendation 3(b): Fish and other biota:
Indications of the assumed reduction in rainfall Hg deposition since the late 1980s may be reflected in the observed declines in fish Hg levels in Gambusia and large-mouth bass (LMB), although the causes of the decline are not known with absolute certainty. It has also been suggested that changes in the load of sulfate to various parts of the region may be responsible via a decrease in the production of monomethyl mercury (MeHg) by sulfate reducing bacteria (SRB). Regardless of the causes, it is essential to continue monitoring programs for LMB, Gambusia, wading birds, and other biota. Any efforts to reduce the rate of Hg loading or the rate of MeHg production will ultimately be reflected in Hg levels in the biota.

Recommendation 3(c): Water Quality:
As efforts to restore the water budgets and water quality to the various parts of the region continue, water quality monitoring is essential to quantify the success of those efforts. Since sulfate loading has been identified as a likely culprit for enhanced MeHg production, it is essential to continue that monitoring. In addition to the DBHYDRO and EcoDB databases, the SFWMD should make available all water quality data that has been collected by district staff (or contractors) so that scientists studying the impacts of sulfate loading on MeHg production are working with the most complete data set.

Information was recently provided by Nicole Howard (SFWMD) regarding the availability of District sulfate data: “Chloride and sulfate are part of the same analytical test, so if chloride is analyzed, sulfate is also analyzed. In the past, however, if sulfate was not a requested analyte, the District did not validate and load analytical results from LIMS to DBHYDRO due to the associated costs. In approximately 2008 or 2009, the need for additional sulfate data was identified and the District began validating and loading all sulfate data to DBHYDRO, regardless of whether or not that test was requested. Sulfate data prior to 2008 or 2009 is stored in the District’s current LIMS, which dates back to October 2006. Unfortunately, data preceding the current LIMS is not available. Anyone interested in retrieving the sulfate data stored in LIMS can do so by contacting the LIMS administrator Madhavi Vadde mvadde@sfwmd.gov.

Recommendation 4: Dissolved organic matter (DOM).
DOM has been shown to influence the bioavailability of Hg to SRB, to influence the binding of Hg(II) to sediments, and is involved in the photochemical reduction of Hg(II) and the

photochemical breakdown of MeHg. Because the concentrations and nature of the DOM in the system have such a large impact on Hg biogeochemistry, it is recommended that regular monitoring of DOM concentrations be continued and expanded. There are some sensors that can be utilized for continuous monitoring of DOM, and the USGS is interested in developing additional sensor capabilities. There are also a number of analytical measurements for discrete DOM samples that can reveal important information about the nature of the DOM. High temperature catalytic oxidation methods can quantify the carbon (DOC) and nitrogen (DON) content of the DOM. Techniques are also available to measure the dissolved organic phosphorus (DOP) and sulfur (DOS) concentrations. Specific UV absorbance (SUVA) and 3-D fluorescence can be used to quantify the "nature" of the DOM, such as the aromatic carbon content. It is recommended that the district initiate discussions with DOM experts to establish a cost-effective set of measurements for monitoring DOM in the system, and to pursue offers from the USGS to develop and deploy continuous sensors for DOM.

Recommendation 5: Mercury Methylation and Demethylation.
A recent review of the literature on the impact of sulfate on methylmercury in sediments and soils was conducted by Cynthia Gilmour, via a contract with FDEP (Gilmour, 2011). She concluded that, "Taken together, the literature shows that net MeHg production is most favored under biogeochemical conditions where sulfate is sufficient to support significant rates of microbial sulfate reduction, without much accumulation of aqueous sulfide. The research reviewed here demonstrates that sulfate additions to freshwater sediments often stimulate MeHg production; and that anthropogenic sulfate contamination of freshwater ecosystems from sources like acid deposition, acid-mine drainage, agriculture and eutrophication have the potential to increase MeHg levels in freshwater ecosystems."

The impacts of sulfate additions on the formation of MeHg and its impacts on biota in Everglades ecosystems was recently summarized by Axelrad et al. (2011). The need for further research on rates of demethylation of MeHg (biological, abiotic, and photochemical) was discussed at the workshop, yet the workshop participants generally agreed that the state of the knowledge on the effects of sulfate pollution on MeHg production in the Everglades is sufficiently mature that it is time to address solutions to the problem; namely reducing sulfate pollution in Everglades ecosystems.

