



Investigating Boron Isotopes for Identifying Nitrogen Sources Supplied by Submarine Groundwater Discharge to Coastal Waters

Joseph Tamborski^{1,2}, Caitlin Brown^{3†}, Henry Bokuniewicz^{4*}, J. K. Cochran⁴ and E. T. Rasbury³

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*Correspondence:

Henry Bokuniewicz
henry.bokuniewicz@stonybrook.edu

† Present address:

Caitlin Brown,
US Environmental Protection Agency,
Boston, MA, United States

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¹ Woods Hole Oceanographic Institution, Woods Hole, MA, United States, ² Centre for Water Resources Studies, Dalhousie University, Halifax, NS, Canada, ³ Department of Geosciences, Stony Brook University, Stony Brook, NY, United States, ⁴ School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, NY, United States

Stable isotopes of oxygen, nitrogen, and boron were used to identify the sources of nitrate (NO_3^-) in submarine groundwater discharge (SGD) into a large tidal estuary (Long Island Sound, NY, United States). Potential contaminants such as manure, septic waste and fertilizer overlap in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ but have been shown to have distinctive $\delta^{11}\text{B}$ in non-coastal settings. Two distinct subterranean estuaries were studied with different land-use up gradient, representative of (1) mixed medium-density residential housing and (2) agriculture. These sites have overlapping $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ measurements in NO_3^- and are unable to discriminate between different N sources. Boron isotopes and concentrations are measurably different between the two sites, with little overlap. The subterranean estuary impacted by mixed medium-density residential housing shows little correlation between $\delta^{11}\text{B}$ and [B] or between $\delta^{11}\text{B}$ and salinity, demonstrating that direct mixing relationships between fresh groundwater and seawater were unlikely to account for the variability. No two sources could adequately characterize the $\delta^{11}\text{B}$ of this subterranean estuary. Groundwater N at this location should be derived from individual homeowner cesspools, although measured septic waste has much lower $\delta^{11}\text{B}$ compared to the coastal groundwaters. This observation, with no trend in $\delta^{11}\text{B}$ with [B] indicates multiple sources supply B to the coastal groundwaters. The agricultural subterranean estuary displayed a positive correlation between $\delta^{11}\text{B}$ and [B] without any relationship with salinity. Binary mixing between sea spray and fertilizer can reasonably explain the distribution of B in the agricultural subterranean estuary. Results from this study demonstrate that $\delta^{11}\text{B}$ can be used in combination with $\delta^{15}\text{N}$ to trace sources of NO_3^- to the subterranean estuary if source endmember isotopic signatures are well-constrained, and if the influence of seawater on $\delta^{11}\text{B}$ signatures can be minimized or easily quantified.

Keywords: submarine groundwater discharge, boron, nitrogen, nitrate, fertilizer, wastewater, septic waste

INTRODUCTION

Submarine groundwater discharge (SGD) is an important vector for the delivery of nutrients to the coastal ocean (e.g., Taniguchi et al., 2019). While once thought to be a relatively minor component of the overall coastal nitrogen budget, studies have shown that non-point-sources of diffuse SGD can supply as much nitrogen into coastal waters as rivers (Slomp and Van Cappellen, 2004; Kroeger and Charette, 2008; Rodellas et al., 2015). The extent of SGD's effect on coastal water quality has been difficult to establish because SGD consists of a fresh groundwater component and a seawater component that mix in a biogeochemically reactive subterranean estuary (STE; Moore, 1999; Burnett et al., 2003; Slomp and Van Cappellen, 2004). The terrestrial, fresh component of SGD (FSGD) represents a source of new N to coastal waters and, if significant, can help sustain primary production and even coastal algal blooms (Gobler and Sanudo-Wilhelm, 2001), thus fueling coastal eutrophication (Paerl, 1995; Howarth and Marino, 2006).

Isotopes of N and O in nitrate (NO_3^-) have a proven utility in sorting out the sources of nitrogen delivered to groundwaters (Aravena et al., 1993; Bateman and Kelly, 2007; Bannon and Roman, 2008; Kendall et al., 2008). In particular, $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ can distinguish between NO_3^- fertilizers, atmospheric NO_3^- , manure and sewage-derived NO_3^- (Kendall, 1998; Kendall et al., 2008). However, the overlapping $\delta^{15}\text{N}$ signatures of soil N, animal and human waste, and nitrification of NH_4^+ in fertilizer and precipitation, as well as the biological modification of nitrogen and oxygen isotopes, can limit their utility in fully identifying anthropogenic sources of nitrogen. In addition, the speciation and attenuation of nitrogen may be modified in the STE before it reaches the coastal ocean (Kroeger and Charette, 2008; Erler et al., 2014). For example, changes in dissolved oxygen (DO) in groundwater may cause changes in N and O isotopic composition by nitrifying NH_4^+ to NO_3^- or denitrifying NO_3^- to N_2 . NH_4^+ volatilization and nitrogen remineralization may also alter N speciation (Charbonnier et al., 2013) and isotopic composition. Therefore, the groundwater isotopic signatures of N and O of an inland groundwater source may differ from that delivered to the coastal ocean, making it difficult to track anthropogenic sources of NO_3^- through the STE (Anschutz et al., 2016). The addition of other tracers may be useful in resolving these problems, including boron (B) isotopes.

Boron is added to groundwater both naturally and with contaminants such as NO_3^- in association with borate minerals used in fertilizers and detergents through septic systems or sewage (Barth, 1998; Vengosh, 1998; Vengosh et al., 1999). B is added to groundwater naturally via precipitation and water-rock interactions that include sorption reactions with clay minerals and iron hydroxides (Demetriou and Pashalidis, 2012). Anthropogenic sources of B to groundwaters include fertilizers and septic systems or sewage (Vengosh et al., 1999). Plants require B as an essential micronutrient for growth and therefore borate minerals are commonly added to commercial fertilizers (Shireen et al., 2018). Detergents and household

cleaning products contain elevated [B] that is subsequently transported to septic systems.

Boron is highly soluble in groundwater and is therefore a co-migrant of groundwater NO_3^- , including fertilizer and septic sources. B is not removed by wastewater treatment nor is it affected by processes that alter N concentration, such as nitrification and denitrification; however, B speciation is controlled by pH. At low pH boric acid (BOH_3) is the dominant species, while at high pH borate (BOH_4^-) dominates, with a pKa of 9.2 in fresh water (McPhail et al., 1972). There is an isotope fractionation between these species that makes borate isotopically enriched in ^{10}B . Boric acid is conservative, but borate has a strong affinity for positively charged particle surfaces (e.g., clays) because of its negative charge (Palmer et al., 1987). This can result in changes in the isotope ratio as B can be fractionated by processes such as adsorption and desorption of borate onto iron oxides and clay minerals (McPhail et al., 1972; Goldberg and Glaubig, 1985; Glavee et al., 1995; Lemarchand et al., 2007; Demetriou and Pashalidis, 2012). However, these processes are pH dependent, where adsorption is greatest at pH 9 and decreases to less than 10% adsorption at pH 5 and lower (Bloesch et al., 1987; De La Fuente and Camacho, 2009; Demetriou and Pashalidis, 2012). The large relative mass differences between ^{11}B and ^{10}B means that isotope fractionation leads to a wide range of isotopic values in nature. The combined use of $\delta^{11}\text{B}$ and $\delta^{15}\text{N}$ to trace NO_3^- sources has been successfully applied in terrestrial and aquatic environments (Komor, 1997; Widory et al., 2004, 2005, 2013; Seiler, 2005; Bronders et al., 2012; Lindenbaum, 2012; Briand et al., 2013, 2017; Eppich et al., 2013; Saccon et al., 2013; Ransom et al., 2016; Guinoiseau et al., 2018; Kruk et al., 2020); however, the use of $\delta^{11}\text{B}$ and $\delta^{15}\text{N}$ has yet to be tested in the STE of coastal systems.

Site Description

Long Island Sound (LIS) is a coastal estuary that lies between the south shore of Connecticut and the north shore of Long Island, NY, United States (**Figure 1**). The southern shoreline of LIS is cut into an unconfined, unconsolidated, sole-source aquifer (the Upper Glacial Aquifer) of glacial deposits with a hydraulic conductivity between 7 and 70 m d^{-1} (Buxton and Modica, 1992). The hydraulic gradient has been estimated to be 0.001 (McClymonds and Franke, 1972) with a vertical hydraulic gradient between 0.02 and 0.08 in the upper meter of sediment at the shoreline. Under these conditions, significant SGD has been documented along the shores of LIS (Durand, 2014; Garcia-Orellana et al., 2014; Bokuniewicz et al., 2015; Young et al., 2015; Tamborski et al., 2017a,b). FSGD-driven N loads to Smithtown Bay ($1\text{--}13 \times 10^6 \text{ mol N y}^{-1}$), an embayment of LIS, rivals that of the local Nissequogue River ($4\text{--}10 \times 10^6 \text{ mol N y}^{-1}$) and has been implicated as the primary new N source to LIS (Tamborski et al., 2017a).

