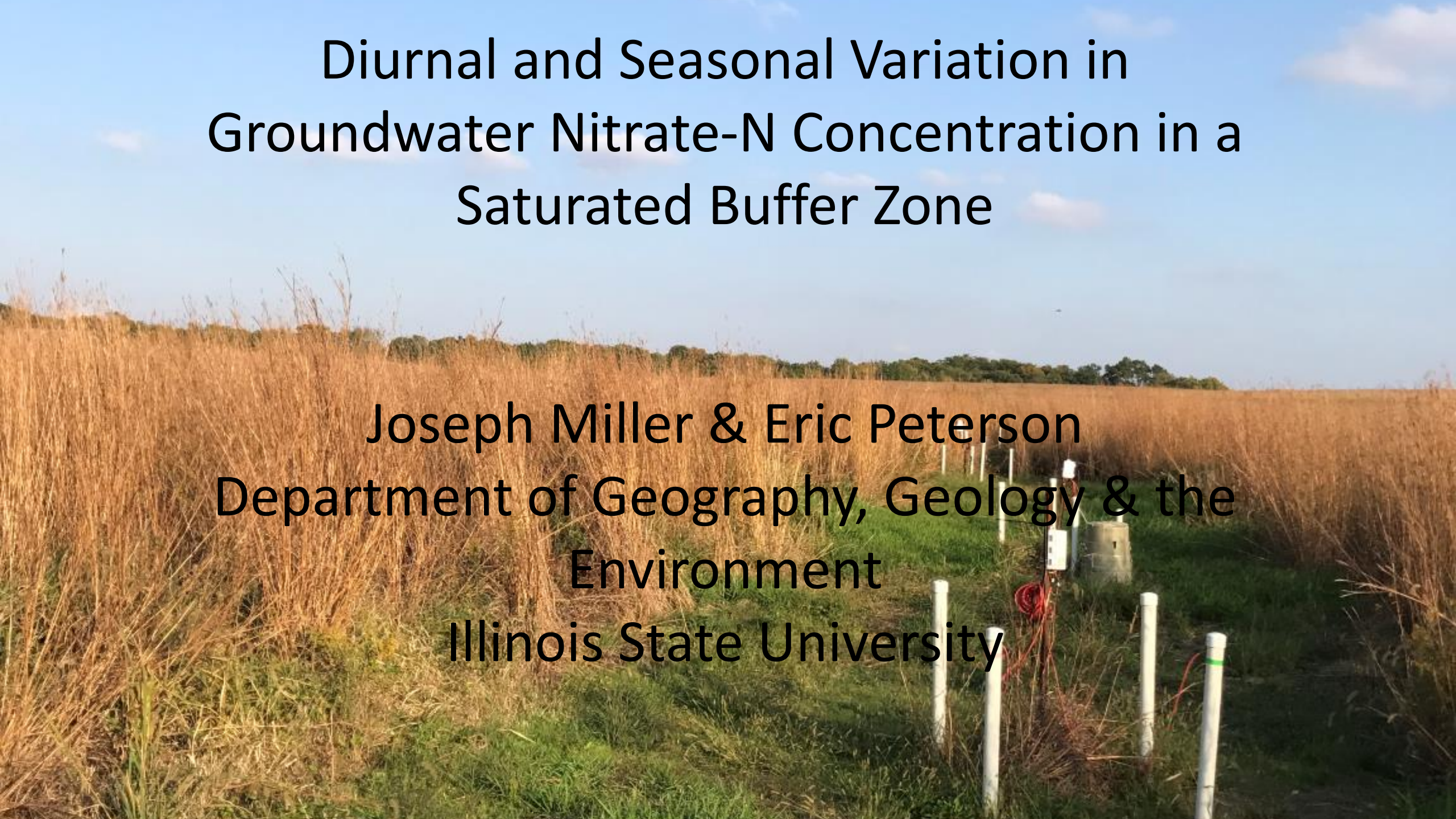


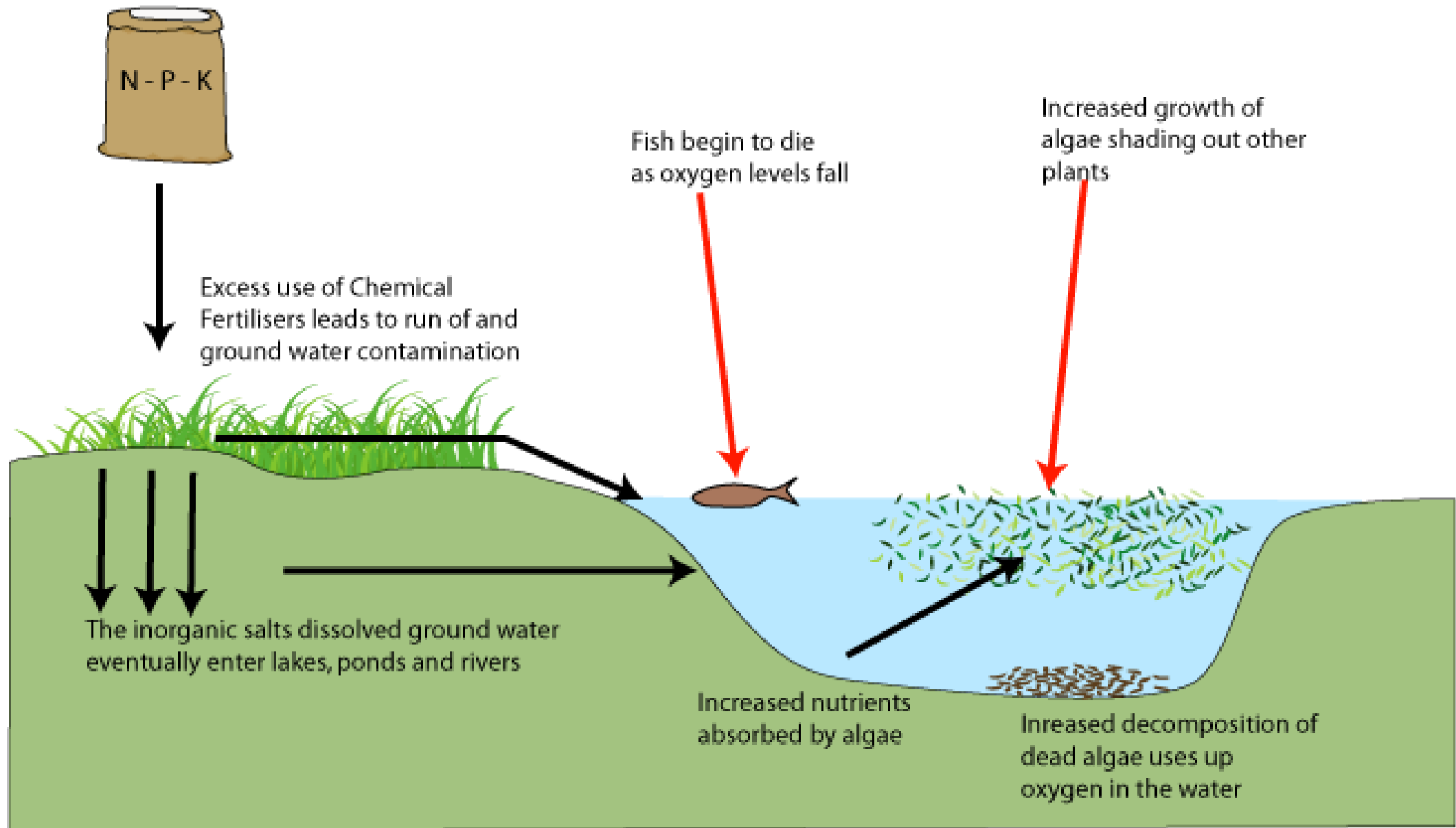
Diurnal and Seasonal Variation in Groundwater Nitrate-N Concentration in a Saturated Buffer Zone

