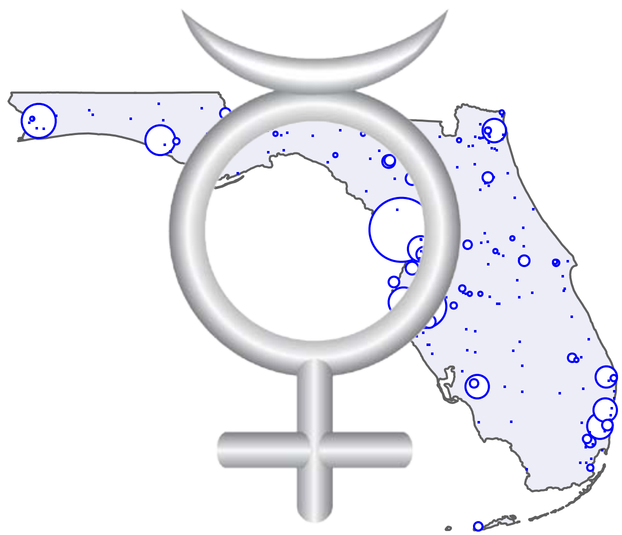
The Florida Statewide Hg TMDL Project – Annual Stakeholders' Meeting

Aquatic Modeling

PRELIMINARY RESULTS



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January 4, 2011

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AQUATIC MODELING OBJECTIVES

PRELIMINARY RESULTS

- Overall goals are to:
  1. Determine the magnitude of aquatic resources (freshwater lakes and streams) in Florida that are impaired.
  2. Predict how the current distribution will change in response to changes in atmospheric deposition fluxes of Hg.

Goal – Determine the Magnitude of Impaired Resources

PRELIMINARY RESULTS

It is not feasible to sample the full breadth of all 77,500 km of streams and rivers and 12,760 lakes in Florida.

- Develop empirical (statistical) models to predict the relationship between between water chemistry variables and LMB Hg concentrations.
  - Approach takes advantage of the fact that the variance in fish Hg concentrations *across* lakes largely reflects variations in biogeochemistry and other edaphic factors other than simply variations in atmospheric loadings of Hg.

Goal – Determine the Magnitude of Impaired Resources

PRELIMINARY RESULTS

- Need to determine the endpoint of interest.
  - Largemouth bass (LMB) sized 15 inches; and
  - LMB Hg concentrations greater than 0.2 mg/kg (preliminary threshold)
- Use the statistical models in conjunction with ambient water quality collected for Florida lakes and streams as part of the FDEP SMN to predict LMB distributions across the state.
  - Use SMN scaling factors for individual TMDL basins (total of 28 freshwater basins) to develop *cfd's*.

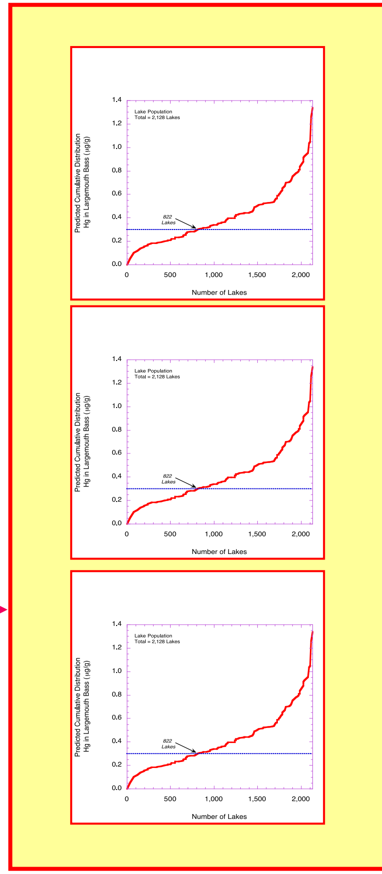
Goal – Determine the Magnitude of Impaired Resources

PRELIMINARY RESULTS

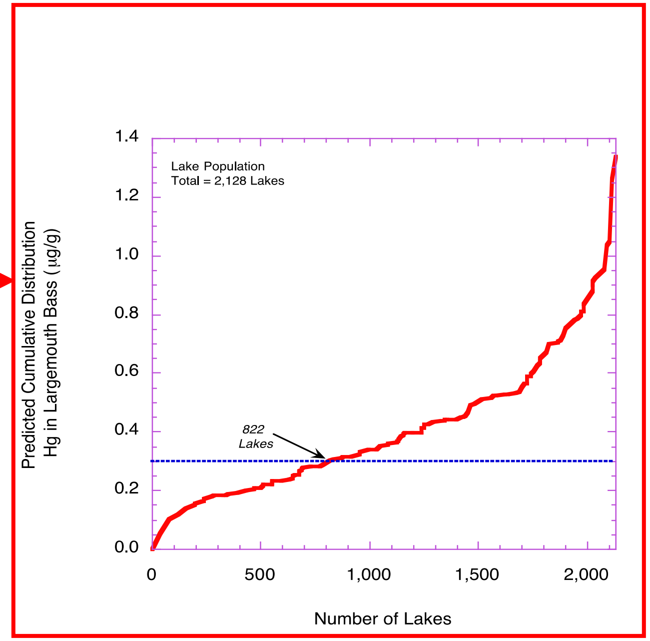
Sample lakes using balanced bins
125 bins
N = 128

Develop Empirical Model

Apply model to each TMDL basin using randomized, stratified sampling



Cfd's for individual TMDL basin



Cfd for entire State of Florida

Elements of Aquatic Modeling

PRELIMINARY RESULTS

- Develop approach to normalize individual measurements of LMB Hg concentrations to the target endpoint (15” LMB) for each lake and stream/river segment.
- Develop integrated statistical database
  - Water quality
  - Atmospheric deposition fluxes
  - Sediment chemistry
  - Normalized fish tissue Hg concentrations – EHg_{15}
- Develop statistical models for streams and lakes
- Develop estimates of LMB Hg *cfd* in the Everglades using REMAP data for *Gambusia* and inferred estimates of LMB Hg based on co-located samples.
- Develop estimates of Hg fluxes to surface waters via permitted point source discharges

