Surface Water Sulfate Dynamics in the Northern Florida Everglades

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Sulfate contamination has been identified as a serious environmental issue in the Everglades ecosystem. However, it has received less attention compared to P enrichment. Sulfate enters the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge), a remnant of the historic Everglades, in pumped stormwater discharges with a mean concentration of approximately 50 mg L^{-1}, and marsh interior concentrations at times fall below a detection limit of 0.1 mg L^{-1}. In this research, we developed a sulfate mass balance model to examine the response of surface water sulfate in the Refuge to changes in sulfate loading and hydrological processes. Meanwhile, sulfate removal resulting from microbial sulfate reduction in the underlying sediments of the marsh was estimated from the apparent settling coefficients incorporated in the model. The model has been calibrated and validated using long-term monitoring data (1995–2006). Statistical analysis indicated that our model is capable of capturing the spatial and temporal variations in surface water sulfate concentrations across the Refuge. This modeling work emphasizes the fact that sulfate from canal discharge is impacting even the interior portions of the Refuge, supporting work by other researchers. In addition, model simulations suggest a condition of sulfate in excess of requirement for microbial sulfate reduction in the Refuge.

The interior marsh of the Refuge is an impounded remnant of the historic Everglades in Palm Beach County, Florida. The Refuge was established in the 1950s for wildlife habitat preservation as well as a source of water supply and flood protection (USFWS, 2000). Sulfur is an element of great mobility, and sulfate contamination has been identified as a serious environmental issue for the Everglades ecosystem including the Refuge (Bates et al., 1998, 2002; Orem et al., 2002; Gilmour et al., 1998, 2007).

The Refuge is designated by the State of Florida as an outstanding Florida water (OFW). Despite this and other legal protections, recent studies have shown that even the interior marsh in the Refuge has been affected by canal water intrusion (Harwell et al., 2008; Surratt et al., 2008), and that surface water in marsh areas near the canals may be characterized as highly enriched in sulfate (e.g., Gilmour et al., 2007). Sulfur isotope studies (e.g., Bates et al., 1998, 2002; Orem et al., 2002) indicated that stormwater runoff from the upstream Everglades Agricultural Area (EAA) is the major source of sulfate contamination in marsh surface waters. Constructed wetlands, termed stormwater treatment areas (STAs), bordering the northern part of the Refuge treat this runoff. While the STAs were created to treat total phosphorus (TP), often remove more than 80%, they remove <20% of sulfate (He, 2007).

Sulfate contamination could greatly affect the structure, functions, and health of the Refuge ecosystem. Previous studies (Bates et al., 1998; Gilmour et al., 1998, 2007) indicated that the high levels of sulfate entering the Everglades marsh could stimulate microbial sulfate reduction, buildup of sulfide in porewater, and production of methylmercury (MeHg, a neurotoxin to fish and other wildlife). Further, high sulfate inputs could impact macrophyte growth and vegetation distribution by changing redox conditions in the underlying soil, and remobilizing nutrients (Bates et al., 2002; Gilmour et al., 2007). Elevated sulfate may induce internal eutrophication, a process in which P bound to

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Abbreviations: EAA, Everglades Agricultural Area; MeHg, methylmercury; OFW, outstanding Florida water; RMSE, root mean square error; SO_4, sulfate; SRR, sulfate reduction rate; STAs, stormwater treatment areas; TP, total phosphorus.

sediments is released into sediment porewater, thus significantly influences the plant species composition of freshwater wetlands (Lamers et al., 1998; McCormick and Harvey, 2007).

The primary goal of this study is to examine the utility of simple sulfate modeling in contrast to more complex modeling approaches (e.g., Gilmour et al., 2008) to examine the linkages between water movement and marsh surface water sulfate concentration in the Refuge in the absence of Refuge-specific details of complex sulfur cycling interactions. This modeling is a part of a broader project modeling hydrology and surface water constituents in the Refuge (Brandt et al., 2004; USFWS, 2007). Current modeling of linked hydrologic and sulfate transport and transformation models of the Refuge combines a mass balance water budget and a simplified water quality model to examine the responses of the surface water sulfate to changes in hydrological processes especially focused on canal water intrusion. We further examine the supposition that sulfate in the Refuge interior is rainfall-driven through a sensitivity simulation. Finally, the model also provides an opportunity to estimate sulfate reduction rate (SRR) across the Refuge from the apparent settling coefficients in the model rather than site-specific field measurements and/or laboratory experiments.

Materials and Methods

Study Area

The Refuge is located in the subtropical region of South Florida (Fig. 1). Much of the average annual rainfall, approximately 1400 mm, occurs during the May to October wet season, and more than half of this annual rainfall occurs between June and September (USFWS, 2000). The marsh soil elevation in the Refuge interior ranges from approximately 3.2 to 5.6 m (1929 NGVD), and gently declines from north to south (USFWS, 2007). The Refuge covers approximately 57,085 ha (141,000 acres) of marsh. The marsh is a mosaic of habitats including slough, wet prairie, sawgrass, brush, tree islands, and cattail (USFWS, 2000). The Refuge provides habitat for more than 300 vertebrate species including the endangered snail kite (*Rostrhamus sociabilis*) and wood stork (*Mycteria americana*) (USFWS, 2000).

