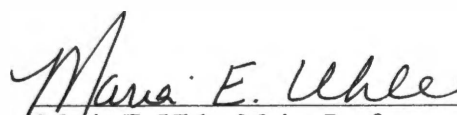
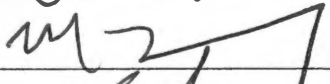
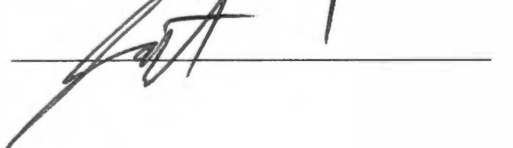


To the Graduate Council:

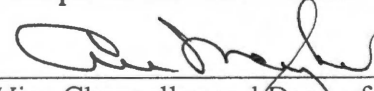
I am submitting herewith a dissertation written by Benjamin Ryan Tanner entitled "C3/C4 Variations in High Salt Marsh Sediments: An Application of Compound Specific Isotopic Analysis of Lipid Biomarkers to Late Holocene Paleoclimatic Research." I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Geology.

  
Maria E. Uhle, Major Professor

We have read this dissertation and  
recommend its acceptance:

Acceptance for the Council:

  
Vice Chancellor and Dean of  
Graduate Studies



**C3/C4 VARIATIONS IN HIGH SALT MARSH SEDIMENTS: AN APPLICATION OF  
COMPOUND SPECIFIC ISOTOPIC ANALYSIS OF LIPID BIOMARKERS TO LATE  
HOLOCENE PALEOCLIMATIC RESEARCH**

**A Dissertation  
Presented for the  
Doctor of Philosophy  
Degree  
The University of Tennessee, Knoxville**

**Benjamin Ryan Tanner  
August 2005**

Copyright © 2005 by Benjamin Ryan Tanner  
All rights reserved.

Thesis  
2005b  
T337

## DEDICATION

This dissertation is dedicated to my wife and children, Wendy, Sophie, and Saben/Mena(??!) Tanner, my parents, Bruce and Bonnie Tanner, and my brother, Brandon Tanner, for your love and support, and to my late grandfather, William F. Tanner, for planting a seed.

*“...we should, make the world more beautiful, somehow, someday, and we each know we will when we think of a way.”*

-quote from Wendy Tanner’s version of Miss Rumphius by Barbara Cooney

## ACKNOWLEDGEMENTS

This research was supported by two Geological Society of America research grants, a Sigma Xi research grant, a University of Tennessee SARIF, two fellowships from the Mayo foundation, and NSF (EAR004104) for technician support in the lab. This work was indirectly supported by the Jones endowment to Dr. Maria Uhle, and the Carden endowment to Dr. Claudia Mora.

I would like to express gratitude to all of those who have been an important part of my professional development over the past four years, including my committee members, Dr. Maria Uhle, Dr. Claudia Mora, Dr. Joseph Kelley, Dr. Jake Weltzin, and Dr. Michael McKinney. Maria, I am grateful for your guidance, never-ending understanding, and continued support. I consider myself fortunate to have been one of your students. Claudia, thank you for giving me so many opportunities and so much support. Your class inspired my work. Joe, you have gone out of your way to help see me through this project while expecting nothing in return. I am honored to have had you serve on my committee and am thankful for your guidance. Dr. Dan Sandweiss, Dr. Ed Perfect and Dr. Terry Bunde have also been especially instrumental in my professional development.

I am also appreciative for the significant help that I received in the lab from Dr. Zhang Hua Lee, Dr. Kaycie Billmark, Chad Lane, Melissa Hage and Patrick Schuneman. Dr. Beverly Johnson, Dr. Joseph Kelley, and Wendy Tanner assisted me in the field.

Finally, I would like to thank my parents, Bruce and Bonnie Tanner, and my brother, Brandon Tanner, for their unfailing love and support, my wife's parents, Dave

and Sue Richard, for the use of their barn on Swan's Island while writing, a truly inspiring spot (!), and my wife, Wendy Tanner for her love, friendship, support, sense of humor, and sense of the important things in life.

## ABSTRACT

### Chapter 1

Bulk carbon isotopes were previously used as a tool to differentiate between C3 and C4 plant communities in ancient salt-marsh deposits (Chmura and Aharon 1995). However, the bulk carbon values reflect organic matter contributions not only from salt-marsh plants, but also from algal and bacterial inputs, as well as allochthonous terrestrial organic matter. The introduction of gas chromatography-isotope ratio mass spectrometry (GC-IRMS) allows for the separation of algal vs. higher plant contributions to the sediment pool. In the present study, this technique is applied to a core and modern plant samples collected from two Maine salt-marshes. We sampled 10 plant species common to Maine marshes including *Spartina alterniflora*, *Spartina patens*, *Juncus Gerardi*, *Solidago sempervirens*, *Salicornia europa*, *Potentilla anserina*, *Atriplex patula*, *Plantago maritima*, *Suaeda maritima*, and *Limonium nashii*. Isolation of two *n*-alkanes (C-27 and C-29) present in marsh plant samples allows for the reconstruction of past plant communities present in a Machiasport, Maine salt-marsh core. Observed  $\delta^{13}\text{C}$  values for the C-27 and C-29 homologues are  $\sim 10\text{‰}$  more negative than what would be expected using bulk isotopic analysis. For the C-27 and C-29 homologues there is a 3-10‰ separation in carbon isotopic composition between C3 and C4 species. Carbon isotopic values down core show a transition from a C4 dominated plant community to a C3 dominated community, attributable to the migration of lower marsh zones onto higher marsh zones due to documented late Holocene sea-level rise (Gehrels et al., 1996). The

two homologues used have the potential to provide paleoenvironmental information in future core work, where the sea-level variable will be controlled.

## Chapter 2

Sources of sedimentary organic matter to a Morse River, Maine (USA) salt marsh over the last 3390 $\pm$ 60 RCYBP 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 zone 1B deposits, implying that the deposits were laid down ~0.2m to 0.5m above mean high water. Distributions of *n*-alkanes show a primary contribution from higher plants, confirmed by an average ACL value of 27.5 for the core sediments, and CPI values all >3. Many sample depths have a maximum abundance at the C<sub>25</sub> alkane. The ACL value for the average of 10 common marsh species is 29.1. *Salicornia europaea* has a similar *n*-alkane distribution to many of the salt marsh sediments, and we suggest that it 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<sub>27</sub> alkane are on average 7.2‰ depleted relative to bulk values, but the two records are strongly correlated ( $R^2 = 0.87$ ), suggesting that marsh plants are “swamping” 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.

## Chapter 3

A record of late Holocene sediment, foraminiferal, compound specific carbon isotope, and organic geochemical stratigraphy is presented for a series of radiocarbon-dated cores from four Maine, USA salt marsh sites. Though we present some evidence for correspondence between foraminiferal records, that indicate mean high water, and carbon isotope values, that record plant community fluctuations ( $p < 0.05$ ), there are also significant excursions in isotope values within specific foraminiferal zones. These excursions are not predictable, do not correspond between field sites, and cannot be related with any confidence to environmental variables. We suggest that salt marshes in Maine undergo a major change in water level, photosynthetic plant community, or sediment influx on average at least once every 288 years, and probably much more frequently. We question the recent use of salt marshes as recorders of ancient climate change and urge caution in the interpretation of marsh plant community records.

## Chapter 4

Average fractal dimensions (D) are calculated for Maine's four coastal compartments using a GIS approach and digitized USGS 7.5 minute series topographic quadrangle maps. The D values indicate relatively little complexity for the southwest coastal compartment (Avg.  $D=1.11$ ), higher complexity for the south-central compartment (Avg.  $D=1.35$ ), and intermediate complexity for the north-central compartment (Avg.  $D=1.23$ ). Our analysis suggests that the northeastern compartment

should be further divided into two sub-compartments (Cobscook Bay and Non-Cobscook Bay), which have Average D values of 1.37 and 1.18 respectively. Subdivision of the northeast coastal compartment is also supported by the geologic makeup of the region. Statistical tests show that all of the geologically-different coastal compartments can be discriminated in terms of D at the 95% confidence level, while the geologically similar compartments (south-central compartment and Cobscook Bay sub-compartment) cannot be statistically distinguished. Further research along previously glaciated shorelines should be carried out to build upon our results.

## TABLE OF CONTENTS

|                                                                                                                                                                                                                              |        |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|
| <b><u>Introduction</u></b>                                                                                                                                                                                                   | 1      |
| Previous Studies                                                                                                                                                                                                             | 3      |
| Hypothesis                                                                                                                                                                                                                   | 4      |
| Approach                                                                                                                                                                                                                     | 6      |
| <br><b><u>Chapter 1: C3/C4 Variations in Salt-marsh Sediments: An Application of Compound Specific Isotopic Analysis of Lipid Biomarkers to Late Holocene Paleoenvironmental Research</u></b>                                | <br>8  |
| Introduction                                                                                                                                                                                                                 | 8      |
| Methodology                                                                                                                                                                                                                  | 12     |
| Field Methods                                                                                                                                                                                                                | 12     |
| Sample Treatment                                                                                                                                                                                                             | 15     |
| Chemical and Isotopic Characterization                                                                                                                                                                                       | 16     |
| Results                                                                                                                                                                                                                      | 17     |
| Discussion                                                                                                                                                                                                                   | 19     |
| Conclusion                                                                                                                                                                                                                   | 23     |
| <br><b><u>Chapter 2: Comparison of Bulk and Compound-Specific <math>\delta^{13}\text{C}</math> Analyses and Determination of Carbon Sources to Salt Marsh Sediments Using <i>n</i>-Alkane Distributions (Maine, USA)</u></b> | <br>25 |
| Introduction                                                                                                                                                                                                                 | 25     |
| Methodology                                                                                                                                                                                                                  | 28     |
| Field Methods                                                                                                                                                                                                                | 28     |
| Foraminifera Sample Preparation and Analysis                                                                                                                                                                                 | 31     |
| Compound Separation and Analysis                                                                                                                                                                                             | 32     |
| Bulk Isotope Sample Preparation and Analysis                                                                                                                                                                                 | 34     |
| Radiocarbon Dating                                                                                                                                                                                                           | 35     |
| Results                                                                                                                                                                                                                      | 36     |
| Chronology                                                                                                                                                                                                                   | 36     |
| Sediment and Foraminiferal Stratigraphy                                                                                                                                                                                      | 36     |
| <i>n</i> -Alkane Distributions                                                                                                                                                                                               | 37     |
| $\delta^{13}\text{C}$ of Organic Matter                                                                                                                                                                                      | 38     |
| Discussion                                                                                                                                                                                                                   | 39     |
| Foraminiferal and Floral Stratigraphy                                                                                                                                                                                        | 39     |
| <i>n</i> -Alkanes                                                                                                                                                                                                            | 40     |
| Carbon Isotopes                                                                                                                                                                                                              | 43     |
| Conclusion                                                                                                                                                                                                                   | 45     |
| <br><b><u>Chapter 3: Compound Specific Isotopic Analysis of <i>n</i>-alkanes and Distributions of Foraminifera from Four Maine, USA Salt Marsh Sites Record Marsh Responses to Frequent Late Holocene Disturbance</u></b>    | <br>46 |
| Introduction                                                                                                                                                                                                                 | 46     |

|                                                                                    |     |
|------------------------------------------------------------------------------------|-----|
| <b>Methodology</b>                                                                 | 49  |
| Field Methods                                                                      | 49  |
| Foraminifera Sample Preparation and Analysis                                       | 52  |
| Compound Separation and Analysis                                                   | 53  |
| Radiocarbon Dating                                                                 | 56  |
| <b>Results</b>                                                                     | 56  |
| Radiocarbon Chronology                                                             | 56  |
| Macroscopic Core Descriptions                                                      | 57  |
| Foraminiferal Stratigraphy                                                         | 58  |
| <i>n</i> -Alkane Distributions                                                     | 59  |
| Compound Specific Isotopic Analysis                                                | 60  |
| <b>Discussion</b>                                                                  | 62  |
| Plant Samples and Core Samples                                                     | 62  |
| Core MC2                                                                           | 64  |
| Core GC3                                                                           | 65  |
| Core MO2                                                                           | 66  |
| Core SP2                                                                           | 67  |
| Disturbance Regime                                                                 | 68  |
| Climate Correlation                                                                | 69  |
| <b>Conclusion</b>                                                                  | 73  |
| <br><b><u>Chapter 4: Fractal Analysis of Maine's Glaciated Shoreline Tests</u></b> |     |
| <b><u>Established Coastal Classification Scheme</u></b>                            | 74  |
| Introduction                                                                       | 74  |
| Methodology                                                                        | 77  |
| Results and Discussion                                                             | 78  |
| Conclusion                                                                         | 82  |
| <br><b><u>Conclusions</u></b>                                                      | 83  |
| <br><b>References</b>                                                              | 85  |
| <br><b>Appendices</b>                                                              | 95  |
| <br><b>Vita</b>                                                                    | 141 |

## LIST OF TABLES

### Table

|    |                                                                                                                                                    |     |
|----|----------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 1  | Foraminiferal faunal zones and floral zones with their associated dominant species                                                                 | 118 |
| 2  | $\delta^{13}\text{C}$ values for the C-27, C-29, and C-31 alkanes from the Machiasport plants                                                      | 119 |
| 3  | GC/MS reported abundances for <i>n</i> -alkanes from the Machiasport salt marsh plants including CPI and ACL values                                | 120 |
| 4  | GC/MS reported abundances for <i>n</i> -alkanes from the Morse River core including CPI and ACL values                                             | 121 |
| 5  | Approximate elevations of foraminiferal faunal zones in three of the four salt marshes relative to local mean high water (data from Gehrels, 1996) | 122 |
| 6  | Radiocarbon dates associated with the core deposits                                                                                                | 123 |
| 7  | GC/MS reported abundances for <i>n</i> -alkanes from core MC2 including CPI and ACL values                                                         | 124 |
| 8  | GC/MS reported abundances for <i>n</i> -alkanes from core GC3 including CPI and ACL values                                                         | 125 |
| 9  | GC/MS reported abundances for <i>n</i> -alkanes from cores MO2 and SP2 including CPI and ACL values                                                | 126 |
| 10 | Previously published fractal dimension (D) values calculated for various coastlines.                                                               | 127 |
| 11 | Mean values and standard deviations (SD) calculated for the different coastal compartments and sub-compartments discussed in this study.           | 128 |

## LIST OF FIGURES

### Figure

|    |                                                                                                                                                                                                 |     |
|----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 1  | Generalized stratigraphic cross section of the Machiasport Sanborn Cove marsh showing the core recovered from the present study along with SN-VC-3                                              | 96  |
| 2  | Map of coastal Maine showing the location of field Sites discussed in text (adapted from Kelly, 1987; Tanner et al., in revision)                                                               | 97  |
| 3  | Absolute abundances of <i>n</i> -alkanes for common New England salt marsh plants                                                                                                               | 98  |
| 4  | Absolute abundances of <i>n</i> -alkanes for the Machiasport core to a depth of 150cmbs                                                                                                         | 99  |
| 5  | Absolute abundances of <i>n</i> -alkanes for the Machiasport core to a depth of 230cmbs                                                                                                         | 100 |
| 6  | Carbon isotopic compositions of the C-27 and C-29 alkanes for the Machiasport core along with Gehrels (1994a) interpretation of peat stratigraphy (center) from identification of plant remains | 101 |
| 7  | Foraminiferal distributions for the Morse River core with the associated faunal and floral zones                                                                                                | 102 |
| 8  | Bulk $\delta^{13}\text{C}$ and compound specific $\delta^{13}\text{C}$ for the C <sub>27</sub> homologue from the Morse River core                                                              | 103 |
| 9  | Bulk $\delta^{13}\text{C}$ and compound specific $\delta^{13}\text{C}$ for the C <sub>27</sub> homologue from the Morse River core                                                              | 104 |
| 10 | Macroscopic core stratigraphy                                                                                                                                                                   | 105 |
| 11 | Foraminiferal percentages with interpreted faunal zones for core MC2                                                                                                                            | 106 |
| 12 | Foraminiferal percentages with interpreted faunal zones for core GC3                                                                                                                            | 107 |
| 13 | Foraminiferal percentages with interpreted faunal zones for core MO2                                                                                                                            | 108 |
| 14 | Foraminiferal percentages with interpreted faunal zones for core SP2                                                                                                                            | 109 |
| 15 | $\delta^{13}\text{C}$ as a function of depth below surface for the C <sub>27</sub> alkane from the different core samples                                                                       | 110 |

|    |                                                                                                                                                       |     |
|----|-------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 16 | $\delta^{13}\text{C}$ as a function of $^{14}\text{C}$ years for the $\text{C}_{27}$ alkane from the different core samples                           | 111 |
| 17 | $\delta^{13}\text{C}$ of the $\text{C}_{27}$ alkane for core SP2 plotted against core MO2.                                                            | 112 |
| 18 | $\delta^{13}\text{C}$ of the $\text{C}_{27}$ alkane for core MC2 plotted against core MO2.                                                            | 113 |
| 19 | $\delta^{13}\text{C}$ of the $\text{C}_{27}$ alkane for core SP2 plotted against core MC2.                                                            | 114 |
| 20 | Map of Maine's shoreline showing the four previously established coastal compartments (from Kelley, 1987).                                            | 115 |
| 21 | Typical $\log(\text{Nr})$ vs. $\log(r)$ plot showing the regression equation, which gives a value of $D=1.19$ .                                       | 116 |
| 22 | Map of Maine's Shoreline showing the further division of the NE compartment into the NE-1 and NE-2 sub-compartments (map modified from Kelley, 1987). | 117 |

## **Introduction**

Salt marshes are zoned stands of intertidal rooted vegetation that are alternately inundated and drained by tidal action. The salt marsh ecosystem is essentially an interface between terrestrial and marine habitats. It is shaped by the interactions of plants, animals, and microbes, all of which contribute to and are influenced by their surrounding environment. Marshes are abundant along the east coast of North America, and their distribution is related to a number of factors including salinity, sediment input, geomorphology, hydrology, and several climatic parameters (Mitsch and Gosselink, 1986). Changing climatic conditions, sea-level rise, and human influence have certainly contributed to spatial changes in marsh distribution.

In the northeastern U.S., salt marshes are divided into a number of zones that represent different assemblages of plant species and foraminifera (Table 1, Appendix B). The low marsh falls within the range of mean high water, while the higher marsh zones may be inundated only monthly or seasonally by the highest tides. A number of researchers have used carbon isotope values to distinguish between different marsh zones in cores (Byrne et al., 2001; Chmura and Aharon, 1995; Choi et al., 2001; Malamud-Roam and Ingram, 2004). In general, for the northeastern US, marsh plants that photosynthesize using the C<sub>3</sub> pathway (Calvin Cycle) can be found in the higher marsh zones, while those that use the C<sub>4</sub> pathway (Hatch-Slack) dominate the low marsh (Figure 1, Appendix A; Table 1, Appendix B)(Chmura and Aharon, 1995; Gehrels et al., 1996). Within salt marshes, high salt concentrations in soil water cause drought stress for higher plants. The C-4 plants have an additional photosynthetic pathway that is

associated with adaptations to avoid drought stress, and C4 plants have an obvious advantage in desert environments as well as in salt marsh systems (Ehleringer et al., 1997). During photosynthesis, C3 plants discriminate against  $^{13}\text{C}$  to a greater extent than do C4 plants, and the large (~10‰) carbon isotopic difference between the plants can be used to quantify the proportion of C3 and C4 species contributing to a mixture of plant material (Cerling, 1989).

While C3/C4 variations have been used to delineate marsh zones for sea level studies (Choi et al., 2001), to assess relative rates of sea level rise and marsh aggradation (Shaw and Ceman, 1999), to investigate salinity variation (Byrne et al., 2001), and for other purposes (Chmura and Aharon, 1995), little has been done to address the issue of C3/C4 variation within specific marsh zones. Evidence from the northeastern U.S. and eastern Maritime Canada indicate that marsh foraminifera can be used to accurately identify four different marsh zones within cores (Table 1, Appendix A)(Gehrels, 1994; Scott and Medioli, 1978; Smith et al., 1984; Thomas and Varekamp, 1991). Gehrels (1994a) demonstrated that marsh zones in Maine are more accurately identified on the basis of foraminifera than by documenting changes in plant community.

Data derived from other studies (Shaw and Ceman, 1999) indicate that carbon isotope values fluctuate within specific foraminiferal zones. The cause of  $^{13}\text{C}$  variation within these zones is unclear. It has been demonstrated that plants utilizing the C3 photosynthetic pathway prefer cooler, wetter conditions and also high atmospheric  $\text{CO}_2$ , while C4 plants are more tolerant of hot, arid conditions, lower atmospheric  $\text{CO}_2$ , and higher salinities (Chmura and Aharon, 1995; Ehleringer et al., 1997). Therefore,  $\delta^{13}\text{C}$  variation within salt marshes can potentially serve as a climate proxy and could also be

used to observe climatic variation in conjunction with relative sea level fluctuations. Conversely, isotope excursions within particular foraminiferal zones may be more related to isolated events specific to the individual marsh, such as disturbance episodes, plant competition, etc.

### **Previous Studies**

Little work has been done to address the issue of climatically influenced C3/C4 variation within salt marshes. Byrne et al. (2001) and Malamud-Roam and Ingram (2004) have used a combination of diatoms, pollen, and carbon isotopes to monitor salinity variation in a San Francisco estuary. These researchers have proposed that by looking at all three types of data in combination, they could determine past marsh community compositions, and furthermore, they could observe changes in marsh composition along a salinity gradient up the estuary. During times of increased fresh water outflow from the estuary (increased precipitation), they observed a shift in plant communities.

Other studies have used carbon isotopes to address the issue of sea level change by delineating transitional zones in cores (Choi et al., 2001; Gehrels et al., 1996; Shaw and Ceman, 1999), however, these studies have not addressed the issue of carbon isotopic variation within specific salt marsh zones. While carbon isotopes have certainly been used in sea level studies, more research is needed to address the issue of carbon isotopic fluctuations within specific salt marsh zones.

I have constructed a means to investigate plant community changes within specific marsh zones independent of sea level fluctuations. I test the hypothesis that

secular changes within marsh zones are related to (a) localized effects, or (b) more broad-scale climatic influences. To this end, a radiocarbon dated transect of cores at multiple field sites combined with analysis of foraminiferal assemblage and compound specific carbon isotopic composition is used to account for C3/C4 variation within specific foraminiferal zones.

## **Hypothesis**

In order to test for potential causal mechanisms of high marsh plant community variation, I propose two hypotheses:

- (1) C3/C4 variation within specific salt marsh zones can be accounted for by localized effects and will show no correlation between field sites.
- (2) C3/C4 variation within specific salt marsh zones can be attributed to broader scale climatic influences, and this variation will show correlation between field sites.

In the case of (1), localized effects could include: deposition of tidal wrack or other disturbance episode, increased or decreased tidal inundation frequency, interspecific plant competition, or some other unknown mechanism. A disturbance episode (i.e. deposition of tidal wrack) should appear stratigraphically, and disturbed sections of cores can be left out of the isotopic analysis. Increased/decreased tidal inundation frequency should be apparent from foraminiferal distributions and can thus be accounted for. Other localized disturbance episodes and interspecific plant

competition could be a controlling factor in marsh plant community distribution, and could potentially be an underlying mechanism if hypothesis (1) is accepted.

Interspecific plant competition in New England salt marshes has been studied in some detail (Bertness and Ewanchuk, 2002). In a series of transplant experiments, these authors found that *Juncus gerardi* competitively dominated *Spartina patens* and *Distichlis spicata*, a species common in disturbed habitats. *Juncus gerardi* seems to dominate the terrestrial border by competitively excluding *Spartina patens* and *Distichlis spicata* to lower marsh level, while *Distichlis spicata* is competitively restricted to disturbed habitats by the other two species. However, bare patches, which are hypersaline due to increased evaporative water loss, are first colonized by the competitive subordinates, which facilitate the subsequent colonization of *Juncus gerardi* by shading the bare patch and reducing pore-water salinity. This model of interspecific plant competition can be tested in a salt marsh core. Using the above model, the high marsh should tend to be dominated on the upland border by *Juncus gerardi*. However, after a disturbance episode (potentially indicated by a sediment influx), any bare patch would tend to be colonized by *Distichlis spicata* (C4), which in a normal successional sequence would give way to *Spartina patens* (C4) and finally *Juncus gerardi* (C3). It should be possible to observe this succession in a core, where a clay lens would indicate a disturbance episode, which would be followed by a C4 carbon isotopic spike, leading finally to C3 values.

In the case of (2), climatic variation could be attributed to three potential sources: moisture, temperature, and salinity (Ehleringer et al., 1997). Temperature, precipitation and salinity variation are related effects and within the salt marsh environment,

precipitation can potentially be reconstructed by looking at salinity variations. Higher temperature, lower precipitation, and higher salinity all favor C4 plants, so carbon isotopes can potentially be used in salt marsh deposits to derive information about past conditions.

## **Approach**

My research is focused on three field locations in Maine: Machiasport, Gouldsboro, and Phippsburg (Morse and Sprague River marshes) (Figure 2, Appendix A). These sites have already been subject to extensive sea level research (Gehrels et al., 1996), and the present author's work at these locations has focused on the characterization of the modern marsh environment, as well as the recovery of a series of Eijkelkamp hand cores from each site. Collected cores were subject to foraminiferal and carbon isotopic analysis.

Because carbon isotopic signatures of salt marsh sediments indicate the sum of contributions from marsh plants, plankton, eroded riverine soils, and marine algae (Hernandez et al., 2001), I utilize compound specific isotopic analysis in order to eliminate the effects of non-plant material on the isotopic composition of the marsh (Bull et al., 1999). By using gas chromatography combustion-isotope ratio monitoring mass spectrometry (GCC-IRMS) it is possible to determine the carbon isotopic composition of specific sedimentary lipids derived from the biomass inputs of primary producers (e.g. Salt marsh plants). In this study, nearly 100 samples underwent compound specific isotopic analysis.

This thesis is divided into four chapters. In chapter 1, I use samples collected from the Machiasport marsh (Figure 2, Appendix A) to test the hypothesis that compound specific isotopic analysis (CSIA) of higher chain length, odd *n*-alkanes can be used to monitor fluctuating plant communities within Maine salt marshes. Isotopic compositions and distributions of *n*-alkanes are determined for 10 common salt marsh plants. A core that contains a known plant community zone transition is analyzed using CSIA and *n*-alkane distributions.

In the second chapter, I explore the possibility of bacterial degradation and algal contributions to the Morse River marsh. CSIA of the C<sub>27</sub> alkane is compared with bulk carbon isotope analyses for a 2.6 meter long marsh core, and *n*-alkane distributions are used to determine sources of organic matter to the marsh, and to evaluate degradation.

In the third chapter, I test the hypothesis that fluctuating salt marsh plant communities can be used to infer changing climate using a series of dated cores from the four Maine field sites. Foraminiferal counts are used as a control for sea level variations, and a regional strategy is used to determine co-variation between field sites, thus providing a test for local (i.e., disturbance episodes) vs. regional (i.e., climate) influences on plant community compositions. Distributions of higher-chain length, odd *n*-alkanes are used to determine sources of organic matter to the sediment pool. CSIA is employed to determine the carbon isotopic composition of individual *n*-alkanes from dominant salt marsh plants, and to monitor fluctuations in C3 vs. C4 plant communities through time.

Separately, the fourth chapter demonstrates variations in complexity along the Maine coastline using fractal techniques. In this chapter, Maine's four-compartment coastal classification scheme is tested using a fractal approach.

**Chapter 1 - C3/C4 Variations in Salt-marsh Sediments: An Application of  
Compound Specific Isotopic Analysis of Lipid Biomarkers to Late Holocene  
Paleoenvironmental Research**

This chapter is a revised version of an invited paper by the same name submitted to a special volume of the journal *Organic Geochemistry* in 2003 by Benjamin Tanner, Maria Uhle, and Joseph Kelley.

My use of “we” in this chapter refers to my co-authors and myself. My primary contributions to this paper include (1) selection of the topic and development of the problem into a work relevant to my study of salt marsh plant community dynamics, (2) design of a field strategy, (3) vegetation and sediment sampling and analysis, (4) most of the gathering and interpretation of the literature, (5) most of the writing.

**Introduction**

Salt-marshes in the northeastern United States are typically composed of a number of species that are segregated into bands along a salinity gradient paralleling the shoreline. The low marsh falls between mean water level and mean high water, while the higher marsh zones are typically inundated only monthly or seasonally by the highest tides (Gehrels et al., 1996). New England salt-marshes are populated by a variety of species, with most of the species being present in the “background matrix” created by the dominant abundance of *Spartina alterniflora*, *Spartina patens* and *Juncus gerardi*

(Bertness and Ewanchuk, 2002). *Spartina alterniflora* dominates lower marsh areas while *Spartina patens* and *Juncus gerardi* are, respectively, the most abundant species found at the seaward and landward edges of the high marsh. *Spartina alterniflora* also occurs in the high marsh, but is usually confined to disturbed areas.

Most northeastern U. S. salt-marshes are composed of plants utilizing either the C3 (Calvin-Benson cycle) or C4 (Hatch-Slack) photosynthetic pathways. For the three “turf dominants”, *Spartina alterniflora* and *Spartina patens* both utilize the C4 photosynthetic pathway, while *Juncus gerardi* utilizes the C3 pathway. Other common marsh plants that were sampled, including *Solidago sempervirens*, *Potentilla anseria*, *Atriplex patula*, *Plantago maritima*, *Suaeda maritima*, and *Limonium nashi*, utilize the C3 photosynthetic pathway with the exception of *Salicornia europaea*, which is a CAM (Crassulean Acid Metabolism) plant that is found in several marsh floral zones, and in disturbed areas. The C4 plants have an additional photosynthetic pathway that is associated with adaptations to avoid drought stress, and C4 plants have an obvious advantage in desert environments as well as in elevated-salinity salt-marsh systems (Chmura and Aharon, 1995). During photosynthesis, C3 plants discriminate against  $^{13}\text{C}$  to a greater extent than do C4 plants, and the large (~10‰) carbon isotopic difference between the plants can be used to quantify the proportion of C3 and C4 species contributing to a mixture of plant material (Cerling, 1989). CAM plants have carbon isotopic values that can vary within the range of C3 and C4 values.

Salt-marsh deposits have been used as a proxy to decipher changes in several environmental variables. Researchers have used marsh chemistry as well as floral and faunal distributions to interpret sea level changes (Gehrels et al., 1996), determine rates

of marsh aggradation or carbon sequestration (Choi et al., 2001; Shaw and Ceman, 1999; Watson, 2004), study the response of plant communities to climate change (Bertness and Ewanchuk, 2002), and to investigate salinity dynamics (Byrne et al., 2001; Chmura and Aharon, 1995; Malamud-Roam and Ingram, 2004).

Within terrestrial environments, carbon isotopic values have been used to determine ancient C3/C4 plant distributions and to infer changing climatic conditions (Ehleringer et al., 1997). Within salt-marshes, C3/C4 plant distributions can provide information on salinity conditions (Chmura and Aharon, 1995; Malamud-Roam and Ingram, 2004). Since salinity is strongly influenced by tidal inundation frequency, there is a general decrease in the salt tolerance of marsh plants from the tidal channel to the upland border. Therefore, saline low marsh (LM) areas are dominated by C4 plants, while high marsh (HM) areas are C4 dominated with some C3 contribution, higher high marsh (HHM) areas are mostly C3 with some C4 contribution, and along the upland border, the brackish marsh (BM) and freshwater marsh (FM) are C3 dominated. Some of the other factors that affect species composition within the marsh include oxygen levels in the substrate (Portnoy and Valiela, 1997), episodic disturbance (Bertness et al., 1992; Reidenbaugh and Banta, 1980), groundwater movement and flow in the soil (Hemond and Fifield, 1982; Silvestri et al., 2005; Thibodeau et al., 1998), and interspecific plant competition (Bertness, 1991; Crain et al., 2004).

While it is possible to infer changing salinity dynamics with a multi-proxy approach (i.e., Byrne et al., 2001), the use of bulk isotope values alone cannot account for algal inputs to the sediment pool, thus complicating the results of studies utilizing only bulk carbon isotopic analysis. Residual differences between predicted isotopic values

determined from surficial plant communities and observed values of surface soils have been partly attributed to algal inputs (Malamud-Roam and Ingram, 2001). Reported carbon isotopic values for algae range from a low of -30.9‰ to a high of -4.9‰ (PDB), effectively covering the ranges reported for salt-marsh plants, which range from a C3 low of -33.6‰ to a C4 high of -10.0‰ (Chmura and Aharon, 1995). If C3/C4 plant distributions are to be utilized in salt-marsh sediments to make inferences regarding changing salinity conditions, a record is needed that circumvents the algal contribution to the sediment pool.

The use of gas chromatography-isotope ratio monitoring mass spectrometry (GC-IRMS) allows measurement of the isotopic ratios of specific compounds, including those derived from higher plants, thus factoring out non-plant contributions to the sediments. Using GC-IRMS it is possible to select a lipid that is present in the profiles of salt-marsh plant communities and absent from indigenous algal communities. With algal contributions ruled out, carbon isotope ratios of higher plant lipids present in salt-marsh sediments can be used to monitor the contributions of C3 and C4 species (Bull et al., 1999).

The objective of this study is to track changes in the carbon isotopic composition of specific organic compounds within a salt-marsh core to infer contributions of C3 and C4 plant communities, and provide a test for the hypothesis that compound specific carbon isotopic analysis can be used to monitor salinity dynamics within salt-marshes. Data derived from sediment and floral samples recovered from a Maine, U.S.A. salt-marsh are presented herein. The carbon isotopic compositions of lipids derived from the three marsh dominants, *Spartina alterniflora*, *Spartina patens*, and *Juncus gerardi*, as

well as other common marsh species including *Solidago sempervirens*, *Salicornia europa*, *Potentilla anseria*, *Atriplex patula*, *Plantago maritima*, *Suaeda maritima*, and *Limonium nashi* are presented and the values are used to interpret the dominant plant community present through time in a 240cm deep core.

There is an expected transition from a mixed marsh to a brackish/freshwater marsh plant community as a result of late Holocene sea-level rise demonstrated at this field site by previous researchers using foraminiferal reconstructions (Gehrels et al., 1996). It is proposed that carbon isotopes should record the transition from a mixed marsh (C3 and C4) to a brackish/freshwater marsh (C3) plant community. If isotopic compositions of higher chain-length *n*-alkanes record this transition, then these compounds can be used in future core work with greater confidence. To our knowledge, this is the first study of its kind conducted on the New England coast.