SEDIMENT SAMPLING

PRELIMINARY RESULTS

- Sample lakes @ location in each lake sampled previously by FWC
- Collect vertical profile of DO and temperature, pH, specific conductance. Measure secchi transparency.
- Sample surficial sediments with Ekman > Petit Ponar > Core
- Split sample between FDEP and UM
- Analytes measured:
  - FDEP: Al, As, Cd, Co, Cr, Cu, Fe, Hg, K, MeHg, Mg, Mn, Ni, Pb, Sb, Se, Sr, Ti, V, Zn, TC, TOC, TP, TKN
  - UM: Stable Hg isotopes
- Sampling and trace element analyses for all 131 lakes have been completed by FDEP and a QA'ed data set supplied to *ALL* in mid-December 2010.

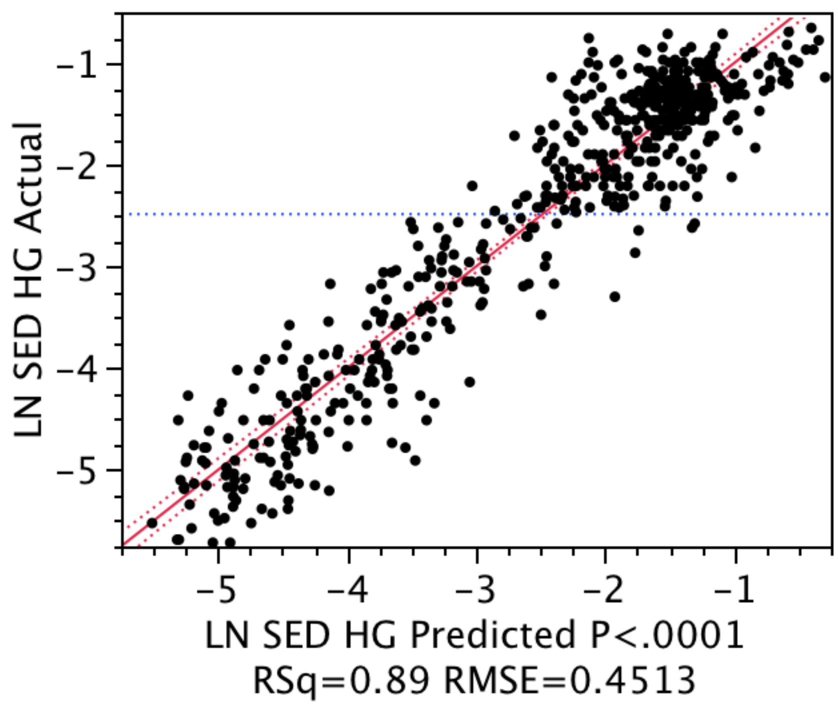
Initial Approach to Computing Hg Enrichment in Sediments

PRELIMINARY RESULTS

1. Use Florida DEP SMN database on concentrations of trace elements and nutrients in Florida lakes.
2. Total *N* = 747 observations. Samples collected in:
   - 2004
   - 2005
   - 2006
3. Screen data to remove qualified observations. Total *N* reduced to 620 observations.
4. Remove multivariate outliers (using ln-transformed Al, Cr, Cu, Fe, Hg, Ni, Pb, Zn, TP, TKN, and TOC as variables) based on Mahalanobis distance. Final *N* = 567 observations.
5. Calculate Hg enrichment attributable to smaller scale processes (local to sub-regional) using PCA and absolute factor score analyses (Thurston and Spengler, 1985).

Predicted* vs. Observed Sediment Hg Concentrations (ln-transformed) in SMN Lakes

PRELIMINARY RESULTS

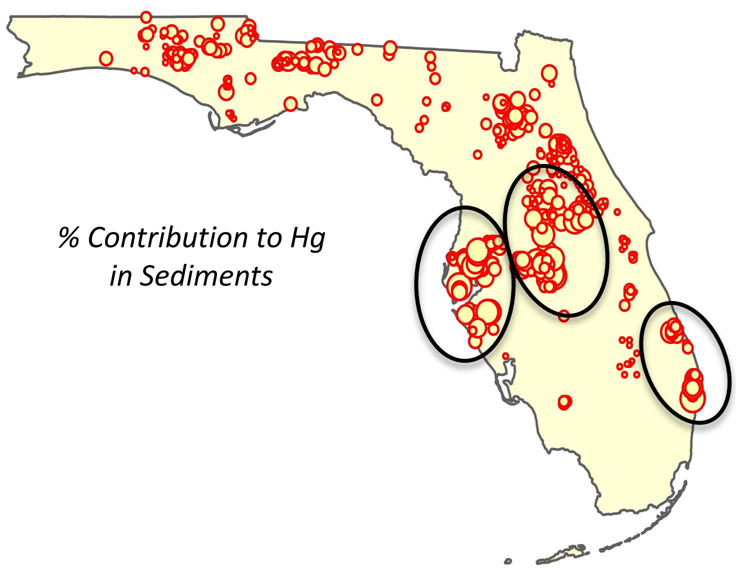


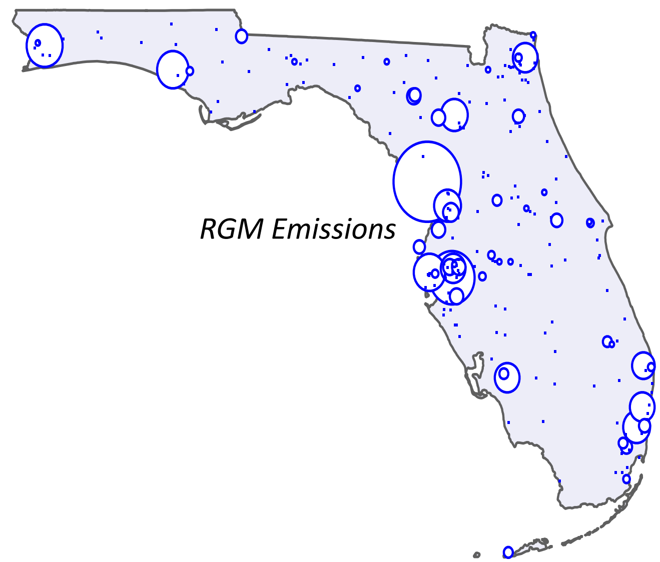
*Predicted concentrations based on PCA model with three extracted components. Model variables include ln-transformed Al, Cr, Cu, Fe, Hg, Ni, Pb, Zn, TP, TKN, and TOC.

