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
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
Effect of light intensity on the diurnal changes in net $\text{NO}_3^-$ uptake rate ($J_{\text{NO}_3^-$}) in 20 day old soybean plants (Delhon et al., 1996).

- 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 $\text{NO}_3^-$-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
Results and Discussion

Daily $\text{NO}_3^-$-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 $\text{NO}_3^-$-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 \( \text{NO}_3^- \)-N concentration trends by season.
The increase trend is:
- Most frequent in the spring and summer
- Least frequent in fall
- Explained in 3 ways

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

Aerobic Only

Ammonium accumulation until oxygen is available
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 $\mu$ difference [NO$_3^-$-N] are present among seasons.

- Majority of differences are <1mg/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 NO₃⁻-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 (δ¹⁸O & δ¹⁵N)
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References


• Ribas, D., Calderer, M., Martí, V., and Rovira, M., 2015, Effect of different seasonal conditions on the potential of wetland soils for groundwater denitrification: Desalination and Water Treatment, v. 53, no. 4, p. 994-1000.


• Eutrophication Image. https://iboess.wikispaces.com/5.4+Eutrophication