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Ecosystem-Scale Modeling and Field Observations of Sulfate and Methylmercury Distributions in the Florida Everglades: Responses to Reductions in Sulfate Loading

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Abstract

The Florida Everglades has one of the most severe methylmercury (MeHg) contamination issues in the USA, resulting from factors including high rates of atmospheric mercury (Hg) deposition and sulfate inputs from agricultural lands. Sulfate loading stimulates microbial sulfate reduction and production of toxic and bioaccumulative MeHg. Controls on regional Hg emissions have been successful in reducing Hg deposition and MeHg production in wetlands in other areas, but this has not been the case for the Everglades as the Hg deposited here appears to come from unknown global sources of emissions. We posit that reductions in sulfate loading to the Florida Everglades can be an effective alternative approach used to reduce MeHg production. This study tested this hypothesis (1) by evaluating temporal trends in MeHg concentrations in response to a reduction in sulfate loading at a site in central Water Conservation Area (WCA) 3 and (2) using ecosystem-scale models to predict the effects of reductions in sulfate loading on sulfate concentrations in surface water and MeHg Risk. At the WCA site, we report a decline in sulfate concentrations (from about 9 mg/L in the late 1990s to levels of <1 mg/L by 2001) due to changes in water delivery as part of Everglades restoration. Concurrent with the decline in sulfate, declines in MeHg concentrations in surface water and fish and wading bird tissues were observed at this site. These results suggest the efficacy of reducing MeHg production and bioaccumulation in the ecosystem through a reduction in sulfate loading. A previously developed model was used to predict the effects of reductions in sulfate loading (97%, 33%, and 10% reduction scenarios) on sulfate concentrations in surface water and MeHg Risk in the Everglades. The model identified areas of the ecosystem where MeHg Risk is most sensitive to the reductions in sulfate loading. Results show that reductions of $>33\%$ in sulfate loading will significantly benefit the Everglades by reducing MeHg Risk.

Keywords Sulfur · Methylmercury · Modeling · Everglades · Mitigation

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George R. Aiken: Deceased.

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Abbreviations

ALT	Alternative reductions in sulfate loading used in the model (e.g., 1, 2, or 3)
EAA	Everglades Agricultural Area
ENP	Everglades National Park
EPA	Everglades Protection Area (Water Conservation Areas and Everglades National Park)
FLDEP	Florida Department of Environmental Protection
MeHg	Methylmercury
MSR	Microbial sulfate reduction
POS	Period of study (1978–2000)
SRS	Shark River Slough
STA	Stormwater treatment area
WCA	Water Conservation Area

1 Introduction

The Florida Everglades is a large, subtropical wetland ecosystem that stretches for over 95 km (east to west) and 160 km (north to south) at the southern tip of the Florida Peninsula (Davis et al. 1994). This ecosystem has been extensively impacted by anthropogenic activities (e.g., agricultural and urban development, canal construction, chemical contaminants, and invasive species) and is currently the focus of extensive restoration activities (Sklar et al. 2005). A map of south Florida showing the major features mentioned in the text is shown in Fig. 1. Among the major issues facing the Everglades is water quality. Agricultural development in the Everglades Agricultural Area (EAA) to the north of the Everglades has resulted in the input of chemical substances into the Everglades, most notably phosphorus and sulfate. The phosphorus contamination of the Everglades has been well documented (Davis et al. 1994; McCormick et al. 2002), and sulfate contamination of the ecosystem has received increased attention (Scheidt and Kalla 2007; Orem et al. 2011). Background levels of sulfate in the freshwater Everglades wetlands are typically <1 mg/L (Orem et al. 2011). However, sulfate levels in canals draining the EAA average between 40 and 70 mg/L and can range up to 200 mg/L (Orem et al. 2011). Canal water discharged into the Everglades has resulted in sulfate levels elevated above background (e.g., >1 mg/L) in at least 60% of the marshes within the ecosystem (Scheidt and Kalla 2007). Note that all references to sulfate concentration in this manuscript are as mg/L sulfate (SO_4^{2-}) and not mg/L sulfur.

Sulfate inputs to the Everglades have several impacts on the ecosystem: altered microbial ecology (increased microbial sulfate reduction or MSR), enhanced carbon biodegradation and nutrient recycling in organic peat soil through MSR, and accumulation of sulfide in wetland soils (by-product of MSR) that is highly toxic to animals and plants (Beauchamp et al. 1984; Bagarinao 1993) and reactive with trace metals and organic substances (Orem et al. 2011; Poulin et al. 2017). However, the most important impact of sulfate loading on the Everglades is the stimulation of mercury (Hg) methylation by MSR and the production of methylmercury (MeHg). Many sulfate-reducing bacteria are known to contain the genes for mercury methylation (Gilmour et al. 2013). While methanogenic archaea present in low-sulfate regions of the Everglades (areas of low MeHg levels) may also possess the genes for Hg methylation (Gilmour et al. 2013; Bae et al. 2014), it is unclear if the metabolic rates of methanogenic archaea are sufficient to produce the levels of MeHg observed

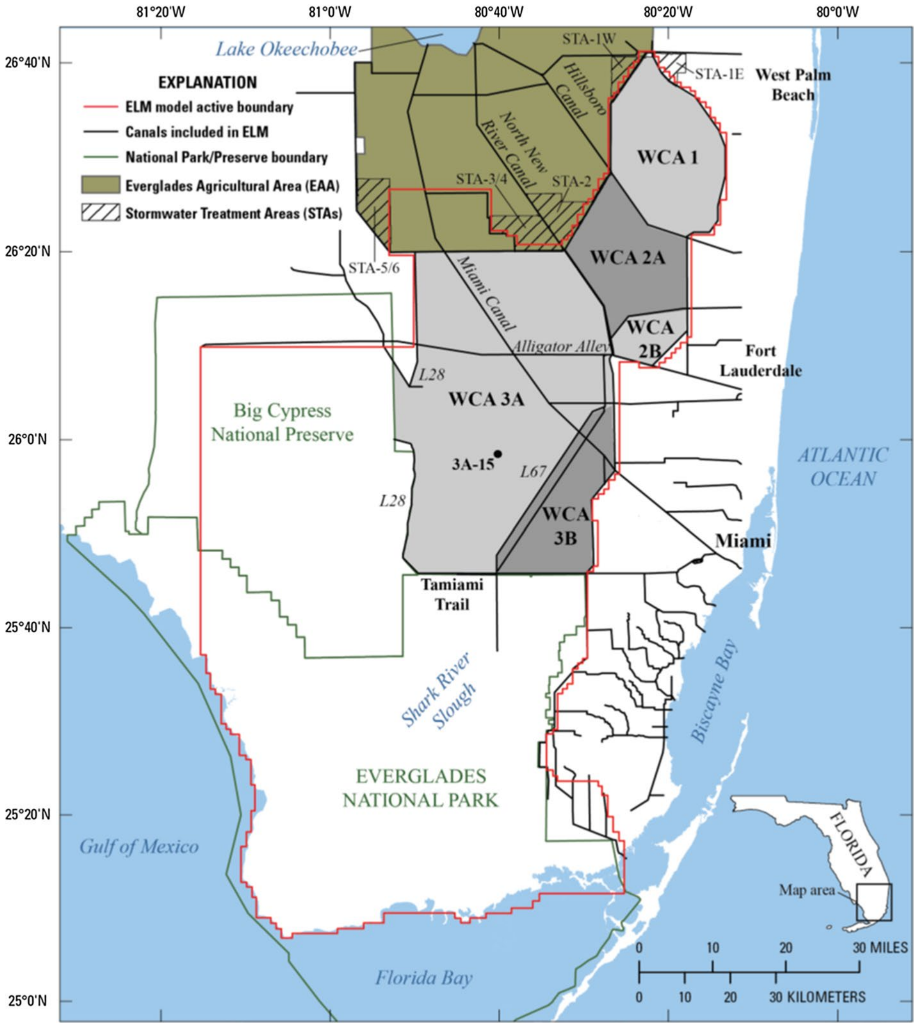

Fig. 1 Map of south Florida and the Everglades showing Site WCA3A-15, and roadways, canals, and other features mentioned in the text

in the Everglades. MSR is considered the principal microbial process driving MeHg production in the Everglades (Gilmour et al. 1998; Orem et al. 2011).

MeHg is a potent neurotoxin (Rice et al. 2014) and endocrine-disrupting chemical (Tan et al. 2009) and is among the most bioaccumulative of contaminants in the environment (Morel et al. 1998; Grandjean et al. 2010; Driscoll et al. 2013). The Everglades has one of the more severe MeHg contamination issues on record (Jurczyk 1993; Rumbold et al. 2008) due to high atmospheric deposition rates of inorganic divalent mercury (Hg(II)) (Dvonch et al. 2005; Coburn et al. 2016), the extensive wetland environment, high dissolved organic matter content, and high sulfate loading. The biogeochemistry of Hg methylation in the Everglades is complex and has been discussed in detail elsewhere (Gilmour et al. 1998; Axelrad et al. 2008, 2009; Orem et al. 2011). The high levels of MeHg production in the Everglades result in increased bioaccumulation in fish, with high levels of MeHg in fish posing a serious risk to piscivorous wildlife, notably wading birds (Frederick et al. 1997), and to human health through fish consumption (Díez 2009). Fish consumption advisories for mercury are posted throughout the Everglades (Florida Department of Health 2003), with the biggest risk to pregnant women through neurological effects on developing fetuses (Kajiwara et al. 1996; Kerper et al. 1992).

The environmental and human health risks associated with high levels of MeHg in the environment have prompted efforts to reduce MeHg production and bioaccumulation. Loading of inorganic mercury (usually via atmospheric deposition) is one major driver of MeHg production (Hammerschmidt and Fitzgerald 2006; Harris et al. 2007). Nationwide efforts to reduce emissions of Hg from anthropogenic sources (e.g., coal-fired power plants, chloralkali plants, cement manufacturing) and thereby to reduce deposition of Hg (mostly Hg^{2+}) on the landscape have been highly successful in reducing levels of MeHg in many environments (Driscoll et al. 2007). In order to reduce Hg deposition on the Everglades and MeHg production in the ecosystem, the Florida Department of Environmental Protection (FLDEP) undertook an effort in the 1990s to reduce Hg emissions in south Florida (Atkeson et al. 2003, 2005). This effort resulted in an estimated 90% reduction in Hg emissions. However, little impact on Hg deposition on the Everglades was observed, and studies have indicated that most Hg deposited on the ecosystem comes from sources outside of south Florida, possibly distant global sources (Pollman et al. 1995; Coburn et al. 2016). As the Hg sources are unknown and not local, it is unlikely that reductions in Hg emissions are a viable approach to reducing Hg deposition on the Everglades and in turn limit MeHg formation and uptake in the food web. We have previously proposed that a reduction in sulfate loading to the Everglades ecosystem may be a more viable strategy to reduce MeHg levels in the biota (Orem et al. 2011). Sulfate is known to be a major control on mercury methylation in the Everglades and in other wetland environments (Gilmour et al. 1992; Branfireun et al. 1999; Jeremiason et al. 2006; Achá et al. 2012; Coleman-Wasik et al. 2015). In many of these other wetland environments, sulfate primarily enters the system from the atmosphere in the wet deposition of industrial contaminants (e.g., acid rain). In contrast, most of the sulfate discharged into the Everglades in canal water originates from the EAA from agricultural use of sulfur in fertilizers and soil amendments, soil oxidation (releasing old sulfur from agricultural soils), and other sources (Gabriel et al. 2010; Corrales et al. 2011; Orem et al. 2011; Landing 2015). Field surveys in the Everglades indicate low levels of MeHg in areas of low sulfate concentration, and results of mesocosm studies that varied sulfate concentration in the water column also reduced MeHg production (Gilmour et al. 1998, 2007a, b). However, it is not known how reductions in sulfate loading will impact MeHg levels and distributions in the ecosystem.