Enrichment of Hg in Florida Lake Sediments - % Contribution of Apparent Local Sources and Spatial Distribution of RGM Emissions

N = 567 Lakes

PRELIMINARY RESULTS





Speciated emissions from 2005 NEI with some source corrections for Florida (F. Marsik, unpublished data). Maximum RGM emission = 209 kg/yr.

Maximum apparent local contribution = 85%, median contribution = 9%

VALIDATION OF PCA MODEL APPROACH TO PREDICTING SEDIMENT HG

PRELIMINARY RESULTS

Use PCA model developed for SMN lake sediments to predict Hg in:

- Hg TMDL lake sediment data set (*N* = 131)
  - 2009 (55 lakes)
  - 2010 (76 lakes)
- Biernacki *et al.* reference lakes and streams data set (46 lakes and 74 streams)
  - 1997

Validation of SMN PCA Model using Hg TMDL & Biernacki et al. Sediment Data Sets

PRELIMINARY RESULTS

Hg TMDL

Biernacki et al.

1:1 Line

Lakes

Streams

–6 –

–8 –

-

APPLICATION OF SMN PCA MODEL TO HG TMDL & BIERNACKI *ET AL*. SEDIMENT DATA SETS – ANALYSIS OF RESIDUALS*

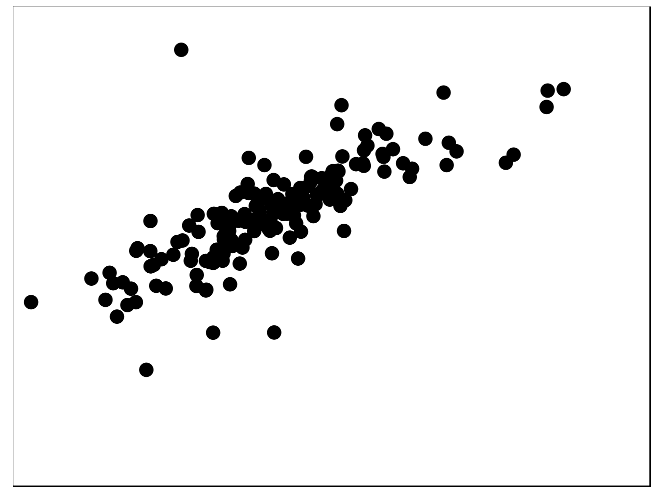
PRELIMINARY RESULTS

–0.2 –

*Positive residuals – Observed values > predicted values

New PCA Model Using All 3 Sediment Data Sets and Including Transformed Year as a Variable

