COMPOUND SPECIFIC RADIOCARBON AND STABLE ISOTOPES OF LIGNIN BIOMARKERS: A STUDY OF TERRESTRIAL ORGANIC CARBON IN THE ALTAMAHA RIVER, ESTUARY AND SOUTH ATLANTIC BIGHT

by

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(Under the Direction of John Noakes)

ABSTRACT

The source and preservation of organic matter in rivers, estuaries and the coastal ocean are important factors for understanding the global carbon budget. The stable carbon isotope ratios of organic matter, including compound specific ratios, have been used rigorously to assess the inputs, origins and preservation mechanisms of organic carbon in the marine environment. More recently, radiocarbon (^{14}C) signals carried by organic matter have been used to assess residence time and distinguish organic inputs to the marine environment based on the age of sediments and the individual compounds found therein.

Recent advances in chromatographic separation of individual compounds from complex mixtures, and subsequent isotopic analysis, have enhanced our understanding of organic carbon distribution in the marine environment. The coupling of these techniques allows determination of the stable isotopic composition of specific biomarkers like lignin phenols. Due to their source specificity to terrestrial vascular plant matter and their refractory nature, lignin phenols represent a very important fraction of the organic matter found in the marine environment.

My overall research objective is to examine the relative contributions of river delivered terrestrial organic carbon from both C_3 and C_4 sources in the Georgia coastal marine environment by determining molecular isotopic signatures and their response to variations in flow rate, degradation and mineral interaction. Specifically I plan to 1. Demonstrate the feasibility of isolating individual lignin phenols from terrestrial organic materials and measure their respective ^{14}C age using accelerator mass spectrometry (AMS). 2. Determine the seasonal variation in isotopic abundance of ^{14}C and $\delta^{13}C$ in sediment, as affected by factors such as soil erosion, biochemical degradation, mineral association, and transport pathway. 3. Determine the relative inputs of organic matter from C_3 or C_4 plants and soil erosion or plant litter, by measurement of ^{14}C and $\delta^{13}C$ abundance of specific lignin phenols respectively, to enable a distinction to be made between terrestrial plants and marine plankton. 4. Compare the ^{14}C age of lignin phenols with the concentration of the acid and aldehyde lignin phenols to test the applicability of the acid to aldehyde ratio as an indicator of degradation status. 5. Compare lignin phenol ^{14}C content in various mineral grain size fractions to understand the transport pathways of various terrestrial organic matters into the ocean.

INDEX WORDS: Radiocarbon, Stable Isotopes, Compound Specific Radiocarbon Analysis, GC/IRMS, Preparative Fraction Collection, Lignin, Terrestrial Carbon, Sediment, Particulate Organic Matter, Altamaha River, South Atlantic Bight, Estuary.

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DEDICATION

I dedicate this dissertation to my wife Donna for her loving and tireless support in my quest to complete this milestone. To my sons for their encouragement all these years and to my mother and father for inspiring me to accomplish what I set out to do.

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1. INTRODUCTION AND LITERATURE REVIEW:

Organic matter transported by river systems, originating in the terrestrial environment, accounts for a significant quantity of carbon deposited in, or transported through estuarine systems. It is estimated 0.4 x 10^{15} grams carbon (Meybeck, 1982) is delivered from land to estuaries each year. Nearly half this amount is as particulate organic matter suspended, deposited and re-suspended within the water column and eventually deposited in coastal marine sediments with the balance as dissolved organic carbon (Spitzy and Ittekkot, 1991). It is estimated deltaic and shelf sediments account for 90% of the total organic carbon burial in the ocean (Berner, 1982, Prahl et al., 1994) and represent only 10% of the world seafloor. Based on modern ocean productivity rate of 50 x 10^{15} grams carbon per year and sediment burial rate of 0.16 x 10^{15} grams carbon per year, organic preservation is less than 0.5% efficient (Hedges and Keil, 1995). Although the mechanisms that govern preservation of organic matter in the ocean and especially in estuarine environments remain unclear, the predominant source of organic matter transported by rivers to the ocean is plants. It is therefore the major emphasis of this research to study the biogeochemical role of plants and their products, derived solely from the terrestrial environment, and their distribution and fate in the Altamaha River, estuary and offshore on the Atlantic Ocean shelf.

To properly study such a complex system with numerous inputs, processes and depositions occurring over time, a number of analytical techniques were applied. Classical, well developed, analytical techniques such as total organic carbon and nitrogen to newly developed hyphenated techniques appending gas chromatographic separation of complex mixtures to

accelerator mass spectrometry analysis for radiocarbon dating of individual compounds were used in this investigation. Investigation of origin and fate of terrestrial organic matter in this study began with analysis of total organic carbon and nitrogen along with their respective stable isotopic ratios of bulk sediment and particulate organic matter. This was followed by the separation of lignin biomarkers from sediment and particulate organic matter to enhance specificity of analysis to terrestrially derived components. Gas chromatographic mass spectrometry and gas chromatographic isotope ratio mass spectrometry were used to measure concentrations and carbon isotopic ratios of specific lignin biomarkers in the study. Radiocarbon analysis was performed on bulk sediment, total lignin isolates and finally specific isolated and concentrated lignin compounds. Figure 1 displays a flow chart of the analytical approach used in this study. By merging these analytical capabilities to measure source specific compounds I planned to 1. Demonstrate isolation and detection of ^{14}C in individual lignin biomarkers to apply terrestrial biomarker age in sediment processes. 2. Determine the relative inputs of C_3 and C_4 plants in the Altamaha River by measuring $\delta^{13}C$ of individual lignin compounds and assess their isotopic and chemical variation based on seasonal sampling. 3. Compare ^{14}C age of sediment with their degree of degradation based on specific lignin ratios of acid to aldehyde groups and finally compare lignin ^{14}C ages with their host sediment and in various particle size fractions to correlate their transport potential and preference for export to the inner shelf.

Why is it important to understand the quantity and type of terrestrial organic matter from those autochthonous, such as phytoplankton derived materials within the marine environment? There is no consensus on the fate of organic matter outside the riverine environment. Does the hydrodynamic sorting based on particle density effect the preferential offshore transport and deposition as suggested by Goñi et al., (1998)? Is the bulk of terrestrial organic carbon deposited

on the inner shelf with little or no export to the outer shelf and slope as proposed by Hedges and Parker (1976)? Or, is a significant amount of organic matter delivered to the pelagic sediments but uncharacterizable by current terrestrial biomarker techniques (Druffel et al., 1986, Gagosian et al., 1983)?

If a higher terrestrial organic carbon component persists in outer shelf and slope sediments that would require lower estimates of past primary production and autochthonous carbon flux to sediments and its re-mineralization. Also, nutrient cycling estimates in marine sediment would be affected because of lower inputs of nitrogen and phosphorus in terrestrially derived organic matter relative to marine organic carbon (Müller and Suess, 1979, Redfield et al., 1963). Equally important for terrestrial source apportionment would be the isotopic makeup of potentially higher terrestrial organic carbon. Low latitude rivers dominate sediment discharge (Milliman and Meade, 1983) and tropical and temperate grasslands, typically composed of C_4 plant material, occupy nearly 20% of the earth's surface (Parton et al., 1993). The significance of C_4 grassland soil and sediment could be considerable as Gordon and Goñi (2003, 2004) suggest when using bulk $\delta^{13}C$ analysis to proportion marine and terrestrial sources.

1.1 Bulk Chemical Analysis:

The bulk chemical analysis of carbon and nitrogen are important parameters in studying marine systems as they represent two of six principle elements; C, H, N, O, P and S, in living systems. Carbon and nitrogen exist in living and dead organic forms and a few non-biological forms like inorganic carbonate. Transfer of carbon and nitrogen through major biogeochemical cycles, whether through oxidation, reduction, nitrification or de-nitrification, are important quantifiers used to clarify processes such as formation, transmittance and deposition of carbon and nitrogen within the terrestrial and marine environments.

The majority of carbon resides in the sedimentary carbonate and organic carbon reservoirs. Far less carbon cycles through, although more frequently, the oceanic inorganic, atmospheric, and both terrestrial and marine biomass reservoirs. The carbon reservoirs are detailed in Garrels et al., (1975) and Deines, (1980).

Some fractions of organic carbon are rapidly decomposed while others are preserved on a geologic time scale. Total organic carbon (TOC) and nitrogen (TN) are measured and used extensively in the marine environment to determine not just concentrations of carbon and nitrogen in various systems but rate constants based on their measurements over time. However, to enhance the accuracy and precision of determinations of parameters such as preservation or degradation, and improve our ability to distinguish physical and chemical processes in marine environments, additional techniques such as stable isotope ratio measurements of carbon and nitrogen along with radiocarbon measurement in milligram quantities have been introduced.

1.2 Stable Isotope Analysis:

The advent of stable isotope geochemistry has allowed for rapid development of source apportionment in terrestrial and marine environments. Measurement of stable isotope ratio of carbon, $^{13}C/^{12}C$ ($\delta^{13}C$) and nitrogen $^{15}N/^{14}N$ ($\delta^{15}N$) permits distinction of organic matter from various sources based on isotope fractionation during photosynthesis and consumer trophic level (Smith and Epstein, 1971, Cifuentes et al., 1988, McClelland, J.W. and Valiela, I, 1998). Natural abundance differences of carbon isotopes are the result of plants discrimination, in favor of the lighter isotope ^{12}C, during photosynthesis. Stable isotopic composition of plants, as a result, exhibit negative or depleted values relative to the atmosphere.

The carbon isotopic composition of plants is primarily determined by enzymatic pathways during photosynthesis. Photosynthetic plants biosynthesize organic carbon by using

either ribulose bisphosphate as part of the Calvin-Benson cycle or C_3 pathway, or by using phosphoenolpyruvate as part of the Hatch-Slack cycle or C_4 pathway, or a combination of both in CAM plants (Crassulacean Acid Metabolism). Higher plants including most terrestrial plants fix carbon dioxide using the C_3 pathway and fractionate the heavier ^{13}C preferentially to lighter ^{12}C, or put another way, discriminate against the heavier mass ^{13}C, resulting in an isotopic ratio $\delta^{13}C$ that is -17 to -27‰ relative to atmospheric carbon dioxide $\delta^{13}C$ value. In contrast, tropical grasses, desert, salt marsh and aquatic plants discriminate carbon isotopes less and exhibit $\delta^{13}C$ values typically between -10‰ and -19‰ using the C_4 pathway (Bender, 1971, Smith and Epstein, 1971). Although these groups are isotopically distinct, there exists considerable overlap in the $\delta^{13}C$ value due to multiple sources and biogeochemical processes making source assessment difficult. Measurements of $\delta^{13}C$ have been used to distinguish C_3 plants from C_4 plants in major river systems (Hedges et al., 1984; Gordon and Goñi, 2003, 2004). Carbon isotope ratios of the total organic carbon pool, would typically increase, or become enriched from river to offshore due to addition of marine phytoplankton enriched in $\delta^{13}C$. Two-member mixing models were used to delineate organic source material in marine environments where terrestrially derived C_3 plant debris is diluted by phytoplankton detritus. This simplified model, however, is not applicable in regions with both C_3 and C_4 plants growing within the drainage basin are found. Mixing of equal amounts of C_3 and C_4 plant detritus result in an isotopic ratio remarkably similar to that of typical marine phytoplankton $\delta^{13}C$ value. For example, rivers draining the Great Plains like the Mississippi, discharge mixed C_3 and C_4 plant debris, isotopically similar to marine plankton. The interpretation of these isotopic abundances as plankton derived has lead to an underestimation of the relative amount of C_3 and C_4 terrestrial materials reaching the continental shelf.

Early stable isotope investigations were able to make accurate distinctions between recent to upper Paleozoic age coal and petroleum oil based on their biologic source material, marine and non-marine organisms, and distinguish the isotopically lighter lipids compounds from their whole plant precursor (Craig, 1953, Silverman and Epstein, 1958). Marine sediments were found by Sackett (1964) to exhibit $\delta^{13}C$ ranging between -16‰ and -28‰ and suggested this was caused by the variations in relative amounts of land and marine synthesized organic carbon. This was an early proposal that marine sediments contained a variety of organic compounds unique to different source materials.

Studies in the Gulf of Mexico correlated terrestrial organic carbon range of deposition with increasing $\delta^{13}C$ value and concluded that the organic carbon source is limited to a short distance from the river mouth (Shultz and Calder, 1976). Similarly, lithological changes in pelagic Gulf of Mexico sediments correlated with heavier $\delta^{13}C$ values for foraminifera oozes, evident of marine deposition, overlying lighter $\delta^{13}C$ values for olive grey clay minerals, evident of a terrestrial input at the Holocene-Pleistocene transition (Parker et al., 1972).

Numerous studies have been directed to salt-marsh estuaries, such as along the Georgia coast, and their influence on stable isotope biogeochemistry. Salt marshes occupy approximately 1500 km^2 of Georgia's coast where approximately 80-96% of net primary production is due to *Spartina* alterniflora and 10% or less from phytoplankton and other microorganisms (Howard and Frey, 1985). These estuaries are characterized by intense bacterial degradation and intense bioturbation leading to mixing of surficial sediment layers (Pomeroy and Wiegert, 1981, Benner et al., 1986).

Spartina contains the distinct isotopic composition of a C_4 plant contained within its chemical composition including the geopolymer lignin. It has been shown to undergo selective

degradation of the polysaccharides relative to lignin (Fogel et al., 1989, Hedges et al., 1985). In general, cellulose is heavier in $\delta^{13}C$ by up to 4‰ (Spiker and Hatcher, 1987) and during decomposition the isotopically lighter lignin is concentrated due to preferential loss of cellulose compounds. This selective decomposition of polysaccharides relative to lignin creates a total sediment isotopic signature more negative (isotopically lighter) than it was originally (Hodson et al., 1984, Benner et al., 1987).

Fogel et al., (1989) and Ember (1987) revealed a slight change in $\delta^{13}C$ due to selective decomposition of labile polysaccharides and residual, isotopically light, lignin in the particulate organic matter (POM) fraction of Georgia's and South Carolina's salt marshes. They found that most POM is microbially degraded material of $\delta^{13}C$ ranging from -15‰ to -22‰, due to the heterogeneous mixture of *Spartina* fragments, associated bacterial biomass and phytoplankton. They also found, preferential consumption of lipids leaves residual *Spartina* with a highly variable $\delta^{13}C$ signature. Gromley and Sackett (1977) found the maturation of depleted lipids led to even greater $\delta^{13}C$ depletion in the sediment organic matter. Decomposition rate measurements of lipids under anaerobic conditions decomposed at rates equal or greater than aerobic decomposition (Sun and Wakeham, 1994, Sun et al., 1996) in support of previous findings. This implies anoxic sediments may not necessarily enhance organic matter preservation and the isotopic $\delta^{13}C$ signature of salt marsh sediments is very complex.

Other studies revealed similar diagenetic effects on organic matter decomposition. Recent marine sediments contain a varied but substantial amount of preserved insoluble humic substances. These macromolecular compounds are formed (though still debated) by condensation-polymerization reactions and selective preservation of biologically resistant compounds exhibiting depleted $\delta^{13}C$ values relative to local plants. Loss of the $\delta^{13}C$ enriched

carboxyl carbon during diagenesis (Brown et al., 1972) could account for some isotopic depletion. Deines (1980) reported carbohydrates in plants to be enriched in ^{13}C by up to 10‰ relative to lipid compounds and 5‰ relative to lignin. Spiker and Hatcher (1984) correlated the decrease in carbohydrate carbon content in marine sediments with a corresponding decrease in $\delta^{13}C$ in the humic substances as well as in degraded wood by 1 to 2‰. These studies highlight the difficulty to quantify terrestrial inputs in sedimentary organic matter based on bulk isotopic analysis.

Other elemental stable isotope ratios have been used to evaluate the fate of organic matter in estuaries and other marine basins. Using a multiple isotope approach, Peterson and Howarth (1987) used stable isotope ratios $\delta^{34}S$, $\delta^{13}C$ and $\delta^{15}N$ to trace organic matter and illustrated unique isotopic compositions of upland plants, plankton and *Spartina* in Georgia's Sapelo Island marshes. Their data highlights earlier work by Haines (1976) who determined $\delta^{13}C$ values for seston and filter feeders in tidal creeks of the Duplin River were more similar to plankton than *Spartina*. This revised thinking that phytoplankton and benthic diatoms are as important in fueling secondary production in the Georgia estuaries as *Spartina* was a consequence of stable isotope determinations.

Chang et al., (2002) studied riverine nitrates and their associated $\delta^{15}N$ and $\delta^{18}O$ values to conclude moderately distinct isotopic signatures could be used to characterize regions of the river basin. Some areas had isotopic signatures resembling farmland and agricultural use while others resembled livestock or urban land use.

Smith and Epstein (1970) measured $\delta^{13}C$ and δD in salt marsh biota and found a large discrimination against ^{13}C, especially by lipid compounds. Deuterium/Hydrogen (δD) ratio was found to have only a small fractionation between external and intracellular water or between

intracellular water and lipid compounds. More recently Sauer et al., (2000) indicated specific algal sterol lipids exhibited an apparent fractionation with environmental water of approximately -200‰. They suggested environmental water is the primary variable controlling the sterols δD ratio and may be used to reconstruct source-water δD in certain environments, with paleo-climatic implications.

Gordon and Goñi (2003) investigated suspended and surficial shelf sediments from the Atchafalaya and Mississippi Rivers draining to the Gulf of Mexico by a multi-analytical approach combining elemental parameters C/N, the isotopic ratio of $\delta^{13}C$ and ^{14}C abundance, surface area and terrestrial lignin phenol concentrations. These measurements indicated a mixture of marine phytoplankton and terrestrial material. However, C/N ratios were similar to those found in soil-derived organic matter. The $\delta^{13}C$ ratios of river suspended sediment samples were between -24‰ and -25‰, and a slight enrichment in $\delta^{13}C$ (-21‰ to -23‰) was found for the Mississippi Delta and offshore sediments. The authors suggested a contribution of C_4 grasses ($\delta^{13}C$ enriched) from this drainage basin to account for this enrichment. Goñi et al., (1998), had revealed that a significant portion of terrestrial material in suspended sediments in the Gulf of Mexico was of C_4 plant origin by targeting specific compounds such as lignin phenols. By this method, the author was able to determine vegetative sources of C_3 versus C_4 plants and their degradation history.

Megens et al., (2002), developed a 3-member mixing model using stable carbon isotopes, found in the Ems-Dollard Estuary, bordering the Netherlands and Germany, soil derived and vascular plant organic matter accounted for 79% of total organic carbon in near shore sediments but 66% of organic matter deposited offshore was from marine source. They concluded terrestrial organic matter is therefore 40% higher in inshore and 85% higher in offshore

sediments than earlier predicted by previous two end-member models. This study suggested that a multi-disciplined approach using elemental, isotopic and biomarker data to evaluate organic matter in coastal sediments must be developed.

These molecular isotopic measurements confirmed the uncertainty in interpreting organic carbon sources by bulk stable carbon isotope values alone. Nonetheless, $\delta^{13}C$ determinations are typically made on bulk sediment after de-mineralization of all inorganic carbon, for total organic carbon $\delta^{13}C$ signature. Bulk $\delta^{13}C$ measurements, although representative of combined pool of poorly constrained organic components, are determined as a normalizing value representing all organic carbon in the sample.

1.3 Biomarker Analysis:

Biomarkers are compounds that preserve their structure in sediments similar to their original and identifiable biological source. When these biomarkers are unique to their environment, source material or a specific process, they allow for an added level of specificity in analytical studies.

Numerous biomarkers have been used to identify specific source materials in the marine environment. Franks et al., (2000) used $\delta^{13}C$ values of short-chain organic acids associated with oilfields to suggest the isotopic composition of aliphatic carbons in organic acids reflect the co-produced oil from either Miocene or Eocene age deposits in the San Joaquin Basin. Biomarkers have been used for reconstructing paleo-environments and conditions of marine deposition. Long chain alkyl compounds, alkanes and terpenoids can be preserved in sediment and like lignin, cutin and suberin are diagnostic of vascular plant inputs to marine environments (Wakeham, 2004). By using GC/IRMS determinations of terrestrial alkanes and carbohydrates along with radiocarbon dating, Glaser and Zech (2005) were able to substantiate C_4 plant origin in paleo-

sediments deposited over 15ka BP (15,000 years before present). Similarly, Yamada and Ishiwatari (1999) found temporal variations of $\delta^{13}C$ values for plant derived n-alkanes averaged 1‰ depletion during colder climates than those in warmer climates. There results covering the last 30ka BP, indicated an abrupt change in the $\delta^{13}C$ value around 10ka BP in relation to the glacial-interglacial cycle revealing a close correlation of these events with stable carbon isotope ratios. Ingalls et al., (2004) measured ^{14}C of diatom bound polyamines to arrive at an accurate date of the diatoms formation in the surface ocean.

