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Indicators of nutrient pollution in Long Island, New York, estuarine environments

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Abstract

Roughly eight million people live on Long Island, including Brooklyn and Queens, and despite improvements in wastewater treatment, nearly all its coastal waterbodies are impaired by excessive nitrogen. We used nutrient stoichiometry and stable isotope ratios in estuarine biota and soils to identify water pollution hot spots and compare among potential indicators. We found strong gradients in $\delta^{15}\text{N}$ values, which were correlated with watershed land cover, population density, and wastewater discharges. Weaker correlations were found for $\delta^{13}\text{C}$ values and nutrient stoichiometric ratios. Structural equation modeling identified contrasts between western Long Island, where $\delta^{15}\text{N}$ values depended on watershed population density, and eastern Long Island where $\delta^{15}\text{N}$ values reflected agriculture and sewage discharges. These results illustrate the use of stable isotopes as water quality indicators, and establish a baseline against which the efficacy of strategies to reduce nutrients can be measured.

Keywords

Eutrophication; stable isotope; denitrification; urbanization; pollution monitoring; water treatment

1. Introduction

The extent and severity of surface and groundwater impairments due to excessive nitrogen (N) is an issue of concern for Long Island, New York residents, ecosystems, utility providers, and regulatory agencies (Suffolk Co. 2014). The combination of high population density, inadequate and aging infrastructure, geographic isolation, and porous unconsolidated soils contribute to a wide variety of water quality issues, including drinking

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water contamination, combined and sanitary sewer overflows, and poor estuarine water quality (Eckhardt and Stackleberg 1995; Protopapas 1999; Wallace and Gobler 2015). Despite improvements in wastewater treatment, many of which occurred after the passage of the Clean Water Act in 1972 when most of the region's wastewater treatment plants (WWTPs) were upgraded (Brosnan and O'Shea 1996), nearly all New York City and Long Island coastal waterbodies are listed as impaired or impacted with respect to excessive N inputs (NYSDEC 2016). Poor water quality in Long Island estuaries has been linked to harmful algae blooms (Anderson et al. 2008), declines in shellfish and eelgrass beds (Gobler et al. 2009), and possible loss of tidal wetlands (Wigand et al. 2014). Groundwater is the sole source of potable water for Nassau and Suffolk Counties (2.8 million residents) (Kimmel 1984), yet some Long Island wells exceed the EPA 10 mg L⁻¹ standard for nitrate in drinking water, and nitrate levels in groundwater have increased significantly over past decades (Suffolk Co. 2014). In addition, changing climatic conditions, such as increasing frequency of extreme precipitation events (Easterling et al. 2000) and higher air and sea surface temperatures (Hayhoe et al. 2008) are likely to exacerbate water quality issues further (Whitehead et al. 2009). Addressing water quality issues as a component of climate adaptation planning is both timely and essential for the restoration and protection of ground and surface water as well as coastal habitats such as seagrass beds that depend on clean water.

Principal sources of N to Long Island watersheds include wastewater, atmospheric deposition, and fertilizer use (Kinney and Valiela 2011; Vaudrey et al. 2016). On western Long Island, wastewater derived N-loads are high as many WWTPs lack tertiary treatment, and in New York City combined sewer overflows are common. On eastern Long Island, much of Suffolk County (~90%) and parts of Nassau County rely on cesspool or septic systems for wastewater treatment, which are poor removers of nutrients (Nixon et al. 2008), and within a geologic setting of permeable outwash soils, contribute to poor water quality in estuaries through nitrate-enriched groundwater underflow (Johannes 1980). Atmospheric deposition, which accounts for a significant proportion of land-derived N loads in the region, is derived primarily (ca. 90%) from fossil fuel burning (i.e. vehicle emissions, electrical utilities, industrial boilers) occurring in the airshed. Fertilization is also thought to play a significant role in watershed N loads on Long Island (Flipse et al. 1984). Lawns occupy a substantial portion of landcover for Nassau and Suffolk Counties (25% for Suffolk Co. in 1970s; Koppelman 1978), the majority of Long Island home water use goes towards lawns (Jones 2013), and a large fraction of fertilizer sales in Suffolk County are for home use (Suffolk Co. 2014).

Several approaches have been undertaken or are being considered to improve water quality for drinking water and downstream ecological communities both on Long Island and in urban areas around New York City. N removal upgrades required under the Long Island Sound TMDL (2000) have been completed for WWTPs discharging into Long Island Sound, and an oceanic outfall is being considered for the discharge of wastewater from Bay Park WWTP in southwest Nassau County. In Suffolk County, which encompasses the eastern two-thirds of Long Island, the portion of homes connected to sanitary sewers increased from 2% in 1969 to 25% in 2014. In addition, zoning laws limit the density of new housing construction in areas not served by sewage treatment, sewer line installation has been

prioritized based on depth to water table, housing density, and waterbody impairment status (Suffolk Co. 2014), and subsidies are available for installation of advanced septic systems (Grymes 2017). Connecticut's Department of Energy and Environmental Protection has developed an innovative incentive-based N-trading program that has led to substantial reductions in N loading to Long Island Sound from Connecticut, which could improve water quality along Long Island's northern coast (Bennett et al. 2000). In nearby New Jersey, home fertilizer use has been restricted, with the goal of improving aquatic ecosystem health (Kennish et al. 2016). In response to recent reports documenting continued water quality declines (Suffolk Co. 2014), and major water quality issues associated with impacts of Superstorm Sandy in 2012 (Buxton et al. 2013), additional state programs, incentives, and infrastructure developments to improve water quality are proposed.

The aim of this study was to apply stable isotope ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$) and nutrient stoichiometric ratio-based methods (C:N, N:P, C:P) to assess relative nutrient impairment status for Long Island estuaries. This method enhances and offers significant benefits over water quality sampling programs, where sparse data, spatial and temporal biases, and basin heterogeneity complicate interpretations (Smith et al. 1997).

