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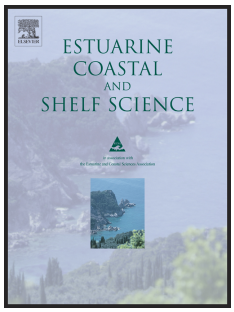

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Comparison of Bulk and Compound-Specific $\delta^{13}C$ Analyses and Determination of Carbon Sources to Salt Marsh Sediments Using *n*-Alkane Distributions (Maine, USA)

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Abstract

Sources of sedimentary organic matter to a Morse River, Maine (USA) salt marsh over the last 3390 +/- 60 RCYBP (Radiocarbon Years Before Present) are determined using distribution patterns of *n*-alkanes, bulk carbon isotopic analysis, and compound-specific carbon isotopic analysis. Marsh foraminiferal counts suggest a ubiquitous presence of high marsh and higher-high marsh deposits (dominated by *Trochammina macrescens forma macrescens*, *Trochammina comprimata*, and *Trochammina inflata*), implying deposition ~0.2 m to 0.5 m above mean high water. Distributions of *n*-alkanes show a primary contribution from higher plants, confirmed by an average chain length value of 27.5 for the core sediments, and carbon preference index values all >3. Many sample depths are dominated by the C_{25} alkane. *Salicornia depressa* and *Ruppia maritima* have similar *n*-alkane distributions to many of the salt marsh sediments, and we suggest that one or both of these plants is either an important source to the biomass of the marsh through time, or that another unidentified higher plant source is contributing heavily to the sediment pool. Bacterial degradation or algal inputs to the marsh sediments appear to be minor. Compound specific carbon isotopic analyses of the C_{27} alkane are on average 7.2 ‰ depleted relative to bulk values, but the two records are strongly correlated (R^2 = 0.89), suggesting that marsh plants dominate the bulk carbon isotopic signal. Our study

underscores the importance of using caution when applying mixing models of plant species to salt marsh sediments, especially when relatively few plants are included in the model.

Keywords: Carbon Isotopes, Saturated Hydrocarbons, Salt Marshes, Sea Level, Carbon Cycle
Regional Terms: USA, Maine, Phippsburg, Machiasport

1. Introduction

Salt marshes exist at the interface between terrestrial and marine habitats and are responsive to changing environmental dynamics including sea level (Gehrels et al., 1996; Shaw and Ceman, 1999), salinity and climate (Byrne et al., 2001; Malamud-Roam and Ingram, 2004; Malamud-Roam et al., 2006; Goman et al., 2008), species invasions (Bull et al., 1999; Zhi et al., 2007), and other disturbances (Bertness et al., 2002). Salt marshes are also a sink for atmospheric CO_2. Chmura et al. (2004) estimate that 44.6 Tg yr^{-1} of carbon is stored in salt marshes globally, and salt marshes are considered to be an important component of the global carbon cycle (Choi et al., 2001; Choi and Wang, 2004).

Carbon isotope ratios and organic biomarkers have contributed to our understanding of ancient vegetation dynamics and have been used to reconstruct plant community structures within salt marsh deposits (Chmura and Aharon, 1995; Bull et al., 1999; Wang et al., 2003). Tidal marshes are composed of plants utilizing either the C3 (Calvin-Benson), C4 (Hatch-Slack), or CAM (Crassulacean Acid Metabolism) photosynthetic pathways. The large (~12 ‰) carbon isotopic difference between the plants operating under these different photosynthetic pathways can be used to quantify the proportion of C3 and C4 species contributing to a mixture of plant

material (Cerling, 1989). Organic biomarkers are used to differentiate primary sources of carbon such as plants, algae, and phytoplankton to the sediment pool (Meyers, 1997).

Bulk isotopic analysis is attractive because there is minimal sample preparation and $\delta^{13}C$ values are commonly presented within radiocarbon reports. However, the use of bulk isotopic values to derive environmental information from salt marsh deposits can be problematic for two reasons. First, bulk isotope values record inputs of carbon from many potential sources, making plant community reconstructions tenuous. Second, diagenetic effects on isotopic values are not well constrained, further complicating environmental interpretations.

France (1995) surveyed 876 $\delta^{13}C$ values of marine phytoplankton and algae and found that they have average values of -22 ‰ and -17 ‰ respectively. These values fall between those reported for C3 and C4 plants, which range from -23 ‰ to -34 ‰ and -9 ‰ to -17 ‰ respectively (Chmura and Aharon, 1995). The rapid decomposition of algae (Harvey et al., 1995) and slower decomposition of plants (Hackney, 1980; Valiela et al., 1985) have led some investigators to conclude that there is little preservation of organic matter derived from phytoplankton and algae (Montagna and Ruber, 1980). Other researchers suggest that sedimentary studies are hampered by the incorporation of organic matter from marine algae into salt marsh sediments (Bull et al., 1999).

Diagenesis of salt marsh sediments can also affect isotope values. Decay estimates range from losses of 25 % to 90 % of original sedimentary organic matter after two years or less (Valiela et al., 1985; Benner et al., 1991; Huller et al., 1996), with less degradation of sediments that are under greater influence from the water table (Lallier-Verges et al., 1998; Goni and Thomas, 2000). The magnitude of the isotope effect resulting from this decomposition is less clear. While some studies suggest little or no effect of degradation on bulk carbon isotopic values

(Johnson and Calder, 1973; Huller et al., 1996; Byrne et al., 2001; Malamud-Roam and Ingram, 2001), even after millions of years (Tu et al., 2002), other studies indicate a depletion of 1 ‰ or more after as little as 18 months (Ember et al., 1987; Benner et al., 1991), or rapid initial depletion with subsequent stasis (Chmura et al., 1987; Fogel et al., 1989).

The potential for distinctive $\delta^{13}C$ source signatures is high in northeastern, USA estuaries because the dominant plant communities should cause a depletion of ^{13}C moving from the low marsh, to the high marsh, and into brackish marsh and freshwater wetlands (Chmura and Aharon, 1995). The origin, distribution and abundance of salt marshes in Maine have been determined (Jacobson et al., 1987; Kelley et al., 1988), and marsh vegetation patterns have been well studied (Jacobson and Jacobson, 1989). Furthermore, previous research reveals ancient (>5,000 cal. yr B.P.) salt marsh deposits (Gehrels et al., 1996). The purpose of this study is to investigate the effects of algae and other non-plant sources of carbon to $\delta^{13}C$ values in salt marsh sediments from the Maine coast through the late Holocene, and to determine if decomposition of the sediments influences bulk $\delta^{13}C$ values.

