Biogeochemical Variables Driving Temporal Dynamics and Spatial Variability in Mercury Bioaccumulation in *Gambusia* in the Everglades – A Model Analysis using R-EMAP

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Introduction

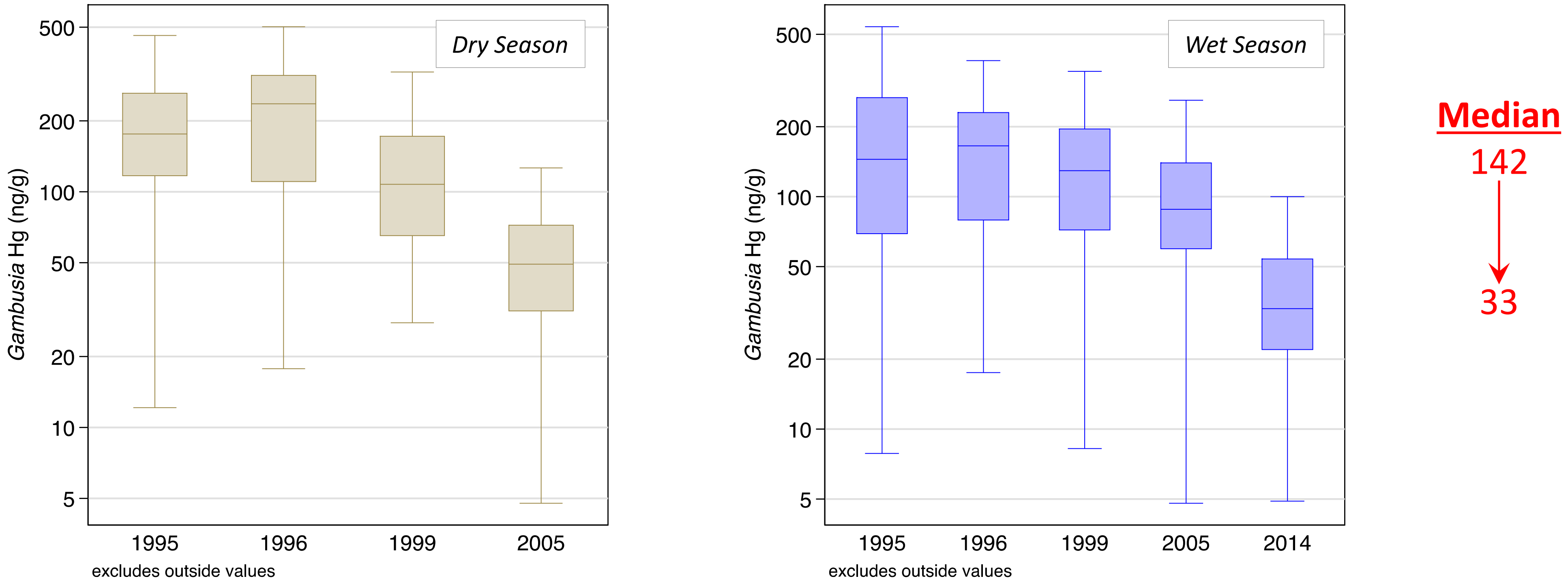
- Between 1995 and 2005 US EPA conducted synoptic field campaigns in the Everglades Protection Area that included measurements of Hg concentrations in *Gambusia* spp. and periphyton, as well as a number of biogeochemical variables that can influence the aquatic cycling of Hg. Eight field campaigns (cycles) were conducted (4 wet and 4 dry) during this period.

- In 2014, *STOTEN* publishes a paper by Pollman that uses structural equation modeling (SEM) to quantify the significance and relative contributions of different biogeochemical pathways – direct and indirect – on fish Hg concentrations. This paper included a model for *Gambusia* Hg specific for the Everglades based on the R-EMAP data for Cycles 0 – 7. The model indicates that sulfate concentrations are an important driver of *Gambusia* Hg.

- In 2014, US EPA conducts another synoptic campaign in the Everglades during the dry season (Cycle 11). A comparison of *Gambusia* Hg results for Cycle 11 with previous cycles indicates a dramatic drop in *Gambusia* Hg during Cycle 11.

Changes in *Gambusia* Hg over Time

R-EMAP data for Dry and Wet Cycles, 1995 - 2014



Objective and Approach

- The primary objective is to use the Pollman (2014) SEM model* to evaluate whether changes in sulfate concentrations – or other variables included in the model – will result in declines in predicted *Gambusia* Hg concentrations consistent with observed declines.

- The model is revised slightly to help account for the fact that, *ceteris paribus, Gambusia* Hg concentrations are generally lower in Everglades National Park.

- The model is calibrated only to Cycles 0 – 7 data to evaluate *post hoc* the predictive performance of the model when applied to Cycle 11 data.