High concentrations of foliar N and phosphorus (P) have been associated with N and P enriched conditions, respectively, in studies involving coastal marsh species (e.g. Broome et al. 1975; Castro et al. 2007), as plants incorporate nutrients in their tissues as a function of supply (US EPA 2002). Tissue molar stoichiometric ratios (C:N, C:P, N:P) are often employed as an indicator of relative nutrient enrichment as ratios are often more consistent across macrophyte species (Sardans et al. 2012).

Stable N isotopes are used to reconstruct N source, as well as to assess N processing. Potential sources of N have contrasting stable N isotope ratios ($\delta^{15}\text{N}$), ranging from -4‰ to $+4\text{‰}$ for nitrate in Long Island Sound (Boon 2008), -2‰ to $+3\text{‰}$ for atmospheric deposition (Elliott et al. 2007), -3‰ to $+2\text{‰}$ for inorganic fertilizers (Kreitler et al. 1978), and $+10\text{‰}$ to $+20\text{‰}$ for human wastewater (Aravena et al. 1993). As the relative percentage of N derived human wastewater increases, the stable isotope ratio of the plant becomes enriched (Cole et al. 2004; Wigand et al. 2007). Additionally, many studies have linked elevated ^{15}N concentrations with elevated water column DIN values (Fry and Allen 2003; Oczkowski et al. 2008). Regardless of the proximate N source, water column denitrification discriminates against the heavier vs. the lighter isotope, leading to a large isotope effect and an ^{15}N enriched DIN pool. Thus elevated $\delta^{15}\text{N}$ may be reflecting either higher source values, processing, or some combination of both. Carbon stable isotopes are also known to reflect nutrient enrichment, as carbon limitation reduces discrimination against ^{13}C in highly productive environments (Livingston et al. 1999; Oczkowski et al. 2014).

In this study, we surveyed the spatial distribution of stable isotope and nutrient stoichiometric ratios for soil, the macrophyte *Spartina alterniflora*, estuarine fish (*Fundulus* spp.) and mudsnail populations (*Nassarius obsoletus*) across the west-east population density gradient of Long Island, and among estuaries whose watersheds vary in land use and WWTP inputs (Fig. 1). We analyzed relationships between isotope and stoichiometric ratios in estuarine biota and population density and land use patterns to characterize the sensitivity of

estuarine biota to anthropogenic nutrient pollution. We also used structural equation modeling to examine interrelationships between different indicators of watershed disturbance, including percentage of agricultural land, percentage of natural lands, sewage inputs, and watershed population density with N isotope response variables. Our research objectives were to screen coastal habitats for evidence of elevated nutrient loads from anthropogenic sources, and to advance interpretation of stable isotope and nutrient stoichiometric ratios in estuarine biota as indicators of nutrient pollution.

2. Materials and Methods

2.1. Study Area

Long Island is a coastal island, part of the U.S. State of New York, and extends 200 km northeastwards from New York harbor into the Atlantic Ocean (Fig. 1). Geologically, Long Island is formed by two spines of glacial moraines and an abutting southerly outwash plain: this geological structure explains the permeable soils, north to south landscape gradients, and forked morphology of eastern Long Island. The southerly expanse of the island is fronted by a system of barrier beaches, spits, and islands intersected by tidal inlets forming a series of embayments, including the Hamptons Bays, Moriches Bay, the Great South Bay, Hempstead Bay, and Jamaica Bay. About 8 million people reside on Long Island, which includes urban and high population density Kings and Queens Counties (the New York City Boroughs of Brooklyn and Queens; which have population densities of 13,656 and 7935 km⁻², respectively), suburban and developed Nassau County (1817 km⁻²), and less densely populated, but rapidly growing Suffolk County (632 km⁻²; US Census 2014). Land use on western Long Island is primarily urban; for eastern Long Island, land use is a mixture of urban (in villages), with forested land on the southern fork (Pine Barrens), and agricultural lands on the north fork. Agriculture is dominated by high-value crops; 75% of sales consist of greenhouse, nursery, floriculture, and sod products (USDA 2009).

2.2. Isotope, Stoichiometric and Soil Analyses

Stable N and carbon isotope ratios ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$) were analyzed for soils, the marsh macrophyte *Spartina alterniflora*, and for two estuarine consumers: the eastern mudsnail *Nassarius obsoletus* and a combination of mummichogs and striped killifish (*Fundulus heteroclitus* and *Fundulus majalis*) collected from 45 study locations in Long Island (Fig. 1; Table 1). Nutrient molar stoichiometric ratios (C:N, C:P, N:P) were analyzed for soils and *S. alterniflora*.

Plant and soil collections targeted populations of *Spartina alterniflora* of intermediate height that were approximately 5m from tidal channels at five separate locations within each estuarine wetland (selected at random, spaced by >10m distant). Soil cores (0–3cm) were dried, and milled using a Spex Shatterbox 8530. Green shoots of *Spartina alterniflora* were collected on one to four occasions spanning seasonal and inter-annual time-scales (2012–2015). Macrophyte shoot samples were processed whole, and clipped, ground, and homogenized using a Thomas Wiley Mini-Mill.

Fish were caught on the marsh platform at high tide or in marsh channels using dip nets. Ten fish of the genus *Fundulus* were caught per site. The heads of the fish were removed, and fish were gutted prior to analysis. Fish were analyzed as composites of five fish each. Fish were homogenized by mortar and pestle. At each site, fifty mudsnails (*N. obsoletus*) were caught, apart from two sites where *N. obsoletus* were not found and *Littorina littorea* (common periwinkle, a non-native species) were collected. All snail samples were gutted and separated into tissue and shell, and homogenized using a Spex Shatterbox. All fish and snail samples were dried at 50° C prior to homogenization.

To measure carbon and N elemental concentrations and stable isotope ratios, subsamples were introduced into a Vario Cube elemental analyzer interfaced to an Isoprime 100 isotope ratio mass spectrometer (IRMS). Isotope ratios for carbon and N are reported in permille

notation as: $\delta^a X = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000 \text{ ‰}$ where R is the abundance ratio of the less

common (a) to more common isotope (Dawson et al. 2002). The standard for N is atmospheric N gas; the standard for carbon is PeeDee Belemnite; by definition standards have $\delta=0$. Percent P was determined using a dry oxidation method modified from Ruttenberg (1992). Solubilized total phosphorus was measured using a Alpkem Autoanalyzer. All samples were analyzed in duplicate for stable isotope and elemental composition (apart from the P analyses, where duplicates were run every 10 samples) with a mean difference between duplicates of 0.1‰ for $\delta^{13}\text{C}$, 0.07‰ for $\delta^{15}\text{N}$, and 0.7 for the C:N ratio.

