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Modeling sulfate transport and distribution and methylmercury production associated with Aquifer Storage and Recovery implementation in the Everglades Protection Area

William Orem [a,*], H. Carl Fitz [b,1], David Krabbenhoft [c], Michael Tate [c], Cynthia Gilmour [d], Mark Shafer [e]

[a] U.S. Geological Survey, Reston, VA, USA
[b] Soil & Water Science Department, IFAS, University of Florida, Davie, FL, USA
[c] U.S. Geological Survey, Middleton, WI, USA
[d] Smithsonian Environmental Research Center, Edgewater, MD, USA
[e] U.S. Army Corps of Engineers, Jacksonville, FL, USA

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ABSTRACT

Aquifer Storage and Recovery (ASR) technology has been proposed to meet the competing ecological and water-supply needs of south Florida and the Everglades Protection Area (EPA). The water recovered from ASR, however, may have altered water quality. Of particular concern is the enrichment of ASR recovery water in sulfate, which can stimulate microbial sulfate reduction and methylmercury (MeHg) production within the EPA. MeHg is already a serious issue with regard to wildlife and human health, and there is concern that ASR might exacerbate the problem. In order to address these concerns, the Lake Okeechobee Environmental Model (LOEM) and the Everglades Landscape Model (ELM) were adapted with sulfur modules to predict concentrations and distributions of sulfate within Lake Okeechobee and the EPA resulting from the release of ASR water. In addition, equations were developed relating the biogeochemistry of sulfate and MeHg production to produce a MeHg production risk assessment from the modeled ASR sulfate loading. Baseline runs (no ASR discharge water), and three different ASR release scenarios with varying sulfate loading were evaluated. Results show that ASR release will temporarily elevate sulfate concentrations in Lake Okeechobee from the present level of about 30 mg/L to as high as 50 mg/L in a worst case scenario, but that this will have little impact on MeHg production in the lake. The model indicates that ASR release will have minimal impacts on sulfate loading to the EPA, primarily because of the already large sulfate loading from other sources within the Everglades Agricultural Area (EAA). Maps of sulfate distributions show that certain locations in the EPA, especially those near canal or Stormwater Treatment Area (STA) discharges, may experience significantly higher sulfate loading from ASR. Overall impacts with regard to increased MeHg production risk are predicted to be low based on this model, although sites with increased ASR sulfate loading (e.g. canal and STA discharge sites) may experience some change in MeHg risk.

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Abbreviations: ALT, various alternate model scenarios; ASR, Aquifer Storage and Recovery; BIR, Basin Indicator Regions; CERP, Comprehensive Everglades Restoration Plan; EAA, Everglades Agricultural Area; ELM, Everglades Landscape Model; ENP, Everglades National Park; EPA, Everglades Protection Area; Hg, mercury; LOEM, Lake Okeechobee Environmental Model; MeHg, methylmercury; SFWMM, South Florida Water Management Model; STA, Stormwater Treatment Area; WCA, Water Conservation Area.

* Corresponding author.
[1] Current address: EcoLandMod, Inc., Fort Pierce, FL, USA.

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1. Introduction

The Everglades ecosystem has been altered from its original state due to anthropogenic actions, including the construction of an extensive canal and levee system, the development of a 700,000 acre agricultural zone to the north of the ecosystem (Scheidt and Kalla, 2007), and a large adjacent urban area (Miller, 1988; Davis and Ogden, 1994). Alterations have resulted in loss of 50% of the historic Everglades; the Everglades Protection Area (EPA) comprising the Water Conservation Areas (WCAs) plus the Everglades National Park (ENP), totals about 2,200,000 acres. Demands on the available freshwater supply in this highly managed landscape by agriculture, the urban area, and the Everglades ecosystem has resulted in a spatially and temporally altered hydroperiod and an altered water distribution pattern (Light and Dineen, 1994; Sklar et al., 2002). Restoring water flows and levels to those approaching pre-development historical conditions is an integral part of Everglades Restoration, as outlined in the Comprehensive Everglades Restoration Plan, CERP (USACE, 1999). An important component of this plan is restoring more "natural" hydrologic conditions; this includes altering the timing of water held and released into the ecosystem to be more representative of pre-development conditions.

Aquifer Storage and Recovery (ASR) has been proposed as a cost-effective approach to help meet the competing water-supply needs of a growing population base, agriculture, recreational interests, and the Everglades (Reese, 2002). In the ASR approach, excess surface water is stored in shallow aquifers during wet periods for recovery during extended dry periods (NRC, 2002). This allows the capture and storage of freshwater previously lost to the sea, and improved management of water quantity, timing and distribution. The CERP plan for ASR includes the construction of over 300 wells for water storage (Fig. 1), with 200 of these around the northern rim of Lake Okeechobee (Reese, 2002).

A problem with the ASR approach is that storage of surface water in subsurface aquifers can significantly alter the quality of freshwater stored. This occurs through mixing of the stored surface water with connate seawater in underground aquifers, and interactions with geologic formations that underlie south Florida. The water mixing and geologic interactions may enrich the stored freshwater in major anions and cations (e.g. chloride, sulfate, sodium, potassium, transition metals). In addition, the surface freshwater used in ASR has already been altered by various substances derived from anthropogenic activities at the surface. For example, sulfate (SO_4^{2-}) concentrations in surface water from Lake Okeechobee and canals are elevated by 20–60 times, respectively, relative to background levels (Orem et al., 2011). The excess sulfate originates from agricultural applications, soil oxidation, and possibly upwelling of groundwater (Bates et al., 2002; Orem et al., 2011).

One particular concern regarding the release of ASR waters is the potential for increased sulfate loading to the Everglades and resultant increased production of toxic methylmercury (MeHg); the links between sulfate loading and MeHg production are well established (Krabbenhoft, 1996; Gilmour et al., 1998; Orem et al., 2011; Gabriel et al., 2014). A previous study evaluated the potential for *in situ* MeHg production during aquifer storage periods and showed that this was not the case (Krabbenhoft et al., 2007). The current study was devised to assess the potential for an implemented ASR program to increase sulfate loading to the ecosystem, thereby exacerbating the MeHg exposure problem in Everglades foodwebs.

Elevated levels of mercury (Hg) in the Everglades food web (up to 3 mg/kg and present in biota as methylmercury or MeHg) have been known since the mid 1980's (Ware et al., 1990), and are comparable to levels at sites highly contaminated with mercury (Schaefer et al., 2004). These high levels of MeHg pose a threat to piscivorous and higher trophic level wildlife, including endangered species in the Everglades, and to human health through fish consumption. The high levels of MeHg in Everglades biota result from a number of factors that are all known to promote MeHg formation, including: elevated levels of atmospheric Hg deposition (http://nadp.sws.uiuc.edu/mdn/), extensive wetland area, abundant organic soils, and moderate to high sulfate and high dissolved organic matter (DOC) concentrations in surface waters.

Sulfate loading drives microbial sulfate reduction in anoxic wetland soils, which is a primary causal process leading to the formation of MeHg in the environment (Hsu-Kim et al., 2013). The relationship between sulfate loading to the ecosystem and MeHg production is complex, however, due to the opposing effects of stimulation of sulfate-reducing bacteria by sulfate at low-to-high concentrations, and inhibition of methylation because of diminished Hg bioavailability for sulfate-reducing bacteria at high sulfate concentrations (sulfide is an endproduct of sulfate reduction and may complex Hg) (Gilmour et al., 1998). This complex relationship between sulfur biogeochemistry and MeHg production is reflected in the observation of maximum MeHg concentration generally associated with moderate sulfate concentrations. Likewise lower MeHg concentrations are observed at low (substrate limitation) and high sulfate (sulfide inhibition) conditions (Orem et al., 2011). This nonlinear relationship leads to a spatially complicated picture of sulfate and MeHg across the Everglades. CERP plans call for major modifications to water use and routing in south Florida, which in some cases could give rise to more MeHg production in some areas, and less MeHg production in others. In order to provide a more complete spatial understanding of MeHg levels in the Everglades, and to improve our ability to anticipate the outcome of possible changing sulfate loads owing to the implementation of the ASR program, the U.S. Army Corps of Engineers, U.S. Geological Survey, and the University of Florida initiated a multi-component study to incorporate sulfur cycling and MeHg production routines into the Everglades Landscape Model (ELM) (Fitz et al., 2011). The overall goal of this study was to provide a tool to anticipate the MeHg production response due to altering sulfate loading from different ASR scenarios.

