New Approaches for Determining Aquatic Metal Toxicity for Mining Impacted Sediments and Waters

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Environmental Contamination in the Hydrosphere and Lithosphere
Organized by
Korean Society for Economic and Environmental Geologists
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The Problem: Impact on Water Quality of Metal-Contaminated Solids Associated with Mining

Mining wastes near Black Hawk, CO

Contaminated sediments in Clear Creek

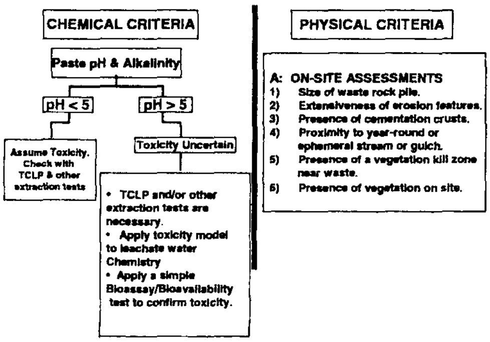
Project Goals

- Site Characterization & Exposure Assessment
  - Evaluate new approaches based on bioavailability to:
    - Screen mining wastes for possible environmental impacts
    - Prioritize sites for remediation
    - Evaluate effectiveness of remediation approaches
    - Improve water quality criteria for sites impacted by mining

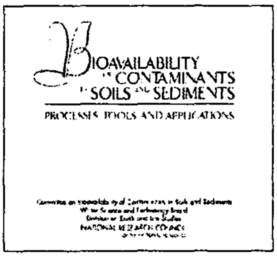
Demonstration Sites

- Clear Creek Watershed, Jefferson County, CO
- Korean Mining Sites
  - *Deuk-Um*

Decision Tree for Ranking Mine Wastes



Bioavailability in Risk Assessment



2003 NRC Publication which elaborates on incorporation of bioavailability into risk assessment

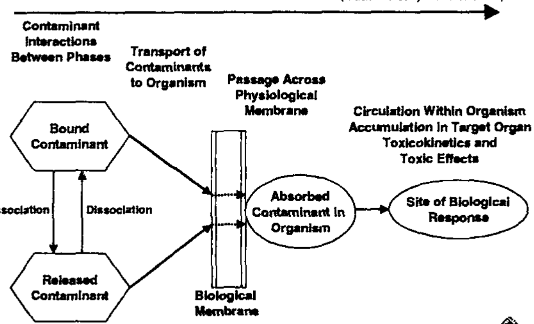
Importance of speciation and environmental chemistry for metals toxicity evaluation

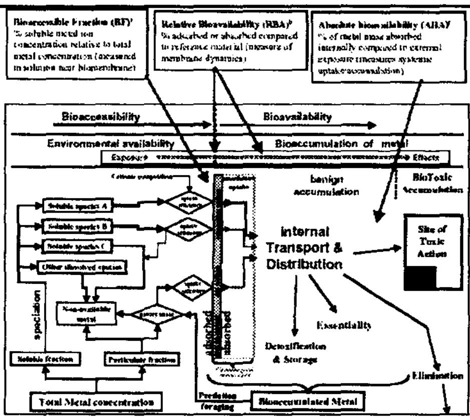
Important Definitions

- Bioaccessibility
  - Bioaccessible metals are metals in the environment that are and/or can become in a biologically available chemical state.
- Bioavailability
  - Bioavailable metals are metals in such a biologically available chemical state that they can be taken up by an organism and can react with its metabolic machinery.
- Toxicity
  - The ability of a substance to cause an adverse and/or harmful effect to an organism.