PRELIMINARY RESULTS



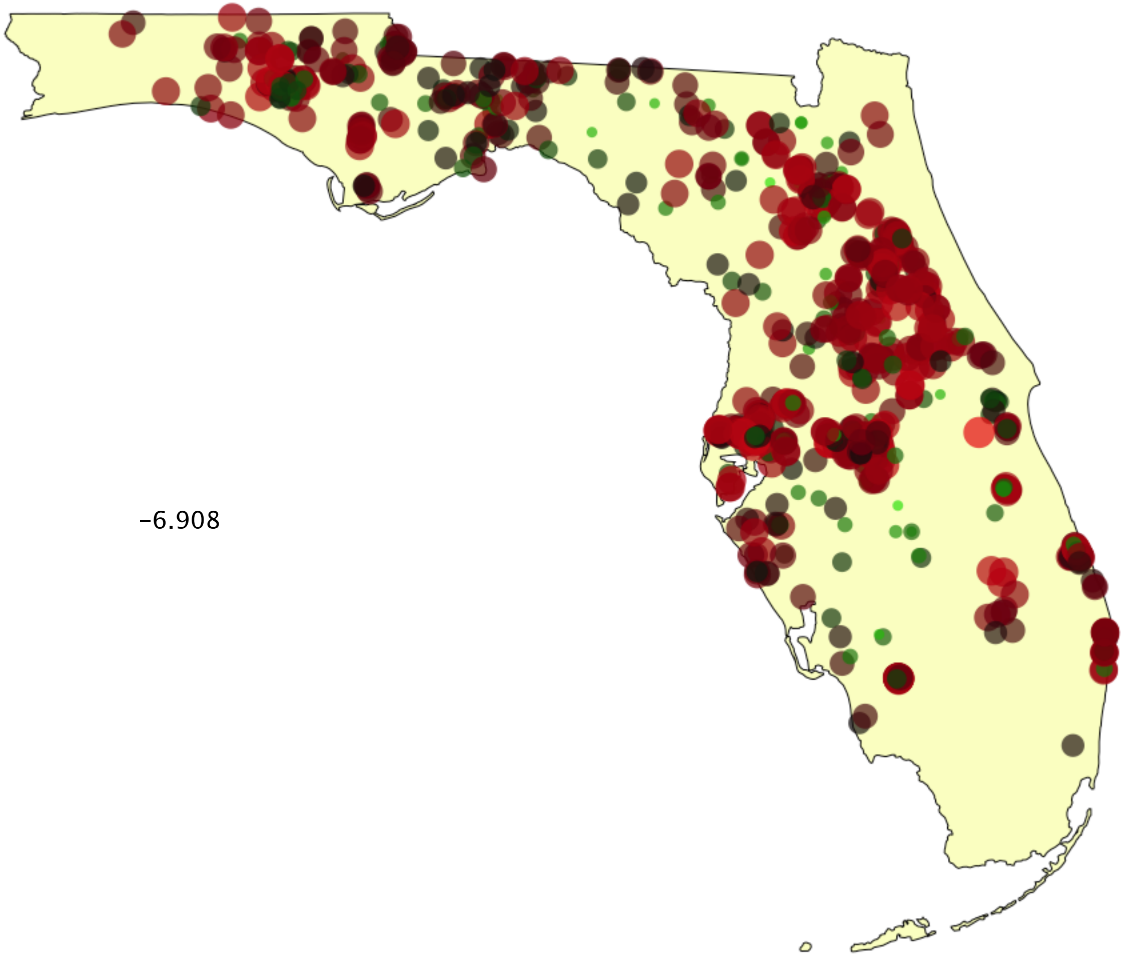
–7 –

Standardized β coefficients indicate following order of variable importance contributing to measured Hg concentrations:

Selective size sorting > volatile trace elements > weathering > non-volatile trace elements

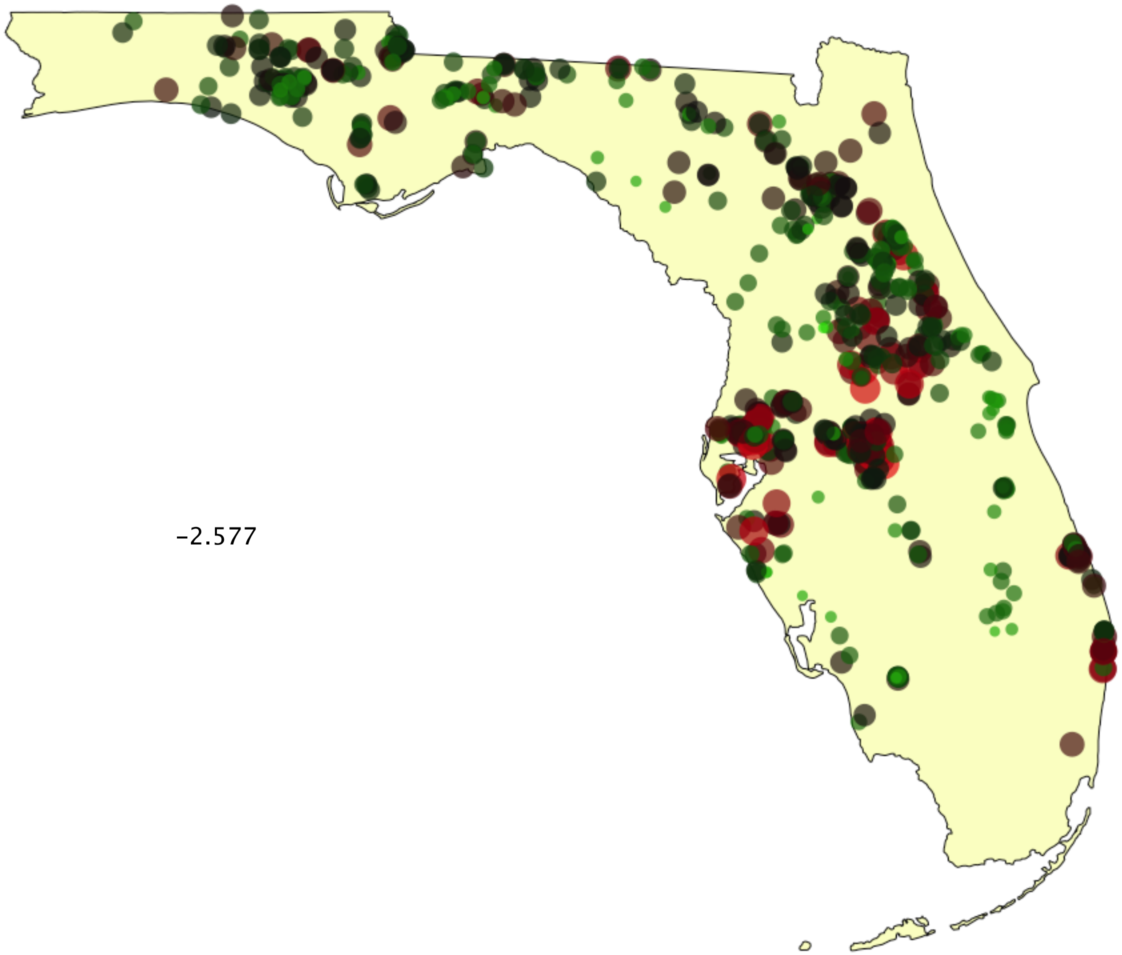
Sediment Sampling Results – Spatial Distribution of Hg in Surficial Lake Sediments

