U.S. Fish & Wildlife Service

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Completely Mixed Flow (CMF) Water Quality Modeling -- Sulfate

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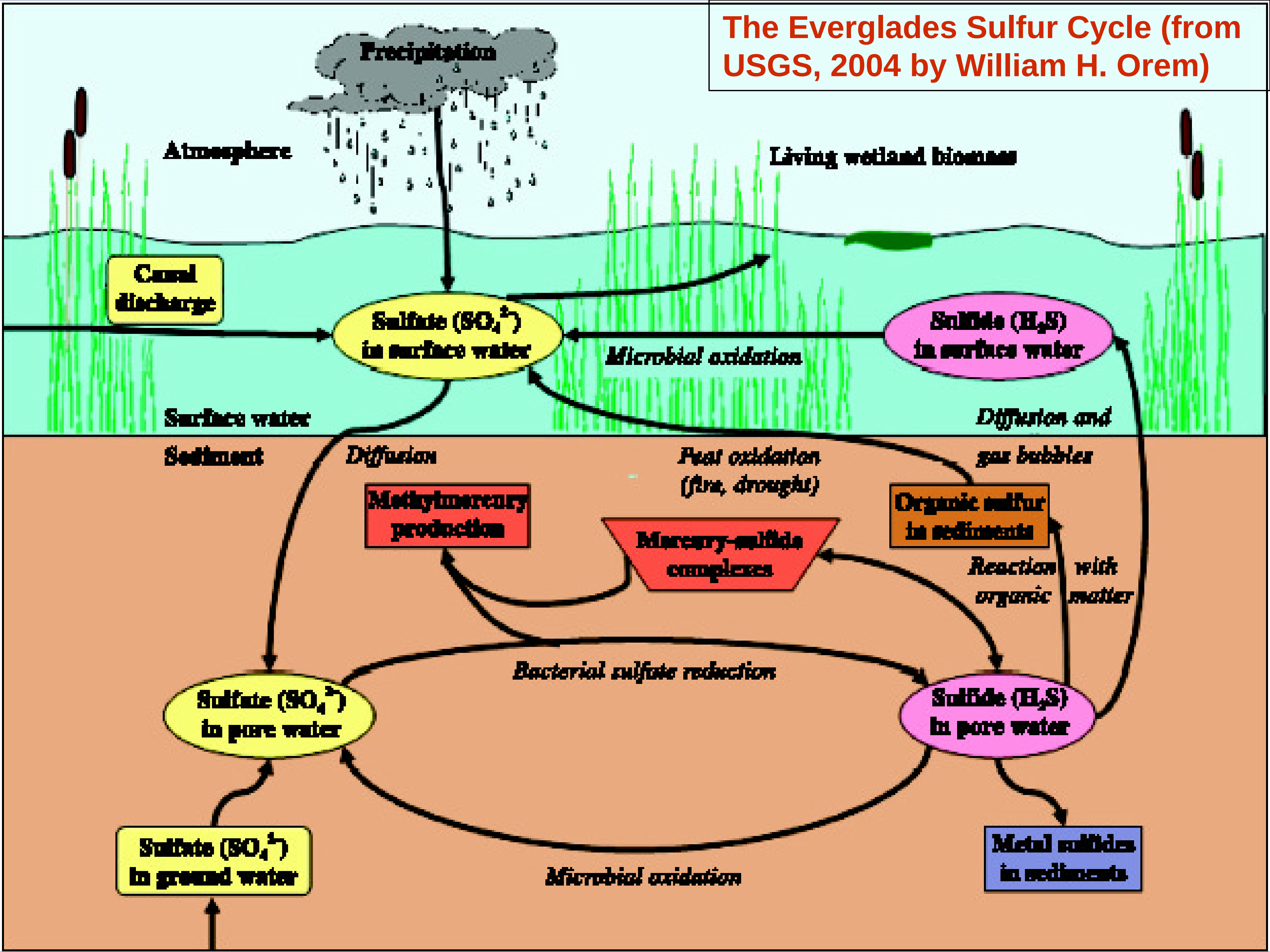
Outline

- Background
- Objectives
- Methods
- Preliminary results
- Conclusions
- Future studies

Background

- Fact
  - Sulfate is greatly elevated in Refuge inflows
- Consequences
  - Changing the S biogeochemistry in the Refuge

The Everglades Sulfur Cycle (from USGS, 2004 by William H. Orem)



Why Model Sulfate?