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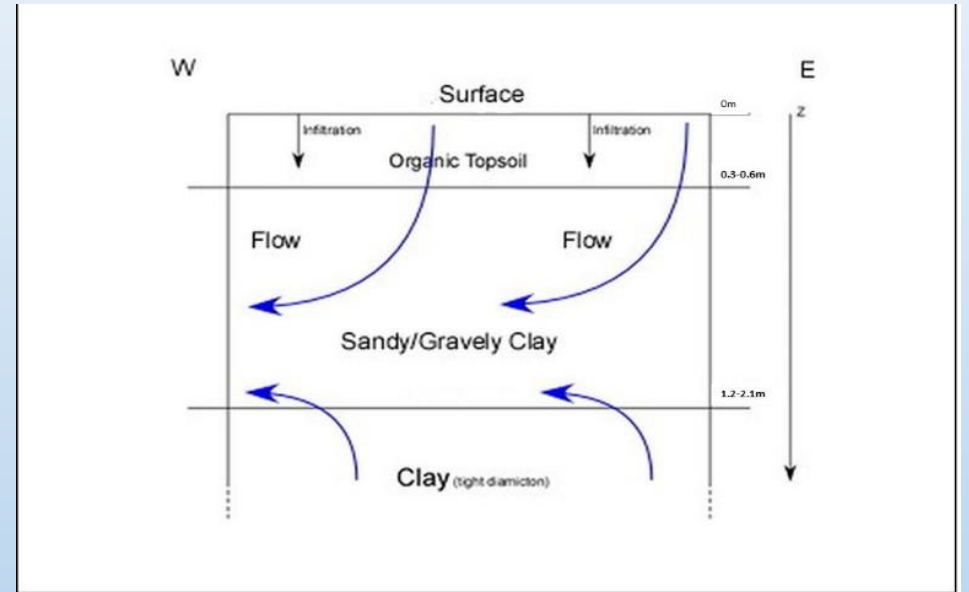
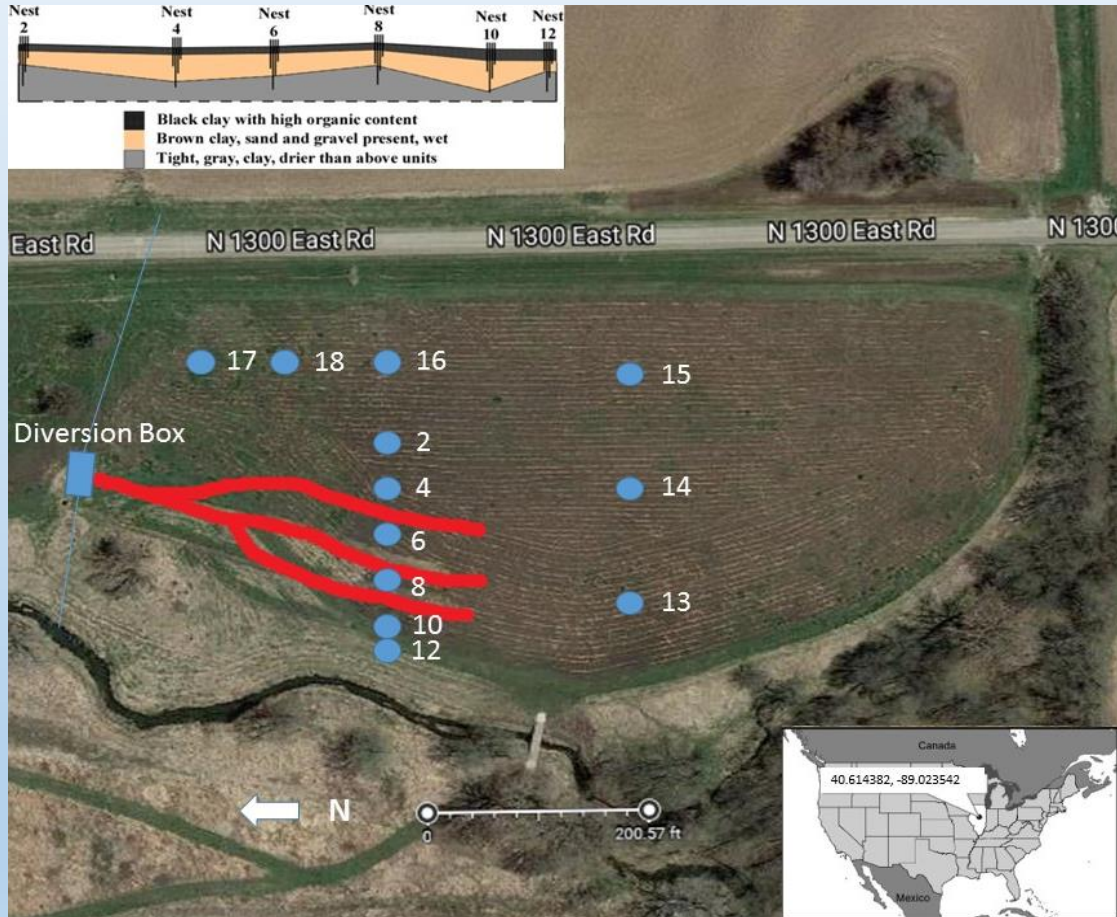
Why do we care about groundwater nitrate?

- Enters system by fertilization of crops
- Concentrations above 10mg/L are considered unsafe (EPA)
- Downstream nitrate transport drives eutrophication



(Eutrophication Image)

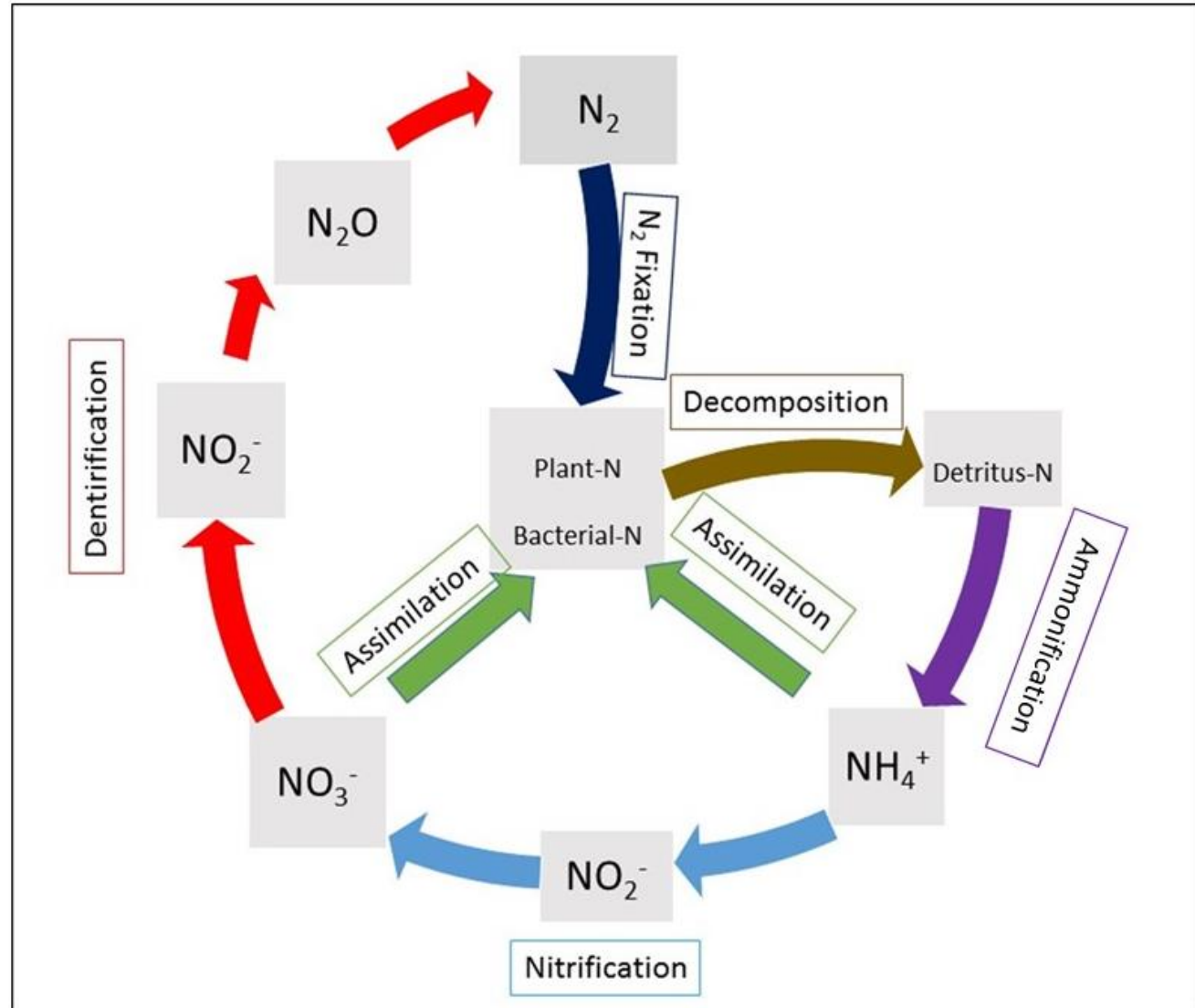
Saturated Buffer Zones can help



- Saturated Buffer Zones are known to facilitate nitrogen cycle transformations
- 2 mechanisms have been identified
 - Denitrification
 - Assimilation

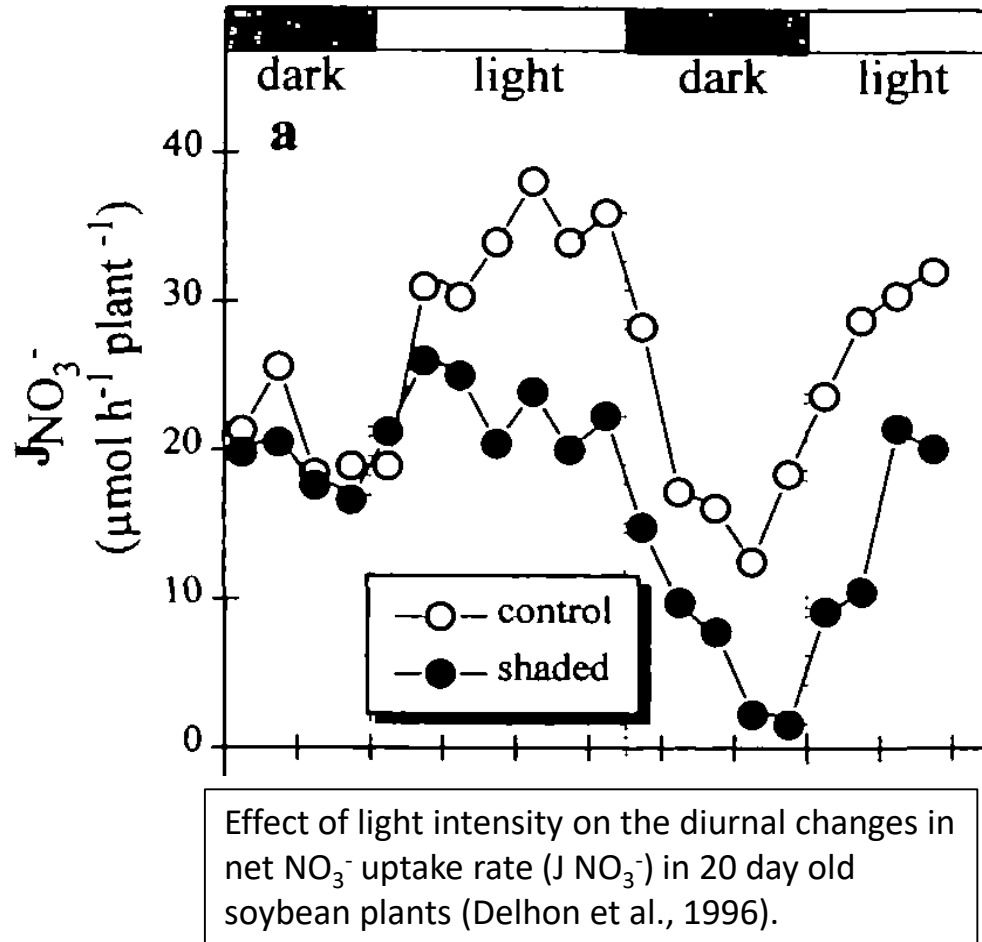
The Nitrogen Cycle

- Denitrification (in red)
- Assimilation (in green)
- These processes are influenced by environmental factors
- Temporal variation on the seasonal and diurnal scales may be present