PRELIMINARY RESULTS



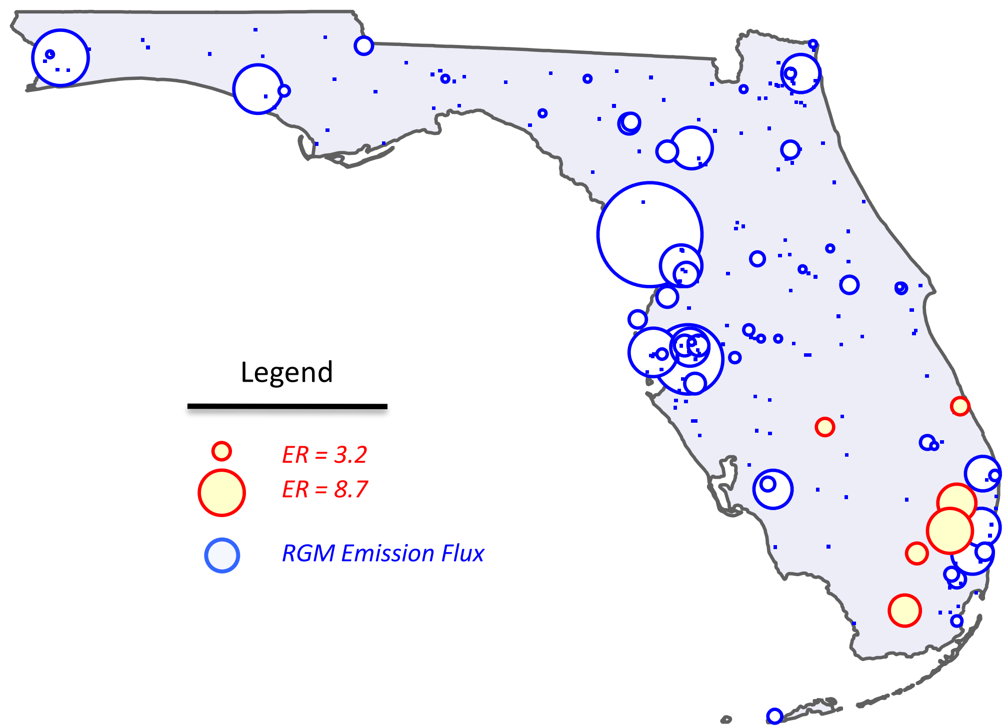
Sediment Sampling Results – Spatial Distribution of Volatile Anthropogenic PCA

PRELIMINARY RESULTS



Sediment Enrichment – Flux Ratios in South Florida Ecosystems and RGM Emissions in Florida

PRELIMINARY RESULTS



Data from Rood *et al.* 1995. *Water Air Soil Poll.* 80: 981-990; and Engstrom, Pollman, and Fitzgerald, *unpublished data.*

Preliminary Modeling – Multiple Linear Regression Model

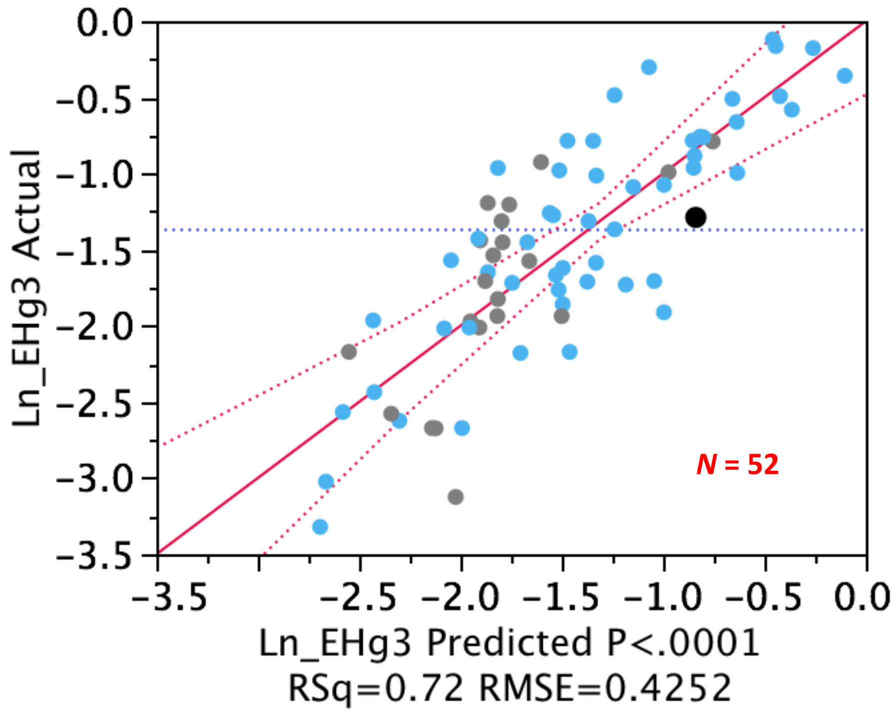
Approach to Preliminary Modeling

PRELIMINARY RESULTS

- Use *ln*-transformed variables to improve model fit and error behavior
- Normalize largemouth bass Hg concentrations for each lake and stream to the same endpoint (age 3).
- Use stepwise regression to identify suite of variables of interest
- Check for IV collinearity (VIF test). Run MLR model iteratively to remove non-significant variables and variables with collinearity problems. Verify individual IV-DV relationships are consistent with theoretical expectations.
- Eliminate obvious outliers based on leverage plots.
- Inspect model residuals.
- Run model for Lange *et al.* data set and compare results.

MLR Fit to Preliminary Hg TMDL Lakes Data

PRELIMINARY RESULTS



*Ln EHg3 = f(Alk, NH_3, Chla, TP, UFMeHg)**

**All variables ln-transformed*

Variable Importance

Term	Estimate	Std Error	t Ratio	Prob>|t|	Std Beta
Ln_UFMeHg	0.41694	0.06900	6.04	<.0001	0.56087
Ln_ALK (ueq/L)	-0.18334	0.03472	-5.28	<.0001	-0.45114
Ln_TP	-0.19881	0.07370	-2.70	0.0097	-0.26125
Ln_CHLA	-0.17321	0.06301	-2.75	0.0085	-0.25498
Ln_NH3 (ueq/L)	-0.08877	0.05131	-1.73	0.0903	-0.15584
Intercept	0.41423	0.43363	0.96	0.3444	.