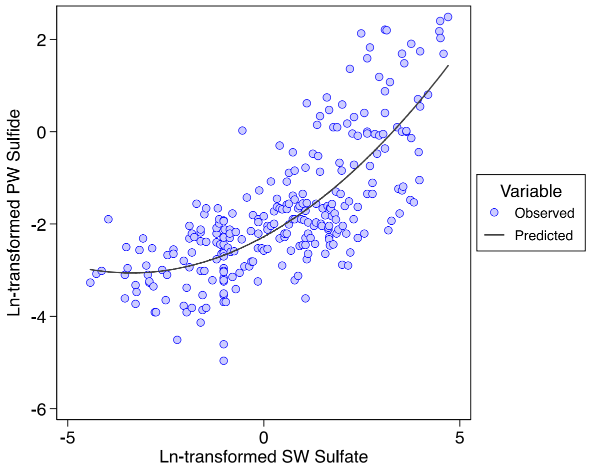
*Pollman, C.D. 2014. Mercury cycling and trophic state in aquatic ecosystems: Implications from structural equation modeling. Sci. Tot. Env. 499:62-73.

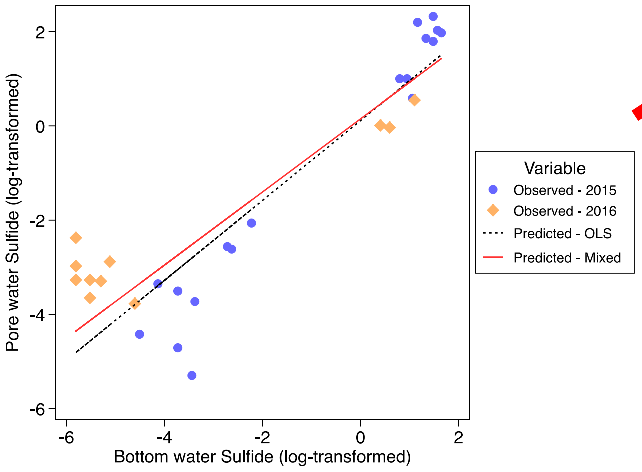
Pollman (2014) SEM Model Modifications

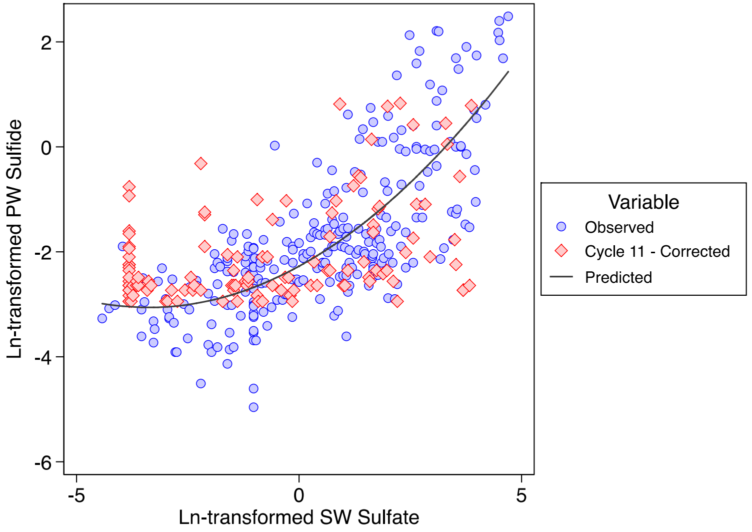
- Include dummy variable for whether sites are located in the ENP
- Use inferred PW sulfide values for Cycle 11 obtained for mixed level regression modeling of bottom water – PW sulfide relationship, and adjusted for surface water sulfate concentrations.
- Modifications to how periphyton MeHg concentrations are aggregated by compartment to ensure consistency across all cycles, including cycle 11.

Inferring Porewater Sulfide for Cycle 11

Use sulfate relationship from previous cycles to identify constant for shift in PW sulfide inferred for Cycle 11 based on *fixed* relationship with bottom water sulfide







