Validation of Biotic Ligand Model Performance in Extremely Hard Surface Waters

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SETAC NA - Baltimore

Nov. 14, 2005

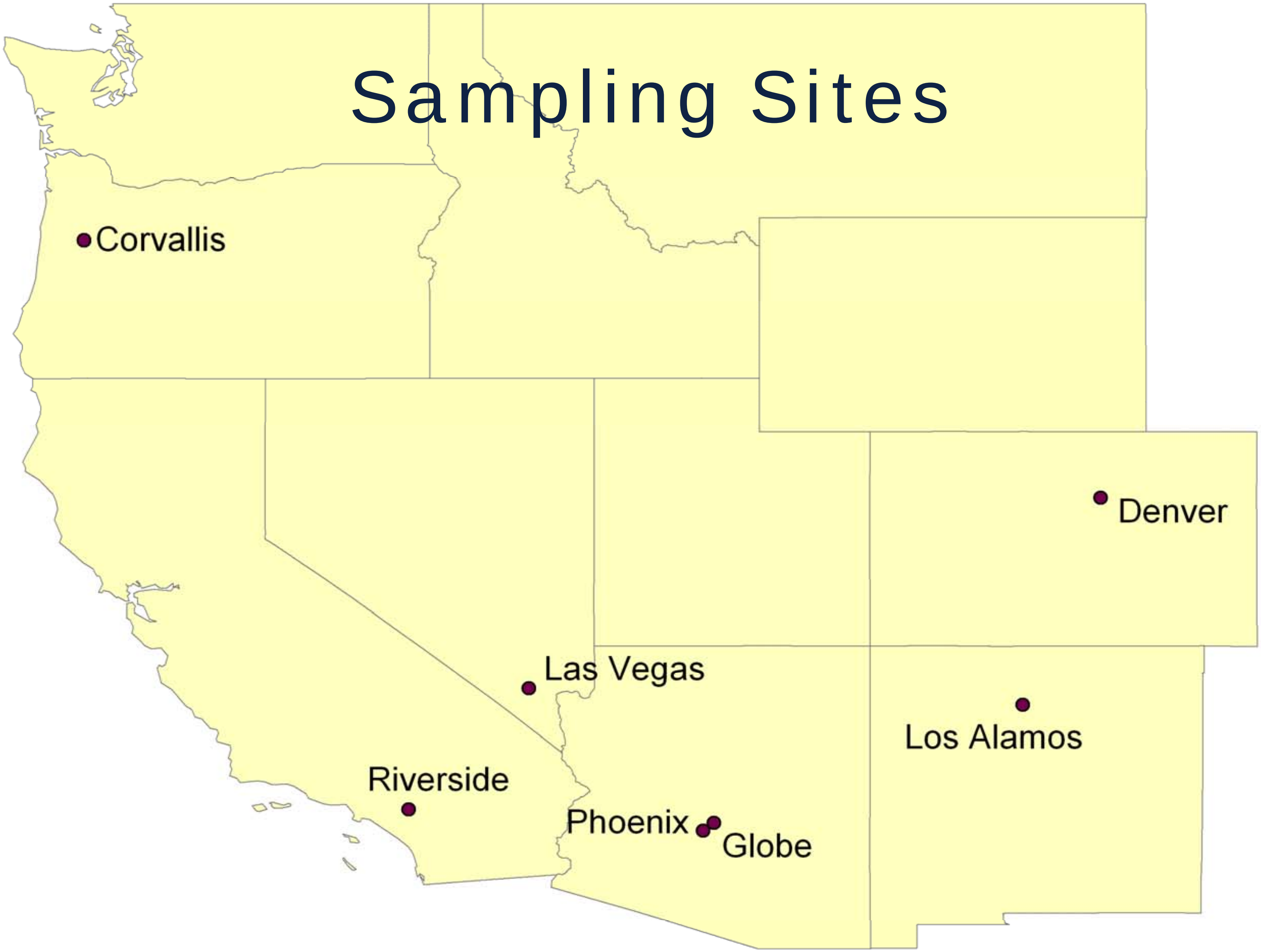
Background

- **Copper regulations inaccurate for Arid West surface waters**
  - **Elevated hardness (e.g., up to 1200 mg/L)**
  - **No co-variance between hardness and alkalinity**
- **Dischargers create effluent-dependent ecosystems**

Project Objectives

- **Conduct series of acute Water Effect Ratio studies with a range of natural waters**
  - **3 species (*C. dubia, D. pulex, P. promelas)***
  - **7 sites to encompass range of WQ conditions**
  - **High- vs. low-flow conditions**
- **Statistical comparison of BLM and empirical results**
  - **Focus on role of alkalinity vs. hardness in very hard waters (> 400 mg/L)**
  - **Under what conditions are BLM predictions more or less valid?**

