THE EFFECT OF LAND USE CHANGE ON STABLE ISOTOPE (δ¹³C AND δ¹⁵N) COMPOSITION AND HEAVY METAL CONCENTRATIONS IN CONNECTICUT WETLANDS DURING THE HOLOCENE

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INTRODUCTION

The New England region exhibits an extensive variation in vegetation, natural disturbances and processes, and cultural history (Foster et al., 2008). The region has been shaped and modified by many episodes of glaciation, with the most recent reaching its maximum approximately 21,000 years ago (Dyke and Prest, 1987; Thorson, 2002). During glaciation, the Laurentide Ice Sheet (LIS) scoured the land, plucking and depositing bedrock material across the North American region (Thorson, 2002). As the LIS retreated from the region between 20,000 and 17,000 years ago, glacial till and glacio-fluvial sediments were deposited throughout the landscape and over the exposed bedrock, shaping regional topography, stream drainage, and soils (Foster et al., 2008). The soils that formed as a result of ice sheet retreat were rich with glacial till, providing well-drained, fertile land for settlers to cultivate (Thorson, 2002).

While the extent of forest management prior to European contact is poorly constrained, the landscape of the eastern United States has undergone considerable change since European settlement (Foster and Motzkin, 1998). Prior to contact, the New England region was heavily forested and highly dynamic in response to changing climate and natural disturbance processes. During 17th to late 19th century agrarian and industrial expansion, forest cover was reduced dramatically (Foster and Motzkin, 1998; Foster et al., 2008). Mature, old growth forests were cleared for timber and agriculture and stonewalls were built from abundant till on the landscape (Foster and Motzkin, 1998; Foster et al., 2008; Thorson, 2002). Some estimates suggest a greater than 50% reduction in forest cover in New England and perhaps up to 70% reduction in Connecticut by 1860 (Foster et al., 2008). After the regional decline in agriculture post-1860 that resulted from industrialization and westward expansion, forest cover and age experience a dramatic recovery, though never reaching pre-contact extent (Foster and Motzkin, 1998).

Changes in forest cover and land use affect soil development and sediment transport, leaving physical and geochemical signatures of change (Pederson et al., 2005; Sritrairat et al., 2012;). The presence of abandoned stonewalls in forested areas attests to the extensive landscape clearing for agricultural purposes, fencing in livestock, charcoal production, or mill damming. Airborne light detection and ranging (LiDAR) has become a useful tool for detecting forest features below the canopy that are otherwise hidden in aerial and satellite imagery (Johnson and Ouimet, 2014). LiDAR analysis readily highlights old roads, building foundations, stonewalls, mills and dams within the modern, forested landscape (Fig. 1). These cultural landscape features represent areas that were once cleared for agriculture or pastures and are reforested with new growth forests.

In New England, glaciation led to a period of dynamic instability during which soils and streams readjusted for thousands of years (Thorson et al., 1998). After

a second wave of landscape instability caused by European settlement, ecosystem response mimicked that of the late-glacial recovery period, a period that it is still recovering from today (Thorson et al., 1998). Both of these are preserved in sedimentary records. European settlement and land use change perhaps most substantially impacted wetlands in the Northeastern United States (Foster and Motzkin, 1998; Thorson et al., 1998; Pederson et al., 2005; Sritrairat et al., 2012). Intense land-use was often accompanied by draining of wetlands, development of new wetlands through extensive river damming, and alteration of landscape runoff and drainage patterns.