The Refuge is a remnant of the once contiguous Everglades that extended from the Kissimmee Chain of Lakes south to Florida Bay. In the historic Everglades, water flowed generally from north to south following the natural elevation gradient as sheetflow. The Refuge presently is impounded by levees, and encircled by canals on the marsh interior side of these levees. The levees and associated canals were completed by the U.S. Army Corps of Engineers in the early 1960s. Presently, inflows to the Refuge primarily originate as pumped stormwater runoff from agricultural lands that were formerly a part of the Everglades (USFWS, 2007). Some of the water and contaminants discharged into the Refuge perimeter canals flows through the canals to hydraulic structures that discharge to other areas, but much of the inflow enters the Refuge interior marsh as overbank flows from the canals (Surratt et al., 2008).

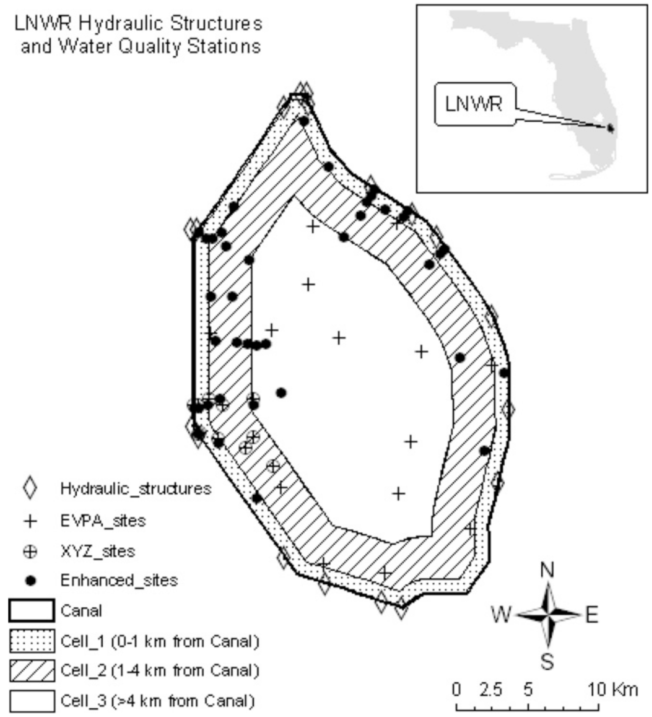

Fig. 1. Map of the Arthur R. Marshall Loxahatchee National Wildlife Refuge showing model segmentation, hydraulic structures along the perimeter canals, and water quality monitoring stations used as data sources. Note that the diamond symbols for the hydraulic structures are larger than the width of the narrow canal cell.

The Refuge Water Quality Model

The Refuge Water Quality Model (RWQM) was implemented using the U.S. Environmental Protection Agency's (EPA) Water Quality Analysis Simulation Program (WASP) model, a dynamic compartmental water quality model (http://www.epa.gov/athens/wwqtsc/html/wasp.html). The RWQM assumes a one-dimensional geometry with four compartments simulating one canal, and three marsh compartments (Fig. 1). The marsh compartment areas were based on analysis of the typical distribution of chloride and P concentrations with distance away from the canal (Arceneaux et al., 2007). The model compartments are designated as canal (403 ha), perimeter marsh (canal to 1.0 km into the interior [8933 ha]; Cell 1), transition marsh (1.0–4.0 km from the canal [22,401 ha]; Cell 2) and interior marsh (>4.0 km from the canal [24,647 ha]; Cell 3).

The RWQM hydrologic time series for canal-marsh interchange flow and seepage are derived from a separate water budget model (Arceneaux et al., 2007). This simple hydrologic model integrates net inflow minus outflow for each compartment to provide a daily estimate of stage and volume within each compartment. The user provides a daily time-series of pumped inflow, structure outflow, precipitation, and evapotranspiration. The model calculates flow between the canal and marsh, groundwater recharge including levee seepage loss, and evaporation and transpiration. The structure and equations of the water budget model are detailed in Arceneaux et al. (2007) and USFWS (2007).

Sulfate is modeled using the WASP carbonaceous biological oxygen demand (CBOD) state-variable within the Eutrophication module. Sulfate disappearance is modeled using a first-order apparent settling (Kadlec and Knight, 1996; Raghunathan et al., 2001; DeBusk et al., 2004) to describe the net effects of physical, biological, and chemical processes that act to change sulfate concentration within a model compartment:

$$[dhC(i)/dt] = -k(i)C(i) + L(i) \quad [1]$$

where h is depth in m, $C(i)$ is the compartment i sulfate concentration (mg SO_4 L^{-1}), $k(i)$ is the apparent settling coefficient (m yr^{-1}). $L(i)$ is the sulfate loading rate in the compartment (g m^{-2} yr^{-1}), representing the net total loading rate from advective and dispersive transport, and external loading. The settling coefficient for the canal is set to zero.

Apparent settling of sulfate from the marsh water column is assumed to represent loss by sulfate reduction, and sulfate reduction rate (SRR) can be estimated by equation:

$$SRR(i) = k(i)\overline{C}_{avg}(i) \quad [2]$$

where $\overline{C}_{avg}(i)$ is the average observed sulfate concentration for compartment i, respectively. It is noted that the estimated rate from settling coefficient is net reduction (i.e., gross reduction rate– reduced sulfur oxidation rate) although oxidation is less important because of the high sulfate concentrations in much of the marsh.

