Appendix 3B-2: Peer-Review Report on the Everglades Agricultural Area Regional Sulfur Mass Balance: Technical Webinar

William Landing[1]

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Peer Review Report on the Everglades Agricultural Area Regional Sulfur Mass Balance: Technical Webinar: November 20, 2013

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Introduction:

The Everglades Agricultural Area Regional Sulfur Mass Balance: Technical Webinar was held on November 20, 2013 in West Palm Beach, FL, with participation from staff and scientists from the Florida Department of Environmental Protection (FDEP), the South Florida Water Management District (SFWMD), the University of Florida's Institute of Food and Agricultural Sciences (IFAS), and the U.S. Geological Survey (USGS). The designated peer reviewer, Dr. William M. Landing, participated in the workshop.

Six separate presentations were made during the webinar, covering many aspects of the sulfur cycle in the Everglades Agricultural Area (EAA):

1. **EAA Soils, Geology, Land Use and Best Management Practices.** Timothy Lang, Samira Daroub, and Jehangir Bhadha, University of Florida – IFAS, Everglades Research and Education Center, Belle Glade, FL.
2. **Proposed Sugarcane Elemental Sulfur Recommendations and Sulfur Removed by Sugarcane Harvest**. Mabry McCray, University of Florida – IFAS, Everglades Research & Education Center, Belle Glade, FL.
3. **EAA Sulfur Mass Balance**. Alan L. Wright, Mabry McCray, and Rongzhong Ye, University of Florida – IFAS, Everglades Research & Education Center, Belle Glade, FL.
4. **The Sulfate Budget of Lake Okeechobee**. R. Thomas James, Lake and River Ecosystem Section, Applied Sciences Bureau, Water Resources Division, SFWMD, West Palm Beach, FL.
5. **EAA Sulfate (SO_4) Measurements and Mass Balance for WY1980 - WY2009**. Lucia Baldwin, Compliance Assessment & Reporting Section, Water Quality Bureau, Water Resources Division, SFWMD, West Palm Beach, FL.
6. **Connate Seawater as a Source of Sulfate in the Northern Everglades: Discussion of Available Evidence**. Curtis D. Pollman, Aqua Lux Lucis, Inc., Gainesville, FL., William H. Orem, USGS, Reston, VA.; Nenad Iricanin, Compliance Assessment & Reporting Section, Water Quality Bureau, Water Resources Division, SFWMD, West Palm Beach, FL.

The presentations are available from Paul Julian of FDEP at: paul.julian@dep.state.fl.us.

Part 1 of this report represents a review of the presentations from the November 2013 webinar. An updated table of the various sulfur fluxes into and out of the EAA is discussed in Part 2, followed by a discussion of our progress on the recommendations from the Peer Review Report on the Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands (June 21-22, 2011).

The agenda for the meeting is attached as Appendix I. Appendix II contains a copy of the "Regional Sulfur Mass Balance Centered on the EAA: An Outline for Investigations" (July 30, 2013 draft) prepared by Garth Redfield, Ben Gu, and Ming Chen of the SFWMD Water Quality Bureau.

Part 1: Review of the presentations from the November 30, 2013 webinar: Everglades Agricultural Area Regional Sulfur Mass Balance Technical Webinar

The context for the webinar is covered in the document "Regional Sulfur Mass Balance Centered on the EAA: An Outline for Investigations" (July 30, 2013 draft) prepared by Garth Redfield, Ben Gu, and Ming Chen of the SFWMD Water Quality Bureau (Appendix II).). This document begins with the statement, "Refining the regional mass balance for sulfur is worthwhile", and this is still true. There is evidence that sulfate fluxes through the EAA and into the Everglades Protection Area (EPA) play an important role in the mercury cycle in the EPA, such that understanding how (and whether) we can reduce methyl mercury in fish throughout the system requires a better understanding of the sulfur cycles. While there is still a great deal of information needed to accomplish this task, the reports from the November 30, 2013 webinar add to our understanding of sulfur cycling in Lake Okeechobee, the EAA, and the fluxes of sulfur and sulfate to and from the various "basins" in this portion of the Everglades.

Page 2 of the Redfield et al. (2013) draft document summarizes general observations on the regional mass balance for sulfur, and outcomes from the July 2011 "Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands." Since the July 2011 workshop, several projects have been completed and were reported at the November 2013 webinar. These presentations are reviewed not in the order of their presentation, but in sequence from Lake Okeechobee, to the EAA, to the potential impacts on the EPA.

1. **The Sulfate Budget of Lake Okeechobee**. R. Thomas James, Lake and River Ecosystem Section, Applied Sciences Bureau, Water Resources Division, SFWMD, West Palm Beach, FL.

Dr. James summarized the mass balances for water, chloride, and sulfate in Lake Okeechobee since 1975, as published in James and McCormick (2012). The sulfate burden in the lake has declined rather steadily since ca. 1990 due to declining sulfate concentrations in the inflows from northern sub-watersheds and the EAA, and reduced back-pumping from the EAA. The loading of sulfate from the EAA to the lake accounted for ca. 50% of the total sulfate loading prior to the late 1980s, but now accounts for only 10-20%. The slight negative bias in the residuals from their mass balance calculations suggest that the lake acts as a small net sink for sulfate. The net loading of sulfate from the lake to the EAA has therefore declined to ca. 14,000 tons of sulfate per year (for the period 2007-2011). Using the atomic weight of sulfur (32.066) and the molecular weight of sulfate (96.062), this converts to a loading of ca. 4,700 tons of sulfur per year. However, this loading was calculated using only dissolved sulfate data, and did not include potential dissolved or particulate forms of organic sulfur (these are not routinely measured).

This reviewer finds that:
The sulfate to chloride mass ratio in the lake is on the order of 0.6, compared to the seawater mass ratio of 0.14. If 100% of the chloride in the lake was ultimately due to the atmospheric deposition of marine aerosols (aka "sea spray") to the lake watershed and input of connate (relict) seawater due to an upward flux of groundwater, and if the sulfate to chloride ratios in those two sources were both ca. 0.14, then one can calculate that ca. 77% of the sulfate in the lake is "excess" sulfate. The majority of the excess sulfate is presumably due to applications of

sulfur in the watershed for agriculture and ranching. Some of the excess sulfate could also come from runoff of excess sulfate due to atmospheric deposition in the watershed, since the majority of sulfate in the atmosphere is “excess” due to coal combustion. Direct atmospheric deposition of sulfate to the lake is a very small term in the sulfate mass balance for the lake (3%, as reported by James and McCormick, 2012).

During discussion of the potential impacts from connate seawater to the sulfate budget for the EAA (discussed in more detail below), it was suggested that application of potassium chloride (KCl; as a fertilizer for crops) could be responsible for some fraction of the chloride load in these watersheds. If this is significant in the Lake Okeechobee watershed, then less of the chloride in the lake would have come from sea-spray or connate seawater, and the percentage of excess sulfate would therefore be higher than 77%.

2. **EAA Soils, Geology, Land Use and Best Management Practices.** Timothy Lang, Samira Daroub, and Jehangir Bhadha, University of Florida – IFAS, Everglades Research and Education Center, Belle Glade, FL.

Dr. Lang reported on “EAA Soils, Geology, land Use and Best Management Practices”. He notes that sugarcane represents 75-80% of the crops grown in the EAA. Soil subsidence due to soil oxidation was initially at a rate of about 1” per year (from 1923-1980) and has since slowed to about 0.5” per year. He discussed the hydrology of the EAA, noting how farmers control the water elevation in the fields by pumping water in and out. He discussed the success of the BMP program for phosphorus control, noting that P loading out of the EAA has been reduced by about 55% since 1995. He presented some useful ambient data for sulfate and chloride concentrations in farm canals from the EAA.

This reviewer finds that:
There is a need to quantify the vertical movement of water from the shallow layer of porous shell material through the overlying soils during periods of low water and back again during periods of high water in order to evaluate the influence of connate seawater that may be percolating upwards. The sulfate and chloride data from the farm canals show that there is a significant amount of excess sulfate in the canals, and the data should be used to calculate the concentrations of “excess” sulfate in the farm canals.

3. **Proposed Sugarcane Elemental Sulfur Recommendations and Sulfur Removed by Sugarcane Harvest.** Mabry McCray, University of Florida – IFAS, Everglades Research & Education Center, Belle Glade, FL.

Dr. McCray presented data on sulfur removal from the EAA via sugarcane burning and harvesting and suggested new BMPs for agricultural sulfur applications. He reported that the harvest of sugarcane directly removes 0.52 lbs. of sulfur per ton of harvested cane; also expressed as 21 lb. of sulfur per “40 ton acre” of crop. He reported that burning of the fields prior to harvest removes an additional 13 lb. sulfur per “40 ton acre”, which converts to 0.32 lbs. sulfur per ton of harvested cane, for a total removal of 0.84 lb. sulfur per ton of harvested cane. McCray also discussed their results on sugarcane crop yields from controlled applications of sulfur and manganese. Their recommendation is to apply 250-500 lbs. of sulfur

per acre (pre-plant in furrow) for soils with pH>7.5, 100-250 lbs. of sulfur per acre for soils with pH between 7.2-7.4, and 100 lbs. of sulfur per acre using STM5 (5% Mn) for soils with pH<7.1 every 3-4 years. These application rates are significantly lower than the current recommendation to apply 500 lbs. of sulfur per acre for soils with pH > 6.6.

This reviewer finds that:
If the typical sugarcane harvest is on the order of 17 million tons per year, the removal of sulfur from sugarcane harvesting should be on the order of 6,500 tons of sulfur per year:

0.84 lb. sulfur/ton cane x 17,000,000 tons cane/year x 1 ton/2200 lbs. = 6,491 tons sulfur/year

Lang et al. (2013 Webinar presentation, cited above) reported that sugarcane represented about 75-80% of the crop activity in the EAA, and if the removal of sulfur from the harvest of other crops (vegetables, rice, sod) removed similar amounts of sulfur per ton of harvested crops, the crop harvest estimate would increase to ca. 8,100 tons sulfur per year. This estimate is only about 33% of "EAA crop harvest" estimates for sulfate removal from the EAA shown in Table 1 (see Part 2 below; taken from James and McCormick, 2012), and suggests that the EAA crop removal estimates are still very uncertain.

One can also express the sulfur removed by harvesting of sugarcane and other crops as an equivalent amount of sulfate:

6,500-8,100 tons sulfur/year x (96.062 g SO4/32.066 g S) = 19,500-24,300 tons SO4/year

The new recommendations for sulfur application rates are well below the older 500 lbs. sulfur per acre (for soil pH>6.6), although McCray pointed out that growers recognize that the previously recommended rate was not cost-effective (and is probably not being used). During discussion, it was mentioned that elemental sulfur is not the only form of sulfur that is applied; some sulfate salts such as ammonium sulfate may be used. McCray was not able to estimate how much sulfur is actually being applied across the EAA (or in what forms), thus, we still do not have a reliable estimate for the amount of agricultural sulfur being applied in the EAA.

The sulfur application rates in the EAA that had been used in previous sulfur budget calculations by Schueneman (2001), Wright et al. (2008), Corrales et al (2011) and Gabriel et al (2010) were summarized by James and McCormick (2012). Those rates are reported as "Assumed agricultural sulfur application rates" (see caption to Table 5 in James and McCormick, 2012), and ranged from 16-37 kg/ha/year. Using the rate of 22.4 kg/ha/year from Gabriel et al. (2010), that converts to an application rate of about 60 lbs. per acre every 3 years, or 12% of the maximum "recommended" rate of 500 lbs. per acre every 3 years. Is this reasonable?