SEM Model

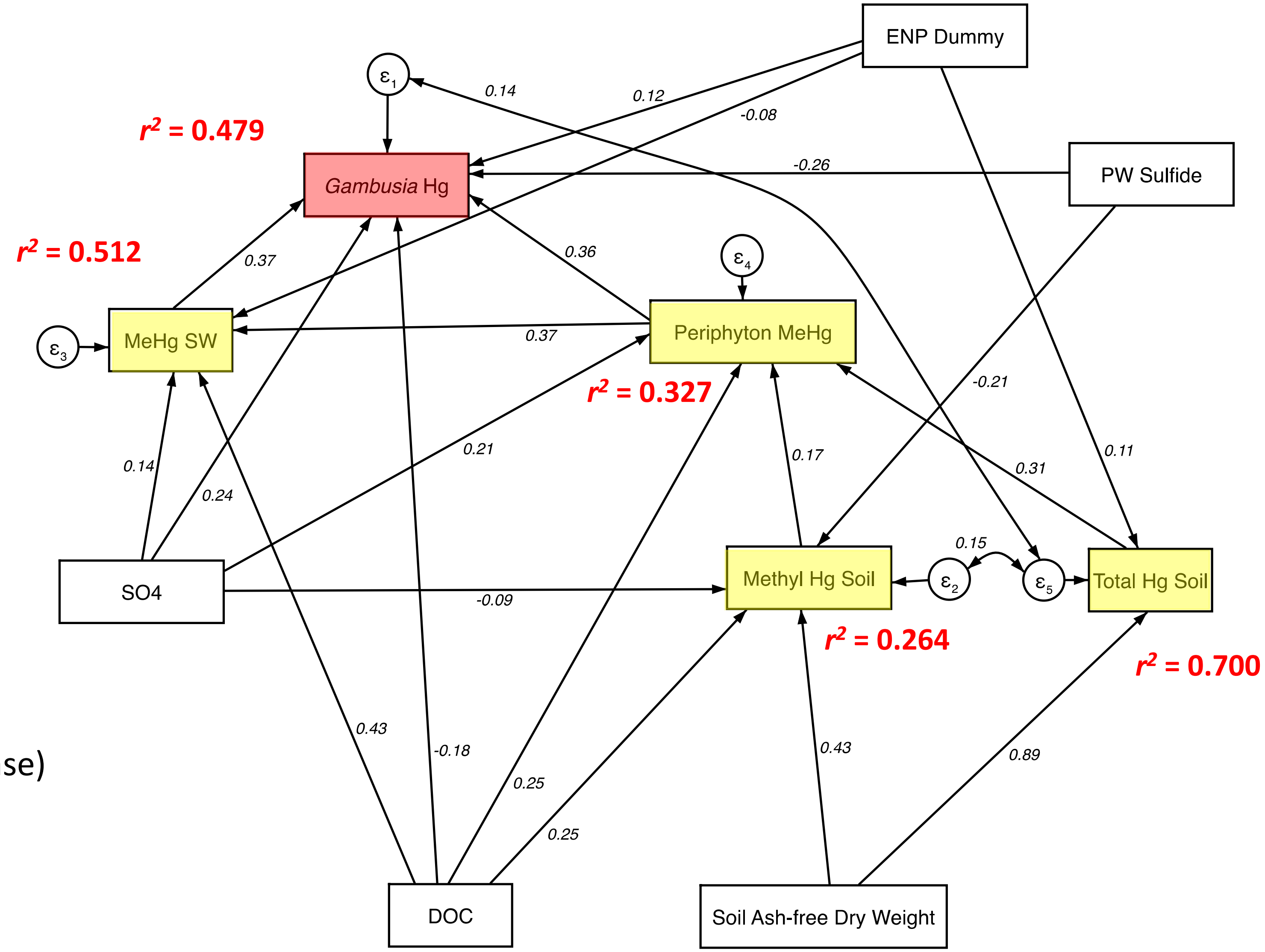
All path coefficients significant @ *p* < 0.001, except for:

ENP_Dummy → MeHg SW (*p* = 0.015)

ENP_Dummy → *Gambusia* Hg (*p* = 0.001)

SO4 → MeHg Soil (*p* = 0.010)

ENP effect in *Gambusia* Hg is 0.125 *ln* units (increase)



SEM Fit Statistics

Cycles 0 – 7; N = 579

Fit statistic	Value	Description
Likelihood ratio		
chi2_ms(13)	12.830	model vs. saturated
p > chi2	0.461	
chi2_bs(35)	1765.645	baseline vs. saturated
p > chi2	0.000	
Population error		
RMSEA	0.000	Root mean squared error of approximation
90% CI, lower bound	0.000	
upper bound	0.041	
pclose	0.989	Probability RMSEA <= 0.05
Information criteria		
AIC	15354.608	Akaike's information criterion
BIC	15581.396	Bayesian information criterion
Baseline comparison		
CFI	1.000	Comparative fit index
TLI	1.000	Tucker-Lewis index
Size of residuals		
CD	0.883	Coefficient of determination

