BORON ISOTOPE VARIABILITY WITHIN A COASTAL LONG ISLAND SALT MARSH

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Introduction and Background

Few studies have used boron isotopes as tracers for anthropogenic contaminants within an ecosystem. Studies of watersheds and potential contaminants however show unique boron isotope signatures (Barth, 1998; Vengosh, 1998; Vengosh et al., 1999). Flax Pond, a local wetlands system with a research center run by SoMAS offers great potential to consider how boron is cycled in a tidally influenced coastal wetlands ecosystem. Flax Pond is adjacent to a residential area and is a well-used recreation area. Runoff as well as natural spring seepage could be impacting the boron concentration gradient within the marsh while seawater is expected to dominant the boron isotope signature in this system. Boron concentration and ratios have been measured for water, soil, and phragmites (*Phragmites spp.*) samples in order to characterize boron throughout the marsh. The Long Island Sound (LIS) has historically been known for having bad water quality and high levels of nitrogen loading (Tamborski et al., 2019; Young et al., 2015). By characterizing the boron gradient within a coastal tidal marsh with direct access to local residents and significant wildlife activity, our study shows the potential to use boron as a tracer of contaminants in a coastal marsh with connections to the LIS.

A tidal marsh is a wetland characterized by tidal influence and the presence of herbaceous plant life. Flax Pond is a biodiverse saltwater tidal marsh with a direct connection to the LIS. While Flax Pond is monitored by the Department of Environmental Conservation (DEC), it is not free from the impacts of anthropogenic activities, particularly those that affect the LIS itself. Given the conditions and accessibility of sites by foot for sampling, Flax Pond is a natural laboratory that we can use to characterize boron compositions and ratios and work to better understand boron composition across plants, soil, and water in an ecosystem dominated by seawater. Due to its proximity to the Stony Brook University (SBU) campus, we were able to sample in the spring and fall, allowing us to characterize the boron behavior across seasons.

Flax Pond has a long history of being a site for scientific research. Given its easy accessibility and unique biodiversity, numerous studies have been conducted, including marine nutrient cycling and phytoplankton dynamics. Flax Pond was formed from glacial activity during the last ice age. The pond originally had no connection to the ocean and was a closed-off freshwater system. The pond was used for flax production and watering of cattle by European settlers. Once the flax industry was no longer profitable, an inlet was dredged, creating the input of seawater from the LIS. Once the inlet was created, a profitable shellfish industry was established at the site. In the 1950's, the water quality at Flax Pond had begun to decline dramatically due to pollution input and anthropogenic actions that led to spiked nutrient levels, resulting in ecological issues including fish kills and algal blooms. In response, restoration efforts began. Currently, SBU's School of Marine and Atmospheric Sciences runs a laboratory at the site that examines the local ecology of the pond, its energy budget as a salt marsh, and the impacts of pollutants on the pond's biodiversity. Phragmites, a non-native species, is particularly dominant throughout the marsh (and marshes across the temperate northeastern United States), and because it exists across salinity gradients it is well suited to study boron uptake in plants.