Sampling Sites

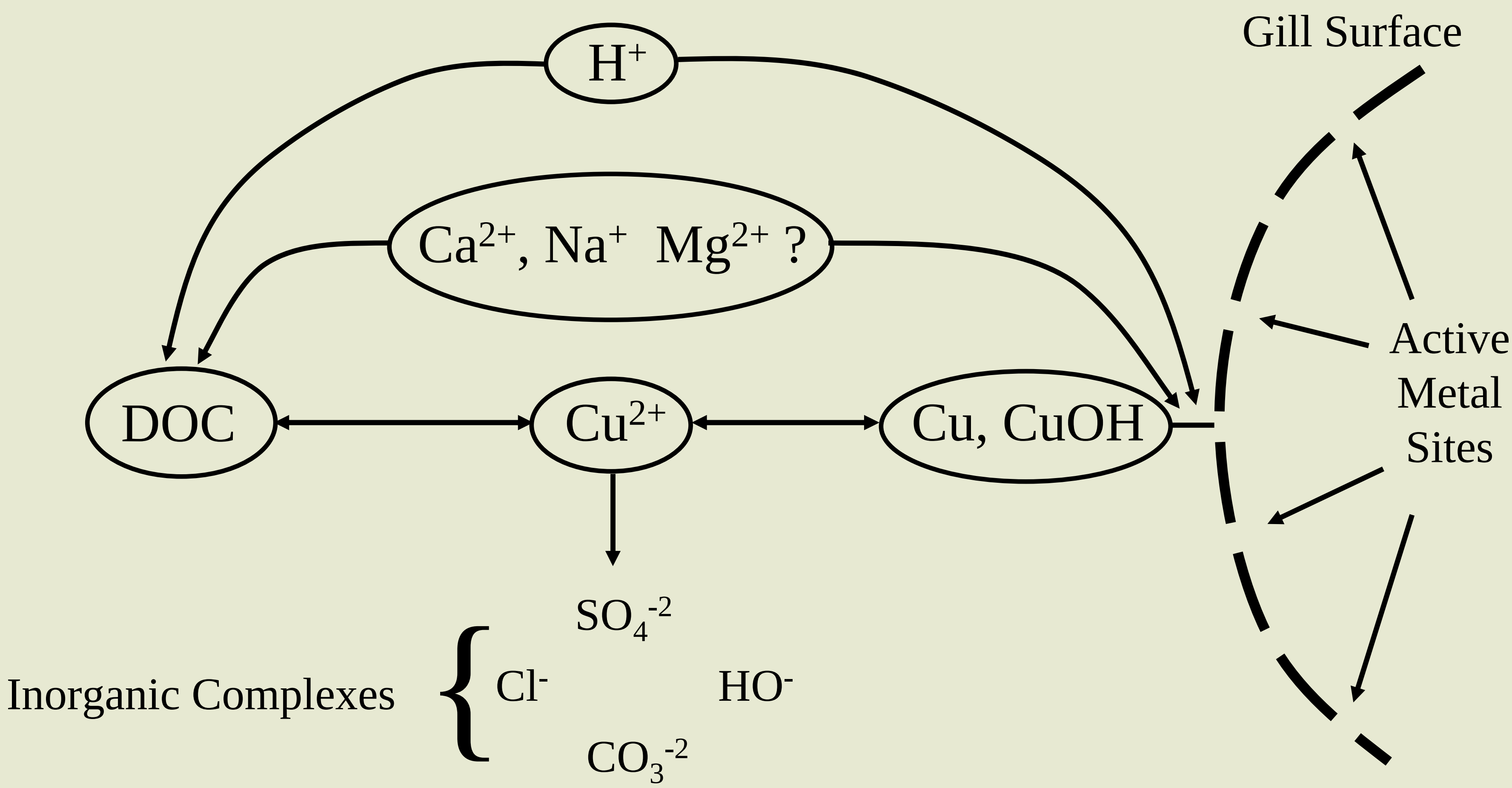


WER Study Locations

Biotic Ligand Model (BLM)

- **Uses water chemistry and metal-organism interactions to predict metal toxicity.**
- **Toxicity occurs when metal accumulation reaches a critical concentration within the most sensitive tissue (e.g., the gills of freshwater fish).**
- **Relates Cu toxicity to pH, DOC, Ca, Mg, alkalinity.**
- **Key component of freshwater CMC in draft AWQC (USEPA 2003)**

BLM Basis



[DiToro, 2000]

BLM Input Data

- **Water chemistry from WER studies**
  - **Site and lab waters**
  - **All flow conditions**
- **Water chemistry from calcium/ magnesium studies**
  - **Influence of elevated Ca (30 – 400 mg/L) and Mg (30 – 250 mg/L) on copper toxicity to fish and daphnids**