This study focuses on two distinct STE's along the north shore of Long Island at Callahans Beach (adjacent to Smithtown Bay) and at Iron Pier Beach (on the North Fork of Long Island; **Figure 1**). Anthropogenic contaminant sources including cesspools, septic systems and fertilizers are implicated in

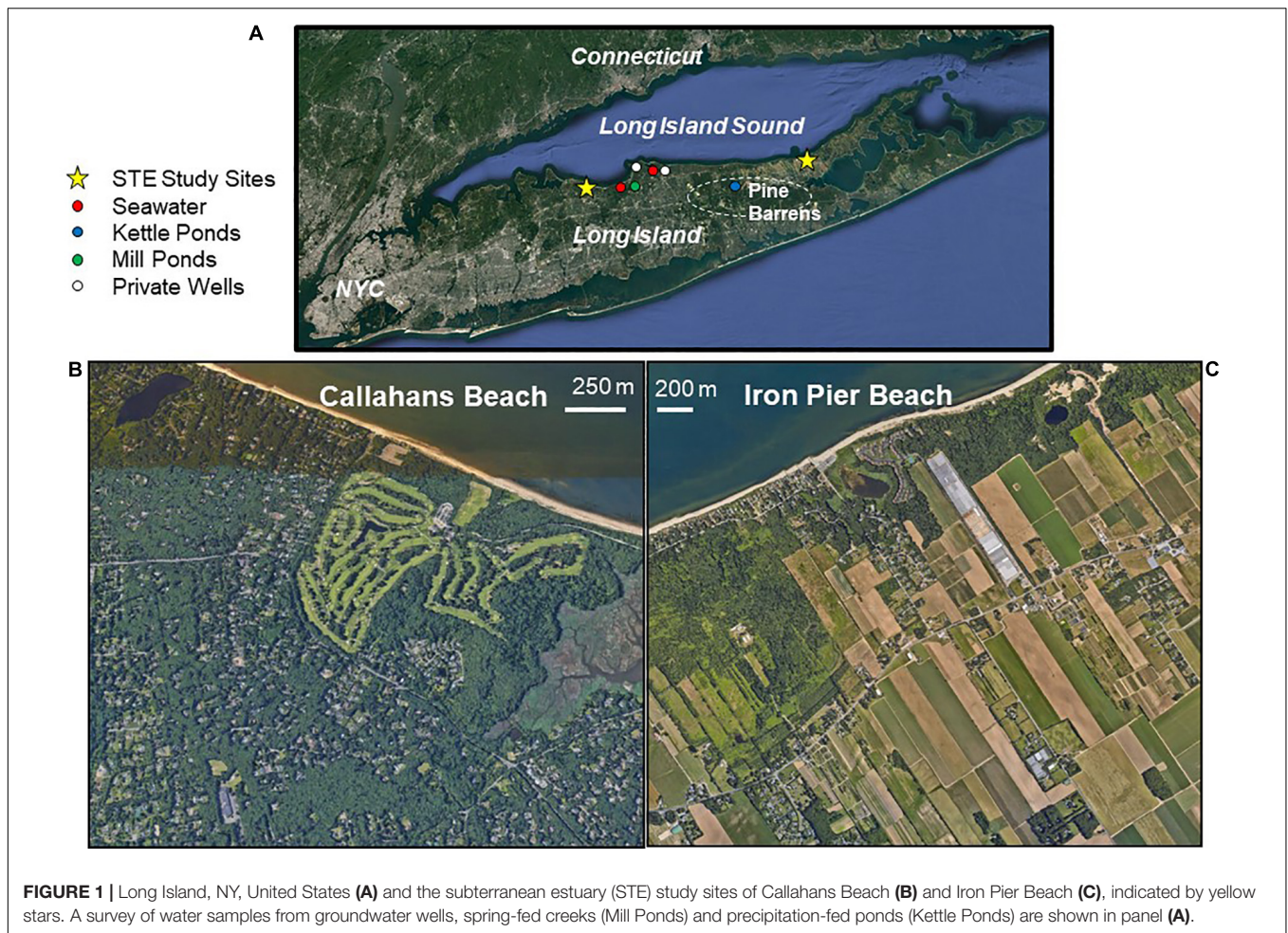


FIGURE 1 | Long Island, NY, United States (A) and the subterranean estuary (STE) study sites of Callahans Beach (B) and Iron Pier Beach (C), indicated by yellow stars. A survey of water samples from groundwater wells, spring-fed creeks (Mill Ponds) and precipitation-fed ponds (Kettle Ponds) are shown in panel (A).

producing elevated NO_3^- levels seen in Long Island's unconfined Upper Glacial Aquifer (Bellone, 2015). Land cover within the watershed of Callahans Beach is composed of medium-density residential housing ($2770 \text{ people km}^{-2}$; town of Fort Salonga); the beach itself is directly down-gradient from a golf course (Figure 1). This site has been well studied (Tamborski et al., 2015, 2017a,b) and was chosen to represent a shoreline impacted by mixed anthropogenic N sources (fertilizer, manure and/or septic); there was no evidence of groundwater denitrification or nitrogen attenuation in the STE (Tamborski et al., 2017a). At Callahans Beach, SGD rates vary tidally and can reach 50 cm d^{-1} near low tide (Tamborski et al., 2015). Land cover within the watershed of Iron Pier Beach is predominantly used for agriculture and this lower population density site ($470 \text{ people km}^{-2}$; town of Northville) was chosen to represent a shoreline impacted by a fertilizer N source. At Iron Pier Beach, SGD was measured at rates up to 75 cm d^{-1} via manual seepage meter measurements (Brown, 2018). Identifying the sources of nitrogen in groundwater is of particular importance to managers here because an effort to reduce nitrogen in Suffolk County, NY, United States, called "Reclaim our Water Initiative," is predicated on nitrogen pollution from septic systems (Suffolk County Government, 2019).

MATERIALS AND METHODS

Field Methods

Multi-level cluster wells were installed above the spring high tide elevation at Callahans Beach in 2014 at depths of 3.0 m, 5.0 m, 6.0 m, and 7.0 m below surface, and at Iron Pier Beach at 1.5 m, 3.0 m, and 4.5 m depths in 2017 using a track-mounted Geoprobe. Multi-level cluster-well installation at Callahans Beach is described in Tamborski et al. (2017b). Groundwater was collected from cluster wells monthly at both sites using a peristaltic pump, from June to December 2017, for nutrient analyses. Temperature, conductivity, salinity, DO, ORP and pH were measured in the field using a YSI-566 multi-probe. Groundwater samples for N, O, and B isotopic analysis were collected from June through October. Water samples for nutrient concentrations and N and O isotopes were filtered in the field ($0.2 \mu\text{m}$), collected in 15 mL falcon tubes and kept on ice. Samples were frozen upon returning to the lab and kept frozen until analyzed. The water samples for B isotope analysis were filtered in the field ($0.2 \mu\text{m}$), collected in 50 mL polypropylene centrifuge tubes and were kept refrigerated until analyzed.

A variety of possible endmembers were sampled to further constrain potential B sources. To estimate the contribution

of B from seawater, we analyzed coastal seawater samples ($n = 10$) from Port Jefferson Harbor (**Figure 1**). Precipitation was collected from acid cleaned rain gauges on four separate occasions (at Stony Brook University). Surface waters were collected from protected precipitation-fed lakes (i.e., kettle ponds; Pine Barrens region; $n = 3$) and spring-fed ponds (Mill Pond and Setauket Pond; $n = 8$). Private wells ($n = 5$) in Smithtown and Old Field were sampled at the houses before the filter (which was disconnected). Septic waste ($n = 3$) was collected from private residences on Long Island with a peristaltic pump from a pump chamber (immediately downfield from the septic tank prior to the drain-field) and stored in 1 L plastic containers with no processing (e.g., no filtering, pH adjustment). All surface and groundwater samples were collected in acid cleaned 50 mL polypropylene bottles. The bottles were rinsed with the water that was being collected and then collected to avoid air space. Temperature, DO, and salinity were measured at the time of collection. Samples were prepared for B analyses in the same way that SGD samples described above were prepared.

Analytical Methods & Endmember Experiments

In order to obtain $\delta^{11}\text{B}$ and to estimate how much [B] could be expected from commercial products, tap water was used to leach five commonly applied fertilizers, one manure sample purchased locally and one locally collected Canada goose dropping. The tap water represents water that would be used for irrigation of lawns, making the leach a more realistic value for what might be delivered to groundwater. The fertilizers and manure were put in 50 mL centrifuge tubes up to the 5 mL mark, filled to the 50 mL mark with tap water and placed on a shaker table at room temperature for several hours.

Boron concentrations were measured with an Agilent 7500cx Quadrupole ICP-MS using a standard bracketing routine with background subtraction. After concentrations were established, approximately 250 ng of B was separated from the matrix using Amberlite IRA 743, a B-specific resin. Samples were adjusted to a pH of ~ 9 before adding to the columns, washed with pH 9 adjusted DI water, and eluted with 2% nitric acid following a modified procedure from Lemarchand et al. (2002). Boron isotope ratios were measured using a Nu Instruments Plasma II multi-collector ICP-MS using a standard bracketing routine that included a background between each sample and standard. These background measurements were averaged and subtracted from the sample and standards before using the average of bracketing standards (NBS 951, which is taken as 0‰) to calculate $\delta^{11}\text{B}$. Measurement precision is between 0.5 and 1.0‰. Archived groundwater samples from Callahans Beach, collected during July 2014 and May 2015, were additionally analyzed for [B] and $\delta^{11}\text{B}$.

