Diel processes in streams: Overview
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- Sunlight
- Temperature
- Streamflow
- Suspended solids
- pH
- Hardness
- Dissolved oxygen
- Seasonal changes
- Lakes vs. rivers
Photosynthetically-active radiation (PAR)

PAR detector (in the water)

Note how the cloudy period between noon and 3 PM caused a dip in pH

Silver Bow Creek, summer, 2008
Diel changes in sunlight

**Importance**
- Light drives river biology
  - animal behavior
  - plant photosynthesis
  - pH, DO cycles
- Temperature changes
- Photochemistry
  - Fe photoreduction
  - Breakdown of DOC
  - H$_2$O$_2$ cycling

**Causes**
- Rotation of earth
- Weather
- Seasonal effects
- Latitude effects
  - Higher UV
Diel changes in temperature

- T changes are greatest for small, shallow streams.
- T maxima usually in mid-to late afternoon, minima at dawn.

Gammons et al., 2005
Diel changes in temperature

**Importance**
- Ecological stress
- Influences *kinetics* and *equilibrium* of aqueous reactions
  - Microbial reactions
  - Mineral and gas solubility
  - Adsorption

**Causes**
- Solar heating
- Radiational cooling
- Groundwater inflow
  - Can contribute to night-time cooling in summer
Diel changes in streamflow

Shape, timing of flow cycles can change with time of year or position within the watershed.
Diel changes in streamflow: importance

- Influence solute concentrations

- Influence solute loads

Load = concentration \times discharge

kg/day = mg/L \times L/day \times 1 \text{ kg/}10^6 \text{ mg}
Diel changes in streamflow: causes

- Freeze/thaw
  - Ice formation
  - Snow/ice melt
- Anthropogenic
  - Sewage discharge
  - Irrigation withdrawals
  - Hydroelectric power
- Evapotranspiration
- “Algal dams”
Evapotranspiration and streamflow

- Flow decreases during the day
- Can cause up to ± 20% change in flow
- May cease after first killing frost
Diel changes in suspended solids

- “Suspended solid” is operationally defined by filter size (often 0.45 µm)
- Includes clays and mineral colloids, as well as algae, bacteria, protists

Clark Fork River, Montana
Parker et al., 2007
Diel changes in suspended solids

**Importance**
- Many MCL’s are based on “total recoverable” concentrations
- TSS can dominate total load of many toxic substances

**Causes**
- Changes in flow
- Biological factors
  - Photosynthesis
  - Macroinvertebrate activity
  - Livestock
- T-related changes in water viscosity
- Changes in rates of formation of hydrous metal oxides

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- Changes in rates of formation of hydrous metal oxides
Diel changes in pH

- pH changes are greatest for high-productivity streams with neutral to alkaline pH
- pH maxima in mid- to late afternoon, minima at dawn (similar to water temperature)

3 streams near Anaconda, MT
Gammons et al., 2007a
Diel changes in pH: importance

- Ecological stress
  - e.g., toxicity of ammonia is pH dependent
  - trout stressed at pH > 9

- pH-dependent reactions
  - Mineral and gas solubility
  - Adsorption

Big Hole River, Montana during drought of August, 2000
Diel changes in pH: causes

- Changes in temperature
- Changes in rate of groundwater inflow
- **Biological C cycling**

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{CH}_2\text{O} + \text{O}_2
\]

When pH is > 9 and CO\(_2\) is low, plants switch to HCO\(_3^-\):

\[
\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 + \text{OH}^-
\]

- **Diel pH changes in acidic streams are usually minor**, since pH is not controlled by CO\(_2/\text{HCO}_3^-\)**
Diel changes in hardness

- Hardness is proportional to Ca, Mg concentration

- **Importance:** MCL’s for many toxic metals are hardness-dependent

- **Causes:** diel changes in flow regime, or cyclic precipitation/dissolution of CaCO$_3$

- Uncommon (?)
Diel cycles in dissolved oxygen

- Biggest DO changes occur in slow-moving, high-productivity streams
- DO usually peaks at noon, when sun is directly overhead

![Graph showing diel cycles in dissolved oxygen with data points at 10:00, 18:00, and 02:00 for DO in mg/L and DO % saturation.](image)
Diel cycles in DO: Importance

- Ecological stress
  - e.g., fish may die during night-time hypoxia
  - fish also have trouble with very high DO
- May induce diel cycles in concentration and speciation of redox-sensitive solutes
  - Trace metals, especially Fe, Mn
  - Nutrients, especially N
  - In extreme cases, may lead to sulfate reduction (to H₂S) or methanogenesis
Diel cycles in DO: Causes

- Temperature changes
- Changes in rate of groundwater inflow
- **Biological O\(_2\) cycling**

\[
\text{CO}_2 + \text{H}_2\text{O} \quad \text{Day} \quad \text{CH}_2\text{O} + \text{O}_2 \quad \text{Night}
\]

\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}
\]

- ammonium
- nitrate
Research in progress: Diurnal changes in isotopic composition of dissolved oxygen (DO) and dissolved inorganic carbon (DIC)

\[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{CH}_2\text{O}(\text{org.}) + \text{O}_2(\text{aq}) \]
Diel cycling in biofilms vs. bulk water

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

Parker et al., 2007
Seasonal changes in diurnal cycles

- As long as there is open water and the sun is shining, there are diurnal cycles.

Big Hole River in winter
Lakes vs. rivers

- Lakes and ponds tend to “even out” diel cycles in rivers
- Tailwaters may show few diel cycles
- Good opportunity for longitudinal gradient studies

Gammons et al., 2007b
Not all streams exhibit diel cycling

Big cycles

- Low Q
- Shallow, clear
- Large T changes
- High productivity

Silver Bow Creek, Montana

Small or nonexistent cycles (?)

- Very large Q
- Deep, turbid
- Small T changes
- Low productivity

Mississippi River
Sources of data