## **Methodology**

### **Field Methods**

The reported core was collected at the Machiasport marsh during the month of June, 2003. Marsh floral samples were collected from the Machiasport marsh (Sanborn Cove), ME during the month of August, 2004 (Figure 2, Appendix A). The Machiasport site is located within Maine's north-central (NC) coastal compartment (Kelly, 1987; Tanner et al., in revision). The NC compartment is characterized by abundant granitic plutons. The relative resistance of the plutonic bodies to erosion has resulted in a

coastline that contains broad estuaries with numerous granitic islands. According to published literature (Gehrels, 1994b; Kelley et al., 1988), the Machiasport site can be classified as a “bluff-toe” marsh, as its sediment is derived from nearby eroding bluffs. This 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, 1994b; Gehrels et al., 1996).

Marsh plants were sampled by establishing a transect line, with collection of unique species located within 10m 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. Collection of plant roots is important because below ground production of roots and rhizomes exceeds above ground production for some salt marsh plants (Good et al., 1982; Schubauer and Hopkinson, 1984). All plant samples were photographed, catalogued, placed in ashed tin foil, and stored in freezers at the University of Maine and finally transported on dry ice to the University of Tennessee.

The 240cm long core was extracted from a high marsh zone at the Machiasport marsh using an Eijkelpkamp hand corer, which consists of a semi-closed tube of 1m length and 3cm diameter. We noted a mixture of *Juncus gerardi* and *Spartina patens* on the marsh surface where the core was collected. The core was recovered in 1m increments and coring proceeded downward to refusal (glaciomarine sediments). The sampled deposits (Figure 1, Appendix A) were collected adjacent to core SN-VC-3 recovered by previous sea level investigators. SN-VC-3 had a reported basal date of  $3,010 \pm 70$ ka (Gehrels et al., 1996). After recovery, the collected core was logged, photographed,

video-taped, wrapped in ashed tin foil and plastic, placed in a split PVC tube and stored as described for the plant samples.

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 the following general characteristics (Belknap et al., 1989; Gehrels, 1994):

- LM: Muddy or sandy matrix with low density of organic material, in situ *Spartina alterniflora* roots and rhizomes. Usually found adjacent to the tidal channel.
- TM: Fibrous high marsh peat with abundant *Spartina alterniflora* remains in addition to remains of *Spartina patens*. Occasionally present between the low and high marsh.
- HM: Dark brown to grayish brown peat characterized by an interwoven, dense network of fine *Spartina patens* roots. Often divides the low marsh from the higher high marsh
- HHM: Light brown peat containing remains of *Juncus gerardi* roots (wavy) and rhizomes (smooth and reddish-brown) with *Solidago sempervirens* tissue (woody) and stele ('fishbone'). Often found adjacent to the upland border.
- BM: Characterized by *Scirpus* remains, black and triangular in cross section, and containing peat with a "coffee grounds" texture.
- FM: Dark-brown to black structureless peat with remains of *Typha angustifolia* plants and the presence of leaves, bark, and other detrital material.

Once in the lab, core samples were sectioned into 10cm increments and divided for foraminiferal, radiocarbon, and isotopic analysis. Core and plant samples were then air dried at 60° C for 24 hours before being further processed. Core samples to be used for bulk and compound-specific isotopic analysis were then crushed using a mortar and pestle. Plant samples were shredded using a coffee grinder.

### Sample Treatment

Compounds from all plant and core samples were extracted using a Dionex ASE 300. Samples were flushed with dichloromethane (40%) and methanol (60%) at 125° C and 1500 p.s.i. for 10 min. This process was repeated four times for each sample. After drying down, 3ml of 5% KOH in MeOH:H<sub>2</sub>O (80:20; pre-extracted with chloroform) was added to each sample. Samples were then flushed with nitrogen, sealed tightly and placed in a heat block at 80° C for 2 hrs. The pH of each sample was checked to ensure that the solutions were still basic. Approximately 3mls of Milli-Q H<sub>2</sub>O were added to each sample, and samples were extracted three times with 3ml of hexane:chloroform (4:1). Total neutrals were then separated from fatty acids using a separatory funnel. Samples were concentrated using a rotovap, and were then analyzed using a gas chromatography-mass spectrometer (GC-MS) and gas chromatography-isotope ratio mass spectrometer (GC-IRMS).

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

$$\delta^{13}\text{C} = \left( \frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} - 1 \right) \times 10^3$$

## Chemical and Isotopic Characterization

### *Gas Chromatography-Mass Spectrometry (GC-MS)*

Individual alkanes were separated and characterized using an Agilent 6890 Series GC interfaced to an Agilent 5973N mass selective detector (MS). Compound separation was achieved using a 30m x 0.25mm i.d. x 0.16 $\mu\text{m}$  film thickness VF-5 column. Oven temperature was set initially at 130°C for 2 minutes, then was ramped at 10°C/min. to 300°C and held for 23min. The detector interface was set at 280°C. Injections were performed in split mode and 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  $m/z$  10 to 500 was scanned at 1.3 scans/sec. Individual peaks in chromatograms were identified by matching their mass spectra to standard reference mass spectra within the National Institute of Standards and Technology (NIST) library. Identification was further confirmed using retention times of GC/MS mass chromatograms of authentic reference compounds.

### *Compound Specific Isotope Analysis (CSIA)*

An Agilent 6890 Series gas chromatograph (GC) was interfaced to a Finnigan Delta Plus XL isotope ratio mass spectrometer (IRMS) through a combustion furnace (GC-IRMS). Injections into the GC were performed in split mode with ultrapure helium employed as carrier gas. The GC column and program were identical to that indicated for GC/MS analyses. Compounds were first combusted in a ceramic furnace at 850° C, passed through a nafian membrane water trap, and then were introduced into the mass spectrometer as pulses of CO<sub>2</sub>. The  $\delta^{13}\text{C}$  values of replicate analyses for the cores typically ranged from 0.1‰ to 1‰. Plant samples were run in triplicate with no standard deviation >1‰.

### **Results**

The absolute abundances of identified *n*-alkanes present in the sampled marsh plants show a strong odd/even carbon number predominance (Figure 3, Appendix A). In addition, *n*-alkanes with chain lengths of less than 21 were almost absent, and no *n*-alkanes above chain length 34 were detected. All plants sampled showed greatest abundance at either C-25 (10%), C-27 (10%), C-29 (30%), C-31 (40%), or C-33 (10%). The two C4 species, *Spartina alterniflora* and *Spartina patens*, show peak abundances at C-29, while the CAM species, *Salicornia europaea*, peaks at C-25. Peak abundances for the C3 species are more variable. The only *n*-alkanes present in all plants studied were those with chain lengths of C-27, C-29, and C-31.

Table 2 (Appendix B) reports the isotopic compositions of the C-27, C-29, and C-31 alkanes for all of the plant samples. The isotopic composition of the C-31 alkane is not reported for *Spartina alterniflora* because it was not detected by GC-IRMS. The isotopic composition of the C-31 alkane is also not reported for *Suaeda maritima* because of co-elution problems. Reported  $\delta^{13}\text{C}$  values for the C4 species range from a C-27 high of -19.78‰ to a C-31 low of -23.87‰. Reported  $\delta^{13}\text{C}$  values for the C3 species range from a C-27 high of -26.37‰ to a C-31 low of -36.69‰. The CAM species displayed C3-like  $\delta^{13}\text{C}$  values ranging from a C-29 high of 30.28‰ to a C-31 low of -32.49‰. Our isotopic values are consistent with those reported for *n*-alkanes in other studies (Canuel et al., 1997).

Absolute abundances for identified *n*-alkanes are presented for all core samples (Figures 4 and 5, Appendix A). The odd/even predominance observed for the plant samples is likewise present for all core samples studied. The odd/even predominance of *n*-alkanes is indicative of a dominant contribution from higher plants (Collister et al., 1994), and is consistent with other studies of salt-marsh plants (Wang et al., 2003). Carbon isotopic compositions of the C-27 and C-29 homologues are presented for all core sample increments (Figure 6, Appendix A). Isotopic values for the C-31 homologue are not presented for the core samples because this compound was not detected by GC-IRMS for *Spartina alterniflora*, one of the turf dominants.

## Discussion

To reconstruct the distribution of C3 and C4 plant communities from a core sample, it is necessary to choose an organic compound that is abundant in all plant samples studied, is present at roughly the same concentration in all of the plants studied, and for which the isotopic values between the C3 and C4 plants are widely separated. Once these criteria are met, the isotopic value of the compound in question can be used to monitor the fluctuation of plant communities through time in a core sample.

Low concentrations of even chain *n*-alkanes make these compounds unsuitable for isotopic analysis. The C-21, C-23, C-25, and C-33 homologues are present in detectable quantities in only some of the sampled plants, making these compounds unsuitable as well. The C-27, C-29, and C-31 homologues are abundant in all plant samples studied. However, the C-31 homologue was not detected by GC-IRMS for one of the turf dominants (*Spartina alterniflora*), making this compound unsuitable for use with cored deposits. Also, the abundance of the C-31 homologue is highly variable between the different plant samples, having a coefficient of variation of 134.17% (Table 2, Appendix B). The C-27 homologue has the lowest coefficient of variation between plant samples (61.95%), with the C-29 homologue having slightly more variable abundance (coefficient of variation = 79.20%). The C-27 homologue is highly abundant in all plant samples studied, and it also shows the least variability in abundance, making it a good choice for use in the core samples. However, the C-27 homologue only has a 3‰ range between its C4 low value and C3 high value (Table 1, Appendix B), thus limiting its potential sensitivity to changes in organic matter contributions. Though the C-29 homologue has

higher variability in absolute abundance between studied plants, it has a 6.38‰ separation between its C4 low value and C3 high value, and thus may be a more sensitive responder to changes in organic matter inputs to the marsh.

The C-27 and C-29 homologues meet the criteria for selection as they are relatively abundant in all plant samples studied, have a relatively low variability in absolute abundance between the different plant samples compared with the other homologues, and have separated carbon isotopic values between the C3 and C4 components. Isotope values for the C-27 and C-29 chain lengths are depleted by ~6-10‰ relative to what would be expected for a bulk C3 or C4 value. A similar depletion of the carbon isotopic composition of *n*-alkanes has also been reported by other researchers (Shi et al., 2001).

For the coréd deposits, carbon isotopic values for the C-27 and C-29 alkanes covary, showing a C3-dominated signal for most sample intervals (Figure 6, Appendix A). The C-27 homologue indicates a mixed plant community near the surface, transitioning to a C4-dominated community at 20cmbs (centimeters below surface), back to a C3-dominated plant community at 40cmbs. The C-27 alkane also shows excursions to less-negative values at 80-90 and 190cmbs. The C-29 homologue shows the same fluctuations, but all indications of a C4-dominated plant community are muted. At the marsh, we noted a mixed C3/C4 plant community at the surface, containing ~50% *Juncus gerardi* and ~50% *Spartina patens*. The C-27 homologue indicates a mixed community near the surface, while the C-29 homologue suggests a C3 dominated plant community.

In an earlier sea-level study, Gehrels et al. (1994a) reported on a core (SN-VC-3) that was recovered on the same transect directly adjacent to our core (Figure 1, Appendix

A). SN-VC-3 stratigraphy was correlated with the core reported herein using depth to glacial marine sediments and other markers as reference points. Gehrels et al. reported marsh deposits to a depth of ~230 cmbs, associated with the  $3,010 \pm 70$  ka radiocarbon date. The researchers noted species composition down-core by observing plant fragments in the cored deposits and suggested two excursions to a mixed plant community (HM) at 60-120 and 180-193 cmbs (Figure 6, Appendix A). While the C-27 and C-29 homologues both show these excursions at the correct sample depths, the C-27 alkane is more suggestive of a mixed plant community signal, indicated by less-negative carbon isotopic values. The interpretation of the plant stratigraphy does show a plant community that would be C3-dominated for most core depths, in agreement with our results. The only disagreement is the interpretation of a HHM plant community from the surface to a depth of ~60cm. Gehrels (1994a) did show a mixed HM/HHM interpretation for this depth interval on a more generalized cross section (Our Figure 1, Appendix A). We noted a HM plant community near the surface with a mix of *Spartina patens* and *Juncus gerardi*. Our interpretation is supported by the intermediate (suggesting a mixed plant community) isotopic values at this level. The general transition to brackish/freshwater marsh deposits at depth is supported by a late-Holocene sea level rise at the site reconstructed using distributions of salt marsh foraminifera (Gehrels et al., 1996), and is consistent with our more negative (C3 dominated) isotopic values.

From our observations of surface plant community composition and Gehrels (1994a) observation of macroscopic plant fragments down-core, it is apparent that the C-27 homologue is providing the most accurate record of salt marsh plant community composition. Though the C-29 alkane co-varies with the C-27 homologue ( $R^2=0.75$ ),

variations in the C-29 carbon isotopic values are more muted. It is possible that a C3 species like *Suaeda maritima* is strongly influencing the carbon isotopic values for the C-29 alkane because of the strong abundance of the homologue in the plant sample (Figure 3, Appendix A), while no individual plant species is controlling isotopic values for the C-27 alkane. The C-29 homologue does have a higher coefficient of variation for absolute abundance between the different plant samples than the C-27 homologue (79.20% vs. 61.95%). Taking these data into account, we suggest that the C-27 alkane is the most useful homologue to utilize for monitoring plant community fluctuations within Maine salt marshes.

While the eventual transition from a mixed plant community to a C3 dominated community is expected (moving from high marsh deposits to brackish/freshwater marsh deposits), the rapid excursions to less-negative (C4) values below 40cmbs are not well understood. Additional work is needed to determine the causes of these significant (up to 4‰) fluctuations. It is possible that plant communities within the marsh are responding to salinity changes that are not a direct result of sea level rise (i.e. addition or subtraction of freshwater inputs to the marsh). Other factors such as disturbance episodes could be responsible for the transitions. In addition, the “patchiness” of the high marsh could account for some of the variation.

Our isotope values are likely a result of a marsh succession that is a response to a late Holocene relative sea-level rise. This rise has been reported at many locations along the Maine coast (Barnhardt et al., 1997; Belknap et al., 1989; Gehrels, 1994b; Gehrels and Belknap, 1993; Gehrels et al., 1996; Kelley et al., 1995). While our results demonstrate that the C-27 and to some extent the C-29 alkane can be used to distinguish

between C3 and C4 species in northeastern, USA salt-marsh deposits, it will be necessary to control for sea level rise if isotope values are to be used to provide additional paleoenvironmental information, since sea level likely exerts a strong influence on plant community patterns within the marsh. Sea-level controls can be accomplished through analysis of foraminiferal distributions that are thought to be controlled by tidal inundation frequency, thus providing an accurate sea-level indicator (Gehrels, 1994b). Once this control is provided for sea-level, analysis of the carbon isotopic composition of *n*-alkanes within specific salt-marsh zones (i.e. high marsh) and their fluctuation between C3 and C4 values may provide information on additional environmental variables, such as plant community changes as a response to changing climatic conditions (eg. salinity variations due to precipitation or temperature fluctuations). Future work will incorporate this type of analysis, and will address the issue of carbon isotope fluctuations within specific *foraminiferal* salt-marsh zones.

## Conclusion

The C-27 and C-29 *alkanes* are abundantly present in the plant communities that are prolific in Maine salt-marshes. These compounds provide a means to monitor plant community changes while ruling out potential contributions to isotopic values from different algal species. Comparison of carbon isotopic values for the C-27 and C-29 homologues with data derived from macroscopic core descriptions suggest that the C-27 alkane is the better choice for monitoring marsh plant composition through time. Isotopic values for the different homologues are ~6-10% more depleted than would be expected

from bulk analysis. A strong odd/even predominance of identified *n*-alkanes from core samples is indicative of dominant contributions from higher plants. In our core,  $\delta^{13}\text{C}$  values for the C-27 homologue suggest a mixed (C3 and C4) signal near the modern marsh surface, becoming more depleted down core, implying a switch to a C3 dominated community. This successional sequence is most likely the result of late Holocene sea-level rise. Additional isotopic fluctuations observed within the cored deposits agree with macroscopic plant identification, but are presently not well understood. Future work will address these transitions. In order to use carbon isotope values to provide additional paleoenvironmental information, it is necessary to have a control for sea-level rise. Foraminiferal distributions should provide this control, and future research will incorporate this type of analysis.

**Chapter 2 - Comparison of Bulk and Compound-Specific  $\delta^{13}\text{C}$  Analyses and Determination of Carbon Sources to Salt Marsh Sediments Using *n*-Alkane Distributions (Maine, USA)**

This chapter will be submitted for publication in an appropriate journal after completion of the dissertation.

My use of “we” in this chapter refers to my co-authors and myself. My primary contributions to this paper include (1) selection of the topic and development of the problem into a work relevant to my study of salt marsh plant community dynamics, (2) design of a field strategy, (3) vegetation and sediment sampling and analysis, (4) most of the gathering and interpretation of the literature, (5) most of the writing.

**Introduction**

Salt marshes represent a dynamic interface between terrestrial and marine habitats and are responsive to changing environmental conditions including sea level (Gehrels et al., 1996; Shaw and Ceman, 1999), salinity and climate (Byrne et al., 2001; Malamud-Roam and Ingram, 2004), species invasions (Bull et al., 1999), and other anthropogenic disturbances (Bertness et al., 2002). Salt marshes are also a sink for atmospheric  $\text{CO}_2$ , storing at least 44.6 Tg of carbon per year globally (Chmura et al., 2004), making them an important component of the global carbon cycle (Choi et al., 2001; Choi and Wang, 2004).

Carbon isotope ratios and organic biomarkers are central to our understanding of ancient vegetation dynamics and are used to reconstruct plant community structures within salt marsh deposits (Bull et al., 1999; Chmura and Aharon, 1995; 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 (~10‰) carbon isotopic difference between the plants 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 bulk  $\delta^{13}\text{C}$  values are reported with radiocarbon dates. 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  $\delta^{13}\text{C}$  values and found that marine phytoplankton and algae 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 (Benner et al., 1991; Huller et al., 1996; Valiela et al., 1985), with less degradation of sediments that are under greater influence from the water table (Goni and Thomas, 2000; Lallier-Verges et al., 1998). 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 (Byrne et al., 2001; Johnson and Calder, 1973; Huller et al., 1996; Malamud-Roam, 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 (Benner et al., 1991; Ember et al., 1987), or rapid initial depletion with subsequent stasis (Chmura et al., 1987; Fogel et al., 1989).

The potential for distinctive  $\delta^{13}\text{C}$  source signatures is high for northeastern, USA estuaries (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, extensive sea level research reveals ancient (>5,000 yrs BP) 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 salt marsh sediments from the Maine coast through the latter Holocene, and to determine if degradation of the sediments influences bulk  $\delta^{13}\text{C}$  values.

Using a salt marsh core from Phippsburg, ME, we compare bulk  $\delta^{13}\text{C}$  values with compound specific  $\delta^{13}\text{C}$  values of high chain length, odd numbered *n*-alkanes, thought to be a refractory biomarker for higher plant inputs (Cranwell, 1973; Eglinton and Hamilton, 1967; Huang et al., 2000; Pearson and Eglinton, 2000; Rieley et al., 1991), being only a minor component in marine organisms (Sakata et al., 1997), and surviving in salt marsh deposits for up to 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). Isotope values and *n*-alkane distributions from cored deposits are compared with those determined from samples of 10 abundant plant species from a Machiasport, ME salt marsh, representing the most comprehensive number of species used in this type of analysis for the northeastern US.

## Methodology

### Field Methods

The reported core was collected at the Morse River marsh near Phippsburg, ME during the month of August, 2003. Marsh floral samples were collected from the Machiasport marsh (Sanborn Cove), ME during the month of August, 2004 (Figure 2, Appendix A). The Machiasport site is located within Maine's north-central coastal compartment (Kelly, 1987; Tanner et al., in revision). The NC compartment is characterized by abundant granitic plutons. The relative resistance of the plutonic bodies

to erosion has resulted in a coastline that contains broad estuaries with numerous granitic islands. According to published literature, the Machiasport site can be classified as a “bluff-toe” marsh, as its sediment is derived from nearby eroding bluffs (Gehrels, 1994a; Kelley et al., 1988).

The Morse River site is located within Maine’s southcentral (SC) coastal compartment. The southcentral (SC) coastal compartment is characterized by north-striking metasedimentary rocks with deep, glacially scoured valleys. 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, 1994a; Kelley et al., 1988). These two field sites were 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, 1994a; Gehrels et al., 1996).

Marsh plants were sampled by establishing a transect line, with collection of unique species located within 10m 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. Collection of plant roots is important because below ground production of roots and rhizomes exceeds above ground production for some salt marsh plants (Good et al., 1982; Schubauer and Hopkinson, 1984). All plant samples were photographed, catalogued, placed in ashed tin foil, and stored in freezers at the University of Maine and finally transported on dry ice to the University of Tennessee.

The 260 cm long core was extracted at the Morse River marsh using an Eijkelpkamp 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 layer of salt marsh sediment). After recovery the collected core was logged, photographed, video-taped, wrapped in ashed tin foil, wrapped in plastic, and placed in a split PVC tube and stored as described for the plant samples.

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 the following general characteristics (Belknap et al., 1989; Gehrels, 1994a):

- LM: Muddy or sandy matrix with low density of organic material, in situ *Spartina alterniflora* roots and rhizomes. Usually found adjacent to the tidal channel.
- TM: Fibrous high marsh peat with abundant *Spartina alterniflora* remains in addition to remains of *Spartina patens*. Occasionally present between the low and high marsh.
- HM: Dark brown to grayish brown peat characterized by an interwoven, dense network of fine *Spartina patens* roots. Often divides the low marsh from the higher high marsh.
- HHM: Light brown peat containing remains of *Juncus gerardi* roots (wavy) and rhizomes (smooth and reddish-brown) with *Solidago sempervirens* tissue (woody) and stele ('fishbone'). Often found adjacent to the upland border.
- BM: Characterized by *Scirpus* remains, black and triangular in cross section, and containing peat with a "coffee grounds" texture.

FM: Dark-brown to black structureless peat with remains of *Typha angustifolia* plants and the presence of leaves, bark, and other detrital material.

Once in the lab, core samples were sectioned into 10cm increments and divided for foraminiferal, radiocarbon, and isotopic analysis. Plant samples were rinsed in deionized water. Core and plant samples for chemical analysis were then air dried at 60° C for 24 hours before being further processed. Core samples to be used for bulk and compound-specific isotopic analysis were then crushed using a mortar and pestle. Plant samples were shredded using a coffee grinder.

#### Foraminifera Sample Preparation and Analysis

Foraminifera were processed according to established techniques (Scott and Medioli, 1980). Cores were split into sections measuring 10cm in length and 1.5cm in diameter. The 10cm increments were further divided into sections measuring 10cm x ~0.5cm<sup>2</sup>, resulting in individual sample sizes of ~2.5cm<sup>3</sup>. Samples were then wet sieved through 0.5mm and 0.063mm sieves. Foraminifera were collected from the 0.063mm screen. Fine organic material was separated from the foraminifera by decantation.

Foraminifera were subsequently dried and then counted under a microscope.

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

water, and faunal zone 2A to extend from just above to ~0.2m above mean high water. A Ward's cluster analysis was employed to validate the faunal zone designations. Each sample point from the core was assigned by the computer 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.

### Compound Separation and Analysis

Compounds from all plant and core samples were extracted using a Dionex ASE 300. Samples were flushed with dichloromethane (40%) and methanol (60%) at 125° C and 1500 p.s.i. for 10 min. This process was repeated four times for each sample. After drying down, 3 ml of 5% KOH in MeOH:H<sub>2</sub>O (80:20; pre-extracted with chloroform) was added to each sample. Samples were then flushed with nitrogen, sealed tightly and placed in a heat block at 80° C for 2 hrs. The pH of each sample was checked to ensure that the solutions were still basic. Approximately 3 mls of Milli-Q H<sub>2</sub>O were added to each sample, and samples were extracted three times with 3 ml of hexane:chloroform (4:1). Total neutrals were then separated from fatty acids using a separatory funnel. Samples were concentrated using a rotovap, and were then analyzed using a gas chromatography-mass spectrometer (GC-MS) and gas chromatography-isotope ratio mass spectrometer (GC-IRMS).

All carbon isotope values for bulk and compound-specific isotopic analysis are reported in conventional delta ( $\delta$ ) notation in per mil (‰) relative to the Pee Dee

Belemnite (PDB) standard. The  $\delta^{13}\text{C}$  notation expresses the  $^{13}\text{C}/^{12}\text{C}$  ratio as defined by the equation:

$$\delta^{13}\text{C} = \left( \frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} - 1 \right) \times 10^3$$

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  $\text{C}_{23}$  to  $\text{C}_{34}$  where,

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

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

$$\text{ACL} = \sum [C_i]i / \sum [C_i]$$

where *i* is the carbon number from  $\text{C}_{23}$  to  $\text{C}_{34}$  and  $[C_i]$  is the concentration. CPI values were calculated using GC/MS reported concentrations, with a few being less than  $0.5\mu\text{g}$ . Therefore, while values of “O” may appear in table 3 (Appendix B) for the concentration value for some of the compounds, the small values for these compounds are used in the calculations. CPI values for the plants range from 3.8 to 34.2. No even chain lengths were detected for *Spartina alterniflora*, making calculation of CPI impossible for this species. ACL values average 29.1 for the plants with a standard deviation of 1.0.

## *Gas Chromatography-Mass Spectrometry (GC-MS)*

Individual alkanes were separated and characterized using an Agilent 6890 Series GC interfaced to an Agilent 5973N mass selective detector (MS). Compound separation was achieved using a 30m x 0.25 mm i.d. x 0.16 $\mu$ m film thickness VF-5 column. Oven temperature was set initially at 130°C for 2 minutes, then was ramped at 10°C/min. to 300° C and held for 23 min. The detector interface was set at 280°C. Injections were performed in split mode and 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  $m/z$  10 to 500 was scanned at 1.3 scans/sec. Individual peaks in chromatograms were identified by matching their mass spectra to standard reference mass spectra within the National Institute of Standards and Technology (NIST) library. Identification was further confirmed using retention times of GC/MS mass chromatograms of authentic reference compounds.

## **Bulk Isotope Sample Preparation and Analysis**

Core samples were pretreated with hydrochloric acid to remove carbonates and were then combusted to yield CO<sub>2</sub> for isotopic analysis using established techniques (Boutton, 1991). Carbon isotope ratios were measured on a dual inlet Finnigan Delta XL.

For the Morse River core, bulk isotope values represent the mid-points of 10cm core sample increments, except for the 100cm to 120cm 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 20cm long sampling increment, and was reported with the radiocarbon date. Compound specific isotope data points represent the mid-points of 10cm sample sections. Sections of 10cm were skipped between sample intervals (e.g. samples are from 0-10, 20-30, 40-50, etc.).

#### *Compound Specific Isotope Analysis (CSIA)*

An Agilent 6890 Series gas chromatograph (GC) was interfaced to a Finnigan Delta Plus XL isotope ratio mass spectrometer (IRMS) through a combustion furnace (GC-IRMS). Injections into the GC were performed in split mode with ultrapure helium employed as carrier gas. The GC column and program were identical to that indicated for GC/MS analyses. Compounds were first combusted in a ceramic furnace at 850° C, passed through a nafian membrane water trap, and then were introduced into the mass spectrometer as pulses of CO<sub>2</sub>. Plant and core samples were run in triplicate with a standard deviation of less than 1‰ for each sample set. Multiple runs of the DNAP standard returned a standard deviation of 0.3‰.

#### *Radiocarbon Dating*

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

sediments. Calibrations are reported using the INTC AL 98 calibration database.

Although one of the radiocarbon dates reported for our core is a “basal” date, we did not penetrate the Pleistocene substrate, but rather refused on compact marsh sediments, making humic acid contamination unlikely (Belknap et al., 1989).

## Results

### Chronology

The radiocarbon measurement associated with the deepest section of the Morse River core, 240cm to 260cm below the surface, returned a conventional date of 3390 $\pm$ 60 RCYBP, with a 2 $\sigma$  cal. age range of 3820 to 3470 YBP. The second assay represents the section from 100cm to 120cm below the surface, which was dated at 1160 $\pm$ 60 RCYBP, with a 2 $\sigma$  cal. age range of 1240 to 950 YBP.

### Sediment and Foraminiferal Stratigraphy

Stratigraphic interpretations for the Morse River core are presented in Figure 7, Appendix A along with foraminiferal distributions. Foraminiferal abundances were determined for individual 10cm 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 *Tiphotocha comprimata* are presented (Figure 7,

Appendix A). 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, Appendix B) 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 35cm below surface, indicating a faunal zone 1B/2A assemblage and (2) Dominance of *Trochammina macrescens* forma *macrescens* and absence of *Tiphotocha comprimata* around 160cm 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,  $p = 0.05$ )

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

#### *n*-Alkane Distributions

While construction of a mixing model using two plant species is mathematically clean (Bull et al., 1999; Wang et al., 2003), the marsh landscape is complex and is not realistically represented by a model with only two end members. We 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* (see chp. 1, this volume). In addition, other abundant salt marsh species were sampled including *Salicornia europa*, *Atriplex patula*, *Potentilla anserina*, *Plantago maritima*, *Suaeda maritima*, and *Limonium nashii*. Alkane distributions are presented for the plant species with the species' associated photosynthetic pathway, carbon preference index (CPI), and average chain length (ACL) (Table 3, Appendix B).

Distributions of *n*-alkanes are presented for the Morse River core deposits (Table 4, Appendix B). 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 55cm (11.2), 95cm (71.4), 115cm (15.3), 125cm (23.7), 145cm (14.5), and 215cm (13.0). The core deposits remain fairly steady down-core, and have an average ACL value of 27.5 with a standard deviation of 0.6.

#### $\delta^{13}\text{C}$ of Organic Matter

Bulk  $\delta^{13}\text{C}$  values are presented with compound-specific  $\delta^{13}\text{C}$  values for the Morse River core (Table 4, Appendix B). Compound-specific isotope values for the core deposits are reported for the  $\text{C}_{27}$  homologue only, as our research suggests that it best represents Maine salt marsh plant communities (Tanner et al., this volume), being abundant in all plants studied, and having the lowest coefficient of variation between plant samples (61.95%) for the different homologues (Table 3, Appendix B). The coefficient of variation is presented for the  $\text{C}_{27}$ ,  $\text{C}_{29}$ , and  $\text{C}_{31}$  alkanes because these three compounds were detected in all plant samples studied. Values of  $\delta^{13}\text{C}$  for the  $\text{C}_{27}$  alkane are also presented (Table 3, Appendix B).

When plotted together, the isotope curves show several common excursions (Figure 8, Appendix A). Isotopic values for the C<sub>27</sub> 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 ( $R^2=0.87$ ; Figure 9, Appendix A). Both isotope records (bulk and C<sub>27</sub>) show intermediate values near the surface, moving to less negative (C4) values by 25cm below the surface. Both records show a dominantly C4 (less negative) signal down-core, with excursions to C3 values (more negative) around 145cm and 225 cm below the surface.

## **Discussion**

### **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, 1994a; 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, 1994a; 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 (Goni and Thomas, 2000; Lallier-Verges et al., 1998), 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 (Figure 7, Appendix A).

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, Appendix B), so it is not surprising that these floral zones are solely present in the Morse River core.

#### *n*-Alkanes

The recognition of the ubiquitous presence of faunal zone 1B deposits 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 years (from radiocarbon chronology). An obvious trend of both the plant and core *n*-alkane distributions is the dominant presence of odd, higher chain length homologues (Tables 3 and 4, Appendix B), suggestive of primary inputs from higher plants. Peak abundances of *n*-alkanes from higher plants are generally within the C<sub>27</sub> to C<sub>33</sub> range (Chikaraishi and Naraoka, 2003; Collister et al., 1994; Cranwell, 1973; Eglinton and Hamilton, 1963; Freeman and Colarusso, 2001; Lockheart et al., 1997; Rieley et al., 1993), and most of the Machiasport plants peak within this range. A notable exception is *Salicornia europa*, the only CAM plant found in the marsh, which peaks at C<sub>25</sub> (Table 3, Appendix B). Non-emergent, freshwater plants can also be characterized by an enrichment in C<sub>25</sub>, with C<sub>23</sub> also common (Chikaraishi and Naraoka, 2003; Ficken et al., 2000), while algal and cyanobacterial inputs are signaled by a higher abundance of C<sub>17</sub>, or C<sub>15</sub>, C<sub>17</sub>, and C<sub>19</sub> (Blumer et al., 1971; Cranwell et al., 1987; Han et al., 1968; Gelphi et al., 1970; Giger et al., 1980), or C<sub>15</sub> to C<sub>32</sub> without an odd/even preference (Weete, 1976). C<sub>14</sub> to C<sub>20</sub> *n*-

alkanes without an odd/even preference are a biomarker for photosynthetic bacteria (Albro, 1976), while non-photosynthetic bacteria produce *n*-alkanes ranging from C<sub>26</sub> to C<sub>30</sub> without an odd/even preference.

Distributions of *n*-alkanes for the core deposits show abundances maximizing at C<sub>25</sub> (n=12), C<sub>27</sub> (n=8), and C<sub>29</sub> (n=5), certainly within the range of higher plants and non-emergent freshwater plants (C<sub>25</sub>). If non-emergent, freshwater plants were contributing significantly to the sedimentary *n*-alkane fraction, we might expect there to be maxima at C<sub>23</sub> for some of the core depths, which is not the case. *Zostera marina* is a submerged, saltwater plant common to Maine estuaries. Canuel et al. (1997) found that *Zostera m.* has an *n*-alkane distribution that ranges from C<sub>17</sub> to C<sub>27</sub>, peaking at C<sub>21</sub>, and is dominated by odd-numbered compounds. If *Zostera m.* was significantly represented in the marsh sediments, there would be a high abundance at C<sub>21</sub>, which is not the case. Also, if *Zostera m.* was present in significant quantities, C<sub>17</sub> and C<sub>19</sub> alkanes should be more abundant in the marsh sediments.

An alternative possibility is that *Salicornia europaea* is contributing heavily to the carbon pool where C<sub>25</sub> 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. Finally, there could be another, non-sampled marsh plant with a C<sub>25</sub> maximum that is contributing heavily to the marsh sediments. We did not profile *Ruppia maritima*, another submerged saltwater plant. *Ruppia m.* is a significant floral component of salt pannes in Maine marshes, and it is possible that this species could be contributing to the *n*-alkane pool of the marsh sediments. Salt pannes are notoriously difficult to identify in salt marsh deposits (Gehrels, 1994a), and it is possible that these deposits could be identified in

cores using *Ruppia m.* biomarkers. More work is needed to profile *Ruppia m.* organic compounds in order to find a biomarker to use for future core work.

