**Setauket Pond: An Anthropogenically Influenced Natural Laboratory to Study Boron Isotopes**

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**Introduction:**

Many surface water systems on Long Island, including Setauket Pond, Setauket, NY, experience algal blooms. These algal blooms result from eutrophication, or the excess presence of nitrates. Long Island is known to experience different types of algal blooms including, brown tides, red tides and rust tides (*Environmental-Quality/Ecology/Harmful-Algal-Blooms*). Algal blooms can foul the water making finding the sources of nitrates in this area a priority.

Nitrate concentrations in the shallow aquifers on Long Island are generally elevated, and in some places has been shown to be above established drinking water standards. To mitigate the problem, it is essential to determine the source of nitrate. Nitrogen (N) and oxygen (O) isotopes do not allow us to discriminate between the two most likely anthropogenic sources on Long Island, which are septic and fertilizer (Tamborski et al., 2020). With that said, an early study using N and O isotopes of nitrates found that the most likely source in the Northport area, which has had periods with nitrate levels above drinking water standards, was fertilizer with some influence from septic waste (Bleifuss et al., 2000).

With the difficulties of using N and O isotopes to identify nitrate sources, a proxy was sought. The proxy needed to be an element that was frequently associated with anthropogenic nitrates, and boron fit these needs. Studies have used boron isotopes as a proxy for nitrates (Ravenscroft and McArthur, 2006; Tamborski et al., 2020; Vengosh, 1998; Widory et al., 2013). These studies have focused on characterizing anthropogenic contaminant sources around the world, since boron is frequently included with nitrates in fertilizer and in detergents (Barth, 1993). Boron is a powerful tracer because it behaves conservatively and is mostly unchanged along the transport path, while nitrogen isotopes change as denitrification or nitrification occurs, often obscuring the original source (Widory et al., 2013). However, a study of boron isotopes in Subterranean Groundwater Discharge (SGD) into the Long Island Sound found a large range of $\delta^{11}B$ that is not easily attributed to septic or fertilizer (Tamborski et al., 2020). The two sites studied by (Tamborski et al., 2020), were selected to examine the impact of residential versus agricultural influence and the $\delta^{11}B$ is distinctly different between these two areas. The work of Tamborski et al (2020) is encouraging but more work is needed to work out the details of using boron as a tracer of pollutants on Long Island. This study of the Setuaket Pond will work through some of these details by examining inputs and details of boron concentrations and isotope ratios throughout this system.

**Setting of the Natural Laboratory:**

Setauket Pond is one of many spring-fed ponds across Long Island. The spring-fed water is transported via a stream, originating near Detmer Farm, that flows into Setauket Pond (Fig. 1). The freshwater pond is separated from the Long Island Sound by a dam (Fig. 1). The water flow from the spring changes throughout the year with rainfall, and is typically very low in the late fall. Based on this, the system appears to be responsive to surface processes. Hudson (2017) analyzed pH, nitrates, temperature, water velocity, and nitrogen of Setauket Pond and the spring stream water during the fall of 2017 and found elevated nitrate levels relative to the rest of Suffolk

County (Hanson and Schoonen, 1999). Because the spring-fed creek and Setauket Pond make a relatively small system in close proximity to the university, it provides an excellent laboratory for working to establish additional controls on the boron concentrations and compositions in Long Island groundwater. We have sampled along the spring-fed creek over the past three years, collecting water and algae. Additionally, we collected a variety of potential inputs to the system, including rainwater, goose and swan feces, fertilizers, and manure that might have been used on lawns. We also analyzed septic waters collected by the New York Clean Water Technology Center.