Vegetation Uptake

NO_3^- uptake rate in soybean light vs. dark

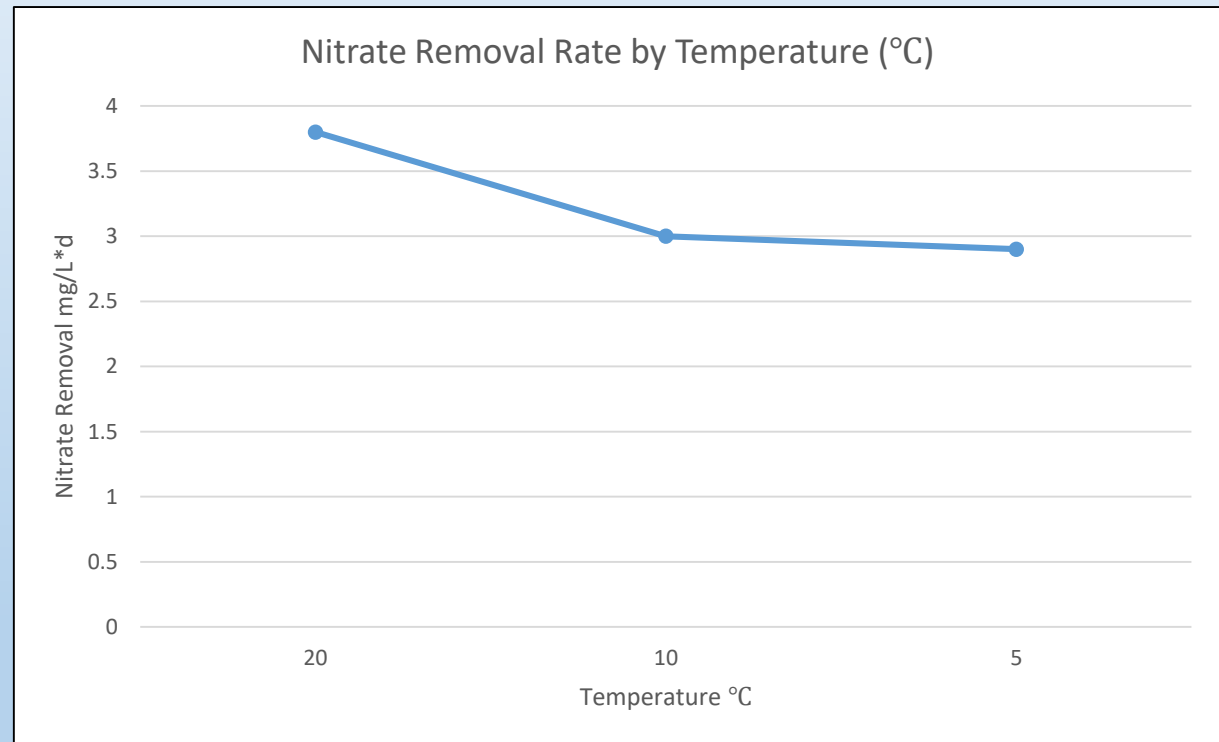


Picture of study site

- Studies show nitrate uptake in plants to vary with photoperiod
- Diurnal variation may be observable in groundwater

Denitrification

- Studies show denitrification to vary by temperature on a threshold
- Experiments performed under laboratory conditions demonstrate biologic denitrification to decrease abruptly at 5°C to 10°C (Ribas et al., 2015; Stanford et al., 1975).
- From 15°C to 35°C the coefficient of denitrification rate is 2. From 35°C to 45°C denitrification rate does not change (Stanford et al., 1975).



Data obtained from (Ribas et al., 2015)

Question

Does riparian zone shallow groundwater NO_3^- concentration vary temporally?

- 1) Does NO_3^- -N concentration vary over a 24-hour period in each season?
- 2) Does time of maximum and minimum NO_3^- -N concentration vary seasonally?
- 3) Does mean daily NO_3^- -N concentration vary seasonally?
- 4) Does the magnitude of mean difference between daily maximum and minimum NO_3^- -N concentration vary seasonally?

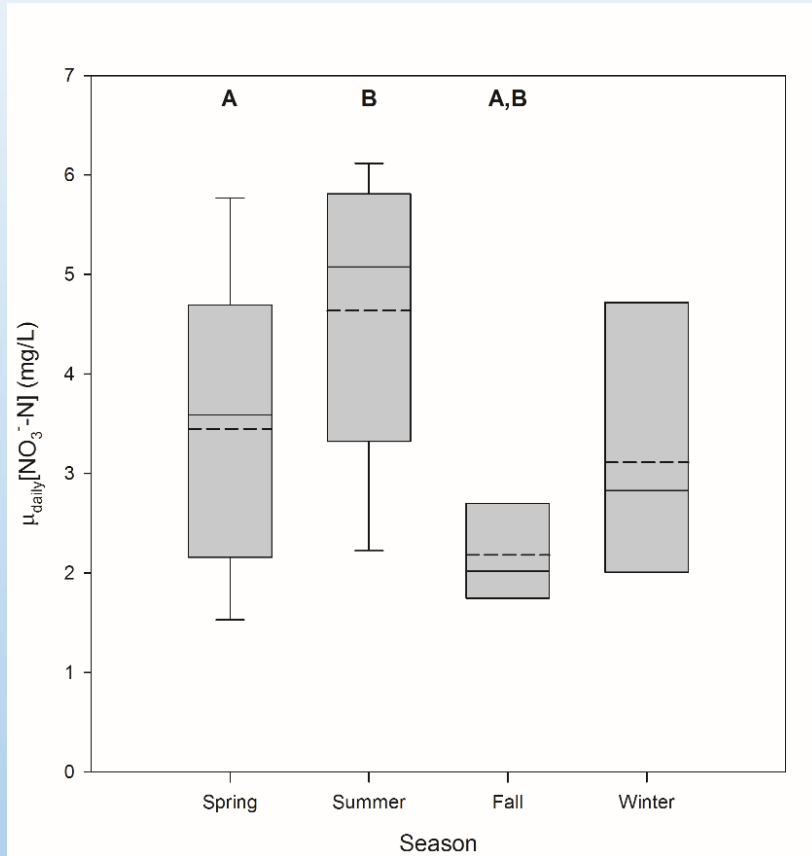
Methods

- 24hr sampling event weekly for a year -> samples taken out of well screened at 1.5m (5ft)
- DIONEX ICS-1100 Ion Chromatography to quantify NO_3^- -N and Cl^-
- Collection of air/water temperature , dissolved oxygen, light intensity, and water table height data
- Data analysis by a *t*-Tests and Pearson Correlation

