

**STABLE ISOTOPE ANALYSIS IN THE HUDSON RIVER MARSHES –  
IMPLICATIONS FOR HUMAN IMPACT, CLIMATE CHANGE, AND TROPHIC  
ACTIVITY**

A Final Report of the Tibor T. Polgar Fellowship Program

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## ABSTRACT

Heightened anthropogenic activities such as land-use change and nutrient loading have been shown to affect both the biodiversity and sedimentation dynamics of wetlands, but how have the marshes of the Hudson River Valley been affected by these changes? The study of stable carbon and nitrogen isotopes provides useful records of eutrophication, carbon cycle balance, biological productivity shifts, and trophic linkages pertaining to the wetlands of the Hudson River Valley. To answer the proposed question, records of stable isotopes  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in sediment cores from the marshes of Iona Island, Piermont, Staten Island, and Jamaica Bay were measured using an isotope ratio mass spectrometer (IRMS). Results suggest that  $\delta^{15}\text{N}$  levels in the marshes have increased over time since the first European contact due to agricultural and wastewater input, but decreased in the 1970s due to the increase in the use of synthetic fertilizers. Increasing human populations, however, have possibly caused  $\delta^{15}\text{N}$  to continue to rise in the past couple of decades. The  $\delta^{13}\text{C}$  signal decline in the marshes parallels the disturbance characterized by a rise in the settlement indicator ragweed (*Ambrosia*). However, the signal fluctuates with time, reflecting shifts in the dominant plant species composition within the respective marshes. There also exist gradients in the  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  levels along the transect of the Hudson River. From north to south, the signals for both  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  are enriched, probably due to population increases and sewage effluent in the south and C3 plant dominance in the north and C4 plant dominance in the south, respectively. Results of this research provide important background information for future studies on trophic dynamics in the Hudson River.

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## INTRODUCTION

Often considered the most productive and biologically diverse ecosystems on Earth, tidal river marshes function as habitats for both estuarine and marine life, flood control, and shoreline protection (Morris and Bradley 1999). With intensified anthropogenic alterations in surrounding regions, the need to understand the effects on biological and geological processes in wetlands becomes increasingly more important (Mitsch and Gosselink 2007). Regional land use changes, such as land clearance and nutrient loading, have been shown to affect both the biodiversity and sedimentation dynamics of lakes and marshes (i.e., Chang et al. 2009; Hubeny et al. 2009). However, it is difficult to assess the health of these marshes because baseline data of pre-anthropogenic estuarine conditions are lacking.

Fortunately, the high depositional rates of Hudson River wetlands allow for high-resolution analysis of vegetation shifts and climate change archived in sediment cores (Pederson et al. 2005; Peteet et al. 2006). These characteristics make the marshes useful study sites for paleoenvironmental reconstruction, where a rich and continuous historical record is needed to understand the past.

The study of stable carbon and nitrogen isotopes and C:N ratios, in particular, provides useful records of eutrophication (Hubeny et al. 2009), biological productivity shifts (Hubeny et al. 2009; Chang et al. 2009), the carbon cycle balance (Morris and Bradley 1999), climate shifts (Minckley et al. 2009), and trophic positions (Abrantes and Sheaves 2010; Litvin and Weinstein 2003; Schiesari et al. 2009; Weinstein et al. 2009). A knowledge of all of these factors throughout a long time scale is important because they determine the health and functioning of an ecosystem, and any significant changes

that are noted may indicate a response to either natural or anthropogenic forcings. Stable isotope analysis can help identify many of these signals. This study examined the  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and C:N records in sediment cores from the marshes of Iona Island, Piermont, Staten Island, and Jamaica Bay (Figure 1) to analyze the implications of human impact, climate change, and the food web in the Hudson River Valley. The variability of these isotopes down each core was compared with existing pollen, microfossil and elemental X-ray fluorescence spectrometer (XRF) data (Kenna et al. 2011) to analyze vegetation shifts, land-use changes and pollution history in these sites . Multi-proxy information provides useful evidence of human impact in the region, ranging from European colonization to land clearance and the use of fertilization in modern society. The differences between biochemical processes in fresh and saltwater marshes were also targeted in this study.

#### *Historic record of land use*

It is important to understand the historic timeline of anthropogenic contact with the Hudson River Marshes to correlate land use changes with stable isotope ratios. The Europeans first colonized the Hudson River Valley region in A.D. 1683 (NERR 2009). The clearance of land was a common activity for farms and homes, and vegetation was also cleared for use in construction, fuel, and defense. Iona Island, for example, was used for commercially growing fruits (NERR 2009). During the Revolutionary War, forests in the Hudson River Valley were not only cleared for battles, but also burned to produce charcoal used in the production of iron (Cronon 1983). In Rockland County, where Piermont Marsh and Iona Island are located, the population increased from a total of 219 people in 1693 to a total of 6000 in a 1790 census (Cole 1884). Later on, the Industrial Revolution and national expansion of agriculture would further transform the ecology of

the marshes (Cronon 1983).