Wetland environments are highly variable and have individualistic responses to natural and anthropogenic perturbations (Thorson et al., 1998). The invasive nature of colonial agricultural technology and its pervasiveness through time ensured permanent change in the chemistry and composition of soils and streams in southern New England. Strata from wetlands can therefore be reliable archives of land use change because they are sites of net deposition and can record variations in the flux of nutrients and sediment composition (Thorson et al., 1998; Sritrairat et al., 2012). Before European settlement, streams were small channels with extensive vegetated wetlands that accumulated little sediment but stored substantial organic carbon (Walter and Merritts, 2008). When settlers cleared forests for timber and farming, it resulted in an abrupt increase in erosion and the import of organic material to freshwater streams and wetlands (Bierman et al., 1997; Pederson et al., 2005; Sritrairat et al., 2012) through increased hillslope erosion (Bierman et al., 1997; Sritrairat et al., 2012)

This project examined the physical and geochemical records of late Holocene and Anthropocene landscape change in Southern New England. Specifically, we collected and analyzed four sediment cores from wetlands in eastern Connecticut for stable isotope and heavy metal analysis. Carbon and nitrogen isotope values and heavy metal concentrations were evaluated to assess how wetlands reacted to the changing landscapes and to determine the source of organic matter and nutrients in these wetlands.
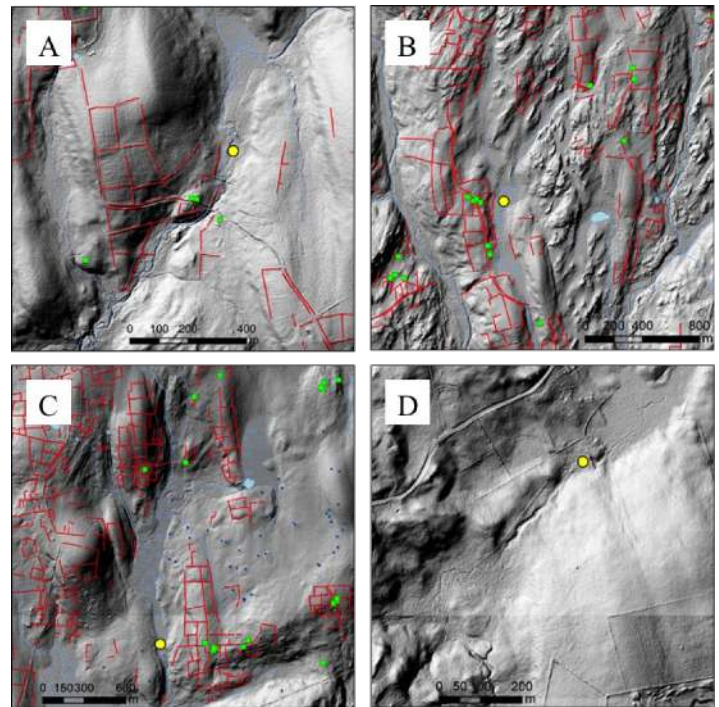

Figure 1. Hillshade maps of 1m LiDAR DEM data illustrate the site locations for the four sediment cores sampled in eastern Connecticut. Red lines denote abandoned stonewalls, blue circles mark charcoal kilns, green squares mark house foundations, and yellow circles indicate core locations. (A) ASYF1 push core from a wetland in Yale Forest, Ashford, CT. (B) ASBP1 vibracore from behind an earthen dam (and current beaver pond) in Ashford, CT. (C) ESBB1 push core from a wetland in the Natchaug State Forest, Eastford, CT. (D) Short PT1 push core from behind an earthen dam in Putnam, CT.

METHODS

Field Methods

We collected three push cores and one vibracore sample from wetlands situated near abandoned agricultural fields or milldams in eastern Connecticut. LiDAR imagery reveals old roads, abandoned stonewall and house foundations around each study site (Fig. 1). The datum was recorded by measuring the top of the core to the sediment. The sediment-water interface was measured to the top of the core from the interior of the aluminum tubing. To calculate core compaction, the datum was subtracted from the total length of the aluminum tubing. The empty space inside the core below the sediment interface was subtracted from the total length of the core in the ground.