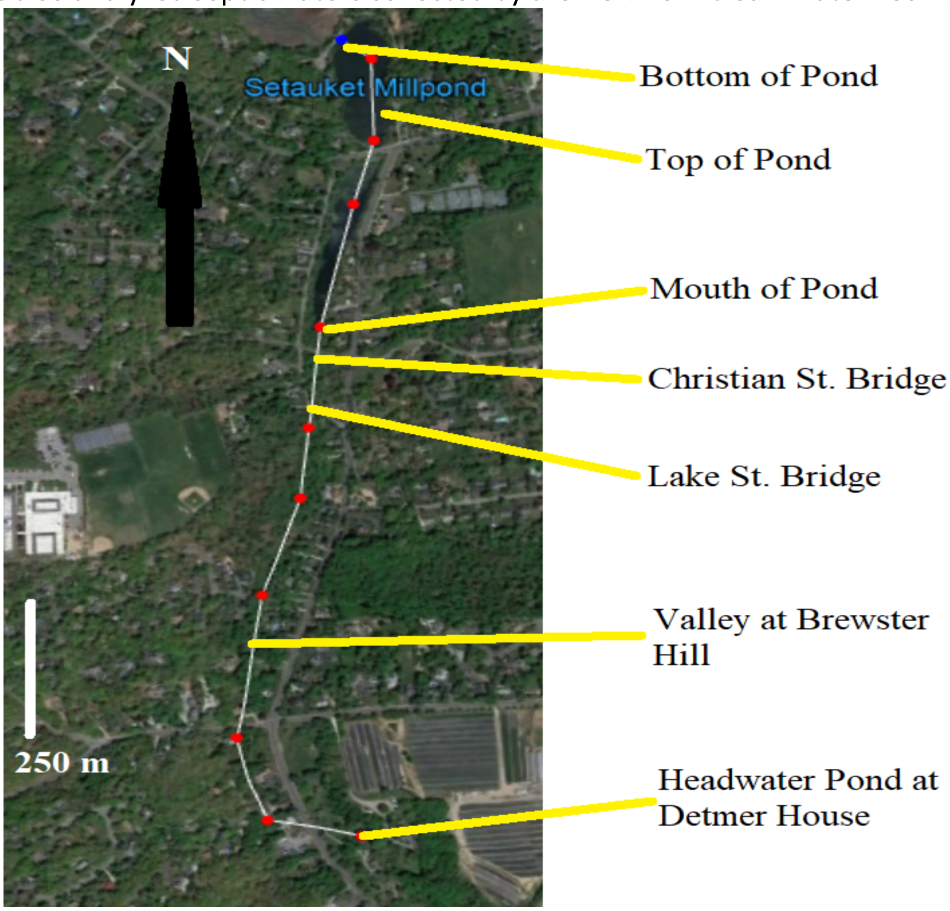



**Figure 1: Google Earth image of the spring creek that feds the Setauket Millpond with locations relevant to this study (from Hudson, 2017).**

**Materials and Methods:**

Water samples were taken from Setauket Pond and the surrounding area (Table 1, Table 2, Table 3). Water samples were collected in cleaned 125mL Nalgene narrow mouth bottles. Samples were also taken of possible sources of contamination to the area. These included clay from a local tennis court, pond algae, septic water, and fertilizer samples (Table 4).

One sample of tennis court clay from the Three Village Club, Setauket, NY, which drains into the pond, was also leached in 2M nitric for 1 week. Fertilizers and septic water samples were leached in deionized water for a week. Supernatants for all samples were filtered to remove organic materials before ion exchange chemistry was performed.

In preparation for boron chemistry, all samples were pH adjusted to approximately 9 using high purity ammonia. Boron chemistry, to remove non-boron ions from the samples, was done using boron-specific resin (Amberlite IRA 743), and was based on the chemistry method developed by Lemarchand et al., 2002. Samples and standards were loaded into the Amberlite IRA 743 columns, with the removal of non-boron ions being done by adding 9 pH adjusted DI water. To elute and collect sample boron, 2% nitric acid was added to the resin.