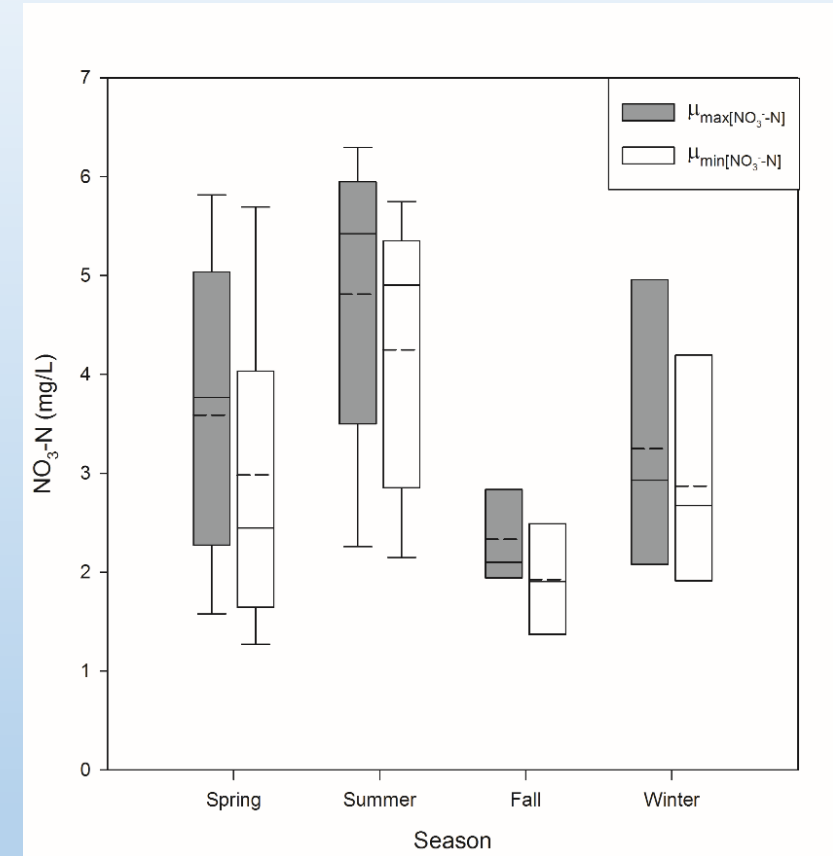


T3 wells and autosampler

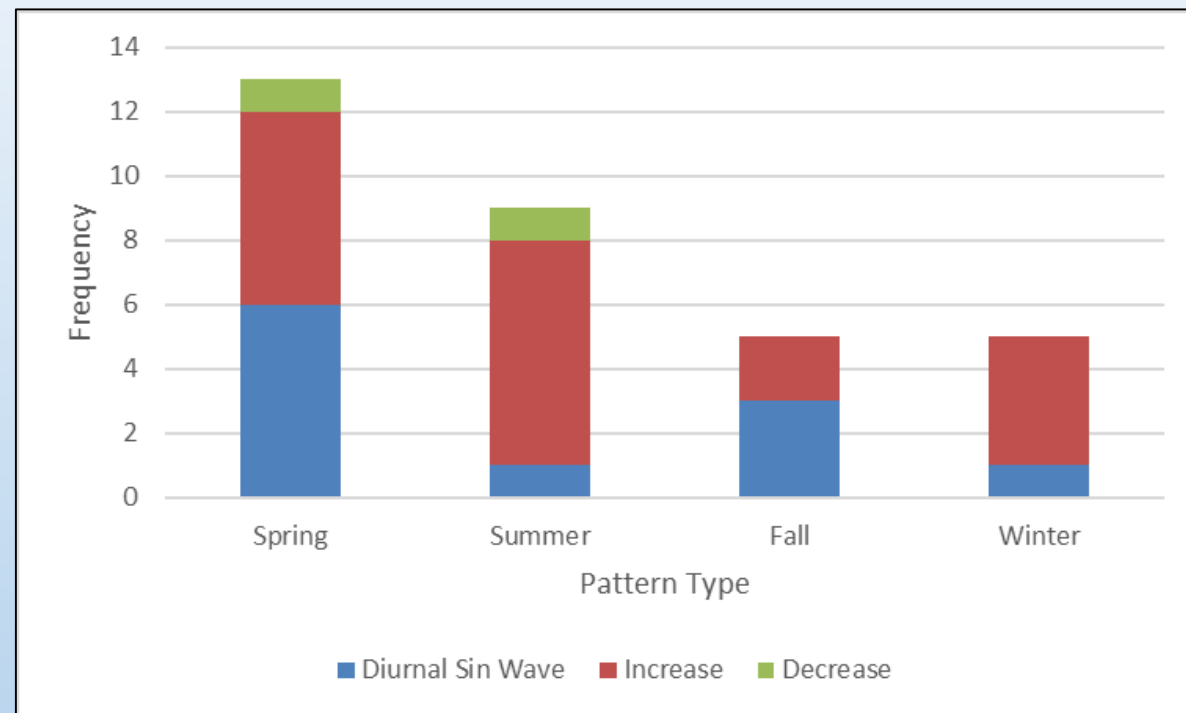
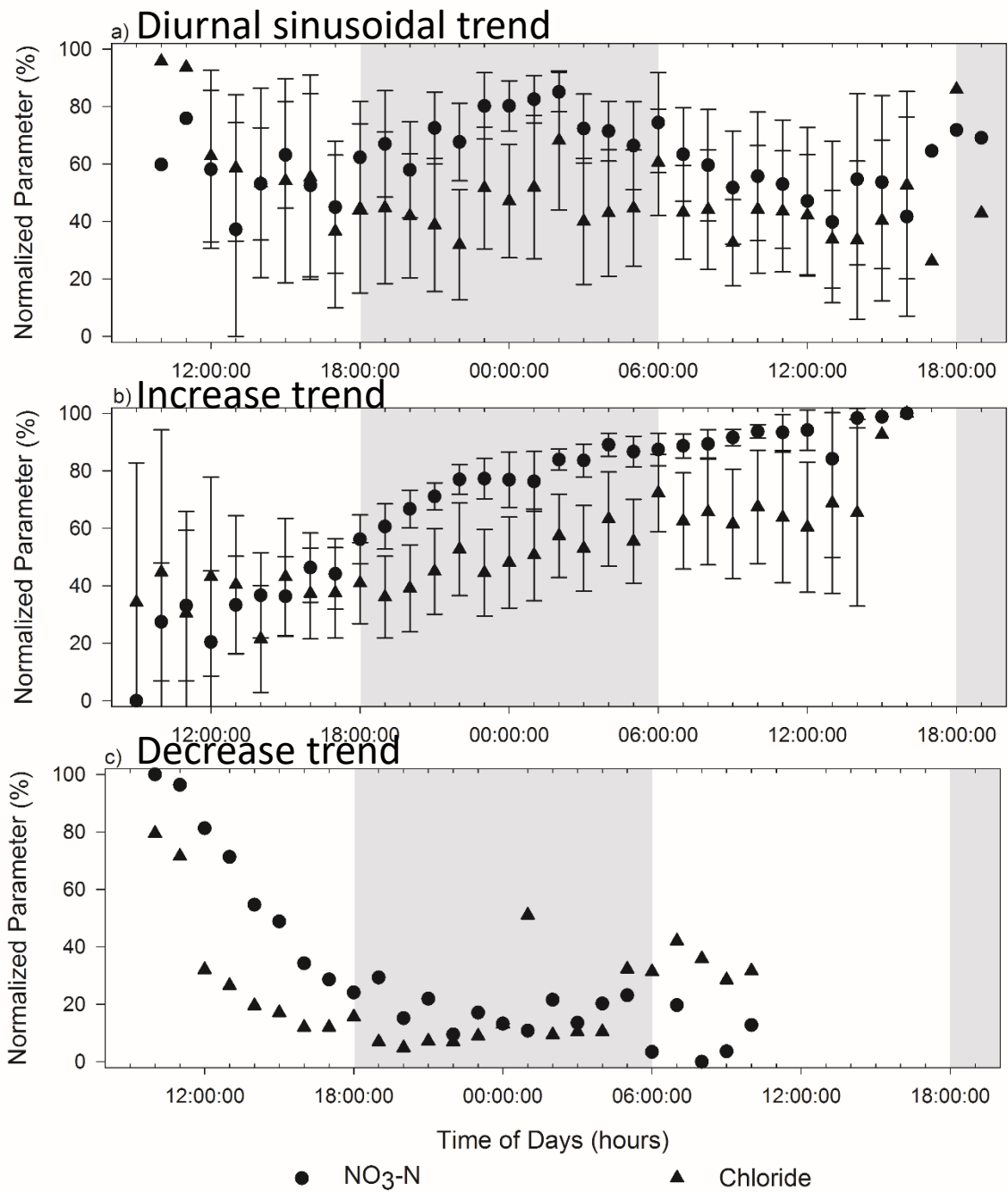
Results and Discussion



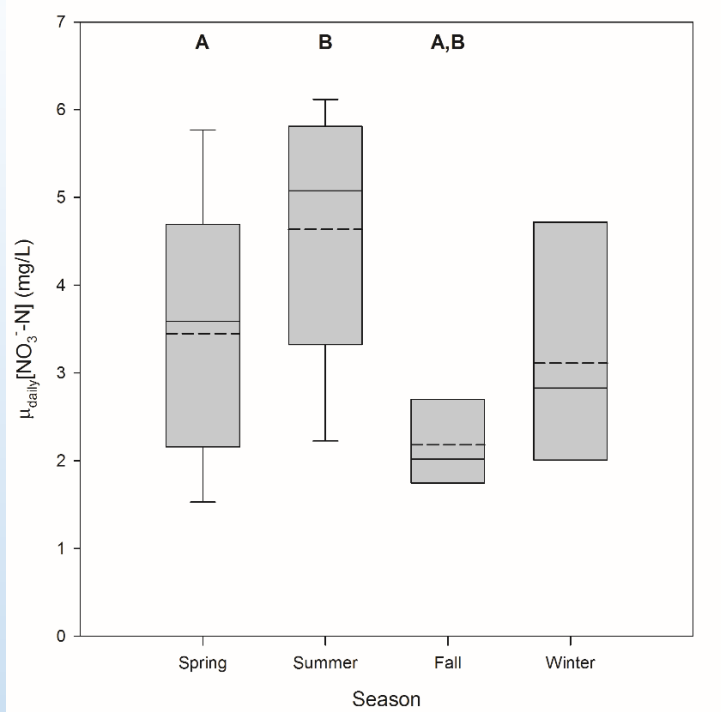
Daily NO_3^- -N concentration by season. Statistically significant difference between $\mu_{\text{daily}}[\text{NO}_3^- \text{-N}]$ indicated by A and B.



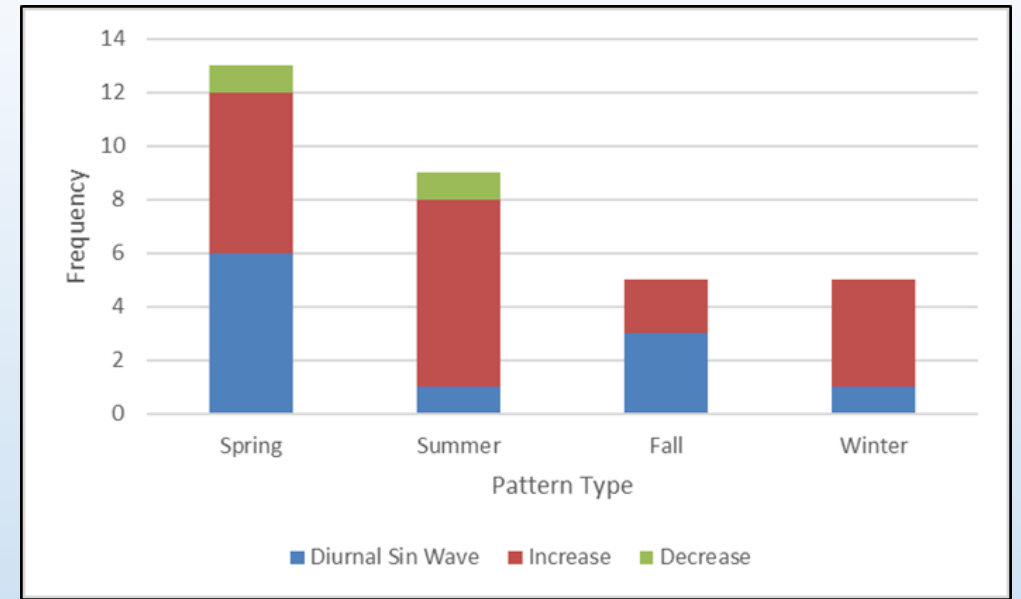
Daily maximum and minimum NO_3^- -N concentrations for each season. Within each season $\mu_{\text{max}}[\text{NO}_3^- \text{-N}]$ and $\mu_{\text{min}}[\text{NO}_3^- \text{-N}]$ are statistically significantly different.



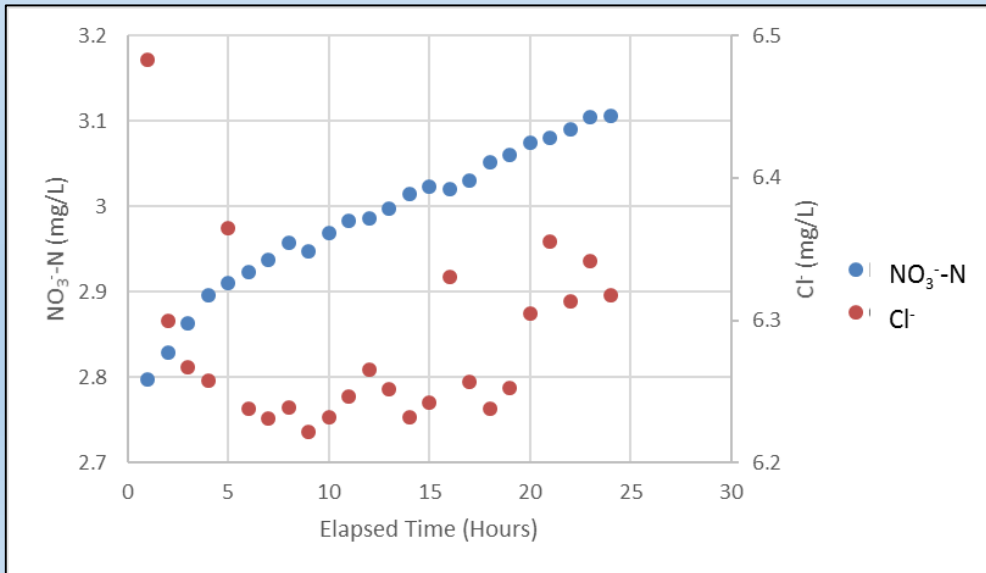
Frequency of NO₃⁻-N concentration trends by season.



