Are nutrients affected by diel cycles in streams? Study of a low-discharge stream in middle TN

Hannah Zanibi[1], John C. Ayers[1]

[1] Earth and Environmental Sciences Department, Vanderbilt University, Nashville, Tennessee

Correspondence: Hannah Zanibi (hannah.r.zanibi@vanderbilt.edu), John C. Ayers (john.c.ayers@vanderbilt.edu)

Monitoring Stream Health: Variability of Surface Water Quality

- Sources of variability in surface water quality include anthropogenic activity, weather patterns, and climate conditions
- Diel or 24-h cycles result from variation in **solar radiation** causing **stream temperature** to increase during the day and decrease at night.
- Diel cycles also affect water chemistry primarily through **biological processes** dominated by in-stream photoautotrophs that photosynthesize during the day and respire at night.

Stream Site along East Fork Creek, a tributary of the Harpeth River south of Nashville, TN

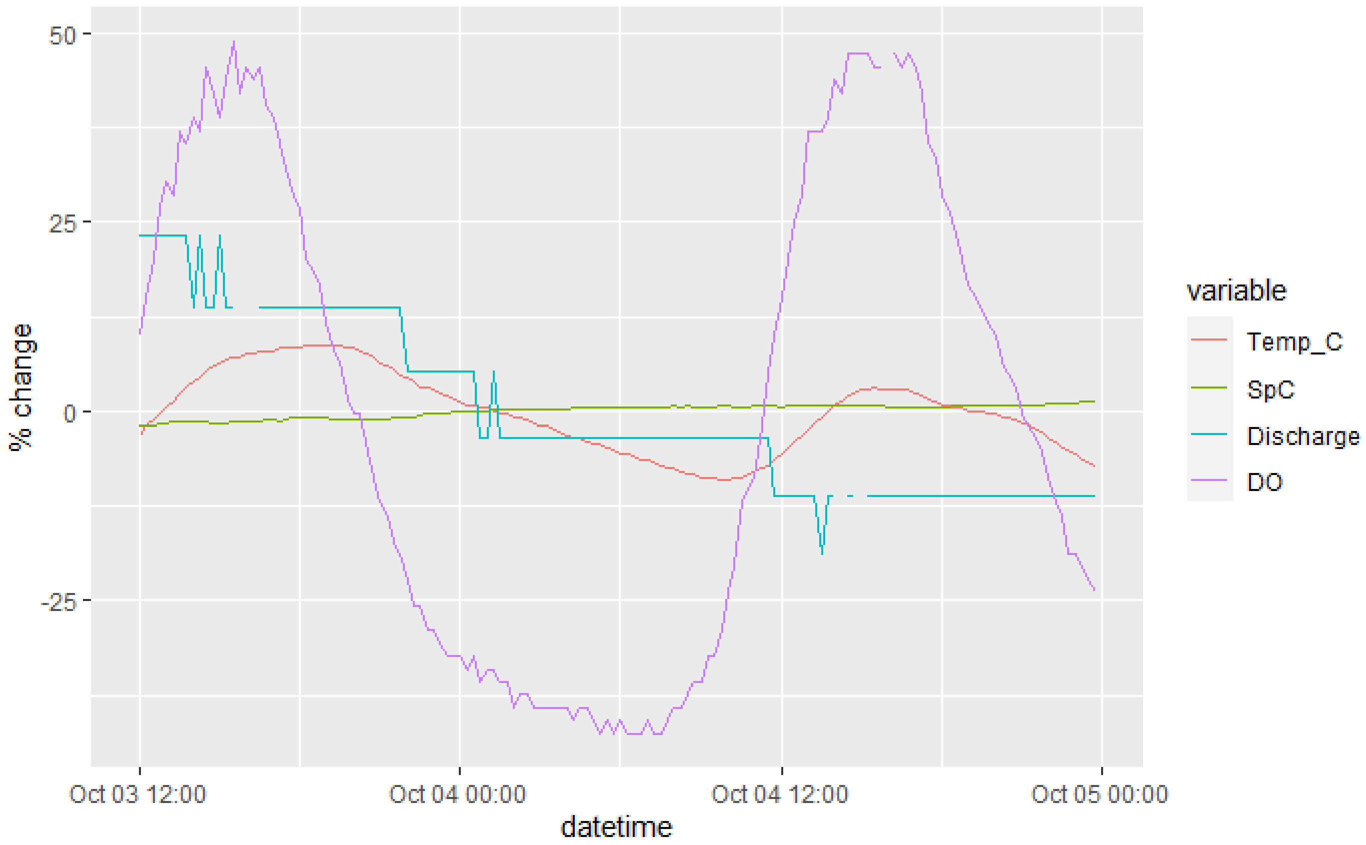
Key Diel Biogeochemical Processes

Photosynthesis: $H_2O + CO_2 = CH_2O + O_2$

Parameter	Daytime	Nighttime
Solar Radiation	↑	↓
T_{air}	↑	↓
T_{water}	↑	↓
Evapotranspiration	↑	↓
pH	↑	↓
Dissolved O_2	↑	↓
Dissolved CO_2	↓	↑
Streamflow	↑ or ↓	↑ or ↓
Eh	↑	↓

Table showing observed diel cycling in key parameters in neutral-to-alkaline streams. Adapted from Nimick et al. (2011).