4. **EAA Sulfur Mass Balance.** Alan L. Wright, Mabry McCray, and Rongzhong Ye, University of Florida – IFAS, Everglades Research & Education Center, Belle Glade, FL.

Dr. Wright summarized data on soil oxidation as a source of sulfate, the partitioning of soil sulfur between elemental sulfur, water-soluble sulfate and water-soluble organic sulfur in the EAA, and results from time-course monitoring of sulfur speciation in soils after application of elemental sulfur in sugarcane fields. Using a soil leaching analytical method (water extraction, Ye et al., 2010), he reported that control soils had about 320 mg water-soluble SO_4-S/kg wet soil, 55 mg water-soluble organic-S/kg wet soil, and insignificant amounts of elemental sulfur. Note that Wright is reporting all of his sulfur results on the same mass basis (a sulfur mass basis) so that they can be directly compared.

The time-course data after two months showed that application of 448 kg of elemental sulfur per hectare (400 lbs. per acre) in furrows prior to planting of sugarcane yielded ca. 480 mg elemental S/kg wet soil after two months, 120 mg water-soluble SO4-S/kg wet soil, and ca. 10 mg water-soluble organic-S/kg wet soil (values corrected for control soils with no sulfur addition). Note that the concentrations of water-soluble organic S were not significantly different between the various treatments, suggesting that the elemental sulfur that was applied was not converted appreciably into water-soluble organic sulfur. Applications of elemental sulfur at lower levels (112 kg/ha and 224 kg/ha) yielded intermediate levels of elemental S and water-soluble sulfate in the soils. The concentrations of elemental sulfur in the soil declined to background levels after 13 months (at harvest), yet the concentrations of water-soluble sulfate also declined to background levels over the same time period. This suggests that either the growing sugarcane sequestered the sulfate, that the sulfate was lost to greater depths in the soil (via reduction to sulfide), or that it was washed from the soil by rainfall/irrigation. Wright could not make any definitive statement about where the sulfate could have gone, and concluded that additional research was needed to resolve this.

One discussion item was whether the observed concentrations of elemental sulfur after two months could be compared to the amount that was initially applied. Wright replied that this would require new measurements of the bulk density of the soil and the depth to which the elemental sulfur might have mixed into the soil, however data exist to start this calculation. The bulk density of EAA soils under sugarcane cultivation is reported to be ca. 0.47 g (dry)/cm^3 (470 kg (dry)/m^3) (http://edis.ifas.ufl.edu/ss514) and the depth of sampling was 6 inches (0.15 m), thus:

(448 kg S applied/ha)/(470 kg dry soil/m^3)/(0.15 m depth) x 1 ha/10,000m^3 = 635 mg S/kg dry soil

If the wet density of the soil was 1,200 kg/m^3, the same sulfur application rate (mixed to 0.15m depth) should have produced 248 mg S/kg wet soil. This is only about half of the 480 mg S/kg wet soil observed two months after application, and this discrepancy further highlights the need for wet and bulk density measurements of the EAA peat soils used for this experiment.

5. **EAA Sulfate (SO4) Measurements and Mass Balance for WY1980 - WY2009.** Lucia Baldwin, Ph.D., Compliance Assessment & Reporting Section, Water Quality Bureau, Water Resources Division, SFWMD, West Palm Beach, FL.

The gross and net inflows of sulfate from Lake Okeechobee to the EAA, canal outflow of sulfate from the EAA to the Water Conservation Areas (WCAs), and from the WCAs to the Stormwater Treatment Facilities (STAs) have been calculated from DBHYDRO data using the "Fortran Program for Calculating EAA Basin Flows and Phosphorus Loads" (www.sfwmd.gov/portal/page/portal/...pdf/40e_63_everglades_prog.pdf). Dr. Baldwin described declining trends in sulfate concentrations and reported "EAA sulfate" loads, which represent the difference between the outflow of sulfate from the EAA (to Lake Okeechobee and the STAs) and the inflow of sulfate to the EAA (from Lake Okeechobee and other adjacent basins). The difference should be the net mobilization of sulfate from all sources within the EAA. The values ranged from 26,214 to 193,535 tons of sulfate per year (average 82,342). Dr. Baldwin compared these "EAA sulfate loads" to values reported by Shueneman (2001), Wright et al. (2008) and Corrales et al. (2011). The calculations were done for water years 1980-1995 (pre-BMP implementation) and 1996-2009 (post-BMP implementation) and for the total 1980-2009 period. While the sulfate measurement program at the interface between the EAA and Lake Okeechobee ended in 2009, the data from 22 stations show lower median sulfate concentrations for the period 1996-2009 than for the period 1989-1995.

This reviewer finds:
Dr. Baldwin's fluxes are all calculated using DBHYDRO data, where sulfate concentrations are reported in mg SO4/L, so her fluxes and loads are expressed as mass of sulfate (not sulfur). In addition, Dr. Baldwin reports that she converted fluxes that had been reported in the literature on a mass of sulfur basis to a mass of sulfate basis. As will be discussed in detail in Part 2 of this report, it is often not clear in the literature on what basis many of the sulfur fluxes have been reported.

On Slide 12, this statement appears, "The model does not account for the loads associated with irrigation flow from the lake into the EAA basin." I questioned this statement, since my interpretation of this statement was that water from the lake that was used for irrigation within the EAA was not being included as an Inflow of sulfate to the EAA, and it would be a mistake not to do so. Dr. Baldwin has replied:
"I understand how the statement could be misleading. The intended message is that the model used does not rigorously quantify how much of Lake Okeechobee water is retained in EAA for irrigations; for such a term a more thorough mass balance (containing rain, evapotranspiration, seepage, etc.) is needed. The model used focuses on estimating mainly the flow-through."

My interpretation of this explanation is that the modelling does not explicitly quantify the fraction of the Inflow water from Lake Okeechobee to the EAA that it used for irrigation within the EAA. Since that fraction represents an internal cycling term for water and sulfate within the EAA, it is not needed to calculate the mass balance of sulfate fluxes for the EAA.

On the original Slide 13 (attached), Dr. Baldwin has a map with the pump stations highlighted in various colors. The legend says red arrows are for "Inflow to EAA Basin" and blue arrows are for "Outflow from EAA basin (runoff)", and purple arrows are for "Lake Flow Through Inflow to the EAA (calculated value)". The equation at the bottom says red arrows are for "Outflow", blue arrows are for "Inflow" and purple arrows are for "Lake Flow Through". I assumed that the

colors for the red and blue arrows in the equation had been mislabeled, and to be consistent with the map the red arrows meant Inflow and the blue arrows meant Outflow. Dr. Baldwin has since confirmed this, and has provided a revised Slide 13 (attached).

On both versions of slide 13, Dr. Baldwin separates Inflow into two categories; purple arrows represent flow from the lake into the EAA basin and red arrows represent flow from adjacent areas into the EAA basin, while blue arrows represent flow out of the EAA (to Lake Okeechobee, to the STAs, to Rotenberger, to the Holey land, and to WCA2 and WCA3).

I had questioned the meaning of “Lake Flow Through”, and Dr. Baldwin explained that it represents an Input; Lake Okeechobee water that enters the EAA canals and passes through the EAA without much interaction (water or sulfate exchange), then exits the EAA as part of the total Outflow. This explanation is consistent with the equation at the bottom of original Slide 13 showing a “mass balance of sulfate fluxes” approach to estimating the amount of sulfate added to the water in the EAA. The “EAA Load” is the net amount of sulfate added to the water from all sources and sinks within the EAA between the time water enters and leaves the EAA:

EAA Load = Outflow – Inflow – Lake Flow Through

The revised Slide 13 provided by Dr. Baldwin shows a different equation that shows how the “Lake Flow Through” is calculated. Dr. Baldwin provided this explanation for the new equation:

“Of the Lake water (~500-600 thousand ac-ft) entering the EAA canals from the Lake, only a small fraction (~100 thousand ac-ft) is purposefully directed south (Flow through) to the EPA or urban areas for environmental or water supply needs. Therefore, the Flow through component is estimated by comparing the total lake inflows to the total basin outflows plus the adjacent inflows on a daily basis as:

$$\text{Flow through}_{\text{Basin}} = \text{minimum}\,(\text{Inflow}_{\text{Lake}}, \text{Outflow}_{\text{Basin}} - \text{Inflow}_{\text{Adjacent}})\text{”}$$

I point out that while I wanted the “Lake Through Flow” term to be defined, it is not essential to know how the “Lake Flow Through” term has been calculated in order to estimate the most important term; the “EAA Load”.

The original Slide 15 (attached) shows a purple arrow (labeled 3) and the text says it is the “Flow through from the lake Okeechobee to downstream.” Because this was confusing to me, Dr. Baldwin has submitted a revised Slide 15 (attached) where the purple arrow has been modified so that it merges with the Outflow (1) from the EAA to “downstream”. This revised image is consistent with the explanation of the “Lake Flow Through” term above.

The original Slide 15 repeats the mass balance of sulfate fluxes that is used to calculate the “EAA Load”. The revised Slide 15 shows a different equation where a new term has been introduced; “$\text{Runoff}_{\text{basin}}$”. This has been defined by Dr. Baldwin as:

“Runoff: The "EAA runoff" is defined as the term for the total water discharged at the southern boundaries minus the "flow through" water.

$$\text{Runoff}_{\text{Basin}} = \text{Outflow}_{\text{Basin}} - \text{Flow through}_{\text{Basin}}$$

My interpretation of this definition is that this term is a water flux term, not a sulfate flux term, and while it is embedded in the calculation of sulfate fluxes, it is not essential to an evaluation of the sulfate fluxes into and out of the EAA.

The mass balance of sulfate fluxes equation on the original Slide 13 and Slide 15 represents how one can calculate the net loading of sulfate from all activities within the EAA.

EAA load = Total outflow loads (1) - Adjacent Basin Inflow Loads (2) - Flow-through (3)

This EAA Load is then compared to other published estimates of the “Total Annual EAA SO4 Load” on both versions of Slide 15, although the estimates from the literature were revised downward slightly in the new version of Slide 15. I questioned whether everyone was expressing this critically important term on a mass of sulfur or a mass of sulfate basis, and also whether everyone was doing the calculation the same way. In different versions of Table 1 from Landing (2011), Table 5 from James and McCormick (2012) and Table 1 from Redfield et al. (2013), various input and output terms for sulfur and sulfate into and out of Lake Okeechobee, the EAA, and the ENP have been presented. My re-analysis of these flux estimates and the different versions of the flux tables is presented below in Part 2.

As will be discussed in more detail in Part 2, I would set things up a little differently for a “mass balance of sulfate fluxes” equation, putting all outputs on one side of an equation and all inputs on the other side:

Outputs: EAA to Lake O(out) + EAA to STAs(out) + crop harvesting + any other outputs =

Inputs: Lake O to EAA(in) + Adjacent basins to EAA(in) + soil ox. + Ag. Appl. + groundwater + atmospheric dep. + any other inputs

Re-arranging the terms into an equation for Outputs - Inputs:

[EAA to Lake O(out)+EAA to STAs(out)-Lake O to EAA(in)-Adjacent basins to EAA(in)] + crops + any other outputs - soil ox. - Ag Appl. - groundwater - atm dep - any other inputs = 0?