A Nu Instruments Plasma II multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) was used for the isotope analyzes. Samples were tested for concentrations and then diluted to 50 ppb to match the 50 ppb NBS 951 standard. Boron is run as a wet plasma using a "twizler" type spray chamber that is cooled to 7°C with a Peltier system. A 100 microliter/minute quartz glass nebulizer was used to aspirate solution into the spray chamber. The sample is injected into the plasma through a glass torch. We measure $\delta^{11}B$ in Faraday cup H5 and $\delta^{10}B$ in Faraday cup L6 and align these masses with the quad values. There is a small quadruply charged Ar peak on the left shoulder of $\delta^{10}B$ but it is far enough from the peak center that it does not bias our results. During analysis, standards and samples are bracketed using the same 2% nitric acid used for boron elution during columns chemistry, and for dilution of the standards and the samples for analysis. In this way, the small (< 1 ppb) addition of boron by the acid is subtracted.

**Results:**

Repeated sampling for boron over three years shows that the spring-fed stream and pond have mostly low boron concentrations (23-35 ppb) and a range of $\delta^{11}$B (Table, 1; Table 2; Table 3). There are differences along the trend of the pond, from the bank into the center of the pond, and with depth in the pond.

A transect from the lower part of the pond to the upper part of the pond (Fig. 2) shows a trend in $\delta^{11}$B from 8.3-15.6‰ (Table 1). Temperatures taken at the same time show a range of 20.4 to 23.5°C, and have a linear relationship with the $\delta^{11}$B (Fig. 3).

A survey of the Pond's shoreline, with variation in sampling depth, was conducted south of the Old Field Road and near the Three Village Tennis Club (Fig. 4). These samples had a range of concentrations of 22.1 to 29.1 ppb and $\delta^{11}$B values of 11.8 to 19.3‰ (Fig 5).

A transect along the east side of the Setauket Pond near the Setauket Neighborhood House and the Three Village Tennis Club (Fig. 4) reveals that background levels at this part of the pond are about 20 ppb and 12‰ (Fig. 5). The transect shows an elevation in both concentrations and $\delta^{11}$B between SP21-SP29. The north driveway from the tennis court is a focus of runoffs during rainstorms and the culvert system #1 (at about SP31) was sampled right in this area. While this makes an appealing source of boron to the pond, having a high boron concentration (61 ppb), the isotope composition is light (-3.1‰), suggesting it cannot be the source for the elevated pond values. The tennis courts are watered daily, and the HarTru clay was sampled directly to

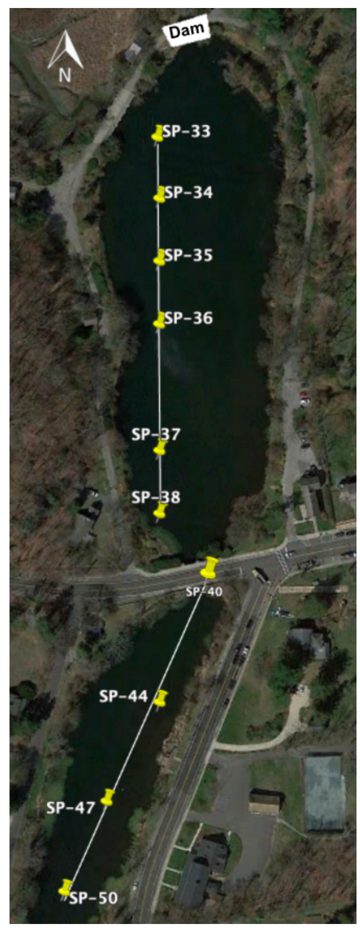
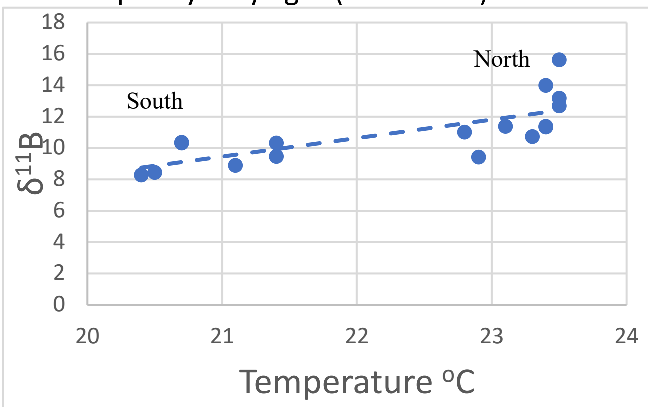