### *Stable Isotopes*

The study of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  provide biochemical information on organic matter in the marsh and estuary ecosystems (i.e., Hubeny et al. 2009). These  $\delta$  values, in ‰, are calculated using the equation  $(R_{\text{sample}}/R_{\text{standard}} - 1) * 1000$ , where R is the ratio of rare versus abundant isotope of either C or N with the respective standard (PD-Belemnite and air respectively). Nitrogen is a necessary element for plant, algal, and microbial production. Previous research has indicated that increases in plant biomass and height could result from excess nitrogen in the estuary (Morris 1991). Thus, studying nitrogen stable isotopes is vital in order to gain a better understanding of nutrient changes and to determine whether or not they can be associated with anthropogenic forcings. The study of the stable nitrogen isotope provides a historical record of eutrophication in the regions of interest.

Most of the carbon in marshes is *in situ* and reflects the local dominant vegetation (Brickerurso et al. 1989; Connor et al. 2001; Rooth et al. 2003). Thus the  $\delta^{13}\text{C}$  signature in the marshes reflects the local marsh vegetation composition and decomposition within the marshes. Differences in photosynthetic pathways of two different groups of plants – C3 and C4 plants – result in different degrees of fractionation of atmospheric  $\text{CO}_2$  (Smith and Epstein 1971). Consequently, the two groups of plants have distinct ranges of  $\delta^{13}\text{C}$ . C3 plants have ranges from -23 to -34‰ while C4 plants range from -9 to 17‰ (Chmura and Aharon 1995). Since  $\delta^{13}\text{C}$  in sediments in marshes is mainly derived from the local dominant vegetation (Chmura and Aharon 1995), changes in species composition of vegetation in the marshes will reflect in the shifts in the stable isotope profile. A more

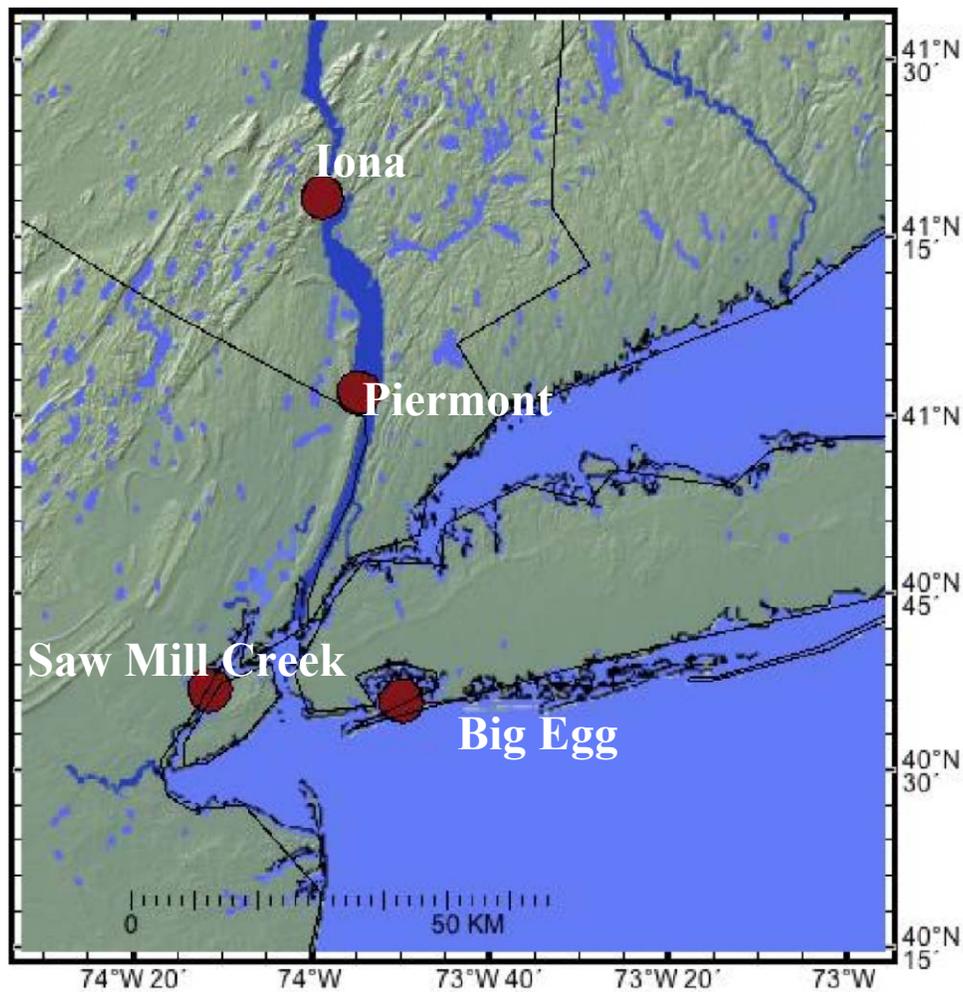
enriched C4 source (i.e. *Spartina*) would have a high  $\delta^{13}\text{C}$  value, whereas  $\delta^{13}\text{C}$  in C3 plants (i.e. *Phragmites*) and aquatic algae sources fluctuate at lower values (Hubeny et al, 2009; Varekamp et al. 2010; McKinley et al. 2009). Stable isotopes of carbon have also been used to better understand the importance of salt marsh primary production in the flux of nutrients to higher consumers (Litwin and Weinstein 2003). The same authors showed that although anthropogenic inputs from upriver may play a minor role in Delaware Bay, local inputs in tidal estuaries are important and detectable. In this study, the organic component of carbon, which required the removal of carbonates, was used to detect the  $\delta^{13}\text{C}$  signature of the sediment, and how it has changed through time.