Soil salinity was measured by reconstituting dried homogenized soils with a 5:1 ratio of water to soil, allowing the mixture to equilibrate, centrifuging, measuring salinity on the supernatant, then back-calculating soil salinity based on the original measured soil moisture (Watson and Byrne 2009). Salinity was measured using a YSI 63 handheld conductivity meter.

2.3. Geospatial Analyses

Catchment areas were delineated for each estuary using the National Hydrography Watershed Boundary Dataset (WBD) at the subwatershed hydrologic unit level (12) (USGS 2013). Land use patterns for each watershed were assessed by clipping NOAA 2011 land cover data (Homer et al. 2015) to each hydrologic unit. Land use patterns were recalculated excluding areas of open water (15–60% of the watersheds) and herbaceous wetlands. Population patterns were examined by clipping the WBD dataset to census block level tiger/line shapefiles (US Census 2016) with a joined population geodatabase. Population density was calculated for each sub-watershed.

WWTP outfalls within 10 km of each sampling location were identified and mapped using the New York State Pollutant Discharge Elimination System (SPDES) (NYSDEC 2004). An index of WWTP influence was calculated for each sampling site as:

$$WWTP \text{ Index} = \sum_{i=1}^n \frac{D_1}{d_1} + \frac{D_2}{d_2} + \frac{D_3}{d_3} + \dots + \frac{D_n}{d_n}$$

where D is the permitted discharge for each outfall (in millions of gallons per day) within 10-km and d is the proximity of the outfall in km to the collection site.

2.4. Data Analysis

Hierarchical cluster analysis was used to group together estuaries with similar chemical signatures using average linkages based on squared Euclidean distances. A correlation matrix was produced to examine relationships between nutrient stoichiometric and stable isotope ratios. Spatial patterns in chemical signatures of estuarine biota, and mean values by water body were tabulated and compared statistically using ANOVA. For two of the variables (soil C:N ratio and macrophyte $\delta^{15}\text{N}$), data did not meet equal variance assumptions for a parametric test, and were calculated on ranks.

Principal components analysis (PCA) was used to collapse correlated data ($\delta^{15}\text{N}$ of sediment, snails, fish, and macrophytes, and C:N and C:P ratios of plants and soils) to one significant principal component (PC). The first PC score was then regressed against land use and population density for sub-watersheds, the WWTP index, salinity, and longitude using partial least squares (PLS) regression. Population density and the WWTP index were log-transformed prior to analysis. Longitude was included as a predictor variable primarily as a proxy for the influence of the position of the site within the broader east-west gradient in population density and land use found on Long Island. The relative impacts of predictor variables were examined using variable importance for projection (VIP) coefficients for the full model, and step-wise PLS regression models that left out certain classes of variables. PLS regression analysis was used to identify which stable isotope and stoichiometric ratios were most reflective of indicators of nutrient pollution (longitude, land use, WWTP discharges, salinity as an indicator of freshwater inputs, and population density) based on correlation.

Seasonal variability was analyzed for marsh macrophyte $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, and C:N ratio from five focus sites that varied in watershed land use and population density using repeated measures ANOVA. Within-site variability was assessed for macrophyte shoots collected 18–20 August 2014. For all data analyses that required observations for each variable (including SEM analyses described below), mean values were substituted where data was unavailable (e.g., snails were not located at two sites).

2.5 Structural Equation Modeling

Structural equation modeling (SEM) is an approach that statistically tests networks of dependencies rather than the overall net effects typically addressed through multivariate regression. SEM models include latent variables that were not directly measured, but for which measured variables serve as indicators. Researchers build and specify an *a-priori* model based on acquired knowledge, which is tested and adjusted based on observed variables. The null hypothesis (H_0) of SEM is $H_0: \Sigma = \Sigma(\theta)$ where Σ = the model calculated covariance matrix and $\Sigma(\theta)$ = the observed data covariance matrix, where SEM seeks acceptance of the null hypothesis (Grace 2006; Paudel and Montagna, 2014). Here, SEM was used to examine dependencies between indicators of watershed disturbance and N inputs with $\delta^{15}\text{N}$ values for soil, macrophytes, and resident estuarine biota. Specific

indicators of disturbance in N inputs included population density, the percentages of developed, agricultural, and natural land at the sub-watershed hydrologic unit level, and permitted sewage inputs using the WWTP index detailed above. Watershed development, nutrient sources, habitat-N, and biota-N were considered latent variables. Data were divided into two different data sets to identify where significant differences in relationships occurred in eastern vs. western Long Island. Alternative models were tested, and models that fit the data well were selected.

Unstandardized path coefficient represent the effects of predictor variables on response variables based on the absolute slope of relationship (Grace 2006). Maximum likelihood was used to evaluate the goodness of fit between observed and predicted covariance. The SEM model was evaluated using a chi-square test and the ratio of chi-squared to degrees of freedom as indicator resilient to the impacts of sample size (Schermerle-Engel et al., 2003; Paudel and Montagna, 2014). The root mean squared error of approximation (RMSEA) and standardized root mean square residual (SRMR) were used as an index of overall model fit. Bentler's comparative fit index (CFI) was used as an index for model comparison. The LAVAAN and SEM packages in R were used to perform and compare SEM models. The model summary was obtained by syntax fit.measures=TRUE (Supplementary Material).

