Fascinating Biogeochemistry: How Diel Cycling Complicates Surface-Water Monitoring

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Definitions

- **Periodicity of 24 hours:**
  
  - Diel or Diurnal Cycles

- **Activity:**
  
  - Diurnal
  - Nocturnal
Session I1: Effects of Diel Cycling on Stream Conditions
Thursday 10:00-11:30 AM

- Pamela Reilly: Diel Cycles in Major and Trace Elements in Streams: Anthropogenic Effects on, and Additions to, Natural Cycles
- Richard Inouye: Diel Variation of Sediment Load in a 5th Order River in SE Idaho—Temporal Variation and Impacts on Load Estimates
- Briant Kimball: Diel Cycles Confound Synoptic Sampling in a Metal-Contaminated Stream
- Alba Argerich: Effects of Daily Fluctuations in Streamflow on Stream Metabolic Activity Calculations
- POSTER 13B. Pamela Reilly: Diel Biogeochemical Processes and Their Effects on Sample Design and Trend Analysis: A Study Looking at Diurnal Arsenic Cycling in a NJ Stream
Outline

- What is Diel Cycling?
- Diel Cycling Mechanisms
- Examples of Diel Cycles
  - Field parameters
  - Other common cycles
  - Nutrients
  - Metals
- Implications for Monitoring Water Quality
  - Examples (How you can get into trouble!)
  - Monitoring guidelines (How to stay out of trouble!)
  - Instrumentation

Madison River, Montana
The Rest of Our Research Team

Chris Gammons
Montana Tech, Butte, Montana

Steve Parker
Variability in Water Quality

- Changing conditions (weather, seasonal, annual)
- Episodic events (rainfall runoff, spills)
- Anthropogenic activity (WWTP effluent, reservoir release for power generation, irrigation withdrawal)
- Diel biogeochemical cycling

"Intensity of monitoring likely controls your perception of variability"

(Don Essig, Idaho DEQ)
Variability in Water Quality

“Water quality is more variable than we know, and the more we look, the more we find.”

(Don Essig, Idaho DEQ)
Diel Biogeochemical Cycling

\[ \text{hv} \uparrow \uparrow, \quad \text{T}_{\text{air}} \uparrow, \quad \text{ET} \uparrow \]

\[ \text{Fe}^{3+} \rightarrow \text{Fe}^{2+}, \quad \text{DOC} \rightarrow \text{DIC} \]

\[ \text{CO}_2 \]

\[ \text{Zn}^{2+} \]

\[ \text{H}_2\text{AsO}_4^- \]

\[ \text{O}_2 \]

\[ \text{NO}_3^- \rightarrow \text{N}_2 \]

\[ \text{MnO}_x \rightarrow \text{Mn}^{2+} \]

\[ \text{FeO}_x \rightarrow \text{Fe}^{2+} \]

\[ \text{biofilm} \]

\[ \text{P} > \text{R} \]

\[ \text{R} > \text{P} \]

\[ \text{hv} \downarrow \downarrow, \quad \text{T}_{\text{air}} \downarrow, \quad \text{ET} \downarrow \]

\[ \text{pH} \uparrow \]

\[ \text{T}_{\text{water}} \uparrow \]

\[ \text{DO, Eh} \uparrow \]

\[ \text{streamflow} \downarrow \text{or} \uparrow \]

\[ \text{NH}_4^+ \rightarrow \text{NO}_3^- \]

\[ \text{Mn}^{2+} \rightarrow \text{MnO}_x \]

\[ \text{Fe}^{2+} \rightarrow \text{FeO}_x \]

\[ (\text{Nimick et al., 2011}) \]
Diel Cycles: Mechanisms

Physical Processes
- Water temperature
- Streamflow
- Particle settling
- Nocturnal aquatic activity

Biogeochemical Processes
- Photosynthesis/respiration
- Photochemical reactions
- Reductive dissolution
- Adsorption/desorption
- Mineral and gas solubility
- Biological assimilation

White = primary process driven directly by sunlight
Pink = secondary process reacting to a primary process
Diel Temperature Cycles

Causes
- Solar heating
- Radiative cooling
- Groundwater inflow

Importance
- Ecological stress
- Influences \textit{kinetics} and \textit{equilibrium} of aqueous reactions
  - Microbial reactions
  - Mineral and gas solubility
  - Adsorption
- Water viscosity
  - Streambed hydraulic conductivity
  - Particle settling

Downstream change in diel temperatures

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram}
\caption{Fisher Creek, Montana (Gammons et al., 2005a)}
\end{figure}
Importance of Temperature

Silver Bow Creek, Montana

(USGS long-term monitoring data for 2002-2011)
Diel pH changes are greatest for high-productivity, neutral-to-alkaline streams.