**Figure 2: Google Earth map of the Setauket Pond with yellow pins marking the locations of water samples taken from a Kayak in the Summer of 2021. These are the data points in Figure 3 and Table 1.**

establish its $\delta^{11}B$. The HarTru boron concentrations are low (19 ppb) and the $\delta^{11}B$ is lighter (11.5‰) than the background water value of 12‰.

An area on the east side of the pond near the Setauket Neighborhood House and across from the Three Village Club tennis courts has anomalously higher concentrations (54-88 ppb) and are isotopically very light (-7.7to -8.8).



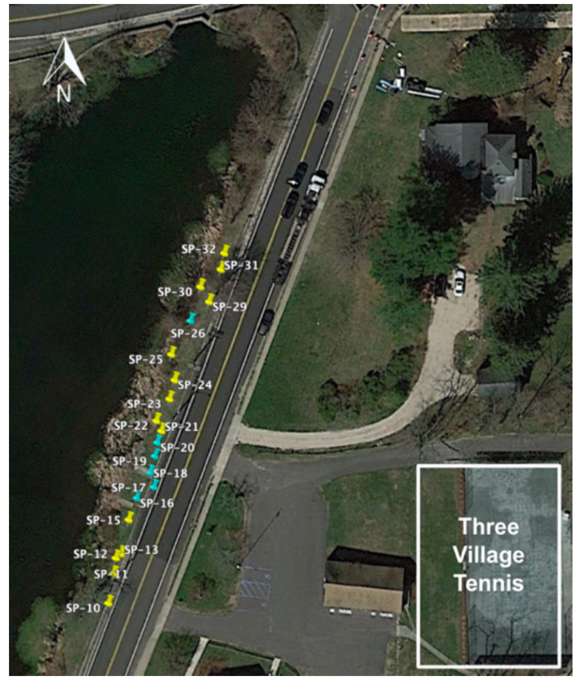




**Figure 3 (left): $\delta^{11}B$ and temperature for samples taken from the southern part of the pond. Figure 4 (right): GoogleEarth map showing the locations of samples taken along the east shore of the Setauket Pond. Blue pins are those where depth analyses were conducted. Yellow pins indicate where only surface samples were collected.**