3. Results

3.1 Stable Isotopes and Nutrient Stoichiometric Ratios

Analysis of stable isotope composition of soils and estuarine biota revealed strong gradients in $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values across Long Island. Cluster analysis revealed that clusters based on nutrient stoichiometry and stable isotope ratios largely reflected the east-west gradient in watershed development, with estuaries that fringed the same water bodies having more similar nutrient profiles than estuaries that fringed distant water bodies (Fig. 2). This analysis also permitted identification of estuaries that were associated with significantly higher or lower nutrient loads than other surrounding estuaries. For example, West Harbor, Barleyfield Cove (on Fishers Island), and Ram Island (off Shelter Island) clustered with estuaries on Long Island Sound (Hutchinson River in the Bronx, Frost Creek and East Creek). These estuaries were therefore found to be associated with more degraded water quality than expected based on their location away from population centers on western Long Island. Hospital Point, in the Great South Bay, clustered with areas with better water quality.

Analyses of the inter-relationships between nutrient stoichiometry of soils and macrophytes, and stable isotope ratios of soil, macrophytes, snails, and fish revealed strong positive correlations between $\delta^{15}\text{N}$ in estuarine biota and soils $0.50 < r^2 < 0.65$ (Fig. 3). Interrelationships for $\delta^{13}\text{C}$ in estuarine biota and soils were generally weaker. Moderate correlations were found amongst soil and macrophyte stoichiometric ratios, and weak correlations were found between soil and macrophyte stoichiometric ratios and stable isotope indicators (Fig. 3).

Stable isotope ratios of estuarine soils and biota varied based on water body (Fig. 4, 5). Higher $\delta^{15}\text{N}$ and lower $\delta^{13}\text{C}$ values were found for wetlands in Jamaica Bay, Hempstead Bay, and fringing Long Island Sound, and lower $\delta^{15}\text{N}$ values and more enriched $\delta^{13}\text{C}$ values

were found for Shelter Island Sound and the Peconic Bays. For $\delta^{15}\text{N}$ values, the greatest separation between waterbodies was found for soil values, which ranged from 0.89 to 10.2‰ (Fig. 5). Although similarly wide ranges were found for macrophyte and killifish $\delta^{15}\text{N}$ values (ranges of 9.3 and 9.2‰, respectively), less statistically significant differences were found among waterbodies (Fig. 5). Mudsnailed had the smallest difference between minimum and maximum $\delta^{15}\text{N}$ values (7.5‰), and a low level of separation among water bodies. For $\delta^{13}\text{C}$ values, the greatest amount of separation among water bodies was found for macrophyte values, which only varied by 1.7‰. There were no significant differences among waterbodies for macrophyte and soil stoichiometric ratios, nor for soil $\delta^{13}\text{C}$ ratio (Fig. 5).

Mapping spatial patterns in stable isotope ratios showed strong east-west gradients in $\delta^{15}\text{N}$ ratios across Long Island (Fig. 4a). This was confirmed by regression analysis that showed significant relationships between longitude and stable N isotope ratios for soil, mudsnails, and killifish (Table 2). A significant east-to-west correlation was also found for macrophyte $\delta^{13}\text{C}$ ratios (Fig. 4b; Table 2).

Results of the PCA for the chemical indicators suggested that PCA analysis was appropriate based on the Kaiser-Meyer-Olkin measure of sampling adequacy (>0.5), Bartlett's test of sphericity ($p<0.0001$) and anti-image correlations. The first principal component (PC), accounted for 35.6% of the variance and had an eigenvalue of 5.0. Loadings in order of weight for the first PC (largest to smallest) were: snail $\delta^{15}\text{N}$ (0.91), macrophyte $\delta^{15}\text{N}$ (0.87), soil $\delta^{15}\text{N}$ (0.86), fish $\delta^{15}\text{N}$ (0.81), soil $\delta^{13}\text{C}$ (0.51), and fish $\delta^{13}\text{C}$ (0.35).

The combination of population density, longitude, the WWTP index, salinity, and land use categories accounted for 61% of the variability in the composite chemical index ($r^2=0.61$, $p<0.0001$). The variable importance for projection factors were significant for all predictors except the developed open space and shrub/scrub land use category. The values that the model weighted highest were population density, longitude, and the mixed forest land use category. Building step-wise PLS regression models revealed that substituting summary land use values (agricultural, developed, and natural land cover) rather than the detailed categories resulted in a significant drop in the predictive power of the model (r^2 of 0.51 vs. 0.61). Leaving out other individual indicators (salinity, population density, longitude, and the WWTP) did not reduce the predictive power of the model due to the large amount of overlap between predictors.

A significant relationship between predictor variables and chemical indicators was present for all stable isotope and stoichiometric ratios measured (Table 2). The amount of variance explained ranged from 29% for the soil CP stoichiometric ratio to 80% for soil $\delta^{15}\text{N}$. For $\delta^{15}\text{N}$, values were greater in estuarine soils and biota where population density was higher, WWTPs were higher, and land cover included mostly developed categories. For stable carbon isotopes, $\delta^{13}\text{C}$ values were more negative for macrophytes and soil in western Long Island, while $\delta^{13}\text{C}$ values for fish and snails were more closely correlated with salinity and land use, with more negative $\delta^{13}\text{C}$ values found for areas with high forest cover and low salinity. Soil and macrophyte C:N and C:P ratios generally followed expected patterns with high population density and more developed land use categories associated with lower ratios

(i.e., more N and P relative to C). Macrophyte NP ratios were higher for western Long Island.

Holding the plant species and collection zone constant, the standard deviation of $\delta^{15}\text{N}$ values for macrophytes collected in August 2014 ranged from 0.5 to 2.1‰ within each site, and from 0.1 to 0.2‰ for $\delta^{13}\text{C}$ (Fig. 6). The standard deviation for macrophyte C:N ratios ranged from 3.1 to 14.5. For plant samples collected across seasons and years, neither $\delta^{15}\text{N}$ nor $\delta^{13}\text{C}$ values were found to vary significantly between seasons ($F_{1,9}=1.05$, $p=0.29$; $F_{1,9}=1.63$, $p=0.22$). Late fall macrophyte samples were found to have significantly lower C:N ratios ($F_{1,9}=14.1$, $p=0.02$). Qualitatively, the highest separation between site C:N values was observed for spring-collected samples (Fig. 6).

