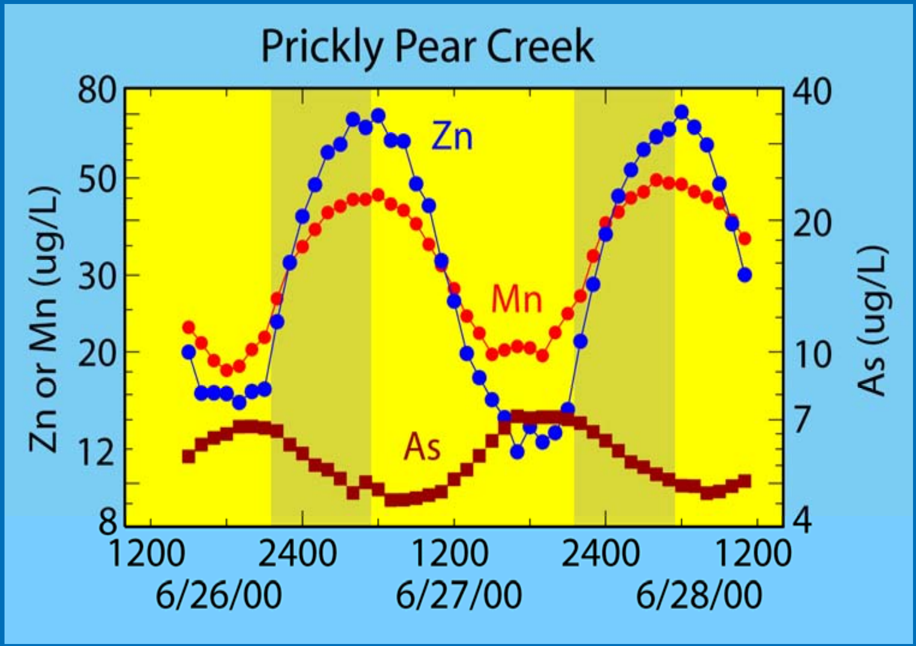
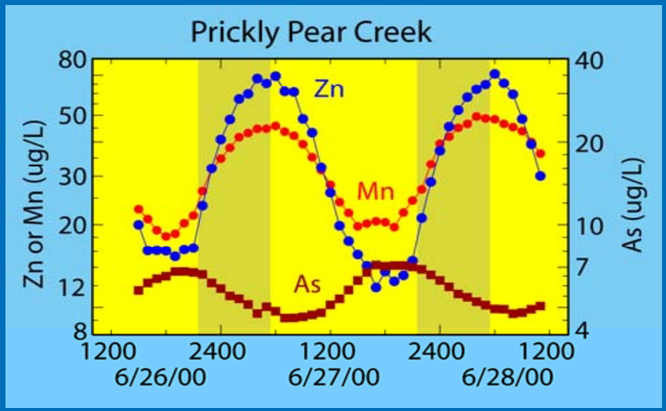
Fascinating Biogeochemistry: How Diel Cycling Complicates Surface-Water Monitoring

David Nimick
U.S. Geological Survey
Helena, Montana



Definitions

- **Periodicity of 24 hours:**



Diel *or* Diurnal Cycles

- **Activity:**

Diurnal

Nocturnal

USGS

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

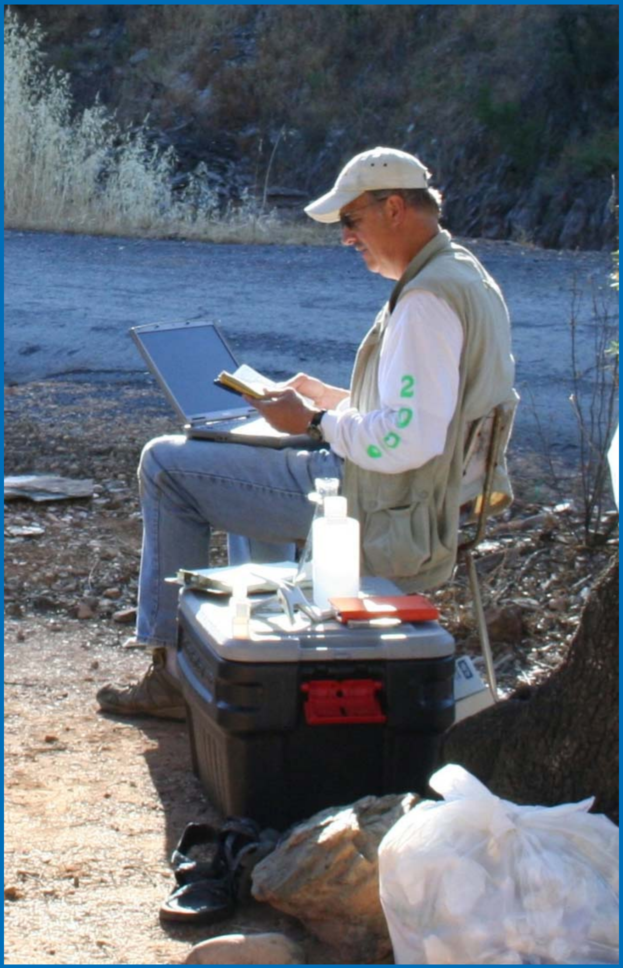
Outline

- 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

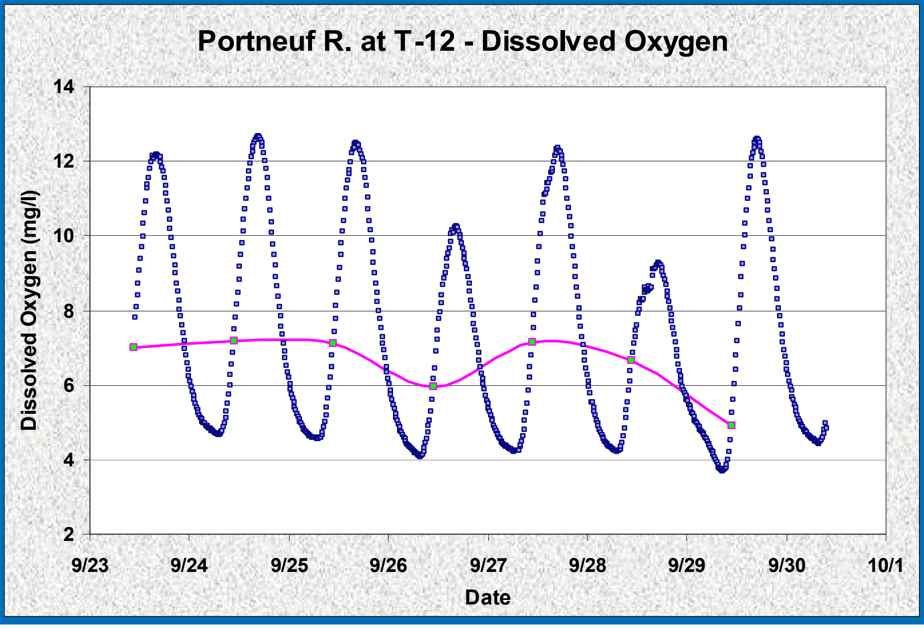


Steve Parker

Montana Tech, Butte, Montana

Variability in Water Quality

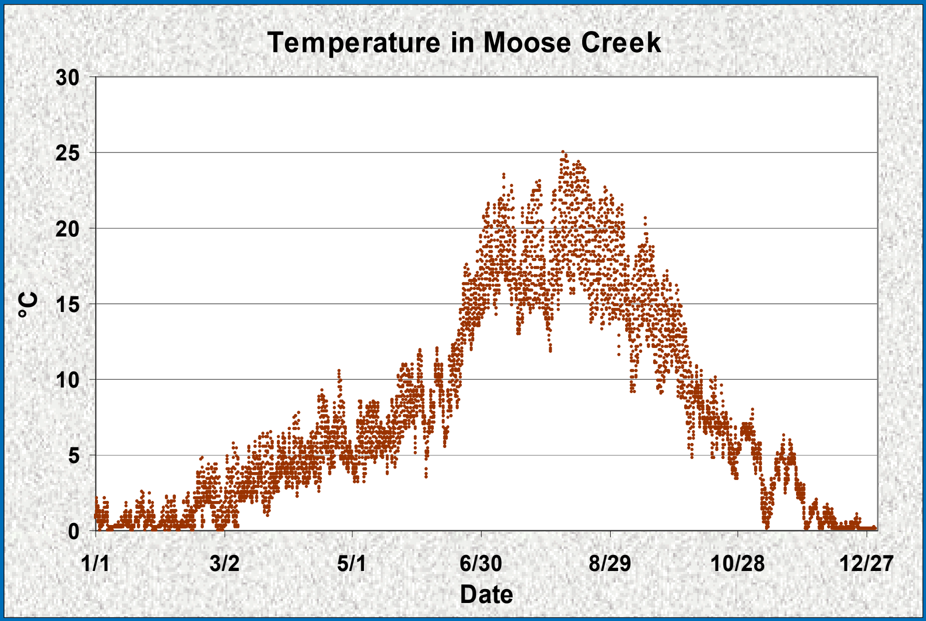
- Changing conditions (weather, seasonal, annual)
- Episodic events (rainfall runoff, spills)
- Anthropogenic activity (WWTP effluent, reservoir release for power generation, irrigation withdrawal)
- Diel biogeochemical cycling

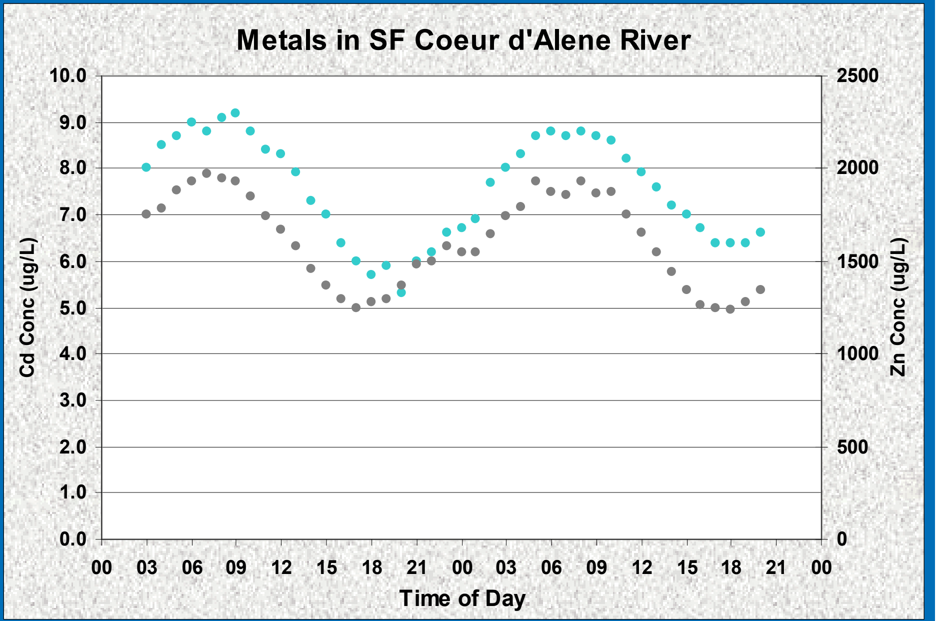


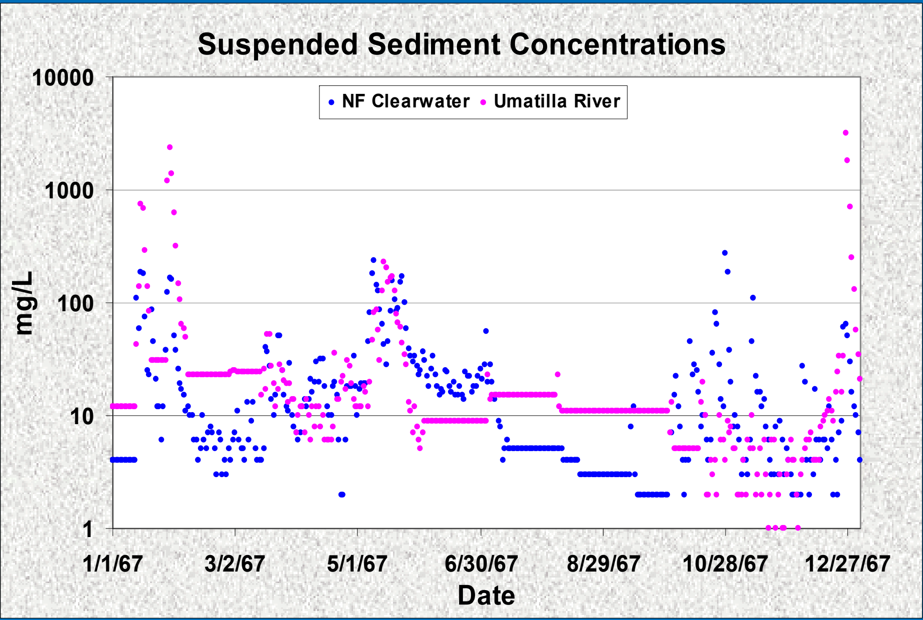
"Intensity of monitoring likely controls your perception of variability"

(Don Essig, Idaho DEQ)

Variability in Water Quality



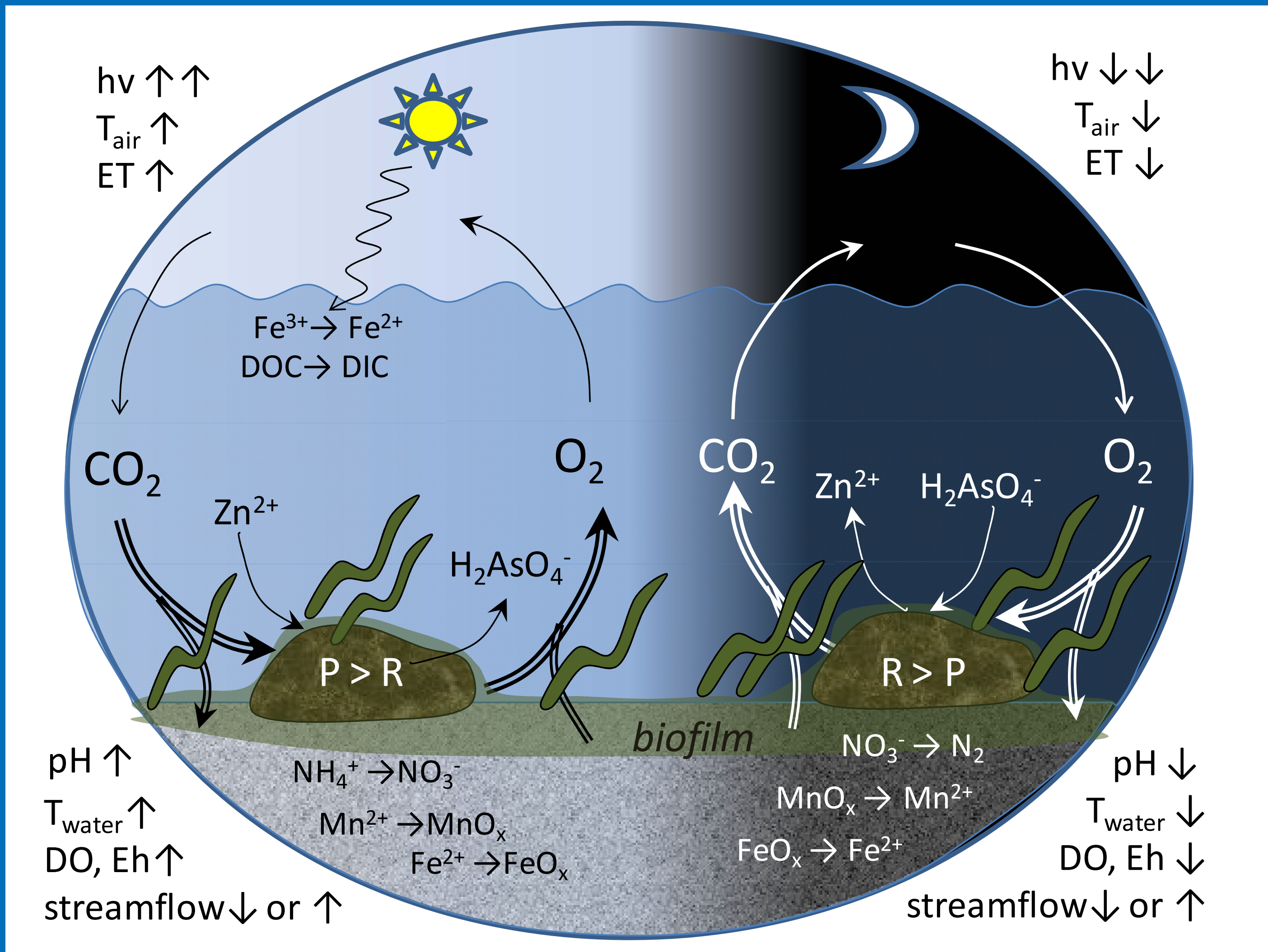




"Water quality is more variable than we know, and the more we look, the more we find."

(Don Essig, Idaho DEQ)

Diel Biogeochemical Cycling



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(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

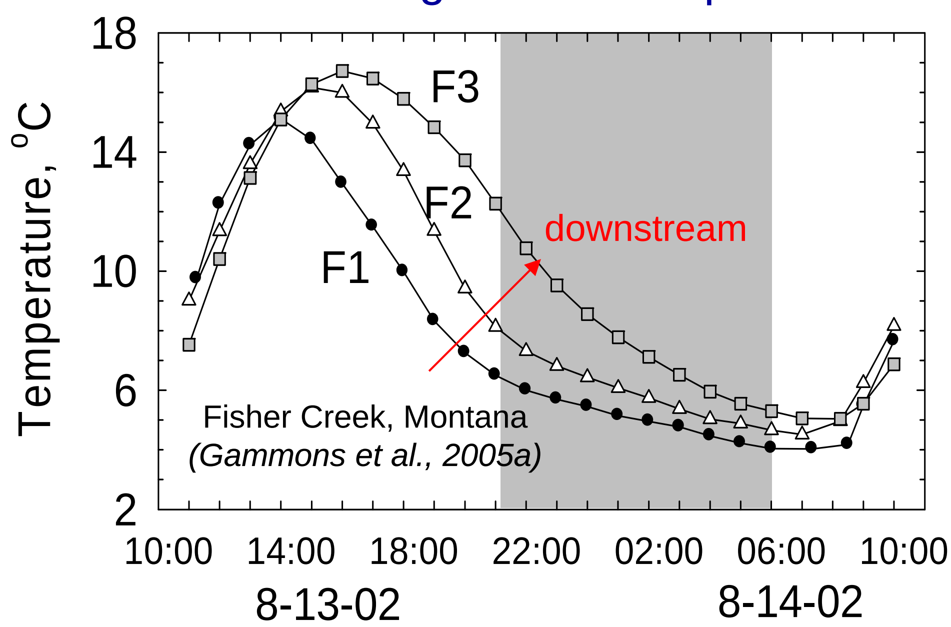
Pink = secondary process reacting to a primary process