2. Methods

The model used for this study is described in detail below, and applied in the EPA (Fig. 1) using data from ASR wells (Fig. 2A) located at the northern end of the ecosystem, especially around Lake Okeechobee. The simulation modeling chain

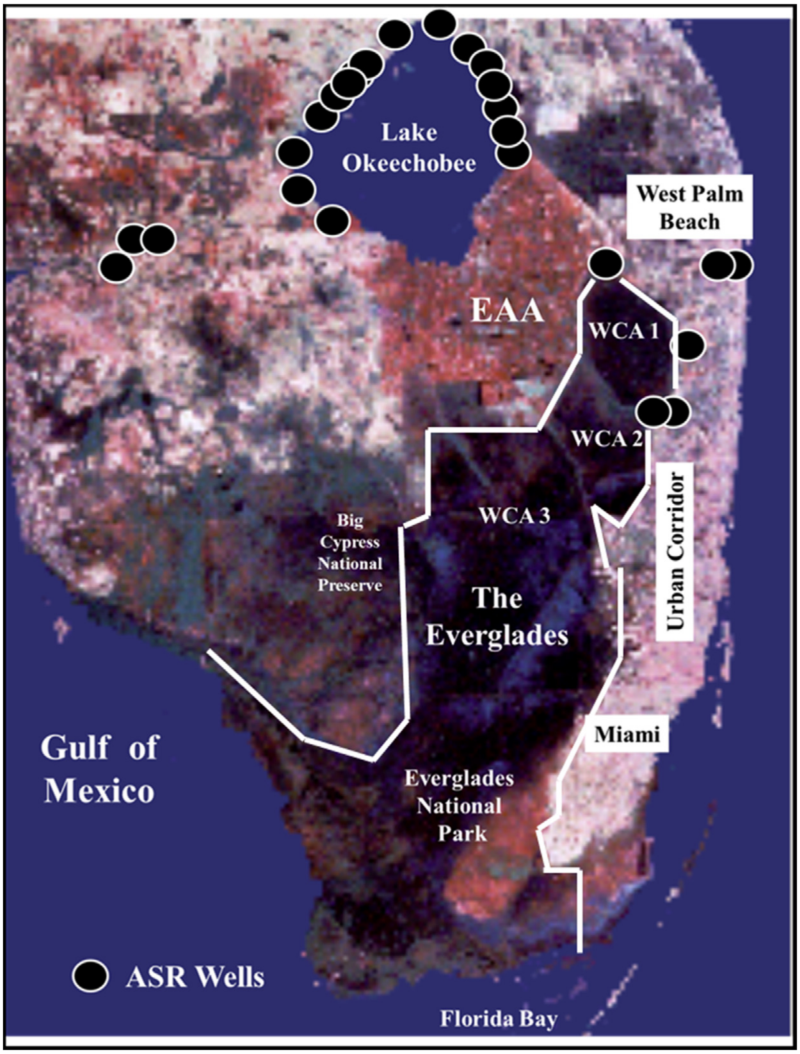

Fig. 1. Map of south Florida showing the Everglades Protection Area outlined in white and the generalized locations of ASR wells, with concentration of wells along the northern perimeter of Lake Okeechobee.

is shown in Fig. 2B. Inflows and outflows of ASR water to Lake Okeechobee were estimated using a modified version of the Lake Okeechobee Operations Screening (LOOPS) model version 5.71 (Neidrauer et al., 2006). The predicted volume of recovered ASR water discharged to Lake Okeechobee during recovery events was 2940 ac-ft/day for both ALT2C and ALT2V and 1170 ac-ft/day for ALT4V. The timing and duration of discharge events is shown in Table 1. The Lake Okeechobee Operations Screening model hydrology was matched with estimated sulfate concentrations in the recovered ASR water. ASR flows from the Lake Okeechobee Operations Screening model were used as boundary conditions for the Lake Okeechobee Environmental Model (LOEM), which simulates ASR impacts to Lake Okeechobee water quality (Jin et al., 2007). Because the simulation period for the LOEM model (2000–2009) did not overlap with the ELM model simulation period, linear regression equations were developed from the LOEM output to predict lake sulfate concentrations for simulated ASR recovery periods before 2000.

2.1. ASR sulfur model

The Everglades Landscape Model (ELM v2.8.6) was the primary modeling framework, which included a new sulfate module for this study. The model was applied to evaluate relative differences in sulfate distributions across the Everglades Protection Area using several ASR Project Alternatives. The sulfate module uses a first order, net settling rate equation. New data for the ELM sulfate module included the addition of sulfate boundary conditions, a net settling rate map, and observed data for calibrating model performance. The historical (1981–2000) model-data calibration resulted in an overall median predictive bias of 0 and −2 mg/L in 78 marsh and canal sites, respectively. Statistical and graphical assessments of model performance were consistent with other ELM-simulated water quality variables (e.g. phosphorus), and the sulfate module was

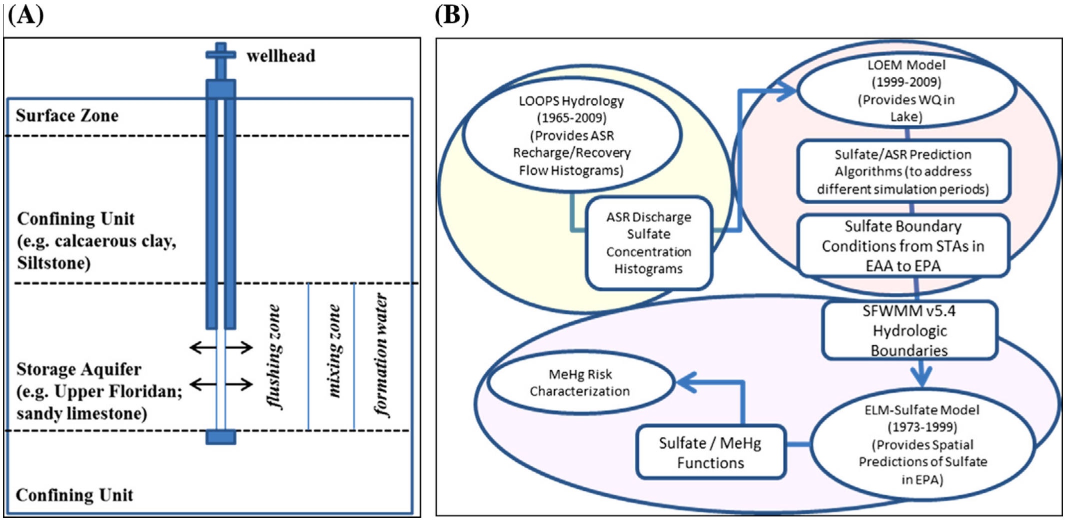

Fig. 2. Diagram of ASR well (A), and simulation modeling chain (B).

Table 1
ASR recovery events as simulated using LOOPS model.

Start of recovery	End of recovery	Duration (days)
4/1/1974	6/28/1974	88
12/6/1980	3/3/1982	452
5/20/1985	9/28/1985	131
6/7/1987	10/16/1987	131
4/27/1989	12/4/1989	221

Table 2
Description of baseline and ASR alternative scenarios applied to Everglades Landscape Model (ELM) in this study.

Simulation	Type	Description
ASR_Base	Baseline	CERP Scenario without ASR (CERP0; update of CERP)
2050B2	Baseline	2050 future baseline scenario without CERP
ALT2C	ASR alternative	CERP0 plus ASR water from 200 wells in Upper Floridan Aquifer discharging to Lake Okeechobee sulfate in ASR recovered water set to aquifer baseline levels of 200–300 mg/L
ALT2V	ASR alternative	CERP0 plus ASR water from 200 wells in Upper Floridan Aquifer discharging to Lake Okeechobee sulfate in water discharged to Lake Okeechobee varied from surface water baseline of 30 mg/L at start of ASR recovery, to aquifer baseline levels of 200–300 mg/L at end of ASR recovery
ALT4V	ASR alternative	CERP0 plus ASR water from 200 wells (48 in Upper Floridan, 32 in Avon Park Producing Zone, 120 in Boulder Zone) discharging to Lake Okeechobee; recovery efficiency for ASR water set at 70% for Upper Floridan, 30% for Avon Park Producing Zone, and 0% for Boulder Zone; sulfate in water discharged to Lake Okeechobee varied from surface water baseline of 30 mg/L at start of ASR recovery and increases to groundwater baseline levels as ASR recovery proceeds; sulfate levels in Avon Park Producing Zone higher than 200–300 mg/L found in Upper Floridan

acceptable for applications to evaluate future scenarios of multi-decadal sulfate dynamics across the greater Everglades region. Thus, the sulfate module was accepted and used to examine sulfate dynamics across the EPA in relation to ASR. Details on the development and calibration/testing of ELM v2.8.6 are detailed by Fitz (2014a).