Here, we present field data from a natural experiment in the ecosystem at a site in Water Conservation Area (WCA) 3 that experienced a decline in sulfate levels due to changes in water flow patterns accompanying Everglades Restoration. This natural experiment between 1995 and 2007 demonstrates the ecosystem responses to declines in sulfate concentrations regarding MeHg levels. Next, we use a previously developed model to evaluate how reductions in sulfate loading to the ecosystem change: (1) the concentrations and distributions of sulfate in surface water and (2) MeHg Risk distributions across the Everglades. This model was used previously to examine the ecosystem response (sulfate and MeHg Risk distributions) to additions of sulfate from Aquifer Storage and Recovery plans as part of the Everglades Restoration (Orem et al. 2015a). Results of the natural experiment in WCA 3 and the model provide a novel examination of how reductions in sulfate loading to the ecosystem may be used to reduce MeHg levels and risk in the greater Everglades ecosystem.

2 Model

The modeling of sulfate and MeHg Risk covers the entire Everglades Protection Area (EPA), including the WCAs and Everglades National Park (ENP). Big Cypress National Preserve, Florida Bay, and Lake Okeechobee are excluded from the modeling.

Sulfate model The Everglades Landscape Model (ELM v2.8.6) was used as the basic modeling framework (Fitz and Trimble 2006; Fitz 2013; http://www.ecolandmod.com/publications). A sulfate module was integrated into ELM for determining sulfate concentrations across the Everglades Protection Area (EPA). Additional details on the development and calibration/testing of ELM v2.8.6 may be found elsewhere (Fitz 2013; 2014a, b, c), and model results and calibrations are available under the heading *Everglades regional: sulfur and MeHg*, at http://www.ecolandmod.com/projects/ELMreg500mSulfur/. This model was previously used to evaluate how increases in sulfate loading to the EPA would impact sulfate distributions across the ecosystem (Orem et al. 2015a).

Here, the model was used to evaluate how reductions in sulfate loading to the ecosystem affected relative differences in sulfate distributions across the EPA. Three alternative (ALT) reduction scenarios in sulfate loading were used (Table 1): ALT 1—97% reduction, ALT 2—33% reduction, and ALT 3—10% reduction. These reductions were based on mass balance studies of sulfate sources in the Everglades (Gabriel et al. 2010; Corrales et al. 2011). ALT 1 (97% reduction) represents a reduction in all sulfur sources except rainfall; ALT 2 (33% reduction) includes implementation of best management practices (BMPs) limiting sulfur use in the EAA and slowing soil oxidation by 50%; ALT 3 (10% reduction) represents an implementation of BMPs only with no reduction in soil oxidation. Each ALT was run for the entire period of study (mean for 1974–2000), an average precipitation year (1974 wet and dry seasons), a dry year (1989 wet and dry seasons), and a wet year (1994 wet and dry seasons). Results of the model are presented in a series of maps of sulfate concentration for each ALT scenario, with each map showing baseline conditions for the time frame (left maps), results of the model ALT scenario (right maps), and a difference map indicating baseline minus ALT concentrations (middle maps). The difference map is particularly useful in identifying areas of the ecosystem where sulfate concentrations are most affected by the reduction in sulfate loading.

The sulfate module in the model uses a first-order, net settling rate equation and includes sulfate boundary conditions, a net settling rate map, and observed data for calibrating model performance. The settling rate equation is based on rates of removal of sulfate from surface water. In the Everglades, this involves diffusion of sulfate from surface water into soils, reduction to sulfide by MSR, and reaction of sulfide with metal ions or organic matter to produce metal sulfides or organic sulfur sequestered in the soils. Some sulfide may diffuse back to the surface water and be oxidized to sulfate. Statistical and graphical assessments of model performance were consistent with other ELM-simulated water quality variables (e.g., phosphorus), and the sulfate module was acceptable for applications to evaluate scenarios of sulfate dynamics across the EPA.

The ELM v2.8.6 evaluations used the South Florida Water Management Model (SFWMM) v5.4 hydrologic simulations to drive all managed water control structure flows for the year 2050 future baseline and the future Comprehensive Everglades Restoration Plan (CERP), recently updated to "CERP0." These SFWMM simulations were drivers of managed water flows for ELM v2.8.6 simulation runs (Fitz 2014b). The climate time period used in the SFWMM and ELM future simulation runs for reductions in sulfate loading was 01/01/1974 to 04/30/2000 (i.e., the SFWMM and ELM assumed that past climate

Table 1 Alternatives (ALT) used in model for examining effects of reductions in sulfate loading on sulfate concentrations and methylmercury (MeHg) risk in the Everglades, Florida

ALT	Reduction in sulfate loading (%)	Scenarios	Year	Figure
1	97	Sulfate concentration—period of study	1974–2000	S2b
1	97	Sulfate reduction rate—period of study	1974–2000	S2a
1	97	Sulfate concentration—average year (dry season)	1978	S2c
1	97	Sulfate concentration—average year (wet season)	1978	S2d
1	97	Sulfate concentration—dry year (dry season)	1989	S2e
1	97	Sulfate concentration—dry year (dry season)	1989	S2f
1	97	Sulfate concentration—wet year (dry season)	1994	S2g
1	97	Sulfate concentration—wet year (dry season)	1994	S2h
2	33	Sulfate concentration—period of study	1974–2000	4; S3b
2	33	Sulfate reduction rate—period of study	1974–2000	S3a
2	33	Sulfate concentration—average year (dry season)	1978	S3c
2	33	Sulfate concentration—average year (wet season)	1978	S3d
2	33	Sulfate concentration—dry year (dry season)	1989	S3e
2	33	Sulfate concentration—dry year (dry season)	1989	S3f
2	33	Sulfate concentration—wet year (dry season)	1994	S3g
2	33	Sulfate concentration—wet year (dry season)	1994	S3h
3	10	Sulfate concentration—period of study	1974–2000	5; S4b
3	10	Sulfate reduction rate—period of study	1974–2000	S4a
3	10	Sulfate concentration—average year (dry season)	1978	S4c
3	10	Sulfate concentration—average year (wet season)	1978	S4d
3	10	Sulfate concentration—dry year (dry season)	1989	S4e
3	10	Sulfate concentration—dry year (dry season)	1989	S4f
3	10	Sulfate concentration—wet year (dry season)	1994	S4g
3	10	Sulfate concentration—wet year (dry season)	1994	S4h
1	97	MeHg Risk—period of study	1974–2000	6; S5a
1	97	MeHg Risk—average year (dry season)	1978	S5b
1	97	MeHg Risk—average year (wet season)	1978	S5c
1	97	MeHg Risk—dry year (dry season)	1989	S5d
1	97	MeHg Risk—dry year (dry season)	1989	S5e
1	97	MeHg Risk—wet year (dry season)	1994	S5f
1	97	MeHg Risk—wet year (dry season)	1994	S5g
2	33	MeHg Risk—period of study	1974–2000	7; S6a
2	33	MeHg Risk—average year (dry season)	1978	S6b
2	33	MeHg Risk—average year (wet season)	1978	S6c
2	33	MeHg Risk—dry year (dry season)	1989	S6d
2	33	MeHg Risk—dry year (dry season)	1989	S6e
2	33	MeHg Risk—wet year (dry season)	1994	S6f
2	33	MeHg Risk—wet year (dry season)	1994	S6g
3	10	MeHg Risk—period of study	1974–2000	8; S7a
3	10	MeHg Risk—average year (dry season)	1978	S7b
3	10	MeHg Risk—average year (wet season)	1978	S7c
3	10	MeHg Risk—dry year (dry season)	1989	S7d
3	10	MeHg Risk—dry year (dry season)	1989	S7e

Table 1 (continued)

ALT	Reduction in sulfate loading (%)	Scenarios	Year	Figure
3	10	MeHg Risk—wet year (dry season)	1994	S7f
3	10	MeHg Risk—wet year (dry season)	1994	S7g

was replicated in future years). Changes in climate (rainfall and temperature) could impact these simulations in the future, as these factors impact both sulfate concentration and MeHg Risk through changes in hydrology and biogeochemistry (Orem et al. 2015b; Flower et al. 2019). Various methods were used to develop sulfate concentrations for ELM boundary conditions detailed by Fitz (2014c). Simulations routed sulfate through canals and then into the Everglades stormwater treatment areas (STAs, constructed wetlands designed for phosphorus removal), which then discharged into the WCAs in the EPA domain of ELM. In summary, a simple STA model, SFWMM v5.4 hydrology, and other quantitative tools were used to establish: (1) the sulfate loadings at model boundaries into the Everglades and (2) ELM-simulated downstream landscape patterns of sulfate availability over decadal timescales in the EPA.

The models were well calibrated and deemed acceptable for applications. However, we recognize that there are uncertainties associated with results due to the linkages among multiple models and complex spatial relationships of the different study areas (among the EAA, canals, STAs, and the greater Everglades). It is important to understand that the model(s) are not predicting absolute values in exact locations in the future. However, the results are useful in comparing the multi-decadal, spatial trends in the relative differences of sulfate concentrations across the landscape among future alternatives.

Methylmercury (MeHg) Risk assessment The MeHg production risk in the ecosystem was evaluated by applying numerical functions relating sulfate concentration to MeHg production risk; see details at http://www.ecolandmod.com/projects/ELMreg500mSulfer/. These functions were developed from empirical data gathered during many years of research and monitoring in the Everglades (Orem et al. 2011), to the predicted sulfate outcomes from the ELM v2.8.6 simulation. The sulfate concentration and MeHg production relationship in surface waters is nonlinear, commonly exhibiting a unimodal shape. Therefore, a maximum in MeHg concentration is commonly observed at moderate sulfate levels, but the position of the maximum in MeHg with respect to sulfate concentration may vary due to several biogeochemical factors, such as soil metal and organic matter content, which can modulate the levels of free sulfide present in the pore water (Gilmour et al. 1992, 1998; Benoit et al. 2001; Benoit and Miller 2003; Orem et al. 2011). This relationship between MeHg production and sulfate concentration has been observed in the Everglades and other wetland environments from field studies, field experiments (mesocosm studies), and laboratory microcosm experiments (Orem et al. 2011).

