AN ORGANIC MOLECULAR RECORD OF POST-GLACIAL CLIMATE AND FIRE OCCURRENCE IN A SOUTHERN NEW ENGLAND WETLAND CORE

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INTRODUCTION

Southern New England has experienced considerable changes in climate and vegetation since the end of the last glacial period ~15,000 years before present (Shuman et al, 2004). These changes have produced significant shifts in the distribution of vegetation, fire-prone plant types and the frequency of fires; however, there still remains uncertainty as to how climate conditions and/or humans have affected the frequency of fires over the past 15,000 years. Our goal was to develop an organic molecular record of post-glacial paleoenvironment and fire history for the Southern New England region. This work utilized sedimentary plant wax distributions, stable carbon isotopic composition and polycyclic aromatic hydrocarbon abundances from a ~6 meter sediment core from a paleo-channel wetland at the confluence of the Ten Mile and Housatonic Rivers in western Connecticut. ^{14}C dating of sedimentary organics in this core provides a detailed chronology of organic deposition and environmental change over the last ~13,000 years.

Long chain normal alkanes (n-alkanes) are straight-chain hydrocarbons synthesized by terrestrial plants to produce leaf waxes that function to protect against predation and to reduce water and/or nutrient loss (Bush & McInerney, 2013). n-Alkanes are stable molecules over geologic time with minimal or no isotopic alteration and occur in measurable abundances in modern and ancient leaves, soils, and sediments (Bush & McInerney, 2013). Stable isotopic data ($\delta^{13}C_{n\text{-}alkane}$) from higher plant waxes record environmental variations such as changes in precipitation or carbon dioxide isotopes, plant types or ecosystems, and plant-specific responses to changing environmental

conditions (Sachse et al., 2012, Chikaraishi et al., 2004). n-Alkanes also provide qualitative records of environmental variability and the distribution of these molecules responds to the same perturbations that can alter carbon isotopic compositions (Bush & McInerney, 2013). Two qualitative measures of paleoenvironment include average chain length (ACL), which represents the weighted average carbon chain length for all higher plant waxes, and carbon preference index (CPI), which quantifies the extent to which alkanes with an odd number of carbon atoms dominate over those with an even number. (Bush & McInerney, 2013). n-Alkane distributions in plant waxes have been studied extensively as proxies for paleo and recent environments.

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds composed of multiple fused benzene rings that are produced during incomplete combustion of organic material (Beriro et al., 2014, Friedman et al., 2013). PAHs are environmentally persistent compounds emitted by both natural and anthropogenic sources, and are therefore ubiquitous in nature (Abdel-Shafy & Mansour, 2015). Anthropogenic PAH sources mainly occur from oil-derived products and from the incomplete combustion of fossil fuels, while natural emissions are primarily the result of natural fire and volcanic processes (Berrojalbiz et al., 2011, Ugungbuyi et al., 2013). PAHs are divided into two groups: low molecular weight (LMW) compounds which have fewer than 4 rings and form under low to moderate temperatures and high molecular weight (HMW) compounds which have 4 or more rings and form under higher temperatures (EPA, 2007, Mai et al, 2003). Because of their hydrophobic and persistent properties, PAHs are

capable of residing in the environment for extensive periods of time and are subject to various transport mechanisms (Kim et al., 2011). Recent work (Kim et al., 2011, Ugungbuyi et al., 2013, Tang et al., 2014) shows that various PAH distributions preserved in sediment and soil archives can be indicative of natural and/or anthropogenic activity. These compounds provide a qualitative and quantitative record of fire frequency and intensity (Denis et al., 2012).

MATERIALS AND METHODS

Site and Sampling Methods

We collected sediments from an ancient meander located >4 m above the active channel of the Ten Mile River in western Connecticut (Fig. 1). We obtained an approximately 6 meter long core by Vibracoring with a 20-foot long, 3-inch diameter aluminum tube. The sediment core was split in the laboratory at UConn, logged, imaged, and sampled soon after collection. We collected a total of 36 samples at regular intervals throughout the core for isotopic and organic molecular analyses. Sample intervals range from 2 cm (28 samples) to 11 cm (8 samples) based on organic content. Larger sample sizes collected in the upper core (containing higher amounts of organic matter) were required for geochemical analyses. We sampled wood and macroscopic organic material for ^{14}C dating at 44 cm, 156 cm, 363 cm, and 482 cm depths.

Figure 1. Site map showing core location (red dot). The site is a paleo-channel wetland located at the junction of the Ten Mile River and Housatonic River in western Connecticut. Regional map highlighting Ten Mile watershed and Housatonic River by K. Musser, published on Wikipedia.