## METHODS

### 1. Study Sites

Along the 240-km stretch of the Hudson River estuary between New York City and Troy lie a range of wetland habitats. Iona Island is a component site of the Hudson River National Estuarine Research Reserve (HRNERR). Located the furthest north of the four study sites, about 72 km from the Atlantic, the wetlands of Iona Island are slightly brackish (NERR 2009). The salinity values at Iona range from 3-6 ppt (Winogron 1997). There, habitats include brackish intertidal mudflats, brackish tidal marsh, freshwater tidal marsh, and deciduous forested uplands (NERR 2009). The vegetation of Iona Island's marshes is dominated by narrowleaf cattail (*Typha angustifolia*), common reed (*Phragmites australis*), and swamp rose mallow (*Hibiscus moscheutos*) (Buckley and Ristich 1976; NERR 2009). Deciduous forest also covers the island and mainland slopes, including species such as red oak (*Quercus rubra*), chestnut oak (*Quercus prinus*), and pignut hickory (*Carya glabra*) (NERR 2009).

Piermont Marsh , another HRNERR component site, is located approximately 40 km north of the river's mouth (Pederson et al. 2005). There, mean salinity is also 3-6 ppt (Winogron 1997), and the habitats include brackish tidal marsh, shallows, and intertidal flats (NERR 2009). The marsh vegetation of Piermont is dominated by invasive *Phragmites australis*, but species such as saltmarsh cordgrass (*Spartina alterniflora*), saltmeadow cordgrass (*Spartina patens*), big cordgrass (*Spartina cynosuroides*), sturdy bulrush (*Schoenoplectus robustus*), and chairmaker's bulrush (*Schoenoplectus americanus*) are present (Lehr 1967; Blair and Nieder 1993).



**Figure 1. Map of Iona Island marsh, Piermont marsh, Saw Mill Creek marsh, and Big Egg marsh (GeoMapApp, Ryan et al., 2009).**

In comparison, the salt marshes of Staten Island are located along the lower transect of the Hudson River and closer to the Atlantic Ocean, thus having higher salinity values. Saw Mill Creek, located in the northwestern part of Staten Island, is part of the Arthur Kill Complex, which has salinity values ranging from 17 to 27 ppt (U.S. Fish and Wildlife Service 2005). The marshes of Staten Island make contact with the Atlantic Ocean, and are composed of broad expanses of salt meadow fringed by low marsh, forested uplands, rock outcrops, a swamp forest, and many small, spring-fed ponds (DEC 2010). Saw Mill Creek marsh, in particular, is dominated by *Spartina alterniflora*, *Spartina patens*, *Distichlis spicata*, and *Phragmites australis*, which were affected by the oil spill into the marsh in 1990 (DEC 2010).

Lastly, Jamaica Bay, which is the southernmost site, is a back-barrier lagoon containing salt marshes with an average salinity range of 20.5 to 26 ppt (Waldman 2008). These marshes make contact with the Atlantic Ocean via Rockaway Inlet and the system has been designated as a National Wildlife Refuge since 1972 (NY Harbor Parks 2010). However, much of the original tidal wetlands of Jamaica Bay have disappeared as a result of infrastructure development and other contributing factors (Hartig et al. 2002). The marsh is also home to over 330 species of birds, over 60 species of butterflies, and has one of the largest populations of horseshoe crabs in the northeast (NY Harbor Parks 2010). The low marsh is dominated by *Spartina alterniflora*; *Spartina patens* characterizes the high marsh. Where disturbed, invasive *Phragmites australis* is present. The high marsh also has a greater variety of species, such as salt grass (*Distichlis spicata*), black grass (*Juncus gerardii*), glasswort (*Salicornia spp.*), and sea lavender (*Limonium carolinianum*) (Mack and Feller 1990). Big Egg, a high marsh that is part of

the Jamaica Bay marsh system, is the study site. The contrast of the marshes of Staten Island and Jamaica Bay against the less saline marshes of Iona Island and Piermont allows for comparative data in the stable isotope analysis, which provides useful information of stable isotope signatures

### *Sediment Coring*

Sediment cores (each 1 meter in length) were collected from the marshes of Iona Island, Piermont, Staten Island, and Jamaica Bay with a Dachnowski corer from 2007 to 2008. These cores were stored in PVC half pipe liners and D-tube containers with a wet sponge to preserve moisture levels and kept in a refrigerator. The 1 m cores span approximately 1000 years, thus include the pre-European and post-European contact, providing information prior to and after anthropogenic impact. Table 1 summarizes the cores that were obtained for each marsh.

