Diel biogeochemical processes and their effect on the aqueous chemistry of streams: A review (2010)

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- A review summarizing diel biogeochemical cycles in streams and the changes in water chemistry that come with it

- Sun is the main source of energy on earth

- Many biogeochemical stream processes change on a diel basis, reacting to day and night and the position of the sun

- Small time scale studies and diel changes indicate which instream biogeochemical processes occur or respond quickly
Biogeochemistry of Physical and Chemical Characteristics that Exhibit Diel Cycles in Streams

Water Temperature

- Most consistent diel change
- On average will increase during the day due to the increase in incoming solar radiation and atmospheric temperature and decrease at night
- Air temperature, relative humidity, cloud cover, wind speed all play a role as well
- Diel temperature changes are more pronounced during the summer and in streams that are more shallow and wide
- Groundwater dampens these changes because it stays at a more constant temperature
- Can effect hydraulic conductivity of the bed, solubility of minerals and gases, sorption of metals, metabolic processes, toxicity of contaminants, and ability for aquatic life to live
Biogeochemistry of Physical and Chemical Characteristics that Exhibit Diel Cycles in Streams

Streamflow

- Affected by:
  - Snowmelt - increases streamflow during the day when higher temperatures melt snow and ice more quickly
  - Evapotranspiration - decreases stream flows during the day as more water is evaporated
  - Infiltration - decreases during the day as warmer water lowers the viscosity of the water and therefore infiltrates more easily
  - Anthropogenically by releases of water from wastewater treatment plants and dams

- Overall streams unaffected by snow melt have a lower streamflow during the day
- Streams affected by snow melt have a higher streamflow during the day
- The dominant process that will control diel changes will change with the seasons
- Diel changes in stream flow can cause diel changes in concentrations of substances within the water column
Dissolved Gases: 
\( \text{O}_2 \) and \( \text{CO}_2 \)

- Controlled by:
  - Solubility properties - during the day higher temperatures cause less gases to be dissolved in the water
  - Photosynthesis - increases dramatically during the day with more sunlight input and decreases to nothing at night
  - Respiration - high in the day and decreases slightly at night
- During the day the rate of photosynthesis is higher than that of respiration so DO concentrations increase and dissolved CO\(_2\) concentrations decrease and at night this is reversed
- Cycles can be damped if high turbidity blocks light needed for photosynthesis, or in faster moving streams where there is less photosynthesis and respiration occurring in general
- Have a large control over pH and redox state
- Biggest cause is the daily changes of CO₂ concentration
- Increasing CO₂ decreases the pH meaning it gets more acidic
- pH typically won't fluctuate more than one pH unit* but fluctuations are greater in productive, low flow, not very acidic streams in warmer seasons
- If pH has a diel cycle it is likely that biogeochemical processes like mineral precipitation and dissolution, nitrification, carbonate chemistry, and microbial growth also have diel cycles
Dissolved Inorganic Carbon

- Greatest diel changes are due to dissolution and precipitation of carbonate minerals
- Streams with carbonate rich source water will have large diel changes
- Dissolved inorganic carbon will decrease during the day when higher temperatures decrease solubility and increase CO$_2$ outgassing
- Streams without a carbonate rich source will have little to no diel changes
- During the day, the warm temperature will cause solubility to decrease and more calcite will precipitate and it will stop precipitating or dissolve again during the cooler night
Dissolved Organic Matter

- DOC has very small or no diel cycles, the cause in streams that do have them is likely due to metabolic processes
  - DOC goes down at night, as heterotrophic organisms consume DOC, and up during the day, as autotrophic organism excrete DOC during photosynthesis
- Chlorophyll-A increases during the day as phytoplankton growth increases
- Reports are variable for DOM
Nutrients: N-species

- During normal conditions NO₃⁻ concentrations, which depend on temperature, light conditions, assimilation by primary producers, and rates of activity of autotrophic and heterotrophic organisms, are lowest in the early morning and highest in the late afternoon.

- Downstream of wastewater sources streams can be dominated by denitrification and nitrification and have diel cycles of NO₃⁻, NO₂⁻, and NH₄⁺ concentrations.

- So during the day NO₃⁻ and NO₂⁻ concentrations increase as temperatures, dissolved oxygen, and pH increase promoting more nitrification, and therefore NH₄⁺ concentrations decrease.