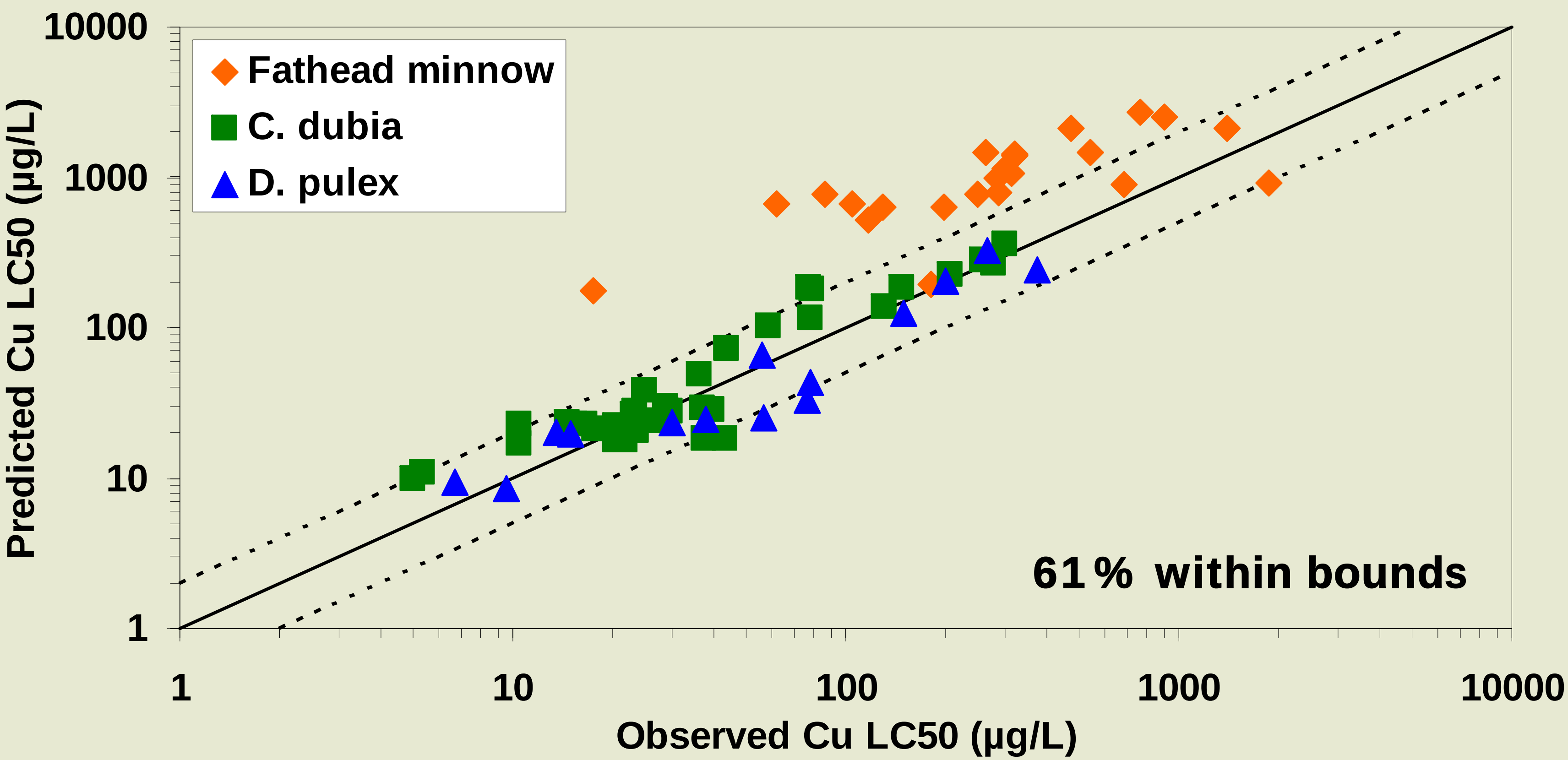
Water Quality – Base Flow

Site	Hardness (mg/L as $CaCO_3$)	Alkalinity (mg/L as $CaCO_3$)	DOC (mg/L)
Sandia Canyon, NM	56	124	4.4
Santa Ana R., CA	188	164	2.5
S. Platte R., CO	280	204	9.8
Calapooia R., OR	284	228	1.2
Salt R., AZ	388	180	6.9
Las Vegas Wash, NV	780	128	5.4
Pinal Cr., AZ	1100	16	0.7

Ca:Mg Study Design

	Ca	Mg	Hardness	Alkalinity
Ca:Mg	mg/L		mg/L as $CaCO_3$	
0.09	43.0	239.0	1070	152
0.11	36.6	189.0	820	144
0.16	42.1	166.0	640	152
0.26	43.5	101.0	420	148
0.67	32.9	31.5	196	144
2.24	105.0	29.0	395	140
3.86	172.0	33.1	580	140
5.48	271.0	29.3	810	140
7.10	383.0	38.6	1030	140