3.2 Structural Equation Modeling

A hypothesized model that assumed WWTP inputs modulated land use and watershed characteristics did not converge (Fig. 7), however an alternative model that considered watershed development and nutrient point sources separately converged and fit well with the data (Fig. 8). Eastern and western Long Island were modeled separately. The key difference between eastern and western Long Island models was that the model for western Long Island included percentage of natural land as an indicator variable for both nutrient point sources and watershed development, while for eastern Long Island, the model did not converge with use of that measured variable. Also, for western Long Island, some nutrient sources (agriculture, WWTP discharges) did not directly significantly impact habitat N availability, while such linkages were found to be present for eastern Long Island. Also, soil salinity did not modulate habitat-N availability for western Long Island, while a slight effect was apparent for eastern Long Island.

The alternative models included four latent variables: watershed development, nutrient point sources, habitat-N availability, and biota-N availability. These alternate models had two indirect paths from watershed development to biota. The fit indices of alternative east and west Long Island models using maximum likelihood estimation identified close fit with the observed data (Table 3). The alternative models explained 38% and 29% of variation in biota-N using east and west Long Island models. All the path coefficients of alternative models were significant at 95% confidence interval.

4. Discussion

4.1 Water Quality Assessment

The strong east-to-west gradient in land use and population density on Long Island was mirrored by the N isotope indicators in estuarine biota. Estuarine fish, snails, plants and soils were found to have elevated $\delta^{15}\text{N}$ values for sites located in western Long Island (Figs. 2,4,5), situated in watersheds with high population density, a high proportion of developed lands, and high WWTP inputs (Table 1). These results agree with previous studies that have associated N pollution with elevated $\delta^{15}\text{N}$ through analysis of seston, algae, macrophytes, fish, mollusks, and corals (Umezawa et al. 2002; Cole et al. 2004; Pruell et al. 2006; Risk et al. 2009).

Exceptions to this overall west-to-east gradient were found for Fishers Island and Ram Island, both off eastern Long Island, where indicators of water quality were found to be more degraded than expected, and for Hospital Point (Great South Bay) where water quality indicators were found to be better than expected. There are many factors that might explain potential poor water quality on Fishers Island: primary sewage treatment (Applied Water Management 2013), a population that swells tenfold during summer (Hamilton 2000), large areas of turf (TNC 2014), and illegal sewage discharges resulting from heavy summer boat traffic. For Ram Island, heavy boat traffic and the proximity between the sampling site and an adjacent large golf course likely explain poor water quality registered by chemical indicators. For the Great South Bay, Hospital Point was located directly adjacent to a new oceanic inlet, breached by Hurricane Sandy, and therefore is well-flushed with a lower residence time than for other regions of the Bay (Hapke et al. 2013).

These exceptions highlight patterns in coastal water quality that are deserving of attention when shifts in management or new regulations are being considered. Residence time is a key modulator of coastal water quality (Cloern 2001), and as such, may exacerbate or ameliorate nutrient pollution originating from uplands. When estuarine residence time is short, land-derived N loads are exported to the ocean (Dettman 2001). In contrast, where residence times are long, N remains in the estuary, and is taken up and recycled by phytoplankton, algae, and estuarine consumers, and denitrified (Josefson and Rasmussen 2000). Long residence times may be especially reflected in stable N isotopes, as extended opportunities are provided for denitrification, and thus enrichment of the nitrate pool in ^{15}N (Oczkowski et al. 2008). While management of tidal exchange is not always possible and may not be the preferred management tactic, it is one intervention to consider for backbarrier estuaries, such as those common in New York.

This study also aimed at comparing eastern with western Long Island in terms of water quality, as symptoms of nutrient pollution have been increasingly documented in eastern Long Island, including harmful algal blooms (Gobler and Sañudo-Wilhelmy 2001), declining seagrass populations (Peterson et al. 2013), and elevated groundwater nitrate concentrations (Suffolk Co. 2014). Stable N isotope analysis suggests that eastern Long Island supports significantly better water quality than western Long Island (Figs. 4), however, given the high population density of western Long Island and known water quality issues (O'Shea and Bronson 2000), that such a contrast exists does not mean that eastern Long Island water quality is acceptable. To better assess current nutrient pollution levels relative to baseline values, studies that focus on proxy records are greatly needed. Such approaches may include the analysis of sediment $\delta^{15}\text{N}$ values in dated sediment cores (Wigand et al. 2014), a comparison of $\delta^{15}\text{N}$ values in modern and fossil mollusk shells (Oczkowski et al. 2016), or analysis of diatoms in dated sediment cores (Anderson et al. 1993).

4.2 Evaluation of Chemical Indicators

Previous studies have applied a N isotope method to assess relative impacts of N pollution and/or wastewater on the coastal marine environment (Tucker et al. 1999; Cole et al. 2004), and this method has additionally been applied in lakes (Lake et al. 2001) and river systems

(Anderson and Cabana 2005). Molar nutrient stoichiometric ratios in macrophytes and soils have also been recommended as a tool to identify patterns of excess nutrient concentrations in aquatic ecosystems (Duarte 1990; US EPA 2002), although such ratios are known to be more sensitive to seasonality than stable isotope ratios (Cloern et al. 2002) and have been more commonly used to identify patterns in nutrient cycling (Bowden 1986).

Here we found that the best separation among sites and the highest correlation between watershed characteristics and chemical indicator was found for $\delta^{15}\text{N}$ in soils (Fig. 5; Table 2). Relative to collection of other specimens, soil collections present less disturbance to a wetland area, and do not require sacrifice of vertebrates or invertebrates. In addition, they likely are subject to less variability across seasons than macrophytes, where previous studies have found seasonal variability of 2–4‰ (Cloern et al. 2002; Pruell et al. 2006). We advocate that condition assessments include measurement of this component.

