Isotopic Evidence in Rainwater for Boron Contribution in Long Island Groundwaters

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Long Island obtains all of its drinking waters from local aquifers and it is crucial to consider pathways of contamination and regulations to prevent them from compromising the quality of our water. Nitrates are one of the main contaminants with some public supply wells having to be abandoned due to concentrations above drinking water standards (Bleifuss, 2000). Numerous studies have suggested that boron isotopes can discriminate between possible sources of nitrate to groundwater. We used a survey approach to study boron isotope composition and boron concentrations in Long Island surface waters. The goal was to determine if boron could be used in a *coastal setting* to identify the source(s) of nitrates in water here on Long Island. Due to the fact that seawater has very elevated isotope ratios and concentrations, we hypothesized that any other signature might be masked. However, we found that the boron isotope compositions vary widely across the island, and that based on Cl^- content, and comparison to water bodies that directly interact with sea water, we can rule out sea spray as an important input to boron in surface waters here on Long Island.

In this study, we examined samples from the spring fed creek that supplies Setauket Mill Pond (Figure 1A). We also examined samples from the Nissequogue River (Figure 1B). Both of these locations were sampled during June of 2019. Finally, we examined rainwater collected from the roof of the Earth and Space Sciences building at Stony Brook University using a rain gauge.

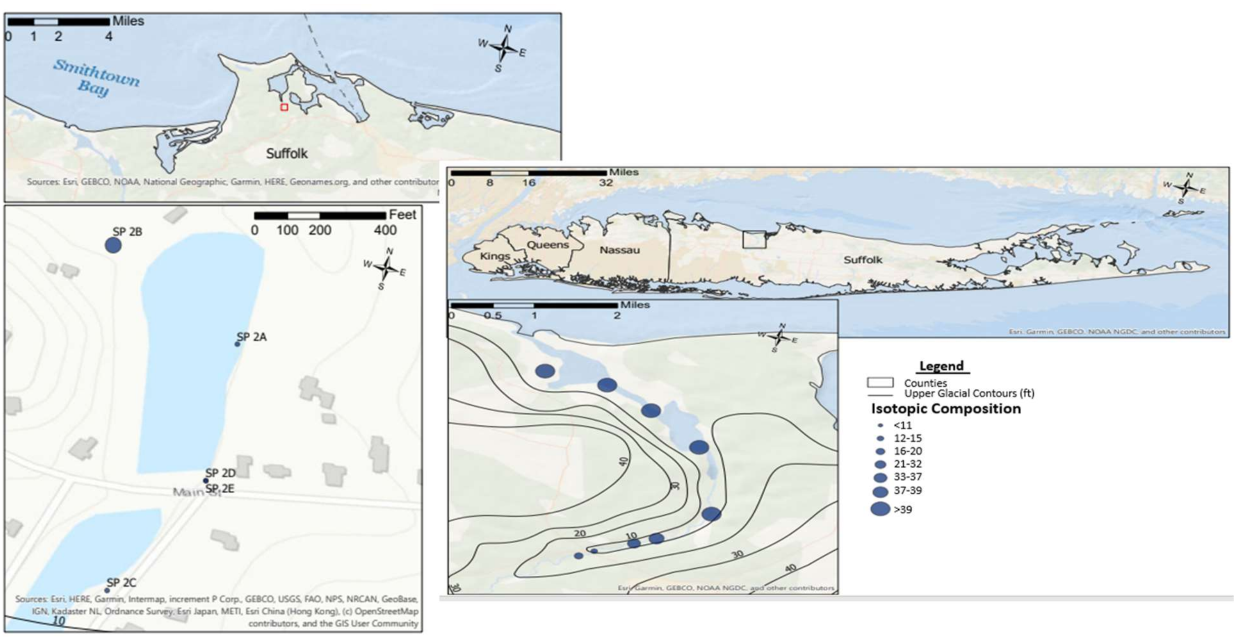

Figure 1: GIS maps of sample localities. Each point represents a sample location and the relative size of the dot represents an isotopic composition range and shown in the legend. **On left:** Setauket Mill Pond transect; **On right:** Nissequogue River transect.

