

Hongqing Wang¹, Michael G. Waldon², Ehab A. Meselhe¹, Jeanne C. Arceneaux³, Chunfang Chen⁴, and Matthew C. Harwell²

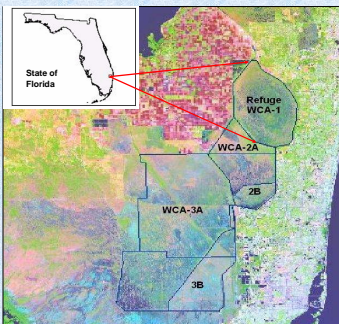
1) Center for Louisiana Water Studies, Institute of Coastal Ecology and Engineering, University of Louisiana at Lafayette, LA 70504; 2) Everglades Program Team, A.R.M. Loxahatchee National Wildlife Refuge, Boynton Beach, FL 33473; 3) C.H. Fenstermaker and Associates, Inc., Lafayette, LA 70504; 4) School of Natural Resources and Environment, University of Florida, Gainesville, FL 32611.

1. Introduction

- Sulfate contamination has been identified as a serious environmental issue for the Everglades ecosystem including the Arthur R. Marshall Loxahatchee National Wildlife Refuge (e.g., Orem et al., 2004).
- There have been no empirical studies of the effects of flow and sulfate concentration in canal water and other hydrological processes on sulfate dynamics in the Refuge.
- The objectives of this modeling study were to (1) develop a simple model for sulfate concentration in surface water linked to an existing water budget based model of stage and canal-marsh water exchange, (2) better understand the spatial patterns and rates of sulfate disappearance, and (3) estimate sulfate reduction rates (SRR) in the Refuge.

2. Study Area

The Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge), overlays Water Conservation Area 1 (WCA-1), which is a freshwater wetland located in Palm Beach County, Florida (Figure 1). It is a remnant of the historical northern Everglades. Agricultural runoff high in sulfate (the mean concentration is approximately 50 mg L⁻¹) is pumped into the perimeter canal, and mixes into the interior marsh (Figure 2), which is characterized by low sulfate (less than 1 mg L⁻¹). Modeling is required to understand the complex interaction between transport and transformation.



Covering Area: 57,000 ha
Mean summer & winter temperature: 31 °C & 13 °C
Annual Rainfall: 1400 mm
Bedrock: Limestone
Soil Type: Peat
Soil Elevation: 3.2 – 5.6 m (NGVD)
Vegetation Types: Sawgrass, Wet prairie, Cattail, Tree islands (Figure 3)



Figure 2. Images of the Refuge's rim canal (left) and marsh areas (right).

Figure 1. Location of the Arthur R. Marshall Loxahatchee National Wildlife Refuge and other Everglades Water Conservation Areas (SFWMD, 2000 at <http://fcelter.fiu.edu/gis/everglades-map>).

3. Model and Data

- Water Flow and Chloride Model:** Driven by simplified flow model (Arceneaux et al., 2007). The flow model was tested using chloride simulations.
Inputs: pumped inflow, structure outflow, precipitation, evapotranspiration (ET);
Outputs: flow between canal and marsh, stage of canal and marsh, groundwater recharge, evaporation, transpiration.

- Sulfate Dynamics:** Using a first order apparent settling rate dynamics (Kadlec and Knight, 1996):

$$\frac{dhC}{dt} = -kC + L$$

where, h is depth in m. C is the sulfate concentration in mg L⁻¹, k is the apparent settling coefficient in m yr⁻¹, L is the sulfate loading rate in the compartment in g m² yr⁻¹, representing the net total loading rate from advective and dispersive transport, and external loading.

The sulfate reduction rates (SRR, g m² yr⁻¹) for the three marsh cells were estimated based on the settling coefficients, or $SRR(i) = k(i) * C(i)$, where $k(i)$ and $C(i)$ are calibrated apparent settling coefficient and average observed sulfate concentration for compartment i , respectively.