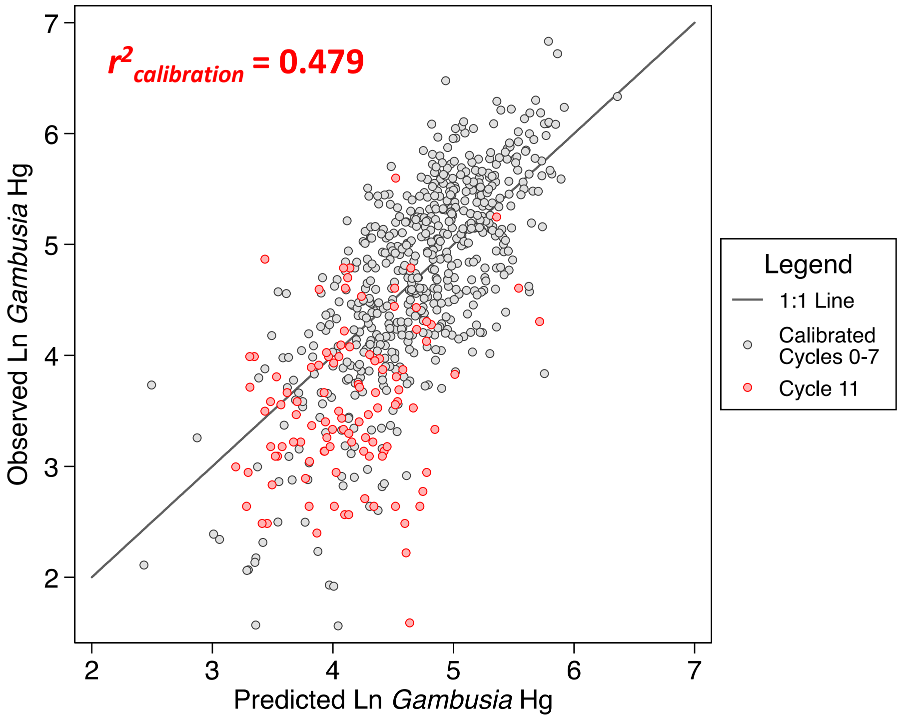
Should be > 0.05

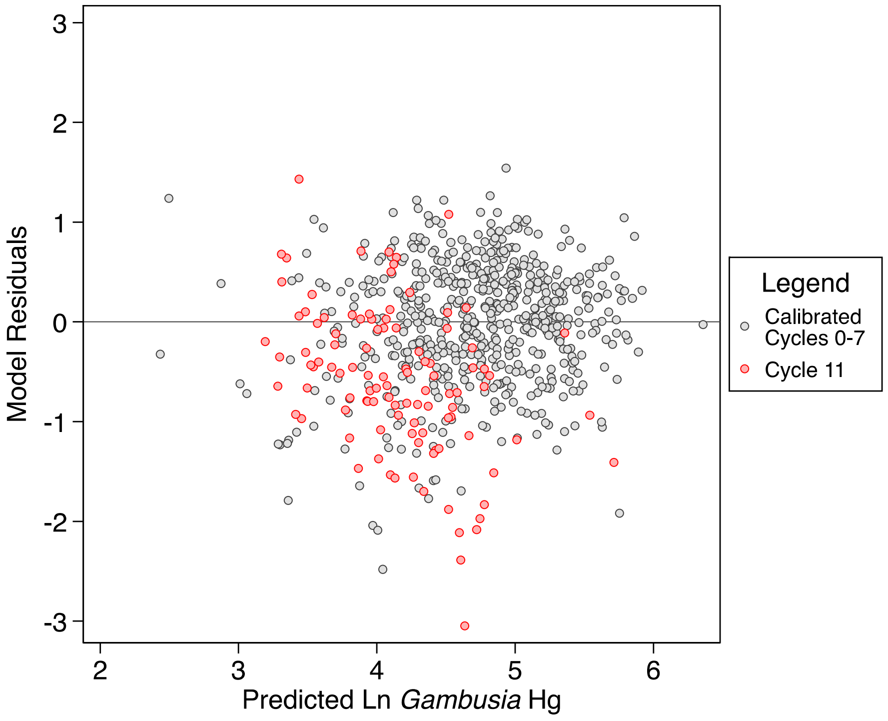
Should be < 0.05

Should be > 0.95

SEM – Observed *vs.* Predicted Values – Model Residuals

Comparison of calibrated results (Cycles 0 – 7) and *post hoc* (Cycle 11) results