Diel Temperature Cycles

Causes

- Solar heating
- Radiative cooling
- Groundwater inflow

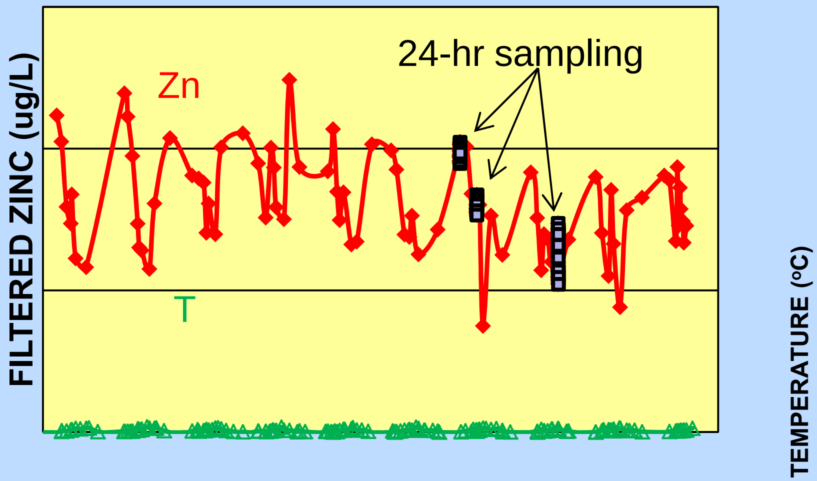
Downstream change in diel temperatures

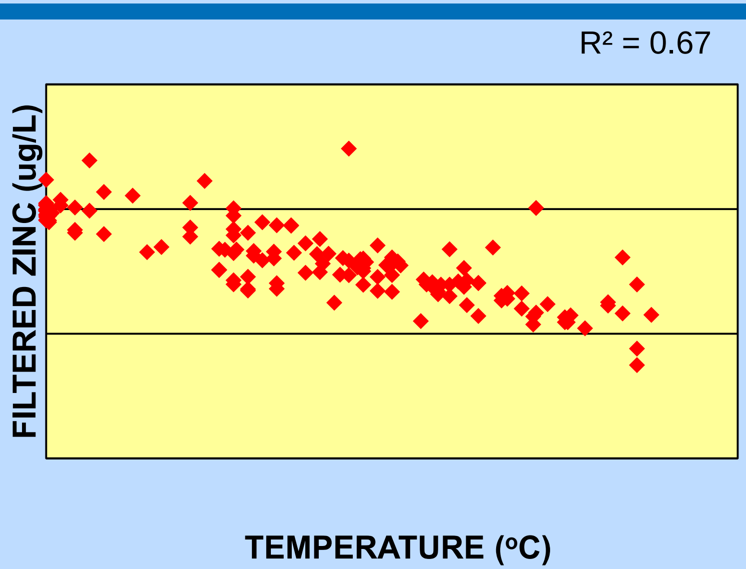


Importance

- Ecological stress
- Influences *kinetics* and *equilibrium* of aqueous reactions
  - Microbial reactions
  - Mineral and gas solubility
  - Adsorption
- Water viscosity
  - Streambed hydraulic conductivity
  - Particle settling

Importance of Temperature



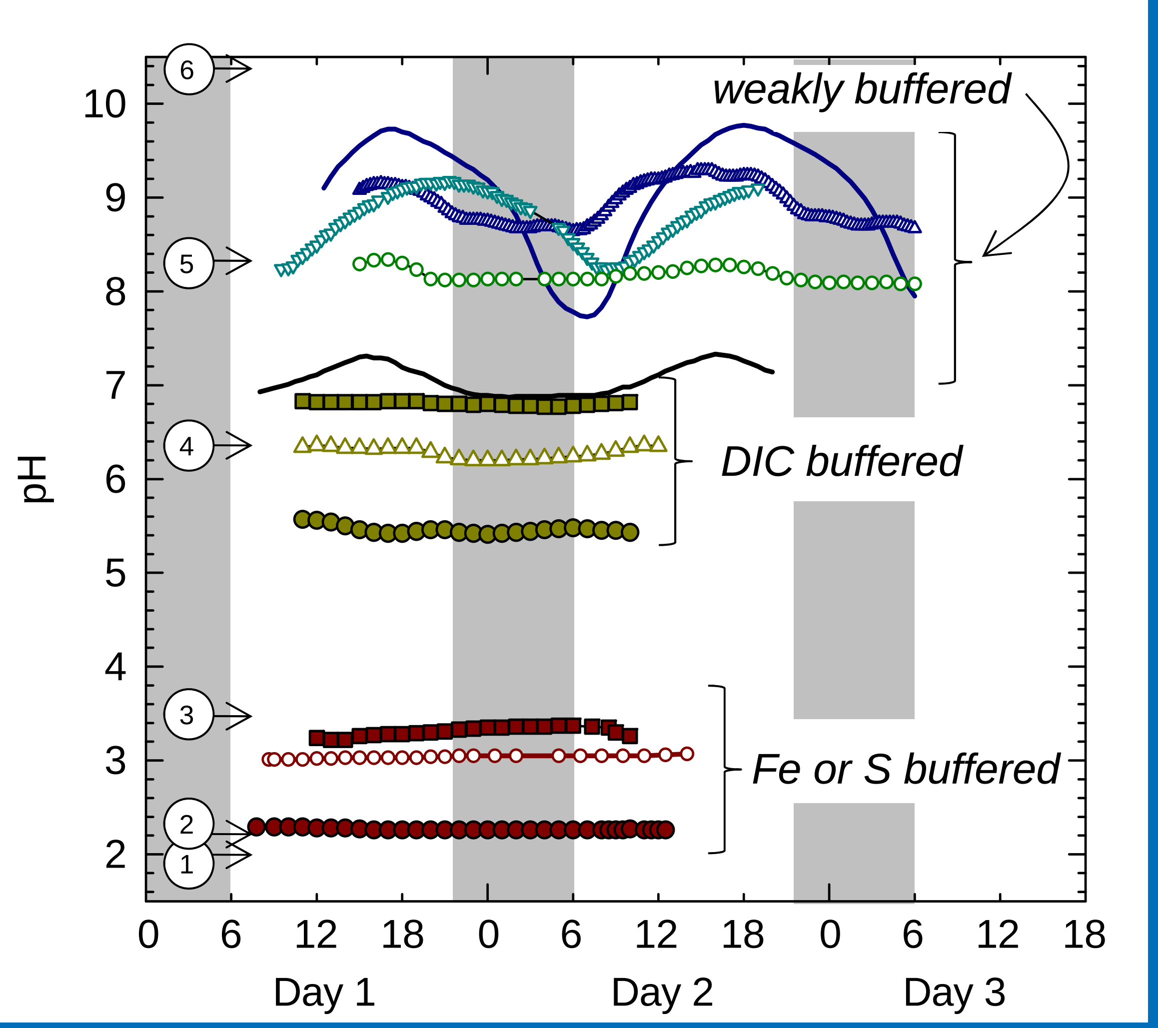


Silver Bow Creek, Montana

(USGS long-term monitoring data for 2002-2011)

Diel pH Cycles

- 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)

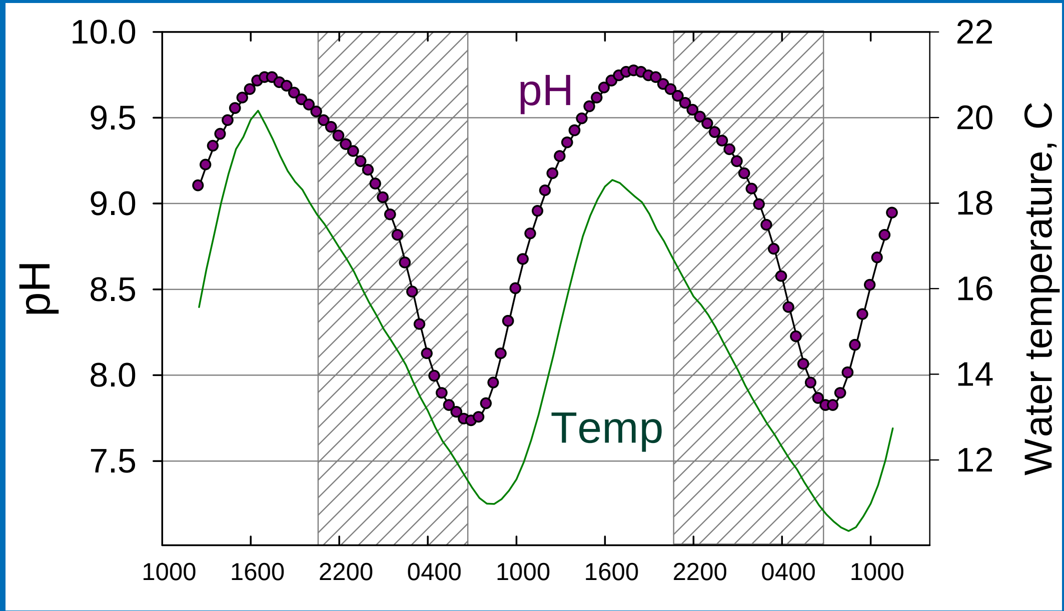
Diel pH Cycles

- Causes
  - Photosynthesis/respiration

$$CO_2 + H_2O \underset{\text{Night}}{\overset{\text{Day}}{\rightleftarrows}} CH_2O + O_2$$

  - Changes in temperature
  - Changes in ground-water inflow
  - Fe chemistry

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



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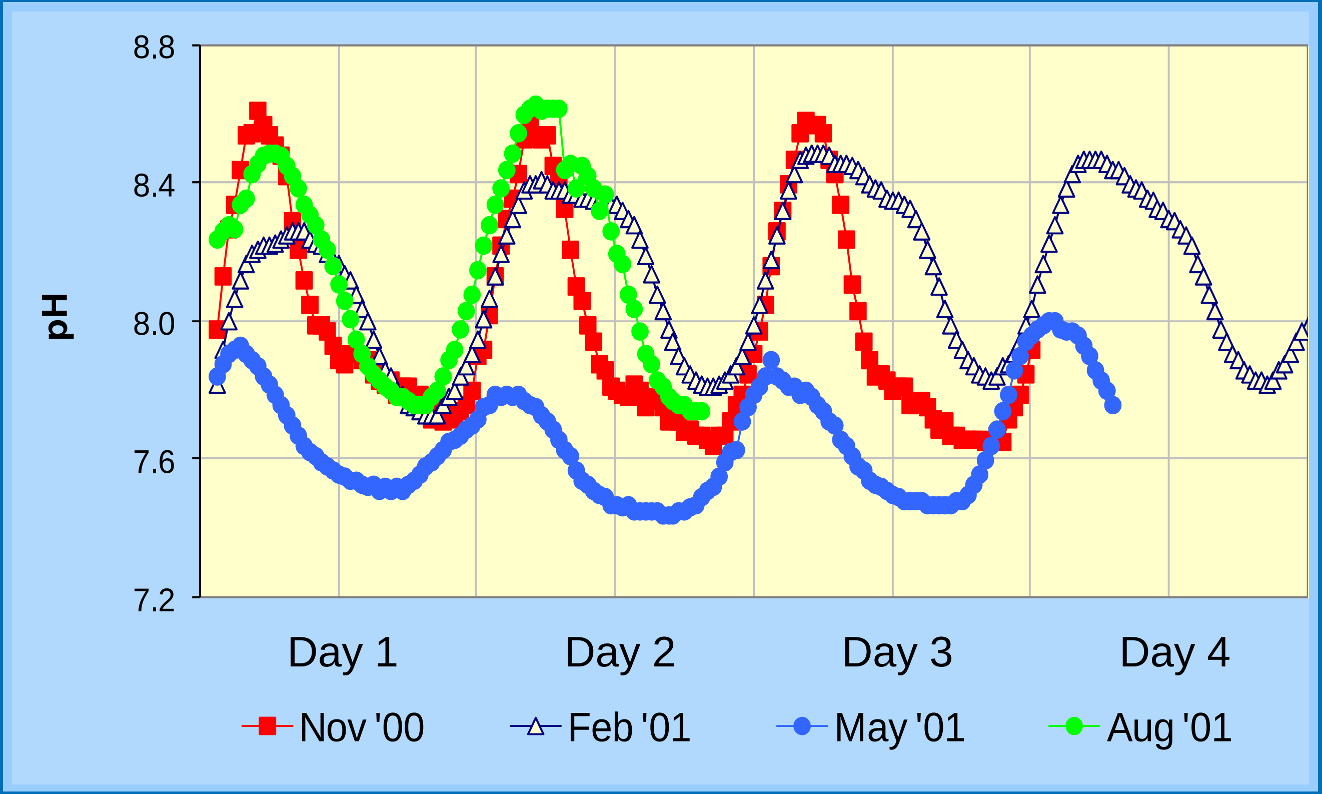
Seasonal Changes in Diel Cycles



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

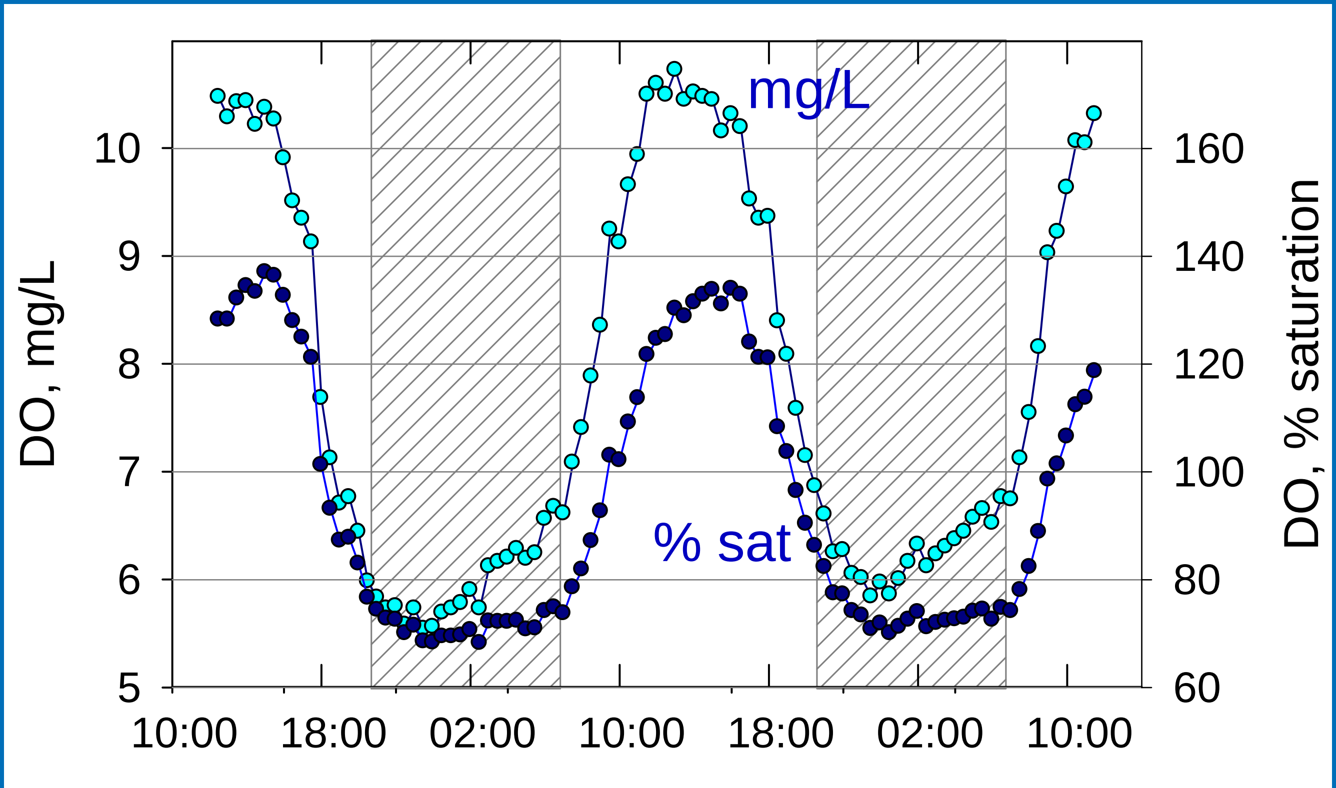
(Chris Gammons, Montana Tech)

Big Hole River in winter

USGS

Diel Cycles in Dissolved Oxygen

Photosynthesis/respiration: $CO_2 + H_2O \underset{\text{Night}}{\overset{\text{Day}}{\rightleftarrows}} CH_2O + O_2$

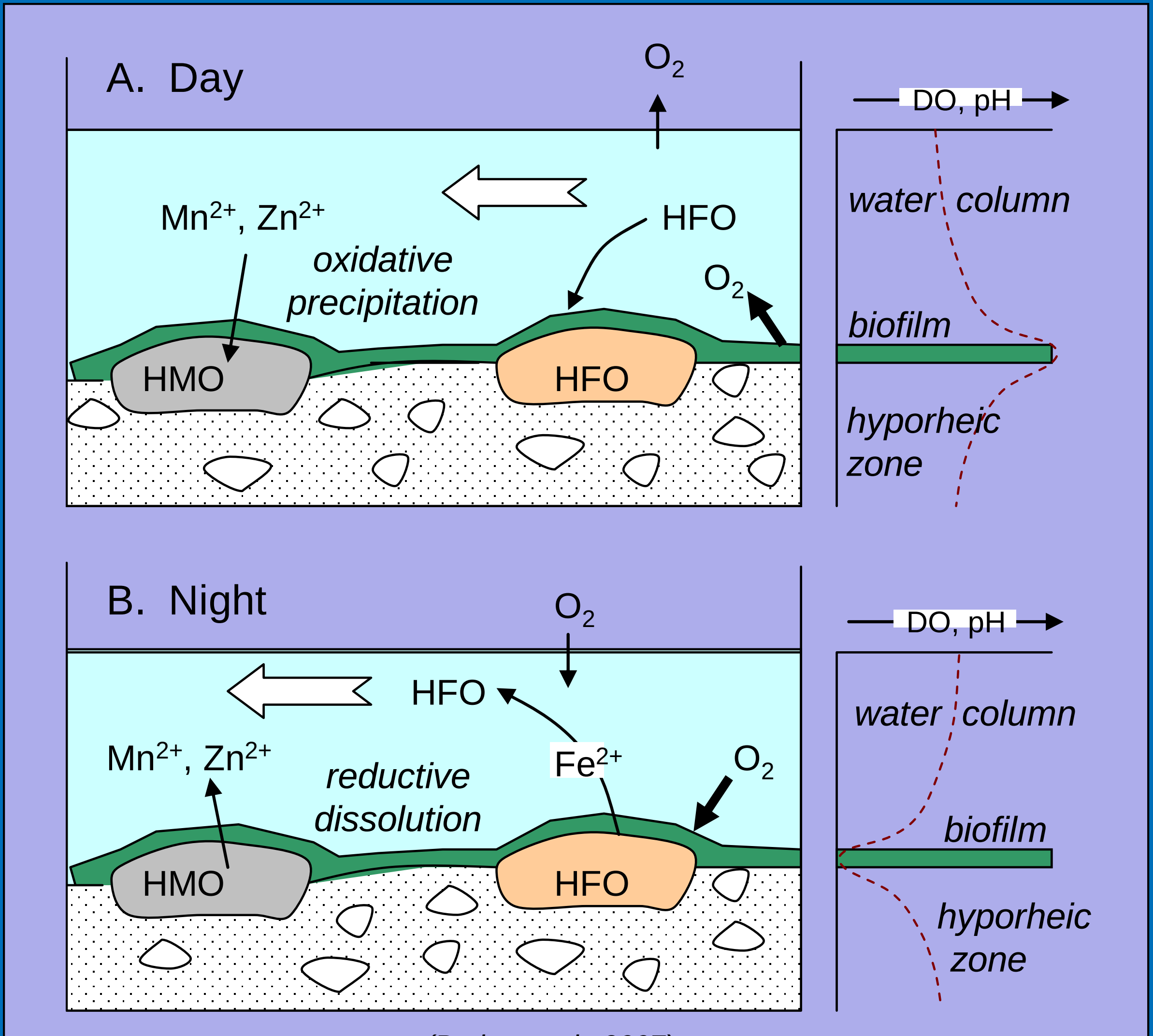


Big Hole River, MT

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

Diel Cycling in Biofilms vs. Bulk Water

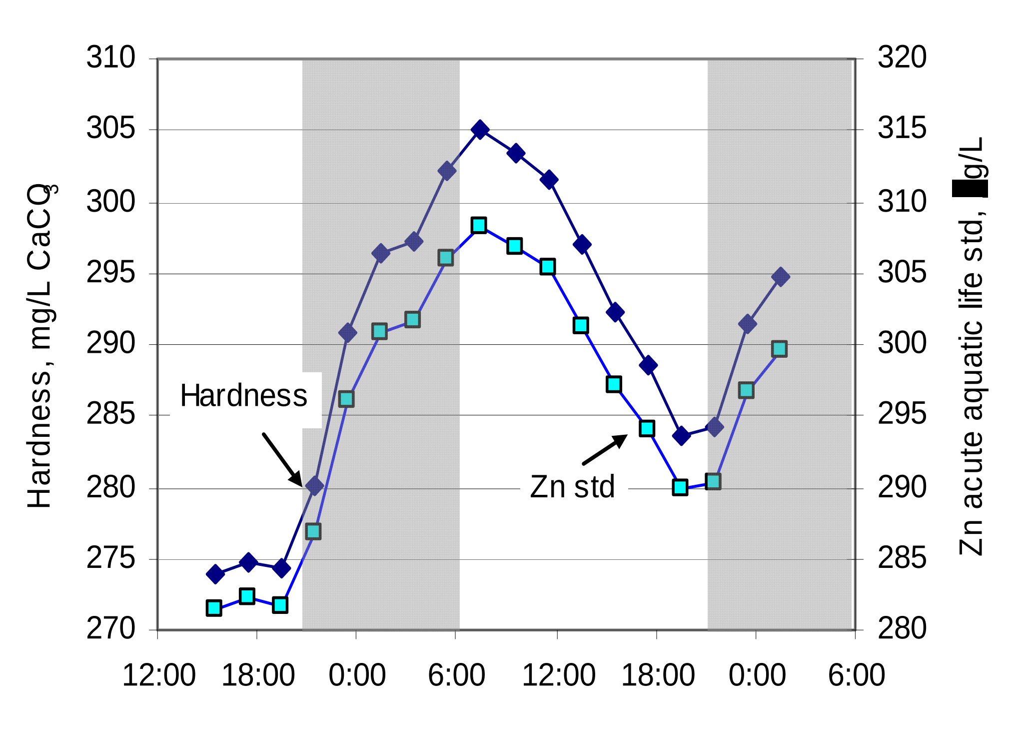
- **Changes in pH, DO, and redox are magnified in biofilms relative to the bulk water!**