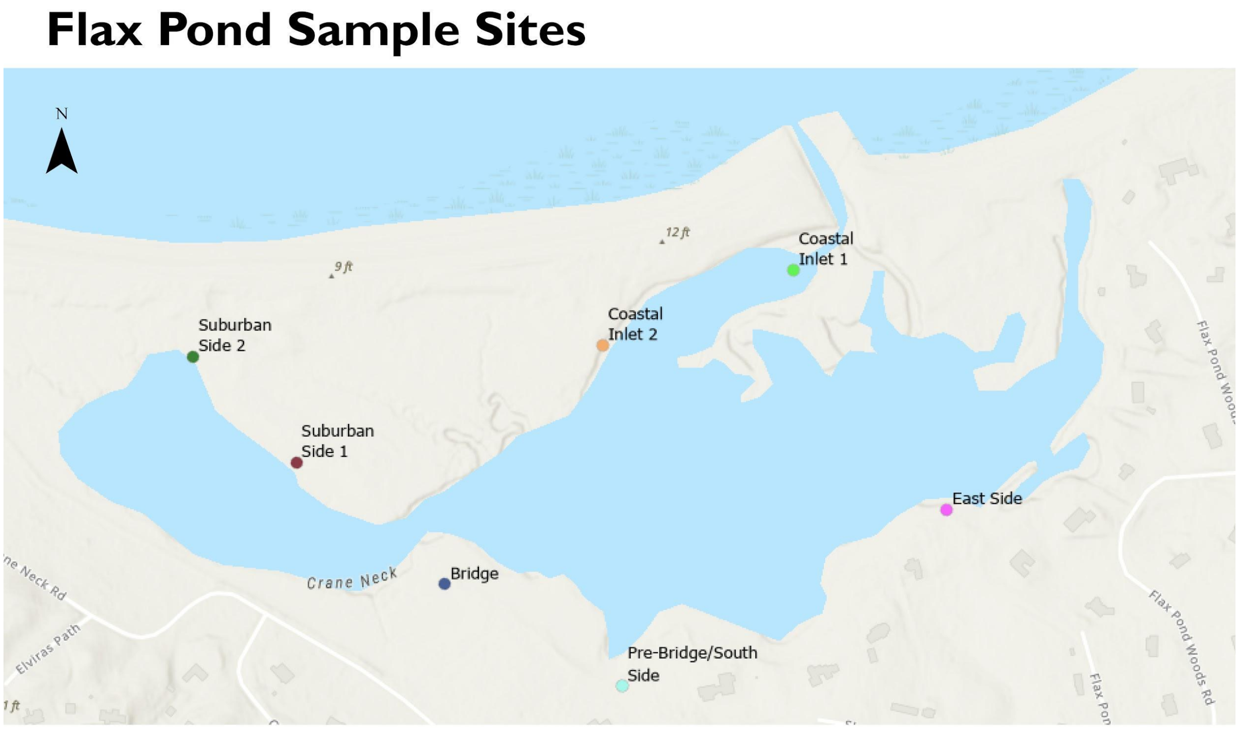

Figure 1. The map above shows a top view of the marsh with the 7 sample sites indicated.

Methods and Materials

Water, soil, and plant samples were collected during low tide from seven sites across Flax Pond in March 2022 (spring) and October 2022 (fall). Sites were chosen based on accessibility and diversity to allow for the greatest view of any potential boron variability in Flax Pond. This resulted in two locations from the west side of the pond (Suburban Side 1 and 2), two from the coastal inlet (Coastal Inlet 1 and 2), one at the southeastern side (East Side), one just below the bridge connecting the two halves of the pond (Bridge), and one from before the bridge (Pre-Bridge) (Figure 1).

Within each sampling location, water samples were collected in pre-washed 125mL bottles, and plant and soil samples were collected in individual plastic bags. Geographic position, temperature, pH, and salinity were measured at each site when possible. In the lab, plant samples were rinsed with DI water to remove any soils and salts, after which both the plant and soil samples were dried for at least 24 hours. Water samples were immediately filtered upon returning to the lab. Around 20 mg of plant sample and 500 mg of soil sample were leached in 2M nitric acid for at least 48 hours and the leaches were then filtered prior to boron separation column chemistry.

All samples were adjusted to pH 9 using high purity ammonia in preparation for column chromatography chemistry. Samples were run through boron-specific resin (Amberlite IRA 743) to remove non-boron ions, and chemistry followed the procedure developed in Lemarchand et al. (2002). The samples were loaded into the resin-filled columns (1–2 mL for plants, 1–3 mL for soils, and 4–5 mL for waters), and non-boron ions were washed out with DI water that had been adjusted to a pH of 9. The boron was then eluted from the columns using 1.2 ml of 2% nitric acid.

Boron analyses were performed on a Nu Instruments Plasma II multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Boron concentrations of the samples were calculated against the standard, boric acid (NBS 951), and subsequently diluted to 50 ppb to match the signal intensity of the standard. Following dilutions, samples were run using a standard bracketing technique with the standard and 2% nitric acid. Seawater was run alongside these unknowns for each batch of chemistry. This tests the boron recovery and any problems with the chemistry. Any boron left on the column or lost in the wash stage would give a boron isotope value that is not correct. The seawater standard run with these experiments gave the correct value within uncertainty. Boron isotope values are reported in per mil (‰) notation which is calculated as:

$$\frac{\left({}^{11}B/{}^{10}B_{sample} - {}^{11}B/{}^{10}B_{NSB\,951}\right)}{{}^{11}B/{}^{10}B_{NSB\,951}} \times 1000$$

Results

Sampling from across Flax Pond during both seasons show a variation in boron concentrations in plants based on season and locality where spring plant sample concentrations are markedly higher than fall plant sample concentrations (Table 1). Spring plants range from 43 ppb to over 100 ppb, while fall plants range from 1 to 24 ppb.