Using a salt marsh core from Phippsburg, ME, we compare bulk $\delta^{13}C$ values with compound specific $\delta^{13}C$ values of high chain length, odd numbered *n*-alkanes. Other researchers have shown that these *n*-alkanes are refractory biomarkers for higher plant inputs (Eglinton and Hamilton, 1967; Cranwell, 1973; Rieley et al., 1991; Huang et al., 2000; Pearson and Eglinton, 2000), being only a minor component in marine organisms (Sakata et al., 1997), and surviving in salt marsh deposits for millions of years (Moreno et al., 1995). We also use *n*-alkane distribution patterns to infer primary organic sediment sources (Meyers, 1997) and foraminiferal analysis to independently determine marsh paleoenvironments and constrain sea level (Scott and Medioli, 1978; 1980). We also calculate carbon preference index values (CPI) and average chain length

values (ACL) for the *n*-alkanes. ACL values are used to assess the dominant *n*-alkane chain length associated with the core sediments and are used as indicators of likely source contributions since certain plant groups peak at different *n*-alkane chain lengths. CPI values are used to indicate odd vs. even *n*-alkane chain length predominance, which can be used to assess microbial degradation of the sediments, which would be indicated by values approaching 1. Isotope values and *n*-alkane distributions from cored deposits are compared with those already reported (Tanner et al., 2007) from samples of 10 abundant plant species from a Machiasport, ME salt marsh, representing the most common plant types found in Maine salt marshes. We also report on the recent analysis of a common plant (*Ruppia maritima*) present in Maine salt pools (water-filled depressions in salt marshes) that could potentially contribute biomarkers to marsh sediments. This species was not reported by Tanner et al. (2007).

2. Methods

2.1. Field Methods

Methodology for the collection and processing of plant samples from the Machiasport marsh (Fig. 1) can be found in Tanner et al. (2007). Briefly, marsh plants were sampled by establishing a transect line, with collection of unique species located within 10 m of the transect line, beginning at the upland boundary and continuing to the tidal channel. The above ground portions of the marsh plants were collected along with their associated roots. All plant samples were photographed, catalogued, placed in ashed aluminum foil, and stored in freezers until analysis. Additionally, a sample of *Ruppia maritima*, a submerged aquatic plant that is common in salt pools in Maine salt marshes, was collected from a salt marsh in Gouldsboro, Maine in 2008.

The reported core was collected from the Morse River marsh during the month of August, 2003 (Fig. 1). The Morse River site is located within Maine's south-central (SC) coastal compartment, which is characterized by north-striking metasedimentary rocks with deep, glacially scoured valleys (Kelley, 1987; Tanner et al., 2006). This combination of bedrock and structure results in a series of northwest-oriented peninsulas with intervening deep, narrow estuaries. The Morse River marsh is a back-barrier marsh (Gehrels et al., 1996; Kelley et al., 1988). This field site was selected for the present study because previous sea level work identified intact marsh deposits with radiocarbon dates that range from the mid- to late-Holocene (Gehrels et al., 1996). The 260 cm long core was extracted at the Morse River marsh using an Eijkelkamp hand corer, which consists of a semi-closed tube of 1 m length and 3 cm diameter. This type of coring device does not compact sediments. The core was recovered in 1 m increments and coring proceeded downward to refusal (clay-rich low marsh deposit). After recovery the collected core was logged, photographed, video-taped, wrapped in ashed aluminum foil, wrapped in plastic, and placed in a split PVC tube and stored in freezers at the University of Maine and finally transported on dry ice to the University of Tennessee.

Visual, macroscopic description of core stratigraphy followed previously established methods where the low marsh (LM), transitional marsh (TM), high marsh (HM), higher-high marsh (HHM), brackish marsh (BM) and freshwater marsh (FM) zones were identified based on visual sediment characteristics and plant remains (see Belknap et al., 1989).

2.2. Laboratory Methods

Once in the lab, core samples were sectioned into 10 cm increments and divided for foraminiferal, radiocarbon, and isotopic analysis. Samples for chemical analysis were then air

dried at 60º C for 24 h before being further processed. Core samples to be used for bulk and compound-specific isotopic analysis were then powdered using a mortar and pestle.

Foraminifera were processed according to established techniques (Scott and Medioli, 1980). Cores were split into sections measuring 10 cm in length and 1.5 cm in diameter. The 10 cm increments were further divided into sections measuring 10 cm x 0.5 cm^2 in order to reduce the number of foraminifera counted, resulting in individual sample sizes of 2.5 cm^3. Samples were then wet sieved through 0.5 mm and 0.063 mm sieves. Foraminifera were collected from the 0.063 mm screen. Fine organic material was separated from the foraminifera by decantation. Foraminifera were subsequently dried and then counted under a microscope at 20x magnification.

Assigned faunal zones for the indicator species are presented along with associated floral communities in Table 1. The upper boundary of faunal zone 1A is approximately the highest astronomical tide mark. For the Morse River marsh, Gehrels (1994b) found the lower boundary of faunal zone 1A to be ~0.5 m above local mean high water, faunal zone 1B to extend from ~0.2 m to 0.5 m above local mean high water, and faunal zone 2A to extend from just above to ~0.2 m above mean high water.

Compounds from all core samples, which are new data, and also the plants that were reported on in Tanner et al. (2007) were extracted and analyzed as described therein. For the subsequent analysis of *Ruppia maritima*, lipid extraction and *n*-alkane separation were preformed following methods outlined by Wang et al. (2003) using laboratory and analytical facilities at Western Carolina University, which necessitated slightly different methodology. Dried and ground vegetation (0.5 g) samples were extracted ultrasonically in 50 ml 9:1 (v/v) dichloromethane/methanol for 10 min each time, and the extraction was repeated three times.

The solvent was removed each time after centrifugation (3500 rpm, 10 min), and all extracts were combined. The total lipid extracts were evaporated to near dryness by rotary evaporation and then re-dissolved in 10 ml hexane. The hexane was further evaporated down to about 2 ml and the sample was transferred to a small glass vial for further column separation. The *n*-alkanes were separated using a 1.0 x 25 cm glass chromatography column packed with activated silica gel (100-200 mesh). On top of the silica gel, about 10 mm activated Cu was added to remove any sulfur in the extracts. After adding the extract to the column using a glass pipette, *n*-alkanes were eluted with 25 ml of hexane. The eluate was rotary evaporated down to about 1 ml, then transferred to a glass vial and further concentrated down to 100 *u*l. The sample was then capped and stored at -20º C until analysis. The sample was then analyzed using a gas chromatography-mass spectrometer (GC-MS) at Western Carolina University.

For *Ruppia maritima*, individual *n*-alkanes were separated and characterized using a Shimadzu QP5050A GC-MS. Compound separation was achieved using a 30 m x 0.25 mm i.d. x 0.25 μm film thickness ZB-5ms column (Phenomenex, CA, USA). Oven temperature was set initially at 130º C for 2 min, then ramped at 10º C min^{-1} to 300º C and held isothermal for 23 min. The detector interface was set at 280º C. Injections were performed in split mode and ultra pure helium was employed as carrier gas. GC/MS analyses were performed in the electron impact (EI) ionization mode with an electron energy of 70 eV and the mass range *m*/*z* 40 to 400 was scanned at 2 scans sec^{-1}. Target analytes were identified within total ion chromatograms by matching their retention times and mass spectra to standard reference materials and the National Institute of Standards and Technology (NIST) 2002 mass spectral library. Concentrations of individual *n*-alkane homologues were calculated based on the standard calibration curve of each corresponding authentic standard.