- In clear streams that light can penetrate easily, photosynthesis by benthic algae limits denitrification during the day.

- But in deeper more turbid streams where benthic algae are less common, denitrification is promoted by the increased nitrification during the day.
Stable Isotopes: C, O, and N

- Photosynthesis by aquatic plants consumes $^{12}\text{CO}_2$ faster than $^{13}\text{CO}_2$, so as a result the concentration of $^{13}\text{C}_{\text{DIC}}$ increases during the day.

- $^{13}\text{C}_{\text{DOC}}$ increases at night because the materials created by photosynthesis are more labile than the rest of the DOC and therefore can be consumed more rapidly.

- Photosynthesis during the day tends to lower the concentration of $^{18}\text{O}$ in a stream and higher rates of respiration at night tend to increase the concentration of $^{18}\text{O}$ at night, so over all the concentration of $^{18}\text{O}$ decreases during the day and increases at night.
Trace Elements: Iron Speciation and Concentration

- Photoreduction, re-oxidation, HFO precipitation and deposition
- pH neutralization and HFO transport
- Alkaline groundwater
- Alkaline groundwater
- HFO settling adsorption/desorption

Fe$^{3+}$

Fe$^{2+}$

C$_i$

C$_i$

Fe$_{part}$

Fe$^{2+}$

pH 3

pH 5

pH 7

Time
In streams with neutral to alkaline pH, highest concentrations of dissolved As occurred during the day, these diel cycles were due to changes in adsorption and desorption in response to the change in pH.

In acidic streams the cycles were opposite to this, due to increased rates of ferrous oxides deposition and therefore As adsorption.
Trace Elements:
Zinc, Cadmium, Manganese, and other Cationic Trace Elements

- Many trace and rare earth metals exhibit diel cycles with highest concentrations shortly after dawn and lowest in the afternoon

- Amplitudes for many are extremely large

- Changes due to cation absorption and desorption which can happen very quickly
Trace Elements: Mercury

- Dissolved gaseous Hg (DGM) and filtered total Hg have their highest concentrations during the day and lowest at night

- Caused by abiotic and biotic production of DGM and evasion and photo-oxidation losses of DGM

- Also adsorption and desorption of Hg$^{2+}$
Trace Elements:
Diel trace-element cycles related to cyanide photodissociation

- There also exist diel cycles of cyanide species
- Silver, gold, and copper complexes with cyanide can therefore also have diel cycles
- Creates more dissolved species during the night and more species attached to sediments during the day
- Turbidity and total suspended solids increase during the night
- Thought to be caused by nocturnal feeding and moving of stream biota or the increased number of bacteria in the water
- Sometimes a season pattern is present where the summer exhibits diel signals whereas the winter does not
Much of the biogeochemistry that controls the water chemistry is thought to take place within the biofilm that coats much of the bed of streams. This biofilm includes bacteria, fungi, archaea, algae, and diatoms. For diel cycles, biofilms play a role in nutrient, DOC, and metal cycling, but most importantly for dissolved gases and pH cycles from changes in photosynthesis and respiration. There is often a bigger amplitude change in the cycles in the biofilm layer and a lag time until the stream feels the changes.
Measurement Methods

- Need smaller time scale measurements
- Often hard to take enough samples back to the lab in terms of space and time involved
- Automated samplers are better but leaving the samples out in the field before long periods of time between analyzing could cause errors
- In situ sensors and analyzers that take readings in the field at real time are on the rise and seem to be the best option, but they are expensive, the accuracy may not be as high on an individual time bases but the long term continuous data is very valuable
- Using surrogate measurements is helpful to if done correctly
Implications

- Diel biogeochemical cycles are all interrelated so it is important to understand all types when researching a particular component

- Not understanding them can lead to inaccurate element cycling models, ineffective management decisions, or bad biological exposure estimates

- By only taking samples during the day, there is potential for inaccurate results

- Fortunately new technologies and more interdisciplinary approaches are helping us to understand more and more about this topic
Discussion Questions

1.) Geology perspective: How could the diel cycles explained in this paper influence potential erosion and deposition diel cycles?

2.) How might someone who only takes samples once a day or once a week correct for diel cycling?

3.) How might a stream’s latitude on earth change the diel cycling? Think Brazil vs. Alaska.