UFMeHg > Alk >> Chl *a*, TP > NH_3

PRELIMINARY RESULTS

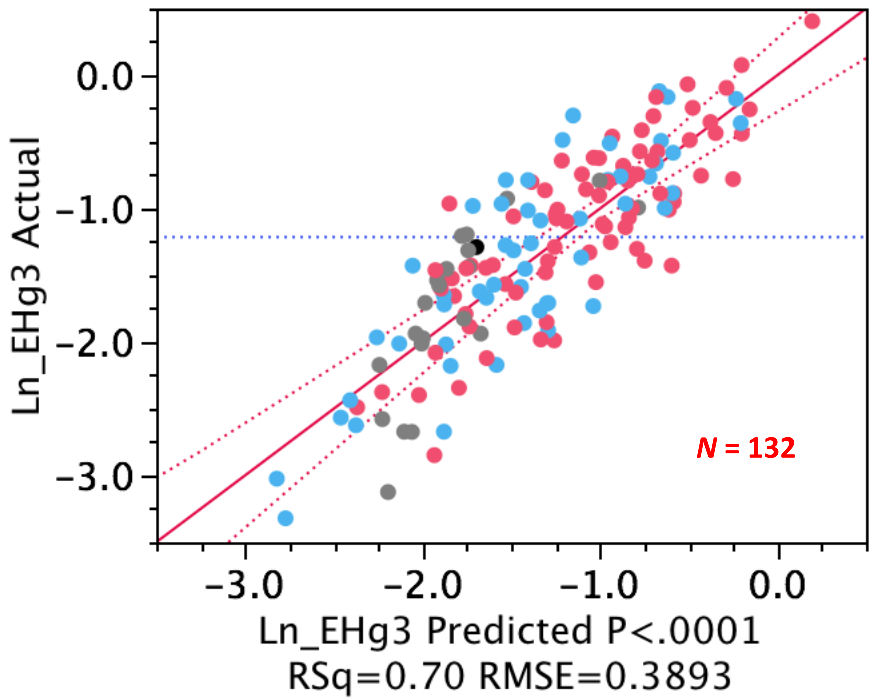
VALIDATION WITH LANGE *ET AL.* DATA SET

PRELIMINARY RESULTS

–3.0 –

COMBINED LAKES MODEL

PRELIMINARY RESULTS



*Ln EHg3 = f(Alk, NH_3, Chla, TP, UFMeHg, UFHg)**

All variables ln-transformed

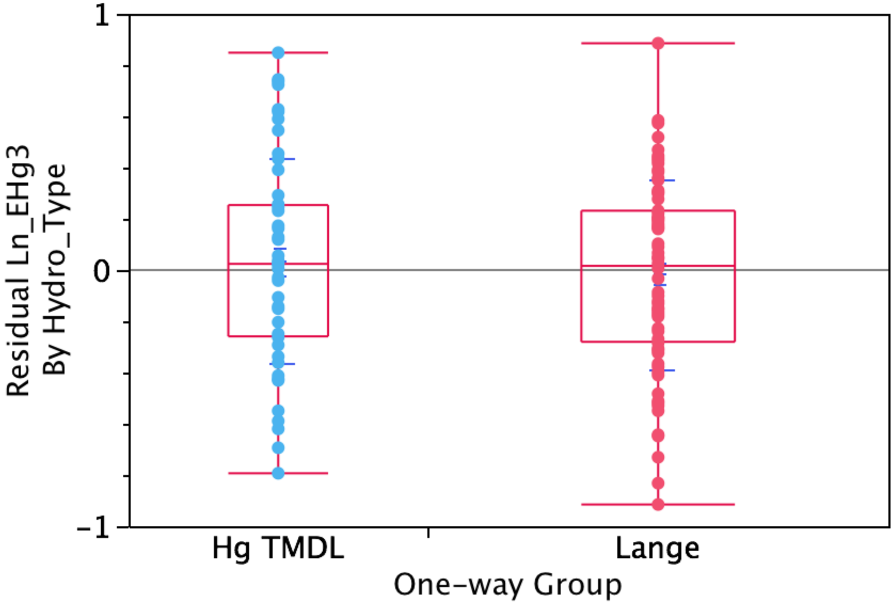
Variable Importance

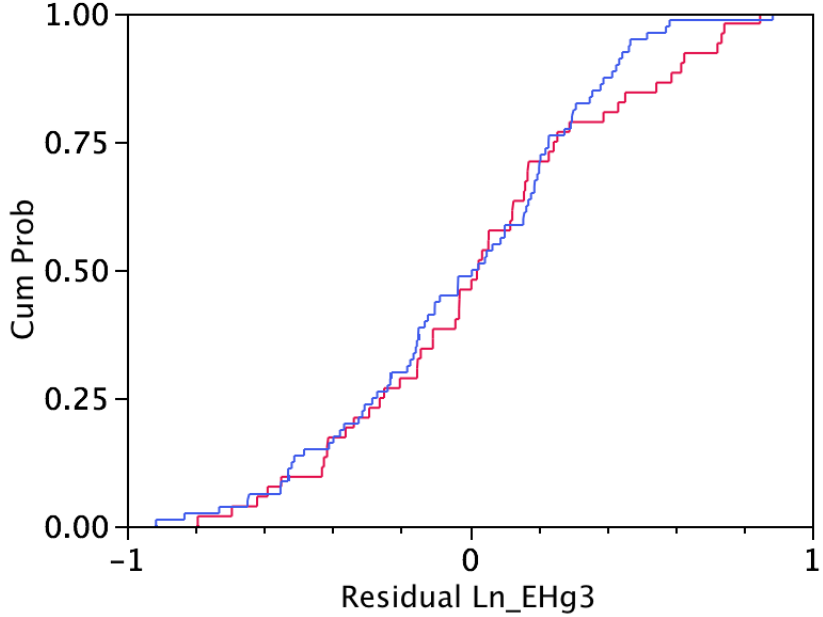
P R E L I M I N A R Y
R E S U L T S

Term	Estimate	Std Error	t Ratio	Prob>|t|	Std Beta
Ln_UFMeHg	0.24931	0.04651	5.36	<.0001	0.36796
Ln_ALK (ueq/L)	-0.12439	0.02634	-4.72	<.0001	-0.31640
Ln_CHLA	-0.15799	0.03225	-4.90	<.0001	-0.30936
Ln_UFHg	0.29626	0.08478	3.49	0.0007	0.29553
Ln_TP	-0.20284	0.05733	-3.54	0.0006	-0.26541
Ln_NH3 (ueq/L)	-0.07940	0.03569	-2.22	0.0279	-0.12530
Intercept	-0.51903	0.36320	-1.43	0.1555	.

