Elevated Dissolved Solids, Biota, and Whole Effluent Toxicity

WaterTec 2015
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Barr Engineering Company
Brief History of Dissolved Solids Toxicity
My View

- The “Gold Book”-1986
- Solids (Dissolved) and Salinity
  - 250 mg/L for chlorides and sulfates in domestic water supplies
- Minnesota and Many States
  - Chronic chloride standard
    - MN 230 mg/L
  - Dissolved salts (solids) standard
    - 700 mg/L for irrigation water
Brief History of Dissolved Solids Toxicity

Key Research

- **Salinity-Toxicity Relationship (FW STR)**
  - Gas Research Institute
  - Multivariet logistic regression approach
  - C. dubia, LC50

[http://en.wikipedia.org/wiki/Logistic_regression]

- **Mount et. al (1997). Env. Tox. and Chem.**
  - Logistic function for C. dubia, D. magna, fathead minnows
  - \( \text{Logit}(P) = B_0 + B_1 X_1 + B_2 X_2 \ldots B_i X_i \)
  - \( \% \text{ Survival} = 100 \times \frac{1}{1 + \exp(-(-64.81 + 2.46 \times \text{Unionized Ammonia} + 0.0068 \times \text{Alkalinity} - 0.0171 \times \text{Chloride} - 0.0262 \times \text{Potassium} - 4.99 \times \text{Aluminum} - 2.93 \times \text{K/NA} - 0.0053 \times \text{SO}_4))} \)
Brief History of Dissolved Solids Toxicity

Key Research


The Potential Influence of Effluent-Related Dissolved Solids On Chronic Whole Effluent Toxicity Test Results With Ceriodaphnia Dubia and Selenastrum Capricornutum

Figure A5  Conductance v. *D. magna* 48-hour Percent Mortality

Ion Pairs of: Cl, K, Na, Mg, Ca, SO4, HCO3
Brief History of Dissolved Solids Toxicity

Key Research

Figure A7  *Daphnia magna* LC$_{50}$ Concentrations for Ion Pairs
(sorted by LC$_{50}$, lowest to highest)
Brief History of Dissolved Solids Toxicity
Sulfate and Chloride Criteria


Fig. 1. Relationship between water hardness (mg/L as CaCO₃) in diluent and 48-h median lethal concentration (LC50s) values for Ceriodaphnia dubia in terms of chloride (mg Cl⁻/L) and total dissolved solids (mg TDS/L).
## Brief History of Dissolved Solids Toxicity

### Sulfate and Chloride Criteria

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Quick Summary
Published Data

• Anions and cations were looking at:
  - Ca, Mg, Na, K, HCO$_3^-$, SO$_4^{2-}$, Cl......(nitrate, pH, OH)

• General ranking of toxicity:
  - K$^+$ > HCO$_2^-$ > Mg$^{2+}$ > Cl$^-$ > SO$_4^{2-}$

• Salt mixtures can have significantly different toxicity
• Additive and antagonistic effects
• Organism specific
Other Relationships
My data: Mine pit water

Chronic sulfate toxicity to C. dubia reduced with humic acid

Filled space = effect of organic carbon addition
### Other Relationships

**My data: Mine pit water**

#### Chronic sulfate toxicity to C. dubia mediated by selenium and zinc deficiency

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<th>Treatment</th>
<th>Mean Young Production</th>
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Other Relationships

My data: Mine pit water

Chronic sulfate toxicity to C. dubia mediated by selenium and zinc deficiency
Other Relationships
My data: Mine pit water

The effect of everything

[Image of a scatter plot showing data points for various categories including Alkalinity, Cations, and Anions, with colors indicating different sources such as Pit 3, Receiving Water, Pit 1 and Pit 2.]
Other Relationships

My data: Industrial discharge

Effect of pH rise on bicarbonate toxicity
Chronic C. dubia WET test

Fluctuating pH environment!
Another Summary

- Ion composition
- Organic carbon
- Micronutrients
- Physical-chemical variables...pH and temperature
In-Stream Biological Monitoring
Dissolved solids effects

- Appalachian region
- Ca$^{+2}$, Mg$^{+2}$, SO$_4^{-2}$, and HCO$_3^{-}$
- 139 biological monitoring sites
- Goal: developed a conductivity-based benchmark
- Benchmark: 300 us/cm
In-Stream Biological Monitoring
Dissolved solids effects