BLM Results



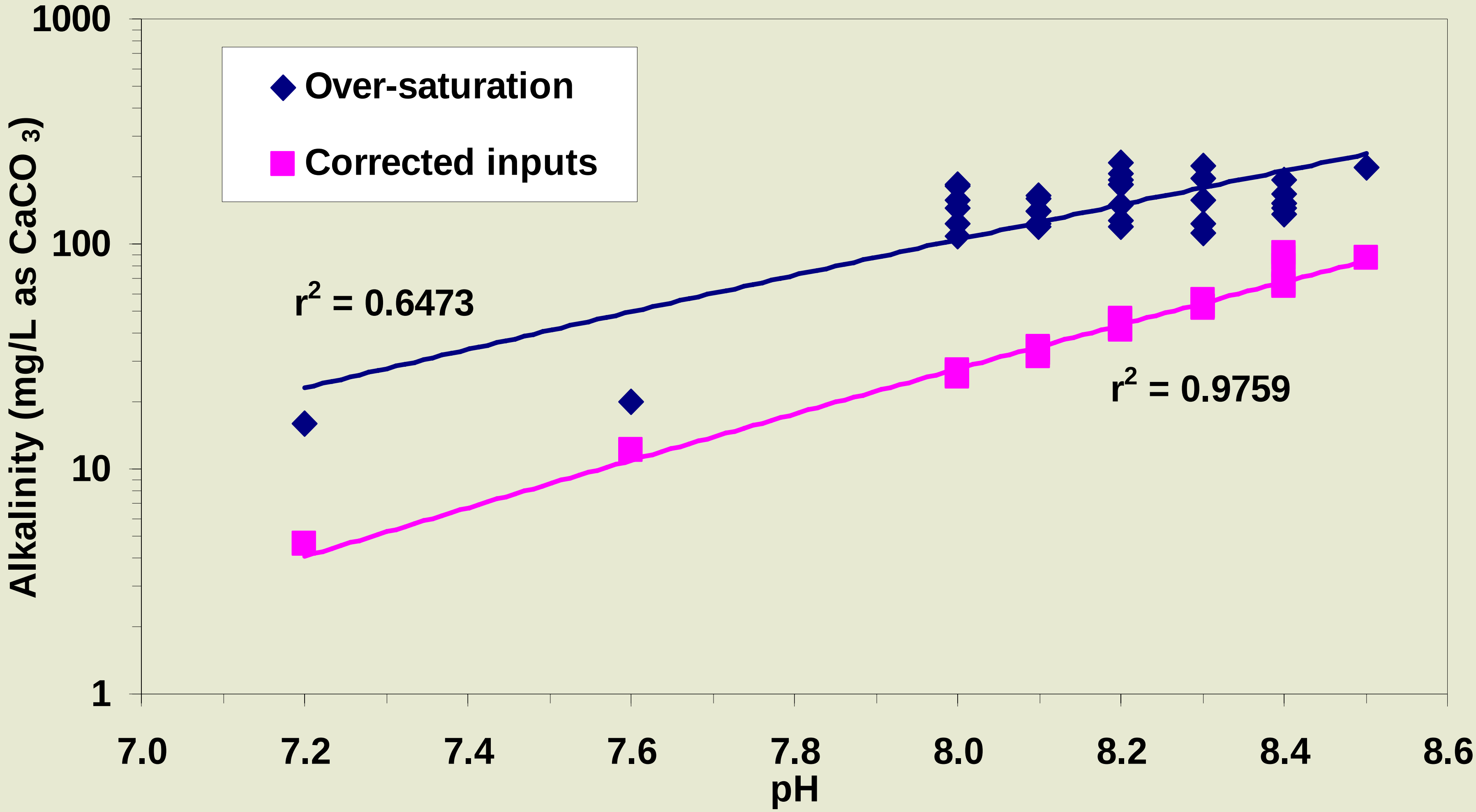
Model Adjustment: None

Potential Solutions

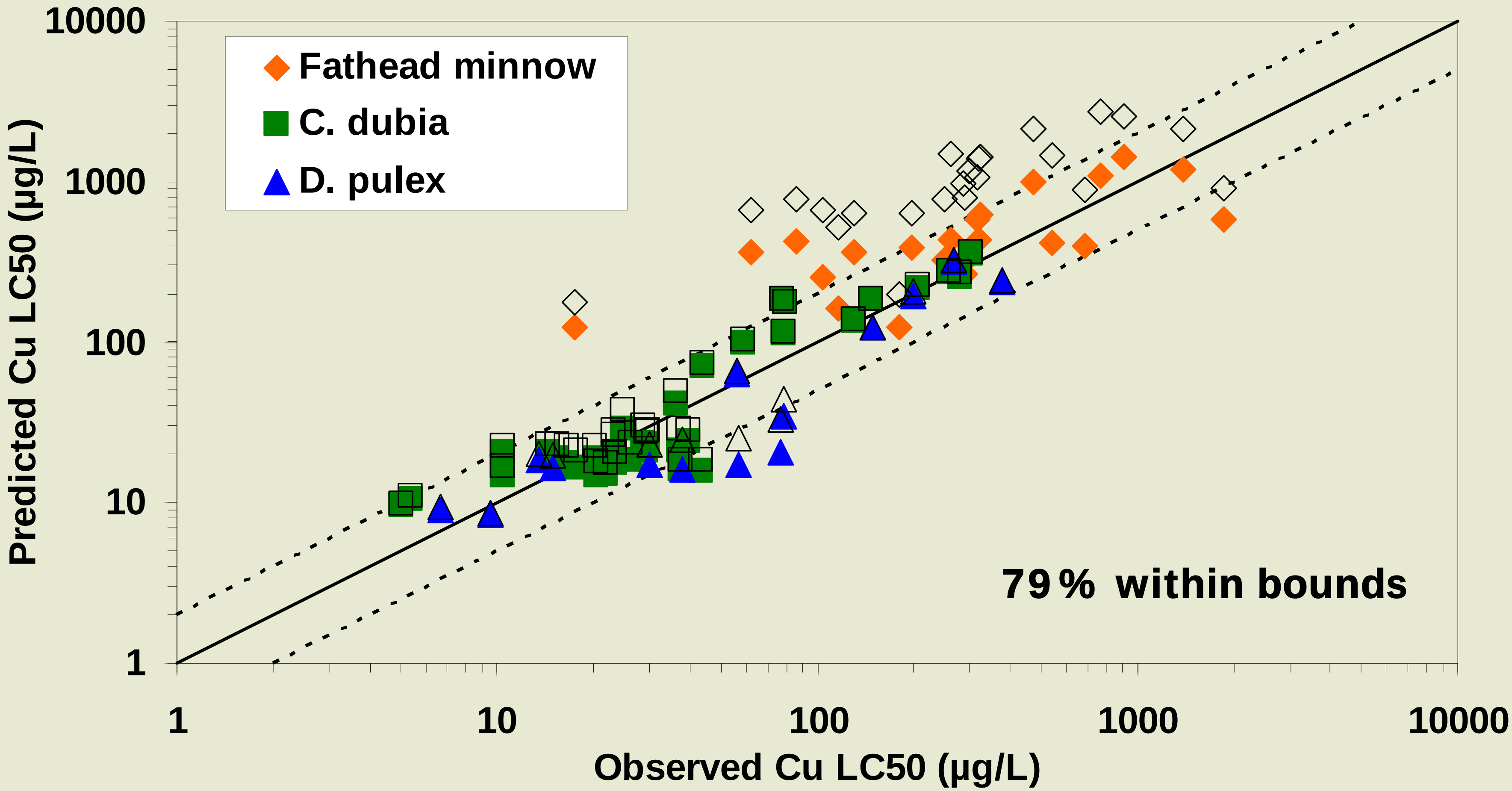
- **Determine impact of individual water quality parameters on model output (i.e., residual analysis)**

- **Characterize the importance of calcium <u>and</u> magnesium on copper toxicity at very high hardness**