(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 ($CaCO_3$) precipitation and dissolution**
- **Importance: Aquatic life standards for many toxic metals are hardness-dependent**



Mill-Willow Bypass, Montana, August 2005
(Gammons et al., 2007)

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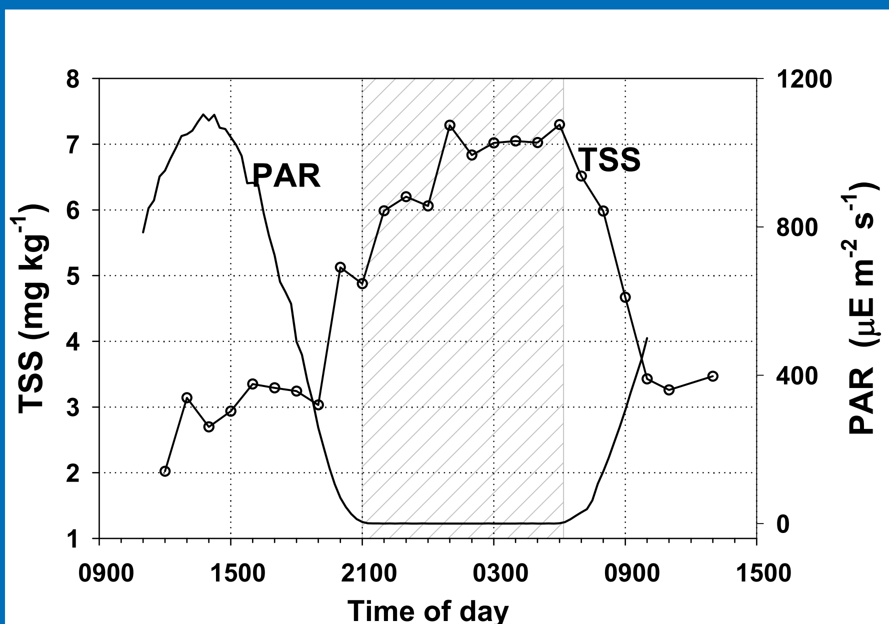
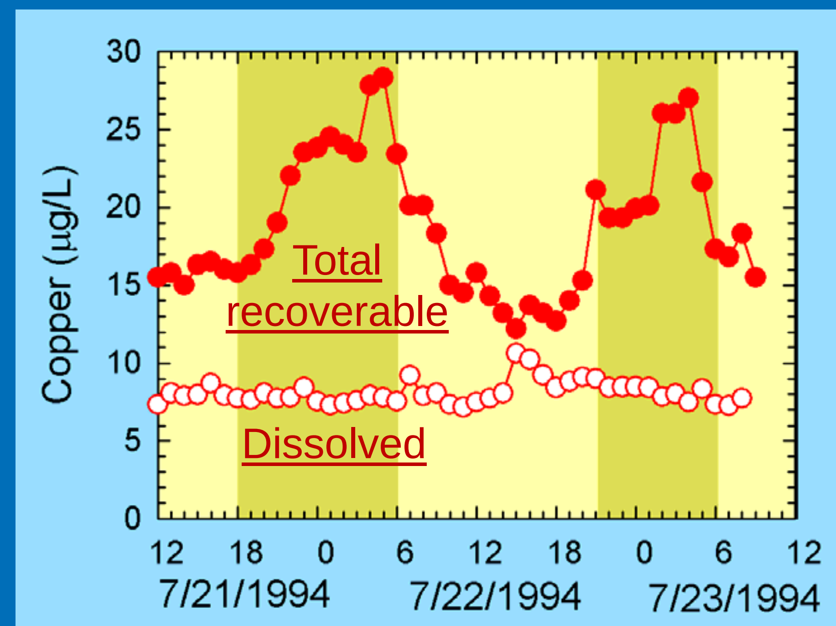
Diel Cycles in Suspended Solids

- **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)

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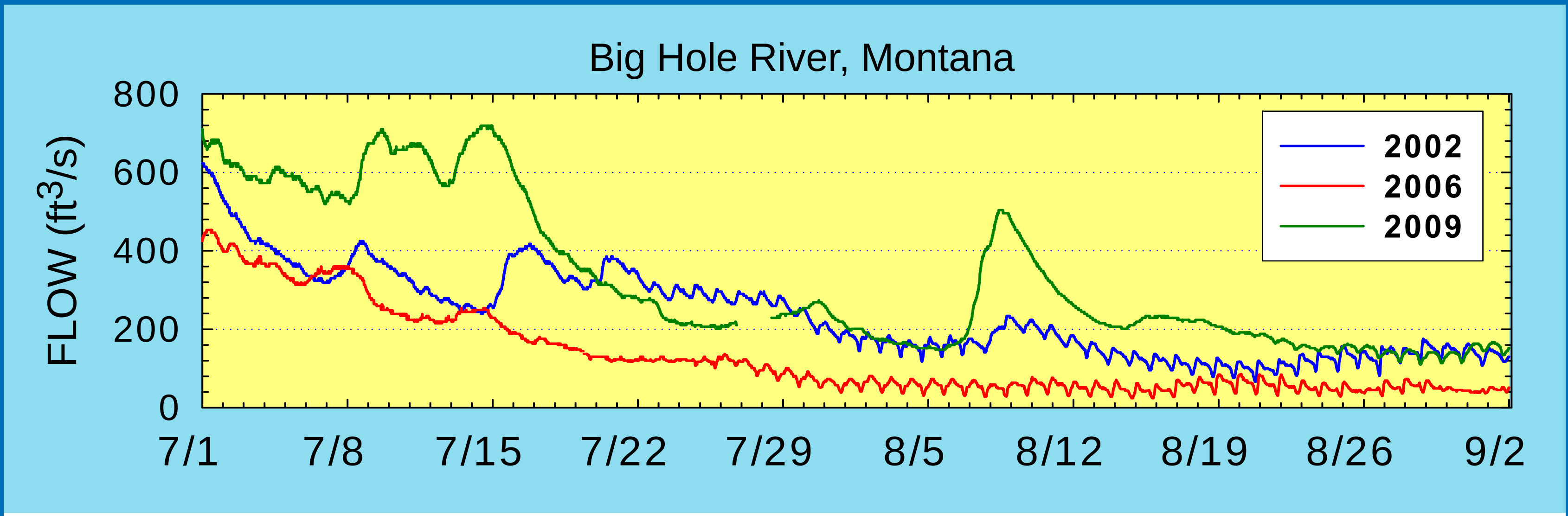
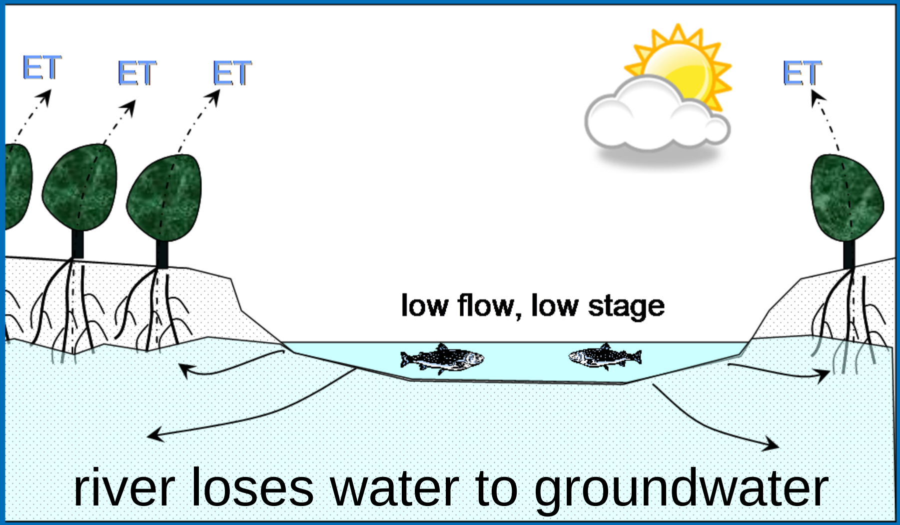
Diel Streamflow Cycles

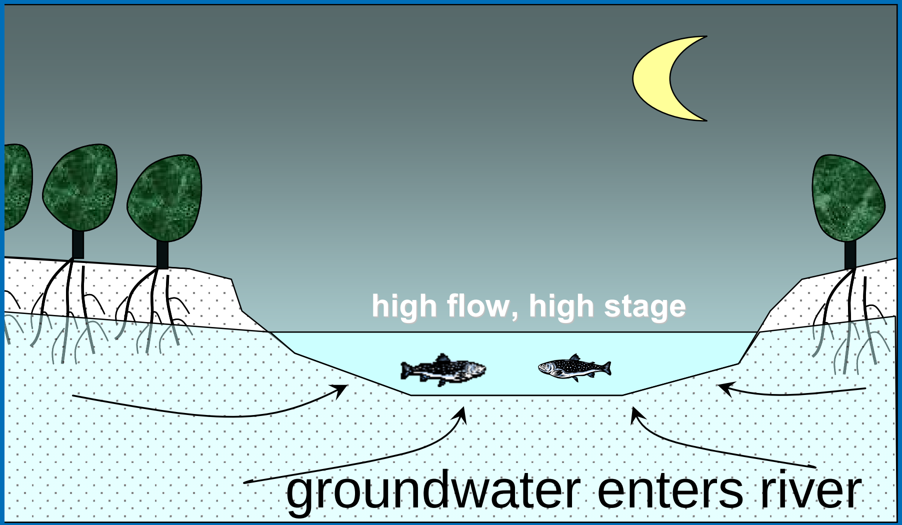
- Freeze/thaw
  - Ice formation
  - Snow melt
- Evapotranspiration
- Temperature-dependent streamflow loss
- Anthropogenic
  - Wastewater or reservoir discharge
  - Irrigation withdrawals
- Macrophyte dams



Diel Streamflow Cycles

Evapotranspiration (ET) typically changes flow by <20%





- Diel streamflow cycles affect:
  - Solute concentration (dilution)
  - Solute load (load = concentration x flow)

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Diel Cycling of Nutrients

NITROGEN

- Nitrate (NO_3^-)
- Nitrite (NO_2^-)
- Nitrous oxide (N_2O)
- Nitrogen (N_2)
- Ammonia (NH_4^+)
- Organic-N
- Suspended solids

PHOSPHORUS

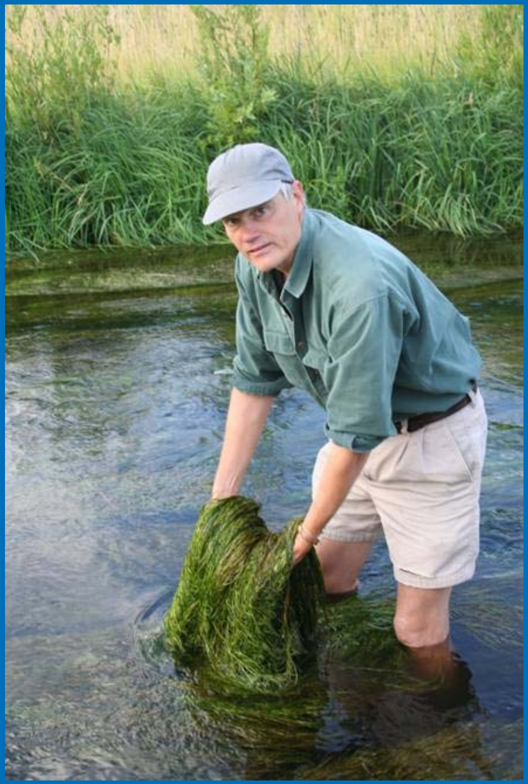
- Orthophosphate (HPO_4^{-2})
- Organic-P
- Suspended solids

Big Hole River, Montana

USGS

Diel Cycling of Nutrients

- Diel redox cycles
  - Nitrification (ammonia + $O_2 \rightarrow$ nitrate)
  - Denitrification (nitrate + organic C $\rightarrow N_2$)
  - Anammox (ammonia + nitrate $\rightarrow N_2$)
- 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

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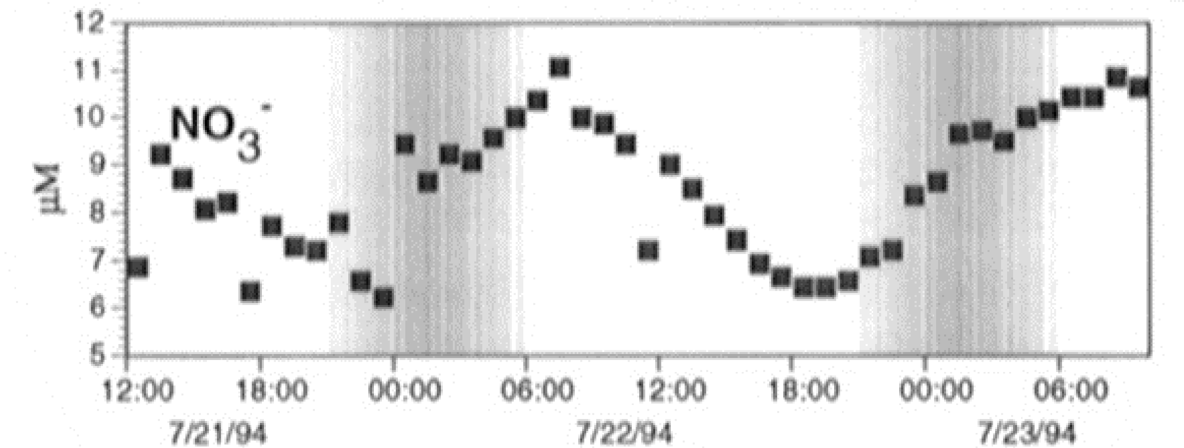
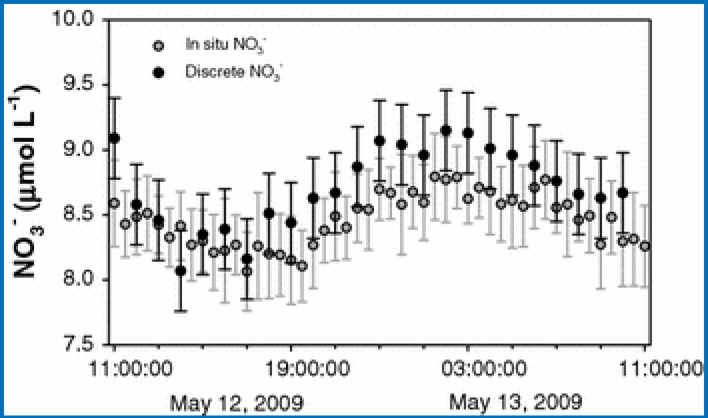
Diel Cycling of Nitrate



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



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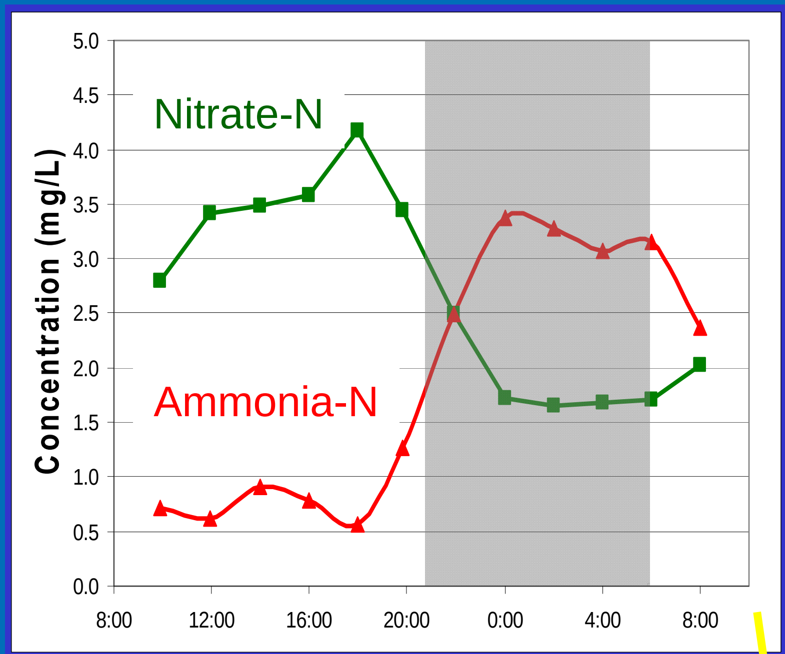
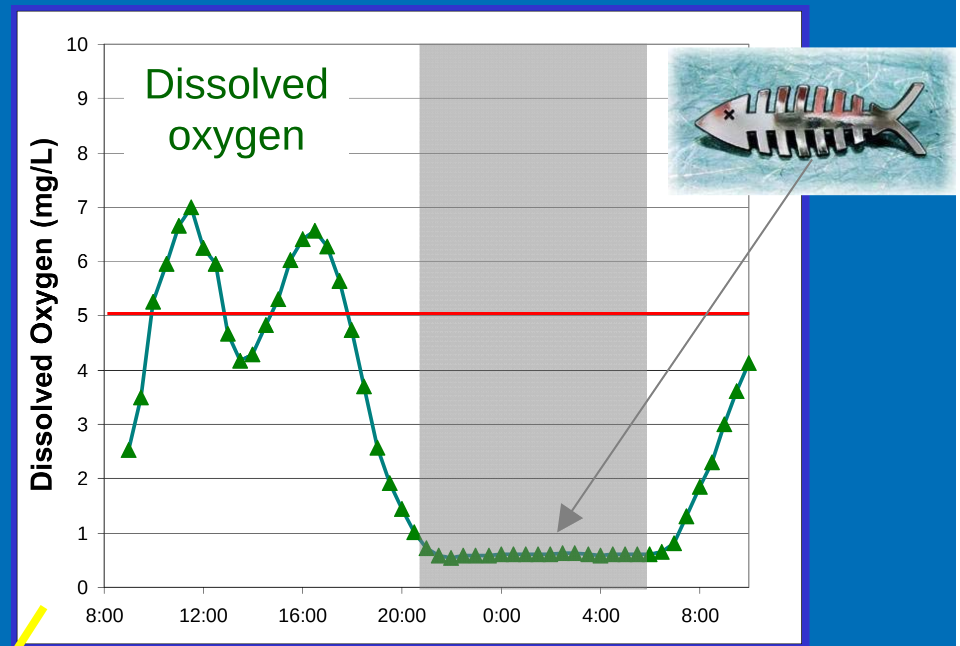
Sleepers River, Vermont (Pellerin et al., 2012)

