Diel cycling of nutrients
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What species of interest?

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

**PHOSPHORUS**
- Orthophosphate
  - $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{\text{-}2}$
- Organic-P
- Suspended solids
  - $\text{PO}_4$ adsorbs *strongly* to carbonates, hydrous metal oxides
What could be going on with N and P?

- Diurnal changes in rate of uptake by biota
- Diurnal changes in delivery rate from hyporheic or benthic zones
- Diurnal redox cycles
  - Nitrification \( (\text{ammonia} + O_2 \rightarrow \text{nitrate}) \)
  - Denitrification \( (\text{nitrate} + \text{org. C} \rightarrow N_2) \)
  - Anammox \( (\text{ammonia} + \text{nitrate} \rightarrow N_2) \)
- Sorption/desorption of P onto carbonates, HFO, etc..
- Others...?
Nutrient cycling below sewage point sources

Diurnal processes
• Rate of ammonia oxidation is faster in warm water
• Rate of denitrification faster in warm water
• Diurnal patterns in nutrient uptake by plants, algae
Hypereutrophic conditions due to poorly treated municipal wastewater (WWTP)
The graphs show the concentration of Nitrate-N and Ammonia-N over time. The concentration of Nitrate-N generally decreases with time, while Ammonia-N shows an initial increase followed by a decrease.

The map indicates that WWTP is 1.36 miles away from the sampling location, and it takes approximately 3 hours to reach there. The distance to the nearest point of interest is 0.74 miles.
Faster rate of microbial oxidation of ammonia in warm day vs. cool night

Less $O_2$ available for ammonia oxidation at night
Diel variations in N species in a sewage-rich canal in Mexico

Like Silver Bow Creek, see decrease in \( \text{NO}_3^- \) and increase in \( \text{NH}_4^+ \) at night. Water column anoxic at night.

Big swings in \( \text{N}_2\text{O} \)... possible role of rivers in global \( \text{N}_2\text{O} \) cycling?
Continuous data collected using nitrate electrode

Scholefield et al. (2005)

River Taw, SW UK

http://www.tawriver.co.uk/sticklepath/images/rivertaw.jpg
Fig. 4. Measurements of (a) nitrate (◇) and reactive phosphorus (●), (b) nitrite (■) and ammonium (◇), (c) pH (◇) and solar energy (●) and (d) river discharge (△) and water temperature (▼) made during a 90-day campaign in the River Taw (June 2001), using manual sampling and laboratory analysis.
Conclusions of Scholefield et al.:

- Diel cycles in N, P are probably biological in origin.
- Cannot discount possible role of physical mixing of water sources.
- Further work is needed on mechanisms:
  - plant uptake?
  - Denitrification? (faster in day*)?

*see Laursen and Seitzinger, 2004*
Evidence from other Montana streams

Brick and Moore, 1996
Clark Fork River, Montana

Gammons et al., 2007
Mill-Willow Bypass, MT
Big Hole River at Wisdom, MT

- **PO$_4$-P**: 50 ppb P (EPA)
- **AsO$_4^{3-}$**: 38 ppb P (Dodds, 1996)
- **pH**: Clark Fork River target

Time of Day

- **P, As Concentration (ppb)**: 7.2, 7.5, 7.8, 8.1, 8.4, 8.7, 9.0

Wenz, 2003
Redox cycling of phosphate?

Light-induced diurnal cycling of PO$_4$ has been documented at lake/sediment interface (e.g., Carlton and Wetzel, 1988). A similar thing could happen in rivers.
Summary (emerging pattern...)

- Nitrate, phosphate concentrations appear to go up at night, down during the day in streams that are far removed from any point-source nutrient loading.
- Dramatic diurnal N-cycling may occur in hyper-eutrophic streams that become anoxic at night.
- Mechanisms still unclear.
- Very little published data... need more case studies.
Diurnal changes in dissolved organic carbon (DOC) in rivers

- DOC is a key input parameter for the Biotic Ligand Model (BLM)
- DOC can complex metals
- DOC is a concern for chlorination of drinking water
- DOC catalyzes many photochemical reactions
Previous studies: DOC cycling

- **Kaplan and Bott (1982)**
  - White Clay Creek, Pennsylvania
  - Robust diurnal cycles in DOC (up to 40%), peaking during afternoon
  - DOC flux controlled by balance between algal secretion and bacterial consumption

- **Dawson et al. (2001)**
  - Acidic peat-land streams, Scotland
  - No evidence of diurnal DOC cycling due to in-stream processes, despite fact that DOC is known to photo-degrade in low-pH waters

- **Spencer et al. (2007)**
  - Hypereutrophic San Joaquin River, CA
  - Diurnal changes in DOC *composition*, but not in total DOC *concentration*
  - Underscores lack of knowledge of processes

- **Steve Parker et al. (MT Tech, in progress)**
  - Big Hole River, MT
  - Large cycles in one summer, no cycles in next
  - Behavior of DOC remains unexplained
Sources of data: nutrients

Sources of data: DOC