The average ACL value for the core deposits (27.5) is lower than the average ACL value for the sampled salt marsh plants (29.1), but is within the range attributed to higher plants in general (Collister et al., 1994; Wang et al., 2003). *Salicornia europa* has a low ACL value, attributable to its large peak at C<sub>25</sub>, and could be a significant contributor to the Morse River marsh sediments, helping to lower ACL values for the core deposits. The 1.6 unit difference between core and plant deposits could also be attributable to degradation, or again, to an as yet unidentified plant source.

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, Appendix B). Johnson and Calder (1973) found that CPI values near one indicate bacterial activity, while vascular plants have values ranging from ~3 to 40 (Chikaraishi and Naraoka, 2003; Collister et al., 1994; 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), 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 europa* contributes 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 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<sub>25</sub> along with the more negative isotope values from 115 to 175cm below the surface suggests that *Salicornia europaea* is highly abundant through these sample depths. Chmura (1995) states 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, coming to a similar conclusion as the present authors, 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.”

The implication of the second possibility, that an as 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. In either 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.

## 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<sub>27</sub> alkane are in good agreement with the bulk values, co-varying, and showing the same excursions down-core (Figure 8, Appendix A). The compound specific isotopic values are depleted by 7.2‰ (Std. Dev. = 1.0‰) on average relative to bulk

values. There is no obvious trend towards lighter or more enriched values down-core, a characteristic that would signal alteration of the isotopic composition due to degradation.

Figure 9 (Appendix A) provides further support of the suggestion that bulk and  $C_{27}$  compound specific carbon isotope values co-vary. The two records are strongly correlated, showing a linear relationship when cross-plotted ( $R^2 = 0.87$ ). 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 (Byrne et al., 2001; Johnson and Calder, 1973; Malamud-Roam, 2001). Also, *n*-alkane distributions indicate that algal contributions are minimal, and their effect on bulk isotope values are being “swamped” by the dominant abundance of plant material.

Bulk and compound specific isotope values are likely recording contributions of  $C_3$ ,  $C_4$ , and CAM plants to the Morse River marsh deposits. Foraminiferal zone 1B is solely present for most sample depths, so there is an expected presence of both  $C_3$  and  $C_4$  species (Table 2, Appendix B; Figure 7, Appendix A). There are two minor changes in faunal zone down-core, with some zone 2A influence (more  $C_4$  expected) from 20cm to 50 cm below the surface, and zone 1A (more  $C_3$  expected) influence from 150cm to 170cm below the surface. There is a trend towards less negative values ( $C_4$ ) at the 20cm to 50cm sample depth. There is also a trend towards more negative values ( $C_3$ ) at and above the 150cm to 170cm 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. Current work at multiple marsh sites is addressing the issue of isotopic fluctuations within specific foraminiferal (mean high water) zones.

## Conclusion

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 carbon fraction is minimal. Bulk carbon isotopic values co-vary with the C<sub>27</sub> homologue, 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<sub>25</sub> homologue down-core implies that either *Salicornia europaea* is an important contributor to the carbon pool, or that there are major contributions from an as yet unidentified plant source. We strongly 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.

### **Chapter 3 - Compound Specific Isotopic Analysis of *n*-alkanes and Distributions of Foraminifera from Four Maine, USA Salt Marsh Sites Record Marsh Responses to Frequent Late Holocene Disturbance**

This chapter will be submitted for publication in an appropriate journal after completion of the dissertation.

My use of “we” in this chapter refers to my co-authors and myself. My primary contributions to this paper include (1) selection of the topic and development of the problem into a work relevant to my study of salt marsh plant community dynamics, (2) design of a field strategy, (3) vegetation and sediment sampling and analysis, (4) most of the gathering and interpretation of the literature, (5) most of the writing.

#### **Introduction**

Stable isotopic values of carbon are often used to provide a signature of plant inputs to salt marsh sedimentary organic matter (Byrne et al., 2001; Chmura and Aharon, 1995; Choi et al., 2001; Malamud-Roam and Ingram, 2004). Salt marshes typically exhibit a zonation pattern that is a reflection of both an ocean-to-land salinity gradient (Chmura et al., 1987) and other individual characteristics of the specific marsh (Silvestri et al., 2005). Since salinity has some effect on species composition, and since salt tolerance is regulated to some extent by the photosynthetic pathway employed by the marsh species, carbon isotopes can be used to distinguish between C4 plants (Hatch-

Slack) that tend to inhabit the lower marsh, and C3 (Calvin-Benson) species that favor higher marsh environments. The large (~10‰) isotopic difference between the plant types can be used to quantify the proportion of C3 and C4 species contributing to a mixture of plant material (Cerling, 1989).

Unfortunately, there is not a one-to-one relationship between flooding-frequency/salinity and the distribution of species within a marsh. Other important factors influencing species distributions include the age and stability of the marsh (Jacobson and Jacobson, 1989; Redfield, 1972), deposition of tidal wrack (Bertness et al., 1992; Reidenbaugh and Banta, 1980) and other disturbance episodes (Clark, 1986; Clark and Patterson, 1985; Ewanchuk and Bertness, 2003), subsurface flow (Hemond and Fifield, 1982; Thibodeau et al., 1998), nutrient availability (Mitsch and Gosselink, 1986; van Wijnen and Bakker, 1999), plant competition (Bertness, 1991; Crain et al., 2004), and sediment supply (Leendertse et al., 1997; Olff et al., 1997). Given the increasing interest in global warming and climate change, researchers are attempting to relate marsh plant community changes to climate (Bertness and Ewanchuk, 2002; Callaway and Sabraw, 1994), even into the past (Byrne et al., 2001; Malamud-Roam and Ingram, 2004).

If, as Malamud-Roam and Ingram (2004) have proposed, estuarine deposits are to be used to "...infer past climate conditions over a large region..." by providing a salinity proxy, it must first be established that the salt marsh can provide a viable record of paleosalinity (hence paleoprecipitation) that is independent from such factors as sea level and tidal range fluctuations, random disturbance episodes, autogenic changes in marsh elevation, etc. It has been recognized for some time that within salt marshes "vegetation changes are environmentally determined, yet environmental and vegetation patterns do

not coincide” and that “the physical setting insures that these variables [regulating species productivity] fluctuate in a stochastic fashion (Clark, 1986).” There is clearly a discrepancy between the contrasting interpretations presented in these two studies.

We test the hypothesis that fluctuating salt marsh plant communities can be used to monitor changing climatic conditions using a series of dated cores from four Maine, USA salt marshes. Climatic parameters that could influence marsh plant distributions include salinity, temperature, and precipitation. Some research suggests that salinity is likely to be the factor dominating marsh plant community dynamics (Chmura and Aharon, 1995). Other climatic factors, including precipitation and temperature, can directly or indirectly affect salinity. In the present study, foraminiferal counts are used as a control for sea level variations, thus factoring out its [probably] substantial effects on marsh plant communities. Salt marsh foraminifera are considered to have a more direct relationship with sea level than marsh plants (Gehrels et al., 1996), since foraminifera live on the marsh surface, or in the uppermost, oxygenated few millimeters of sediment (Nydic et al., 1995). Another important oceanic influence, tidal range amplification, is known for our field sites from previous work (Gehrels, 1994; Gehrels et al., 1996).

A series of cores were collected from four Maine salt marshes, and a regional strategy is used to determine co-variation between field sites, thus providing a test for local (i.e. disturbance episodes) vs. regional (i.e. climate) influences on plant community compositions. Distributions of higher-chain length, odd *n*-alkanes, thought to be a refractory biomarker for higher plant inputs (Cranwell, 1973; Eglinton and Hamilton, 1967; Huang et al., 2000; Pearson and Eglinton, 2000; Rieley et al., 1991), and only a minor component in marine organisms (Sakata et al., 1997), are used to determine

sources of organic matter to the sediment pool. Compound specific isotopic analysis (CSIA) is employed to determine the carbon isotopic composition of individual *n*-alkanes from dominant salt marsh plants, and to monitor fluctuations in C3 vs. C4 plant communities through time. To our knowledge, this combination of peat stratigraphy and foraminiferal stratigraphy along with compound specific isotope and organic geochemical analyses of deep cores and dominant plants from multiple, well-studied field sites, represents the first study of its kind conducted in North America.

## **Methodology**

### **Field Methods**

Marsh floral samples were collected from a Machiasport, Maine marsh (Sanborn Cove) during the month of August, 2004 (Figure 2, Appendix A). The reported cores were collected at the Machiasport marsh (core MC2), the Morse River and Sprague River marshes near Phippsburg (cores MO2 and SP2 respectively), and the Gouldsboro marsh (Grand Marsh, core GC3) during the summer of 2003. The Machiasport and Gouldsboro sites are located within Maine's north-central (NC) coastal compartment (Kelly, 1987; Tanner et al., in revision). The NC compartment is characterized by abundant granitic plutons. The relative resistance of the plutonic bodies to erosion has resulted in a coastline that contains broad estuaries with numerous granitic islands. According to the literature, the Machiasport and Gouldsboro sites can be classified as "bluff-toe" marshes,

as their sediment is derived from nearby eroding bluffs (Gehrels, 1994; Kelley et al., 1988).

The Morse River and Sprague River sites are located within Maine's southcentral (SC) coastal compartment. The SC coastal compartment is characterized by north-striking metasedimentary rocks with deep, glacially scoured valleys. This combination of bedrock and structure results in a series of northwest oriented peninsulas with intervening deep, narrow estuaries. The Morse River and Sprague River marshes are back-barrier (Gehrels, 1994; Kelley et al., 1988). These four field sites were 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, 1994; Gehrels et al., 1996), thus providing a long record of environmental conditions.

Marsh plants were sampled by establishing a transect line, with collection of unique species located within 10m 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. Collection of plant roots is important because below ground production of roots and rhizomes exceeds above ground production for some salt marsh plants (Good et al., 1982; Schubauer and Hopkinson, 1984). Wang et al. (2003) showed variations in carbon isotope values of up to 1.3‰ between roots and certain above-ground counterparts in a Massachusetts salt marsh. All plant samples were photographed, catalogued, placed in ashed tin foil, and stored in freezers at the University of Maine and finally transported on dry ice to the University of Tennessee.

All core sites were located within a surficial high marsh plant community in order to reduce potential variability between sites. The cores were extracted using an

Eijkelpamp 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 cores were recovered in 1 m increments and coring proceeded downward to refusal (usually clay-rich sediments). After recovery the collected cores were logged, photographed, video-taped, wrapped in ashed tin foil, wrapped in plastic, and placed in a split PVC tube and stored as described for the plant samples.

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 the following general characteristics (Belknap et al., 1989; Gehrels, 1994):

- LM: Muddy or sandy matrix with low density of organic material, in situ *Spartina alterniflora* roots and rhizomes. Usually found adjacent to the tidal channel.
- TM: Fibrous high marsh peat with abundant *Spartina alterniflora* remains in addition to remains of *Spartina patens*. Occasionally present between the low and high marsh.
- HM: Dark brown to grayish brown peat characterized by an interwoven, dense network of fine *Spartina patens* roots. Often divides the low marsh from the higher high marsh
- HHM: Light brown peat containing remains of *Juncus gerardi* roots (wavy) and rhizomes (smooth and reddish-brown) with *Solidago sempervirens* tissue (woody) and stele ('fishbone'). Often found adjacent to the upland border.

BM: Characterized by *Scirpus* remains, black and triangular in cross section, and containing peat with a “coffee grounds” texture.

FM: Dark-brown to black structureless peat with remains of *Typha angustifolia* plants and the presence of leaves, bark, and other detrital material.

Once in the lab, core samples were sectioned into 10cm increments and divided for foraminiferal, radiocarbon, and isotopic analysis. Plant samples were rinsed in deionized water. Core and plant samples for chemical analysis were then air dried at 60°C for 24 hours before being further processed. Core samples to be used for compound-specific isotopic analysis were crushed using a mortar and pestle. Plant samples were shredded using a coffee grinder.

#### Foraminifera Sample Preparation and Analysis

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

Assigned faunal zones for the indicator species are presented along with associated floral communities in Table 1, Appendix B. Faunal zone interpretations are determined using relative abundances determined for surficial populations (after Gehrels,

1994; Scott and Medioli, 1980). The upper boundary of faunal zone 1A is approximately the highest astronomical tide mark. Other faunal zone boundaries relative to mean high water are available for three of the marshes (Table 5, Appendix B). A Ward's cluster analysis was employed to validate the faunal zone designations. Each sample point from the four cores was assigned by the computer to a specific cluster, and these clusters were then compared to the designated faunal zones (1A, 1B, 2A, 2B, etc.). A statistical comparison of the categories derived from the cluster analysis with the faunal zone categories was made using a chi-square test.

#### Compound Separation and Analysis

Compounds from all plant and core samples were extracted using a Dionex ASE 300. Samples were flushed with dichloromethane (40%) and methanol (60%) at 125° C and 1500 p.s.i. for 10 min. This process was repeated four times for each sample. After drying down, 3 ml of 5% KOH in MeOH:H<sub>2</sub>O (80:20; pre-extracted with chloroform) was added to each sample. Samples were then flushed with nitrogen, sealed tightly and placed in a heat block at 80° C for 2 hrs. The pH of each sample was checked to ensure that the solutions were still basic. Approximately 3 mls of Milli-Q H<sub>2</sub>O were added to each sample, and samples were extracted three times with 3 ml of hexane:chloroform (4:1). Total neutrals were then separated from fatty acids using a separatory funnel. Samples were concentrated using a rotovap, and were then analyzed using a gas chromatography-mass spectrometer (GC-MS) and gas chromatography-isotope ratio mass spectrometer (GC-IRMS).

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

$$\delta^{13}\text{C} = \left( \frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} - 1 \right) \times 10^3$$

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 that employed by Wang et al. (2003) that are based on the absolute abundance of n-alkanes with chain lengths ranging from  $\text{C}_{23}$  to  $\text{C}_{34}$  where,

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

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

$$\text{ACL} = \sum [C_i]i / \sum [C_i]$$

where *i* is the carbon number from  $\text{C}_{23}$  to  $\text{C}_{34}$  and  $[C_i]$  is the concentration. CPI values were calculated using GC/MS reported concentrations, with a few being less than  $0.5\mu\text{g}$ . Therefore, while values of “O” may appear in the table for the concentration value for some of the compounds, the small values for these compounds are used in the calculations. CPI values for the plants range from 3.8 to 34.2. No even chain lengths were detected for *Spartina alterniflora*, making calculation of CPI impossible for this species. ACL values average 29.1 for the plants with a standard deviation of 1.0.

### *Gas Chromatography-Mass Spectrometry (GC-MS)*

Individual alkanes were separated and characterized using an Agilent 6890 Series GC interfaced to an Agilent 5973N mass selective detector (MS). Compound separation was achieved using a 30m x 0.25 mm i.d. x 0.16 $\mu$ m film thickness VF-5 column. Oven temperature was set initially at 130°C for 2 minutes, then was ramped at 10°C/min. to 300° C and held for 23 min. The detector interface was set at 280°C. Injections were performed in split mode and 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  $m/z$  10 to 500 was scanned at 1.3 scans/sec. Individual peaks in chromatograms were identified by matching their mass spectra to standard reference mass spectra within the National Institute of Standards and Technology (NIST) library. Identification was further confirmed using retention times of GC/MS mass chromatograms of authentic reference compounds.

### *Compound Specific Isotope Analysis (CSIA)*

An Agilent 6890 Series gas chromatograph (GC) was interfaced to a Finnigan Delta Plus XL isotope ratio mass spectrometer (IRMS) through a combustion furnace (GC-IRMS). Injections into the GC were performed in split mode with ultrapure helium employed as carrier gas. The GC column and program were identical to that indicated for GC/MS analyses. Compounds were first combusted in a ceramic furnace at 850° C, passed through a nafian membrane water trap, and then were introduced into the mass

spectrometer as pulses of CO<sub>2</sub>. Most plant and core samples were run in triplicate with a precision of at least 1‰ for each sample set. Some core samples were run in duplicate with a range of <1‰ for each sample set. Multiple runs of the DNAP standard returned a standard deviation of 0.3‰.

## Radiocarbon Dating

The chronology for the four cores is based on a series of bulk radiocarbon dates representing total organic material from 20cm sections of the recovered cores. Analysis was performed by BETA Analytic, Inc. following standard procedures for organic sediments. Calibrations are reported using the INTC AL 98 calibration database. Although one of the radiocarbon dates reported for our core is a “basal” date, we did not penetrate the Pleistocene substrate, but rather refused on compact marsh sediments, making humic acid contamination unlikely (Belknap et al., 1989). Three of the five dates for the MC2 core were from an earlier, directly adjacent core and were “tied in” with our core using foraminiferal stratigraphy and depth to the Pleistocene substrate.

## Results

### Radiocarbon Chronology

Radiocarbon dates are presented along with their associated depth and 2σ cal. age range (Table 6, Appendix B). All of the dates are in stratigraphic order. Three dates from

an earlier core (SN-VC-1; Gehrels et al., 1996) are tied in with core MC3. Though there are differences in the macroscopic stratigraphic descriptions between SN-VC-1 and MC3, foraminiferal zones and depth to Pleistocene substrate match up well (Compare our Figure 11, Appendix A with figure 5a from Gehrels, 1999). Nominal data from macroscopic stratigraphic descriptions are much more subjective than numerical data from foraminiferal counts.

### Macroscopic Core Descriptions

Macroscopic core stratigraphies for the four core sites are presented with their associated radiocarbon ages (Figure 10, Appendix A). The radiocarbon data points within the core sections represent the mid-points of the depth range for the date. Macroscopic stratigraphy shows that three of the four cores are dominated by high marsh deposits. Core SP2 is more variable, having a strong presence of transitional marsh deposits and more minor amounts of low marsh and higher-high marsh deposits. The other Phippsburg core, MO2 has minor amounts of transitional marsh and higher-high marsh deposits. Core GC3 contained some higher-high marsh deposits, with minor freshwater marsh and low marsh. Core MC2 included transitional and low marsh deposits, and also a section of upland soil above the Pleistocene substrate (clay-rich refusal). Cores GC3, MO2, and SP2 all refused on clay-rich estuarine deposits.

Mineral-rich layers with low organic matter are present in Cores SP2, MO2, and MC2. These layers are only present in high marsh deposits, though low marsh and

transitional marsh deposits contained lower amounts of organic matter and had a higher mineral content (estimated visually).

### Foraminiferal Stratigraphy

Relative abundances of foraminifera are presented in Figures 11 through 14 (Appendix A) for the four core sites. Foraminiferal abundances were determined for individual 10cm long core sections and data points on the graphs represent the midpoints of the sampling increments. Six species of foraminifera were identified, and abundances of the four dominant species, *Trochammina macrescens* forma *macrescens*, *Trochammina inflata*, *Tiphotrecha comprimata*, and *Miliammina fusca* are presented. Other species, including *Haplophragmoides manilaensis*, and *Pseudothurammina limnetis*, were also identified, but were not present in significant enough quantities to affect the faunal zone interpretations, and are not presented. Core MO2 contained such minor amounts of *Miliammina fusca* (<1% for any sample depth) that this foraminifer is not included in Figure 13 (Appendix A). 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,  $p = 0.05$ )

Core MC2 (Figure 11, Appendix A) is dominated by faunal zone 1B. There are two transitions to faunal zone 1B/1A within the core, as well as two transitions to faunal zone 1B/2A, all representing short excursions. Core GC3 (Figure 12, Appendix A) shows more fluctuations, with 5 transitions between faunal zones 1B/2A and 1B within the first 110cm of the core, and subsequent transitions to faunal zones 1A and 1A/2B. Core MO2

(Figure 13, Appendix A) is characterized by a dominance of faunal zone 1B, with one excursion to faunal zone 1B/2A, and one excursion to faunal zone 1A/1B. Core SP2 (Figure 14, Appendix A) shows many fluctuations between faunal zones 1B (6 sections), 1B/2A (3 sections), 1A/1B (1 section), and 2A (3 sections).

#### *n*-Alkane Distributions

We 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*. In addition, other abundant salt marsh species were sampled including *Salicornia europa*, *Atriplex patula*, *Potentilla anserina*, *Plantago maritima*, *Suaeda maritima*, and *Limonium nashii*. Alkane distributions are presented for the plant species with the species' associated photosynthetic pathway, carbon preference index (CPI), and average chain length (ACL) (Table 3, Appendix B).

Distributions of *n*-alkanes are presented for all of the collected cores (Tables 7-9, Appendix B). The cores were divided into 10cm increments and indicated depths on the tables represent the mid-points of the sample increments. Core MC2 (Table 7, Appendix B) CPI values range from 3.2 to 66.3. The average ACL value for MC2 is 27.7 with a standard deviation of 0.4. Core GC3 (Table 8, Appendix B) ACL values range from 1.5 to 8.6. The average ACL value for GC3 is 27.7 with a standard deviation of 0.4. CPI and ACL values for both of the Phippsburg cores are presented (Table 9, Appendix B). Core MO2 CPI values range from 3.2 to 71.4. The average ACL value for MO2 is 27.5 with a

standard deviation of 0.6. Core SP2 CPI values range from 3.2 to 20.7. The average ACL value for SP2 is 27.6 with a standard deviation of 0.4.

### Compound Specific Isotopic Analysis

Compound-specific  $\delta^{13}\text{C}$  values for the cores are presented as a function of depth (Figure 15, Appendix A), and as a function of  $^{14}\text{C}$  age (BP)(Figure 16, Appendix B). Linear interpolation was used to estimate ages between dated radiocarbon sample points. Errors associated with the linear interpolation are unknown, but could be substantial. For the core samples, compound specific isotope data points represent the mid-points of 10cm sample sections. Sections of 10cm were skipped between sample intervals (e.g. samples are from 0-10, 20-30, 40-50, etc.). Compound-specific isotope values for the core deposits are reported for the  $\text{C}_{27}$  homologue only, as our research suggests that it best represents Maine salt marsh plant communities (Tanner et al., this volume), being abundant in all plants studied, and having the lowest coefficient of variation between plant samples (61.95%) for the different homologues (Table 3, Appendix B). In table 3 (Appendix B), the coefficient of variation is presented for the  $\text{C}_{27}$ ,  $\text{C}_{29}$ , and  $\text{C}_{31}$  alkanes because these three compounds were detected in all plant samples studied. Values of  $\delta^{13}\text{C}$  for the  $\text{C}_{27}$  alkane are also presented for the 10 plant samples.

The vertical-dashed line in the graphs on figures 15 and 16 (Appendix A) represent an estimation of the average  $\delta^{13}\text{C}$  value for a 50% biomass mixture of the most dominant C3 and C4 salt marsh plants. These include *Spartina alterniflora*, *Spartina*

*patens*, *Juncus gerardi*, and *Solidago sempervirens* (see Table 1, Appendix B). The position of the line is calculated thus:

$$f_{Sp} = C_{Sp}/(C_{Sp}+C_{Sa})$$

where  $f_{Sp}$  is the fractional value of *Spartina patens* representing a 50% mix with *Spartina alterniflora*, and C is the GC/MS reported concentration for that plant sample ( $\mu\text{g/g}$ ). The fraction of *Spartina alterniflora* can then be found as:

$$f_{Sa} = 1 - f_{Sp}$$

The  $\delta^{13}\text{C}$  value of a 1 to 1 mixture of *Spartina alterniflora* and *Spartina patens* is then estimated as follows:

$$\delta_{C4} = f_{Sp}\delta_{Sp} + f_{Sa}\delta_{Sa}$$

The process is repeated to estimate the isotopic value of a 1 to 1 mixture of the C3 plants, replacing *Spartina alterniflora* and *Spartina patens* with *Juncus gerardi* and *Solidago sempervirens*. The average isotopic value of a 1 to 1 mixture of C3 and C4 biomass (25% of each plant sample,  $\delta_{\text{mix}}$ ) is then approximated as follows:

$$f_{C4} = C_{Sp+Sa}/(C_{Sp+Sa}+C_{Jg+Ss})$$

$$f_{C3} = 1 - f_{C4}$$

$$\delta_{\text{mix}} = f_{C4}\delta_{C4} + f_{C3}\delta_{C3}$$

For our plant samples  $\delta_{\text{mix}} = -27.2\text{‰}$  for the  $\text{C}_{27}$  alkane. We interpret values falling to the left of the line as representing C3-dominated plant communities and values falling to the right of the line as C4-dominated plant communities. The center line represents a rough approximation of a 50% mixture. It is either very difficult, or more likely impossible, to calculate precise contributions of particular plant species to the sediment pool when dealing with a system that is beyond a simple binary mixture.

The isotope curves show several excursions within each core (Figure 15, Appendix A). Tanner et al. (this volume) found that isotopic values for the C<sub>27</sub> homologue are depleted by an average of 7.2‰ relative to bulk isotope values for the MO2 core samples (Std. Dev. = 1.0‰).

## Discussion

### Plant Samples and Core Samples

An obvious trend of both the plant and core *n*-alkane distributions is the dominant presence of odd, higher chain length homologues (Tables 2 and 7-9, Appendix B). Peak abundances of *n*-alkanes from higher plants are generally within the C<sub>27</sub> to C<sub>33</sub> range (Chikaraishi and Naraoka, 2003; Collister et al., 1994; Cranwell, 1973; Eglinton and Hamilton, 1963; Freeman and Colarusso, 2001; Lockheart et al., 1997; Rieley et al., 1993), and most of the Machiasport plants peak within this range. A notable exception is *Salicornia europa*, the only CAM plant found in the marsh, which peaks at C<sub>25</sub>.

Distributions of *n*-alkanes for the core deposits show abundances maximizing at C<sub>25</sub>, C<sub>27</sub>, and C<sub>29</sub>. *Salicornia europa* may be contributing heavily to the carbon pool where C<sub>25</sub> is at a maximum, or there could be another, non-sampled marsh plant with a C<sub>25</sub> maximum that is contributing heavily to the marsh sediments (see chapter 2, this volume). Since *Salicornia europa* is a CAM plant, significant contributions to the sediments from the species should be carefully considered. CAM plants are known to have carbon isotopic values that are intermediate between C3 and C4 plants. However,

our measured value of -31.5‰ for the C<sub>27</sub> alkane of *Salicornia e.* (Table 2, Appendix B) is within the range of a C3 plant, in agreement with other studies that have reported on the isotopic composition of *Salicornia sp.* (Chmura and Aharon, 1995; Byrne et al., 2001).

Average ACL values for the four different cores range from 27.5 to 27.7, somewhat lower than the average ACL value for the salt marsh plants (29.1), but within the range attributed to higher plants in general (Collister et al., 1994; Wang et al., 2003). *Salicornia europa* has a low ACL value, attributable to its large peak at C<sub>25</sub>, and could be a significant contributor to the marsh sediments, helping to lower ACL values for the core deposits. The 1.4 to 1.6 unit difference between core and plant deposits could also be attributable to degradation of the sediments, or again, to an as yet unidentified plant source.

CPI values, indicative of odd/even preference, calculated for core deposits are all >3, except for 7 sample depths for core GC3 (Tables 7-9, Appendix B). High CPI values suggest primary input from higher plants and a lack of bacterial degradation. Johnson and Calder (1973) found that CPI values near one indicate bacterial activity, while vascular plants have values ranging from ~3 to 40 (Chikaraishi and Naraoka, 2003; Collister et al., 1994; 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), in agreement with the previous studies. Therefore, based on the CPI index, bacterial degradation of higher chain length *n*-alkanes in cores MC2, MO2, and SP2 seems to be minimal. Bacterial degradation could be affecting the sediments in core GC3 near 125cm and 195cm below the surface, where CPI values begin to approach one.

Analysis of *n*-alkane distributions along with CPI and ACL values suggests that higher plants are the dominant contributor to the sediments at the four salt marshes, and that bacterial degradation of the sediments is minimal. Therefore, carbon isotopic values of the C<sub>27</sub> alkane can confidently be used to monitor plant community fluctuations within the cored marsh deposits.

## Core MC2

Moving from top to bottom of the core, the first faunal zone that is present is 1B/2A (Figure 11, Appendix A), followed by zone 1B beginning at 10cm. This transition is significant, as it means that the surface of the marsh is lower relative to sea level than it was in the near past. The relative fall of the marsh surface, or rise in sea level, is recorded in the isotope curve, which shows C<sub>4</sub> values nearer the surface that become more depleted down-core (Figure 15, Appendix A). Faunal zone 1B is maintained to a depth of 350cm below the surface. The foraminiferal counts do not show any of the macroscopic peat transitions above the 350cm depth (Figure 10, Appendix A). It is possible that some foraminiferal excursions are “averaged out” by the 10cm sampling interval.

The mineral-rich, low marsh section at ~55cm recorded in the macroscopic peat stratigraphy (Figure 10, Appendix A) is not recorded in the isotope stratigraphy. C<sub>4</sub> values would be expected at this sample depth, but C<sub>3</sub> values are indicated (Figure 15, Appendix A). The macroscopic core description is showing an event that is not recorded by the isotopic compositions or the foraminiferal counts, and instead of representing low marsh deposits, the unit is likely to have been deposited during a time of greater sediment

influx to a higher marsh zone. The mineral-rich layers that are present at 115cm, 149cm, and 254 cm below the surface, likely representing significant disturbance episodes, do not affect the foraminiferal counts, and show no consistent isotopic pattern. Isotope values show a trend towards less-negative values after the first event, towards more negative values after the second event, and are seemingly unaffected by the third event, continuing on an already present trend towards more negative values.

The transitional marsh deposits observed in the sediment core above 300cm are recorded as a transition to C4 isotopic values. The three isotope fluctuations between 300cm and 350cm are not explained by any fluctuations in the foraminiferal or peat stratigraphic records. The C4 excursion around 365cm is recorded in the peat stratigraphy as a clay-rich, low marsh unit. The transition to a faunal zone 1B/2A assemblage at 380 cm is supported by less negative (C4)  $\delta^{13}\text{C}$  values. Below 390cm, foraminiferal counts show a transition towards higher-elevation deposits, beginning with faunal zone 1B, moving to 1A/1B, and then to upland or freshwater deposits, indicated by an absence of foraminifera, and by the presence of upland soils in the peat stratigraphy. Isotope values show this “freshening”, with a move to more depleted (C3) values towards the bottom of the core.

### Core GC3

Peat stratigraphic, foraminiferal, and isotopic data for core GC3 are presented in figures 10, 12, and 15 (Appendix A). GC3 shows the same transition from a 1B/2A faunal zone to a purely 1B faunal zone as core MC2, representing either a lowering of the

marsh surface or relative sea level rise. Isotopic values indicate a C4 plant community near the surface, echoing the foraminiferal counts. The transitional marsh deposit at 18cm is consistent with the faunal data, though the isotope data show a mixed plant community at this depth. The interpretation of higher-high marsh and freshwater marsh units from 28cm to 41cm below the surface is not supported by foraminiferal counts, which indicate zone 1B deposits at this depth range. Isotope values continue to show a mixed plant community at these depths. It is apparent that subjective macroscopic stratigraphic assignments are not necessarily supported by faunal and isotopic data, and that interpretations based on macroscopic stratigraphic descriptions of salt marsh deposits should be made cautiously.

From 70cm to 110cm, faunal zone 1B is surrounded by a 1B/2A assemblage. An isotope excursion to C4 values accompanies the faunal zone transition. The sediment stratigraphy continues to show high marsh deposits at these depths. The next isotope fluctuation, towards C3 values, is in agreement the move to faunal zone 1A at 170cm and 1A/1B at 180cm, and to a transition to higher high marsh peat stratigraphy.

#### Core MO2

Peat stratigraphic, foraminiferal, and isotopic data for core MO2 are presented in figures 10, 13, and 15 (Appendix A). C4 values are indicated from the surface to a depth of 105cm. The presence of faunal zone 1B/2A from 20cm to 50cm and transitional marsh deposits from 49cm to 89cm agrees well with the isotope stratigraphy. Two mineral-rich lenses are present within the core, one at 118cm and one at 132cm. Isotope values

indicate a move towards C4 dominance following these disturbance episodes, and suggest the establishment of salt tolerant species. C4 species are considered to be salt-tolerant colonizers (Bertness et al., 1992). Faunal zone 1A/1B is present below the two clay lenses, and the shift towards more depleted isotopic values is in agreement with the move towards fresher conditions on the marsh. Higher high marsh deposits are also indicated at this depth. A transition back to C4 isotopic values is present at the bottom of the core, in good agreement with the stratigraphic change to transitional marsh deposits.

#### Core SP2

Peat stratigraphic, foraminiferal, and isotopic data for core SP2 are presented in figures 10, 14, and 15 (Appendix A). SP2 is characterized by a large number of faunal zone transitions (12), almost all of them between zone 1B and zone 1B/2A or 2A. Twelve transitions are also recorded in the peat stratigraphy, though not always in agreement or at the same depth as the faunal zone transitions. Isotopic values remain fairly stable downcore, suggesting a C4 dominated plant community for most sample depths, in general agreement with the faunal stratigraphy, where the high salinity zone 2A is often present. There are only 2 or 3 sample depths showing a more mixed signal, at 5cm, 65cm, and 105cm.

The interval from 20cm to 50cm is the only section of the core where a C3 signal would be expected from the foraminiferal stratigraphy, given the faunal zone 1A and 1A/1B assemblage. No such isotopic signal is present at these core depths. Higher high marsh is present from 32cm to 62cm, in general agreement with the faunal zone

boundaries. The thick (8cm), mineral-rich mud layer near 18cm is signaled by an isotopic excursion to C4 values. It appears that the rapid movements of the land/water interface, suggested by the many faunal zone transitions, are maintaining the marsh in a disturbed state, where C4 plants appear to be at a competitive advantage.

### Disturbance Regime

The interplay of relative water level, sediment supply, and plant community dynamics in the salt marsh often defy simple cause and effect explanations. Stability is not a characteristic of any of the marshes under consideration. On the contrary, short term disturbance events, many that are likely going unrecognized, maintain the marsh in a state of disequilibrium. Clark's (1986) contention that marsh vegetation is responding to "frequent and severe fluctuations in the physical environment" is supported by our data. From four dated cores, we estimate that a major fluctuation in the marsh, whether a faunal zone transition, an excursion between C3 and C4 values, or a major (catastrophic) sediment influx, occurs at least once every 288 years (disturbance, plant transition, faunal transition divided by summed aged of cores). This figure must be a minimum value, as some major events, such as ice-scouring and deposition of tidal wrack, are likely to go unnoticed. Clark found that "at least every 100 yr along the six transects, sufficient sand was deposited to destroy all [salt marsh] vegetation."