- Hydrological processes are important in Refuge S biogeochemistry
- It is difficulty to measure *in situ* process rates such as sulfate reduction
- Sulfate also provides a non-conservative tracer for water movement, complementing chloride tracer

Objectives

- Calibrate and validate a simple mass balance-based sulfate model
- Conduct sensitivity analysis on sulfate apparent settling coefficients in marsh

Methods

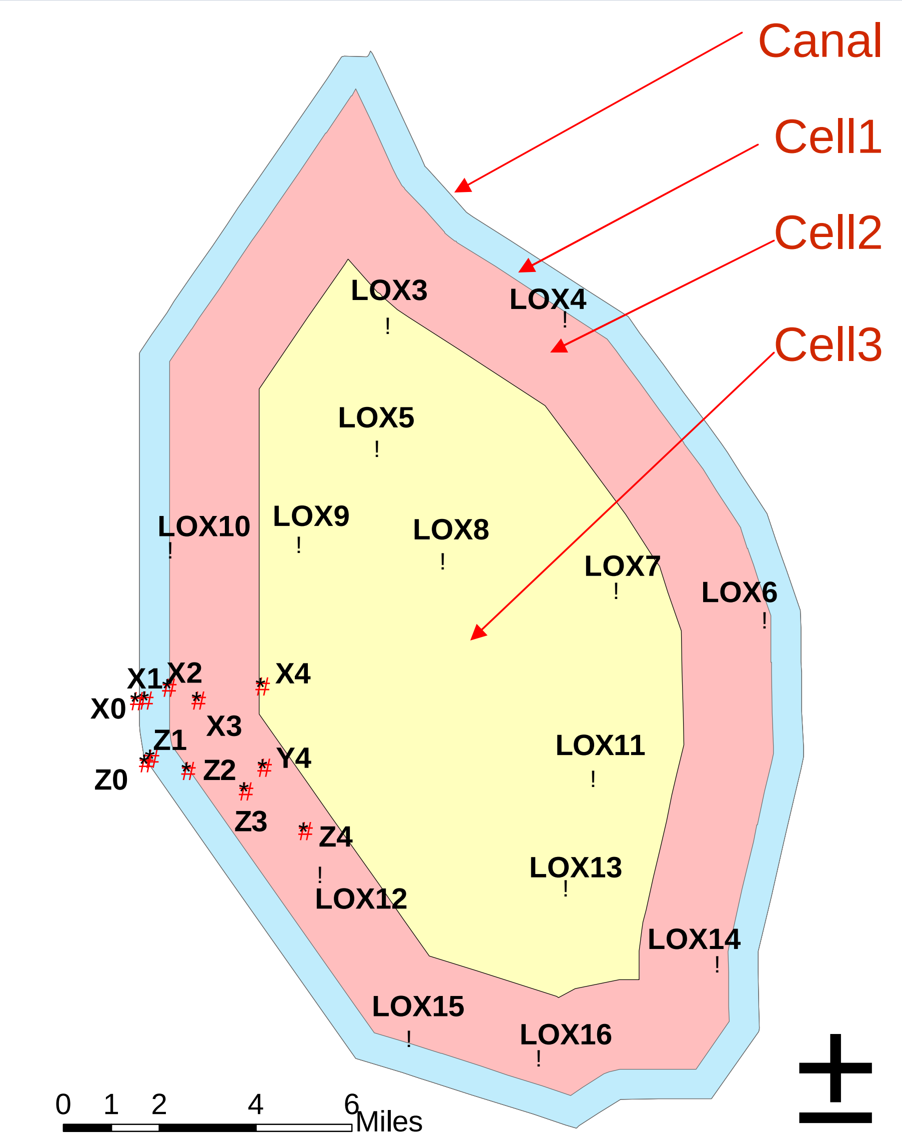
- Refuge Water Budget Model
  - Inputs: daily time-series of pumped inflow, structure outflow, precipitation, and evapotranspiration;
  - Outputs: stage, flow between the canal and marsh, groundwater seepage loss, evaporation and transpiration;
- EPA WASP model

WASP Model

- A dynamic compartment-based WQ model
- Reflecting the time-varying processes of advection, dispersion, point and diffuse mass loading, and boundary exchange

Sulfate WASP Setup

- Four components
- EUTRO Module
- Time Step = 0.1 days



Sulfate “Disappearance”