The first 4 terms on the left in brackets are what Dr. Baldwin calculates from the flow and concentration data; what she calls "EAA load" on the original versions of Slide 13 and Slide 15. If the system is balanced for any given time period (total outputs = total inputs), then we can move all the other terms from the left to the right:

"EAA load" = [Lake O(out)+STAs(out)-Lake O(in)-Adjacent basins(in)] =
-crops - any other outputs + soil ox. + Ag Appl. + groundwater + atm dep + any other inputs

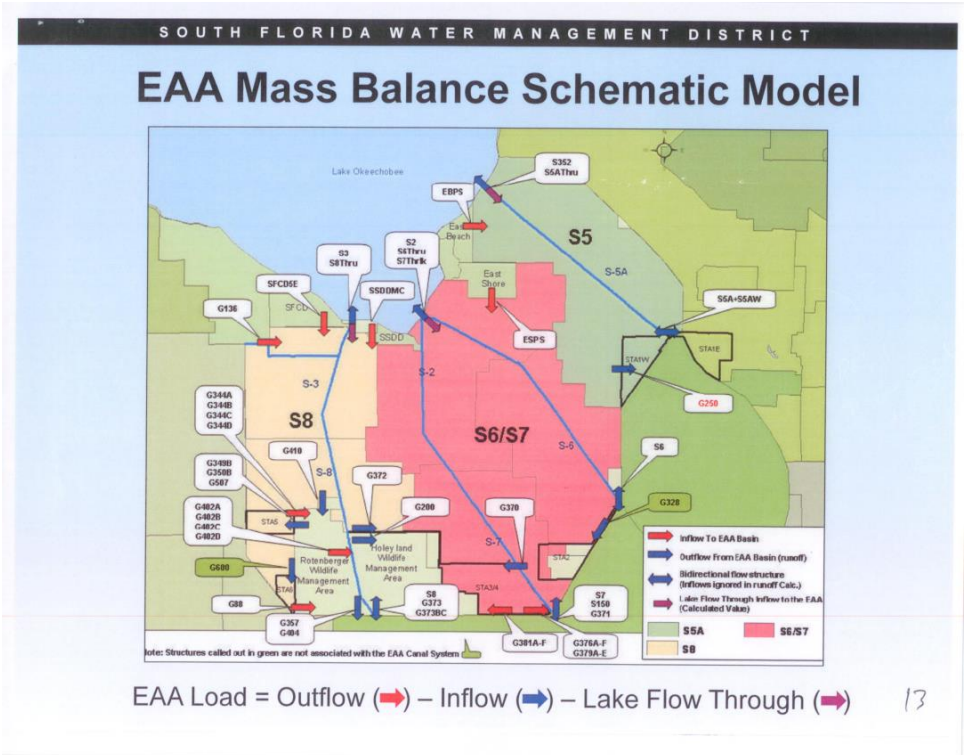
In the table at the bottom of slide 15, Dr. Baldwin compares her "EAA load" values to other published estimates, but as noted above, many of the values in Table 1 (in Part 2 below) are

for the mass of sulfur added or removed from the EAA, while some of the other terms appear to have been based on the mass of sulfate (and will therefore be about 3x higher than if they had been expressed on the mass of sulfur). In Part 2 of this report, I have generated a new table for these comparisons, where all of the fluxes are reported both on the mass of sulfur basis as well as the mass of sulfate basis. I also re-calculate the “EAA Load” term from the earlier published data in order to compare to Dr. Baldwin’s estimate.

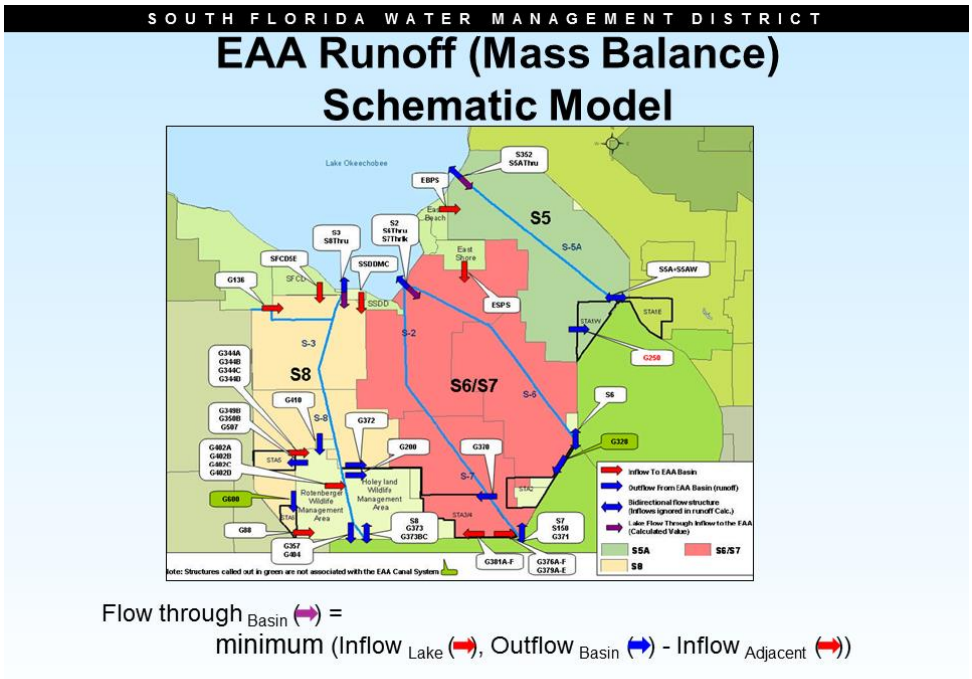
I suggested that Dr. Baldwin’s results would be most useful for estimating the net sulfate loading from Lake Okeechobee to the EAA, since she has all the data to do that. I asked “How does that compare to the 14,000 tons of sulfate per year from the talk by James?” Dr. Baldwin replied:
“This is an important comparison which needs to be performed during the next phase of the analysis. At the current stage, the sulfate loads produced by the EAA are estimated using an ‘off the shelf’ model, which consider slightly different sites at the interface with Lake Okeechobee than the mass balance model used by Tom James for the Lake.”

I suggested that Dr. Baldwin could calculate the total sulfate flux from the EAA to the STAs (the EAA to STAs (out) term), which might be close to what enters the EPA (depending on how much sulfate is retained (or contributed!) by the STAs themselves. That is a number we really need! Dr. Baldwin replied:
“At the second phase of the analysis the sulfate EAA output can be parsed between the neighboring basins. Nevertheless the sulfate export from STA to EPA needs a separate analysis since we do not know how much SO4 is retained in STAs.”

Dr. Lucia Baldwin, original Slide 13



Dr. Lucia Baldwin, revised Slide 13



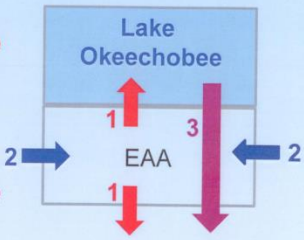
Dr. Lucia Baldwin, original Slide 15

SOUTH FLORIDA WATER MANAGEMENT DISTRICT

SO4 EAA Mass Balance Program Output

Total SO4 loads

1. Total outflow loads to Lake Okeechobee and to Downstream Structures
2. Inflow load from adjacent Basins
3. Flow through from the lake Okeechobee to downstream



EAA load = Total outflow Loads (1) –
- Adjacent Basin Inflow Loads (2) – Flow–through (3)

Output provide values similar to literature values:

Source	Total Annual EAA SO4 load (mt/year)		
	Min	Average	Max
Mass Balance Program for WY80-WY09	26,214	82,342	193,535
Schueneman,2001;Wright et al.,2008		104,904	
Corrales et al.,2011 for WY95-WY09		155,712	

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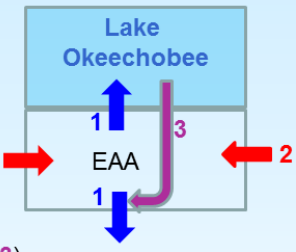
Dr. Lucia Baldwin, revised Slide 15

SOUTH FLORIDA WATER MANAGEMENT DISTRICT

SO4 EAA Runoff (Mass Balance) Program Output

Total SO4 loads

1. Total outflow loads
2. Inflow load from adjacent Basins
3. Flow through from the lake Okeechobee to downstream



Runoff $_{Basin}$ = Outflow $_{Basin}$ (1) - Flow through $_{Basin}$(3)

Output provide values compatible with literature values:

Source	Total Annual EAA SO4 load (mt/year)		
	Min	Average	Max
SO4 EAA Runoff Program Output for WY80-WY09	26,214	82,342	193,535
Schueneman,2001;Wright et al.,2008		92,530	
Corrales et al.,2011 for WY95-WY09		110,303	

6. **Connate Seawater as a Source of Sulfate in the Northern Everglades: Discussion of Available Evidence.** Curtis D. Pollman, Aqua Lux Lucis, Inc., Gainesville, FL, William H. Orem, USGS, Reston, VA, Nenad Iricanin, Compliance Assessment & Reporting Section, Water Quality Bureau, Water Resources Division, SFWMD, West Palm Beach, FL.

The potential importance of connate seawater as a source of sulfate to the EAA and EPA was discussed. The evidence for the importance of connate seawater was based on an analysis of the water quality data for samples taken at the G310 and G335 structures where water is pumped from the STAs into WCA2A and WCA3A. Any alteration of water chemistry between the inflow from the EAA into the STAs and the outflow from the STAs to the WCAs cannot be determined from this report. It was suggested that the STAs can remove a relatively small fraction of the sulfate, but they are unlikely to affect the chloride concentrations.

Pollman shows that chloride behaves relatively conservatively in the canal waters, with a strong linear relationship to sodium. While the slope of the relationship (ca. 0.7 g Na/g Cl) is slightly higher than the Na/Cl ratio in seawater (0.55 g Na/g Cl), he argued that there would be no reason for sodium to respond to chloride input from KCl fertilizer application, thus the strong linear relationship between sodium and chloride suggests that other sources of chloride are not significant. He showed under low flow conditions, when groundwater influenced by connate seawater should be most observable in canal waters, that the sulfate to chloride ratio declines dramatically towards the seawater ratio (0.14 g SO_4/g Cl) and the Na/K ratio increases towards the seawater ratio (27 g Na/g K). His results from PCA analysis of the water quality data showed that 3 components explained 80% of the variance in the data, and concluded that the three components represented “Marine-Deep Groundwater” (Ca, Cl, Na, Mg, and conductivity), “Deep Soil Drainage” (DO and NO_3+NO_2), and “Surface Runoff” (TKN and TP). He used the factor weightings from the PCA analysis to calculate the fraction of sulfate in the canal waters that resulted from connate seawater for the period 2000-2013, resulting in an estimate of 27-36%.

Bill Orem then discussed the evidence against the importance of connate seawater as a source of sulfate to the EAA and the EPA. He said that the sulfur isotopic composition of the canal water in the EAA ($\delta^{34}S$ = +21) was similar to that of agricultural sulfur (+18 to +23) and differed from deep groundwater (+12). He also described the uranium isotope data showing that the $^{234}U/^{238}U$ activity ratio in groundwater (+1.3) is significantly higher than in canal waters (ca. +1) or for uranium in phosphate fertilizer (ca. +1).

In the discussion that followed, it was acknowledged by some that reductions in sulfate loading should decrease methyl mercury formation in the WCAs and ENP, and that while it might be possible to lower sulfate loading from the EAA to the EPA, it would be difficult if not impossible to lower the direct input of sulfate to the EPA from connate seawater.