The MeHg Risk assessment used two parameterizations of surface water sulfate concentration versus MeHg distribution curves from field data: one for the WCAs and the other for ENP (http://www.ecolandmod.com/projects/ELMreg500mSulfer/). The curves are shown in Supplemental Information (Fig. S1). The distinction between these two areas of the Everglades was made because of a clear difference in the observed peak in MeHg accumulation response to sulfate concentration; these occurred at sulfate concentrations of 10–15 and 2 mg/L for the WCAs and ENP, respectively. The reason for this difference is hypothesized to be linked to the higher organic content of the peat soils of the WCAs compared to the marl soils common in

ENP. The organic matter in the peat soil reacts with sulfide from MSR to produce organic sulfur compounds (Bates et al. 1998). This process modulates the amount of free sulfide present in the pore water in the WCAs. The marl soils in ENP (lower overall organic matter content) appear to have a lower capacity to modulate the free sulfide present, and higher sulfide levels occur in ENP porewater compared to the WCAs at comparable surface water sulfate concentrations. This moves the maximum in MeHg to lower sulfate levels in ENP due to higher levels of porewater sulfide that inhibits mercury methylation (Orem et al. 2011). The general equation used, defining the two distributions, was:

$$[\mathrm{MeHg}] = a * \exp(-0.5 * (\ln([\mathrm{SO_4}]) - b/c)^2) + d, \tag{1}$$

where coefficients $a = 1$, $b = 2$, $c = 1$, and $d = 0.05$ for the WCAs and $a = 0.5$, $b = 2$, $c = 3$, and $d = 0.05$ for ENP. The model used basin indicator regions (BIRs) for sulfate loading and used the same ALTs for reductions in sulfate loading applied in the sulfate model: a baseline (2050 future baseline) and three ALT reductions in sulfate loading scenarios (Table 1). With this approach, map-based MeHg Risk performance measures were developed. It should be noted that this dual-function approach to model MeHg Risk results in a visual discontinuity in the results at the interface of the ENP and WCA 3 along Tamiami Trail. This artifact in the model results is not reflected in our field data, which show a more gradual transition. Results are reported as a MeHg Risk (dimensionless) and not as a concentration of MeHg due to the many uncertainties in the prediction of concentration for a reactive constituent like MeHg. Results are useful for identifying the areas and relative intensity of the effect of reductions in sulfate loading under the different ALTs and scenarios on MeHg Risk in the ecosystem.

3 Study Area and Methods

3.1 Study Area

Water chemistry studies were conducted at site 3A-15 located in the center of WCA 3 (25°58.455′ N; 80°40.127′ W; see Fig. 1). During the 1990s, this location had high levels of MeHg in fish and other wildlife (Lange et al. 1999; Stober et al. 1996, 2001; Sepulveda et al. 1999; Rumbold 2004), as well as high levels of MeHg in surface water and sediments (Gilmour et al. 1998). The site was accessed by an airboat. Surface water samples were collected by positioning acid-cleaned Teflon tubing mid-depth in the water column and using a peristaltic pump to filter (0.45 µm) in-line directly into sample vessels. Samples for sulfate analysis were collected into small PVC bottles and stored refrigerated or on water ice until analysis. Samples for filtered MeHg and total Hg were collected in acid-cleaned Teflon bottles and stored as previously described prior to analysis (Olson et al. 1997; DeWild et al. 2002). Peat soil samples for total Hg and MeHg analysis were collected as short cores (@ 10 cm depth) and sectioned (DeWild et al. 2004; Olund et al. 2004). We present results for the top 2 cm of soil, including surface floc when present.

3.2 Analytical Methods

Sulfate was determined on filtered water samples by Dionex ion chromatography with an anion exchange column and a conductivity detector.

Filtered water samples were analyzed for dissolved total Hg using USEPA method 1631 (US Environmental Protection Agency 2002). Samples with high dissolved organic matter content (visible color) were pre-treated in an ultraviolet (UV) digester consisting of three Spectroline X-Series UV lights in a plastic box lined with aluminum foil for reflection (Olson et al. 1997) to oxidize the organic matter. Water samples from the Everglades required 2–5 days of UV pretreatment to remove the visible color. Once the water samples clarified, bromine monochloride (BrCl) was added to oxidize all forms of Hg to Hg(II). After 5 days at 50 °C, BrCl is neutralized with hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) and stannous chloride ($SnCl_2$) is added to reduce Hg(II) to volatile Hg^0; then, Hg^0 is purged from the water and trapped on gold-coated glass beads (used as a sample trap). The Hg^0 is thermally desorbed onto a second gold trap (analytical trap) and again thermally desorbed and detected by cold vapor atomic fluorescence spectroscopy (CVAFS; Tekran® Model 2600 Mercury Detector; Toronto, Canada).

Filtered MeHg in water was analyzed by aqueous phase ethylation, followed by gas chromatographic separation with CVAFS detection (DeWild et al. 2002). This method is applicable for use on water samples with a MeHg range of 0.04–5 ng/L; the upper range may be extended to higher concentrations by distilling smaller sample volumes or ethylating less of the distillate.

Peat soils were analyzed for total Hg and MeHg. Soil cores were frozen in the field immediately after collection (Lutz et al. 2008) and maintained frozen until analysis. Total Hg was analyzed according to the following procedure. Sections of the soil core were thawed and homogenized using a clean Teflon spatula, and a recorded quantity was digested in Teflon® bombs with a strong acid (Olund et al. 2004). Acid extracts were treated with: (1) bromine monochloride, (2) hydroxylamine hydrochloride, and (3) $SnCl_2$ to convert Hg forms to gaseous elemental Hg^0. Gaseous Hg^0 was purged from aqueous solution, captured on a gold trap, thermally desorbed, and then quantified using CVAFS. For soil MeHg measurements (DeWild et al. 2004), field-frozen samples were thawed and homogenized. MeHg was extracted (from a subsample of recorded weight) using potassium bromide, copper sulfate, and methylene chloride and then extracted into Milli-Q® water. The extractant was pH-adjusted and ethylated with sodium tetraethyl borate. The ethylated MeHg species was purged from aqueous solution, trapped, thermally desorbed, separated on a gas chromatographic column, reduced to elemental Hg^0 using a pyrolytic column, and detected using CVAFS.

3.3 Statistical Analysis

The Mann–Whitney rank sum U test was used to examine the significance of differences in MeHg concentrations (median values) before and after 1998 at the WCA 3A-15 site. The dataset (Supplemental Information Table S1) suggested a major decrease in MeHg concentrations after 1998. Mann–Whitney is a nonparametric statistic for examining differences between groups of measurements, testing the null hypothesis that a randomly selected value from one population will be greater than (or less than) a randomly selected value from another population. The many unknowns that could affect the concentrations of MeHg in surface water and the limited data available made the selection of a nonparametric statistic more appropriate than a parametric statistic (e.g., *t* test and ANOVA).

4 Results and Discussion

4.1 Changes in Sulfate Loading and Methylmercury Production in the Central Everglades

Site WCA 3A-15 is in the central part of WCA 3, with the Miami Canal to the north and northeast, and the L67 Canal to the east (Fig. 1). This part of central WCA 3 had high MeHg production and high levels of MeHg in fish (whole fish and fillets) and wading birds (from feather and egg measurements) in the 1990s (Fink et al. 1999). This site was originally established by the South Florida Water Management District for ecosystem studies and was used by the US Geological Survey (USGS) Aquatic Cycling of Mercury in the Everglades (ACME) project for examining the biogeochemistry of Hg in the ecosystem. The ACME project sampled WCA 3A-15 from 1995 to 2007 for a variety of chemical parameters in surface water, soil, and soil pore water, including filtered sulfate, MeHg, and total Hg concentrations in surface water and soil. Results are presented in the Supplementary Information (Table S1); sulfate and MeHg concentrations in surface water and total Hg concentrations in the soil from 1995 to 2007 are shown in Fig. 2.

Consistent with observations of high levels of MeHg in fish and wading birds in this area, MeHg concentrations in surface water at site WCA 3A-15 were elevated in the mid- to late 1990s, ranging from 0.25 to 0.94 ng/L in 1995–1997 (Fig. 2). Sulfate concentrations from 1995 to 1997 ranged from 1 to 9 mg/L (avg. 2.3 mg/L, maximum 8.9 mg/L), which are significantly above background concentrations of sulfate (<0.5 mg/L) observed in

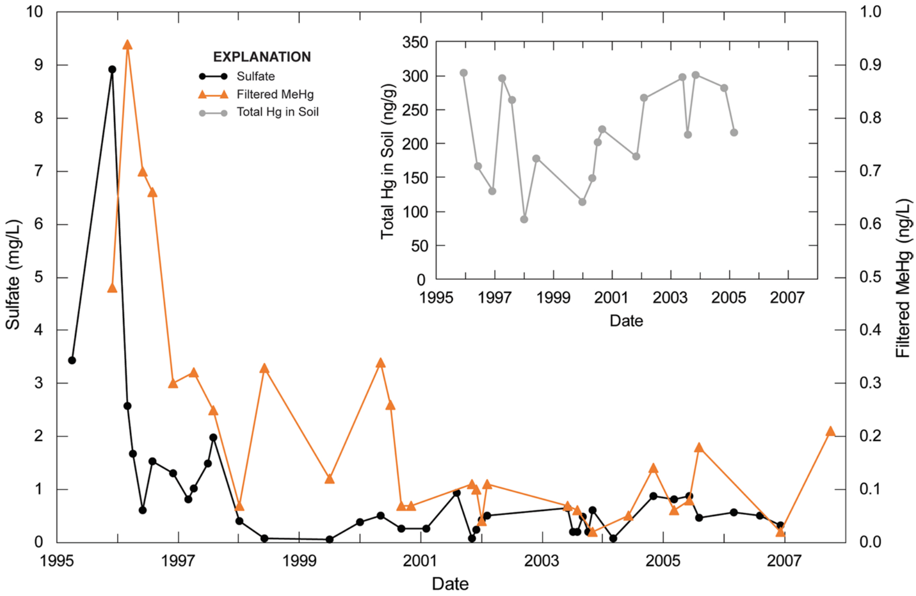

Fig. 2 Time series of sulfate (mg/L) and filtered MeHg (ng/L) concentrations in surface water from site WCA 3A-15 in the central Everglades. The inset plot shows concentrations of total Hg (ng/g) in soil for the same time series and location. Corresponding numerical data are presented in Supplementary Information (Table S1), along with filtered total Hg concentrations (ng/L) in surface water and MeHg concentrations in peat soil from this site

pristine areas of the Everglades (Orem et al. 2011). Beginning in 1998, sulfate concentrations at WCA 3A-15 declined and remained <1 mg/L through the end of sampling in 2007 (1998–2007 avg. = 0.38 mg/L, minimum = 0.05 mg/L). A Mann–Whitney rank sum test of sulfate concentrations before and after 1998 showed that the median values (1.540 mg/L before 1998, $N=13$; 0.420 mg/L in 1998–2006, $N=29$) were statistically significantly different ($P=<0.001$). The difference in the median values between the two groups is greater than would be expected by chance (Mann–Whitney U statistic = 9.000), indicating a systematic change altering sulfate concentrations at this site. The cause of the decline in sulfate beginning in 1998 at WCA 3A-15 is not known. We hypothesize that the site originally received sulfate loading from the Miami and L67 canals through breaks in the canal levees. The opening of the L67 Canal to deliver more water to ENP as part of Everglades Restoration may have reduced the input of canal water to this site after 1998.