Table 1: Boron concentrations from Flax Pond

Location	**Spring**			**Fall**		
	Water ppm	*Soil ppb*	*Plant ppb*	*Water ppm*	*Soil ppb*	*Plant ppb*
Suburban Side 1	2.0	4.5	68.6	2.6	10.9	19.6
Suburban Side 2	2.7	6.1	63.7	2.6	3.9	8.4
East Side	3.2	7.8	90.0	2.9	7.0	1.5
Coastal Inlet 1	2.4	9.4	142.4	2.5	2.2	2.1
Coastal Inlet 2	2.9	2.3	67.8	2.6	3.7	8.1
Bridge	3	15.3	80.5	2.7	3.9	24.7
Pre-Bridge	0.6	25.0	43.8	2.3	16.5	—

Table 2: Boron isotope values from the spring sampling at Flax Pond

Location	**Water $\delta^{11}B$ (‰)**	**2SD**	**Soil $\delta^{11}B$ (‰)**	**2SD**	**Plant $\delta^{11}B$ (‰)**	**2SD**
Suburban Side 1	38.92	1.1	27.2	0.8	19.4	0.1
Suburban Side 2	37.61	0.7	31.6	0.2	23.6	0.4
East Side	40.6	1.4	28.8	0.5	20.6	0.3
Coastal Inlet 1	39.73	1.5	33	1.2	18.7	2.3
Coastal Inlet 2	41.04	1.7	26.5	1.6	24.8	6.6
Bridge	40.24	3.2	31.5	0.9	22.2	1.7
Pre-Bridge	37.58	1.3	32.9	0.5	20	0.5

Water concentrations are mostly consistent between seasons and across localities (Table 1). However, the Pre-Bridge spring water concentration is less than 1 ppm, which is lower compared to its fall concentration of around 2 ppm. Water concentrations, reported in ppm, are significantly higher than plant and soil concentrations, which are reported in ppb.Soil concentrations vary across localities and between seasons, but there is no obvious pattern for the seasonal differences. Some localities are lower in spring than in fall, while the opposite is true for others. Unlike water concentrations, soil concentrations vary across localities and between seasons, but there is no obvious pattern for the seasonal differences.

At present, there is only $\delta^{11}B$ data for spring samples (Table 2). We see a notable offset between water, plant, and soil samples, where water is around 10‰ greater than the soil of the same locality, and the soil is around 10‰ greater than the plant of the same locality. The Coastal Inlet 1 and Coastal Inlet 2 samples do not follow the pattern. The plant and soil samples from those localities are also among the few with significantly higher standard deviations. Water δ^{11}B values are very close to seawater, ranging from 37‰ to 41‰. Given Flax Pond's proximity to the coast, its coastal inlet, and its tidal nature, this is expected.

Discussion

Spatial Trends

Flax Pond is a saltwater tidal marsh significantly impacted by seawater inundation through daily tidal cycles. The boron isotope composition and concentration of the water samples reflect seawater's massive influence on the system. The boron concentration of seawater from the LIS is typically around 4 ppm, which is well within the range of the water samples' concentrations, and the δ^{11}B of seawater is typically around 39‰, also within the range of the water samples' values. Salinity levels at Flax Pond are all similar to that of the Long Island Sound seawater, with the locations averaging at 30 ppt whereas the Long Island Sound has salinity around 27 to 35 ppt. All samples were collected at low tide when the amount of seawater present in the system should be lowest.

The Pre-Bridge location consistently shows unexpected values or values that are significantly different than other locations. Its soil boron concentrations are consistently the highest between seasons, and yet its water concentration was abnormally low (0.7 ppm) in the spring but not the fall. Its plant concentrations are also the lowest out of all locales. These differences may potentially be explained by wildlife activity in the area, but further investigation of possible inputs is required to confirm. For example, if the leachable boron from the soil is from shells, this boron may not be available to plants and would not impact the water. There had been no reported rain up to three days prior to sampling for the fall collection date, but the spring collection date did coincide with rain and snow. As the Pre-Bridge location does not have as much flow as other locations, it is possible that the the precipitation had more of an impact here.

Seasonal Trends

At present, only concentration data is available for both spring and fall samples, and thus, only comparisons of boron concentrations between seasons is currently possible. Concentration data from spring and fall show a significant difference in boron concentrations for plants between the seasons (Table 1), with concentrations being significantly lower in the fall compared to spring (Figure 2). This difference could be explained by the fact that fall generally marks the end of the growing season, and with dropping temperatures, the plants were likely dying, or already dead, thus no longer needing or being able to maintain higher concentrations of boron. This would need to be further tested with a comparison between spring and fall δ^{11}B values in the plants (data forthcoming).