## Climate Correlation

The salt marsh plants could be responding to climate change, which is likely to be responsible for increased or decreased fresh water inflow into the marsh. Freshwater inflow is potentially detectable in the marsh deposits (Byrne et al., 2001). Periods of increased fresh water inflow would tend to favor  $^{13}\text{C}$ -depleted C3 plants, while drier, more saline periods would favor C4 species. Byrne et al. (2001) and Malamud-Roam and Ingram (2004) have attempted to relate C3 and C4 transitions in a San Francisco Bay estuary to climate-induced salinity changes. In order to test the climate/marsh link on the Maine coast, it is important to examine existing late Holocene climate records.

Domack and Mayewski (1999) have correlated an Antarctic Peninsula (Palmer Deep) paleoproductivity record with the GISP2 chloride record for the last 4000 calendar years before 1950 AD. Six warm events are correlated, at 750, 950, 1300, 1650, 1800 (1900 in Antarctica), and 2700 years before present. Three cool events are noted, at 3050, 2500, and 550-250 (Little Ice Age - LIA) years before present. Keigwin (1996) shows a warming event (the Medieval Warm Period - MWP) from 950 to 650 years before present, along with a Little Ice Age event using a  $^{14}\text{C}$  dated surface temperature record from the Sargasso Sea. There is some evidence that sea level changes in Connecticut and Maine record these two climate events. Van de Plassche et al. (1998) and Gehrels (1999) show a rise in mean high water corresponding to the MWP and a fall in mean high water corresponding to the LIA. Pollen records from the northeast do not seem to record all of these events.

A vegetation record from the White Mountains, New Hampshire, suggests cooler, moister conditions from 2000 years ago to the present (Spear et al., 1994), while another study from the northeast suggests that only the LIA may be recorded in fossil pollen in the late Holocene (Davis and Botkin, 1985), or that there has been more precipitation over the last 1000 years than the previous 1000 years (Gajewski, 1988). A pollen record from Mud Pond, Maine, located near the Gouldsboro field site suggests that climate in the region has become cooler and wetter since 1300 years before present (Rhodes and Davis, 1995).

In all, the MWP and LIA events appear to be widely present and relatively well correlated, though not always in the pollen record, and pollen climatic reconstructions suggest wetter conditions since at least 1000 years ago, with drier conditions before.

In order to infer a potential climate change from the salt marsh deposits using carbon isotopes, it is necessary to control for sea level fluctuations as much as possible. Our data suggests that relative water level changes in the marsh, recorded in salt marsh foraminifera, can influence carbon isotope values. The average carbon isotopic value for the C<sub>27</sub> alkane from faunal zone 1B deposits (n=40 sample points) is -26.6‰, a significantly different figure from the -24.3‰ average for zone 1B/2A deposits (n=9; p<0.05). There were not enough isotope data points for any of the other faunal zones to make statistical comparisons meaningful. One isotope value is available for faunal zone 1A deposits (-33.1) and 2A deposits (-25.4). The average isotope value for zone 1A/1B deposits is -27.3‰ (n=4)

The only way to provide a control for sea level is to stay within a narrow range of mean high water. Since there are a significant number of isotope data points for faunal

zone 1B (n=40), which has a direct relationship with mean high water, and since zone 1B deposits have an average carbon isotopic value near our 50% to 50% mixed C3/C4 isotopic value, meaning that both C3 and C4 plant communities are present through time (see Table 1, Appendix B), it is logical to use the isotope values from zone 1B deposits to look for climate fluctuations.

The gray squares on figure 16 (Appendix A) represent data points from faunal zone 1B deposits. We observe no consistent trends between the four different field sites. There is no correlation between the C<sub>27</sub> alkane carbon isotope values for cores MO2 and SP2 ( $R^2=0.02$ ) for faunal zone 1B deposits, even though the two sites are in close proximity (within 5 miles), and have a similar geologic setting (back-barrier marshes within a deep, narrow estuary; Figure 17, Appendix A). Isotope values from core MC2 show a weak, inverse correlation with isotope values from core MO2 ( $R^2=0.34$ ), but show a weak, positive correlation with isotope values from core SP2 ( $R^2=0.13$ ). No attempts at correlation were made for core GC3 because of the low number of isotope values from faunal zone 1B data points (n=4).

The wetter period from 1300 years before present to the present recorded in the pollen record from Mud Pond, Maine, is not consistently seen in our cores. There are no clear and consistent excursions to C3 values over this time period. Moreover, there is no clear and consistent trend that shows a MWP or LIA signal between the different field sites. Fluctuations in the cores are unique to the individual field sites and likely represent individual responses and adjustments of the marshes to localized disturbances. The only consistent trend that we see in the cores is a transition to C4 values near the surface over the last ~400 to 500 <sup>14</sup>C years before the present. Gehrels (1999) notes that “in the past

300 years, sea level has risen by about 0.5m, reaching an unprecedented rate of 2.2mm/yr since 1930..." at Machiasport. Rapid acceleration of sea level rise over the last 300 years is a potential cause for the more recent move towards C4 values in all of our cores.

Another occurrence that might lead to a regional trend is the amplification of the tidal range in the Gulf of Maine. Gehrels et al. (1995) show an amplitude increase of 87cm at Phippsburg, 93cm at Gouldsboro, and 103cm at Machiasport over the last 5,000 years. Since no consistent isotope pattern is observed in our cores, any floral community response to increasing tidal range is being obscured.

Our study suggests that salt marsh vegetation is responding to a multitude of factors and that climate change is not consistently recorded in the marsh vegetation between the field sites, even when water level fluctuations are controlled for. Malamud-Roam and Ingram (2004) came to the opposite conclusion in their study of the San Francisco Bay estuary, tying pollen and isotope fluctuations to salinity changes resulting from variations in freshwater influx. Studying their figures 2 and 3, we fail to see the consistent patterns that they suggest, and are forced to agree with Clark (1986), that salt marsh vegetation change is unpredictable, that vegetation history differs between field sites, and that plant population distributions cannot be related directly to environmental parameters. The San Francisco study does not monitor fluctuations of ocean level relative to the marsh surface, so that effects of sediment subsidence and autocompaction, as well as sea level movement, are not controlled for. Given that there is no obvious, consistent plant community pattern between their field sites, it is at least questionable to suggest that salt marshes show a direct response to climate change, given that so many factors affect marsh plant distributions. Early on, Chapman (1940) recognized that salt marsh plant

community succession was an exceedingly complicated phenomenon. We propose that recent studies of ancient salt marsh deposits do not challenge this view, and urge caution in the interpretation of secular plant community records.

## **Conclusion**

Salt marshes represent a unique environment where disturbance is the norm and stasis the exception. Salt marsh plant communities are certainly responding to environmental variables, but not in a predictable fashion. Foraminiferal zones, indicative of mean high water levels, do show some correspondence with carbon isotope values. However, even within a single faunal zone, isotope fluctuations are frequent and unpredictable. Given the recent interest in the response of salt marshes to climate change, we urge caution in the use of ancient salt marsh plant community records to make inferences regarding climate change.

## **Chapter 4 - Fractal Analysis of Maine's Glaciated Shoreline Tests Established Coastal Classification Scheme**

This chapter is a revised version of a paper by the same name accepted (pending revisions) by the *Journal of Coastal Research* in 2005. Authors include Benjamin Tanner, Ed Perfect, and Joseph Kelley.

My use of “we” in this chapter refers to my co-authors and myself. My primary contributions to this paper include (1) selection of the topic and development of the problem into a work relevant to my study of Maine shoreline morphology, (2) design of a research strategy, (3) most of the data acquisition, analysis, and synthesis, (4) most of the gathering and interpretation of the literature, (5) most of the writing.

### **Introduction**

Coastline description has been a traditional application of fractal analysis after Mandelbrot's (1967) influential paper introduced the concept of fractal dimension (D) to the scientific community. While coastline shape has historically been difficult to quantify, the introduction of D has provided a simple parameter for describing the complexity of shorelines, and D values have been calculated for several coastlines around the world (Table 10, Appendix B). The higher the D value ( $>1$ ) the greater the coastal complexity. While fractal techniques have been used to characterize the complexity of different coastlines (Mandelbrot, 1967; Pennycuick and Kline, 1986; Xiaohua et al., 2004), relatively little work has been done to associate the resulting D values with

geological and geomorphological processes. Data linking fractal dimensions to underlying genetic processes (Gao and Xia, 1996) have thus far have been sparse and inconclusive. Xiaohua et al. (2004) suggest that variations in D values along China's coastline can be related to the strike of faults, while Jiang and Plotnick (1998) relate D values along the Pacific and Atlantic coastlines of the United States to sea floor complexity. Andrieu (1996) found two peaks of complexity for the west coast of Britain, and suggested that granite batholiths and parallel grabens are responsible for larger indentations along the coast, while glacially incised valleys are responsible for smaller indentations. The objective of this paper is to strengthen existing research by investigating D values for a coastline where there is a well-established and accepted coastal classification system in place.

Although Jackson (1837) was the first to subdivide the Maine coast into four compartments, a more formal classification scheme was proposed by Kelley (1987). Glacial ice covered the state of Maine during the last glacial maximum (~20,000 yr B.P.), producing many of the features, either directly or indirectly, that are presently observable along the coast. Kelley considered Maine's glacial history as well as lithology, structure, sediment supply and differential Holocene sea level rise in his work, keeping the four compartment scheme and confirming the four-fold division with statistical testing. Kelley quantified differences in Maine's four coastal compartments using principle components analysis (see Hayden and Dolan, 1979). Kelley's classification attempt is widely accepted and is often cited in literature dealing with Maine coastal research. A visual inspection of a map of coastal Maine reveals that there are differences in shoreline complexity between the four coastal compartments (Figure 20, Appendix A).

Maine's southwestern (SW) coastal compartment is characterized by northeast-striking metasedimentary rocks that are intruded by several plutonic bodies. Extensive glacial sand and mud deposits blanket this section of the coast, leaving an environment that is typified by plutonic capes and intervening sand beaches that front salt marshes.

The southcentral (SC) coastal compartment is characterized by north-striking metasedimentary rocks with deep glacially scoured valleys. This combination of bedrock and structure results in a series of northwest oriented peninsulas with intervening deep, narrow estuaries.

Maine's northcentral (NC) coastal compartment is characterized by abundant granitic plutons. The relative resistance of the plutonic bodies to erosion has resulted in a coastline that contains broad estuaries with numerous granitic islands.

The northeastern (NE) coastal compartment is characterized by relatively resistant northeast-striking metavolcanic rocks with less resistant, glacially scoured metasedimentary rocks comprising Cobscook Bay. The resulting shoreline is typified by high cliffs protecting a highly indented estuary (Cobscook Bay).

The detailed classification of Maine's coast makes its shoreline an ideal location to compare fractal dimensions with geological processes responsible for producing the shoreline. The purpose of this study is to calculate fractal dimensions for Maine's four coastal compartments and to determine if these compartments can be statistically discriminated using this parameter.

## Methodology

The shoreline maps used in this study were digitized by the Maine Geological Survey and are freely available online from the Maine Office of GIS (<http://apollo.gis.state.me.us>). The coastline data are in vector format and are derived from 1:24,000 scale, 7.5 minute series USGS topographic quadrangles. We selected a random sample of 10 quadrangles each from the SC (out of 25 possible) and NC (out of 52 possible) coastal compartments and analyzed the 9 and 10 digital maps that are available for the SE and NW compartments respectively.

We calculated the fractal dimension of the coastline for each of the sampled topographic quadrangles using the box counting method (Klinkenberg and Goodchild, 1992). The box counting method is based on the following equation:

$$N_r = Cr^{-D}$$

Where  $N_r$  is the number of boxes that cover the boundary in question,  $r$  is the side length of the individual square boxes making up the grid,  $D$  is the fractal dimension, and  $C$  is a constant. The log-log form of the above equation follows:

$$\log[N_r] = -D \log(r) + \log(C)$$

$D$  values calculated using this equation are obtained by counting  $N_r$  for different box lengths ( $r$ ). The value of  $D$  is then estimated from the slope of an xy plot of  $\log(N_r)$  vs.  $\log(r)$  using least-squares linear regression (Figure 2). We used box sizes ( $r$ ) of 30m, 100m, 250m, 500m, 1000m, 1500m, and 3000m, thus establishing the fractal character of Maine's coastline over two orders of magnitude (see Avnir et al., 1998). The analysis was performed using ESRI ArcView GIS version 3.2.

Two additional details are of considerable importance regarding the fractal dimensions calculated for the different shoreline segments:

1. The boundaries between rivers and the ocean were visually determined by inspecting river mouths. Narrow river channels were not counted and do not influence the values of D obtained.
2. Islands are included in the analyses since they comprise an important part of the Maine coast, and are of primary importance in the NC coastal compartment. The box counting method is well suited to counting the shoreline compartments of the islands, as well as the adjacent mainland sections (Feder, 1988).

For most of the maps, the grids covered an area of 9,000m x 12,000m, a multiple of the largest box size (3,000m). Several of the maps (<10%) required using a smaller overall grid coverage as a result of an unavoidable intersection of certain linear features (i.e. the Canada/Maine border) with the coastline. The software could not distinguish between these linear features and the coastline, and thus inclusion of these features would have influenced the resulting D values.

## **Results and Discussion**

High  $R^2$  values ( $> 0.99$ ) for all linear regression analyses support the argument that the Maine coast is fractal throughout the range of scales tested (Figure 21, Appendix A). Average fractal dimensions for the four coastal compartments are presented (Table

11, Appendix B). The average D value for the SW compartment (9 quadrangles) is 1.11, the lowest average value for D in this study. The average D value for the SC compartment (sample of 10 quadrangles) is 1.35, the highest average value obtained for any of the four compartments. The NC (sample of 10 quadrangles) and NE (10 quadrangles) compartments had average D values of 1.23 and 1.26 respectively, intermediate between the other two compartments.

Protected (ANOVA) t-tests showed that mean values calculated for the fractal dimension parameter were significantly different (ANOVA,  $p < 0.05$ ) between three of the four compartments (Table 11, Appendix B). Mean D values for the NC and NE coastal compartments were statistically indistinguishable. Close inspection of the data for the NE compartment shows that there is a high standard deviation for the obtained D values and a large range between the lowest (1.13) and highest (1.45) fractal dimensions (Table 11, Appendix B). Recall that the Cobscook Bay region of the NE coastal compartment is geologically different from the rest of the NE compartment. While much of the NE compartment is comprised of resistant metavolcanic rocks, glacially scoured metasedimentary rocks underlie Cobscook Bay. Kelley and Kelley (2004) provide a thorough description of the geology of Cobscook Bay.

Separation of Cobscook Bay (denoted by NE-2, 4 quadrangles) from the rest of the NE section (now NE-1, 6 quadrangles) lowered the standard deviations for both sub-compartments (Figure 22, Appendix A; Table 11, Appendix B). No D values for quadrangles from the two sub-compartments overlapped. The NE-2 sub-compartment has a much higher mean fractal dimension (1.37) than the NE-1 sub-compartment (1.18), indicating a more complex shoreline. Protected t-tests (Table 2) including the two sub-

compartments show that NE-2 and NE-1 are significantly different (ANOVA,  $p < 0.05$ ).

The only coastal compartments that are not significantly different (ignoring the now subdivided NE compartment) are the NE-2 sub compartment and the SC compartment (ANOVA  $p > 0.05$ ). This is not surprising since the underlying geology of these two compartments is generally similar. Both are comprised of metasedimentary rocks that have been deeply scoured by glacial advance and retreat, though the two compartments have been subjected to a different Holocene sea level history and tidal range (Gehrels et al., 1996).

Overall, our results indicate that Maine's four coastal compartments differ in complexity, as is suggested by statistically significant differences in average D values. Unique geological processes are responsible for the differing levels of complexity of the shoreline segments.

SW Compartment – The low average fractal dimension (1.11) reflects a relatively uniform shoreline; in this case comprised of plutonic capes and intervening arcuate sand beaches.

SC Compartment – The relatively high average fractal dimension (1.35) is indicative of a tortuous shoreline, a result supported by visual inspection of a map of coastal Maine. High D values are likely a reflection of the many glacially scoured, northwest-oriented peninsulas with intervening deep, narrow estuaries.

NC Compartment – The average fractal dimension of 1.23 suggests an intermediate level of complexity, reflected by the compartment's broad estuaries and numerous granitic islands.

NE Compartment – Our analysis suggests that this compartment should be further divided into two sub-compartments. This conclusion is supported by the underlying geology of the NE coastal region.

NE-1 Sub-Compartment – The average fractal dimension of 1.18 reflects a relatively uncomplicated shoreline that is distinct from the other segments included in this study. The NE-1 sub-compartment is comprised of relatively straight cliffs of resistant metavolcanic rocks.

NE-2 Sub-Compartment – The average fractal dimension of 1.37 is suggestive of a relatively high level of complexity and cannot be statistically distinguished from the average D value for the SC compartment. The NE-2 sub-compartment is in many respects geologically similar to the SC compartment.

Jiang and Plotnick (1998) calculated fractal dimensions for 1° latitudinal increments covering the Eastern United States coast. They obtained a fractal dimension of 1.11 for the 45° to 44° segment, and a D value of 1.13 for the 44° to 43° segment (covering the Maine coast) using the divider method. Our results support the conclusion of Xiuhua et al. (2004) that D values calculated for an entire coastline are different from average D values for various segments of the same coastline. They are also in agreement with the conclusion of Andrieu (1996) that complexity varies with position along the coastline. Results from the present study suggest that shoreline D values derived from

1:24,000 quadrangles are useful for comparing complexity at scales used in statewide coastal classification schemes.

## **Conclusion**

Relatively little research has been undertaken to associate coastal fractal dimensions to geologic processes. Our study indicates that Maine's coastal geologic compartments can be statistically discriminated using fractal analysis, with the caveat that the NE compartment should be divided into two distinct sub-compartments. This further subdivision is supported by the underlying geology of the NE compartment. The Cobscook Bay segment of the NE compartment (NE-2) is geologically similar to the SC coastal compartment, and D values for the NE-2 and SC compartments are statistically indistinguishable. Although our analysis indicates that D values can distinguish geologically dissimilar segments of the Maine coast, additional research is needed to determine if D values obtained for coastal segments can be further linked to a general set of underlying geological processes. Linking fractal dimensions to coastal geological processes will require an extensive database of shoreline D values. In this regard, it may be worthwhile to apply our approach to similar coastal environments (ie. glaciated shorelines) in other parts of the world.

## Conclusions

In this dissertation, I have used a combination of compound specific isotopic analysis of *n*-alkanes, foraminiferal analysis, bulk isotope analysis, and *n*-alkane distributions from four radiocarbon-dated field sites on the Maine coast, and have come to several conclusions.

First, it is demonstrated in chapter 1 that compound specific isotopic values of the  $C_{27}$  alkane are recording a known shift in the plant community in the cored deposits. Through analysis of 10 common salt marsh plants, it is apparent that the  $C_{27}$  alkane is the most appropriate choice to record plant community fluctuations, as it is relatively abundant in all plant samples studied, and also has the lowest coefficient of variation between the plant samples. The results from chapter 1 lend credibility to the use of the  $C_{27}$  alkane in subsequent chapters, and also allow confidence in the use of the  $C_{27}$  alkane to monitor secular plant community changes.

In chapter 2, it is shown that CSIA of the  $C_{27}$  alkane co-varies with bulk isotope values using a core from Phippsburg, lending credibility to studies that only employ bulk isotopic analysis in salt marshes. Furthermore, *n*-alkane distributions and isotope values show that bacterial degradation of the marsh sediments is minimal, and that algae are not major contributors of organic matter to the marsh sediments. The marsh plants are effectively “swamping” the isotopic signal. It is also proposed in this chapter that *Salicornia europaea* may contribute heavily to the organic carbon pool in salt marsh sediments from Maine.

Finally, in chapter 3, the original hypothesis of this dissertation is tested, namely that isotope fluctuations within specific foraminiferal zones are related to either regional effects (i.e. climate change) or more localized disturbance episodes. Isotope fluctuations within foraminiferal zone 1B cannot be correlated between the different field sites, and the second hypothesis is accepted (e.g. C3/C4 variation within specific salt marsh zones can be accounted for by localized effects and show no correlation between field sites). Through a combination of CSIA, foraminiferal analysis, and radiocarbon dating of the 4 separated field sites, it is shown that processes operating in the salt marshes are unique to the individual marshes, and their effects are not seen on a regional scale.

Separately, in chapter 4 it is demonstrated that the shoreline of Maine is fractal in character. Fractal analysis confirms the separation of previously identified coastal compartments, and suggests the establishment of an additional sub-compartment in the northeastern section of the shoreline.

Many problems remain to be studied. It will be necessary to profile the *n*-alkane distributions of other plants that can potentially contribute to salt marsh sediments, including the submerged species *Zostera maritima* and *Ruppia maritima*, in order to more fully account for contributions to the marsh sediments. Furthermore, if a biomarker can be found for *Ruppia maritima*, it may be possible to confidently identify salt panne deposits within cores, something that is difficult to do at present. Also, since there is little or no correlation between field sites, it would be worthwhile to investigate variability within specific marshes through time in order to elucidate potential causes for plant community fluctuations. This could be accomplished by looking at a series of cores from a single marsh. Future work will be geared towards resolving these remaining problems.

## References

- Albro P. W. (1976) Bacterial waxes. In: Kolattukudy P. E. (ed.), *Chemistry and Biochemistry of Natural Waxes*, Elsevier, Amsterdam., pp. 419-445.
- Andrle R. (1996) The west coast of Britain: Statistical self-similarity vs. characteristic scales in the landscape. *Earth Surface Processes and Landforms* 21(10):955-962.
- Avnir D., Biham O., Lidar D. and Malcai O. (1998) Is the geometry of nature Fractal? *Science* 279:39-40.
- Barnhardt W. A., Belknap D. F. and Kelley J. T. (1997) Stratigraphic evolution of the inner continental shelf in response to late Quaternary relative sea-level change, northwest Gulf of Maine. *GSA Bulletin* 109:612-630.
- Belknap D. F., Shipp R. C., Stuckenrath R., Kelley J. T. and Borns H. W., Jr. (1989) Holocene sea-level change in coastal Maine. *Maine Geological Survey Bulletin* 40:85-105.
- Benner R., Fogel M. L. and Sprague E. K. (1991) Diagenesis of belowground biomass of *Spartina alterniflora* in salt-marsh sediments. *Limnological Oceanography* 36(7):1358-1374.
- Bertness M. D. (1991) Interspecific Interactions Among High Marsh Perennials in a New England Salt-marsh. *Ecology* 72(1):125-137.
- Bertness M. D. and Ewanchuk P. J. (2002) Latitudinal and climate-driven variation in the strength and nature of biological interactions in New England salt-marshes. *Oecologia* 132:392-401.
- Bertness M. D., Ewanchuk P. J. and Silliman B. R. (2002) Anthropogenic modification of New England salt-marsh landscapes. *Ecology* 99(3):1395-1398.
- Bertness M. D., Gough L., and Shumway S. W. (1992) Salt Tolerances and the Distribution of Fugitive Salt-marsh Plants. *Ecology* 73(5):1842-1851.
- Blumer M., Guillard R. R. L. and Chase T. (1971) Hydrocarbons of marine plankton. *Marine Biology* 8:183-189.
- Boutton T. W. (1991) Stable carbon isotope ratios of natural materials: 1. Sample preparation and mass spectrometer analysis. In: Coleman D. C. and Fry B. (eds.), *Carbon Isotope Techniques*. Academic Press, San Diego.
- Bull I. D., van Bergen P. F., Bol R., Brown S., Gledhill A. R., Gray A. J., Harkness D. D., Woodbury S. E. and Evershed R. P. (1999) Estimating the contribution of *Spartina angelica* biomass to salt-marsh sediments using compound specific stable carbon isotope measurements. *Organic Geochemistry* 30:477-483.

- Byrne, R., Ingram B. L., Starratt S. and Malamud-Roam F. (2001) Carbon-isotope, diatom, and pollen evidence for Late Holocene salinity change in a brakish marsh in the San Francisco Estuary. *Quaternary Research* 55:66-76.
- Callaway R. M., and Sabraw C. S. (1994) Effects of variable precipitation on the structure and diversity of a California salt marsh community. *Journal of Vegetation Science* 5(3):433-438.
- Canuel E. A., Freeman K., and Wakeham S. (1997) Isotopic compositions of lipid biomarker compounds in estuarine plants and surface sediments. *Limnological. Oceanography* 42(7):1570-1583.
- Carr J. R. and Benzer W. B. (1991) On the practice of estimating fractal dimension. *Mathematical Geology* 23(7):945-958.
- Cerling T. E., Quade J., Wang Y. and Bowman J. R. (1989) Carbon isotopes in soils and paleosols as ecology and paleoecology indicators. *Nature* 341:138-139.
- Chikaraishi Y. and Naraoka H. (2003) Compound-specific  $\delta D$ - $\delta^{13}C$  analyses of *n*-alkanes extracted from terrestrial and aquatic plants. *Phytochemistry* 63:361-371.
- Chmura G. L. and Aharon P. (1995) Stable carbon isotope signatures of sedimentary carbon in coastal wetlands as indicators of salinity regime. *Journal of Coastal Research* 11(1):124-135.
- Chmura G. L., Aharon P., Socki R. A. and Abernathy R. (1987) An inventory of  $^{13}C$  abundances in coastal wetlands of Louisiana, USA: Vegetation and sediments. *Ooecologia* 74:264-271.
- Chmura G. L., Anisfield S. C., Cahoon D. R. and Lynch J. C. (2004) Global carbon sequestration in tidal, saline wetland soils. *Global Biogeochemical Cycles* 17(4), Article 1111.
- Choi Y. H., Wang Y. (2004) Dynamics of carbon sequestration in a coastal wetland using radiocarbon measurements. *Global Biogeochemical Cycles* 18(4), Article GB4016.
- Choi Y. H., Wang Y., Hsieh Y. P. and Robinson L. (2001) Vegetation succession and carbon sequestration in a coastal wetland in northwest Florida: Evidence from carbon isotopes. *Global Biogeochemical Cycles* 15(2):311-319.
- Clark J. (1986) Dynamism in the barrier-beach vegetation of Great South Beach, New York. *Ecological Monographs* 56(2):97-126.
- Clark J. and Patterson W. A. III (1985) The development of a tidal marsh: upland and oceanic influences. *Ecological Monographs* 55(2):189-217.

- Collister J. W., Rieley G., Stern B., Eglinton T., Fry B. (1994) Compound specific  $\delta^{13}\text{C}$  analyses of leaf lipids from plants with differing carbon dioxide mechanisms. *Organic Geochemistry* 21:619-627.
- Crain C., Silliman B., Bertness S., and Bertness M. (2004) Physical and biotic drivers of plant distribution across estuarine salinity gradients. *Ecology* 85(9):2539-2549.
- Cranwell P. A. (1973) Chain-length distribution of *n*-alkanes from lake sediments in relation to postglacial environmental change. *Freshwater Biology* 3:259-265.
- Cranwell P. A., Eglinton G. and Robinson N. (1987) Lipids of aquatic organisms as potential contributors to lacustrine sediments. *Organic Geochemistry* 11:513-527.
- Davis M. B. and Botkin D. B. (1985) Sensitivity of cool-temperate forests and their fossil pollen record to rapid temperature change. *Quaternary Research* 23:327-340.
- Domack E. W. and Mayewski P. A. (1999) Bi-polar ocean linkages: evidence from late-Holocene Antarctic marine and Greenland ice-core records. *The Holocene* 9(2):247-251.
- Eglinton G. and Hamilton R. J. (1967) Leaf epicuticular waxes. *Science* 156:1322-1335.
- Ehleringer J. R., Cerling T. E. and Helliker B. R. (1997)  $\text{C}_4$  photosynthesis, atmospheric  $\text{CO}_2$ , and climate. *Oecologia* 112:285-299.
- Ember L. M., Williams D. F. and Morris J. T. (1987) Processes that influence carbon isotope variations in salt-marsh sediments. *Marine Ecology – Progress Series* 36(1):33-42.
- Ewanchuk P. J. and Bertness M. D. (2003) Recovery of a northern New England salt marsh plant community from winter icing. *Oecologia* 136:616-626.
- Feder J. (1988) *Fractals*. Plenum Press, New York.
- Ficken K. J., Li B., Swain D. L. and Eglinton G. (2000) An *n*-alkane proxy for the sedimentary input of submerged floating freshwater aquatic macrophytes. *Organic Geochemistry* 31:745-749.
- France R. L. (1995) C-13 Enrichment in benthic compared to planktonic algae – Foodweb implications. *Marine Ecology – Progress Series* 124(1-3):307-317.
- Freeman K. H. and Colarusso L. A. (2001) Molecular and isotopic records of  $\text{C}_4$  grassland expansion in the late Miocene. *Geochimica et Cosmochimica Acta* 65(9):1439-1454.

Fogel M. L., Sprague E. K., Gize A. P. and Frey R. W. (1989) Diagenesis of organic matter in Georgia salt marshes. *Estuarine Coastal and Shelf Science* 28:211-230.

Gao J. and Xia Z. (1996) Fractals in physical geography. *Progress in Physical Geography* 20(2):178-191.

Gehrels, W.R. (1994a) Holocene sea-level changes in the northern Gulf of Maine: Regional trends and local fluctuations determined from foraminiferal analyses and paleotidal modeling. Dissertation, University of Maine, Orono.

Gehrels W. R. (1994b) Determining relative sea-level change from salt-marsh foraminifera and plant zones on the coast of Maine, U.S.A. *Journal of Coastal Research* 10(4):990-1009.

Gehrels, W. R. (1999) Middle and Late Holocene Sea-Level Changes in Eastern Maine Reconstructed from Foraminiferal Saltmarsh Stratigraphy and AMS  $^{14}\text{C}$  Dates on Basal Peat. *Quaternary Research* 52:350-359.

Gehrels W. R. and Belknap D. F. (1993) Neotectonic history of eastern Maine evaluated from historic sea-level data and  $^{14}\text{C}$  dates on salt-marsh peats. *Geology* 21:615-618.

Gehrels W. R., Belknap D. F. and Kelly J. T. (1996) Integrated high-precision analyses of Holocene relative sea-level changes: Lessons from the coast of Maine. *GSA Bulletin* 108(9):1073-1088.

Gehrels W. R., Belknap D. F., Pearce B. R. and Gong B. (1995) Modeling the contribution of  $M_2$  tidal amplification to the Holocene rise of mean high water in the Gulf of Maine and Bay of Fundy. *Marine Geology* 124:71-85.

Gajewski K. (1988) Late Holocene climate changes in eastern North America estimated from pollen data. *Quaternary Research* 29(3):255-262.

Gelphi E., Schneider H., Mann J. and Oró J. (1970) Hydrocarbons of geochemical significance in microscopic algae. *Phytochemistry* 9:603-612.

Giger W. Schaffner C. and Wakeham S. G. (1980) Aliphatic and olefinic hydrocarbons in recent sediments of Greifensee, Switzerland. *Geochimica et Cosmochimica Acta* 44:119-129.

Goni M. A. and Thomas K. A. (2000) Sources and transformations of organic matter in surface soils and sediments from a tidal estuary (North Inlet, South Carolina, USA). *Estuaries* 23(4):548-564.

Good R. E., Good N. F. and Frasco B. R. (1982) A review of primary production and decomposition dynamics of the belowground marsh component. In Kennedy V. S. (ed.), *Estuarine Comparisons*, Academic, pp. 139-157.

Hackney C. T. (1980) In situ decomposition of roots and rhizomes of two tidal marsh plants. *Ecology* 61:226-231.

Han B. J., McCarthy E. D., van Hoesen W., Calvin M. and Bradley W. H. (1968) Organic geochemical studies, II. A preliminary report on the distribution of aliphatic hydrocarbons in algae, in bacteria, and in a recent lake sediment. *Proceedings of the National Academy of Sciences* 59:29-33.

Harvey H. R., Tuttle J. H., Bell J. T. (1995) Kinetics of phytoplankton decay during simulated sedimentation: changes in biochemical composition and microbial activity under oxic and anoxic conditions. *Geochimica et Cosmochimica Acta* 59:3367-3377.

Hayden B. and Dolan R. (1979) Barrier islands, lagoons, marshes. *Journal of Sedimentary Petrology* 49:1061-1072.

Hemond H. F. and Fifield J. L. (1982) Subsurface Flow in Salt-marsh Peat: A Model and Field Study. *Limnological Oceanography* 27(1):126-136.

Hernandez M. E., Mead R., Peralba M. C. and Jaffé R. (2001) Origin and transport of *n*-alkane-2-ones in a subtropical estuary: potential biomarkers for seagrass-derived organic matter. *Organic Geochemistry* 32:21-32.

Huang Y. S., Dupont L., Sarnthein M., Hayes J. M. and Eglinton G. (2000) Mapping of C<sub>4</sub> plant input from North Africa into North East Atlantic sediments. *Geochimica et Cosmochimica Acta* 64:3505-3513.

Huller M. A. J., Fry B., Peterson B. and Wright R. T. (1996) Microbial utilization of estuarine dissolved organic carbon: A stable isotope tracer approach tested by mass balance. *Applied and Environmental Microbiology* 62(7):2489-2493.

Jackson C. (1837) *The geology of the state of Maine*. Smith and Robison Publishing Company, Augusta, ME.

Jacobson H. A. and Jacobson G. L., Jr. (1989) Variability of vegetation in tidal marshes of Maine, U.S.A. *Canadian Journal of Botany* 67:230-238.

Jacobson H. A., Jacobson G. L., Jr. and Kelley J. T. (1987) Distribution and abundance of tidal marshes along the coast of Maine. *Estuaries* 10:126-131.

Jiang J. and Plotnick R. E. (1998) Fractal analysis of the complexity of United States Coastlines. *Mathematical Geology* 30(5):535-546.