Laboratory and Analytical Methods

We freeze-dried sediment samples using a Labconco FreezeZone® 4.5 freeze dryer for 24 hours prior to organic chemical analysis. Sediment splits (~0.5 to 17 g) were sonicated for 15 minutes 4 times in a 2:1 azeotrope of dichloromethane:methanol to extract organics. Compounds were separated by polarity using silica gel column chromatography into *n*-alkane (S1) and PAH-containing (S2) fractions using hexane (S1) and a mixture of 70:30 hexane: dichloromethane (S2). Eluents were forced through a silica gel column with clean nitrogen via positive air pressure and stored in 4 mL vials. When necessary, urea adduction was employed to separate *n*-alkanes from cyclic and branched compounds and silver nitrate column chromatography used to remove any unsaturated lipids. Solvents were evaporated with clean nitrogen, and *n*-alkane and PAH fractions transferred to 2 mL vials for GC analysis on a TraceGC Ultra fitted with a flame ionization detector and DB-1 column (60m x 0.25mm x 0.25μm). Sample traces were compared to known *n*-alkane and PAH standards. We analyzed the δ^{13}C of normal alkanes using a Thermo GC-Isolink attached to a Thermo MAT 253 for all samples with sufficient abundance. Peaks were corrected for area, daily drift of the instrument, and offset from known standards.

The PAH-containing S2 fractions were analyzed on the Trace GC Ultra at 1:50 μL, and PAH peak areas manually identified by retention time relative to a Restek standard containing the 16 EPA priority PAHs. In order to calculate PAH concentrations in each sample, the standard was first run on the GC in solutions equivalent to 0.5 ng, 1 ng, 5 ng, 10 ng, 15 ng, and 20 ng PAH concentrations to develop the abundance calibration line for each compound of interest. Corrected areas were multiplied by volume to find the total concentration of specific PAHs in each sample, then divided by the dry sample mass to calculate the masses of each PAH per mass of sample (ng/g).

To quantify the amount of organic content present, samples were weighed before and after being heated at 550°C for 5 hours. The result weight % loss represents loss on ignition (LOI).
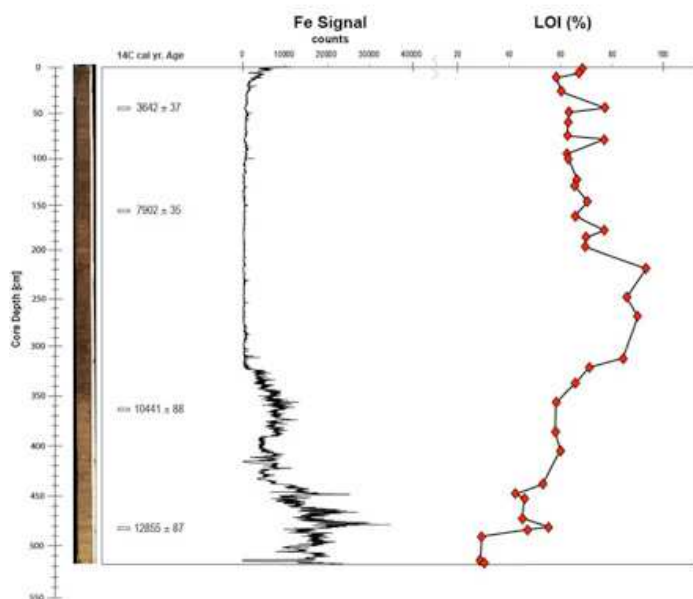
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Figure 2. Elemental XRF iron counts and organic content (loss on ignition %) as a function of depth. High mineral matter and lower organic matter are present at the base of the core and shifts at ~350 cm, marking a transition from a lacustrine system subject to river mineral input to a peat-rich wetland.

RESULTS

[14]C dates and Core Description

[14]C dates ranged from Holocene to Younger Dryas in age, respectively (3,600 to 12,800 years BP). Core sediments transition from lacustrine units with abundant gastropods at the base of the core (395-518 cm) to prolonged deposition of peat (70-350 cm), followed by a shift to a shallow marshland subject to continual infilling from upslope land areas (0-70 cm) (Fig. 2). Over these ranges, elemental XRF iron counts and organic content vary significantly, with iron counts and LOI shifting inversely at depth ~350 cm. In the bottom section of the core, sediments are finely laminated and may represent annual varves in a lake system that was present soon after the glacial retreat. Above 70 cm, the core is characterized dominantly by peat with occasional seed pods and wetland reeds. The uppermost portion (0-70 cm) of the core contains an organic matrix of wetland/reedy vegetation and thin roots.

n-Alkane Distributions and δ^{13}C Compositions

Average chain length (ACL), carbon preference index (CPI), and $\delta^{13}C_{nc27-31}$ data vary throughout the core (Fig. 3). Specifically, ACL values vary from 26.1 to 29.7 with an average of 27.7. ACL shows a gradual increase over time and does not change substantially except between depths 0-2 cm and 9-11 cm, where it decreases by 1.5, and between 56-58 cm and 74-76 cm, where it increases by 1.2. CPI shows an overall positive shift over time, but has several drops at 303-305 cm and 479-481 cm. Weighted $\delta^{13}C_{nc27-31}$ values remain stable at -31 to -33$^0/_{00}$ at the base of the core followed by a shift to more negative values (-36 to -39$^0/_{00}$) at approximately 300 cm.