Diel cycles on Harpeth River in October 2019

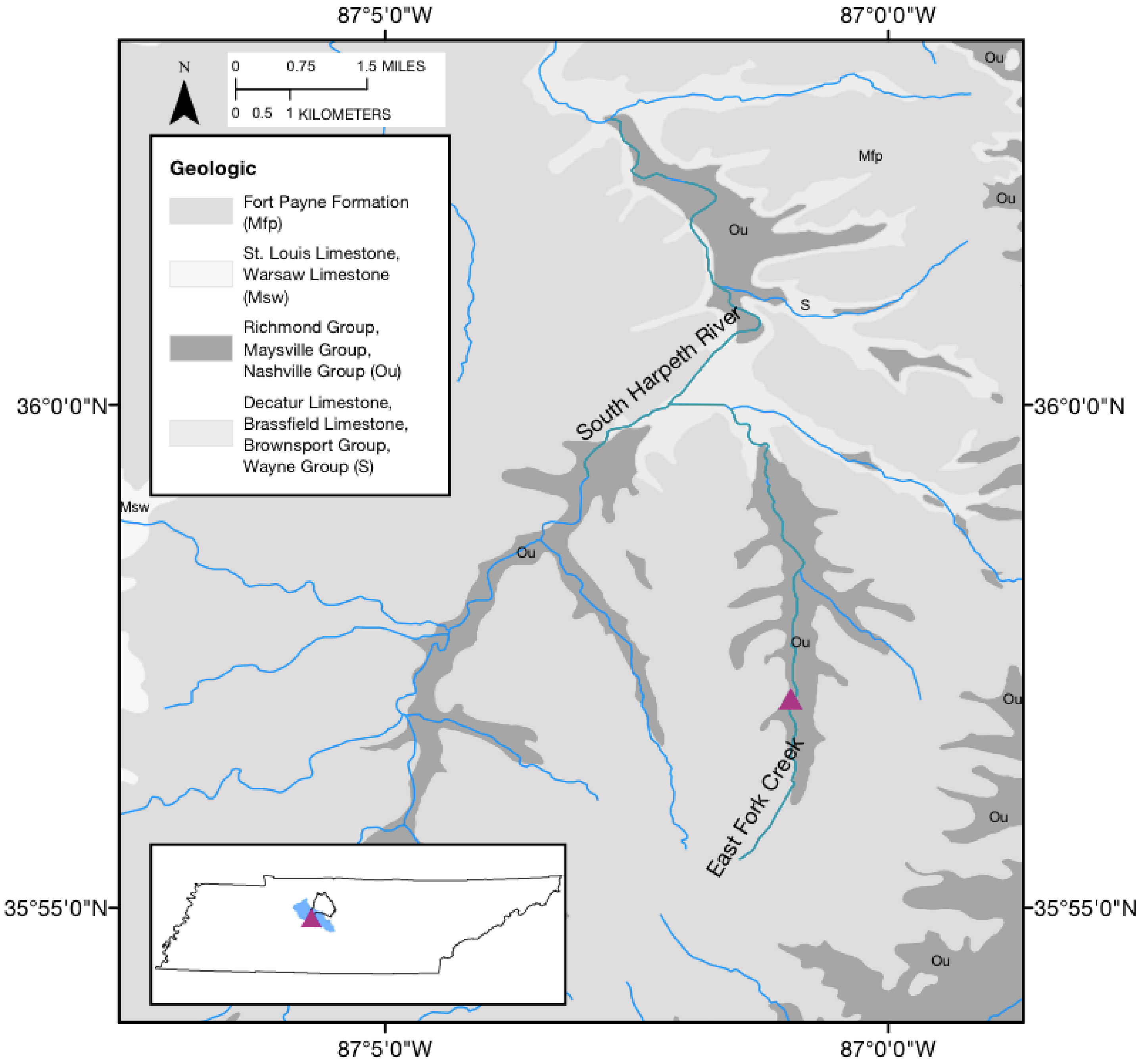


- **Hypothesis**: Nutrient concentrations also show diel cycles resulting from incorporation into organic matter during photosynthesis and release during respiration
- If true, **nutrient concentrations lower during the day** when measurements often made
- Important because nutrients cause cultural eutrophication!

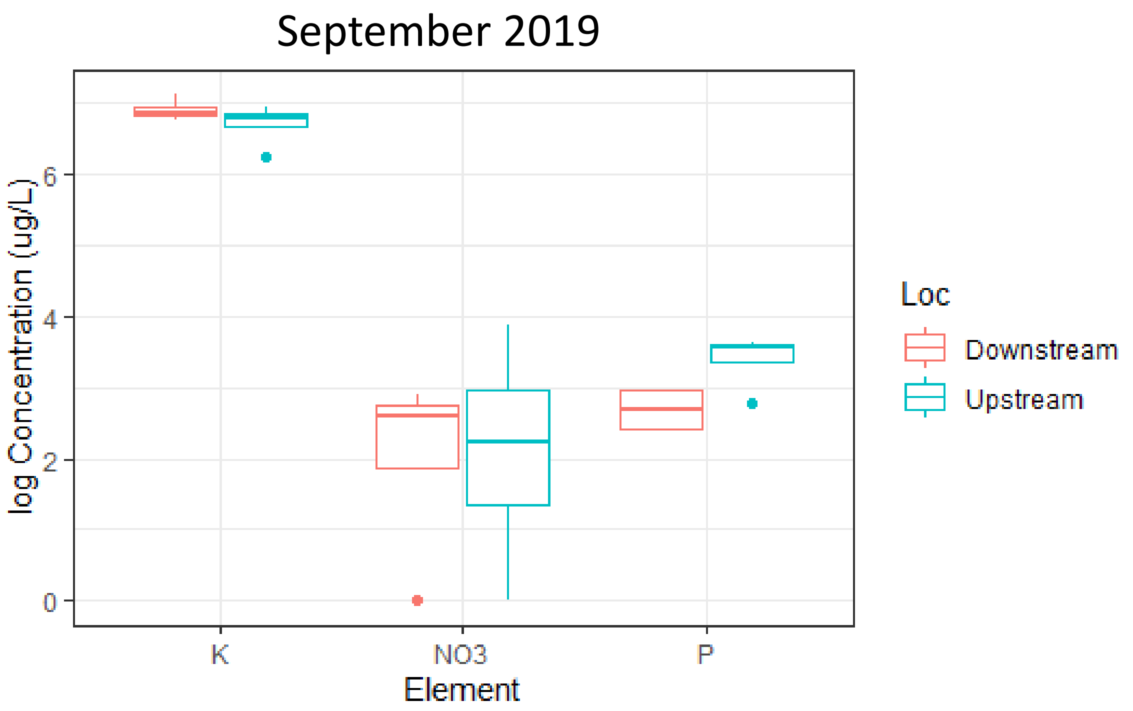
HARPETH RIVER AT BELLEVUE, TN: https://waterdata.usgs.gov/monitoring-location/03433500/