The compound class known as poly-aromatic hydrocarbons (PAHs) has proven to be a valuable biomarker to locate point-source anthropogenic pollutants within marine sediments. The PAH content and isotopic abundance were used to assign an anthropogenic source to an industrial production facility based on organic pyrolysis residue analysis (Webster et al., 2004). Kanke et al., (2004) used PAHs to determine historical proportion of combustion products in sediment cores derived from either fossil fuel combustion or biomass burning. The combination of PAHs and polychlorinated biphenyls (PCBs) biomarkers were studied by Ko et al., (2003) to determine sediment resuspension and settling characteristics in the Chesapeake Bay. They found PAHs and PCBs behave differently in suspended sediments based on their unique source and association with different particles.

Lignin, the structural component of vascular plants and a unique biomarker of terrestrially derived materials, has been studied considerably since early applications by Hedges and Mann (1979 a, b) and Hedges and Ertel (1982). This pioneering research dealt with characterization of plant material sources from various woody and non-woody species found in sediments from the Washington coast. Goñi et al., (1998), using lignin oxidation products, revealed a significant portion of the terrestrial material in suspended sediments in the Gulf of

Mexico was of C_4 plant origin by targeting specific lignin compounds. In addition their degradation history was suggested by the ratio of specific lignin compounds. More recent studies of sediment and lignin biomarkers have been conducted in the Gulf of Mexico by Gordon and Goñi (2003, 2004). They investigated lignin in suspended and surficial shelf sediments from the Atchafalaya and Mississippi Rivers draining to the Gulf of Mexico. They combined terrestrial lignin phenol biomarker concentrations with elemental parameters (C/N), isotopic abundances of $\delta^{13}C$ and ^{14}C and surface area to assess the proportion of terrestrially derived organic. Their measurements confirmed earlier indications of a mixture of marine phytoplankton and terrestrial organic material with a significant contribution of C_4 grasses from this drainage basin.

These molecular isotopic measurements confirmed the uncertainty in interpreting organic carbon sources by bulk stable carbon isotope values alone. By applying unique terrestrial biomarkers such as lignin we can increase the specificity in analytical schemes by eliminating all non-terrestrial inputs. Add to this uniqueness, a dual isotope tracer of $\delta^{13}C$ ratio and ^{14}C abundance a plant source and age of specific compounds can be characterized.

1.4 Chemical Analysis of Lignin Oxidation Products:

Lignin, a structural polymer of vascular plants (Sarkanen and Ludwig, 1971), is a unique biomarker for terrestrial plants that is absent from marine plants and other living organisms. It is a generally refractory polymer that decays slowly in the natural environment. Although monomer phenols making up lignin can be degraded microbially under anaerobic conditions (Healy and Young, 1979), polymeric lignin can eventually become part of the soil organic matter, transported in rivers as dissolved or particulate organic matter and eventually become part of marine sediment for years or eons (Moran et al., 1991, Hopkinson, et al., 1998, Haddad and Martens, 1987). Lignin can be recovered and extracted from sediment and soils through

specific oxidation procedures. These procedures release a variety of specific lignin phenol monomers that are indicative of the type of plants from which they were derived. By analyzing lignin phenols on a gas chromatograph after derivatization, the occurrence and proportion of unique lignin phenols can help establish the plant source (Hedges and Mann, 1979a, Hedges and Ertel, 1982).

Lignin makes up a large portion of terrestrial plant biomass and is present in both angiosperms and gymnosperms, two major classes of vascular plants. Angiosperms include flowering plants, herbs, grasses and hardwood trees. Angiosperms produce vanillyl and syringyl phenols during lignin oxidation. Vanillyl and syringyl phenol groups possess one and two methoxy carbon groups, respectively, on the basic phenol molecule. Gymnosperms, in contrast, include non-flowering plants and coniferous trees. Gymnosperms produce only vanillyl phenols, with a single methoxy carbon functional group, made measurable through lignin oxidation. Other phenol compounds are revealed through the oxidation process as well which contain no methoxy carbons on the basic phenol ring. A third group of lignin phenol substituted compounds are the cinnamyl phenols. These possess an unsaturated double bond within their structure and are found exclusively in non-woody material. Both vanillyl and syringyl phenols are found in woody materials. Therefore, lignin phenols can be used as plant specific biomarkers, indicative of plant type and material not only in terrestrial environments but within marine environments as well. By computing ratios of total syringyl to total vanillyl phenols a relative proportion of angiosperm derived material to gymnosperm derived material can be made since only angiosperm plants produce syringyl phenols. By computing the ratios of total cinnamyl to total vanillyl phenols a relative proportion of non-woody derived material to woody derived material can be made since only non-woody plants produce cinnamyl phenols.

Chemical structure of eleven primary substituted lignin phenols produced by the lignin oxidation (alkaline cupric oxide) process along with two internal recovery compounds; ethyl vanillin and trans-cinnamic acid (not found in terrestrial plants), used during chemical processing, are listed in figure 2 with their respective chemical name. These include the aldehyde, ketone and carboxylic acid substituted para-hydroxy phenols, vanillyl phenols and syringyl phenols and the two carboxylic acid substituted cinnamyl (unsaturated) phenols. Figure 2 also displays the groupings of para-hydroxy, vanillyl, syringyl and cinnamyl phenols along with their respective designation letter and their prevalence in angiosperm and gymnosperm woody and non-woody species.

Wood polymers have been reported to survive millions of years, at least structurally, in kerogen and as petrified (silicified) wood (Sigleo, 1978). Saiz-Jimenez and De Leeuw (1985) used pyrolysis (510°C) in combination with gas chromatography and mass spectrometry to reveal lignin pyrolysis products of softwoods, hardwoods and grasses for application of source apportionment in soils and sediments. Their findings show similar but far more numerous products derived from pyrolysis than derived from current oxidation processes at 150-170°C. However, the principle components derived from pyrolysis showed nearly identical presence of coniferyl or guaiacyl (vanillyl) compounds in gymnosperm species, sinapyl (syringyl) compounds in angiosperm species and coumaryl (cinnamyl) in non-woody grass species. Coniferyl, guaiacyl, sinapyl and coumaryl denote synonymous chemical terms, found in literature, for equivalent mono- and di-methoxy substituted phenols and unsaturated substituted phenols respectively. Similar numbers of lignin oxidation products were derived by Goñi and Hedges (1992) using modified combustion apparatus and a final oxidation temperature of 155°C. They reported a larger more diverse suite of lignin phenols including both monomers and dimers

of both complementary and unique origin information. Another procedural modification was developed by Standley and Kaplan (1998) specifically for lignin phenol analysis of aquatic humic substances of terrestrial origin. Humic substances have been used to trace terrestrial organic matter in the marine environment (Alberts et al., 1992, Moran and Hodson, 1994) but required laborious pretreatment of the humics prior to oxidation. Their method allows for rapid processing of resin material used to isolate, purify and hydrogenate isolated humics. Teflon lined mini-bombs were used for an optimized 3 hour oxidation time. Longer oxidation times were found to have an advantage of creating more oxidized compounds but with greater variation between duplicate analyses and completely destroyed the unsaturated cinnamyl phenols.

Numerous studies have been made based on chemical analysis of lignin via oxidation (Hedges and Mann, 1979, Hedges and Ertel, 1982). Lignin oxidation products were identified in the dissolved organic matter (DOM) from the eastern equatorial Pacific to be compositionally similar to Amazon River water lignin content (Meyers-Schulte and Hedges, 1986). Terrestrial organic components had not previously been identified in the open ocean despite models predicting the existence of terrestrial organic matter transported from river to the ocean. Leopold et al., (1982) using individual lignin proportions along with pollen analyses found regional vegetation differences in Lake Washington sediments. Although the lignin could not distinguish genus-level changes of local vegetation it could be used for distributions and local vegetation characterization. When combined with pollen analysis, the lignin proportions may provide indicators of paleo-vegetation patterns in the sediments. Hedges et al., (1988) used lignin-phenol concentrations along with bulk particulate matter, nitrogen and neutral sugars to determine degradation patterns in the Washington coast Dabob Bay region. Their findings indicate extreme reactivities of nitrogen and neutral sugars approaching 70% of their respective totals in contrast

to essentially no reactivity of vanillyl phenols in the sediment water interface. Higher degradation rates of plankton derived lipids and plant pigments of 90% and 99% respectively, were also found. The implication here is that diversity in reactivities of the local organic material and the low average reactivity of terrestrial organic matter make for a considerable contribution to marine sediment even though they exist in low concentration relative to bulk organic material. Studies in Saanich Inlet, British Columbia, Canada by Hamilton and Hedges (1988) indicate less selective degradation of carbohydrates and lignin although lignin represents only 10-20% of the total organic matter in core samples. They found particulate lignin entering Saanich Inlet was composed of measurably degraded vascular plant debris from predominantly gymnosperm woods and non-woody angiosperm remains. Little aerobic degradation of lignin occurs once in Saanich Inlet water column. However, they found in sedimentary profiles, all organic carbon, nitrogen, polysaccharides and lignin degrading in the reducing sediments of Saanich Inlet.

Goñi et al., (1997) used the analysis of lignin phenols and bulk radiocarbon of sediments to reassess the inputs of terrestrial organic matter to the Gulf of Mexico. Their study, suggested a significant portion of the sedimentary organic matter is composed of old carbon ranging from 2,580 to 6,770 YBP. The carbon isotopic ratio ($\delta^{13}C$) of this organic matter resembled previous studies indicating a dominant autochthonous marine signal over terrestrial organic matter (-22 ‰ and -26‰ respectively). Analysis of lignin phenol concentrations in these sediments revealed a different conclusion. The ratios of the cinnamyl to vanillyl phenols and syringyl to vanillyl phenols indicated a non-woody angiosperm origin to the lignin in these Gulf of Mexico sediments, such as from a C_4 grass. In addition the ratio of vanillyl and syringyl acids to aldehydes, an indicator of degradation, implies these sediments have been highly reworked and possibly derived from old recalcitrant soil matter. Based on lignin and isotopic analysis, the

authors concluded fine grained mineral associated grassland debris, exhibiting an enriched $\delta^{13}C$ signature close to -22 ‰, is transported to interior regions of the Gulf of Mexico and a coarse fraction vascular plant detritus is deposited in the estuaries and inner shelf regions.

A mixture of C_3 and C_4 terrestrial source material found in marine sediments has implications to climate variations. A depleted C_3 terrestrial signature, deposited during glacial epochs is a consequence of low sea level and a greater input of terrestrial C_3 source material. In contrast, C_4 dominance during inter-glacial periods is a consequence of warmer temperature vegetation. In a similar study area, Winyah Bay, S. Carolina, lignin phenol signatures indicated terrestrial organic matter containing fresh vascular plant detritus and degraded soil organic matter. C_3 upland forest was the primary source of sedimentary organic matter with only a small fraction from C_3 marsh plants and no appreciable C_4 source like *Spartina* (Goñi et al., 2003).

Dissolved organic matter (DOM), though not measured in this study, is a dynamic component of marine systems. An isolatable component of DOM is aquatic humic substances (Ertel et al., 1984). Lignin phenol compounds were found to dominate the humic substances in Cullaby Lake, a coniferous forest watershed, and the Williamson River, a marsh-grass source. Since lignin is an exclusively vascular plant product, a significant portion of the humic substances found there must be terrestrially derived, either directly from plants or from plant soil matter. Unlike plant tissue lignin, humic substances found here were considerable higher in acid/aldehyde ratios indicating highly degraded and oxidized humic substances, suggesting an explanation and mechanism of how relatively insoluble lignin might be incorporated into dissolved humic materials. Fulvic acids were found to differ from humic acids by susceptibility to demethylation of methoxy groups by aerobic degradation. This results in loss of identifiable lignin in fulvic acid decomposition. Despite this potential loss of terrestrial signature in the fulvic

acids, the aquatic humic substances may allow for distinguishing autochthonous from allochthonous inputs in the dissolved organic pool. Another argument for POM to DOM conversion is data from Lee (2004) that in the mesopelagic ocean, common bio-chemicals such as amino acids, carbohydrates, lipids and pigments are converted into uncharacterizable matter, at least by conventional methods of detection. She estimated only 4% or less of carbon flux in the water column is physically protected from degradation by the mineral or bio-mineral encasements, too low to explain the large uncharacterizable fraction within sediments.

1.5 Stable Isotope Analysis of Lignin Oxidation Products:

One group of biomarkers, lignin phenols, has been found to be very useful in identifying terrestrial biopolymers from plant tissue, humic extracts and sedimentary mixtures in marine systems. Lignin phenols are utilized due to their inherent stability as a structural component in vascular land plants, subsequent stability in soils, sediment, and particulate matter, their absence from organisms and their ease of analysis through alkaline CuO oxidation of organic matter (Hedges and Ertel, 1982). The carbon stable isotope values of lignin derived biomarkers, range from -16‰ to -18‰ for C_4 plants such as the cord grass *Spartina* and differentiates from those of the C_3 plants which range from -27‰ to -35‰ (Fogel and Cifuentes, 1993, Benner et al., 1987)

Goñi and Eglinton (1996) found a 2-7‰ depletion in all tissue derived lignin phenols relative to their total organic carbon $\delta^{13}C$ value. This is consistent with the more enriched components, carbohydrates and amino acids, also found in plant tissue. They also found differences in isotopic ratios of specific lignin phenol classes within the same plant type. C_3 woods, for example, displayed vanillyl and syringyl phenols in the range of -27 to -30‰ while pine needles and oak leaves exhibited more depleted $\delta^{13}C$ values of -31 and -35‰ respectively. The $\delta^{13}C$ of *Spartina*, a C_4 vascular plant, revealed individual lignin compound $\delta^{13}C$ values

between -13 and -19‰, similar to the bulk isotopic enrichment of C_4 plants relative to C_3 plants. Generally, all lignin phenol compounds derived from C_4 plants had enriched $\delta^{13}C$ values relative to those derived from C_3 plants. In addition, cinnamyl acids, representative of non-woody plants exhibited equally enriched $\delta^{13}C$ values for both C_3 and C_4 plants.

1.6 Substrate Particle Size and Mineral Interaction:

Based on the coastal plain geology and the sampling conducted over the six cruises associated with this study, the general morphology of the riverbed may be one of extensive coastal plain sediment composed of silica sand grains ranging in size from silt to sand and overlain by a random deposition of coarse to fine terrestrial debris and finer silt to clay size particles from both allochthonous and detritus origin. Sand grain size particles are typically associated with lower organic carbon and nitrogen content due to lower surface area to volume ratio and lack of ionic interaction prevalent in fine grained sediments such as those composed of iron and manganese oxides. Hedges and Keil (1995) found 90% of organic matter found in sediments, from a variety of depositional environments, cannot be separated from its mineral matrix. They also found that organic material varies directly with sediment surface area and thus appears to be strongly adsorbed to the mineral grains in the sediment.

Similar studies using lignin biomarkers have shown a specific hydrodynamic sorting of particles to occur in the riverine and near coastal shelf and slope. Bainchi et al. (2002) compared specific lignin biomarker ratios; syringyl, vanillyl and cinnamyl phenols and were able to suggest that woody tissue settles within lower Mississippi River region prior to selective dispersal of both C_3 and C_4 non-woody sources in the Louisiana shelf. Similarly, Washington coast sediments were measured for their lignin, aliphatic hydrocarbon and PAH content and found to be preferentially sorted based on particle size (Prahl, 1985). Based on cinnamyl to vanillyl

phenol ratios, lignin content was computed in sediment to be primarily derived from woody gymnosperms with less prevalent non-woody detritus from angiosperm material. Also observed was the preferential transport of finer grained non-woody angiosperm material to further offshore sediments accompanied by fossil phenanthrene (a PAH class compound). Coarser or larger fraction material was associated with woody gymnosperm material accompanied by plantwax hydrocarbons and combustion derived PAHs. Thus hydrodynamic properties can influence distribution of different organic compounds based on particle size, density and associated mineral grains.

Coarse and fine grained fractions of suspended particulate matter were collected along 1,950 km of the Amazon River for lignin, elemental and isotopic analysis (Hedges et al., 1986). Lignin was found to predominate in fine fractions composed primarily of old, degraded and mostly soil derived matter, while the coarse fraction was composed of recent leaf debris and wood. Interestingly, they found C_4 grasses, abundant in the floodplain, were minor constituents in both coarse and fine fractions. They concluded organic matter carried down the Amazon River is relatively unreactive and conservatively transported by association with mineral particles with only some downstream compositional changes with lignin-poor organic matter in the lower basin. More recent studies from the Amazon River's headwaters have substantiated association of organic matter composition and processing with particle size (Aufdenkampe et al., 2007). This study indicated the controlling process to be mineral association but not necessarily associated with particle size. Sand-sized aggregates were found to behave similarly to fine grained silt-clay fractions with regard to their organic matter association. They also found dissolved organic matter from the high Andes mountains behaved similar to fine grained particulate fractions due to its high inorganic colloid content.

The adsorption processes between fine grained fractions, colloidal materials and larger aggregates may have important implications to the interaction and transfer between dissolved organic matter and particulate organic matter.

1.7 Dissolved Organic Matter and Particulate Organic Matter:

More than half of the estimated terrestrial carbon delivered to estuaries annually is in the form of dissolved organic carbon (DOC) with the balance as particulate organic carbon (POC). However, the quantities of terrestrial biomarkers found in DOC and POC cannot support the terrestrial carbon persisting in the oceans (Raymond and Bauer, 2001). These materials are either re-mineralized to undetectable levels or oxidized significantly, to alter their structure and escape detection by conventional methods or biomarker techniques. The re-mineralized theory is supported in part by CO_2 flux out of rivers and estuaries in excess of organic matter loading (Cai and Wang 1998).

Terrestrial soils constitute a large reservoir of organic carbon, exceeding that of atmospheric or living carbon pools (Schlesinger, 1991). Export of this carbon, other than through decomposition, may be as soluble DOC (Peterson et al., 1994, Mannino and Harvey, 2000). This DOC has been shown to be younger in ^{14}C age than the soil from which it came and in excess of atmospheric ^{14}C levels (Trumbore et al., 1989, 1992). Raymond and Bauer (2001) used paired ^{14}C and $\delta^{13}C$ measurements of POC and DOC and found younger DOC than POC in rivers, but older DOC than POC in coastal offshore area. He concludes younger pools of DOC are preferentially removed during transport which significantly alters ^{14}C and $\delta^{13}C$ by delivering older material to oceans than what is found in rivers. This disputes Hedges et al., (1986) contending rivers export ^{14}C enriched organic matter and Druffel et al., (1992) that old DOC in ocean ages in ocean basins. By utilizing young DOC, post-modern $\Delta^{14}C$ values between 24 –

120‰ were found with some abundances as high as $\Delta^{14}C = 390$ (~140pMC) in Chesapeake Bay DOC. However, some DOC may still contain aged ^{14}C depending on factors such as organic matter development, age of vegetation or source rock from which the soil is derived, regional climate, watershed and the decomposition rate of the soil itself. ^{14}C depleted DOC was observed in samples from Hudson, Rappahanock, Susquehanna and Sacramento rivers (Raymond and Bauer, 2001). These rivers have watersheds containing considerable farm and agricultural lands which by practice rotate soils with ^{14}C ages in excess of 50 years. Wetlands typically are enriched in ^{14}C in their associated DOC. But, as wetlands are reduced and replaced by development and agriculture less enriched ^{14}C will be produced and more ancient ^{14}C soils will be disturbed with a net effect of lowering the ^{14}C content of the DOC (Raymond et al., 2004).

Lignin phenols have also been measured in the high molecular weight (HMW) fraction of dissolved organic matter (DOM) isolated from surface and bottom waters from the Middle-Atlantic Bight (MAB) to provide evidence of terrestrially derived organic matter (Mitra et al., 2000). They suggest coastal sediments may be an important source of organic matter to the deep ocean from HMW DOM derived from older sediments enriched in terrestrial organic matter but deposited below the sediment/water interface. This older, hydro-dynamically fractionated, refractory material may represent a significant source of terrestrial organic matter to the deep ocean.

DOC is formed primarily by chemical weathering of soil and vegetative litter. In contrast, POC forms primarily through mechanical weathering, especially of ancient and relict soil found deeper in the ground. An important aspect of mechanical weathering is the release of minerals of considerable surface area and adsorptive properties. Experiments mixing DOC with Alumino-silicate minerals showed enrichments in certain class compounds like amino acids but also

showed distinct changes in $\delta^{13}C$ values. Therefore, as organic matter fractions convert between DOC and mineral associated particles their respective $\delta^{13}C$ values may change appreciably and lead to further complications in interpretation in process or source of organic carbon (Aufdenkampe et al., 2007).

1.8 Radiocarbon (^{14}C) Age Analysis of Organic Matter:

Radiocarbon (^{14}C) is an unstable isotope of carbon which undergoes radioactive decay exponentially with a half-life of 5730 years (Godwin, 1962). ^{14}C would have decayed completely from Earth if not for its production by cosmogenic neutrons interacting with atmospheric nitrogen. ^{14}C is produced in the upper atmosphere and rapidly combines with oxygen to form $^{14}CO_2$. Plants take this up through photosynthesis and some subsequently consumed by animals. Therefore living organisms are equilibrating ^{14}C uptake with its decay. Once dead, decay continues and the ^{14}C level drops at a measurable decay rate. In addition to this natural process anthropogenic addition of ^{14}C has occurred during atmospheric nuclear bomb testing in the 1950s and 1960s. After the stop of atmospheric bomb testing ^{14}C began to decrease through uptake by other carbon reservoirs and dilution by fossil fuel combustion. Figure 3 indicates the northern hemisphere 1963 peak where most testing occurred and the southern hemisphere peak a few years later indicating the global exchange and precision of data that can be retrieved from this time period.