The first 3-meter push core (ASYF1) was taken from a flooded beaver wetland in the Yale Forest in Ashford, CT (Fig. 1A). The second 3 m vibracore (ASBP1) was taken behind an earthen dam and beaver dam site in Ashford, CT (Fig. 1B). Beaver dams were common throughout the region prior to European contact, but the fur trade eradicated populations in the 17th and 18th centuries. Beaver populations have since recovered and numbers have increased since the mid-20th century – with reoccupation at ASBP1 as an example. The third 3 m push core (ESBB1) was taken in a wetland within Beaver Brook, downstream from the old road in the Natchaug State Forest in Eastford, CT. The area is surrounded by low gradient farms, stonewalls and relict charcoal hearths, which are sites of historic charcoal production (Fig. 1C). The fourth core (PT1) is a one-meter push core take in wetland behind a colonial era earthen dam in Putnam, CT and is also located near stonewalls and agricultural fields (Fig. 1D).

Lab Methods

Sediment cores were taken to the University of Connecticut's Center for Integrative Geosciences and opened, cleaned, described, and sampled. Cores were described based on texture, organic content, grain size, and lithology. Wood material was sampled from each core and sent to the Woods Hole Oceanographic Institution for ^{14}C AMS dating. Samples were taken in 2 cm intervals from significant stratigraphic layers in the described units of each core. Samples were split, placed in crucibles, and dried overnight at 50 °C. Following drying these were baked at 500 °C for 5 hours for loss on ignition (LOI) analysis.

Dried samples were prepared for δ^{13}C and δ^{15}N stable isotope analysis at the Union College Geology Department Stable Isotope Lab. Samples were divided into categories of high, medium, and low organics and weighed on a microbalance based on their organic content. Samples were weighed in tin cups (8 mg, 20 mg, and 40 mg for high, medium, and low organic content respectively) for nitrogen analysis. Samples were weighed in silver cups (3 mg, 7 mg, and 40 mg weights for high, medium, and low organic content respectively) before being treated with HCl for carbon analysis. HCl was added to each silver cup to dissolve inorganic carbonate content. Samples were analyzed

using a Thermo Delta Advantage mass spectrometer in continuous flow mode connected to a Costech Elemental Analyzer via a ConFlo III in the Union College Stable Isotope Lab. The combined uncertainty (analytical uncertainty and average correction factor) for δ^{15}N is ± 0.11‰ (Air) and for δ^{13}C is ± 0.02‰ (VPDB).

Samples were prepared for heavy metal analysis in the Union College Geology Department ICP-MS Analytical Facility. Samples were weighed (50 to 100 mg) in a clean 50 mL falcon tube. Deionized H_2O (9.5 mL) and high-purity HNO_3 (1.0 mL) were added to each sample. All samples were shaken for 12 hours and then refrigerated for 24 hours. After refrigeration, 0.5 mL and 0.05 mL of each sample solution were transferred to two sets of clean ICP-MS tubes. Each sample was analyzed by a PerkinElmer/Sciex Elan 6100 DRC ICP-MS for Co, Cu, Zn, and Pb.

RESULTS

Radiocarbon

Radiocarbon dates display older Holocene ages with depth and younger ages towards the top of the cores. The age at the bottom of ASBP1 at 106 cm is 4,036 ± 41 calendar years BP. The age at the bottom of ESBB1 at 114 cm is 14,449 ± 346 calendar years BP. The age for ASYF1 at depth 74 cm is 223 ± 66 calendar years BP, and the age for ESBB1 at depth 29 cm is 362 ± 54 calendar years BP (Table 1). Ages were calibrated from radiocarbon years to calendar years BP using the calibration curve 'CalPal2007_HULU' (http://www.calpal-online.de/).

Core Name	Depth (cm)	^{14}C Age (yrs BP)	Calibrated ^{14}C Age (yrs BP)[*]
ASYF1	74	205 ± 15	223 ± 66
ESBB1	29	280 ± 15	362 ± 54
ESBB1	114	12300 ± 80	14449 ±346
ASBP1	106	3690 ± 25	4036 ± 41

[*] Calibrated using the calibration curve CalPal2007_HULU
(http://www.calpal-online.de/)