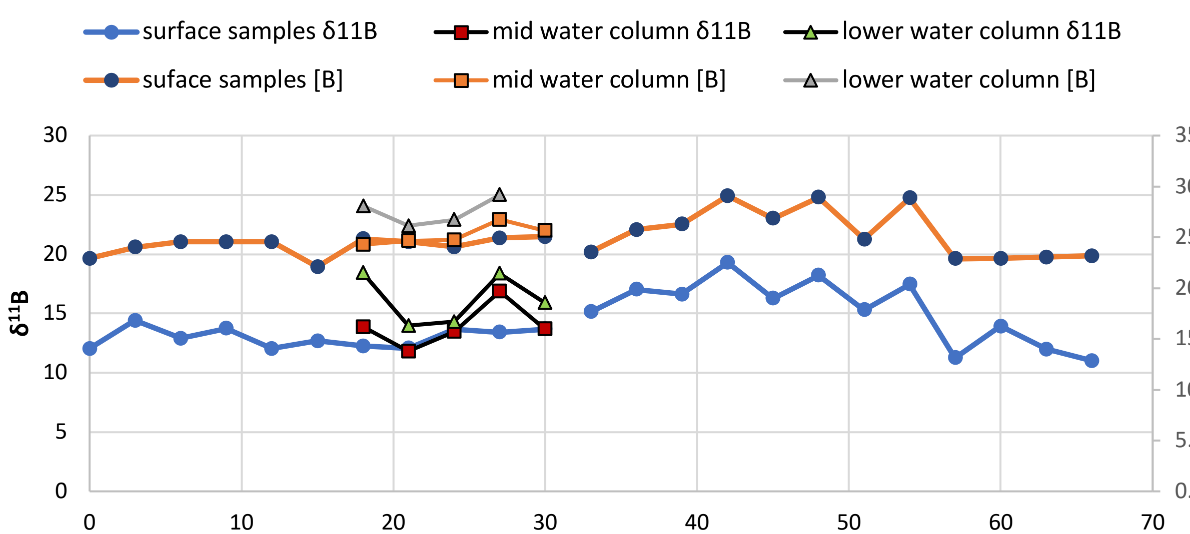



**Figure 5:** Boron concentrations and $\delta^{11}B$ for pond waters on the east side of the Setauket Pond as shown in Fig. 4. The elevated concentration and $\delta^{11}B$ is from about SP21-SP29.

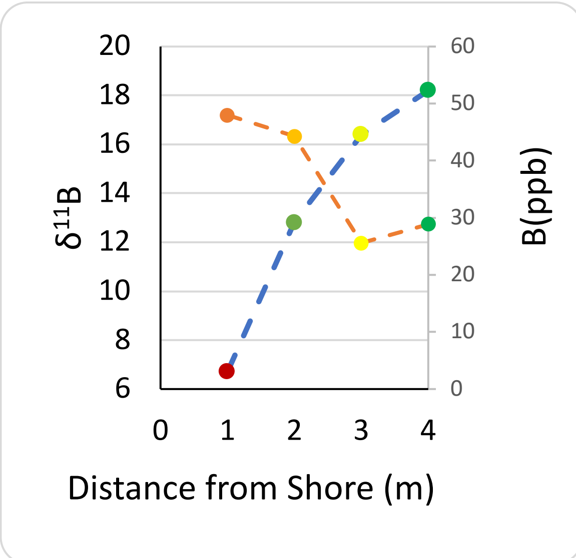



**Figure 6:** Transect from the shore into the pond across from the Three Village Tennis Courts.

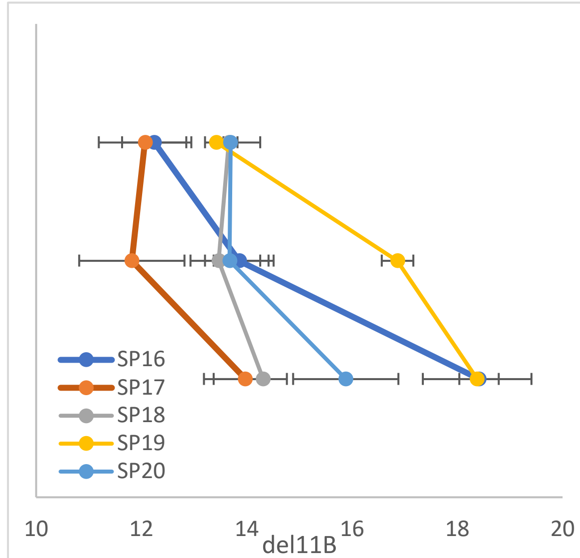



Figure 7: Depth transect across from the Three Village Tennis Courts.

**Discussion:**

While the Setauket Pond appears to be a continuous unit from the spring fed creek through the upper pond on Lake Street into the pond to the north of Old Field Rd, the boron isotopes between the two bodies of water have distinctly different boron isotope results. The low endmember for the upper pond is about 12‰ while the low endmember which starts near the Old Field Road is about 8‰. The upper pond has variability than can be explained by a somewhat stagnant body of water, where the bottom waters are higher concentrations and isotopically heavier. Numerous geese inhabit this area, and the isotope composition (23‰) and high concentrations of goose feces, makes this a likely candidate for the elevated values at the base of the pond.