Methods

At least 125mL of water was collected in cleaned polyethelene bottles. In the lab, aliquots of the water samples were adjusted to pH 9, and then put through Amberlite boron specific resin to separate boron from all other ions. The boron was eluted with 2% nitric, which is the normality of acid we use for analyses. We diluted the solution to 50ppb to match the signal with the standard. We used NBS951, a boric acid standard, to bracket samples and we ran nitric acid blanks between each analyses. This background was averaged and subtracted from each boron analyses and then the average of the bracketing standards were used to calculate the $\delta^{11}B$ using the equation:

$$\delta^{11}B = ({}^{11}B/{}^{10}B_{(sample)} - {}^{11}B/{}^{10}B_{(standard)}) / {}^{11}B/{}^{10}B_{(standard)} \text{ X } 1000$$

We also analyzed the samples for other properties such as pH, chlorine and nitrates using Vernier probes.

Results

Seven samples from the spring fed creek at Detmer Farm to the outlet at the Setauket Pond give a narrow range of concentrations and isotope compositions (Table 1, Figure 2). Two other samples (SP 2B, and SP2I) collected across the dam has much higher boron concentration and has a much heavier $\delta^{11}B$ values than the rest, trending towards seawater values. They were accompanied by higher Cl^- concentrations (Table 1).

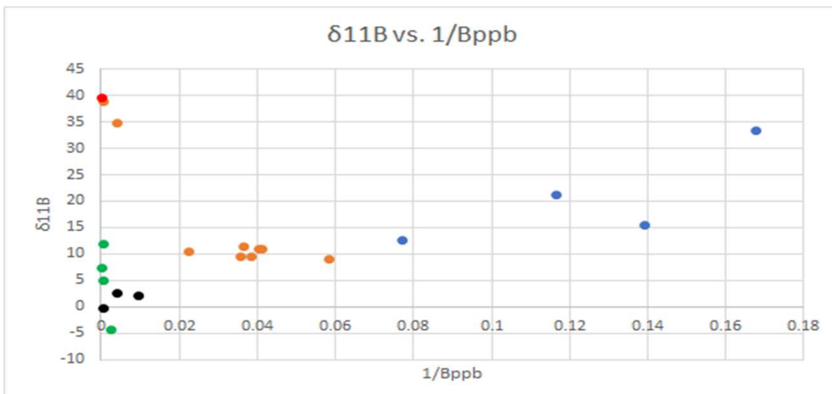

Figure 2: Plot of $\delta^{11}B$vs. 1/B (ppb). The green points are fertilizers, the red is seawater, the black is septic, and the orange are from Setauket Pond and the spring creek that supplies it.

Table 1. Data from the Setauket Pond samples.

Sample	$\delta^{11}B$	B(ppb)	pH	Cl (mg/L)
SP 2A	10.91	24.33	7.08	79.9
SP 2B	38.89	2026.8	7.57	8729
SP 2C	9.47	28.044	6.88	48.1
SP 2D	10.83	24.72	6.97	73.3
SP 2E	9.04	17.17	7.10	63.1
SP 2F	10.47	44.31	N/A	59.4
SP 2G	9.4	25.998	N/A	33.7
SP 2H	11.27	27.32	N/A	61.3
SP 2I	34.73	233.74	N/A	928

Seven samples collected on a transect along the Nissequaogue River show a pronounced influence of seawater toward the Long Island Sound (Table 2; Figure 3). Cl^- concentrations show a strong correlation the B concentrations consistent with a marine influence in this tidally influenced river (Table 2).