Bioavailability Processes

(National Academy of Sciences, 2003)





US EPA Framework for Metals Risk Assessment: EPA/630/P-04/068a July 2004

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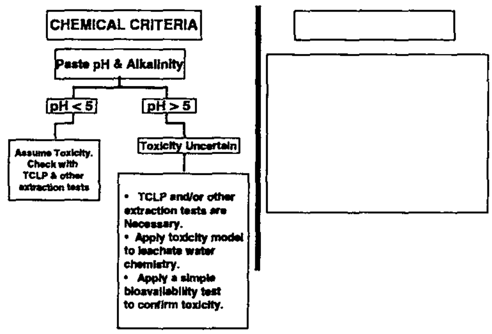


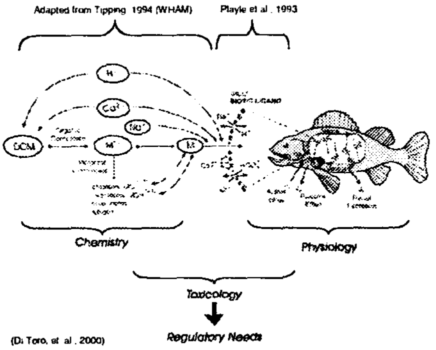
Biotic Ligand Model (BLM)

- In development for Ambient Water Quality Criteria
- In review for "replacement" of hardness equations for Copper Criteria
- Research Questions ?
  - Applicable to Mining Influenced Waters (MIW)
  - Useful for solids characterization (leachates)

The Three C's of the Biotic Ligand Model

- Concentration
- Complexation
- Competition

Biotic Ligand Model (BLM)



(Di Toro, et al., 2000)

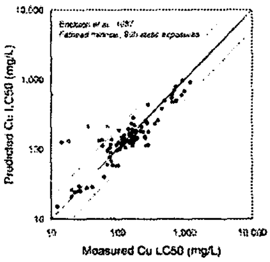
BLM Constants and Correlations

Summary of log conditional binding constants (log K) derived for different versions of the BLM

Interaction	Cu		Ag		Zn		
	FHM[a]	DM[b]	RBT[c]	RBT[d]	DM[e]	RS[f]	RBT[g]
M_{toxic}-BL	7.4	8.0	7.3	7.6	5.3		5.5
Ca-BL	3.6	3.5	2.3	2.3	3.3	3.4	4.8
Mg-BL	–	3.6	–	3.0	3.1	3.9	
Na-BL	3.0	3.2	2.3	2.9	2.4	3.0	
H-BL	5.4	–	4.3	5.9	–		6.7

RBT, rainbow trout; FHM, fathead minnow; DM, *Daphnia magna*; RS, *Raphidocelis subcapitata*; M_{toxic}, toxic metal; and BL, biotic ligand.

[a] Santore et al., 2001
[b] De Schamphelaere and Janssen, 2002.
[c] Paquin et al., 1999
[d] McGeer et al., 2000.
[e] Heijerick et al., 2002a
[f] Heijerick et al., 2002b
[g] Schwartz and Playle, 2001.
[h] Santore et al., 2002



(Paquin et al., 2002)

Current Assumptions & Parameters of the BLM

- Toxicity is directly related to a critical accumulation of metal at the site of uptake
- Accumulation occurs at a constant rate that depends on
  - Quantity of "free" metal in solution
  - Competition between metal and hardness cations and protons
- DOC consists of HA and FA
  - Proportion is adjustable in model (10-60 % HA)
  - Binding properties of DOC are adequetly described by the Windermere Humic Aqueous Model (WHAM VI)
- Biotic ligand can be described by conditional stability constants

BLM Inputs

- BLM Requires Additional Data
  - Hardness
    - Ca and Mg affect different metals & species
  - Alkalinity and pH
    - Inorganic complexes in solution
    - H+ also competes with metals
  - Dissolved Organic Matter
    - Measured as DOC
    - "Controls" free metal concentration
    - Metal binding quantified by WHAM model