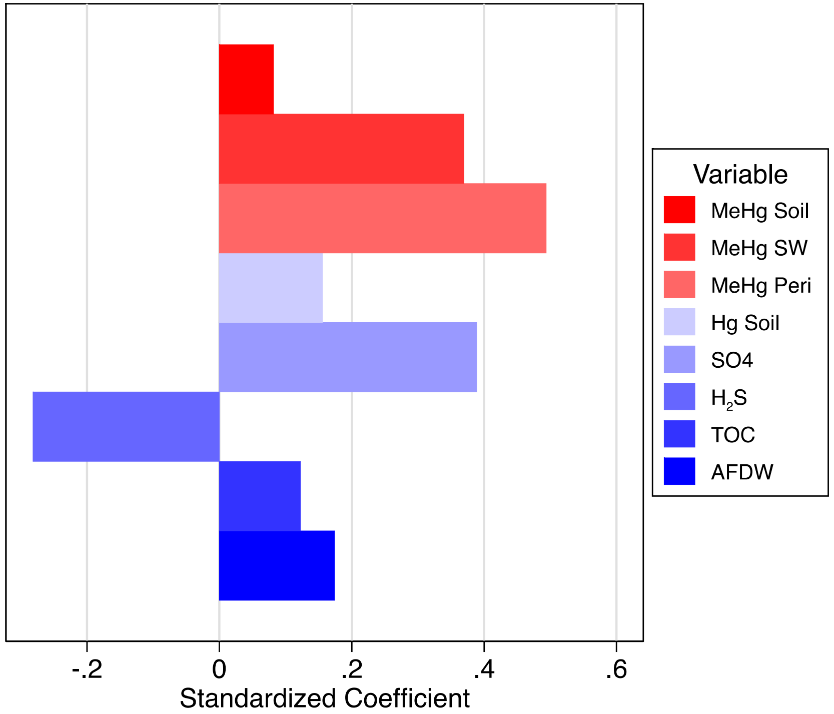




SEM – Variable Contributions to *Gambusia* Hg

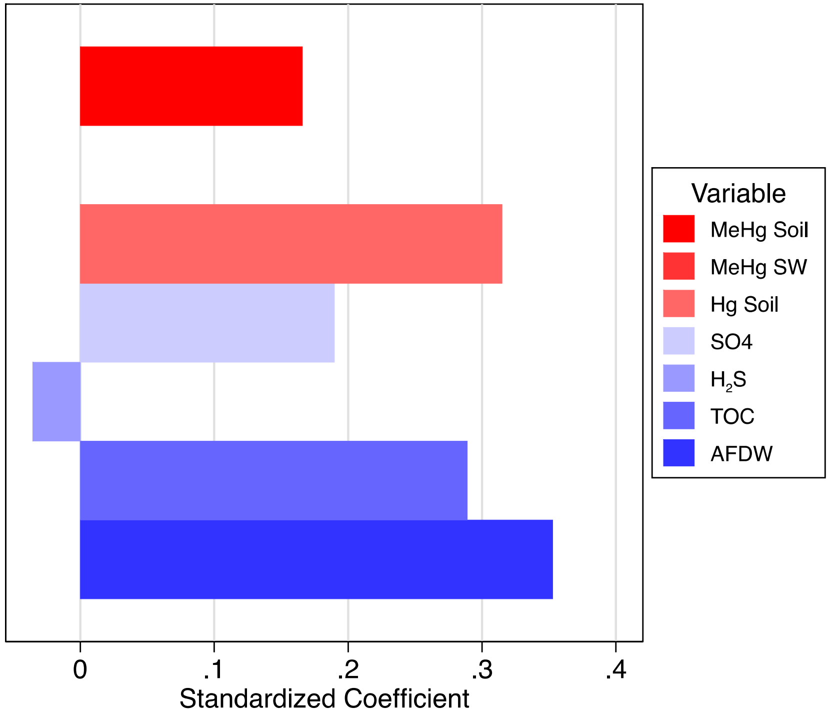
Endogenous variables

Exogenous variables

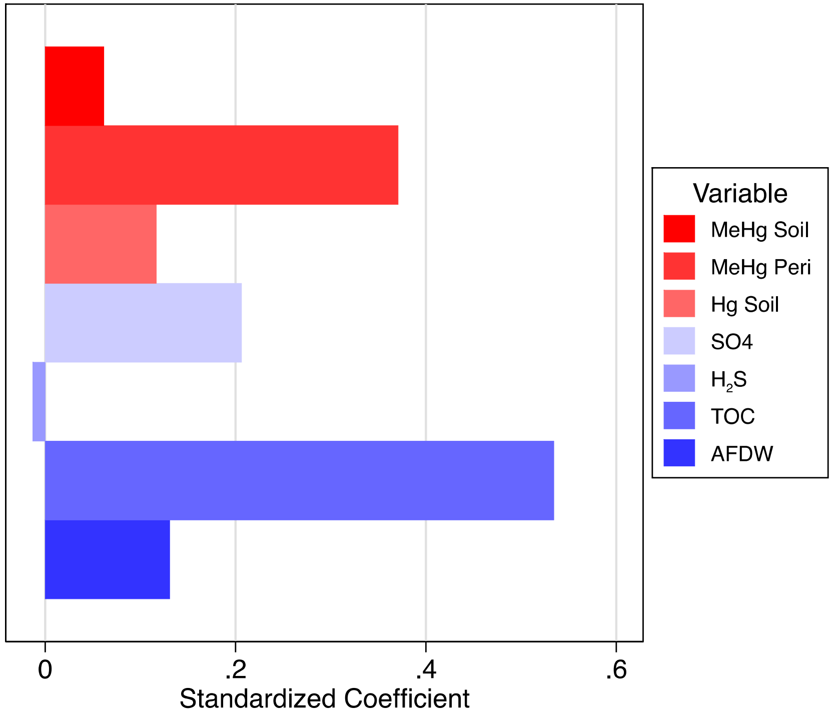


Primary exogenous driving variable in SEM model is sulfate methylation potential, followed by H_2S