- Model Compartments:** Canal, and three marsh cells: Cell1 (0-1 km from canal), Cell2 (1-4 km from canal), and Cell3 (> 4km from canal), see Figure 4.

- Model Platform:** Water Quality Analysis Simulation Program (WASP) of U.S. EPA (<http://www.epa.gov/athens/wqatsc/html/wasp.html>).

- Time Step:** 0.1 days.

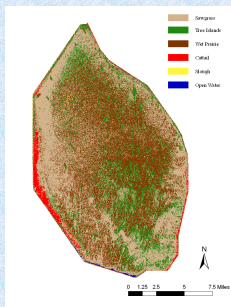
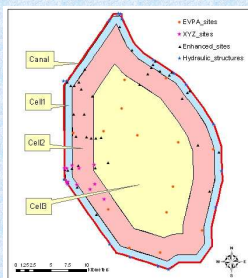


Figure 3. Refuge vegetation map adapted from USFWS (2000).



Data:

Hydrological, meteorological and water quality data are primarily from the South Florida Water Management District (SFWMD)'s DBHYDRO online database (<http://www.sfwmd.gov/org/ema/dbhydro/index.html>).

Water quality stations (Figure 4): Hydraulic structures, EVPA sites, XYZ sites, and the Enhanced sites.

Figure 4. Map of the Refuge model compartments and water quality monitoring stations.

4. Simulation Results

4.1 Our model generally captures the spatial, inter-annual, and seasonal variations in sulfate concentrations in the Refuge (Figure 5; Table 1):

a) Sulfate concentration decreases along a gradient from the canal perimeter to the marsh interior;

b) Sulfate concentrations tend to be higher in wet years and during wet season (May to October), and the peaks are likely to occur because: - more sulfate enters canals from agricultural runoff, - more sulfate transports into Refuge interior when canal stages higher than marsh stages (McCormick and Harvey, 2007; Surratt et al., 2008).

c) The anomalous increase during June 1999 - July 2001 (Figure 5, Table 1), could not solely be explained by canal water intrusion and wet deposition. It was observed that 1999 and 2001 were severe drought years with peat fires in 1999 in northern WCA-3A (Figure 1) that begins ~15 miles southwest of the Refuge (Smith et al., 2001). The dry condition and peat fire could also impact the refuge. Drought could lead to the oxidation of reduced sulfur. Sulfate may then be released upon rewetting.

4.2 Sulfate apparent settling coefficients increased from periphery toward interior marsh (0.5, 1, and 10 m yr⁻¹ for Cell1, Cell2 and Cell3, respectively).

4.3 The estimated SRR for the Refuge marsh as a whole is approximately 14.4 g m² yr⁻¹. The relatively constant SRR across all three marsh zones (14.5, 14.0, 14.9 g m² yr⁻¹ for Cell1, Cell2, and Cell3, respectively) suggests a condition of sulfate in excess of requirement for microbial reduction in the marsh.

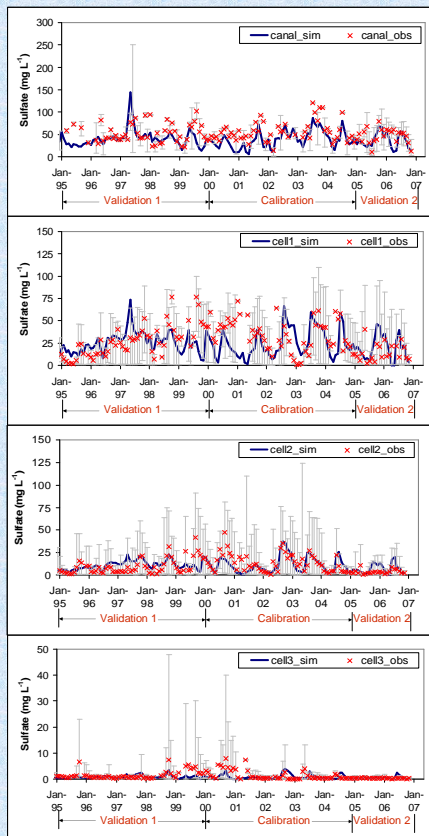


Figure 5. Simulated (line) and observed sulfate concentration (monthly mean) in rim canal, perimeter marsh (Cell1), transition marsh (Cell2) and interior marsh (Cell3) during 1995-2006. Grey bars indicate the range from minimum to maximum of observations.