Data and Simulations

The hydrological, meteorological, and water quality data were primarily obtained from the South Florida Water Management District DBHYDRO database (http://www.sfwmd.gov/org/ema/dbhydro/index.html). The overall study period is from 1 Jan. 1995 to 31 Dec. 2006. Sulfate concentrations at hydraulic structures were sampled quarterly, and daily values were linearly interpolated using SAS 9.1.3 (http://www.sas.com/index.html). Daily sulfate loads were calculated by multiplying interpolated daily concentrations with daily average structure flows. Although wet and dry aerial depositions are small relative to pumped inflow loads, both terms were included in the model. Dry deposition of sulfate, 138.2 mg m^{-2} yr^{-1}, was based on observations from the Air Quality and Deposition module of the EPA's Clean Air Status and Trends Network, CASTNET (http://www.epa.gov/castnet/). Rainwater sulfate concentration in the model was assumed to be a constant 1 mg L^{-1} based on earlier work in the Northern Everglades (Gilmour et al., 2007). This constant is consistent with measured rainfall sulfate concentrations in the STA adjacent to the Refuge, where the 25th, median and 75th percentiles of concentrations during 2001–2005 were 0.715, 0.985, and 1.4 mg L^{-1}, respectively (He, 2007).

Sulfate monitoring data for model calibration and validation are available from water quality monitoring sites (Fig. 1). Observations within the canal are available at outflow hydraulic structures, and monitoring data within the Refuge are available from South Florida Water Management District routine monitoring and research (XYZ) sites (McCormick et al., 2000) and the Refuge's Enhanced Monitoring sites (Harwell et al., 2008; Surratt et al., 2008).

We used data from 2000 to 2004 as the calibration period because a more complete set of observations are available during this period. For validation, we initially used the period from 1995–1999; subsequent extension of the period of record allowed us to also validate for 2005–2006. When observed sulfate concentration was reported as below the limit of quantification, a value of one-half of the quantification limit was applied (USFWS, 2007). To examine the role of surface water inflows on sulfate levels in the interior marsh, a model simulation was run assuming zero sulfate loading in canal water inflows (i.e., a sensitivity scenario).

Statistical Analyses

To describe a large range of model performance, we used several statistics (Nash and Sutcliffe, 1970; Legates and McCabe, 1999) during the calibration and validation, including bias, Root Mean Square Error (RMSE), correlation coefficient (R), variance reduction, and Nash-Sutcliffe Efficiency (Efficiency). Calibration statistics measure the performance of the model during calibration. Furthermore, calibration period statistics provide a quantitative comparison with the validation periods, and any large reduction of statistical performance outside the calibration period suggests that the model fit may be spurious, or that some important factor changed between the periods is not being properly modeled. Bias characterizes the average of the difference between modeled and observed values; a good model exhibits low bias. The RMSE metric characterizes the residual difference between model performance and actual data; a good model will have low RMSE values. The correlation coefficient measures the linear association between the modeled and observed data; a high correlation coefficient is considered desirable. Variance reduction examines how well a model follows variations in observed data, and is unaffected by bias; a large percentage of the variance that is captured by the model is desirable. Finally, Nash-Sutcliffe Efficiency examines the predictive accuracy of a model, with a maximum efficiency of one corresponding to a perfect fit. A value of zero indicates that the model predicts no better than simply using an average observed value. The utility of Nash-Sutcliffe Efficiency is challenged when applied to observations with limited variation about their mean value (Legates and McCabe, 1999).

Results and Discussion

Sulfate Dynamics in Rim Canal and Marsh

Comparison of simulated sulfate concentrations for the four compartments with the average of observed values within each cell (Fig. 2) demonstrates that our model generally captures the spatial, inter-annual, and seasonal variations in sulfate concentrations in the Refuge although we did identify an unusual period of anomalous values from June 1999–July 2001 (see below). Both simulations and observations exhibit a large degree of temporal variability in the canal (Fig. 2a) and throughout the marsh (Fig. 2b-d). Sulfate concentrations in the canal and marsh tend to be higher in wet years and during wet season (May–October),