We tested extraction efficiency for the ASE and sonication techniques separately by adding known amounts of pentacosane (nC$_{25}$) to sub-samples of sediments and plants. The spiked sediments and plants were processed as described for the other samples. Concentrations of the nC$_{25}$ alkane from non-spiked samples were subtracted from concentrations determined for the corresponding spiked sample. The remaining concentration of the nC$_{25}$ alkane was then compared to the amount that was added to the spiked samples. The recoveries of the nC$_{25}$ alkane were all > 95%. Plant and sediment samples were therefore not spiked with internal standards in order to avoid concentration interference.

Bulk isotope analysis followed established techniques (Boutton, 1991). Prior to isotopic analysis, dried and finely ground core samples were pretreated with 10 % hydrochloric acid for one hour to remove carbonates. Samples were then neutralized with distilled water washes and dried overnight at 50° C. After re-grinding the samples, they were then loaded into quartz tubes with 500 mg CU, 500 mg CuO, and a small platinum wire. The quartz tubes were sealed under vacuum and the organic matter combusted at 800° C for three hours. The evolved CO_2 was then cryogenically purified off-line and analyzed using a dual-inlet Finnigan MAT Delta-plus mass spectrometer. For the Morse River core, bulk isotope values represent the mid-points of 10 cm core sample increments, except for the 100 cm to 120 cm sample depth, where the core section intended for bulk analysis was added to the material sent to BETA Analytic for radiocarbon dating. The bulk value for this sample depth represents the mid-point of a 20 cm long sampling increment, and was reported with the radiocarbon date. Compound specific isotope data points represent the mid-points of 10 cm sample sections. Sections of 10 cm were skipped between sample intervals (e.g. samples are from 0-10, 20-30, 40-50, etc.).

Compound specific isotopic analyses were made using an Agilent 6890 Series gas chromatograph (GC) interfaced to a Finnigan Delta Plus XL isotope ratio mass spectrometer (IRMS) through a combustion furnace (GC-IRMS). The technique used is described in Tanner et al. (2007).

All carbon isotope values for bulk and compound-specific isotopic analysis are reported in conventional delta (δ) notation in per mil (‰) relative to the Pee Dee Belemnite (PDB) standard. The $\delta^{13}C$ notation expresses the ^{13}C / ^{12}C ratio as defined by the equation:

$$\delta^{13}C = [(^{13}C_{sample} / {}^{12}C_{sample}) / (^{13}C_{standard} / {}^{12}C_{standard}) - 1] \times 10^{3}$$

The chronology for the Morse River core is based on two bulk radiocarbon dates representing total organic material from 20 cm sections of the recovered core. Analysis was performed by BETA Analytic, Inc. following standard procedures for organic sediments. Calibrations are reported using the INTCAL 98 calibration database.

2.3 Data Reduction

Gehrels (1994a) employed a factor analysis to determine faunal zone designations. It was found that four factors (the four foraminiferal zones) explained 99.3% of the variance of 52 surficial samples collected on Maine marsh surfaces. Factor 1 (Zone 1A) was best represented by a sample consisting of 100% *Trochammina macrescens* forma *macrescens*. Factor 2 (Zone 2B) was best represented by a sample consisting of 85% *Miliammina fusca*, 9% *Trochammina macrescens* forma *macrescens*, and 3% *Trochammina inflata*. Factor 3 (Zone 2A) was best represented by a sample consisting of 70% *Trochammina inflata*, 18% *Trochammina macrescens* forma *macrescens*, 8% *Miliammina fusca*, and 3% *Tiphotrocha comprimata*. Factor 4 (Zone 1B) was best represented by a sample consisting of 80% *Tiphotrocha comprimata*, 16%

Trochammina inflata, and 4% *Trochammina macrescens* forma *macrescens* and 1% *Haplophragmoides manilaensis*. Faunal zone 1A therefore contains an almost pure *Trochammina macrescens* forma *macrescens* assemblage. Zone 1B contains other high marsh species including *Trochammina inflata*, *Tiphotrocha comprimata*, and *Haplophragmoides manilaensis*. *Tiphotrocha comprimata* and *Haplophragmoides manilaensis* are replaced by *Miliammina fusca* in zone 2A and zone 2B is dominated by *Miliammina fusca* with occurrences of *Ammotium salsum*. We employed a Ward's cluster analysis to validate these faunal zone designations. Each sample point from the core was assigned to a specific cluster, and these clusters were then compared to the faunal zone (1A, 1B, 2A, 2B, etc.) assignments. A statistical comparison of the categories derived from the cluster analysis with the faunal zone categories was made using a chi-square test.

Distributions of organic compounds were quantified using the carbon preference index (CPI) and average chain length (ACL). We used versions of the CPI and ACL similar to those employed by Wang et al. (2003) that are based on the absolute abundance of *n*-alkanes with chain lengths ranging from C_{23} to C_{34} where,

$$CPI = \sum \text{odd } C_{23} \text{ to } C_{33} / \sum \text{even } C_{24} \text{ to } C_{34}$$

thus summing the concentrations of the *n*-alkanes in question. The ACL is calculated as follows:

$$ACL = \sum [C_i] \, i / \sum [C_i]$$

where *i* is the carbon number from C_{23} to C_{34} and $[C_i]$ is the concentration. CPI values were calculated using GC/MS reported concentrations, with a few being less than 0.5 μg g^{-1}. Therefore, while values of "0" may appear in tables 2 and 3 for the concentration value for some of the compounds, the small values for these compounds are used in the calculations.

3. Results

3.1. Chronology

The radiocarbon measurement associated with the deepest section of the Morse River core, 240 cm to 260 cm below the surface, returned a conventional date of 3390 +/- 60 ^{14}C yr B.P., with a 2 σ age range of 3820 to 3470 cal. yr B.P. The second assay represents the section from 100 cm to 120 cm below the surface, which was dated at 1160 +/- 60 ^{14}C yr B.P., with a 2 σ age range of 1240 to 950 cal. yr B.P.

3.2. Sediment and Foraminiferal Stratigraphy

Stratigraphic interpretations for the Morse River core are presented in Fig. 2 along with foraminiferal distributions, ACL values, and isotope values. Foraminiferal abundances were determined for individual 10 cm long core sections and data points on the graph represent the midpoints of the sampling increments. Five species of foraminifera were identified, and abundances of the three dominant species, *Trochammina macrescens* forma *macrescens*, *Trochammina inflata*, and *Tiphotrocha comprimata* are presented (Fig. 2). The two non-represented species, *Haplophragmoides manilaensis*, and *Miliammina fusca* were present in minor quantities (5% or less for any data point) and were not used in the faunal zone interpretations. Foraminiferal abundances indicate a 1B assemblage (Table 1) for the majority of the core with two excursions: (1) an increase in the relative abundance of *Trochammina inflata* with an absence of *Trochammina macrescens* forma *macrescens* around 35 cm below surface, indicating a faunal zone 1B/2A assemblage, and (2) dominance of *Trochammina macrescens* forma *macrescens* and absence of *Tiphotrocha comprimata* around 160 cm below surface,

indicating a faunal zone 1A/1B assemblage. The results of the Ward's cluster analysis confirmed our faunal zone designations for the core deposits. These clusters showed no statistically significant difference from the designated faunal zones (chi-square, $p = 0.05$)

Visual, macroscopic analysis of the sediments shows three transitions within a primarily high marsh section. Transitional marsh deposits were present from 49 cm to 89 cm below the surface, and from 250 cm below the surface to the bottom of the core. A single higher high marsh floral zone was present from 142 cm to 168 cm below the surface (Fig. 2).