Coastal groundwater samples for nitrate concentration analysis were prepared using a modified vanadium (III) reduction procedure (Miranda et al., 2001; Doane and Howarth, 2003). Samples for the analysis of ammonium were prepared and analyzed using a mixed-reagent method (Presley and Claypool, 1971). Nutrient (NO_3^- and NH_4^+) concentrations

were measured spectrophotometrically on a BPPBABTECH Omega series microplate reader. $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ were measured at the stable isotope facility at the University of California, Davis by bacterial denitrification assay. Isotope ratios were measured on a ThermoFinnigan GasBench + PreCon trace-gas concentration system interfaced to a ThermoScientific Delta V Plus isotope-ratio mass spectrometer with measurement precision of 0.4‰ for $\delta^{15}\text{N}-\text{NO}_3^-$ and 0.5‰ for $\delta^{18}\text{O}-\text{NO}_3^-$. Nitrogen isotopes are referenced to air while oxygen isotopes are referenced to Vienna Standard Mean Ocean Water (VSMOW). Nitrite was removed prior to analysis (Granger and Sigman, 2009). November and December groundwater samples were not analyzed for $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$.

RESULTS

Possible Sources – Boron

Natural Sources

The survey of local water sources reveals a range in [B] and large variability in $\delta^{11}\text{B}$ (**Table 1**). Rainwater varied from 6 to 13 ppb with a $\delta^{11}\text{B}$ between 12.7 and 33.4‰ (**Table 1**). Kettle ponds in the Pine Barrens region, which is a protected part of the Long Island watershed without farming and residences (**Figure 1**), demonstrated similar [B] as the rainwater samples (6–8 ppb) and somewhat higher $\delta^{11}\text{B}$ values (27.5 to 32.7‰; **Table 1**). These protected ponds are fed by precipitation and should therefore represent the average annual precipitation $\delta^{11}\text{B}$ and [B] endmember.

Private wells to depths of 30 and 90 m in the Upper Glacial aquifer (town of Old Field; **Figure 1**) give a range of [B] of 18–47 ppb and a range of $\delta^{11}\text{B}$ of 19.6 to 36.6‰ (**Table 1**). In contrast, one well from the town of Smithtown (Metcalf) was higher in [B] (67 ppb) and lower in $\delta^{11}\text{B}$ (11‰; **Table 1**). Water collected along two spring-fed creeks (Setauket Mill Pond and Stony Brook Mill Pond) were enriched in [B] (17–25 ppb) and isotopically low ($\delta^{11}\text{B} = 9.0\text{--}15.8\%$; Setauket Pond 2E; **Table 1**) as compared to inland groundwaters. A total of 10 coastal seawater samples were collected along the shoreline of Port Jefferson Harbor; the mean (\pm standard deviation) $\delta^{11}\text{B}$ is $39.4 \pm 0.2\%$ for a [B] of 3580 ppb and a salinity of 27 psu.

Anthropogenic and Animal Sources

The public water supply is used for agricultural and homeowner irrigation; therefore, tap water was used to leach a variety of fertilizers and manure samples. The tap water has relatively low [B] (11 ppb) and elevated $\delta^{11}\text{B}$ (34.9‰; **Table 1**). Leaching with tap water produced a range of [B] and while it is understood that farming and lawn practices are not mimicked by our leaching experiments and attenuation is expected, the $\delta^{11}\text{B}$ values are used in ensuing mixing models (see section “Identifying Potential Sources of Groundwater Nitrate Using Boron Stable Isotopes”). The differences in [B] availability through these qualitative leaching experiments provides order of magnitude concentrations and shows differences among the various potential B sources. The $\delta^{11}\text{B}$ values for five commonly applied commercial fertilizers (Scotts Thick'R Lawn, Holly Tone,

TABLE 1 | Summary of B concentration and $\delta^{11}\text{B}$ isotopic values for natural waters, including precipitation, protected precipitation-fed lakes, spring-fed ponds, groundwater wells, public tap water, and seawater.

| Sample type | $\delta^{11}\text{B}$ (‰) | B (ppb) | Lat | Lon |
|--|---------------------------|---------|---------|----------|
| Precipitation | | | | |
| SBU Rain 1 | 12.7 | 13 | 40.9570 | -73.1251 |
| SBU Rain 2 | 33.4 | 6 | 40.9570 | -73.1251 |
| SBU Rain 3 | 21.3 | 9 | 40.9570 | -73.1251 |
| SBU Rain 4 | 15.6 | 7 | 40.9570 | -73.1251 |
| Precipitation-fed lakes (protected) | | | | |
| Lake Panamoka | 27.5 | 7 | 40.9217 | -72.8543 |
| Ridge Lake | 30.9 | 8 | 40.9169 | -72.8568 |
| Tarkill Pond | 32.7 | 6 | 40.9167 | -72.8551 |
| Spring-fed ponds | | | | |
| Stony Brook Mill Pond 1 | 15.8 | 24 | 40.9149 | -73.1468 |
| Stony Brook Mill Pond 2 | 14.2 | 25 | 40.9145 | -73.1461 |
| Setauket Pond 2A | 10.9 | 24 | 40.9464 | -73.1152 |
| Setauket Pond 2C | 9.5 | 28 | 40.9441 | 73.1158 |
| Setauket Pond 2D | 10.8 | 25 | 40.9452 | -73.1152 |
| Setauket Pond 2E | 9.0 | 17 | 40.9452 | -73.1152 |
| Groundwater wells | | | | |
| Metcaif (Smithtown) | 11.0 | 67 | 40.9589 | -73.0069 |
| 29B Fuller (Old Field) | 19.6 | 47 | 40.9560 | -73.1289 |
| 21A Johnson (Old Field) | 36.6 | 18 | 40.9568 | -73.1288 |
| Johnson #2 (Old Field) | 36.6 | 20 | 40.9570 | -73.1283 |
| 33B Wooton (Old Field) | 36.0 | 26 | 40.9570 | -73.1283 |
| Public (tap) water | 34.9 | 11 | | |
| Seawater | | | | |
| Port Jefferson Harbor ($n = 10$) | 39.4 | 3580 | 40.9664 | -73.0781 |

TABLE 2 | Summary of potential contaminant endmember $\delta^{11}\text{B}$ isotopic values analyzed, including fertilizers, animals waste and septic waste.

| Sample type | $\delta^{11}\text{B}$ (‰) | B (ppb) |
|----------------------|---------------------------|---------|
| Fertilizers | | |
| Scotts Thick'R Lawn™ | 12.6 | 349 |
| Holly Tone™ | 7.4 | 4000 |
| 10-10-10 | 11.9 | 1310 |
| 5-10-5 | 4.9 | 2500 |
| Milorganite™ | -4.4 | 405 |
| Animal waste | | |
| Commercial manure | 25.9 | 92 |
| Goose droppings | 25.8 | 75 |
| Septic waste | | |
| 59R Sewage | -0.2 | 1275 |
| 9B Sewage | 2.5 | 250 |
| CSH Sewage | 2.1 | 105 |

10-10-10, 5-10-5, and Milorganite™ analyzed ranged from -4.4 to 12.6‰ (Table 2). In contrast, commercial manure (animal source unknown) was higher in $\delta^{11}\text{B}$ (25.9‰), and similar to that of Canada goose manure collected from Stony Brook University's campus (25.8‰; Table 2). The $\delta^{11}\text{B}$ of three septic samples ranged between -0.2 and 2.5‰ (Table 2). Milorganite™ is the heat-treated residue from microbes that

were used to break up solids in the public wastewater treatment for the city of Milwaukee, likely accounting for its similar composition (-4.4‰) to the septic samples. These analyses were conducted to better understand potential B endmembers, and N isotope values were not measured.

Subterranean Estuary Groundwaters – Concentrations Callahans Beach

Groundwater salinity remained constant at depth (≤ 0.3 psu) and waters were well-oxygenated (with dissolved oxygen, $[\text{DO}] > 5 \text{ mg L}^{-1}$) at Callahans Beach (Table 3). DO was variable with depth and was generally lower in August and September than it was in the other 4 months. Groundwater pH generally increased with depth but showed some variability being lower in July (4.77–4.98) than at other times (4.80–5.89). [B] did not show a statistically significant correlation with salinity ($R^2 = 0.22$, excluding a high outlier from 6 m depth in July) or with NO_3^- concentrations (Table 3 and Figure 2). B concentrations were variable with depth for each month, ranging from 14 to 47 ppb, with one elevated salinity sample at 73 ppb (Table 3). NO_3^- concentrations in groundwater from Callahans Beach ranged from 3.7 to 19.3 mg L^{-1} (as NO_3^-) with a mean (\pm standard deviation) of $12.7 \pm 4.6 \text{ mg L}^{-1}$ (Table 3 and Figure 2B). NO_3^- concentrations were elevated during June through September and decreased from October through December 2017. NH_4^+ was present at trace levels through the summer and increased slightly in November and December. These differences may have been driven by changes in regional precipitation. October 2017 had about 150 mm of total rainfall, while November and December 2017 had about 50 mm of total rainfall. Tamborski et al. (2017a) monitored these same wells over a 12-month period (2014–2015), during which NH_4^+ concentrations were negligible and NO_3^- was the dominant form of inorganic N.