This reviewer finds that:
The use of water quality data to investigate the influence of connate seawater is very compelling, but that the isotopic data are also very compelling. Pollman concludes that connate seawater could be responsible for ca. 30% of the sulfate in canal water leaving the STAs (and by inference, leaving the EAA). What other evidence is there for this? The SO_4/Cl

ratios in the canal waters in LOX, WCA2A and WCA3A are ca. 0.41 g SO_4/g Cl (vs. the seawater ratio of 0.14), meaning that there is a lot of excess sulfate in the canal waters. Assuming that chloride comes only from connate seawater (with the seawater SO_4/Cl ratio), then the fraction of sulfate from connate seawater is ca. 28-37%, in close agreement to Pollman's estimates:

Connate Seawater Sulfate (%) = 100 x [(Total Cl) x (SO_{4sw})/(Cl_{sw})]/(Total SO_4)

If one believes that there are additional sources of chloride other than connate seawater, then the Total Cl term in Equation (5) should be lowered, which would linearly lower the fraction of sulfate attributed to connate seawater. Once again, the very strong linear relationship between Na and Cl argues against the significance of other sources for chloride.

The isotopic data is also not totally inconsistent with the possibility that a modest fraction of the sulfate comes from connate seawater. If connate seawater is responsible for ca. 25% of the sulfate (with an isotopic value of +12) and agricultural sulfur is responsible for ca. 75% of the sulfate (with an isotopic ratio of +23), then the resulting mixture would have an isotopic ratio of:

$(0.25x12)_{sw} + (0.75x23)_{fert} = 20.3$

This is not far from the measured value (+21) in waters of the EAA.

A similar calculation can be done with the uranium isotope data:

$(0.25x1.3)_{sw} + (0.75x1.0)_{fert} = 1.08$

This result (1.08) is only slightly higher than the ratios measured in canal waters (0.92-0.97). Taking all of the evidence into account, it seems quite possible that connate seawater could indeed contribute on the order of ca. 25% of the sulfate in canal waters.

Finally, no new data on atmospheric deposition or biogenic emissions were presented, but they are still considered to be the smallest terms in the sulfur budget for the EAA and the EPA.

Part 2. Revising the sulfur mass balance estimates for the EAA.

Landing (2011) included a table in his report (taken from the work of Donner and Axelrad, Gu et al., 2012, Table 3B-3) that summarized the various loading estimates for sulfur to and from the EAA. That table was also used by James and McCormick (2012; their Table 5) where their new estimates for the net flux of sulfate from Lake Okeechobee to the EAA were reported. As already noted in Part 1 of this report, the fluxes reported by James and McCormick (2012) were on a mass of sulfate basis, while many of the loading estimates in the original summary by Donner and Axelrad were supposedly expressed on a mass of sulfur basis. It is also clear that sulfate data in the DBHYDRO database are reported as mg SO_4/L (SO_4 basis), and the conversion factor to put the water quality data on a mass of sulfur basis is the atomic weight of sulfur divided by the molecular weight of sulfate (32.066/96.062 = 0.334). Thus, one cannot combine and compare loading estimates if they are not on the same mass basis. In a new Table 1 (below), I have incorporated the new loading estimates from the November 2013 webinar with re-calculated estimates from the older data.

The original table showed sulfur loading estimates from soil oxidation (item 1) ranging from 30,464 to 54,127 tons S per year. Gabriel et al. (2010) used estimates for soil sulfur content, subsidence rate, and bulk density to calculate the loading to the EAA from soil oxidation on a sulfur basis (ca. 30,600 tons S per year). If that sulfur were 100% oxidized to sulfate and washed into the canal waters leaving the EAA, the flux of sulfate would be ca. 92,000 tons SO_4 per year. New data from Wright et al. (2013) presented at the November 2013 webinar shows that water-soluble sulfate in EAA soils is important (320 mg SO_4-S/kg) followed by water-soluble organic sulfur (ca. 55 mg organic-S/kg). He did not report total sulfur or total particulate sulfur or total particulate organic sulfur. The total of the water-soluble species (ca. 375 ppm or 0.0375%) is only about 1/10 of the total soil sulfur content used by previous authors to estimate sulfur input to EAA waters from soil oxidation. In Appendix II, Redfield et al. (2013) pointed out that soil oxidation is not a true input to the EAA, since the soil was already there. However, if soil oxidation leads to sulfate in canal waters, then it must be accounted for when trying to estimate the flux of sulfate from the EAA to the EPA in canal waters. Also, if the EAA soil S content of 0.35% includes remnant sulfur from agricultural applications, then it is possible that some of the agricultural sulfur is being double-counted. Regardless, if soil oxidation leads to soluble sulfate in farm canals, it appears to be the largest source term by far, accounting for ca. 60% of the total sulfur input to the EAA. If all sulfur inputs are equally converted to soluble sulfate and escape via canal outflow to the EPA, then soil oxidation would also account for 60% of the sulfate in the outflow from the EAA to the EPA.

Item (2), estimates for the agricultural applications of sulfur are all similar, and were presumably also expressed on a mass of sulfur basis. The estimate from Gabriel et al. (2010) (ca. 6,300 tons S per year), would convert to ca. 19,000 tons of sulfate per year if it were all oxidized to sulfate and washed into farm canals. The application rate of 22.45 kg/ha/year used by Gabriel et al. (2010) is equivalent to about 20 lbs. S per acre per year, or 60 lbs./ per acre for a 3-year growing cycle. This is the 2nd largest term in the sulfur inputs to the EAA, and could account for about 14% of the sulfate in the farm canals. Since soil oxidation and sulfur application are both due to agricultural practices, together they could be responsible for ca. 75% of the sulfate input to the EAA.

The original table showed net loading from Lake Okeechobee to the EAA (item 3), with values supposedly reported on a mass of sulfur basis, ranging from 28,494 to 40,626 tons per year. The re-analysis of the DBHYDRO data by James and McCormick (2012) yields 14,000 tons SO_4 per year, or 4,700 tons S per year averaged over the period 2007-2011. This strongly suggests that the older estimates (also based on DBHYDRO data) were in fact reported on a mass of sulfate basis instead of a mass of sulfur basis. That those earlier estimates were higher than the most recent estimate is perhaps attributable to the facts that (1) back-pumping from the EAA to the lake has declined greatly since 1990, (2) sulfate concentrations in Lake Okeechobee are declining, and (3) the flux of sulfate to the EAA is therefore also declining. This net flux of sulfate from the lake to the EAA is due primarily to agricultural practices in the Lake Okeechobee watershed, and represents about 10% of the total sulfur inputs to the EAA.

Item (4), inflow from levees of 5,585 tons per year, was only included in the EAA loading estimates of Corrales et al. (2011). That estimate was also based on DBHYDRO data, but supposedly reported on a mass of sulfur basis, according to the authors. If so, it would be greater than the revised net flux estimate for sulfur from Lake Okeechobee to the EAA from James and McCormick (2012) and this does not seem reasonable. Thus, I suspect that the estimate in Corrales et al (2011) was actually calculated on a mass of sulfate basis and was simply used in their publication without converting to a mass of sulfur basis. Correcting this flux to a mass of sulfur basis yields 1,955 tons S per year.

Item (5), groundwater input of 4,055 tons per year, was also only included in the estimates of Corrales et al. (2011), was also based on DBHYDRO data, and was said to be reported on a mass of sulfur basis. If this is true, then it rivals the net sulfur flux from Lake Okeechobee to the EAA from James and McCormick (2012); once again this seems unreasonable. I therefore suspect that this flux was also inadvertently reported on a mass of sulfate basis. Converting this flux to a mass of sulfur basis yields 1,354 tons S per year.

Item (6), atmospheric deposition of ca. 4,000 tons per year has been calculated by most authors using NADP and CASTNET data, where the concentrations of sulfate in rainfall are also reported on a mass of sulfate basis. Using my own data from two continuous years (1995 and 1996) of rainfall monitoring at the ENR site (near the STA1W facility) as part of the FAMS project, and extrapolating to the entire area of the EAA, I find 3,285 tons SO_4 per year in wet deposition, or 1,097 tons S per year. Thus, I suspect that the earlier atmospheric wet deposition estimates were inadvertently reported on a mass of sulfate basis. Dry deposition (Item 7) is often expected to be about one half of wet deposition, so a flux of 529 tons S per year, or 1,585 tons SO_4 per year for aerosol dry deposition, seems reasonable.

The crop harvest output of sulfur (Item 8) has been newly estimated by Mabry (2013) in the November 2013 webinar. He reported a removal rate of 0.52 lb. S/ton of harvested cane plus 0.32 lb. S/ton lost during pre-harvest burning. The total of 0.84 lb. S/ton of cane multiplied by an annual average harvest of 17 million tons yields crop removal of 6,491 tons S per year. Since sugarcane represents about 80% of the harvested crops from the EAA, the removal estimate could be as high as 8,100 tons S per year. Expressing this crop removal flux on a mass of sulfate basis yields 24,300 tons SO_4 per year, which is quite close to the earlier crop

harvest estimates that were supposedly reported on a mass of sulfur basis. This suggests that the earlier estimates may not have been correctly reported.

Finally, if Item (9), the canal flux out of the EAA to the EPA, was based on DBHYDRO data in previous estimates, it may also have been calculated on a mass of sulfate basis, not a mass of sulfur basis. Using the revised flux estimates discussed above, and calculating the outflow flux by difference, I find ca. 38,000 tons S per year or ca. 115,000 tons SO_4 per year. The sulfate flux I calculate by difference is very close to the flux reported by Corrales et al. (2011) (116,360 tons per year), and suggests once again that their use of DBHYDRO data was not properly converted from a mass of sulfate basis to a mass of sulfur basis in their paper.

The other flux estimates in the table fall between the fluxes I calculate on a mass of sulfur basis and those I calculate on a mass of sulfate basis. It is therefore not clear what basis was used to calculate many of the earlier flux estimates.

Comparing the various sets of flux estimates to the “EAA load” estimates from Dr. Baldwin, reported at the November 2013 webinar, is difficult since while the estimates from Baldwin (2013) are clearly expressed on a mass of sulfate basis, it is not clear whether some of the earlier fluxes were also calculated on a mass of sulfate basis or a mass of sulfur basis. In addition, not all of the earlier estimates included all of the same terms. In any event, I calculated the equivalent to Baldwin’s “EAA load” from the data in Table 1 by summing soil oxidation plus agricultural applications plus levee and groundwater input plus atmospheric deposition and subtracting the crop harvest flux. My estimate is about 25% higher than that of Baldwin (2013), and probably well within the uncertainty of many of the input and output terms.

I recommend that Dr. Baldwin use the fluxes she calculated from her re-analysis of the DBHYDRO sulfate data to report the gross flux of sulfate from the EAA to Lake Okeechobee and the gross flux of sulfate from Lake Okeechobee to the EAA. The difference between those two fluxes will hopefully come out close to the net flux of ca. 14,000 tons SO_4 per year reported by James and McCormick (2012). I also recommend that Dr. Baldwin use the data from her re-analysis to calculate the flux of sulfate from the EAA to the STAs, which should be reasonably close to the canal flux into the EPA. Both of these calculations can then be directly compared to fluxes reported in Table 1.

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Revised “Table 1”. Estimates of Sulfur Inputs and Outputs in the EAA. Data are highlighted in yellow signify when it is uncertain whether the flux was calculated on a mass of sulfur basis or a mass of sulfate basis. Data highlighted in blue are calculated by difference, by assuming a mass balance of sulfur (or sulfate) for the EAA; the sum of the inputs equals the sum of the outputs.