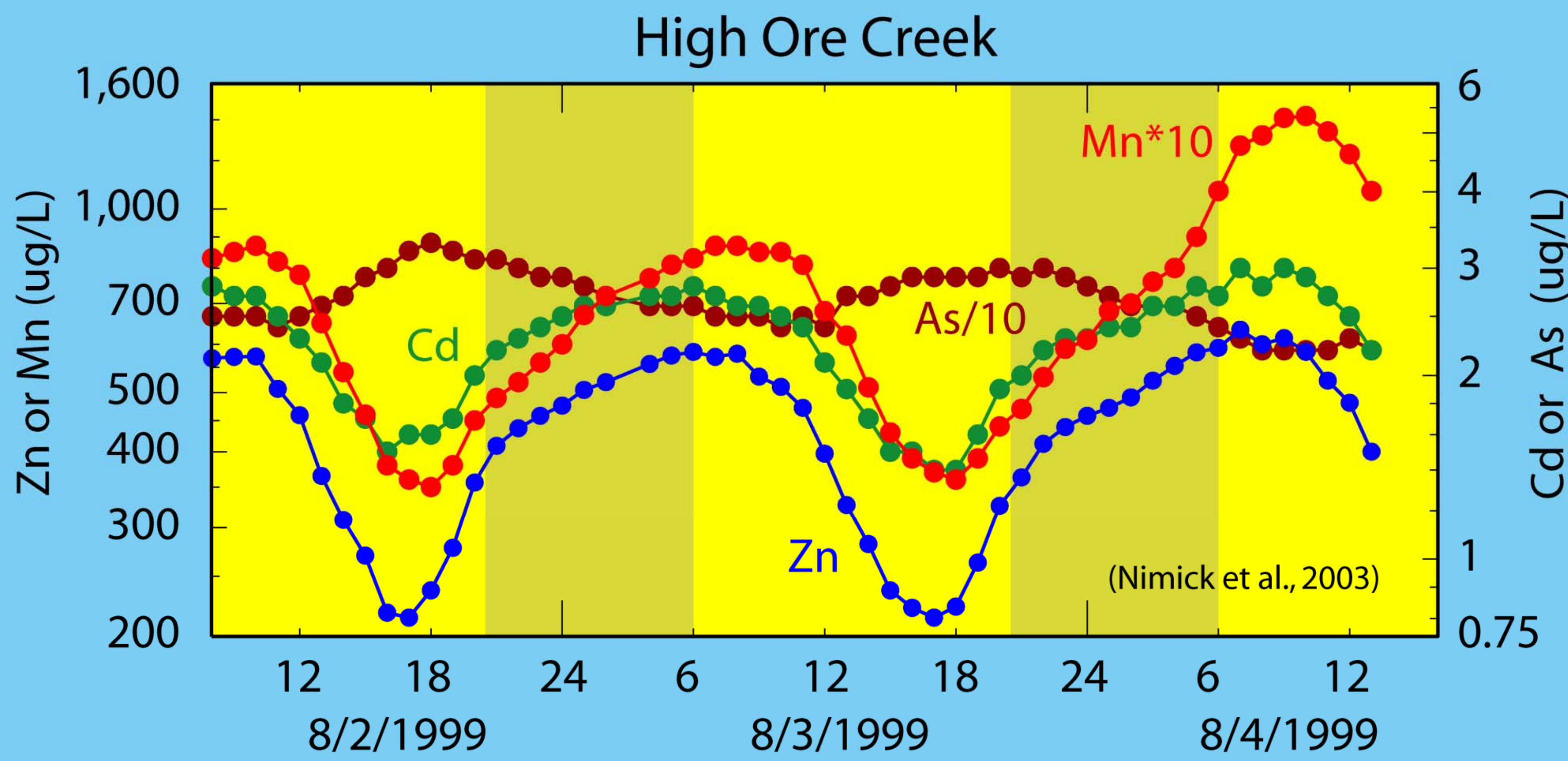
Diel Nutrient Cycling in Silver Bow Creek





(Gammons et al., 2011)

Diel Trace-Element Cycles in Neutral and Alkaline Streams



Arsenic	Cadmium	Manganese	Zinc
22-33 µg/L	1.4-3.0 µg/L	35-142 µg/L	214-634 µg/L
50%	110%	306%	196%

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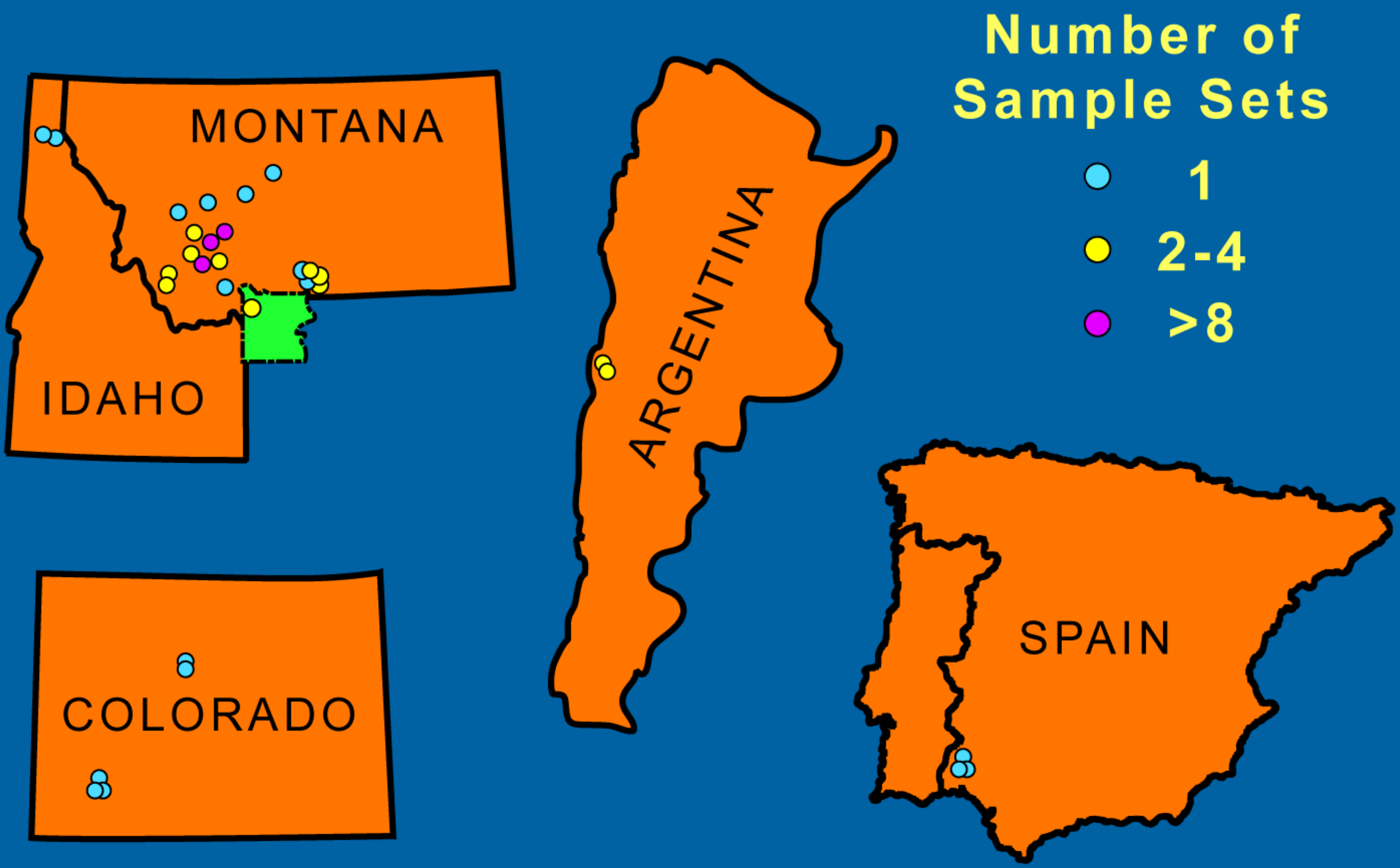
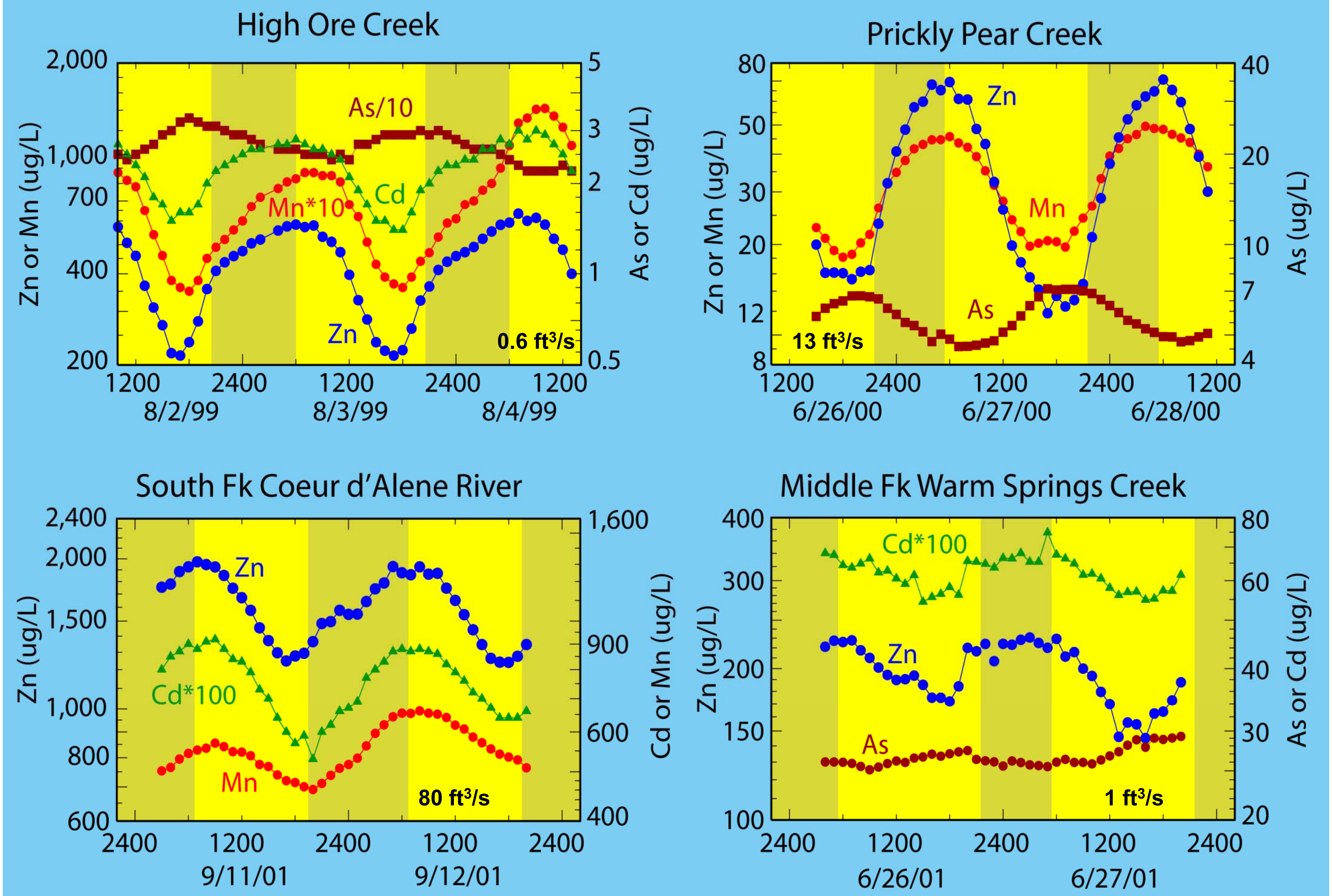
Diel Trace-Element Cycles



Diel sampling sites – 1990-2011



(Nimick et al., 2003)

Magnitude of Diel Cycles for Dissolved Trace Elements

Trace Element[1]	Maximum Daily Increase (%) [2]	Number of Diel Samplings[2]
Zn	990	>35
Rare earth elements	830	2
Cd	330	12
Mn	306	20
Ni	167	1
U	125	2
Methyl Hg	93	2
As	54	>25
Cu (pH = 6.8 – 7)	140	3
Cu (pH > 7)	<10	12
Se	<10	1

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

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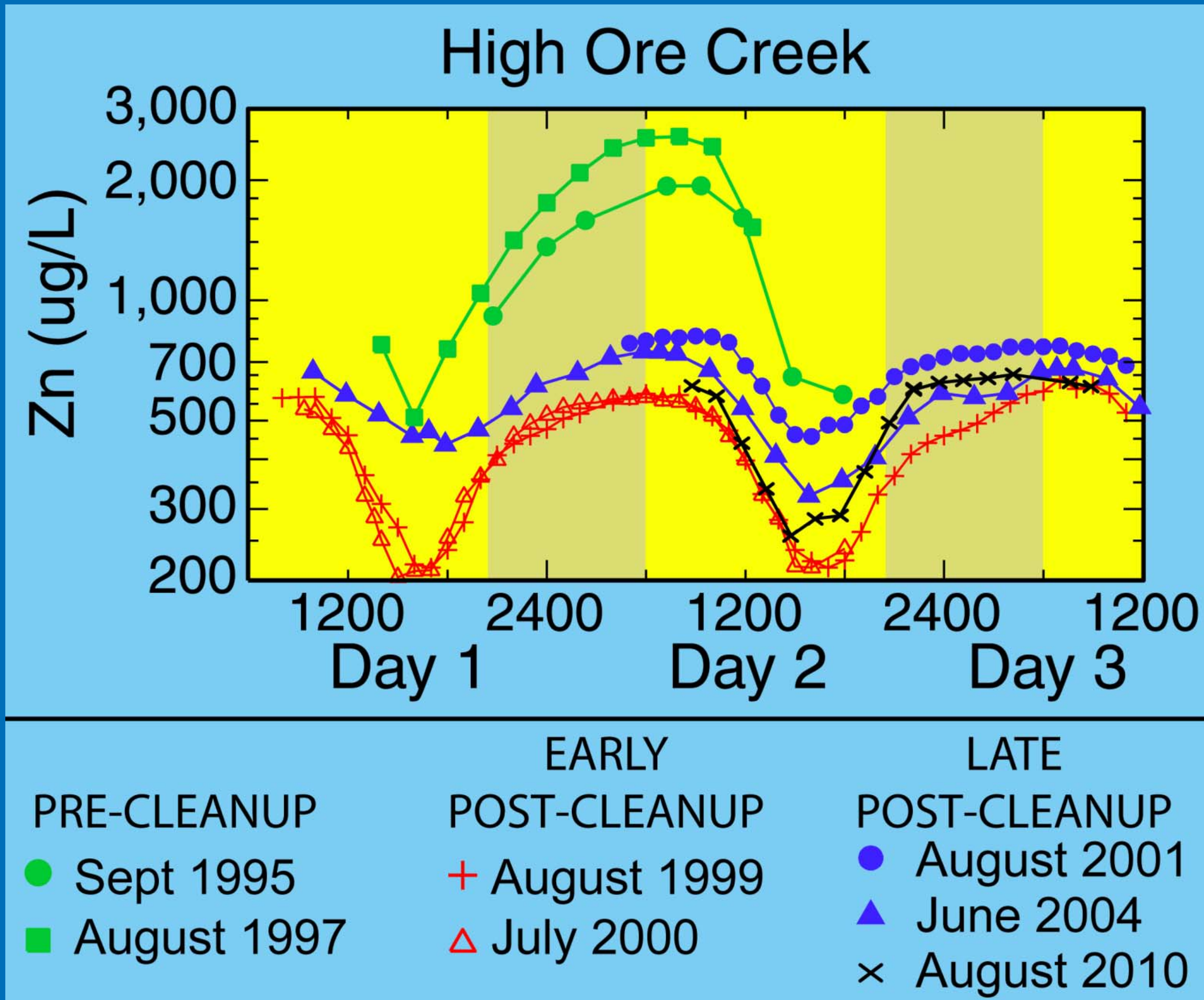
Year-to-Year Variation



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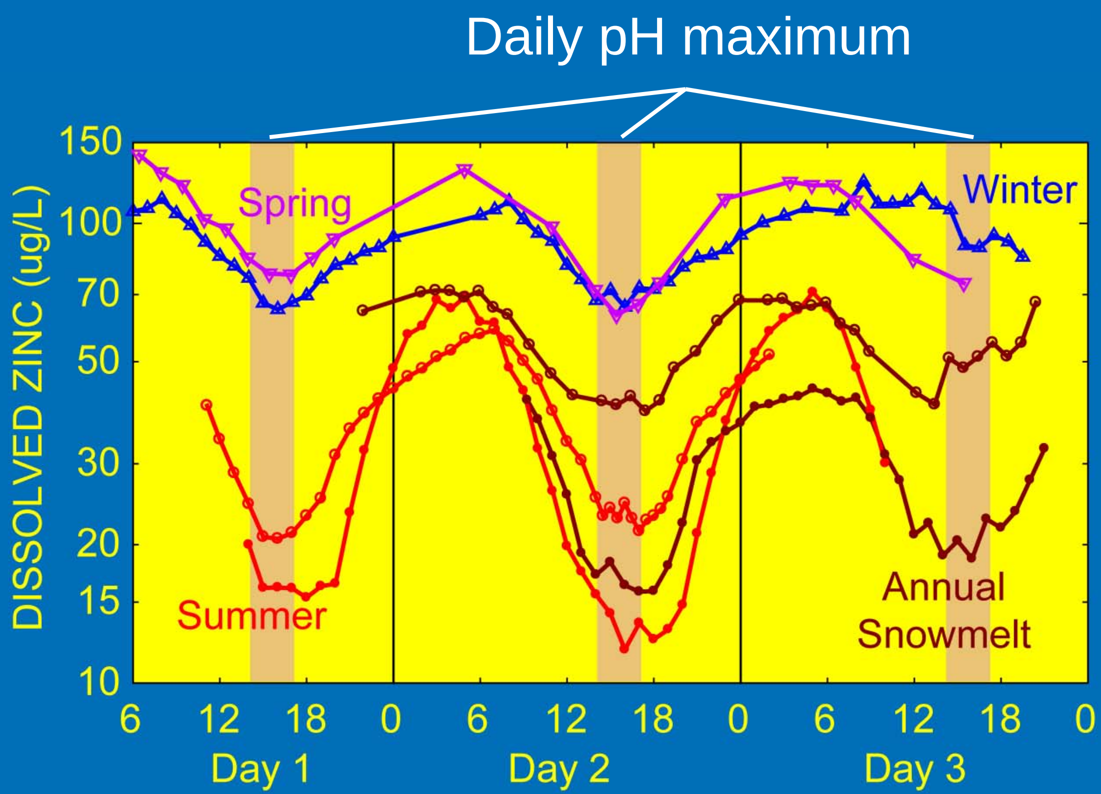
Seasonal Variation

Prickly Pear Creek, Montana



(Nimick et al., 2005)