Iron Pier Beach

At Iron Pier Beach, groundwater salinity was relatively constant with depth (< 0.5 psu), with slightly elevated salinities in July (< 2 psu; Table 4). DO generally decreased with depth but all samples were well-oxygenated ($> 5 \text{ mg L}^{-1}$); DO was slightly higher in summer than in winter. There was variability in pH with depth and pH was lower in June (4.98–5.07) than at other times of the year (5.10–5.92). On average, B concentrations at Iron Pier Beach were higher than those at Callahans Beach (16–98 ppb), variable with depth and were not correlated with salinity (Table 4 and Figure 2A). NO_3^- concentrations were consistently higher at Iron Pier Beach than those at Callahans Beach. The mean (\pm standard deviation) groundwater NO_3^- concentration was $28.2 \pm 9.3 \text{ mg L}^{-1}$ with a range of 9.3 to 52.6 mg L^{-1} . NO_3^- concentrations showed no seasonal differences and generally increased with depth, with minor amounts of NH_4^+ (Table 4).

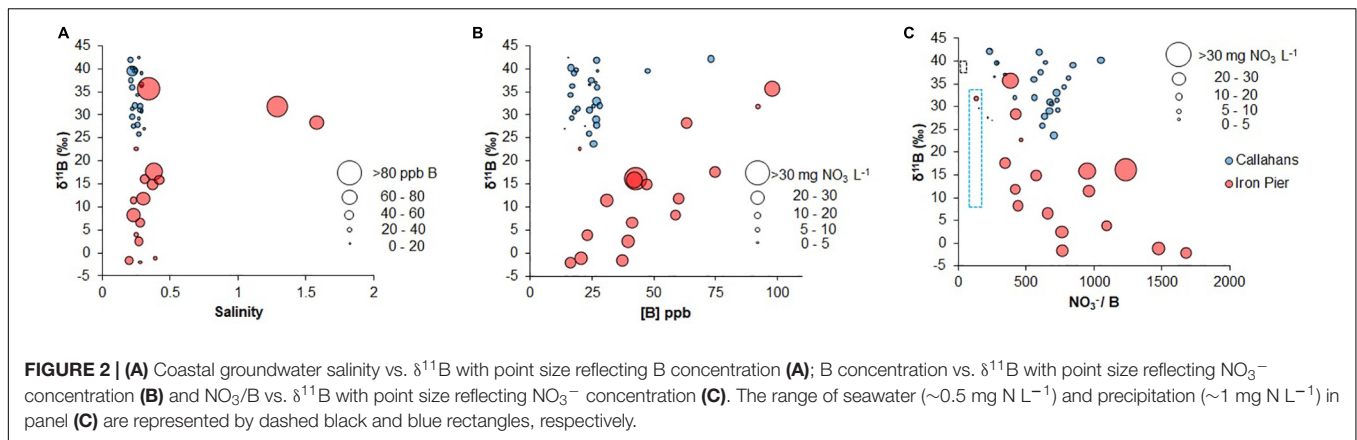
Subterranean Estuary Groundwaters – Stable Isotopes

Groundwater samples from Callahans Beach collected in 2017 gave $\delta^{15}\text{N}-\text{NO}_3^-$ values that ranged from 1.9‰ to

TABLE 3 | Callahans Beach coastal groundwater samples collected in 2017.

| Well | Date | Depth m | T °C | Salinity | DO mg L ⁻¹ | pH | ORP mV | NO _x mg L ⁻¹ | NH ₄ ⁺ mg L ⁻¹ | B ppb | δ ¹⁵ N ‰ - air | δ ¹⁸ O ‰ - VSMOW | δ ¹¹ B ‰ |
|------|--------|------------|---------|----------|--------------------------|------|-----------|---------------------------------------|--|----------|------------------------------|--------------------------------|------------------------|
| CH2 | Jun-17 | -3 | na | na | na | 4.98 | 83 | 19.3 | 0.0 | 27 | 3.6 | 2.2 | 33.0 |
| CH3 | Jun-17 | -5 | na | na | na | 5.22 | 73 | 18.0 | 0.0 | 27 | 3.8 | 0.0 | 29.0 |
| CH4 | Jun-17 | -6 | na | na | na | 5.38 | 48 | 18.0 | 0.0 | 26 | 3.8 | -0.1 | 23.7 |
| CH5 | Jun-17 | -7 | na | na | na | 5.34 | 61 | 9.1 | 0.0 | 26 | 3.8 | -0.1 | 37.1 |
| CH2 | Jun-17 | -3 | 17.1 | 0.28 | 9.4 | 4.80 | 216 | 16.1 | 0.0 | 24 | 3.2 | -0.4 | 31.1 |
| CH3 | Jul-17 | -5 | 16.4 | 0.27 | 10.0 | 4.77 | 209 | 14.6 | 0.0 | 24 | 3.6 | 0.6 | 25.9 |
| CH4 | Jul-17 | -6 | 17.3 | 9.36 | 8.8 | 4.80 | 197 | 16.7 | 0.0 | 73 | 3.6 | 1.1 | 42.2 |
| CH5 | Jul-17 | -7 | 16.4 | 0.29 | 9.5 | 4.79 | 202 | 6.4 | 0.0 | 24 | 4.2 | 0.6 | 36.5 |
| CH2 | Aug-17 | -3 | 25.6 | 0.28 | 5.7 | 5.29 | 256 | 10.7 | 0.0 | 26 | 4.0 | 1.3 | 32.0 |
| CH3 | Aug-17 | -5 | 23.9 | 0.24 | 6.8 | 5.59 | 253 | 15.8 | 8.3 | 28 | 3.9 | 0.3 | 32.0 |
| CH4 | Aug-17 | -6 | 23.1 | 0.26 | 6.5 | 5.66 | 272 | 17.1 | 0.0 | 27 | 3.1 | 1.0 | 27.8 |
| CH5 | Aug-17 | -7 | na | 0.24 | 6.4 | 5.55 | 257 | 7.9 | 0.0 | 27 | 4.6 | 0.5 | 39.6 |
| CH2 | Sep-17 | -3 | 14.4 | 0.22 | 8.3 | 5.45 | 293 | 13.5 | 0.0 | 47 | 4.1 | 1.2 | 39.6 |
| CH3 | Sep-17 | -5 | 14.4 | 0.22 | 8.0 | 5.53 | 308 | 15.1 | 0.0 | 27 | 4.2 | 1.3 | 35.9 |
| CH4 | Sep-17 | -6 | 14.1 | 0.21 | 7.6 | 5.87 | 346 | 16.0 | 0.0 | 27 | 2.8 | 1.3 | 41.9 |
| CH5 | Sep-17 | -7 | 14.1 | 0.22 | 8.0 | 5.68 | 336 | 3.9 | 0.0 | 26 | 4.7 | 0.9 | 29.6 |
| CH2 | Oct-17 | -3 | 19.0 | 0.21 | 7.7 | 5.46 | 253 | 15.0 | 0.0 | 25 | 4.1 | 0.2 | 37.6 |
| CH3 | Oct-17 | -5 | 21.2 | 0.22 | 6.5 | 5.42 | 264 | 14.0 | 0.0 | 19 | 4.0 | 1.0 | 31.4 |
| CH4 | Oct-17 | -6 | 20.0 | 0.22 | 7.8 | 5.60 | 238 | 17.3 | 0.0 | 16 | 1.9 | 1.5 | 40.2 |
| CH5 | Oct-17 | -7 | 18.7 | 0.23 | 6.7 | 5.56 | 250 | 4.8 | 0.0 | 22 | 4.6 | 1.1 | 27.6 |
| CH2 | Nov-17 | -3 | 7.4 | 0.25 | 9.5 | 5.40 | 341 | 12.0 | 0.0 | 19 | na | na | 39.7 |
| CH3 | Nov-17 | -5 | 6.2 | 0.26 | 9.0 | 5.68 | 289 | 12.6 | 3.2 | 16 | na | na | 34.4 |
| CH4 | Nov-17 | -6 | 5.8 | 0.27 | 9.2 | 5.70 | 308 | 3.7 | 2.4 | 15 | na | na | 42.5 |
| CH5 | Nov-17 | -7 | 6.1 | 0.27 | 9.9 | 5.89 | 325 | 12.3 | 0.7 | 17 | na | na | 29.2 |
| CH2 | Dec-17 | -3 | 4.8 | 0.29 | 10.0 | 5.87 | 266 | 13.8 | 0.2 | 17 | na | na | 36.3 |
| CH3 | Dec-17 | -5 | 5.0 | 0.29 | 9.2 | 5.67 | 291 | 12.4 | 0.5 | 18 | na | na | 30.7 |
| CH4 | Dec-17 | -6 | 4.3 | 0.31 | 9.8 | 5.86 | 238 | 3.5 | 0.7 | 14 | na | na | 27.0 |
| CH5 | Dec-17 | -7 | 4.5 | 0.29 | 9.3 | 5.72 | 308 | 15.0 | 0.8 | 18 | na | na | 39.1 |

na, not analyzed.



4.7‰ and $\delta^{18}\text{O}-\text{NO}_3^-$ values that ranged from -0.4‰ to 2.2‰ (Figure 3A). $\delta^{15}\text{N}-\text{NO}_3^-$ was slightly lower at 6 m depth (sample ID = CH4) than at other depths during August, September, and October (Table 3). $\delta^{18}\text{O}-\text{NO}_3^-$ values were generally variable at depth without an obvious trend. The $\delta^{11}\text{B}$ of groundwater at Callahans Beach ranged from 23.7‰ to 42.5‰ with a concurrent change at 6 m depth (Table 3). $\delta^{11}\text{B}$ was significantly higher from July to October, but lower during June, and showed no trend with NO_3^- concentrations (Figure 2B).