- Johnson R. W. and Calder J. A. (1973) Early diagenesis of fatty acids and hydrocarbons in a salt marsh environment. *Geochimica et Cosmochimica Acta* 37:1943-1955.
- Keigwin, L. D. (1996) The Little Ice Age and Medieval Warm Period in the Sargasso Sea. *Science* 274:1504-1508.
- Kelley J. T. (1987) An inventory of coastal environments and classification of Maine's glaciated shoreline. In: Fitzgerald, D., and Rosen, R. (ed.), *Glaciated Coasts*, Academic Press, San Diego, CA., pp. 151-176.
- Kelley J. T., Belknap D. F., Jacobson G. L. Jr., and Jacobson H. A. (1988) The morphology and origin of salt-marshes along the glaciated coastline of Maine, USA. *Journal of Coastal Research* 4:649-665.
- Kelley J. T., Gehrels W. R. and Belknap D. F. (1995) Late Holocene Relative Sea-Level Rise and the Geological Development of Tidal Marshes at Wells, Maine, U.S.A. *Journal of Coastal Research* 11(1):136-153.
- Kelley J. T. and Kelley A. R. (2004) Controls on surficial materials distributed in a rock framed, glaciated, tidally dominated estuary: Cobscook Bay, Maine. *Northeast Naturalist Special Issue # 2* (in press).
- Klinkenberg B. and Goodchild M. F. (1992) The fractal properties of topography: a comparison of methods. *Earth Surface Processes and Landforms* 17:217-234.
- Lallier-Verges E., Perrussel B. P., Disnar J. and Baltzer F. (1998) Relationships between environmental conditions and the diagenetic evolution of organic matter derived from higher plants in a modern mangrove swamp system (Guadeloupe, French West Indies). *Organic Geochemistry* 29(5-7):1663-1686.
- Leendertse P. C., Roozen A. J. M. and Rozema J. (1997) Long-term changes (1953-1990) in the salt marsh vegetation at the Boschplaat on Terschelling in relation to sedimentation and flooding. *Plant Ecology* 132(1):49-58.
- Lockheart M. J., Van Bergen P. F. and Evershed R. P. (1997) Variations in the stable carbon isotope compositions of individual lipids from the leaves of modern angiosperms: Implications for the study of higher land plant-derived sedimentary organic matter. *Organic Geochemistry* 26:137-153.
- Malamud-Roam F. and Ingram B. (2001) Carbon isotopic compositions of plants and sediments of tide marshes in the San Francisco Estuary. *Journal of Coastal Research* 17(1):17-29.

Malamud-Roam F. and Ingram B. (2004) Late Holocene  $\delta^{13}\text{C}$  and pollen records of paleosalinity from tidal marshes in the San Francisco Bay estuary, California. *Quaternary Research* 62:134-145.

Mandelbrot B. B. (1967) How long is the coast of Britain? Statistical self-similarity and fractional dimension. *Science* 156:636-638.

Meyers P. A. (1997) Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Organic Geochemistry* 27(5-6):213-250.

Mitsch, W. J. and J. G. Gosselink (1986) Wetlands. Van Nostrand Reinhold, New York.

Montagna P. and Ruber E. (1980) Decomposition of *S. alterniflora* in different seasons and habitats of a northern Massachusetts salt marsh and a comparison with other regions. *Estuaries* 56:1859-1861.

Moreno O., Martinez M. and Escobar M. (1995) Geoquímica orgánica de los carbones de Fila Maestra, Estado Anzoátegui, Venezuela. *Journal of South American Earth Sciences* 8(2):201-208.

Oloff H., De Leeuw J., Bakker J. P., Platerink R. J., van Wijnen H. J. and De Munck W. (1997) Vegetation succession and herbivory in a salt marsh: changes induced by sea level rise and silt deposition along an elevational gradient. *Journal of Ecology* 85(6):799-814.

Pearson A. and Eglinton T. I. (2000) The origin of *n*-alkanes in Santa Monica Basin surface sediment: a model based on compound-specific  $\delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  data. *Organic Geochemistry* 31:1103-1116.

Pennycuik C. J. and Kline N. C. (1986) Units of measurement for fractal extent, applied to the coastal distribution of bald eagle nests in the Aleutian Islands, Alaska. *Oecologia* 68:254-258.

Phillips J. D. (1986) Spatial analysis of shoreline erosion, Delaware Bay, New Jersey. *Annals of the Association of American Geographers* 76(1):50-62.

Portnoy J. W. and Valiela I. (1997) Short-Term Effects of Salinity Reduction and Drainage on Salt-Marsh Biogeochemical Cycling and *Spartina* (Cordgrass) Production. *Estuaries* 20(3):569-578.

Redfield, A. C. (1972) Development of a New England salt marsh. *Ecological Monographs* 42(2):201-237.

Reidenbaugh T. G. and Banta W. C. (1980) Origin and Effects of a *Spartina* Wrack in a Virginia Salt-marsh. *Gulf Research Reports* 6(4):393-401.

- Rhodes T. E. and Davis R. B. (1995) Effects of late Holocene forest disturbance and vegetation change on acidic Mud Pond, Maine, USA. *Ecology* 76(3):734-746.
- Rieley G., Collier R. J., Jones D. M. and Eglinton G. (1991) The biogeochemistry of Ellesmere Lake, U.K.: Source correlation of leaf wax inputs to the sedimentary record. *Organic Geochemistry* 17:901-912.
- Rieley G., Collister J. W., Stem B. and Eglinton G. (1993) Gas chromatography-isotope ratio mass spectrometry of leaf wax *n*-alkanes from plants of differing carbon dioxide metabolisms. *Rapid Communications in Mass Spectrometry* 7:488-491.
- Sakata S., Hayes J. M., McTaggart A. R., Evans R. A., Lekrone K. J. and Togasaki R. K. (1997) Carbon isotopic fractionation associated with lipid biosynthesis by a cyanobacterium: relevance for interpretation of biomarker records. *Geochimica et Cosmochimica Acta* 24:5379-5389.
- Schubauer J. P. and Hopkinson C. S. (1984) Above and belowground emergent macrophyte production and turnover in a coastal marsh ecosystem, Georgia. *Limnological Oceanography* 29:1052-1065.
- Scott D. B. and Medioli F. S. (1978) Vertical zonations of marsh foraminifera as accurate indicators of former sea-levels. *Nature* 272:528-531.
- Scott D. B. and Medioli F. S. (1980) Quantitative studies of marsh foraminiferal distributions in Nova Scotia: Implications for sea-level studies. *Cushman Foundation for Foraminiferal Research Special Publication* 17.
- Shaw J. and Ceman J. (1999) Salt-Marsh Aggradation in Response to Late-Holocene Sea-Level Rise at Amherst Point, Nova Scotia, Canada. *The Holocene* 9(4):439-451.
- Shi W., Sun M., Molina M. and Hodson R. (2001) Variability in the Distribution of Lipid Biomarkers and their Molecular Isotopic Composition in Altamaha Estuarine Sediments: Implications for the Relative Contribution of Organic Matter from Various Sources. *Organic Geochemistry* 32:453-467.
- Silvestri S., Defina A., and Marani M. (2005) Tidal regime, salinity and salt marsh plant zonation. *Estuarine, Coastal and Shelf Science* 62:119-130.
- Spear R., Davis M. B. and Shane L. C. K. (1994) Late Quaternary history of low- and mid-elevation vegetation in the White Mountains of New Hampshire. *Ecological Monographs* 64(1):85-109.
- Tanner B. T., Perfect E., and Kelley J. T. (n.d.) Fractal Analysis of Maine's Glaciated Shoreline Tests Established Coastal Classification Scheme. Accepted pending revision, *Journal of Coastal Research*.

Thibodeau P. M., Gardner L. R., and Reeves H. W. (1998) The Role of Groundwater Flow in Controlling the Spatial Distribution of Soil Salinity and Rooted Macrophytes in a Southeastern Salt-marsh, USA. *Mangroves and Salt-marshes* 2:1-13.

Tu T., Kvaček J., Uličný D., Bocherens H., Mariotti A. and Broutin J. (2002) Isotope reconstructions of plant paleoecology. Case study of Cenomanian floras from Bohemia. *Palaeogeography, Palaeoclimatology, Palaeoecology* 280:1-28.

Valiela I., Teal J. M., Allen S. D., Van Etten R., Goehring D. and Volkman S. (1985) Decomposition in salt marsh ecosystems: the phases and major factors affecting disappearance of above-ground organic matter. *Journal of Experimental Marine Biology and Ecology* 89(1):29-54.

van de Plassche O. (1998) Sea level-climate correlation during the past 1400 yr. *Geology* 26(4):319-322.

van Wijnen H. J. and Bakker J. P. (1999) Nitrogen and phosphorous limitation in a coastal barrier salt marsh: the implications for vegetation succession. *Journal of Ecology* 87:265-272.

Wang X. C., Chen R. F. and Berry A. (2003) Sources and preservation of organic matter in Plum Island salt marsh sediments (MA, USA): long-chain *n*-alkanes and stable carbon isotope compositions. *Estuarine Coastal and Shelf Science* 58:917-928.

Watson E. (2004) Changing elevation, accretion, and tidal marsh plant assemblages in a South San Francisco Bay tidal marsh. *Estuaries* 27(4):684-698.

Weete J. D. (1976) Algal and fungal waxes. In: Kolattukudy (ed.), *Chemistry and Biochemistry of Natural Waxes*, Elsevier, Amsterdam., pp. 349-418.

Xiaohua Z., Yunlong C. and Xiuchun Y. (2004) On fractal dimensions of China's coastlines. *Mathematical Geology* 36(4):447-461.

## **Appendices**

## Appendix A - Figures

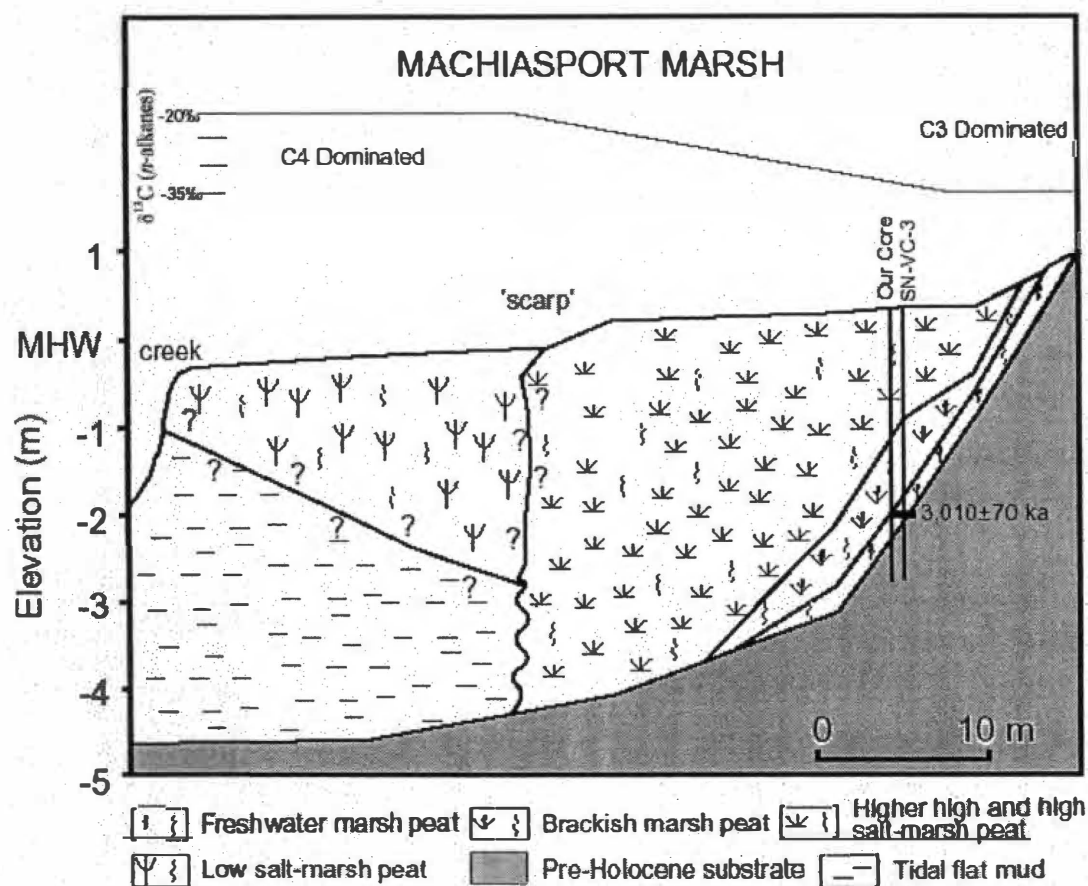


Figure 1. Generalized stratigraphic cross section of the Machiasport Sanborn Cove marsh showing the core recovered from the present study along with SN-VC-3. Note the expected isotopic transition (near top of figure) from a C4 dominated community (low marsh, left) to a C3 dominated community (higher high and brackish/freshwater marsh). Figure modified from Gehrels (1994a).

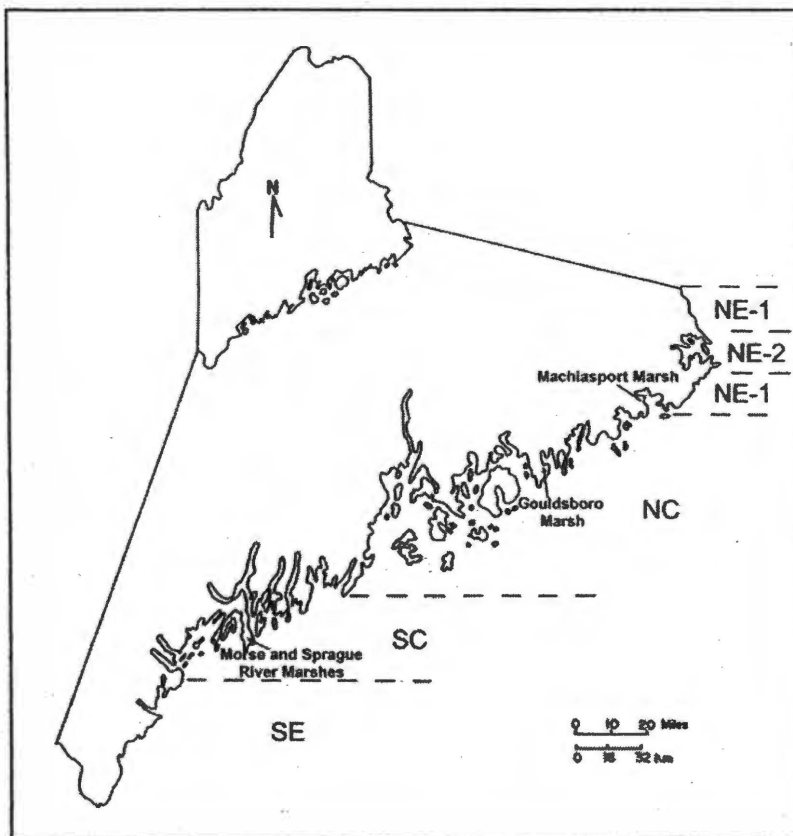


Figure 2. Map of coastal Maine showing the location of field Sites discussed in text (adapted from Kelly, 1987; Tanner et al., in revision).

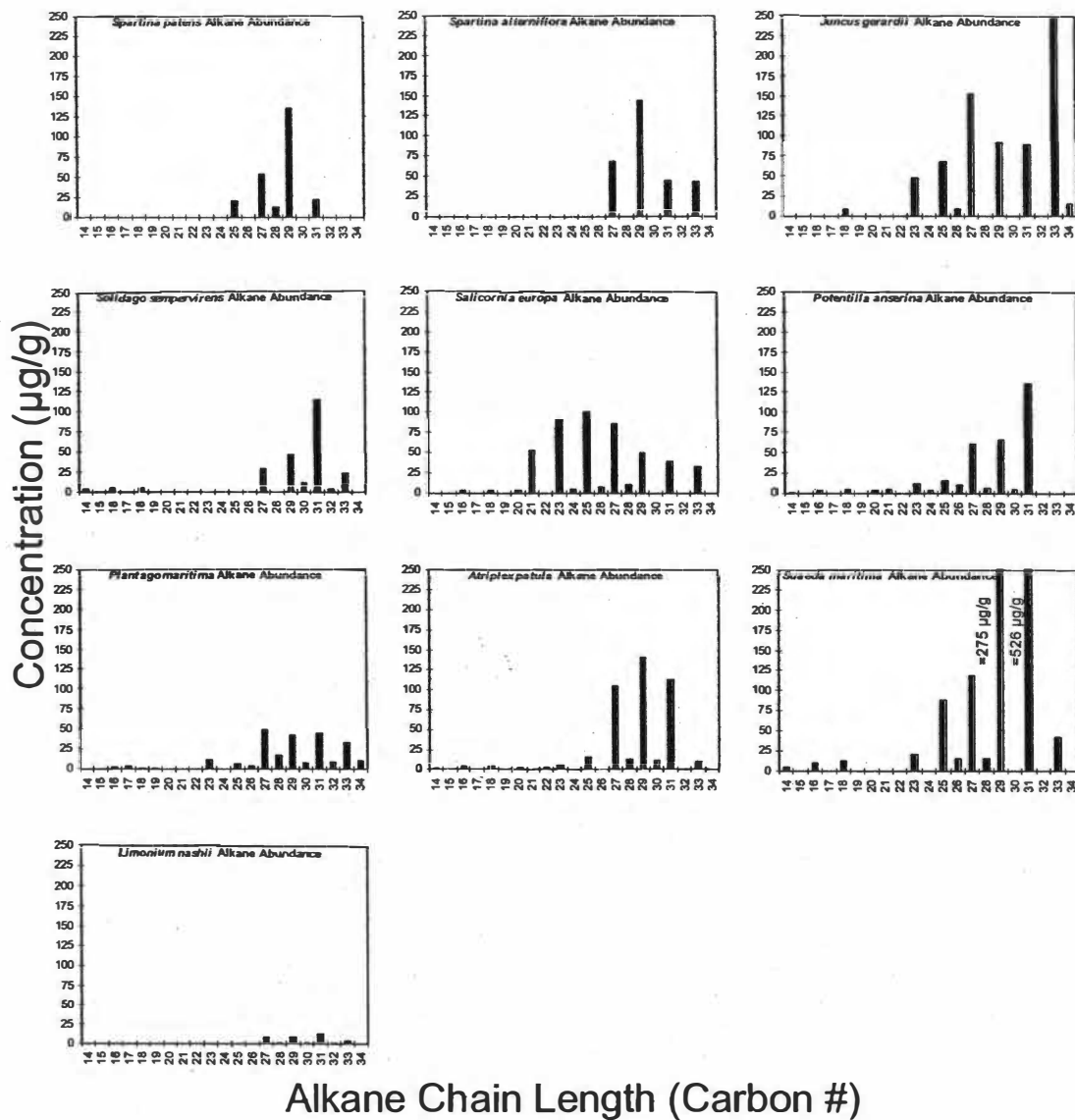


Figure 3. Absolute abundances of *n*-alkanes for common New England salt marsh plants.

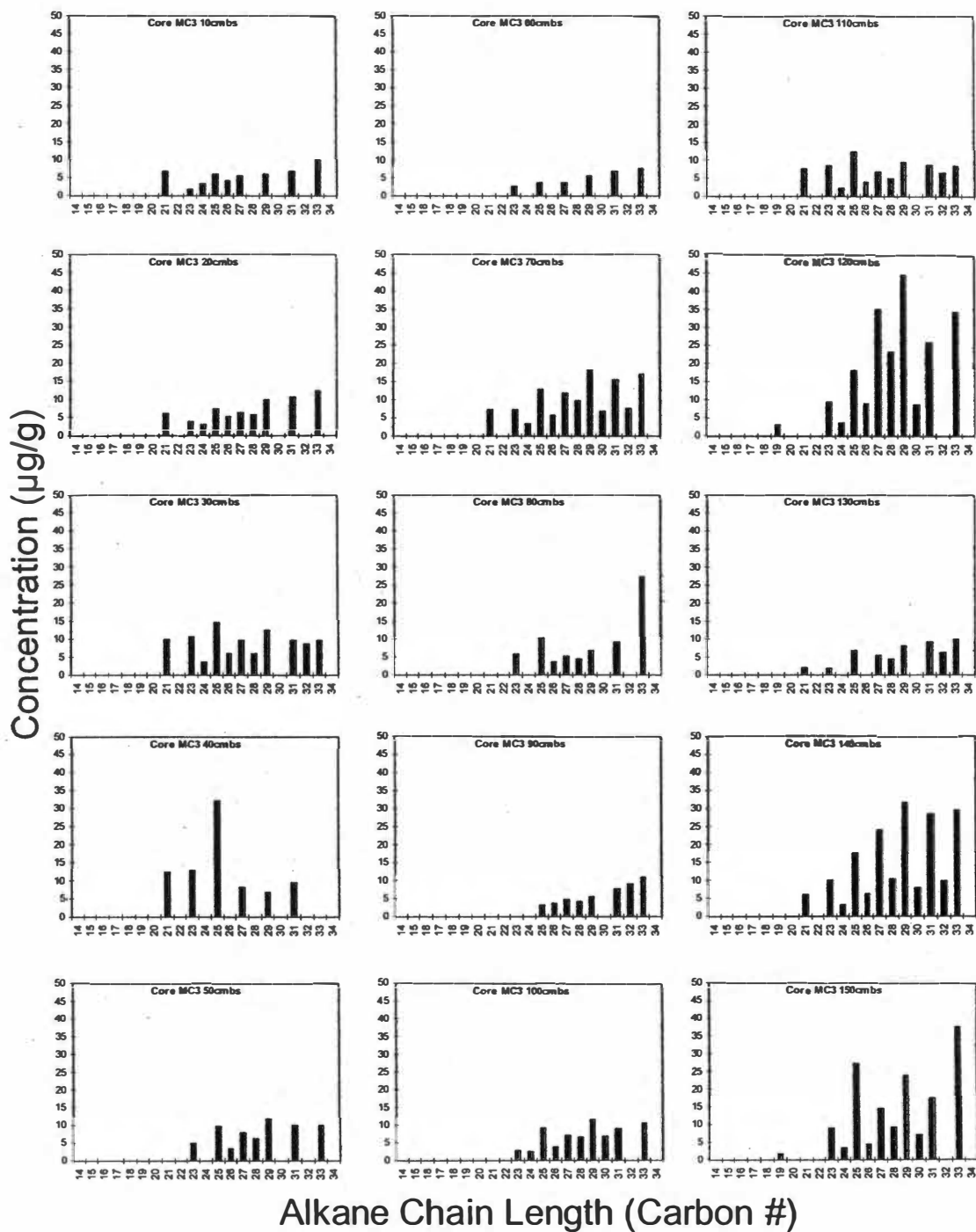


Figure 4. Absolute abundances of *n*-alkanes for the Machiasport core to a depth of 150cmbs.

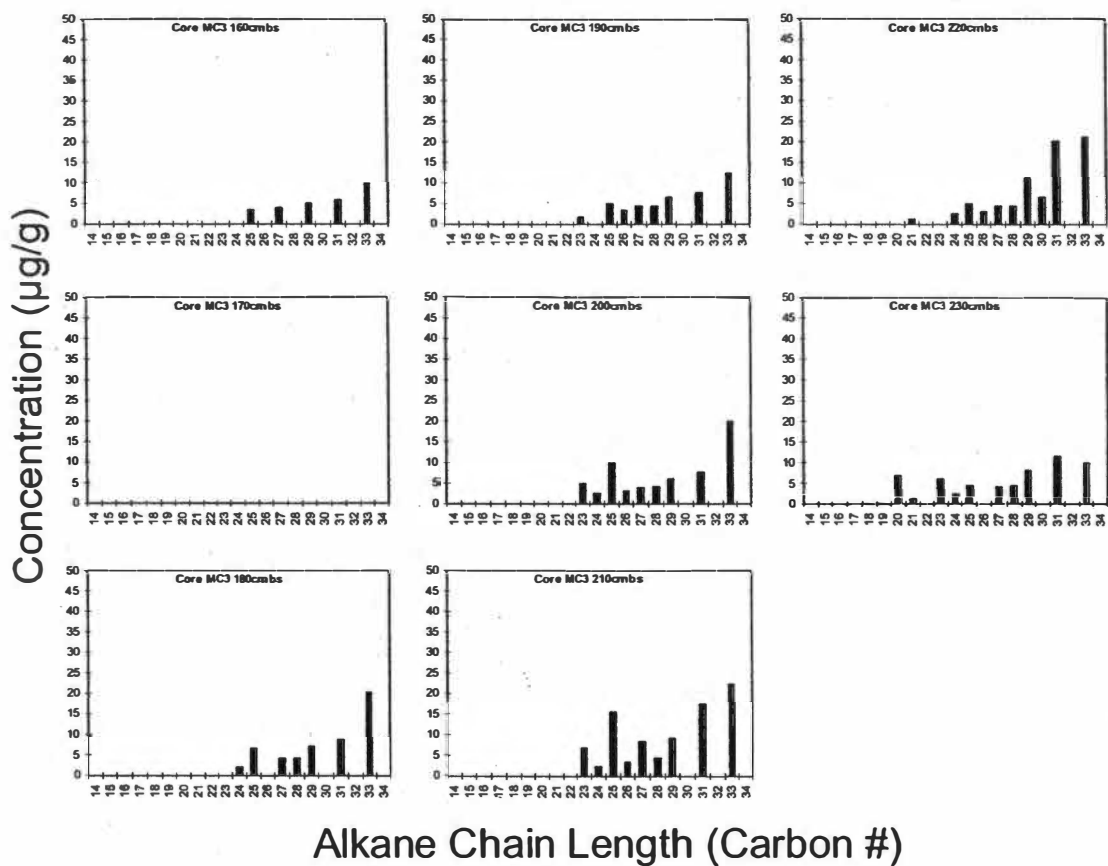


Figure 5. Absolute abundances of *n*-alkanes for the Machiasport core to a depth of 230cmbs.

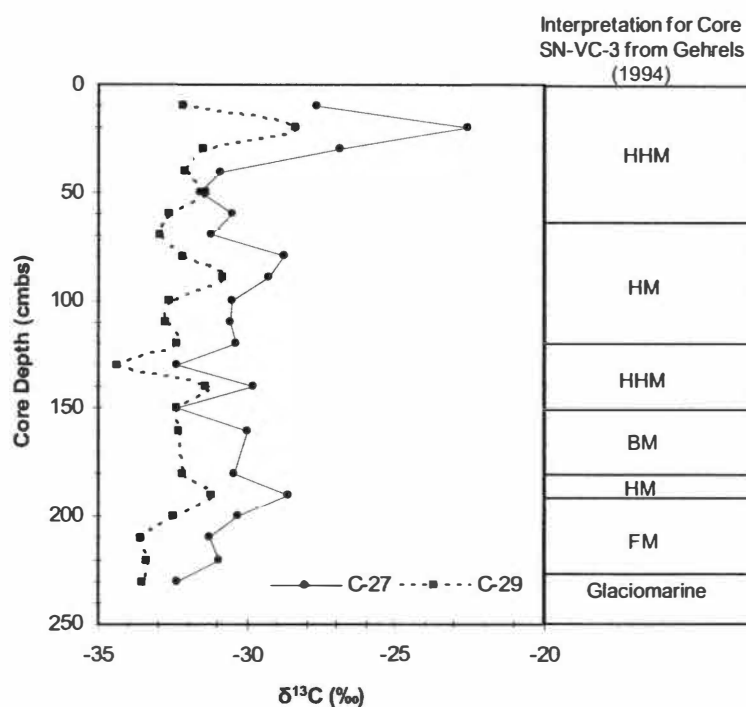


Figure 6. Carbon isotopic compositions of the C-27 and C-29 alkanes for the Machiasport core along with Gehrels (1994a) interpretation of peat stratigraphy (center) from identification of plant remains. Abbreviations are discussed in the text.

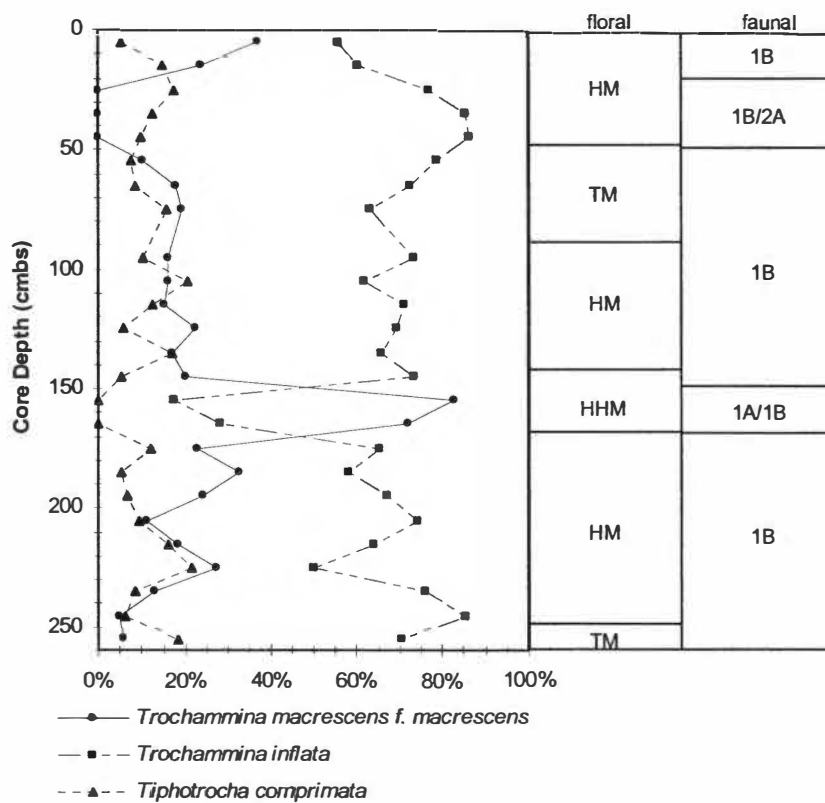


Figure 7. Foraminiferal distributions for the Morse River core with the associated faunal and floral zones.

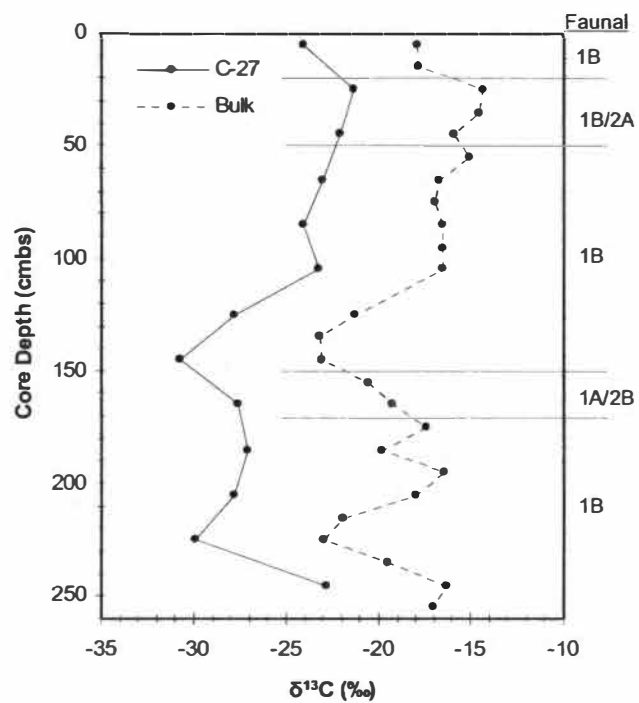


Figure 8. Bulk  $\delta^{13}\text{C}$  and compound specific  $\delta^{13}\text{C}$  for the  $\text{C}_{27}$  homologue from the Morse River core. Associated foraminiferal zones are indicated to the right of the figure.

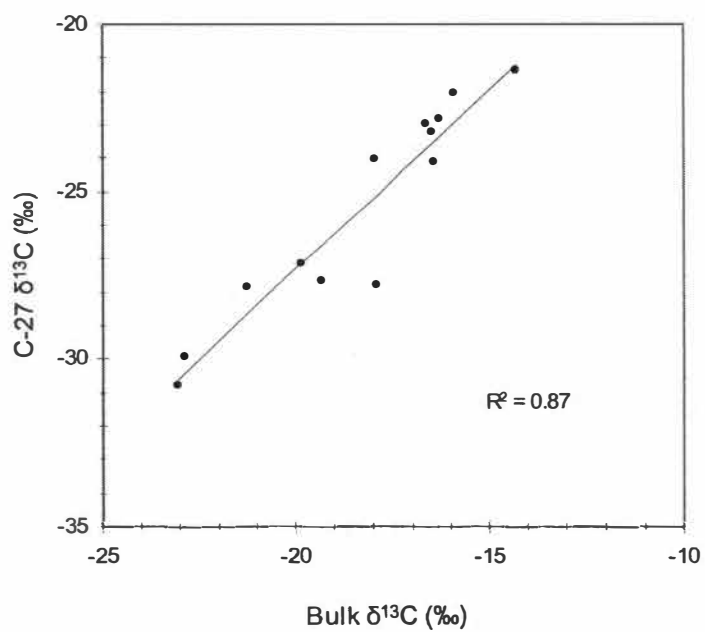


Figure 9. Bulk  $\delta^{13}\text{C}$  and compound specific  $\delta^{13}\text{C}$  for the  $\text{C}_{27}$  homologue from the Morse River core.

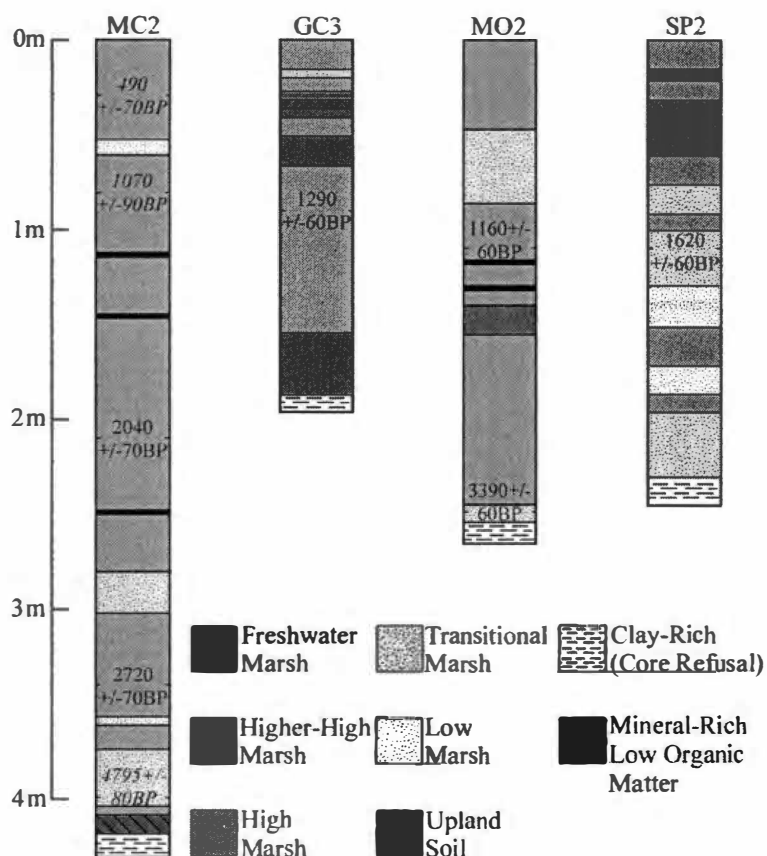


Figure 10. Macroscopic core stratigraphy. All dates are in  $^{14}\text{C}$  years and those in italics are from core SN-VC-1 (Gehrels, 1996).

