Differences in Alkalinity Relative to Denitrification in Mississippi Floodplains

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Abstract:

Agricultural and urban fertilization in the Mississippi River watershed has led to over-fertilization downstream in the Gulf of Mexico, causing excessive algal growth, leading to low oxygen levels that impair water quality and promotes the Dead Zone in the Gulf of Mexico where oxygen levels are so low that fish cannot thrive (Fig 1). Natural respiration of denitrifying microbes remove nitrate from ground water and convert it to nitrogen gas (N_2). When anaerobic bacteria respire, they change the amount of carbon dioxide in the surrounding water that can cause higher alkalinity.

Hypothesis: We hypothesize that higher alkalinity will correspond with higher nitrogen saturation and possibly with faster denitrification rates.

Method Summary: We collected water samples from three sites in the Dogtooth Bend region of the Mississippi River in Southern Illinois and measured nitrogen gas saturation and alkalinity. We collected surface and ground water and sediment samples from Big Cypress, Sandy Ridge, and Grand Lake wetlands. Surface water samples from these three sites were further incubated for 72 hours at 14.5 °C to investigate the effect of alkalinity over time.

Preliminary findings: Although alkalinity levels at field sites trended toward higher values with higher nitrogen saturation, the relationship was not significant.

Importance of research: Resolving nutrient issues can benefit riverine and marine ecosystems.

Objectives:

The objective of our research is to test whether alkalinity measurements cn provide an inexpensive, simple means of measuring denitrification.

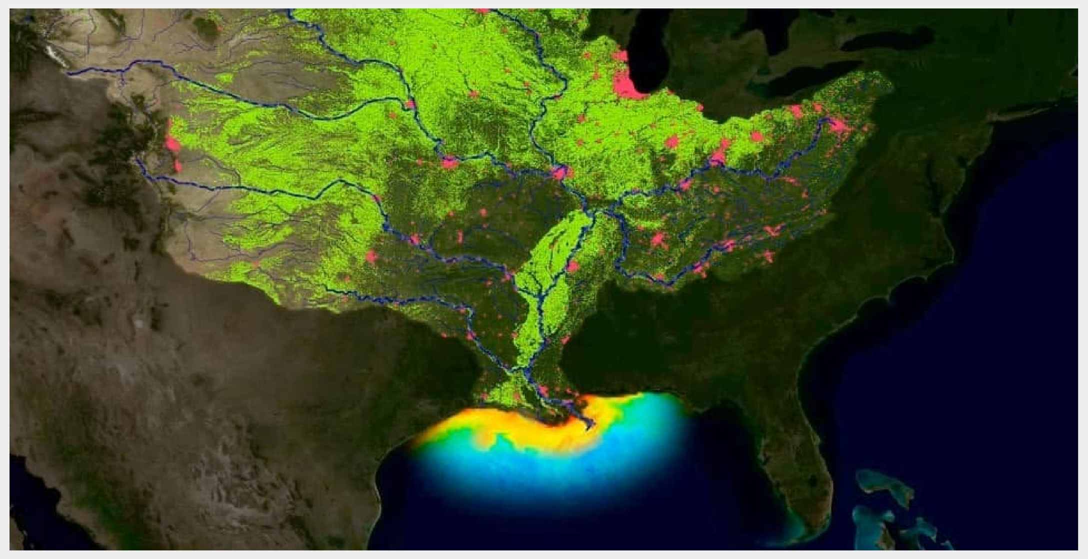

Fig 1. The Dead Zone in the Gulf of Mexico
(https://coastalscience.noaa.gov/news/noaa-forecasts-very-large-dead-zone-for-gulf-of-mexico/)

Methods:

- Samples were collected at three locations of the Dogtooth Bend region of the Mississippi river.
  - Locations include: Grand Lake, Sandy Ridge, and Big Cypress Illinois.
  - Samples were collected with three or more duplicates.
- Denitrification was measured in field samples and incubations time 0 and 72 hours.
  - Wetland sediment samples were brought back and incubated.
- 25 mL of each sample was poured into a beaker for alkalinity and pH testing.
- A pH electrode (Fisher Scientific) was used to get a beginning pH reading of all samples.
- Sulfuric acid (H_2SO_4) was added to each sample while I continuously monitored the pH until it reach a reading of 4.5.
- The amount of H_2SO_4 added was multiplied by a conversion factor of 40 to calculate the final alkalinity.
- We measured N_2 in water samples collected from field sites using a Membrane Inlet Mass Spectrometer (MIMS; Bay Instruments). We analysed samples following methods according to Kana (1994).
- Samples were collected, immediately preserved with 100 µL / 12 mL sample with 50% ZnCl in ultrapure water (weight by volume), and stored at 4 °C until analysis on the MIMS.
- Raw data were analyzed using regression analysis in Excel (Microsoft Office) and R statistical software.