Iron Pier Beach groundwaters had a similar range of $\delta^{15}\text{N}-\text{NO}_3^-$ values (0.5‰ to 5.0‰) as Callahans Beach (Figure 3A). $\delta^{15}\text{N}-\text{NO}_3^-$ values at Iron Pier Beach generally increased with depth (Table 4), while $\delta^{18}\text{O}-\text{NO}_3^-$ values were highest at a depth of 3 m. $\delta^{11}\text{B}$ values were generally lower at Iron Pier Beach than groundwater samples from Callahans Beach and ranged from -2.1‰ to 35.7‰ (Table 4 and Figure 2) and displayed a significant positive correlation with B concentration ($R^2 = 0.56$; Figure 2B). Groundwater NO_3^-/B ratios were significantly greater than seawater and precipitation endmembers for both sites (Figure 2C), demonstrating a significant input of anthropogenic NO_3^- to the STE.

DISCUSSION

Subsurface Processes and Variability

Groundwater pH was low at both sites (Tables 3, 4) and was not correlated with [B] or $\delta^{11}\text{B}$. Therefore, B isotopic signatures are unlikely to be affected by sorption and should only reflect nitrogen source compositions or mixing processes. Coastal groundwaters at both sites were well oxygenated (Tables 3, 4); despite this, denitrification may occur in sedimentary anoxic micro-sites (Brandes and Devol, 1997). There was no evidence of denitrification in the STE (Figure 3A), assuming that denitrification results in a $\delta^{18}\text{O}$ to $\delta^{15}\text{N}$ ratio of 2:1 (Kendall et al., 2008). This is further supported by comparing $\delta^{15}\text{N}$ with $\ln[\text{NO}_3^-]$ and $1/[\text{NO}_3^-]$ (Figure 4). Denitrification should result in trends distinctive from that induced by binary mixing. The narrow range of $\delta^{15}\text{N}$ for the coastal groundwaters coupled with overlapping signatures of $\delta^{15}\text{N}$ in potential endmembers

(Figure 3A) precludes using N alone to untangle mixing sources (Figure 4).

There were no seasonal changes in $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ at Iron Pier Beach, but there were differences with depth (Table 4). The groundwater at 1.5 m depth had a lower $\delta^{15}\text{N}$ value relative to the other groundwater samples at Iron Pier Beach. Lower isotope values for samples at 1.5 m depth may be explained by nitrification processes within the STE where oxic conditions are persistent (Kroeger and Charette, 2008), especially at this shallow depth. Alternatively, differences may be related to geologic heterogeneity. At Callahans Beach, fresh groundwaters at 6 m depth were lower in $\delta^{15}\text{N}-\text{NO}_3^-$ with variable $\delta^{11}\text{B}$, compared to shallower and deeper groundwaters (Table 3). This depth horizon is geologically distinct from neighboring sediments. Indeed, Tamborski et al. (2017b) observed significant radon, radium, and dissolved Mn^{2+} enrichments at this depth horizon. Geologic heterogeneity can act to both modify groundwater flow paths and enhance biogeochemical transformations within the STE (Heiss et al., 2020). However, denitrification cannot explain the differences in $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ compositions (Figures 3A, 4). In the ensuing analysis, we thus interpret changes in stable isotopes to reflect changes in groundwater N (and B) sources, rather than from a biogeochemical process or cycle, unless explicitly stated.

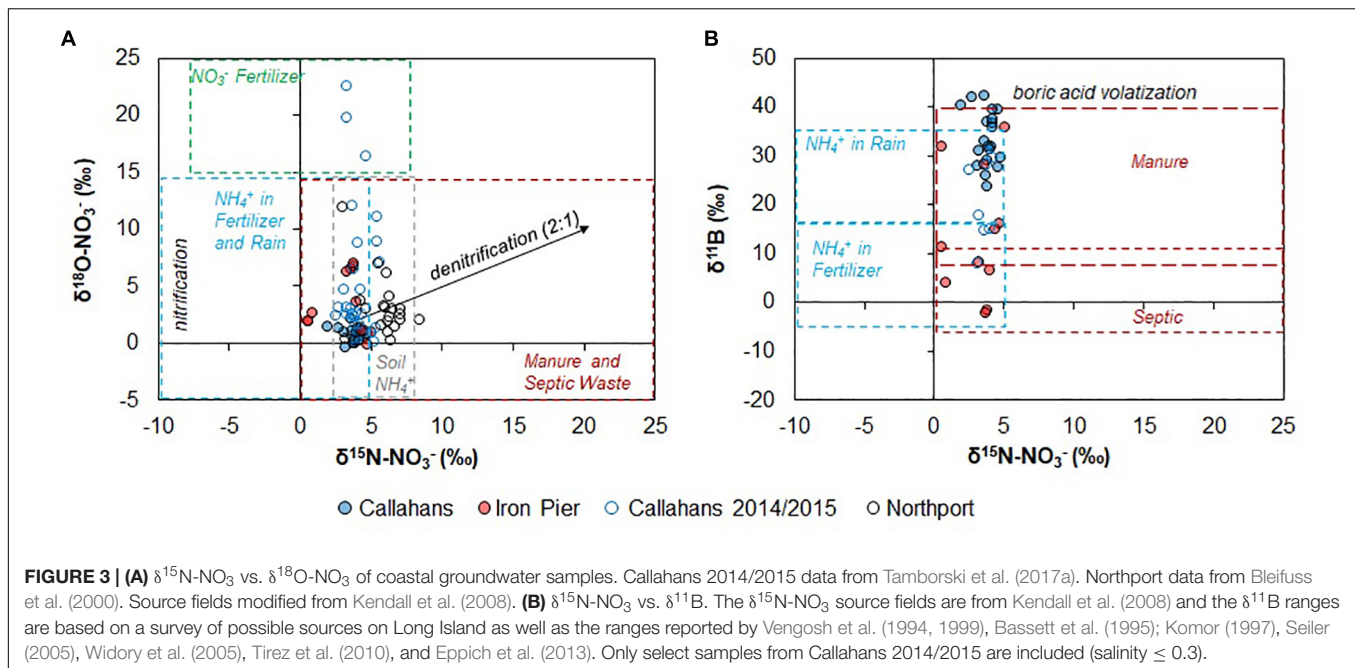
Potential Sources of Groundwater Nitrate Using Nitrate Stable Isotopes

The nitrogen and oxygen isotope values of NO_3^- in groundwater from Callahans Beach show no seasonal trends (Table 3). The samples from this study are similar in $\delta^{15}\text{N}-\text{NO}_3^-$ to previously measured values at that site from 2014 and 2015 (Tamborski et al., 2017a); however, the 2017 samples span a much narrower range in $\delta^{18}\text{O}-\text{NO}_3^-$ (Figure 3A). Samples from both Callahans Beach and Iron Pier Beach plot in the overlapping fields of nitrification of NH_4^+ in fertilizer and precipitation, soil NH_4^+ , manure and septic waste (Figure 3A). Previous studies at Callahans Beach attributed the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of groundwater NO_3^- to either nitrification of septic waste, or to mineral fertilizer (Tamborski et al., 2017a). Studies of drinking supply well samples collected in Northport, a sewered community to the southwest of Callahans

TABLE 4 | Iron Pier Beach coastal groundwater samples collected in 2017.