Saturation Issues in Hard Water



BLM Results



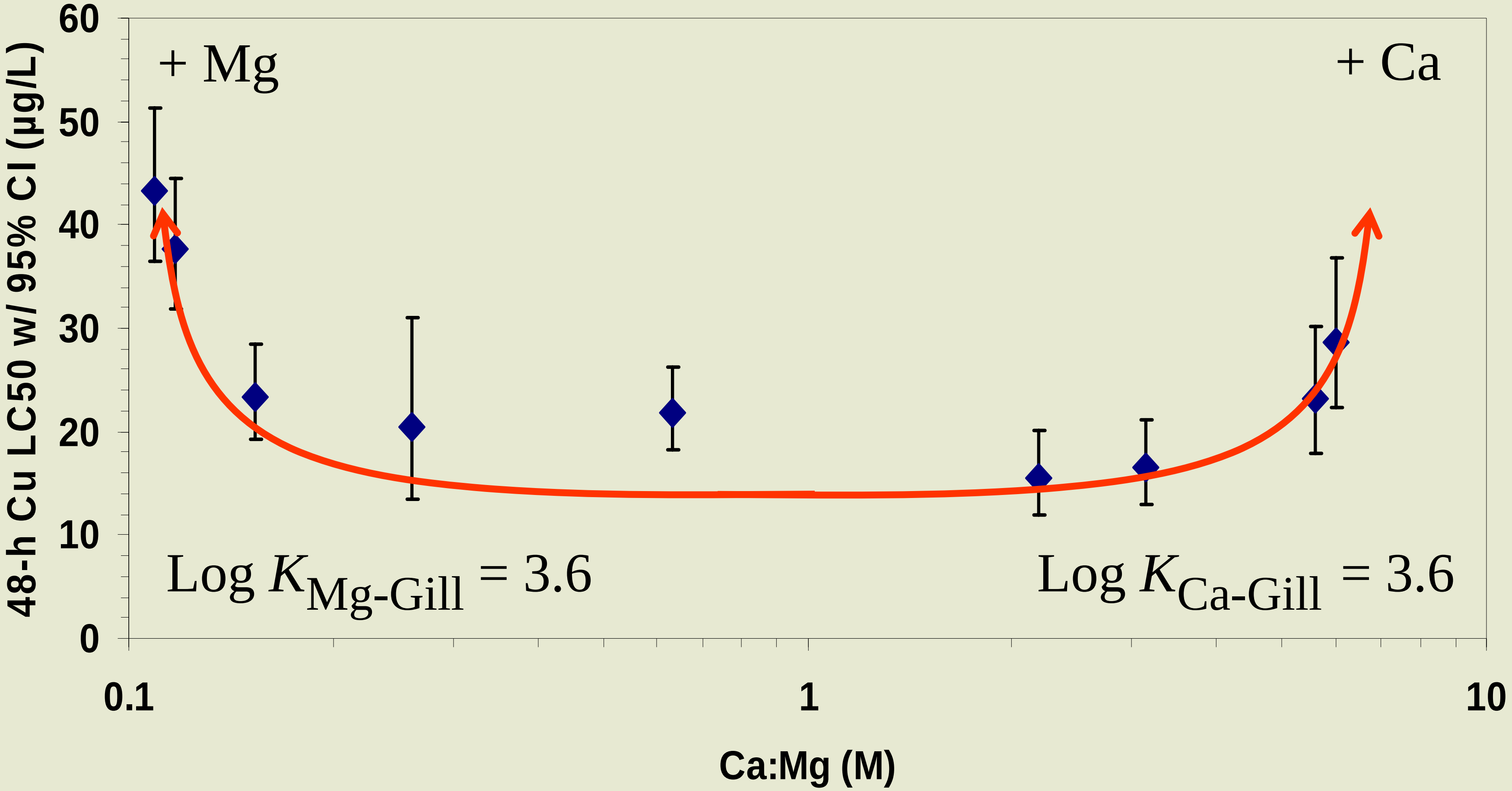
Model Adjustment: Carbonate precipitation by Ca and Mg

Potential Solutions

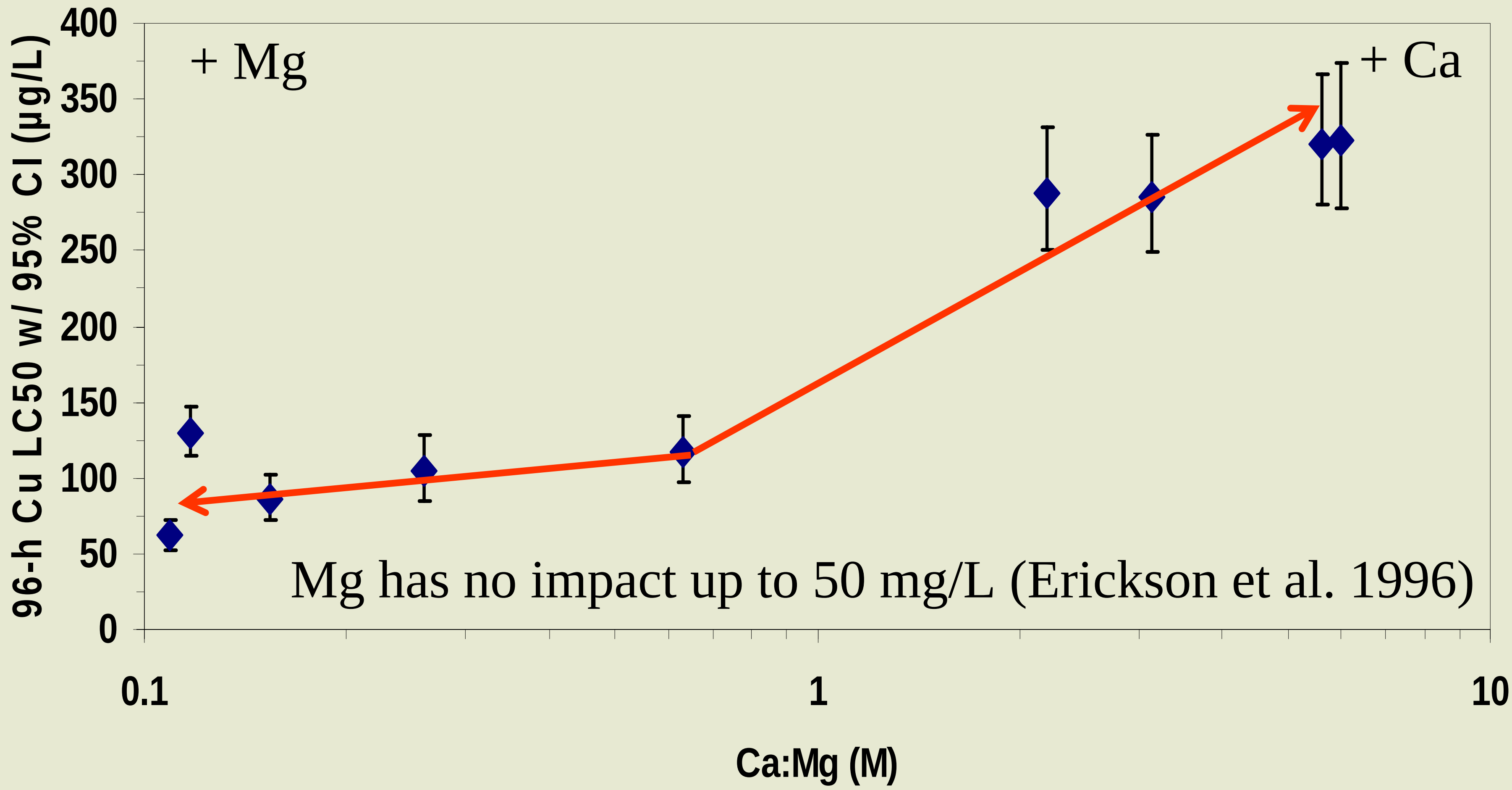
- Determine impact of individual water quality parameters on model output (i.e., residual analysis)