First order concentration model (the k-c* model) by Kadlec and Knight (1996):

$$\frac{dhC}{dt} = -k(C - C^*) = -kC + kC^*$$

h - depth in m

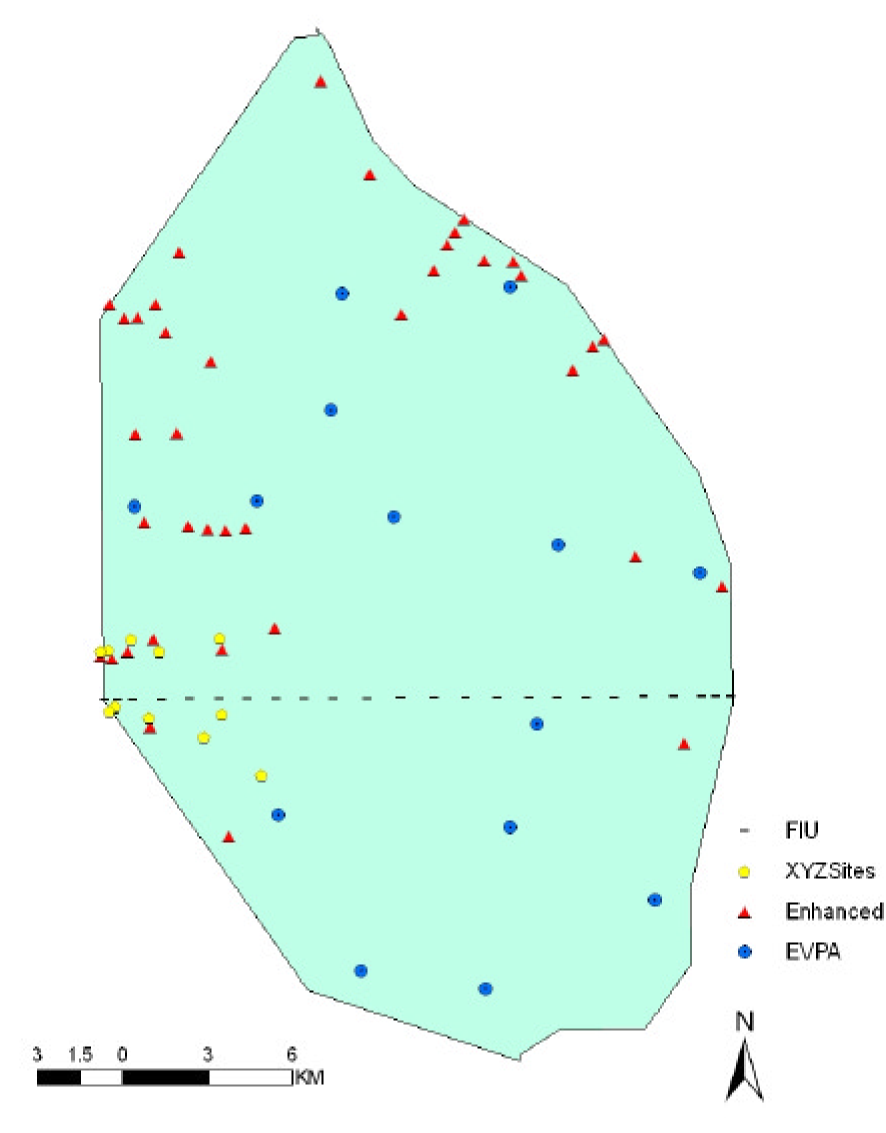
C - the concentration in g/m^3

k - the apparent settling coefficient (m/yr)

C^* - the background concentration (=0)

Data

- Data:
  DBHYDRO
- Calibration:
  2000-2004
- Validations:
  1995-1999
  2005-2006



Statistics

$$Bias = \overline{M} - \overline{O}$$

$$R = \left\{ \frac{\sum_{i=1}^{N} \left(O_i - \overline{O}\right)\left(M_i - \overline{M}\right)}{\left[\sum_{i=1}^{N} \left(O_i - \overline{O}\right)^2\right]^{0.5} \left[\sum_{i=1}^{N} \left(M_i - \overline{M}\right)^2\right]^{0.5}} \right\}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} (O_i - M_i)^2}{N}}$$

$$Variance\ Reduction = 1 - \left(\frac{s_E}{s_O}\right)^2$$

$$Nash\ \ Sutcliffe\ \ Efficiency = 1.0 - \frac{\sum_{i=1}^{N} (O_i - M_i)^2}{\sum_{i=1}^{N} (O_i - \overline{O})^2}$$