Daily NO₃⁻-N concentration by season. Statistically significant difference between $\mu_{\text{daily}}[\text{NO}_3^--\text{N}]$ indicated by * and \diamond .



Frequency of NO₃⁻-N concentration trends by season.

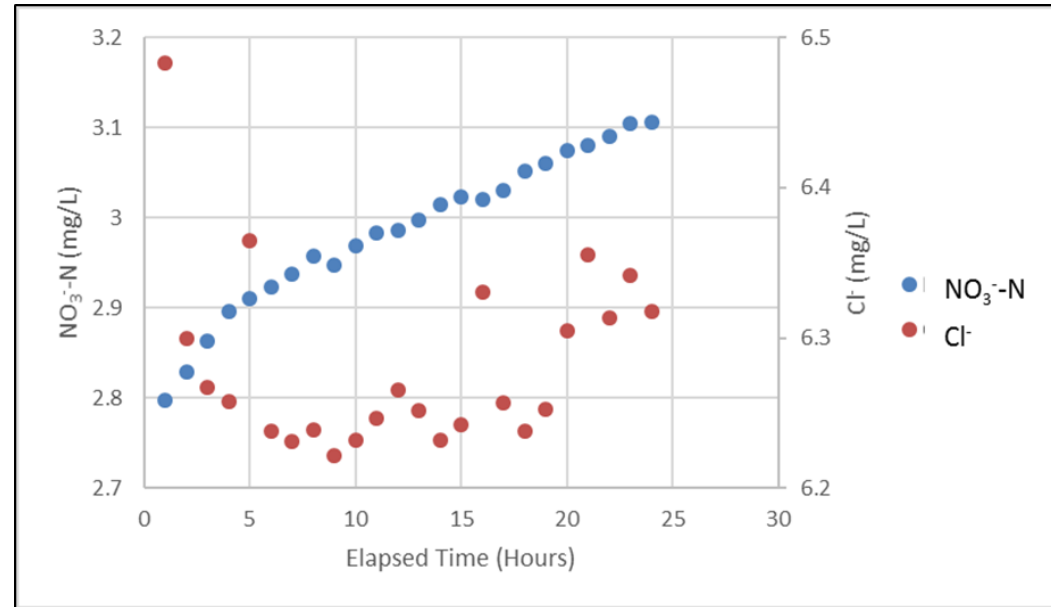
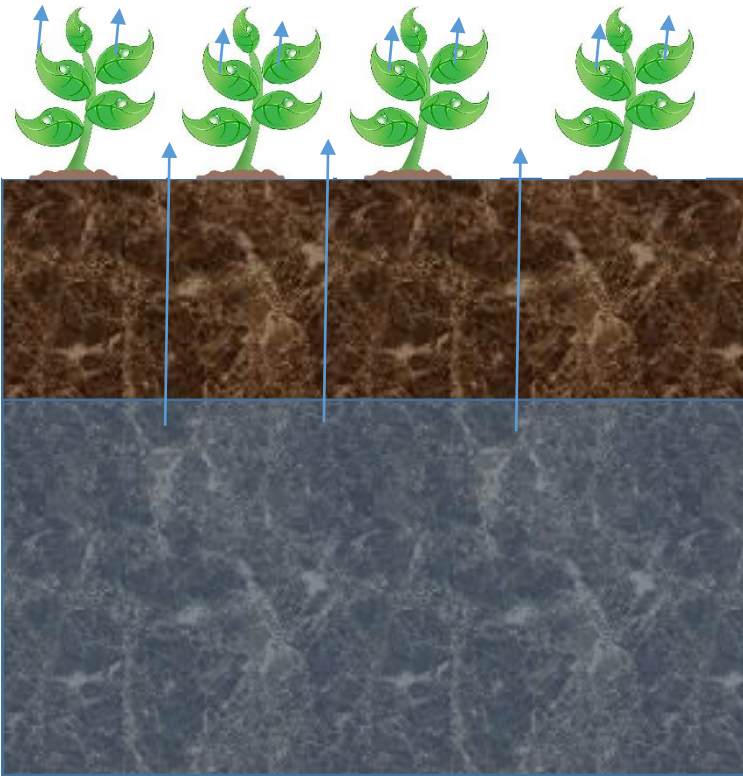


Increase trend

The increase trend is:

- Most frequent in the spring and summer
- Least frequent in fall
- Explained in 3 ways

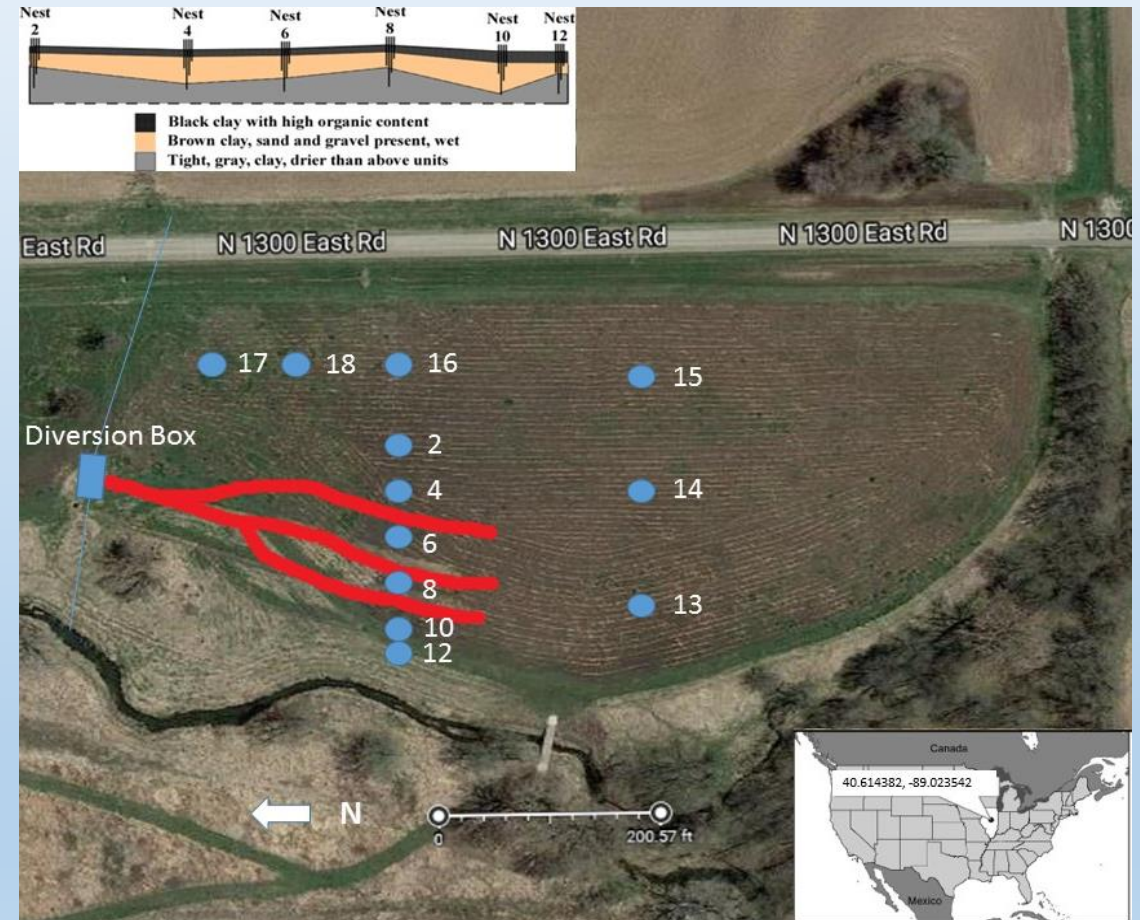
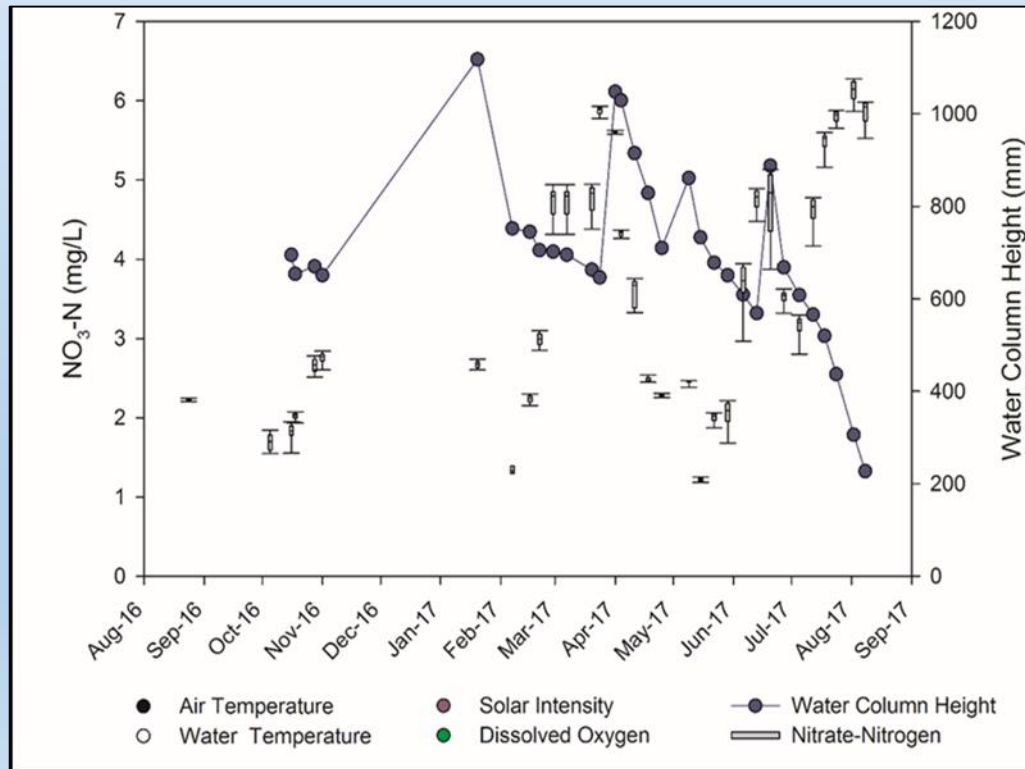
Explanation 1: Evapotranspiration