3.3. *n*-Alkane Distributions

While it is common and mathematically clean to construct a mixing model using two plant species, the marsh landscape is complex, and it is best to consider multiple plant inputs to the marsh sediment pool. We previously sampled all of the dominant low marsh, high marsh, and higher-high marsh plant species common to Maine salt marshes including *Spartina alterniflora*, *Spartina patens*, *Juncus gerardi*, and *Solidago sempervirens* (Tanner et al., 2007). In addition, other abundant salt marsh species were sampled including *Salicornia depressa* (was *Salicornia europaea* – See Haines, 2000), *Atriplex patula*, *Potentilla anserina*, *Plantago maritima*, *Suaeda maritima*, and *Limonium nashii* (Tanner et al., 2007). In general, *Spartina alterniflora* occurs in the low marsh in nearly mono-specific stands. *Spartina patens* is generally present in the high marsh and occurs with other species. *Juncus gerardi* generally dominates the higher-high marsh in Maine, with species richness increasing with proximity to the upland border. All of the other species listed in Table 2 except for *Ruppia maritima* can occur in either the high marsh or higher-high marsh at different abundances, but most are rare in the low marsh (Jacobson and Jacobson, 1989). *Ruppia maritima* occurs in salt pannes. Alkane distributions are presented for

the plant species with the carbon preference index (CPI) and average chain length (ACL) (Table 2). New data for *Ruppia maritima* are also included in the table. CPI values for the plants range from 3.8 to 34.2 (Table 2; Tanner et al., 2007). No even chain lengths were detected for *Spartina alterniflora*, making calculation of CPI impossible for this species. ACL values average 28.7 for the plants with a standard deviation of 1.5.

Distributions of *n*-alkanes are presented for the Morse River core deposits (Table 3). The core was divided into 10cm increments and indicated depths represent the mid-points of those increments. CPI values remain below 10 for most depth intervals, but increase at 55 cm (11.2), 95 cm (71.4), 115 cm (15.3), 125 cm (23.7), 145 cm (14.5), and 215 cm (13.0). ACL values remain fairly steady down-core (Fig. 2), and have an average of 27.5 with a standard deviation of 0.6.

3.4. $\delta^{13}C$ of Organic Matter

Bulk $\delta^{13}C$ values are presented with compound-specific $\delta^{13}C$ values for the Morse River core (Fig. 2). Compound-specific isotope values for the core deposits are reported for the C_{27} and C_{25} homologues. Our research suggests that the C_{27} homologue best represents Maine salt marsh plant communities (Tanner et al., 2007), being abundant in all plants studied, and having the lowest coefficient of variation between plant samples (56 %) for the different homologues. C_{25} is the most abundant *n*-alkane for almost half of the sampled depths. Values of $\delta^{13}C$ for the C_{27} alkane are also presented for the different salt marsh plants (Table 2; Tanner et al., 2007), except for *Ruppia maritima*, which did not undergo compound-specific isotopic analysis. Chmura and Aharon (1995) conducted an extensive survey of bulk biomass $\delta^{13}C$ data and the reader is advised to consult this publication for bulk $\delta^{13}C$ values for salt marsh plants.

When plotted together, the isotope curves show several common excursions (Fig. 2). Isotopic values for the C_{27} homologue are depleted by an average of 7.2 ‰ relative to bulk values for the core samples (Std. Dev. = 1.0 ‰), and the two records are strongly correlated (R^2 = 0.89; Fig. 3). Isotopic values for the C_{25} homologue are depleted by an average of 6.6 ‰ relative to bulk values for the core samples (Std. Dev. = 2.2 ‰), and these two records are also strongly correlated (R^2 = 0.71; Fig. 4). All three isotope records (bulk, C_{25}, and C_{27}) show intermediate values near the surface, moving to less negative (C4) values from 25 cm to 105 cm, 175 cm to 205cm, and 245 cm below the surface. C3 values (more negative) are indicated from 135 cm to 155 cm and 215 cm to 225 cm below the surface (Fig. 2).

4. Discussion

4.1. Foraminiferal and Floral Stratigraphy

Marsh foraminifera have a direct relationship with sea level, and the vertical position of a particular species on the marsh surface is controlled by tidal inundation frequency (Gehrels et al., 1996). Salt marsh foraminifera are used to construct sea level curves because they represent better index points than marsh plant zones (Gehrels et al., 1996). For the present study, foraminiferal zones independently confirm the presence of salt marsh deposits for all sample depths down-core. Given that degradation proceeds more rapidly in upland environments (Lallier-Verges et al., 1998; Goni and Thomas, 2000), our faunal data indicate that there are no upland soils present in the Morse River core, and that all sediments were deposited under broadly similar (zone 1B dominated) environmental conditions (Fig. 2). Plants from the TM (*Spartina patens*), HM (*Spartina patens*), and HHM (*Juncus gerardi and Solidago sempervirens*) are typically found in foraminiferal zone 1B deposits (Table 1). The ubiquitous presence of zone 1B

foraminifera in the core suggests that the sediments represent salt marsh and not freshwater or brackish marsh deposits.

4.2. *n*-Alkanes

The recognition of the ubiquitous presence of faunal zone 1B deposits (sometimes mixed with 1B or 2A) from top to bottom of the Morse River core permits the interpretation of the *n*-alkane distributions as reflecting a continuous record of salt marsh deposition for the last ~3600 cal. yr B.P. (from radiocarbon chronology). An obvious trend of the *n*-alkane distributions from the core sample, especially in the upper meter of the core, is the dominant presence of odd, higher chain length homologues (Table 3), suggestive of primary inputs from higher plants. Peak abundances of *n*-alkanes from higher plants are generally within the C_{27} to C_{33} range (Eglinton and Hamilton, 1963; Cranwell, 1973; Rieley et al., 1993; Lockheart et al., 1997; Freeman and Colarusso, 2001), and most of the Maine salt marsh plants that we have sampled peak within this range (Table 2; Tanner et al., 2007). A notable exception is *Salicornia depressa*, the only CAM plant sampled (see Kwak and Zedler, 1997), which peaks at C_{25}, and *Ruppia maritima*, a non-emergent plant, that also peaks at C_{25} (Table 2). Non-emergent plants are generally characterized by an enrichment in C_{25}, with C_{23} also common (Ficken et al., 2000; Chikaraishi and Naraoka, 2003), while algal and cyanobacterial inputs are signaled by a higher abundance of C_{17}, or the combination of C_{15}, C_{17}, and C_{19} (Han et al., 1968; Gelphi et al., 1970; Blumer et al., 1971; Giger et al., 1980; Cranwell et al., 1987), or C_{15} to C_{32} without an odd/even preference (Weete, 1976). C_{14} to C_{20} *n*-alkanes without an odd/even preference are a biomarker for photosynthetic bacteria, while non-photosynthetic bacteria produce *n*-alkanes ranging from C_{26} to C_{30} without an odd/even preference (Albro, 1976).