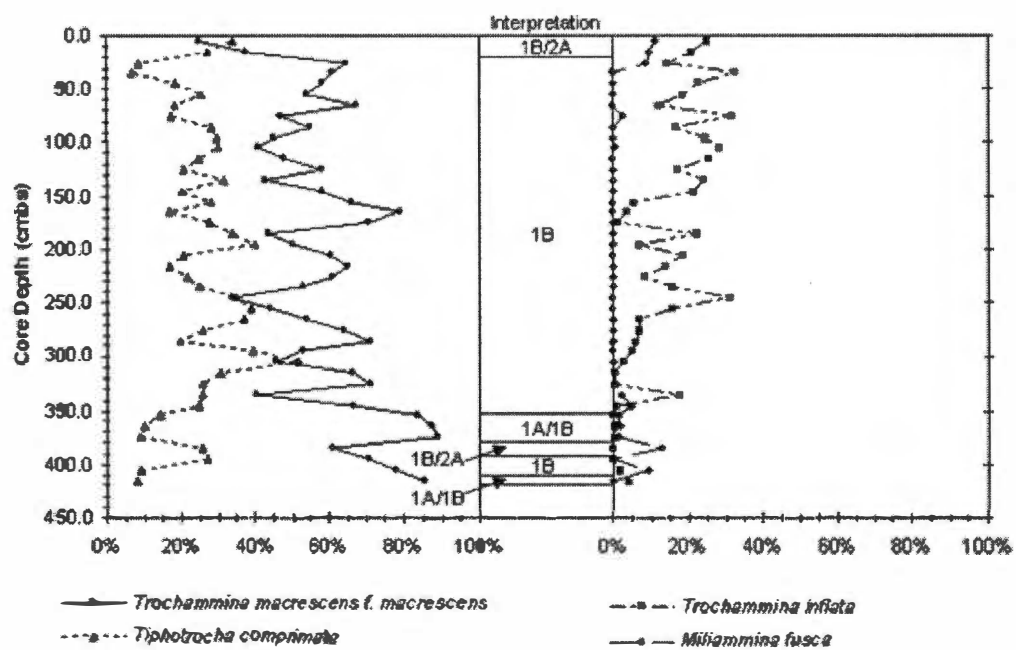


Figure 11. Foraminiferal percentages with interpreted faunal zones for core MC2.

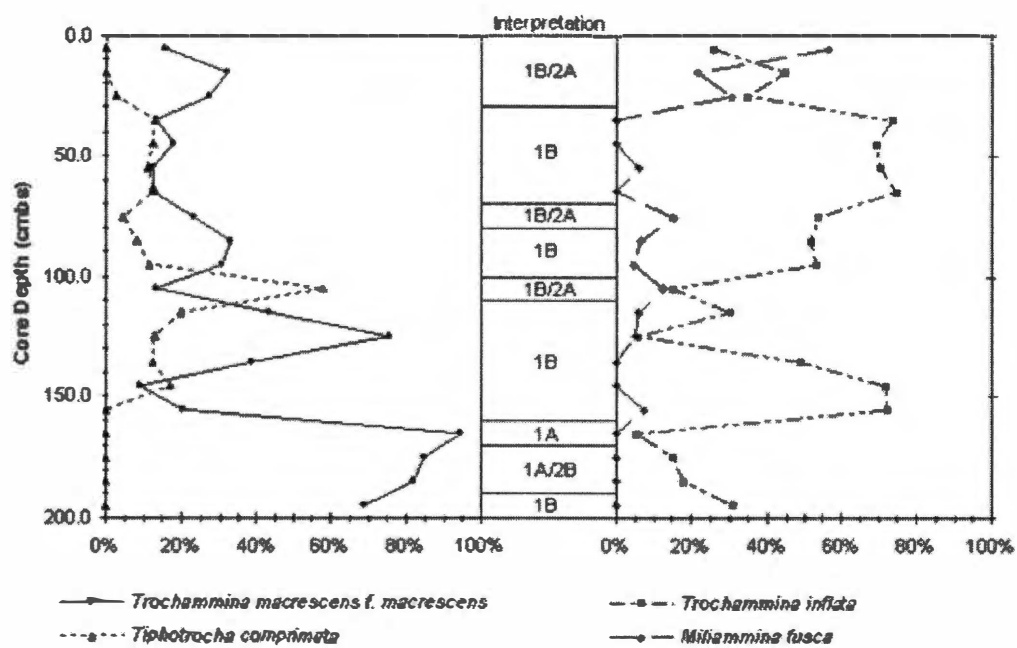


Figure 12. Foraminiferal percentages with interpreted faunal zones for core GC3.

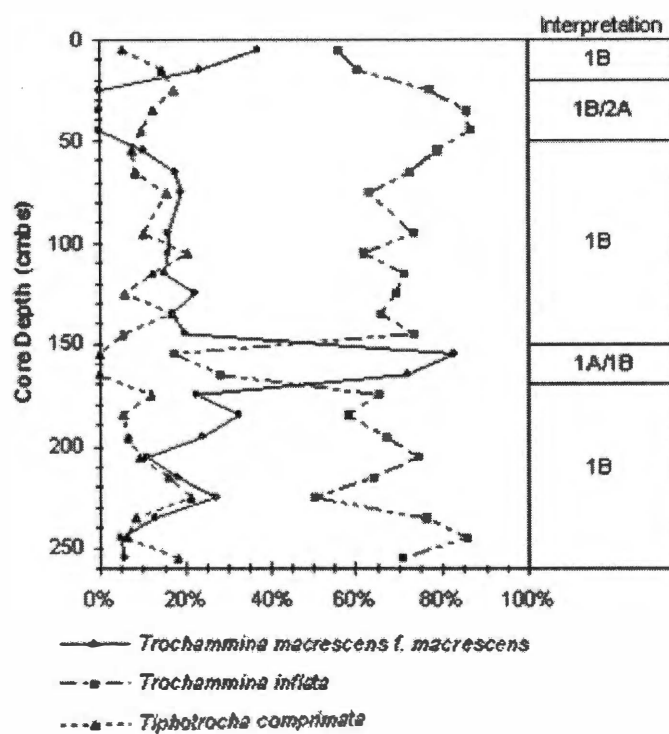


Figure 13. Foraminiferal percentages with interpreted faunal zones for core MO2.

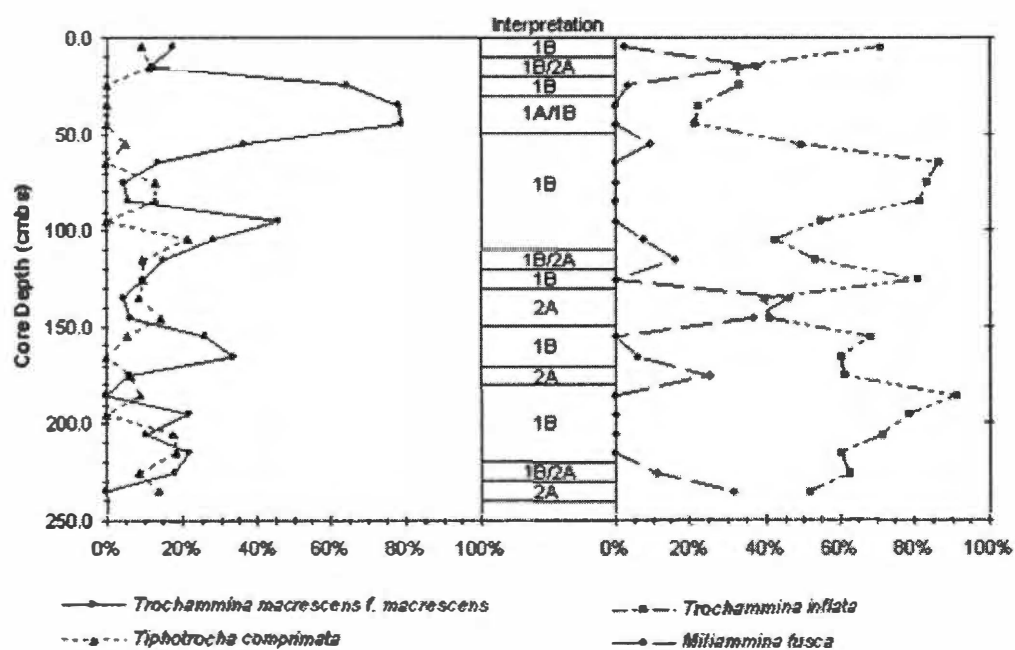


Figure 14. Foraminiferal percentages with interpreted faunal zones for core SP2.

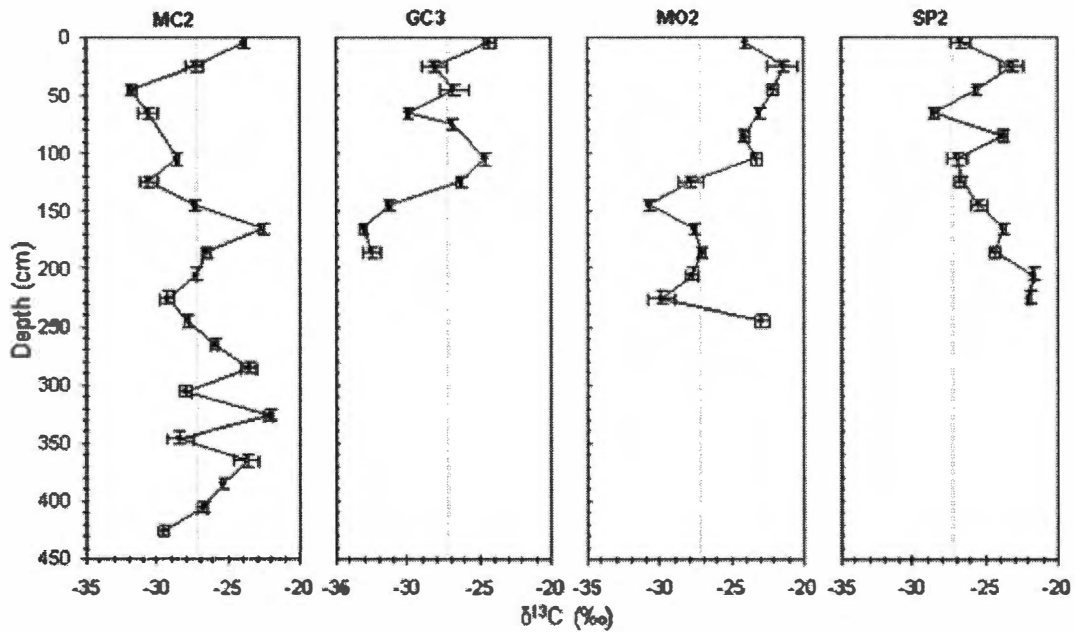


Figure 15.  $\delta^{13}\text{C}$  as a function of depth below surface for the  $\text{C}_{27}$  alkane from the different core samples. Vertical error bars represent the sample intervals (10cm total) and horizontal error bars represent the standard deviations of the isotopic analyses. The vertical, dashed lines represent an estimated 50% mix of C3 and C4 plants.

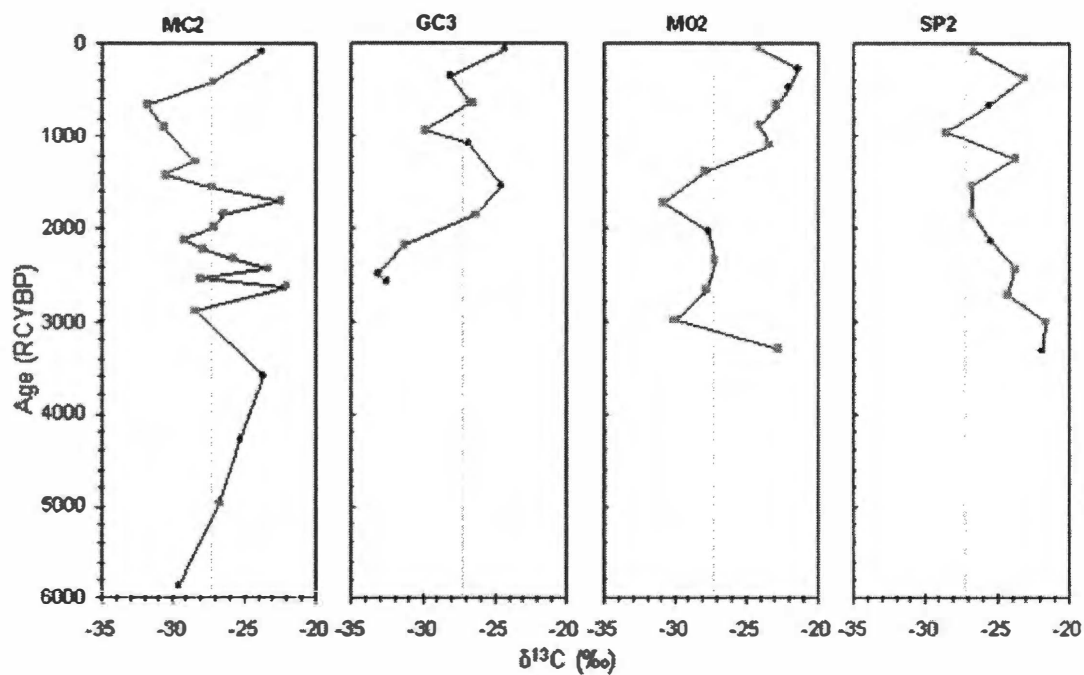


Figure 16.  $\delta^{13}\text{C}$  as a function of  $^{14}\text{C}$  years for the  $\text{C}_{27}$  alkane from the different core samples. The vertical, dashed lines represent an estimated 50% mix of C3 and C4 plants. The gray boxes represent data points from faunal zone 1B deposits.

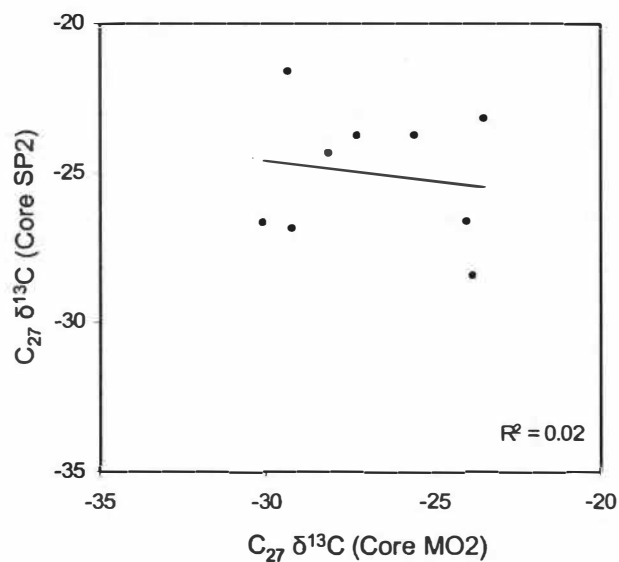


Figure 17.  $\delta^{13}C$  of the  $C_{27}$  alkane for core SP2 plotted against core MO2. Data points were matched using a 3 step procedure as follows: (1) ages of data points were calculated using linear interpolation between dated horizons, (2) data points from core SP2 were matched in time with the nearest data points from core MO2, (3) isotope values for the matched SP2 data points were estimated using linear interpolation.

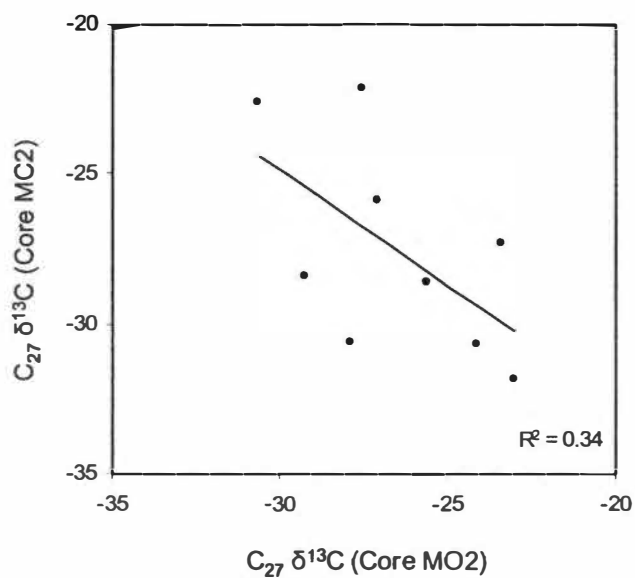


Figure 18.  $\delta^{13}\text{C}$  of the  $\text{C}_{27}$  alkane for core MC2 plotted against core MO2. Data points were matched using a 3 step procedure as follows: (1) ages of data points were calculated using linear interpolation between dated horizons, (2) data points from core MO2 were matched in time with the nearest data points from core MC2, (3) isotope values for the matched MO2 data points were estimated using linear interpolation.

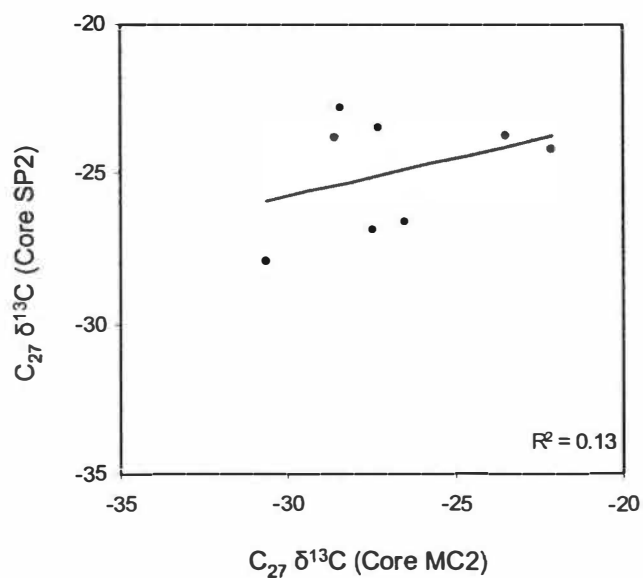


Figure 19.  $\delta^{13}\text{C}$  of the  $\text{C}_{27}$  alkane for core SP2 plotted against core MC2. Data points were matched using a 3 step procedure as follows: (1) ages of data points were calculated using linear interpolation between dated horizons, (2) data points from core SP2 were matched in time with the nearest data points from core MC2, (3) isotope values for the matched SP2 data points were estimated using linear interpolation.

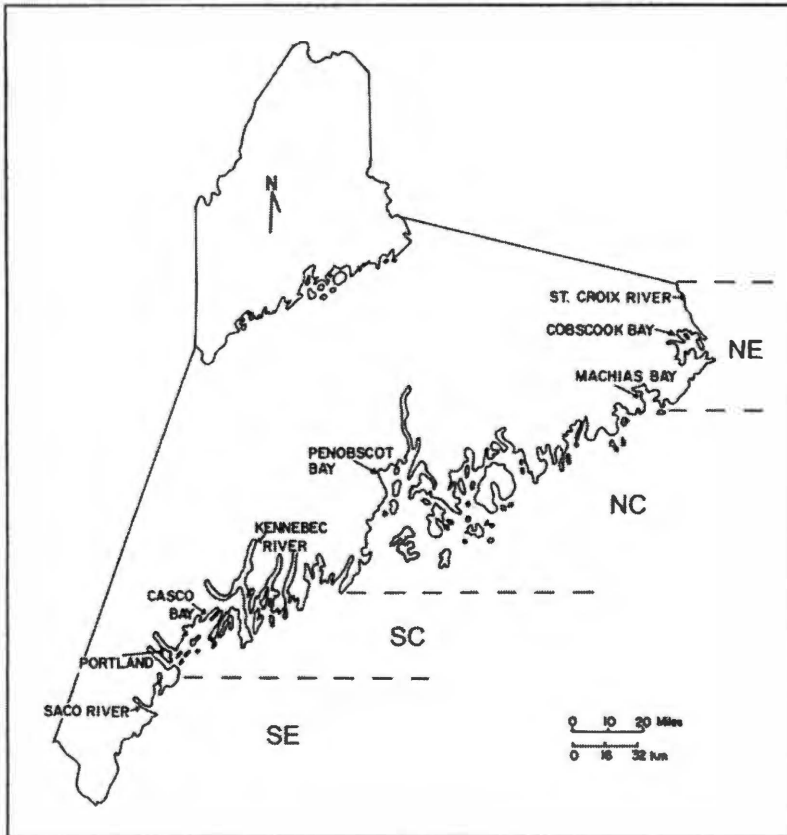


Figure 20. Map of Maine's shoreline showing the four previously established coastal compartments (from Kelley, 1987).

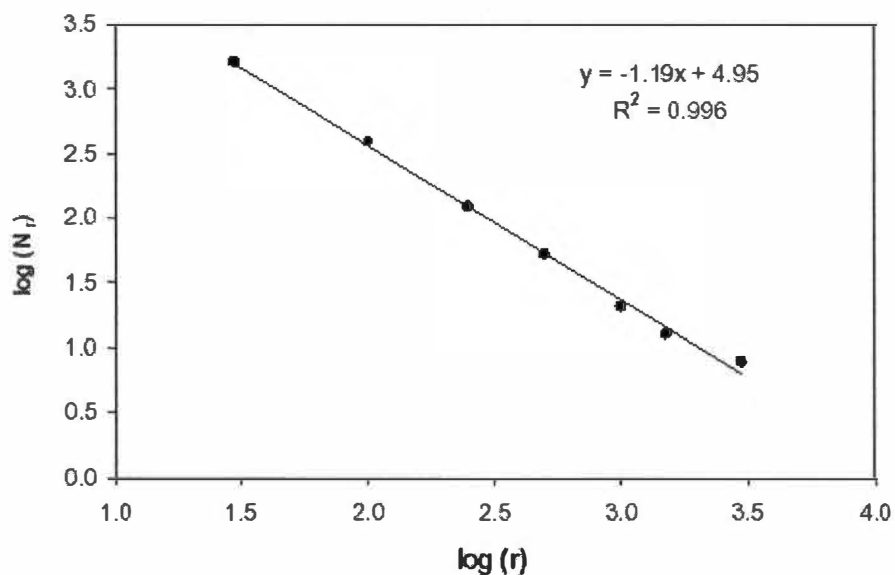


Figure 21. Typical  $\log(Nr)$  vs.  $\log(r)$  plot showing the regression equation, which gives a value of  $D=1.19$ . This log-log plot is for the Kittery quadrangle, the first quadrangle on the Maine coast moving from West to East.

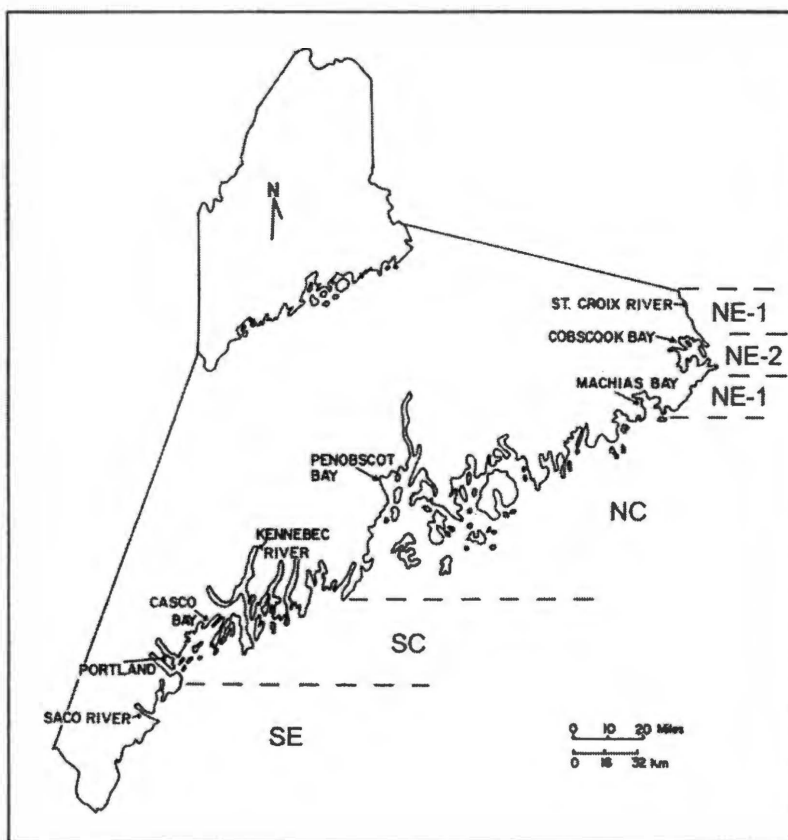


Figure 22. Map of Maine's Shoreline showing the further division of the NE compartment into the NE-1 and NE-2 sub-compartments (map modified from Kelley, 1987).

## Appendix B - Tables

Table 1. Foraminiferal faunal zones and floral zones with their associated dominant species. No vertical scale is implied (modified from Gehrels, 1994).

| Faunal Zone | Foraminifera                                                                                                           | Floral Zone/Plants                                                                          |
|-------------|------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|
| 1A          | <i>Trochammina macrescens</i><br><i>forma macrescens</i>                                                               | Higher high marsh (HHM)                                                                     |
| 1B          | <i>Trochammina macrescens</i><br><i>forma macrescens</i><br><i>Tiphotocha comprimata</i><br><i>Trochammina inflata</i> | <i>Juncus gerardi</i> (C3)<br><i>Solidago sempervirens</i> (C3)<br>-----<br>High Marsh (HM) |
| 2A          | <i>Miliammina fusca</i><br><i>Trochammina inflata</i>                                                                  | <i>Spartina patens</i> (C4)<br>-----                                                        |
| 2B          | <i>Miliammina fusca</i><br><i>Ammotium salsum</i><br><i>Pseudothurammmina limnetis</i>                                 | Low Marsh (LM)<br><i>Spartina alterniflora</i> (C4)                                         |

Table 2.  $\delta^{13}\text{C}$  values for the C-27, C-29, and C-31 alkanes from the Machiasport plants. The coefficient of variation of absolute abundance for the different plant samples is also reported for the C-27, C-29, and C-31 homologues (bottom).

| Marsh Plant                                                                                               | C-27 (‰) | C-29 (‰) | C-31 (‰) |
|-----------------------------------------------------------------------------------------------------------|----------|----------|----------|
| <i>Spartina alterniflora</i> (C4)                                                                         | -19.78   | -22.62   | NA       |
| <i>Spartina patens</i> (C4)                                                                               | -23.37   | -22.92   | -23.87   |
| <i>Salicornia europa</i> (CAM)                                                                            | -31.50   | -30.28   | -32.49   |
| <i>Juncus gerardi</i> (C3)                                                                                | -31.97   | -30.98   | -31.52   |
| <i>Solidago sempervirens</i> (C3)                                                                         | -26.37   | -29.30   | -34.29   |
| <i>Potentilla anseria</i> (C3)                                                                            | -27.26   | -29.84   | -31.35   |
| <i>Atriplex patula</i> (C3)                                                                               | -32.22   | -31.68   | -31.21   |
| <i>Plantago maritima</i> (C3)                                                                             | -34.39   | -34.29   | -36.69   |
| <i>Suaeda maritima</i> (C3)                                                                               | -29.73   | -31.10   | NA       |
| <i>Limonium nashii</i> (C3)                                                                               | -30.65   | -31.25   | -32.26   |
| C3 vs. C4 Min. Difference                                                                                 | 3.00     | 6.38     | 7.34     |
| Coefficient of Variation (%)<br>for absolute abundance of<br>indicated homologue for all<br>plant samples | 61.95    | 79.20    | 134.17   |

Table 3. GC/MS reported abundances for n-alkanes from the Machiasport salt marsh plants including CPI and ACL values. The photosynthetic pathway employed by the plant is also indicated with the  $\delta^{13}\text{C}$  value for the C27 homologue. Bold indicates n-alkane with highest abundance for a particular plant species.

| Plant ID                     | Path. | C <sub>27</sub>       | <i>n</i> -alkane abundance (μg/g) |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 | CPI        | ACL  |                 |                 |
|------------------------------|-------|-----------------------|-----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------|------|-----------------|-----------------|
|                              |       | δ <sup>13</sup> C (‰) | C <sub>15</sub>                   | C <sub>16</sub> | C <sub>17</sub> | C <sub>18</sub> | C <sub>19</sub> | C <sub>20</sub> | C <sub>21</sub> | C <sub>22</sub> | C <sub>23</sub> | C <sub>24</sub> | C <sub>25</sub> | C <sub>26</sub> | C <sub>27</sub> | C <sub>28</sub> | C <sub>29</sub> | C <sub>30</sub> | C <sub>31</sub> | C <sub>32</sub> |            |      | C <sub>33</sub> | C <sub>34</sub> |
| <i>Spartina alterniflora</i> | C4    | -19.8                 | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 68              | 0               | <b>144</b>      | 0               | 44              | 0               | 44              | 0          | NA   | 29.4            |                 |
| <i>Spartina patens</i>       | C4    | -23.4                 | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 21              | 0               | 55              | 13              | <b>136</b>      | 0               | 23              | 0               | 0               | 0          | 18.2 | 28.4            |                 |
| <i>Salicornia europaea</i>   | CAM   | -31.5                 | 0                                 | 4               | 0               | 4               | 0               | 5               | 53              | 0               | 93              | 6               | <b>100</b>      | 8               | 86              | 11              | 50              | 0               | 40              | 0               | 33         | 0    | 16.5            | 26.7            |
| <i>Juncus gerardi</i>        | C3    | -32.0                 | 0                                 | 0               | 0               | 9               | 0               | 0               | 0               | 0               | 48              | 0               | 67              | 9               | 153             | 0               | 92              | 0               | 89              | 0               | <b>248</b> | 16   | 27.1            | 29.5            |
| <i>Solidago sempervirens</i> | C3    | -26.4                 | 0                                 | 5               | 0               | 6               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 29              | 0               | 46              | 12              | <b>115</b>      | 4               | 24              | 0          | 13.6 | 30.3            |                 |
| <i>Atriplex patula</i>       | C3    | -32.2                 | 0                                 | 4               | 0               | 3               | 0               | 3               | 0               | 2               | 5               | 0               | 16              | 0               | 105             | 13              | <b>140</b>      | 12              | 113             | 0               | 11         | 0    | 16.1            | 28.9            |
| <i>Potentilla anseria</i>    | C3    | -27.3                 | 0                                 | 4               | 0               | 5               | 0               | 5               | 5               | 0               | 12              | 4               | 16              | 11              | 61              | 7               | 66              | 6               | <b>136</b>      | 0               | 0          | 0    | 10.6            | 28.9            |
| <i>Plantago maritima</i>     | C3    | -34.4                 | 0                                 | 2               | 3               | 1               | 1               | 0               | 0               | 0               | 11              | 0               | 6               | 4               | <b>49</b>       | 17              | 43              | 8               | 45              | 10              | 33         | 11   | 3.8             | 29.4            |
| <i>Suaeda maritima</i>       | C3    | -29.7                 | 0                                 | 11              | 0               | 14              | 0               | 0               | 0               | 0               | 22              | 0               | 89              | 16              | 120             | 15              | 275             | 0               | <b>526</b>      | 0               | 42         | 0    | 34.2            | 29.4            |
| <i>Limonium nashii</i>       | C3    | -30.7                 | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 9               | 1               | 9               | 1               | <b>13</b>       | 2               | 4               | 0          | 8.5  | 29.8            |                 |
| Coefficient of Var. (%)      |       |                       |                                   |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 | 62              | 79              | 134             |                 |                 |            |      |                 |                 |

Table 4. GC/MS reported abundances for n-alkanes from the Morse River core including CPI and ACL values. Bulk  $\delta^{13}\text{C}$  values are also reported with  $\delta^{13}\text{C}$  values for the  $\text{C}_{27}$  alkane. Radiocarbon dates are also indicated at the appropriate core depth. Bold indicates n-alkane with highest abundance for a particular core depth.