Sample Site

- East Fork Creek: First-order perennial stream in Franklin, TN, south of Nashville
- Sample site located within the Ordovician Nashville Group (Ou) limestones
- Representative soil type is Lindside cherty silt loam



Land-Use Along East Fork Creek

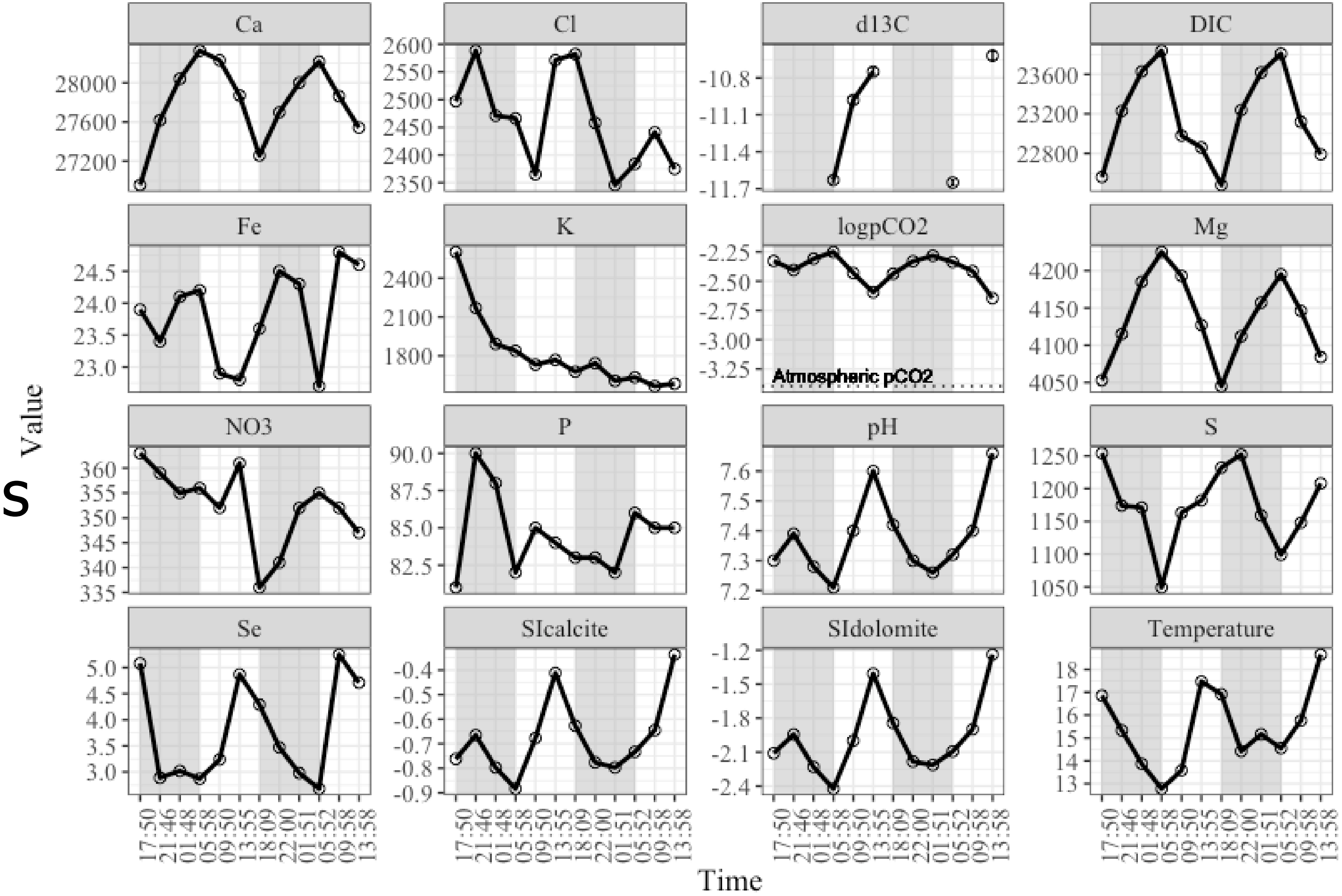


- Minimal agricultural activity, previous research indicates no significant contribution from upstream farm plot
- Mainly undeveloped and forested
- Good overall waterbody condition

Methods

- Measurements and stream grab samples were collected at a single site in East Fork Creek every four hours beginning at 17:50 October 2 and ending at 13:58 on October 4, 2020
- Daytime cloud cover ranged from 0-3% (October 2-3) up to 52 % (October 4) during the sampling campaign
- Samples filtered to 0.45 um and analyzed for dissolved concentrations