PAH Distributions

We analyzed the 16 priority PAHs as defined by EPA (Fig. 4). The distribution of LMW PAHs in the core shows an overall decrease in concentration over time from peak abundances below 300 cm, punctuated by local concentration maxima at depths of 329-331 cm and 349-351 cm. These peaks date to approximately 10,000 to 8,500 years BP. An extreme maximum
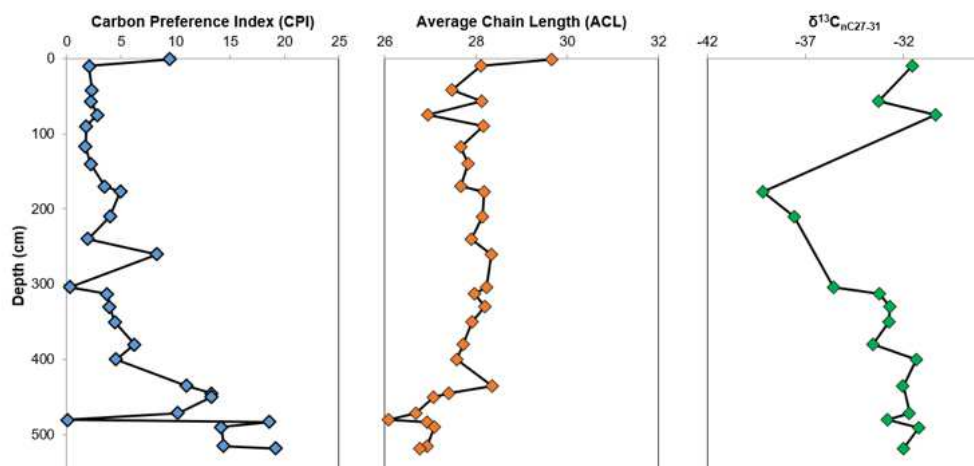

Figure 3. Carbon preference index, average chain length, and $\delta^{13}C27-31$ as a function of depth. CPI shows an overall increase with depth with punctuated minima at 303-305 cm and 479-481 cm. ACL increases gradually over time. $\delta^{13}C27-31$ values shift to more negative values at ~300 cm.
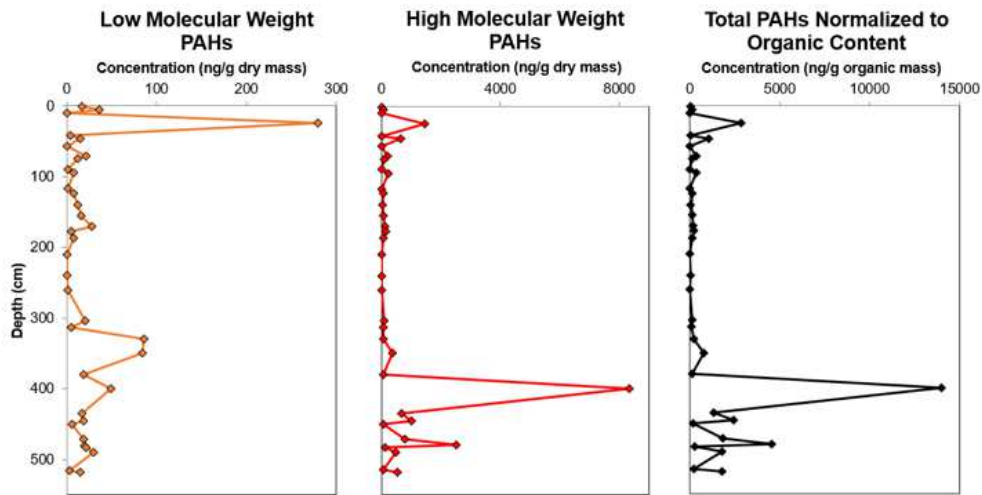
Figure 4. PAH concentrations in ng per g dry mass or ng per g organic mass as a function of depth. LMW concentrations are highest at depth interval 21-28 cm. HMW concentrations display a maximum at depth interval 399-401 cm and also dominate in total PAHs. PAHs collectively show an overall shift to lower concentrations at ~330 cm.