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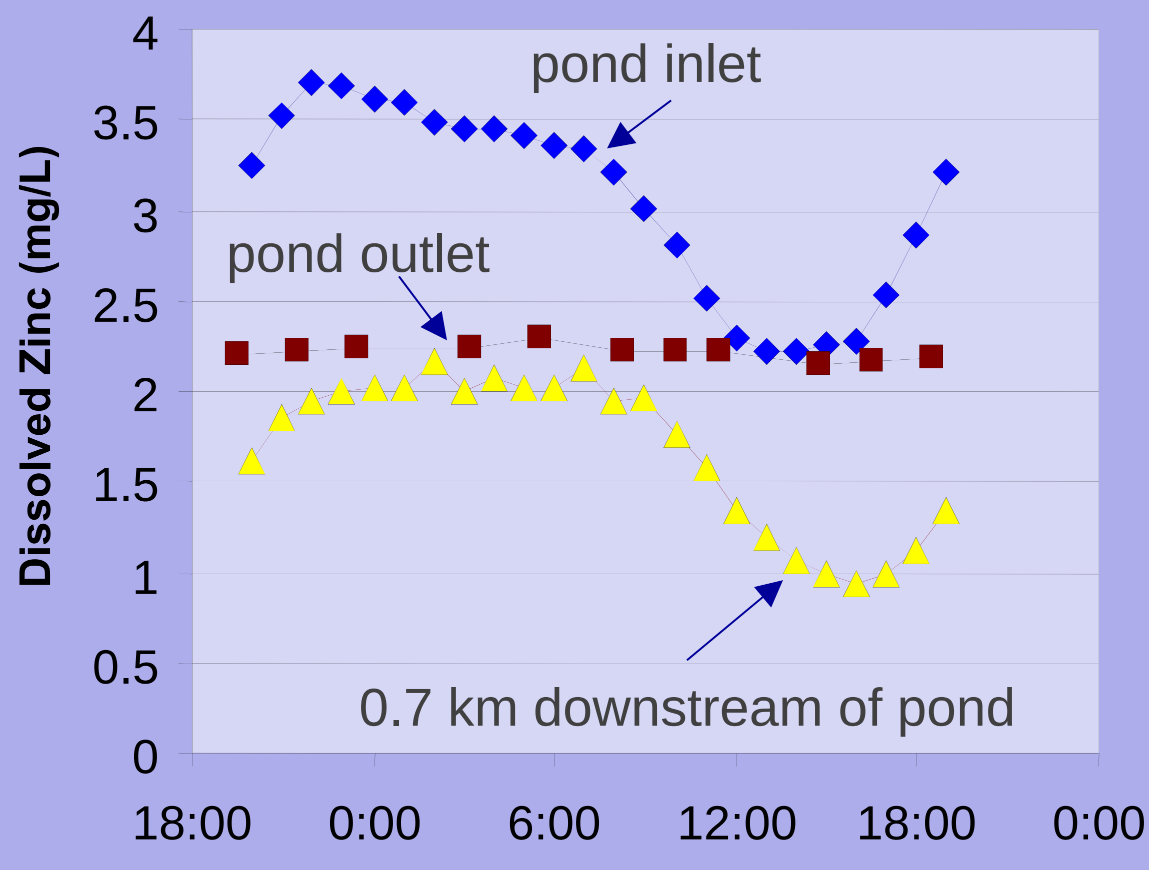
Lakes versus Rivers

- **Lakes and ponds tend to "even out" diel cycles found in streams**



High Ore Creek, MT
(*Gammons et al., 2007b*)

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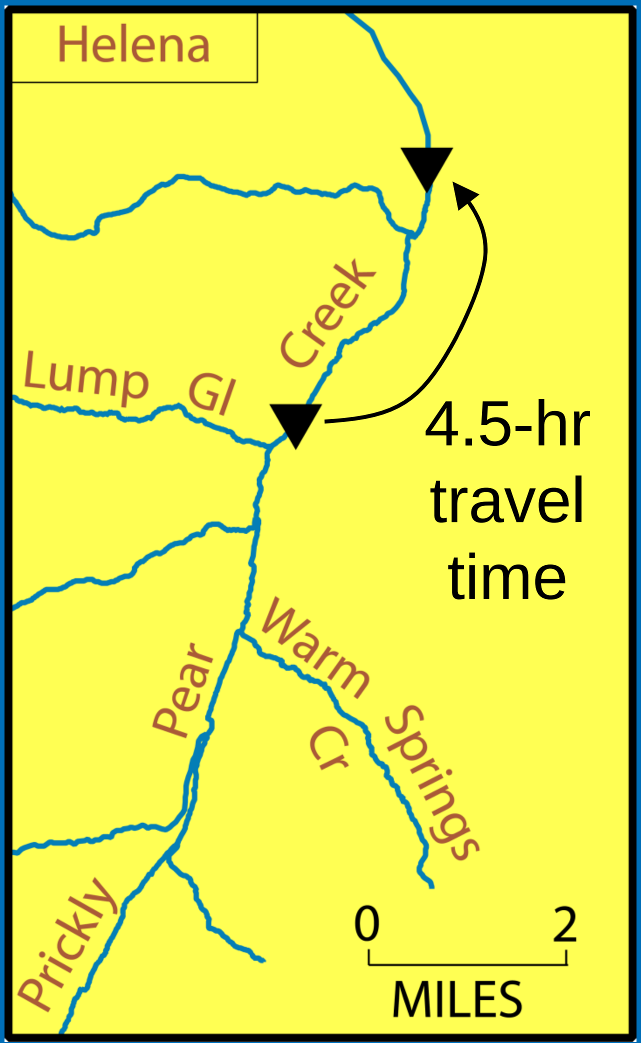
Possible Causes – Dissolved Metal Cycles

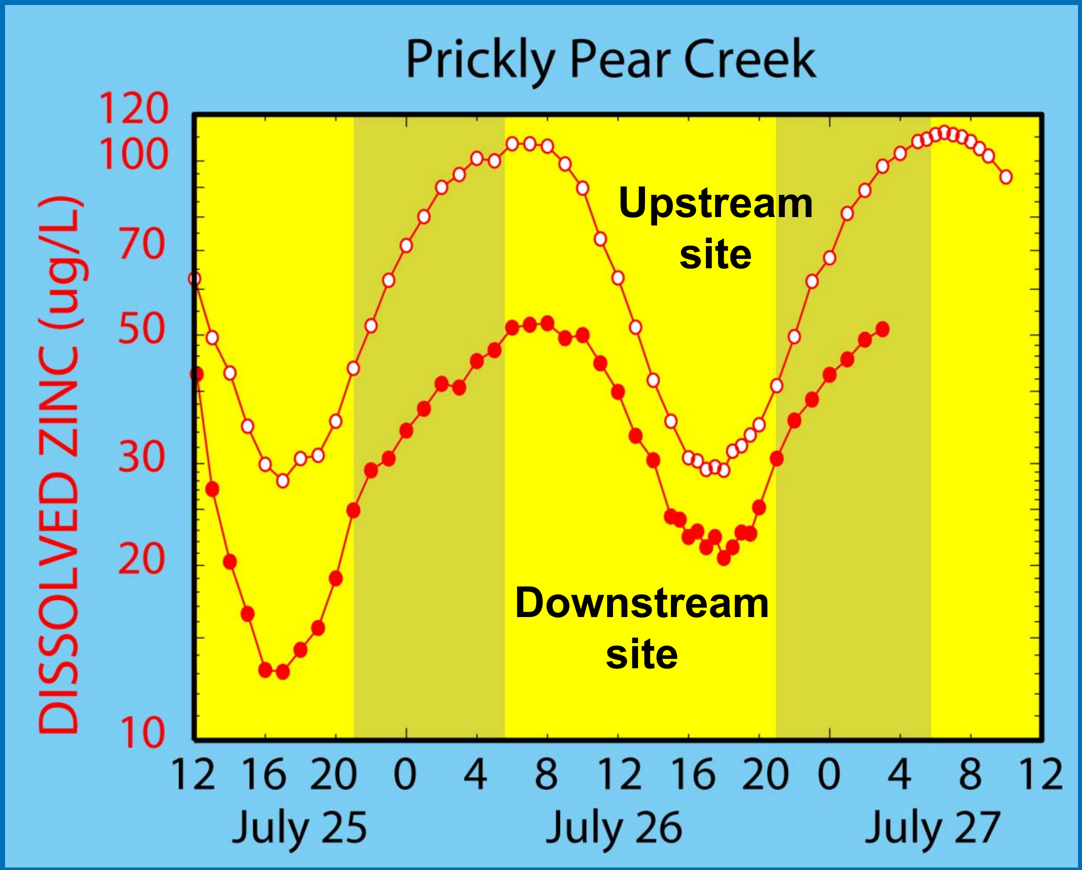
- Diel variation in metal input
- Biological uptake
- Precipitation-dissolution reaction
- Sorption-desorption reaction

South Fork Coeur d'Alene River

USGS

Cause: Diel Source Input or Instream Process?





No lag time means cycles caused by instream process

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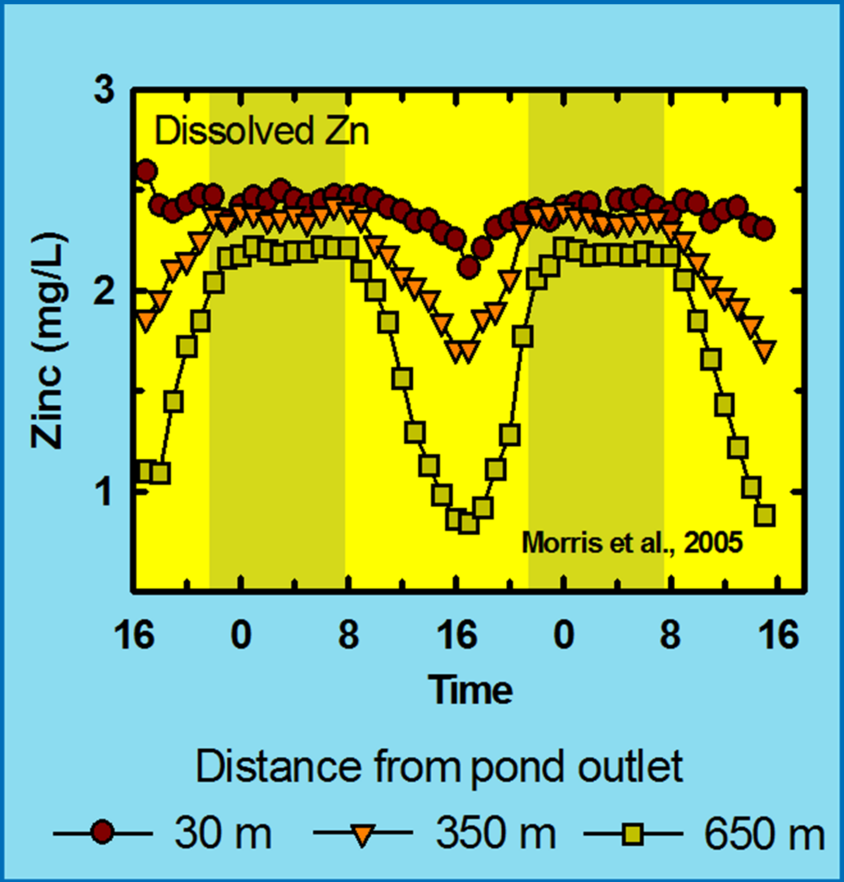
Cause: Biological Uptake

- **Uptake by biofilm and periphyton is plausible reason for Zn cycles but not As cycles, which have opposite timing**

High Ore Creek



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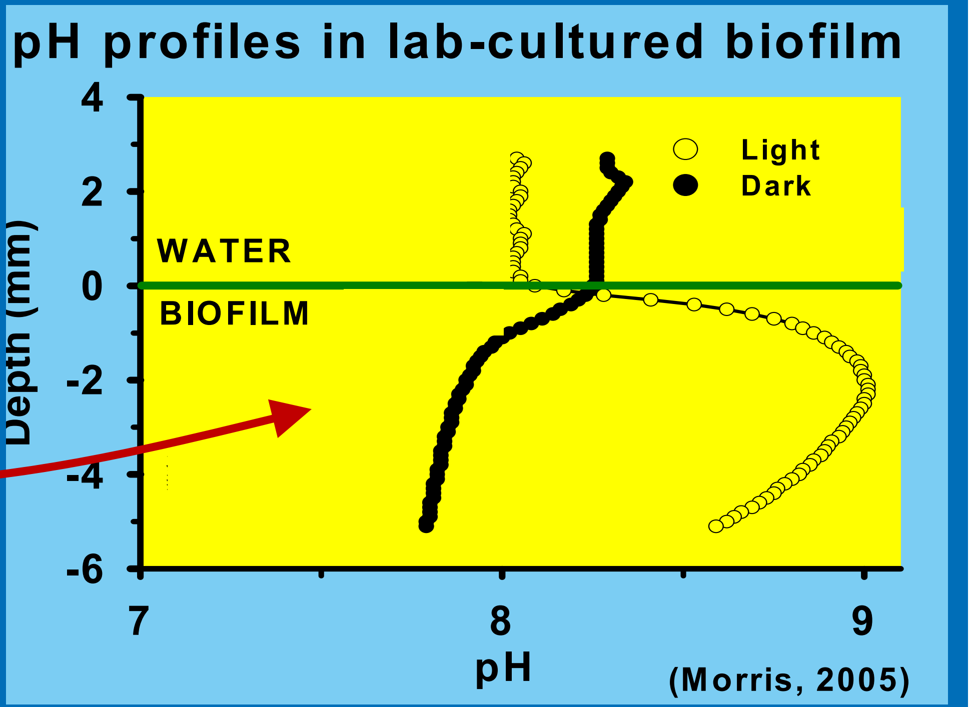
Cause: Precipitation-Dissolution

- Daytime increases in pH and water temperature increase mineral saturation and precipitation
  - $Zn^{+2} + CO_3^{-2} = ZnCO_{3(s)}$ (smithsonite)
  - $Ca^{+2} + CO_3^{-2} = CaCO_{3(s)}$ (calcite)
- Reversible reaction
- pH changes much greater within biological surface
- Does not explain arsenic



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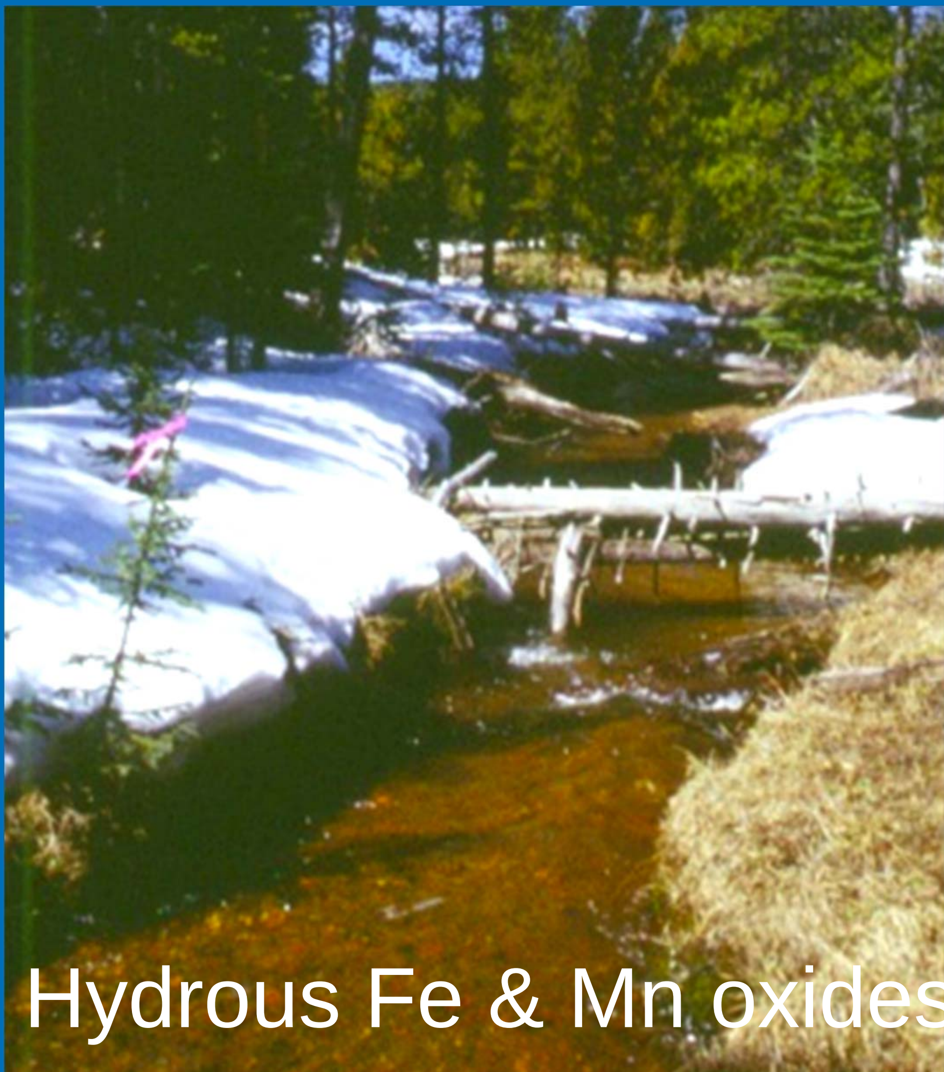
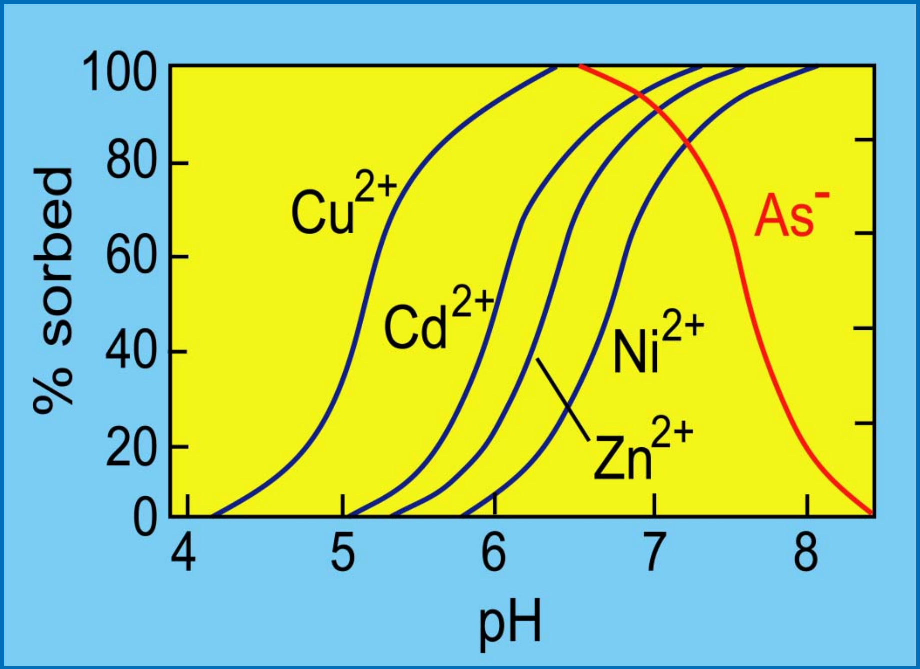
Cause: Sorption-Desorption

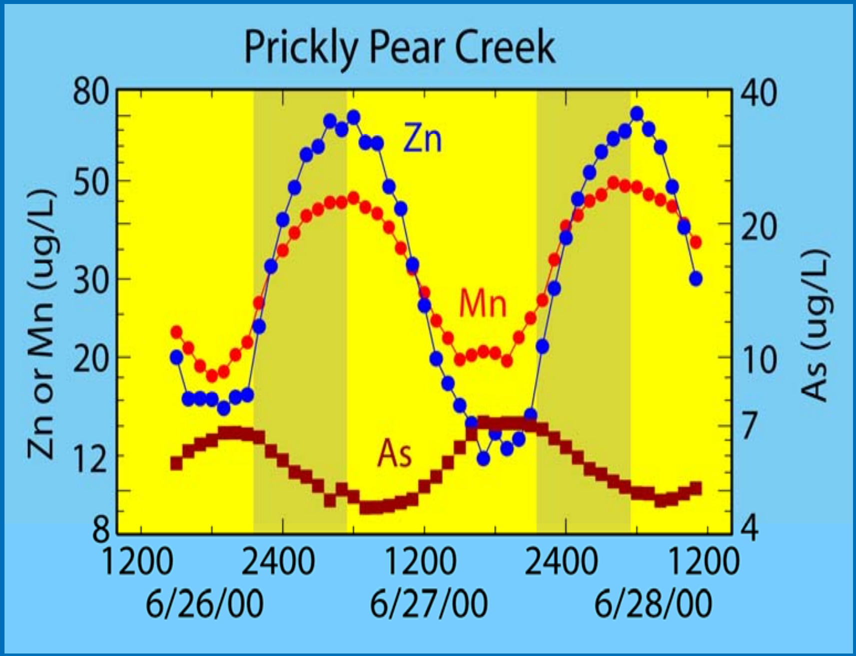


Possible inorganic and organic sorption substrates

Cause: Sorption-Desorption

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





Not All Streams Exhibit Diel Cycling

Big cycles

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

Small or nonexistent cycles

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

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Diel Processes in Acidic Streams