UFMeHg > Alk, Chl *a*, UFHg > TP >> NH_3

Compare Residuals to Test for Bias

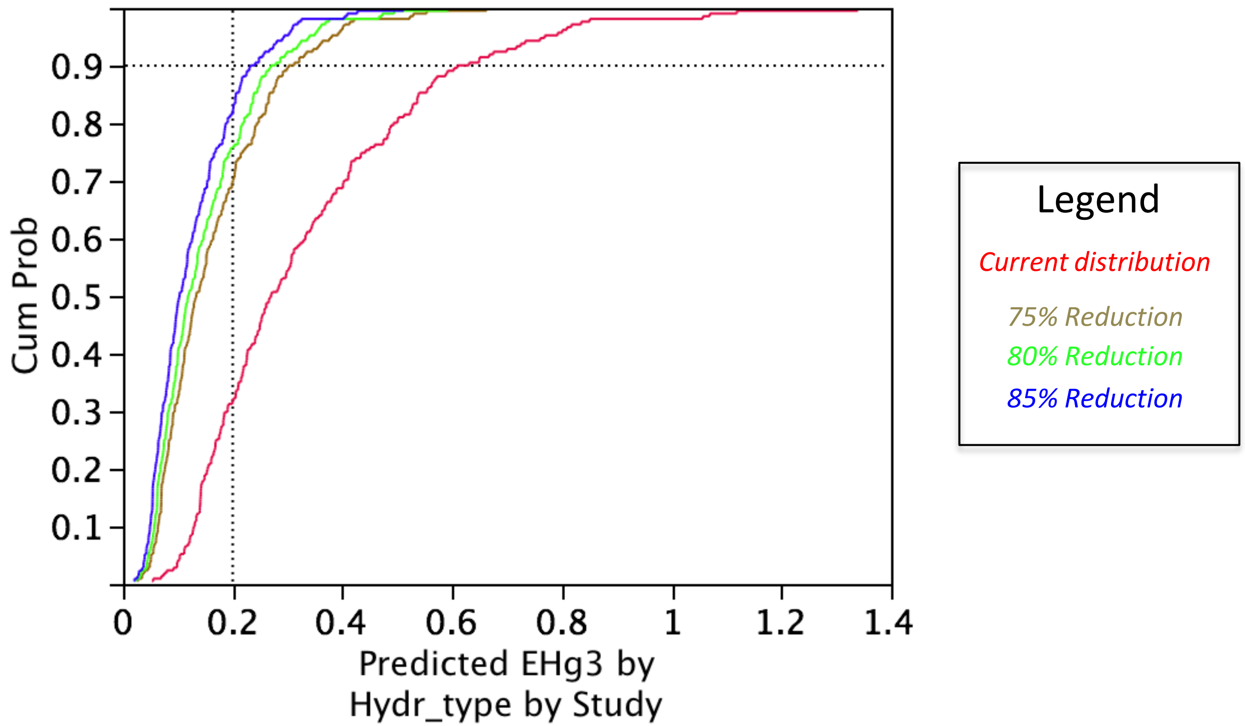




No systematic difference in residuals between the two data sets except at upper end of distribution

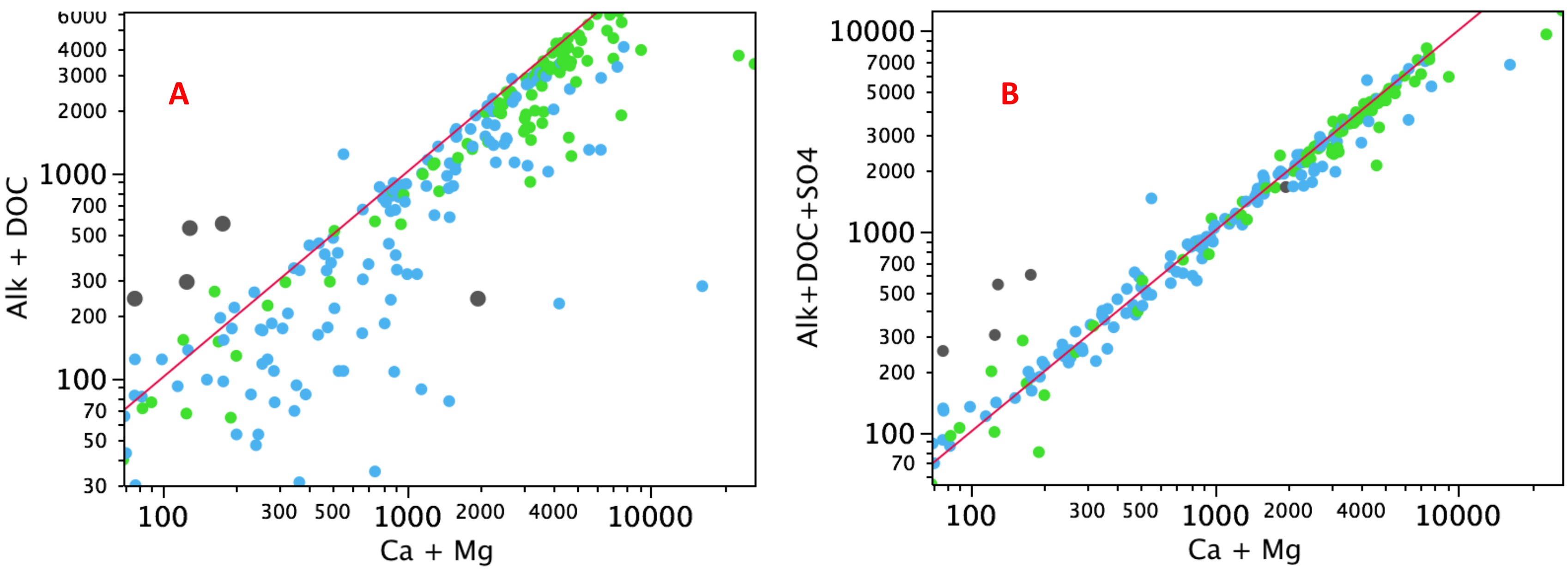
PRELIMINARY CALCULATIONS ON EFFECTS OF REDUCING HG CONCENTRATIONS ON PREDICTED LMB HG DISTRIBUTION IN HG TMDL LAKES

