Diel Cycles: Dissolved Arsenic and Metals

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Diel cycles first studied by Fuller & Davis (1989) in Whitewood Creek (So. Dak.) and then by Nimick et al. (1998) in Madison and Missouri Rivers (Montana)
Diel sampling sites – 1990-2008

Number of Sample Sets
- 1
- 2-4
- >8

USGS
Which Dissolved Metals?

Arsenic
22-33 ug/L  
50%

Cadmium
1.4-3.0 ug/L  
110%

Manganese
35-142 ug/L  
306%

Zinc
214-634 ug/L  
196%

(Nimick et al., 2003)
Year-to-Year Variation

High Ore Creek

Zn (µg/L)

Day 1  1200  2400
Day 2  1200  2400
Day 3  1200  2400

Early
PRE-CLEANUP
- Sept 1995
- August 1997

POST-CLEANUP
- August 1999
- July 2000

Late
POST-CLEANUP
- August 2001
- June 2004
Particulate Metals

- Particulate metal concentrations increase at night:
  - Foraging of benthic macroinvertebrates
  - Oxides form as Fe is released by reductive dissolution in biofilms
  - Particle settling rate decreases as temperature decreases
Filtered Mercury

Mercury in Silver Creek

Unfiltered Metals

(Nimick et al., 2007a)
Possible Causes – Dissolved Metal Cycles

- Diel variation in metal input or ground-water inflow
- Biological uptake
- Precipitation-dissolution reaction
- Sorption-desorption reaction

Coeur d’Alene River
Cause: Downstream Transport or Instream Process?

- No lag time means cycles caused by instream process
Uptake by biofilm and periphyton is a plausible reason for Zn cycles but not As cycles, which have opposite timing.

High Ore Creek
Cause: Precipitation-Dissolution?

- Daytime increases in pH and water temperature increase mineral saturation and precipitation
  - $\text{Zn}^{+2} + \text{CO}_3^{-2} = \text{ZnCO}_3^{(s)}$ (smithsonite)
  - $\text{Ca}^{+2} + \text{CO}_3^{-2} = \text{CaCO}_3^{(s)}$ (calcite)
- Reversible reaction
- pH changes much greater within biological surface
- Does not explain arsenic

![pH profiles in lab-cultured biofilm](Morris, 2005)
Cause: Sorption-Desorption?

Hydrous Fe oxides

Biofilm

Possible inorganic and organic sorption substrates
Cause: Sorption-Desorption?

- Cation sorption increases and anion sorption decreases with either:
  - increased pH, or
  - increased temperature
Temperature- and pH-dependent sorption can explain metal and arsenic cycles.
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Experiments with High Ore Creek “mesocosms”

(Shope et al., 2006)
Conclusions – Diel Metal Cycles

- Have daily changes: ≤500% (Zn, Mn, Ni, Cd, Hg)
  ≤50% (As)
- Are widespread and persistent in streams with pH > ~6.5
- Caused mainly by geochemical processes driven by diel pH and temperature cycles

- Diel variations must be considered when collecting or interpreting water-quality data!
Sources of Data