BLM Output

- Toxicity predictions from water quality data
  - Multiple species and metals

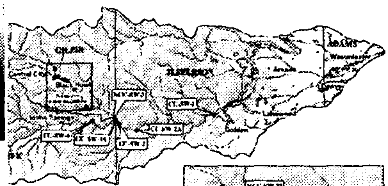
BLM for Mining Influenced Waters

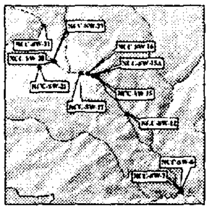
- Data sets used for BLM development generally have co-varying hardness and alkalinity
  - Ca competition vs carbonate complexes ??
- In MIW this is not necessarily true
  - Sulfate balances hardness
  - Mn may make up fraction of hardness

BIM Modeling of MIW: Clear Creek CO

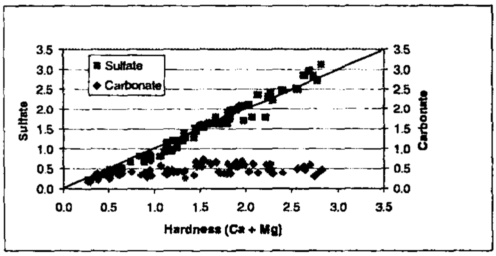
- **Use historical data to look for seasonality of toxicity**
- **Make forward predictions for 2005**
- **Perform toxicity tests to confirm BLM**

Clear Creek CO

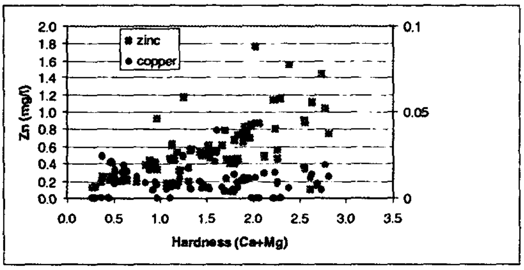


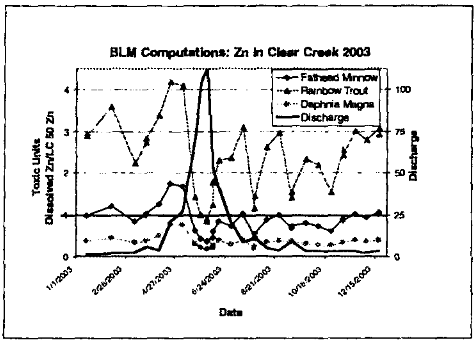


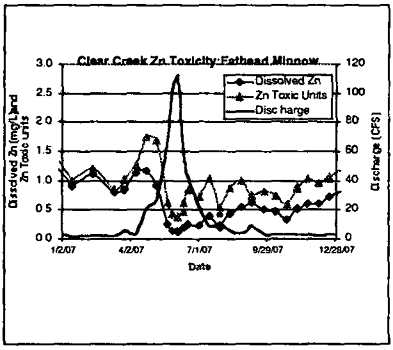
Hardness and Carbonate not covarying



Metals and Hardness



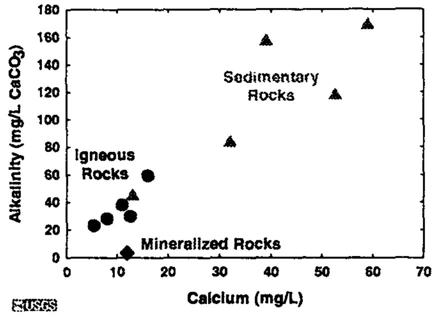




BIM Modeling of MIW: Relating Geology to BLM Parameters

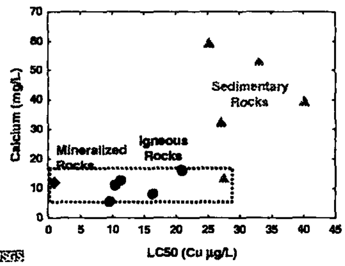
- **Collaboration with Dr. K. Smith, USGS**
- **Apply existing model to historical datasets**
- **Apply existing model to new water samples from diverse geological settings**
- **Confirm predictions with toxicity tests**