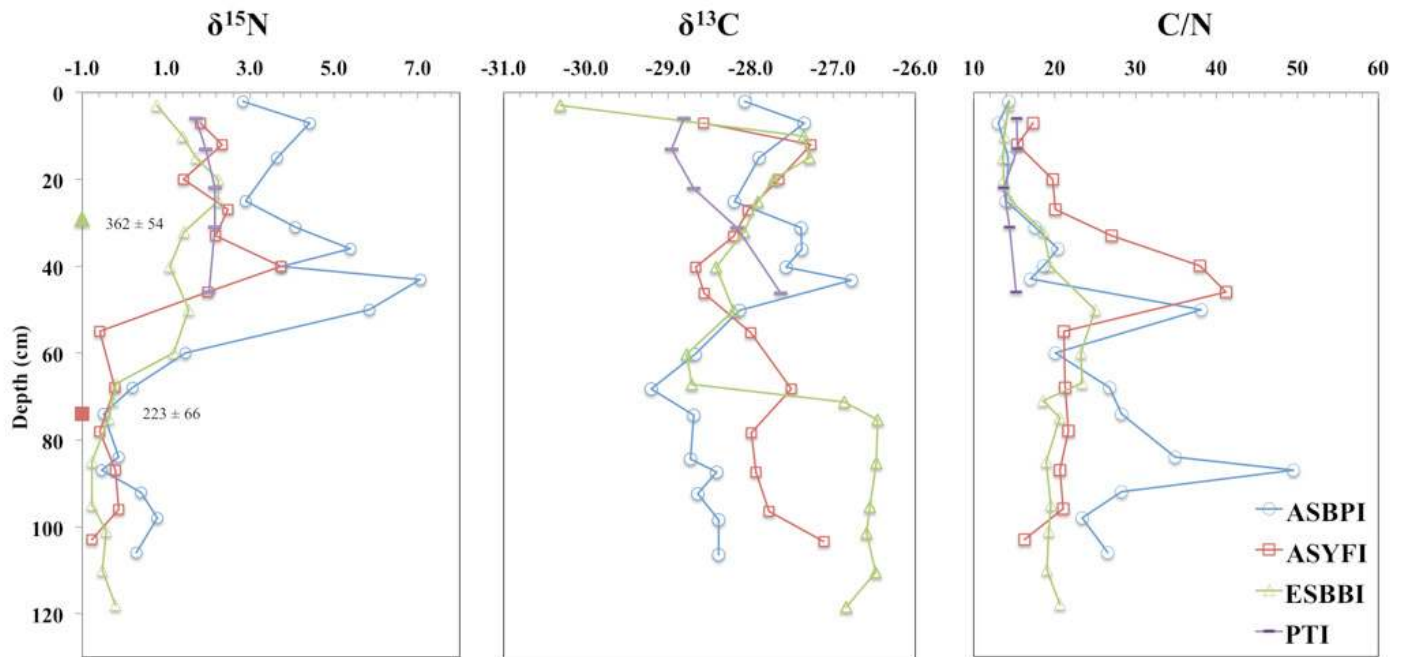*Table 1. Radiocarbon data obtained from grass and wood material in the cores.*

Figure 2. Nitrogen and carbon data for ASBP1, ASYF1, ESBB1, and PT1. Values for carbon and nitrogen exhibit an uncertainty of ±0.02‰ and ±0.11‰, respectively.