The ELM v2.8.6 ASR 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 CERP plan, recently updated to "CERP0". These SFWMM simulations were drivers of managed water flows for all of the ELM v2.8.6 simulation runs (Fitz, 2014b) The climate time period used in the SFWMM and ELM future ASR simulation runs was 01/01/1974–04/30/2000 (i.e., the SFWMM and ELM assumed that past climate was replicated in future years). This climate period includes several long-duration ASR recovery periods which provide the ASR related sulfate load pulses to Lake Okeechobee.

Simulation runs included: a baseline (ASR_BASE) with no contributions from ASR wells, and three alternative scenarios of sulfur flow from ASR wells (ALT2C, ALT2V, ALT4V) involving mixing of surface water (30 mg/L sulfate) with groundwater from ASR wells (Table 2). These different scenarios covered the range of expected sulfate loading from ASR water, with ALT2C having the highest and ALT4V the lowest loading. ASR wells located in the Upper Floridan Aquifer (244–457 m depth), Boulder Zone (853–1067 m), and the Avon Park Producing Zone located near the top of the Avon Park Formation (213–610 m) were considered in this study (Fig. 1). Sulfate levels in different ASR groundwater formations were 200–350 mg/L for the Upper Floridian (depending on location), and 350–550 mg/L for the Avon Park Producing Zone. The ASR_BASE and all ASR Alternatives had the same CERP0 hydrologic flows, but different Everglades sulfate loads due to ASR contributions. Sulfate loads varied due to differences in loading from deep-aquifer sulfate sources under different ASR scenarios.

A variety of methods were used to develop sulfate concentrations for ELM boundary conditions as detailed by Fitz (2014c). All ASR simulations routed ASR-derived sulfate through Lake Okeechobee, then into the Everglades Stormwater Treatment Areas (STAs; constructed wetlands designed for phosphorus removal)), which then discharged into the Water Conservation Areas (WCAs) in the EPA domain of ELM. In summary, the LOEM, a simple STA model, SFWMM v5.4 hydrology, and other quantitative tools were used to establish boundary-condition sulfate loads discharged to the Everglades, and ELM-simulated downstream landscape patterns of sulfate availability over decadal time scales in the EPA. Sulfate concentrations in Lake Okeechobee were of particular interest in developing boundary conditions for ELM because the lake was the direct recipient of all ASR recovery water, and a variable source of water and sulfate loading to STAs, and the EPA. LOEM-simulated daily mean Lake sulfate concentrations varied from long-term means of approximately 30 mg/L (ASR_BASE) to as much as 50 mg/L (ALT2C), and EAA source waters were assumed to have constant sulfate levels of 50 mg/L for all simulations.

Although the models were well-calibrated and deemed acceptable for applications, there are uncertainties associated with results due to the linkages among multiple models and complex spatial relationships (among the aquifers of the ASR wells, Lake Okeechobee, the EAA, and the greater Everglades). It is thus important to understand that the model(s) are not predicting absolute values in exact locations in the future, but the results are useful in comparing the multi-decadal, spatial trends in the relative differences among future alternatives.

2.2. ASR methylmercury model

The MeHg production risk posed by altering sulfate loading from implementation of the ASR program was examined by applying numerical functions relating sulfate concentration to MeHg production that were determined from many years of research and monitoring by our research group in the Everglades (Fig. 3), to the predicted sulfate outcomes from the ELM v2.8.6 ASR simulation. The sulfate concentration and MeHg production relationship in surface waters is highly nonlinear, commonly exhibiting a ‘‘humped” shaped (unimodal) form. Thus, a peak in MeHg concentration is commonly observed at moderate sulfate levels, but the position of the peak in MeHg production with respect to sulfate concentration may vary

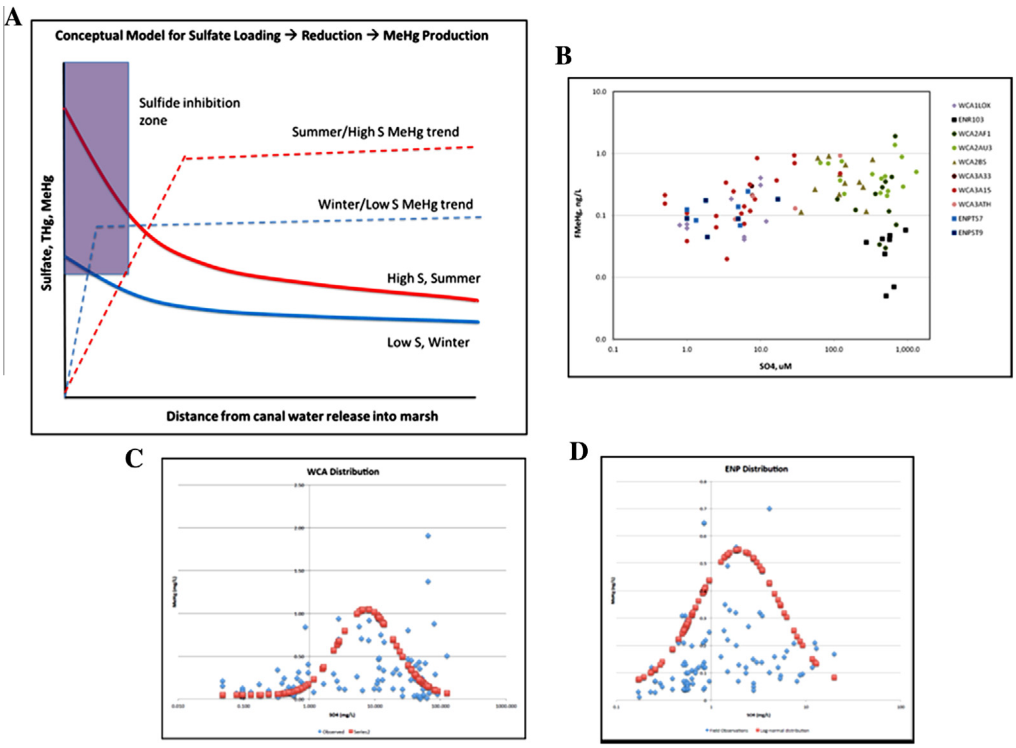

Fig. 3. Relationship between sulfate and MeHg: (A) conceptual model of sulfate concentration and MeHg production with respect to inflow points, and indicating sulfide inhibition zone at high sulfate loading; (B) plot of sulfate versus MeHg production using empirical data from across the EPA; (C and D) plots of sulfate versus MeHg in the WCAs and ENP, respectively and used to develop equations for model.

due to several biogeochemical factors (Gilmour et al., 1992, 1998; Benoit et al., 2001, 2003; Orem et al., 2011). This relationship between MeHg production and sulfate concentration has been observed in field studies, field experiments (mesocosm studies), and lab experiments (microcosm studies) in the Everglades and other wetland environments (Fig. 2).

The mercury model used two parameterizations of sulfate versus MeHg distribution curves from field data: one for the WCAs and one for ENP (Fig. 3). 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; these occurred at sulfate concentrations of 10–15 and 2 mg/L for the WCAs and ENP, respectively. The general equation used, defining the two distributions was: $[MeHg] = a * \exp(-0.5 * (\ln([SO4])-b/c)\text{^}2)+d$; with coefficients of $a = 1$, $b = 2$, $c = 1$, 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 (BIR) for sulfate loading and used the same five simulations applied in the sulfate model: 2 baselines (2050 future baseline, and ASR_Base), and three alternative ASR sulfate loading scenarios (ALT2C, ALT2V, ALT4V). 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 visual discontinuity in the results at the interface of the ENP and WCA3 along Tamiami Trail. This artifact in the model results is not reflected in our field data, which actually show a more gradual transition.