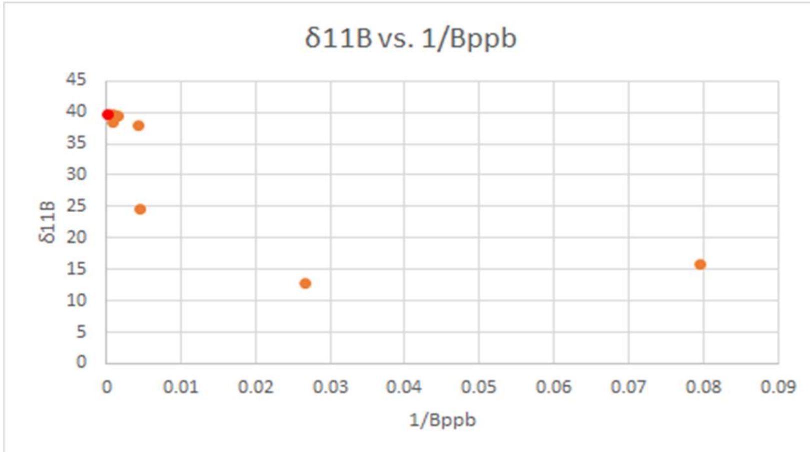

Figure 3: Plot of δ^{11}Bvs. 1/B (ppb). The red point represents seawater and the orange points represent the results of the samples taken along our transect of the Nissequogue River.

Table 2. Data from the Nissequogue River samples.

Sample	$\delta^{11}B$	B(ppb)	pH	Cl (mg/L)	NO_3(mg/L)
NR1	15.91488	12.6	6.9	19.7	4.6
BR2	12.94431	37.67918	6.95	26.6	4.9
NR3	24.65557	230.6621	6.73	1059	15.2
NR4	38.04148	232.8175	6.75	2028	26.8
NR5	39.5113	860.8696	6.73	6908	66.1
NR6	39.46598	704.3478	7.01	7951	78.9
NR7	38.58124	1256.058	7.11	10100	95.4
NR8	39.69573	1387.445	7.2	11100	98.1
NR9	39.44106	988.0292	6.99	8944	74.8

Four rainwater samples collected on the roof of the Earth and Space Sciences Building at Stony Brook University give a range of concentrations from 6-13 ppb and 12.7 to 33.4‰ (Table 3; Figure 4). These are some of the lowest values measured and are similar to tap water from our lab used for leaching fertilizer and manure samples (10 ppb and 33 ‰).

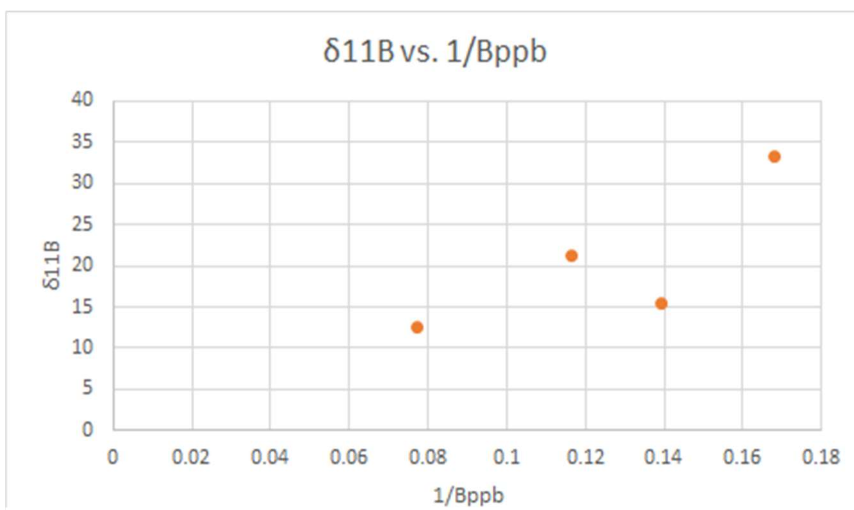

Figure 2: Plot of δ^{11}Bvs. 1/B (ppb) for the rainwater samples.

Table 3. Data from rainwater and tap water samples.