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Appendix I

The Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands
South Florida Water Management District, West Palm Beach, FL

Agenda

June 21 and 22, 2011
The *Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands* will be held in the Storch Room (Bldg B-1, 3rd Floor) at the South Florida Water Management District Headquarters, 3301 Gun Club Road, West Palm Beach, FL 33406, on June 21 and 22, 2011.

This Workshop is organized by the South Florida Water Management District (SFWMD), the U.S. Geological Survey (USGS) and the Florida Department of Environmental Protection (FDEP). It is intended to support activities under the SFWMD's Sulfur Action Plan; the USGS' South Florida Ecosystem Program, and the FDEP's South Florida Mercury Science Program. Through these programs, the three agencies investigate the effects of elevated mercury and sulfur levels on the Greater Everglades, with research emphasis placed on mercury and sulfur biogeochemistry, internal eutrophication, sulfide toxicity, agricultural applications of sulfur, mercury bioaccumulation and levels in biota, and mercury effects on wildlife. The purpose of this workshop is to present data and conclusions from research conducted since the Second Workshop (June 2009), on that basis recommend actions to reduce the harmful ecological effects of mercury and sulfur, and to define additional mercury and sulfur research needs to restore the Greater Everglades.

Workshop Agenda

June 21
10:00a - 10:30a: Attendee Introductions and Workshop Background, Ronnie Best (USGS)

I: Sulfur Distribution, Biogeochemistry and Impacts
Moderator – Ronnie Best (USGS)

10:30a - 11:00a: Sulfur Studies in the South Florida Ecosystem - Present Status and Future Research Needs
Bill Orem, USGS

11:00a - 11:30a: Near Zeroth Order Sulfate Disappearance Rate Estimated using Models of the Arthur R. Marshall Loxahatchee National Wildlife Refuge
Mike Waldon, DOI Everglades Program Team

11:30a - 12:00p: Spatial Patterns of Sulfur Enrichment within the Loxahatchee National Wildlife Refuge
Paul McCormick, SFWMD

12:00p - 1:00p: Lunch

1:00p - 1:30p: Sulfur Use in the Everglades Agricultural Area: Soil Biogeochemical and Crop Responses
Alan Wright, UF

1:30p - 2:00p: Effects of Sulfate Dosing on Phosphorus Mobilization and Vegetation in WCA-3A Mesocosms

Forest Dierberg, DB Environmental Inc.

2:00p - 2:30p: Dryout-Reflood Impacts on Spatial Gradients and Temporal Variations in Surface and Pore Water Chemistry in a South Florida (USA) Stormwater Treatment Area
Tom DeBusk, DB Environmental Inc.

2:30p - 2:45p: Break

Workshop Agenda (*continued*)

II: Mercury Distribution and Methylation

	Moderator – Bill Orem (USGS)
2:45p - 3:15p:	Distribution of Mercury in South Florida Wetlands Sue Newman, SFWMD
3:15p-3:45p:	Distribution of Mercury in Tree Islands and Surrounding Marsh in the Everglades Lena Ma, UF
3:45-4:15p:	Mercury and Methylmercury Distributions, Drivers and Trends in Everglades National Park David P. Krabbenhoft, USGS
4:15-4:45p:	Degradation of Methylmercury and Its Effects on Mercury Distribution and Cycling in the Florida Everglades Yong Cai, FIU

June 22:

II: Mercury Distribution and Methylation (continued)

	Moderator – Bill Orem (USGS)
9:00a – 9:30a:	From Field to Lab: Advances in Understanding the Dissolved Organic Matter-Mercury Connection George R Aiken, USGS