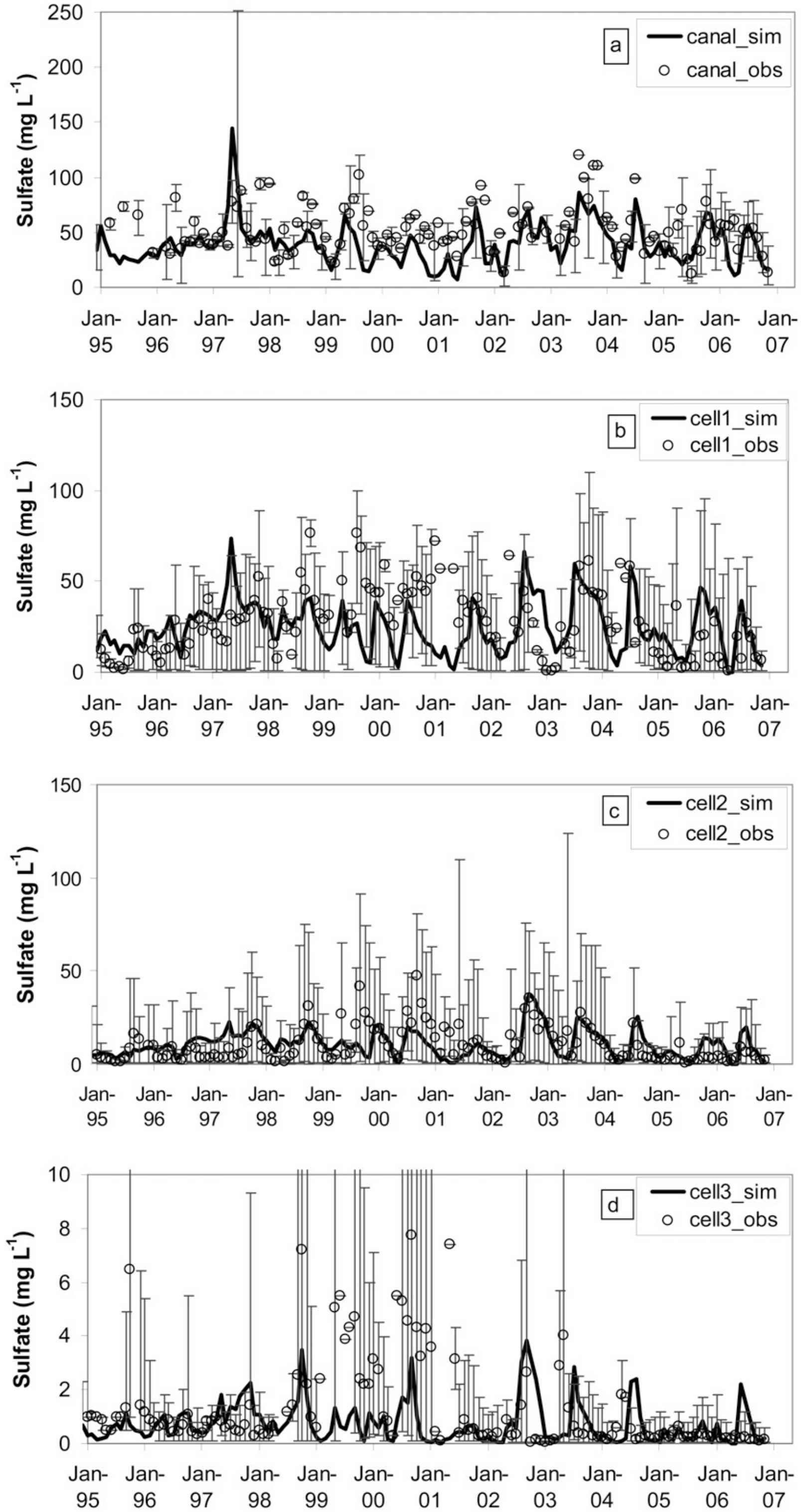

Fig. 2. Monthly average of simulated (line) and observed (circles) sulfate concentrations in rim canal, perimeter marsh (Cell 1), transition marsh (Cell 2) and interior marsh (Cell 3) during 1995–2006. The bars indicate the range from minimum to maximum of observations.

and the peaks of sulfate concentrations are likely to occur during July to October (Fig. 2). The high concentrations of sulfate in the canal and marsh during wet season presumably result from more sulfate entering the canal through runoff from EAA (Chen et al., 2006) and sulfate transport from canal to marsh interior by higher canal-marsh exchange flow as a result of canal stages in excess of that in the marsh interior (McCormick and Harvey, 2007; USFWS, 2007; Surratt et al., 2008).

Sulfate concentrations are observed to decrease along a gradient from the canal to the marsh interior (Gilmour et al.,

Table 1. Assessment of simulations of surface water sulfate concentration for calibration (2000–2004) and validation (1995–1999, 2005–2006) and the estimated sulfate reduction rate in the Refuge marsh from settling coefficients using the mass balance based water quality modeling.

Statistic		Canal	Cell_1	Cell_2	Cell_3	Marsh
(a)		Calibration (2000–2004)				
Avg. observ. (SD)†	mg L^{-1}	55.6 (22.4)	34.7 (17.4)	13.8 (9.8)	1.5 (1.8)	16.3 (7.8)
Min./max. observ.	mg L^{-1}	1.42/120.0	0.37/110.0	0.05/124.0	0.05/40.0	0.05/124.0
Avg. sim. (SD)	mg L^{-1}	39.0 (19.2)	26.0 (15.9)	11.7 (9.2)	0.8 (0.9)	12.5 (8.4)
Bias	mg L^{-1}	−17.37	−8.71	−2.13	−0.68	−3.79
RMSE	mg L^{-1}	23.21	24.13	8.40	2.09	10.24
Variance reduction %		54%	−68%	31%	−9%	−45%
R		0.75	0.09	0.64	0.16	0.33
Efficiency		−0.08	−0.93	0.26	−0.22	−0.69
k (m yr^{-1})		0.0	0.5	1.0	10.0	
SRR (g m^{-2} yr^{-1})		0	14.5	13.9	14.9	14.4
(b)		Validation (1995–1999, 2005–2006)				
Avg. observ. (SD)	mg L^{-1}	49.9 (19.7)	22.2 (17.1)	7.5 (7.7)	1.1 (1.4)	10.2 (8.2)
Min./max. observ.	mg L^{-1}	1.42/120.0	0.37/110.0	0.05/124.0	0.05/13.05	0.05/124.0
Avg. sim. (SD)	mg L^{-1}	40.3 (19.2)	24.3 (12.5)	9.7 (5.4)	0.7 (0.6)	11.5 (5.9)
Bias	mg L^{-1}	−9.60	2.07	2.25	−0.41	1.31
RMSE	mg L^{-1}	24.30	17.61	7.91	1.41	8.23
Variance reduction %		−27%	−5%	4%	15%	3%
R		0.34	0.33	0.38	0.39	0.38
Efficiency		−0.51	−0.07	−0.04	0.07	0.01

† Marsh aggregates the three marsh cells; Avg. = average; Observ. = observed; Min. = minimum of observations; Max. = maximum of observations; Sim. = simulated; SD = standard deviation; RMSE = root mean square error; *R* = correlation coefficient; Efficiency = Nash-Sutcliffe Efficiency; *k* = settling coefficient; SRR (sulfate reduction rate) = settling coefficient × average observed sulfate concentration.