### *Isotope Analysis*

Approximately 5 g of wet sediment was extracted at the surface and every 4 cm for each core (26 samples each) and then freeze-dried overnight. The dry sediment was then ground and homogenized using a ceramic mortar and pestle. Samples were then treated for the removal of carbonates through leaching with 1 M hydrochloric acid. After 24 hours, the samples were rinsed and centrifuged to remove the acid and the water was evaporated overnight at 75°C. Approximately 1 g of the dry residue was homogenized using a mortar and pestle and weighed into tin capsules for stable carbon and nitrogen isotope ratio analysis.

The samples were prepared at the Lamont-Doherty Earth Observatory, while the stable isotope analysis was sent to the Cornell University Isotope Laboratory, where an isotope ratio mass spectrometer (IRMS) was utilized. For quality control, duplicates and standard reference samples were also measured.

*Dating*

Radiocarbon dating has already been determined on macrofossils from Piermont (Pederson et al. 2005), Iona (Chou and Peteet 2010), and Saw Mill Creek (Peteet et al., unpublished data). Macrofossils were selected from sediment cores at these three sites and were radiocarbon dated using an Accelerator Mass Spectrometer (AMS) at Lawrence Livermore National Laboratory. Radiocarbon dates were calibrated using the CALIB program, version 6.0 of Stuiver and Reimer (1993) to determine the calendar ages of the samples.

**Table 1: List of Sediment Cores and Chronology Sources**

<b>Marsh</b>	<b>Sediment Core</b>	<b>Chronology</b>	<b>Source</b>
Piermont	07-Piermont-RC01	Carbon-14 dating; XRF	Pederson et al., 2005
Iona	07-Iona-RC01	Carbon-14 dating; XRF	Chou and Peteet, 2010
Staten Island (Saw Mill Creek)	08-SMC-RC01	Carbon-14 dating, XRF	Kleinstei, D., MS Thesis, 2004; Peteet et al., unpublished data
Jamaica Bay (Big Egg Marsh)	08-Big Egg-RC2	XRF	Sritrairat et al., in prep

## RESULTS

Figures 2 and 3 are downcore profiles of the specified normalized stable isotope versus the respective standard for the four study sites. Each plot has been labeled with calibrated ages based on earlier data (Table 1). The depth at which Pb from XRF results (Sritrairat et al., unpublished) peaked were also marked on the  $\delta^{13}\text{C}$  results of the cores, labeled as the 1970s when Pb in gasoline was banned in the Hudson River Valley region. For all graphs, the y-axis represents the average of the sampling interval of the depth of the sediment core. The x-axis is the normalized stable isotope value in ‰.