III: Mercury and Wildlife

	Moderator – Don Axelrad (FDEP)
9:30a - 10:00a:	Effects of Ecologically Relevant Exposure of White Ibises to Methylmercury: Endocrine and Reproductive Effects Don Axelrad, FDEP
10:00a - 10:35a:	Spatial and Temporal Trends in Mercury Concentrations in Blood and Hair of Florida Panthers (*Puma concolor coryi*) April Brandon, FGCU
10:35a – 10:50a:	Break
10:50a - 11:20a:	Temporal and Spatial Trends of Mercury in Largemouth Bass Ted Lange, FFWCC
11:20a - 11:50a:	Variations of Mercury in Largemouth Bass: Nutrient Enrichment, Trophic Position and Source of Organic Matter Ben Gu, SFWMD
11:50a - 1:00p:	Lunch
1:00p - 3:30p:	Workshop Summary, Conclusions, Recommended Actions, and Future Research Needs

Workshop Organizers:

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Appendix II

Third Annual (2011) Mercury and Sulfur Workshop Attendees

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Charles Wilson	EAA Environmental Protection Division	cfwservices@bellsouth.net
Alan Wright	University of Florida	alwr@ufl.edu
Yingjia Zhu	University of Florida	yjzhu@ufl.edu

Appendix III
Statement of Work for Contract 4500060353, dated May 27, 2001

South Florida Water Management District
P.O. Box 24680
West Palm Beach, FL 33416-4680
Telephone (561) 686-8800

PURCHASE ORDER

FLORIDA SALES TAX EXEMPTION #85-8013149859C-9
FEDERAL TAX EXEMPT #59-74-0072K

THIS NUMBER MUST APPEAR ON ALL PACKAGES, PACKING LISTS, INVOICES, AND CORRESPONDENCE.	PAYMENT TERMS
4500060353	PAY WITHIN 30 DAYS NET.

PRICES QUOTED INCLUDE SHIPPING CHARGES UNLESS OTHERWISE STIPULATED BELOW.

PAGE NO.	DATE OF ORDER	EST. DELIVERY DATE
1 of 1	05/27/2011	06/22/2011

VENDOR NO.	PURCHASING AGENT	PHONE	F.O.B.	CONFIRMING
118582	PATRICK RYAN	561-682-6757	DESTINATION	NO

VENDOR:
WILLIAM M LANDING
304 TIMBERLANE RD
TALLAHASSEE FL 32312
Tel: 850-766-5531 Fax: 850-644-2581
ATTN: WILLIAM M LANDING

SHIP TO:
SOUTH FLORIDA WATER MANAGEMENT DISTRICT
SFWMD: HEADQUARTERS B-2 BUILDING
3301 GUN CLUB ROAD
WEST PALM BEACH FL 33406

LINE ITEMS OF YOUR INVOICE MUST MATCH LINE ITEM NUMBERS ON THIS DOCUMENT

Line	Quantity	Unit	Part Number and Description	Unit Price	Total Amount
			PRICING PER WRITTEN QUOTATION FOR PEER-REVIEW SERVICES AT THE 3RD WORKSHOP ON MERCURY AND SULFUR DATED MAY 27, 2011 BY WILLIAM M. LANDING, PH.D., ENVIRONMENTAL CHEMISTRY AND CHEMICAL OCEANOGRAPHY, FLORIDA STATE UNIVERSITY.		
			DR. LANDING SHALL PERFORM PEER-REVIEW SERVICES AT THE WORKSHOP ON MERCURY AND SULFUR AT THE SFWMD'S HEADQUARTERS LOCATED AT 3301 GUN CLUB ROAD, WEST PALM BEACH, FL ON JUNE 21 AND 22, 2011. DR. LANDING SHALL PERFORM PEER-REVIEW SERVICES IN ACCORDANCE WITH ATTACHMENT 'A", STATEMENT OF WORK ATTACHED TO THIS PURCHASE ORDER AND INCORPORATED HEREIN. THE TOTAL AMOUNT FOR THE PERFORMANCE OF SERVICES SHALL NOT EXCEED $4,894.00.		
1	1	AU	FY11 PEER RVW SVCS 3RD HG SULFUR WRKSHP	4,894.00	4,894.00
THE ITEM COVERS THE FOLLOWING SERVICES:					
10	*4,894*	*EA*	*FY11 DELIVERABLES*	*1.00*	*4,894.00*
			SFWMD CONTACT: BINHE GU, PH.D. AT 561 682-2556		

NOTE: . Prices displayed govern the purchase order transaction.
. Early payment discount invoices receive priority handling.
. The attached Purchase Order terms & conditions, pages 1 through 2 apply