3. Lake Okeechobee sulfur and mercury

3.1. Historical sulfur trends

Excluding ASR inputs, sulfur in Lake Okeechobee (primarily sulfate) is largely sourced from surface runoff, including the upstream Kissimmee River basin and the EAA (including back pumping of agricultural drainage). Historic sulfate concentrations in Lake Okeechobee for the period 1974 to present have varied from about 70 mg/L to present levels of about 22 mg/L in 2005 (Scheidt and Kalla, 2007). Lake sulfate concentrations were about 25 mg/L during 1940–41 (Love, 1955), and 28 mg/L from 1950–1952 (Brown and Crooks, 1955), rising to an average in excess of 60 mg/L during the 1970s as large volumes of EAA runoff were routinely backpumped to the lake, accounting for roughly 50% of the lake's sulfate load. In the 1980s backpumping was reduced in an effort to reduce nutrient loading that was contributing to lake eutrophication. These changes resulted in a substantial decline in sulfate loading and sulfate concentrations in the lake, but in greater discharges of EAA water containing sulfate southward to the WCAs. Since 1985, annual net exports of sulfate from the lake have exceeded imports from the EAA in most years. As a result, during the period of record for this study (1974–2006), Lake Okeechobee represents a modest net input of sulfate (approximately 4500 mt/yr in surface flows) to the EAA canals and the Everglades, driven by surface water runoff to the lake and evapoconcentration. Sulfate concentration in the lake appears to be inversely related to lake stage, likely due to dilution that results from rainfall during wet periods and concentration from evaporation during dry periods. The long-term trend for Lake Okeechobee sulfate concentration is downward since 1980, most likely due to a reduction in back pumping of EAA runoff.

3.2. Sulfur budget

A sulfur budget for Lake Okeechobee (McCormick and James, 2008; James and McCormick, 2012) shows that about 97% of the sulfur entering the lake is from surface water inflow (75,000 metric tons sulfur/year), with the remaining 3% from the atmosphere (2000 metric tons sulfur/year). About 89% of the sulfur in the lake (70,000 metric tons/year) is exported to canals and the Caloosahatchee River, with about 11% (9000 metric tons/year) retained in the lake. Retention is most likely through uptake by aquatic plants, and sequestration in sediments as organic sulfur and metal sulfides after reduction to sulfide by sulfate reducing bacteria in the anoxic sediments. Overall, Lake Okeechobee is more of a reservoir for sulfur than a source or sink.

The most significant current sources of sulfate to Lake Okeechobee are from the Kissimmee Basin, Indian Prairie, and the EAA. Drainages flowing into the lake from the north account for 64% of annual average sulfur loads: 28% from the Indian Prairie/Lake Istokpoga basin, 18% from the Kissimmee River, and 18% from other basins. Runoff, including some back pumping (though much less than in the 1970s) from the EAA, accounts for 36% of the annual average sulfur load to the lake. Direct groundwater discharge appears to contribute little or no sulfate to the lake, and rainfall contributes only a small percentage (about 2–3%) of the lake's sulfate (McCormick, unpublished data). Improved pastures and other agricultural lands, collectively account for 52% of the land-use in the watershed north of the lake, and soil oxidation and fertilizer applications may be important sources of sulfur (Zielinski et al., 2006). The soils in upland areas of the watershed are typically poor in sulfate, although not in all locations.

The concentration of sulfate (and other ions) in this large shallow lake is significantly impacted by evapoconcentration (James et al., 1995). The lake also has limited capacity to effectively sequester sulfur in its sediments. The rocky and sandy bottom of much of the lake and the re-suspension of sediments from the relatively shallow lake bottom during even modest wind events inhibits anoxia in surface sediments and microbial sulfate reduction, limiting sequestration of reduced sulfur species in the lake sediments. Indeed, the residence time of sulfate in Lake Okeechobee is similar to that of unreactive chloride, about 2–3 years on average, showing that sulfate passes through the lake quickly (McCormick, unpublished data). Thus, ASR sulfur in the lake that is discharged to the south will primarily pass through to the canals, STAs and eventually the EPA. It should be understood that most of the ASR sulfate entering the lake would be discharged to the Caloosahatchee and St. Lucie Rivers where most of the lake water is also discharged. Sulfate discharged to these rivers will mostly be transported to the sea.

3.3. Effects of ASR on Lake Okeechobee sulfur

As mentioned, several alternative scenarios were used to model ASR discharges of sulfate to Lake Okeechobee and the EPA (Table 1) using the LOEM and ELM-Sulfate models respectively. Alternative ALT2C assumes 200 Upper Floridan ASR wells placed around the perimeter of the lake. In this alternative, the sulfate concentration in the recovered water discharged to the lake was conservatively assumed to be equal to the background groundwater sulfate concentration, as measured or estimated for each ASR well. Alternative ALT2V also assumes 200 Upper Floridan ASR wells placed around the perimeter of the lake. However, in this alternative, the sulfate concentration in the recovered water discharged to the lake was assumed to vary linearly during the recovery period, ranging between the surface water sulfate concentration (approximately 30 mg/L) to the background groundwater sulfate concentration as measured or estimated for each ASR well (200–350 mg/L). Alternative ALT4V likewise assumes 200 wells with 48 Upper Floridian wells, 32 APPZ wells, and 120 Boulder Zone wells. Wells located in the Avon Park Producing Zone are estimated to recover only 30 percent of the stored volume and wells located in the Boulder Zone are assumed to have no recovery. For this reason, ALT4V has significantly less recovered water volume. In this alternative, the sulfate concentration in the recovered water discharged to the lake was assumed to vary linearly over the recovery period between the above surface water sulfate concentration to the background groundwater sulfate concentration as measured or estimated for the geologic unit for each recovery well. The Upper Floridan estimated sulfate concentrations vary from 200 to 350 mg/L depending upon location; the Avon Park Producing Zone has estimated sulfate concentrations that range from 350 to 550 mg/L. Simulation results indicate that mean lake sulfate concentrations will increase from the long-term background of 30 mg/L to 50 mg/L, 34 mg/L, and 31 mg/L, for scenarios ALT2C, ALT2V, and ALT4V, respectively. The output from the LOEM simulation of lake sulfate concentrations (1999–2009 simulation period) for one baseline and three ASR scenarios are shown in Fig. 4A, and the derived sulfate boundary condition for the 1974–2000 period used in the ELM-Sulfate modeling effort is shown in Fig. 4B.

Lake Okeechobee sulfate concentrations were of particular interest for this study because the lake is planned to be the primary discharge point for ASR recovery water, and a variable source of water and sulfate loading to STAs, and the EPA.

3.4. Sulfate loading from Lake Okeechobee to the STAs

Depending on daily flows quantified by SFWMM outputs, calculated inflows to STAs were a mix of lake outflow and EAA runoff that varied spatially and temporally. The different ASR Alternative simulations all increased sulfate loading from the lake to the STAs compared to the baseline (ASR_BASE). Annual mean sulfate loading from the lake to the STAs were 16,000

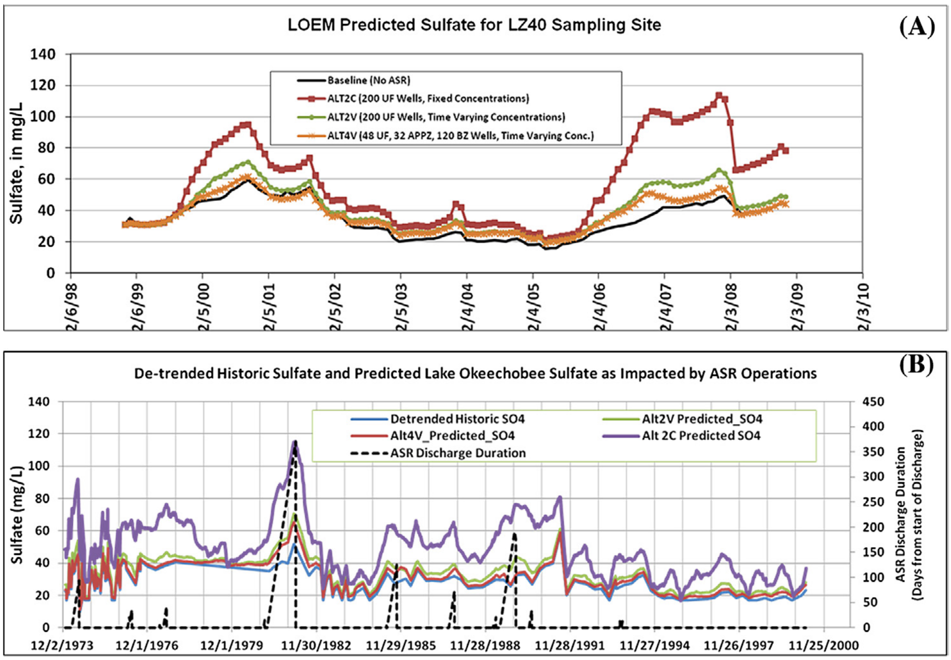

Fig. 4. Simulated sulfate concentration in Lake Okeechobee from LOEM Model for ALT2C, ALT2V, and ALT4V scenarios, including the sulfate baseline concentration signal (no ASR) shown in (A), and derived ELM-Sulfate model boundary conditions shown in (B).