4.4 The sources of simulation errors are uncertainty in data of flow, rainfall, ET, and inflow sulfate concentration; low frequency of water quality monitoring data; coarse spatial resolution; and simplification of complex sulfur biogeochemical processes.

Table 1. Assessment of simulations of surface water sulfate concentrations using the mass balance based Refuge water quality model (Note: Ave.=average; Obs.=observed; Sim.=simulated; sd=standard deviation; Bias = average difference between modeled and observed values; RMSE=root mean square error; R=correlation coefficient; Efficiency= Nash-Sutcliffe Efficiency).

Statistic	Canal	Cell1	Cell2	Cell3	Marsh
Calibration (2000 - 2004)					
Ave. Obs. (sd)	mg L ⁻¹ 55.6 (22.4)	29.1 (17.4)	13.9 (9.8)	1.5 (1.8)	16.3 (7.8)
Ave. Sim. (sd)	mg L ⁻¹ 39.0 (19.2)	26.0 (15.9)	11.7 (9.2)	0.9 (0.9)	12.5 (8.4)
Bias	mg L ⁻¹ -17.37	-3.20	-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
Calibration (August 2001-December 2004)					
Ave. Obs. (sd)	mg L ⁻¹ 60.6 (25.5)	29.9 (17.2)	11.8 (8.7)	0.68 (0.8)	13.9 (7.3)
Ave. 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%	-39%	53%	-12%	-24%
R	0.76	0.29	0.80	0.08	0.52
Efficiency	0.18	-0.39	0.52	-1.27	-0.24
Validation (1995-1999, 2005-2006)					
Ave. Obs. (sd)	mg L ⁻¹ 49.9 (19.7)	22.2 (17.1)	7.5 (7.7)	1.1 (1.4)	10.2 (8.2)
Ave. Sim. (sd)	mg L ⁻¹ 40.3 (19.2)	24.3 (12.5)	9.7 (5.4)	0.7 (0.6)	11.5 (8.9)
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
Validation (January 1995-May 1999, 2005-2006)					
Ave. Obs. (sd)	mg L ⁻¹ 47.8 (18.8)	19.7 (14.6)	6.2 (5.7)	0.85 (1.1)	8.8 (6.6)
Ave. Sim. (sd)	mg L ⁻¹ 40.8 (19.2)	24.7 (12.5)	9.8 (5.5)	0.71 (0.6)	11.6 (8.0)
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	-0.16	0.18	0.03
Anomalous period (Jun 1999-July 2001)					
Ave. Obs. (sd)	mg L ⁻¹ 52.4 (16.3)	46.8 (13.9)	19.1 (11.2)	3.5 (2.1)	22.5 (7.6)
Ave. 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	-5.52
RMSE	mg L ⁻¹ 29.45	33.27	14.06	3.32	10.00
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

5. Conclusions

- Reduction in bias shows the model captures spatial variation well.
- Model temporal projections are less reliable, but generally pass through observed range.
- Sulfate modeling tool, when combined with modeling other water quality constituents, helps better refine science efforts to drive management decisions to protect Refuge resources.

6. Future Development

- Conducting uncertainty analysis (e.g., data uncertainty; parameter uncertainty).
- Dividing Refuge into more compartments for spatial variability in surface water sulfate dynamics.
- Adding "sediment" as a layer to build a sulfate hydro-ecological model.
- Implementing a complex spatially explicit hydrodynamic and constituent model.

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