Sensitivity Analysis

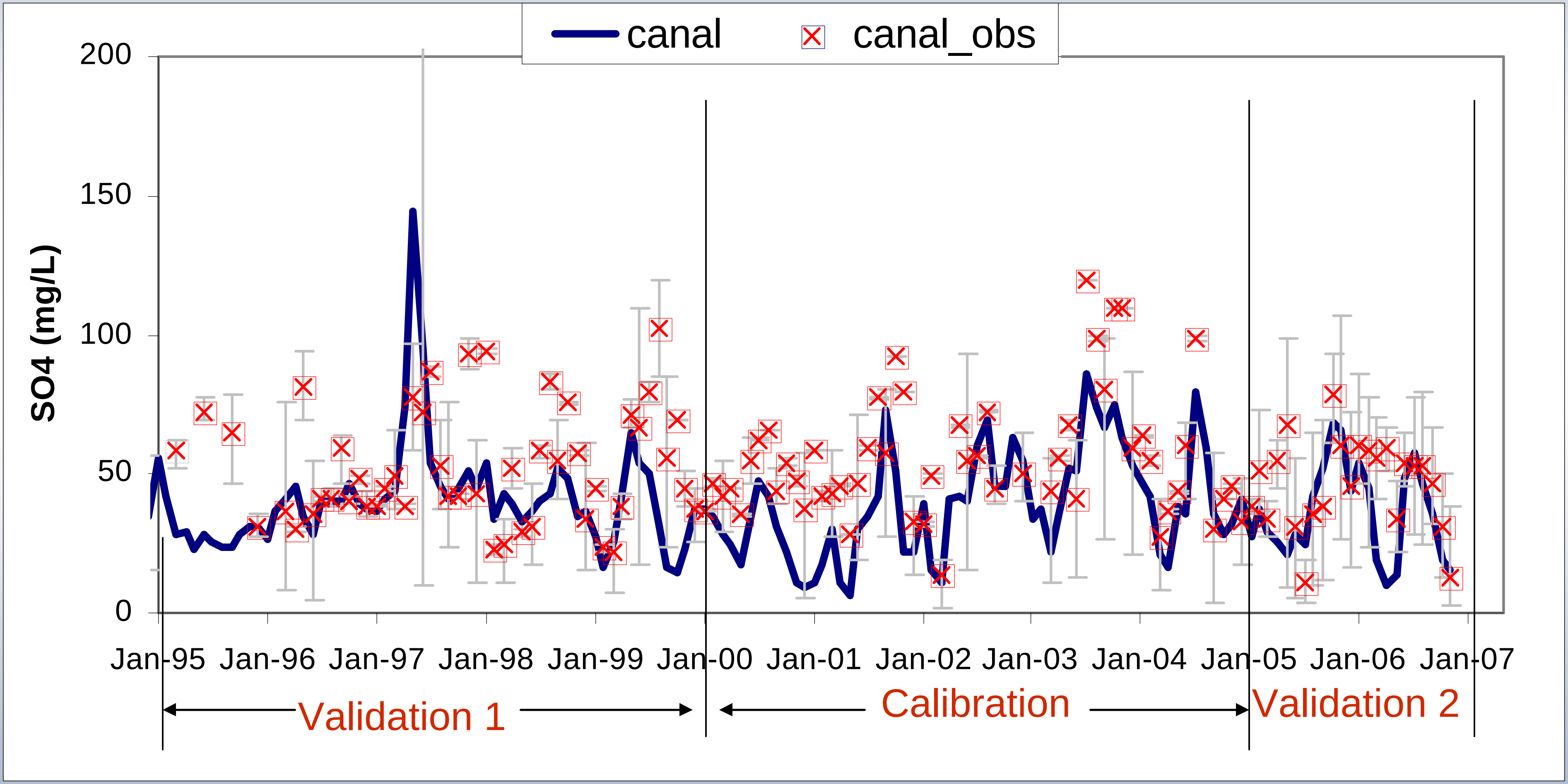
- **Sulfate apparent settling coefficients in Cell 1 (S1), Cell 2 (S2) and Cell 3 (S3)**
  - Calibrated values (S1=0.5, S2=1, S3=10 m/yr)
  - Changed values (0.1,0.5,1.5,1.75,and 2 times of calibrated values)

Normalized Sensitivity Index (NSI)