	Estimates of Sulfur Inputs to and Outputs from canals in the EAA						James &			
		Shueneman/Wright	Corrales	Gabriel et al. 2010			McCormick (2012)	Landing (2014)	Landing (2014)	
		(2001, 2008)	et al. (2011)	Moderate Year	Wet Year	Dry Year	Moderate Year	sulfur basis	sulfate basis	
	EAA area (acres)	700,000	718,073	693,031	693,031	693,031				
	EAA area (Hectares)	283,280	290,594	280,460	280,460	280,460	280,466	280,466	280,466	
	soil oxidation rate (cm/yr)	1.3	1.4	1.3	1.3	1.3				
	Sulfur concentration in soils (percent)	0.96	0.35	0.37	0.37	0.37				
	Sulfur input to EAA									
1	soil oxidation (tons/yr)	54,127	49,169	30,646	30,646	30,646	30,646	30,571	91,583	Gabriel et al (2010) 109 kg-S/ha/year
2	agricultural applications (tons/yr)	2,371	11,775	6,286	6,286	6,286	6,286	6,310	18,905	Gabriel et al. (2010) 22.5 kg-S/ha/year
3	Lake Okeechobee Net (tons/yr)	33,968	35,217	31,057	40,626	28,494	13,948	4,656	13,948	James (2013) 13,948 tons SO4 per year
4	levees (tons/yr)		5,858					1,955	5,858	Corrales et al. (2011) 5,858 ton SO4/year?
5	groundwater (tons/yr)		4,055					1,354	4,055	Corrales et al. (2011) 4,055 ton SO4/year?
6	atmospheric deposition, wet (tons/yr)	2,064	4,229	3,864	2,861	3,295	3,864	1,097	3,285	FAMS Project (ENR site 1995-1996) 3.91 kg-S/ha/year
7	atmospheric deposition, dry (tons/yr)			529	487	508	529	529	1,585	Gabriel et al. (2010)
	Total S (in)	**92,530**	**110,303**	**72,382**	**80,906**	**69,229**	**55,273**	**46,472**	139,218	
	Sulfur Loss from EAA									
8	harvest (tons/yr)		23,182	25,500	25,500	25,500	25,500	8,100	24,266	Mabry (2013) 0.84 lbs. S/ton x 17 million tons/year plus 20%
9	TS out to STAs or WCAs	92,530	116,360	72,382	80,906	69,229	29,773	38,372	114,953	Calculated by difference
	Total S (out)	**92,530**	**139,542**	**97,882**	**106,406**	**94,729**	**55,273**	**46,472**	**139,218**	
	"EAA Load" (1+2+4+5+6+7-8)	58,562	51,904	15,296	14,293	14,727	15,296	33,187	99,420	
								27,486	82,342	Baldwin (2013) 82,342 tons SO4/year

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Part 3: An update on the recommendations from the "Peer Review Report on the Third Annual Workshop on Mercury and Sulfur in South Florida Wetlands (2011)" (Landing, 2011).

Recommendations for Future Research Needs

These five recommendations for future research needs were developed and discussed on the afternoon of Day 2 of the 2011 workshop. The rationale for each recommendation is explained in detail in the following section, and amended as necessary to reflect the new information presented at the November 2013 webinar.

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 Study

There is compelling evidence that elevated levels of sulfate can enhance 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 EPA. Revised estimates for the sulfur budget in the EAA (see Part II, Table 1) implicate the same three processes for the majority of the sulfate loading reaching the EPA via flow from the EAA: sulfate release from soil oxidation, sulfate input from Lake Okeechobee (and other surrounding basins), and agricultural applications of sulfur and sulfate salts.

Table 1 (Part II, above) shows that there are still large variations in the individual input and output estimates, some of which I now believe are due to mix-ups in the conversion between loading on a mass of sulfur basis vs. a mass of sulfate basis.

The release of sulfur from soil oxidation in the EAA is one of the largest terms in all of the EAA sulfur input budgets (66%), yet it is still highly uncertain due to uncertainty in the rate of soil oxidation and the sulfur and water content of the soils. The most recent estimates by Gabriel et al. (2010) may be the most reliable, but additional work on this topic is clearly needed. It is also important to conduct soil oxidation studies on background soils that have never received agricultural sulfur inputs in order to avoid "double-counting" agricultural

sulfur during soil oxidation and release of sulfate. Since the fate of sulfate resulting from soil oxidation is not currently known, studies should be conducted to determine how much sulfate is actually released to farm canals as a function of the sulfur speciation in the soils and the water management practices within the EAA.

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. The agricultural application rate used in previous estimates ranges over a factor of ~4. As noted above, the application rate of 22.45 kg/ha/year used by Gabriel et al. (2010) is equivalent to about 20 lbs. S per acre per year, or 60 lbs./ per acre for a 3-year growing cycle, and accounts for ca. 13.5% of the total sulfur input to the EAA. This may be reasonable, however it cannot be verified without additional data from the farmers who are actually applying sulfur containing fertilizer in the EAA. It is also important to get data on the form of sulfur applied (elemental sulfur vs. sulfate salts).

The latest data for the net input of sulfate from Lake Okeechobee (James and McCormick, 2012) of ca. 14,000 tons of sulfate per year (4,656 tons of sulfur per year) may be the most reliable. Interestingly, Orem et al. (2011) estimated that the net flux of sulfate from the lake to the EAA was only 4,500 tons of sulfur per year, and this agrees very well with the latest estimate when both are expressed on a mass of sulfur basis.

Only the budget from Corrales et al. (2011) includes flow over levees and a groundwater flux. These two fluxes were estimated using DBHYDRO data, and appear to have been inadvertently reported on a mass of sulfate basis in their original paper. When expressed on a mass of sulfur basis, they represent 4.2% and 2.9% of the total sulfur input to the EAA, respectively. If the original estimates by Corrales et al. (2011) were in fact correctly reported on a mass of sulfur basis (as they asserted in the paper and confirmed in a recent phone conversation with me), then these two fluxes would each represent about 10% of the total sulfur input to the EAA, which is not insignificant. Additional re-analysis of DBHYDRO data should be conducted to better quantify these two fluxes.

My own data on wet deposition of sulfate to the EAA (two years of data from 1995-1996) yields a flux of sulfur that is about 1/3 of the previous estimates, suggesting that the earlier estimates may have also been inadvertently reported on a mass of sulfate basis. Using my data, atmospheric deposition only represents about 3.4% of the total sulfate input to the EAA. While it would be useful to re-analyze the NADP and CASTNET atmospheric deposition data to determine whether the earlier estimates were expressed on a mass of sulfur or a mass of sulfate basis, it is probably a small term in the overall budget and there is not much that can be done anyway to lower that input flux. EPA regulations that will continue to reduce the emission of SO_2 from coal-fired power plants should serve to lower this flux in the coming decade.

With these new flux estimates, it still appears that crop harvesting can approximately balance the estimated application rate of agricultural sulfur. However, release of sulfate from soil oxidation (66%) and net inflow of sulfate from Lake Okeechobee (10%) together

account for ca. 76% of the total sulfur input to the EAA and are both due to man's agricultural activities in the Lake Okeechobee watershed and the EAA. If all of the sulfate burden in the EAA behaves similarly, then one can infer that "agricultural" sulfate will be responsible for ca. 76% of the sulfate flowing from the EAA to the EPA. This estimate is also consistent with the conclusions of Pollman et al. (2013) that connate seawater can account for about 30% of the sulfate in canal waters entering the EPA from the EAA.

However, because of the uncertainties in the various flux estimates (especially whether they were calculated on a mass of sulfur or a mass of sulfate basis), it is still not 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. While the water and sulfate mass balances for Lake Okeechobee are now much better constrained (James and McCormick, 2012; James, 2013), 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 should be more accurately quantified across the EAA via a comprehensive soil survey. Measurements of sulfur speciation in soil cores (Wright et al., 2013 Webinar presentation) have shown that water-soluble sulfate is important, however it is still necessary to acquire new data (or evaluate existing data) on all forms of sulfur in EAA soils, both water-soluble and particulate forms.

IFAS may soon recommend revised best management practices (BMPs) to reduce the agricultural application of sulfur in the EAA, from the previous recommendation of 500 lbs. per acre to as low as 100 lbs. per acre (Mabry, 2013 Webinar presentation).

Recommendation 2: Modeling Studies

It must be 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 application of the EAA phosphorus model to sulfate (Baldwin, 2013 Webinar presentation) has provided better constraints on the flows of sulfate into and out of the EAA.

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. Based on the time-series modeling presented by James (2013 Webinar presentation) and Baldwin (2013 Webinar presentation), it is clear that there are large inter-annual variations in the fluxes of sulfate in canal waters into and out of the EAA. Either all groups should adopt time-series modeling, or a fixed time period should be chosen (for example 2000-2010) to compare models that rely on average concentrations and fluxes.

Another suggestion/recommendation which was not discussed during the 2011 workshop or the 2013 webinar is to conduct metadata analysis using the historic water quality data (sulfate, DOC, color, etc.). The purpose of 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. Data presented at the 2013 webinar have already shown declines in the sulfate concentrations (and inventories) in Lake Okeechobee and the EAA between 1975 and the present. The DBHYDRO database almost certainly contains additional data that can be mined to reveal trends in sulfate concentrations and inventories in all of the sub-basins with the entire system.

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).
(NB: Monitoring of rainfall Hg deposition was not discussed at the 2013 webinar. Recommendation 3(a) is repeated here with modification to reflect that the Florida Mercury TMDL draft report was released in May 2012).

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 draft report from the FDEP-sponsored Florida Freshwater TMDL study was released in May 2012. The report states that the mass of Hg released from Florida sources was 25 kg for the base model year compared to a total atmospheric deposition loading of 6,043 kg for 2009. While some sites in Florida are more affected by local Hg emissions than others, Fig. 7 from the report shows that atmospheric mercury deposition to the Everglades is predominantly derived from long-range transport from non-Florida sources.

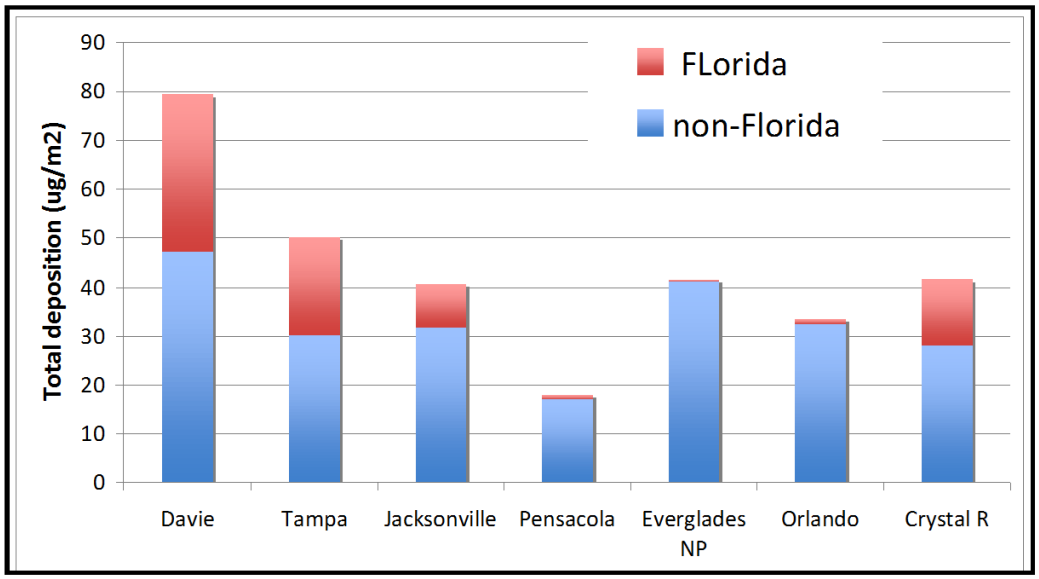

Figure 7. Annual (2009) total mercury deposition (µg/m^2) results from CMAQ partitioned into Florida and non-Florida sources (partition based on Florida and non-Florida tags) for 7 sites.