Sample	$\delta^{11}B$	B(ppb)
SBU Rain 6.11.19	12.7	13.0
SBU Rain 9.16.19	15.56	7.19
SBU Rain 10.27.19	33.43	5.97
SBU Rain 11.12.19	21.26	8.60
Stony Brook University tap water	33	10

Discussion

Rainwater samples from four different months, June, September, October, and November, have a small range in concentrations and a rather large range of isotopic values. Summer rainwater samples (June and early September) have lower isotopic values than those taken in October and November (Figure 4). The data is not dense enough to tell if there is a mixing relationship, but it appears that isotope values are higher when concentrations are lower. To compare to the literature we need to also analyze for nitrate concentrations, which will be higher if the light boron is from biomass burning.

Springs represent places where the groundwater table intersects the land surface. Springs are common across Long Island and are a major component to all rivers and streams. The system is dynamic with recharge in the winter and spring. Evapotranspiration in the summer prevents infiltration so groundwater discharge is at its lowest in late summer and fall. The headwaters of the Setauket Mill Pond spring is a depression near Detmer farm, and the stream flows through a medium density residential area, suggesting a possible fertilizer or septic source of nitrates. This depression is where the water table intersects the surface, and it also acts as a recharge basin, collecting water from rain events. In dry summer months it is nearly empty while during wet seasons it is nearly full. Water samples taken during June 2019 have boron concentrations that are about double that of the rainwater sampled across the same early summer months (Figure 2). The range of rainwater from 13-33 ‰ contrasts with the small range of values from the spring fed creek and Setauket Mill Pond of 9-11 ‰. This increase in concentration and decrease in $\delta^{11}B$ compared to rainwater suggests that a large part of the boron is added as rainwater interacts with soils. The fact that the concentration and isotope values do not change from the headwaters to the Setauket Mill Pond suggests that boron (and thus nitrate that comes with it) is introduced before the water flows into the creek.

Setauket Pond is prone to algal blooms in the late summer and often harmful algal blooms. In part this is due to decreased runoff in the summer months leading to water stagnation, but excess nutrient loading is responsible for stimulating the algal blooms. In order to consider the possible source of the eutrophication in the Setauket Mill Pond, we did a survey of leached fertilizers purchased locally and septic waters from nearby homes representing the most likely sources of nitrates and phosphates to these waters. While we expected fertilizers to be the most important source because the headwaters is near a farm and this is a medium to low density residential area, many of the fertilizer samples are isotopically heavier than the Setauket Mill Pond (Figure 5). Septic waters are isotopically lighter ranging from -2 to 2.5 ‰ (Figure 5), and thus may represent a more important source of boron to this system.