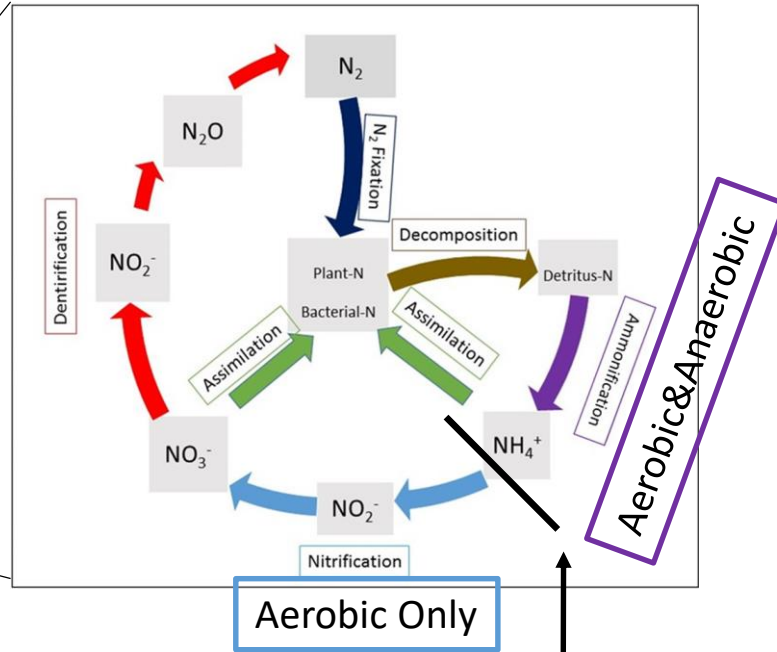
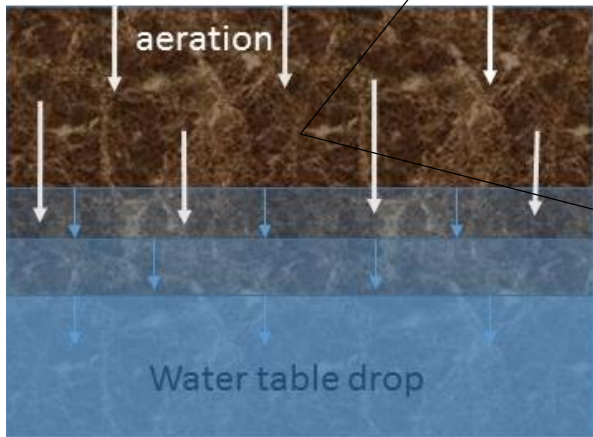
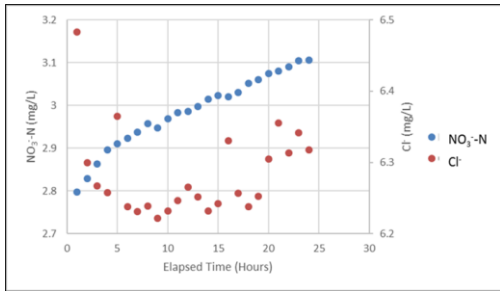
- Concentration of solute by evapotranspiration
- Data does not support, as chloride does not increase in parallel to nitrate

Explanation 2: Nitrate Plume

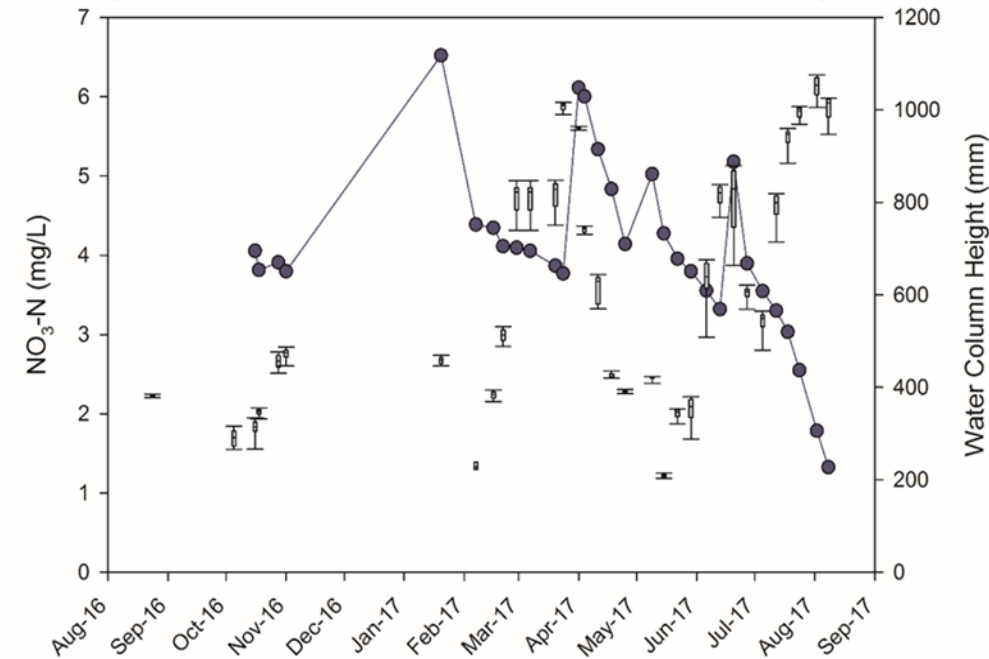
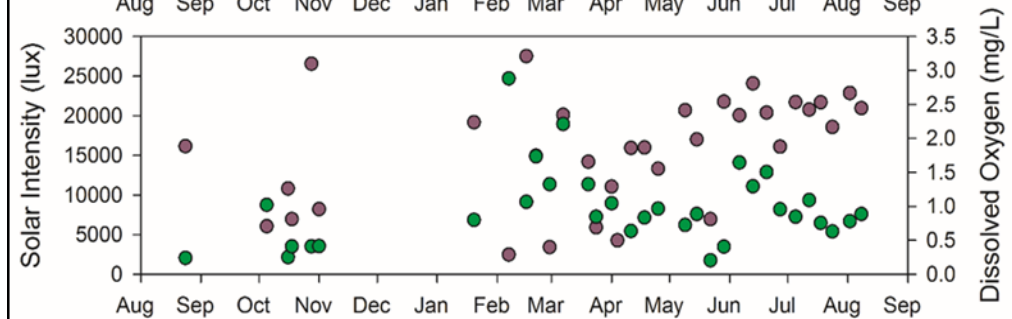
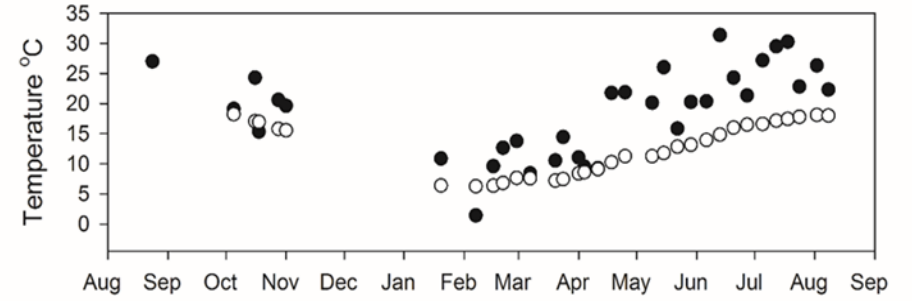
- Nitrate plume could have passed through the saturated buffer from the agricultural land use upgradient



