BORON ISOTOPIC EVIDENCE FOR COMPARTMENTALIZATION OF THE UPPER GLACIAL AQUIFER

Deanna Downs, Brooke Peritore, Kathleen Wooton, and Troy Rasbury
Department of Geosciences and FIRST, Stony Brook University

Introduction

Long Island's source of drinking water is from local aquifers. The Upper Glacial aquifer is an unconfined aquifer that intersects with the surface as evidenced by the abundant spring fed creeks across Long Island. This makes the aquifer particularly susceptible to anthropogenic contamination. While not the main source for public supply wells, the Upper Glacial Aquifer is used for private wells and recharges the underlying Magothy Aquifer (Figure 1). The Upper Glacial Aquifer consists of Pleistocene aged glacial deposits including glacial till, outwash, and glaciolacustrine deposits, which have a range of hydrological characteristics (McClymonds & Franke 1972).

Figure 1. Generalized north-south cross section of Long Island, displaying the main aquifers and confining layers (Cohen et al., 1968).

Nitrate concentrations in some areas on Long Island are higher than drinking water standards. Studies in other regions have shown that boron isotopes can be an important tracer of the source of nitrates because boron is conservative and co-migrates with the nitrates (Leenhouts et al., 1998, Bronders et al., 2012; Widory et al., 2005). In this study we used boron concentrations and isotope compositions to evaluate the potential for determining sources of nitrate contamination to the Upper Glacial Aquifer. We measured boron concentrations and isotope compositions of rainwater, leaches of fertilizers and manures, and septic waters to constrain possible source endmembers. We also measured boron concentrations and isotope composition of waters from ponds in the Pine Barrens, spring fed creeks and the reservoirs they supply, and some private wells to survey the concentration and isotope composition across the aquifer. Because the Upper Glacial Aquifer intersects the surface (Figure 2), it is particularly vulnerable to contamination from lawn fertilization, agriculture, sewage and septic systems. This water discharges into the Long Island Sound and the flux of nitrate to the Long Island Estuary from this subterranean groundwater discharge is quite high (Tamborski et al., 2017, Brown et al., in revision).