| Well | Date | Depth m | T °C | Salinity | DO mg L ⁻¹ | pH | ORP mV | NO _x mg L ⁻¹ | NH ₄ ⁺ mg L ⁻¹ | B ppb | δ ¹⁵ N ‰ - air | δ ¹⁸ O ‰ -VSMOW | δ ¹¹ B ‰ |
|------|--------|------------|---------|----------|--------------------------|------|-----------|---------------------------------------|--|----------|------------------------------|-------------------------------|------------------------|
| IP1 | Jun-17 | 1.5 | 18.4 | 0.23 | 12.9 | 4.98 | 54 | 29.9 | 0.0 | 31 | 0.5 | 1.9 | 11.4 |
| IP2 | Jun-17 | 3 | 19.4 | 0.20 | 9.4 | 5.41 | 77 | 28.6 | 0.0 | 37 | 3.8 | 6.7 | -1.6 |
| IP3 | Jun-17 | 4.5 | 18.4 | 0.31 | 10.3 | 5.07 | 105 | 52.6 | 0.1 | 43 | 4.7 | -0.2 | 16.1 |
| IP1 | Jul-17 | 1.5 | 18.6 | 1.29 | 9.8 | 5.87 | 170 | 12.4 | 0.0 | 92 | 0.6 | 1.9 | 31.9 |
| IP2 | Jul-17 | 3 | 16.8 | 1.58 | 10.1 | 5.57 | 147 | 26.6 | 0.0 | 63 | 3.6 | 6.5 | 28.3 |
| IP3 | Jul-17 | 4.5 | 16.5 | 0.37 | 10.2 | 5.35 | 123 | 26.8 | 0.0 | 47 | 4.4 | 1.1 | 14.9 |
| IP2 | Aug-17 | 3 | 19.1 | 0.28 | 6.9 | 5.64 | 288 | 27.1 | 0.0 | 16 | 3.7 | 7.0 | -2.1 |
| IP3 | Aug-17 | 4.5 | 18.0 | 0.28 | 7.6 | 5.68 | 319 | 27.0 | 0.1 | 41 | 4.0 | 3.7 | 6.6 |
| IP1 | Oct-17 | 1.5 | 15.6 | 0.25 | 8.4 | 5.82 | 184 | 25.2 | 0.0 | 23 | 0.8 | 2.7 | 3.9 |
| IP2 | Oct-17 | 3 | 12.5 | 0.23 | 8.4 | 5.59 | 230 | 25.8 | 0.0 | 59 | 3.2 | 6.2 | 8.3 |
| IP3 | Oct-17 | 4.5 | 12.6 | 0.34 | 7.8 | 5.72 | 120 | 37.7 | 0.0 | 98 | 5.0 | 0.9 | 35.7 |
| IP1 | Nov-17 | 1.5 | 8.2 | 0.25 | 9.3 | 5.10 | 250 | 9.3 | 0.8 | 20 | na | na | 22.7 |
| IP2 | Nov-17 | 3 | 7.8 | 0.27 | 8.7 | 5.72 | 302 | 30.1 | 0.0 | 40 | na | na | 2.5 |
| IP3 | Nov-17 | 4.5 | 7.4 | 0.38 | 8.6 | 5.92 | 321 | 25.7 | 0.0 | 75 | na | na | 17.6 |
| IP1 | Dec-17 | 1.5 | 7.4 | 0.30 | 9.6 | 5.72 | 262 | 25.2 | 0.0 | 60 | na | na | 11.8 |
| IP2 | Dec-17 | 3 | 7.1 | 0.39 | 8.9 | 5.84 | 3 | 30.2 | 0.2 | 20 | na | na | -1.1 |
| IP3 | Dec-17 | 4.5 | 7.1 | 0.42 | 9.0 | 5.90 | 260 | 39.9 | 0.5 | 42 | na | na | 15.9 |

na, not analyzed.



Beach, have NO_3^- concentrations less than 10 mg L^{-1} (Bleifuss et al., 2000). These sewered community groundwaters have higher $\delta^{15}\text{N-NO}_3^-$ values compared with those from Iron Pier and Callahans Beach (hollow black circles; **Figure 3A**). The $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values from the Northport supply wells were attributed to nitrification of NH_4^+ in fertilizer, with small inputs from septic waste (Bleifuss et al., 2000); we note that the soil NH_4^+ and manure/septic waste source fields also overlap in $\delta^{15}\text{N-NO}_3^-$ for these supply well samples (**Figure 3A**).

Residences in the watershed of Callahans Beach are unsewered and use individual, homeowner septic systems for wastewater disposal (i.e., cesspools); thus, a septic waste N signature is expected for Callahans Beach. Callahans Beach is located immediately down-gradient of a golf course, and in the vicinity of communities that fertilize their lawns (**Figure 1**), and so a N and B source from fertilizers is also expected. Based on the $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ data and the endmember source fields identified in Kendall et al. (2008), it is unclear what the dominant source of NO_3^- is to the groundwaters of the Callahans Beach STE (**Figure 3A**). Iron Pier Beach is located down-gradient from agricultural fields, so a fertilizer source for the NO_3^- was expected. Based on $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ is unclear, however, if the Iron Pier Beach samples are sourced from nitrification of NH_4^+ in fertilizer and precipitation, soil NH_4^+ , manure or septic waste.

Identifying Potential Sources of Groundwater Nitrate Using Boron Stable Isotopes

Stable isotope measurements of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ are unable to discriminate NO_3^- sources in the STE, despite local knowledge of each study site's primary NO_3^-

sources. Comparison of $\delta^{15}\text{N}$ and $\delta^{11}\text{B}$ values has allowed the discrimination of anthropogenic NO_3^- sources in other terrestrial and aquatic-based studies (Komor, 1997; Widory et al., 2004, 2005, 2013; Seiler, 2005; Bronckers et al., 2012; Lindenbaum, 2012; Briand et al., 2013, 2017; Eppich et al., 2013; Saccon et al., 2013; Guinoiseau et al., 2018; Kruk et al., 2020). Callahans Beach and Iron Pier Beach have distinct land-use patterns within their respective coastal watersheds (**Figure 1**). A *posteriori* knowledge of each site, and of the Long Island region (Bellone, 2015), provides a unique opportunity to compare “known” nitrogen sources to those estimated from $\delta^{11}\text{B}$ and $\delta^{15}\text{N-NO}_3^-$ versus $\delta^{18}\text{O-NO}_3^-$.

Endmember Mixing and N Sources

Comparison between $\delta^{11}\text{B}$ and $\delta^{15}\text{N}$ provides qualitative information on potential groundwater N sources (**Figure 3B**). Endmember source fields of $\delta^{11}\text{B}$ from this study (**Tables 1, 2**), with additional constraints as summarized by Eppich et al. (2013), suggests that groundwater NO_3^- for Iron Pier Beach is derived from either nitrification of NH_4^+ in fertilizer or septic waste. In contrast, groundwater NO_3^- at Callahans Beach is interpreted to reflect either nitrification of NH_4^+ in precipitation or an animal manure source. Precipitation can supply, at most, 1 mg L^{-1} of NO_3^- to the groundwater system of Long Island; therefore, precipitation is not the primary source of the observed N concentrations (**Table 3**) or $\delta^{11}\text{B}$ (**Figures 2C, 5**). Binary mixing models were used to investigate theoretical mixing between different sources of B in the STE. Assuming that B is not attenuated by *in situ* biogeochemical processes, then mixing between two different endmembers may be quantitatively approximated as:

$$[B] = C_1^*X + C_2^*(1 - X) \quad (1)$$

$$\delta^{11}B = ((\delta^{11}B_1^*C_1^*X) + (\delta^{11}B_2^*C_2^*(1 - X))) / (C_1^*X + C_2^*(1 - X)) \quad (2)$$

where X is the fraction of endmember 1 in the coastal groundwater, C_1 and $\delta^{11}B_1$ are the concentration and isotope

composition of endmember 1 and C_2 and $\delta^{11}B_2$ are the concentration and isotope composition of endmember 2. Estimated endmembers (**Figure 5**) were used to investigate potential mixing relationships between natural sources (precipitation or seawater) with contaminant sources B (fertilizer, septic waste or animal waste). We note that endmember mixing models may be improved with a Bayesian statistical analysis, which accounts for the degree of overlap and uncertainty of different sources (Ransom et al., 2016); however, a more comprehensive analysis of potential endmembers is required here. The two different subterranean estuaries studied have relatively distinct ranges of $\delta^{11}B$ (**Figure 2**) and therefore we treat each site as a separate system in the ensuing discussion.

Iron Pier Beach

Agriculture dominates the lower population density (470 people km^{-2}) watershed of Iron Pier Beach. Groundwater NO_3^- at this site should be derived from mineral fertilizers. Fresh groundwater samples from Iron Pier Beach are systematically lower in $\delta^{11}B$ compared to Callahans Beach (**Figure 2**). Iron Pier groundwater $\delta^{11}B$ increases nearly linearly with increasing B concentration (**Figure 2B**), suggesting that binary mixing occurred between an isotopically enriched B source and an isotopically depleted, lower [B] source. Precipitation has isotopically high $\delta^{11}B$ but is too low in [B] to explain the higher $\delta^{11}B$ values of the Iron Pier groundwater (**Figure 5**). Animal manure is an alternative endmember; however, three coastal groundwater samples are higher in $\delta^{11}B$ than the two measured manure samples (**Figure 5**). Either two samples are insufficient to adequately characterize the $\delta^{11}B$ of animal manure (Eppich et al., 2013), or this is not an appropriate endmember for this site.

Seawater has elevated $\delta^{11}B$ and [B] and may therefore constitute one endmember for Iron Pier Beach (**Figure 5**). Groundwater salinities are on the order of 0.3 psu (**Table 4**); direct mixing between a contaminant endmember and seawater (25–28 psu) would mean that seawater contributes between 1 and 2% of the observed salinity. This amount of seawater [B] could be

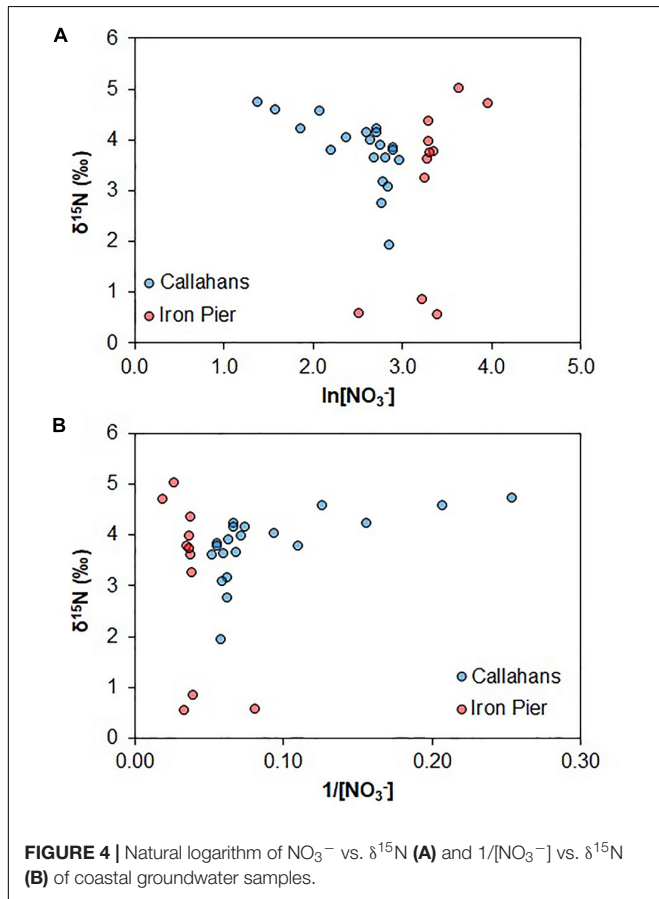


FIGURE 4 | Natural logarithm of NO_3^- vs. $\delta^{15}\text{N}$ (A) and $1/[\text{NO}_3^-]$ vs. $\delta^{15}\text{N}$ (B) of coastal groundwater samples.