Ca vs alkalinity



Copper toxicity vs Ca

Daphnia Magna
DOC = 1 mg/L



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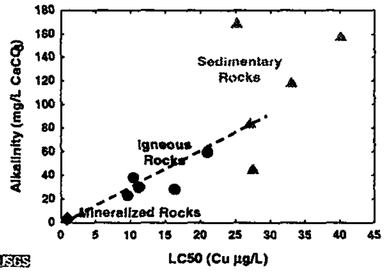

Current BLM Research Directions

- Compare current BLM predictions to *Ceriodaphnia dubia* toxicity tests for different USA and Korean geological settings
  - Especially for variable hardness:alkalinity ratios
- Mixed Metals experiments
  - Binary systems of Cu, Zn, Cd, Ni
    - Synergistic vs antagonistic effects
- Compare Effect of DOC source on toxicity

Metal Mixtures: Toxic Units Approach

- $TTM = \Sigma(C_i / WQG_i)$
- TTM > 1 mixture exceeds water quality criteria
- TTM = Predicted Total Toxicity of the Mixture
- C_i = the concentration of the component
- WQG_i = the guideline for that component
- (ANZECC and ARMCANZ 2000)

Metal Mixtures

- Synergistic
- Strictly Additive
- Antagonistic

- Greater than additive
- Less than additive

W.P. Norwood, U. Borgmann, D.G.Dixon, and A. Wallace (2003) Effects of Metal Mixtures on Aquatic Biota: A Review of Observations and Methods. Hum Ecol. Risk Assess, 9: 795-811.

Table 3. Interactions of metals in binary mixtures based on reinterpretation of published data and comparison to original interpretation by the authors.

		Less Than Additive	Strictly Additive	More Than Additive	Total Tests
	Zn	27	8	17	52
	[illegible]	21	8	21	50
	Cu	24	14	13	[illegible]
	Hg	[illegible]	[illegible]	11	42
	Ni	[illegible]	2	[illegible]	24
	Pb	[illegible]	[illegible]	3	[illegible]
	Al	3	1	0	4
	Mn	6	0	2	8
	[illegible]	7	0	2	[illegible]
	V	[illegible]	0	[illegible]	[illegible]
	[illegible]	4	0	2	[illegible]
	As	[illegible]	2	[illegible]	[illegible]
	Mo	5	0	0	5
	Mg	1	0	0	1
This	Total	134	52	84	270
Analysis	Percent	[illegible]	[illegible]	[illegible]	100.0
Author	Total	145	114	100	359
Interpretation	Percent	40.4	[illegible]	27.9	100.0

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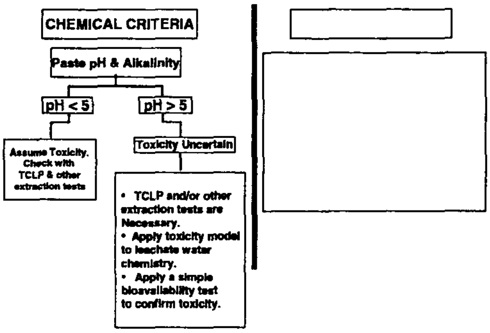


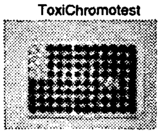
Bioassays

Ceriodaphnia dubia *E. coli*

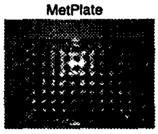
Standard Aquatic Toxicity Tests

Microbial Enzyme Activity Tests

ToxiChromotest



MetPlate

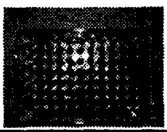


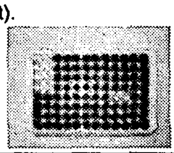
Aquatic Organisms

- *Daphnia*
  - USEPA (EPA 1994a,Test Method 1002.0)
    - *Ceriodaphnia dubia*
    - 48 hour test
    - Endpoint: Survival or Reproduction
  - OECD
    - (OECD guideline for testing of chemicals 202)
    Acute immobilization Test, 24 hr. *Daphnia magna* or *Daphnia pulex*
    - (OECD guideline for testing of chemicals 211)
    Daphnia magna Reproduction Test. At least 14 days.