Distributions of *n*-alkanes for the core deposits show abundances maximizing at C_{25} (n=12), C_{27} (n=8), and C_{29} (n=5), certainly within the range of higher plants and non-emergent plants (C_{25}). *Zostera marina* is another non-emergent plant common to Maine estuaries that occurs seaward of salt marshes and also within salt pools. Canuel et al. (1997) found that *Zostera marina* has an *n*-alkane distribution that ranges from C_{17} to C_{27}, peaking at C_{21}, and is dominated by odd-numbered compounds. If *Zostera marina* was significantly represented in the marsh sediments, there would be a high abundance at C_{21}, which is not the case. Also, if *Zostera marina* was present in significant quantities, C_{17} and C_{19} alkanes should be more abundant in the marsh sediments. Canuel et al. (1997) report a bulk $\delta^{13}C$ value of -10‰ for *Zostera marina*, a bulk value much higher than any in the sediments studied (see Fig. 2).

An alternative possibility is that *Salicornia depressa* or *Ruppia maritima* is contributing heavily to the carbon pool where C_{25} is at a maximum, or there is significant degradation of the sediments, and higher chain length *n*-alkanes are not as refractory as they are believed to be. Or, there could be another, non-sampled marsh plant with a maximum abundance at C_{25} that is contributing heavily to the marsh sediments. Finally, there could be a combination of two or more plants where low chain length distribution(s) (like *Zostera marina*) overlaps with high chain length distribution(s) (like *Spartina alterniflora*) with this leading to a maximum at C_{25} at certain sample depths. If this were the case, though, one would expect higher abundances for the lower chain lengths that are the primary constituents of plants like *Zostera marina* than is observed. It is also possible that upland plants, which were not sampled, contribute *n*-alkanes to the sediments in the marsh. The visual appearance of the peat recovered from the marsh suggests strongly that salt marsh plants are the dominant contributor to the organic matter present within

the core deposits. However, our organic geochemical and isotope data cannot be used to distinguish between upland and certain salt marsh plant sources.

The average ACL value for the core deposits (27.5) is lower than the average ACL value for the salt marsh plants (28.7), but is within the range attributed to higher plants in general (Collister et al., 1994; Wang et al., 2003). *Salicornia depressa* and *Ruppia maritima* have low ACL values, attributable to their large peaks at C_{25}, and could be significant contributors to the Morse River marsh sediments, helping to lower ACL values for the core deposits. The 1.2 unit difference between core and plant deposits could also be attributable to degradation, or again, to an as yet unidentified plant source or a mixture of many plant sources (though this latter possibility is unlikely, as explained above).

CPI values, indicative of odd/even preference, calculated for core deposits are all > 3, suggesting primary input from higher plants and a lack of bacterial degradation (Table 3). Johnson and Calder (1973) found that CPI values near one indicate bacterial activity, while vascular plants have values ranging from ~3 to 40 (Collister et al., 1994; Chikaraishi and Naraoka, 2003; Wang et al., 2003). The plant samples from the Machiasport marsh fall within the range attributable to higher plants, measuring 3.8 to 34.2 (Table 2; Tanner et al., 2007), in line with the previous studies. Therefore, based on the CPI index, bacterial degradation of higher chain length *n*-alkanes in the Morse River core seems to be minimal, leaving two possibilities: (1) *Salicornia depressa* or *Ruppia maritima* contribute heavily to the marsh sediments at many sample depths, or (2) a non-sampled plant is contributing heavily to the marsh sediments.

The implication of the first possibility is that a marsh plant (*Salicornia depressa*) that is usually not assumed to be a dominant species is an underappreciated and more important component of northeastern, US salt marsh biomass through time than previously thought. In our

core, the dominance of C_{25} along with the more negative isotope values from 115 cm to 175 cm below the surface suggests that *Salicornia depressa* may be highly abundant through these sample depths. Chmura and Aharon (1995) state that "the occasional *Salicornia* or other forb (non-grassy herb) adds little in terms of plant biomass" to the low marsh in northeastern, US estuaries. However, in a landmark pollen study of Great South Beach, New York, Clark (1986) states that "as found in other palynological studies…, pollen of *Salicornia*, an early successional genus…, was abundant over extended periods." Conversely, *Ruppia maritima* could be contributing to the marsh sediments at these sample depths, suggesting that we cored a relict salt pool deposit, as *Ruppia maritima* is common in Maine salt pools (Wilson et al., 2009).

The implication of the second possibility, that an as of yet unidentified plant is contributing largely to historic marsh biomass, is that caution must be used when applying simple mixing models of relatively few dominant surface plants to core deposits. We sampled 11 plant species, but it is common to sample only several species that are then used in stratigraphic interpretations. Whatever the case, it is apparent, and cannot be emphasized enough, that it is important to study as many species on the surface of the marsh as possible before making environmental interpretations about core deposits.

4.3. Carbon Isotopes

If bacterial degradation of higher chain length *n*-alkanes is minimal for the Morse River core, which is suggested by our *n*-alkane data, then bacterial degradation seems to have a negligible effect on bulk carbon isotopic values. Compound specific isotopic values of the C_{25} and C_{27} alkanes are in good agreement with the bulk values, co-varying, and showing the same excursions down-core (Fig. 2). There is no obvious trend towards lighter or more enriched values

down-core, characteristics that would signal alteration of the isotopic composition due to degradation. Chmura and Aharon (1995) found that low marsh (C4 dominated) sedimentary organic matter had a $\delta^{13}C$ value of -15.5 ‰, while high marsh (C3/C4 mix) and brackish marsh (C3 dominated) sedimentary organic matter had $\delta^{13}C$ values of -17.8 ‰ and -23.4 ‰ respectively. Our bulk $\delta^{13}C$ values for the Morse River core fluctuate between -14.3 ‰ and -23.1 ‰, suggesting transitions between C3 and C4 dominated plant communities, an interpretation that is consistent with our compound specific *n*-alkane $\delta^{13}C$ values from the same core.

Figures 3 and 4 provide further support of the suggestion that bulk, C_{25}, and C_{27} compound specific carbon isotope values co-vary. The records are strongly correlated, showing a linear relationship when cross-plotted ($R^2 = 0.71$ for C_{25} and $R^2 = 0.89$ for C_{27}). Our results indicate that bulk isotope values are recording changing plant community structure in the marsh, and support the assertion that there is little or no effect of microbial degradation on bulk carbon isotopic values within salt marsh sediments (Johnson and Calder, 1973; Byrne et al., 2001; Malamud-Roam and Ingram, 2001; Johnson et al., 2007). Also, *n*-alkane distributions indicate that algal contributions are minimal, and their effects on bulk isotope values are being negated by the dominant abundance of plant material.