Boron isotopes have been used as a monitor of nitrate source because boron is in high concentration in fertilizer and sewage and is not changed along the flow path as it co-migrates with nitrate. At the pH of rainwater and groundwater, boric acid dominates. Boric acid is conservative and therefore changes little through interaction along the water path (Leenhouts et
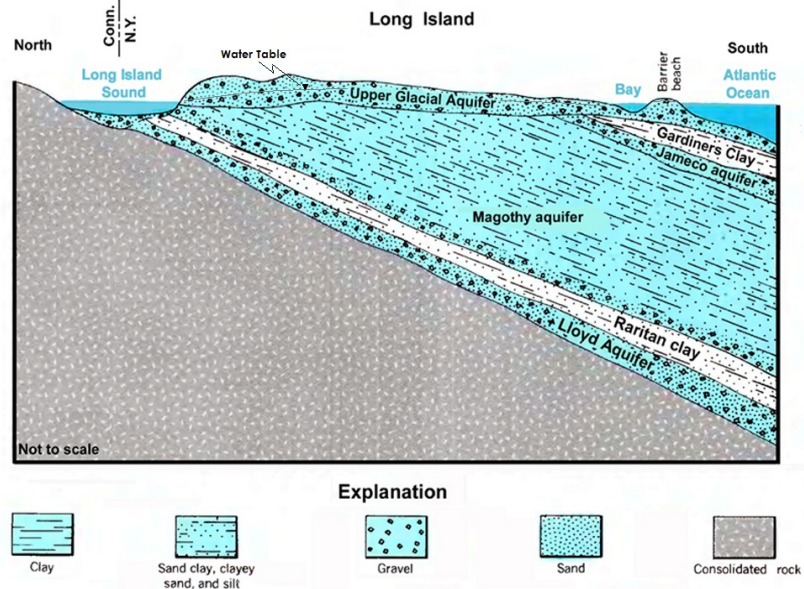
al., 1998, Widory et al., 2005). Boron is added to fertilizers as an essential nutrient (Barth, 1998), is found in septic/sewage due to its use in bleach and detergents (Barth, 1998) and can be contributed through atmospheric sources such as biomass burning (Chetelat et al., 2005) and flyash (Vengosh et al., 1998). Numerous studies in non-coastal regions have shown that boron can be used as a tracer of nitrate contamination (Leenhouts et al., 1998, Widory et al., 2005). In coastal areas, seawater, which has a heavy boron isotope signature, can provide boron to surface and groundwater through boric acid volatilization and atmospheric rainout (Chetelat et al., 2005).
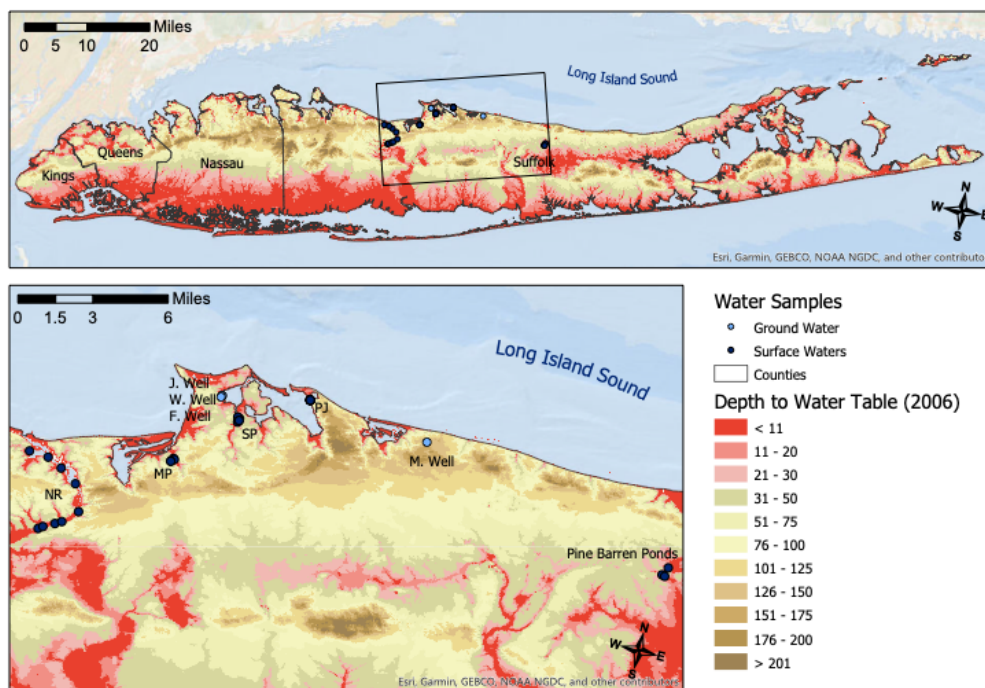

Figure 2. Depth to the water table across Long Island and location of the samples collected on the north shore.

Methods

Samples were collected in pre-cleaned 125mL plastic bottles. When necessary, samples containing organic solids were filtered prior to boron ion exchange chemistry. The samples were then pH-adjusted to pH 9 and put through Amberlite boron specific resin to obtain purified boron samples for isotope analyses (Hemming & Hanson, 1994). Boron is easily fractionated in column chemistry, so each batch of samples was tested in multiple ways to demonstrate reliability of the results. A seawater sample was put through chemistry with each batch of unknown samples. Additionally, the concentrations of each of the samples were measured before chemistry to determine the amount of sample needed to provide a minimum of 50 ng of boron. This concentration was compared with the elution concentration as a monitor of recovery. Additionally, many of the samples were put through chemistry twice to test for reproducibility.