- **Characterize the importance of calcium and magnesium on copper toxicity at very high hardness**

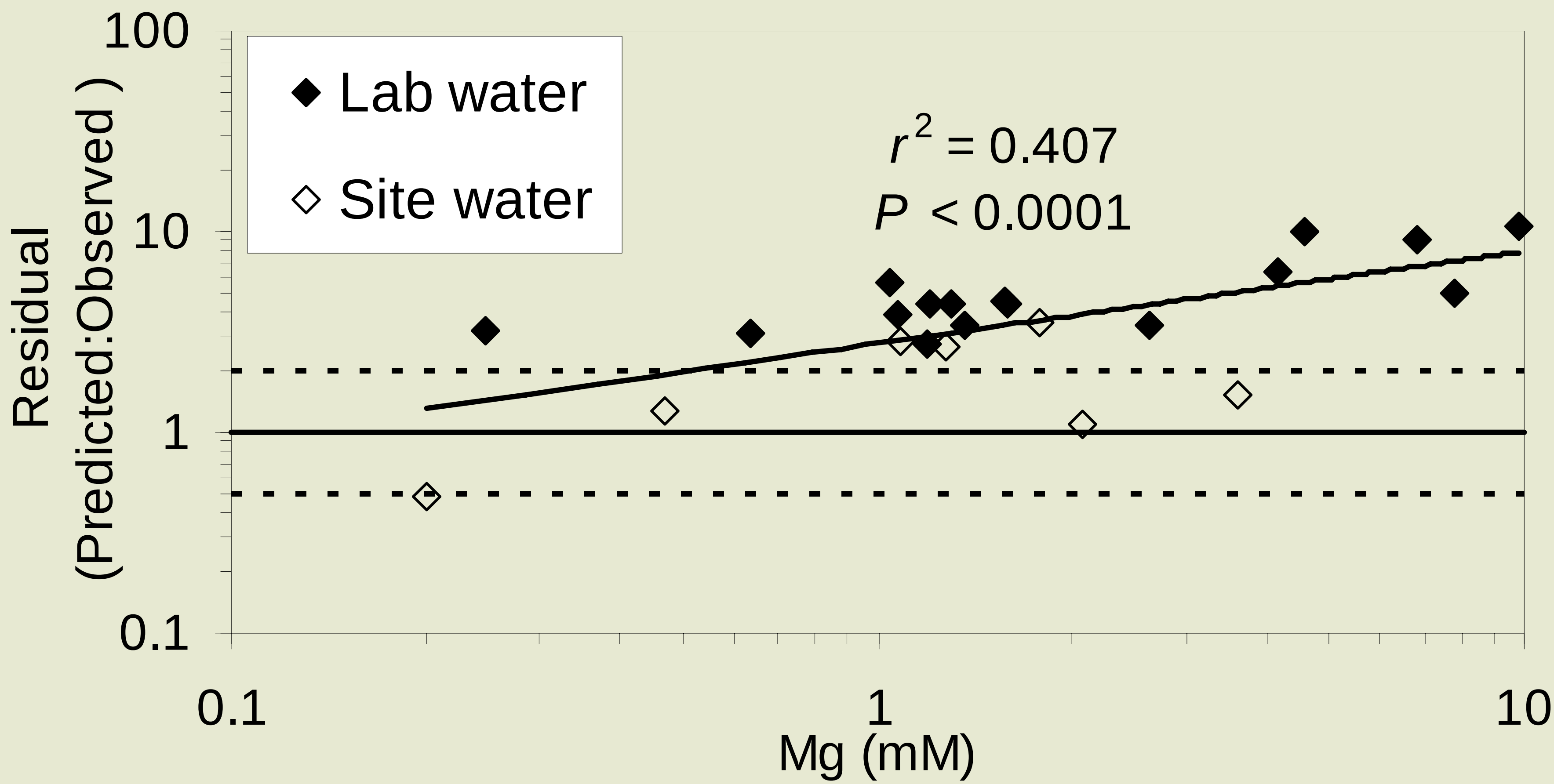
Ca:Mg Results
- *Ceriodaphnia dubia* -



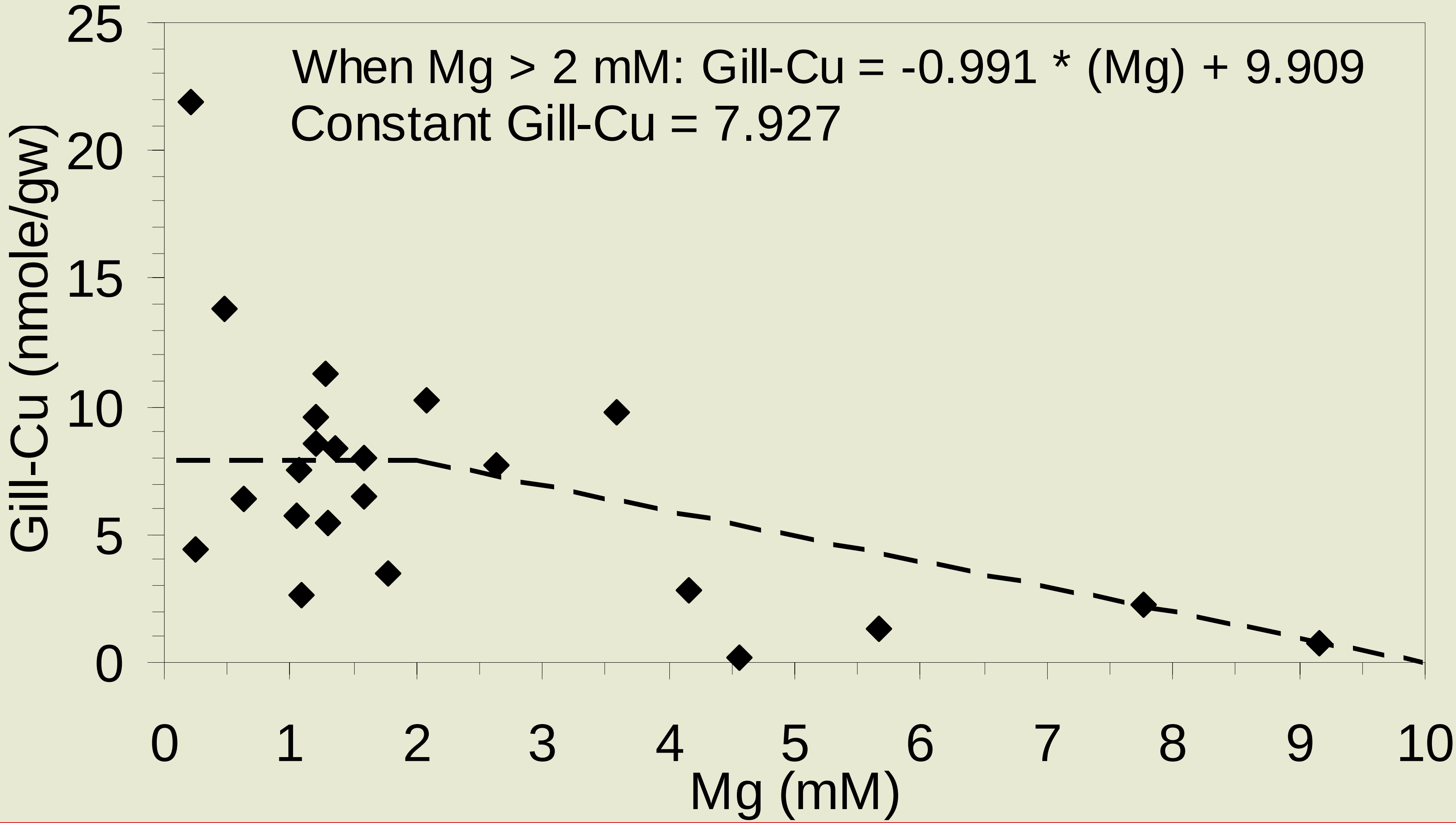
Ca:Mg Results
- Fathead minnows -



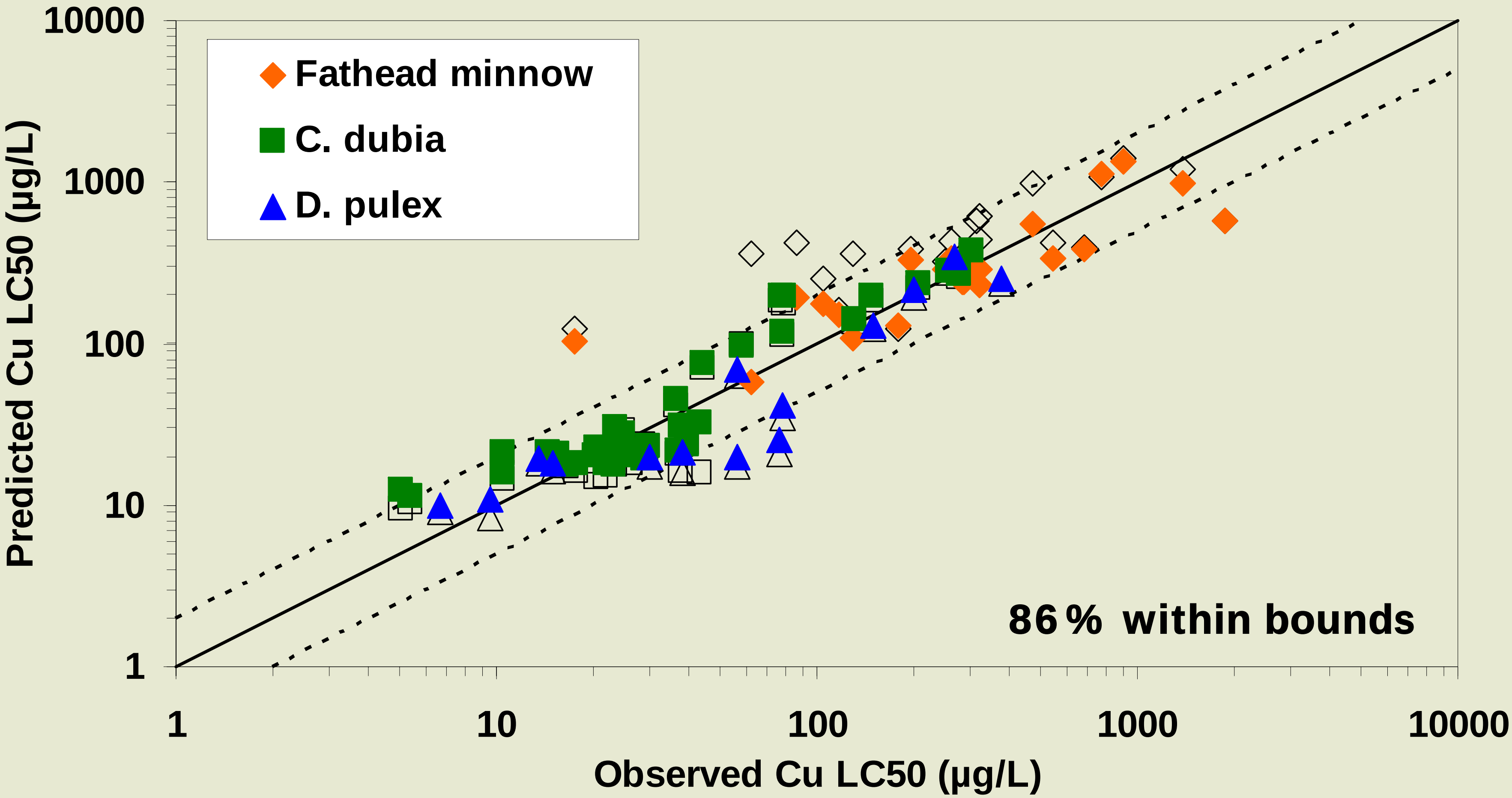
Mg Influence on FHM Predictions



Mg Influence on Gill-Copper Accumulation