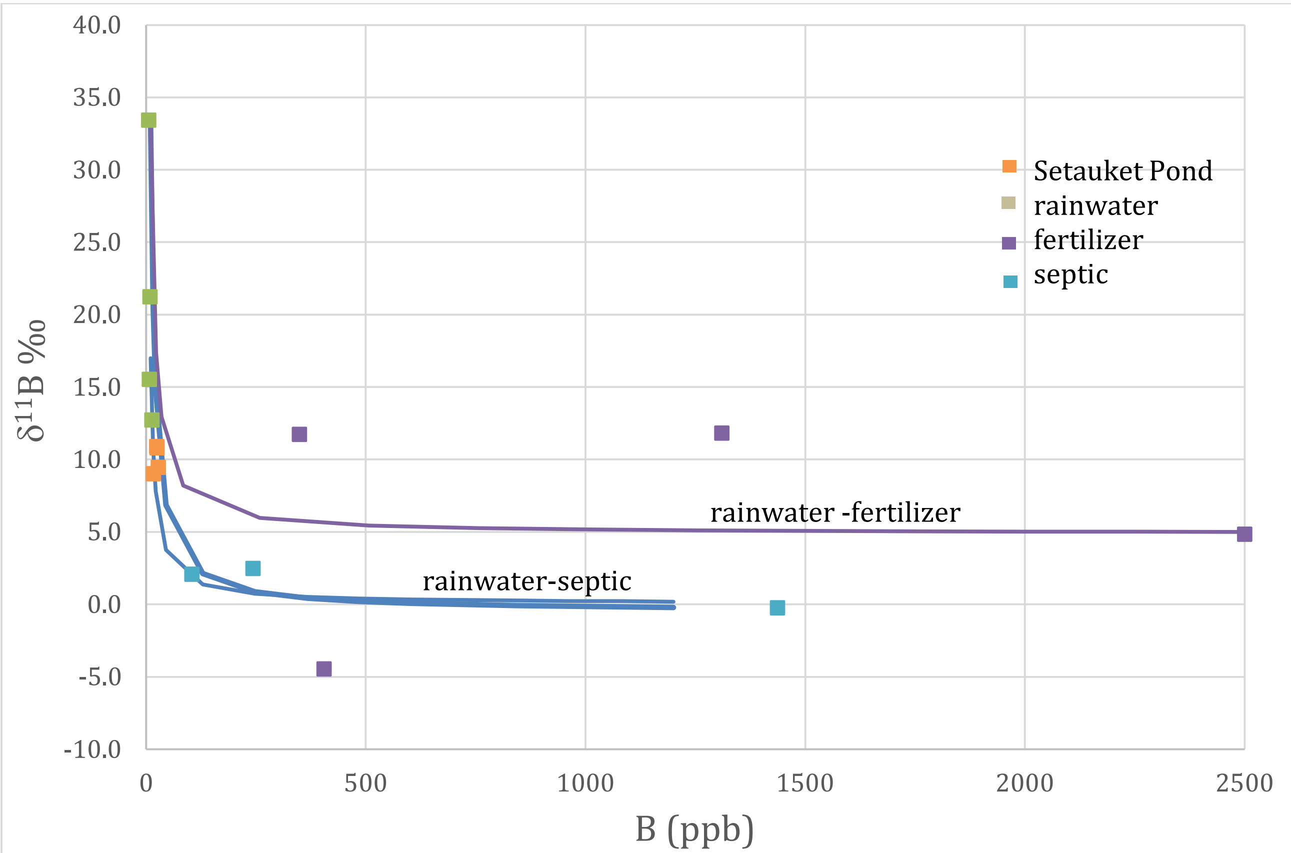

Figure 5: Mixing curves based on rainwater (grey) and septic (blue) and fertilizer (purple) to explain the concentration and boron isotope values of Setauket Pond waters.

Rainwater samples have heavy boron isotope compositions but have low boron concentrations and very low salinity (Figure 5). This means that uncontaminated freshwater is distinct from the possible contaminant sources we evaluated. However, the range of rainwater $\delta^{11}B$ from the 4 rains we sampled is large and thus we need to understand what controls the differences and to better understand the proportions of different boron isotope values delivered to the recharging waters. We hypothesize that rain sourced from different directions may have unique values. For example, Chetalet et al, 2005, showed that the atmospheric component of boron in coastal regions is a mix between boric acid volatilization from seawater, which is isotopically heavy, and biomass burning, which is isotopically light. In the northeast United States, the light component could be from coal burning.

Taking rainwater as the fresh endmember for waters that we find in the Setauket Pond, we considered how much boron could have been contributed by septic and fertilizers by making mixing curves between the isotopically heaviest rainwater and septic samples and the isotopically lightest rainwater and sewage (Figure 5). These mixing curves demonstrate that much of the boron in the groundwater is introduced after rain infiltrates the soil, as the concentration is near double that of rainwater. Further, because the manure and fertilizer samples that we analyzed (Downs et al., 2020) are isotopically heavier than the Setauket Pond waters, any addition of these would have to be offset by a component with a lighter boron isotope composition. Septic waters have elevated boron concentrations and are isotopically light. Therefore, septic waters are the most likely candidate for contributing boron, and thus nutrients co-migrate with the boron, to the Setauket Pond system.

Citations

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Chetelat, B., Gaillardet, J., Freydier, R., & Négrel, P. (2005). Boron isotopes in precipitation: experimental constraints and field evidence from French Guiana. *Earth and Planetary Science Letters*, *235*(1-2), 16-30.

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