concentration of 279 ng per g dry material is present at depth interval 21-28 cm, which corresponds to modern age. Acenaphthylene, phenanthrene, and fluoranthene are the primary LMW constituents in this depth interval. The distribution of HMW PAHs in the core shows a maximum at depth 399-401 cm with progressive decrease over time, punctuated by several smaller spikes in concentration at depth intervals 479-481 cm and 21-28 cm. The maximum concentration was calculated to be 8346 ng per g dry material and corresponds to 11,500 to 9,000 years BP at the time of deposition. Indeno[1,2,3-cd]pyrene comprises 68% of this maximum concentration and Benzo[a]anthracene makes up 13%. A study by Yunker et al. (2002) showed that PAH samples with an Anthracene/(Anthracene + Phenanthrene) ratio of >0.10 are indicative of pyrogenic processes. 26 of 36 samples collected from Housatonic-Ten Mile have An/(An + Phe) ratios >0.10, which is interpreted to reflect natural fire occurrences.

DISCUSSION

The distributions of PAHs, *n*-alkanes, and $\delta^{13}C$ compositions from the HSTM core can be interpreted to reflect changes in the abundance of dominant plant species, fire occurrence, and anthropogenic impact throughout the past ~13,000 years. As glaciers retreated and climate warmed 12,000 years BP, a period of tundra was followed by boreal forest and succeeded by pine forest with rapidly increasing deciduous species by 8,000 BP. The $\delta^{13}C$ isotope values at 300 cm are consistent with those observed in modern riparian broad-leaf angiosperms in Connecticut (Fig. 5). The transition to more negative

$\delta^{13}C$ isotope values at 300 cm can be interpreted to reflect a shift from pine to deciduous forest regimes which is known to have occurred between 11,000 and 8,000 years BP. This shift occurs within the core's peat layers, which leads to the interpretation that the material was not an immediate influx but instead was collected from the surrounding landscape. Higher carbon preference index and shorter average chain length at ~400-518 cm can be interpreted to reflect cooler conditions, which is consistent with the post-glacial history of the region of approximately 12,000 years ago.
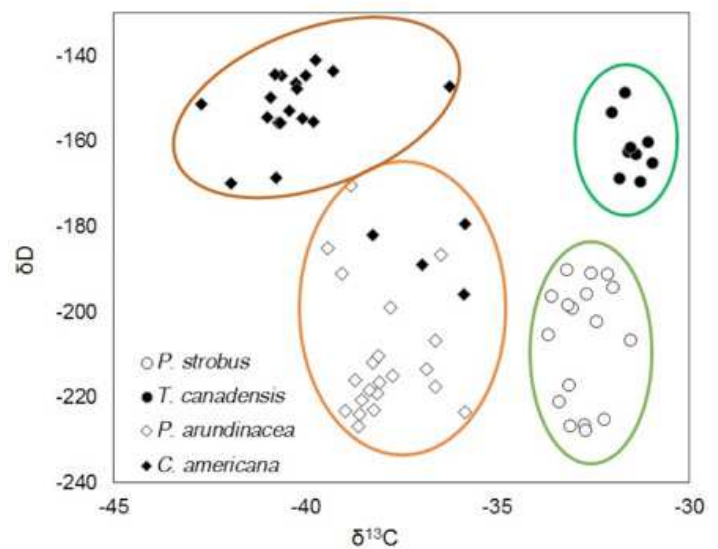

Figure 5. $\delta^{13}C$ and δD values for plant species common in the northeastern United States (adapted from Oakes and Hren, in Review): white pine (P. strobus), eastern hemlock (T. canadensis), reed canary grass (P. arundinacea), and American Hazelnut (C. americana). Composition of $\delta^{13}C$ for coniferous species trends towards less negative values and for deciduous species trends towards more negative values.

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Furthermore, PAH concentrations begin decreasing at ~330 cm, which coincides with this coniferous-deciduous transition in vegetation. Higher PAH abundance in the lower section of the core reflects potentially higher fire occurrence and in combination with the increased HMW PAHs, may be associated with greater burning temperatures of coniferous plant species. Natural fire occurrence is more prevalent between 11,000 and 8,000 years BP. Coincidentally, although humans are considered responsible for suppression of naturally-occurring forest fires, PAHs peak again at depth 21-28 cm, which may reflect fire-related anthropogenic activities (i.e. clearcutting, wood burning).

CONCLUSION

This is the first study that uses *n*-alkane and PAH distributions, as well as $\delta^{13}C$ isotopic compositions, to evaluate temporal shifts in New England paleoenvironment from early post-glacial to modern time. Understanding the natural mechanisms that control fire occurrence requires continuous records of past fires over many years. Anthropogenic fire suppression has left few natural fire ecosystems, so reconstructions of fire history provides understanding of how climate influences natural fire regimes. Future work includes analyzing δD isotopes to better understand past temperature and precipitation conditions of the region. Bulk carbon and nitrogen isotope fractionation may also be conducted to better understand organic compositions throughout the core.

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