Large spatial and temporal variation was found in northeastern rivers using ^{14}C measurements of DOC, POC and DIC (Raymond et al., 2004). Their ^{14}C data showed export of old dissolved organic carbon to the Middle Atlantic Bight from the Susquehanna, Delaware and Hudson rivers. The Hudson River exhibited the oldest ^{14}C values found which was attributed to a significant decrease in ^{14}C activity of DOC (decrease of young DOC) possibly from loss of

wetlands and export of ancient marine shale deposits in this river. They also suggested a positive relationship between ^{14}C and $\delta^{13}C$ values of DIC and DOC. Their proposed explanation of this correlation was that allochthonous DOC is re-mineralized to DIC in soils and rivers and DOC are produced from autotrophic DIC uptake. Old ^{14}C organic matter may well be produced from autochthonous production when ^{14}C depleted DIC is consumed.

Other studies of the Middle Atlantic Bight involved particulate organic carbon where low ^{14}C values ($\Delta^{14}C$ as low as -476‰ for deep slope waters) were indicative of either highly aged terrestrial materials or natural hydrocarbon seepage (Bauer et al., 2002). Hydrocarbon seepage, for which evidence exists (Boehm and Requejo, 1986) in the Atlantic and Gulf of Mexico, could provide background level ^{14}C and depleted ^{13}C DOC and POC to parts of the MAB. If the POC contains very aged ^{14}C values it likely is due to lateral transport of mineral derived particles from the slope/shelf system since they found little evidence of a ^{14}C aged POC from rivers and estuaries ($\Delta^{14}C$ up to +78‰). Druffle et al., (1992) found open ocean highly depleted ^{14}C and ^{13}C DOC and ^{13}C depleted suspended POC along with land plant lignin. Indicating inputs of old terrestrial organic matter may not be only in the coastal ocean.

Radiocarbon studies combined with carbon isotopes ($\delta^{13}C$) in the northeastern Pacific Ocean involved analysis of select chemical classes; hydrolysable amino acids, carbohydrates, lipids and acid insoluble fractions separated from plankton, sediment floc and seafloor sediments (Wang et al., 1998). Their work indicated rate constants for the early diagenesis of these compound classes in order from amino acids = carbohydrates > total organic carbon > lipids based on concentration profiles in sediment. The ^{14}C values were found to decrease in the order from plankton in the surface water, sediment floc in the water column to seafloor sediment. Distinctive differences were also found within each of the compound classes for sediment floc

and seafloor sediments. The ^{14}C ages decreased similarly to the compound class degradation rate. Amino acids and carbohydrates were youngest followed by total organic carbon with lipids being the oldest of the classes studied. Actual age differences measured between these classes exceeded 2,000 years. Additionally, their individual organic fraction profiles indicate significant percentages of each class were not decomposed deep within the sediment. Adsorption processes are suggested as the cause, primarily by sorption to mineral surfaces, for stabilizing or slowing remineralization rates. Despite the range of ^{14}C values found for these compound classes, the $\delta^{13}C$ values were similarly enriched and resembling plankton values suggesting they were derived from primarily marine sources.

A similar study of these compound classes was undertaken for Southern Ocean samples (Wang and Druffel, 2001). Differences in organic carbon production and deposition accounted for the observed variations in ^{14}C and $\delta^{13}C$ values. Carbohydrates had younger ^{14}C values than amino acids and in the Southern Ocean lipids did not exhibit older ^{14}C ages than the other class compounds. A more rapid and higher organic deposition rate in the Northeast Pacific Ocean as well as less bioturbation may account for some observed differences in ^{14}C ages. Southern Ocean sediments had lower organic carbon contents with older ^{14}C signatures indicating extensive degradation. The refractory nature of these sediments and uncharacterized organic fraction dominate these sediments and their respective isotopic signatures. However, the isotopic distinction between compound classes in sediments suggests processes unique to each class can effect their preservation through, for example, mineral surface adsorption.

^{14}C has been used to establish chronology in sediment deposition. Glaser and Zech (2005) used ^{14}C measurements along with compound specific isotope ratio mass spectrometry to reconstruct climate and landscape changes during the late glacial and Holocene in a high

mountain lake in Nepal. Their study of terrestrial sugars and n-alkanes, aquatic alkanes and microbial sugars revealed distinctively C_4 plant sources in the sediments at 15 ka BP. This time period, beginning around 18 ka BP, saw an immergence of C_4 plants due to a very dry climate resulting in formation of steppe-like vegetation surrounding this lake. Lignin compounds were identified but unfortunately of too low concentration from these samples for measurement.

The combination of age dating using ^{14}C and source apportionment using $\delta^{13}C$ of specific biomarkers has increased our ability to monitor impact of climate change and its consequences on preservation and transport of organic carbon. Goñi et al., (2005) used a dual isotope tracer technique to study fate of organic matter in the Canadian Beaufort Shelf from the Mackenzie River. Sediment compositions and bulk ^{14}C and $\delta^{13}C$ of lignin oxidation products were investigated. It was found that 70% of particle bound organic matter exported by the Mackenzie River is highly degraded and very old (7 ka BP), consistent with other eastern Siberian shelf measurements (Guo et at., 2004), but in contrast with findings of young dissolved organic carbon from North American Rivers (Benner et al., 2004). The other 30% of POM was derived from modern vascular plants of C_3 origin based on the lignin phenol $\delta^{13}C$. They suggest the source of this older terrestrial carbon is from fossil carbon (kerogen) from eroding sedimentary rocks or degraded soil carbon. Post-deposition mineralization is minimized due to inherent recalcitrance of this material which allows for its wide distribution in the shelf. This study demonstrates the need for critical baseline information in sensitive regions affected by climate change. Terrestrial carbon, released from erosion of permafrost during warmer climate alters input of fossil and degraded soil to arctic rivers. These allochthonous inputs will likely change organic carbon in the arctic marine as climate warms.

A minimal amount of terrestrially derived POC or DOC is found in the open ocean. One explanation is terrestrial organic matter is modified or remineralized prior to introduction into the ocean (Raymond and Bauer, 2001). They conclude rivers export a certain fraction of old ^{14}C depleted DOC and POC to the oceans, in contrast to rivers exporting ^{14}C enriched organic matter to the oceans (Hedges et al., 1986). Preferential removal of labile and younger ^{14}C by bacteria during transport would retain an older material delivered to the oceans. Young ^{14}C DOC content in plant litter and upper soil horizons from rivers draining into the Arctic Ocean were also found by Benner et al., (2004). Close correlation between ^{14}C age of DOC and the concentration of dissolved lignin phenol was observed with higher lignin concentrations associated with younger ^{14}C DOC. They found ^{14}C content of DOC in Ob river samples indicate the presence of bomb ^{14}C levels in nearly all samples with $\Delta^{14}C$ values exceeding 300‰.Young ^{14}C ages of the terrestrial biomarker in the DOC in these rivers indicates little mobilization of old carbon from the arctic soils although radiocarbon ages have been recorded into past millennia for these soils (Schell, 1983).

The above study and others have demonstrated the association of DOC with the POC in marine systems and although different in isotopic abundance, have the potential for defining processes occurring in the marine environment especially in response to terrestrial inputs. Although Benner et al. (2004) found high lignin phenol content associated with higher ^{14}C levels in the DOC, enough variation in the composition of DOC in these arctic rivers could exist that the high ^{14}C of lignin phenols, indicating terrestrial source material, should be substantiated by the direct ^{14}C measurement of individual lignin compounds.

1.9 Compound Specific Radiocarbon Analysis:

The capability of compound specific stable isotope ratio mass spectrometry has been rigorously demonstrated in the assessment of inputs and preservation mechanisms of organic carbon in the marine environment (Hayes et al., 1990, Augenstein, 1999, Glaser and Zech, 2005). The development of accelerator mass spectrometry (AMS) for the determination of ^{14}C at quantities as low as 20 micrograms (Kirner et al., 1997) can now provide an equally beneficial characterization of source materials because of the potential for compound specific radiocarbon analysis (CSRA). The isolation of specific compounds followed by radiocarbon dating measurement can help determine residence time in specific reservoirs, reactivities of individual compounds and reveal presence of anomalous materials, such as organic contamination, based on ^{14}C content. Isolation and ^{14}C measurement of individual lignin phenols will give unequivocal assessment of rates and ages of terrestrial sources.

Molecular level age determination was developed and tested on plant lipids and petroleum whose age ranged from modern to fossil and contained various compounds such as lipids, hydrocarbons and sterols (Eglinton et al., 1996). Comparison between bulk ^{14}C and compound specific ^{14}C for homogeneous samples agreed within ±10%. Compound specific isotope ratio mass spectrometry was used to determine isotopic fractionation and correct for it when necessary. Principle causes of fractionation were poorly resolved chromatographic peaks, incomplete peak isolation or co-elution with other peaks. Contamination is far more critical in this technique as a modern ^{14}C contaminant can cause just as severe problems with interpretation of data as a fossil fuel ^{14}C contaminant can by either increasing or decreasing the ^{14}C activity unintentionally. Sources of contamination were from column bleed from the gas

chromatographic column and incomplete removal of solvent after sample transfer prior to combustion to CO_2.

Many studies using CSRA have focused on soil organic carbon and its transformation within various environments (Trumbore et al., 1996). Compound specific radiocarbon measurements were used to determine the assimilation of different substrates during biomass synthesis (Rethemeyer et al., (2005). Specifically, short-chain phospholipid fatty acids (PLFA) were measured after gas chromatographic separation of monounsaturated and saturated PLFAs. Based on ^{14}C ages, monounsaturated PLFAs were synthesized from close to modern level soil organic carbon while saturated PLFAs were synthesized from sub-recent soil matter. The latter was indicated by higher ^{14}C activity levels due to the bomb-^{14}C effect in sub-surface soils. The former, monounsaturated PLFAs also showed minor ^{14}C decrease through topsoil. This indicates possible incorporation of modern level ^{14}C from plant residues transported deep into topsoil as dissolved organic matter.

Another application of CSRA is direct isotopic analysis of polyaromatic hydrocarbons in atmospheric aerosols. Aerosols derived from either fossil fuel or biomass burning is of considerable environmental concern. Complex combustion products have until recently prevented accurate apportionment of sources. Currie et al. (1997) showed capability to separate and collect six individual PAH compounds using preparative capillary gas chromatography (PCGC). Their results indicate the PAHs dated were of fossil origin but source assessment was tentative due to interference from un-resolved compounds. Kanke et al., (2004) analyzed PAHs by compound specific ^{14}C in sediments from a Tokyo urban reservoir where they varied from 6 to 21 pMC (% Modern fraction) or $\Delta^{14}C$ of -940 to -790‰. Individual compounds separated by PCGC and ^{14}C dated were found to be fossil derived, although some compounds such as

phenanthrene received a larger input from biomass burning than from fossil fuel combustion, based on its ^{14}C measurement. This technique would allow for the proper allocation of sources of either fossil fuel or biomass produced products over historical times. In addition, potential interference from compounds not removed completely from the purified compound was likely. Proper application of this technique makes it possible to assign a radiocarbon date to a molecular level compound to test for not only source verification but authenticity of artifacts, forensic samples and those used in trade or commerce.

CSRA has also been used to study fatty acids used as proxies of organic carbon in marine sediments. Uchida et al., (2000) measured fatty acid methyl esters in Tokyo Bay sediments to provide information on sources and depositional history. Their study revealed considerable differences between fatty acids and bulk sediment ^{14}C content. Phytoplankton and bacteria derived fatty acids were as old as 1.4ka BP (1,400 years before present) dependent upon the specific fatty acid collected and measured. The bulk organic matter age was determined to be 5.0ka BP and the $C_{22:0}$ fatty acid originating from terrestrial plants had a ^{14}C age of over 17ka BP. Possible explanations for very old $C_{22:0}$ fatty acid include an overlap of old relict carbon and modern plant derived carbon in sediments and changes in inputs due to environmental changes in estuaries over time. Similarly, Matsumoto et al., (2004) measured ^{14}C and $\delta^{13}C$ of individual fatty acids in an aerosol sample and compared the CSRA data to the previous year aerosol sample. The $\delta^{13}C$ value indicated animal and marine algae origins for the C_{16}-C_{19} fatty acids and terrestrial C_3 plants for $C_{>20}$ fatty acids. Not only were variations found between adjacent years aerosols but a large variation was found within fatty acids within each aerosol sample. $\Delta^{14}C$ values ranged from 83.5 to -89.7‰ or a range in excess of 800 calendar years with the $C_{>20}$ fatty

acids being oldest at 755 yr BP. Soils transported from the Asian continent are suggested as the older terrestrial source of these ^{14}C ages.

Pearson and Eglinton (2000) studied the Santa Monica Basin sediments of the southern California coast using CSRA of individual long-chained C_{24} to C_{33} n-alkanes. Based on ^{14}C abundance and $\delta^{13}C$ values they simulated contributions of three end-members using a model without any marine end member since n-alkanes are minor constituents in marine organisms. Their model concludes 80% of surface sediment in Santa Monica Basin is terrestrial, based on plant-wax end member, and of modern age. Fossil carbon made up 12% based on high-wax petroleum end member and the balance 8% from shale as a second fossil end member. Their three end member model also predicted the average terrestrial $\Delta^{14}C$ value at +235‰ for the post-bomb surface sediment (0-2.5 cm) and ~0‰ for pre-bomb sediment (2.7-7.5 cm). Based on their CSRA data and modeling, presence of fossil carbon in marine sediments could be significant and help explain aged organic carbon in sediments rather than relying on aged terrestrial carbon alone. CSRA techniques applied to the terrestrial biomarker lignin may certainly assist in clarifying sources of old organic carbon in marine sediments. McNichol et al., (2000) showed the capability of CSRA technique to isolate, collect and measure ^{14}C on lignin-derived phenol compounds. Their analysis of vanillin, cinnamic acid and various woods indicate good agreement to bulk samples. Although their samples were pure compounds or those isolated from relatively pure materials the technology is poised for application to naturally occurring samples. The main obstacle to this technique regardless of the compounds made amenable to chromatographic separation is quality of separation of analytical peaks of interest and absence of baseline contamination in the spectra which equate directly to the quality of the isolated and collected compounds. Chromatographic separation capacity also depends and begins with the

quality of isolation chemistry devoted to compound class separation techniques such as lignin oxidation.

2. STUDY AREA:

The study area encompasses the lower eight miles of the Altamaha River proximal to the Georgia Coast, and extends out an additional 20 miles to Gray's Reef National Marine Sanctuary on the inner Atlantic Shelf. The Altamaha River Basin, one of the three largest river basins on the Atlantic Seaboard, has a watershed of 14,400 square miles, covering nearly one-quarter of the state of Georgia. The Altamaha River is formed by the confluence of the Oconee and Ocmulgee rivers, the Altamaha river flows for nearly 140 miles through hardwood forests, cypress swamps and tidal marshes to its terminus near Darien, Georgia. Annual flow varies from approximately 5,000 cubic feet per second (cfs) in the fall to over 25,000 cfs during spring flooding.

Twelve locations were selected for multiple sampling in the study area. The furthest upriver station was located near Two-Way fish camp, just east of the US17 overpass and approximately 8 miles upstream of the coast. Eight additional sampling stations extended downriver to just outside the Altamaha River Sound. Three additional sampling stations on the inner Atlantic Shelf extended in a linear configuration toward the Gray's Reef National Marine Sanctuary, approximately 20 miles east-northeast of the Altamaha River Sound. A single sampling station, approximately 70 miles upriver from the coast near US15, 12 miles north of Baxley, was designated as "Hatch", a freshwater station outside the influence of saltwater incursion. One single sediment sample was collected from the South Atlantic Bight approximately 46 miles offshore in 35 meters water depth by Dr. Cai during a separate cruise in May, 2006 and is designated "SAB".

3. METHODS:

3.1 Sampling of the Altamaha River and South Atlantic Bight:

Surface sediment samples and surface particulate matter were collected from the Altamaha River and inner Atlantic Shelf locations during six cruises conducted between March 2002 and March 2007. The research vessel *Spartina* from the University of Georgia's Marine Institute on Sapelo Island was used as the support vessel for five of these cruises, conducted in March and November 2002, November 2005, March 2006, and March 2007. Dr. Ji-Hong Dai provided samples from nine locations along the Altamaha River, collected during the 2002 cruises. The same nine Altamaha locations, in addition to three sites on the inner Atlantic shelf, were sampled during the November 2005, March 2006 and March 2007 cruises. An October 2006 cruise made use of the University of Georgia's Center for Applied Isotope Studies' 20-foot MonArk vessel, which precluded sampling of the three offshore locations, but due to its shallow draft did allow for additional surface sediment and seawater sampling in the Mud River and Doboy Sound. The November 2005, March 2006 and March 2007 cruises aboard the *Spartina* also included sample collection of surface seawater for filtration of particulate matter. The offshore sampling stations 1-4 and SAB and inland station Hatch are depicted in figure 4 in reference to the coastline of Georgia and the Southeastern United States. Figure 5 depicts the sampling stations within the Altamaha River and Estuary along with additional samplings in the Little Mud and South River.

3.2 Sample Collection:

All six cruises included the GPS monitoring of latitude and longitude at each sampling station. The March 2002 samplings included surface salinity and water temperature measurements and the November 2002 samplings included surface salinity measurements. The three cruises between November 2005 and October 2006 included measurement of surface salinity, water temperature, water depth and time of sampling. These physical parameters as well as sampling location, date, and water volume collected at each sampling station for each cruise are listed in table 1. Surface temperature and salinity measurements were made using Orion Corp. model 140 conductivity, temperature, salinity meter.

Surface sediment samples were collected using either a Ponar brand clamshell dredge or a box corer measuring 6 inches by 6 inches by 12 inches (depth). Both devices yielded satisfactory surficial sediment samples, but the box corer allowed retrieval of a more undisturbed sample at depth in areas where the sediment was less consolidated. Most sampling required the use of the Ponar clamshell dredge, however, due to the underlying hard packed sand of the river bottom, and the minimal penetrating ability of this particular box corer. Both sampling devices were washed thoroughly with water between sample stations to minimize residual sediment.

The sediment sampling process consisted of removal of overlying water followed by scooping out of sediment from the topmost portion of the sampler's contents. The amount of sediment collected on each sampling attempt varied considerably, and was dependent on the location within the river and prevailing sediment type (sand, silt or clay), as well as the collection efficiency of the sampler. Collection efficiency was controlled by technique – the lowering of the sampler in conjunction with the ship's velocity relative to both surface and bottom currents. The most successful sampling occurred with minimal ship movement and a rapid, straight

descent of the sampler. Sediment samples were transferred to plastic bags using pre-washed stainless steel utensils. The samples were double bagged and identified by time, date and station number, and then placed in a cooler with ice for transfer back to the laboratory. Ship position, date and time of collection and water depth were noted in a log book for each sample location.

For one deeply-penetrating box core sample collected in November 2005, a 2 inch polycarbonate coring tube was used to sample the undisturbed sediment. A core tube of approximately 8 inches of sediment was recovered and placed on ice until transferred to a laboratory freezer.

Water, collected for suspended particle analysis, was sampled from the opposite side of the boat to eliminate or minimize sampling of suspended material brought up by the sediment sampling device. In most cases, the water sampling was carried out before the sampler was dropped to the seabed to ensure an uncontaminated sample. In the few situations where sediment sampling was unsuccessful at a particular site, the water samples were discarded, a new sediment site selected and new water samples drawn. Water samples were collected in one liter polypropylene bottles, rinsed with seawater prior to filling, and placed on ice until transferred to a laboratory refrigerator.

Larger volume water samples of up to 100 gallons were collected from each of the three offshore sampling stations due to the limited organic carbon content. Collection was conducted concurrent with sediment sampling to minimize time at the offshore stations. A submersible pump connected to 0.5 inch ID rubber tubing was lowered over the side of the boat to a depth of between 2 and 4 feet below the surface. The pump was turned on and the output run into three 35 gallon polypropylene containers set on the aft deck of the boat, filling the containers at a rate of 10 gallons per minute. Once the containers were filled, the submersible pump was placed into

one of the containers along with the output hose. A special bypass line, which could sub-sample the main flow at reduced pressure and flow, was connected to a dual filtration apparatus housing two 130mm diameter glass fiber filters. Each filter, pre-burned at 550°C to remove organic carbon, could be removed individually through the use of an isolation valve when they became clogged. Filtration rates slowed as filters clogged, but the process was continued until all water samples had been filtered. Each loaded filter was removed with stainless steel tools and placed onto aluminum foil, wrapped securely, and placed in an ice chest for transport back to the laboratory.

3.3 Sample Treatment:

Sediment samples collected during cruises were either sub-sampled immediately upon returning to the laboratory, or thawed temporarily before sub-sampling. Approximately 200 grams of sediment was treated with warm 1N HCl to remove carbonates from the sample. The samples were rinsed thoroughly in de-ionized water until a pH of 6-7 was reached. The samples were centrifuged for 5 minutes, the water poured off and the sediment scooped into aluminum dishes for drying at 50°C. After thoroughly drying, the samples were homogenized by physical mixing with stainless steel utensils or mortar and pestle. Sediment samples treated in this fashion were ready for further analysis.