The decline in sulfate at site WCA 3A-15 is mirrored by a concomitant decline in MeHg concentrations in surface water (Fig. 2). Average filtered MeHg concentrations in surface water were 0.52 ng/L in 1995–1998 compared to 0.12 ng/L from 1998 to 2007. Filtered MeHg concentrations were as high as 0.94 ng/L in 1996 and as low as 0.02 ng/L in November 2003 and December 2006 (Table S1 in SI). Concentrations of MeHg at this site were particularly low from 2001 to 2007 (average value of 0.09 ng/L). Comparing the MeHg surface water data prior to 1998 and from 1998 to 2007 using a Mann–Whitney rank sum test indicated that median values (0.48 ng/L before 1998, $N=9$; 0.08 ng/L from 1998 to 2007, $N=23$) were significantly different ($P<0.001$), with a Mann–Whitney U statistic of 7.000. Concentrations of MeHg in soil also appear to decline after 1998 at this site (Table S1 in SI) though the dataset for soil MeHg is less complete for this date range. The production of MeHg is dependent on the availability of divalent inorganic mercury (Hg(II)) as a substrate. To assess if the observed temporal differences in MeHg concentration could be explained by Hg(II) concentration, we evaluated surface water and soil total Hg levels. Although both surface water and soil levels of total Hg exhibit interannual variability from 1995 to 2007 (Fig. 2; Table S1 in SI), perhaps reflecting changes in rainfall, there is no systematic change in total Hg levels at WCA 3A-15. Therefore, we consider it unlikely that changes in Hg deposition at this site explain the observed decline in MeHg concentrations in surface water.

This dataset suggests that a decline in sulfate concentration at WCA 3A-15 resulted in a decline in MSR and MeHg production, with resulting lower concentrations of MeHg in surface water. Lower production of MeHg at this site may also be a major factor in the decline of MeHg in fish and wading birds observed here after 1999 (Fink et al. 1999).

These data, therefore, support the hypothesis that the decline in MeHg in surface water observed at this site is a result of a decline in sulfate concentrations. It should also be noted that MeHg levels were tightly coupled to sulfate concentration. Thus, reductions in sulfate loading to the Everglades are anticipated to result in a substantial and rapid (within a few years) reduction in MeHg levels in surface water.

4.2 Model Results for Sulfate Distributions Following Reduction to Sulfate Loading

Alternative 1 (97% reduction in sulfate loading) Model results for mean sulfate distributions for the period of study (POS, 1974–2000) are illustrated as three maps (Fig. 3), with color coding indicating sulfate concentration (mg/L). The left map illustrates baseline (unaltered) conditions, the right map illustrates sulfate concentrations after ALT 1 is applied, and the middle map is the difference between baseline and ALT 1 maps. All results for reductions in sulfate loading in the following sections are presented as maps and follow this same presentation format. Mean POS sulfate concentration maps for the different alternatives are shown in Figs. 3, 4 and 5; additional maps of other scenarios are presented in Supplemental Information (Figs. S2a–h, S3a–h, S4a–h; see Table 1 for details). All maps are also available on the Web site (http://www.ecolandmod.com/projects/ELMreg500mSulfer/).

The baseline map (Fig. 3 left map) for the POS mean sulfate concentration shows the extensive penetration of sulfate into the Everglades. This reflects the high loading of sulfate from canal water draining the EAA, minimal uptake of sulfate by plants, and the slow rate of diffusion of sulfate into the anoxic soil where sulfur is sequestered following MSR and reaction of the produced sulfide with organic matter and metals. Virtually, all of WCAs 2A and 2B have elevated levels of sulfate. A "halo" of sulfate along the outer margins of WCA 1 (ARM Loxahatchee National Wildlife Refuge) reflects sulfate entering from canal water leakage into the refuge. In WCA 3, elevated levels of sulfate are observed over large swaths of marsh with the highest concentrations near canals and points of canal discharge. For example, elevated sulfate is observed in a marsh along the Miami Canal in northern WCA 3, at the discharge of the L28 Canal in west central WCA 3, along the L67 Canal in southeastern WCA 3, and at the southern boundary of WCA 3 along the Tamiami Trail. ENP exhibits a plume of water with elevated sulfate in the northern portion of Shark River Slough (SRS) that reflects discharge from the L67 Canal and southern WCA 3. ENP also has high sulfate along the coast from seawater sulfate.

ALT 1 has a large impact on sulfate distributions across the Everglades (Fig. 3, right map). The ALT 1 POS map may be a reasonable approximation of sulfate concentration and distributions in the pre-development Everglades, given that the 97% reduction represents the elimination of all non-atmospheric sulfur sources. Some faintly shaded areas are present along canals, but the ecosystem has very low overall levels of sulfate except for the coastal zone due to the presence of marine sulfate. The difference map (Fig. 3, middle map) illustrates areas where the largest reductions in sulfate concentration occur and closely resembles the baseline map, emphasizing the near-total reduction in sulfate concentration across the ecosystem. Especially important is the decrease in sulfate concentration in northern SRS in ENP, a region of increasing concern for sulfate contamination and MeHg production (Orem et al. 2011).

The mean POS maps for sulfate reduction rate in g/m^2 year^1 (Supplemental Information, Fig. S2a) reflect the settling rate or removal rate for sulfate from surface water (generally sequestered as reduced sulfur in soils; see Orem et al. 2011). Sulfate reduction rates are the highest in areas of high sulfate concentration, with conditions conducive to reduction and sequestration of sulfur (e.g., anoxic soils). Thus, the baseline map for the sulfate reduction rate (Fig. S2a left map) closely resembles the map for sulfate concentration (Figs. 3 and S2b). ALT 1 produces very low sulfate reduction rates across the ecosystem (Fig. S2a right map) reflecting the very low sulfate concentrations. Only areas close to canals or canal discharge show sulfate reduction due to the sequestration of residual canal-derived sulfate in the system. The difference map (middle map in Fig. S2a) shows areas where sulfate reduction rates decreased the most, especially marsh areas at the outer edges of canal or STA discharge points.

The 1978 (year of average precipitation) maps for ALT 1 (Fig. S2c and d) resemble the mean POS maps (Figs. 3 and S2b), with much lower sulfate concentrations throughout the ecosystem. Changes in sulfate concentration (as shown in the difference maps in the middle) are most pronounced near points of canal or STA discharge and along canals where leakage of canal water can occur. Again, the large decline in sulfate concentration in

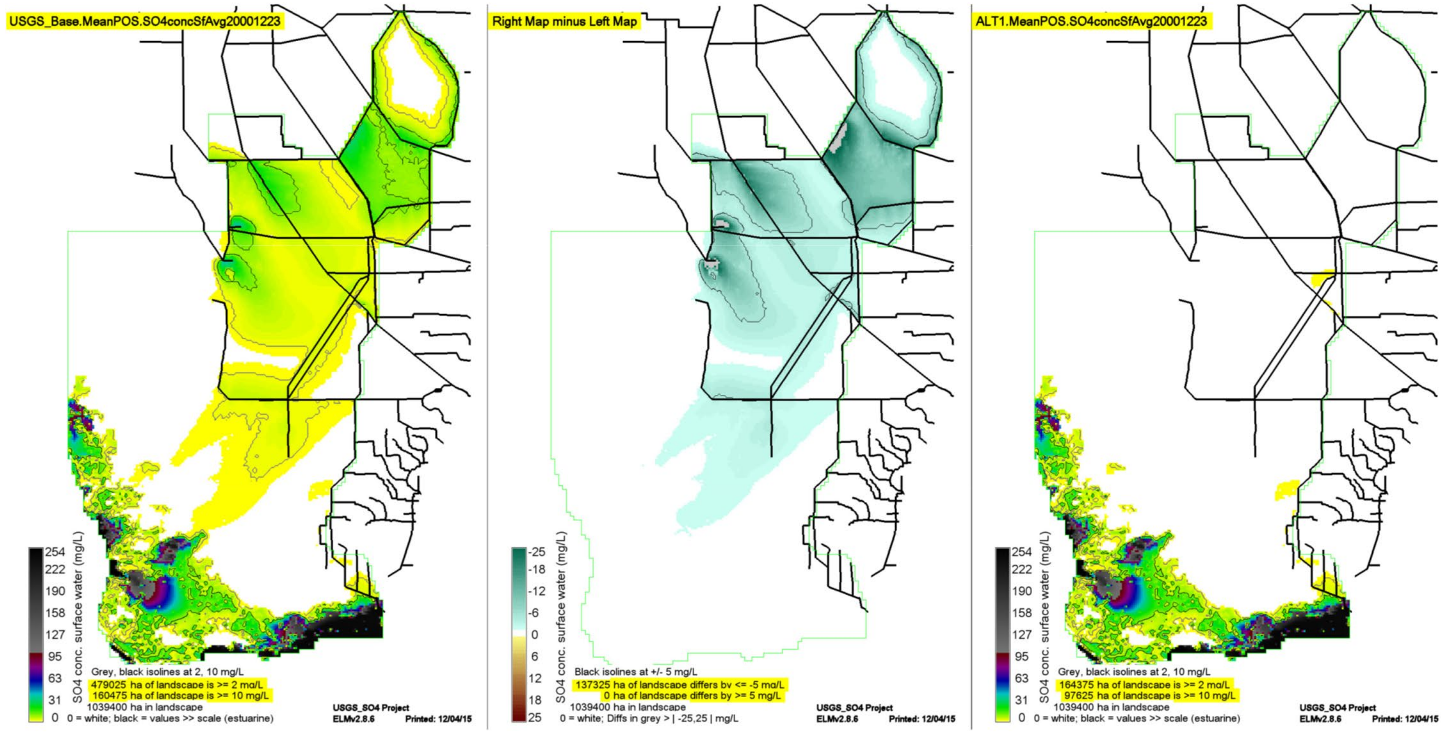

Fig. 3 Maps of model results for Alternative 1 (97% reduction in sulfate loading) for sulfate concentrations across the Everglades. The left map shows baseline conditions, the right map shows sulfate concentrations after a 97% reduction in sulfate loading, and the middle map shows the difference between baseline and Alternative 1