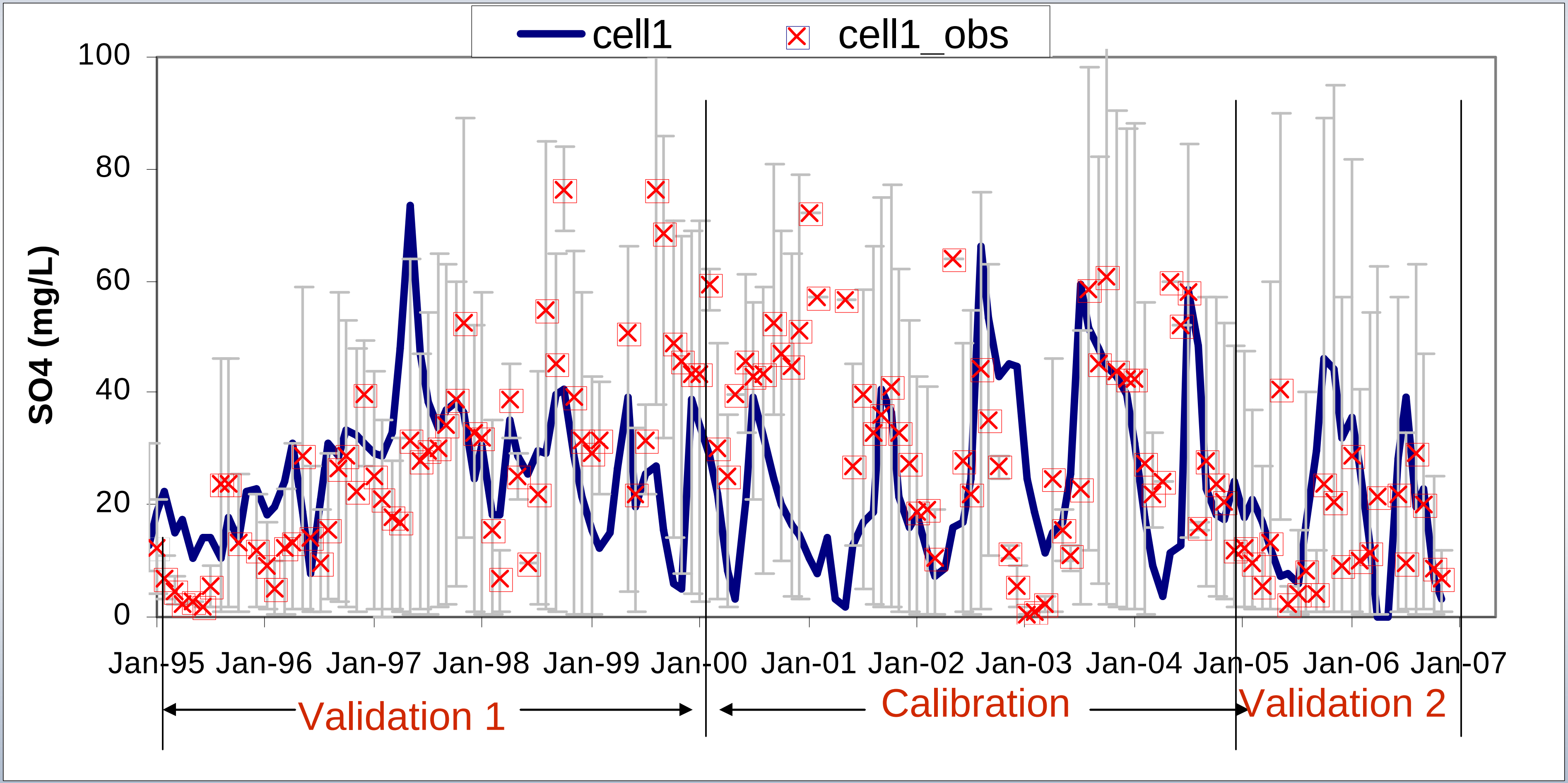
$$NSI = \frac{(\Phi - \Phi_0)/\Phi_0}{(P - P_0)/P_0}$$

- F_0 and P_0 -- mean marsh sulfate concentration and settling coefficients at calibrated condition
- F and P -- mean marsh sulfate concentration and settling coefficients at changed condition