(ASR_BASE), 25,000 (ALT2C), 19,000 (ALT2V), and 17,000 (ALT4V) metric tons. However, the annual mean surface water sulfate load (i.e., excluding atmospheric inputs) to the downstream WCAs was more than 5× that of the lake-only (ASR-influenced) inflow loads to the STAs. Thus, while ASR variations had meaningful effects on lake-derived loads to STAs and WCAs, on average the EAA sulfate loads to STAs and the Everglades were dominant.

3.5. ASR sulfate loading and methylmercury in Lake Okeechobee

Simulation results indicate that mean lake sulfate concentrations will increase from the long-term background of 30 mg/L to 50 mg/L, 34 mg/L, and 31 mg/L, for scenarios ALT2C, ALT2V, and ALT4, respectively. However, this additional sulfate loading is expected to have minimal impacts on MeHg production in Lake Okeechobee if the relationship between sulfate and MeHg is similar to the WCAs and ENP. Although no detailed studies of Hg methylation in Lake Okeechobee have been conducted, Hg levels in the muscle of gar and other top predator fish collected from Lake Okeechobee are similar to, or lower than, those generally reported from other areas of the United States (Burger et al., 2004). Thus, although the levels of Hg in fish from the Everglades to the south of Lake Okeechobee are sufficiently high to result in human fish consumption advisories, there are no similar advisories for Lake Okeechobee. The reasons for this are not presently known, but there are several likely explanations. First, although there are some areas of mud and peat bottom sediments, most of the lake bottom consists primarily of rubble and sand with relatively low organic carbon content. This type of sediment is not generally associated with sulfate reduction and MeHg formation. Second, observed sulfate levels of ~30 mg/L in the lake place its condition in the zone of inhibition (Fig. 3C and D). Third, several lines of evidence suggest that microbial sulfate reduction is not prevalent in Lake Okeechobee. Sulfur models for Lake Okeechobee indicate that it is more of a reservoir of sulfate within the ecosystem, and there is no source of sulfate and minimal retention of sulfur within the lake. The lack of sulfur retention further suggests that limited sedimentary sulfate reduction is occurring within the lake. Thus, Lake Okeechobee receives sulfate inflow from rivers to the north, backpumping from the EAA, and small amounts from rainfall, some evapoconcentration of sulfate occurs due to the large surface area of the lake, and the sulfate passes through on its way to the EPA. Fourth, Lake Okeechobee does not commonly stratify with regard to oxygen, which is a condition commonly observed in lakes with elevated MeHg (Rask et al., 2010). Last, eutrophic lakes like Lake Okeechobee generally exhibit low MeHg levels, likely due to bio-dilution effects (Chen and Folt, 2006).

4. Everglades Protection Area

4.1. Sources and distributions of sulfur in the EPA

Sulfur in the EPA is primarily derived from canal discharge (pumping stations), STA discharge (with canals the main source of sulfur passing through the STAs), and passive movement through breaks in canal levees. The form of sulfur entering the EPA is overwhelmingly sulfate (Orem et al., 2011). The canals receive sulfate from Lake Okeechobee loads, EAA runoff (soil oxidation, and sulfate added as agricultural amendments), and possibly groundwater. Surface water sulfate concentrations (1993 through 2005) show that the highest average surface water sulfate concentrations in the EPA are found in canal water in (and just downstream of) the EAA (Scheidt and Kalla, 2007; Orem et al., 2011). Average sulfate concentrations in EPA marshes over the period of record ranged from <0.05 mg/L at sites distant or protected from canal discharge, to 100 mg/L at sites near canal discharge (Scheidt and Kalla, 2007; Payne et al., 2009; Orem et al., 2011). At interior marshes within the WCAs, there is an overall gradient in sulfate concentration from north to south, with the exception of WCA 1 (the Arthur R. Marshall Loxahatchee National Wildlife Refuge), which is somewhat protected from canal inputs by a rim canal. Recent data show that during the wet season sulfate from canal water penetrates into interior marsh in WCA 1 (Wang et al., 2009). Elevated sulfate concentrations occur near major canals throughout the ecosystem, even in areas to the south, such as along the L-67 canal in southern WCA 3A and where the L-67 canal terminates in ENP.

Sulfate from STAs and canal discharge points penetrates much farther into the marsh than phosphorus. Sulfur is a plant nutrient required at roughly the same levels as phosphorus and is removed from surface water by aquatic plants (Hawkesford and DeKok, 2007), but sulfur (as sulfate) is discharged into the EPA at mg/L levels compared to μg/L levels for phosphate. The 1000× higher loading of sulfate compared to phosphorus means that plant uptake has little effect on the sulfate concentration. Microbial sulfate reduction in soils also removes sulfate from surface water and sequesters it as insoluble reduced sulfur in soils, but this process is slow relative to sulfate loading rates to the EPA. Hence, as water flows across the EPA, phosphorus concentrations are rapidly attenuated with distance from the canals by plant uptake, whereas sulfate concentrations are reduced much more slowly.

Datasets from the U.S. Geological Survey, U.S. Environmental Protection Agency, and the South Florida Water Management District are all in close agreement for sulfate concentrations and distributions across the EPA (Scheidt and Kalla, 2007; Scheidt et al., 2000; Orem et al., 2011). Surface water sulfate concentrations in the EPA tend to be highest during the wet season due to the pumping of stormwater from the EAA into the Everglades for flood control (Scheidt et al., 2000). The most sulfate-enriched marshes are in WCA 2A, and northern WCA 3A. STA 2 discharges water with sulfate concentrations as high as 100 mg/L during the wet season into northwestern WCA 2A (Scheidt and Kalla, 2007; Garrett and Ivanoff, 2008). Sulfate concentrations in WCA 3A generally have been highest in the north and east, and at sites near the

Miami and L67 Canals. Sulfate concentrations up to 100 mg/L were observed in surface water at sites in WCA 3A near points of canal discharge, though average levels in most of northern WCA 3A range from 5 to 20 mg/L. Sulfate concentrations in WCA 3A decrease toward the south and west. STA 3/4 as well as the HoleyLand and Rotenberger Wildlife management Areas discharge into WCA 3 at its northern intersection with the EAA.

In the freshwater parts of ENP, sulfate concentrations in surface waters are naturally low (<<1 mg/L), but are elevated substantially from this background at points near canal releases to the marsh. EPA REMAP data from the 1995, 1996, 1999, and 2005 wet seasons indicate elevated sulfate levels (5–10 mg/L) well into the Shark River Slough marsh near the L-67 canal terminus within ENP (Stober et al., 2001; Scheidt and Kalla, 2007). In Big Cypress National Preserve sulfate concentrations are generally <1 mg/L, except for marshes just north of Big Cypress National Preserve (2–3 mg/L sulfate) and canals such as the L28 (10 mg/L sulfate) that surround Big Cypress National Preserve (Orem et al., 2011).

4.2. Temporal changes in sulfur in the EPA

Sulfate concentrations in marsh surface waters exhibit substantial temporal variability due to changes in rainfall, canal discharge, seasonal drying and rewetting cycles, and perhaps the timing of additions of agricultural chemicals to soils in the EAA. For example, sulfate concentrations in WCA 2A near the center of the area, and near the S-10C canal discharge structure have ranged from 5 to 100 mg/L at various times during the course of a year. Long-term temporal trends are superimposed on this shorter-term variability. For example, surface water sulfate concentrations at marsh sites in eastern WCA 2A have shown significant downward trends over time (Orem et al., 2011). This trend reflects a decrease in the volume of water discharged from the S-10 outflow structures on the Hillsborough Canal into northeastern WCA 2A, and not a decline in sulfate concentration in canal water (Gilmour et al., 2007). Significant declines in surface water sulfate have also occurred in central WCA-3A, more remote from the EAA. Sulfate concentrations here dropped from about 10 mg/L in the mid-1990's to <0.1 mg/L by about 1999, and have remained low since then. The reason for this decline is more difficult to determine because canal loads to WCA 3A occur through levee breaks rather than control structures. However, sources of sulfate to this site probably include Miami and L-67 canal water, and the observed decline in sulfate here may reflect changes in water management accompanying the Everglades restoration plan. In contrast, sulfate has increased in the northwest corner of WCA 2A. Prior to 2000 sulfate concentrations there ranged from 5 to 17 mg/L, but since the opening of STA 2 in 2000 the average sulfate concentration has risen to 60–70 mg/L, consistent with sulfate levels found in STA 2 discharge water (Garrett and Ivanoff, 2008).