Bulk and compound specific isotope values are likely recording contributions of C3, C4, and CAM plants to the Morse River marsh deposits. Foraminiferal zone 1B is dominant for most sample depths, so there is an expected presence of both C3 and C4 species (Table 1; Fig. 2). There are two minor changes in faunal zone down-core, with some zone 2A influence (more C4 expected) from 20 cm to 50 cm below the surface, and zone 1A (more C3 expected) influence from 150 cm to 170 cm below the surface. There is a trend towards less negative values (C4) at the 20 cm to 50 cm sample depth. There is also a trend towards more negative values (C3) at and

above the 150 cm to 170 cm sample depth. At these sample depths, the interplay of the marsh surface with sea level is likely causing fluctuations in plant communities, with the isotopes recording these fluctuations. The other isotope excursions, towards more negative values at ~225 cm below the surface and towards less-negative values towards the bottom of the core, happen within the same faunal zone, and are not as yet well understood. Additional work at multiple marsh sites will address the issue of isotopic fluctuations within specific foraminiferal (mean high water) zones.

5. Conclusions

An abundance of high chain length, odd carbon number *n*-alkanes in a Morse River, ME salt marsh core reveals that higher plants are the dominant contributor of organic matter to the marsh sediments. CPI values, all >3 for all core depth intervals, suggest that bacterial degradation of the *n*-alkane organic matter fraction is minimal. Bulk carbon isotopic values co-vary with the C_{25} and C_{27} homologues, suggesting that the bulk values are being dominated by contributions from the marsh plants, and that bulk isotope values are minimally affected by degradation. The abundance of the C_{25} homologue down-core implies that either *Salicornia depressa* or *Ruppia maritima* is an important contributor to the carbon pool, or that there are major contributions from an as yet unidentified plant source. We suggest that researchers using geochemical methods to study plant community dynamics in ancient salt marsh deposits incorporate as many plant species as possible into their mixing models.

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Figure Captions

Fig. 1. Map of coastal Maine showing the location of field sites discussed in text (adapted from Kelley, 1987; Tanner et al., 2006).

Fig. 2. Bulk $\delta^{13}C$ and compound specific $\delta^{13}C$ for the C_{27} homologue, foraminiferal distributions, and foraminiferal abundances for the Morse River core with the associated faunal and floral zones.

Fig. 3. Bulk $\delta^{13}C$ vs. $\delta^{13}C$ for the C_{27} homologue from the Morse River core and the associated regression line.

Fig. 4. Bulk $\delta^{13}C$ vs. $\delta^{13}C$ for the C_{25} homologue from the Morse River core and the associated regression line.

Table 1. Foraminiferal faunal zones and floral zones with their associated dominant species. No vertical scale is implied (modified from Gehrels, 1996).

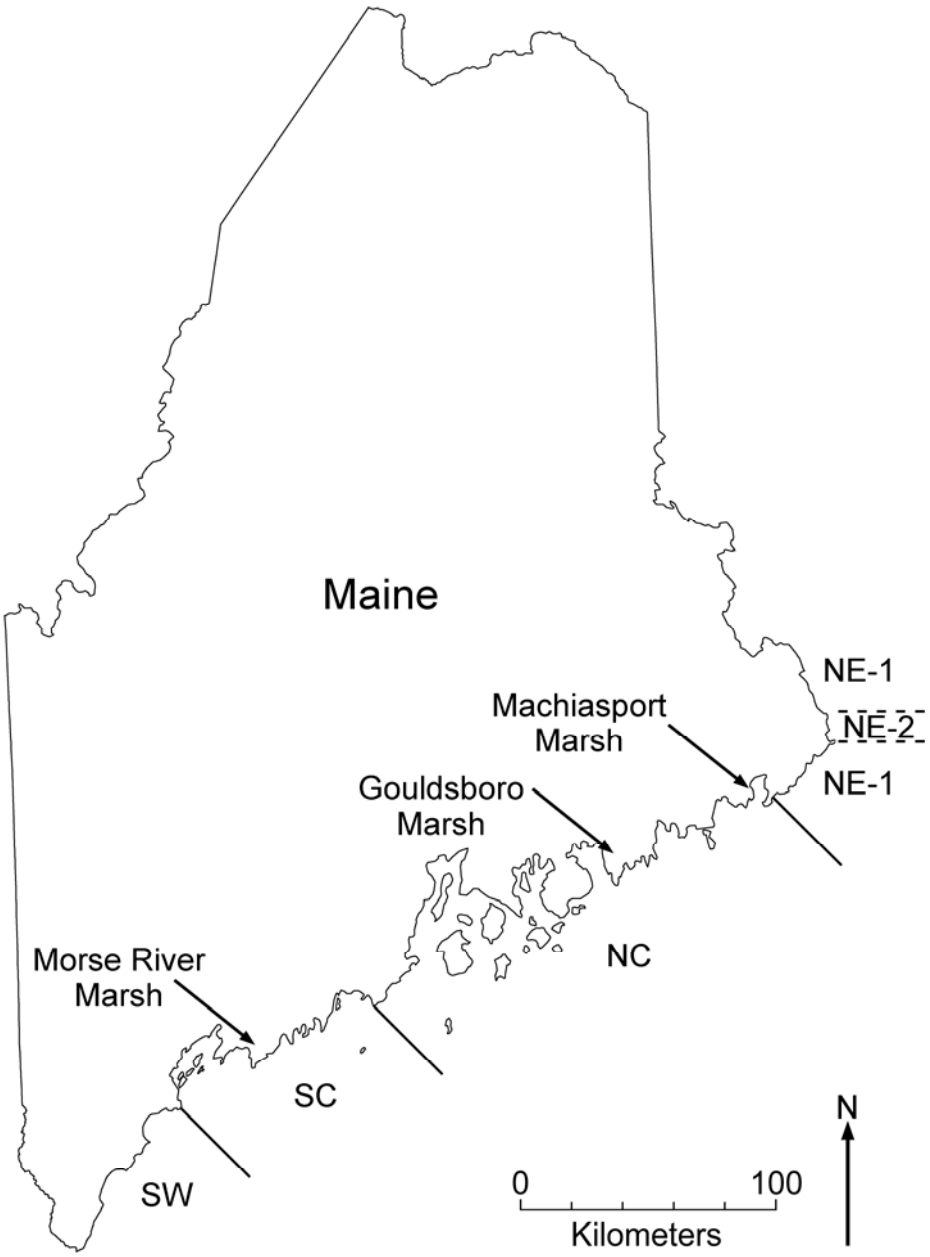
Faunal Zone	Foraminifera	Floral Zone/Plants
1A	*Trochammina macrescens forma macrescens*	Higher high marsh (HHM)
1B	*Trochammina macrescens forma macrescens*	*Juncus gerardi* (C3) *Solidago sempervirens* (C3)
	Tiphotrocha comprimata *Trochammina inflata*	High Marsh
2A	*Miliammina fusca* *Trochammina inflata*	*Spartina patens* (C4)
2B	*Miliammina fusca* *Ammotium salsum* *Pseudothurammina limnetis*	Low Marsh *Spartina alterniflora* (C4)