A select few samples from the Altamaha sound and offshore stations were prepared for particle size analysis and separation into four size classes: greater than 20 mesh (1 millimeter pore size), greater than 35 mesh (500 micron pore size), greater than 60 mesh (250 micron pore size) and less than 60 mesh. These particular samples were selected because of their varied particle size distribution, unlike the upriver sediments which consisted primarily of fine-grained silt and clay of less than 250 micron diameter particles. These samples were not treated with

dilute acid initially, as a large fraction of their particles consisted of carbonate shells. Approximately 200 grams of sample sediment was wet sieved through screens and rinsed into beakers for carbonate removal using dilute acid as described above. The de-ionized water rinsed sediment was transferred to aluminum dishes for drying at 50°C and subsequent analysis.

The core sample recovered from a box core in November 2005 was removed from the polycarbonate tube by cutting away the tube while it was still frozen. The sediment core was divided into 20 millimeter sections from the top down, and portions of these sections were acid treated and dried as above. The remainder was re-packaged and re-frozen for future processing.

The small water samples recovered in one liter polypropylene bottles were filtered through 0.45 micron PTFE filters using a sink aspirator for vacuum. The particulate matter recovered on the filters was rinsed into aluminum drying dishes for drying at 50°C. Some samples were filtered through pre-combusted glass fiber filters and remained integrally imbedded in the filter. Weight of filtered material was determined with less precision due to the mass of the filter and low particulate weight.

3.4 Bulk Chemical and Isotopic Analysis (TOC, TN, $\delta^{13}C$ and $\delta^{15}N$):

Chemical analysis was carried out on sediment and filtered particulate organic matter (POM) by pre-treating the sediment samples with 1N HCl to remove any associated carbonate minerals and shell material. The samples were rinsed to neutral pH and dried at 50°C. Suspended particulate matter was filtered through a 0.45 micrometer Millipore HA Teflon filter, rinsed thoroughly and washed onto an aluminum dish, and dried at 50°C. Approximately 100 milligrams of sediment or POM was combusted to carbon dioxide, in a continuous flow of helium using a Carlo-Erba elemental analyzer coupled to a Finnigan MAT Delta S isotope ratio mass spectrometer (EA/IRMS). Simultaneous collection of both total organic carbon and

nitrogen concentrations as well as the stable isotope ratios of $^{13}C/^{12}C$ ($\delta^{13}C$) and $^{15}N/^{14}N$ ($\delta^{15}N$) on each combusted sample can be achieved through the use of this type of instrumentation. Duplicate analyses were performed on the bulk sediment samples collected from the 2002, 2005 and 2006 cruises. POM samples were very limited and duplicates were run for only a few. Results for TOC, TN, C/N, $\delta^{13}C$ and $\delta^{15}N$ for sediment and POM samples are listed in table 2.

Samples were also prepared using a sealed tube method by loading samples into pre-combusted 6 or 9 mm diameter quartz tubes, with adequate copper oxide to quantitatively combust the organic carbon in each sample to carbon dioxide at 900°C. The quantity of sediment sample loaded was dependent on percent organic carbon, which was estimated for each sample based on visual estimation of sediment composition. The carbon dioxide was then cryogenically purified and separated on a specialized high vacuum processing line. At this point, the collected carbon dioxide was then available for measurement of the stable isotope ratios of $^{13}C/^{12}C$ using a Finnigan MAT 252 Isotope Ratio Mass Spectrometer, or could be further prepared to graphite for ^{14}C measurement by accelerator mass spectrometry (AMS) using a National Electrostatics Corporation 0.5MeV pelletron accelerator.

3.5 Lignin (CuO) Oxidation:

The formation of lignin monomers from the phenolic polymers within vascular land plants can be achieved using CuO oxidation (Hedges and Ertel, 1982; Goñi and Hedges, 1992). Recently, there have been modifications or improvements to the technique of lignin oxidation to reduce reaction time (Goñi and Montgomery, 2000). Some of these improvements were incorporated into the following method. Up to 500 milligrams (higher mass for low %OC samples) of sediment was loaded into a stainless steel reactor with internal dimensions 22mm diameter by 41 mm high. Added to the sediment was 50mg ferrous ammonium sulfate, 500mg

CuO and a stainless steel ball to facilitate mixing. The reactors were placed inside of a glove bag where through successive nitrogen gas fillings and evacuations, oxygen was eliminated by replacement with pure nitrogen. Approximately 7 ml of 2N NaOH was added to each reactor. A viton o-ring was affixed to the reactor's o-ring groove and the top was sealed with four bolts. The reactors were placed into a 170°C rotary heater for 3 hours. After 3 hours the cells were immediately placed into an ice bath to cool and stop the reaction. Once cool, the reactors were opened, the steel ball removed and two internal standards - 500 μg each of trans-cinnamic acid and ethyl vanillin – were added as recovery standards. The reactor's contents were rinsed into 50ml centrifuge cups with 1N NaOH. The cups were centrifuged for 10 minutes and NaOH solution was collected in 250ml flasks. This process was repeated twice, combining the NaOH extracts. The NaOH solution was brought to pH<1 with concentrated HCl and stored in a refrigerator overnight. The acidic aqueous solution was extracted with three 20ml portions of distilled ethyl acetate. The extracts were combined and then reduced in volume to a few milliliters on a rotary-evaporator under nitrogen and mild heat. The extract was passed through a small bed of anhydrous sodium sulfate to remove water and foreign matter, and the ethyl acetate evaporated to dryness in a pre-combusted gas chromatographic vial.

3.6 Chemical Analysis of Lignin Oxidation Products (GC/MS):

Dried extract from the CuO oxidation was taken up in either 200 or 400 microliters (μL) of pyridine. The amount of solvent used was dependent on the amount of total lignin that was recovered from a particular sediment sample and the number of gas chromatographic runs that may be required of a particular sample. The latter is important when sample limited by low organic carbon content. Derivatization of lignin oxidation products is required because of low volatility of these compounds. To make lignin phenols amenable to gas chromatographic

separation the hydroxyl hydrogen are converted to esters of trimethyl siloxane. A 50μL aliquot of the extract was transferred to pre-combusted (550°C) gas chromatographic (GC) vial. 50μL of N,O bis(trimethylsilyl)-trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) (Supelco Co.) was added to the vial and immediately closed and placed into a 60°C dry bath for 10 minutes to derivatize or silylate all exchangeable hydrogen in the phenolic compounds. This derivatized lignin sample was then ready to be analyzed on an Agilent 6980 GC with 5973 mass selective detector (MSD) for compound identification and quantification, analyzed on a Agilent 6890 GC with Thermo-Finnigan Delta plus XL isotope ratio mass spectrometer (GC/IRMS) for the $\delta^{13}C$ measurement of individual compounds, or processed on a Agilent 5890 GC with a flame ionization detector (FID) and Gerstel preparative fraction collector (GC/PFC) for the identification and collection of specific target compounds. The quantitative analysis using the 6980/5973 GC/MS is typically run immediately after derivatization, as any evaporation of original pyridine solvent or derivatizing solvent could adversely effect the concentration of LOPs and result in higher peak areas and inaccurate quantification. Immediate measurement by for GC/IRMS and GC/PFC methods of analysis is not as critical, as they are less concentration dependent. However, to maintain correct isotopic ratios and minimize any fractionation of individual compounds, samples were kept frozen in both derivatized and underivatized form until ready for analysis.

Quantitative analysis was performed on the Agilent 6980 GC with 5973 mass selective detector (MSD). Samples were injected in triplicate using a small volume, 0.2 μL, auto-injector connected to the GC splitless injector set at 250°C. A DB5-MS (5% methyl silicone) fused silica capillary column 30 meters long by 0.32 mm internal diameter, coated to 0.25 micron film thickness and programmed from 100°C to 180°C at 3° per minute and 180°C to 300°C at 20° per

minute, was used to facilitate individual component separation. Individual compounds were detected using an Agilent 5973 mass selective detector (MSD) (electron impact at 50eV) with identification by mass fragment pattern comparison to the NBS database of mass spectra. A suite of standards was used to quantify retention times, response factors and mass fragment patterns for each of the 13 lignin phenol compounds identified in this study. Standard solutions of lignin phenols were prepared in reagent grade and petrochemically-derived pyridine. From concentrated stock solutions, various combinations of groups of LOPs were prepared for quantification and determination of GC/MS response factors used for quantification of unknown LOPs. Table 3 lists 13 lignin phenol compounds with their primary fragment pattern masses.

Other compounds of interest were identified but are not listed in this study, including 3,5-dihydroxy phenol and dihydroxy benzoic acid. Standards were run on a daily basis after tuning the MSD to optimize the quantification of unknown samples. The internal recovery standards, trans-cinnamic acid and ethyl vanillin, were used to determine chemical yield of lignin phenols after oxidation and extraction. By applying recovery yields, and comparing response factor and retention times to standards, an accurate assessment of concentration and distribution of lignin phenols in unknown samples was achieved. Triplicate analyses were performed on most unknowns, with duplicates as a minimum, for better precision. GC/MS quantified lignin phenols for the separate sampling cruises are listed in nanograms per gram (ng/g) sediment in appendix A and after averaging duplicate or triplicate analysis and normalization to organic carbon concentration (mg/100mgOC) the results for all sampling cruises are listed in table 4.

3.7 $\delta^{13}C$ Analysis of Lignin Oxidation Products (GC/IRMS):

The $\delta^{13}C$ ratio of individual lignin phenols were measured using an Agilent 6890 GC with Thermo-Finnigan Delta plus XL isotope ratio mass spectrometer (GC/IRMS). Just as the

quantitative analysis of the LOPs by GC/MS required derivatization of hydroxyl group hydrogen, so too did GC/IRMS analysis. Samples either freshly derivatized, as described above, or those derivatized earlier and kept frozen until use, were injected into the GC for separation and subsequent analysis. Samples were injected in triplicate, using a programmed 0.3 to 2.0μL injection via an A200S auto-injector connected to the Agilent 6890 gas chromatograph. Injections were made in splitless mode at 250°C. A DB5-MS (5% methyl silicone) fused silica capillary column 30 meters long by 0.32 mm internal diameter, coated to 0.25 micron film thickness and programmed from 100°C to 180°C at 3° per minute and from 180°C to 300°C at 20° per minute, was used to facilitate individual component separation using similar order and retention times for the GC/MS instrument. The $\delta^{13}C$ values for the individual LOPs were measured using Finnigan MAT Isodat software with automatic background subtraction and peak identification, and were calculated relative to PDB carbon standard using Equation 1.

$$\delta^{13}C = \left[\frac{\left({}^{13}C/{}^{12}C\right)_{Sam}}{\left({}^{13}C/{}^{12}C\right)_{Std}} - 1 \right] \times 1000 \qquad \text{Equation 1.}$$

Where Sam and Std designate sample and standard $^{13}C/^{12}C$ ratios respectively.

Due to the complexity of these chromatograms, each peak of interest was reviewed and individual backgrounds applied along with re-integration for their respective $\delta^{13}C$ values. Standard reference peaks composed of high purity carbon dioxide used as the reference for computation of $\delta^{13}C$ values were injected prior to and after the LOPs of interest. Corrections were made when reference peaks varied within a chromatogram, indicating instability in the IRMS.

Identification of 13 LOP standards in the GC/IRMS spectra were determined by comparison to the spectra generated by the GC/MS. Although a slight difference in transfer

columns existed between the two instruments, retention times varied slightly but still followed similar peak heights and order of elution from the chromatographic column. Relative peak heights based on unique response factors of each lignin phenol created a pattern of spectra which assisted in the proper identification of the retention time of each standard and was applied to more complex samples. The oxidation reaction can produce other monomers and dimers from an assortment of compound classes resulting in a complex chromatogram. Although other compounds are small in relative mass, proper definition of LOP retention times is critical when spectra become crowded with numerous peaks, of various intensities, derived from compounds other than LOPs.

The suite of standard LOPs were made from pure chemicals purchased from Aldrich Chemical Company. A few milligrams of these pure standards were combusted at high temperature with CuO in an evacuated ampoule. The resulting carbon dioxide retained the stable isotopic signature of the pure chemical, for which a $\delta^{13}C$ value was determined based on the average of triplicate analyses on the Finnigan MAT 252 dual inlet IRMS. The dual inlet mode allows for the alternating measurement of the unknown carbon dioxide against a known and calibrated carbon dioxide for a high precision isotopic ratio measurement approaching 0.01‰. Accurate $\delta^{13}C$ values were determined for the 13 LOP standards in this way and accepted as the true $\delta^{13}C$ value for each LOP standard. Once diluted into pyridine and derivatized with TMCS, the original carbon abundance and isotopic composition will have changed by the addition of three or six derivatization carbons for each hydroxyl-hydrogen replaced. No alteration of pre-existing carbons occurs, so ideally the original $\delta^{13}C$ value should be revealed once derivatizing carbons have been mathematically removed. The calculation of the $\delta^{13}C$ value of the original underivatized sample is based on Equation 2:

$$\delta^{13}C_{Under} = \frac{\left(\delta^{13}C \cdot \#C\right)_{Der} - \left(\delta^{13}C \cdot \#C\right)_{TMCS}}{\#C_{Under}}$$ Equation 2

Where $\delta^{13}C_{Under}$, $\delta^{13}C_{Der}$ and $\delta^{13}C_{TMCS}$ are the $\delta^{13}C$ values for the underivatized LOP, derivatized LOP and derivatizing agent TMCS respectively, and #C represents the number of carbons in each respective compound. Samples either had 3 additional carbons substituted at the hydroxyl position, or six carbons with an additional substitution at the carboxyl hydrogen.

Recovery standards ethyl vanillin and trans-cinnamic acid were used to determine yield loss during extraction of lignin oxidation products. These two standards were also used as a check of correction for added carbons during derivatization according to equation 2.

Variations between batches of the derivatization TMCS exist. Therefore it is critical to measure the isotopic value for each new batch of material used. A variation of $\delta^{13}C$ values of up to 4‰ were found for a number of different batches of TMCS used during this study. It was advantageous to combine more batches of TMCS into one for a more uniform and consistent derivative $\delta^{13}C$ value. By combining up to five batches of one milliliter each of TMCS and keeping it under nitrogen and refrigerated between use, nearly one hundred derivatizations could be carried out using the same batch value for TMCS $\delta^{13}C$.

It is difficult to assess all the potential variations possible in this chemical manipulation of these natural bio-polymers. The efficiency of lignin oxidation was studied thoroughly while optimizing oxidation and extraction parameters and varied in technique only slightly from that described by other researchers in this field. Consistent derivatization of the various compounds of interest is dependent on the ability to substitute trimethyl siloxane group for hydroxyl hydrogen in a few specific functional groups. Some of the compounds exhibit a considerable steric hindrance to complete substitution, which can only be assessed by this analytical

technique. Proper assignment of background isotopic abundance and peak integration parameters, of individual peaks, especially when co-eluting or near neighboring peaks, is important for accurate results. However, by maintaining consistent treatment of both samples and standards throughout the study a reasonable assessment of the original $\delta^{13}C$ values can be made.

3.8 ^{14}C Preparation and AMS Measurement of Bulk Sediment:

Bulk sediment samples were prepared for radiocarbon dating by first pre-treating sediment samples with 1N HCl to remove carbonate minerals and marine shell. Samples were exposed to acid treatment for a minimum of 4 hours under mild heating. All indication of bubbling caused by neutralization to carbon dioxide had ceased within 4 hours and pH less than 2 maintained. Samples were then centrifuged for ten minutes and the supernatant decanted off. Sediment was rinsed with de-ionized water, shaken and centrifuged another ten minutes and supernatant decanted off. This process was repeated until the supernatant was at pH 6-7. Sediment was transferred with minimum water to an aluminum dish and dried at 50°C for a minimum of 12 hours. Specific weights of sediment samples, based on previously determined percent carbon, were loaded into quartz ampoules with CuO, evacuated and sealed, and combusted at 900°C. Resulting carbon dioxide was cryogenically purified on a high vacuum preparation line and split into two 80 micromole aliquots of carbon dioxide. One split was used for dual inlet stable isotope analysis as described above. A second split was attached to a high vacuum processing apparatus for conversion of carbon dioxide to graphite and measurement using the University of Georgia's Center for Applied Isotope Studies accelerator mass spectrometer (UGAMS).

Carbon dioxide is reduced to graphite in the presence of hydrogen over iron catalyst. Our apparatus is modified from Vogel, et al. (1984) and is composed of Pyrex glass with minimal use

of metal fittings. An advantage to this apparatus is its ease of disassembly and baking at high temperature to remove any organic residue from the walls of the glass tubing. Stainless steel Cajon Ultra-torr fittings, used here, have the advantage of leak tight capability when properly greased and maintained but can have active sites for adsorption and therefore are used minimally. Stainless steel pressure transducers are used for reaction monitoring. Samples, equivalent size standards and background carbon dioxide are all run on the same preparation line to insure low blank levels and consistent results. National Institute for Standards and Technology (NIST) Oxalic Acid I and II are used as primary standards. Either anthracite coal or high purity petrochemically-derived carbon dioxide, devoid of ^{14}C, is used as background carbon dioxide. Graphite produced is pressed into aluminum targets at approximately 200 psi to insure target integrity. The targets for AMS analysis are loaded into a sample wheel in groups composed of twelve unknowns, four standards (mixture of primary and secondary) and one background target.

AMS analysis was performed using the National Electrostatics Corporation (NEC) 0.5 MeV tandem pelletron accelerator with 134 sample capability at the University of Georgia (Roberts et al. 2004). Sample analysis is conducted by measuring all three isotopes ^{12}C, ^{13}C and ^{14}C for each target for a pre-selected time and replicates. Beam line currents for each isotope are acquired and set as a ratio $^{14}C/^{12}C$ and $^{14}C/^{13}C$. Statistical analysis consists of chi square testing or other rejection criteria based on NEC algorithms. Results are reported in percent Modern Carbon (pMC) as well as Radiocarbon age (5568 half-life) and can be converted to $\Delta^{14}C$ (Stuiver and Polach 1977). Stable carbon isotope $\delta^{13}C$ correction is applied to all samples and standards.

3.9 ^{14}C Preparation and AMS Measurement of Particulate Organic Matter:

Particulate organic matter was prepared for radiocarbon dating by first rinsing the filtered materials with deionized water to remove salts. The materials were then exposed to 1N HCl to

remove the carbonate minerals. Samples were rinsed to a neutral pH and dried as above. The same procedure for combustion, purification, graphitization and analysis as above for the bulk sediment samples was used for the particulate organic matter samples.

3.10 ^{14}C Preparation and AMS Measurement of Lignin Oxidation Products:

Select samples prepared and isolated as lignin oxidation products (LOP) described previously were measured for ^{14}C content. Those selected samples were maintained in a dry state after removal of ethyl acetate solvent using dry nitrogen gas. The LOP were transferred to pre-combusted (575°C) quartz ampoules using a minimum quantity of acetone. The acetone was thoroughly removed with dry nitrogen gas and CuO was added to each ampoule. The ampoules were evacuated, sealed and combusted at 900°C. The carbon dioxide produced from reaction was processed on a high vacuum processing line, isolating and purifying the carbon dioxide for collection of at least two CO_2 samples of approximately 80 μmoles each. One CO_2 sample was analyzed for $\delta^{13}C$ of total LOP on the Finnigan MAT 252 IRMS. The second CO_2 sample was converted to graphite and analyzed on a NEC AMS as described above.

Measurements of $\delta^{13}C$ were made on selected sediment samples to assist in determining source and biogeochemical process undergone and to correct for isotopic fractionation of ^{14}C. Some samples that underwent lignin oxidation processing were selected for quantitative and stable isotopic analysis, requiring internal standards trans-cinnamic acid and ethyl vanillin to be added as recover standards. These particular standards had been selected from chemical manufacturers synthesizing these compounds from fossil fuel and therefore are devoid of ^{14}C. By measuring ^{14}C activities of these standards their fossil fuel origin was verified. Added carbon from these recovery standards, although devoid of ^{14}C would impart a dilution of the ^{14}C activity of the original LOPs ^{14}C activity. The amount of the diluted ^{14}C activity contributed by the added

"dead" carbon in the two recover standards relative to the total LOP could be corrected, since a quantitative analysis of the principle LOP compounds including the recover standards had previously been made. Mass balance equation 3 below, similar to equation 2, was applied for this purpose. However, instead of correcting for added carbons and the derivatizing $\delta^{13}C$ value the mass fraction (mf) of added carbon from t-cinnamic acid and ethyl vanillin and there ^{14}C activities were used in place of $\delta^{13}C$ and #C as shown below.

$$\Delta^{14}C_{LOP} = \frac{\left(\left(\Delta^{14}C \cdot mf\right)_{DerLOP} - \left(\Delta^{14}C \cdot mf\right)_{LOP+STDs}\right)}{mf_{LOP}} \qquad \text{Equation 3:}$$

Where $\Delta^{14}C_{\ LOP}$, $\Delta^{14}C_{\ DerLOP}$ and $\Delta^{14}C_{\ LOP\ +\ STDs}$ are the ^{14}C activities ($\Delta^{14}C$) for the undiluted LOPs, derivatized LOPs plus trans-cinnamic acid and ethyl vanillin and ^{14}C activities ($\Delta^{14}C$) for trans-cinnamic acid and ethyl vanillin (already confirmed as zero) respectively, and mf represents the mass fraction of the respective LOPs and standards.