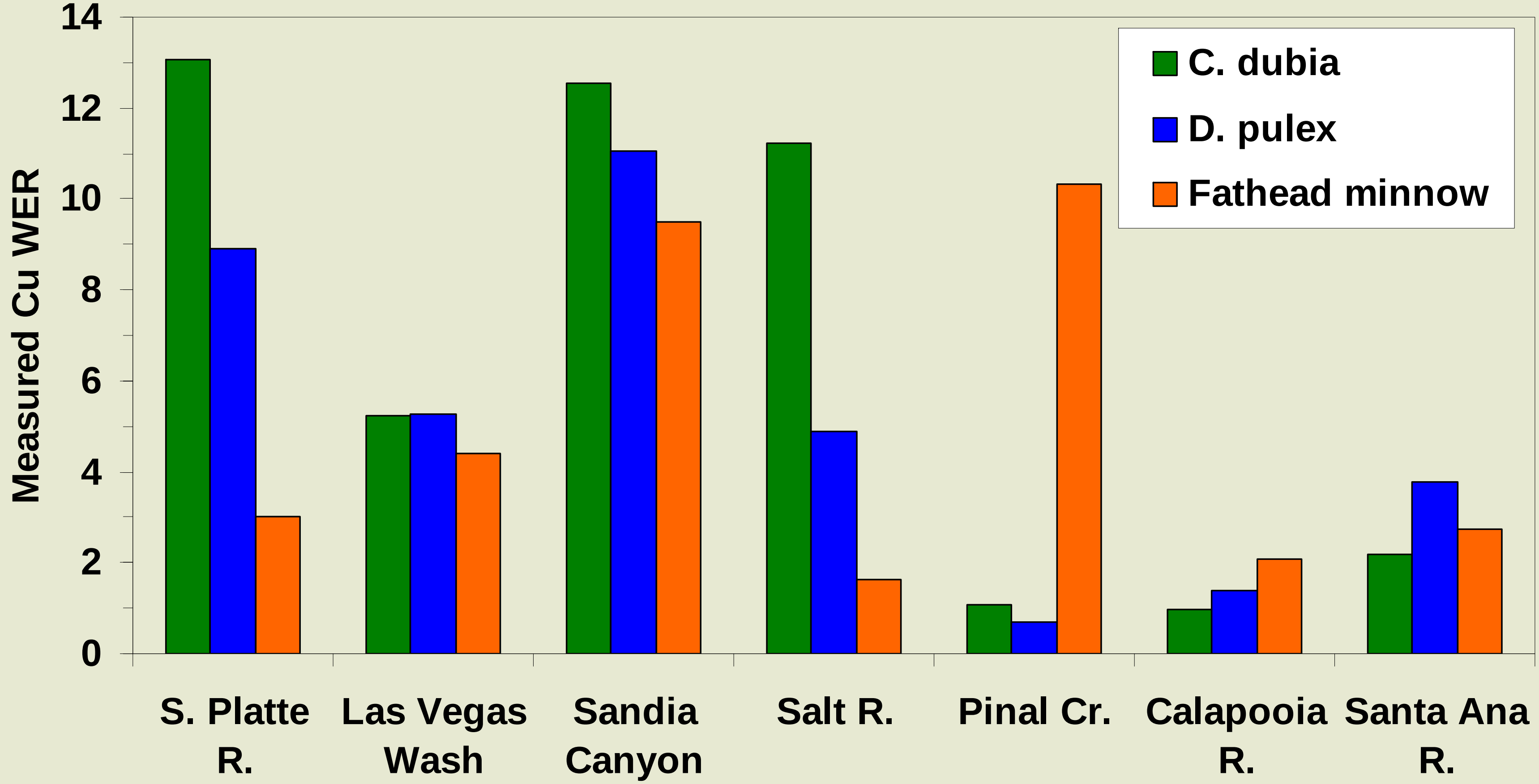


BLM Results



Model Adjustment: Carbonate <u>and</u> Mg Influence

Water Effect Ratio Results
- Measured -



WER = Site LC50 / Lab LC50

Conclusions

- **BLM predictions accurate for the most sensitive aquatic organisms**
- **BLM input corrections should be considered in high hardness surface water**
- **Model performance improved by incorporating Mg-biotic ligand interactions**

Acknowledgements

- Funding from Arid West Water Quality Research Project; Pima County, Tucson, AZ

- Sampling Crews
  - Denver Metro Wastewater Reclamation, City of Riverside, City of Phoenix, City of Las Vegas, Los Alamos National Lab, Pinal Creek Group

- PERL Staff
  - Carrie Smith, Aaron Edgington, Allison Cardwell, Amber Young, Dinah Nasvik