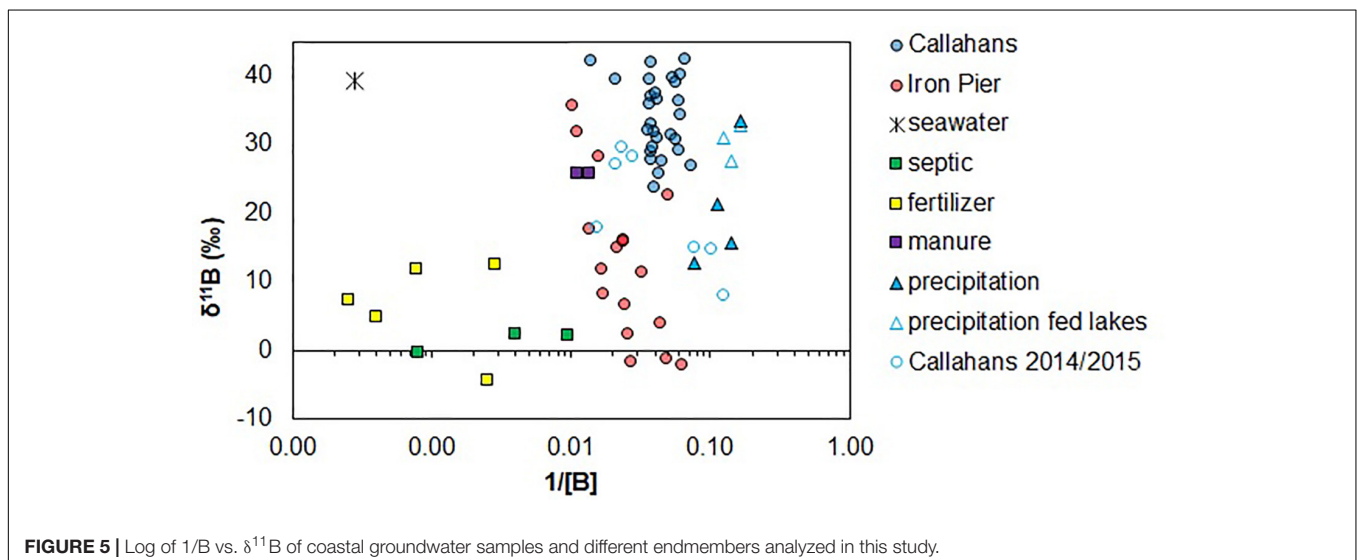
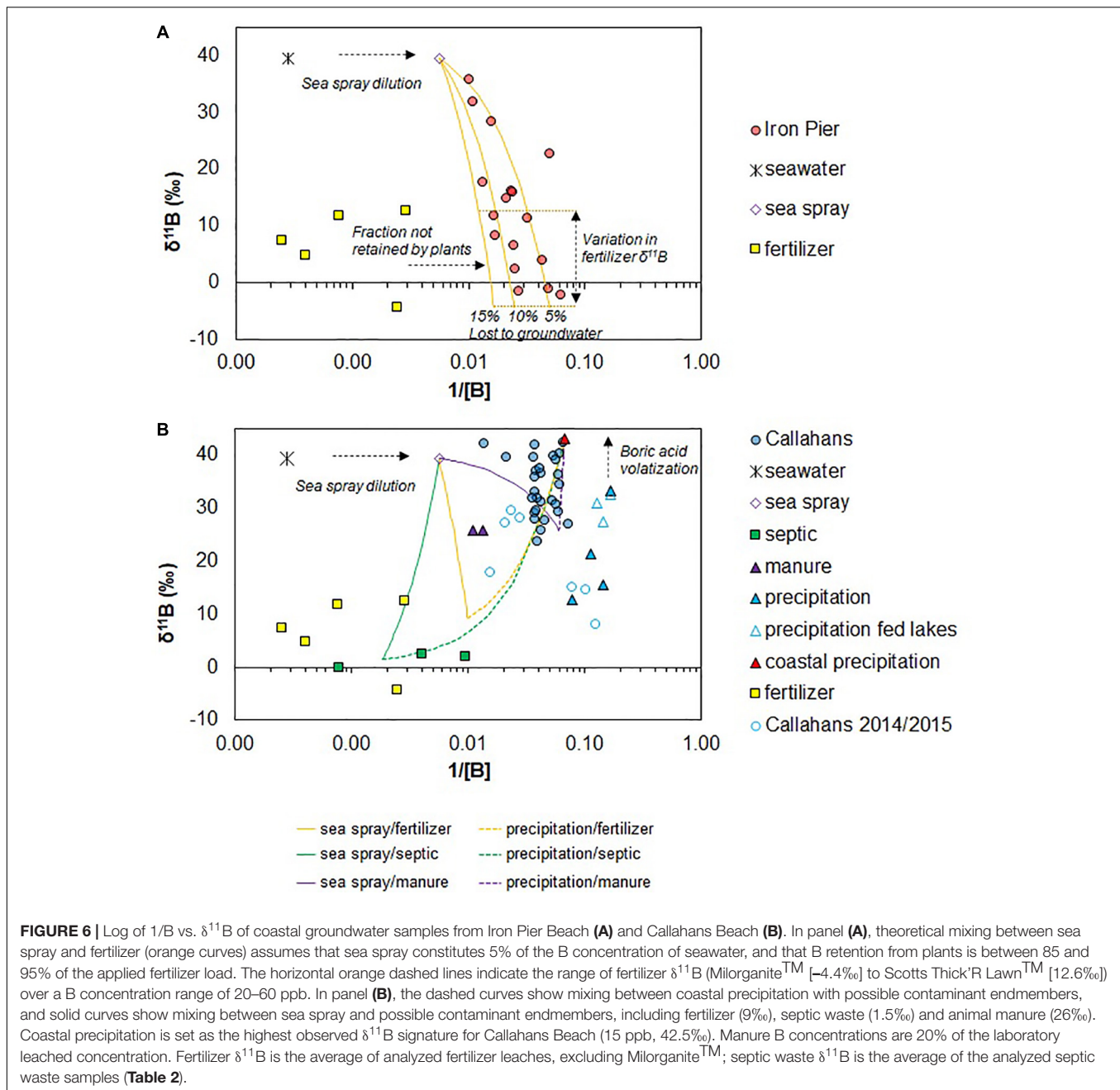


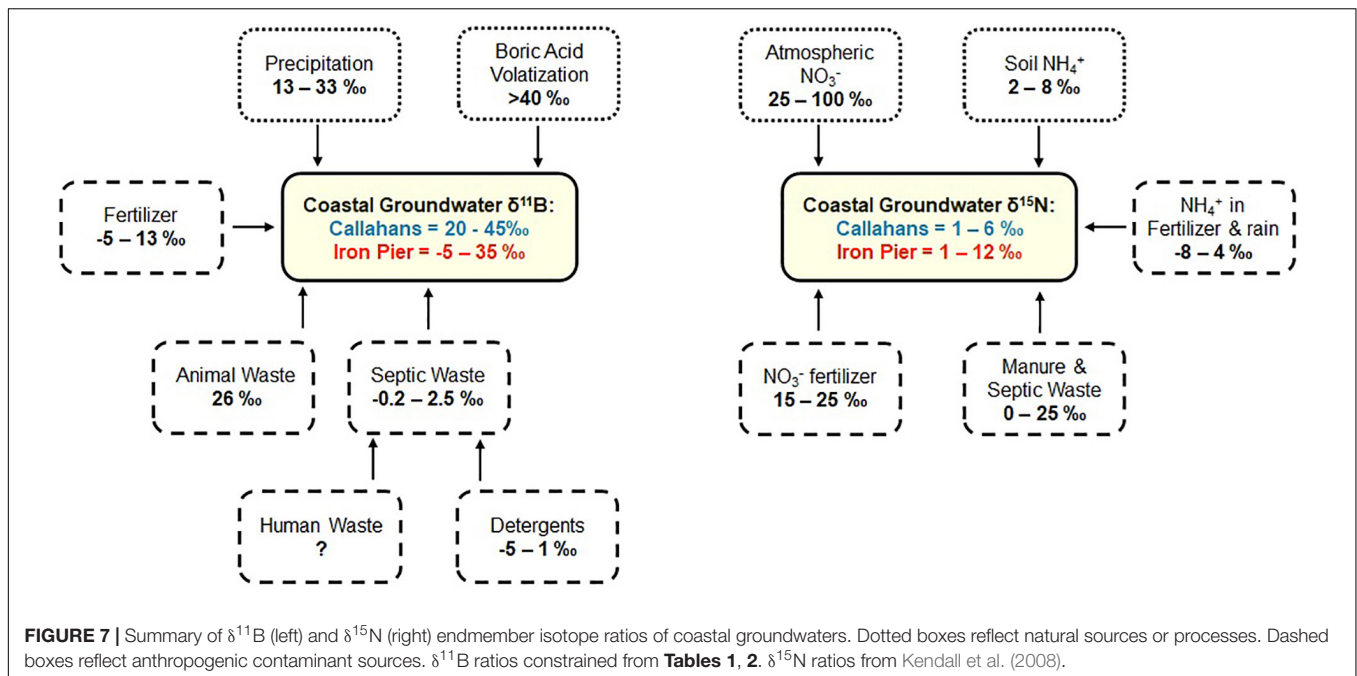
FIGURE 5 | Log of $1/B$ vs. $\delta^{11}B$ of coastal groundwater samples and different endmembers analyzed in this study.