A similar correction is required for the added carbons from the TMCS derivatizing compound for samples and standards undergoing derivatization for chromatographic separation prior to ^{14}C measurement. In an analogous way, correction for added derivatizing carbons, this time, from confirmed fossil fuel derived BSTFA/TMCS is given in equation 4.

$$\Delta^{14}C_{Under} = \frac{\left(\left(\Delta^{14}C \cdot \#C\right)_{Der} - \left(\Delta^{14}C \cdot \#C\right)_{TMCS}\right)}{\#C_{Under}} \qquad \text{Equation 4:}$$

Where $\Delta^{14}C_{\ Under}$, $\Delta^{14}C_{\ Der}$ and $\Delta^{14}C_{\ TMCS}$ are the ^{14}C activities ($\Delta^{14}C$) for the underivatized LOP, derivatized LOP and derivatizing agent BSTFA/TMCS respectively, and #C represents the number of carbons in each. Some of the sediment samples were processed strictly for the ^{14}C measurement by AMS. These samples, after oxidation of the lignin phenols, had no recover standards added. This eliminated any added carbon, even that devoid of ^{14}C.

3.11 Preparative Fraction Collection of Lignin Oxidation Products and AMS Measurement of ^{14}C:

The primary analytical task of this study is to ascertain the radiocarbon age of specific compounds as proxies for the age of specific terrestrial components found in the sediment derived from the Altamaha River. Using the previously described procedure to isolate lignin oxidation products from the selected sediment samples, these components were further separated on a gas chromatographic column, as previously described, for quantitative and isotopic analysis. Confirmation of lignin phenols peak retention times within chromatograms was accomplished by comparison with standards of identical chemical composition.

Instrumentation used for this purpose was an HP5890 gas chromatogram with an auto-injector with DB5-MS column of dimensions 30 meter long by 0.32 internal diameter and 0.25μm film coating. The temperature program was identical to that used for quantitative and isotopic analysis on their respective gas chromatographs: 100°C to 180°C at 3° per minute, then 180°C to 300°C at 20° per minute. Flame ionization detection (FID) set at 250°C was used to detect individual components representing approximately 1% of effluent stream from the column. The majority and balance of the chromatographic effluent passed into a preparative fraction collector (PFC). The PFC is composed of a specialized back-pressure controlled splitting device (valve) where seven separate outlets can be opened at pre-programmed times. Opening and closing times were determined by retention times of chromatographic peaks and transfer times through the PFC. Additional time was added to FID-determined retention time to compensate for the additional 800 mm of column length into and through the PFC apparatus.

Collection of peaks of interest and isolation of specific compounds was accomplished by cooling nominal 10 μL volume glass U-traps connected at the outflow lines that followed the

diverter valve. The temperature of the traps was optimized at 10°C by determining maximum collection efficiency of the analytes of interest without collection of interfering material. The helium column flow continued through the selected trap during collection, but flow stopped for all other traps at this time. This flow stoppage through non-selected traps allowed for a static condition in the transfer line and the possible condensation of moisture when lower collection temperatures were maintained, despite the back-pressure valve being off. Multiple sample injections were required to collect adequately-sized samples for further testing.

A model HP7673 auto-injector was connected to the injector of the GC and allowed for the continuous and uninterrupted injections of the same GC vial for up to 60 injections. More injections could be made by adding another GC vial to the next position within the auto-injector and programming its use. Potentially, hundreds of same sample injections could be made. However, traps were typically removed after 30 to 50 injections to minimize the potential contamination of the collected analyte. The traps were immediately rinsed with 3- 20μL aliquots of ethyl acetate using a fine tipped pipette, and flushed into a pre-combusted GC vial with pre-combusted insert for small-volume samples. It was found that under these particular trapping conditions, the initial washings from the inlet side of the traps, where analytes predominately collected, efficiently transferred sample to the GC collection vial. Once collected in the GC vial, yield and purity of the analyte of interest was determined using GC/MS and GC/IRMS to determine the concentration and carbon stable isotopic ratio, respectively. After the isolated compound of interest was compared to the previously determined retention time and peak area, and the isotope ratio determined within the mixture of lignin phenols and found to be of adequate yield and purity, separate aliquots of the same sample could be combined and further processed for radiocarbon measurement.

The primary goal of this technique was to determine radiocarbon age of specific compounds found within lignin oxidation products from sediments. It was critical to maintain purity of the isolated compounds by eliminating contamination in all processing and achieving clean complete gas chromatographic separation and collection with minimal baseline contamination. Pre-combusted (575°C) glassware was used to reduce any potential organic contamination in either GC vials or glass apparatus used in processing. Samples were evaporated to dryness using dry nitrogen to remove any ethyl acetate solvent. The removal of the ethyl acetate, previously determined to be of petroleum derivation by its background ^{14}C content, was necessary so as not to dilute the sample of interest with additional carbon. The GC vial insert containing the isolated compound was inserted into a 9mm Pyrex ampoule with an adequate amount of CuO to facilitate complete combustion of the organic compound to carbon dioxide (CO_2) at 575°C over a 6 hour period. The resulting CO_2 was measured for carbon stable isotope ratio on a Finnigan MAT 252 IRMS. Due to the small quantity of CO_2 recovered from the PFC the CO_2 was frozen back into the transfer bulb once analyzed on the IRMS. This analysis was discontinued after finding the GC/IRMS gave substantial confirmation of the recovered compounds $\delta^{13}C$ value. The CO_2 was transferred to a reactor, where the CO_2 was reduced to graphite with hydrogen over an iron catalyst. The graphite formed was pressed into an aluminum target and loaded into a sample wheel containing other unknown samples, standards and background targets. ^{14}C measurements were made using NEC 0.5 MeV AMS.

Standard solutions were prepared to test and determine the fractionation and collection efficiency of the PFC methodology. Mixtures of standards of accurately known concentration and isotopic abundance ($\delta^{13}C$ and ^{14}C) of three lignin phenols were prepared for these tests. One standard was of modern ^{14}C activity while the other two were of fossil fuel ^{14}C activity. Each

displayed unique $\delta^{13}C$ values predetermined by measurement on a Finnigan MAT 252 dual inlet IRMS. PFC collection times and durations were optimized by studying the collection efficiency and purity determined by GC/MS analysis. At the same time, modifying the trapping duration to collect varying amounts of baseline components was made. By this method, comparison of both $\delta^{13}C$ and ^{14}C values before separation and isolation on the PFC and after would indicate potential success on real samples and acquiring accurate $\delta^{13}C$ and ^{14}C signatures.

Sample ^{14}C analysis was determined by measurement and normalization to known ^{14}C activity standards, NIST Oxalic Acid I or II, and comparison to secondary standards. Background ^{14}C activity was measured and subtracted with each group of unknowns using anthracite coal. Extremely low quantities of carbon were recovered from preparative fraction collection and subsequent graphitization of both standard mixtures and samples. Carbon recoveries ranged from <10 micrograms (not measurable) to over 200 micrograms. Primary and secondary standards and background coal were prepared to bracket the mass of carbon in the samples. This was necessary for accurate measurement of ^{14}C in the AMS.

4. RESULTS:

4.1 Physical and Chemical Measurements:

As part of the overall study plan physical parameters were measured at most of the stations on most sampling cruises including water salinity, temperature and depth. These parameters, along with latitude and longitude determined from GPS for each station and each cruise, and surface water volume sampled is listed in table 1. Surface salinity for five cruise dates are displayed in figure 6. All salinity measurements were taken with Orion Corp. model 140 CDS temperature/salinity probe suspended 2 feet below the surface and acclimated to the seawater being measured for at least 2 minutes prior to measurement.

Surface temperatures were recorded using the same Orion Corp. model 140 CDS probe and are listed in table 1. Surface temperature data for four cruise dates are displayed in figure 7.

Chemical analyses were performed on sediment samples retrieved during all the sampling cruises. These analyses included measurement of total organic carbon and total nitrogen in sediment. The %TOC and %TN are listed in table 2 and illustrated in figure 8 representing two spring samplings; March 2002 and 2006, and three winter samplings; November 2002 and 2005 and October 2006. Stations listed on each figure include upriver stations A through H and vary slightly with inclusion of offshore stations such as Sea buoy (SB) and 2 through 4 in March 2006, and South Atlantic Bight (SAB) in May 2006 and a series of M denoted samples from the Little Mud and South River in October 2006. Percent TOC and TN axes are consistent at 0 to 10% and 0 to 0.5% respectively. Figure 9 displays sediment C/N ratio for the first five sampling cruises.

4.2 Lignin Oxidation Products (LOP):

Eleven primary substituted lignin phenols produced by the alkaline cupric oxide process along with the two internal recovery compounds were identified and compared in this study. These thirteen compounds are listed in table 3 along with their abbreviation and mass fragment ions for identification by GC/MS. The complete GC/MS data for all samples are listed in Appendix A.

Table 4 lists percent organic carbon (%OC) and lignin concentrations (mg/100mg OC) by sampling date and material tested. Table 5 lists the sums and ratios of concentrations of different lignin phenol groups which can be used to indicate proportions of angiosperm and gymnosperm, and woody and non-woody plants. Ratios of vanillyl and syringyl acids to their aldehydes are also listed as a description of potential degradation processes. Because the para-hydroxy phenols made up a small portion of the total lignin phenol concentration, the alternative Λ_6 and Λ_8 representing the sum of all vanillyl and syringyl phenols and sum of all vanillyl, syringyl and cinnamyl phenols respectively, were used. The following abbreviations are used throughout the data tables: V = sum of vanillyl phenols, S = sum of syringyl phenols, C = sum of cinnamyl phenols, Λ_6 = vanillyl phenols plus syringyl phenols, Λ_8 = vanillyl phenols plus syringyl phenols plus cinnamyl phenols, Vd = vanillic acid, Vl = vanillin, Sd = syringic acid and Sl = syringaldehyde.

Figure 10 shows the distribution of S/V (syringyl phenols/ vanillyl phenols) versus C/V (cinnamyl phenols/ Vanillyl phenols) ratios for surface sediment samples collected from three sampling cruises; November 2005, March 2006 and October 2006 and the core sample from November 2005 station D. Figure 11 displays the S/V versus C/V ratio and the variation found in particulate organic matter, collected from surface water at each sampling stations during four

separate cruises; November 2005, March 2006, October 2006, and March 2007. The presentation of data in figures 10 and 11 are modeled from previous researchers, particularly the late John Hedges, a pioneer in lignin geochemistry, and modified according to Goñi et al., (2003) as an illustrative means for deciphering plant sources (Hedges et al., 1986, Meyers-Schulte and Hedges, 1986). Boxes represent the typical ratios for angiosperm and gymnosperm woody and non-woody plants. Ovals represent the loci of ratio values for each sampling date. Figure 12 shows the total vanillyl, syringyl and cinnamyl phenols per 100mg carbon versus sampling station for each of five cruises March and November, 2002, March and November, 2005 and October 2006.

4.3 Bulk Sediment $\delta^{13}C$ and $\delta^{15}N$:

Stable isotope measurements were made on acid treated sediment samples collected from five sampling cruises. An isotopic composition was determined with respect to carbon and nitrogen on the bulk material because this represented all sources of organic carbon and nitrogen found in both terrestrial and marine environments. Stable isotopic values are reported relative to the international standard V-PDB for carbon isotopes and to international standard air for nitrogen isotopic values. Isotopic $\delta^{13}C$ and $\delta^{15}N$ data is listed in table 2. Figure 13 illustrates the $\delta^{13}C$ and $\delta^{15}N$ variation from upriver sites to Altamaha Sound (A through I) including the Mud River samples (M) and a few offshore stations SB (Sea buoy at sound), 2, 3, and 4 (seaward to Gray's Reef) and SAB (South Atlantic Bight) station for the first five sampling cruises. Figure 14 illustrates a combination of all $\delta^{13}C$ values for the first five sampling cruises. To help decipher a seasonal dependence on isotopic abundance, composite data is reformatted in figure 15 beginning with upriver "A" followed by all of collective data for that station, in sequential order, to offshore "SAB" station. Included in this data are samples collected from the Mud River

and Altamaha Sound during October 2006 and March 2007 sampling cruises. A general trend of enrichment in sediment $\delta^{13}C$ from upriver stations to lower river stations and variable but generally enriched $\delta^{13}C$ values within the Altamaha sound, Mud River and Doboy sound are revealed.

4.4 Lignin Oxidation Products (LOP) $\delta^{13}C$:

Lignin biomarkers are useful in identifying terrestrial biopolymers from plant tissue, humic extracts and sedimentary mixtures in marine systems. Lignin phenols are utilized due to the stability of lignin in vascular land plants, their absence from organisms and their ease of analysis through alkaline CuO oxidation of organic matter (Hedges and Ertel, 1982). The $\delta^{13}C$ value of lignin derived biomarkers, range from -16‰ to -18‰ for C_4 plants such as *Spartina* and differentiates from those of the C_3 plants which range from -27‰ to -35‰ (Fogel and Cifuentes, 1993, Benner et al., 1987, Goni and Eglinton, 1996).

A comparison between sediment and total LOP $\delta^{13}C$ is portrayed in figure 16. Lignin isolation was performed as per the method previously described and modified from Goni et al (2005). An untreated sediment sample along with its LOP extract were combusted at 900°C and carbon dioxide was used for stable carbon isotopic analysis using a dual inlet IRMS with typical $\delta^{13}C$ precision ± 0.02. The $\delta^{13}C$ values of these particular samples are listed in table 6.

During the November 2005 and March 2006 cruises, surface seawater samples were collected for particulate organic matter (POM) measurements. These determinations should clarify the abundance and nature of the suspended material transported down the Altamaha River to the Atlantic Ocean. These samples were limited in their recovered quantities which allowed for only a few selected measurements. The $\delta^{13}C$ of the POM and sediment samples for these two cruises are listed in table 6 and figure 17.

4.5 Continuous Flow versus Dual-Inlet $\delta^{13}C$ Measurements:

Two separate sample introduction techniques were used during this study for isotopic ratio analysis. Bulk carbon isotopes in our acid treated sediment samples from the various sampling cruises were used to compare both continuous mode analyses to confirm reliability of data between these two techniques. One using a Carlo-Erba elemental analyzer (EA) interfaced to a Thermo Finnigan IRMS housed in the University of Georgia's Institute of Ecology and from a Finnigan MAT 252 dual inlet IRMS at the CAIS. Data generated from this comparative analysis is listed in appendix B. Figure 18 displays graphically the comparison of over 50 samples between the two techniques.

4.6 GC/IRMS $\delta^{13}C$ of Lignin Oxidation Products:

Accuracy of GC/IRMS continuous flow measurement of lignin oxidation products was substantiated using individual lignin phenol standards first characterized isotopically by off-line combustion and dual inlet mode analyses on a Finnigan MAT 252 IRMS. High purity (>99%) Aldrich and Fluka Chemical Company standards of thirteen lignin phenols were combusted at high temp (900°C) in quartz ampoules and processed without derivatization to CO_2.

Three methods of derivatization correction were considered. First, according to Goñi and Eglinton (1996) ethyl vanillin could be used to determine the value of the TMCS by using equation 5 below. This calculated TMCS value would be used in equation 2 to derive an underivatized $\delta^{13}C$ value for an unknown compound. A second method is to measure the TMCS $\delta^{13}C$ on a high precision IRMS without derivatization carbons being added. These two techniques could be used with any number of standards including the t-Cinnamic acid standard. Although the average corrected value of each compound was similar to their underivatized analog, the variance was greater with the trans-cinnamic acid standard relative to the ethyl

vanillin standard. As a result, ethyl vanillin was used as the primary correcting standard. A third approach used to determine the underivatized LOP value was to apply a correction value to each of the 13 LOP based on their computed TMCS $\delta^{13}C$ value. This approach minimized variations due to the derivatization efficiency of a specific compound, or its ability to fully substitute the hydroxyl hydrogen without fractionation. Because this method forced the standard LOP to their respective off-line determined $\delta^{13}C$ values, no measurement of derivatization error could be determined. However, replicate analyses of each standard were performed and can be used as a measure of the precision of this technique. A comparison of results based on the first two methods above is displayed graphically in figure 19. The single correction algorithm based on ethyl vanillin or the dual inlet measured TMCS correction algorithm results in very similar $\delta^{13}C$ values for a number of isotopically defined standards.

A complete list of Lignin Oxidation Products analysis by GC/IRMS for all sediment, particulate organic matter and core sample is presented in table 7. Derivatization correction was made using dual-inlet IRMS measured BSTFA/TMCS $\delta^{13}C$ values and equation 2. Results are relative to international standard PDB and units of ‰.

To assess the derivatization efficiency of each of the principal compounds in this study the computation of $\delta^{13}C$ using the TMCS was determined for comparison to the off-line determined value. The average $\delta^{13}C$ value for each LOP standard was determined from replicate analysis and the resulting value applied to the following equation 5:

$$\delta^{13}C_{TMCS} = \frac{\left(\delta^{13}C \cdot \#C\right)_{Der} - \left(\delta^{13}C \cdot \#C\right)_{Under}}{\#C_{TMCS}} \qquad \text{Equation 5.}$$

Where $\delta^{13}C_{Under}$, $\delta^{13}C_{Der}$ and $\delta^{13}C_{TMCS}$ are the $\delta^{13}C$ values for the underivatized LOP, derivatized LOP and derivatizing agent TMCS respectively, and #C represents the number of

carbons in each respective compound. The computed TMCS $\delta^{13}C$ values are listed in table 8 along with values for the 13 LOP standards indicating good agreement to the off-line value, measured previously at -40.50 ‰.

Table 8 lists the $\delta^{13}C$ values and standard deviations, based on a minimum of triplicate analyses for IRMS determined standards under the heading "accepted". Also included in table 8 are the results of the two different calculation algorithms for the computation of underivatized LOP based on measured $\delta^{13}C$ values and either measured or computed $\delta^{13}C$ values of derivatizing agent BSTFA/TMCS.

$\delta^{13}C$ values are graphically displayed in figures 20 and 21 for the eight primary lignin phenol components extracted and isolated from sediments from November 2005 and March 2006 samplings and extracted and isolated from both sediment and POM from the October 2006 sampling, respectively. Sampling stations from upriver station "A" through Altamaha Sound station "H" and continuing offshore to SAB are listed in both figures.

4.7 ^{14}C Content of Sediment, LOP and POM:

Samples were collected for ^{14}C measurement during six sampling cruises between March 2002 and March 2007 on the Altamaha River and out an additional 20 miles to Gray's Reef National Marine Sanctuary on the inner Atlantic Shelf. The first two sets of samples from March and November 2002 were provided by Dr. Ji-Hong Dai and the May, 2006 SAB sample provided by Dr. Wei-Jun Cai. All other samples were collected personally with assistance from colleagues at the University of Georgia Center for Applied isotope Studies, Marine Science department and Captain and crew of the RV Spartina of Sapelo Island Marine Institute.

Samples consisted of surficial sediment samples (SED) collected using box corer or Ponar dredge sampler; surface seawater, for particulate organic matter (POM), collected during

most cruises and sampling stations; and total lignin oxidation products prepared from sediment and particulate organic matter samples. All samples prepared for ^{14}C measurement underwent acid treatment to remove carbonates, combustion to carbon dioxide and graphitization over iron catalyst. Carbon dioxide was either split for $\delta^{13}C$ analysis for ^{14}C correction or measured using IRMS and the CO_2 recovered for graphitization. Duplicate sample analyses were run on approximately 5% of the samples. Complete data tables for Sediment and POM samples are listed in table 9 and for LOP samples are listed in table 10.

Measurements of ^{14}C are reported in percent modern carbon (pMC) relative to NIST Oxalic Acid 1 and the 1950 activity level of 13.56 disintegrations per minute per gram carbon (dpm/gC) or 100% modern (pMC) and by convention use the Libby half-life of 5568 years (Libby, 1955). Conversion to radiocarbon age, reported as years before present (YBP) and per mil ^{14}C ($\Delta^{14}C‰$) is done mathematically. Results are reported using a 1-sigma standard deviation and $\delta^{13}C$ is used to correct for isotopic fractionation of ^{14}C activity based on equation 6 below.

$$\Delta^{14}C_{Corr} = \Delta^{14}C_{Meas}\left[1 - \frac{\left(2(25 + \delta^{13}C\right)}{\left(1000\right)}\right] \qquad \text{Equation 6.}$$

Figures 22, 23 and 24 portray the ^{14}C data, for November 2005, March and October 2006 sampling cruises, allowing an overview of an entire single survey data set. Figures 22 and 23 include SED (total carbonate free sediment), LOP (lignin oxidation phenols) and POM (particulate organic matter) ^{14}C data while figure 24 includes only SED and LOP ^{14}C data. All three figures include sample stations “A” through “H” and additional stations I, SB, 2, 3, 4, SAB (South Atlantic Bight), the furthest station sampled offshore, and Mud River samples denoted by prefix M. All figures include the NIST ^{14}C OXI standard activity line (dashed horizontal)

representing 104.6 pMC. This ^{14}C activity line is meant only as a reference for comparison and is approximately 2% lower than the present day $^{14}CO_2$ activity level of the atmosphere. It is denoted on the graphs as "Modern" to reflect this activity level.