Diel Biogeochemical Cycling is Observed in Numerous Dissolved Species

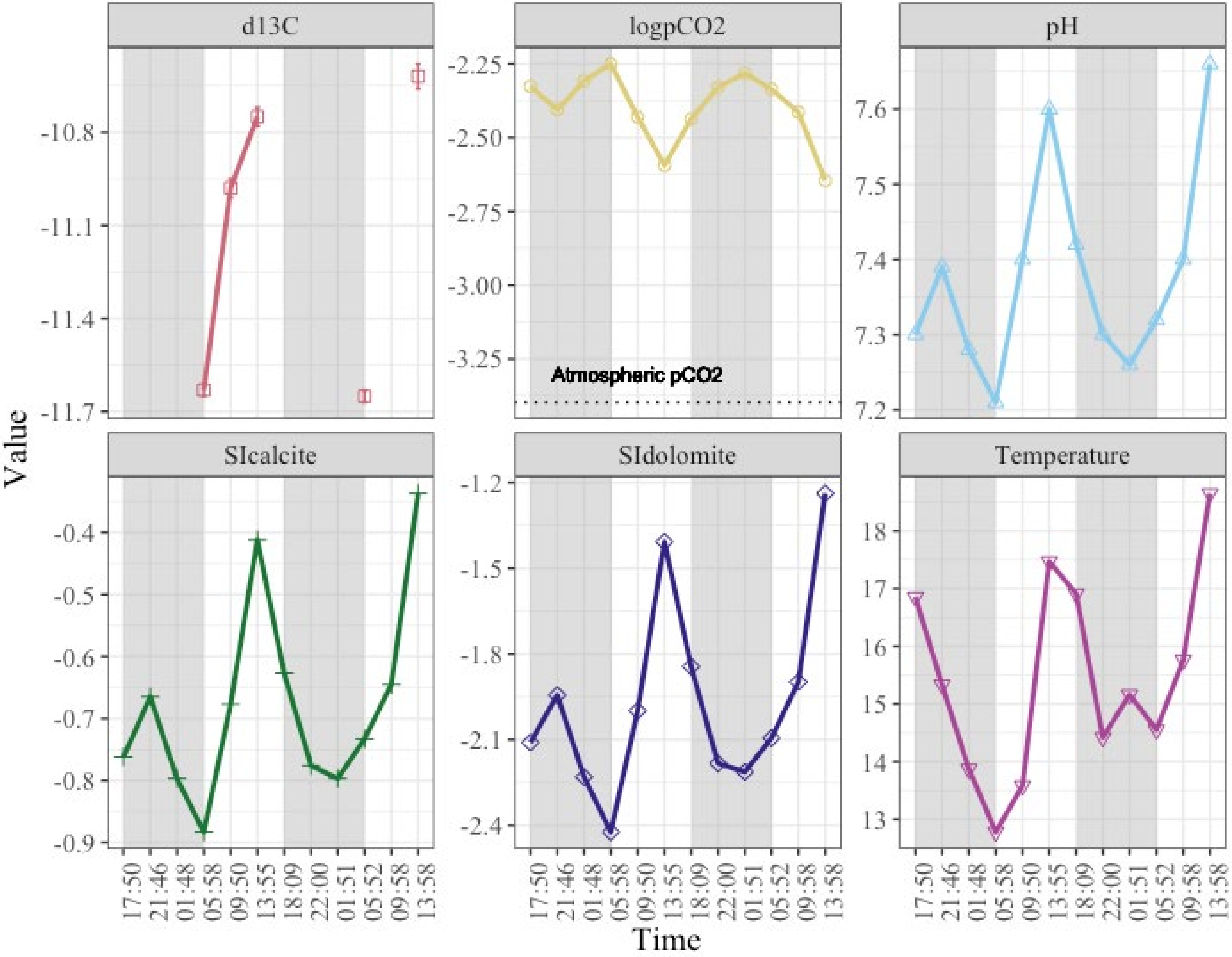


Note that night is shaded grey in all time series plots

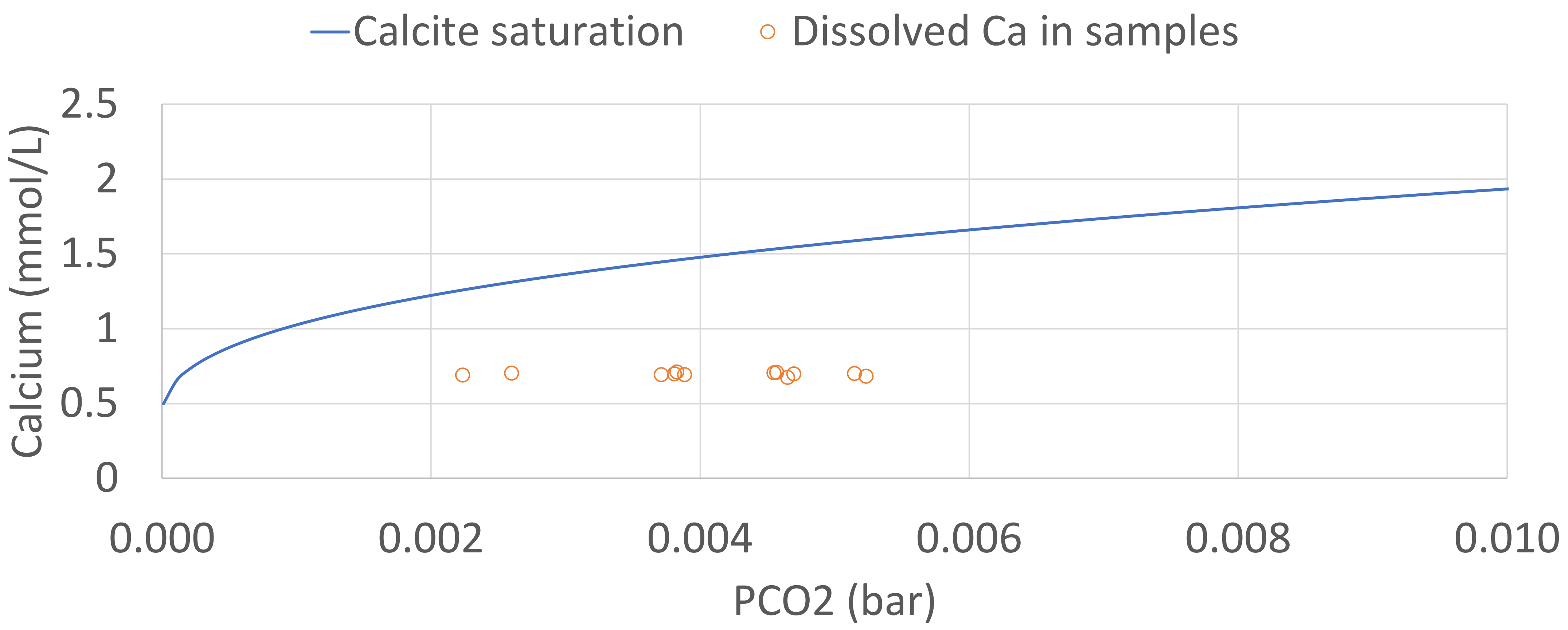
Ancillary Parameters

Parameter	Magnitude Change (%)
$SI_{calcite}$	63.49
$SI_{dolomite}$	50.60