(Gammons et al., 2010)

(Gammons et al., 2005a,b)

(Gammons et al., 2008)

(Parker et al., 2008)

Fe(III) Photoreduction

$Fe^{3+} + H_2O + h\upsilon \rightarrow Fe^{2+} + H^+ + OH^\bullet$

Rio Tinto, Spain

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

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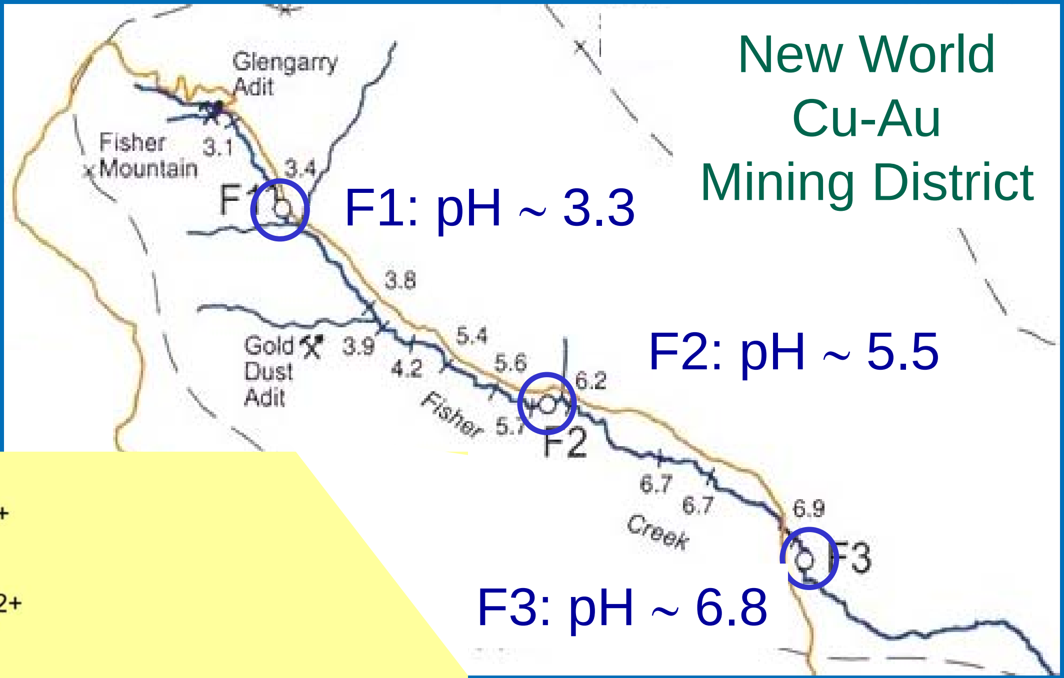
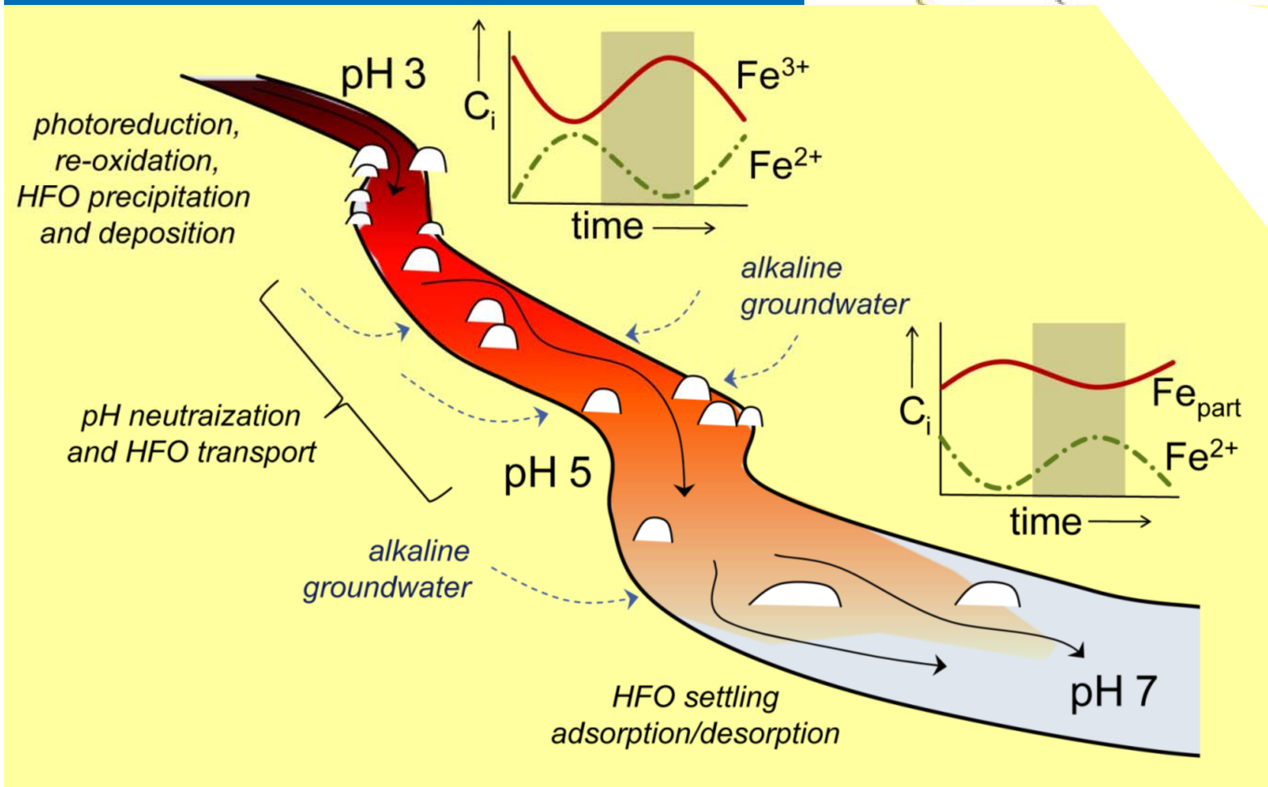
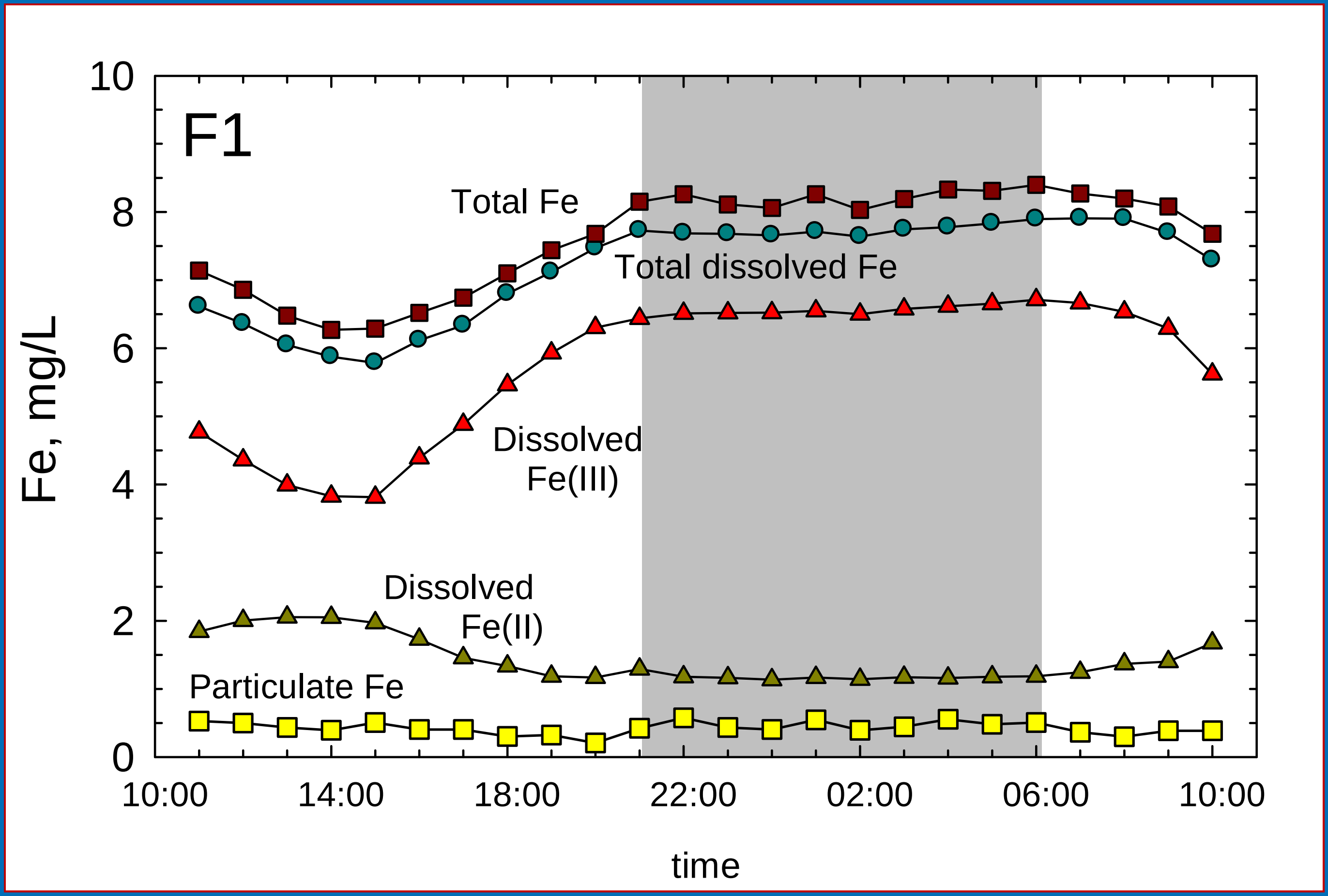
Fe Chemistry along a pH Gradient

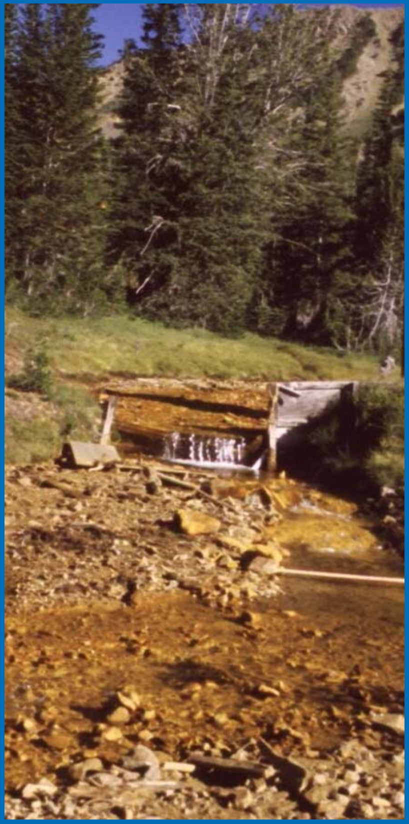




Fisher Creek, Montana
(Gammons et al., 2005a)

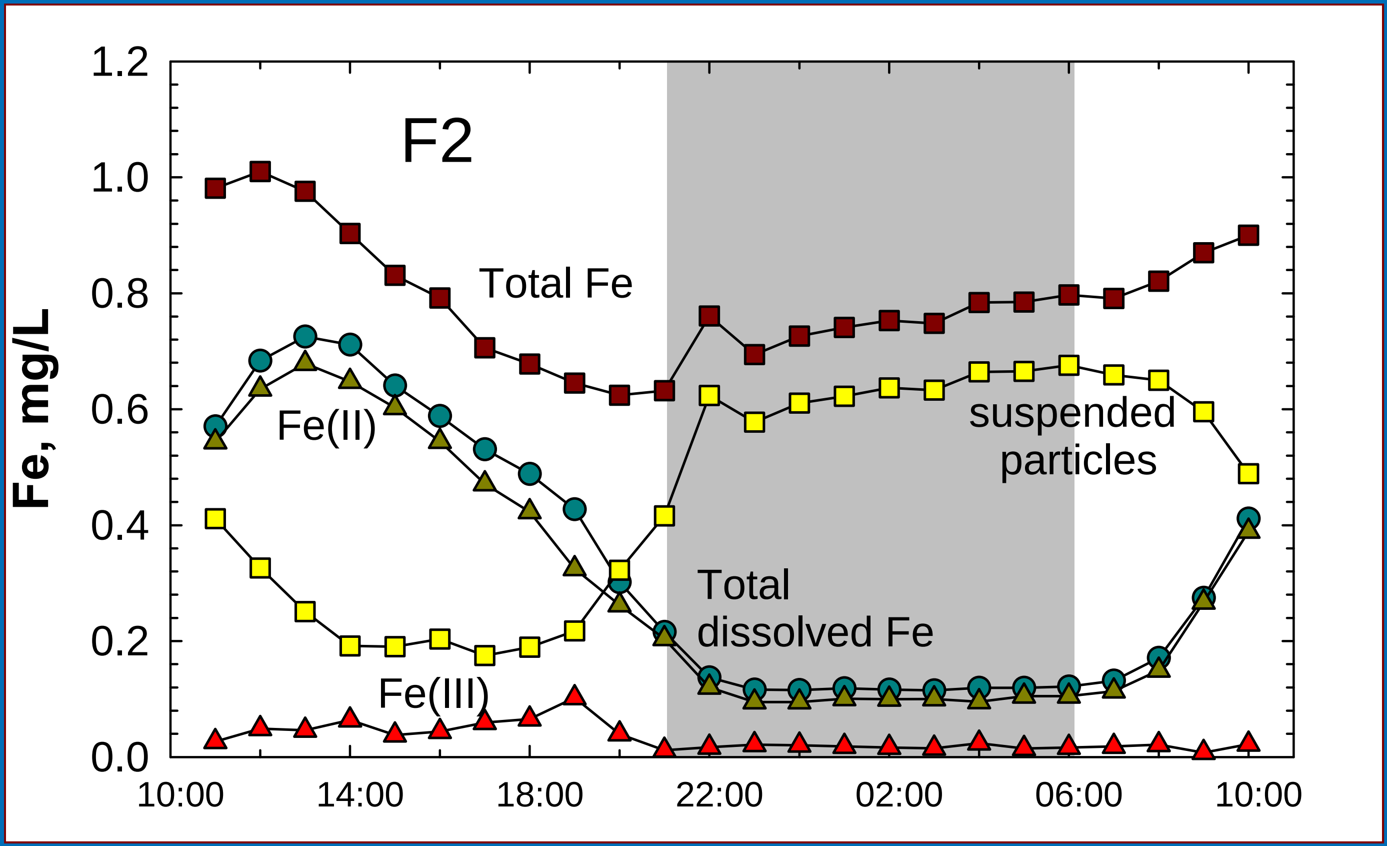
Fisher Creek F1 site: pH ~ 3.3





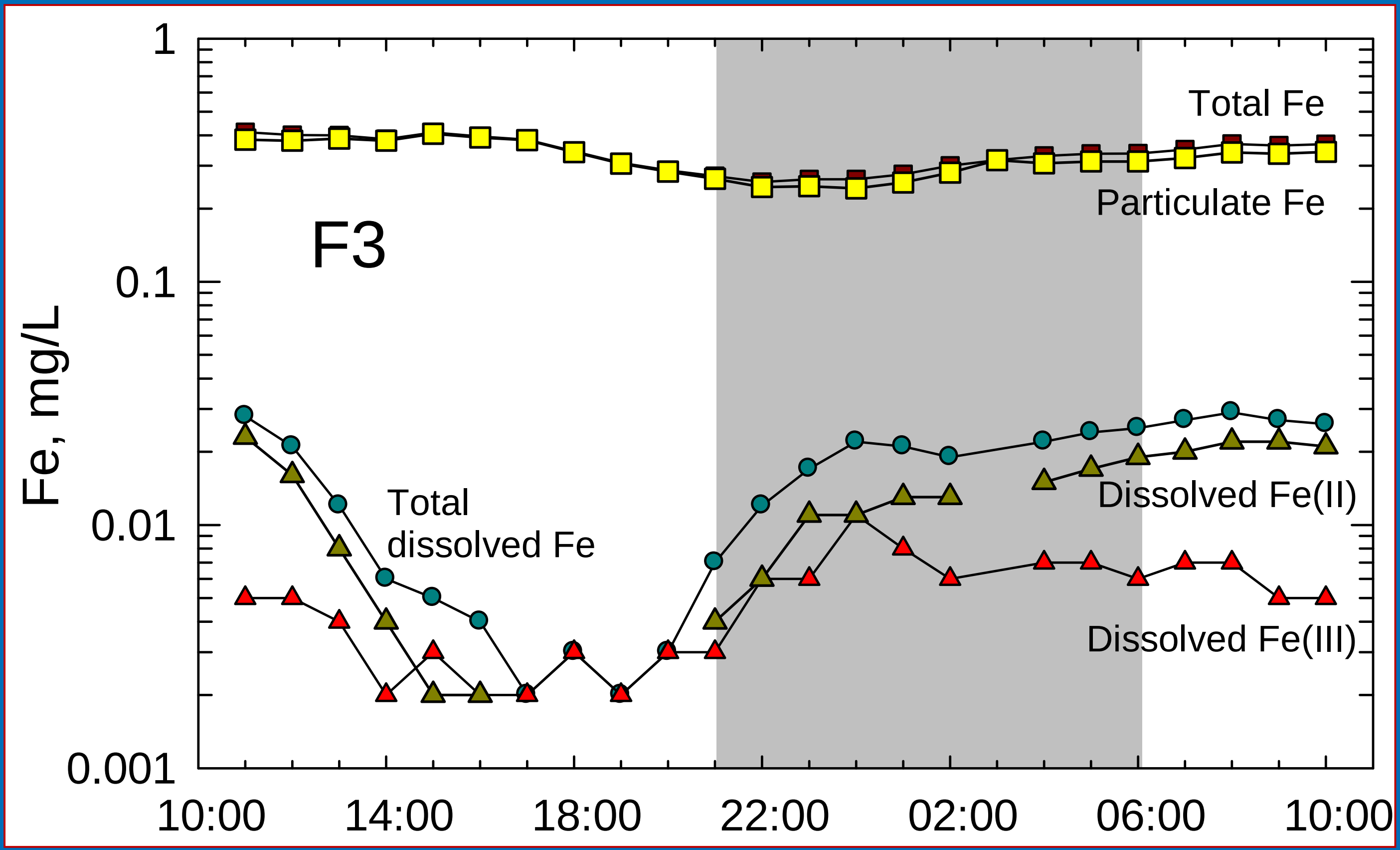
- Daytime decrease in total Fe (solubility of Fe ↓ as T ↑)
- Daytime photoreduction of Fe(III) to Fe(II)

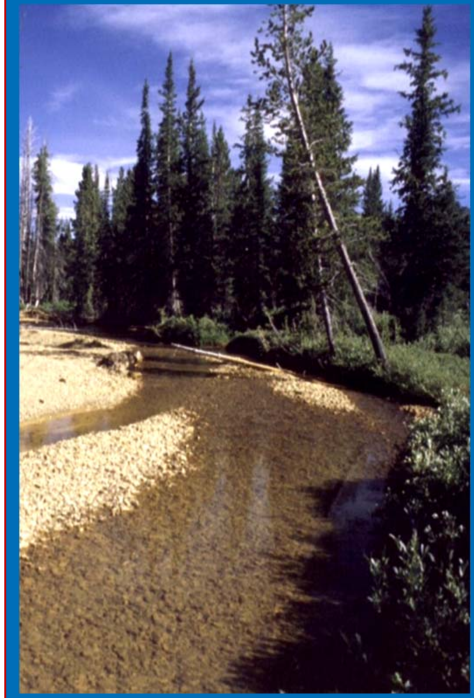
Fisher Creek F2 site: pH ~ 5.5



- Photoreduction of HFO causes daytime increase in Fe(II) and total dissolved Fe concentrations
- Fe mainly dissolved during day, particulate at night