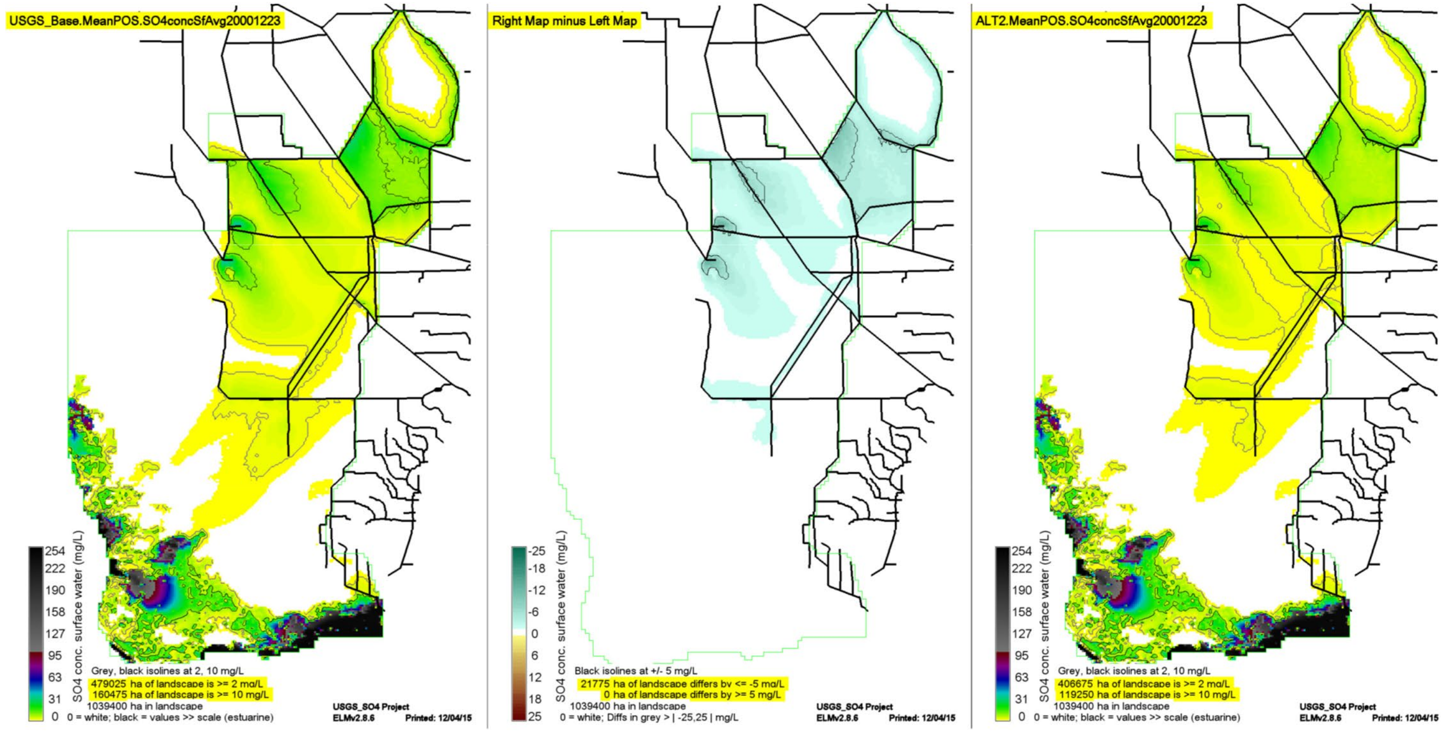

Fig. 4 Maps of model results for Alternative 2 (33% reduction in sulfate loading) for sulfate concentrations across the Everglades. The left map shows baseline conditions, the right map shows sulfate concentrations after a 33% reduction in sulfate loading, and the middle map shows the difference between baseline and Alternative 2

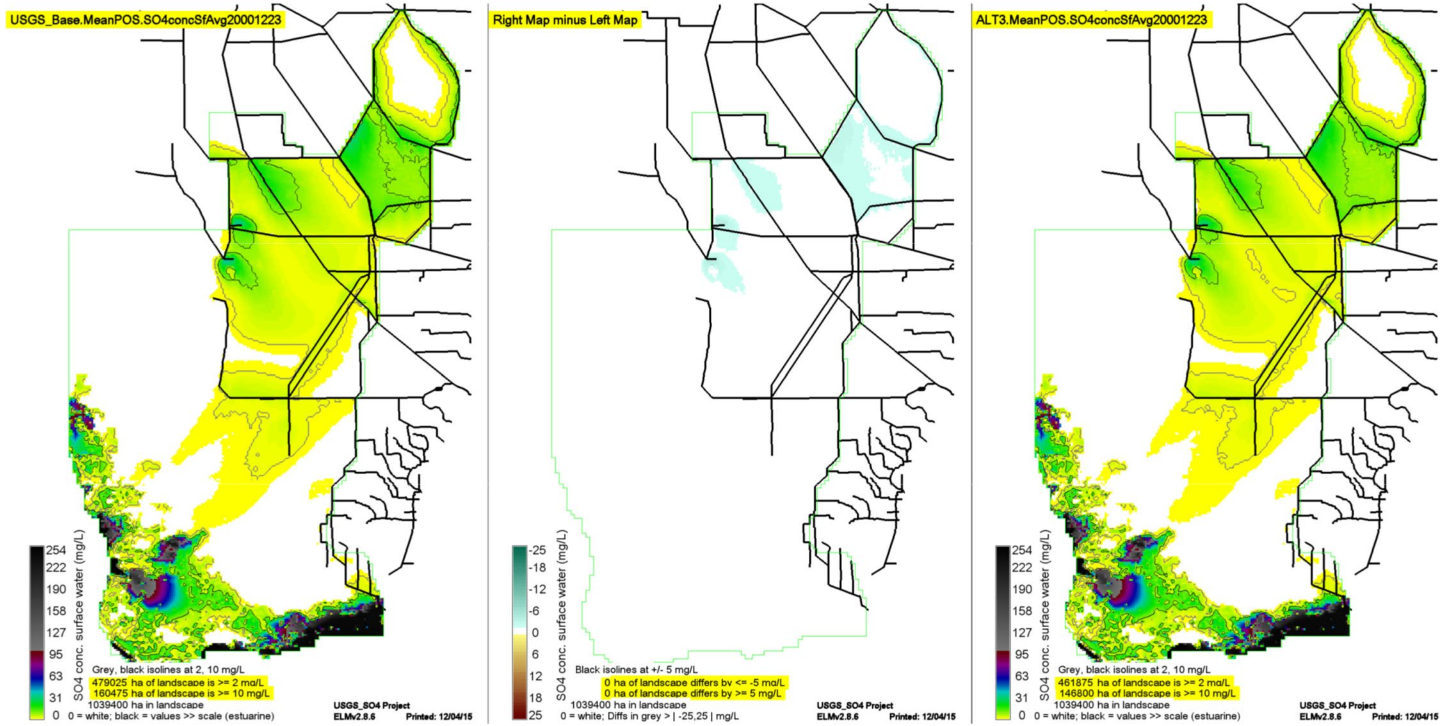

Fig. 5 Maps of model results for Alternative 3 (10% reduction in sulfate loading) for sulfate concentrations across the Everglades. The left map shows baseline conditions, the right map shows sulfate concentrations after a 10% reduction in sulfate loading, and the middle map shows the difference between baseline and Alternative 3

northern SRS in ENP is noteworthy. There are differences in the baseline sulfate concentration maps between the 1978 dry (November through April) and wet seasons (May through October), reflecting generally lower sulfate loading during the dry season. This has been observed in field investigations of sulfate concentrations in dry and wet seasons (Scheidt and Kalla 2007). Higher rainfall in the wet season may mobilize more sulfate from agricultural fields in the EAA to canals, resulting in higher sulfate loading to the Everglades.

Baseline sulfate maps (Fig. S2e and f, left maps) for a drier than average year (1989) were lower across the ecosystem, especially in the dry season, compared to baseline for the POS. ALT 1 produces large decreases in sulfate during the wet season, but more modest declines during the dry season of the dry year because of lower baseline sulfate concentrations. Declines in sulfate during the dry season are mostly near canals and canal discharge points: northwestern WCA 2A where STA 2 discharges canal water, at the terminus of the L28 Canal in western WCA 3, and at the junction of the Miami and L67 canals in east central WCA 3. One aspect the model does not capture is the release of sulfate during peat oxidation or fire, which could occur during a dry year, especially in the dry season. Oxidation of reduced sulfur in peat soil to sulfate can occur during a dry-down period and result in the remobilization of sulfate during rewetting (Orem et al. 2011). The amount of sulfate remobilized depends on the degree of peat oxidation, which can vary depending on the nature of the dry-down (Gilmour et al. 2007a, b).

Wet year (1994) maps (Fig. S2g and h) show extensive baseline sulfate concentrations across the ecosystem for both the wet and dry seasons. ALT 1 produces large declines in sulfate concentrations throughout the Everglades. The difference maps (middle maps in Fig. S1g and h) indicate decreases in sulfate concentration across most of WCAs 2 and 3 and around the edges of WCA 1. Sulfate is transported into ENP from the EAA through the canal system and southern WCA 3, especially in a wet year. A 97% reduction in sulfate loading (ALT 1) virtually eliminates transport of sulfate in canal water and limits sulfate sources in ENP to rainfall and sulfate recycled from soils during dry-downs or fires (exclusive of the coastal zone where sulfate originates from seawater).

The ALT 1 scenario produces large declines in sulfate levels across the ecosystem to conditions approximating sulfate concentrations prior to development in the early 1900s. The decline in sulfate concentrations from ALT 1 is likely to have effects on MeHg production, as discussed in Sect. 4.3. The effect on MeHg production resulting from the reduction in sulfate concentration is likely to be rapid (several years or less), based on the rapidity of MeHg decline following the reduction in sulfate loading at site WCA 3A-15 (see Sect. 4.1). The decline in sulfate levels with ALT 1 may also result in large decreases in sulfide concentrations in soils throughout the ecosystem as MSR becomes sulfate-limited. Under current conditions, sulfide levels are observed to range up to 13,000 ppb in soils and 300 ppb in surface water (exceeding EPA standards) in heavily sulfate-impacted areas such as northwestern WCA 2A (Orem et al. 2011). Sulfide levels under the ALT 1 scenario would likely decrease to below detection (< 1 ppb) throughout most of the ecosystem over time (e.g., several years). As sulfide is toxic to plants and animals (Koch and Mendelssohn 1989; Koch et al. 1990; Wang and Chapman 1999) and may alter trace metal biogeochemistry, this large reduction in sulfide concentrations would benefit ecosystem health. The limitation of MSR by lower sulfate loading will restore most soil microbial communities in the Everglades to domination by fermentation and methanogenesis. This will likely slow biodegradation of soil organic matter and nutrient recycling and may increase peat accumulation.

Even with the large reduction in sulfate concentrations predicted by the ALT 1 model results, periodic plumes of sulfate could be produced during drought and fire events

(Gilmour et al. 2004). These events oxidize peat soil and reduced sulfur species (organic sulfur and metal sulfides), releasing sulfate following rewet. Increases in drought and fire may occur in the Everglades under climate change scenarios (Orem et al. 2015b; Flower et al. 2019). Sulfur sequestered in peat soils during decades of high sulfate loading to the Everglades will remain a reservoir for sulfate release during drought/fire until burial by low sulfur-containing peat soils occurs.

Alternative 2 (33% reduction in sulfate loading) The complete dataset of maps for ALT 2 is presented in Supplementary Information (Fig. S3a–h; see Table 1). Note that baseline maps for ALT 2 and 3 in all scenarios are the same as the corresponding maps for ALT 1. Sulfate concentration maps of the baseline conditions, ALT 2, and the difference between baseline and ALT 2 are shown for the POS in Fig. 4. ALT 2 has far less effect on sulfate concentration across the ecosystem compared to ALT 1. Under ALT 2, WCAs 2 and 3 still have significant sulfate concentrations, but reduced scope. The difference map for sulfate concentration for ALT 2 POS (middle map in Figs. 4 and S3b) illustrates where major reductions in sulfate concentration are occurring. Sulfate concentration in central and southern parts of WCA 2 is reduced to 20–30 mg/L (compared to about 40 mg/L under baseline), and in the northwestern parts of WCA 2 (STA 2 discharge area) to 40–50 mg/L (compared to 60 + mg/L under baseline). In WCA 3, a broad area of the northwest and central region and an area just north of the Tamiami Trail sulfate concentrations decline to 5–10 mg/L (compared to 10–15 mg/L under baseline). In northwest WCA 3 along the Miami Canal, in the west just north of Alligator Alley, and near the L28 terminus, sulfate concentrations decline to 10–15 mg/L with ALT 2 (compared to 15–20 mg/L under baseline). The ring of sulfate around the edges of WCA 1 is reduced in both extent and intensity under ALT 2. One important result is the greatly reduced size of the plume of sulfate in northern SRS in ENP that would reduce MeHg and benefit this vulnerable area, as discussed in Sect. 4.3.