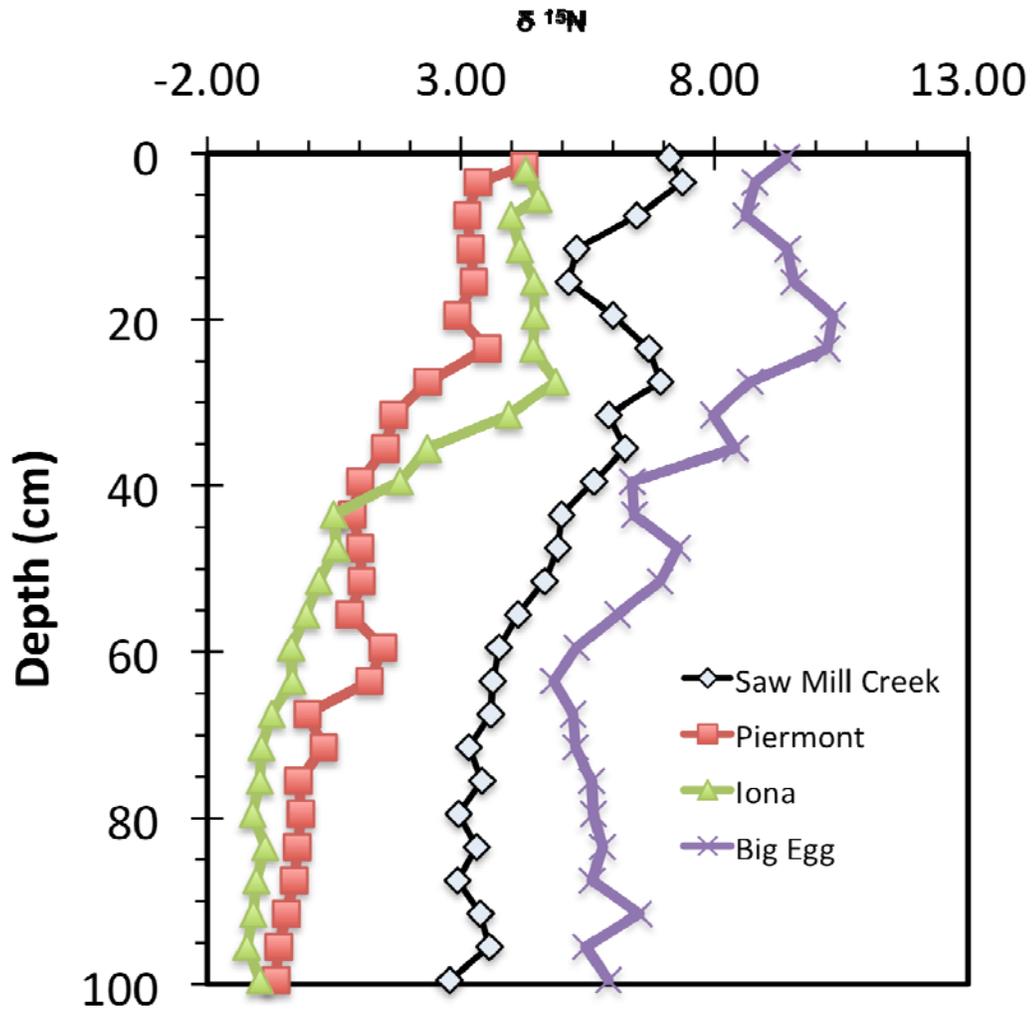


Figure 2:  $\delta^{15}\text{N}$  results

## *Nitrogen*

Figure 2 shows that the  $\delta^{15}\text{N}$  value for the Iona core at the bottom of the meter core is 0.96‰ (the most negative value) and remains stable until about 70 cm. The values increase between 70 and 30 cm, decline slightly between about 30 and 8 cm below the surface, then slightly increase at 5 cm, before decline from 5 cm to the surface. Iona's nitrogen signal is more negative in comparison to the Piermont signal at the bottom of the core, but is more positive than Piermont above 40 cm.

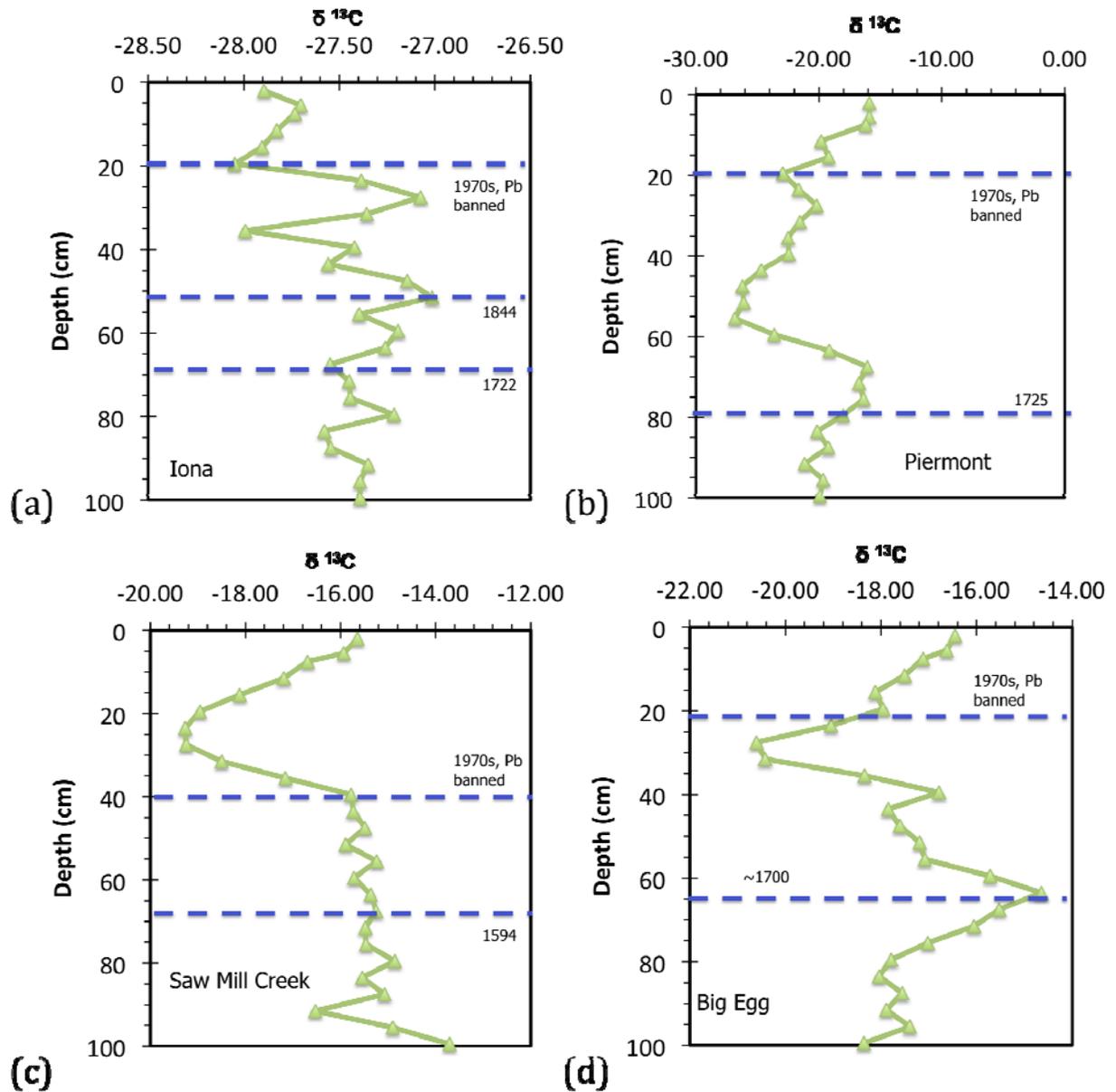
At Piermont, Figure 2 also shows that  $\delta^{15}\text{N}$  initially are -0.64‰ for the Piermont core, and the overall trend is an increasing one. The profile of the stable isotope remains somewhat stable until a depth of about 80 cm, then sharply increases up to 60 cm, then stabilizes from 60 cm to 40 cm but increases again from 40 cm to 20 cm. The values stabilize from 20 cm to 5 cm, but then increase at the surface.