2007; Harwell et al., 2008), and this spatial gradient is well characterized by our model despite limitations in input data discussed below. Although model spatial resolution is limited, the low bias during most simulation periods demonstrates that the model quantitatively captures the spatial pattern of sulfate concentration (Table 1). Temporal discrepancies between simulations and observations in each compartment may reflect the spatial variation within each compartment that cannot be captured at this level of spatial resolution.

Another likely cause of the discrepancies is the limited sampling frequency of sulfate concentration. For most monitoring stations in the marsh areas, sulfate concentrations are only measured when clear water depth exceeds 20 cm; sulfate in most inflows is measured quarterly. Sampling sites are also not evenly distributed among compartments, and at times only a single monthly measurement was available within a compartment, occurring six times for the canal, three times for the perimeter marsh (Cell 1), and one time for the interior marsh (Cell 3). This single-measurement issue may cause larger discrepancies between simulated and average observed sulfate concentrations at these times, particularly when the sampled station is not representative of the whole compartment. Sulfate concentrations were much lower in the interior marsh (Cell 3) compared to perimeter marsh (Cell 1) and transition marsh (Cell 2); however, elevated sulfate concentrations in the interior marsh occurred in both simulations and field data (Fig. 2). While many observations were below the detection level (0.1 mg L^{-1}), the maximum and average of observations in the interior marsh (Cell 3) could be as high as 40 and 8 mg L^{-1}, respectively (Fig. 2).

Variance reductions and Nash-Sutcliffe efficiencies are low or negative, indicating that the model is less successful at explaining the temporal patterns of sulfate within each compartment. Although the model does capture the observed magnitude of sulfate variations, it less reliably recreates the timing of these variations. This discrepancy may be due to the coarse spatial resolution of the model, temporal variations in actual sulfate reduction rates not included in the model, or reaction kinetics and other biological and chemical interactions (Marnette et al., 1993) are not modeled here. Factors such as local variations in topography and patterns of vegetative resistance to flow affect canal water intrusion into different parts of the Refuge (McCormick and Harvey, 2007; Surratt et al., 2008), and SRR may vary with changes in sediment types, topography, dissolved oxygen, vegetation types and organic carbon content (e.g., Ingvorsen et al., 1981; Urban et al., 1994), therefore causing spatial variations in sulfate disappearance from Refuge marsh surface water.

Models can provide a quantitative tool for identifying conditions or periods when the model data or assumptions are inadequate (Marnette et al., 1993). Indeed, in complex systems it may be difficult to clearly identify these anomalous situations without the use of a statistical or empirical model to examine a longer period of record. Weaver and Payne (2004) identified a period of dramatic increase in sulfate levels in the Refuge marsh from May 2002 to April 2003 that they deemed anomalous. However, our model was able to capture this increase very well, indicating that that this event was well explained by canal water intrusion and should not merely be considered anomalous. In our study, we identified the period from June 1999 to July as characterized by elevated sulfate concentrations in the marsh relative to model projections (Fig. 2). This difference is especially clear in the transition marsh (Cell 2) and the interior marsh (Cell 3). Observed average marsh concentrations were more than double modeled values during this period (Table 2a). The sulfate increase identified here (from June 1999–July 2001) could not be solely ex-

Table 2. Assessment of simulations of surface water sulfate concentration for identified anomalous period (June 1999–July 2001) and calibration and validation excluding the anomalous period.

Statistic		Canal	Cell_1	Cell_2	Cell_3	Marsh
(a)		Anomalous period (June 1999–July 2001)				
Ave. observ. (SD)†	mg L^{-1}	52.4 (16.3)	46.8 (13.9)	19.1 (11.2)	3.5 (2.1)	22.5 (7.6)
Avg. sim. (SD)	mg L^{-1}	28.4 (15.1)	19.8 (11.7)	9.5 (6.4)	0.8 (0.7)	9.7 (6.1)
Bias	mg L^{-1}	–24.00	–27.08	–9.53	–2.76	–12.74
RMSE	mg L^{-1}	29.45	33.27	14.06	3.32	15.36
Variance reduction %		–1%	–74%	17%	28%	–18%
R		0.46	–0.02	0.44	0.58	0.29
Efficiency		–2.26	–4.65	–0.59	–1.59	–3.13
(b)		Calibration (August 2001–December 2004)				
Avg. observ. (SD)	mg L^{-1}	60.8 (25.5)	29.9 (17.2)	11.8 (8.7)	0.68 (0.8)	13.9 (7.3)
Avg. sim. (SD)	mg L^{-1}	45.1 (19.7)	28.7 (16.8)	12.5 (9.9)	0.85 (1.0)	13.8 (9.0)
Bias	mg L^{-1}	–15.74	–1.27	0.71	0.18	–0.06
RMSE	mg L^{-1}	23.07	20.26	6.05	1.28	8.11
Variance reduction %		57%	–38%	53%	–122%	–24%
R		0.76	0.29	0.80	0.08	0.52
Efficiency		0.18	–0.39	0.52	–1.27	–0.24
(c)		Validation (January 1995–May 1999, 2005–2006)				
Avg. observ. (SD)	mg L^{-1}	47.8 (18.8)	19.7 (14.6)	6.2 (5.7)	0.85 (1.1)	8.8 (6.6)
Avg. sim. (SD)	mg L^{-1}	40.8 (19.2)	24.7 (12.5)	9.8 (5.5)	0.71 (0.6)	11.6 (6.0)
Bias	mg L^{-1}	–7.07	5.07	3.65	–0.13	2.83
RMSE	mg L^{-1}	21.97	14.74	6.20	1.03	6.55
Variance reduction %		–22%	10%	23%	20%	22%
R		0.40	0.49	0.61	0.46	0.57
Efficiency		–0.36	–0.02	–0.18	0.18	0.03