Benchmark from extirpation concentration (XC)

$XC = \text{concentration at which genus becomes absent}$

Figure 8. The species sensitivity distribution. Each point is an $XC_{95}$ value for a genus. There are 163 genera. The $HC_{05}$ (295 μS/cm) is the conductivity at the intercept of the SSD with the horizontal line at the 5th centile.
Mayflies were lost first

Figure A-1. The genera in the Order Ephemeroptera, as a group, are extirpated at lower conductivity levels than many other taxonomic groups. The plot is a species sensitivity distribution (SSD). Open circles represent the 95th centile extirpation concentration (XC95) for a genus. The closed circles are genera of the Order Ephemeroptera. The genus at 230 μS/cm is Cinygmula and at 3,923 μS/cm is Caenis.
Biological Monitoring and Whole Effluent Toxicity: Industrial Discharge

Instream biological monitoring as permit condition for a specific conductance variance
Biological Monitoring and Whole Effluent Toxicity: Industrial Discharge
Biological Monitoring and Whole Effluent Toxicity: Industrial Discharge

CD45

SH03 (control)

SH01 (downstream)
Specific Conductance Upstream of the 1st Monitoring Site CD45

- Fall, Spring, Winter: discharge
- Summer: no discharge
Chemistry In the Receiving Stream

Bicarbonate Upstream of the 1st Monitoring Site

Alkalinity (mg/l as CaCO3)

Chemistry In the Receiving Stream

Chloride Upstream of the 1st Monitoring Site

Chloride (mg/l)

0 50 100 150 200 250 300 350 400 450

Chemistry In the Receiving Stream

Magnesium Upstream of the 1st Monitoring Site

Magnesium (mg/l)
Chemistry In the Receiving Stream

Potassium Upstream of the 1st Monitoring Site

Potassium (mg/l)

Dates:
- 17/02/2005
- 05/09/2005
- 24/03/2006
- 10/10/2006
- 28/04/2007
- 14/11/2007
- 01/06/2008
- 18/12/2008
Reference Site Specific Conductance
Discharge Chemistry

Specific Conductance

- HCO₃ (mg/L), 1033
- Ca (mg/L), 121
- Cl (mg/L), 110
- SO₄ (mg/L), 218
- Na (mg/L), 230
- Mg (mg/L), 230
- K (mg/L), 235

Specific Conductance (us/cm)

- 9/1/02
- 1/14/04
- 5/28/05
- 10/10/06
- 2/22/08
- 7/6/09
- 11/18/10
- 4/1/12
Macroinvertebrate Indices


- Sensitive Species Dominant
- Pre-discharge
- Tolerant Species Dominant
- Control

- CD45ALT
- SH01
- SH03
Macroinvertebrate Indices

Macroinvertebrate Groups

Macroinvertebrate abundance for Orders, 2014.
Macroinvertebrate abundance for Orders, 2011.
The metrics used for this study were described in Bailey et. al., 1992.
Whole Effluent Toxicity (acute)

C. dubia Average Percent Survival by Test Year

Potassium Controlled
Ammonia Controlled
Alum and Acid Eliminated

Testing Season (fall to spring)
What About the High Alkalinity

C. dubia Percent Survival

Potassium (mg/L)

Alkalinity = 1030 mg/L
Alkalinity = 800 mg/L
Alkalinity = 1500 mg/L
What About the High Alkalinity

Percent Survival = 100*1/(1 + exp(-(8.685-0.001*Alkalinity+0.004*Chloride-0.956*Ammonia as N+0.015*Sulfate+1.008*Aluminum -0.020*Potassium-0.008*Sodium))}

R² = 0.9266
Relative Effect of Potassium in Effluent Matrix

9/19/11--Potassium Spike Test

12/12/12--Potassium Spike Test

10/17/11--Potassium Spike Test

11/7/11--Potassium Spike Test

1/9/12--Potassium Spike Test

11/28/11--Potassium Spike Test
Synopsis

- Be careful!
- Things that modify dissolved solids toxicity:
  - Hardness, chloride, pH, organic carbon (NOM), micronutrient (trace metals), acclimatized population
- My toxicity ranking
  - $\text{HCO}_3^- = \text{SO}_4^{2-} = \text{Cl}^{-2}$
  - $\text{K} > \text{Mg} > \text{Ca} = \text{Na}$
- Use multivariate logistic regression