At Saw Mill Creek, Figure 3 shows that  $\delta^{15}\text{N}$  begins at a higher value of 2.78‰ and the overall trend is increasing. A shift is noticeable at 60cm and reaches a peak at 30 cm depth, where values decrease between 30 and 20 cm. The increasing pattern returns above 10 cm.

Finally, the initial value of  $\delta^{15}\text{N}$  at Big Egg is depicted to be 5.91‰ – the highest of all four marshes. The overall trend is again the increasing  $\delta^{15}\text{N}$  values toward the surface. The rise in  $\delta^{15}\text{N}$  is most evident at just below 60 cm below the surface. The increase in  $\delta^{15}\text{N}$ , however, changes at about 20 cm below the surface between 10 and 20 cm, when values decline. Above 10 cm,  $\delta^{15}\text{N}$  again increase.

Carbon

Figure 3a shows that the  $\delta^{13}\text{C}$  value for the Iona core begins at -27.39‰. The values oscillate below 60 cm, but the oscillation trends towards the left and increases in magnitude above 60 cm.



**Figure 3: Delta 13C results with years obtained from C-14 dating and XRF results: (a) 07-Iona-RC01(b) 07-Piermont-RC01 (c) 08-SMC-RC01(d) 08-Big Egg-RC2**

In the Piermont results, the  $\delta^{13}\text{C}$  value starts at  $-19.91\text{‰}$  (Figure 3b). The values oscillate at the bottom of the core, but there is a trend towards higher values until about 70 cm. Above 70 cm, the  $\delta^{13}\text{C}$  values decrease from  $-16.06$  to  $-26.83 \text{‰}$  (at 55 cm). The values then increase above this depth until about 30 cm. Between 20-30 cm below the surface, the values decrease a small amount, but increase again above 20 cm. Above 30 cm, the values have reached a level that is more positive than the initial values.

Figure 3c depicts the  $\delta^{13}\text{C}$  profile with depth for Saw Mill Creek. The starting value at 100 cm below the surface is  $-13.71\text{‰}$ , and values remain close to  $-15\text{‰}$  up to 40 cm. The values then decline to  $-19\text{‰}$  at 25 cm. Above 25 cm, the values increase back to  $-15\text{‰}$ .

For Big Egg marsh, the value of  $\delta^{13}\text{C}$  is  $-18.36\text{‰}$  at 100 cm below the surface (Figure 3d). The values increase between 100 and 60 cm below the surface, decrease between 60 and 30 cm below the surface, and then increase above 30 cm.

## **DISCUSSION**

Marked changes in the stable isotope profiles are observed throughout the sediment record for the marshes of Piermont, Iona Island, Staten Island, and Jamaica Bay. These shifts in the profiles of the stable isotopes reflect changing conditions in the environment at specific points in the sediment record. The observed perturbations are likely to be indicative of changes in climate and human alterations of the marshes that affect species composition and sediment dynamics in the marshes.

### *Stable Nitrogen Isotope*

The chronology associated with the stable isotope profiles suggests that an isotopically heavy source of nitrogen dominated the marshes after European contact with the Hudson River Valley in the 1700s at between 80 and 65 cm depth. Manure and septic effluent is enriched in  $\delta^{15}\text{N}$  (Aravena et al. 1993; Bedard-Haughn et al. 2003), and if released into the environment can result in an output of higher  $\delta^{15}\text{N}$  in the marsh vegetation (Cole et al. 2004). Increasing livestock and human population after European settlement in the Hudson River Valley intensified wastewater input and agricultural runoff, and probably contributed to the significant increase in  $\delta^{15}\text{N}$  that was observed in all of the marshes after the 1700s.

The significant increase in the usage of nitrogen in the United States (Vitousek et al. 1997) has also resulted in eutrophication throughout many bodies of water in the country (Howarth et al. 1991). Eutrophication results in algal blooms and consequently anoxic or hypoxic waters in many estuaries and coastal seas, and poses a serious threat to marine and estuarine wildlife (Bonsdorff et al. 1997; Howarth et al. 1991; Price et al. 1985). Eutrophication furthermore can increase denitrification through anoxic conditions (Childs et al. 2002; Cole et al. 2004), thus enriching  $\delta^{15}\text{N}$  in macrophytes and marsh sediments even further (Cole et al. 2005; Cole et al. 2004).