Boron isotopes are reported in per mil notation (‰) which is calculated as:

$$\delta^{11}\text{B } \text{‰} = \frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}} - (^{11}\text{B}/^{10}\text{B})_{\text{std.}}}{(^{11}\text{B}/^{10}\text{B})_{\text{std.}}} \times 1000$$

Where the reference standard is NIST951 boric acid. We used a Nu Instruments Plasma II multi-collector ICPMS to measure boron isotopes. Samples and standards were bracketed by blanks (background) which was averaged and subtracted before applying the equation above to the bracketing averaged standards to calculate the $\delta^{11}B$ of the sample. All samples were run at least three times to monitor for reproducibility. The uncertainties in the measurements are based on reproducibility of the standards as well as of the replicates of the samples.

Results

Freshwater Endmembers

Rainwater analyses are presented in a companion abstract (Peritore et al., 2020). The rainwater samples were collected at Stony Brook University in June, September, October, and November of 2019. The range in boron concentrations is 4-15 ppb and the range in $\delta^{11}B$ is 12.5-33.4‰ (Peritore et al., 2002). Samples from Pine Barrens ponds have a similar range in boron concentrations (6-8 ppb) but generally fall on the heavy end of the rainwater values with a range from 27.5-32.7‰ (Table 1). The Pine Barrens is a protected area on Long Island with low residential density and no agriculture, and the similarities in these waters to rainwater suggests they represent a good estimate for the average contribution from atmospheric sources to Long Island groundwater. This is considered a good estimate of the uncontaminated endmember.

Table 1. Boron concentration and composition Pine Barrens Ponds.

Body of Water	Sample ID	B (ppb)	$\delta^{11}B$ (‰)
Pine Barren Ponds	RL 1	8.0	30.85
Pine Barren Ponds	P 1	7.0	27.54
Pine Barren Ponds	TP 1	6.0	32.71

Nitrate Endmembers

The nitrate endmembers display high boron concentrations and a range of isotope composition. The fertilizers range from 349ppb to 4000ppb in concentration and from -4.43‰ to 11.85‰ in composition (Table 2). The sewage samples range from 104.6ppb to 1436.7ppb in concentration and from -0.21‰ to 2.5‰ in composition (Table 2).

Table 2. Boron concertation and composition of anthropogenic nitrate sources sampled in this study.

Samples	Sample ID	B (ppb)	$\delta^{11}B$ (‰)
Fertilizers	Hollytone	4000.0	7.38
Fertilizers	40461	1310.0	11.85
Fertilizers	Milorganitte	405.0	-4.43
Fertilizers	37021	2500.0	4.86
Fertilizers	Scott's	349.0	11.77
Sewage	59R Sewage	1436.7	-0.21
Sewage	9B Sewage	243.7	2.50
Sewage	CSH Sewage	104.6	2.11

Surface Waters

       Springs and spring fed creeks and rivers are common on the north shore of Long Island. We have studied a number of these including the Stony Brook Mill Pond, the spring and the spring fed creek that supply the Setauket Pond, the Carmans River and the Nissequogue River (Table 3). All of the springs sampled have boron concentrations that are higher than rainwater and the Pine Barrens control samples (Table 1). Each of the springs have unique boron isotope compositions.

Table 3. Boron concentration and composition of the Carmans River and Stony Brook Mill Pond. Values for the Setauket Pond and Nissequogue River can be found in a companion abstract (Peritore et al., 2020).

Body of Water	Sample ID	B (ppb)	$\delta^{11}B$ (‰)
Carmans River	CA	14.3	17.35
Carmans River	CB	14.0	18.28
Carmans River	CC	14.2	18.18
Carmans River	CD	14.0	17.81
Carmans River	CE	16.0	15.46
Carmans River	CF	13.7	17.86
Carmans River	CZ	11.3	12.56
Stony Brook Mill Pond	MP 1	23.5	15.79
Stony Brook Mill Pond	MP 2	24.7	14.16

Private Wells

       Four private wells were sampled to represent the Upper Glacial Aquifer. The composition of the well samples (11-37‰) are similar to rainwater (12-33‰), yet the well waters have a broader range. In contrast, the range in boron concentration (18-67ppb) is greater than the freshwater endmembers (8-15ppb).