Diel pH changes in acidic streams are usually small.

(Nimick et al., 2011)
**Diel pH Cycles**

**Causes**
- Photosynthesis/respiration
  \[\text{CO}_2 + \text{H}_2\text{O} \xleftrightarrow{\text{Day}} \text{CH}_2\text{O} + \text{O}_2\]  
  \[\xrightarrow{\text{Night}}\]
- Changes in temperature
- Changes in groundwater inflow
- Fe chemistry

**Importance**
- Many reactions are pH-dependent:
  - Mineral solubility
  - Gas solubility
  - Adsorption

**Graph:**
- pH vs. Water temperature, C
- Diel pH Cycles
- Day and Night reactions

*USGS*
As long as the sun shines and the water is open, there are diel cycles!

(Chris Gammons, Montana Tech)
Diel Cycles in Dissolved Oxygen

- DO changes are largest in slow-moving, high-productivity streams
- DO usually peaks at noon (sun is directly overhead)

Photosynthesis/respiration: \( \text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{Day}} \text{CH}_2\text{O} + \text{O}_2 \xleftarrow{\text{Night}} \)
Diel Cycling in Biofilms vs. Bulk Water

- Changes in pH, DO, and redox are magnified in biofilms relative to the bulk water!

(Parker et al., 2007)
Diel Cycles in Hardness

- Hardness is proportional to Ca & Mg concentration
- Diel hardness cycles caused by diel changes in
  - Streamflow
  - Calcite (CaCO₃) precipitation and dissolution
- Importance: Aquatic life standards for many toxic metals are hardness-dependent

Mill-Willow Bypass, Montana, August 2005 (Gammons et al., 2007)
Diel Cycles in Suspended Solids

- Particulate 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

Clark Fork River, Montana
(Parker et al., 2007)

Clark Fork River, Montana
(Brick and Moore, 1996)
Diel Streamflow Cycles

- Freeze/thaw
  - Ice formation
  - Snow melt
- Evapotranspiration
- Temperature-dependent streamflow loss

- Anthropogenic
  - Wastewater or reservoir discharge
  - Irrigation withdrawals
  - Macrophyte dams

Big Hole River, Montana
Diel streamflow cycles affect:

- Solute concentration (dilution)
- Solute load (load = concentration x flow)

Evapotranspiration (ET) typically changes flow by <20%
Diel Cycling of Nutrients

**NITROGEN**
- Nitrate (NO$_3^-$)
- Nitrite (NO$_2^-$)
- Nitrous oxide (N$_2$O)
- Nitrogen (N$_2$)
- Ammonia (NH$_4^+$)
- Organic-N
- Suspended solids

**PHOSPHORUS**
- Orthophosphate (HPO$_4^{2-}$)
- Organic-P
- Suspended solids

Big Hole River, Montana
Diel Cycling of Nutrients

- Diel redox cycles
  - Nitrification (ammonia + O₂ → nitrate)
  - Denitrification (nitrate + organic C → N₂)
  - Anammox (ammonia + nitrate → N₂)
- Diel changes in rate of uptake by biota
- Diel changes in delivery rate from hyporheic or benthic zones
- Sorption/desorption of P

Silver Bow Creek, Montana
Diel Cycling of Nitrate

Clark Fork River, Montana (Brick and Moore, 1996)

Sleepers River, Vermont (Pellerin et al., 2012)
Diel Nutrient Cycling in Silver Bow Creek

- **Nitrate-N**
- **Ammonia-N**

Dissolved Oxygen (mg/L)

- **Dissolved oxygen**

~3 hours 1.4 miles

WWTP

(Gammons et al., 2011)
Diel Trace-Element Cycles

Diel sampling sites – 1990-2011
Dissolved As, Cd, Cu, Mn, Zn data (Nimick et al., 2003)

- **High Ore Creek**
  - Zn or Mn (μg/L) vs. Time (8/2/99 to 8/4/99)
  - As/10, Mn*10, Cd, Zn (0.6 ft³/s)

- **Prickly Pear Creek**
  - Zn or Mn (μg/L) vs. Time (6/26/00 to 6/28/00)
  - Mn, As (13 ft³/s)

- **South Fk Coeur d’Alene River**
  - Zn (μg/L) vs. Time (9/11/01 to 9/12/01)
  - Cd*100, Mn (80 ft³/s)