Temperature	45.93
log pCO_2	13.99
pH	6.24

- P_{CO2} is greater than atmospheric P_{CO2}, suggesting groundwater input
- Calcite and dolomite undersaturated despite stream being in limestone terrane



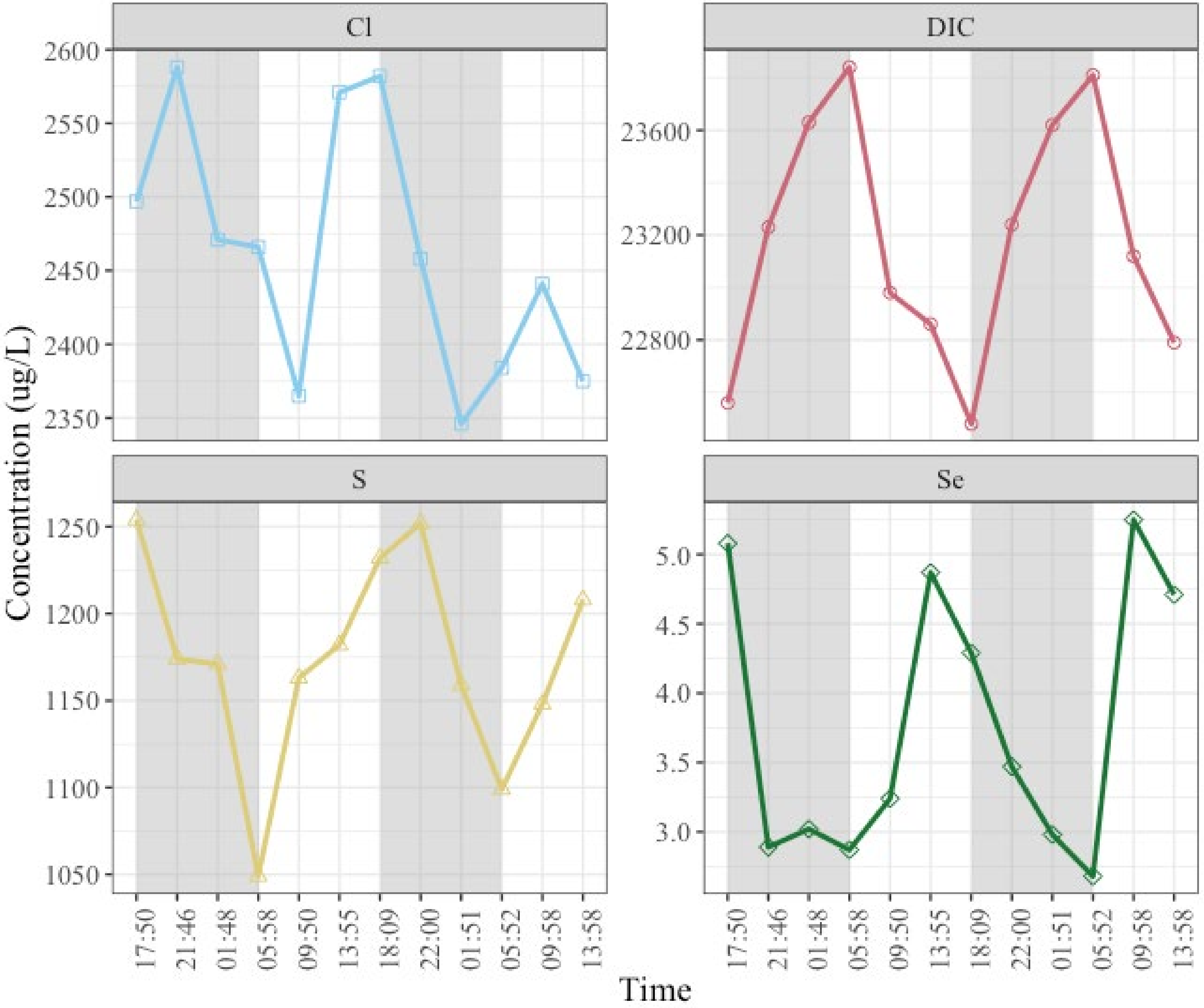
Calcite undersaturation due to mixing of surface and ground waters?