Explanation 3: Nitrification

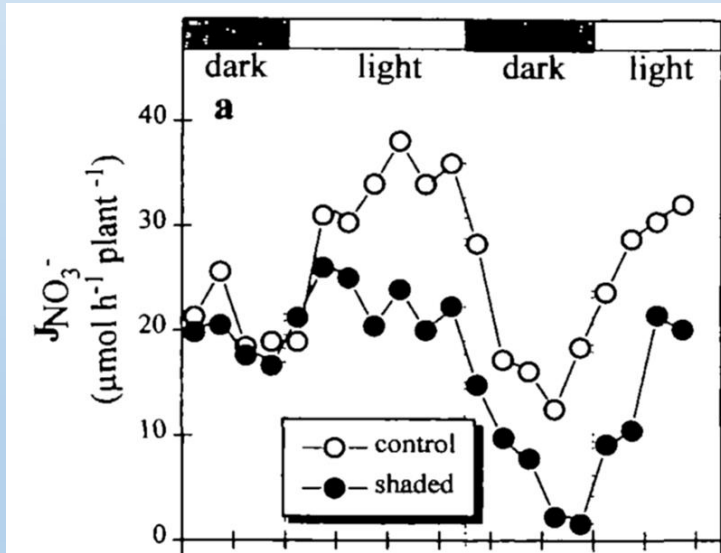
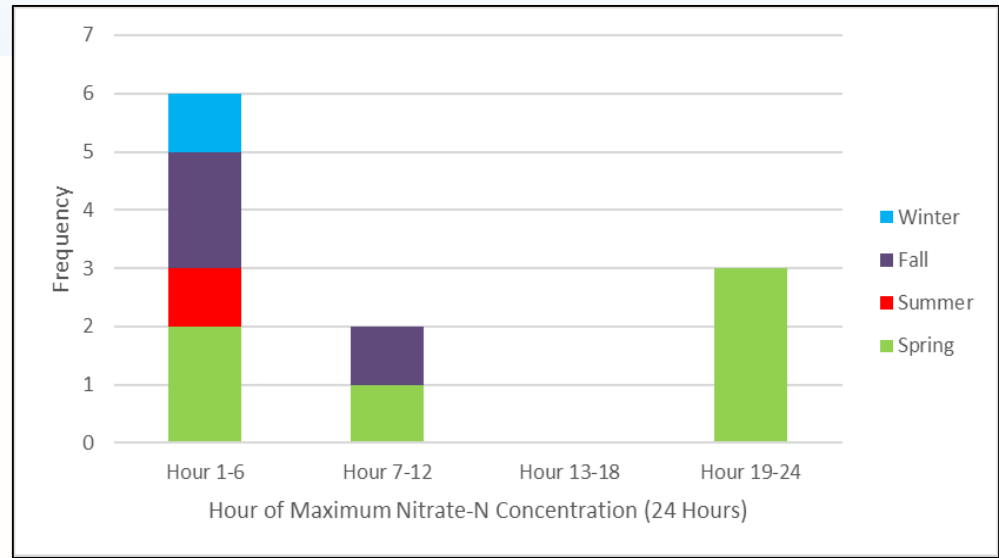
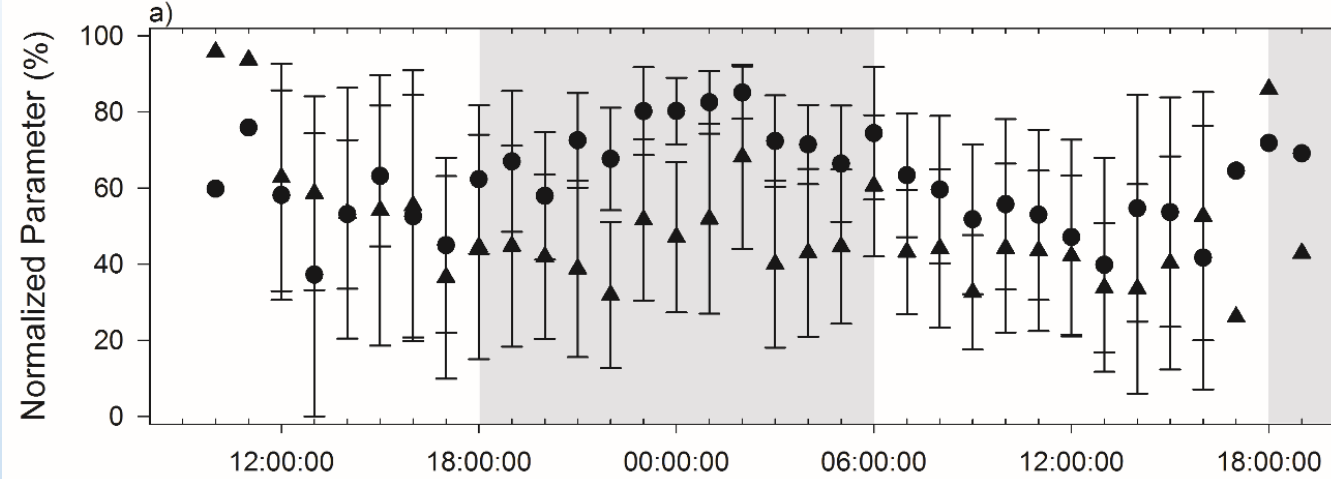


Ammonium accumulation until oxygen is available

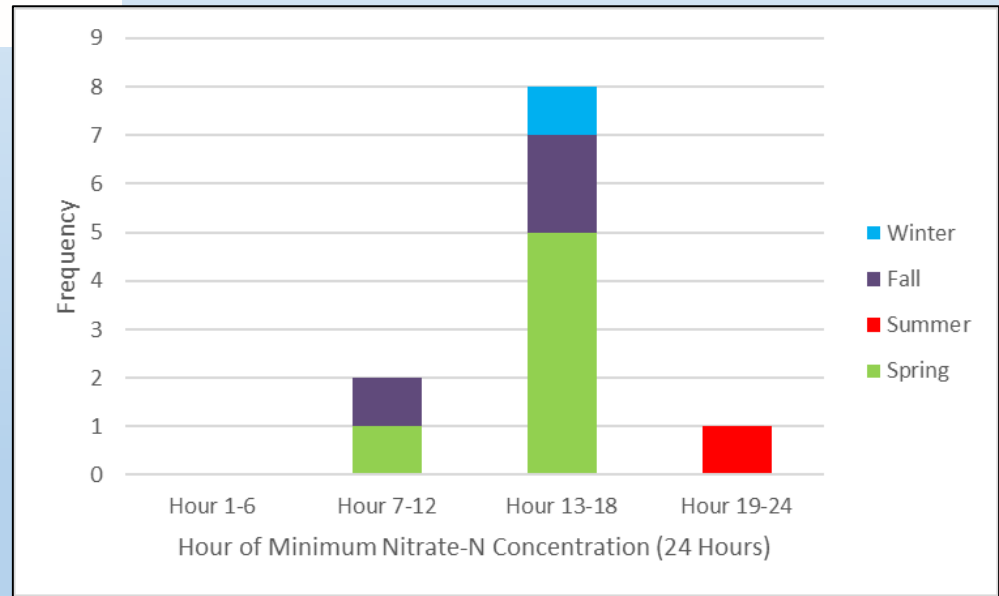


- Air Temperature
- Water Temperature
- Solar Intensity
- Dissolved Oxygen
- Water Column Height
- Nitrate-Nitrogen

Diurnal sinusoidal trend

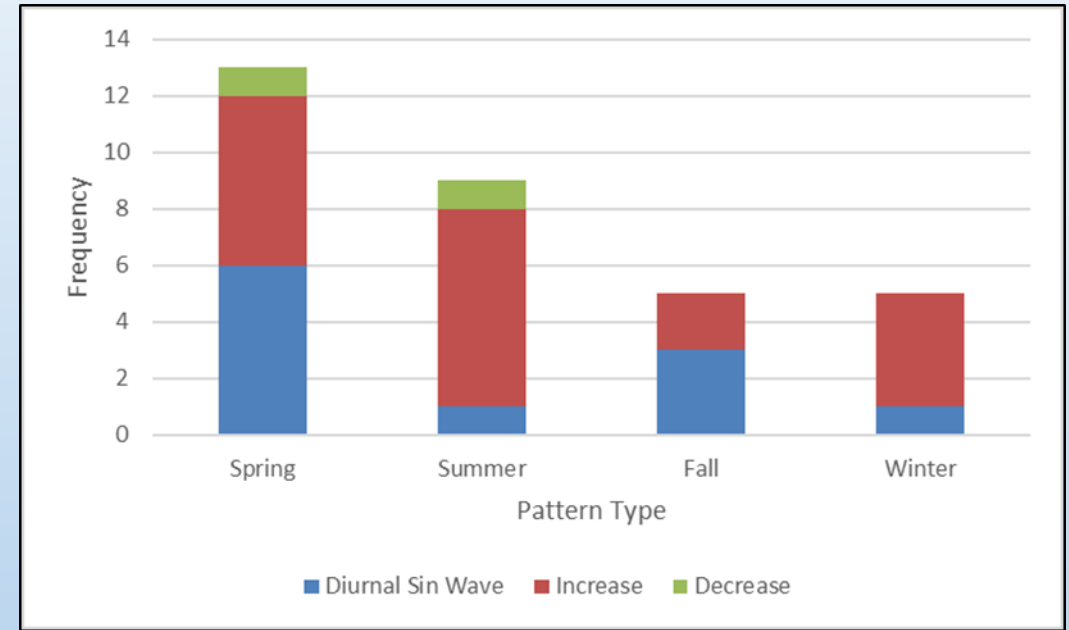
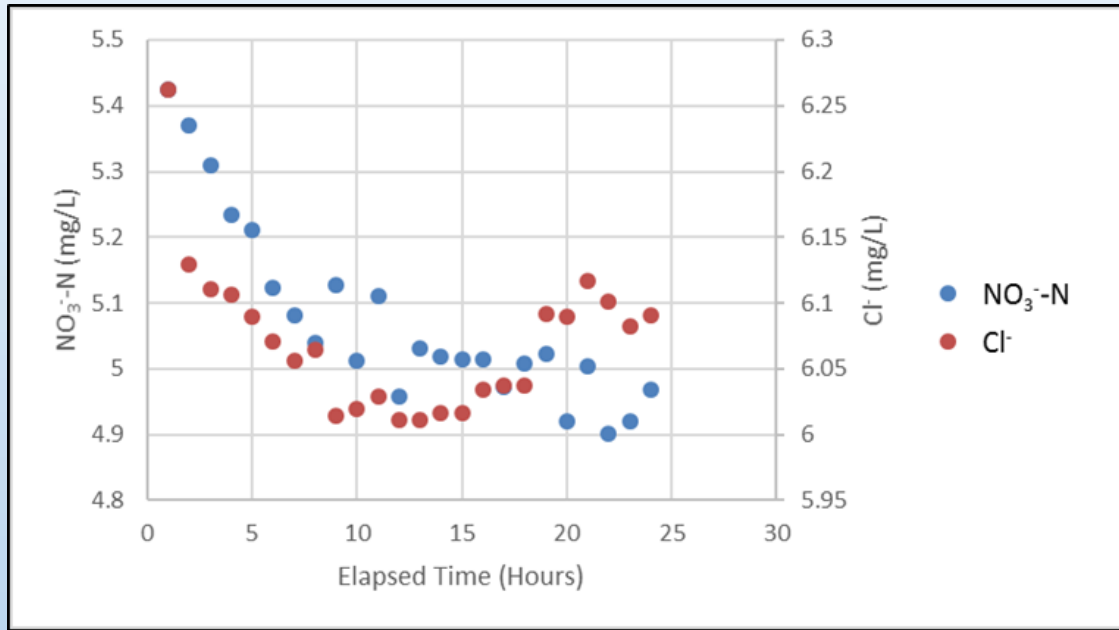


Effect of light intensity on the diurnal changes in net NO_3^- uptake rate (J NO_3^-) in 20 day old soybean plants (Delhon et al., 1996).