The POS sulfate reduction rates map for ALT 2 (Fig. S3a) shows that the greatest decreases occur in areas of the highest sulfate concentration: areas near discharges (e.g., northwestern WCA 2, L28 Canal terminus in western WCA 3) or along canals where leakage can occur under or through levees (e.g., north central WCA 3 along the Miami Canal). Much of WCAs 1, 2, and 3 and ENP show only a modest decrease in sulfate reduction rates.

In the average year (1978), the wet season sulfate concentration results (Fig. S3d) resemble those for the POS (Fig. 4), with reductions in sulfate concentration across WCAs 2 and 3, especially near canal water discharge points or along canal levees. Reductions in sulfate concentration in the ring of sulfate contamination along the edges of WCA 1 and in northern ENP and SRS are also observed during the 1978 wet season. The ALT 2 results for the dry season of 1978 (Fig. S3c) show a similar pattern to the wet season, but the effects are muted due to the overall lower sulfate loading to the ecosystem in the dry season compared to the wet season.

Dry year (1989) results for ALT 2 for the dry season (Fig. S3e) resemble the corresponding maps for ALT 1 (Fig. S2e). In a dry year, there is little sulfate loading to the Everglades, especially during the dry season. With little sulfate washing from agricultural fields, differences between ALT 1 and 2 are minimal. The 1989 ALT 2 dry season results show some reduction in sulfate concentrations along the Miami Canal in north central WCA 3, at the terminus of the L28 in western WCA 3A, along the L67 canal in eastern WCA 3, in northwestern WCA 2 (near STA 2 discharge), and in southern WCA 3 just north of Tamiami Trail. Sulfate concentrations in northern ENP are reduced to values < 1 mg/L, approaching pre-development levels. Higher sulfate concentrations are observed during the wet season of 1989 (Fig. S3f) compared to the dry season, as indicated by the baseline map. The effects of ALT 2 during the wet season are seen throughout all the WCAs, with reductions in concentration and extent of sulfate contamination in north central WCA 3, western WCA 3 at L28 terminus, western WCA 3 just north of Alligator Alley, northwestern WCA 2 (STA 2 discharge), and the edges of WCA 1. Sulfate concentrations in ENP are reduced to a small area near the L67 terminus. High concentrations (> 10 mg/L) of sulfate remain in northwestern WCA 2, north central WCA 3, western WCA 3, and the edges of WCA 1.

Wet year (1994) results for ALT 2 are shown in Fig. S3g and h. In a wet year, there are significant baseline sulfate concentrations throughout the Everglades in both dry and wet seasons. Application of ALT 2 for the dry season of 1994 reduces sulfate concentrations throughout WCAs 2 and 3, around the edges of WCA 1, and in northern ENP. The largest effects occur where sulfate enters the ecosystem: northwestern WCA 2 and north central (along Miami Canal) and western (terminus of L28 Canal) WCA 3. Areas of very low sulfate (< 1 mg/L) in WCA 3 increase in extent, and central WCA 2 shows significant reductions in sulfate though levels remain > 10 mg/L here. In SRS and northern ENP, ALT 2 reduces the extent and concentration of sulfate, but in this wet year there is still extensive sulfate contamination entering ENP. In the wet season of 1994 (Fig. S3h), high sulfate concentrations (> 10 mg/L) are present throughout WCA 2 (except a strip down the very center), in north central and western WCA 3, and around the edge of WCA 1. A large plume of moderate sulfate concentration (1–5 mg/L) is present in northern ENP and SRS. ALT 2 reduces sulfate concentrations in areas of high sulfate loading and increases the extent of low-sulfate areas in central WCA 2 and WCA 3 during the wet season of 1994. The plume in northern ENP and SRS is smaller but remains. Overall, the effects of ALT 2 during the wet season of a wet year are not large, and high sulfate concentrations remain in large areas of WCAs 2 and 3.

ALT 2 produces benefits by reducing sulfate loading overall, but sulfate concentrations remain > 10 mg/L over large portions of the WCAs. This concentration is high enough to drive MSR and MeHg production over large portions of the Everglades, though less than under baseline conditions. Perhaps, the greatest benefit is the reduction in the plume of sulfate in SRS in northern ENP to near background levels (e.g., < 1 mg/L), except during wet years. This could assist in reducing MeHg production in ENP and help protect wildlife from the impacts of this neurotoxin and endocrine disruptor. Reductions in sulfate in the WCAs under ALT 2 would likely reduce sulfide levels in soils, but not as dramatically as observed under ALT 1. Sulfide levels would likely still be > 500 ppb in soil over much of WCA 2A. MSR would remain a dominant microbial process over much of the WCAs, though northern ENP (especially during average or dry years) may return to a microbial community dominated by fermentation and methanogenesis.

Alternative 3 (10% reduction in sulfate loading) ALT 3 (10% reduction in sulfate loading) has only minimal effects on sulfate concentrations in the Everglades. The POS baseline and ALT 3 maps (Figs. 5 and S4b) are similar in terms of both extent of sulfate contamination and color intensity (concentration). The difference map highlights areas where some diminution of sulfate concentration is seen: west and northwest WCA 2 (STA 2 discharge and flow path), northeast WCA 2 along the Hillsboro Canal, slight change in the southern part of WCA 1, north central WCA 3 along the Miami Canal, and western WCA 3 around Alligator Alley and the L28 Canal terminus. A little reduction in sulfate concentration or areal extent was observed in southern WCA 3 or in northern ENP and SRS.

ALT 3 has somewhat greater effects on sulfate concentrations in the average precipitation year (1978) in both the dry and wet seasons (Fig. S4c, d) compared to the POS (Fig. 5).

Although the baseline and ALT 3 maps appear to be similar, the difference map illustrates areas where sulfate concentrations are lower under ALT 3. In the dry season, sulfate concentrations decrease in much of WCA 2, in central and western WCA 3, around the edges of WCA 1, and slightly in northern ENP. However, the decrease is not large (1–5 mg/L). The wet season map shows a similar decrease in sulfate concentration (1–5 mg/L), but over a larger area of the marsh compared to the dry season. Virtually, all WCA 2, the fringe of WCA 1, and northern, western, and central WCA 3 show small reductions in sulfate concentration. Northern ENP and southern WCA 3 (north of Tamiami Trail) also see a small decrease in sulfate concentration during the wet season.

Dry year (1989) results for ALT 3 (Fig. S4e, f) are comparable to ALT 1 and 2. Baseline sulfate concentration is low overall due to low sulfate (little rainfall runoff from agricultural fields). The difference map (middle map in Fig. S4e) shows that ALT 3 has a little impact in further reducing the minimal sulfate entering the Everglades during the dry season of a dry year. There is a larger impact of ALT 3 in the wet season of 1989, and the difference map pinpoints areas of lower concentration: the outer margins of WCA 1 (especially in the south), northwest and west WCA 2 (STA 2 discharge and flow path), north central and western WCA 3 (along Miami Canal, around Alligator Alley, and near the L28 terminus), and a small reduction in sulfate in northern ENP. Sulfate concentrations remain high in much of WCA 2 and 3 and around the rim of WCA 1 (right map in Fig. S4f).

Overall, ALT 3 had minimal impacts on sulfate concentration in the Everglades, although slight declines were observed in some areas. There is more of an impact of ALT 3 during the 1994 wet year (Fig. S4g, h), especially compared to the 1989 dry year. MSR would remain the dominant microbial process over much of the Everglades under ALT 3, with attendant effects (MeHg and sulfide production).

4.3 Model Results for Methylmercury Risk Following Reductions to Sulfate Loading

Alternative 1 (97% reduction in sulfate loading) Maps for methylmercury risk (dimensionless) resulting from the various ALT scenarios for reductions in sulfate loading follow a format analogous to that for the sulfate concentration maps discussed in Sect. 4.2 and are described in Table 1.

ALT 1 produces a significant decline in sulfate concentration in surface water throughout the Everglades for the POS (Fig. 3) as discussed above, and a similar result for MeHg Risk during the POS is observed (Fig. 6). Under the baseline conditions (Fig. 6 left map), high MeHg Risk is observed across wide swaths of marsh in all three WCAs and northern ENP and SRS. These model results are consistent with observations of elevated MeHg across these same regions of the Everglades and fish consumption advisories throughout the ecosystem. Areas of low risk under baseline conditions (Fig. 6 left map) include central WCA 1, portions of WCA 3, and ENP outside of the SRS flow path. ALT 1 (97% reduction in sulfate loading) reduces MeHg Risk across most of the affected areas for the POS (Fig. 6 right map). The difference map (Fig. 6 middle map) illustrates the areas of the highest reduction in MeHg Risk, including the inner part of the high MeHg perimeter of WCA 1, northeast and western WCA 2, large swaths of WCA 3 near canals or discharge areas, and northern ENP and SRS flow path.

Results for an average precipitation year (1978) are shown in Supplementary Information (Fig. S5b and c). As with the POS map (Fig. 6), baseline maps for both the wet and dry seasons of 1978 show much of the Everglades with a high MeHg Risk. A greater extent of the ecosystem has elevated MeHg Risk during the wet season. An interesting aspect of