† Marsh aggregates the three marsh cells; Avg. = average; Observ. = observed; Min. = minimum of observations; Max. = maximum of observations; Sim. = simulated; SD = standard deviation; RMSE = root mean square error; *R* = correlation coefficient; Efficiency = Nash-Sutcliffe Efficiency.

plained by canal water intrusion. Further, there is no evidence of greatly increased aerial deposition during this period. Water stages in the Refuge were not unusual in 1999 or 2000, but 2001 was an unusually dry year (Arceneaux et al., 2007). Thus, these elevated sulfate concentrations also are not explained by effects of drought and soil oxidation.

During the calibration period, our model was more effective in capturing sulfate dynamics in the canal and transition marsh (Cell 2) as indicated by higher values of variance reduction, correlation coefficient, and Nash-Sutcliffe efficiency (Table 1). For the validation period, statistics were significantly improved for perimeter marsh (Cell 1), interior marsh (Cell 3), and marsh as a whole as indicated by all statistical parameters (Table 1). The model was unable to describe sulfate dynamic in the marsh during the anomalous period (June 1999–July 2001) as indicated by the large values of bias and RMSE as well as large negative Nash-Sutcliffe efficiencies (Table 2a). When using data without this anomalous period for both calibration and validation, the model simulated the sulfate dynamics in canal and three marsh zones well, with largely improved statistical parameters except the variance reduction, correlation coefficient (*R*), and Nash-Sutcliffe efficiency for interior marsh (Cell 3) in calibration period, bias for perimeter marsh (Cell 1), transition marsh (Cell 2) and marsh as a whole, and Nash-Sutcliffe efficiency for transition marsh in validation period (Table 2b and 2c).

Estimate of Sulfate Reduction Rate in Refuge Marsh

Sulfate apparent settling coefficients determined through calibration increased by more than an order-of-magnitude from periphery toward marsh interior (Table 1). In contrast, SRR for the three marsh cells calculated from settling coefficients and mean sulfate concentrations (Eq. [2]) are similar across the marsh cells (Table 1), which leads us to estimate that SRR is approximately 14.4 g m^{-2} yr^{-1} throughout the Refuge. This estimate falls within the range of 0.8 to 43 g m^{-2} yr^{-1} for net SRR that has been reported from limited research in freshwater wetlands (e.g., Giblin and Wieder, 1992). The relatively constant SRR across all three marsh zones implies that microbial reduction is reaching steady state throughout the Refuge marsh, and suggests that sulfate is in excess of the requirement for microbial reduction in the Refuge marsh. In freshwater environments, sulfate reduction is often reported to be limited by the low concentrations of sulfate (e.g., Ingvorsen et al., 1981). Sulfate concentrations of approximately 30 to 300 mg L^{-1} in freshwater environment has been reported to be in excess of microbial requirements (Ingvorsen et al., 1981) with some research indicating an even lower threshold of sulfate-in-excess condition for microbial reduction in freshwater sediments at approximately 3 mg L^{-1} (Lovley and Klug, 1985). Since the average observed sulfate concentration in marsh interior (Cell 3) is approximately 1.5 mg L^{-1}, we infer that surface sulfate concentrations in the Refuge higher than 1.5 mg L^{-1} are in excess of microbial requirements.

Pumped inflow loading of sulfate over the period of simulation, 1995 to 2006, averaged 36,220 t per year, which distributed across the entire Refuge marsh area, is 63.5 g m^{-2} yr^{-1}. Thus loading exceeded modeled Refuge-wide settling by more than a factor of four. Excess sulfate is transported from the Refuge primarily as outflow to other Everglades wetlands downstream of the Refuge, and discharges to Florida Lower East Coast water users. A small mass of excess sulfate is also transported in the model through groundwater recharge and levee seepage.

Most water entering the Everglades is now treated by constructed wetlands called stormwater treatment areas (STAs). Typical STA sulfate loading rates exceed 500 g m^{-2} yr^{-1}. Thus, the SRR found here is consistent with the observation that Everglades STAs remove only a small fraction of the sulfate in treated water (He, 2007).