Page Total	4,894.00
Grand Total	4,894.00

SEND ALL INVOICES TO:
South Florida Water Management District
P.O. Box 24682
West Palm Beach, FL 33416-4682

Patrick M. Ryan
Authorized Agent
SOUTH FLORIDA WATER MANAGEMENT DISTRICT
An Equal Opportunity Employer - M/F/H/V

ATTACHMENT "A"

STATEMENT OF WORK
Peer-Review Services for the Third
Workshop on Mercury and Sulfur in South Florida Wetlands

Introduction/Background

The *Third Workshop on Mercury and Sulfur in South Florida Wetlands*, to be held June 21 and 22, 2011, at the South Florida Water Management District (District or SFWMD) headquarters in West Palm Beach, FL, is intended to support activities associated with the District's Sulfur Action Plan, the United States Geological Survey's (USGS) South Florida Ecosystem Program, and the Florida Department of Environmental Protection's (FDEP) South Florida Mercury Science Program. Through this interagency coordination, related efforts are focused on investigating the effects of elevated mercury and sulfur levels throughout the Greater Everglades, with an emphasis on research of mercury and sulfur interactions, internal eutrophication (sulfate-induced nutrient release from sediments), sulfide toxicity, agricultural applications of sulfur, and geographic sulfur mass balance. The primary goals of this workshop are to present and deliberate recent research findings on mercury and sulfur biogeochemistry and ecological effects on South Florida wetlands since the last workshop was held in June 2009, and to determine and prioritize future research needs regarding the impacts of mercury and sulfur on South Florida wetlands.

Dr. William M. Landing (Expert) shall (1) actively participate in the two-day public workshop (Appendix 1); (2) critically review the District's Sulfur Action Plan (Appendix 2) and recent findings on the sulfur and mercury monitoring and research in South Florida wetlands and provide a written report on the (A) critical review of the Sulfur Action Plan and (B) workshop conclusions and recommendations for future research needs on sulfur and mercury in South Florida wetlands.

Work Breakdown

<u>Task 1.</u> Participate in two-day public workshop

The Expert shall actively participate in the interagency workshop at the District's West Palm Beach headquarters on June 21 and 22, 2011, and interact with other meeting participants and attendees. The Expert shall help moderate the discussion session of the workshop (see Appendix 1).

Prior to the workshop, the Expert shall read the District's Sulfur Action Plan and other reports/journal publications (see Appendix 2) provided by the District Project Manager (Dr. Ben Gu) to obtain a basic understanding of the status of sulfur and mercury monitoring and research in South Florida wetlands.

Deliverable 1: Participate in the two day workshop
The Expert shall participate in the two-day workshop on June 21 and 22, 2011, and help moderate the discussion session of the workshop.

Date Due: June 21 and 22, 2011

Task 2. Provide a written report on critical review of the (1) District's Sulfur Action Plan and (2) workshop final conclusions and recommendations for future research needs

Task 2 consists of two sub-tasks, Tasks 2.1 and 2.2. In Task 2.1, the Expert shall conduct a critical review of the District's Sulfur Action Plan, which shall comprise Part 1 of the Expert's Draft Report and Final Report deliverables. In Task 2.2, the Expert shall provide a written report on the final workshop conclusions and recommendations for future research needs, which shall comprise Part 2 of the Expert's Draft Report and Final Report deliverables. The Expert shall submit the Draft Report and Final Report deliverables to the District Project Manager in Microsoft Word format, with an estimated length between 5 and 10 pages, respectively. The content of the Draft Report and Final Report shall include a title page, introduction, critical review of the District's Sulfur Action Plan (Part 1), workshop conclusions and recommendations (Part 2), and literature cited.

The District's Sulfur Action Plan is designed to address 15 management questions regarding the impacts of sulfur loading into South Florida wetlands. Research findings will provide critical information on the mechanisms that may lead to elevated methylmercury in water and biota, sulfate-induced internal eutrophication, sulfide toxicity and agricultural applications of sulfur, and geographic sulfur mass balance. This information is intended to aid in supporting the agency's ecosystem restoration efforts and water management decisions. In Task 2.1, the Expert shall critically review the Sulfur Action Plan and provide written comments and suggestions, including but not limited to the following three questions:

(1) Are data gaps sufficiently identified?
(2) Should other questions on the impacts of sulfur to South Florida wetlands be considered?
(3) Can research projects be further prioritized based on the importance of information needed to address the impacts of sulfur to South Florida wetlands?