The temporal variability of sulfate concentrations in different parts of the EPA highlights the many factors that influence sulfate levels, most importantly the discharge of sulfate-enriched canal water. Some temporal trends can be linked to changes in water management operations (e.g., initiation of new canal water release points from STAs), whereas the cause of others is less clear. Thus, the use of sulfate-enriched canal water to increase hydroperiod in ENP as part of the restoration plan will inevitably lead to increased sulfate loading in the absence of any changes to sulfate use and releases in the northern portions of the ecosystem. This has significant consequences for the ecosystem, especially with regard to MeHg production and bioaccumulation, and the resulting impacts on the ecosystem. The release of ASR water into the EPA could also impact temporal trends in sulfate levels based on release times of the ASR water.

4.3. Effects of ASR on the EPA

Five boundary condition datasets for sulfate concentration were developed for the northern end of the EPA using output from Lake Okeechobee scenarios described earlier. The calibration boundary conditions are for the period from 1980 to 2000, and the baseline and ASR scenario conditions are for the period from 1965 to 2000. Baseline and three ASR scenario boundary (ALT-2C, ALT-2V, ALT-4V) condition datasets were based upon LOEM output for with/without ASR discharges of sulfate. Sulfate loads and concentrations from Lake Okeechobee are adjusted to account for sulfate loss or addition within the STAs and EAA, usually sulfate loss in the STAs and sulfate addition from the EAA. Estimates of sulfate removal in each STA were based on inflow versus outflow sulfate concentrations from limited datasets: 10% STA 1E, 33% STA 1W, 15% STA 2, 26% STA ¾, 60% STA 5, and 58% STA 6.

Calculated inflows to STAs were a mixture (varying spatially and temporally) of Lake Okeechobee outflows and runoff from the EAA. The various ASR scenarios used (Table 1) all increased the sulfate loading from Lake Okeechobee to the STAs compared to the baseline run, as expected. Annual mean sulfate loads to the STAs were 16,000 metric tons for the baseline scenario (e.g. no ASR sulfate), and varied from 17,000 to 25,000 metric tons for the various ASR addition scenarios. Annual mean surface water sulfate loading to the WCAs (excluding small input from the atmosphere), however, were more than 5× that of ASR-influenced Lake Okeechobee inflow loads to the STAs. This excess loading to the EPA predominantly originates from the EAA, and includes sulfate from soil oxidation (including historical agricultural sulfur applications), recent agricultural sulfur applications (Bates et al., 2002; Orem et al., 2011), and possibly contributions from groundwater. Thus, although ASR had some impact on lake-derived sulfate loads to STAs and to the EPA, the EAA sulfate loading to STAs and the Everglades were dominant, as they are at present in the absence of any ASR additions.

The area of the EPA (total area 1,039,400 hectares (ha) as used in this study) impacted by ASR sulfate loading under different scenarios is shown as a series of bar graphs in Fig. 5. The area of the EPA exceeding 2 and 10 mg/L sulfate were the criteria used in developing these bar graphs. These concentrations were chosen as meaningful tipping point concentrations

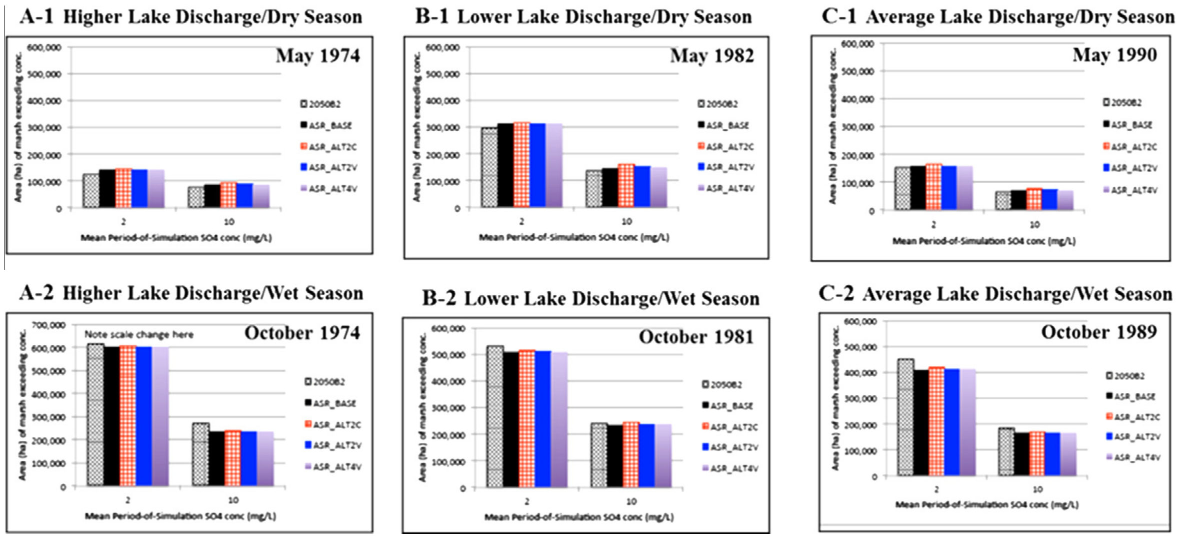

Fig. 5. Bar plot of area of the EPA marsh exceeding two sulfate criteria (2 mg/L and 10 mg/L) for future 2050 estimated baseline conditions, ASR baseline conditions, and the three ASR sulfate addition scenarios (ALT2C, ALT2V, ALT4V) from ELM model simulation with sulfate module. Results are reported for dry season and wet season during three periods of study: (A-1) wetter period/dry season (May 1974), (A-2) wetter period/wet season (October 1974), (B-1) drier period/dry season (May 1982), (B-2) drier period/wet season (October 1981), (C-1) average rainfall period/dry season (May 1990), (C-2) average rainfall period/wet season (October 1989).

relating to sulfate stimulation/inhibition of MeHg production impacting the ecosystem. The 2050B2 and ASR_Base simulations, and the three ASR simulations (ALT2C, ALT2V, ALT4V) are shown in each plot. Results are reported for dry season and wet season during three periods of study that correspond with the timing of significant ASR recovery events as shown in Table 1: a wetter than average period (1974) with A-1 and A-2 representing the dry season (May 1974) and wet season (October 1974), respectively; a drier than average period (1981/1982) with B-1 and B-2 representing the dry season (May 1982) and wet season (October 1981), respectively; and an average rainfall period (1989/1990) with C-1 and C-2 representing the dry season (May 1990) and wet season (October 1989), respectively.

For all three periods of study (1974, 1981/1982, 1989/1990) the model predicts a greater extent of the EPA exceeding both the 2 and 10 mg/L criteria (developed for the ENP and WCAs respectively) used during the wet season. This prediction is consistent with observations from ecosystem-wide water quality surveys (Scheidt et al., 2000), and largely reflects greater runoff from the EAA during the wet season. Consistent with this observation, the model predicts the greatest occurrence of sulfate levels exceeding both the 2 and 10 mg/L criteria in the EPA during the wet season of the wetter than average period of study (1974). Scheidt and Kalla (2007) reported that about 60% and 20% of the EPA has sulfate levels exceeding 2 and 10 mg/L, respectively. Our model results compare well with these observations under the mean baseline (ASR_Base) hydrologic conditions with 46% and 15% of the EPA exceeding the 2 and 10 mg/L, respectively. The close comparison of these results is encouraging given that the prediction periods for the model runs and the field surveys are not coincident. The most important feature of the simulations from the perspective of ASR is that all alternative simulations of ASR inputs to the EPA are either not discernably different, or only very slightly elevated from the ASR baseline run for both the 2 and 10 mg/L sulfate criteria. This suggests that the release of ASR water to the EPA via the Lake Okeechobee-canal-STA-EPA routing has little impact on the area of the EPA exceeding 2 and 10 mg/L sulfate. There are likely several reasons for this including: the ASR sulfate loading is small compared to that discharged from the EAA, dilution of the ASR signal by the large area of the EPA marshes, and some removal of sulfate from ASR in Lake Okeechobee and the STAs.