PRELIMINARY RESULTS



Preliminary Analysis of Effects of Excess SO4 on Alkalinity

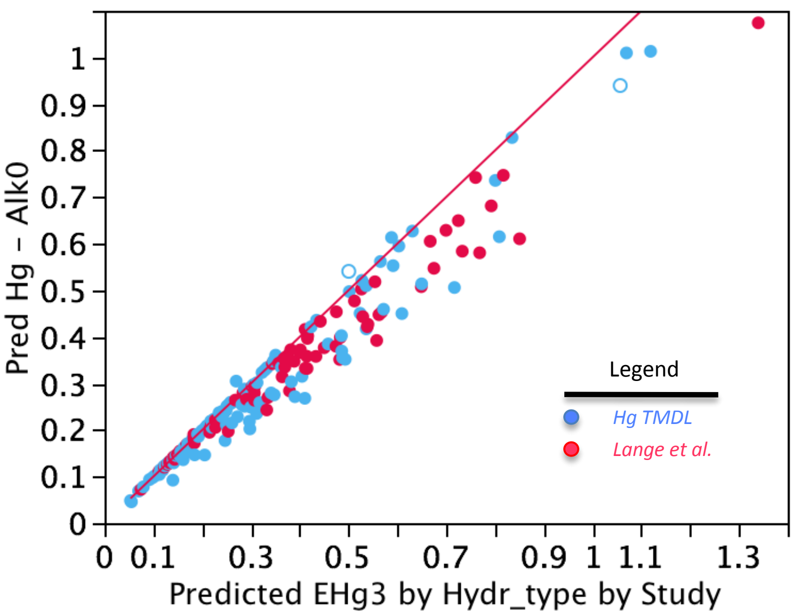
PRELIMINARY RESULTS



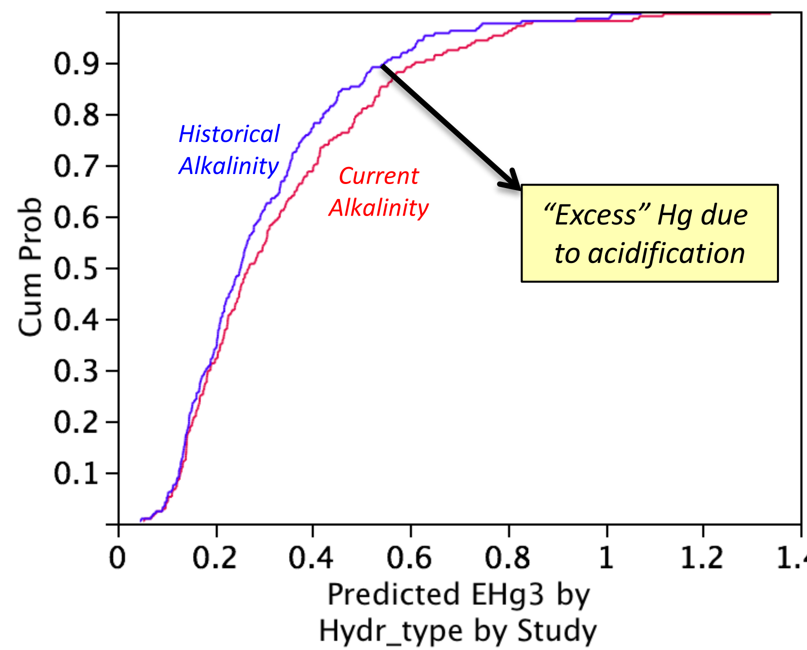
1. Excess Ca+Mg primarily reflects titration of alkalinity by acidic deposition (excess SO4).
2. Outliers above expected line may have analytical problems – verified by cross check with cation-anion balance.

Effects of Reducing Excess SO4 on Predicted LMB Hg Distribution in Hg TMDL and Lange et al. Lakes*

Estimated Historical EHg3 *vs.* EHg3 predicted as function of current alkalinity



Predicted Historical and Current EHg3 Distribution



*Note – First order analysis assuming excess sulfate results in a 1:1 equivalent reduction in alkalinity and that historical concentrations of Ca + Mg were equivalent to current levels. Excess sulfate is calculated as the difference between observed and expected concentrations based on ambient chloride concentrations (marine contributions).

Aquatic Modeling Status - Conclusions

P R E L I M I N A R Y R E S U L T S

- Lake and stream water quality and fish tissue sampling for all 256+ lakes and streams has been completed. Full data set should be internally available within a couple of weeks.
- Sediment sampling and analysis has been completed, and a working data set has been delivered to *ALL.*
- Preliminary PCA modeling of occurrence of Hg in lake sediments has been completed using data collected as part of the SMN between 2004-2006.
- Preliminary results from the SMN model suggest a median local signal contribution ~ 9%, and maximum contribution of 85%
- The recent Hg TMDL data set was used to validate the SMN approach to predicting sediment Hg concentrations.
- SMN model validation also suggests that the sediment Hg signal has declined across a large number of lakes since 1997.
- Preliminary MLR modeling was conducted with an early (incomplete) set of results for 52 lakes.
- Validation of the preliminary Hg TMDL MLR model predictions using the Lange *et al.* lakes data set shows promising results. MLR modeling using the combined data sets shows no consistent difference in residuals except at the upper tail of residuals *cfd*. This will need to be explored more fully in future modeling efforts.
- Analysis of alkalinity (corrected for DOC) as a function of Ca + Mg concentrations shows the titration effects of excess SO4 on alkalinity. First order analyses were conducted illustrating the likely effects of lake acidification on exacerbating the Hg signal in LMB.