| Depth<br>(cm) | 2σ Cal. Age | C <sub>27</sub><br>δ <sup>13</sup> C (‰) | Bulk<br>δ <sup>13</sup> C (‰) | <i>n</i> -alkane abundance (μg/g) |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 | CPI             | ACL  |      |
|---------------|-------------|------------------------------------------|-------------------------------|-----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------|------|
|               |             |                                          |                               | C <sub>15</sub>                   | C <sub>16</sub> | C <sub>17</sub> | C <sub>18</sub> | C <sub>19</sub> | C <sub>20</sub> | C <sub>21</sub> | C <sub>22</sub> | C <sub>23</sub> | C <sub>24</sub> | C <sub>25</sub> | C <sub>26</sub> | C <sub>27</sub> | C <sub>28</sub> | C <sub>29</sub> | C <sub>30</sub> | C <sub>31</sub> | C <sub>32</sub> | C <sub>33</sub> | C <sub>34</sub> |      |      |
| 5             |             | -24.1                                    | -18.0                         | 2                                 | 0               | 0               | 2               | 0               | 0               | 7               | 2               | 10              | 8               | 31              | 11              | 45              | 16              | 46              | 13              | 39              | 4               | 15              | 0               | 3.6  | 28.1 |
| 15            |             |                                          | -17.8                         | 0                                 | 0               | 0               | 1               | 0               | 0               | 0               | 0               | 2               | 0               | 9               | 3               | 12              | 2               | 4               | 0               | 2               | 0               | 4               | 0               | 6.3  | 27.3 |
| 25            |             | -21.4                                    | -14.3                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 5               | 1               | 23              | 8               | 24              | 4               | 7               | 1               | 3               | 0               | 4               | 0               | 4.8  | 26.8 |
| 35            |             |                                          | -14.5                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 3               | 3               | 20              | 10              | 24              | 5               | 15              | 0               | 0               | 3               | 7               | 0               | 3.2  | 27.3 |
| 45            |             | -22.1                                    | -15.9                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 2               | 2               | 18              | 9               | 19              | 1               | 10              | 0               | 3               | 0               | 7               | 0               | 5.0  | 27.2 |
| 55            |             |                                          | -15.0                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 3               | 1               | 4               | 0               | 2               | 0               | 1               | 0               | 3               | 0               | 11.2 | 28.3 |
| 65            |             | -23.0                                    | -16.6                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 1               | 0               | 8               | 2               | 7               | 0               | 5               | 0               | 2               | 0               | 3               | 0               | 9.7  | 27.6 |
| 75            |             |                                          | -16.9                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 1               | 0               | 6               | 1               | 6               | 0               | 6               | 0               | 2               | 1               | 3               | 0               | 9.1  | 28.2 |
| 85            |             | -24.1                                    | -16.5                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 1               | 0               | 7               | 1               | 8               | 1               | 9               | 1               | 6               | 1               | 2               | 0               | 8.0  | 28.2 |
| 95            |             |                                          | -16.4                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 1               | 0               | 2               | 0               | 3               | 0               | 1               | 0               | 1               | 0               | 71.4 | 28.7 |
| 105           | 1240 to     | -23.2                                    | -16.5                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 2               | 1               | 3               | 0               | 3               | 0               | 1               | 1               | 1               | 0               | 6.5  | 28.4 |
| 115           | 950 BP      |                                          |                               | 0                                 | 0               | 0               | 1               | 0               | 0               | 0               | 0               | 1               | 0               | 5               | 1               | 4               | 0               | 4               | 0               | 1               | 0               | 2               | 0               | 15.3 | 27.7 |
| 125           |             | -27.8                                    | -21.2                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 8               | 0               | 10              | 0               | 16              | 2               | 11              | 0               | 9               | 0               | 2               | 0               | 0               | 0               | 23.7 | 26.1 |
| 135           |             |                                          | -23.2                         | 0                                 | 0               | 0               | 1               | 0               | 0               | 9               | 1               | 25              | 1               | 49              | 1               | 20              | 4               | 20              | 7               | 25              | 4               | 5               | 0               | 9.0  | 27.1 |
| 145           |             | -30.8                                    | -23.1                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 10              | 0               | 18              | 0               | 29              | 1               | 9               | 1               | 16              | 0               | 12              | 3               | 7               | 0               | 14.5 | 27.1 |
| 155           |             |                                          | -20.6                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 5               | 0               | 28              | 1               | 57              | 11              | 23              | 15              | 23              | 0               | 33              | 0               | 6               | 0               | 6.4  | 26.9 |
| 165           |             | -27.6                                    | -19.3                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 5               | 0               | 29              | 1               | 64              | 9               | 47              | 24              | 60              | 20              | 55              | 11              | 0               | 0               | 3.9  | 27.7 |
| 175           |             |                                          | -17.4                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 2               | 0               | 11              | 0               | 38              | 6               | 32              | 7               | 23              | 4               | 16              | 3               | 4               | 0               | 5.8  | 27.3 |
| 185           |             | -27.1                                    | -19.8                         | 0                                 | 0               | 0               | 1               | 0               | 0               | 4               | 0               | 14              | 1               | 32              | 9               | 19              | 3               | 33              | 6               | 22              | 3               | 3               | 0               | 5.5  | 27.5 |
| 195           |             |                                          | -16.4                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 2               | 0               | 13              | 4               | 17              | 3               | 5               | 0               | 4               | 2               | 4               | 0               | 4.7  | 27.4 |
| 205           |             | -27.8                                    | -17.9                         | 0                                 | 0               | 0               | 1               | 0               | 0               | 13              | 1               | 15              | 1               | 26              | 6               | 25              | 9               | 22              | 6               | 10              | 2               | 3               | 0               | 4.1  | 27.2 |
| 215           |             |                                          | -21.8                         | 0                                 | 0               | 0               | 0               | 0               | 0               | 7               | 0               | 9               | 1               | 16              | 4               | 19              | 1               | 16              | 1               | 7               | 0               | 4               | 0               | 13.0 | 27.2 |
| 225           |             | -29.9                                    | -22.9                         | 0                                 | 0               | 0               | 2               | 0               | 0               | 9               | 0               | 6               | 0               | 9               | 0               | 15              | 2               | 16              | 0               | 0               | 4               | 0               | 0               | 7.9  | 27.2 |
| 235           |             |                                          | -19.5                         | 0                                 | 0               | 0               | 1               | 0               | 0               | 7               | 0               | 10              | 1               | 39              | 8               | 30              | 10              | 32              | 6               | 23              | 4               | 0               | 0               | 4.6  | 27.5 |
| 245           | 3820 to     | -22.8                                    | -16.3                         | 0                                 | 0               | 0               | 1               | 0               | 0               | 1               | 1               | 5               | 2               | 33              | 10              | 26              | 9               | 25              | 0               | 9               | 3               | 0               | 0               | 4.1  | 27.1 |
| 255           | 3470 BP     |                                          | -17.0                         | 0                                 | 0               | 0               | 1               | 0               | 0               | 1               | 2               | 6               | 1               | 31              | 6               | 28              | 7               | 30              | 7               | 12              | 3               | 0               | 0               | 4.5  | 27.4 |

Table 5. Approximate elevations of foraminiferal faunal zones in three of the four salt marshes relative to local mean high water (data from Gehrels, 1996).

| Site          | Mean        | Faunal Zone |          |           |          |
|---------------|-------------|-------------|----------|-----------|----------|
|               | Tidal Range | 1A Upper    | 1B Upper | 2A Upper  | 2B Upper |
| Machiasport   | 3.84m       | +0.7m       | +0.5m    | +0.1m     | -0.25m   |
| Gouldsboro    | 3.29m       | +0.95m      | +0.75m   | +0.4/0.2m | -0.1m    |
| Morse River   | 2.56m       | -           | +0.55m   | +0.25m    | -        |
| Sprague River | 2.56m       | -           | -        | -         | -        |

Table 6. Radiocarbon dates associated with the core deposits.

| Core                  | Depth       | <sup>14</sup> C Age (ybp) | 2σ Cal. Age | Reference             |
|-----------------------|-------------|---------------------------|-------------|-----------------------|
|                       | Range (m)   |                           | Range (ybp) |                       |
| SN-VC-1 <sup>§</sup>  | 0.27 - 0.28 | 490±70                    | 595-641     | Gehrels et al. (1996) |
| SN-VC-1 <sup>§</sup>  | 0.8 - 0.83  | 1070±90                   | 782-1171    | Gehrels et al. (1996) |
| MC2                   | 2.0 - 2.2   | 2040±70                   | 1860-2150   |                       |
| MC2                   | 3.3 - 3.5   | 2720±70                   | 2740-2960   |                       |
| SN-VC-1 <sup>§#</sup> | 3.98 - 4.0  | 4795±80                   | 5318-5664   | Gehrels et al. (1996) |
|                       |             |                           | 5699-5701   |                       |
| GC3                   | 0.8 - 1.0   | 1290±60                   | 1070-1300   |                       |
| GC3                   | 1.7 - 1.9   | 2740±60                   | 2750-2960   |                       |
| MO2                   | 1.0 - 1.2   | 1160±60                   | 950-1240    |                       |
| MO2                   | 2.5 - 2.7   | 3390±60                   | 3470-3820   |                       |
| SP2                   | 1.0 - 1.2   | 1620±60                   | 1380-1630   |                       |
|                       |             |                           | 1660-1690   |                       |

<sup>§</sup>Core from previous sea level research (Gehrels, 1996) recovered directly adjacent to MC2 and stratigraphically correlated using foraminiferal zones and depth to Pleistocene substrate

<sup>#</sup>AMS date of plant fragment

Table 7. GC/MS reported abundances for n-alkanes from core MC2 including CPI and ACL values.

| MC2   |    |                           |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |       |      |                           |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |      |      |
|-------|----|---------------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-------|------|---------------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|------|------|
| Depth |    | n-alkane abundance (µg/g) |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    | 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  | (cm)                      | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | CPI  | ACL  |
| 5     | 0  | 0                         | 0  | 0  | 0  | 1  | 0  | 3  | 1  | 4  | 0  | 5  | 0  | 1  | 0  | 0  | 0  | 12.2  | 27.3 | 225                       | 0  | 0  | 0  | 6  | 0  | 4  | 0  | 6  | 2  | 9  | 2  | 10 | 0  | 2  | 1  | 7  | 0  | 6.8  | 28.1 |
| 15    | 0  | 0                         | 0  | 3  | 0  | 1  | 0  | 2  | 1  | 5  | 0  | 4  | 0  | 1  | 0  | 0  | 0  | 13.0  | 27.2 | 235                       | 0  | 0  | 0  | 3  | 0  | 3  | 0  | 6  | 1  | 6  | 0  | 7  | 0  | 2  | 1  | 6  | 0  | 9.8  | 28.2 |
| 25    | 0  | 0                         | 0  | 4  | 0  | 2  | 0  | 4  | 0  | 4  | 0  | 5  | 0  | 1  | 1  | 0  | 0  | 10.9  | 27.3 | 245                       | 0  | 0  | 0  | 3  | 0  | 6  | 0  | 13 | 2  | 11 | 2  | 10 | 1  | 3  | 1  | 5  | 0  | 8.2  | 27.4 |
| 35    | 0  | 0                         | 0  | 4  | 0  | 3  | 0  | 6  | 2  | 10 | 1  | 11 | 0  | 2  | 1  | 2  | 0  | 7.7   | 27.5 | 255                       | 0  | 0  | 0  | 4  | 0  | 6  | 0  | 12 | 2  | 10 | 1  | 10 | 0  | 5  | 0  | 5  | 0  | 14.4 | 27.4 |
| 45    | 0  | 1                         | 0  | 6  | 0  | 5  | 0  | 7  | 1  | 10 | 2  | 13 | 0  | 2  | 1  | 6  | 0  | 9.5   | 27.9 | 265                       | 0  | 0  | 0  | 5  | 0  | 5  | 1  | 7  | 3  | 8  | 1  | 7  | 1  | 2  | 1  | 7  | 0  | 5.8  | 27.9 |
| 55    | 0  | 0                         | 0  | 1  | 0  | 2  | 0  | 3  | 0  | 2  | 0  | 4  | 0  | 1  | 0  | 3  | 0  | NA    | 28.0 | 275                       | 0  | 0  | 0  | 12 | 0  | 7  | 0  | 8  | 1  | 12 | 3  | 12 | 1  | 2  | 2  | 3  | 0  | 6.2  | 27.4 |
| 65    | 0  | 0                         | 0  | 6  | 0  | 6  | 0  | 8  | 1  | 9  | 2  | 12 | 1  | 2  | 2  | 5  | 0  | 8.8   | 27.7 | 285                       | 0  | 0  | 0  | 2  | 0  | 5  | 1  | 10 | 4  | 11 | 1  | 9  | 1  | 3  | 2  | 5  | 0  | 5.6  | 27.4 |
| 75    | 0  | 0                         | 0  | 4  | 0  | 6  | 0  | 11 | 0  | 6  | 0  | 9  | 0  | 3  | 0  | 5  | 0  | 48.5  | 27.4 | 295                       | 0  | 0  | 0  | 3  | 0  | 6  | 0  | 7  | 2  | 8  | 0  | 8  | 1  | 2  | 2  | 9  | 0  | 8.3  | 28.1 |
| 85    | 0  | 0                         | 0  | 6  | 0  | 6  | 0  | 9  | 1  | 10 | 2  | 12 | 1  | 3  | 1  | 8  | 0  | 8.7   | 27.9 | 305                       | 0  | 0  | 0  | 4  | 0  | 4  | 0  | 5  | 1  | 5  | 1  | 6  | 1  | 1  | 1  | 5  | 0  | 7.5  | 27.8 |
| 95    | 0  | 0                         | 0  | 3  | 0  | 3  | 0  | 3  | 0  | 4  | 0  | 7  | 0  | 1  | 0  | 3  | 0  | NA    | 27.9 | 315                       | 0  | 0  | 6  | 0  | 0  | 5  | 0  | 9  | 2  | 11 | 2  | 10 | 1  | 3  | 1  | 5  | 0  | 6.8  | 27.7 |
| 105   | 0  | 0                         | 0  | 3  | 0  | 3  | 0  | 4  | 0  | 4  | 0  | 5  | 0  | 1  | 1  | 5  | 0  | 13.1  | 28.4 | 325                       | 0  | 0  | 0  | 2  | 0  | 5  | 1  | 30 | 9  | 22 | 3  | 16 | 1  | 4  | 0  | 7  | 0  | 5.9  | 27.0 |
| 115   | 0  | 0                         | 0  | 3  | 0  | 6  | 0  | 10 | 1  | 7  | 1  | 8  | 1  | 3  | 0  | 5  | 0  | 14.9  | 27.4 | 335                       | 0  | 0  | 0  | 3  | 0  | 6  | 0  | 11 | 3  | 12 | 2  | 10 | 1  | 2  | 2  | 15 | 0  | 7.0  | 28.3 |
| 125   | 0  | 0                         | 0  | 6  | 0  | 5  | 0  | 6  | 1  | 7  | 2  | 8  | 1  | 1  | 1  | 5  | 0  | 7.2   | 27.7 | 345                       | 0  | 0  | 0  | 5  | 0  | 4  | 0  | 8  | 2  | 9  | 2  | 9  | 1  | 2  | 2  | 5  | 0  | 6.2  | 27.7 |
| 135   | 0  | 0                         | 0  | 6  | 0  | 6  | 0  | 8  | 1  | 8  | 2  | 9  | 1  | 2  | 1  | 7  | 0  | 8.1   | 27.8 | 355                       | 0  | 0  | 0  | 5  | 0  | 8  | 1  | 25 | 8  | 26 | 4  | 21 | 2  | 6  | 3  | 11 | 0  | 5.7  | 27.5 |
| 145   | 0  | 0                         | 0  | 1  | 0  | 3  | 0  | 6  | 1  | 4  | 0  | 5  | 0  | 1  | 0  | 5  | 0  | 17.5  | 27.7 | 365                       | 0  | 0  | 0  | 1  | 0  | 1  | 0  | 3  | 1  | 4  | 0  | 3  | 0  | 1  | 0  | 2  | 0  | 11.1 | 27.6 |
| 155   | 0  | 0                         | 0  | 0  | 0  | 3  | 0  | 6  | 4  | 8  | 0  | 3  | 0  | 2  | 0  | 0  | 0  | 4.8   | 26.4 | 375                       | 0  | 0  | 0  | 1  | 0  | 4  | 1  | 11 | 4  | 10 | 2  | 9  | 0  | 3  | 0  | 5  | 0  | 6.4  | 27.3 |
| 165   | 0  | 0                         | 0  | 4  | 0  | 5  | 1  | 12 | 7  | 14 | 2  | 9  | 0  | 2  | 0  | 4  | 0  | 4.5   | 27.0 | 385                       | 0  | 0  | 0  | 3  | 0  | 5  | 0  | 12 | 4  | 12 | 2  | 11 | 1  | 4  | 0  | 4  | 0  | 7.7  | 27.4 |
| 175   | 0  | 0                         | 0  | 3  | 0  | 7  | 1  | 11 | 4  | 13 | 2  | 13 | 1  | 3  | 2  | 9  | 0  | 5.9   | 27.7 | 395                       | 0  | 0  | 0  | 3  | 0  | 3  | 0  | 5  | 1  | 5  | 1  | 6  | 0  | 1  | 1  | 4  | 0  | 9.1  | 28.0 |
| 185   | 0  | 0                         | 0  | 7  | 0  | 8  | 0  | 16 | 5  | 16 | 4  | 15 | 0  | 8  | 1  | 6  | 0  | 6.7   | 27.5 | 405                       | 0  | 0  | 0  | 4  | 0  | 5  | 0  | 7  | 2  | 7  | 0  | 6  | 1  | 3  | 2  | 2  | 0  | 7.4  | 27.3 |
| 195   | 0  | 0                         | 0  | 5  | 0  | 4  | 0  | 6  | 1  | 6  | 1  | 7  | 0  | 1  | 1  | 6  | 0  | 8.1   | 28.0 | 415                       | 0  | 0  | 0  | 6  | 0  | 7  | 0  | 7  | 1  | 5  | 0  | 7  | 0  | 5  | 2  | 9  | 0  | 14.0 | 28.3 |
| 205   | 0  | 0                         | 0  | 2  | 0  | 2  | 0  | 4  | 1  | 4  | 0  | 4  | 0  | 1  | 2  | 3  | 0  | 8.5   | 27.9 | 425                       | 1  | 0  | 0  | 1  | 0  | 2  | 0  | 7  | 0  | 3  | 0  | 2  | 0  | 2  | 0  | 3  | 0  | 66.3 | 27.4 |
| 215   | 0  | 0                         | 0  | 0  | 0  | 2  | 2  | 10 | 7  | 14 | 1  | 9  | 1  | 2  | 2  | 3  | 0  | 3.2   | 27.4 | 435                       | 0  | 0  | 0  | 1  | 0  | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 0  | NA   | 28.7 |

Table 8. GC/MS reported abundances for n-alkanes from core GC3 including CPI and ACL values.

| GC3           |                                   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |     |     |      |
|---------------|-----------------------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|-----|------|
| Depth<br>(cm) | <i>n</i> -alkane abundance (µg/g) |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    | CPI | ACL |      |
|               | 18                                | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 |     |     | 34   |
| 5             | 2                                 | 0  | 2  | 0  | 0  | 0  | 0  | 3  | 2  | 3  | 2  | 4  | 0  | 3  | 0  | 0  | 0   | 3.1 | 27.7 |
| 15            | 2                                 | 0  | 2  | 0  | 0  | 0  | 2  | 4  | 2  | 3  | 2  | 3  | 0  | 2  | 0  | 0  | 0   | 2.0 | 27.0 |
| 25            | 2                                 | 0  | 2  | 2  | 0  | 2  | 2  | 3  | 3  | 7  | 2  | 6  | 0  | 3  | 0  | 3  | 0   | 3.3 | 27.7 |
| 35            | 1                                 | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 1  | 2  | 1  | 1  | 0  | 1  | 0  | 2  | 0   | 3.3 | 28.7 |
| 45            | 1                                 | 0  | 1  | 0  | 0  | 1  | 0  | 2  | 1  | 1  | 1  | 1  | 0  | 1  | 0  | 3  | 0   | 4.3 | 28.3 |
| 55            | 1                                 | 0  | 1  | 2  | 0  | 2  | 0  | 3  | 2  | 3  | 1  | 3  | 1  | 2  | 0  | 1  | 0   | 3.9 | 27.7 |
| 65            | 2                                 | 0  | 0  | 2  | 0  | 2  | 0  | 2  | 0  | 3  | 2  | 3  | 0  | 2  | 0  | 2  | 0   | 8.6 | 28.0 |
| 75            | 2                                 | 0  | 2  | 1  | 0  | 1  | 1  | 1  | 1  | 2  | 1  | 2  | 0  | 2  | 0  | 2  | 0   | 2.9 | 27.8 |
| 105           | 0                                 | 0  | 0  | 1  | 0  | 1  | 0  | 2  | 1  | 2  | 1  | 5  | 1  | 2  | 0  | 1  | 0   | 4.6 | 28.3 |
| 115           | 2                                 | 0  | 2  | 1  | 0  | 1  | 1  | 1  | 1  | 3  | 1  | 3  | 1  | 2  | 0  | 0  | 0   | 2.5 | 27.4 |
| 125           | 0                                 | 0  | 0  | 0  | 0  | 1  | 1  | 2  | 2  | 4  | 1  | 2  | 1  | 1  | 1  | 0  | 0   | 1.5 | 27.1 |
| 135           | 2                                 | 0  | 2  | 0  | 0  | 2  | 2  | 3  | 4  | 7  | 2  | 7  | 2  | 4  | 1  | 2  | 0   | 2.3 | 27.8 |
| 145           | 2                                 | 0  | 2  | 3  | 0  | 3  | 0  | 3  | 2  | 6  | 3  | 3  | 0  | 2  | 0  | 2  | 0   | 3.7 | 27.5 |
| 155           | 2                                 | 0  | 2  | 5  | 0  | 2  | 0  | 2  | 2  | 8  | 2  | 6  | 0  | 2  | 0  | 2  | 0   | 5.3 | 27.7 |
| 165           | 2                                 | 0  | 0  | 3  | 0  | 2  | 0  | 2  | 2  | 6  | 2  | 5  | 0  | 3  | 0  | 0  | 0   | 4.3 | 27.4 |
| 175           | 0                                 | 0  | 0  | 2  | 0  | 2  | 0  | 0  | 3  | 7  | 3  | 3  | 0  | 3  | 0  | 2  | 0   | 3.0 | 27.9 |
| 185           | 2                                 | 0  | 2  | 2  | 0  | 2  | 2  | 5  | 5  | 16 | 5  | 5  | 2  | 5  | 0  | 2  | 0   | 2.5 | 27.4 |
| 195           | 0                                 | 0  | 0  | 0  | 0  | 0  | 0  | 1  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 1  | 0   | 1.6 | 27.9 |

Table 9. GC/MS reported abundances for n-alkanes from cores MO2 and SP2 including CPI and ACL values.

| MO2   |    |                                   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |      | SP2  |      |       |    |                                   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |      |      |  |  |
|-------|----|-----------------------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|------|------|------|-------|----|-----------------------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|------|------|--|--|
| Depth |    | <i>n</i> -alkane abundance (μg/g) |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |      |      |      | Depth |    | <i>n</i> -alkane abundance (μg/g) |    |    |    |    |    |    |    |    |    |    |    |    |    |    |      |      |  |  |
| (cm)  | 18 | 19                                | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | CPI  | ACL  | (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 | 5    | 2     | 2  | 0                                 | 3  | 1  | 5  | 2  | 16 | 3  | 17 | 3  | 16 | 2  | 5  | 0  | 11 | 0  | 6.8  | 27.8 |  |  |
| 15    | 1  | 0                                 | 0  | 0  | 0  | 2  | 0  | 9  | 3  | 12 | 2  | 4  | 0  | 2  | 0  | 4  | 0  | 6.3  | 27.3 | 15   | 0     | 0  | 1                                 | 2  | 0  | 1  | 0  | 4  | 1  | 4  | 0  | 6  | 1  | 1  | 1  | 2  | 0  | 5.5  | 28.0 |  |  |
| 25    | 0  | 0                                 | 0  | 0  | 0  | 5  | 1  | 23 | 8  | 24 | 4  | 7  | 1  | 3  | 0  | 4  | 0  | 4.8  | 26.8 | 25   | 2     | 0  | 0                                 | 1  | 0  | 3  | 0  | 13 | 4  | 18 | 2  | 14 | 0  | 3  | 0  | 4  | 0  | 8.2  | 27.4 |  |  |
| 35    | 0  | 0                                 | 0  | 0  | 0  | 3  | 3  | 20 | 10 | 24 | 5  | 15 | 0  | 0  | 3  | 7  | 0  | 3.2  | 27.3 | 35   | 2     | 0  | 2                                 | 11 | 2  | 10 | 0  | 16 | 5  | 20 | 3  | 19 | 6  | 13 | 3  | 11 | 0  | 5.1  | 28.1 |  |  |
| 45    | 0  | 0                                 | 0  | 0  | 0  | 2  | 2  | 18 | 9  | 19 | 1  | 10 | 0  | 3  | 0  | 7  | 0  | 5.0  | 27.2 | 45   | 0     | 0  | 0                                 | 27 | 1  | 17 | 1  | 8  | 2  | 5  | 1  | 9  | 0  | 7  | 0  | 3  | 0  | 13.2 | 26.6 |  |  |
| 55    | 0  | 0                                 | 0  | 0  | 0  | 0  | 0  | 3  | 1  | 4  | 0  | 2  | 0  | 1  | 0  | 3  | 0  | 11.2 | 28.3 | 55   | 0     | 0  | 0                                 | 42 | 2  | 30 | 3  | 15 | 14 | 4  | 20 | 43 | 6  | 13 | 3  | 9  | 0  | 2.5  | 27.4 |  |  |
| 65    | 0  | 0                                 | 0  | 0  | 0  | 1  | 0  | 8  | 2  | 7  | 0  | 5  | 0  | 2  | 0  | 3  | 0  | 9.7  | 27.6 | 65   | 0     | 0  | 0                                 | 18 | 1  | 19 | 3  | 28 | 18 | 64 | 20 | 37 | 7  | 8  | 3  | 9  | 0  | 3.3  | 27.3 |  |  |
| 75    | 0  | 0                                 | 0  | 0  | 0  | 1  | 0  | 6  | 1  | 6  | 0  | 6  | 0  | 2  | 1  | 3  | 0  | 9.1  | 28.2 | 75   | 0     | 0  | 0                                 | 4  | 0  | 7  | 2  | 19 | 11 | 24 | 3  | 16 | 1  | 4  | 2  | 3  | 0  | 3.8  | 26.9 |  |  |
| 85    | 0  | 0                                 | 0  | 0  | 0  | 1  | 0  | 7  | 1  | 8  | 1  | 9  | 1  | 6  | 1  | 2  | 0  | 8.0  | 28.2 | 85   | 0     | 0  | 0                                 | 1  | 0  | 1  | 0  | 4  | 2  | 6  | 0  | 4  | 0  | 1  | 1  | 1  | 0  | 6.3  | 27.5 |  |  |
| 95    | 0  | 0                                 | 0  | 0  | 0  | 0  | 0  | 1  | 0  | 2  | 0  | 3  | 0  | 1  | 0  | 1  | 0  | 71.4 | 28.7 | 95   | 0     | 0  | 0                                 | 1  | 0  | 2  | 0  | 4  | 1  | 5  | 0  | 3  | 0  | 1  | 1  | 1  | 0  | 12.6 | 27.2 |  |  |
| 105   | 0  | 0                                 | 0  | 0  | 0  | 0  | 0  | 2  | 1  | 3  | 0  | 3  | 0  | 1  | 1  | 1  | 0  | 6.5  | 28.4 | 105  | 1     | 0  | 0                                 | 3  | 1  | 4  | 1  | 9  | 5  | 13 | 2  | 9  | 3  | 3  | 1  | 2  | 0  | 3.5  | 27.3 |  |  |
| 115   | 1  | 0                                 | 0  | 0  | 0  | 1  | 0  | 5  | 1  | 4  | 0  | 4  | 0  | 1  | 0  | 2  | 0  | 15.3 | 27.7 | 115  | 0     | 0  | 0                                 | 1  | 0  | 1  | 0  | 6  | 2  | 8  | 1  | 7  | 1  | 3  | 1  | 1  | 0  | 4.5  | 27.7 |  |  |
| 125   | 0  | 0                                 | 0  | 8  | 0  | 10 | 0  | 16 | 2  | 11 | 0  | 9  | 0  | 2  | 0  | 0  | 0  | 23.7 | 26.1 | 125  | 0     | 0  | 0                                 | 3  | 1  | 3  | 1  | 11 | 3  | 14 | 4  | 13 | 4  | 11 | 1  | 3  | 0  | 4.5  | 28.0 |  |  |
| 135   | 1  | 0                                 | 0  | 9  | 1  | 25 | 1  | 49 | 1  | 20 | 4  | 20 | 7  | 25 | 4  | 5  | 0  | 9.0  | 27.1 | 135  | 1     | 0  | 1                                 | 5  | 1  | 4  | 1  | 28 | 8  | 22 | 9  | 22 | 8  | 18 | 3  | 3  | 0  | 3.2  | 27.7 |  |  |
| 145   | 0  | 0                                 | 0  | 10 | 0  | 18 | 0  | 29 | 1  | 9  | 1  | 16 | 0  | 12 | 3  | 7  | 0  | 14.5 | 27.1 | 145  | 0     | 0  | 0                                 | 1  | 0  | 2  | 0  | 11 | 3  | 12 | 1  | 11 | 2  | 5  | 2  | 2  | 0  | 5.5  | 27.7 |  |  |
| 155   | 0  | 0                                 | 0  | 5  | 0  | 28 | 1  | 57 | 11 | 23 | 15 | 23 | 0  | 33 | 0  | 6  | 0  | 6.4  | 26.9 | 155  | 0     | 0  | 0                                 | 2  | 0  | 2  | 0  | 6  | 1  | 7  | 1  | 7  | 1  | 3  | 2  | 0  | 0  | 6.4  | 27.7 |  |  |
| 165   | 0  | 0                                 | 0  | 5  | 0  | 29 | 1  | 64 | 9  | 47 | 24 | 60 | 20 | 55 | 11 | 0  | 0  | 3.9  | 27.7 | 165  | 1     | 0  | 1                                 | 4  | 1  | 6  | 3  | 25 | 14 | 33 | 6  | 28 | 6  | 24 | 3  | 3  | 0  | 3.7  | 27.8 |  |  |
| 175   | 0  | 0                                 | 0  | 2  | 0  | 11 | 0  | 38 | 6  | 32 | 7  | 23 | 4  | 16 | 3  | 4  | 0  | 5.8  | 27.3 | 175  | 1     | 0  | 0                                 | 3  | 0  | 7  | 2  | 24 | 12 | 32 | 4  | 28 | 2  | 9  | 5  | 4  | 0  | 4.0  | 27.4 |  |  |
| 185   | 1  | 0                                 | 0  | 4  | 0  | 14 | 1  | 32 | 9  | 19 | 3  | 33 | 6  | 22 | 3  | 3  | 0  | 5.5  | 27.5 | 185  | 0     | 0  | 0                                 | 13 | 0  | 9  | 2  | 34 | 12 | 48 | 8  | 44 | 3  | 33 | 8  | 5  | 0  | 5.4  | 27.9 |  |  |
| 195   | 0  | 0                                 | 0  | 0  | 0  | 2  | 0  | 13 | 4  | 17 | 3  | 5  | 0  | 4  | 2  | 4  | 0  | 4.7  | 27.4 | 195  | 1     | 0  | 0                                 | 5  | 0  | 6  | 1  | 13 | 6  | 21 | 2  | 15 | 0  | 5  | 2  | 3  | 0  | 5.9  | 27.3 |  |  |
| 205   | 1  | 0                                 | 0  | 13 | 1  | 15 | 1  | 26 | 6  | 25 | 9  | 22 | 6  | 10 | 2  | 3  | 0  | 4.1  | 27.2 | 205  | 0     | 0  | 0                                 | 13 | 1  | 6  | 2  | 31 | 16 | 50 | 6  | 44 | 1  | 18 | 7  | 5  | 0  | 4.8  | 27.7 |  |  |
| 215   | 0  | 0                                 | 0  | 7  | 0  | 9  | 1  | 16 | 4  | 19 | 1  | 16 | 1  | 7  | 0  | 4  | 0  | 13.0 | 27.2 | 215  | 0     | 0  | 0                                 | 0  | 0  | 1  | 0  | 18 | 6  | 31 | 3  | 35 | 3  | 26 | 5  | 3  | 0  | 6.8  | 28.4 |  |  |
| 225   | 2  | 0                                 | 0  | 9  | 0  | 6  | 0  | 9  | 0  | 15 | 2  | 16 | 0  | 0  | 4  | 0  | 0  | 7.9  | 27.2 | 225  | 1     | 0  | 0                                 | 2  | 1  | 2  | 1  | 34 | 8  | 35 | 6  | 38 | 1  | 18 | 8  | 4  | 0  | 5.5  | 27.8 |  |  |
| 235   | 1  | 0                                 | 0  | 7  | 0  | 10 | 1  | 39 | 8  | 30 | 10 | 32 | 6  | 23 | 4  | 0  | 0  | 4.6  | 27.5 | 235  | 0     | 0  | 0                                 | 1  | 0  | 1  | 0  | 10 | 0  | 14 | 2  | 18 | 1  | 7  | 0  | 2  | 0  | 20.7 | 28.0 |  |  |
| 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 |      |       |    |                                   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |      |      |  |  |

Table 10. Previously published fractal dimension (D) values calculated for various coastlines.

| Coastline                 | D         | Reference                   |
|---------------------------|-----------|-----------------------------|
| West Coast, Great Britain | 1.25      | Mandelbrot (1967)           |
| South Coast, Norway       | 1.52      | Feder (1988)                |
| North Coast, Australia    | 1.19      | Carr and Benzer (1991)      |
| South Coast, Australia    | 1.13      | Carr and Benzer (1991)      |
| West Shore, Puget Sound   | 1.19      | Carr and Benzer (1991)      |
| East Shore, Puget Sound   | 1.15      | Carr and Benzer (1991)      |
| West Shore, Gulf of CA    | 1.03      | Carr and Benzer (1991)      |
| East Shore, Gulf of CA    | 1.02      | Carr and Benzer (1991)      |
| Deleware Bay, NJ          | 1.46      | Phillips (1986)             |
| Adak Island, AK           | 1.20      | Pennycuick and Kline (1986) |
| Amchitka Island, AK       | 1.66      | Pennycuick and Kline (1986) |
| Pacific Coast, USA        | 1.00-1.27 | Jiang and Plotnick (1998)   |
| Atlantic Coast, USA       | 1.00-1.70 | Jiang and Plotnick (1998)   |
| Jiangsu Province, China   | 1.07      | Xiaohua et al. (2004)       |
| China                     | 1.16      | Xiaohua et al. (2004)       |
| Taiwan Island             | 1.04      | Xiaohua et al. (2004)       |

Table 11. Mean values and standard deviations (SD) calculated for the different coastal compartments and sub-compartments discussed in this study.

| Compartment | n <sup>a</sup> | D Values |      |      |      | t-tests <sup>b</sup> |               |
|-------------|----------------|----------|------|------|------|----------------------|---------------|
|             |                | Low      | High | Mean | SD   | NE                   | NE-subdivided |
| SW          | 9              | 1.02     | 1.21 | 1.11 | 0.06 | A                    | A             |
| SC          | 10             | 1.25     | 1.43 | 1.35 | 0.06 | B                    | B             |
| NC          | 10             | 1.19     | 1.27 | 1.23 | 0.04 | C                    | C             |
| NE          | 10             | 1.13     | 1.45 | 1.26 | 0.11 | C                    | -             |
| NE-1        | 6              | 1.13     | 1.25 | 1.18 | 0.05 | -                    | D             |
| NE-2        | 4              | 1.28     | 1.45 | 1.37 | 0.07 | -                    | B             |

<sup>a</sup>Total number of USGS topographic quadrangle maps sampled for each compartment.

<sup>b</sup>Probability at the 95% confidence level that the mean fractal dimension for each coastal compartment was drawn from a different population. Compartments that share the same letter cannot be statistically discriminated from one another at the 95% confidence level. ANOVA was run separately for each group of data (NE and NE-subdivided).