An important part of this study was to investigate the effect of local mineralogy and particle size on the bulk sediments, suspended particles and particularly lignin distribution in the shelf region beyond the Altamaha Sound. Four size fractions were selected based on average particle size for sediments collected between stations H and SAB, beyond Gray's Reef. Coarse size greater than 20 mesh (standard sieve) or 1 mm nominal diameter, greater than 35 mesh or 0.5 mm diameter, greater than 60 mesh or 250 micron diameter and the pan or residual less than 60 mesh grain size. These size fractions were separated using the wet-sieve method on sediment samples collected at stations "H, 2, 3, 4 and SAB". The collected size fractions were acid treated to remove inorganic carbonates, rinsed and dried at 50°C overnight. The fractions were weighed and a display of normalized weight fraction is shown in Figure 25.

^{14}C activity was determined on each fraction of the acid treated sediment (SED) fractions when adequate carbon was available. Total lignin phenols (LOP) were recovered from each of the same sediment fractions. The ^{14}C and $\delta^{13}C$ for each fraction and type (SED or LOP) is listed in table 11 for each of 5 sampling stations "H" through "SAB". Figure 26 displays the same data graphically as 14C activity for sediment and LOP for four different particle size fractions from five different stations offshore Altamaha Sound. Missing data points are due to unrecoverable material.

4.8 Compound Specific Radiocarbon (^{14}C) Analysis:

Prior to analyzing unknown samples through the CSRA technique some preliminary analysis of standard materials and recoveries needed to be established. Because chromatographic

separation, and trapping in the case of preparative fraction collection, could lead to isotopic fractionation of both $\delta^{13}C$ and ^{14}C it is critical to separate and isolate chromatographic peaks efficiently and without contamination. Standard solutions of known lignin compounds were prepared and analyzed under varying conditions of fraction collection. Extended baseline collection was made on standard solutions around selected peaks to determine background contribution to the ^{14}C content. A second series of standards was sent to another AMS facility for confirmation of results. Data is presented in table 12 for these standard recovery tests. Once the proper chromatographic conditions and recovery conditions were applied, a suite of samples from stations within the Altamaha River, estuary and offshore, sampled at different seasons, were analyzed by CSRA and listed in table 13.

5. DISCUSSION OF RESULTS:

5.1 Physical and Chemical Measurements:

Surface salinity increased from upriver stations to the Altamaha Sound as expected from estuarine dynamics. As can be seem in figure 6, surface salinity exhibited a greater rate of change during the winter sampling in 2002 relative to other sampling dates. Also, the level of salinity at upriver station A and progressing toward the sound was higher during winter samplings in 2005 and 2006 than during spring sampling of those same years. The lowest upriver salinities were determined from station A through F in both March 2002 and March 2006 samplings. These correspond to higher discharge of the Altamaha River during spring flooding maintaining a freshwater load further downriver than in winter. Coastal seawater salinities of greater than 30 parts per thousand were attained past station H and within Altamaha Sound, for all sampling seasons. Mud river samplings indicate a high salinity is maintained even during winter due to its proximity to Altamaha sound and tidal zone.

Water temperatures were highest, indicated in table 1 and figure 7, for samples from March 2002 but differ by no more than 5 degrees from other seasonal samplings at all upriver stations except A. A discernable cooling of the surface seawater was determined for the off-shore stations during the March 2002 and 2006 samplings. The consistency of the March 2006 surface water temperature measurements approaching Gray's Reef, approximately 20 miles offshore, is an indication of the extent of off-shore currents bringing cooler water along the coast during late winter and early spring. A slight increase of seawater surface temperature was recorded during November 2005 approaching Gray's Reef indicating increasingly warmer surface water currents

offshore. It may also reflect the influence of cooler river water diluting this warmer off-shore surface water as it flows from the sound. The Mud River surface water temperature may support this observation in that all the surface seawater temperatures measured during the October 2006 sampling cruise fall within the average of the upriver and offshore surface water temperatures during the November 2005 sampling.

%TOC and %TN exhibit characteristic decrease in values as we progress from upriver to the offshore stations, as shown in figure 8, with the exception of the October 2006 sampling. This particular sampling cruise, indicate a trend of increased %TOC and %TN for both stations A through H and for stations M1 through M7. Mud River stations are in proximity to both Altamaha and Doboy Sound. Within this tidally dominated region, it is possible stations M1 through M7 would not show a pattern of decreasing TOC or TN within its boundaries. The observed trend in stations A through H during the October 2006 sampling may be due to different particle size distribution in sediment affecting availability of material. Even in higher flow spring samplings, lower TOC and TN were observed for station A sample which were predominantly composed of sand and silt size particles. Lower %TOC and %TN was observed for other downriver stations, where higher levels might be expected, possibly due to varying particle size distribution. This is evident in both November 2005 and October 2006 upriver stations where collected sediment samples were composed of sand size particles dominating this upriver region.

The largest downriver variation in %TOC and %TN were found during March of 2002 and 2005 samplings with %TOC and %TN approaching 10 and 0.5% respectively. High flow rate of the Altamaha River at this time of year is responsible for conducting a high load of organic carbon from more distant points of origin and depositing it further offshore than in

winter. In contrast, November 2002 and 2005 and October 2006 samplings have lower upriver %TOC and %TN values, but appear to persist longer downriver than those observed during spring samplings.

C/N ratios were determined for Altamaha River and offshore sampling stations for five sampling cruises and are presented in figure 9. C/N ratio indicates a general decreasing ratio from upriver station A to offshore station 4 at Gray's Reef. The November 2005 station "A" value was displayed to indicate how very low organic carbon content samples (0.1% TOC) can exhibit C/N ratios far removed from the normal trend-line.

5.2 Lignin Oxidation Products (LOP):

The organic carbon content of the samples collected as part of this study varied considerably from kilometers upriver to kilometers offshore of the coast. This is a direct indication of the complexity of the carbon sources and sinks within an estuarine system. The major thrust of this study was to use specific compounds, indicative of terrestrial plants to isolate this carbon source from those of the marine environment. The particular biomarker lignin was selected for its unique association to land derived vascular plants and its stability in nature. Lignin polymers make up the structural components of most all land plants and are therefore quite ubiquitous in nature. However, when these structural macromolecules are broken down, by well established chemical processes, into monomers of substituted phenols, their products can reveal the particular plant source of origin.

Lignin makes up a large portion of terrestrial plant biomass and is present in two major classes of vascular plants. Angiosperms include flowering plants, herbs, grasses and hardwood trees and produce vanillyl and syringyl phenols during lignin oxidation. Gymnosperms, in contrast, include non-flowering plants and coniferous trees and produce only vanillyl phenols

during lignin oxidation. A third group of lignin phenol substituted compounds are the cinnamyl phenols which possess an unsaturated double bond within their structure and are found exclusively in non-woody material. Both vanillyl and syringyl phenols are found in woody materials. Therefore, lignin phenols can be used as plant specific biomarkers, indicative of plant type and material not only in the terrestrial environment but within the marine environment as well. By computing the ratios of total syringyl to total vanillyl phenols a relative proportion of angiosperm to gymnosperm derived material can be made since only angiosperm plants produce syringyl phenols. By computing the ratios of total cinnamyl to total vanillyl phenols a relative proportion of non-woody to woody derived material can be made since only non-woody plants produce cinnamyl phenols.

The lignin phenols recovered from sediments and suspended particles within this study varied considerably due to sediment morphology across the sampling region. Finer grained sediments and suspended particles contained higher organic carbon concentrations and therefore potentially a higher proportion of lignin phenols. In contrast, coarse sandy sediments recovered from off-shore shelf locations such as Gray's Reef, had much lower organic carbon concentrations and accordingly much lower recoverable lignin phenols. To compensate for this proportion and allow for correlation to the total organic carbon in the samples, lignin phenol concentrations are normalized to 100 grams of organic carbon. This is accomplished by first quantitatively determining, using GC/MS, the concentrations of the unknown samples by comparison to the retention times and retention factors (unit area per nanogram) of a standard suite of the thirteen phenols. Duplicate and triplicate analyses of both standards and unknowns were measured after derivatization and statistically reviewed for outlier data. Second, the total organic carbon concentration of the sediment was determined after acid treatment to remove

inorganic carbon such as marine shell material. Total organic carbon was determined by direct high temperature combustion and isolation of combustion gases including carbon dioxide which can be equated to the original organic carbon concentration. Lignin phenol concentrations are then normalized to the total organic carbon concentration and listed in milligram per 100 milligrams OC (mg/100mgC).

Tables 4 and 5 reveal a few general aspects of terrestrial organic matter transported down and deposited within the Altamaha River. Of the 47 sediment samples analyzed, average normalized concentration of all syringyl phenols (angiosperm plant derived) was 2.63 ± 1.14 mg per 100 mg OC. This constitutes approximately 42 ± 18% by weight of total lignin phenols. Similar, but slightly lower was the concentration of vanillyl phenols, common to both gymnosperm and angiosperm plants, at 2.19 ± 0.90 mg per 100 mg OC or 35 ± 14% by weight of total phenols. Cinnamyl phenols, derived exclusively from non-woody plants, made up 17 ± 12% by weight with an average concentration of 1.04 ± 0.76 mg per 100mg OC. The 7% balance is made up other lignin phenols such as the para-hydroxy phenols and others not tested for in this study. On average, these values would suggest a rather heterogeneous mixture of plant derived material transported within the Altamaha River. The large watershed composed of coniferous forests, hardwoods trees, flowering plants and extensive agriculture, certainly would support a diverse input of terrestrial carbon into the Altamaha River.

The proportions of individual or grouped lignin phenols found in these samples are descriptive of the variety and extent of plant sources from which they occur. Because vanillyl phenols are common to both gymnosperms and angiosperms, we use this group of phenols to ratio with syringyl phenols, found only in angiosperm hardwoods and flowering plants, and with cinnamyl phenols, found only in non-woody plants. S/V to C/V ratios shown in figures 10 and

11, reveal a rather heterogeneous mixture of plant derivations with no single source of lignin within sediment or particulate organic matter. This is evident based on the absence of data points on either axis which would indicate the absence of either syringyl or cinnamyl component. This is not the case here, rather, the cluster of points slightly above S/V =1 imply a slightly higher proportion of syringyl to vanillyl phenols. Likewise, the cluster of points around C/V = 0.4 imply a vanillyl proportion nearly twice that of cinnamyl phenols. Although the S/V or C/V ratios do not appear to be dependent on upstream or downstream sampling location, the mean value and trend of each sampling time differ enough to imply a distinct variability in deposition patterns within these sampling times. For example the two winter samplings, November 2005 and October 2006, exhibit a rather narrow range of variation in syringyl phenol content across the sampling sites relative to the March 2006 samplings. This can also be seen in figure 12 comparing total vanillyl and syringyl versus station and date of sampling. However, the October 2006 samplings during low flow exhibit considerably more diversity in both the C/V and S/V ratios. This could imply varying regions and conditions of deposition and re-suspension of bottom sediment within the same season. A similar diversity may be evident for samples collected during high flow periods such as March 2002 and 2006 as well. This is also evident from the total vanillyl and syringyl versus station in figure 12. March 2002 samples exhibit low diversity in both S/V and C/V ratios whereas March 2006 samples exhibit a large range for both S/V and C/V ratios, although both have similar averages when all samples within a single collection time are considered.

S/V versus C/V ratio of particulate organic matter in figure 11 indicates unique lignin phenol signatures for each set of surface water samplings. November 2005 sampling exhibits data with low but fairly consistent S/V ratios across a broad variation in C/V ratio. C/V ratios

again imply a very diverse environment with regard to terrestrial inputs. C/V ratios in figure 11 for the November 2005 sampling range from 0 at a mid-river sampling station, indicating absence of non-woody material, to nearly a one-to-one ratio of C/V indicating a large proportion of non-woody angiosperm plant matter. One data point, associated with the sampling station just upriver of the Hatch power generating station 70 miles upstream of the sound and salt-marsh environment, exhibits a very low C/V value indicating very little non-woody material. Based on the evidence, supporting absence of non-woody cinnamyl phenols at this upriver site and absence of *Spartina* cordgrass this far from the coast it may be reasonable to assume the principle supplier of cinnamyl phenols downriver within the estuary is the prominent cordgrass *Spartina*. Data points for the October 2006 sampling of POM are also unique in regard to their very low S/V ratio. This implies very low syringyl phenol content, suggesting low angiosperm content relative to other stations and sampling times. A single core section recovered during the November 2005 sampling exhibits a consistent level of syringyl phenols relative to the vanillyl phenols. However, nearly a five-fold change can be seen in the C/V ratio within the core sections analysis indicating variation in source material over time.

The relative abundance of specific lignin phenols have been used to distinguish woody from non-woody plants as well as angiosperm from gymnosperm species, (Moran and Hodson, 1994, Onstad et al., 2000, Hopkinson et al., 1998). In addition, the ratio of specific lignin phenols, specifically the acids to aldehydes, can reveal the degree of oxidative degradation in organic matter. However, the amount of degradation of organic matter is difficult to assess in most environments and can be misinterpreted due to other acidic components in the organic matter derived by fungal or microbial alteration (Goni et al., 1993). Table 5 data reveals a relatively consistent vanillyic acid to vanillin (Vd/Vl) ratio and syringic acid to syringaldehyde

(Sd/Sl) ratio for sediment samples collected during the first five sampling cruises. Ratio of Vd/Vl range between 0.14 and 0.45 and display only minor variation and trend toward highest ratios nearest Altamaha Sound. Ratio of Sd/Sl range similarly with most data for the same sampling cruises falling between 0.15 and 0.35 with less of a trend toward higher ratios toward the Altamaha Sound. This information suggests a consistent level of degradation throughout the Altamaha River including older sediments. The results from table 4 would support this conclusion as the aldehyde concentrations for both vanillin and syringaldehyde are typically 3 times higher than the acid equivalent suggesting a low level of degradation.

The diversity of carbon sources, especially those of terrestrial origin, particle transport and sediment hydrodynamics make source plant allocation difficult in the Altamaha River, by classical chemical and lignin phenol analysis alone. Possibly, with the addition of ^{14}C age to the equation, a better understanding of the degradation processes and level may be realized.

5.3 Bulk Sediment $\delta^{13}C$ and $\delta^{15}N$:

Figure 13 portrays variability in isotopic composition in organic carbon and nitrogen that would be expected from sediment in such a complex environment as the Altamaha River estuary. A minor correlation exists between $\delta^{13}C$ and $\delta^{15}N$ values along sampling transect from upriver stations to the sound within each cruise. Although this correlation does not follow a similar pattern between sampling cruises, it does signify how enrichment processes that occur through degradation or through transport processes affect both isotopic abundances in a similar manner. Unfortunately, only a few per mil enrichment is observed for sampling stations at or beyond the Altamaha Sound such as station I, SB (Sea buoy at sound), 2, 3, and 4 (seaward to Gray's Reef) and SAB (South Atlantic Bight) station. This would be expected as greater input of marine phytoplankton in the lower reaches of the river find its way to the sediment and dilutes a

terrestrial plant signal, assuming an exclusively C3 plant origin. However, this assumption is not valid in either scope of this study to delineate C_3 and C_4 terrestrial inputs or based on knowledge of botanical assemblages within the Altamaha River basin.

As indicated in the composite of five samplings in figure 14, the majority of sediment data falls within $\delta^{13}C$ range of -21.22 to -24.50 ‰ (average -22.86 ± 1 sigma), other than a few outlying data points such as November 2002 station D at -15.82 ‰ and November 2005 station A at -27.85 ‰. This range is consistent with a combination of earlier estimates of $\delta^{13}C$ values for C_3 and C_4 plants (Bender, 1971, Goni et al., 1998), and suggests a mixture of plant groups of not only C_3 and C_4 photosynthetic pathway but of terrestrial and marine derivation. Only a slight enrichment in $\delta^{13}C$ value can be seen for each sampling cruise from upriver stations to the South Atlantic Bight except for November, 2002 where an enrichment of $\delta^{13}C$ value is evident beyond station "D".

To help decipher a seasonal dependence on isotopic abundance, composite data is reformatted in figure 15 beginning with upriver "A" followed by all of collective data for that station, in sequential order, to offshore "SAB" station. Included in this data are samples collected from the Mud River and Altamaha Sound during October 2006 and March 2007 sampling cruises. A general trend of enrichment in sediment $\delta^{13}C$ from upriver stations to lower river stations and variable but generally enriched $\delta^{13}C$ values within the Altamaha sound, Mud River and Doboy sound are revealed.

5.4 Lignin Oxidation Products (LOP) $\delta^{13}C$:

In this study, lignin phenols were extracted from a number of sediment and particulate organic matter samples recovered during six sampling cruises. Some lignin extracts were prepared for total lignin $\delta^{13}C$ and ^{14}C analysis. These specific samples were extracted from

sediment and their lignin phenol compounds recovered by the previously described and modified method (Goni et al., 2004) into ethyl acetate. Samples were dried under nitrogen, combusted at 900°C to carbon dioxide which was measured with typical $\delta^{13}C$ precision ± 0.02 using a dual inlet IRMS. Data comparing the $\delta^{13}C$ of these sediment, particulate organic matter and lignin oxidation products are listed in table 6.

The data presented in figure 16 indicate depletion in $\delta^{13}C$ of lignin phenols relative to the bulk sediment $\delta^{13}C$ by an average 1.89 ‰ for nearly all samples. Lignin phenols in general are consistently lighter in $\delta^{13}C$ relative to sediment. Previous research has demonstrated variation in isotopic $\delta^{13}C$ abundance based on organic compound class (Fogel, et al 2003). The variation can be based on factors such as selective degradation or availability for bacterial consumption or substrate size (Benner et al, 1989). Lignin, known to be more refractory in sediments than other organic substrates such as proteins and carbohydrates, exhibits a regular depletion in $\delta^{13}C$ relative to sediment $\delta^{13}C$. The March 2006 samples shown in figure 16 for offshore stations 3 and 4 are the exception. Total lignin phenol $\delta^{13}C$ for these samples are 5 and 8‰ depleted relative to sediment $\delta^{13}C$. The $\delta^{13}C$ of these particular samples is the average for two size fractions: larger than 1 mm (20 mesh) and smaller than 250 μm (60 mesh), representing 33 and 38% of total sediment mass respectively. These size fractions were used for both bulk sediment and lignin isolation as part of another portion of this study for ^{14}C abundance but were used here as well to demonstrate the substantial effect due to particle size. Also significant is a general trend of $\delta^{13}C$ values and their magnitude for sets of sediment samples and their associated lignin fraction. A general enrichment of up to 4‰ is indicated for most sets and greater than 6‰ indicated by November 2002 station D samples. Enriched $\delta^{13}C$ values may indicate a greater proportion of C_4 plant material, primarily *Spartina*, as its abundance increases downriver. This is

indicated by bulk sediment and lignin $\delta^{13}C$ values tracking to enriched values downstream. If the bulk isotopic value was due to a greater proportion of marine organisms, devoid of lignin, rather than a C_4 plant, the sediment $\delta^{13}C$ would not have been as enriched in $\delta^{13}C$ as observed here.

A comparison of sediment $\delta^{13}C$ and POM $\delta^{13}C$ from identical cruise stations is made in figure 17. The POM $\delta^{13}C$ values displayed are consistently depleted relative to sediment $\delta^{13}C$ except at the upriver station "A". Very slight seasonal difference can be concluded from this data as the spring POM $\delta^{13}C$ values reflect less change from upriver values to the Altamaha Sound. Higher flow rates and faster transport times may reduce variation seen in both sediment and POM samples from upriver stations to the Altamaha Sound. Also apparent from this data is the influence of increasingly diverse organic matter content on surface sediments as $\delta^{13}C$ values become enriched toward the lower Altamaha River near station "E" and remain moderately enriched in $\delta^{13}C$ to Altamaha Sound.

5.5 Continuous Flow versus Dual-Inlet $\delta^{13}C$ Measurements:

Numerous comparisons of stable carbon isotopic abundance have been made so far with respect to parameters such as location, season and chemical class. These previous measurements have been made using an isotopic technique incorporating a dual inlet source and relatively large volumes of sample (2 – 100 μmoles CO_2) run against a standard reference carbon dioxide at the same relative volume resulting in a high precision analysis of 0.01‰. This analysis is considered more accurate and precise than the "continuous flow" method where either gas chromatographically separated components, at concentrations as low as 10 nanograms, is followed by combustion to CO_2 and isotopic measurement by GC/IRMS or EA/IRMS where samples of concentrations as low as 10 micrograms are combusted first followed by chromatographic separation of combustion gases followed by isotopic measurement. Both

require standard gas introduction at the beginning of a measurement and sometimes strategically placed within the run as compared with dual inlet mode where standards and samples are alternatively analyzed for maximum precision. Figure 18 displays the good agreement (F-test =0.46) found for over 50 samples between the two techniques and substantiated our confidence in using both of these techniques in this study.