Microbial Assays (Surface Water)

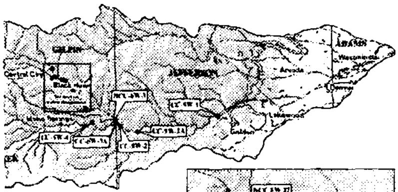
- MetPlate™ & Toxi-Chromotest ®
  - Based on enzyme (β-galactosidase) inhibition
  - Uses a 96-well microplate
  - Endpoint is determined by the absorbance measured at 575nm (MetPlate), and 615nm (Toxi-Chromotest).

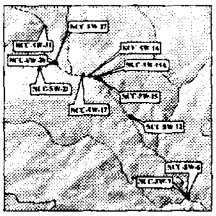




Clear Creek Study (August 2003)

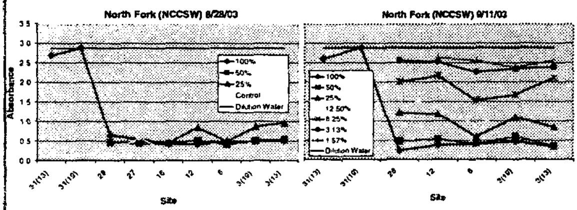
Toxicity Sites
CC-SW-21,
CC-SW-3A,
CC-SW-2,
CC-SW-1,
NCC-SW-31,
NCC-SW-28,
NCC-SW-16,
NCC-SW-12,
NCC-SW-6,
NCC-SW-3





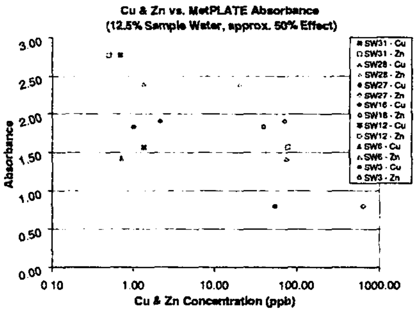
Aquatic and Sediment Toxicity
Water and Sediment Chemistry
Hydrogeology
Colorado Division of Public Health and the Environment
U.S. Environmental Protection Agency, Region 8
U.S. Environmental Protection Agency, Cincinnati
Colorado School of Mines
U.S. Geological Survey

Microbial Assays (MetPLATE™)



Control: no bacteria added, no color change of chromophore.
Dilution water: no inherent toxicity, greatest change of chromophore

Microbial Assays (MetPLATE™)



Ceriodaphnia dubia %Survival

SITE	SW3		SW6	SW12	SW16	SW27	SW28	SW31	
	8/13/03	8/19/03	8/19/03	8/19/03	8/19/03	8/19/03	8/19/03	8/13/03	8/19/03
USGS100%	98	89	88	91	69	0	76	97	91
USGS 50%	96	85	96	95	72	0	70		
EPA 100%	45		35	55	0		95	100	95
EPA 50%			80		95				
EPA 25%	95		75		100				
EPA 12.5%			80		95				

Preliminary Results

- Metplate™ shows the greatest response
  - nearly complete reduction in Absorbance for undiluted (100%) samples
- Toxi-chromotest® is next most sensitive
  - 66% reduction in Absorbance for undiluted (100%) samples
  - Shows minor downstream trend
- Standard 48 hour *Ceriodaphnia dubia* test showed less survival than Ceriodaphtoxkit F for undiluted sample
  - Example: SW-6 (undiluted) 35% vs 88% survival

Current Bioassay Research

- More comparisons between standard toxicity tests and enzyme bioassays
- Application to
  - Mine site characterization
  - Remediation
  - Surface water monitoring
  - Bioavailability process research

Acknowledgements

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  - Eric Blumenstein CSM
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  - USEPA Region VIII