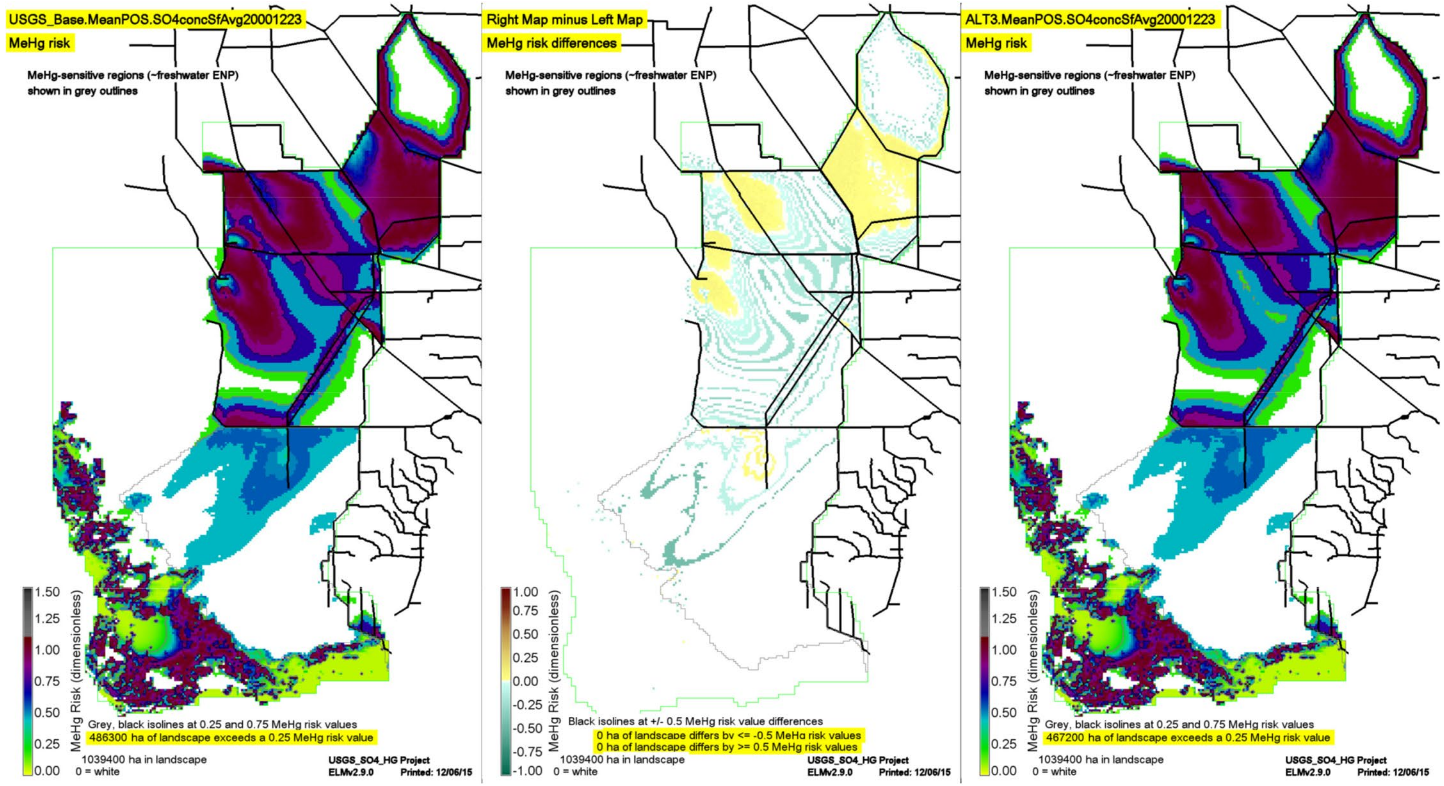

Fig. 6 Maps of model results for Alternative 1 (97% reduction in sulfate loading) for methylmercury risk (dimensionless) across the Everglades. The left map shows baseline conditions, the right map shows methylmercury risk after a 97% reduction in sulfate loading, and the middle map shows the difference between baseline and Alternative 1

the baseline map is that western WCA 2 near the STA 2 discharge has moderately lower MeHg Risk in the wet compared to the dry season despite higher sulfate loading from STA 2 during the wet season. We interpret this observation to be a result of elevated sulfide from MSR that decreases the potential for the methylation of inorganic Hg and therefore MeHg Risk at high concentrations (Orem et al. 2011). ALT 1 lowers MeHg Risk across the ecosystem in both the dry and wet seasons. Areas of MeHg Risk remaining in the ALT 1 scenario for 1978 include southern WCA 2, northern WCA 3 along the Miami Canal, WCA 3 near the junction of the L67 and Miami Canals, far northern and southeastern ENP, and central WCA 1.

The dry year (1989) simulations differ for the dry and wet seasons (Fig. S4d and e). Baseline results for sulfate concentration during a dry year are very low in the model output, and this decreases MeHg Risk throughout the ecosystem. Only portions of the ecosystem with the highest sulfate concentrations have any MeHg Risk under baseline conditions during the dry season of a dry year (e.g., western and southern WCA 2, northern and eastern WCA 3 along the Miami and L67 Canals, western WCA 3 near the L28 Canal terminus, southern WCA 3 along Tamiami Trail, and a small area of northern ENP). ALT 1 reduces MeHg Risk in the dry season to small areas in northern, eastern, and southern WCA 3 along the Miami and L67 Canals and Tamiami Trail. For the dry year, baseline sulfate levels for the wet season produce overall higher MeHg Risk across the ecosystem compared to the dry season, reflecting higher sulfate loading during the wet season. ALT 1 greatly reduces wet season MeHg Risk across the ecosystem. Remaining areas of modest MeHg Risk include southern WCA 1 and WCA 2, eastern WCA 3 along the Miami and L67 Canals, southern WCA 3 along Tamiami Trail, and a small portion of ENP to the north and southeast. This pattern may reflect the residual effect of sulfate already in the system.

Wet year (1994) results for ALT 1 (Fig. S4f and g) show extensive MeHg Risk under baseline conditions, with somewhat less risk during the dry season. ALT 1 virtually eliminates MeHg Risk from the ecosystem during the dry season of a wet year (only small areas of risk in northern WCA 2, eastern WCA 3, and southeastern ENP; Fig. S4f). ALT 1 also reduces MeHg Risk for the wet season of 1994 to small, low-risk areas in central WCA 1, southern WCA 2, eastern WCA 3, and northern and southeastern ENP (Fig. S4g). These likely represent areas of residual sulfate in the system.

ALT 1 changes the Everglades ecosystem from one with high MeHg Risk over large areas to one with overall low MeHg Risk. Consistent with the observations at site WCA 3A-15 (Sect. 4.1), reducing sulfate loading by 97% reduces MSR and MeHg Risk to manageable levels. This reduction in sulfate loading would be likely to reduce the MeHg burden in wildlife over time, with resulting benefits to both neurologic health and reproductive success. Fish consumption advisories may be able to be removed after a generation of fish has been replaced.

Alternative 2 (33% reduction in sulfate loading) Although ALT 2 reduced MeHg Risk in many parts of the ecosystem, the risk remained elevated across the Everglades under various hydrologic conditions. This is best illustrated in the POS maps for ALT 2 (Figs. 7 and S6a). Baseline risk is high across the system in the model results, as previously discussed. The ALT 2 map (right map in Fig. 7) appears similar to the baseline map. However, the difference map (Fig. 7 middle map) shows that there is some reduction in MeHg Risk throughout the system. The inner part of the perimeter ring of MeHg Risk in WCA 1 is reduced, and WCA 2 shows some reduction in MeHg Risk, especially in the south. Reductions of MeHg Risk in WCA 3 are mostly concentrated in the center of this large area, with some additional risk reduction in the north and in the southwest along Tamiami

Trail. ENP has reductions in MeHg Risk, especially along the front of the risk plume in the flow path of SRS.

The average precipitation year (1978) results (Fig. S6b and c) are comparable to those for the POS maps for both the dry and wet seasons. There appear to be only modest changes in MeHg Risk between baseline and the ALT 2 maps. However, the difference map shows reductions in risk around the perimeter of WCA 1, in the center of WCA 2, and north, central, and southwest WCA 3. Reductions in MeHg Risk in SRS in ENP are apparent in the difference map. The dry season shows reductions in MeHg Risk over a greater portion of WCA 3 and in central WCA 2 compared to the wet season.

ALT 2 results for the dry year of 1989 (Fig. S6d and e) are like ALT 1 for 1984. Baseline MeHg Risk is lower throughout for the dry season of the dry year compared to all other scenarios. As previously discussed, this reflects low rainfall resulting in minimal mobilization of sulfate from agricultural fields in the EAA. ALT 2 results for the dry season (right map in Fig. S6d) resemble the baseline, except for some reduction in MeHg Risk in central and western WCA 3. The difference map (Fig. S6d middle map) shows these reductions, as well as scattered reductions in MeHg Risk in other parts of the WCAs, but the magnitude and extent of risk reduction are not large. Greater impacts from ALT 2 are apparent during the wet season, as increased rainfall means more sulfate for potential mitigation in the model run. The baseline map for the wet season of the dry year (left map in Fig. S6e) has an overall greater MeHg Risk compared to the dry season. The ALT 2 map (right map in Fig S6e) is comparable to the baseline (indicating the effect of ALT 2 is not large overall), but with reductions in risk in northern ENP and in northern and western WCA 3. MeHg Risk increases with ALT 2 in western WCA 2 (near STA 2 discharge) as lower sulfate loading removes the sulfide inhibition to MeHg production (Orem et al. 2011). This increase in MeHg Risk illustrates the complexity of the sulfate/MeHg relationship. The difference map indicates areas where MeHg Risk is reduced under ALT 2, including the inner perimeter of WCA 1; eastern and southern WCA 2; western (outer edges of sulfate plume from L28 Canal terminus), southwestern, and northeastern WCA 3; along the L67 Canal in WCA 3; and northern ENP.

Results for MeHg Risk for the wet year (1994) for ALT 2 are presented in Fig. S6f and g. Baseline maps for the dry and wet seasons show extensive risk throughout the system, but more extensive in the wet season (especially in WCA 1 and ENP). The difference maps for both the dry and wet seasons show that ALT 2 reduces MeHg Risk to a moderate degree around the edges of WCA 1; central WCA 2; north, central, and southwestern WCA 3 (larger area of reduction during the dry season); and at the leading edge of the front in SRS in ENP (reflecting the leading edge of the sulfate loading in ENP). Overall, the effects of ALT 2 are modest with respect to the reduction in the intensity of MeHg Risk, but are spatially extensive across the Everglades ecosystem, possibly due to the extensive mobility of sulfate within the wetland ecosystem.

Alternative 3 (10% reduction in sulfate loading) Overall reductions in MeHg Risk under ALT 3 are modest. The POS difference map in Fig. 8 indicates scattered small reductions in MeHg Risk across the ecosystem: the perimeter of WCA 1, southern WCA 2, north and central WCA 3, and the outer edges of the MeHg Risk plume in SRS in ENP. The 1978 average precipitation year results for ALT 3 (Fig. S7b and c) are comparable to the POS map, with small scattered reductions in risk across WCAs 1, 2, 3, and ENP. Dry year 1989 (Fig. S7d and e) and wet year 1994 (Fig. S7f and g) results are similar. The dry season of the dry year map (Fig. S7d) shows a very little reduction in MeHg Risk.

A 10% reduction in sulfate loading is not insignificant, yet it produces only modest reductions in MeHg Risk in the model scenarios. This may reflect how sulfate discharged