Fisher Creek F3 site: pH ~ 6.8



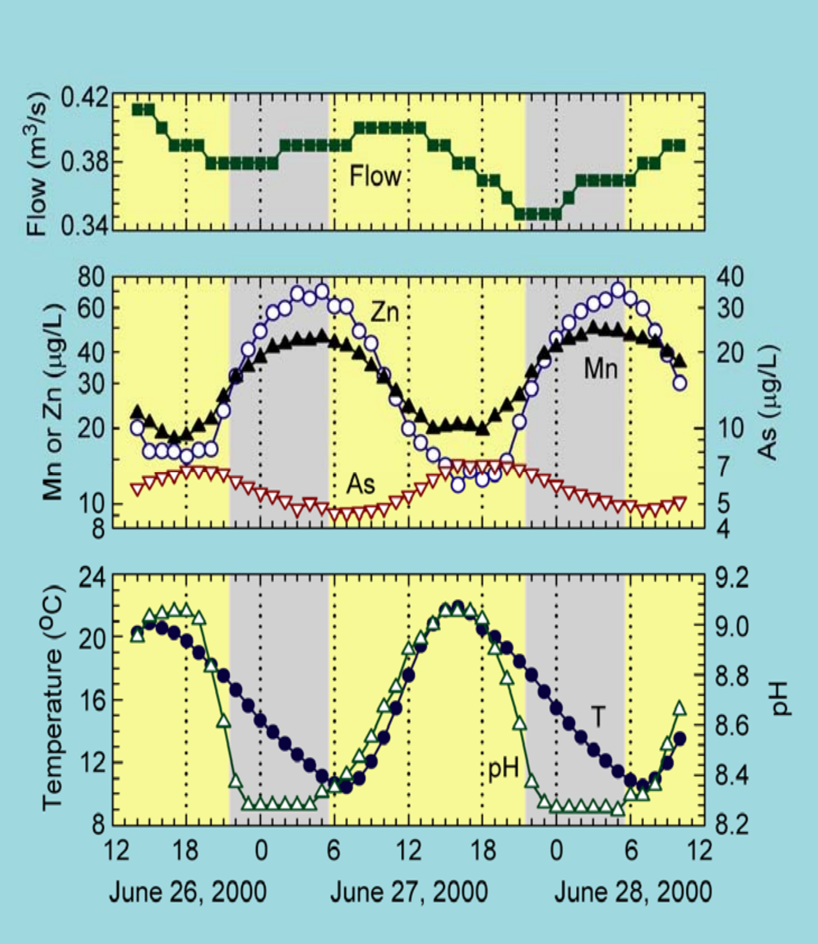


- No evidence of Fe(III) photoreduction
- Night-time increase in Fe(II) and total dissolved Fe mainly due to temperature-dependent sorption

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!*



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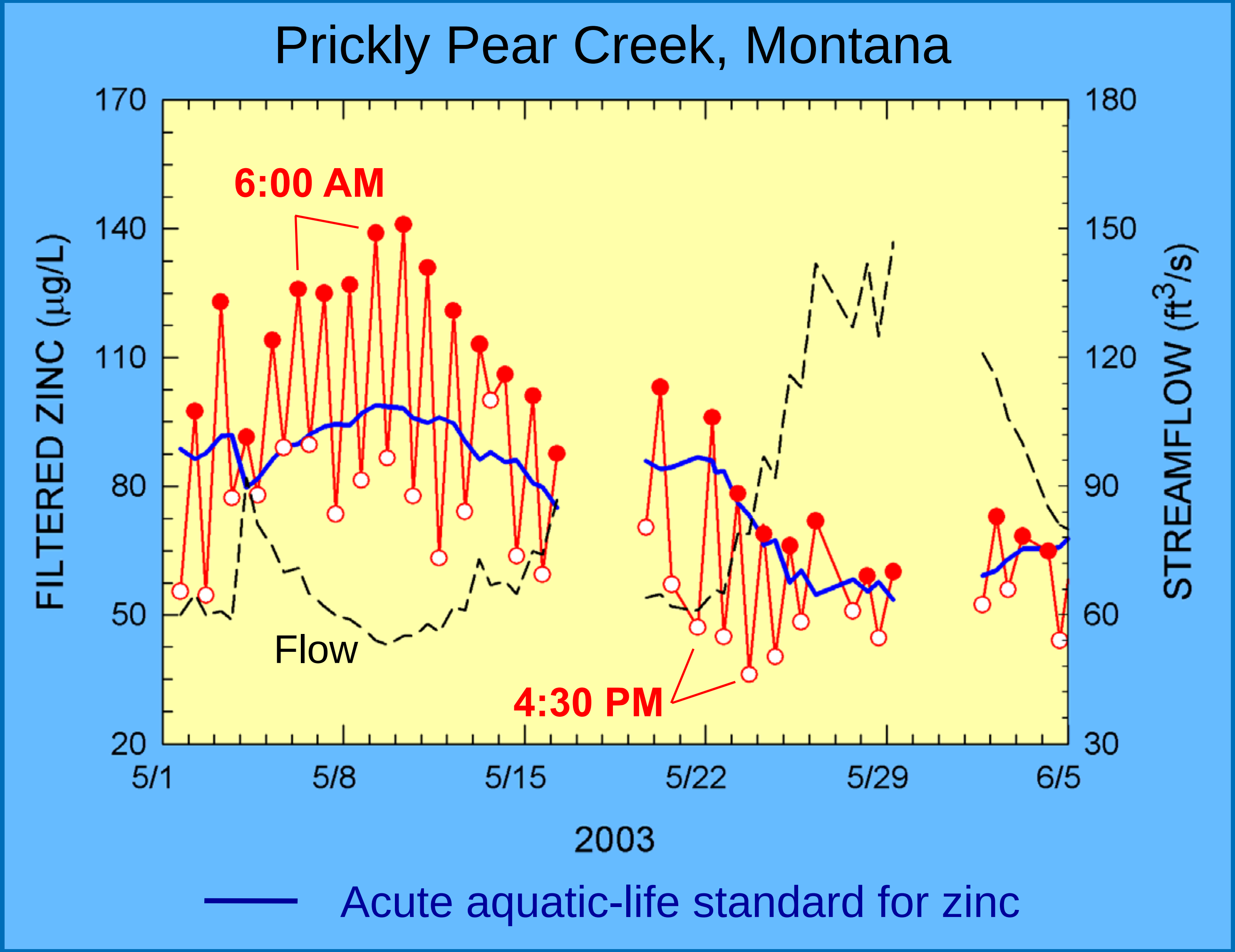
Implications: Time of Sampling Important!



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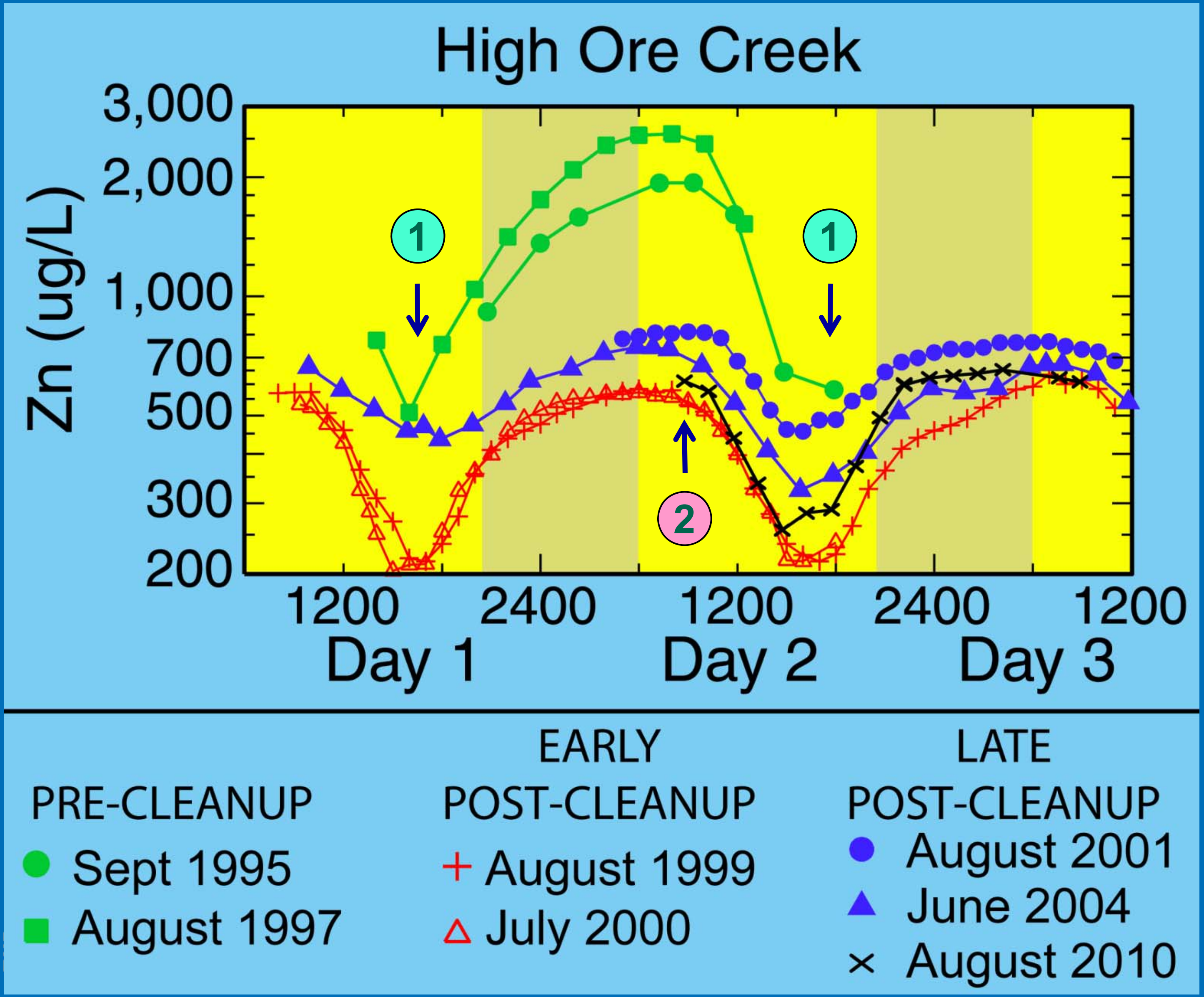
Implications: Time of Sampling Important!

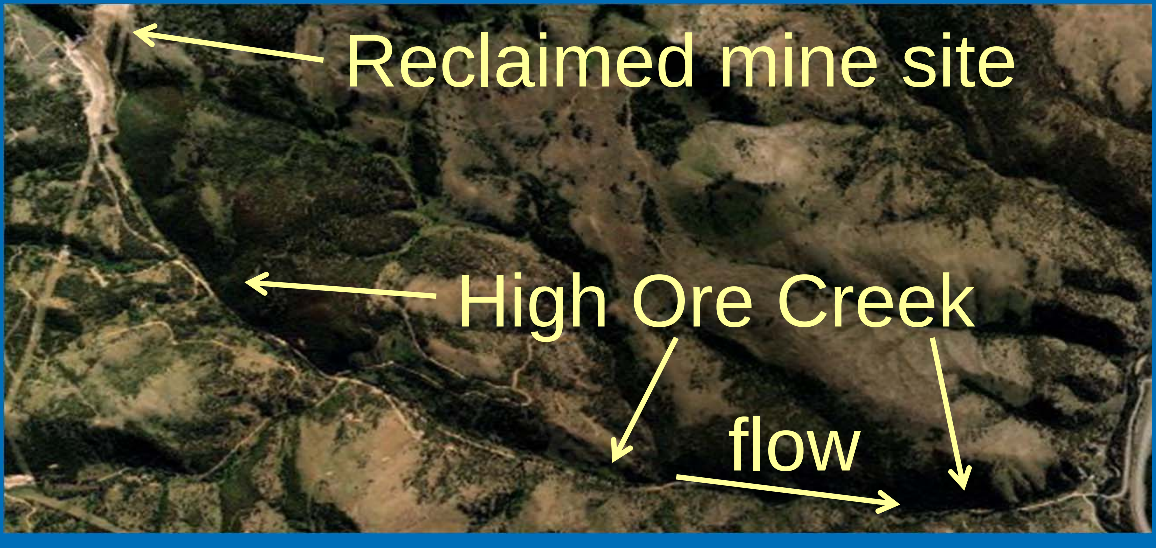


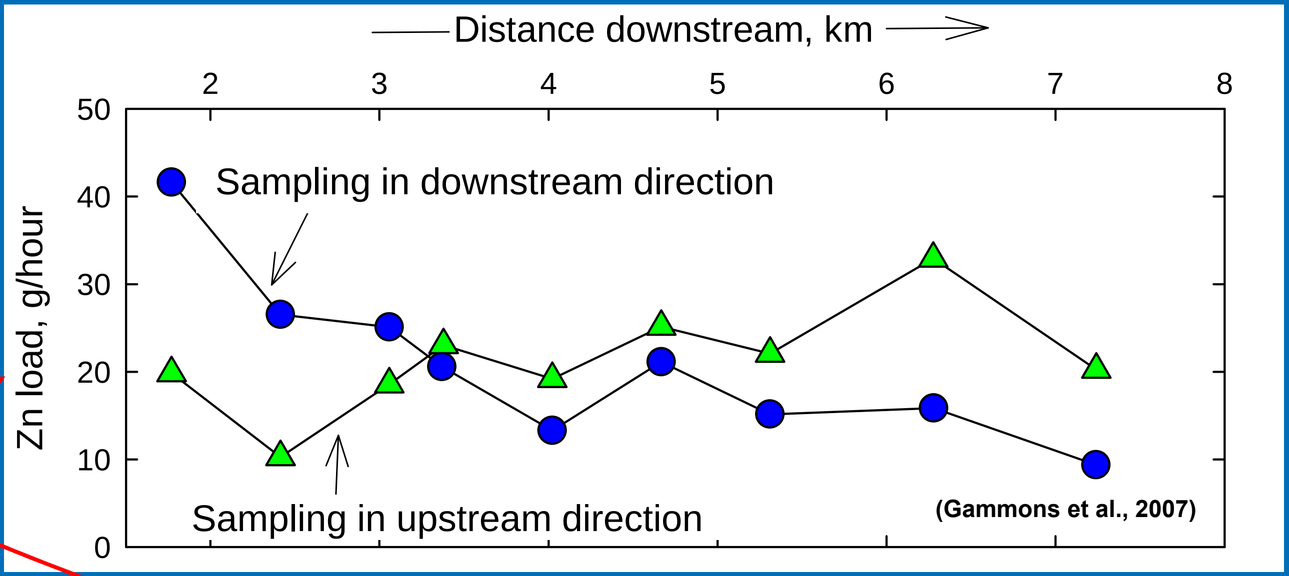
Sampling time:

1 Afternoon

2 Morning

Implications for Synoptic Sampling: Example 1





Load = Concentration x Flow

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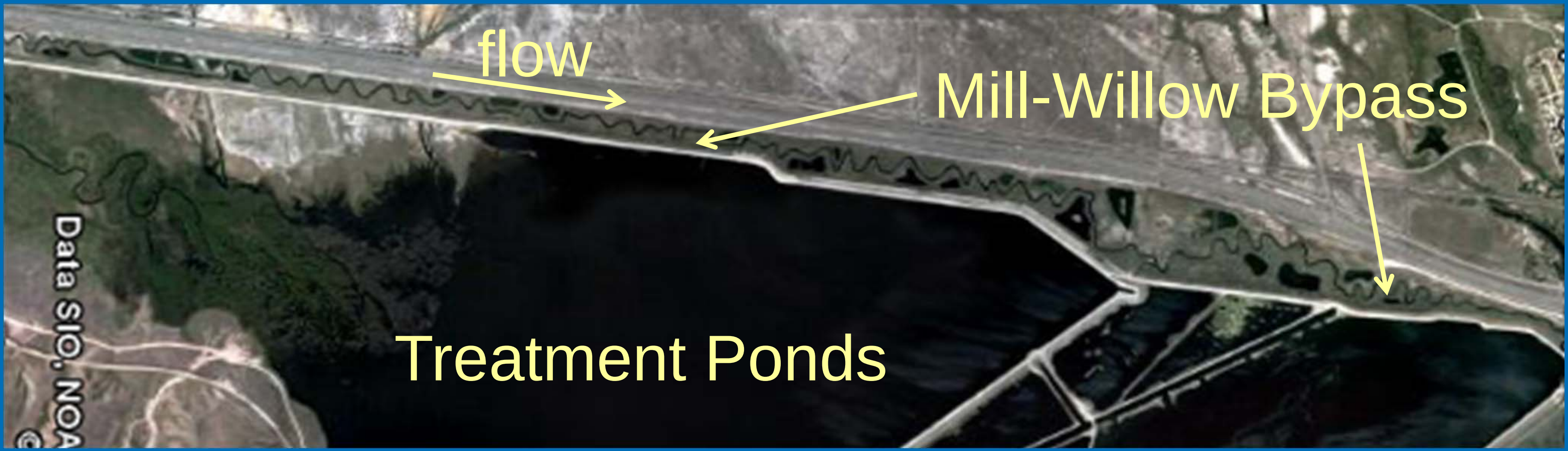
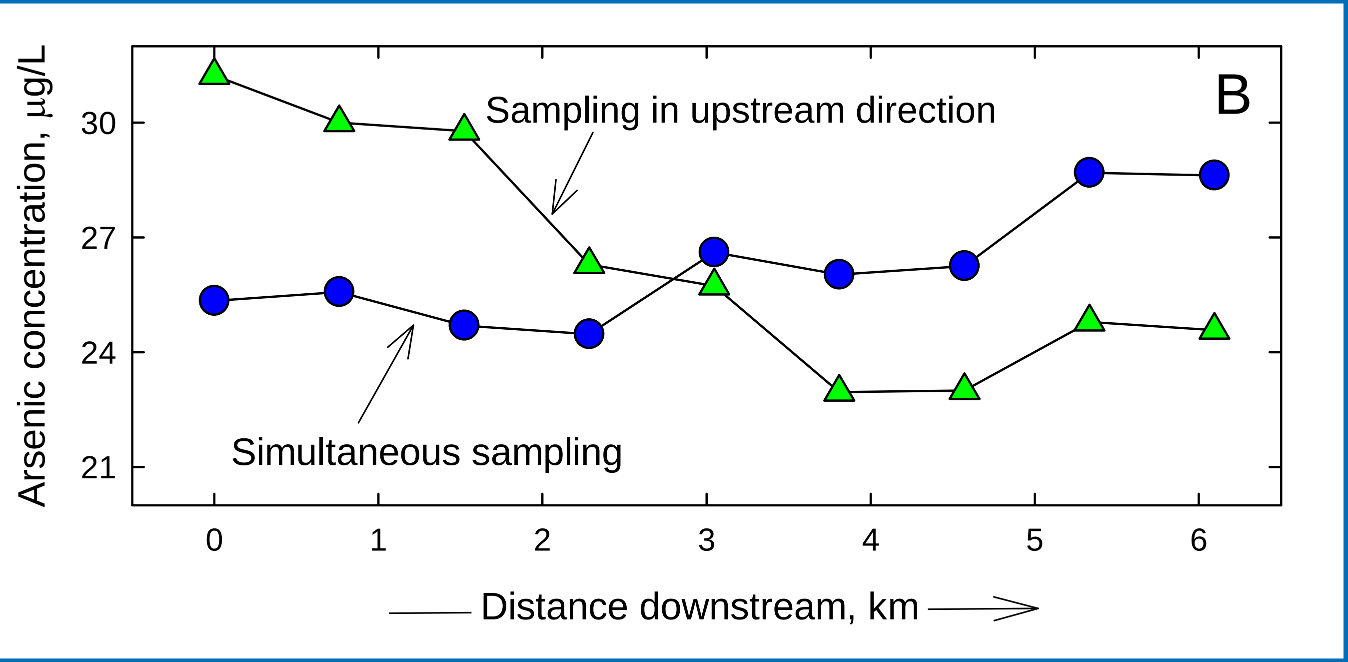
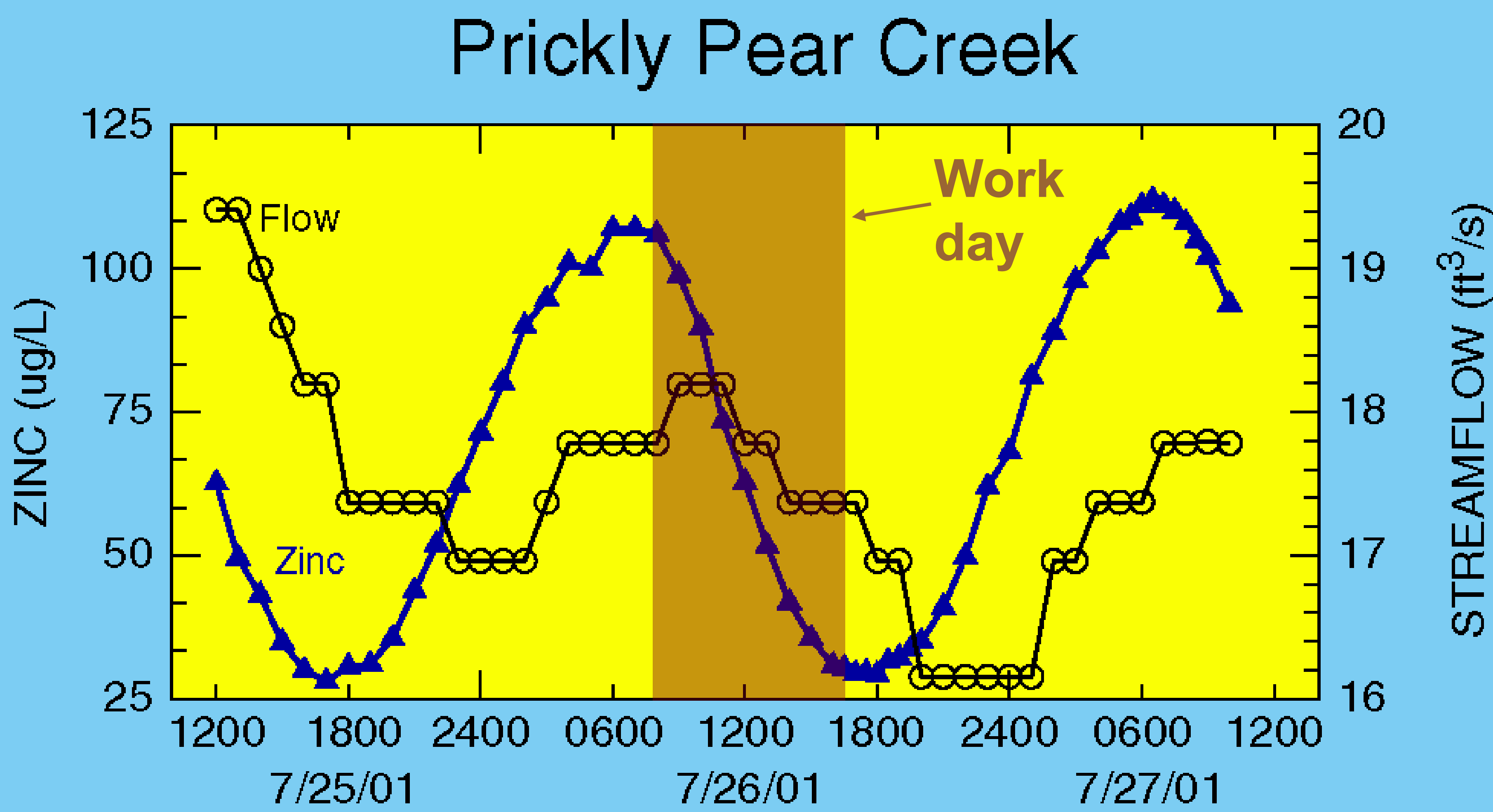
Implications for Synoptic Sampling: Example 2

