Diel Phosphorus Variation and the Stoichiometry of Ecosystem Metabolism in a Spring-Fed River

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Coupling of Elements: From Cells to the Biosphere

- Elements can constrain metabolism.
  - Increasing availability can lead to excess C fixation
  - Organism stoichiometry differs from supply
- Metabolic activity couples element cycles across scales
  - Ecosystem scale is of particular interest
- Coupling is direct + indirect
  - Direct autotroph assimilation
  - Indirect effects on redox, pH, heterotrophs

Gruber and Galloway 2008
“Ecology in Streams”
Streams as Model Ecosystems

- Flow creates coherent (diel) downstream signals from ecosystem metabolic processes

- **Carbon**: Diel $O_2$ for riverine GPP, $R$ (Odum 1956)

- **Nitrogen**: Diel $NO_3$ for autotrophic N demand (Heffernan and Cohen 2010)
North Florida’s Springs as Model Rivers

• High GPP (clear water)
• Stable flow; no scouring floods
• Constant source water chemistry
• Constant temperature

• **Natural laboratory for coupled elemental cycling in ecosystems**
Coupled Carbon and Nitrogen Cycles

- **DIRECT**: Net primary production and $U_{a,N}$ are strongly correlated and yield plausible C:N

- **INDIRECT**: $U_{den}$ is correlated with $R$ and previous days’ GPP (short and long term coupling)
Research Questions: Coupled Carbon and Phosphorus Cycles

• Is there a coherent diel SRP signal?

• Is the diel signal controlled by metabolic processes?
  – Directly via autotrophic assimilation?
  – Indirectly via pH or redox sensitive geochemical reactions (e.g., Ca, Fe)?

• What is the stoichiometry (C:N:P) of ecosystem metabolism and how does it vary?
  – Does it indicate the dominant autotrophs?
  – Does it change at daily and seasonal time-scales?
Conceptual Model of Diel P Dynamics

- Assumes all diel variation due to assimilation.
- No P uptake at diel maximum.
- Assumes diel variation due to assimilation and calcite co-precipitation.
- Assumes in-phase P removal mechanisms.
- Extracts P removal due to assimilation and co-precipitation which produce signals that are out of phase.

**Graph:**
- Assimilation (green)
- Calcite (gray)
- FW Input (dashed line)

**Time (h):**
- 0:00, 6:00, 12:00, 18:00
Site

- Ichetucknee River
  - High Flow ~ 6 - 9 m³/s
  - Constant input chemistry
    - FW NO₃ ~ 620 ppb, PO₄ ~ 48 ppb
  - High GPP (5 ± 2 g C m⁻² d⁻¹)

- 8 deployments, 5-12 days
  - Sensors at South Take Out, 5 km from Ichetucknee Headspring

Sensors

- C fluxes + calcite dynamics
  - YSI 6920, Optical DO, SpC

- N fluxes from nitrate
  - Satlantic SUNA (UV NO3)

- P fluxes from phosphate
  - Wetlabs Cycle-PO4
Geochemical Interactions

- Diel $S_{\text{cal}}$ responds to GPP
  - Day: Precipitation, Night: nothing
- No other significant geochemical sinks

- $[\text{Ca}]$ well predicted by specific conductance ($\text{SpC}$)
- Calcite co-precipitation kinetics from House (1990)
Raw Data (March 2011)
Unexpected Timing of P Dynamics

- NITRATE
- SRP
- [Ca]
- SRP uncorrected
- SRP corrected
P Assimilation vs. GPP

Uncorrected - C:P ~ 945:1

Corrected - C:P ~ 466:1

\[ U_{\text{a-raw},P} = 0.60 \times \text{GPP} - 0.59 \]
\[ R^2 = 0.53 \]

\[ U_{\text{a-cor},P} = 1.20 \times \text{GPP} - 1.06 \]
\[ R^2 = 0.84 \]

C:P\text{\_vascular} \sim 480:1
C:P\text{\_algae} \sim 430:1
P Removal in Context

• Uptake dominates removal
  – Biotic removal ~ 70%
  – Co-precipitation ~ 30%
    (exported as calcite particles?)

• Spiraling metrics indicate huge supply vs. demand
  – Uptake length ~ 42 km
  – Matches 5th order river spiraling (Ensign & Doyle 2006)
  – Zeroth order removal?

Ichetucknee is a NET SOURCE of P
A Phosphorus Source?

- Magnitude inferred from varying [SRP] baseline
- Baseline covaries with respiration and flow
  - Redox sensitivity? Hydraulic gradient?
- Interstitial porewater has high SRP (ca. 150 ppb)
  - H1: [SRP] varies with R
  - H2: P flux varies with hydraulic gradient

\[
\Delta [\text{SRP}]_{\text{max, cor}} = -1.51 \times \text{ER} + 22.6 \\
R^2 = 0.71
\]

\[
\Delta [\text{SRP}]_{\text{max, cor}} = -4.10 \times Q + 39.9 \\
R^2 = 0.75
\]
Predicting Diffuse Flow: Evidence from P Mass Balance

- Assuming porewater [SRP] (150 ppb), what is diffuse lateral flow to close river P budget?
- Strong f(flow), declining inputs at high stage
- Matches [Cl] budgeting
  - 0.6 m$^3$ s$^{-1}$ (de Montety et al. 2011)
Ecosystem C:P Stoichiometry

Plausible mixture

Weak phenology

Graphs showing molar C:P ratios for ecosystem, algae, and vascular plants, as well as a scatter plot correlating C:P ratios with gross primary production (g O₂ m⁻² d⁻¹). The equation for the regression line is C:P = -8.65 * GPP + 569, with R² = 0.19.
P Assimilation LAGS Primary Production

• H: Ribosome production occurs when cell energy stores are maximum
  – Ribosomes dominate P demand (Falkowski 2000, Elser and Sterner 2002)
  – Literature evidence that rRNA maximum is at midnight (Paul et al. 1988)
  – $H_1$: Diel rRNA:DNA variation with peak at maximum P removal
Summary:

Ecosystem Scale C and P Coupling

• Coherent diel [SRP] signal, varying amplitude
• Signal is convolution of 2 out-of-phase processes
  – Calcite co-precipitation (ca. 30% of removal)
  – Biotic assimilation (ca. 70% of removal)
  – Combined removal < 10% of total P flux
• Calcite-corrected removal yields plausible C:P
• Discrete springs are NOT the only source of P
  – Lateral seepage flux controlled by $R_{eco}$ and hydraulics
• P assimilation lags GPP by ca. 8 hours
  – Signal from the cell to the ecosystem?
Thank You.
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