In the upper pond we found a small area with light boron (-7 to -8‰) with elevated concentrations (>50 ppb). The only possible sources that we have measured with this value is a fertilizer called Milorganite, made from kiln dried micro-organisms that have been used to break down solid waste in a Milwaukie wastewater plant. We consider this an interesting point source to the pond (which could also be septic), but impressively, we do not see evidence for it meters away, even though this anomaly was observed three years in a row.


**Figure 8:** GoogleEarth map showing the locations of samples taken for year-to-year analysis.

The lower pond appears to have a new source that is isotopically light. While water flows from the upper pond to the lower pond, the boron isotopes are quite distinct. This suggests that there are multiple springs with different paths feeding into the pond system. The trend to higher values with higher temperatures seems consistent with contamination of a lighter boron isotope spring water that is interacting with something in the environment to become heavier. Again, the large numbers of geese around the pond with prolific green feces everywhere appears to be a natural source of the boron, and very likely comes with substantial nitrate as well.

The ponds are characterized by strong gradients in isotope compositions, suggesting that they are not well mixed. A transect from the north side of the lower pond to the south revealed a simple mix of isotopically light and lower temperature water at the south side of the pond. A transect from the east side of the upper pond into the pond, only 4 meters, revealed an even greater change in the boron isotopes. Similarly, a trend from the surface to the bottom of the upper pond, only a few meters in depth, reveals variable values and pretty strong gradients.

Given the heterogeneity found across the pond, we can see that compartmentalization due to the geology, bringing in springs in multiple places, combined with the variety of inputs from runoff of the area is likely a key factor in determining the large range in isotopic ratios. While our results cannot point to septic or fertilizers as a source of the boron (or nitrate) perhaps the heterogeneity we see helps to explain the large range in $\delta^{11}$B in SGD found in the Tamborski et al. (2020) study. Future work will be conducted to create a three-dimensional understanding of the area. Particularly, spring water will have lower temperatures and mapping the temperature across this system with respect to contaminants and boron isotopes would help to constrain when these are being added to the pond.

**Acknowledgements:**
We would like to acknowledge and thank Lise Hintze and Kristin Norton from Frank Melville Park for allowing us to collect samples from the pond.

**Tables:**

Table 1. Kayaking Transect Samples.

| Sample Name | $\delta^{11}B$ (‰) | 2SD | B (ppb) | Latitude | Longitude | Temperature (°C) |
|---|---|---|---|---|---|---|
| **SP33** | 13.5 | 1.8 | 19.5 | 40.946944 | -73.115833 | N/A |
| **SP34** | 14.0 | 1.0 | 18.4 | 40.946667 | -73.115833 | 23.4 |
| **SP35** | 13.2 | 1.9 | 19.2 | 40.946389 | -73.115833 | 23.5 |
| **SP36** | 15.6 | 2.5 | 20.3 | 40.946111 | -73.115833 | 23.5 |
| **SP37** | 12.7 | 1.7 | 19.1 | 40.945556 | -73.115833 | 23.5 |
| **SP38** | 11.3 | 0.3 | 20.4 | 40.945278 | -73.115833 | 23.4 |
| **SP39** | 10.7 | 0.4 | 20.8 | 40.945278 | -73.115833 | 23.3 |
| **SP40** | 11.4 | 0.7 | 20.4 | 40.945000 | -73.115556 | 23.4 |
| **SP41** | 11.4 | 0.4 | 19.6 | 40.944722 | -73.115556 | 23.1 |
| **SP42** | 11.0 | 0.4 | 20.4 | 40.944722 | -73.115556 | 22.8 |
| **SP43** | 10.3 | 0.9 | 19.6 | 40.944722 | -73.115556 | 21.4 |
| **SP44** | 10.4 | 0.8 | 18.4 | 40.944444 | -73.115833 | 20.7 |
| **SP45** | 10.3 | 0.2 | 19.2 | 40.944444 | -73.115833 | 20.7 |
| **SP46** | 9.4 | 0.2 | 24.0 | 40.944444 | -73.115833 | 22.9 |
| **SP47** | 9.5 | 0.8 | 19.3 | 40.943889 | -73.115833 | 21.4 |
| **SP48** | 8.9 | 1.4 | 19.3 | 40.943889 | -73.115833 | 21.1 |
| **SP49** | 8.3 | 0.1 | 19.6 | 40.943889 | -73.115833 | 20.4 |
| **SP50** | 8.5 | 0.5 | 23.3 | 40.943611 | 73.116389 | 20.5 |