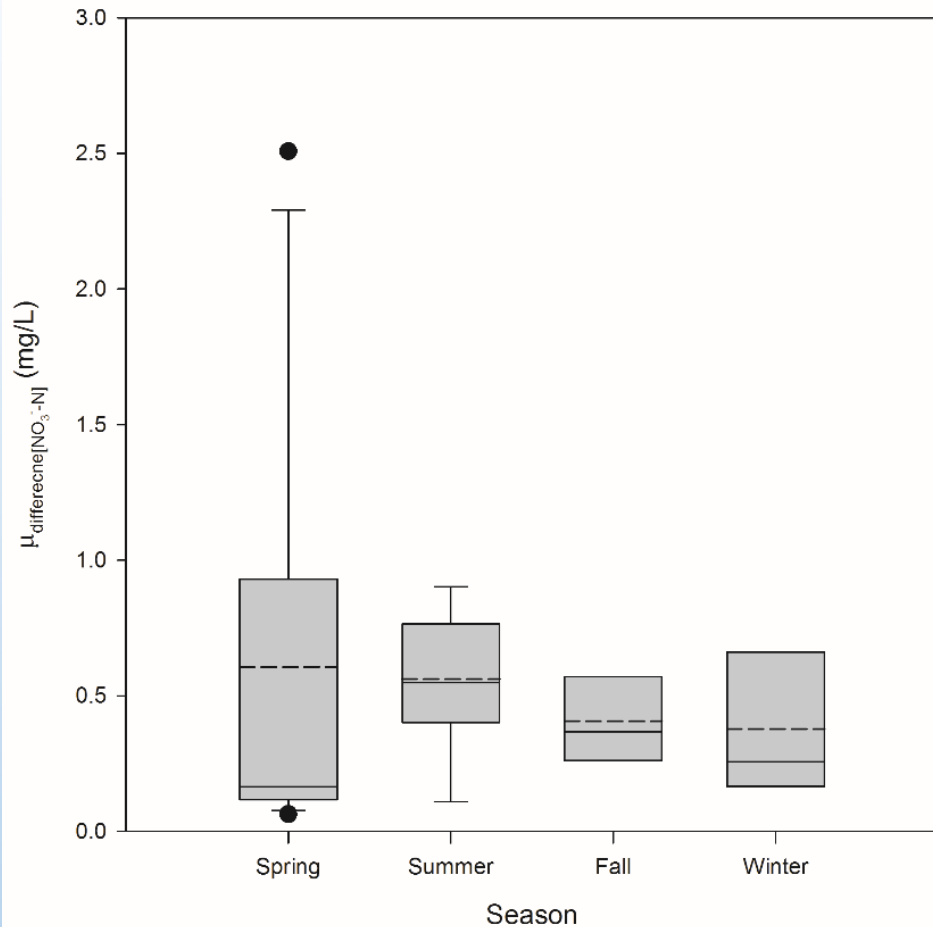


Histogram of maximum and minimum NO_3^- -N concentration time-of-day for diurnal pattern events (**hour 1 = 1:00am**)

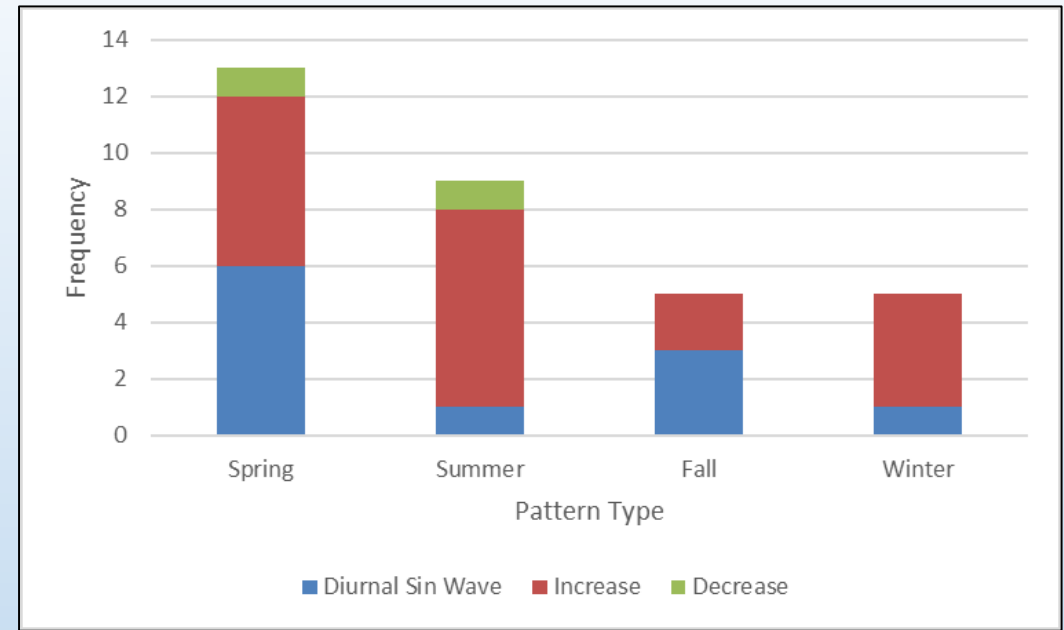
Decrease Trends



- Decrease trends are infrequent
- Nitrate and chloride decrease in parallel
- Sampling events occurred after recharge events

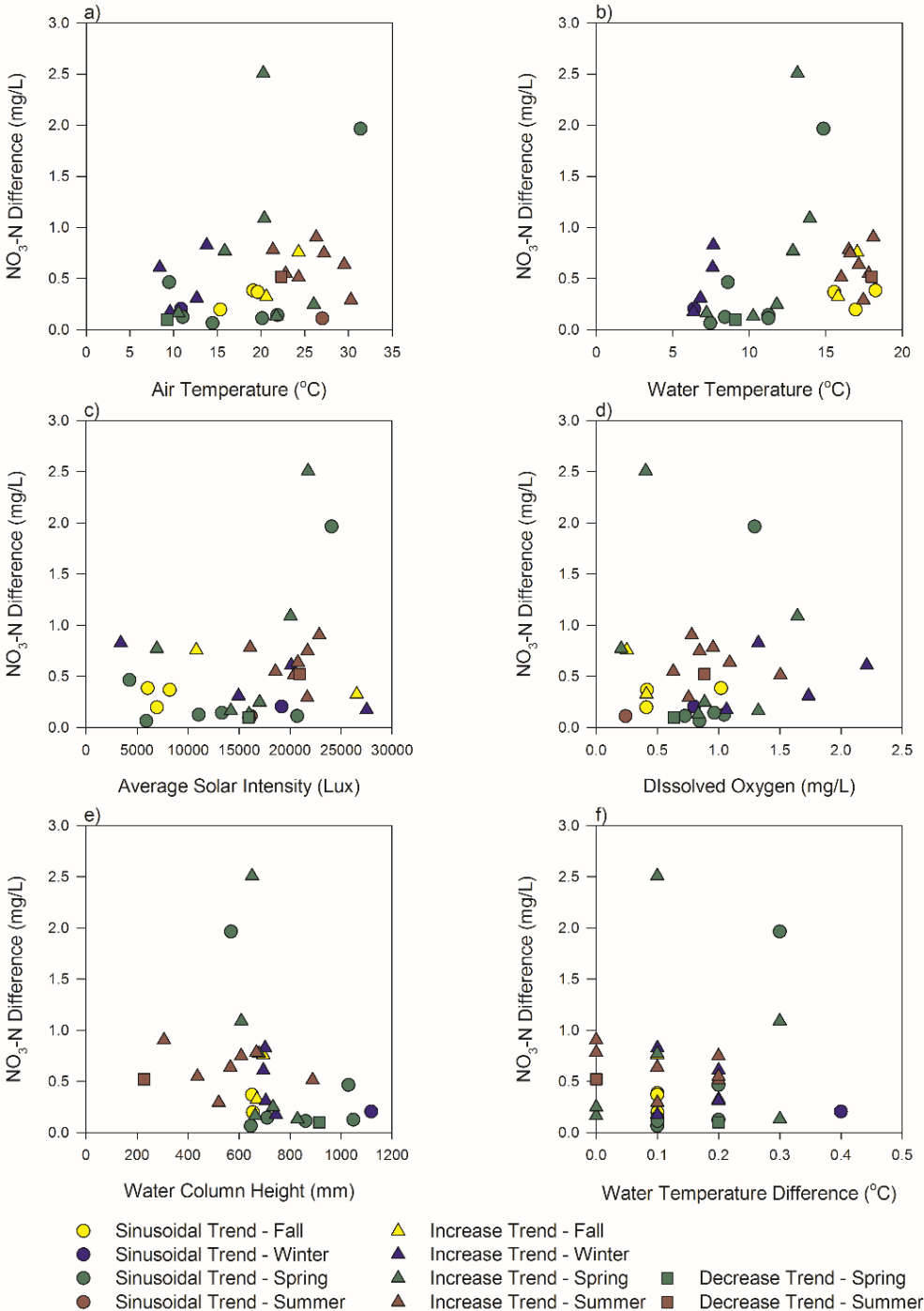


Differences between daily maximum and minimum NO_3^- -N concentration for each season. No statistically significant differences in $\mu_{\text{difference}[\text{NO}_3^- \text{-N}]}$ are present among seasons.



Frequency of NO_3^- -N concentration trends by season.

- Majority of differences are $<1\text{mg/L}$
- Magnitude of difference over 24-hours may be physically limited by groundwater movement
- Biologically mediated reactions may have similar reaction rates



Environmental factor correlations

- Grouped as all data, increase/decrease trend days, and diurnal sinusoidal trend days
- No significant correlations



Conclusions

- Seasonal and diurnal changes in NO_3^- -N concentration exist
- Measurable differences occur throughout the year
- Vegetation uptake is measurable
- Water table location matters
- Future work should focus on water table variation and stable isotope methods for nitrate source and fate ($\delta^{18}\text{O}$ & $\delta^{15}\text{N}$)

Acknowledgements

- The City of Bloomington, Rick Twait
- Geologic Society of America
- Illinois Groundwater Association
- The Illinois Water Resources Center



References

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- Eutrophication Image. <https://iboess.wikispaces.com/5.4+Eutrophication>
- Fertilizer application Image.
<http://www.christiancountyfs.com/agronomy/Pages/Custom-Application.aspx>