Task 2.2. The Expert shall provide final conclusions and recommendations based on the literature review, workshop presentations, consensus from the workshop discussion session, and understanding of the sulfur and mercury issues in South Florida wetlands.

Deliverable 2.1: Draft Report on the critical review of the Sulfur Action Plan and workshop conclusions and recommendations for future research needs

Date Due: June 30, 2011

SFWMD staff will review the Expert's Draft Report and the District Project Manager will submit District's comments to the Expert within one week (by July 7, 2011) upon receiving the draft deliverable.

Deliverable 2.2: Submit Final Report on the critical review of the Sulfur Action Plan and workshop conclusions and recommendations for future research needs

The Expert shall review and address agency comments in the Final Report and submit the final deliverable to the District Project Manager within one week after receiving these comments.

Date Due: July 14, 2011

Evaluation Criteria for Acceptance of Deliverables

Task 1. Successful completion of Task 1 will be evidenced by the Expert's active participation in the two-day public workshop, thoughtful interaction with other workshop participants, and help in moderating the discussion sessions.

Task 2. Successful completion of Task 2 (including Tasks 2.1 and 2.2) will be evidenced by submitting Draft and Final Reports (including incorporating one round of agency comments into final deliverable), which respectively comprise (1) a critical review of the District's Sulfur Action Plan, and (2) final conclusions and recommendations that reflect key findings from the workshop presentations, consensus reached during the workshop discussion session, and understanding of the sulfur and mercury issues in South Florida wetlands.

Responsibilities of the District's Project Manager

The District Project Manager, Dr. Ben Gu (bgu@sfwmd.gov; 561-682-2556), will provide the Expert with:

- District's Sulfur Action Plan and nine reports and journal publications on sulfur and mercury research and monitoring in South Florida wetlands (listed in Appendix 2) for critical review (at least one week prior to the workshop).
- Copies of workshop presentations (at least one week prior to the workshop).
- Copies of workshop notes taken during workshop (within two days after the workshop).

Summary of Timeline and Responsibilities for Each Task

Copies of Reports/Journal Publications and Workshop Presentations	Ben Gu	Expert	June 15, 2011
Participation in two-day public workshop (Task 1)	Expert	Workshop	June 21 and 22, 2011
Copies of Workshop Notes	Ben Gu	Expert	June 24, 2011
Draft Report (Task 2.1)	Expert	Ben Gu	June 30, 2011
District Comments on Draft Report	Ben Gu	Expert	July 7, 2011
Final Report (Task 2.2)	Expert	Ben Gu	July 14, 2011

Payment for Services: An honorarium of $4,894.00 will be paid to the Expert for participation in the workshop and providing final report on the critical review of the Sulfur Action Plan and the workshop conclusions and recommendations.

Appendix IV: Responses to SFWMD staff comments on draft peer review report submitted June 27, 2011.

District Feedbacks on Dr. Landing's Draft Workshop Report: received 7/7/2011

Reviewer 1

1. Introduction should also include a description of what Dr. Landing is doing for the District.
Response: Appendix III: the peer review contract has been was added.

2. At the end of Project 1, the conclusions are helpful. It is also worth noting that field data in WCA-2 is consistent with their findings: even in high S environments in the middle of WCA-2, TP levels are extremely low. Notice also that much of the research done to develop the TP criterion of 10 ppb was done in WCA-2 under enriched S conditions.
Response: Thanks for pointing out this agreement.