5.6 GC/IRMS $\delta^{13}C$ of Lignin Oxidation Products:

The GC/IRMS technique requires derivatization of less volatile substances prior to analysis. This is the case with lignin phenols which require the replacement of hydroxyl hydrogen bound in their structure to make them amenable to chromatographic separation. The TMCS derivatization reagent described earlier replaces 3 methyl groups for each of the hydroxyl hydrogen. Since each compound had either 3 or 6 methyl groups added (acids had 6) an accurate measurement and apportionment of these derivatization carbons must be made. The measurement of the derivatization agent TMCS was made using ampoule combustion and dual inlet analysis using the Finnigan MAT 252 IRMS. The same TMCS was used for hundreds of derivatizations. By combining at least five 1ml ampoules together and analyzing the composite an accurate correction for added carbons during derivatization was applied. The $\delta^{13}C$ value for triplicate analyses of the TMCS was -40.50 ± 0.05. Equation 2 was used to correct for the additional carbons according to isotopic mass balance:

$$\delta^{13}C_{Under} = \frac{\left(\delta^{13}C \cdot \#C\right)_{Der} - \left(\delta^{13}C \cdot \#C\right)_{TMCS}}{\#C_{Under}} \qquad \text{Equation 2.}$$

Where $\delta^{13}C_{Under}$, $\delta^{13}C_{Der}$ and $\delta^{13}C_{TMCS}$ are the del values for the underivatized lignin phenol, derivatized lignin phenol and derivatizing agent TMCS, and #C represents the number of carbons in each respective compound.

The lignin phenol standards were accurately defined without derivatization on a dual inlet IRMS and these were considered the "accepted" $\delta^{13}C$ value for each standard. These values were then compared to the derivatized standards measured on a Delta XLplus GC/IRMS after correction for the added carbons. A comparison was made between the accepted $\delta^{13}C$ value and GC/IRMS corrected values using the $\delta^{13}C$ value measured on the TMCS by dual inlet measurement. An example containing one set of triplicate analysis shows the variation of this suite of thirteen lignin phenol compounds after such treatment. Numerous suites of standards were measured with similar variations but not systematic with regard to particular lignin phenols. Even though TMCS was accurately defined with regard to its associated carbons, repeated measurements of standards indicated variability between standards within the mixture of thirteen compounds. Variability was likely a result of incomplete substitution, possible isotopic fractionation of derivatized compound or poor chromatographic integration by the isotopic software. The former is suggested because a comparison of chromatographic peak heights, determined during GC/IRMS runs varied by as much as 20% in some standards. This indicates loss of specific compounds, incomplete derivatization or even loss of derivatization carbons. This last point was revealed during GC/MS analysis where ion fragment patterns indicated presence of both derivatized and underivatized standards within the same sample, possibly due to high temperatures within the GC oven. The poor chromatographic integration was a problem as well but in most cases could be corrected by manually reintegrating and computing a new corrected isotopic value. The approach suggested by Goni and Eglinton (1996) was also applied where the internal standard compounds ethyl vanillin and trans-cinnamic acid were used to correct for variability in derivatization as well as for process variation. Results using ethyl vanillin were more consistent than with trans-cinnamic acid. Possibly because of the formers

similarity to phenols in general and the acids lack of phenolic hydroxyl group. The approach made use of the ethyl vanillin and trans-cinnamic acids derivatized $\delta^{13}C$ value to compute the TMCS value rather than use the "accepted value" defined by dual inlet IRMS. Using the following equation ethyl vanillin was forced to match its accepted value by computing an appropriate TMCS $\delta^{13}C$ value. This $\delta^{13}C$ was then used to correct the other derivatized standards according to equation 5.

$$\delta^{13}C_{TMCS} = \frac{\left(\delta^{13}C \cdot \#C\right)_{Der} - \left(\delta^{13}C \cdot \#C\right)_{Under}}{\#C_{TMCS}} \qquad \text{Equation 5.}$$

Where $\delta^{13}C_{Under}$, $\delta^{13}C_{Der}$ and $\delta^{13}C_{TMCS}$ are the del values for the underivatized LOP, derivatized LOP and derivatizing agent BSTFA/TMCS, and #C represents number of carbons in each respective compound.

Figure 19 indicates most of the "accepted" $\delta^{13}C$ values for the lignin phenol standards fall between values determined by one or the other of these two methods of calculation of underivatized $\delta^{13}C$. Based on numerous analyses of the 13 lignin phenol standard suite, it was determined the more appropriate correction algorithm made use of the IRMS determined TMCS value. As indicated graphically below, EV calculated TMCS value matched the accepted $\delta^{13}C$ value for syringic acid (Sd) far better than measured TMCS value. This prevalent lignin phenol is characteristic of angiosperm plants and has application to the degree of degradation when ratioed with syringaldehyde (Sl). Therefore, its correct isotopic assessment is important in interpretation of this data. To that end, another algorithm was designed based on individual compounds. A slight modification to the "accepted value" for the TMCS can be made using the approach by Goni and Eglinton (1996) but rather than use the internal standard ethyl vanillin (EV) as normalizing $\delta^{13}C$, the standard LOP for a specific compound of interest, such as syringic acid

(Sd) would be used to determine the TMCS value and subsequent correction algorithm. Data in table 8 indicate no particular correction algorithm is best. The single value TMCS correction makes calculations simpler but lacks accuracy for all LOPs, whereas individually determined TMCS values for each standard could be more accurate but far more cumbersome and excessive relative to inherent precisions of GC/IRMS.

By applying the primary correction algorithm using dual-inlet IRMS measured TMCS $\delta^{13}C$ the measured GC/IRMS data for all six sampling cruises were corrected for their added derivatization carbons. A complete list of GC/IRMS derivatization corrected data is presented in table 7. $\delta^{13}C$ values are graphically displayed in figures 20 and 21 for the eight primary lignin phenol components extracted and isolated from sediments from November 2005 and March 2006 samplings and extracted and isolated from both sediment and POM from the October 2006 sampling, respectively. Sampling stations from upriver station "A" through Altamaha Sound station "H" and continuing offshore to SAB are listed in both figures. Each figure maintains for comparison the same Y-axis $\delta^{13}C$ range from -5 to -45 (per mil scale relative to PDB standard). Vanillyl groups are labeled as square shapes and syringyl groups as diamonds, each aldehyde as filled shape, ketones as gray shape and acids as open shapes. Para-coumaric acid is labeled as open triangles and ferulic acid as open circles. Missing data points indicate inadequate sample for lignin recovery.

The first observation from figures 20 and 21 is although the component $\delta^{13}C$ values vary considerably downriver to the sound, the series of level of depletion in $\delta^{13}C$ progresses from the cinnamyl to vanillyl to syringyl lignin in sediment as well as POM. Indicating syringyl lignin (angiosperm derived) is lighter and more depleted in $\delta^{13}C$ relative to vanillyl and cinnamyl lignin. The cinnamyl lignins; coumaric and ferulic acid, represent non-woody plant material and

display the most enriched $\delta^{13}C$ values near -10 to -20‰ for nearly all sampling cruises. Values this enriched in $\delta^{13}C$ are also found in offshore station SAB during November, 2005 sampling. This would indicate a C_4 plant source makes up a significant proportion of the non-woody component in lignin within these sediments. A likely candidate for this C_4 plant could be *Spartina* grass found throughout this coastline in the expansive salt-marshes. Another explanation may be the formation of higher concentrations of the cinnamyl acids by degradation from fungi and wood rot organisms as suggested by Goni et al., (1993). However, certain acidic compounds indicative of these decomposition pathways such as 3, 4-dihydroxy benzaldehyde were absent from the mass spectra for these samples.

Stations "F" and "G" from earlier samplings display enriched $\delta^{13}C$ values for cinnamyl phenols as did stations "F" and "G" in the November 2005 sampling shown in figure 20. This station is located at the confluence of Buttermilk Sound and South Altamaha River upriver of Egg Island. This area could have a higher deposition or retention of *Spartina* grass and its decomposition products based on a combination of sediment morphology including silt and clay content and transport processes at this juncture and time. This could explain a higher C_4 component and enriched $\delta^{13}C$ values at or near these stations.

Syringyl lignin is uniformly the most depleted in $\delta^{13}C$ of the three classes displayed. Only vanillyl lignin samples from March 2006 indicate a depletion exceeding that of syringyl lignin. This may well be the consequence of its source material from upland hardwoods and flowering plants. These angiosperm plants are most likely dominated by C_3 plants evidenced by depleted $\delta^{13}C$ relative to C_4 plants. The already depleted $\delta^{13}C$ signal in the syringyl lignin is slightly more depleted in the winter time cruise of November 2005 than the spring cruise in March 2006. It is possible the lower flow of the Altamaha River during November 2005 allowed for degradation

and consumption of isotopically heavier lignin components. This is also evident, albeit slightly, in other sampling times where both syringyl and vanillyl lignin is slightly more depleted near the Altamaha Sound. This could be a consequence of selective feeding of isotopically heavier lignin or a transport phenomenon with heavier, possibly C_4 enriched, lignin is moved faster to the Atlantic Ocean shelf.

Sediment and POM samples from the Hatch station, approximately 70 miles upriver from the sound, indicate $\delta^{13}C$ depleted character of upriver plants or an abundance of C_3 plants at this site. Each lignin class indicates depletion of $\delta^{13}C$ and in general, only hardwood and coniferous trees, shrubs and bushes populate this upriver region. The absence of saltwater tolerant plants is evident.

Figure 21 represents the individual lignin $\delta^{13}C$ values from POM for all the stations during the October 2006 cruise. Other than a large excursion of vanillin from stations B through D, the isotopic values resemble their sediment analog and would support some fraction of sediment being derived from upriver suspended particulate matter. The enriched vanillin from stations B through D is mirrored by a more depleted acetovanillone and vanillic acid components. This may follow the slight trend of increasing vanillic acid to vanillin and syringic acid to syringaldehyde in table 5 indicating a higher degradation state for samples taken during the October 2006 cruise. Further study will have to be conducted to determine if isotopic enrichment of the aldehydic lignin occurs concurrent with the isotopic depletion of the acidic lignin in either vanillyl or syringyl lignins as their respective acid to aldehyde ratios increase during degradation.

5.7 ^{14}C Content of Sediment, LOP and POM:

Figures 22, 23 and 24 portray the ^{14}C data, for November 2005, March and October 2006 sampling cruises. Figures 22 and 23 include SED (total carbonate free sediment), LOP (lignin oxidation phenols) and POM (particulate organic matter) ^{14}C data while figure 24 includes only SED and LOP ^{14}C data. All three figures include sample stations "A" through "H" and additional stations I, SB, 2, 3, 4, SAB (South Atlantic Bight), the furthest station sampled offshore, and Mud River samples denoted by prefix M. All figures include the NIST ^{14}C OXI standard activity line (dashed horizontal) representing 104.6 pMC. This ^{14}C activity line is included as a reference for comparison and is approximately 2% lower than the present day $^{14}CO_2$ activity level of the atmosphere. It is denoted on the graphs as "Modern" to reflect this activity level.

An important observation from these figures and their accompanying tables 9 and 10 is that total lignin ^{14}C activities do not exceed the "Modern" level at any sampling stations and lignin is nearly always lower in ^{14}C activity than sediment from which it was derived. In contrast, a few samples of total sediment, station "I" in both 2002 samplings, "B" and "H" in November 2005 and station "4" (Gray's Reef), 20 miles offshore, in March 2006 sampling, exceed the "Modern" activity line, some considerably. This could be explained by the ^{14}C "bomb" activity still detectable in various substrates today. For example, trees grown during the last 100 years would display, within their annual growth rings, the high ^{14}C activity that approached 200 pMC in 1964, decreasing annually to approximately 107 pMC today. Therefore, based on relatively young land plants and marine plankton taking up CO_2 via the atmosphere or equilibrated in ocean water, their inherent ^{14}C content may range from well above "Modern" levels, as high as 200 pMC, to well below "Modern" activity levels based on radioactive decay of ^{14}C over time. The combination of fresh plant matter with altered or degraded soil matter could results in a

similar mixture of high ^{14}C activities diluted by older and depleted ^{14}C abundances (Goñi et al., 2003, Goñi and Thomas, 2000).

Particulate organic matter (POM) illustrated in both the November 2005 and March 2006 samplings show a difference in pattern with respect to their ^{14}C activity relative to both SED and LOP ^{14}C activities. In the case of November 2005 sampling low flow conditions prevailed and surface seawater particulate (POM) ^{14}C activities remained relatively constant. In contrast, the POM ^{14}C activities during March 2006, though fewer in number, are 5-10 pMC lower in ^{14}C activity relative to their November 2005 counterparts. This may be explained by the combination of chemical data with ^{14}C activity. Earlier displayed Vd/Vl and Sd/Sl ratios for March 2006 sampling indicate more degraded material in stations A through C upriver of this lower ^{14}C activity POM sample at station D. It is possible the lower ^{14}C activity is a consequence of re-suspension of older degraded sediments (400-800 years older based on 5-10 pMC lower ^{14}C activities) re-deposited down river at station D. This theory may be supported by data from March 2007 sampling during high flow conditions but restricted to the lower 1 km of the Altamaha River, just inside the sound. Fifteen surficial sediment samples, collected in this area, resulted in average ^{14}C activities of 92 pMC, equivalent to at least 500 year old organic carbon. The suspended particulate matter (POM) from three samples in the same area is as low in ^{14}C activity as the surficial sediment organic carbon. The re-suspension of older surficial sediment during high flow rates may have a significant influence on the distribution of particulate organic carbon distributed to off-shore locations. ^{14}C activity data from the first 5 sampling cruises for the first 8 stations “A” through “G” for total sediment and the first 7 stations “A” through “F” for LOPs display little correlation between sediment or lignin phenol age with season of sampling. The close resemblance of both SED and LOP age for the March and November 2002 samplings

especially at station "D" would suggest little or no seasonal variation based on the ^{14}C data other than a few unique locations discussed above.

During the November 2005 sampling successful collection of a full box-core sample at station "D" was accomplished which allowed an intact 2 inch diameter core sample to be removed. This core was sectioned into ten 20mm sections from top to bottom and portions of each section processed as described earlier. The data in tables 9 and 10, illustrates minimal ^{14}C activity variation down-core except at 0-20 mm and 80-100 mm sections. The higher ^{14}C activity at the top of the core may be due to bio-turbation and modern ^{14}C activity organisms consuming or contributing to surface carbon. The lignin phenol Vd/Vl and Sd/Sl ratios were also greater at the top of the core supporting a higher degradation in this section. The LOP ^{14}C activities decrease rapidly in the first two sections and then much slower throughout the remaining core. A slight decrease in the sediment ^{14}C activity is observed coincident with an abrupt color change in the core tube from a green brown to black possibly indicative of an oxic/anoxic interface.

The mechanism of preservation of lignin phenols in sediment and suspended particles is not well defined, anymore than the process of degradation of lignin in marine sediment. The association of lignin phenols, ^{14}C and $\delta^{13}C$ with specific grain size fractions has been suggested by numerous researchers (Hedges et al., 1986, Hedges and Keil, 1995, DeMaster et al., 2002, Onstad et al., 2000). Lower ^{14}C activities are typically associated with coarse fraction mineral grains along with depleted $\delta^{13}C$ (Hedges and Oades, 1997). In contrast the younger material with enriched $\delta^{13}C$ is associated with finer grain size particles similar to POM. Finer grain size was also associated with higher lignin content in the form of unaltered plant debris which exhibit lower Sd/Sl ratios. In contrast is research by Bianchi et al., (1999) who found finer particles were

more altered and displayed lower ^{14}C activities and higher Sd/Sl ratios. The affects of particle size and mineral grain adsorption is clearly not well defined.

The sampling of Altamaha River and off-shore stations during this study revealed sediment morphology of coarse grain silica sand underlying the region, as expected from regional geology of the Piedmont and coastal plain. Varying amounts of detritus and allochthonous fine grained sediment, primarily silt size with minor clay, are distributed throughout this region. Due to the generally coarse size of the surficial sediment in the Altamaha Sound and on the offshore shelf, four size fractions were selected for particle size separation and analysis. Coarse size greater than 20 mesh (standard sieve) or 1 mm nominal diameter, greater than 35 mesh or 0.5 mm diameter, greater than 60 mesh or 250 micron diameter and the pan or residual less than 60 mesh grain size. These size fractions were separated using the wet-sieve method on sediment samples collected at stations "H" through "SAB", inside the Altamaha Sound and extending beyond the Gray's Reef offshore station. The collected size fractions were acid treated to remove inorganic carbonates, rinsed and dried at 50°C overnight. The fractions were weighed and a display of normalized fraction weight is shown in Figure 25. It indicates fine fraction sediment is minimal in content just inside Altamaha Sound at station "H" and is at its maximum at offshore station 2 decreasing steadily to SAB station, furthest offshore. Coarse fraction sediment decreases rapidly, relative to the finer fraction, inside the Sound and then increases steadily out to SAB station. This may be indicative of the prevailing surface and bottom currents just off Altamaha Sound where abrupt reduction in current at the mouth allows for settling of finer grained materials. This is followed by a steadily decreasing finer particle size mixture as they are winnowed by long shore currents.

The size fractionated samples were further processed by combustion at 900°C, isolation of resultant CO_2, measurement of $\delta^{13}C$ and graphitization for AMS ^{14}C measurement. Lignin phenols were also isolated from each of these size fractions, when enough lignin phenols were available. They too were processed for AMS ^{14}C measurement. The results of the ^{14}C activity for total acid treated sediment (SED) and lignin oxidation phenols (LOP) are listed in table 11 along with their fraction weights and normalized proportions and their respective $\delta^{13}C$ values.

^{14}C activities are distributed uniquely based on fractional size of sediment and material. ^{14}C activities span a wide range of ages from nearly 10,000 years before present (YBP) to post-Modern levels at or slightly above ^{14}C bomb peak activity. Horizontal lines representing constant ^{14}C activity are added to the figure for reference only. They include peak ^{14}C activity in 1964 during atmospheric atomic bomb testing, "Modern" level ^{14}C activity approximately reflecting today's ^{14}C level, and 5,000 and 10,000 YBP levels of ^{14}C activity.

The ^{14}C activities displayed in figure 26 indicate association of high ^{14}C levels with coarse grained materials at offshore stations. Highest activity levels are found at station 2, 10 miles offshore, and decrease below "Modern" levels at Gray's Reef, 20 miles offshore. The ^{14}C activities generally decrease with decreasing particle size at each station, >20 mesh being highest and <60 mesh being lowest. No data was available for station H fraction >35 mesh due to extremely low organic content. Although this data suggests a residual high ^{14}C activity prevails in the surface sediments for a considerable distance offshore, the lignin isolated from the same sample is very old in these offshore stations, although at very low concentration. ^{14}C activity of lignin is slightly above the "Modern" activity level just inside the Sound for the coarse >20 mesh fraction sample as might be expected by its association with coarse woody debris of "Modern" ^{14}C activity level. Contrasting this is lignin derived from the fine grain <60 mesh fraction

indicating aged lignin association. This is in agreement with previous investigations suggesting larger size fractions were associated with younger ^{14}C ages. Fine grain, <60 mesh, samples reported here may also be mineral associated organic fractions which are preserved through intimate association with iron and manganese oxide coatings of fine grain sediment. Further investigation of particle size distribution and associated isotopic abundance of ^{14}C and ^{13}C in these sediments is needed to fully explain these observations.

5.8 Compound Specific Radiocarbon (^{14}C) Analysis:

Once lignin phenols have been isolated and prepared for chromatography they are processed through a GC and selected compounds collected using a preparative fraction collector. This technique, referred to as preparative capillary gas chromatography (PCGC) uses repeated injection and collection until an adequate mass of the specific target compound has been recovered. The advantage of off-line preparation and measurement is more control of intermediate products through independent measurement to confirm purity of chromatographically separated and collected compounds by GC. In addition, as technology develops, a thorough comparison of off-line prepared, compound specific, radiocarbon measurements will be needed to "ground-truth" new GC/AMS techniques.

The instrumentation used for the CSRA work here made use of a Gerstel Corp. Preparative Fraction Collector (PFC) interfaced to an Agilent Technologies (formerly Hewlett Packard) 5890 GC. The GC, in its optimum configuration, can process sample loadings of up to 2 μL per injection. With typical concentration of the source specific biomarker, such as syringaldehyde, at approximately 1 μg per 2 μL injection nearly 200 individual injections and subsequent collections are needed to recover 200 μg of syringaldehyde for further processing and ^{14}C analysis. New gas chromatographic injection systems are available which allow for removal

of solvent in which the analyte is dissolved, prior to chromatographic separation. Using such an injection system, fewer injections would be required to collect the target 200 μg of analyte or larger recovery weights can be achieved for the by injecting the same number of injections. For now, the existing GC injection system, column and fraction collector were optimized for the samples prepared earlier for GC/IRMS analysis.