Although ASR sulfate loading is not predicted to be a dominant source of sulfate to the EPA overall and does not appear to significantly alter the total area of the EPA impacted, it may have ecosystem effects locally. For example, localized ASR sulfate loading near discharge points during certain time periods could produce critical tipping points with regard to stimulation/inhibition of MeHg production (Orem et al., 2011). In order to examine this, we used map-based performance measures to examine the downstream patterns of sulfate loading to the EPA using the previously described ASR scenarios. As described earlier, the ALT2C model conditions showed the largest impact on ecosystem sulfate levels. Even for this ALT2C, however, the mean sulfate concentrations for all periods of study showed little difference between the ASR additions and baseline (Fig. 6). Small increases in mean sulfate concentrations as affected by ALT2C were observed in northwestern and central western WCA3A. The maps in Fig. 6 show the distribution of predicted sulfate concentrations in the EPA for the ASR_BASE (baseline) for May 1982 (Fig. 7A), the ALT2C scenario for May 1982 (Fig. 7B), and the difference (B-A) shown in Fig. 7C. This particular scenario showed the largest ASR impact on predicted sulfate levels of all the scenarios tested. The difference map highlights

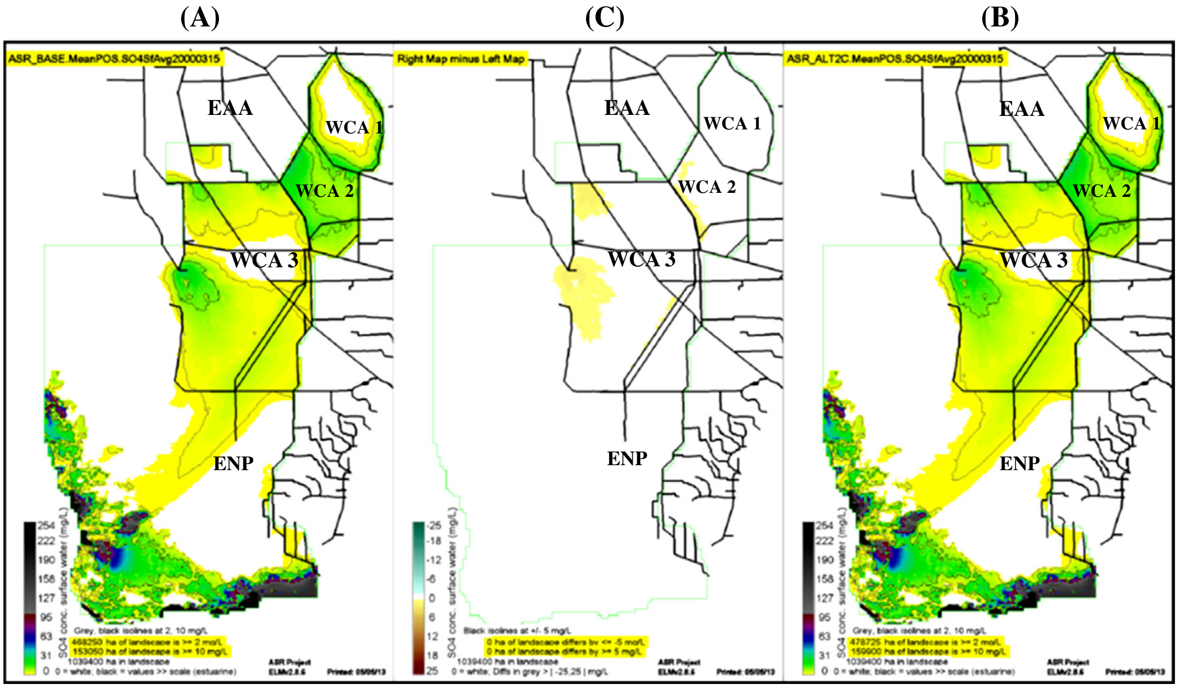

Fig. 6. Maps of mean sulfate concentration for all runs for ASR_Baseline representing baseline conditions (A), ALT2C (B), and the difference map (B-A) shown in (C). The yellow areas in the northwest and center west of WCA 3A are the areas of ASR impact on sulfate concentrations, which are seen to be minimal.

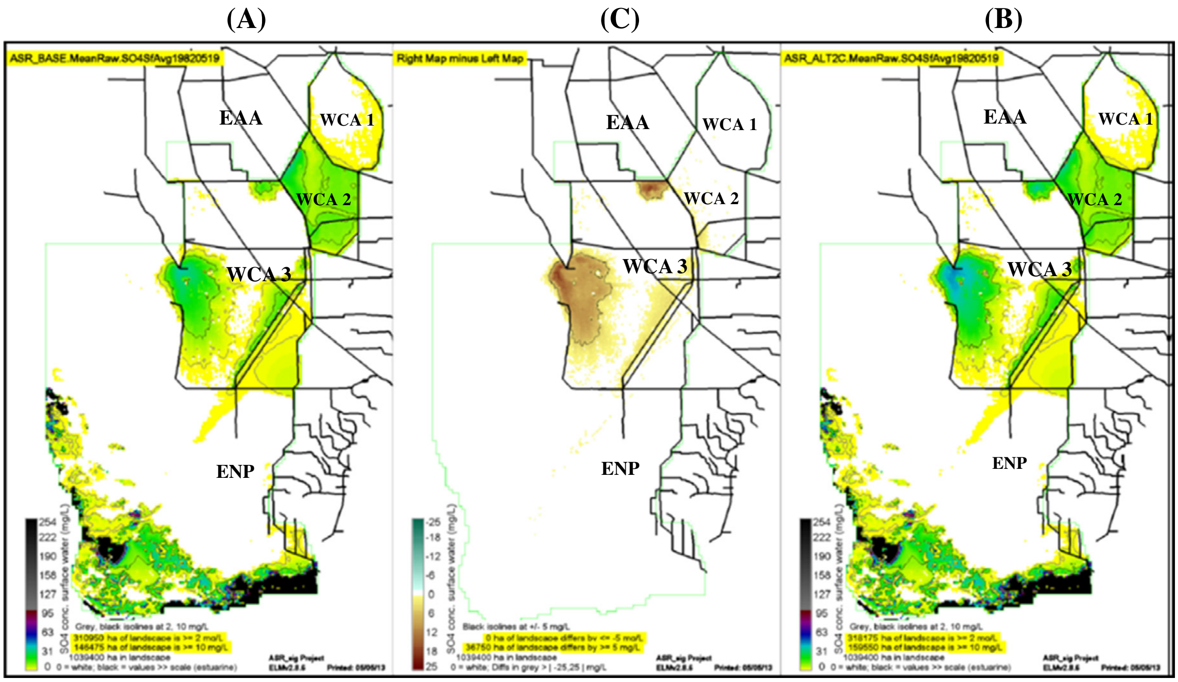

Fig. 7. Maps of sulfate concentration for ASR_Baseline representing baseline conditions (A), ALT2C (B), and the difference map (B-A) shown in C for May 1982 (dry season in a lower than normal Lake Okeechobee discharge year), the period of study with the greatest observed impact from the model runs. Note the areas of greatest ASR impact in the northeastern and west central portions of WCA 3A.

areas where the added ASR discharge has the most pronounced effect on sulfate concentrations in western WCA 3A (L28 canal discharge) and northeastern WCA 3A (STA 3/4 discharge).

The largest differences between baseline runs and various alternative scenarios were observed in the sulfate reduction performance measure (data not shown). Relative to baseline conditions, increases (15,875 ha) in total marsh area that exceeded the 15 g/m^2-y sulfate reduction rate criteria were observed, mostly in northwest and western WCA 3A marshes downstream of inflow structures, the same areas where sulfate concentrations were affected.