## Appendix C – Supplementary Data

| Plant Sample                 | <i>n</i> -alkane Chain Length | Average $\delta^{13}\text{C}$ (‰) | Standard Deviation |
|------------------------------|-------------------------------|-----------------------------------|--------------------|
| <i>Spartina alterniflora</i> | C-25                          | -16.32                            |                    |
| <i>Spartina alterniflora</i> | C-27                          | -19.78                            | 0.65               |
| <i>Spartina alterniflora</i> | C-29                          | -22.62                            | 0.58               |
| <i>Spartina alterniflora</i> | C-31                          |                                   |                    |
| <i>Spartina patens</i>       | C-25                          | -20.71                            | 0.50               |
| <i>Spartina patens</i>       | C-27                          | -23.37                            | 0.37               |
| <i>Spartina patens</i>       | C-29                          | -22.92                            | 0.10               |
| <i>Spartina patens</i>       | C-31                          | -23.87                            |                    |
| <i>Juncus gerardi</i>        | C-25                          | -30.23                            | 0.10               |
| <i>Juncus gerardi</i>        | C-27                          | -31.97                            | 0.27               |
| <i>Juncus gerardi</i>        | C-29                          | -30.98                            | 0.90               |
| <i>Juncus gerardi</i>        | C-31                          | -31.52                            | 0.94               |
| <i>Solidago sempervirens</i> | C-25                          | -27.44                            | 0.66               |
| <i>Solidago sempervirens</i> | C-27                          | -26.37                            | 0.35               |
| <i>Solidago sempervirens</i> | C-29                          | -29.30                            | 0.55               |
| <i>Solidago sempervirens</i> | C-31                          | -34.29                            | 0.54               |
| <i>Potentilla anserina</i>   | C-25                          | -20.54                            | 0.99               |
| <i>Potentilla anserina</i>   | C-27                          | -27.26                            | 0.26               |
| <i>Potentilla anserina</i>   | C-29                          | -29.84                            | 0.22               |
| <i>Potentilla anserina</i>   | C-31                          | -31.35                            | 0.30               |
| <i>Salicornia europa</i>     | C-25                          | -33.18                            | 0.16               |
| <i>Salicornia europa</i>     | C-27                          | -31.50                            | 0.31               |
| <i>Salicornia europa</i>     | C-29                          | -30.28                            | 0.53               |
| <i>Salicornia europa</i>     | C-31                          | -32.49                            | 1.32               |
| <i>Atriplex patula</i>       | C-25                          | -29.85                            | 0.15               |
| <i>Atriplex patula</i>       | C-27                          | -32.22                            | 0.02               |
| <i>Atriplex patula</i>       | C-29                          | -31.68                            | 0.34               |
| <i>Atriplex patula</i>       | C-31                          | -31.21                            | 0.28               |
| <i>Plantago maritima</i>     | C-25                          | -30.18                            | 0.38               |
| <i>Plantago maritima</i>     | C-27                          | -34.39                            | 0.70               |
| <i>Plantago maritima</i>     | C-29                          | -34.29                            | 0.90               |
| <i>Plantago maritima</i>     | C-31                          | -36.69                            | 0.21               |
| <i>Suaeda maritima</i>       | C-25                          | -26.18                            | 0.76               |
| <i>Suaeda maritima</i>       | C-27                          | -29.73                            | 0.26               |
| <i>Suaeda maritima</i>       | C-29                          | -31.10                            | 0.18               |
| <i>Suaeda maritima</i>       | C-31                          |                                   |                    |
| <i>Limonium nashii</i>       | C-25                          | -28.74                            | 0.75               |
| <i>Limonium nashii</i>       | C-27                          | -30.65                            | 0.11               |
| <i>Limonium nashii</i>       | C-29                          | -31.25                            | 0.16               |
| <i>Limonium nashii</i>       | C-31                          | -32.26                            | 0.11               |

| Core | Depth (cmbs) | <i>n</i> -alkane Chain Length | Average $\delta^{13}\text{C}$ (‰) | Standard Deviation |
|------|--------------|-------------------------------|-----------------------------------|--------------------|
| MC2  | 0            | C-25                          | -23.95                            | 0.16               |
| MC2  | 0            | C-27                          | -23.87                            | 0.10               |
| MC2  | 0            | C-29                          | -25.33                            | 0.07               |
| MC2  | 0            | C-31                          | -25.78                            | 0.28               |
| MC2  | 20           | C-25                          | -25.03                            | 0.63               |
| MC2  | 20           | C-27                          | -27.29                            | 0.65               |
| MC2  | 20           | C-29                          | -28.20                            | 0.14               |
| MC2  | 20           | C-31                          | -28.66                            | 0.16               |
| MC2  | 40           | C-25                          | -31.15                            |                    |
| MC2  | 40           | C-27                          | -31.81                            | 0.28               |
| MC2  | 40           | C-29                          | -32.89                            | 0.12               |
| MC2  | 40           | C-31                          |                                   |                    |
| MC2  | 60           | C-25                          |                                   |                    |
| MC2  | 60           | C-27                          | -30.65                            | 0.68               |
| MC2  | 60           | C-29                          | -31.71                            | 0.48               |
| MC2  | 60           | C-31                          |                                   |                    |
| MC2  | 100          | C-25                          |                                   |                    |
| MC2  | 100          | C-27                          | -28.58                            | 0.08               |
| MC2  | 100          | C-29                          | -31.31                            | 0.40               |
| MC2  | 100          | C-31                          |                                   |                    |
| MC2  | 120          | C-25                          | -29.02                            | 0.45               |
| MC2  | 120          | C-27                          | -30.60                            | 0.66               |
| MC2  | 120          | C-29                          | -32.72                            | 0.12               |
| MC2  | 120          | C-31                          |                                   |                    |
| MC2  | 140          | C-25                          |                                   |                    |
| MC2  | 140          | C-27                          | -27.43                            | 0.13               |
| MC2  | 140          | C-29                          | -29.83                            | 0.19               |
| MC2  | 140          | C-31                          |                                   |                    |
| MC2  | 160          | C-25                          | -22.53                            | 0.03               |
| MC2  | 160          | C-27                          | -22.58                            | 0.19               |
| MC2  | 160          | C-29                          | -27.66                            | 0.49               |
| MC2  | 160          | C-31                          |                                   |                    |
| MC2  | 180          | C-25                          |                                   |                    |
| MC2  | 180          | C-27                          | -26.49                            | 0.31               |
| MC2  | 180          | C-29                          | -30.34                            | 0.42               |
| MC2  | 180          | C-31                          | -31.40                            | 0.49               |
| MC2  | 200          | C-25                          | -26.70                            |                    |
| MC2  | 200          | C-27                          | -27.26                            |                    |
| MC2  | 200          | C-29                          | -30.19                            |                    |
| MC2  | 200          | C-31                          |                                   |                    |
| MC2  | 220          | C-25                          | -26.69                            | 2.27               |
| MC2  | 220          | C-27                          | -29.31                            | 0.54               |
| MC2  | 220          | C-29                          | -32.95                            | 0.60               |
| MC2  | 220          | C-31                          | -33.33                            |                    |

| Core | Depth (cmbs) | <i>n</i> -alkane Chain Length | Average $\delta^{13}\text{C}$ (‰) | Standard Deviation |
|------|--------------|-------------------------------|-----------------------------------|--------------------|
| MC2  | 240          | C-25                          |                                   |                    |
| MC2  | 240          | C-27                          | -27.91                            | 0.20               |
| MC2  | 240          | C-29                          | -30.54                            | 0.07               |
| MC2  | 240          | C-31                          |                                   |                    |
| MC2  | 260          | C-25                          | -25.52                            | 0.10               |
| MC2  | 260          | C-27                          | -25.90                            | 0.24               |
| MC2  | 260          | C-29                          | -30.98                            | 0.21               |
| MC2  | 260          | C-31                          |                                   |                    |
| MC2  | 280          | C-25                          | -23.55                            | 0.82               |
| MC2  | 280          | C-27                          | -23.47                            | 0.62               |
| MC2  | 280          | C-29                          | -27.43                            | 0.83               |
| MC2  | 280          | C-31                          |                                   |                    |
| MC2  | 300          | C-25                          | -27.45                            | 0.08               |
| MC2  | 300          | C-27                          | -28.01                            | 0.44               |
| MC2  | 300          | C-29                          | -30.36                            | 0.25               |
| MC2  | 300          | C-31                          | -31.81                            |                    |
| MC2  | 320          | C-25                          | -20.67                            | 0.08               |
| MC2  | 320          | C-27                          | -22.11                            | 0.32               |
| MC2  | 320          | C-29                          | -23.64                            | 0.07               |
| MC2  | 320          | C-31                          |                                   |                    |
| MC2  | 340          | C-25                          | -27.40                            | 0.36               |
| MC2  | 340          | C-27                          | -28.41                            | 0.96               |
| MC2  | 340          | C-29                          | -31.12                            | 0.96               |
| MC2  | 340          | C-31                          | -32.11                            |                    |
| MC2  | 360          | C-25                          | -23.42                            | 0.37               |
| MC2  | 360          | C-27                          | -23.66                            | 0.89               |
| MC2  | 360          | C-29                          | -26.96                            | 0.17               |
| MC2  | 360          | C-31                          |                                   |                    |
| MC2  | 380          | C-25                          |                                   |                    |
| MC2  | 380          | C-27                          | -25.37                            | 0.10               |
| MC2  | 380          | C-29                          | -28.52                            | 0.17               |
| MC2  | 380          | C-31                          | -31.93                            | 0.21               |
| MC2  | 400          | C-25                          | -26.46                            | 0.20               |
| MC2  | 400          | C-27                          | -26.79                            | 0.44               |
| MC2  | 400          | C-29                          | -29.71                            | 0.06               |
| MC2  | 400          | C-31                          | -32.06                            | 0.23               |
| MC2  | 420          | C-25                          |                                   |                    |
| MC2  | 420          | C-27                          | -29.56                            | 0.32               |
| MC2  | 420          | C-29                          | -30.69                            | 0.06               |
| MC2  | 420          | C-31                          | -30.54                            | 0.44               |
| MO2  | 0            | C-25                          | -23.13                            | 0.46               |
| MO2  | 0            | C-27                          | -24.05                            | 0.00               |
| MO2  | 0            | C-29                          | -25.11                            | 0.37               |
| MO2  | 0            | C-31                          | -25.64                            |                    |

| Core | Depth (cmbs) | <i>n</i> -alkane Chain Length | Average $\delta^{13}\text{C}$ (‰) | Standard Deviation |
|------|--------------|-------------------------------|-----------------------------------|--------------------|
| MO2  | 20           | C-25                          | -21.41                            | 0.55               |
| MO2  | 20           | C-27                          | -21.38                            | 0.99               |
| MO2  | 20           | C-29                          | -23.30                            | 0.81               |
| MO2  | 20           | C-31                          | -25.29                            | 0.43               |
| MO2  | 40           | C-25                          | -20.68                            | 0.39               |
| MO2  | 40           | C-27                          | -22.07                            | 0.39               |
| MO2  | 40           | C-29                          | -23.89                            | 0.09               |
| MO2  | 40           | C-31                          | -22.33                            |                    |
| MO2  | 60           | C-25                          | -21.40                            | 0.94               |
| MO2  | 60           | C-27                          | -22.98                            | 0.12               |
| MO2  | 60           | C-29                          | -23.47                            | 0.60               |
| MO2  | 60           | C-31                          |                                   |                    |
| MO2  | 80           | C-25                          | -22.55                            | 0.58               |
| MO2  | 80           | C-27                          | -24.10                            | 0.30               |
| MO2  | 80           | C-29                          | -24.76                            | 0.71               |
| MO2  | 80           | C-31                          | -23.82                            | 0.89               |
| MO2  | 100          | C-25                          | -20.69                            | 0.38               |
| MO2  | 100          | C-27                          | -23.24                            | 0.43               |
| MO2  | 100          | C-29                          | -22.61                            | 0.72               |
| MO2  | 100          | C-31                          | -21.06                            |                    |
| MO2  | 120          | C-25                          | -25.46                            | 0.69               |
| MO2  | 120          | C-27                          | -27.85                            | 0.84               |
| MO2  | 120          | C-29                          | -29.68                            | 0.94               |
| MO2  | 120          | C-31                          | -28.37                            |                    |
| MO2  | 140          | C-25                          | -31.89                            | 0.76               |
| MO2  | 140          | C-27                          | -30.77                            | 0.03               |
| MO2  | 140          | C-29                          | -31.58                            | 0.47               |
| MO2  | 140          | C-31                          | -34.37                            |                    |
| MO2  | 160          | C-25                          | -28.53                            | 0.27               |
| MO2  | 160          | C-27                          | -27.65                            | 0.14               |
| MO2  | 160          | C-29                          | -28.40                            | 0.11               |
| MO2  | 160          | C-31                          | -29.92                            |                    |
| MO2  | 180          | C-25                          | -28.87                            | 0.09               |
| MO2  | 180          | C-27                          | -27.13                            | 0.28               |
| MO2  | 180          | C-29                          | -26.11                            | 0.26               |
| MO2  | 180          | C-31                          | -28.96                            |                    |
| MO2  | 200          | C-25                          | -28.84                            | 0.94               |
| MO2  | 200          | C-27                          | -27.77                            | 0.45               |
| MO2  | 200          | C-29                          | -29.81                            | 0.22               |
| MO2  | 200          | C-31                          | -31.94                            |                    |
| MO2  | 220          | C-25                          | -29.09                            |                    |
| MO2  | 220          | C-27                          | -29.93                            | 0.95               |
| MO2  | 220          | C-29                          | -31.08                            | 0.30               |
| MO2  | 220          | C-31                          |                                   |                    |

| Core | Depth (cmbs) | <i>n</i> -alkane Chain Length | Average $\delta^{13}\text{C}$ (‰) | Standard Deviation |
|------|--------------|-------------------------------|-----------------------------------|--------------------|
| MO2  | 240          | C-25                          | -21.68                            | 0.23               |
| MO2  | 240          | C-27                          | -22.85                            | 0.58               |
| MO2  | 240          | C-29                          | -23.26                            | 0.59               |
| MO2  | 240          | C-31                          | -24.78                            |                    |
| SP2  | 0            | C-25                          | -23.86                            | 0.01               |
| SP2  | 0            | C-27                          | -26.65                            | 0.72               |
| SP2  | 0            | C-29                          | -28.45                            | 0.31               |
| SP2  | 0            | C-31                          | -30.31                            |                    |
| SP2  | 20           | C-25                          | -22.01                            | 0.76               |
| SP2  | 20           | C-27                          | -23.16                            | 0.87               |
| SP2  | 20           | C-29                          | -23.64                            | 0.17               |
| SP2  | 20           | C-31                          | -26.25                            |                    |
| SP2  | 40           | C-25                          | -25.77                            | 0.04               |
| SP2  | 40           | C-27                          | -25.55                            | 0.16               |
| SP2  | 40           | C-29                          | -24.56                            | 0.24               |
| SP2  | 40           | C-31                          | -31.30                            |                    |
| SP2  | 60           | C-25                          | -23.59                            | 0.37               |
| SP2  | 60           | C-27                          | -28.45                            | 0.29               |
| SP2  | 60           | C-29                          | -27.74                            | 0.23               |
| SP2  | 60           | C-31                          | -28.16                            |                    |
| SP2  | 80           | C-25                          | -22.15                            | 0.21               |
| SP2  | 80           | C-27                          | -23.78                            | 0.28               |
| SP2  | 80           | C-29                          | -24.48                            | 0.17               |
| SP2  | 80           | C-31                          | -24.93                            |                    |
| SP2  | 100          | C-25                          | -23.80                            | 0.53               |
| SP2  | 100          | C-27                          | -26.88                            | 0.71               |
| SP2  | 100          | C-29                          | -26.18                            | 0.46               |
| SP2  | 100          | C-31                          | -25.35                            |                    |
| SP2  | 120          | C-25                          | -25.42                            | 0.94               |
| SP2  | 120          | C-27                          | -26.69                            | 0.41               |
| SP2  | 120          | C-29                          | -26.57                            | 0.22               |
| SP2  | 120          | C-31                          | -28.44                            |                    |
| SP2  | 140          | C-25                          | -25.44                            | 1.68               |
| SP2  | 140          | C-27                          | -25.43                            | 0.54               |
| SP2  | 140          | C-29                          | -26.87                            | 0.76               |
| SP2  | 140          | C-31                          | -28.55                            |                    |
| SP2  | 160          | C-25                          | -22.89                            | 0.05               |
| SP2  | 160          | C-27                          | -23.76                            | 0.09               |
| SP2  | 160          | C-29                          | -24.95                            | 0.28               |
| SP2  | 160          | C-31                          | -24.37                            |                    |
| SP2  | 180          | C-25                          | -22.87                            | 0.14               |
| SP2  | 180          | C-27                          | -24.36                            | 0.31               |
| SP2  | 180          | C-29                          | -26.34                            | 0.79               |
| SP2  | 180          | C-31                          | -23.62                            | 1.89               |

| Core | Depth (cmbs) | <i>n</i> -alkane Chain Length | Average $\delta^{13}\text{C}$ (‰) | Standard Deviation |
|------|--------------|-------------------------------|-----------------------------------|--------------------|
| SP2  | 200          | C-25                          | -22.34                            | 2.31               |
| SP2  | 200          | C-27                          | -21.63                            | 0.06               |
| SP2  | 200          | C-29                          | -22.59                            | 0.21               |
| SP2  | 200          | C-31                          | -22.42                            |                    |
| SP2  | 220          | C-25                          | -20.29                            | 0.47               |
| SP2  | 220          | C-27                          | -21.92                            | 0.09               |
| SP2  | 220          | C-29                          | -21.96                            | 0.21               |
| SP2  | 220          | C-31                          | -20.67                            |                    |
| GC3  | 0            | C-25                          |                                   |                    |
| GC3  | 0            | C-27                          | -24.30                            | 0.42               |
| GC3  | 0            | C-29                          | -24.79                            | 0.28               |
| GC3  | 0            | C-31                          |                                   |                    |
| GC3  | 20           | C-25                          | -28.02                            |                    |
| GC3  | 20           | C-27                          | -28.13                            | 0.84               |
| GC3  | 20           | C-29                          | -28.38                            | 0.19               |
| GC3  | 20           | C-31                          |                                   |                    |
| GC3  | 40           | C-25                          | -26.68                            |                    |
| GC3  | 40           | C-27                          | -26.74                            | 1.06               |
| GC3  | 40           | C-29                          | -26.00                            | 0.70               |
| GC3  | 40           | C-31                          | -28.34                            |                    |
| GC3  | 60           | C-25                          |                                   |                    |
| GC3  | 60           | C-27                          | -29.90                            | 0.13               |
| GC3  | 60           | C-29                          | -29.59                            | 0.33               |
| GC3  | 60           | C-31                          |                                   |                    |
| GC3  | 70           | C-25                          | -26.17                            |                    |
| GC3  | 70           | C-27                          | -26.88                            |                    |
| GC3  | 70           | C-29                          | -26.85                            |                    |
| GC3  | 70           | C-31                          |                                   |                    |
| GC3  | 100          | C-25                          |                                   |                    |
| GC3  | 100          | C-27                          | -24.58                            |                    |
| GC3  | 100          | C-29                          | -23.97                            | 0.67               |
| GC3  | 100          | C-31                          |                                   |                    |
| GC3  | 120          | C-25                          | -25.77                            | 1.18               |
| GC3  | 120          | C-27                          | -26.33                            | 0.21               |
| GC3  | 120          | C-29                          | -26.62                            | 0.12               |
| GC3  | 120          | C-31                          |                                   |                    |
| GC3  | 140          | C-25                          |                                   |                    |
| GC3  | 140          | C-27                          | -31.26                            | 0.09               |
| GC3  | 140          | C-29                          | -30.14                            | 0.25               |
| GC3  | 140          | C-31                          |                                   |                    |
| GC3  | 160          | C-25                          |                                   |                    |
| GC3  | 160          | C-27                          | -33.05                            | 0.23               |
| GC3  | 160          | C-29                          | -31.93                            | 0.77               |
| GC3  | 160          | C-31                          | -30.88                            |                    |

| Core | Depth (cmbs) | <i>n</i> -alkane Chain Length | Average $\delta^{13}\text{C}$ (‰) | Standard Deviation |
|------|--------------|-------------------------------|-----------------------------------|--------------------|
| GC3  | 180          | C-25                          | -31.38                            | 0.18               |
| GC3  | 180          | C-27                          | -32.42                            | 0.60               |
| GC3  | 180          | C-29                          | -31.82                            | 0.38               |
| GC3  | 180          | C-31                          | -30.40                            | 0.38               |

| core | depth | <i>Trochammina inflata</i> | <i>Trochammina macrescens</i> | <i>Miliammina fusca</i> | <i>Tiphotrecha comprimata</i> | <i>Haplophragmoides manilaensis</i> | <i>Pseudothurammina limnetis</i> | UID |
|------|-------|----------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------------------|----------------------------------|-----|
| GC3  | 5     | 27                         | 17                            | 60                      | 0                             | 2                                   | 0                                | 0   |
| GC3  | 15    | 64                         | 46                            | 32                      | 0                             | 2                                   | 0                                | 0   |
| GC3  | 25    | 16                         | 12                            | 14                      | 1                             | 2                                   | 0                                | 0   |
| GC3  | 35    | 19                         | 4                             | 0                       | 3                             | 0                                   | 0                                | 0   |
| GC3  | 45    | 63                         | 17                            | 0                       | 11                            | 0                                   | 0                                | 0   |
| GC3  | 55    | 22                         | 4                             | 2                       | 4                             | 0                                   | 0                                | 0   |
| GC3  | 65    | 40                         | 7                             | 0                       | 7                             | 0                                   | 0                                | 0   |
| GC3  | 75    | 50                         | 22                            | 15                      | 4                             | 3                                   | 0                                | 0   |
| GC3  | 85    | 85                         | 54                            | 11                      | 14                            | 0                                   | 0                                | 0   |
| GC3  | 95    | 62                         | 36                            | 5                       | 14                            | 0                                   | 0                                | 0   |
| GC3  | 105   | 17                         | 15                            | 14                      | 63                            | 0                                   | 1                                | 0   |
| GC3  | 115   | 31                         | 45                            | 6                       | 21                            | 0                                   | 0                                | 0   |
| GC3  | 125   | 7                          | 81                            | 5                       | 14                            | 0                                   | 0                                | 0   |
| GC3  | 135   | 51                         | 40                            | 0                       | 13                            | 0                                   | 0                                | 0   |
| GC3  | 145   | 33                         | 4                             | 0                       | 8                             | 0                                   | 1                                | 0   |
| GC3  | 155   | 49                         | 14                            | 5                       | 0                             | 0                                   | 0                                | 0   |
| GC3  | 165   | 6                          | 101                           | 0                       | 0                             | 0                                   | 0                                | 0   |
| GC3  | 175   | 3                          | 17                            | 0                       | 0                             | 0                                   | 0                                | 0   |
| GC3  | 185   | 6                          | 29                            | 0                       | 0                             | 0                                   | 0                                | 0   |
| GC3  | 195   | 6                          | 12                            | 0                       | 0                             | 0                                   | 0                                | 0   |

| Core | Depth | <i>Trochammina inflata</i> | <i>Trochammina macrescens</i> | <i>Miliammina fusca</i> | <i>Tiphotrecha comprimata</i> | <i>Haplophragmoides manilaensis</i> | <i>Pseudothuramina limnetis</i> | UID |
|------|-------|----------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------------------|---------------------------------|-----|
| SP2  | 5     | 19                         | 76                            | 10                      | 2                             | 0                                   | 0                               | 0   |
| SP2  | 15    | 13                         | 36                            | 13                      | 41                            | 5                                   | 2                               | 0   |
| SP2  | 25    | 26                         | 13                            | 0                       | 1                             | 0                                   | 0                               | 0   |
| SP2  | 35    | 25                         | 7                             | 0                       | 0                             | 0                                   | 0                               | 0   |
| SP2  | 45    | 33                         | 9                             | 0                       | 0                             | 0                                   | 0                               | 0   |
| SP2  | 55    | 44                         | 60                            | 6                       | 11                            | 0                                   | 0                               | 0   |
| SP2  | 65    | 11                         | 65                            | 0                       | 0                             | 0                                   | 0                               | 0   |
| SP2  | 75    | 3                          | 45                            | 7                       | 0                             | 0                                   | 0                               | 0   |
| SP2  | 85    | 5                          | 61                            | 10                      | 0                             | 0                                   | 0                               | 0   |
| SP2  | 95    | 32                         | 37                            | 0                       | 0                             | 0                                   | 0                               | 0   |
| SP2  | 105   | 20                         | 30                            | 15                      | 5                             | 0                                   | 0                               | 0   |
| SP2  | 115   | 12                         | 43                            | 8                       | 13                            | 4                                   | 1                               | 0   |
| SP2  | 125   | 4                          | 32                            | 4                       | 0                             | 0                                   | 0                               | 0   |
| SP2  | 135   | 4                          | 36                            | 8                       | 42                            | 0                                   | 1                               | 0   |
| SP2  | 145   | 4                          | 26                            | 9                       | 23                            | 0                                   | 1                               | 0   |
| SP2  | 155   | 25                         | 64                            | 5                       | 0                             | 0                                   | 0                               | 0   |
| SP2  | 165   | 17                         | 31                            | 0                       | 3                             | 0                                   | 0                               | 0   |
| SP2  | 175   | 4                          | 42                            | 5                       | 17                            | 0                                   | 1                               | 0   |
| SP2  | 185   | 0                          | 56                            | 6                       | 0                             | 0                                   | 0                               | 0   |
| SP2  | 195   | 16                         | 55                            | 0                       | 0                             | 0                                   | 0                               | 0   |
| SP2  | 205   | 6                          | 41                            | 10                      | 0                             | 0                                   | 0                               | 0   |
| SP2  | 215   | 18                         | 50                            | 15                      | 0                             | 0                                   | 0                               | 0   |
| SP2  | 225   | 19                         | 65                            | 9                       | 12                            | 0                                   | 0                               | 0   |
| SP2  | 235   | 0                          | 36                            | 10                      | 22                            | 0                                   | 2                               | 0   |

| Core | Depth | <i>Trochammina inflata</i> | <i>Trochammina macrescens</i> | <i>Miliammina fusca</i> | <i>Tiphotrocha comprimata</i> | <i>Haplophragmoides manilaensis</i> | <i>Pseudothurammina limnetis</i> | UID |
|------|-------|----------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------------------|----------------------------------|-----|
| MC2  | 5     | 10                         | 10                            | 5                       | 13                            | 0                                   | 2                                | 0   |
| MC2  | 15    | 12                         | 22                            | 6                       | 16                            | 0                                   | 2                                | 0   |
| MC2  | 25    | 15                         | 69                            | 9                       | 10                            | 0                                   | 4                                | 0   |
| MC2  | 35    | 9                          | 17                            | 0                       | 2                             | 0                                   | 0                                | 0   |
| MC2  | 45    | 11                         | 28                            | 0                       | 9                             | 0                                   | 0                                | 0   |
| MC2  | 55    | 14                         | 40                            | 0                       | 19                            | 1                                   | 0                                | 0   |
| MC2  | 65    | 9                          | 50                            | 0                       | 14                            | 1                                   | 0                                | 0   |
| MC2  | 75    | 18                         | 27                            | 2                       | 10                            | 0                                   | 0                                | 0   |
| MC2  | 85    | 10                         | 32                            | 0                       | 17                            | 0                                   | 0                                | 0   |
| MC2  | 95    | 14                         | 26                            | 0                       | 17                            | 0                                   | 0                                | 0   |
| MC2  | 105   | 17                         | 24                            | 0                       | 18                            | 0                                   | 0                                | 0   |
| MC2  | 115   | 19                         | 36                            | 0                       | 19                            | 1                                   | 0                                | 0   |
| MC2  | 125   | 23                         | 76                            | 0                       | 28                            | 5                                   | 0                                | 0   |
| MC2  | 135   | 15                         | 27                            | 0                       | 20                            | 1                                   | 0                                | 0   |
| MC2  | 145   | 3                          | 9                             | 0                       | 3                             | 0                                   | 0                                | 0   |
| MC2  | 155   | 1                          | 8                             | 0                       | 3                             | 0                                   | 0                                | 0   |
| MC2  | 165   | 0                          | 7                             | 0                       | 2                             | 0                                   | 0                                | 0   |
| MC2  | 175   | 0                          | 19                            | 0                       | 8                             | 0                                   | 0                                | 0   |
| MC2  | 185   | 7                          | 13                            | 0                       | 10                            | 0                                   | 0                                | 0   |
| MC2  | 195   | 1                          | 8                             | 0                       | 7                             | 1                                   | 0                                | 0   |
| MC2  | 205   | 3                          | 8                             | 0                       | 3                             | 0                                   | 0                                | 0   |
| MC2  | 215   | 3                          | 15                            | 0                       | 4                             | 1                                   | 0                                | 0   |
| MC2  | 225   | 2                          | 12                            | 0                       | 4                             | 2                                   | 0                                | 0   |
| MC2  | 235   | 3                          | 9                             | 0                       | 4                             | 1                                   | 0                                | 0   |
| MC2  | 245   | 4                          | 4                             | 0                       | 5                             | 0                                   | 0                                | 0   |
| MC2  | 255   | 3                          | 9                             | 0                       | 8                             | 0                                   | 0                                | 0   |
| MC2  | 265   | 2                          | 13                            | 0                       | 9                             | 1                                   | 0                                | 0   |
| MC2  | 275   | 1                          | 11                            | 0                       | 4                             | 1                                   | 0                                | 0   |
| MC2  | 285   | 1                          | 12                            | 0                       | 3                             | 1                                   | 0                                | 0   |
| MC2  | 295   | 1                          | 7                             | 0                       | 5                             | 0                                   | 0                                | 0   |

| Core | Depth | <i>Trochammina inflata</i> | <i>Trochammina macrescens</i> | <i>Miliammina fusca</i> | <i>Tiphotrecha comprimata</i> | <i>Haplophragmoides manilaensis</i> | <i>Pseudothurammina limnetis</i> | UID |
|------|-------|----------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------------------|----------------------------------|-----|
| MC2  | 305   | 0                          | 5                             | 0                       | 6                             | 0                                   | 0                                | 0   |
| MC2  | 315   | 1                          | 60                            | 0                       | 28                            | 2                                   | 0                                | 0   |
| MC2  | 325   | 1                          | 67                            | 0                       | 25                            | 2                                   | 0                                | 0   |
| MC2  | 335   | 3                          | 6                             | 0                       | 4                             | 2                                   | 0                                | 0   |
| MC2  | 345   | 0                          | 12                            | 1                       | 5                             | 1                                   | 0                                | 0   |
| MC2  | 355   | 0                          | 34                            | 1                       | 6                             | 0                                   | 0                                | 0   |
| MC2  | 365   | 0                          | 35                            | 1                       | 4                             | 0                                   | 0                                | 0   |
| MC2  | 375   | 0                          | 55                            | 1                       | 6                             | 0                                   | 0                                | 0   |
| MC2  | 385   | 0                          | 5                             | 1                       | 2                             | 0                                   | 0                                | 0   |
| MC2  | 395   | 0                          | 7                             | 0                       | 3                             | 0                                   | 0                                | 0   |
| MC2  | 405   | 1                          | 24                            | 3                       | 3                             | 0                                   | 0                                | 0   |
| MC2  | 415   | 0                          | 7                             | 0                       | 1                             | 0                                   | 0                                | 0   |

| Core | Depth | <i>Trochammina inflata</i> | <i>Trochammina macrescens</i> | <i>Miliammina fusca</i> | <i>Tiphotrecha comprimata</i> | <i>Haplophragmoides manilaensis</i> | <i>Pseudothurammina limnetis</i> | UID |
|------|-------|----------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------------------|----------------------------------|-----|
| MO2  | 5     | 50                         | 33                            | 0                       | 5                             | 0                                   | 0                                | 0   |
| MO2  | 15    | 19                         | 7                             | 0                       | 5                             | 0                                   | 0                                | 0   |
| MO2  | 25    | 13                         | 0                             | 0                       | 3                             | 1                                   | 0                                | 0   |
| MO2  | 35    | 28                         | 0                             | 0                       | 4                             | 1                                   | 0                                | 0   |
| MO2  | 45    | 52                         | 0                             | 0                       | 6                             | 2                                   | 0                                | 0   |
| MO2  | 55    | 44                         | 6                             | 0                       | 4                             | 0                                   | 0                                | 0   |
| MO2  | 65    | 61                         | 15                            | 0                       | 7                             | 0                                   | 0                                | 0   |
| MO2  | 75    | 78                         | 24                            | 0                       | 20                            | 0                                   | 0                                | 0   |
| MO2  | 95    | 0                          | 18                            | 0                       | 11                            | 0                                   | 0                                | 0   |
| MO2  | 105   | 61                         | 16                            | 0                       | 21                            | 0                                   | 0                                | 0   |
| MO2  | 115   | 68                         | 15                            | 0                       | 12                            | 0                                   | 0                                | 0   |
| MO2  | 125   | 69                         | 22                            | 0                       | 6                             | 0                                   | 0                                | 0   |
| MO2  | 135   | 28                         | 7                             | 0                       | 7                             | 0                                   | 0                                | 0   |
| MO2  | 145   | 17                         | 5                             | 0                       | 1                             | 0                                   | 0                                | 0   |
| MO2  | 155   | 5                          | 25                            | 0                       | 0                             | 0                                   | 0                                | 0   |
| MO2  | 165   | 10                         | 24                            | 0                       | 0                             | 0                                   | 0                                | 0   |
| MO2  | 175   | 11                         | 4                             | 0                       | 2                             | 0                                   | 0                                | 0   |
| MO2  | 185   | 8                          | 5                             | 0                       | 1                             | 0                                   | 0                                | 0   |
| MO2  | 195   | 28                         | 10                            | 0                       | 3                             | 0                                   | 0                                | 0   |
| MO2  | 205   | 39                         | 6                             | 1                       | 5                             | 0                                   | 0                                | 0   |
| MO2  | 215   | 37                         | 11                            | 0                       | 9                             | 0                                   | 0                                | 0   |
| MO2  | 225   | 32                         | 17                            | 0                       | 14                            | 0                                   | 0                                | 0   |
| MO2  | 235   | 48                         | 8                             | 0                       | 6                             | 0                                   | 0                                | 0   |
| MO2  | 245   | 76                         | 5                             | 0                       | 6                             | 0                                   | 0                                | 0   |
| MO2  | 255   | 52                         | 4                             | 0                       | 14                            | 0                                   | 0                                | 0   |

## **Vita**

Benjamin Ryan Tanner was born in Winter Park, FL on February 21, 1976. He was raised in Palatka, FL and Tallahassee, FL and graduated from Leon High School in 1994. From there, he went to Tallahassee Community College and on to the Florida State University where he received a B.S. in anthropology in 1999. He then went to the University of Maine where he received an M.S. in quaternary and climate studies in 2001. From there, he went to the University of Tennessee, Knoxville and received a Ph.D. in geology in 2005.

Benjamin is currently an Assistant Professor of Geosciences and Natural Resource Management at Western Carolina University.

4535 0545 18

11/09/05

MRB