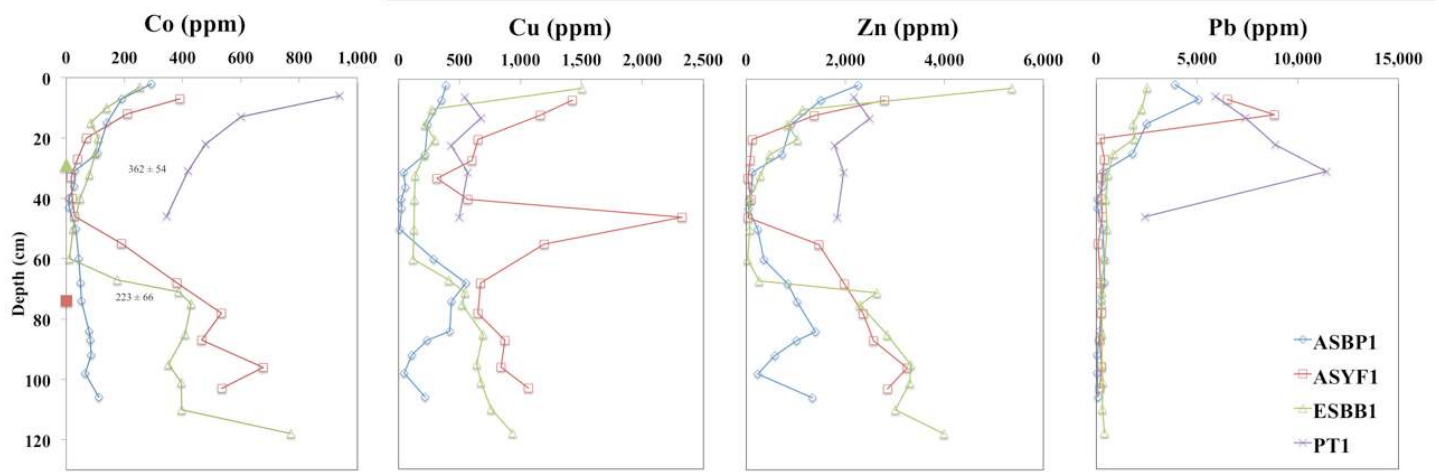*Figure 3. Co, Cu, Zn, and Pb concentrations in parts per million (ppm) for cores ASBP1, ASYF1, ESBB1, and PT1.*

Nitrogen

Isotopic $\delta^{15}N$ values exhibit clear trends throughout the four cores. Isotopic $\delta^{15}N$ values range from -2.0 to 8.0‰. Each of the four cores display similar trends, demonstrating lower values at the bottom of the core (-1.0 to 1.0‰), abruptly shifting to higher values at around 50 cm (2.0 to 7.0‰), and decreasing towards the top of the core (1.0 to 5.5‰) at around 40 cm (Fig. 2). ASBP1 displays the most noticeable trend, as it is less ^{15}N-enriched (0.3‰) at depth (~115 cm), becomes heavier (1.5‰) at 60 cm, and abruptly increases in value (7.1‰) at 40 cm. Values are less ^{15}N-enriched at the surface of the core (2.8‰) at about 2 cm. ASYF1 presents similar trends, as it has low $\delta^{15}N$ values (-0.8‰) at 100 cm depth, and sharply increases in value (3.7‰) at 40 cm. Values are lower near the surface (1.7‰) at about 6 cm. ESBB1 exhibits a more gradual trend, as it displays lighter values at depth 118 cm (-0.2‰), increases slightly at 60 cm (1.2‰), and

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has higher values at 25 cm (2.2‰). Values become lighter at the surface (0.8‰) at about 3 cm. PT1 shows higher $\delta^{15}N$ values (2.0‰) at 50 cm, and lower values at the surface (1.7‰).

Carbon

Bulk organic $\delta^{13}C$ values show less variation or consistency between the four cores. Values are low (-27.0 to -30‰) at the surface of each core relative to the bottom (-26.0 to -28.0‰) (Fig. 3). ESBB1 had the highest $\delta^{13}C$ values of the four cores (-27.0) at depth 118 cm and lowest (-30.0‰) at the surface. ASYF1 shows high values (-28.0‰) at 100 cm depth. ASBP1 displays heavier values (-29.0‰) at 106 cm depth. PT1 exhibits higher values (-28.0‰) at 46 cm. All four cores display variability in $\delta^{13}C$ values throughout the core.

C/N Ratios

Carbon to nitrogen ratios are variable throughout the cores, but ultimately range from higher ratios (20.0 to 50.0) at the bottom of the cores to lower ratios (10.0 to 20.0) at the top of the cores (Fig. 4). ASBP1 exhibits an abrupt increase (to 50.0) at 87 cm, before decreasing (to 13.0) towards the top of the core. ASYF1 displays lower ratios with depth (20.0), but increases (40.0) suddenly at 46 cm. The remaining two cores, ESBB1 and PT1, show more gradual decreases in ratios from the bottom to the surface (20.0 at the bottom to 15.0 at the surface).