Table 2. Samples for depth profile.

| Sample Name | $\delta^{11}B$ (‰) | 2SD | B (ppb) | Latitude | Longitude |
|---|---|---|---|---|---|
| **SP10** | 12.0 | 1.2 | 22.9 | 40.943999 | -73.115795 |
| **SP11** | 14.4 | 0.4 | 24.0 | 40.944048 | -73.115784 |

| | | | | | |
|---|---|---|---|---|---|
| **SP12** | 12.9 | 4.5 | 24.5 | 40.944074 | -73.115779 |
| **SP13** | 13.7 | 0.4 | 13.7 | 40.944081 | -73.115767 |
| **SP14** | 12.0 | 0.1 | 12.0 | N/A | N/A |
| **SP15** | 12.7 | 1.0 | 12.7 | 40.944138 | -73.115750 |
| **SP16S** | 12.2 | 0.6 | 12.2 | 40.944174 | -73.115732 |
| **SP16M** | 13.9 | 0.7 | 24.3 | 40.944174 | -73.115732 |
| **SP16B** | 18.4 | 0.4 | 28.1 | 40.944174 | -73.115732 |
| **SPculv2** | 17.8 | 0.4 | 16.9 | 40.944174 | -73.115732 |
| **SP17S** | 12.1 | 0.9 | 24.6 | 40.944193 | -73.115692 |
| **SP17M** | 11.8 | 2.7 | 24.6 | 40.944193 | -73.115692 |
| **SP17B** | 14.0 | 0.8 | 26.1 | 40.944193 | -73.115692 |
| **SP18S** | 13.7 | 0.3 | 24.0 | 40.944217 | -73.115701 |
| **SP18M** | 13.5 | 1.1 | 24.7 | 40.944217 | -73.115701 |
| **SP18B** | 14.3 | 2.6 | 26.7 | 40.944217 | -73.115701 |
| **SP19S** | 13.4 | 0.2 | 24.9 | 40.944245 | -73.115690 |
| **SP19M** | 16.9 | 0.0 | 26.7 | 40.944245 | -73.115690 |
| **SP19B** | 18.4 | 1.0 | 29.2 | 40.944245 | -73.115690 |
| **SP20S** | 13.7 | 0.1 | 25.0 | 40.944268 | -73.115684 |
| **SP20M** | 13.7 | 0.7 | 25.6 | 40.944268 | -73.115684 |
| **SP20B** | 15.9 | 1.4 | 25.6 | 40.944268 | -73.115684 |
| **SPculv1** | -3.1 | 1.2 | 61.4 | 40.944268 | -73.115684 |
| **SP21** | 15.1 | 0.8 | 23.5 | 40.944288 | -73.115674 |
| **SP22** | 17.0 | 0.6 | 25.7 | 40.944305 | -73.115686 |
| **SP23** | 16.6 | 1.4 | 26.3 | 40.944342 | -73.115655 |
| **SP24** | 19.3 | 0.3 | 29.1 | 40.944374 | -73.115643 |
| **SP25** | 16.3 | 2.7 | 26.8 | 40.944417 | -73.115650 |
| **SP26M** | 18.2 | 0.8 | 28.9 | 40.944423 | -73.115619 |
| **SP26 ~3m** | 16.4 | 2.6 | 25.6 | 40.944423 | -73.115619 |
| **SP26 ~2m** | 12.8 | 3.2 | 44.3 | 40.944423 | -73.115619 |
| **SP26 Shore** | 6.7 | 0.5 | 48.0 | 40.944423 | -73.115619 |
| **SP27** | 15.8 | 1.1 | 24.8 | N/A | N/A |
| **SP28** | 17.0 | 0.9 | 28.9 | N/A | N/A |
| **SP29** | 13.3 | 4.0 | 22.9 | 40.944505 | -73.115562 |
| **SP30** | 13.7 | 0.5 | 22.9 | 40.944530 | -73.115582 |
| **SP31** | 12.2 | 0.4 | 23.0 | 40.944559 | -73.115535 |
| **SP32** | 12.7 | 3.3 | 23.2 | 40.944586 | -73.115527 |