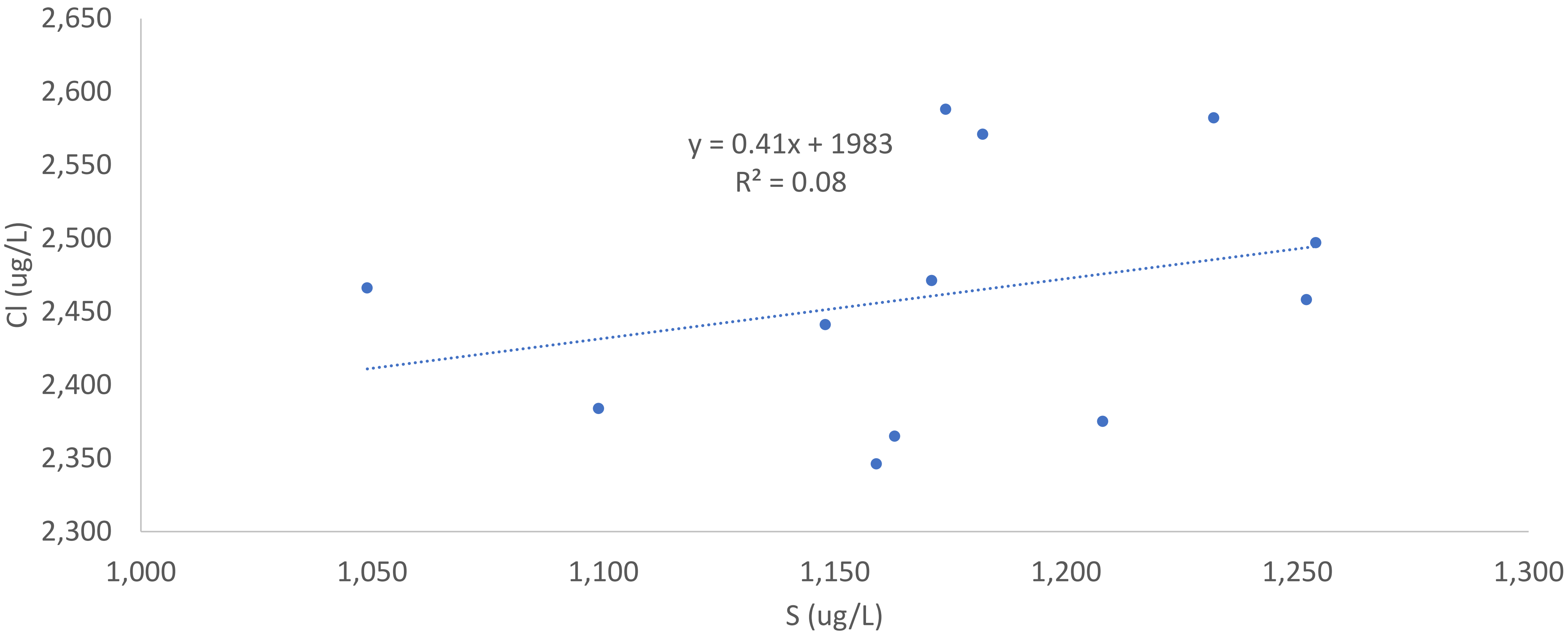
Anions

- Strong Diel Cycling of Selenium Not Previously Observed in Diel Studies
- Cl and S ↑ during day; evapo-transpiration?

Parameter	Magnitude Change (%)
Se	95.90
S	19.54
Cl	10.32
DIC	6.05



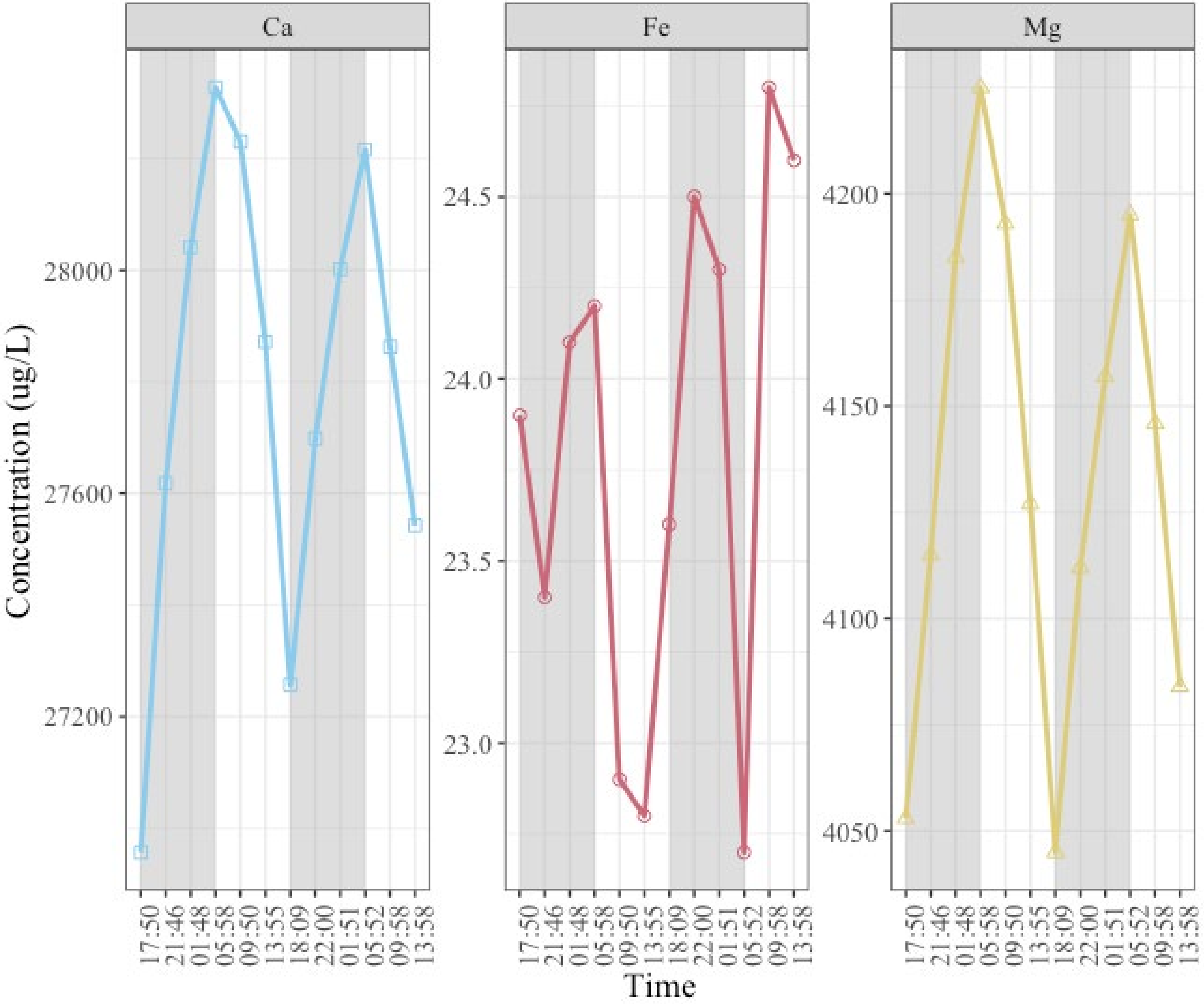
Are Cl and S variations due to variable groundwater inputs caused by evapotranspiration?