SEM – Variable Contributions to Periphyton and Surface Water Methyl Hg



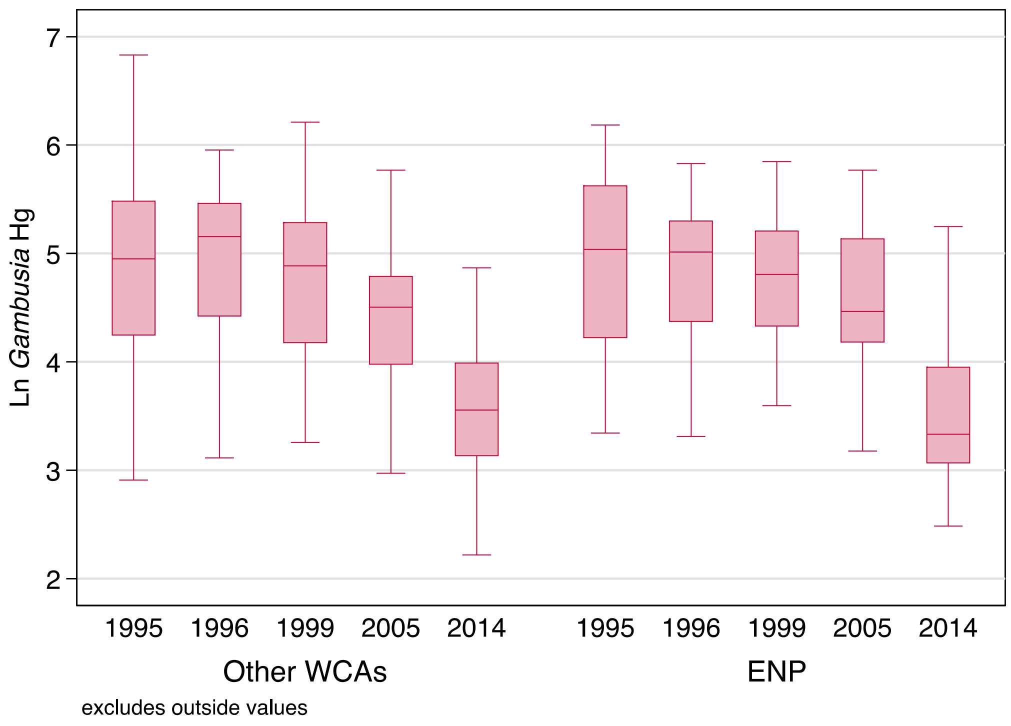
Periphyton Methyl Hg

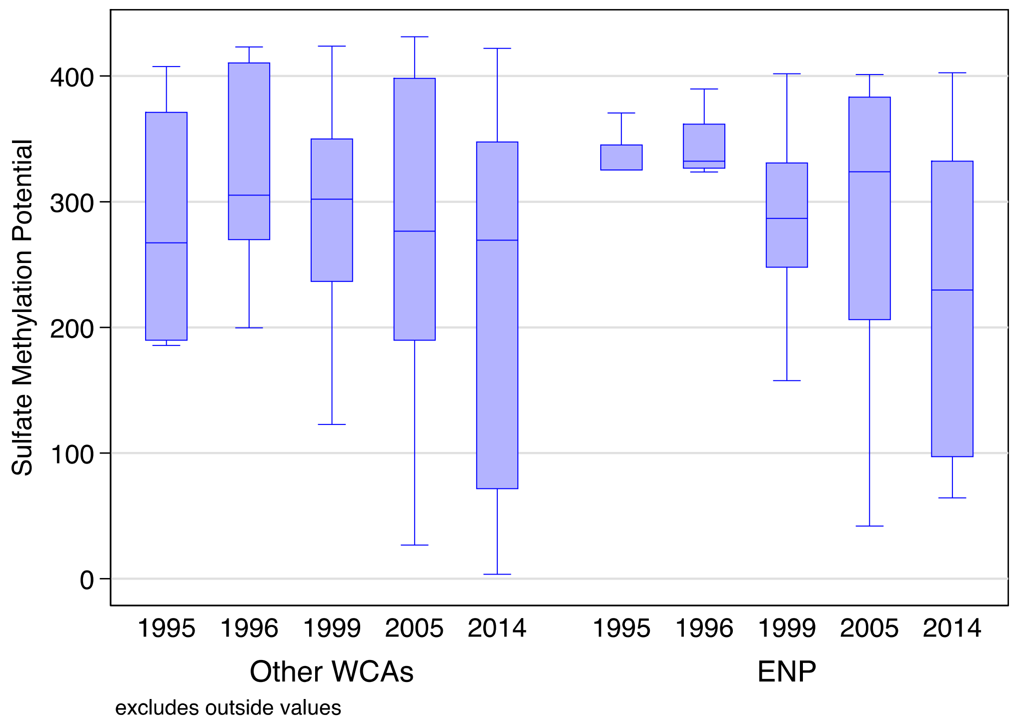


Surface Water Methyl Hg

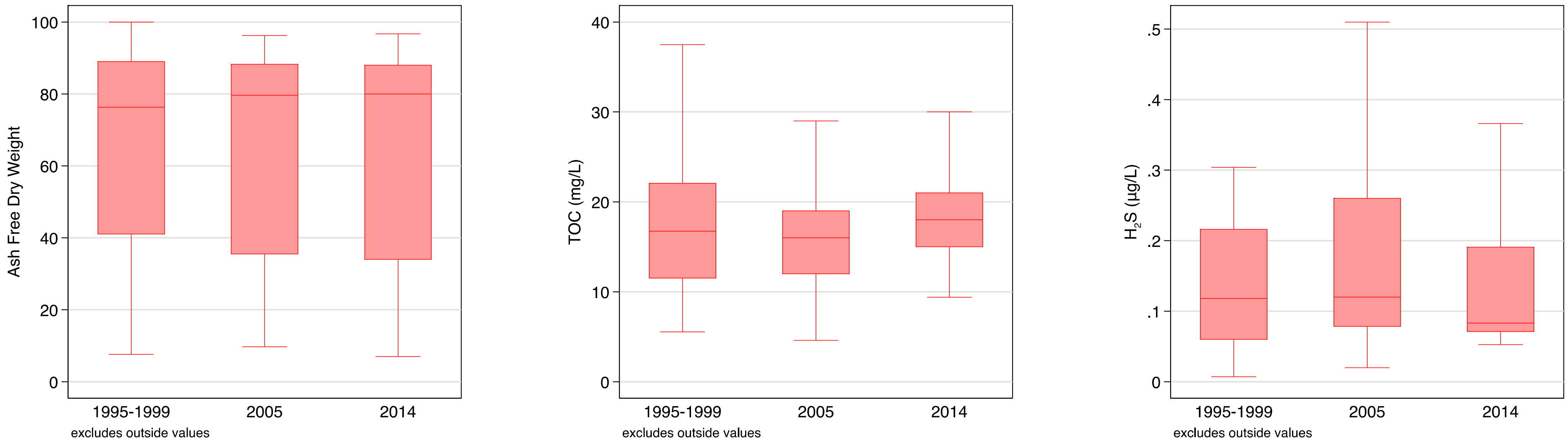
Trends in SEM Contributing Variables

Sulfate Methylation Potential



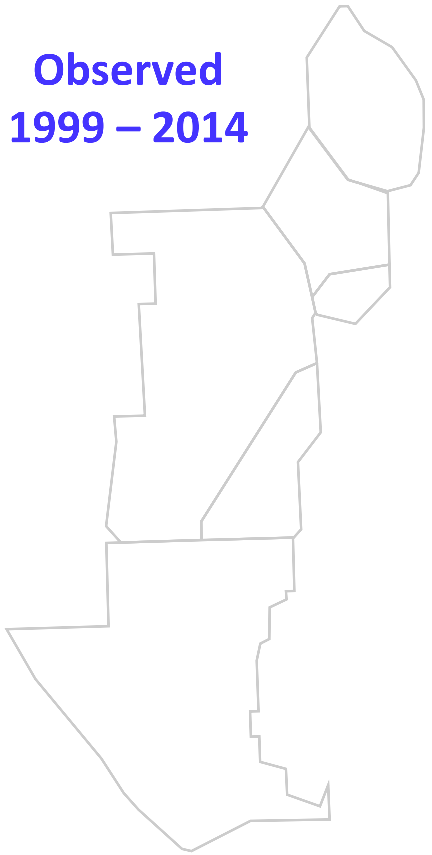


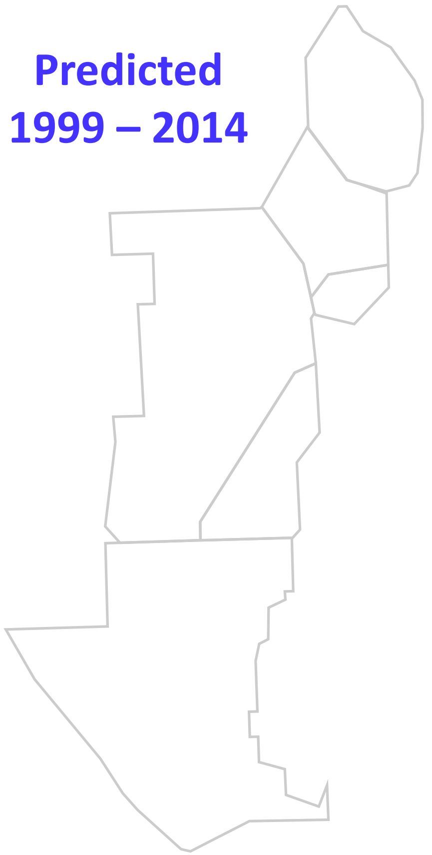
Trends in Other Model Exogenous Variables



Comparison of Observed with Predicted Changes in *Gambusia* Hg between 1999 and 2014

Dry season / Co-located sites*



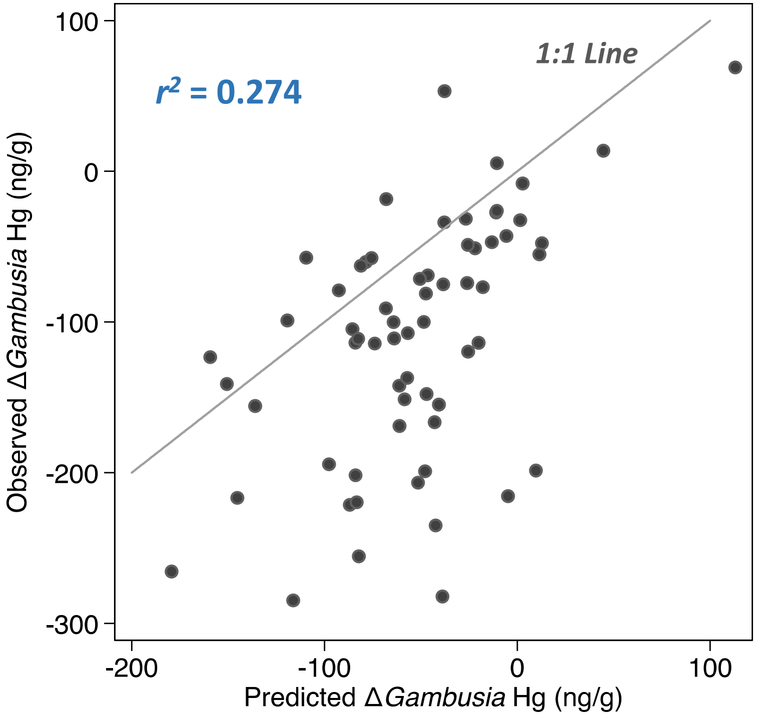


*Pollman (2012) grid system for identifying proximal sites.

Model Prediction Bias

Dry season / Co-located sites / *N* = 64 sites

Δ = 2014 – 1999



SEM model under predicts magnitude of change between 1999 and 2005 by an average value of 42%

Conclusions and Next Steps