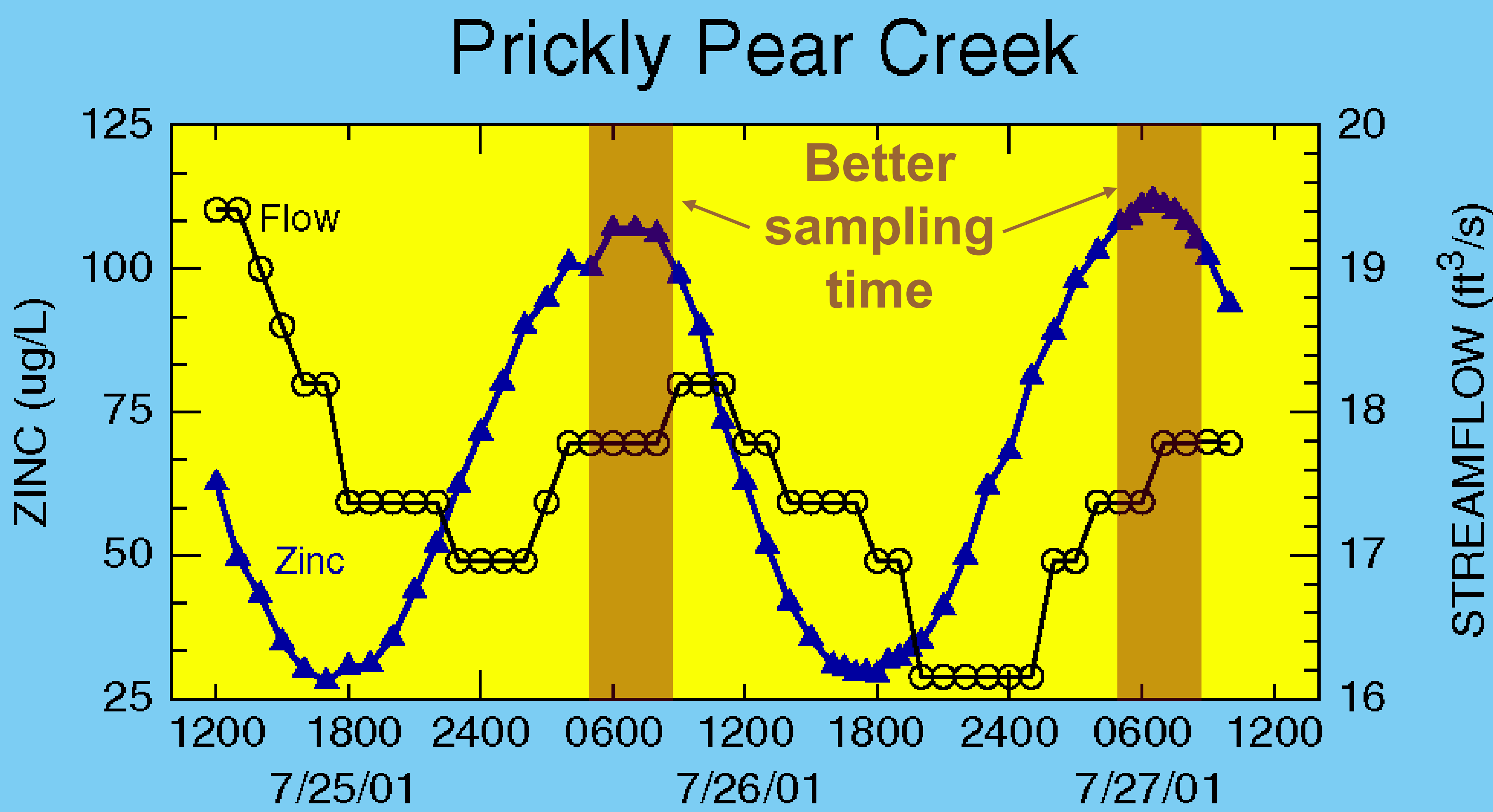




Implications for Synoptic Sampling: Example 3

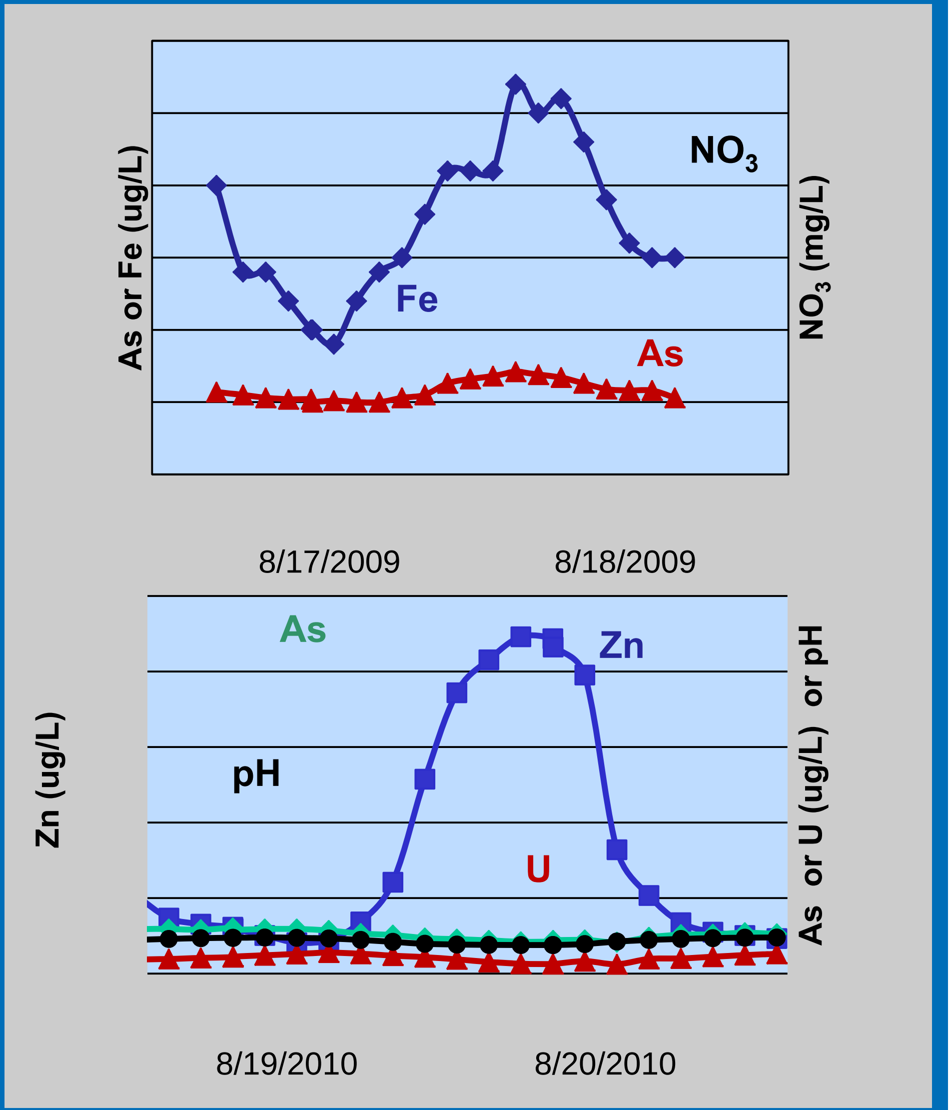


Implications for Synoptic Sampling: Example 3



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



Silver Bow Creek, Montana

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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

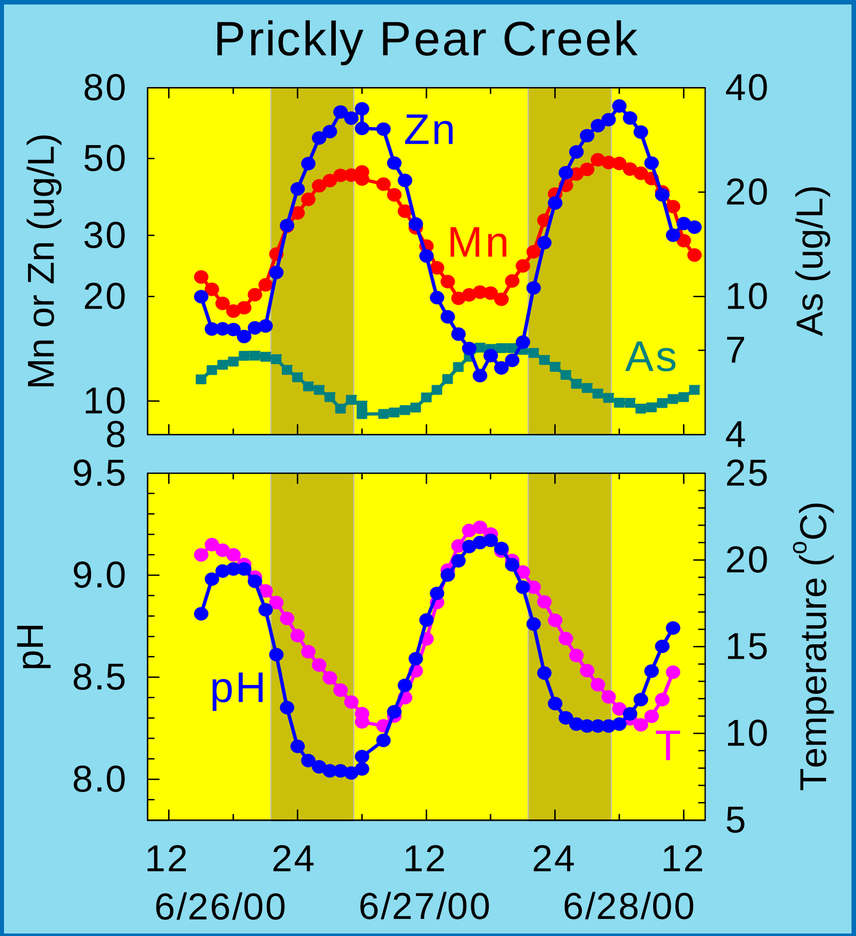

Multi-sensor sonde


In-situ analyzer

Water-Quality Criteria and Monitoring

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



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Water-Quality Criteria and Monitoring: Temperature

Criteria:

Maximum daily maximum
Maximum weekly maximum
Maximum daily average
Maximum weekly average

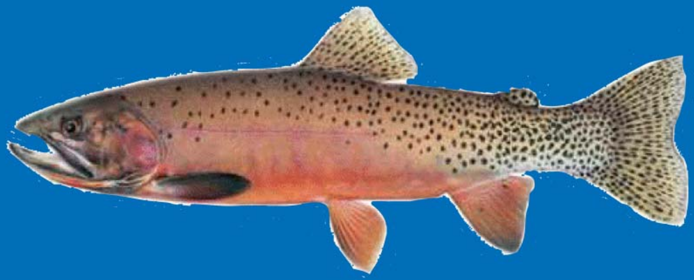
Monitoring:

Hobos, Tidbits, data sondes

Easy calibration, accurate, no drift

Conclusion:

Monitoring capability is out in front of criteria



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Water-Quality Criteria and Monitoring: Dissolved Oxygen

Criteria:

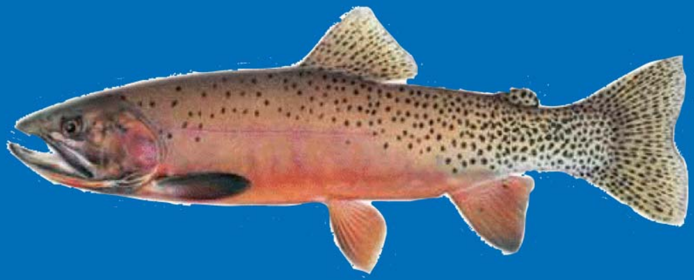
- Minimum
- 7-day average minimum
- 30-day average

Monitoring:

- Data sondes
- Need periodic calibration and maintenance to offset drift and fouling

Conclusion:

Monitoring capability has caught up with criteria



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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:

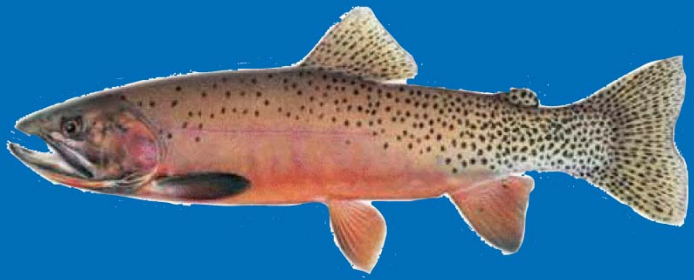
Site visits needed

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.



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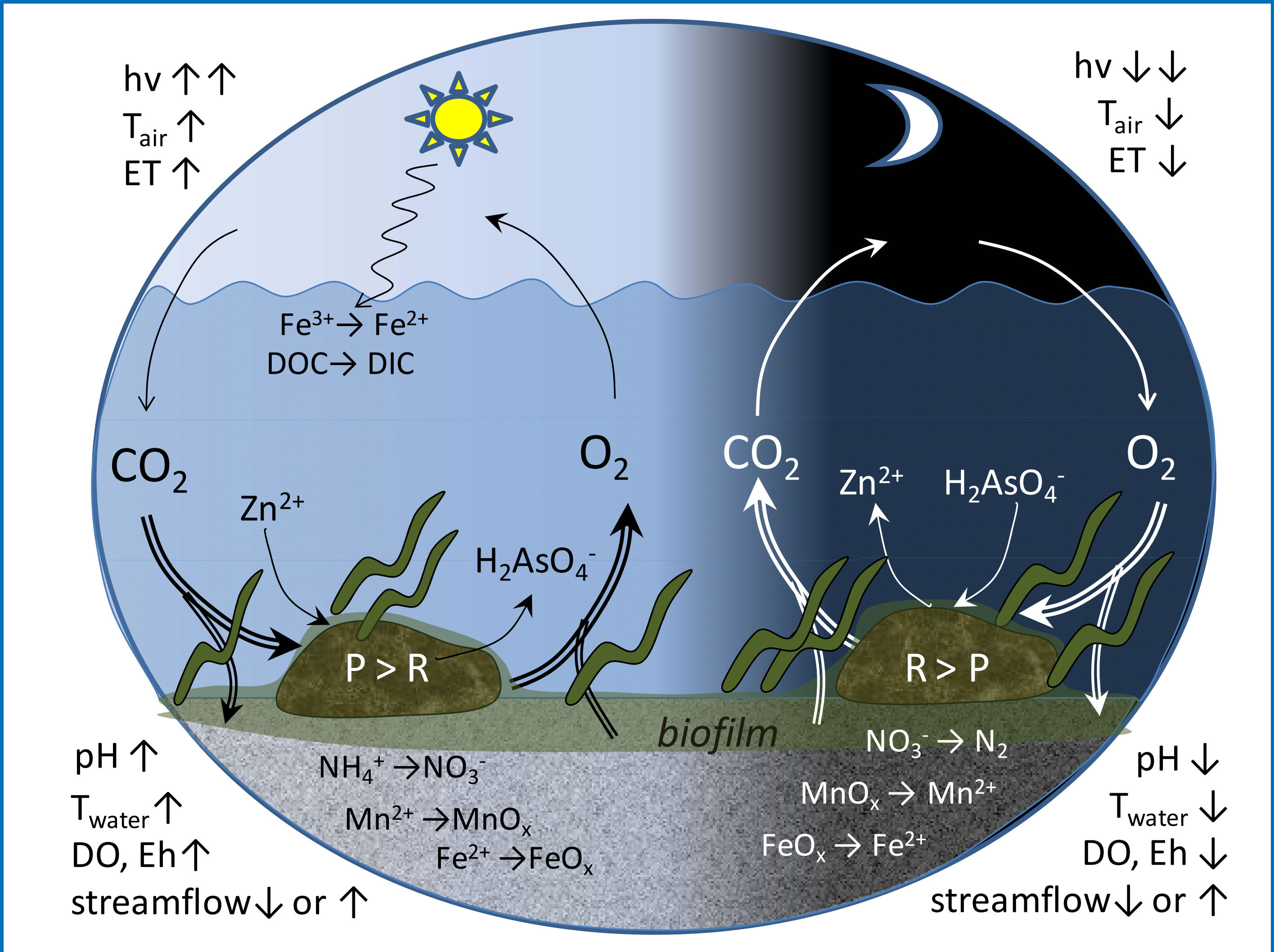
Questions?



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