In this study, we found that macrophyte $\delta^{13}\text{C}$ was a strong indicator of watershed nutrient inputs, with light carbon isotopic ratios associated with greater nitrogen levels. Stable carbon isotope fractionation is well documented in plants exposed to fertilization and water stress, although the effect of N availability on shoot $\delta^{13}\text{C}$ varies between C3 and C4 plants due to differences in their photosynthetic systems (Farquhar et al. 1989). High N availability combined with salt water stress has been associated with more negative shoot $\delta^{13}\text{C}$ for *S. alterniflora* in this study, and for C4 plants in general (Dercon et al. 2006). High N availability tends to increase CO_2 uptake, while the effect of water stress is to limit stomatal exchange, which together lead to stronger gradients between atmospheric and intercellular $^{13}\text{C}/^{12}\text{C}$ ratios, and thus more fractionation in shoot tissue (Lasa et al. 2011). In contrast, high N availability in C3 plants has been associated with less carbon isotope fractionation (Cernusak et al. 2008). We also investigated soil salinity as a potential indicator of water stress, but found no relation between macrophyte $\delta^{13}\text{C}$ and salinity. The results of this study suggest that $\delta^{13}\text{C}$ can be indicator of nutrient availability if the taxon is held constant.

In this study, we also found that soil $\delta^{13}\text{C}$ values mimicked the relationship between macrophyte $\delta^{13}\text{C}$ and urbanization (although with less fidelity), as the source of organic matter in the soil is largely *S. alterniflora*. Although fish and snail $\delta^{13}\text{C}$ also reflected environmental variables, their relationship was not as strong as for macrophyte $\delta^{13}\text{C}$, and was largely related with salinity, and to a lesser extent land cover. Here, we hypothesize that more terrestrial detrital material (with a C3 $\delta^{13}\text{C}$ signature) is present in coastal estuaries when salinities are lower or forest cover is greater. Such a pattern is found in Delaware Bay, where particulate organic matter isotope composition is more reflective of terrestrial carbon sources in the upper estuary (e.g., -24‰) with more phytoplankton and algal carbon sources in the lower estuary (-18‰) (Cifuentes et al. 1988).

While previous studies have used the $\delta^{15}\text{N}$ isotopes as water quality indicators, uncertainty in interpretation remains for watersheds where both agricultural fertilizers and human wastewater are large potential sources of nitrate. Although studies have associated high ^{15}N signatures with overall N inputs, as ^{15}N is concentrated through denitrification (Oczkowski et al. 2008), human wastewater tends to be enriched in ^{15}N (Aravena et al. 1993), while inorganic fertilizer is depleted ^{15}N (Gautam and Iqbal 2010). Thus, interpretation of $^{15}\text{N}/^{14}\text{N}$

signatures is often context dependent – with both lighter and heavier $\delta^{15}\text{N}$ potentially indicative of excessive N inputs (Oczkowski et al. 2011). In this context we found that even for sites with large areas of agriculture or turf, we did not see a consistent pattern of lighter than expected $\delta^{15}\text{N}$ based on watershed characteristics. For instance, the most heavily agricultural watershed (Indian Island, at 36% of landcover) had a soil $\delta^{15}\text{N}$ of more than 7‰, well above the average for Long Island. Fishers Island – where golf courses make up 20%+ of the island – also had higher than average $\delta^{15}\text{N}$ signatures (Fig. 5). In contrast, sites with high natural land cover on Shelter Island had the lowest $\delta^{15}\text{N}$ signatures. These results are additionally supported by a previous study of nitrate $\delta^{15}\text{N}$ in shallow groundwater on agricultural fields on Long Island, which found strong contrasts between the N isotope composition of nitrate in fertilizer (–5.9–0.2‰) and shallow groundwater (6.2–6.5‰) suggesting that the “light” signature of fertilizer is not retained even on limited spatial scales (Flipse and Boner 1985). Collectively, these results suggest that $\delta^{15}\text{N}$ in estuarine biota found on Long Island is largely reflective of N load and residence time rather than N source. We caution that context should be considered when employing stable nitrogen isotope ratios as indicators.

4.3 Insights from the Structural Equation Modeling Approach

SEM development provided additional insights into contrasts that exist between eastern and western Long Island and for interpretation of soil and biota $\delta^{15}\text{N}$ ratios. Eastern Long Island estuaries appear to be more sensitive to agricultural and sewage point sources of N, as path coefficients from these variables were significant. In contrast with western Long Island, this path was not found to be significant. Considered in context, this contrast suggests that the high population density on western Long Island and intense development (Eckhardt and Stackelberg 1995) overwhelms other sources, while for eastern Long Island, the influence of human wastewater and agricultural activities are discernable from a background of overall lower nutrient concentrations (LaRoche et al. 1997).

Contrasting models also identified a significant impact of soil salinity on habitat-N for eastern Long Island but not for western Long Island. We hypothesize that lower salinity reflects higher nutrient availability in enriched terrestrial runoff (Paudel et al. 2016). Again, this appears to be plausible for eastern Long Island, but not for western Long Island. We propose that the long residence time of nutrients in Jamaica Bay (Beck et al. 2009) and western Long Island Sound (Williams et al. 1997) reduces effects of dilution by comparatively low-nutrient seawater. Lastly, some contrasts were found between habitat-N and soil and plant $\delta^{15}\text{N}$, suggesting stronger relationship between habitat-N and plant $\delta^{15}\text{N}$ for eastern Long Island, and stronger relationships between habitat-N and soil $\delta^{15}\text{N}$ for western Long Island. It is possible that higher denitrification levels, expected with high nutrient inputs, would be more directly reflected by soil than macrophyte $\delta^{15}\text{N}$ (Kendall et al. 2007). More broadly, this may highlight the importance of soil $\delta^{15}\text{N}$ as a potential indicator or proxy for denitrification, especially in urbanized areas with high nutrient loads.