Recommendation 3(b): Fish and other biota:
(NB: Hg concentrations in fish and other biota were not discussed at the 2013 webinar. Recommendation 3(b) is repeated without modification).

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 contributing to net 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.

The information presented at the 2013 webinar indicates that this is happening, although it is also clear that there are many data gaps at many of the monitoring sites. It may also be true that the SFWMD has gone to less frequent monitoring at some sites. It is important to identify the canal and control structure sites where the majority of the flow (and sulfate fluxes) are occurring, and to continue to collect water quality samples from those sites into the future. Since the equations one can use to calculate “excess” sulfate (presented in Part 1 of this report) can be more accurate when data are collected for chloride, sulfate, sodium and potassium, these parameters should be measured.

Recommendation 4: Dissolved organic matter (DOM)
(NB: DOM was not discussed at the 2013 webinar, so Recommendation 4 is repeated without modification)

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
(NB: Mercury methylation and demethylation were not discussed at the 2013 webinar. Recommendation 5 is repeated without modification).

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

Regional Sulfur Mass Balance Centered on the Everglades Agricultural Area
Technical Webinar, Review of Scientific Investigations
November 20, 2013, 8:30 am – 12:30 pm
Agenda

Introduction and Initial Observations on Regional Sulfur Mass Balance

1. Welcome and background on context of the workshop.	Paul Julian, FDEP	8:30 - 8:35
2. Everglades Agricultural Area (EAA) and prior EAA Sulfur mass balances.	Garth Redfield, SFWMD	8:35 - 8:40
3. EAA soils, geology, land use and best management practices.	Tim Lang, UF IFAS	8:40 - 9:05

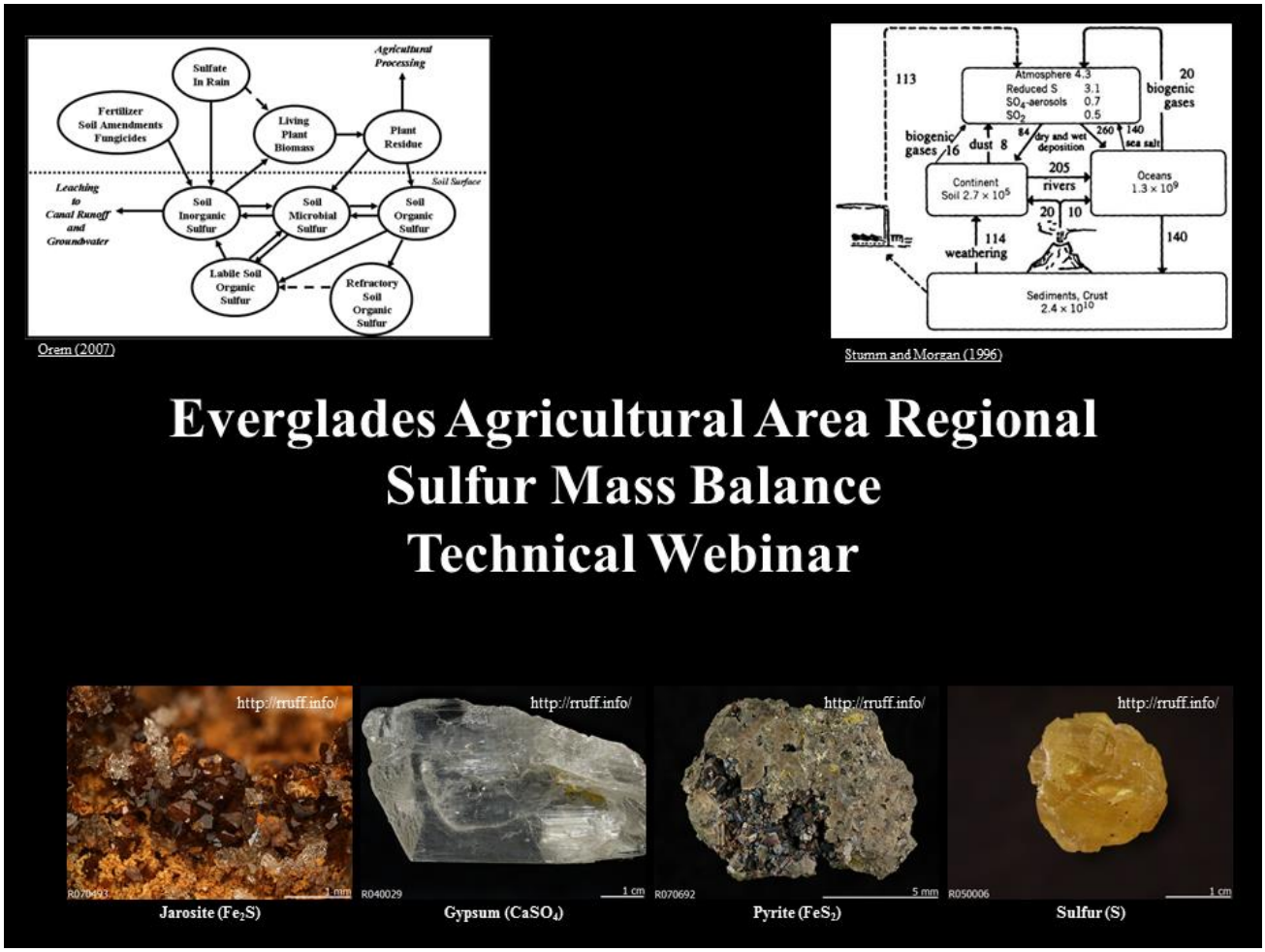
EAA Sulfur Mass Balance – Soil and Agricultural Parameter Estimates

4. Agricultural uses of sulfur, rates of application in the EAA and sulfur export through sugarcane harvesting, burning and movement from soils into canals.	Mabry McCray, UF IFAS	9:05 - 9:30
5. Sulfur storage, speciation and distribution in EAA soils.	Alan Wright, UF IFAS	9:30 - 9:55
6. Break.		9:55 - 10:05

EAA Sulfur Mass Balance – Estimating Sulfur Imports and Exports for the EAA

7. Relationship of total dissolved and particulate sulfur to sulfate in water and soils; role of organic Sulfur in the EAA Sulfur mass balance.	Alan Wright, UF IFAS	10:05 - 10:30
8. The Sulfate Budget of Lake Okeechobee.	Tom James, SFWMD	10:30 - 10:55
9. EAA Sulfate Measurements and Mass Balance for the Interval WY1980-WY2009.	Lucia Baldwin, SFWMD	10:55 - 11:20
10. Break.		11:20 - 11:30
Panel Discussion: 11. The role of groundwater, including the importance of connate seawater and other marine-derived deposits.	Nenad Iricanin, SFWMD Bill Orem, USGS Curt Pollman, Aqua Lux Lucis	11:30 - 12:10
12. Concluding Remarks and Follow-up Discussion.	Paul Julian, FDEP	12:10 - 12:30

“Welcoming” slides from the Everglades Agricultural Area Regional Sulfur Mass Balance Technical Webinar (November 20, 2013).



Orders of Business

- In Person Attendees
  - Please mute cell-phone
  - Bathrooms
  - Coffee
  - Questions

- Webinar
  - Please refrain from putting the telecon. on hold.
  - If you can't hear please let us know.
  - Questions

- Presentations and reference material will be made available on the webinar FTP site: (*ftp://ftp.dep.state.fl.us/pub/outgoing/Sulfur%20Mass%20Balance%20Webinar/*).

- If the FTP site link becomes broken email *Paul.Julian@dep.state.fl.us* for copies of material.

Baker , W., J. Madden and P. Wade. 2014. Chapter 4: Nutrient Source Control Programs. In: 2014 *South Florida Environmental Report – Volume I*. South Florida Water Management District, West Palm Beach, FL, USA.

Appendix II

"Regional Sulfur Mass Balance Centered on the EAA: An Outline for Investigations" (July 30, 2013 draft) prepared by Garth Redfield, Ben Gu, and Ming Chen of the SFWMD Water Quality Bureau.

Regional Sulfur Mass Balance Centered on the EAA: An Outline for Investigations

Garth Redfield, Ben Gu and Ming Chen, Water Quality Bureau
July 30, 2013 draft

Refining the Regional Mass Balance for Sulfur is Worthwhile

The 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 (SFWMD), West Palm Beach, Florida) emphasized the need to continue improving estimates of regional sulfur (S) mass balance and transport. The workshop report by Landing (2011) and Wright (2011) identified a series of data and information gaps that merit attention. This recommendation is fully consistent with Project 2 of the Sulfur Action Plan which also called for a regional mass balance for sulfur. The fundamental motive for seeking more information on S sources and sinks is based on the 'Goldilocks' concept describing a bell-shaped relationship between the availability of S and the production of methyl mercury (see review by Gilmour, 2011). The District and Florida Department of Environmental Protection (FDEP) agree with other workshop participants that refining a regional sulfur mass balance is an important next step in our understanding of sulfur as a water quality constituent in South Florida. Again this year, the 2013 South Florida Environmental Report (SFER) Peer Review Panel noted the need to continue improving our understanding of sulfate sources and their effects in South Florida.

The Comprehensive Everglades Restoration Plan (CERP) (2002) is based on a balanced approach to getting 'the water right' in quantity, quality, timing and distribution. CERP also requires due consideration of water quality constituents such as sulfur that may have significant direct and indirect environmental effects must be factored into restoration planning as described at Implement Principles and Guidelines, **http://www.evergladesplan.org/about/rest_plan_pt_05.aspx**: "During implementation, we will ensure that the components of the Plan are located, designed, and operated consistently with existing and future water quality protection criteria and restoration targets." The importance of sulfur to restoration is specifically addressed in a 'CERP System-wide Performance Measure - Greater Everglades Wetland Sulfate Concentrations in Surface Water', available at the same URL. This outline for investigations supports both CERP and the Central Everglades Planning Project (CEPP) with the recognition that understanding sulfur from the EAA area is important to water quality planning in restoration of the Everglades Protection Area (EPA).

This outline for investigations is a living document aimed at organizing and prioritizing studies of the sources, sinks and transport of sulfur primarily in the Everglades Agricultural Area (EAA). As emphasized by Landing (2013), each subject considered in the mass balance needs to be approached in a 'risk analysis' framework considering the potential magnitude of the term and the likelihood of making progress at a reasonable cost. These concepts are embedded in the topics considered in the following outline for investigations.

General Observations on a Regional Mass Balance for Sulfur

For the workshop, Landing (2011; Table 1) utilized various sources of data and information on sulfur mass balance for the EAA summarized by Donner and Axelrad and published in Table 3B-3 of Gu et al. (2012). These estimates were based on those published by Gabriel et al. (2010), Corrales et al. (2011) and Orem et al. (2011) and have recently been modified with new lake sulfate loads by James and McCormick (2012). The canal outflow of sulfate is the dominant loss term from the EAA to the Water Conservation Areas (WCAs) and from the WCAs to the Everglades National Park (ENP), while atmospheric deposition and biogenic emissions (output) are the smallest terms (Gabriel et al., 2010; Axelrad et al., 2011). For the EAA, the mass balance estimates of Corrales et al. (2011) and Shueneman (2001) suggest that soil oxidation is one of the dominant factors in mobilizing sulfur from the EAA to the downstream areas (49,169 & 54,127 metric tons per year, resp.).