Figure 3. Graph depicting the boron concentrations for spring and fall samples of *Phragmites*.

The water concentrations remain relatively consistent between seasons (Figure 3), save for the Pre-Bridge location, which may be influenced more by shells or meteoric water than seawater. Water samples show small differences (generally less than 1 ppm) between

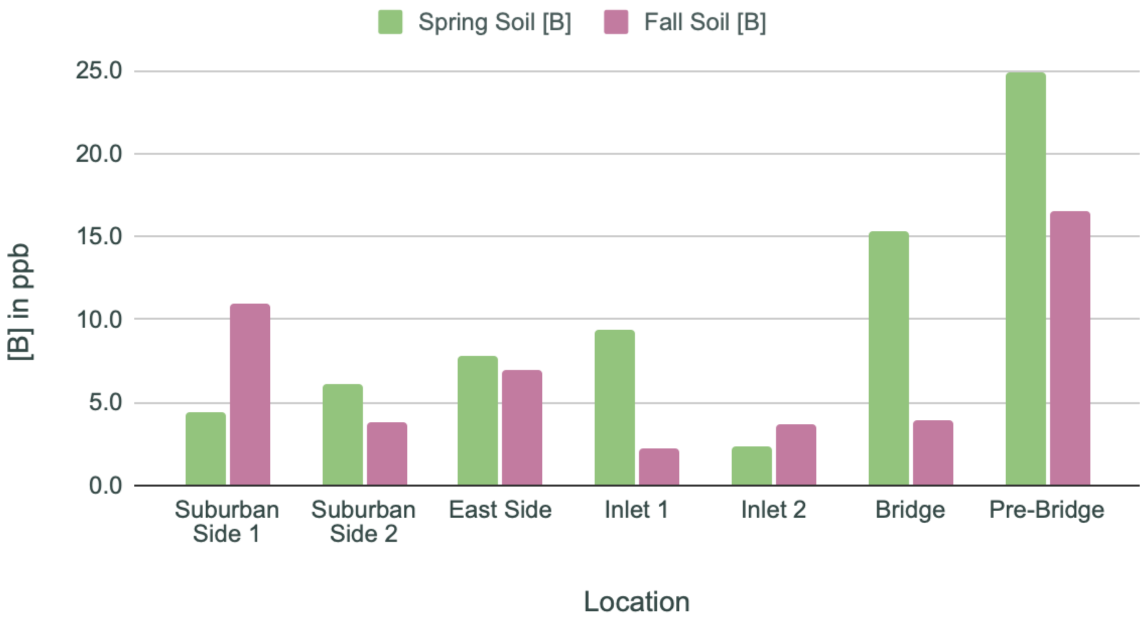

Figure 4. Graph depicting the boron concentrations for spring and fall soil samples.

seasons compared to that of the plants or even the soils. Water pH did not change significantly between sampling sessions in the locations where data was available.

Soil concentrations between Spring and Fall show differences, but not as drastically as the plant concentrations (Figure 4). One possible explanation for variability in soil concentrations might be linked to animal activity, or lack thereof. Shellfish hibernate or go dormant in colder temperatures, burrowing into the soil, and the spring collection took place during a time that was more than 10°C colder than the fall collection. It is thus reasonable to assume that shellfish were hibernating during the spring collection but not the fall. Suburban Side 1 and Inlet 2 did have an inordinate amount of fiddler crabs during the fall, which could explain why the boron concentrations of these sites does not follow the pattern for fall soil boron concentrations. Plant activity could also have an effect on the boron concentrations of the soil, particularly as we see major changes in the plants that suggest boron is lost from plants in the fall (Table 1). However, at the depths the soil was collected (around 5 cm), this is less likely (see Cividini et al., 2010). In future efforts we will make sure to remove shells from the soils before leaching.

Water, Soil, and Plant Differences

For the spring data, there is an around 10‰ stepwise decrease in $\delta^{11}B$ values from water samples to soil samples to plant samples (Figure 5). The stepwise decrease between plants and the soil are consistent with values reported in Mao et al. (2019) and Cividini et al. (2010), which investigates weathering and plant/soil boron cycling. A large offset between plant and soil is similarly found in Cividini et al. (2010), but the mechanism behind this offset is complex, as the soil matrix at these depths (5-10 cm) is also heavily influenced by seasonal precipitation and dissolution of fiddler crabs and other shells in the Flax Pond setting. The decrease in $\delta^{11}B$ values from water samples to soil samples likely results from the leaching of carbonate shells from the soils. We do not know if this boron is available to the plants. It is also not clear if the boron in the plants comes primarily from the soil, or if it is directly from the water in this system where boron concentrations are so much higher in the water. If the boron comes from the water, the phragmites is showing a -20‰ offset from the water, similar to what Wright et al. (2021) found with seaweed from seawater. In both cases the offset to lower $\delta^{11}B$ values indicates that the plant is preferentially uptaking borate. We have also seen this in controlled garden experiments with tomatoes (Rasbury et al., 2022).