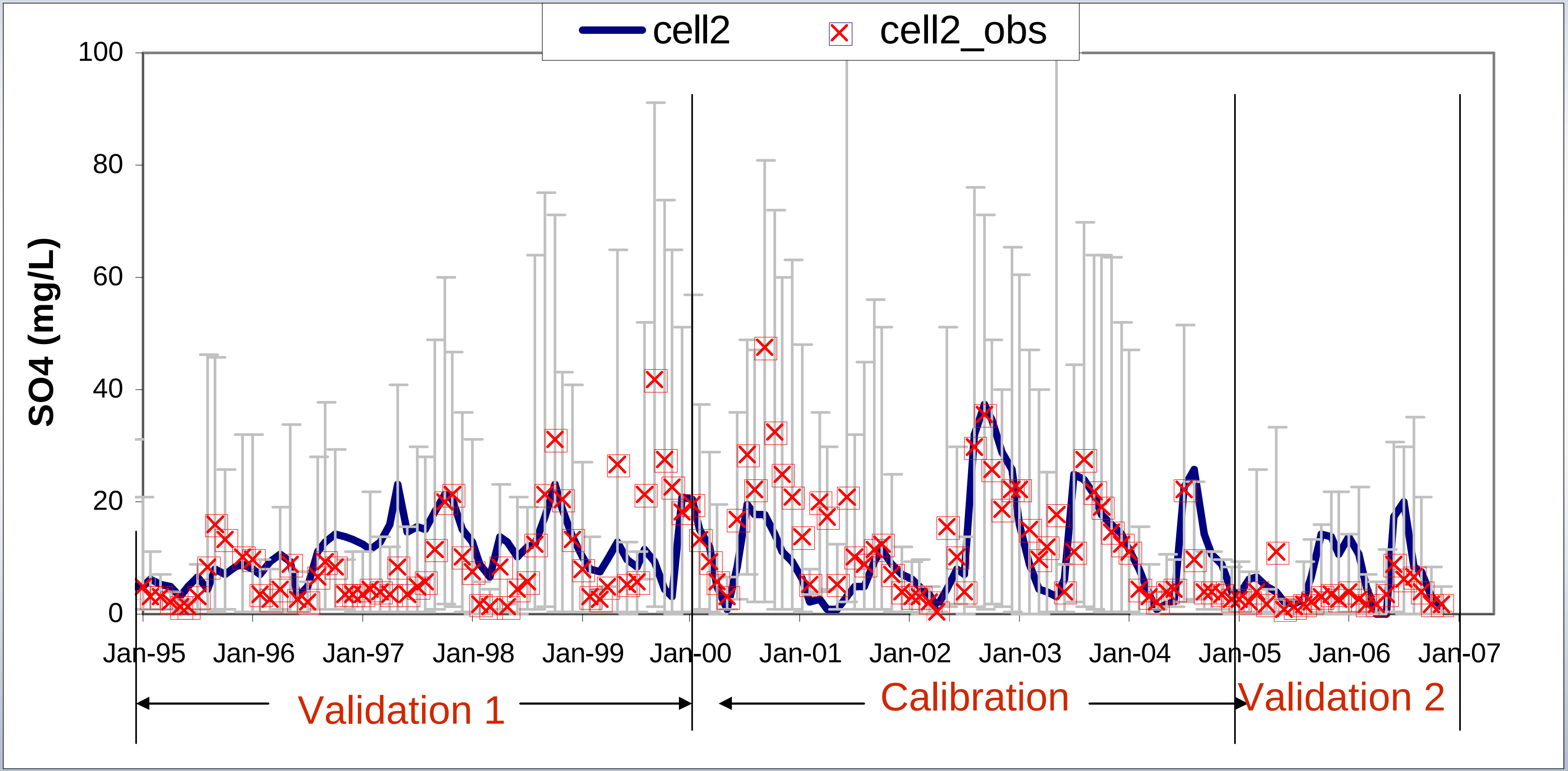
Preliminary Results - Canal



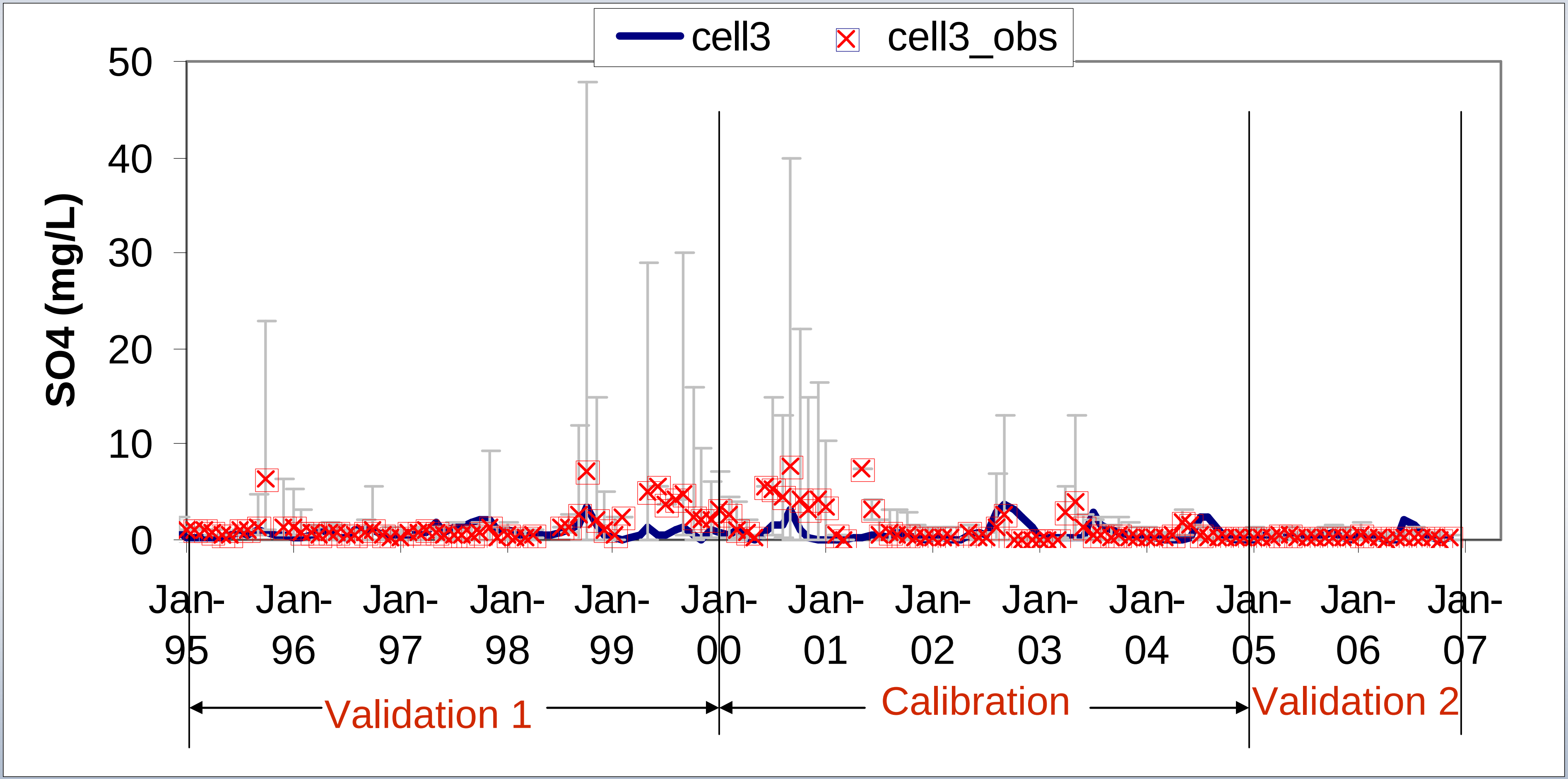
Preliminary Results – Cell 1



Preliminary Results – Cell 2



Preliminary Results – Cell 3



Statistics – Calibration 00-04

Statistic		canal	cell_1	cell_2	cell_3	marsh
Bias	mg/l	-17.37	-8.70	-2.13	-0.68	-3.79
RMSE	mg/l	23.21	24.13	8.40	2.09	10.24
Variance reduction		54%	-68%	31%	-9%	-45%
R (Correl Coef)		0.75	0.09	0.64	0.16	0.33
Nash-Sutcliffe Eff		-0.08	-0.93	0.26	-0.22	-0.69

Statistics – Validation 95-99

Statistic		canal	cell_1	cell_2	cell_3	marsh
Bias	mg/l	-9.41	-0.79	1.73	-0.65	0.31
RMSE	mg/l	26.81	18.25	8.58	1.65	8.43
Variance reduction		-41%	-7%	3%	12%	2%
R (Correl Coef)		0.30	0.29	0.32	0.34	0.35
Nash-Sutcliffe Eff		-0.33	-0.07	-0.01	-0.05	0.02