Poor correlation. Also do not see diel variation in conductivity/salinity, so no good evidence for hyporrheic exchange

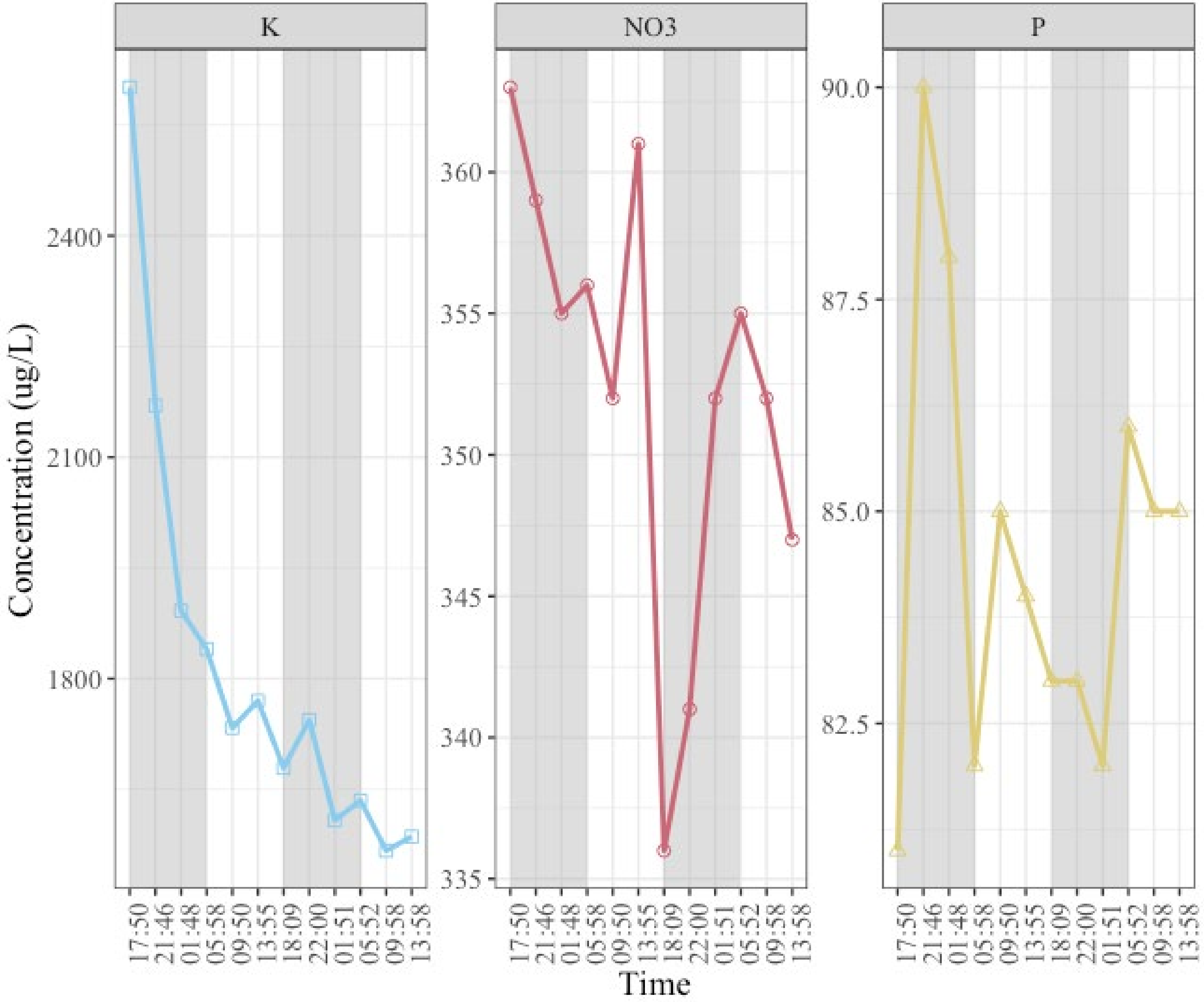
Cations

- Concentrations of Ca and Mg exhibited similar diel cycling
- Fe more complicated