3. As is discussed later in his report, Dr. Landing correctly discussed the contribution of oxidation to S exports from the EAA. Project 2, paragraph 4, is very important and statements need to be very exact. Soil oxidation is NOT an agricultural phenomenon alone and it will not stop unless the EAA is back under water. Importantly, stopping ALL agricultural S subsidies CAN NOT alter exports significantly based on current estimates. Lake inputs and oxidation overwhelm local activities. As this paragraph is honed, it must be remembered that water does not move through the EAA in a traditional upstream, downstream pattern. It can be recycled multiple times as it gradually moves south through irrigation and stormwater discharges.
Response: The text in Part 1, pg. 4-5 and in Part 2 (Recommendations), pg. 15-16 has been carefully written to reflect the information that was presented at the workshop and discussed on Day 2. Soil oxidation in the EAA is exclusively an agricultural phenomenon, since it was a flooded wetland where peat soil was accumulating prior to the onset of agricultural activity. It is not recommended that all agricultural use of sulfur be halted; only that Best Management Practices be developed to minimize export of sulfate from the EAA to the EPA. The north to south gradient in sulfate from the EAA to the ENP demonstrates the dominant influnce of sulfate from agricultural activities, despite the vagaries of water movement throughout the system.

4. On Projects 3 and 4, we must be cautious about interpretations of site specific studies. Any climate cycle or hydroperiod alteration will alter the site mass balance, giving the impression of in situ trends when surface water is simply reflecting changes in import and export at the site. Just a cm or two can alter site specific loading, so we must be careful in data interpretation. In other words, a site can potentially show a multiple year decline in both S and Hg having NOTHING to do with the interaction thereof, just small landscape changes in water movement.
Response: The recommendation for supporting modeling work has been edited to emphasize the need for coupled hydrologic and biogeochemical modeling.

5. I would like to see more provocative thoughts from Dr. Landing regarding Part 2 on the presentations. Did he agree with all the author's assertions?

Response: The peer review contract does not call for a detailed review of each presentation. Significant comments from the discussion of the authors' conclusions have been added where appropriate.

The Waldon et al. zero order work may have huge implications. Does Dr. Landing agree with this mixed reactor kind of modeling? Interesting, there are huge mass differences reflected in REMAP S data across the Everglades between wet and dry seasons, and the relatively high reduction flux found by Waldon et al. COULD account for this.
Response: There wasn't adequate time at the workshop for Waldon to thoroughly describe his modeling framework, and I have not seen any hard copy reports or publications on this issue. However, I would point out the following. From Waldon's presentation (slide 9):

Within a single model compartment:

$$d(hC)/dt = L - kC \qquad (1)$$

where

C = concentration of surface water (g/m3)
h = depth (m)
L = net loading rate in the cell (g/m2 yr)
k = disappearance rate (m/yr)
t = time (yr)

I would start by writing:

$$d(C)/dt = L/h - fC \qquad (2)$$

C = concentration of surface water (g/m3)
h = depth (m)
L = net loading rate in the cell (g/m2 yr)
f = pseudo-first order rate constant for sulfate removal (1/yr)
t = time (yr)

multiplying through by h yields:

$$d(hC)/dt = L - (f*h)C \qquad (3)$$

so that Waldon's "k" is now recognized as the pseudo-first order rate constant multiplied by the depth of the compartment. The depth of each compartment is not constant, and there is no reason to believe that the pseudo-first order rate constant should in fact be a constant; thus there is no reason for "k" to be constant. The pseudo-first order rate constant for sulfate removal will not be a constant for the following reasons. The sulfate removal presumably actually happens in the upper pore water of the sediment where sulfate reduction takes place. The rate of sulfate reduction is a function of many things (organic substrate availability, temperature, bacterial assemblage) and it would surprise me if it were constant across WCA-1.

If we assume that sulfate removal from the water column of a compartment is via sulfate reduction in the sediments, then the proper way to express the equation is:

$$d(C)/dt = L/h - (Dz * \Delta C/\Delta z)/h \qquad (4)$$

Dz = effective diffusion coefficient for sulfate mixing into the pore water
$\Delta C/\Delta z$ = concentration gradient for sulfate across the sediment water interface

Multiplying through by h yields:

$d(hC)/dt = L - (Dz * \Delta C/\Delta z)$ vs. Waldon's $d(hC)/dt = L - kC$

Can we relate $(Dz * \Delta C/\Delta z)$ to Waldon's kC? Not without some assumptions.