It has been reported that usually a detectable fraction of marsh surface-water originated as pumped inflow into the canal (USFWS, 2007; Surratt et al., 2008). Furthermore, groundwater is not an important sulfate source in the Refuge, nor is atmospheric deposition (e.g., Orem et al., 2002; He, 2007). Our results also support the conclusion that atmospheric deposition plays a minor role, compared to canal water, as a source of sulfate in the Refuge marsh. For example, in our mass balance calculation, from 1995 to 2006, the average sulfate loading from the atmosphere is approximately 2158 kg d^{-1}, which is only 2.17% of the loading from sulfate in canal inflows (99,232 kg d^{-1}). Sulfate in the interior marsh has been termed rainfall-driven (e.g., McCormick and Harvey, 2007). However, sensitivity analysis indicates that if there were no sulfate loading from canal water, such that sulfate originated only from atmospheric deposition, the mean values of sulfate concentration in the three marsh compartments, Cell 1, Cell 2, and Cell 3, would be reduced by 98, 95, and 89%, respectively. The range of the sulfate concentrations in the Refuge marsh without loading from pumped inflows tended to be <0.1 to 1.1 mg L^{-1}. Therefore, a significant source of sulfate contamination in interior marsh, particularly in the wet season from May to October, occurs from canal water intrusion.

Our sulfate modeling efforts have improved our understanding and enhanced the credibility of our underlying hydrological model. Traditionally, models use a conservative constituent, such as chloride used for our hydrological modeling, for testing the performance of a model. The nonconservative nature of sulfate in the water column complements traditional conservative tracer model testing because marsh sulfate concentrations are more strongly related to recent water movements and thus more clearly identify the times of reduced hydrological model performance.

Conclusions

The modeling approach presented here, applying highly simplified modeling assumptions, contrasts with the recent modeling approach of Gilmour et al. (2008) that incorporates complex interactions between multiple state-variables in surface water and soil, and explicitly models soil diagenesis. Both complex and simplified approaches have value in specific applications, and both should be used together where appropriate. Often simplified approaches provide insights that are less apparent in more complex models. Our modeling results demonstrate there is a strong linkage between hydrological surface water transport processes and the sulfate transformations which together determine marsh sulfate concentrations. Our compartmental modeling approach provides a straightforward and robust tool for examining wetland surface water sulfate dynamics along the gradient from canal to marsh interior, and for estimating marsh sulfate reduction rates.

Water quality in the interior portions of the Refuge marsh has, in the past, often been described as rainfall-driven. We conclude that most sulfate in the interior area of the Refuge originates as pumped inflow rather than rainfall, and thus a categorization of rainfall-driven for surface water sulfate is not appropriate. Given the low sulfate removal efficiency in STAs relative to P, any sulfate reduction rates within the STAs similar to that found for the Refuge indicates that source control of sulfate contamination may be the only practical approach to remove the excess sulfate load discharged into the Refuge.

The finding that at most times sulfate within the Refuge is in excess of microbial requirement needs further study. Our continuing modeling efforts are directed at better defining the relationship of SRR to sulfate concentration, and improving the spatial resolution of our models. Continued routine monitoring should be coupled with future targeted field research.

In a hydrologically managed system such as the modern Everglades, availability of linked hydrological and water quality models provides needed management decision support. These tools quantify the implications of future water management decisions on Refuge water quality and habitat suitability. The sources of simulation errors include uncertainty in data of flow, rainfall, ET, and sulfate inflow concentration; low frequency of monitoring data; coarse spatial resolution; and simplification of complex sulfur biogeochemical processes. Nevertheless, within the limits of uncertainty and applicability, these models may help us to better manage these outstanding ecological resources.

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References

Arceneaux, J.C., E.A. Meselhe, and M.G. Waldon. 2007. The Arthur R. Marshall Loxahatchee National Wildlife Refuge water budget and water quality models. Rep. LOXA07-004. Available at http://loxmodel.mwaldon.com/ (verified 18 Dec. 2008). U.S. Fish and Wildlife Service, Boynton Beach, FL.

Bates, A.L., W.H. Orem, J.W. Harvey, and E.C. Spiker. 2002. Tracing sources of sulfur in the Florida Everglades. J. Environ. Qual. 31:287–299.

Bates, A.L., E.C. Spiker, and C.W. Holmes. 1998. Speciation and isotopic composition of sedimentary sulfur in the Everglades, Florida. Chem. Geol. 146:155–170.

Brandt, L.A., M.C. Harwell, and M.G. Waldon. 2004. Work plan: Water quality monitoring and modeling for the A.R.M. Loxahatchee National Wildlife Refuge. Available at http://sofia.usgs.gov/lox_monitor_model/

workplans/2004-2006_workplan.html#pdf (verified 18 Dec. 2008). Arthur R. Marshall Loxahatchee National Wildlife Refuge, U.S. Fish and Wildlife Service, Boynton Beach, FL.

Chen, M., S.H. Daroub, T.A. Lang, and O.A. Diaz. 2006. Specific conductance and ionic characteristics of farm canals in the Everglades Agricultural Area. J. Environ. Qual. 35:141–150.

DeBusk, T.A., K.A. Grace, F.E. Dierberg, S.D. Jackson, M.J. Chimney, and B. Gu. 2004. An investigation of the limits of phosphorus removal in wetlands: A mesocosm study of a shallow periphyton-dominated treatment system. Ecol. Eng. 23:1–14.

Giblin, A.E., and R.K. Wieder. 1992. Sulfur cycling in marine and freshwater wetlands. *In* R.W. Howarth et al. (ed.) SCOPE 48 Sulphur cycling on the continents: Wetlands, terrestrial ecosystems, and associated water bodies. Wiley, UK.