Nutrients

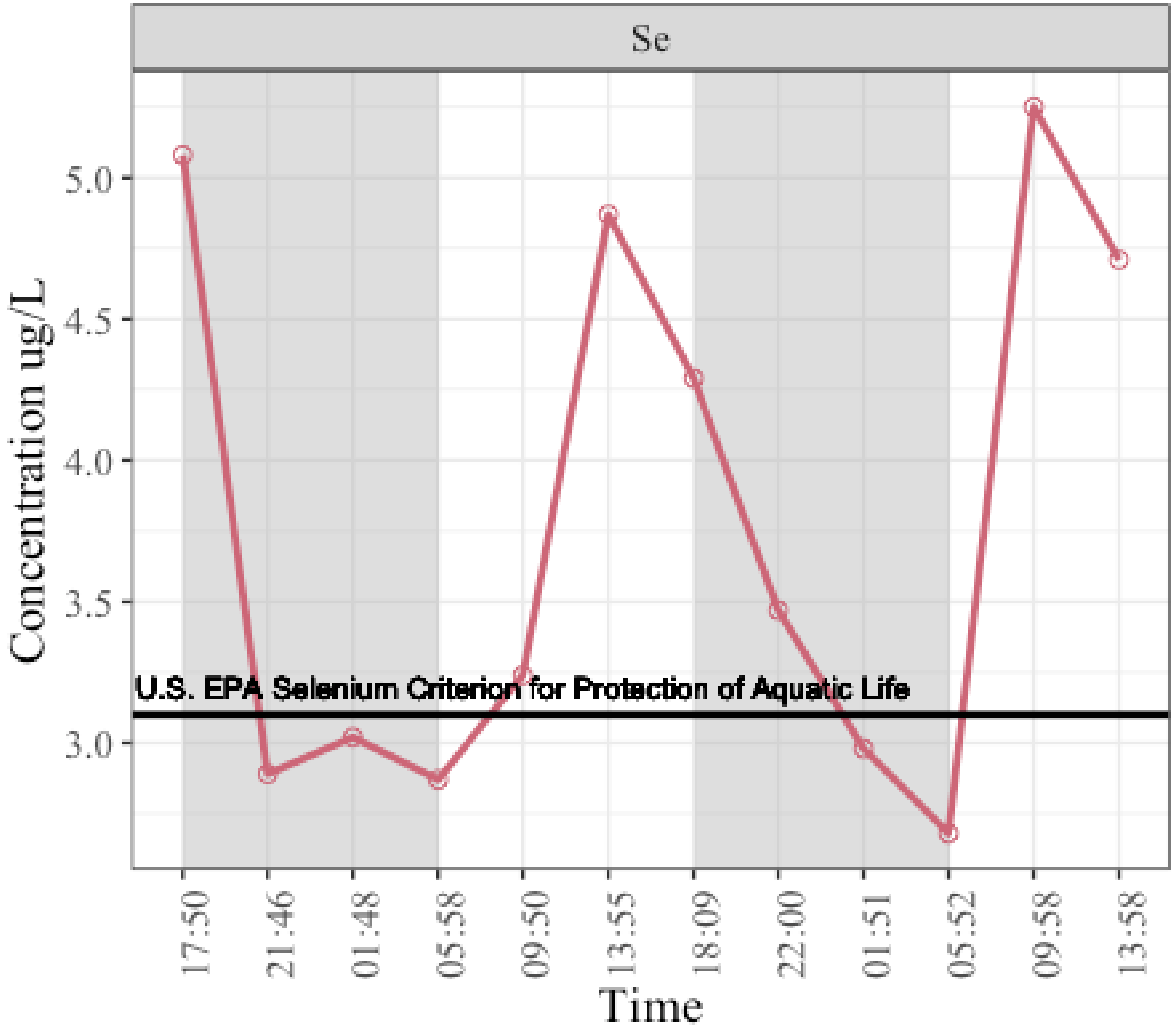
- **K:** cause of nearly continuous decrease unclear
- **NO3:** final six samples for nitrate show diel signal. Perhaps samples must be analyzed immediately?
- **P**: Like Fe, often in colloidal material, so we may need to filter to 0.2 um to see the dissolved phosphorous signal clearly



Implications for Stream Health

- Diel variability in sampling
- Additional consideration of Se in current water quality criterion
- Harm to aquatic organisms when concentrations are above 3.1 ug/L (U.S. EPA, 2016)

Parameter	Magnitude Change (%)
Se	95.90
K	65.99
$SI_{calcite}$	63.49
$SI_{dolomite}$	50.60
Temperature	45.93
S	19.54
log pCO_2	13.99
P	11.11
Cl	10.32
Fe	9.25
NO_3	8.04
pH	6.24
DIC	6.05
Ca	5.08
Mg	4.45



Biological activity is a major control of diel cycles

Parameter	Daytime	Nighttime	Cause of variation
T_{water}	↑	↓	Solar radiation, heat exchange
pH	↑	↓	CO_2 solubility, biological activity
Dissolved CO_2	↓	↑	Biological activity, groundwater inputs
$\delta^{13}C$	↑	↓	Biological activity
Cl^-, SO_4^{2-}	↑	↓	Groundwater inputs?
Se	↑	↓	Chemical weathering, sorption/desorption behavior
Ca and Mg	↓	↑	Streamflow, biological activity
$SI_{calcite}$ and $SI_{dolomite}$	↓	↑	Chemical weathering of limestone
DIC	↓	↑	Biological Activity
Fe	↓	↑	Oxidation Rates
K	↓	↓	Cycling on longer timescales
P	Inconclusive	Inconclusive	?
NO_3^-	Inconclusive	Inconclusive	?

Conclusions

- Diel cycles observed for temperature, pH, P_{CO2}, saturation indices of calcite and dolomite, and concentrations of Ca, Mg, Se, Fe, Cl, SO_4, DIC, and $\delta^{13}C$-DIC.
- Selenium had the highest magnitude of increase, 96%, over the stream campaign, and 7 of the 12 samples had Se concentrations greater than the maximum EPA WQC of 3.1 ug/L for lotic aquatic systems.
- P and N did not show clear diel cycles, despite being incorporated into organic matter during photosynthesis.
- Future work:
  - Use an autosampler
  - Continuous field measurements
  - Nitrogen species will need to be measured immediately using a Hach spectrophotometer
  - Piezometers to measure groundwater compositions and inputs to stream

Questions?

Email: john.c.ayers@vanderbilt.edu