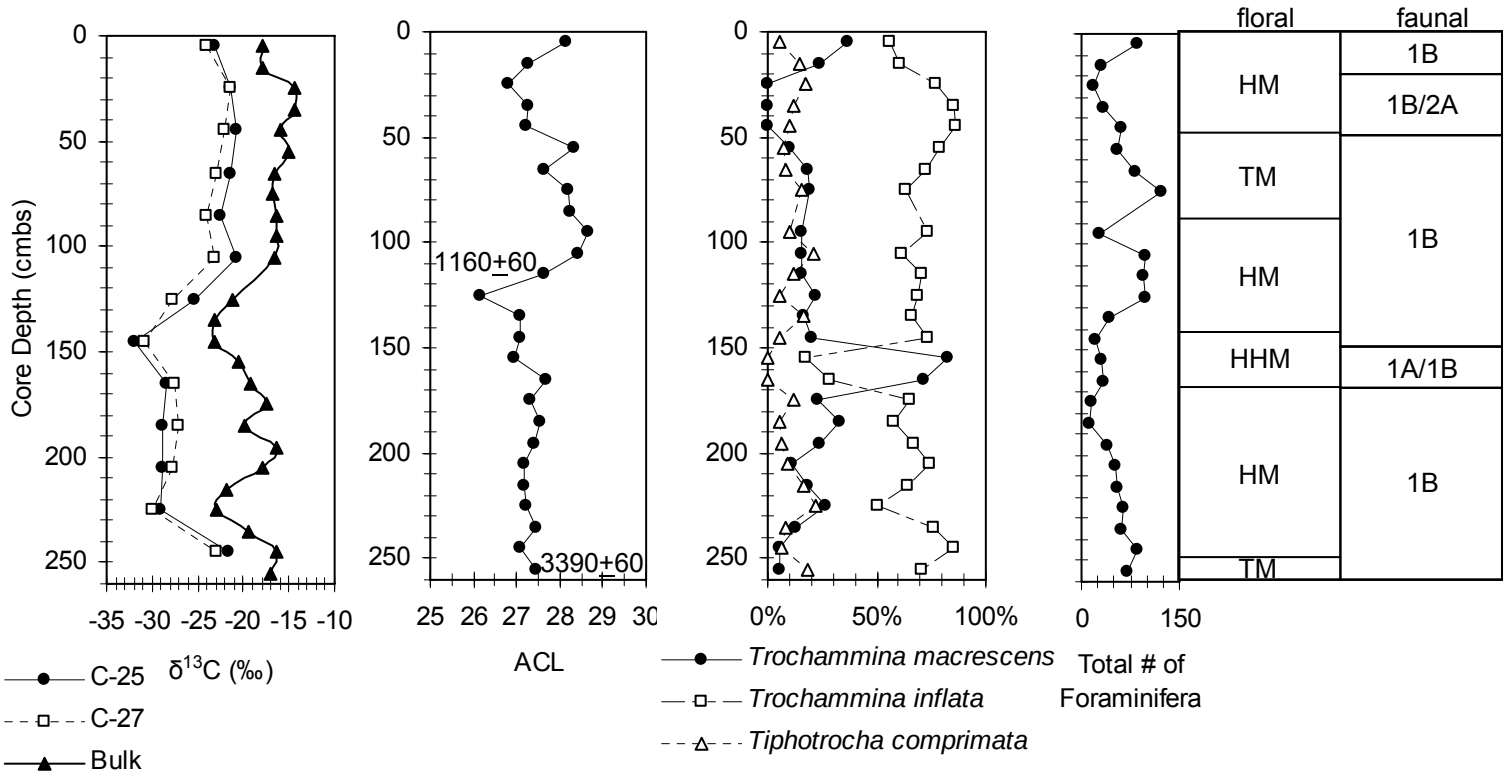
Table 2. GC/MS reported abundances for *n*-alkanes from the salt marsh plants including CPI and ACL values and $\delta^{13}C$ values for the C_{27} alkane. Bold indicates the n-alkane with the highest abundance for a particular plant species (Table modified from Tanner et al., 2007).

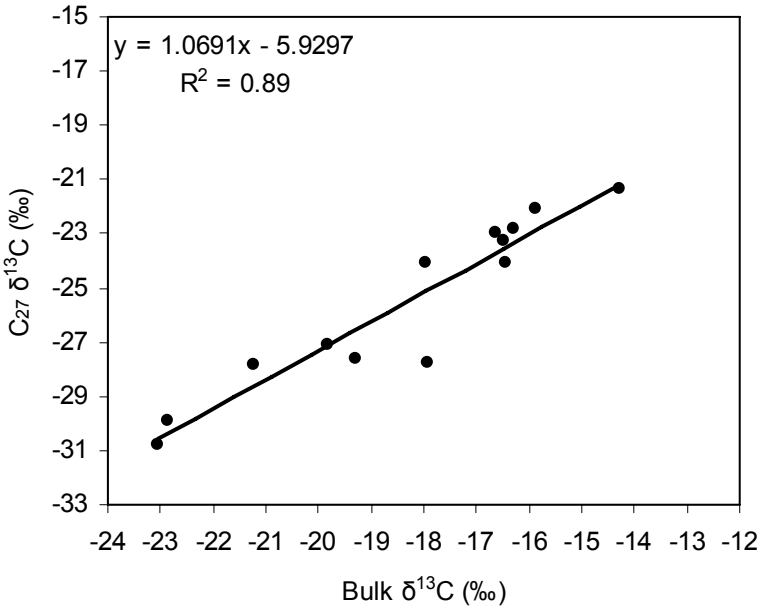
		C_{27} $\delta^{13}C$	*n*-alkane abundance (µg/g)																				
Plant ID	Path.	(‰)	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}	C_{34}	CPI	ACL
Spartina alterniflora	C4	-19.8	0	0	0	0	0	0	0	0	0	0	0	0	68	0	**144**	0	44	0	44	0	NA	29.4
Spartina patens	C4	-23.4	0	0	0	0	0	0	0	0	0	0	21	0	55	13	**136**	0	23	0	0	0	18.2	28.4
Salicornia depressa	CAM	-31.5	0	4	0	4	0	5	53	0	93	6	**100**	8	86	11	50	0	40	0	33	0	16.5	26.7
Juncus gerardi	C3	-32.0	0	0	0	9	0	0	0	0	48	0	67	9	153	0	92	0	89	0	**248**	16	27.1	29.5
Solidago sempervirens	C3	-26.4	0	5	0	6	0	0	0	0	0	0	0	0	29	0	46	12	**115**	4	24	0	13.6	30.3
Atriplex patula	C3	-32.2	0	4	0	3	0	3	0	2	5	0	16	0	105	13	**140**	12	113	0	11	0	16.1	28.9
Potentilla anseria	C3	-27.3	0	4	0	5	0	5	5	0	12	4	16	11	61	7	66	6	**136**	0	0	0	10.6	28.9
Plantago maritima	C3	-34.4	0	2	3	1	1	0	0	0	11	0	6	4	**49**	17	43	8	45	10	33	11	3.8	29.4
Suaeda maritima	C3	-29.7	0	11	0	14	0	0	0	0	22	0	89	16	120	15	275	0	**526**	0	42	0	34.2	29.4
Limonium nashii	C3	-30.7	0	0	0	0	0	0	0	0	0	0	0	0	9	1	9	1	**13**	2	4	0	8.5	29.8
Ruppia maritima	ND	ND	0	0	0	17	14	0	40	24	**186**	25	53	25	74	25	56	0	16	0	0	0	5.1	25.4
Coefficient of Var. (%)													90		56		78		138					