Gilmour, C., W.H. Orem, D. Krabbenhoft, I. Mendelssohn, and S. Roy. 2007. Preliminary assessment of sulfur sources, trends and effects in the Everglades. 2007 South Florida Environmental Report. Available at http://www.sfwmd.gov (verified 18 Dec. 2008). South Florida Water Management District, West Palm Beach, FL.

Gilmour, C., G.S. Riedel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.G. Gill, and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry 40:327–345.

Gilmour, C., E. Roden, and R. Harris. 2008. Approaches to modeling sulfate reduction and methylmercury production in the Everglades. 2008 South Florida Environmental Report. Available at http://www.sfwmd.gov (verified 18 Dec. 2008). Florida Water Management District, West Palm Beach, FL.

Harwell, M.C., D.D. Surratt, D.M. Barone, and N.G. Aumen. 2008. Conductivity as a tracer of agricultural and urban runoff to delineate water quality impacts in the northern Everglades. Environ. Monit. Assess. 147:445–462. doi: 10.1007/s10661-007-0131-3.

He, G. 2007. Efficiency of stormwater treatment areas in removing contaminants. Everglades National Park and University of Miami/RSMAS-MGG, Homestead, FL.

Ingvorsen, K., J.G. Zeikus, and T.D. Brock. 1981. Dynamics of bacterial sulfate reduction in a eutrophic lake. Appl. Environ. Microbiol. 42:1029–1036.

Kadlec, R.H., and R.L. Knight. 1996. Treatment wetlands. CRC Press, Boca Raton, FL.

Lamers, L.P.M., H.B.M. Tomassen, and J.G.M. Roelofs. 1998. Sulfate-induced eutrophication and phytotoxicity in freshwater wetlands. Environ. Sci. Technol. 32 (2):199–205.

Legates, D.R., and G.J. McCabe, Jr. 1999. Evaluating the use of "goodness-of-fit" measures in hydrologic and hydroclimatic model validation. Water Resour. Res. 35:233–242.

Lovley, D.R., and M.J. Klug. 1985. Model for the distribution of sulfate reduction and methanogenesis in freshwater sediments. Geochim. Cosmochim. Acta 50:11–18.

Marnette, E.C.L., H. Houweling, H. Van Dam, and J.W. Erisman. 1993. Effects of decreased atmospheric deposition on the sulfur budgets of two Dutch moorland pools. Biogeochemistry 23:119–144.

McCormick, P.V., and J.W. Harvey. 2007. Influence of changing water sources and mineral chemistry on the Everglades Ecosystem. Administrative Rep. Available at http://water.usgs.gov/nrp/sheetflow/publications.html (verified 18 Dec. 2008). U.S. Geological Survey, Reston, VA.

McCormick, P.V., S. Newman, G. Payne, S. Miao, and T.D. Fontaine. 2000. Ecological effects of phosphorus enrichment in the Everglades. *In* G. Redfield (ed.) Everglades Consolidated Rep. Available at http://www.sfwmd.gov (verified 18 Dec. 2008). South Florida Water Management District, West Palm Beach, FL.

Nash, J.E., and J.V. Sutcliffe. 1970. River flow forecasting through conceptual models: Part I. A discussion of principles. J. Hydrol. 10:282–290.

Orem, W., H. Lerch, A. Bates, M. Corum, and M. Beck. 2002. Sulfur contamination and geochemistry of the Everglades. USGS Open-File Rep. 03-54. Available at http://sofia.usgs.gov/publications/ofr/03-54/ (verified 18 Dec. 2008). USGS, Tallahassee, FL.

Raghunathan, R., T. Slawecki, T.D. Fontaine, Z. Chen, D.W. Dilks, V.J. Bierman, Jr., and S. Wade. 2001. Exploring the dynamics and fate of total phosphorus in the Florida Everglades using a calibrated mass balance model. Ecol. Modell. 142:247–259.

Surratt, D.D., M.G. Waldon, M.C. Harwell, and N.G. Aumen. 2008. Time-series and spatial tracking of polluted canal water intrusion into wetlands of a national wildlife refuge in Florida, USA. Wetlands 28:176–183.

Urban, N.R., P.L. Brezonik, L.A. Baker, and L.A. Sherman. 1994. Sulfate reduction and diffusion in sediments of Little Rock Lake, Wisconsin. Limnol. Oceanogr. 39:797–815.

USFWS. 2000. Arthur R. Marshall Loxahatchee National Wildlife Refuge comprehensive conservation plan. Available at http://www.fws.gov/southeast/planning/Loxahatchie%20Final%20Pg.html. U.S. Fish and Wildlife Serv., Boynton Beach, FL.

USFWS. 2007. A.R.M. Loxahatchee National Wildlife Refuge—Enhanced monitoring and modeling program–2nd Annual Report–February 2007. LOXA06-008. Available at http://sofia.usgs.gov/lox_monitor_model/reports/2nd_annual_07.html#pdf (verified 18 Dec. 2008). U.S. Fish and Wildlife Service, Boynton Beach, FL.

Weaver, K.C., and G.G. Payne. 2004. Status of water quality in the Everglades Protection Area. *In* G. Redfield (ed.) Everglades Consolidated Report. Available at http://www.sfwmd.gov (verified 18 Dec. 2008). South Florida Water Management District, West Palm Beach, FL.