Amongst all of the four marshes, Big Egg Marsh at Jamaica Bay had the highest initial level of  $\delta^{15}\text{N}$  at 5.91‰, which reached a maximum of 10.34‰ at 19.5 cm below the surface (Figure 2). Saw Mill Creek Marsh in Staten Island had the second highest starting level at 2.78‰ (Figure 2), with Iona Island and Piermont marshes having relatively similar starting values at -0.96 and -0.64‰ respectively (Figure 2). Big Egg

Marsh perhaps has the highest levels because of wastewater collection in the marsh due to its location inside a cove that is nearby extensive wastewater treatment plants. The difference in the levels of  $\delta^{15}\text{N}$  may indicate an influence by species composition or salinity levels in the marshes. The  $\delta^{15}\text{N}$  levels for Iona Island exceeded that of Piermont just below 40 cm, perhaps due the rapid increase in population in the 20<sup>th</sup> century in regions local to the Iona Island marsh. However, more research would be necessary to better understand this change as well as to better understand the differences in  $\delta^{15}\text{N}$  levels that exists along the transect of the Hudson River.

In all of the marshes there is a reversal in the rise of  $\delta^{15}\text{N}$  near the top of the cores, corresponding to about the 1970s. This perhaps reflects the increase in the use of synthetic fertilizers, which has increased by almost twenty-fold over the latter end of the 20<sup>th</sup> century (Glass 2003). Synthetic fertilizers have a lower  $\delta^{15}\text{N}$  range than manure and septic effluent, as synthetic fertilizers range from -5 to 5‰ while manure and septic effluent range from 10 to 20‰ (Bottcher et al. 1990). The increase of synthetic fertilizer consumption may have decreased the  $\delta^{15}\text{N}$  levels in marsh sediments, but the  $\delta^{15}\text{N}$  profile also shows an increase in  $\delta^{15}\text{N}$  levels again above 5 cm for most of the marshes (Figure 2). This may indicate an even higher increase in wastewater and agriculture due to increasing population in the region in recent decades.

### *Stable Carbon Isotopes*

The stable carbon isotope profiles in the four marshes reflect a more complicated history. With time, degradation of organic material can result in an enrichment of  $\delta^{13}\text{C}$  in the sediment. Furthermore, decomposition preserves  $^{13}\text{C}$ -depleted components such as

lignin at the surface (Chmura and Aharon 1995; Hornibrook et al. 2000). The resulting effect would be low  $\delta^{13}\text{C}$  values near the surface of the core, and higher values with increasing depth below the surface. However, the stable isotope profiles do not reflect this pattern. Since the situation was more complicated than initially hypothesized, individual marshes will be examined to better understand the stable isotope profiles.

The pollen record for Iona Marsh shows an increase in ragweed pollen (*Ambrosia*) at 60 cm (Chou and Peteet 2010), which dates to the early 1800s. *Ambrosia* requires plentiful sunlight, and as a result a disturbance such as land clearance that perturbs the forests would allow for *Ambrosia* to thrive (Pederson et al. 2005). This suggests that the 60 cm mark in the Iona sediment core signifies the beginning of major anthropogenic alterations in the region, and this same anthropogenic alteration affects the nutrient balance in the estuary, with the decrease of  $\delta^{13}\text{C}$  in the sediment core record (Figure 3a). The decrease in the carbon signal possibly also reflects increased C3 runoff from the uplands into the marsh. However, the shifts in the carbon isotopes are minor, with the total around 1‰. The fluctuations in the  $\delta^{13}\text{C}$  profile are indicative of the change in species composition in the marshes, and Iona has many species. Pollen and macrofossil records for the marsh suggest that the marsh was predominantly *Scirpus americanus* (-26.0‰), and may have shifted to *Typha* species (27-28‰) (Chmura and Aharon 1995) above 60 cm, which decreased overall  $\delta^{13}\text{C}$  levels. The subsequent shifts back to enriched levels up to 30 cm are difficult to understand without the known values of all species from the marsh.

Macrofossil and pollen data for Piermont marsh shows a rise in ragweed at 80 cm (Pederson et al. 2005), and a decrease in  $\delta^{13}\text{C}$  levels occurs at 70 cm (Figure 3b). The

decline in the signal can also be due to invasive C3 species from the uplands entering the marsh as the region was cleared. Above 40 cm, the signal becomes enriched, suggesting that C4 plants had a greater influence on the marsh. Interestingly, the rise of *Phragmites* (-24.6‰ to -29.4‰) in the marsh (Pederson et al. 2005; Chmura and Aharon 1995) would deplete the signal, but enrichment in the  $\delta^{13}\text{C}$  signal was seen towards the top, suggesting other species are affecting the signal, possibly including more algae.

At Saw Mill Creek, preliminary pollen results indicate that the sustained rise in *Ambrosia* occurred at the same depth interval as the decline in  $\delta^{13}\text{C}$  (Kleinstein 2004), suggesting more of a C3 signal in the marsh, possibly from uplands in the 1800s as the region was heavily modified. This is also possibly concurrent with a vegetation shift to C3 salt marsh plants such as *Salicornia* (-26‰) and *Atriplex patula* (-25.0‰ to -27.8‰) (Chmura and Aharon 1995) that have more depleted isotopic signatures than the original C4 grasses present in the marsh. The fluctuation at 30 cm below the surface to increased  $\delta^{13}\text{C}$  levels, however, suggests that C4 grasses dominate the marsh again as they do at the surface today (Figure 3c), and there is possibly less input from land clearance.