- Pollman (2014) SEM model was recalibrated to R-EMAP Cycles 0-7 data to help resolve some bias in predicted *Gambusia* concentrations in Everglades National Park.
- The recalibrated model was used to predict *post hoc Gambusia* Hg concentration for R-EMAP Cycle 11 sampling (2014 wet season).
- SEM predicts a large decline in *Gambusia* Hg concentrations across the model domain between 1999 and 2005.
- Based on pairwise comparison of co-located sites, median predicted decline is 48 ng/g.
- Examination of trends in SEM independent variables suggests that a large shift in sulfate methylation potential is largely responsible of predicted declines. No other shifts in variable distributions appear to support the declines.

Conclusions and Next Steps

- Pairwise comparison of changes in *Gambusia* Hg concentrations for proximal sites between 1999 and 2014 indicate that the SEM under-predicts the magnitude of observed changes by an average of 42%.
- Plots of spatial changes for 1999-2014 time interval also indicates some concordance between observed and predicted changes. Overall comparison shows a highly significant correlation between observed and predicted *Gambusia* Hg equal to $r^2 = 0.274$ ($p < 0.0001$).
- Modeling supports the notion that Everglades biota Hg concentrations will react favorably to changes in sulfate methylation potential related to appropriate changes in sulfate concentrations, although it also indicates other variable dynamics (either not included or not measured) are likely important as well.
- Uncertainty in these effects could be evaluated with more work, including Monte Carlo simulations.
- Further model evaluation should be undertaken to identify further improvements (if possible given possible limitations to R-EMAP database).

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