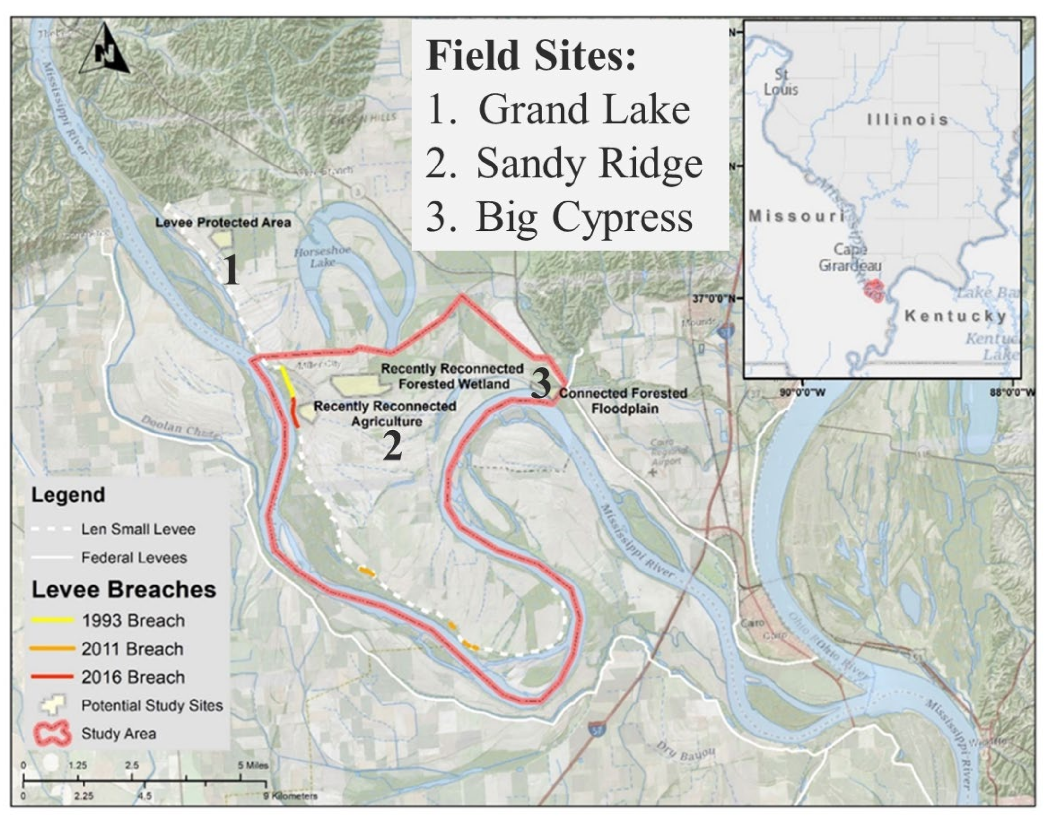

Fig 2. Dogtooth Bend of the Mississippi River in Illinois (map courtesy of Dr. Jon Remo).

Results:

Our preliminary results show that alkalinity is positively correlated with nitrogen saturation across field locations.