Heavy Metals

Sedimentary extractable metal concentrations of Co, Cu, Zn, and Pb (in parts per million, ppm) are illustrated in Fig. 3. Co, Cu, and Zn concentrations are elevated at depth in each of the four cores and decrease to a minima at ~40-60 cm. All cores show an increase in these metals in the upper 40 cm. Pb concentrations are near detection limits for all sites in the lower parts of the core but increase dramatically in the uppermost portion of the core, with PT1 and ASYF1 showing concentrations of ~10,000 ppm. Pb increases occur near 20 cm for ASBP1, ASYF1, and ESBB1 and 40 cm for PT1.

DISCUSSION

Stable nitrogen and carbon isotope values reveal dynamic responses to changes in landscape over the past couple hundred years. The abrupt increase of $\delta^{15}N$ values from the bottom of the cores to the surface reveals a shift from natural to anthropogenic waste input. Human and animal waste input can result in high $\delta^{15}N$ values, due to the uptake of the lighter ^{14}N isotope in microbial decay (Aravena et al., 1992; Sritrairat et al., 2012). The correlating $\delta^{15}N$ trends throughout the four cores suggest that colonial land use change over time delivered human and animal waste to these water bodies. This shift in nitrogen correlates with the age date assigned to ASYF1 (Table 1). Humans have modified the New England landscape on a large scale for the past 200 years, so the age at depth 74 cm (223 ± 66 cal. yr. BP) implies a correlation between $\delta^{15}N$ enrichment and colonial settlement.

Isotopic $\delta^{13}C$ values are less informative, however. Organic $\delta^{13}C$ values are highly variable throughout the cores, yet may indicate shifts in vegetation between C3 and C4 plants. C3 plants, such as trees, are the most abundant plant species and contain lighter $\delta^{13}C$ values (-35 to -20‰). C4 plants, such as corn and some grasses and shrubs, are less abundant in nature and exhibit higher $\delta^{13}C$ values (-20 to -8‰) (Kohn, 2010; Austin, 2011). These isotopic carbon trends can be suggestive of a switch in native vegetation due to land use change and logging. Additionally, C/N ratios throughout the four cores indicate a shift in vegetation composition from aquatic to terrestrial plants. Autochthonous organic matter contains low C/N ratios (<10), while allochthonous terrestrial organic matter contain much higher C/N ratios (~20-30) (Dean, 1999). Ratios for the four cores are higher with depth and lower towards the surface, indicating a shift from terrestrial material to aquatic material. This is possibly due to deforestation at the onset of colonial settlement and land use change, and subsequent land abandonment and forest regrowth over time.

Heavy metal concentrations in the four cores reveal the influence of land use change in eastern Connecticut. During European land settlement, milldams were emplaced on small streams as a power source (Walter and Merritts, 2008; Niemetz et al., 2012). As population grew, increased agriculture and

land clearance led to increased rates of erosion and sediment transport (Bierman et al., 1997). Sediments transported via streams were eventually trapped behind these milldams, leading to an accumulation of excess fertilizers and trace metals (Niemetz et al., 2012). The watersheds in this study were most likely affected by intensive land use during European settlement. Agricultural fertilizers, pesticides, and herbicides may have influenced the accumulation of heavy metals in soils (Niemetz et al., 2012). This may explain the high concentrations of Co, Cu, and Zn in the four cores. The increased concentrations of Pb may be due to leaded gasoline combustion emissions or agricultural soil amendments over the past 100 years (Niemetz et al., 2012).

Sudden $\delta^{15}N$ enrichment and high concentrations of Co, Cu, Zn, and Pb at the tops of each core mark the beginning of the Anthropocene. However, nitrogen values increase before the metal concentrations. These markers suggest that agricultural land use changes occurred in the region before industrialization, and that there are two geochemical signatures of the New England Anthropocene.

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