4.4. Methylmercury risk from ASR

Similar to the modeled sulfate results, impacts to MeHg risk from ASR releases of sulfate were predicted using the same three ASR scenario boundary condition datasets (ALT-2C, ALT-2V, ALT-4V). The dimensionless MeHg risk maps are derived by translating the sulfate distribution maps discussed above with the non-linear sulfate-MeHg relation shown in Fig. 3. The maps on Fig. 8 show the distribution of predicted MeHg risk (dimensionless) associated in the EPA for the ASR_BASE (baseline) for May 1982 (A), the ALT2C scenario for March 1982 (B), and the difference (B-A) shown in Fig. 8C. Much like Fig. 7, the focus area of anticipated change is near the canal discharge points for the L28 canal and STA 3/4 in western WCA 3A, north-central and southern WCA2, and the Shark River Slough in ENP. Unlike the predicted sulfate changes, however, the MeHg risk maps show both increased and decreased risk in areas of predicted maximum increases in sulfate concentration. This result is due to the non-linear nature of the sulfate-MeHg relationship, whereby the regions of greatest predicted sulfate increase near the discharge points result in reduced risk because the resulting change in sulfate concentration exceeds the apical MeHg sulfate concentration (about 10 ppm sulfate). In other words, if the predicted sulfate change exceeds the 10 ppm criteria for the WCAs there is a net decrease in MeHg risk. On the other hand, if the change in sulfate is less than 10 ppm but is still positive, a net increase in MeHg is predicted. For each of the areas of greatest predicted change in MeHg risk, the area closest to the discharge point exhibits reduced MeHg risk, whereas the more distant areas from the source have increased risk. The large circular area of predicted MeHg risk change near the L28 discharge point illustrates this condition nicely with reduced risk (negative values) encircled by increased risk regions. It is important to note that this particular model output showed the greatest net change in risk associated with the ASR conditions, and most of the other scenarios showed far less change. This result is similar to the sulfate change maps discussed previously, suggesting that the ASR program will have little impact on the overall MeHg risk in the Everglades, and that most of the MeHg risk distribution across the model domain is driven by the releases of other sulfate sources, predominantly from EAA canals.

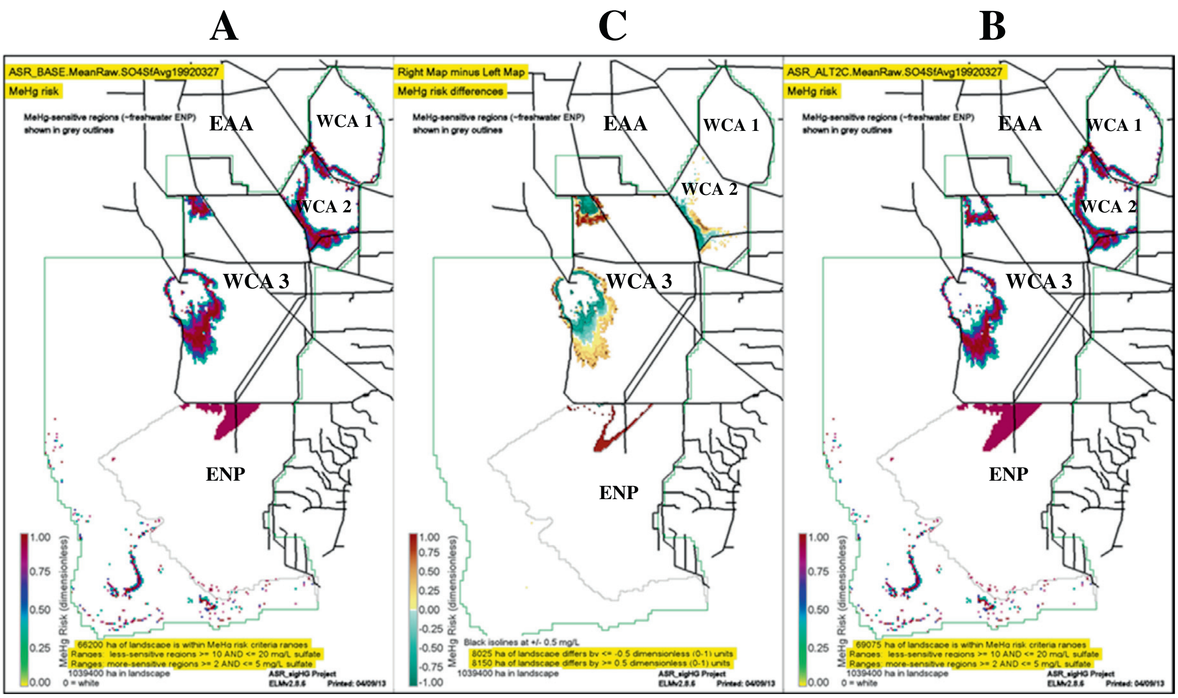

Fig. 8. Maps of predicted MeHg risk from ASR discharges for ASR_Baseline representing baseline conditions (A), ALT2C (B), and the difference map (B-A) shown in (C) for March 2000 the period of study with the greatest observed impact from the model runs. Note the areas of greatest ASR impact in the northwestern and west central portions of WCA 3A.

5. Conclusions

In this study, the ELM model was adapted with the addition of a sulfate module to predict the impacts of ASR water on sulfate loading to Lake Okeechobee and the EPA for different ASR scenarios and for different time periods. The different time periods (periods of study) were designed to examine ASR impacts under different environmental conditions, such as wet season (May–October) and dry season (October–May) in south Florida, and periods of variable flow from Lake Okeechobee (high, low, and average lake discharge). These different time courses are important because most CERP ASR water is designed to be discharged into Lake Okeechobee and from the lake through the STAs before being discharged into the EPA. Model baseline runs using current conditions were also used in the various ASR scenarios, and a year 2050 future baseline scenario was used to normalize the impact of ASR water on the EPA. Baseline runs provided realistic sulfate concentrations and distributions based on observed conditions for sulfate within the ecosystem, thereby validating the model.

The model suggests that the discharge of ASR will result in an increase in Lake Okeechobee sulfate levels from about 30 to about 50 mg/L. Scenario ALT2C involving discharge of ASR water from 200 Upper Floridan wells (Table 2) was found to have the greatest impact on Lake sulfate levels. Although some sulfate from surface inflow to Lake Okeechobee is sequestered within the lake, most sulfate added to the lake exits as discharge. This means that little ASR sulfate is retained in the lake. Similarly, STAs appear to remove little sulfate from surface water under current inflow/outflow conditions. Thus, most sulfate discharged from ASR wells will enter the EPA in water discharged from STAs and canals.

The model shows that ASR water entering the EPA does increase overall sulfate loading, but only during certain time periods and primarily in areas directly adjacent to STA or canal discharge. When normalized to the ASR_BASE (baseline) sulfate scenario, the impacts of ASR sulfate are minimal. This is primarily due to the dominance of EAA discharge with regard to sulfate loading to the ecosystem, loss of sulfate from Lake Okeechobee in water discharged to the Caloosahatchee and St. Lucie Rivers, and dilution effects on the ASR discharge to the extensive EPA marshes. ALT2C was determined to have the biggest impact on sulfate loading to the EPA. Evaluation of long-term averages and short-term "ASR stress periods" indicate that although sulfate loading from ALT2C was small compared to other sources, this scenario should be considered with caution, regarding the potential to increase sulfate concentrations within important localized regions of the marshes of WCA 3A. Western WCA (L28 discharge), northeastern WCA 3A (STA 3/4 discharge), and northwestern WCA 3A were most impacted by ASR sulfate loading in the model runs. However, due to hydrogeologic constraints, ALT2C is not the most realistic ASR scenario, and the assumptions used to derive ALT2C sulfate boundary conditions were very conservative (possibly higher than would occur under real world conditions). The more realistic ASR alternative (ALT4V), which include varying sulfate concentrations and less recovered water, exhibited some increases in sulfate loading relative to the ASR_BASE, but these were very limited in magnitude and extent. It is worth noting that in freshwater wetland ecosystems not as impacted by sulfate loading as the Everglades is, the effects of ASR sulfate would be much more pronounced. In the Everglades, ASR sulfate loading is dwarfed by that from EAA sulfate loading.

Overall, the areas of changed MeHg risk attributable to the ASR operations are predicted to be minimal, and are located near major canal water release points in western WCA3, north-central WCA2, and northern Shark River Slough. Because the relationship between sulfate and MeHg production is nonlinear and hump-shaped, the model generally predicts both regions of net increases and net decreases in MeHg risk in near proximity to each other, producing a halo effect on the maps. That is not to say, however, that sulfate releases from ASR or other canal water sources are not important, because in the absence of sustained sulfate loading to this ecosystem, MeHg levels in the EPA would be substantially reduced – once internal recycling of sediment sulfate pools subsided.

This study was undertaken as part of a comprehensive evaluation of the engineering and ecological risks associated with the implementation of CERP ASR facilities (USACE, 2015). The modeling tool (ELM-Sulfate) and approach developed in this study could also be applied to investigate the impact of other CERP-related hydrologic modifications such as those planned as part of the Central Everglades Planning Project. The Central Everglades Planning Project will increase sulfate loading and potentially alter MeHg risk by increasing flows through WCA-3A by approximately 20%.

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