$\Delta C/\Delta z$ is expanded as $(Cpw-C)/\Delta z$ where Cpw is the pore water sulfate at some appropriate distance (Δz) into the sediment. If the Cpw were to go to zero, then:

$$d(hC)/dt = L - (Dz * C/\Delta z) = L - Dz/\Delta z * C$$

and one could try to relate $Dz/\Delta z$ to Waldon's "k" parameter. Dz might be reasonably constant, but the distance Δz into the sediment where Cpw goes to zero will not be. So, either way, there should be no expectation that Waldon's "k" should be a constant across WCA-1.

I do not understand why they don't use something like Eqn (4), unless it is because they do not know the $\Delta C/\Delta z$ for their compartments.

6. Did Dr. Wright concur with the estimates of agricultural application rates in mass balance studies?
Response: Dr. Wright says: "Any rate is just a crude estimate. I suppose the rate mentioned below (37 kg/ha/yr) is as good as any. But some growers do not apply any S, some may put on a little. Perhaps it would be good to state that any estimate (or even better a range of estimates) is based on the Schueneman paper about 10 years ago.

7. Recommendations for future research: On S mass balance studies, be careful on back pumping assertions. Back pumping is only done under high water conditions and much of the S may have come from the lake in the first place. Huge S inputs to the lake are from mass loading through northern tributaries. More definitive tracking is needed. Why the assertion on agricultural applications when the data on the next page demonstrates on the order of 10 % of mass moving south can be associated with applications? Reducing uncertainties is very important for mass balance, but most management decisions can be based on constrained estimates even if imprecise.
Response: This issue is addressed in Part 1, pg. 4-5 and in Part 2, pg. 15-16.

Reviewer 2
I read through the report quickly and do not have any major comments except to note that Tom James and I did an analysis of the Lake O sulfate budget a few years ago (FLMS abstract and

presentation) so, contrary to what is indicated in the report, there is some information on this. This information was summarized in Orem et al. 2011 (Critical Reviews in Environmental Science and Toxicology).
Response: This is extremely relevant to my review of the 2009 SFWMD Sulfur Action Plan. However, from my reading of Orem et al. (2011), I am not sure that the Lake Okeechobee sulfur mass balance has been “nailed down” completely. Since the inputs and outputs vary over time, it is necessary to actually keep a running inventory for each compartment in the system from Lake Okeechobee to the ENP.

Reviewer 3

I have read through Bill’s report and do not have anything to add or any edits. It is a nice summary but he doesn’t give any “peer review”, any analysis of the presentations or information presented or the quality or value of the information.
Response: It was not within the scope of the contract to provide a detailed analysis of the presentations, however I have added comments where I felt there was a significant issue to be raised. In general, I did not hear things in the workshop presentations that sounded unreasonable. Ultimately, it is a judgment call on the part of the SFWMD staff as to the value of the information as it pertains to their goals.

Reviewer 4

1. Regarding sulfur –caused P release from DB Environ’s study, they did not find any significant release of P. One of the possibilities is that the P release under high SO4 is quickly assimilated by the plant community, resulting in no net increase in water column P. This might be especially true for WCA-2 U3 site where P is depleted.
Response: The implication is that plant growth would be enhanced. Macrophytes or epiphytes or algae or all? DBE looked at sawgrass leaf elongation for evidence of sulfide toxicity and saw no increase or decrease. Does this mean that the plant growth rates did not change? The district may wish to add plant growth monitoring (macrophytes and epiphytes and algae) to this study.

2. Regarding the review of sulfur action plan: I would like to see more comments and recommendations from the peer reviewer. Does the plan provide a full coverage of critical research on sulfur/mercury? Is there any project that is not critical or considered as low priority in the plan?
Response: I understood that the goal of the workshop was to identify data gaps and research needs with respect to the action plan, not to question the value of the items already in the plan (which I assume had been thoroughly vetted by many people).

3. Page 6 (the peer reviewer should number the pages): Point 2 of the 2nd para: MeHg (monomethyl mercury) is not the most toxic form of mercury, the dimethyl mercury is.
Response: Page numbers have been added for ease of reviewing and reference. While it is true that dimethylmercury is more toxic that monomethyl mercury, MeHg is far more abundant in this system and is the form that biomagnifies into fish tissue.