Water samples are dominated by seawater, both in $\delta^{11}B$ value and in boron concentrations. This does not change much across locations or seasons (save for Pre-Bridge). Despite the pattern seen in $\delta^{11}B$ values, though, plant and soil boron concentrations do not follow a pattern with water concentrations. This is likely due to the differing influences on the amount of boron in a system for plants, soils, and water. Plants will be influenced by activity in the soils, within the plant itself, and in the water, and given that there is a boron necessity in plants, it is reasonable to assume that plants would have a higher boron concentration than soils, particularly at the start of a growing season (i.e., spring).

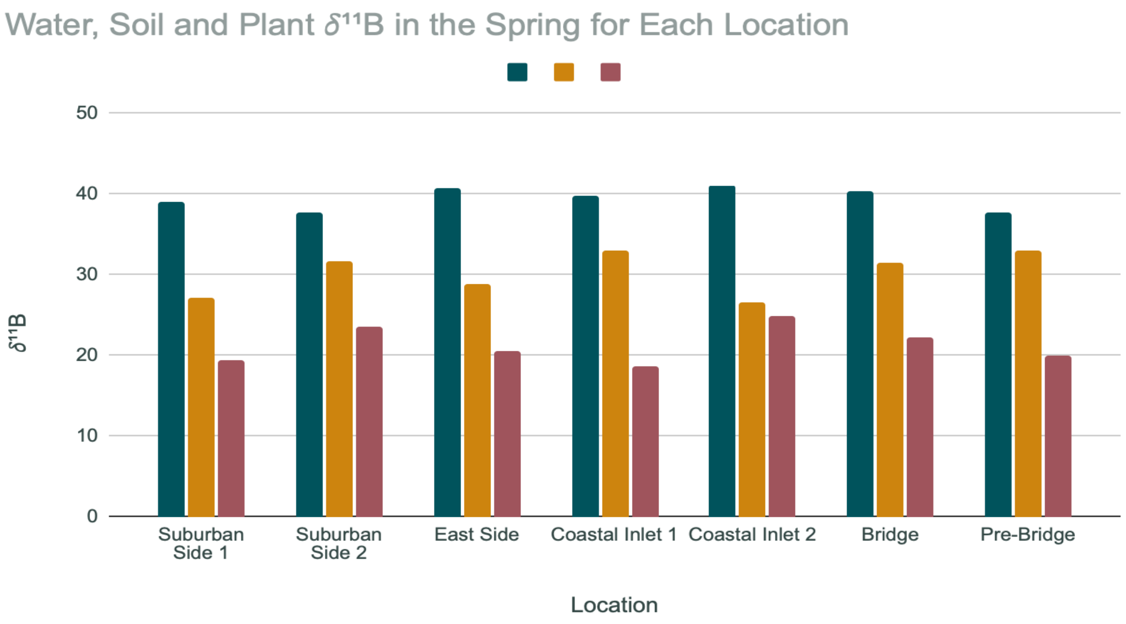

Figure 5. Graph depicting the boron isotope values for water (blue), soil, (orange) and plant (red) samples, collected Spring 2022.

Future Work

Further research will provide essential information to help trace pollutants and sources within the ecosystem. We will collect phytoplankton samples to analyze them for boron concentrations and δ^{11}B values to understand better how they interact with the environment. Boron analysis will be conducted on water, plant, and soil samples from fall to address differences in boron concentrations and potentially reveal a pattern between boron and the growing season. To better understand where anthropogenic or natural activities are impacting the marsh, we will collect and analyze potential sources of boron in the system, such as run-off, animal droppings, and rainwater. Other isotope analyses, like nitrogen, are also possible, and may provide more insight into the impact of anthropogenic input on the system. To fully understand the way boron cycles through phragmites over its life cycle, the next steps will be to focus on a single plant from Flax Pond over the course of the year and periodically sample it to see how boron is changing as it grows and subsequently dies.

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