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 (Bates et al., 2002; Orem et al., 2011). Unfortunately, this consistency does not link quantitatively to sources so that the relative amount of sulfur from agriculture, lake water and groundwater cannot be determined from the isotopic mixture alone. Landing (2011) suggests review of isotopic data to determine whether sources are different enough to allow source apportionment in waters leaving the EAA. The isotope data do suggest that some sulfate released from soil oxidation is partially sulfur from current and 'legacy' agricultural applications. Prior to development as agricultural land, the areas south of Lake Okeechobee were accumulating peat soil with presumably relatively low sulfur content (ca. 0.4 %). However, background sulfur content of peat soils in South Florida needs to be investigated and quantified sub-regionally. If useful data do not already exist, new sampling and analysis is warranted. Results from earlier work on sulfur in soils were synthesized by Gabriel et al. (2010) in the 2010 SFER available at: http://www.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_sfer/tab2236037/2010%20report/v1/chapters/v1_ch3B.pdf.

Input of sulfate from Lake Okeechobee to the EAA is comparable albeit somewhat less than that released via soil oxidation, although this input term is complicated by the tradeoff between runoff from the lake and "back-pumping" from the EAA to the lake. After 1983, the role of "back-pumping" was reduced greatly and net export from the lake to the EAA increased; over the period of record since 1975, the lake has been a net exporter of sulfur to the EAA (James and McCormick, 2012). Orem et al. (2011) asserted that agricultural back-pumping is a major source of sulfur to the lake. The thorough analysis of Lake Okeechobee sulfur inputs and outputs by James and McCormick (2012) does not support this view and provides enough information on the linkage between the lake and the EAA that additional information as part of the EAA sulfur mass balance is probably not needed. James and McCormick (2012) estimate that on the average over the past five years, about 13,000 mt of sulfur was imported to the EAA from the lake. This loading rate is substantially lower than earlier mass balance studies of Corrales et al. (2011), Gabriel et al. (2010), and Schuenemann (2001).

Mass Balance Estimates Provide a Starting Point for Future Studies

Landing (2011) provided recommendations based on the third annual workshop discussion and his interpretation thereof. The first recommendation was: conduct careful water and sulfur mass balance studies for the entire system, from the tributaries to Lake Okeechobee to the outflow from the ENP. This section of his workshop report is included here *verbatim* (Landing, 2011, pp. 17 – 19):

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).

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).

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

Estimates of Sulfur Inputs to and Outputs from the EAA					
	Shueneman (2001)	Corrales et al.	Gabriel et al. (2010)		
	Wright et al. (2008)	(2011)	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					

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 the University of Florida Institute of Food and Agriculture (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.

Reducing Uncertainties in the Regional Mass Balance for Sulfur

The headings of Landing (2011, Table 1) provide a good starting point to organize an outline of components of an S mass budget and they also encompass the mass balance outline presented by Wright (2011). Landing (2013) recommends an S mass balance for each WCA as part of this process. While this is a good recommendation for the long-term, priority should be given to the EAA as an S source to downstream marshes in the EPA. Each element of the mass balance below is discussed by **what is known, what is not known and what is recommended** as next steps for information gathering on the regional mass balance for sulfur centered on the EAA.

I. Background State Constants

a. EAA land area (acres)

- What is known: In terms of land area acting as a drainage basin for mass balance, the EAA is approximately 693,031 acres as used by Gabriel et al. (2010) in their S mass balance estimate.
- What is not known: The effective area covered as Stormwater Treatment Areas (STAs), internal and external levees, urban areas, areas in different crop types and canal area is not now clear or readily available.
- What is recommended: Add detail on how land area is accounted for in the mass balance for the EAA. STA land area needs to be handled separately in the S budget. Geographical information system (GIS) experts can assist in accounting for all aspects of land structure. While the overall improvement in S mass balance may be minor with these refinements, it is a relatively straightforward effort to better account of land areas in the EAA.

b. Soil oxidation rate

- Sulfur in Soils: Landing (2013) and the mass balance studies referenced above, report oxidation as an input term in the mass balance. If surface water is the mass balance target, then oxidation can be viewed as an input. As a land mass, however, sulfur in EAA peat soils is a resource pool of various forms of sulfur which is dominated by organic sulfur. The organic S in the pool can be transformed by oxidation into sulfate which is readily available to plant uptake or can be reduced to sulfide by sulfate-reducing bacteria under anaerobic conditions. Therefore, consideration of soil oxidation rates in the context of an EAA mass balance provides information transformation for apportioning S sources, not as an estimate of *de novo* inputs or outputs.
- What is known: When virgin peat or muck soil is brought into use for farming the rate of subsidence or natural oxidation is rapid at first then it decreases with time. The rate of subsidence appears closely proportional to the depth of water table (Jones, 1948; Snyder, 2005). Also, soil oxidation rates in the EAA appear to be lower than in the past due to better land management techniques, including best management practices, BMPs, for nutrient control. The rates used by Gabriel et al. (2010) and others are from 1.30 to1.40 cm oxidized per year (Table 1). The range of available values is quite high, however, and when this uncertainty is considered with associated soil S content and bulk density, the overall uncertainty in estimating oxidative release of S is substantial. Gabiel et al. (2010) used an estimated oxidative release rate of 109 kg/ha/yr of total S in the EAA. Soil

oxidation is a large term of the S mass balance in the EAA and uncertainty in this estimation should be reduced greatly if possible.

- What is not known: In addition to the uncertainties just noted, it is not known how much of S released through decomposition is exported into canals then out of the EAA, how much is held on site and how much enters groundwater.
- What is recommended: A team effort is needed to improve estimates of oxidative release and export to canals in the EAA through both surface and groundwater. The soil oxidation rate of 1.30 cm per year is an estimation based on a series of historical studies conducted by IFAS (Jones, 1948; Snyder, 2005). A new soil survey in the EAA may be useful to fine-tune the current and site-specific soil oxidation rates, which could possibly be less than 1.30 cm per year as discussed earlier. In addition, it may be feasible to geo-reference rates using GIS and global positioning system (GPS) technologies to permit the incorporation of spatial variation. Based on initial estimates reviewed by Landing (2011 and 2013), this pathway for S must be better quantified as it may represent a 30 to 40 % apportionment of S outputs from the EAA. The role of organic sulfur should also be better understood and the mass balance cannot be based solely on imports and exports of sulfate. Direct measurements of the total sulfur pools in soils, groundwater and surface water are needed.

c. Sulfur concentration in soils (percent or mass / soil mass)

- What is known: EAA peat soils contain about 0.37 % TS (Gabriel et al., 2010) and it is notable that this content falls in the same range as TS in unfarmed peat from the Okefenokee Swamp in Georgia (0.26 – 0.48%, Price and Casagrande, 1991). The relative proportion of inorganic SO_4^{2-} of the total S (TS) in 208 soils from different regions of the world averages 5.2% but varies widely, according to soil type and depth within the soil profile. In calcareous soils much of the S exists as SO_4^{2-} co-crystallized with the $CaCO_3$ and thus a smaller proportion of the TS exists in organic forms (Frency, 1986).
- What is not known: Reasons for the large range of values both in the EAA and in the literature need to be clarified and information is needed on the forms of S and their distribution. If more sub-regional values could be developed, the EAA S content could be more accurate.
- What is recommended: One of the biggest differences between the three estimates for sulfur input to EAA as indicated in Table 1 is because of the EAA soil TS contents used by different researchers (Schueneman, 2001; Wright et al., 2008; Corrales et al., 2011; Gabriel et al., 2010). We need additional direct systemic measurements of TS and the organic and inorganic forms of the TS in the EAA soil profiles and get values from other freshwater peats. In addition to percent TS and organic and inorganic S, good estimates of bulk density are essential for comparable data.

d. Other considerations

- When soil TS concentration and soil oxidation rates are used for the calculation of the EAA TS release, earlier studies need to be reviewed to make sure that geometric means instead of arithmetic means were used for the calculation.
- The relative proportion of sulfate to TS in canal water needs to be determined for both imports from the lake and exports to the Everglades.

II. Sulfur Inputs to the EAA and Transformations (metric tons / yr)

a. Soil oxidation

- What is known: There are substantial uncertainties involved in estimating soil oxidation as noted above (I. b.). The amount of S mineralized from organic form to inorganic form has been found to be directly proportional to pH and $CaCO_3$ addition (Frency, 1986). Oxidation is not an input to the EAA as Corrales et al. (2011) indicate; it is a transformation process of TS in the soils and sediments, facilitating movement into the water column and out into canals when conditions are right. Downward movement of sulfate (SO_4^{2-}) is reduced when soils contain appreciable quantities of organic matter, and occurs more rapidly with increasing pH (Hagstrom, 1986). Landing (2013) views oxidative release as an input term to surface water; here, we are using mass balance as a geographic term and surface water and ground water as a vehicle for import and export. Good estimates of oxidation are useful for apportionment of sources to canal exports.
- What is not known: How much of the transformed TS is transported to surface water, ground water, local drainage canals and into EAA canals? How much oxidized TS is captured by adsorption or precipitation and how much is reduced and sequestered as metal halides? Even if oxidation is well estimated, that amount does not equate directly to a mass exported by canals.
- What is recommended: Available information on transformations and transport from soils and sediments needs to be summarized. Any direct measurements of organic and inorganic forms of S in the EAA using batch, column or field lysimeter studies should be examined in different soil environments (water levels, soil pH, land use type, etc.). Smaller scale mass balance studies are needed to estimate net export of S once it is released and should include measurements of organic S. Wright (2011) makes these and additional recommendations. Landing (2013) suggests attention to iron levels, sulfide formation, and possible adsorption of sulfate to peat soils.

b. Gas emissions

- What is known: Gabriel et al. (2010) added a component of the mass balance for gas emissions not considered by Corrales et al. (2011) or Shueneman (2001) and reviewed key literature to estimate possible rates for reduced gases of sulfur (hydrogen sulfide, carbonyl sulfide, di-methyl sulfide and di-methyl di-sulfide). Flux rates vary widely for individual gases and collectively; Gabriel et al. (2010) elected to use a combined rate of 7.3 µg/m2/hr as a net output term. It is expected that the importance of gas emissions will vary with the degree of nutrient enrichment, being higher in the STAs and northern Everglades and lower in more oligotrophic areas. James and McCormick (2012) report that the lake shows a small net removal of sulfate, but oxic conditions at the sediment-water interface may constrain gas emission rates from the lake and sulfide accumulation in the sediments.
- What is not known: The actual rate of S gas flux into the atmosphere is not known, although literature values suggest that this component is not large at least on a square meter basis. However, EPA marshes and EAA fields provide a huge surface area for gas flux and the overall regional importance of this output should be considered.
- What is recommended: Some direct measurements in the EAA would be desirable at least to bracket the range of possible emission rates; this effort is not a priority however.