4. Line 6 from bottom, page 6: regarding sulfate reduction: it is mentioned here any significant reduction is likely to provide benefits to the ecosystem as whole. I think there will be shifts/increases of mercury hotspots as sulfate concentrations are reduced to lower levels that fall into the Goldilocks region. It is not known how long the optimal level of sulfate will last because this optimal level ranges wildly from above 1 to 20mg/L. We might see the worst mercury problem for a long time before it gets resolved.
Response: I disagree with this comment. We have seen the “Goldilocks” zone shift south in the EPA as the sulfate plume has also moved south. Reductions in sulfate loading from the north should serve to shift the zone back north (where MeHg production may increase again), but regions farther south should see reductions in MeHg formation.

5. Page 9: On Sue Newman’s presentation. Point 6: I don’t think there is a conflict between Sue and Dave’s data. The similarly low levels of TS and THg in the soil from the Park have nothing to do with the high THg in Gambusia. This is consistent with the view that it is not mercury but sulfate (maybe combined with DOC) that leads to elevated mercury methylation in south Florida.
Response: Agreed. Newman was referring to sediment levels of total sulfur and total Hg and Krabbenhoft was referring to sulfate concentrations in the water column.

6. Recommendations: first, please number all recommendations.
Response: Done

Second, I would like to see a concise/bullet point type summary of each recommendation (as a separate section?). This is especially useful to the agency managers.
Response: Done

Finally, I don’t think it is clear yet under what conditions (SO4, H2S and DOC) that will stimulate the highest methyl mercury production (regarding Mercury methylation and demethylation). The relationship between sulfate and methylmercury rate is a mess (see Corrales et al. 2011 STE). I believe more work should be done.
Response: Agreed (see Recommendation 5), however the consensus from the workshop participants was that we know enough about the relationships between sulfate and MeHg production already that we should focus on reducing sulfate pollution.

7. Format: Please place the title of this report, reviewer’s name/affiliation and contract number in the first page.
Response: Done.

District Feedbacks on Dr. Landing’s Draft Workshop Report: Received 7/14/2011

Recommendation 1: should "water" mass balance be mentioned here? The district has various hydrological models for the Everglades and hydrology will be used in sulfur mass balance.
Response: It doesn't hurt to specify "water" along with sulfur, although I think we all assume that hydrologic modeling would be part of any detailed sulfur mass balance modeling.

Recommendation 2: This looks very general. Various biogeochemical models have been developed for the Everglades. It seems we should be more specific to sulfur and mercury modeling here.
Response: I agree. I have changed the first line of the recommendation to read:
Recommendation 2: Support development of models for the various biogeochemical and physical components of the system focused on mercury, sulfate, DOM.

Recommendation 3: It has been suggested that this recommendation should be placed as #1.
Response: That was not the sense I got from the discussion among the workshop attendees on the afternoon of Day 2.

Recommendation 4: TOC and DOC have been routinely monitored by the district although the numbers of site have been reduced. I suggest the language be modified to "continue and expand" instead of "add". DOM/DOC monitoring is especially important in the interior sites.
Response: Agreed. Text has been changed to reflect this.

Recommendation 5: Should we say "Continue to conduct field surveys and experiments...."
Response: Agreed. Text has been changed to reflect this.

Recommendation 3(c): In addition to DBHYDRO which hosts district's database for monitoring and some research projects, the District also has a database named EcoDB which hosts exclusively experiment/survey data generated by district scientists and contractors (for example, Tetra Tech's mercury hotspot study results will be loaded into EcoDB).
Response: I now mention DBHYDRO and EcoDB explicitly. What I heard from the ACME team at the discussion session of the workshop was that they did not think they had access to all of the district's sulfate data. So, I am simply stressing the need to make all data available.
Reply from Ben Gu: The district is looking into resource availability for loading the unrequested
sulfate data into DBHYDRO.

Recommendation 4: "regular monitoring of DOM concentrations be initiated": I suggest this statement be changed to "regular monitoring of DOC concentrations be continued and expanded (or other language of your choice). As mentioned earlier, the district monitors DOC which can be easily converted to DOM (if needed).
Response: Agreed. The text has been changed to reflect this.

END OF REPORT