Table 3. Year to year sampling

| Sample Name | $\delta^{11}B$ (‰) | 2SD | B (ppb) | Latitude | Longitude |
|---|---|---|---|---|---|
| **SP3* (2019)** | 10.9 | 0.6 | 24.3 | 40.9464 | -73.1152 |
| **SP5* (2019)** | 10.8 | 0.4 | 25.0 | 40.9452 | -73.1152 |
| **SP6* (2019)** | 38.9 | 0.9 | 2026.8 | 40.947 | -73.1164 |
| **SP7* (2019)** | 9.5 | 0.3 | 28.0 | 40.9441 | -73.1158 |
| **SP2F (2019)** | 10.6 | 0.3 | 44.3 | 40.9417 | -73.1170 |
| **SP2G (2019)** | 9.2 | 1.3 | 26.0 | 40.933056 | -73.117203 |
| **SP2H (2019)** | 11.8 | 1.4 | 27.3 | 40.1341 | -73.1177 |
| **SP2I (2019)** | 34.9 | 1.5 | 233.7 | 40.9494 | -73.1164 |
| **SP1 (2020)** | -7.7 | 0.2 | 53.7 | 40.944444 | -73.116111 |
| **SP2 (2020)** | 10.9 | 1.0 | 29.6 | 40.946944 | -73.116111 |
| **SP3 (2020)** | 11.9 | 0.8 | 24.4 | 40.9464 | -73.1152 |
| **SP4 (2020)** | 14.7 | 1.7 | 35.0 | 40.947222 | -73.115 |
| **SP5 (2020)** | 12.3 | 0.0 | 28.7 | 40.9452 | -73.1152 |
| **SP1 (2021)** | -8.8 | 0.8 | 88.0 | 40.944444 | -73.116111 |
| **SP2 (2021)** | 14.4 | 0.2 | 31.4 | 40.946944 | -73.116111 |
| **SP3 (2021)** | 14.4 | 0.2 | 22.5 | 40.9464 | -73.1152 |

| | | | | | |
|---|---|---|---|---|---|
| **SP5 (2021)** | 13.6 | 2.1 | 22.7 | 40.9452 | -73.1152 |

*Indicates sample from Peritore et. al. (2020).

Table 4. Possible Sources.

| Sample Name | | $\delta^{11}B$ (‰) | 2SD | B (ppb) |
|---|---|---|---|---|
| Pond Algae | | -4.6 | 2.6 | 366 |
| Tennis Clay | | 11.5 | 2.9 | 19 |
| Goose Poop | | 25.8 | 0.9 | 264 |
| Swan Poop | | 0.1 | 1.7 | 1445 |
| Fertilizers | Scott's Grass Mix | 12.6 | 0.6 | 349 |
| | Hollytone | 7.4 | 0.8 | 4000 |
| | 10-10-10 | 11.8 | 0.2 | 1310 |
| | Miloragnite | -4.4 | 0.8 | 405 |
| | 5-10-5 | 4.9 | 0.2 | 2500 |
| Septic | 9P | 2.0 | 0.5 | 250 |
| | 59R | 0.1 | 0.4 | 1275 |

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