5. Conclusions

Measurement of N stable isotope ratios ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$) in estuarine biota revealed strong gradients in $\delta^{15}\text{N}$ values, which largely matched the east-to-west gradient in population density and land use found on Long Island. Specific values for $\delta^{15}\text{N}$ ratios ranged from 0.89–10.2‰ for soils, 1.26–13.0‰ for *Spartina alterniflora*, 5.26–14.5‰ for *Fundulus* spp., and 6.64–14.1‰ for *Nassarius obsoletus*. The $\delta^{15}\text{N}$ values measured in the plants, animals, and soils as part of this study were reflective of overall N loads, rather than the $\delta^{15}\text{N}$ signatures of those sources, as we did not see a consistent pattern of lighter than expected $\delta^{15}\text{N}$ in agricultural watersheds. Macrophyte carbon stable isotopes – and to a lesser extent soil $\delta^{13}\text{C}$ – also had a strong relationship with indicators of watershed impairment. In contrast with N stable isotopes, molar nutrient stoichiometric ratios were not found to be highly correlatory with watershed characteristics, and did not display strong patterns of correlation with $\delta^{15}\text{N}$. Monitoring stoichiometric and stable isotope ratios of macrophytes through the growing season and over several years documented seasonal variability in both signatures and ranges between sites, suggesting that the use of $\delta^{15}\text{N}$ or C:N as indicators requires collecting macrophytes during the same season. SEMs suggested that eastern Long Island estuaries are more sensitive to sources of N such as agriculture and WWTP discharges, while for western Long Island high population densities within watersheds overwhelmed the impacts of other sources. It is clear that the high population and poor wastewater treatment infrastructure of Long Island contribute to poor coastal water quality, and that western Long Island's water quality is more impaired than eastern Long Island. Future studies could help clarify impairment status using pre-anthropogenic baselines derived from analysis of dated fossil materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- We investigated water quality indicators for Long Island estuaries
- Stable nitrogen isotopes reflected nutrient pollution
- Structural equation modeling identified geographic contrasts in N sources

Figure 1.

Map of Long Island showing sampling locations, permitted wastewater treatment outfalls (in millions of gallons per day) (NYDEC 2004), population density in people per square km (US Census 2016), and dominant 2011 land cover type (Homer et al. 2015). Numbers for research sites are listed in Table 1. Counties are shown in bold, water bodies in italics.

Figure 2.
Dendrogram of hierarchical cluster analysis based on average linkages of squared Euclidean distances.

Figure 3.

Correlation matrix showing inter-relationships between $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values and molar nutrient stoichiometric ratios in estuarine biota. Where Pearson product-moment correlation coefficients were found to be significant at the $p < 0.01$ level, they are shown in bold. Where coefficients were not found to be significant at the $p < 0.05$ level, they were listed as 'NS' or non-significant.

Figure 4.

(a) Spatial patterns in stable nitrogen isotope ratios across Long Island, including the NYC boroughs of Brooklyn and Queens in soils, macrophytes, snails, and fish. (b) spatial patterns in stable carbon isotope values.

Figure 5.

Differences in stoichiometric and stable isotope ratios in estuarine biota along different waterbodies. Analysis of variance indicated statistically significant differences between sites for $\delta^{15}\text{N}$ for soil ($F_{7,37} = 9.841$; $p < 0.001$), macrophytes ($F_{6,35} = 5.941$; $p < 0.001$), snails ($F_{6,34} = 5.945$; $p = 0.002$), and fish ($F_{6,36} = 6.015$; $p < 0.001$), and for $\delta^{13}\text{C}$ for macrophytes ($F_{6,35} = 4.547$; $p = 0.02$), snails ($F_{6,34} = 3.280$; $p = 0.01$), and fish ($F_{6,36} = 6.377$; $p < 0.001$), although not for molar C:P, C:N, or N:P ratios for soil or macrophytes, nor $\delta^{13}\text{C}$ values for soils. Box and whisker plots denotes range (whiskers), interquartile range (boxes), and

median (vertical line). Results of LSD post-hoc tests are denoted by letters on the figures, with different letters signifying statistically significant differences between sites.

Figure 6.

Within-site and season variability in macrophyte $\delta^{15}\text{N}$ and molar C:N ratios. Within-site variability samples were collected in August 2014, and plots show boxes that encompass minimum and maximum observations and all observed values as lines. Seasonal samples were collected across years: May and July samples were collected in 2013, August samples were collected in 2014, and October samples were collected in 2012. Seasonal variability plots are labeled BB (Black Bank, Jamaica Bay), EC (East Creek, Long Island Sound), FC (Frost Creek, Long Island Sound), HC (Hubbard Creek, The Peconic Bays), and BC (Bass

Creek, Shelter Island Sound). For seasonal variability in macrophyte C:N ratios, different letters reflect differences between sampling dates. Station locations are given in Table 1.

Figure 7.

Initial hypothesized model to predict change in stable nitrogen isotope signature in estuarine biota as a function of watershed characteristics. Arrows show directionality between independent and predictor variables. Ovals represent latent variables, and variables in rectangles were measured. Small arrows denote measurement error.

Figure 8.

This model reflects observed dependencies between watershed characteristics and estuarine soils and biota. Values of path coefficients in bold represent relationship variables in the western Long Island model, while coefficients in italics represent relationship variables for the eastern Long Island model. Dashed lines and dashed box represents variable present in the western Long Island model only. Zero values represent path restrictions present in western Long Island model.

Table 1

Land use and population density for sub-watershed study locations. Developed lands includes developed open spaced, low, medium, and high density development and barren land. Natural land cover includes deciduous forest, evergreen forest, mixed forest, shrub/scrub, grassland, and wooded wetlands. Agricultural lands include pasture and cultivated crops. WWTP discharges are summed for all permitted discharges less than 10km distant.