Measurements could span zones of nutrient enrichment and emission rates should be part of small scale mass balance studies mentioned repeatedly in this document. Landing (2012) indicates that if the Gabiel (2010) estimate is representative, the gas release pathway is a very small part of the local mass balance and less than dry deposition inputs. It does not appear worthwhile to invest resources in constraining gas emission rates for the EAA based on existing information. With more information, gas emission outputs may be more significant to the downstream EPA marshes.

c. Agricultural applications of sulfur

- What is known: The pH values of the EAA virgin peats tended to increase from ~5.0 to 6.0 and up to 7.5 after brought to use in agriculture (personal communication). The agriculture industry in the EAA has used sulfur containing additives to lower soil pH, especially when pH is above 7.5, and promote nutrient availability. It is likely that application rates in the past were higher than today and actual rates on the farm are difficult to estimate. Application rate estimates vary greatly (37 via Wright et al. [2008] to 187 kg/ha as a recommendation [500 lbs. per acre over 3 years] via Wright [2011]). Gabriel et al. (2010) decided to apply a rate of 22 kg/ha/yr, while recognizing that a wide range of possible application rates have been reported.
  Forms of sulfur applied in the EAA include: elemental sulfur (90% granular S) and STM5 (granular S with 80% S and 5% manganese). Over time, various sulfate fertilizers have been used: Copper sulfate to correct sulfate deficiency; ammonium sulfate; SPM (sulfate of potash magnesia); magnesium sulfate and sulfate forms of micronutrients; and sulfur-coated urea largely used on golf courses and turf grasses.
- What is not known: Actual forms, including organic forms of S as sludge/manure, and rates of S applied today in the EAA are not easily estimated. Even if overall rates are quantified, the amount of S available for release and movement is not known and various forms of S can result in very different rates of transformation and export.
- What is recommended: Better estimates of agricultural TS application rates and chemical forms are very important, both current and historical. These data could possibly be collected from direct survey of the EAA farmers, regional fertilizer retailers, as well as from the published annual agricultural statistics. Small scale mass balance studies mentioned above are needed to improve our predictive capacity for S transformations and movement into canals. Sulfur stable isotopic ratios for S agricultural applications need to be reexamined in light of a large amount of information available on the applications of sulfur stable isotopes in nature. A recent publication from IFAS recommends at least 25 lbs. of TS per acre for good tomato yields.

d. TS Loading from Lake Okeechobee

- What is known: The TS loading from Lake Okeechobee to the EAA represents from about one-third to one half of total TS inputs. A recent analysis by James and McCormick (2012) suggests that an average of about 14,000 mt of sulfate for 2007 – 2011 is imported from the lake, a smaller tonnage than other mass balance studies. It is notable however that any additional water moved south into the Everglades for restoration will increase this loading in the future and TS will be higher than sulfate loading.
- What is not known: It will be a challenge to deal with net inputs. When lake water is moved it can sometimes move through the EAA with little local interaction. Deciding

how to deal with Lake Okeechobee inputs and associated outputs could be difficult. More information on TS and the relative amount of organic S is needed for lake inputs.

- What is recommended: A priority project is to conduct data mining and loading derivation for the EAA from the lake using all available data for structures S2 and S3 which can deliver back pumped water to the lake and discharge water to the EAA. James and McCormick (2012) provide a solid background for this and short-term mass balance studies for the canals should be considered for water management situations like irrigation needs, water supply for southern areas, stormwater releases etc. Getting more information on canal-groundwater interactions would be highly desirable. Landing (2013) recommends a canal mass balance model to reveal internal recycling and possible interactions with groundwater. Organic S contribution to TS in surface water can be variable but substantial (Edwards et al., 1992). New data on the role of organic and total sulfur to S loading is needed for the EAA and should include any effects of filtration on dissolved and particulate estimates.

e. S Loading to Lake Okeechobee from the EAA

- What is known: Since 1983, back-pumping into the lake from the EAA has been restricted to high water periods, and the in-lake sulfate concentration has been decreasing over the last two decades. Inflow volumes to the lake from the EAA have been reduced, but concentrations from the EAA tend to be higher in sulfate than other inflows to the lake (James and McCormick, 2012). The net relationship between the EAA and the lake is variable across years, but overall the lake is a net S exporter to the EAA. After 1982, the lake has exported about 21,000 mt sulfate net per year to the EAA. Orem et al. (2011) suggest that back-pumping has provided a substantial portion of the S contained in the lake. After 1983, this assertion is not correct – export to the EAA exceeds import from the EAA. James and McCormick (2012) provide the best available long-term estimates of net loading between the lake and the EAA.
- What is not known: None of the studies reviewed by Landing (2011) estimated the movement of TS from the EAA to the lake via back-pumping, although he mentioned that it should be estimated. While back-pumping is expected to be a relatively minor source for the lake today and in the future, it could be more important to the EAA budget during very wet years.
- What is recommended: Back-pumping events should be analyzed quantitatively building on the data summary of James and McCormick (2012). Landing (2013) stresses need to look at the relative contributions of dissolved and particulate TS and to validate the estimates of James and McCormick (2012).

f. Levees

- What is known: Corrales et al. (2011) added a term in their mass balance for inputs from levees. This component appears correct as an input from the C-139 basin via G136 and G88 structures, although it may be a relatively minor input to the EAA. This is an input from the C-139 basin runoff, not from levees per se.
- What is not known: The availability of water quality data for G88 and G136 needs to be confirmed.
- What is recommended: It is important to include C-139 inputs as part of the EAA TS mass balance.

g. Groundwater

- What is known: Groundwater can have substantial amounts of TS which appear to increase with depth in the EAA. Some areas of the EAA have shallow groundwater and evidence suggests that both connate seawater and soil oxidation may be an important source of sulfate in EAA groundwater. There is evidence that TS increases with depth presumably from reduced S moving down and forming insoluble chemical forms. Connate seawater deserves particular attention because seawater contains about 2700 mg-SO_4/kg (28 mM) so that even small additions can supply substantial sulfur. There are several studies of the EAA canal water that point strongly to connate seawater as a source of chloride, conductivity and at least by inference, sulfur (e.g., Chen et al., 2006; Harvey and McCormick, 2009).
- What is not known: The role of connate seawater entering from groundwater needs to be confirmed because even a small amount entering the primary canals could result in substantial TS loads to the EPA. Also, shallow groundwater may carry elevated TS concentrations and could be an important source from local soils.
- What is recommended: Using ionic relationships in ambient canal data from the EAA or stable isotope studies should allow an investigation of sources of chloride and sulfate, and provide better evidence on the role of connate seawater. Finding the means to distinguish TS originating from relict deposits in surficial groundwater or from that in deep aquifers is important for source studies in EAA canals. Earlier studies conducted by the U.S. Geological Survey (USGS) and IFAS scientists need to be reviewed and evidence for the role of groundwater and ancient marine inputs deserves investigation. The movement of TS from water and sediments down into deeper strata needs to be considered as an export from the EAA and Landing (2012) suggests hydrological mass balance studies as a starting point.

h. Atmospheric deposition, wet and dry

- What is known: Data from the CASTNET (Clean Air Status and Trends Network) monitoring network provides very reasonable data from both wet and dry deposition, although station locations are not in the EAA. The NADP/NTN monitoring network provides estimated wet sulfate deposition rate of about 10.5 kg/ha/yr with a standard deviation of 1.6; rates are highest in the summer and lowest in the winter and are well correlated with precipitation (Irick, unpublished data)
- What is not known: The possibility of local sources needs consideration and some investigation of how well CASTNET or NADP/NTN data reflects deposition to vegetated and aquatic surfaces merits review.
- What is recommended: Some additional effort is needed to address CASTNET and NADP/NTN data, as indicated above. Small improvements in atmospheric input rates are not expected to affect the mass balance in any significant way. Possible application of the University of Michigan's community multi-scale air quality (CMAQ) modeling might be considered; the model was set up for FDEP and the mercury total maximum daily load (TMDL) development process. Landing (2013) notes that local sources can be constrained by looking at 'excess' sulfate from data on sodium or chloride and sulfur isotopes can be useful for source apportionment.

i. Internal loading of sulfur

- What is known: Internal release of sulfur from soil oxidation and plant decomposition can be important sources of sulfur locally.
- What is not known: The quantity released during various dry out events needs to be quantified and considered as part of the total budget for sulfur.
- What is recommended: Flux measurements across environmental gradients are needed at a regional level. These could be done partially with the small scale mass balance studies. It is also important to assess the duration of internal loading following a dry out. Core studies both in the EAA and other areas should be considered to assess net vertical movement of TS.

III. Sulfur Outputs from the EAA

a. TS exported by sugarcane harvest

- What is known: Corrales et al. (2011) estimated the removal of S from the EAA via the harvesting of sugarcane using the mass estimated by Gabriel (2009). Gabriel et al. (2010) assumed the TS content for sugarcane of 0.15 percent and estimated 25,500 mt removed each year by harvest.
- What is not known: The detailed methods used to estimate harvest removal are not certain and the potential errors involved are therefore not known.
- What is recommended: The parameters used to estimate TS exported by crop harvest need to be examined from Gabriel (2009). Was burning and green harvesting practices included as an export? Were other crops (turf, tree, vegetable, corn, rice, etc.) besides sugarcane included? Is the S content of crops estimated with reasonable certainty? TS export in crops appears very important and is a priority for further study.

b. Canal exports from EAA to the STAs

- What is known: Permit reporting for the STAs contains inflow and outflow sulfate data. The difference in concentration is quite variable, but often shows that the STAs retain or lose 10 – 30 % of inflowing sulfate.
- What is not known: The cycling of sulfur in the STAs has not been quantified, but the loads imported and exported can be calculated.
- What is recommended: All available data on the STAs for sulfate should be used to document mass exports from the EAA to the STAs, as well as retention and loads moving south into the EPA. The nature of STA retention is important as well to indicate the permanence of removal.

c. Canal exports to the EPA from the EAA

- What is known: Most (about 80 %) of TS leaving the EAA moves south into the EPA through canals after treatment through the STAs. There is large variation in the amount

retained in the STAs, but they often show about a 20 % reduction from inflow to outflow S concentrations.

- What is not known: Seasonality and flow-weighted concentrations have not been analyzed and the role of organic S is not known.
- What is recommended: Use all available S data to develop a data set of monthly flows and S loads from the EAA. Conduct intensive data evaluation to explore the dynamics of S loading. Consider developing a loading model for the basin to allow estimation of seasonal and annual variations in loads and sensitivity analyses for S inputs.

IV. Modeling of Mass Balance

a. Estimating sulfur mass balance loads using the EAA BMP model

- The EAA Best Management Practices (BMP) model is developed to track phosphorous loads from the EAA as required by the Everglades Forever Act (EFA). District scientists are attempting to modify this model for the purpose of estimating of sulfur loads to and from EAA basin. The model output will provide surface water sulfate loadings by inflow, outflows and flow-through structures.
- Currently, sulfate data from the monitoring stations within EAA basin for the water years (WY) 2000 to 2012 are downloaded from the District DBHYDRO database. Out of 43 stations with both flow and TP data, only 22 stations have sulfate data. District scientists will look into the availability of measured but not archived (not required by permits or requested by clients) sulfate data for stations in DBHYDRO. If no sulfate data are available, surrogate data sets may be used for stations without sulfate measurements to fulfill the load calculation needs.
- If the modified EAA model calibrates successfully, it will then be used for evaluating questions related to long-term storage and sourcing of sulfur in the EAA. If feasible, additional data (such as particulate sulfur, flux of sulfur from sediment) and parameter estimates may be added to the model to allow operation at smaller scales. The model outputs may also be used to assess the historic trends, and the source and sink of sulfur when analyzed together with conservative elements such as chloride.
- The data used to run the EAA BMP S model will also be used for other analyses. Trend analyses will be done on both concentration and flow-weighted concentrations in inflow and outflow data sets. Advanced statistical techniques will be applied to sulfate and associated parameters. In addition, water quality data sets will be evaluated to assess the importance of connate seawater as a source of canal sulfate. Both geochemical and mass balance data will be evaluated for a weight of evidence on sulfate sources in the EAA.

Working Draft Notes

This nature and scope of this study will be refined at a technical workshop with sulfur and mercury experts. The sulfur mass balance efforts in this document will require multiple projects over several years. Funding from the Everglades Trust Fund would be desirable.

This 7/30/13 draft responds to comments and additions by Ming Chen, Ben Gu and Curt Pollman, and a detailed review by Landing (2013). Their teamwork is appreciated.....GR

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