Table 4. Boron concertation and composition of the four private wells sampled during this study and their depths.

Body of Water	Sample ID	B (ppb)	$\delta^{11}B$ (‰)	Depth (ft)
Private Wells	M. Well	66.8	11.04	175
Private Wells	W. Well	25.5	36.01	80
Private Wells	J. Well	18.4	36.61	90
Private Wells	F. Well	46.9	19.55	90

Discussion

Private Wells

       The W. Well and J. Well are located on the same property, with the F. Well less than a 500ft from the other two (Figure 4). Given the proximity between the wells, the difference in isotope composition and concentration are quite surprising. The W. Well and J. Well are 80ft and 90ft deep respectively. The boron concentration of these wells varies slightly, although the difference in depth does not seem to play a role in the isotope composition. The F. Well is 90ft in depth and is in close proximity to the W. Well and J. Well geographically, yet the isotope composition varies quite drastically from them. The F. Well is isotopically lighter (19.6‰) than

the two wells previously discussed but has a greater boron concentration (47ppb). The variance in isotope composition within the same aquifer is unusual given the small distance between the sites. The fourth well sampled is the M. Well, located 6 miles east of the other three and is 175ft deep (Figure 4). This well has the highest concentration of boron and the lightest isotope composition out of the four sampled. Although these wells are sampling the same aquifer, there are several bodies of water between the M. Well and the other three that could contribute to the differences in boron.
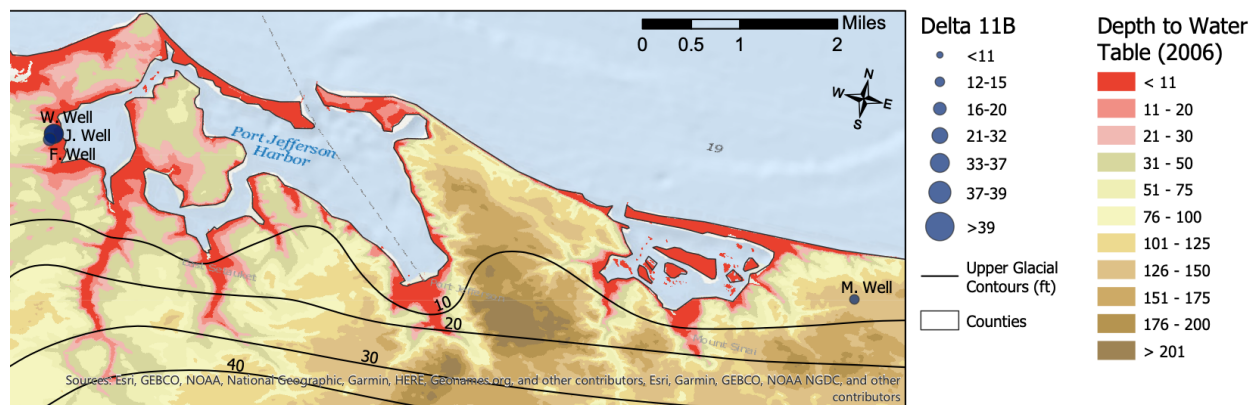

Figure 4. Location of the private wells we collected samples from, their $\delta^{11}B$, depth to water table, and depth to the Upper Glacial Aquifer.

The light isotope values and high concentration of the springs and creeks relative to rainwater suggests that a light isotope source such as septic water or fertilizer has been added. The differences across the springs suggest that the aquifer is compartmentalized, and the springs are reflecting only the local recharge. Compartmentalization could be due to the variety sediment deposits within the Upper Glacial Aquifer. Poorly permeable layers within the aquifer can restrict the lateral flow of water resulting in varying isotope values. This may present the opportunity to examine land use around the catchments to each of the springs to better understand sources of contamination to the aquifer.