- **Middle Fk Warm Springs Creek**
  - Zn (μg/L) vs. Time (6/26/01 to 6/27/01)
  - As (1 ft³/s)

(Nimick et al., 2003)
Magnitude of Diel Cycles for Dissolved Trace Elements

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>Maximum Daily Increase (%)</th>
<th>Number of Diel Samplings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>990</td>
<td>&gt;35</td>
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<tr>
<td>Rare earth elements</td>
<td>830</td>
<td>2</td>
</tr>
<tr>
<td>Cd</td>
<td>330</td>
<td>12</td>
</tr>
<tr>
<td>Mn</td>
<td>306</td>
<td>20</td>
</tr>
<tr>
<td>Ni</td>
<td>167</td>
<td>1</td>
</tr>
<tr>
<td>U</td>
<td>125</td>
<td>2</td>
</tr>
<tr>
<td>Methyl Hg</td>
<td>93</td>
<td>2</td>
</tr>
<tr>
<td>As</td>
<td>54</td>
<td>&gt;25</td>
</tr>
<tr>
<td>Cu (pH = 6.8 – 7)</td>
<td>140</td>
<td>3</td>
</tr>
<tr>
<td>Cu (pH &gt; 7)</td>
<td>&lt;10</td>
<td>12</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;10</td>
<td>1</td>
</tr>
</tbody>
</table>

1. Near-neutral to alkaline streams unless otherwise noted
2. See Nimick et al. (2011) and Balistrieri et al. (2012) for references
Year-to-Year Variation

High Ore Creek

Zn (μg/L)

<table>
<thead>
<tr>
<th>Day</th>
<th>1200</th>
<th>2400</th>
<th>1200</th>
<th>2400</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>500</td>
<td>700</td>
<td>1000</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Day 2</td>
<td>300</td>
<td>500</td>
<td>800</td>
<td>1000</td>
<td>1200</td>
</tr>
<tr>
<td>Day 3</td>
<td>200</td>
<td>400</td>
<td>600</td>
<td>800</td>
<td>1000</td>
</tr>
</tbody>
</table>

EARLY
PRE-CLEANUP
- Sept 1995
- August 1997

POST-CLEANUP
- August 1999
- July 2000

LATE
POST-CLEANUP
- August 2001
- June 2004
- August 2010

USGS
Seasonal Variation

Prickly Pear Creek, Montana

(Nimick et al., 2005)
Lakes and ponds tend to “even out” diel cycles found in streams (Gammons et al., 2007b)
Possible Causes – Dissolved Metal Cycles

- Diel variation in metal input
- Biological uptake
- Precipitation-dissolution reaction
- Sorption-desorption reaction

South Fork Coeur d’Alene River
Cause: Diel Source Input 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.
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

(Morris, 2005)
Cause: Sorption-Desorption

Hydrous Fe & Mn oxides

Possible inorganic and organic sorption substrates

Biofilm
Cation sorption increases and anion sorption decreases with either:
- increased pH, or
- increased temperature

Cause: Sorption-Desorption
Not All Streams Exhibit Diel Cycling

Big cycles
- Shallow, clear
- High productivity
- Large pH and T changes

Silver Bow Creek, Montana

Small or nonexistent cycles
- Deep, turbid, shaded
- Low productivity
- Small pH and T changes

Coeur d’Alene River, Idaho
Diel Processes in Acidic Streams

- Coal mine drainage, Montana (Gammons et al., 2010)
- Fisher Creek, Montana (Gammons et al., 2005a,b)
- Rio Tinto, Spain (Gammons et al., 2008)
- Rio Agrio, Argentina (Parker et al., 2008)
Fe(III) Photoreduction

\[ \text{Fe}^{3+} + \text{H}_2\text{O} + h\nu \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{OH}^- \]

- Light can reduce Fe(III) in both dissolved and solid forms
- Less important at pH > 6
- \((h\nu = \text{photons})\)

Rio Tinto, Spain
Fe Chemistry along a pH Gradient

Fisher Creek, Montana (Gammons et al., 2005a)

- F1: pH ~ 3.3
- F2: pH ~ 5.5
- F3: pH ~ 6.8

New World Cu-Au Mining District
Fisher Creek F1 site: pH ~ 3.3

- Daytime decrease in total Fe (solubility of Fe ↓ as T ↑)
- Daytime photoreduction of Fe(III) to Fe(II)
Fisher Creek F2 site: pH ~ 5.5

- Photoreduction of HFO causes daytime increase in Fe(II) and total dissolved Fe concentrations
- Fe mainly dissolved during day, particulate at night
No evidence of Fe(III) photoreduction

Night-time increase in Fe(II) and total dissolved Fe mainly due to temperature-dependent sorption
Conclusions – Diel Cycling

- Parameters and constituents:
  - Streamflow
  - pH
  - Temperature
  - Dissolved oxygen
  - Trace elements
  - Nutrients
  - Hardness and alkalinity
  - Suspended particles

- *Diel variations must be considered when collecting or interpreting water-quality data!*
Implications: Time of Sampling Important!