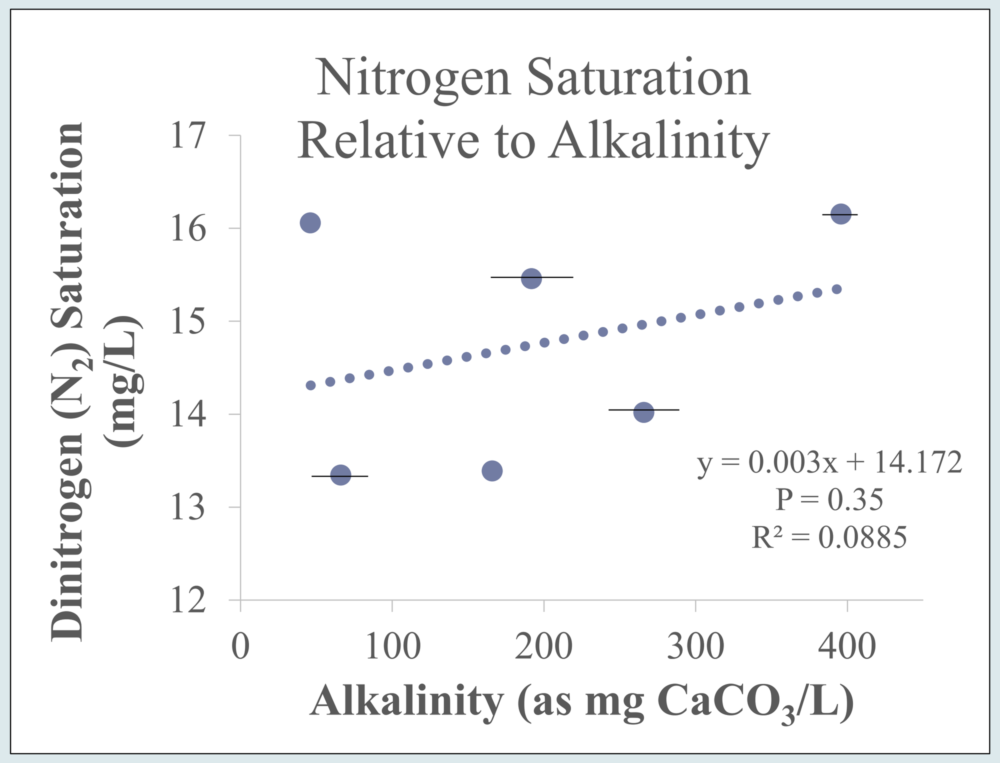

Fig 3. Dinitrogen (N_2) saturation relative to alkalinity. Error bars for nitrogen and some alkalinity values are too small to extend beyond symbols. Where visible, standard deviations are shown for alkalinity.

Sample	pH (mg/L) Avg ± SD	Alkalinity (mg/L) Avg ± SD
GLSW	8.24 ± 0.41	266.00 ± 48.08
GLGW	8.51 ± 0.43	396.00 ± 22.627
SRSW	8.56 ± 0.03	166.00 ± 2.83
SRGW	7.87 ± 0.77	192.00 ± 56.57
BCSW	8.04 ± 0.23	66.20 ± 36.49
BCGW	4.64 ± 0.25	46.20 ± 8.20
GLSW T0	8.23 ± 0.15	244.00 ± 16.97
SRSW T0	8.26 ± 0.09	150.00 ± 19.80
BCSW T0	7.87 ± 0.05	64.00 ± 22.63
GLSW T72	8.63 ± 1.15	256.00 ± 18.33
SRSW T72	8.00 ± 0.15	183.33 ± 9.02
BCSW T72	7.27 ± 0.12	46.67 ± 2.31

Table 1. Alkalinity and pH Results. Key: GL = Grand Lake, SR = Sandy Ridge, BC = Big Cypress, SW = surface water, GW = ground water. Data from time zero (T0) and 72 h (T72) incubations are shown for interest.

Fig 4. Alkalinity Testing Setup

Discussion:

The general trend between nitrogen saturation and alkalinity indicates that as anaerobic, denitrifying microbes respire and produce nitrogen gas (N_2), they may influence alkalinity. However, the correlation is not statistically significant. Thus, based on these preliminary data alone, we do not recommend that alkalinity be used as an indicator of the magnitude of denitrification in environmental samples. Several potential errors that could alter the results included sampling error during titrations with the sulfuric acid. We anticipate that clearer findings will emerge as the number of field sites is expanded from 3 to 4 locations and repeat sampling occurs quarterly throughout the next year.

Future Directions:

Based on our preliminary findings, we will continue to test whether alkalinity is a good predictor of denitrification activity. The nitrogen levels from laboratory incubations conducted under controlled conditions are not yet complete. We expect those findings will likely yield more insights.

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