References

Barth, S., 1998. Application of boron isotopes for tracing sources of anthropogenic contamination in ground- water. Water Res. 32, 685–690

Bronders, J., Tirez, K., Desmet, N., Widory, D., Petelet-Giraud, E., Bregnot, A., and Boeckx, P. (2012). Use of Compound-Specific Nitrogen ($\delta^{15}N$) Oxygen ($\delta^{18}O$), and Bulk Boron ($\delta^{11}B$) Isotope Ratios to Identify Sources of Nitrate-Contaminated Waters: A Guideline to Identify Polluters. Environmental Forensics 13:32-38.

Brown C., Tamborski, J., Bokuniewicz, H., Conchran, K., & Rasbury, T. (in revision). Investigating boron isotopes for identifying nitrogen sources supplied by submarine groundwater discharge to coastal waters.

Chetelat, B., Gaillardet, J., Freydier, R. and Ph. Negreic. 2005. Boron isotopes in precipitation: Experimental constraints and field evidence from French GuianaEarth and Planetary Science Letters 235:16-30.

Cohen, P. M., Franke, O. L., & Foxworthy, B. L. (1968). *An atlas of Long Island's water resources* (Vol. 62). State of New York.

Hemming, N. G., & Hanson, G. N. (1994). A procedure for the isotopic analysis of boron by negative thermal ionization mass spectrometry. *Chemical geology*, *114*(1-2), 147-156.

Leenhouts, J., Bassett, R., & Maddock, T. (1998). Utilization of intrinsic boron isotopes as co-migrating tracers for identifying potential nitrate contamination sources. *Ground Water*, *36*(2), 240–250.

McClymonds, N.E., & Franke, O.L. (1972). Water-transmitting properties of aquifers on Long Island, New York. Geological Survey Professional Paper 627-E, p. 24

Monti, J., & Busciolano, R. (2009). Water-table and potentiometric-surface altitudes in the Upper Glacial, Magothy, and Lloyd Aquifers beneath Long Island, New York. (2006). U.S. Geological Survey. [February 2020].

New York State Civil Boundaries. (2019). [downloaded file]. NYS Office of Information Technology Services GIS Program Office (GPO). [November 2019].

Palmer, M. R., Spivack, A. J., & Edmond, J. M. (1987). Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clay. *Geochimica et Cosmochimica Acta*, *51*(9), 2319-2323.

Peritore, B., Downs, D., Wooton, K., & Rasbury, T. (2020). Isotopic evidence in rainwater for boron contribution in Long Island groundwaters. [Abstract]. 27th Conference on the Geology of Long Island and Metropolitan New York.

Tamborski, J.J., J.K. Cochran, and H.J. Bokuniewicz. 2017. Submarine groundwater discharge driven nitrogen fluxes to Long Island Sound, NY: Terrestrial vs. marine sources. Geochimica et Cosmochimica Acta 218: 40-57.

USGS National Hydrography Dataset. (2019). [downloaded file]. U.S. Geological Survey, Rolla, MO. [November 2019].

Vengosh, A. (1998). The isotopic composition of anthropogenic boron and its potential impact on the environment. Biological Trace Element Research 66: 145–151.

Widory, D., Petelet-Giraud, E., Négrel, P., & Ladouche, B. (2005). Tracking the sources of nitrate in groundwater using coupled nitrogen and boron isotopes: a synthesis. *Environmental Science & Technology*, *39*(2), 539-548.

Widory, D., W. Kloppmann, L. Chery, J. Bonnin, H. Rochdi, and J. L. Guinamant. 2004. Nitrate in groundwater: an isotopic multi-tracer approach. J Contam Hydrol 72:165-188.

Vengosh, A., Kolodny, Y., & Spivack, A. J. (1998). *Ground-water pollution determined by boron isotope systematics* (No. IAEA-TECDOC--1046).

Yingkai, X.; Lan, W. The effect of pH and temperature on the isotopic fractionation of boron between saline brine and sediments. *Chem. Geol.* 2001, *171*, 253-261.