Prickly Pear Creek, Montana

6:00 AM

Acute aquatic-life standard for zinc
Implications: Time of Sampling Important!

Sampling time:
1. Afternoon
2. Morning

High Ore Creek

<table>
<thead>
<tr>
<th>Zn (ug/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,000</td>
</tr>
<tr>
<td>2,500</td>
</tr>
<tr>
<td>2,000</td>
</tr>
<tr>
<td>1,500</td>
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<tr>
<td>1,000</td>
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<tr>
<td>700</td>
</tr>
<tr>
<td>500</td>
</tr>
<tr>
<td>300</td>
</tr>
<tr>
<td>200</td>
</tr>
</tbody>
</table>

Day 1  2400  1200  1200  2400  1200
Day 2
Day 3

Early
PRE-CLEANUP
- Sept 1995
- August 1997

POST-CLEANUP
- August 1999
- July 2000

Late
POST-CLEANUP
- August 2001
- June 2004
- August 2010
Implications for Synoptic Sampling: Example 1

Reclaimed mine site

High Ore Creek

flow

Distance downstream, km

Load = Concentration x Flow

Gammons et al., 2007
Implications for Synoptic Sampling: Example 2

Treatment Ponds

Flow

Mill-Willow Bypass

Distance downstream, km

Arsenic concentration, $\mu$g/L

Upstream sampling

Simultaneous sampling

Sampling in upstream direction

Distance downstream, km
Implications for Synoptic Sampling: Example 3

Prickly Pear Creek

Better sampling time

ZINC (µg/L)

Flow

Zinc

STREAMFLOW (ft³/s)

7/25/01  7/26/01  7/27/01

1200  1800  2400  0600  1200  1800  2400  0600  1200
Sampling Strategies

- **Chronic standards**
  - Sample at equal time intervals to obtain 4-day mean
- **Acute standards**
  - Pick sample time to coincide with daily maximum
- **Temporal or spatial analysis**
  - Always sample at same time or collect 24-h samples
- **Comparison of loads (temporally or spatially)**
  - Collect samples and measure flows over 24 hours
Continuous Collection Methods

- Electrometric & optical sensors (pH, DO, SC, T, turbidity, NO$_3$, chlorophyll, fluorescence, CDOM)
- In-situ analyzers that use bench-chemistry methods (NO$_3$, SiO$_2$, Cl, P, …)
- Lab on the streambank (GC/MS, metals, …)
- Surrogates (e.g., measure turbidity to quantify bacteria)
- Automated samplers
Environmental protection may be most effective when:

- Criteria are set with true variability and toxicity in mind
- Criteria are set with monitoring practicality in mind

**Water-Quality Criteria and Monitoring**

![Graph showing Prickly Pear Creek water quality criteria and monitoring data](chart.png)
Water-Quality Criteria and Monitoring: Temperature

Criteria:
- Maximum daily maximum
- Maximum weekly maximum
- Maximum daily average
- Maximum weekly average

Monitoring:
- Hobos, Tidbits, data sondes
- Easy calibration, accurate, no drift

Conclusion:
Monitoring capability is out in front of criteria
Water-Quality Criteria and Monitoring: Dissolved Oxygen

Criteria:
Minimum
7-day average minimum
30-day average

Monitoring:
Data sondes
Need periodic calibration and maintenance to offset drift and fouling

Conclusion:
Monitoring capability has caught up with criteria
Water-Quality Criteria and Monitoring: Metals

Criteria:
Acute standard:
  1-hour average concentration
Chronic standard:
  4-day average concentration
  .... not to be exceeded more than once in three years

Monitoring:
Site visits needed
Automatic samplers require attention in the field but may let you sleep
Diel variability difficult and expensive to address

Conclusion:
Criteria are out in front of monitoring. A more practical expression of criteria may be needed.


Sources of Data


Sources of Data