For Big Egg Marsh at Jamaica Bay, anthropogenic influence in the marsh begins at 60 cm below the surface, but the shift from background levels of Pb in the XRF data to a significant rise is after 40 cm (Figure 3d). The decrease in  $\delta^{13}\text{C}$  perhaps represents the dominance of invasive species such as *Phragmites australis* and *Typha* or other upland influence as land was cleared. The increase in  $\delta^{13}\text{C}$  above 30 cm, however, is perhaps indicative of increased algae species in the waters due to increased wastewater input into the New York Harbor or a rise of C4 plants such as *Spartina*.

The carbon stable isotope pattern also reveals the salinity gradient in the plants

dominant in the marshes along the transect of the Hudson River. The two marshes in the lower part of the river (Saw Mill Creek and Big Egg) are more enriched in  $\delta^{13}\text{C}$  compared to the two marshes in the upper transect (Iona and Piermont) (Figure 3). This agrees with the occurrence of C4 plants that are more prominent in the southern marshes, while C3 plants dominate the two northern marshes.

### *Prospects for Trophic Activity*

Recent studies have also used stable isotope ratios to determine trophic activity in marsh ecosystems (Abrantes and Sheaves 2009, 2010; Litvin and Weinstein 2003; Schiesari et al. 2009; Weinstein et al. 2009), and thus this research can act as a foundation for future research on the subject for the Hudson River estuary. Trophic positions in the food web can be identified by looking for a consistent relationship between the isotopic signatures of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in organisms and primary producers. Researchers have shown 1) that variations exist in trophic linkages along the salinity gradient of the Delaware Bay (Litvin and Weinstein 2003), 2) the existence of significant feeding niche differentiation in species from six different wetlands on the University of Michigan's E.S. George Reserve (Schiesari et al. 2009), 3) the trophic relationships between *P. australis* and resident mummichog (*Fundulus heteroclitus*) and marine transient species from Sandy Hook Bay, New Jersey (Weinstein et al. 2009), and 4) the variations in trophic positions and trophic lengths between the primary producers, primary consumers and secondary consumers of the Ross River estuary in northern Australia (Abrantes and Sheaves 2010).

The role of "specialized" habitats such as Piermont Marsh in the trophic activities

of Hudson fish warrants further investigation, as these marshes may serve as overwintering areas for specific species (Weinstein et al. 2009). The isotopic signatures of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in the sediment record can be compared to present isotopic signatures in existing vegetation in the Hudson River wetlands. Thus, isotopic results from this study can consequently function as background data in future research identifying the role of wetland producers in the trophic activities of Hudson River fish throughout the transect of the estuary.

The Hudson River Valley has provided the structural framework for human development over hundreds of years by linking communities economically, culturally and ecologically. Increased anthropogenic activities, however, can be detrimental to estuarine health, thus requiring a more thorough understanding of the chemistry and organic matter of the wetlands and how these environments behave in response. This research project has shed light on the effects of anthropogenic forcings, such as the use of fertilizers and land development, and upon the dynamics of the nitrogen and carbon cycles in Hudson River wetlands on a much longer time scale than instrumental measurement allows. Understanding the natural responses of these diverse ecosystems to human activities will provide a history of biochemical processes and physical and ecological shifts as a result of human activities. A more thorough understanding of the natural responses of the wetland ecosystem to human activities will not only document the historical effects of anthropogenic forcings, but also yield public awareness and facilitate conservation and restoration efforts.

## CONCLUSIONS

- (1) There exists a gradient in the  $\delta^{15}\text{N}$  levels along the transect of the Hudson River.  
From north to south, the signal enriches, probably due to population increases and sewage effluent in the south.
  
- (2)  $\delta^{15}\text{N}$  levels in Hudson River marshes have increased since European impact due to agricultural and wastewater input. These human-induced changes have also increased eutrophication levels in marshes, further enriching  $\delta^{15}\text{N}$  in marsh sediments through denitrification. Anthropogenic alterations in marshes have therefore changed nutrient dynamics.
  
- (3) Increased use of synthetic fertilizers has apparently decreased the  $\delta^{15}\text{N}$  signal in marshes during the 1970s, since synthetic fertilizers have a lower  $\delta^{15}\text{N}$  range than manure and septic effluent. With increasing population levels, however, and more wastewater and agricultural inputs, it appears that the  $\delta^{15}\text{N}$  signal has increased again.
  
- (4) The  $\delta^{13}\text{C}$  signal is enriched from North to South along the transect of the Hudson River, as expected from the present distribution of increased salinity and the gradient in plant composition from fresh (depleted) to brackish to salt marsh species (enriched) at the mouth.

- (5) The rise in ragweed (*Ambrosia*) in the uplands parallels an initial decrease in the  $\delta^{13}\text{C}$  value in marshes, sometimes due to invasive influence, possibly from uplands, or possibly from increased deposition of eroded upland plant material.
- (6) Fluctuations in  $\delta^{13}\text{C}$  since European impact indicates a complex sequence of changing species composition, and further research on the isotopic signature of marsh species will help us define these shifts.

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