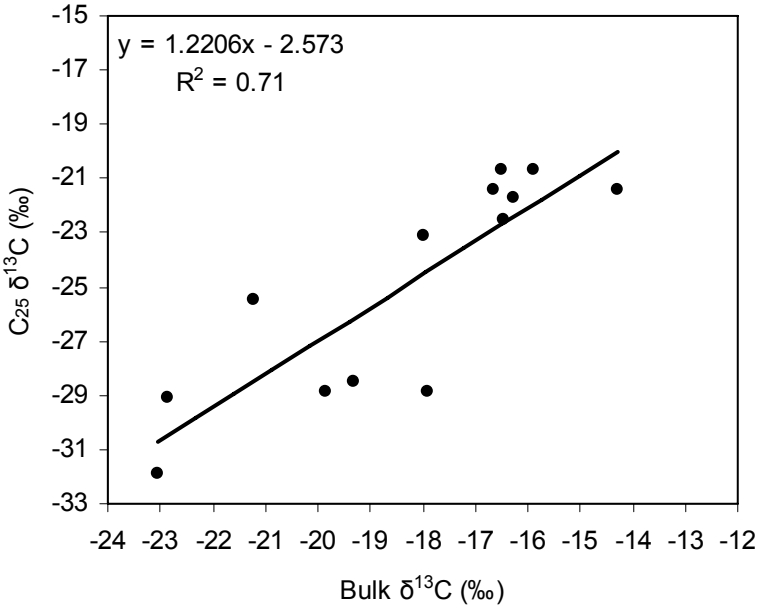
Table 3. GC/MS reported abundances for n-alkanes from the Morse River core including CPI and ACL values. Bold indicates n-alkane with highest abundance for a particular core depth.

Depth	*n*-alkane abundance (µg/g)																		
(cm)	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	CPI	ACL
5	2	0	0	7	2	10	8	31	11	45	16	**46**	13	39	4	15	0	3.6	28.1
15	1	0	0	0	0	2	0	9	3	**12**	2	4	0	2	0	4	0	6.3	27.3
25	0	0	0	0	0	5	1	23	8	**24**	4	7	1	3	0	4	0	4.8	26.8
35	0	0	0	0	0	3	3	20	10	**24**	5	15	0	0	3	7	0	3.2	27.3
45	0	0	0	0	0	2	2	18	9	**19**	1	10	0	3	0	7	0	5.0	27.2
55	0	0	0	0	0	0	0	3	1	**4**	0	2	0	1	0	3	0	11.2	28.3
65	0	0	0	0	0	1	0	**8**	2	7	0	5	0	2	0	3	0	9.7	27.6
75	0	0	0	0	0	1	0	6	1	**6**	0	6	0	2	1	3	0	9.1	28.2
85	0	0	0	0	0	1	0	7	1	8	1	**9**	1	6	1	2	0	8.0	28.2
95	0	0	0	0	0	0	0	1	0	2	0	**3**	0	1	0	1	0	71.4	28.7
105	0	0	0	0	0	0	0	2	1	**3**	0	3	0	1	1	1	0	6.5	28.4
115	1	0	0	0	0	1	0	**5**	1	4	0	4	0	1	0	2	0	15.3	27.7
125	0	0	0	8	0	10	0	**16**	2	11	0	9	0	2	0	0	0	23.7	26.1
135	1	0	0	9	1	25	1	**49**	1	20	4	20	7	25	4	5	0	9.0	27.1
145	0	0	0	10	0	18	0	**29**	1	9	1	16	0	12	3	7	0	14.5	27.1
155	0	0	0	5	0	28	1	**57**	11	23	15	23	0	33	0	6	0	6.4	26.9
165	0	0	0	5	0	29	1	**64**	9	47	24	60	20	55	11	0	0	3.9	27.7
175	0	0	0	2	0	11	0	**38**	6	32	7	23	4	16	3	4	0	5.8	27.3
185	1	0	0	4	0	14	1	32	9	19	3	**33**	6	22	3	3	0	5.5	27.5
195	0	0	0	0	0	2	0	13	4	**17**	3	5	0	4	2	4	0	4.7	27.4
205	1	0	0	13	1	15	1	**26**	6	25	9	22	6	10	2	3	0	4.1	27.2
215	0	0	0	7	0	9	1	16	4	**19**	1	16	1	7	0	4	0	13.0	27.2
225	2	0	0	9	0	6	0	9	0	15	2	**16**	0	0	4	0	0	7.9	27.2
235	1	0	0	7	0	10	1	**39**	8	30	10	32	6	23	4	0	0	4.6	27.5
245	1	0	0	1	1	5	2	**33**	10	26	9	25	0	9	3	0	0	4.1	27.1
255	1	0	0	1	2	6	1	**31**	6	28	7	30	7	12	3	0	0	4.5	27.4


Maine
NE-1
Machiasport
Marsh
NE-2
NE-1
Gouldsboro
Marsh
NC
Morse River
Marsh
SC
SW
N
0
100
Kilometers


floral
faunal
Core Depth (cmbs)
0
50
100
150
200
250
-35 -30 -25 -20 -15 -10
δ13C (‰)
C-25
C-27
Bulk
1160±60
3390±60
25 26 27 28 29 30
ACL
0%
50%
100%
Trochammina macrescens
Trochammina inflata
Tiphotrocha comprimata
0
150
Total # of Foraminifera
HM
TM
HM
HHM
HM
TM
1B
1B/2A
1B
1A/1B
1B


y = 1.0691x - 5.9297
R2 = 0.89
C27 δ13C (‰)
Bulk δ13C (‰)
-15
-17
-19
-21
-23
-25
-27
-29
-31
-33
-24 -23 -22 -21 -20 -19 -18 -17 -16 -15 -14 -13 -12


y = 1.2206x - 2.573
R2 = 0.71
C25 δ13C (‰)
Bulk δ13C (‰)
-15
-17
-19
-21
-23
-25
-27
-29
-31
-33
-24 -23 -22 -21 -20 -19 -18 -17 -16 -15 -14 -13 -12