delivered via sea spray that is diluted by rainfall. Septic waste and fertilizer endmembers (Table 2) are isotopically light enough to serve as the second endmember for Iron Pier Beach. However, B concentrations of the leaches are 1–3 orders of magnitude higher (lower $1/B$; Figure 5) than the isotopically lowest $\delta^{11}B$ groundwater sample (16 ppb; -2.1‰ ; Table 4). The $[B]$ of the fertilizers determined from the leaching experiments are not representative of a natural system. Borate minerals are added to commercial fertilizers because B is an essential micro-nutrient for plant growth (Shireen et al., 2018); therefore, a significant fraction of the B from a fertilizer application should be retained by the plant-root system. Further, the leaching experiment used a small

amount of water so the leach is much more concentrated than what would be found in irrigation water even if the plant roots were inefficient at utilizing the B.

Theoretical mixing between highly diluted sea spray and fertilizers reasonably explains the coastal groundwater B data of Iron Pier Beach (Figure 6A). These mixing curves represent an isotopically light fertilizer (Table 2) assuming that 5, 10 or 15% of the applied B is lost to the groundwater system. Note that a higher $\delta^{11}B$ signature for fertilizer (12.6‰) would simply shift these mixing curves upward toward higher $\delta^{11}B$ values, assuming that B concentration ranges remain the same (Figure 6A). Given these assumptions, groundwater N at Iron Pier Beach must be



predominantly sourced from nitrification of NH_4^+ in fertilizer (**Figures 3B, 6A**), consistent with our working knowledge of this agricultural coastal system. Notably though, there is no trend in NO_3^- with [B] (**Figure 2B**), and therefore a simple two-component mix cannot explain the source of NO_3^- at Iron Pier Beach using N alone (**Figure 4**).

Callahans Beach

Callahans Beach is directly down-gradient from medium-density residential housing (2770 people km^{-2}) and a public golf course. Groundwater NO_3^- at this site should be derived from septic (i.e., cesspool) waste, with minor contributions from fertilizers. The coastal groundwater $\delta^{11}\text{B}$ of Callahans Beach reflects a much heavier $\delta^{11}\text{B}$ source compared to measured septic waste ($-0.2 - 2.5\text{‰}$) and fertilizer (**Table 2**). Anthropogenic B compounds used in detergents and cleaning products have a $\delta^{11}\text{B}$ signature between -5 and 1‰ (Vengosh et al., 1999), such that the $\delta^{11}\text{B}$ signature of the measured septic waste may be dominated by detergents, rather than human waste.

The highest $\delta^{11}\text{B}$ signatures ($>39\text{‰}$) suggest a contribution of B from seawater, although coastal groundwater salinities are low (<0.3) and do not show a trend with [B] or $\delta^{11}\text{B}$ (**Figure 2A**). Sea spray was invoked as the isotopically high $\delta^{11}\text{B}$ endmember for Iron Pier Beach (**Figure 6A**). At Callahans Beach, B concentrations are systematically lower than Iron Pier Beach, and so despite appreciably high $\delta^{11}\text{B}$ signatures, [B] cannot be explained by sea spray alone. $\delta^{11}\text{B}$ signatures higher than seawater isotope values may be derived from boric acid volatilization of seawater (Chetelat et al., 2005). The highest $\delta^{11}\text{B}$ we measured for rainwater is 33.4‰ (**Table 1**), but coastal precipitation can be much heavier (Chetelat et al., 2005). Therefore, we suggest that the high $\delta^{11}\text{B}$ endmember of Callahans Beach results from boric acid volatilization of seawater,

resulting in a higher $\delta^{11}\text{B}$ coastal precipitation endmember (**Figure 6B**). The highest $\delta^{11}\text{B}$ value for Callahans Beach, 42.5‰ (CH4, November 2017; **Table 3**) has relatively low NO_3^- concentrations ($3.7 \text{ mg NO}_3^- \text{ L}^{-1}$ or 0.84 mg N L^{-1}), similar to the N concentration of regional precipitation (Suffolk County Government, 2019). In the ensuing analysis, this sample is assumed to represent the B endmember of regional coastal precipitation.

Mixing relationships between sea spray and coastal precipitation were examined with respect to septic waste (1.5‰), animal manure (26‰) and fertilizer (9‰ ; **Figure 6B**). Sea spray B concentrations were assumed to represent 5% of measured seawater concentrations. Notably, because there is little change in [B] for a large range in $\delta^{11}\text{B}$, no single mixing curve will fit all of the Callahans Beach data. Therefore, it is not possible to demonstrate with certainty using B whether the N source is derived from fertilizer or septic waste (via individual homeowner cesspools). However, the range of values demonstrates that there is not one single endmember, consistent with our knowledge that groundwater NO_3^- within this watershed is derived from multiple non-point sources.

Coastal groundwaters collected during 2014 and 2015 are distinct in $\delta^{18}\text{O}-\text{NO}_3^-$ and $\delta^{11}\text{B}$ compared to samples from the same wells collected during 2017 (**Figure 3**). The B signatures of several 2015 samples match precipitation endmember B signatures, suggesting that recently recharged groundwaters obtain B and N from precipitation (**Figure 6A**). Importantly, this data demonstrates annual variability in groundwater flow and contaminant transport to LIS. While coastal groundwaters collected throughout 2017 showed relatively higher values of $\delta^{11}\text{B}$, it remains to be seen how contaminant delivery varies over longer time periods for this sole-source, unconfined aquifer.

Synthesis and Conceptual Model

In the coastal systems studied here, B and NO_3^- are added to the groundwater system in different ways, and are impacted by precipitation and seawater (sea spray versus boric acid volatilization) differently (Figure 7). Precipitation and seawater both have relatively low N concentrations ($<1 \text{ mg L}^{-1}$). Seawater is a distinct endmember, due to its high [B] and its isotopically high $\delta^{11}\text{B}$ signature (Figure 7). Boric acid volatilization of seawater produces isotopically high B, and thus gives a very distinctive low B concentration endmember for coastal precipitation. It is interesting that two subterranean estuaries from similar settings have distinct sources of 'uncontaminated' waters. One has to consider differences in pathways for B from both fertilizer and septic waste. In the case of fertilizer, plants use B as a micro-nutrient, and so the concentration of B that is added to the groundwater system will be lower than what was applied to the land surface. In contrast, [B] in septic waste does not change. Therefore, homeowner cesspools likely reflect different sources of B and NO_3^- to the groundwater system (Figure 7). Septic waste $\delta^{11}\text{B}$ integrates multiple contaminant sources, including detergents, commercial cleaning products and human waste. Given the low $\delta^{11}\text{B}$ signature of septic waters (Table 2), B in detergents must dominate the B signature of septic waste. In contrast, human waste is the primary N source in septic waste and therefore B and N are decoupled in septic systems (Figure 7). Importantly, there is no relationship between B and NO_3^- concentrations in either of the studied subterranean estuaries (Figure 2).

CONCLUSION

Application of boron isotopes in coastal settings is vulnerable to the influence of seawater (via sea spray), which has orders of magnitude higher boron concentrations compared to various contaminant sources. Identification and discrimination of NO_3^- and B sources in coastal settings thus requires (1) adequate characterization of local sources (both natural waters and contaminants) and (2) an understanding of biogeochemical processes within the STE. Coastal groundwaters are collected from beaches in SGD studies to integrate terrestrial

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groundwater flow paths over the entirety of the coastal watershed and to account for any biogeochemical processes (i.e., denitrification) in the STE that would influence N concentration and speciation prior to discharge. The advantage of collecting coastal groundwater to account for N transformation may thus hinder the utility of B as an auxiliary N source tracer if seawater significantly modifies subsurface geochemical signatures. The results from this study demonstrate the utility of multi-isotope tracing techniques to identify N sources in polluted coastal aquifers. Future studies should explicitly measure isotopic values of different possible endmembers in order to constrain local variability in N and B sources.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

CB and JT collected the field data under the supervision of HB, JC, and ER. Boron isotopes were analyzed in the lab of ER. All authors participated in the data analysis and interpretation.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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