Map #	Study Site	Northing	Easting	Developed land use (%)	Natural land cover (%)	Agricultural land cover (%)	Population Density km ⁻¹	WWTP Discharge MGD
1	Saw Mill Creek	40.6098	-74.1939	92.13	7.79	0.07	2980	0
2	Spring Creek	40.6595	-73.8561	91.34	8.54	0.12	8540	130.00
3	Blank Bank	40.6225	-73.8305	91.34	8.54	0.12	8540	243.08
4	Big Egg	40.5973	-73.8250	91.34	8.54	0.12	8540	243.08
5	Hutchinson River	40.8732	-73.8207	93.19	6.78	0.03	4090	438.60
6	Pelham Bay Cove	40.8710	-73.8089	93.19	6.78	0.03	2030	293.60
7	Udalls Cove	40.7789	-73.7448	96.04	3.96	0.00	3130	91.30
8	Idlewild	40.6471	-73.7436	97.72	2.28	0.00	4010	78.58
9	Lawrence Marsh	40.5945	-73.7178	96.00	4.00	0.00	1850	123.58
10	East Creek	40.8651	-73.7106	63.65	35.23	1.12	3620	28.40
11	North Greensedge	40.6203	-73.6814	96.00	4.00	0.00	1850	78.58
12	Bay Park Outfall	40.5971	-73.6734	96.00	4.00	0.00	1850	78.58
13	East Meadow North	40.6218	-73.6592	96.00	4.00	0.00	1850	78.58
14	East Meadow East	40.6122	-73.6543	96.00	4.00	0.00	1850	78.58
15	Oceanside Nature Area	40.6188	-73.6205	97.37	1.60	1.03	2310	76.50
16	North Cinder	40.6125	-73.6096	97.37	1.60	1.03	2310	147.50
17	Frost Creek	40.9041	-73.5946	52.58	44.89	2.53	878	7.31
18	Bayville	40.9014	-73.5723	49.35	50.44	0.21	419	7.31
19	Cold Spring Harbor	40.8675	-73.4623	52.58	44.89	2.53	878	4.30
20	Huntington Harbor	40.8971	-73.4330	65.48	31.22	3.29	1370	4.64
21	Northport	40.8930	-73.3548	76.59	23.26	0.15	607	2.84
22	Crab Meadow	40.9240	-73.3234	77.49	22.28	0.23	750	4.04
23	Flax Pond	40.9623	-73.1429	60.81	37.68	1.50	434	3.49
24	Watch Hill	40.6968	-72.9794	82.85	16.55	0.59	499	0.50

Map #	Study Site	Northing	Eastings	Developed land use (%)	Natural land cover (%)	Agricultural land cover (%)	Population Density km ⁻¹	WWTP Discharge MGD
25	Carmans River	40.7676	-72.8941	45.96	49.79	4.26	596	1.99
26	Hospital Point	40.7305	-72.8936	82.85	16.55	0.5	499	1.40
27	Wading River	40.9640	-72.8631	57.51	39.06	3.42	510	0.07
28	Forge River	40.7921	-72.8257	74.60	22.53	2.87	688	0.25
29	Great Gun	40.7628	-72.7787	74.60	22.53	2.87	688	0
30	Indian Island	40.9306	-72.626	24.11	40.07	35.82	178	1.34
31	Hubbard Creek	40.9080	-72.5655	24.11	40.07	35.82	178	1.55
32	Pine Neck	40.8409	-72.5649	64.96	32.35	2.68	215	0
33	Goose Creek	41.0422	-72.4259	46.54	29.86	23.59	150	0.66
34	Hashamomuck	41.0845	-72.4012	46.54	29.86	23.59	150	0.66
35	Cedar Beach	41.0338	-72.3891	36.73	60.48	2.79	82	0.91
36	Pipes Cove	41.0950	-72.3741	46.54	29.86	23.59	150	0.66
37	Ram Island	41.0890	-72.3227	41.93	54.88	3.19	122	0.66
38	Orient Point	41.1408	-72.3178	46.54	29.86	23.59	150	0.66
39	Miss Annie's Creek	41.05432	-72.3096	36.73	60.48	2.79	82	0.91
40	Bass Creek	41.0434	-72.2913	36.73	60.48	2.79	82	0.91
41	Mashomack Point	41.0282	-72.2798	36.73	60.48	2.79	82	0.25
42	Accabonac Harbor	41.0262	-72.1487	56.11	56.11	5.41	70	0.05
43	West Harbor, Fishers Is.	41.2660	-72.0017	25.01	73.99	1.00	304	0.02
44	Barleyfield Cove	41.2771	-71.9548	33.93	66.07	0.00	35	0.02
45	East Harbor, Fishers Is.	41.2863	-71.9386	25.01	73.99	1.00	304	0.02

Table 2

Relationship between predictors and chemical indicators modeled using PLS regression.

Chemical Indicator	r^2	p	Relationship(s)
Soil $\delta^{15}\text{N}$	0.80	<0.0001	More urban ~ high $\delta^{15}\text{N}$
Soil $\delta^{13}\text{C}$	0.37	<0.0001	More urban ~ more negative $\delta^{13}\text{C}$
Soil C:N ratio	0.44	<0.0001	No individual correlations $p>0.10$
Soil C:P ratio	0.29	<0.0001	Western Long Island ~ low CP ratios
Soil N:P ratio	0.32	<0.0001	No individual correlations $p>0.10$
Macrophyte $\delta^{15}\text{N}$	0.61	<0.0001	More urban ~ high $\delta^{15}\text{N}$
Macrophyte $\delta^{13}\text{C}$	0.56	<0.0001	More urban ~ more negative $\delta^{13}\text{C}$
Macrophyte C:N ratio	0.39	<0.0001	More urban ~ low CN ratio
Macrophyte C:P ratio	0.41	<0.0001	High barren land cover ~ high CP ratios Sewage inputs ~ low CP ratios
Macrophyte N:P ratio	0.27	0.0003	High shrub cover ~ high NP ratios Western Long Island ~ low NP ratios
Snail $\delta^{15}\text{N}$	0.62	<0.0001	More urban ~ high $\delta^{15}\text{N}$
Snail $\delta^{13}\text{C}$	0.36	<0.0001	High forest cover ~ more negative $\delta^{13}\text{C}$ Low salinity ~ more negative $\delta^{13}\text{C}$
Fish $\delta^{15}\text{N}$	0.57	<0.0001	More urban ~ high $\delta^{15}\text{N}$
Fish $\delta^{13}\text{C}$	0.49	<0.0001	Low salinity ~ more negative $\delta^{13}\text{C}$

Table 3

Model fit indices for eastern and western Long Island SEM models depicted by Fig. 9.

Model fit indices	Eastern Long Island Model	Western Long Island Model
$\frac{\chi^2}{df}$ (p value for close fit)	1.34 (0.13)	1.46 (0.08)
SRMR	0.10	0.12
RMSEA	0.11	0.14
RMSEA 90% confidence interval	0.00 – 0.20	0.00 – 0.21
P of close fit	0.18	0.11
CFI	0.94	0.92