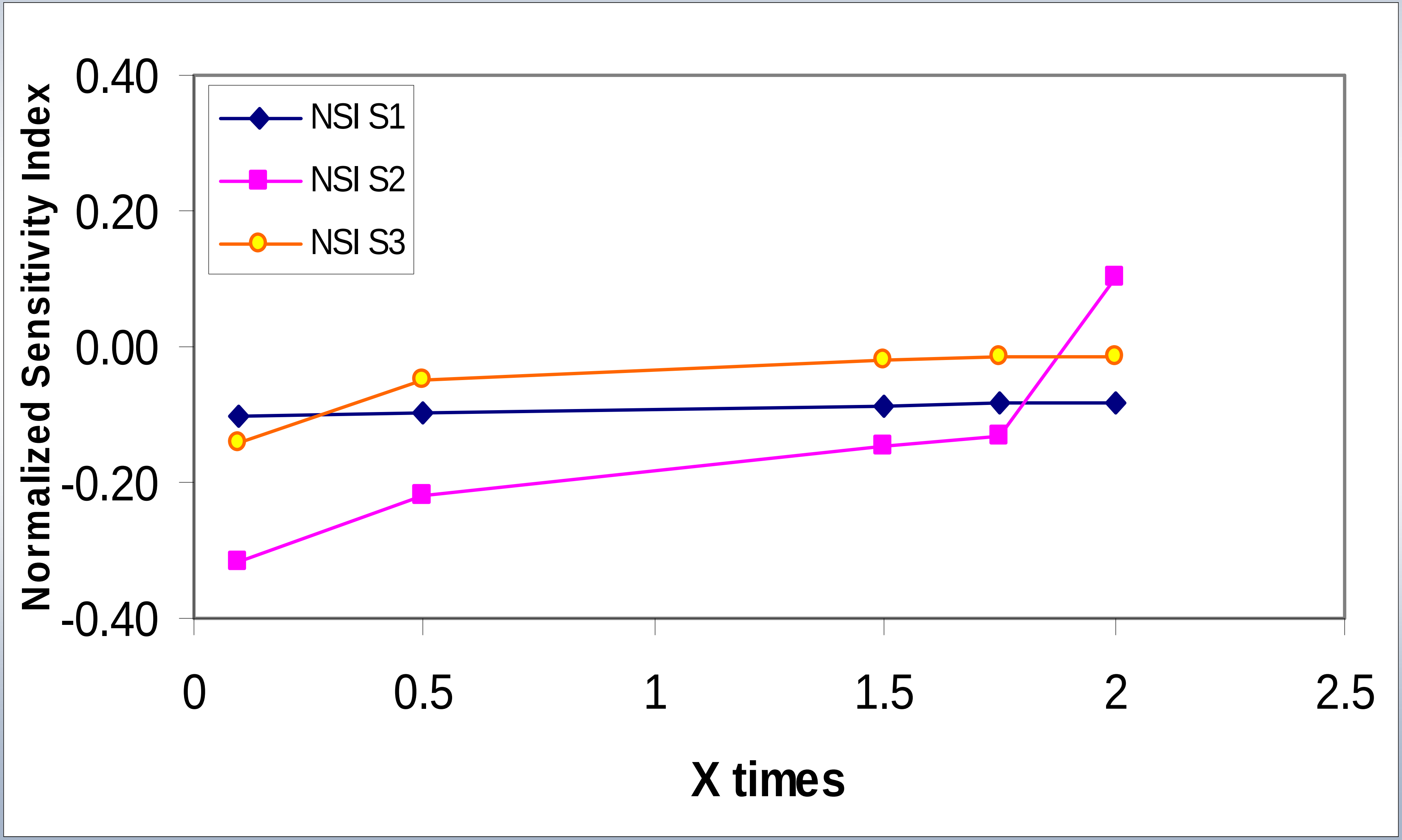
Statistics – Validation 05-06

Statistic		canal	cell_1	cell_2	cell_3	marsh
Bias	mg/l	-7.13	7.50	4.10	0.19	3.93
RMSE	mg/l	16.85	15.81	6.33	0.58	7.23
Variance reduction		16%	-101%	-247%	-1981%	-131%
R (Correl Coef)		0.55	0.25	0.45	0.05	0.30
Nash-Sutcliffe Eff		-0.04	-1.63	-5.20	-22.54	-2.35

General Evaluation of Sulfate Simulations

- Effective in examining Sulfate dynamics
- Sources of uncertainty
  - Model structure (e.g., 4 segments; no biological processes involved: reduction rate by OM,NO_3,veg.,microbial community)
  - Water budget model (e.g., Transpiration % in ET: not cell-specific, not seasonal)
  - Data (e.g., monthly average from quarterly obs.)

SA: Sulfate Settling Coefficients



Sulfate Disappearance Rate (sulfate reduction)

	Cell 1	Cell 2	Cell 3
Settling coefficient (m/yr)	0.5	1	10
Mean concentration (mg/L)	32.9	13.8	1.4
Disappearance rate (g/m^2.yr)	16.45	13.8	14

- Disappearance rate (g/m^2.yr) = K * C

Conclusions

- Canal water is the primary source of sulfate contamination in marsh interior
- Rate of sulfate disappearance (reduction flux) is relatively constant (~15 g/m^2.yr) - not sulfate limited

Future Studies

- Dividing Refuge into more segments for spatial variability in surface water sulfate dynamics
- Conducting uncertainty analysis (e.g., data uncertainty; parameter uncertainty)
- Adding “sediment” as a component to build a hydro-ecological model