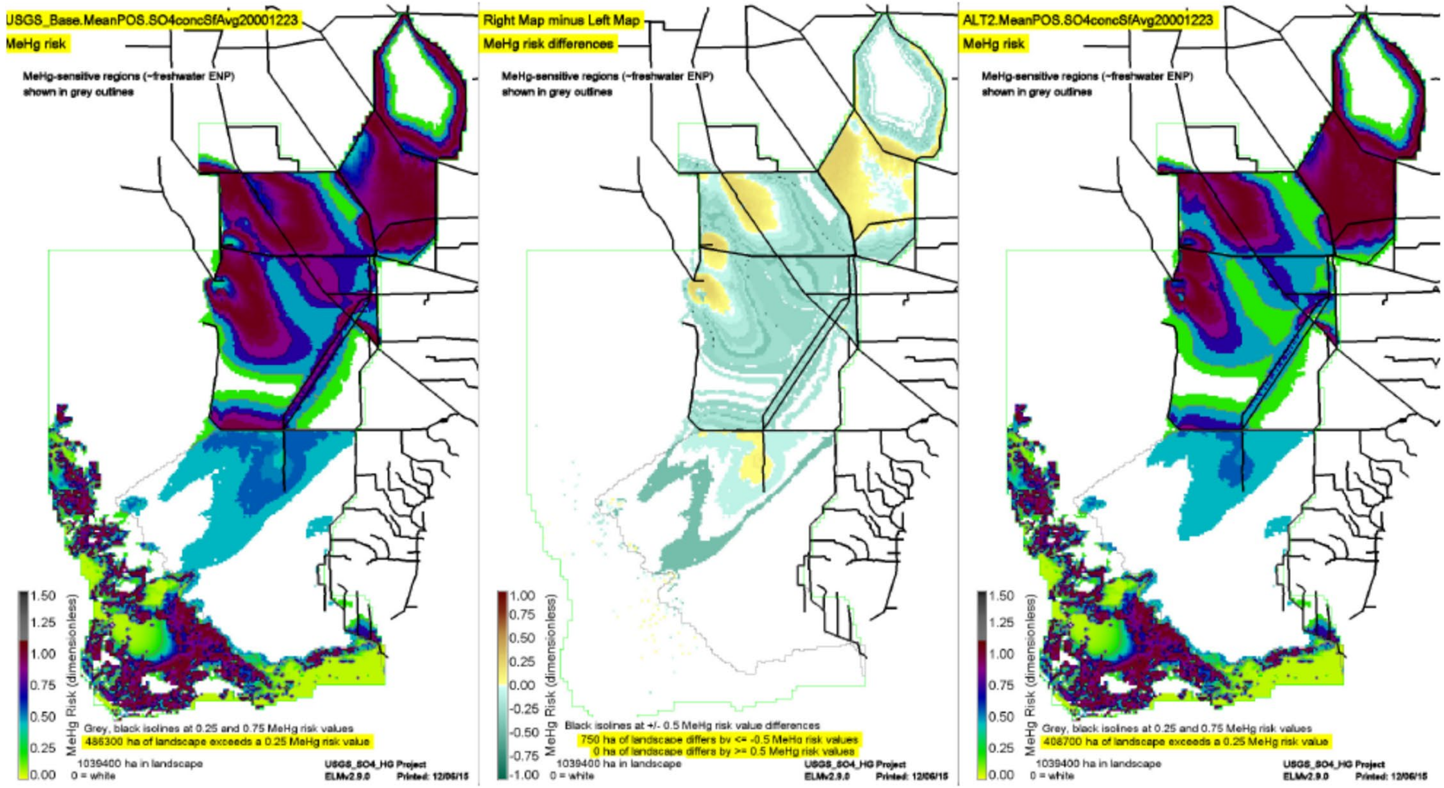

Fig. 7 Maps of model results for Alternative 2 (33% reduction in sulfate loading) for methylmercury risk (dimensionless) across the Everglades. The left map shows baseline conditions, the right map shows methylmercury risk after a 33% reduction in sulfate loading, and the middle map shows the difference between baseline and Alternative 2

into the ecosystem from STAs or canals quickly penetrates the wetland with little to retard its spread. Wetland plants do not take up enough sulfate to make any difference in retarding the sulfate plume, and MeHg is only produced after the sulfate diffuses (a slow process) into anoxic wetland soils where MSR and mercury methylation occur. Effects of reductions in sulfate loading are spread over large areas of wetland, with more extensive (small effects over a large area) rather than intensive (large effects in a small area) impacts.

5 Conclusions

MeHg production and bioaccumulation remain a serious environmental concern for the Everglades and a threat to wildlife and human health through fish consumption (Perry 2008). The production of MeHg in the Everglades ecosystem is controlled by numerous factors including the atmospheric deposition of mercury, dissolved organic matter concentration and composition, and sulfate loading. Although the areas of the ecosystem most impacted by MeHg have changed over time, both production and bioaccumulation of MeHg remain high. Attempts to mitigate MeHg production in the Everglades through controls on local Hg emissions have not greatly reduced Hg deposition on the ecosystem. Reducing sulfate loading to the Everglades provides an alternative approach to reducing MeHg production by removing the electron acceptor needed to support MSR and MeHg production. Results presented here from site WCA 3A-15 in the central Everglades, where hydrologic controls caused a decrease in sulfate concentrations in the late 1990s and concomitant declines in MeHg concentrations in surface water, demonstrate the potential effectiveness of such an approach (Fig. 1; Table S1). No other factors (e.g., Hg deposition) accounting for the decline in MeHg in surface water here could be discerned. The area around this site (central WCA 3A) also experienced a decline in MeHg in fish and wading birds at the same time. Previous mesocosm experiments in the Everglades also showed that reduction in sulfate loading resulted in declines in MeHg production (Gilmour et al. 2004).

A model was used to examine how decreases in sulfate loading to the Everglades would affect distributions of sulfate concentration and MeHg Risk (Figs. 3, 4, 5, 6, 7, 8 and S2–S7). The model applied three alternative scenarios (ALT) of reduction in sulfate loading: 97%, 33%, and 10% reduction. While model results should not be interpreted to predict specific sulfate concentrations or MeHg Risk levels at a specific location, they do provide an overall spatial pattern of the predicted effects of reductions in sulfate loading on MeHg Risk under different conditions and areas of the ecosystem most impacted by these changes. As expected, ALT 1 (97% reduction in sulfate loading) dramatically reduced sulfate concentration and MeHg Risk across the Everglades. Areas of high sulfate concentration, such as most of WCA 2, the edges of WCA 1, north central and western WCA 3, and northern ENP and SRS, had sulfate concentrations reduced to near background levels (<1 mg/L) with resulting declines in MeHg Risk. ALT 2 scenarios (33% reduction in sulfate loading) produced far less dramatic reductions in sulfate concentration and MeHg Risk. However, significant reductions in both sulfate concentration and MeHg Risk were apparent for the entire POS in western WCA 2 (near STA 2 discharge), along the Miami Canal in northern WCA 3, in western WCA 3 around Alligator Alley and the L28 Canal terminus, and even in the outer edges of WCA 1. Sulfate concentration and MeHg Risk in northern ENP and SRS were reduced during the average precipitation (1978) and wet (1994) years under ALT 2, and reductions in sulfate concentration and MeHg Risk in WCA 1, 2, and 3 were greater during the average precipitation and wet years compared to the

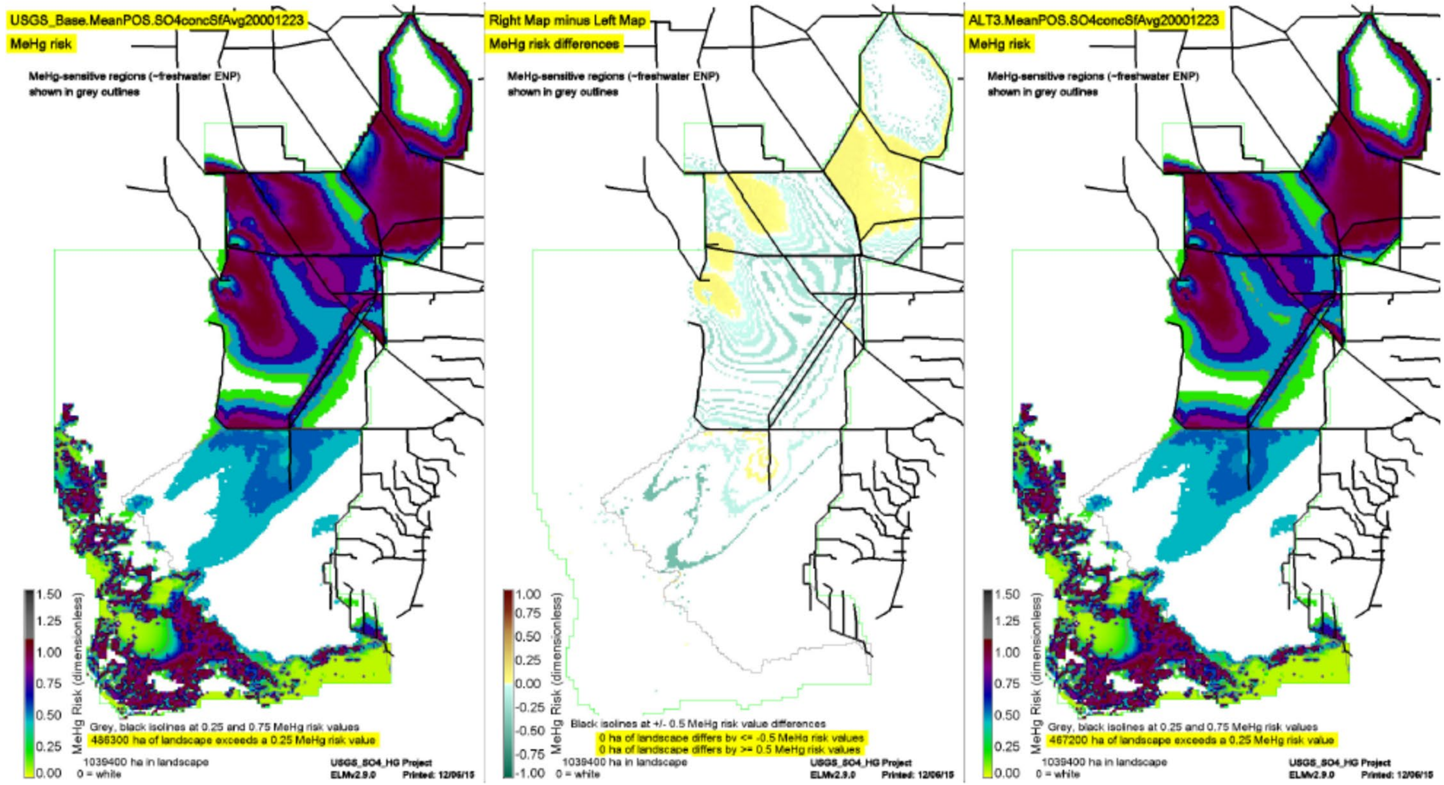

Fig. 8 Maps of model results for Alternative 3 (10% reduction in sulfate loading) for methylmercury risk (dimensionless) across the Everglades. The left map shows baseline conditions, the right map shows methylmercury risk after a 10% reduction in sulfate loading, and the middle map shows the difference between baseline and Alternative 3

POS. This likely reflects the greater sulfate present in the system during wetter years and the wet season, as sulfate is mobilized from soils in the EAA (Scheidt and Kalla 2007; Orem et al. 2011). ALT 3 (10% reduction in sulfate loading produced only modest reductions in sulfate concentration and MeHg Risk, even during a wet year. Some parts of WCA 3 near the junction of the Miami and L67 canals showed a modest zone of decline in sulfate concentration and MeHg Risk, but overall reductions were not large and very scattered. Overall, the model results seem to suggest that a > 33% reduction in sulfate loading to the ecosystem will be needed to significantly impact the MeHg problem in the Everglades, although any reduction will reduce MeHg Risk and have value for some portions of the ecosystem. Further modeling will be needed to fully evaluate the levels of reductions needed to protect, especially sensitive areas (e.g., WCA 1 and ENP).

As mentioned, the model uses past climate information in the simulations and assumes that past climate is replicated in future years. However, the rapidly changing climate may result in changes in rainfall and temperature in south Florida (Obeysekera et al. 2011). These changes will likely impact hydrology and biogeochemistry affecting both sulfate and MeHg concentrations and distributions (Orem et al. 2015b; Flower et al. 2019) and may need to be considered in future uses of the model developed for this study. It is also important to emphasize that the model is not intended to predict specific concentrations of sulfate or MeHg at a particular point in the ecosystem. Rather, it provides a guide for how changes in sulfate loading may affect overall distributions and changes in concentration and regions of the Everglades that would be most affected. The model is specific for the Everglades. However, the complex (nonlinear) biogeochemical relationship between sulfate and MeHg appears to be more general, and similar modeling approaches could be taken in other ecosystems.

Approaches to achieving reductions in sulfate loading have been discussed elsewhere (Orem 2007). These approaches include best management practices for sulfur use and reduction in soil oxidation in the EAA, reducing deep groundwater leakage (such as from fractures in canal bottoms), and adapting STAs to increase the removal of sulfate. It is anticipated that a combination of these strategies will be needed to achieve a > 33% reduction in sulfate loading suggested from the modeling results.

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