The CSRA technique requires the complete chromatographic separation of target compounds sometimes only achievable by derivatization. Such is the case with the lignin phenols. Just as in the GC/IRMS determination of compound specific $\delta^{13}C$ measurement, the added derivatizing carbons must be accounted for. The same is true for the additional carbon added when ^{14}C is calculated. The correction of added carbon in ^{14}C analysis is far simpler when the derivatizing carbons are devoid of ^{14}C. To insure the use of ^{14}C free derivatization compounds and solvents used to dissolve samples, the ^{14}C activity was determined and confirmed to be zero by off-line combustion and graphitization of the BSTFA/TMCS derivatizing agent and solvents such as pyridine, ethyl acetate, hexane and acetone. The ^{14}C activities, along with their respective $\delta^{13}C$ values, of these solvents and compounds are listed at the bottom of table 12.

The chromatographic purity and collection efficiency of the preparative fraction collector was the next quality control feature to be assessed in this study. Quality control standards were prepared using fossil fuel derived (synthetic) syringaldehyde and syringic acid and modern botanically derived vanillin. A mixture of these three compounds was used as the primary standard for collection efficiency studies for our CSRA. Because we had pre-determined the $\delta^{13}C$ values and ^{14}C activities of these standards individually, we hoped to be able to replicate their individual isotopic abundances again once separated, collected individually and re-analyzed.

Briefly, approximately 100-2μL injections were made of mixed standard containing 1000 ng/μL of each standard. Collection efficiencies were computed based on theoretical recovery of 200 μg of each standard. The collection efficiencies for all three compounds varied systematically with changes in trapping temperature and duration as well as lag time on measured retention time from the GC's internal flame ionization detector (FID). Efficiency values range from a high of 85% (average of all three compounds) to a low of 0%. Based on optimized efficiencies, expected recovery of each standard would be slightly less than 200μg. Considering the percent carbon of these lignin phenol compounds expected carbon mass available for CSRA would be around 50 to 100μg carbon. This mass of carbon is within the lower optimum range for ^{14}C measurement on the NEC 0.5 MeV AMS here at the University of Georgia. To insure the most accurate measurement of these extremely small samples, standards and background targets were prepared to bracket the expected mass of graphite derived from these standards.

Baseline contamination, or the collection of non-analyte compounds near the analytical peak of interest, is a major concern in this method due to the extremely small mass of carbon attempting to be recovered. To test the magnitude of this potential contamination, the trapping times were extended on a few collections of a three standard mixture to intentionally collect material from around the peak of interest. These samples are identified with the suffix +15 and +30, denoting the additional seconds the trap is open preceding and following the analytical peak.

Preliminary analysis of standard materials indicate little or no fractionation of the carbon isotopes during chromatographic separation, fraction collection or transfer from collection trap to ampoule for conversion to CO_2 and graphite. Table 12 displays the initial and recovered $\delta^{13}C$ and ^{14}C isotopic abundances for standards indicating some expected variation in the $\delta^{13}C$ and ^{14}C

abundances. Along with the calculated mass of carbon in the sample, table 12 lists the original dual inlet measured $\delta^{13}C$ values along with the GC/IRMS measured values post collection. Measured ^{14}C activities are low due to added derivatization carbons from the ^{14}C free TMCS agent. Once these carbons are mathematically backed out using equation 4 the corrected ^{14}C activity is derived and compared to the accepted or pre-determined ^{14}C level. The solvent $\delta^{13}C$ and ^{14}C values were from underivatized samples so no correction for derivatized carbon was necessary. Collection of standards with extended trapping times showed little evidence of contamination from baseline chromatography beyond the average 5% variation found in all analyses of standard compounds. However, more complex spectra may be required to apply this test to actual samples exhibiting a GC complexity like lignin phenols. Knowledge gained from GC/IRMS spectra, for measurement of compound specific $\delta^{13}C$, will be extremely useful for determining peak purity and potential interfering or co-eluting peaks. Since GC/IRMS reveal precisions sometimes on the order of 1‰ for lignin analysis, we should not expect better than 1‰ for ^{14}C determinations under the best conditions.

Table 13 displays a suite of samples from similar stations within the Altamaha River, estuary and shelf but sampled at different seasons and analyzed by CSRA. This data indicates compound specific ages for certain lignin phenols to resemble their total lignin precursors but exceed the age of bulk LOP ^{14}C. In four stations, with measured ^{14}C activities for both vanillin and syringaldehyde, vanillin age exceeds the syringaldehyde age by as much as 3400 years for the SAB sample and approximately 1500 years for the C and D station samples from November, 2005 and March, 2006 respectively. The magnitude of ^{14}C age difference between these two unique source biomarkers indicates the large potential for two unique sources for these lignin biomarkers. Although the ^{14}C activities vary between the lignin phenol compounds the average

of the two falls relatively close to the ^{14}C activity of the total lignin. This would support their individual contribution, albeit a fraction of total lignin, to the bulk lignin age. In only one case the individual lignin ^{14}C ages are younger than the total lignin age. These samples of syringaldehyde and syringic acid from March, 2006 station F exhibit similar but older ^{14}C ages relative to the bulk sediment but are younger by nearly 500 years relative to total lignin. Although the vanillin was not measured, it may have presented an age closer and exceeding the total lignin age similarly to other samples tested here.

6. CONCLUSIONS:

The Altamaha River's complex and diverse chemical and isotopic abundances are a testament to its extensive watershed and myriad of inputs and processes it contains. A significant variation spatially and temporally was found along the main sampling sites from station A through H within the river and estuary. Less distinct variation was found for the offshore sites due to less frequent sampling and low organic carbon.

Trends in salinity and temperature were consistent with flow patterns and seasonal variation expressed by lowest salinity during high flow spring flooding for stations A through H. Lower surface water temperatures were measured offshore relative to the river during this spring flooding in contrast to the winter sampling when cooler river water warmed as it transected the Altamaha Sound on it way offshore. Also found was a general decrease in total organic carbon and nitrogen from upriver stations to offshore or the Altamaha Sound as expected from a general decrease in source material and dilution within the coastal ocean. The C/N ratio also decreases as expected with the increase of proportion of marine derived nitrogen compounds in relation to the higher carbon containing terrestrial components. Absolute seasonal variation in either total organic carbon or nitrogen or their ratio is difficult to express from the sediment and particulate organic matter (POM) data from this study.

The utilization of biomarker lignin phenols allowed for the refinement of the aforementioned data to specific terrestrial source materials measured in sediments and POM. A general correlation of low lignin phenol content with lower organic carbon was revealed as expected. However, chemical analysis indicated consistent but variable concentration of the

syringyl groups (angiosperm plants) and vanillyl groups (gymnosperm plants) within a number of the sampling cruises conducted. An average concentration was found for syringyl phenols representing 42 ± 18% of the total lignin phenols analyzed. This was followed closely by the vanillyl phenols at 35 ± 14% and cinnamyl phenols at 17 ± 12%. The only variation to this trend was in particulate organic matter samples from November 2005 when vanillyl phenols outnumbered syringyl phenols. These trends suggest a rather uniform but variable mixture of source materials within the Altamaha River. Although quite variable within the scope of this study, nearly 75% of the lignin phenol concentration can be attributed to woody angiosperm and gymnosperm sources. Assuming there is minimal contribution from cinnamyl phenols as an intermediate compound in the formation of lignin and minimal preferentially lost during degradation, approximately 17% of the lignin phenols are derived from non-woody terrestrial material as indicated by para-coumaric and ferulic acids. These compounds are most likely derived from the prevalent salt-marsh grasses *Spartina* and *Juncus* and are likely the major source of this biomarker in the sediment. Although a slight refinement of this conclusion may be required based on observed S/V and C/V ratios for sediment and core sample (figure 10) and particulate organic matter (figure 11). These plots express the variation of ratios of syringyl and cinnamyl phenols to their vanillyl content with sampling time as well within each sampling date. The loci of points for each sampling date are very diverse and differ from one another in range of variation. Only for a single sample, November 2005 station E, does POM indicate the absence of cinnamyl or non-woody lignin phenol. It is apparent from this data that sediment exhibits a larger range of variation in cinnamyl to vanillyl and syringyl to vanillyl phenols than POM samples. Sediment C/V ratios average around 0.6 and range as high as 1.4 whereas POM C/V ratios average 0.3 with a high of less than 1.0. Similarly, S/V ratios for sediment average 1.2 and range

from 0.5 to 2.5 whereas POM S/V ratios average near 1.0 and range from 0 to 2.0. This may well be the consequence of the residence time of sediment in comparison to POM residence time in the Altamaha River. The possible accumulation of cinnamyl phenols, likely derived from non-woody tissue, relative to vanillyl phenols, is more likely in sediment than in POM. Unfortunately, the seasonal differences between POM plots cannot resolve this residence time response on such a short time scale even though low cinnamyl content from high flow March POM samples may support this conclusion.

The use of vanillic acid to vanillin and syringic acid to syringaldehyde concentrations as indicators of degradation of organic matter in Altamaha River sediments has not proven as valuable as hoped. Based on the data for sediments, POM and a single core sample to 200 millimeter depth, a moderate but consistent degree of degradation is evident. Although a significant amount of acidic compounds were quantified they exist in low proportion to the aldehyde phenols. Typical ratios, in sediment samples, of the acid to aldehyde for vanillyl and syringyl groups range from 0.06 to 0.86 and 0.14 to 0.76 respectively, with averages of 0.28 and 0.25 respectively, indicating a moderate degree of degradation in the sediment. Ratios of acid to aldehydes in POM were slightly higher with averages of 0.48 and 0.50 respectively. The only significant deviation from this trend was the ratio from the top section of the sediment core collected from station D in November 2005. Because of its proximity to marsh grass, this sample may have an unusual degree of degradation on the surface sediment relative to the core at depth. A consistent level of acid to aldehyde ratios were found for the remainder of core sections down to a depth of 200 millimeters revealing a similar rate of degradation in Altamaha River sediment. Although this degradation rate may be moderate, the consequence of selective decomposition of

labile compounds, newly formed, and uncharacterizable decomposition products make conclusions from the variations found by chemical analysis and compound ratios very elusive.

The stable carbon isotopic ratio, $\delta^{13}C$ indicate a general trend from a more depleted terrestrial source material to an enriched marine source material along the sampling sites out to the sound. An enrichment of approximately 4-5‰ was observed in an averaged trend-line for sediment samples collected from station A through H. Consistent with an increase in highly variable autochthonous derived carbon in the sound, Mud River and offshore, $\delta^{13}C$ values average -22‰ but vary considerably. POM $\delta^{13}C$ varied similarly from station A to H but was consistently depleted by 2-3‰ relative to sediment $\delta^{13}C$. Data from two sampling cruises indicated less enrichment in the POM $\delta^{13}C$ toward station H relative to sediment. This may be due to a higher incorporation of C_4 plant (*Spartina*) material in sediment within this area effectively enriching sediment $\delta^{13}C$.

Total lignin oxidation products (LOP) $\delta^{13}C$ follow a similar isotopic trend as sediment $\delta^{13}C$ from stations A through H but at a depleted level relative to their host sediment by 2-3‰. This observed depletion is likely due to the refractory nature of lignin and its persistence in sediment while other more labile components such as amino acids, proteins and carbohydrates get selectively removed. This depletion is also evident regardless of the C_3 or C_4 plant precursor as indicated from data in this study. The $\delta^{13}C$ of lignin maintains its depleted isotopic abundance offshore as well. Despite the enriched nature of the total sediment $\delta^{13}C$, terrestrially derived lignin resembles and is unique to its source material, even 20 miles offshore.

Compound specific stable isotopic analysis allows an even greater specificity to the terrestrial components in the Altamaha River and offshore. Sediment and POM samples from three sampling cruises indicate syringyl lignin (angiosperm derived) is lighter or more depleted

in $\delta^{13}C$ relative to vanillyl and cinnamyl lignin. The cinnamyl phenols; p-coumaric acid and ferulic acid, represent non-woody plant material and generally display enriched $\delta^{13}C$ values by 10 to 20‰ relative to the syringyl phenols. Values this enriched in $\delta^{13}C$ are also found in offshore station SAB samples, although more depleted ferulic acid was found in March 2006 samples throughout the offshore stations. C_4 plants may account for a significant proportion of the non-woody component found in lignin within these sediments. A likely candidate for this C_4 plant could be *Spartina* grass found throughout the Georgia coast in expansive salt-marshes.

Although the $\delta^{13}C$ of the individual biomarker lignin compounds vary considerably from station to station and from different sampling cruises, a pattern may exist for the degradation of aldehydic compounds to their acid analogs. As indicated by LOP $\delta^{13}C$ data from the October 2006 POM sampling, isotopically enriched vanillin is accompanied by isotopically depleted vanillic acid. Further study will have to be conducted to determine if isotopic enrichment of aldehyde compounds occur concurrently with the isotopic depletion of the acid compounds during degradation.

Stable isotopic $\delta^{13}C$ determinations, of the entire suite of sediment and POM samples, made on individual lignin compounds by GC/IRMS support the use of continuous flow measurement as a viable means of generating precise isotopic measurements. During GC/IRMS data acquisition, the difficulty of correcting for added carbons during chemical derivatization and proper application of correcting algorithms was shown to be reasonably robust for this particular biomarker class. Variations of a few per mil based on different algorithms were found to have a small impact on the variation of sample $\delta^{13}C$ abundances and well within the typical error of approximately 1-2‰ for measurements by this method.

^{14}C activities in sediment and LOP from the Altamaha River to the South Atlantic Bight present some interesting and provocative data. In general, POM ^{14}C illustrates the consistency of particulate matter transported in the water column and its minimal residence time relative to sediments. POM ^{14}C may be as close a representative of the DOC ^{14}C as any of the substrates tested within this study. POM ^{14}C is slightly lower in ^{14}C activity than the atmospheric ^{14}C level indicating close correlation with modern derived plants or marine organisms. A few anomalously low ^{14}C activities were observed for POM at the upriver stations A, B and D during March, 2006 as well as the 70 mile upriver station "Hatch" which exhibited POM of ^{14}C age near 700 years old (YBP). These were similar in location to areas having potentially re-suspended matter and thus may be bringing older seafloor sediment to the suspended sediment in the water column.

Sediment ^{14}C activities were found to range from nearly 4000 year old to post-modern (bomb ^{14}C) levels from the early 1960s. The unusual mixture of ages determined in sediment samples is a consequence of the diversity of carbon sources and processes within the Altamaha River and offshore. Older, refractory and persistent organic compounds whether sequestered on mineral grains, or degraded to uncharacterizable form within the sediment are but one source of ^{14}C depleted sediments. Erosion of relict soils and fossil carbon can also contribute to the older age of riverine sediment. In contrast, the autochthonous production within the living carbon pool, freshly decomposed terrestrial litter or soil, dissolved and re-adsorbed organic matter within recently weathered mineral grains add a near-modern, even post-modern, ^{14}C component to marine sediment. This combination of sources and processes can reconcile the extremely old organic carbon ages found within a mile of extremely young organic carbon, even carbon that is enriched in ^{14}C from exchange with the atmosphere in the 1960s. Similarly, the total LOP ^{14}C frequently tracks along with the variation of sediment age within the Altamaha River but is

nearly always older by at least 500 years. This is a consequence of the selective degradation of the more labile younger constituents resulting in old recalcitrant compounds such as lignin persisting within sediments.

The association with mineral grains is likely the most important controlling parameter for preservation of organic matter in the marine environment. Not solely the mineral interaction but also specific particle size interaction may be the determinant factor for long term organic compound sequestering. A high residual ^{14}C activity was determined in various coarse grain size sediment fractions, for a considerable distance offshore. In contrast, lignin isolated from the same size fractions is considerably old in these offshore stations, even though at very low concentration. This data indicates a direct association of organic carbon age with specific particle size minerals. The highest lignin ^{14}C activity, slightly above the "Modern" activity level, was from just inside the Altamaha Sound and associated with coarse >20 mesh fraction. This could well be expected by this size fractions association with coarse woody debris of "Modern" ^{14}C activity level. Contrasting this is lignin derived from the fine grain <60 mesh fraction indicating aged lignin association. This is in agreement with previous investigations suggesting larger size fractions were associated with younger ^{14}C ages. Further investigation of particle size distribution and associated isotopic abundance of ^{14}C and $\delta^{13}C$ in these sediments is needed to fully explain these observations.

The primary goal of this study was to demonstrate the ability of isolating the source specific biomarkers of the terrestrial environment and determine their respective age by AMS. The primary roadblock to accomplishing this goal was the ability to collect an adequate amount of a specific compound of sufficient purity for measurement of ^{14}C activity. The preparative fraction collection system used for this task has been developed to that potential. Test mixtures

have been processed to verify the collection efficiency and parameters to be used on real samples derived from Altamaha River and offshore lignin. Results from the standard mixtures indicate the ability of the fraction collector to sample an analytical peak without substantially increasing the interfering carbon from sources such as chromatographic baseline, column bleed or derivatizing carbons. While conducting this research it was determined a more efficient collection of individual components could be accomplished with a few modifications to the existing equipment. 1. A wide or mega bore column for higher loading capacity within the gas chromatograph is recommended with length appropriate for complete separation of the compounds of interest and baseline resolution. 2. A cooled injection system allowing solvent to be removed for maximizing column loading thereby reducing the number of replicate GC runs required for collection of an adequate mass of selected compound. 3. Cryogenic focusing system to enhance the separation of large volume components in the GC column. 4. Development of more efficient and robust derivatizing agents.

Despite the need or desire for improvements to the present system, the accomplishment of preliminary tests on real samples collected from the Altamaha River demonstrate the application of this technique for the unambiguous determination of the age of individual compounds, derived from terrestrial carbon from a major river system. Compound specific ^{14}C data for selected lignin phenol compounds from the Altamaha River and South Atlantic Bight sediments has been acquired. In a similar pattern to total lignin phenols being older than their precursor sediments, so to, selected individual lignin phenols are typically older than their total lignin age. Vanillin was found to be older than the total lignin age while syringaldehyde was typically younger while both averaged closely to the total lignin age.

The age of the respective biomarkers is a direct indication of the age and long term processes occurring in the marine environment, particularly with regard to the terrestrial biomarkers. The individuality of lignin biomarkers in this particular setting is clearly evident with even this small set of data. Although a complete mass balance of lignin compounds cannot be accomplished with this limited data set it does lend support to the large variation in ages of these lignin compounds indicating the processes, both formation and degradation, unique to the different classes of plants. The syringaldehyde derived from angiosperm plants obviously degrade or are sequestered in sediment differently than the gymnosperm derived vanillin compounds.

This study was designed to sequentially increase the specificity of analysis to help determine the sources and fates of organic matter in the Altamaha River and South Atlantic Bight. As in most analytical schemes, an increase in resolving power is proportional to an increase in complexity. To resolve the isotopic composition of individual molecular biomarkers is no exception. The ability to isolate individual compounds of adequate purity and mass for measurement on high precision AMS machines will soon be commonplace in research facilities. The use of such a technique has application to urgent problems such as climate change, forensics and medicine, but these are only a few of the potential fields it may benefit.

Table 1. General Sampling Data for Six Sampling Cruises

Station	Lat.(N)	Lon.(W)	Sal.(o/oo)	Temp.(C)	depth (ft)	Vol.(L)
Mar., 2002						
A	31 19.89	81 26.11	0	26.4		
B	31 18.71	81 25.94	0	22.4		
C	31 18.51	81 24.25	1.1	21.9		
D	31 18.27	81 23.89	1.5	21.9		
E	31 18.78	81 22.87	2.8	21.9		
F	31 19.00	81 21.76	7.5	22.1		
G	31 18.95	81 19.87	14.7	21.9		
H	31 19.31	81 17.95	12.5	21.9		
I	31 18.48	81 15.04	30.4	20.4		
Nov., 2002						
A	31 19.89	81 26.11	0.3			
B	31 18.71	81 25.94	2.1			
C	31 18.51	81 24.25	11.7			
D	31 18.27	81 23.89	13.5			
E	31 18.78	81 22.87	15.9			
F	31 19.00	81 21.76	20.6			
G	31 18.95	81 19.87	25.8			
H	31 19.31	81 17.95	30			
I	31 18.48	81 15.04	31.4			
Nov., 2005						
A	31 19.92	81 26.29	3.2	18.6	15.1	4
B	31 18.61	81 25.80	3.9	18.9	27.5	4
C	31 18.58	81 23.93	5.6	19.1	31.5	4
D	31 18.26	81 23.63	5.5	19.1	16.3	4
E	31 19.24	81 22.52	6.4	19.4	12.5	4
F	31 19.00	81 21.34	5.9	19.5	10.8	4
G	31 19.05	81 19.51	6.7	19.1	9.0	4
H	31 18.99	81 18.11	6.2	19.3	8.0	4
I	31 18.51	81 15.13	30.8	19.6	15.3	0
1	31 18.25	81 14.41	30.8	19.6	16.7	194
2	31 21.22	81 09.65	31.5	20.6	32.0	330
3	31 22.78	81 01.59	32.3	21.9	49.0	388
4	31 25.26	80 51.74	34.2	22.3	55.0	388
Mar., 2006						
A	31 19.80	81 26.30	0.0	17.7	20.4	6
B	31 18.59	81 25.67	0.0	17.9	2.8	6
C	31 18.55	81 23.88	0.1	17.6	5.0	6 + 116
D	31 18.06	81 23.60	0.1	17.8	8.8	6 + 116
E	31 18.69	81 22.91	0.5	18.0	7.9	4 + 116
F	31 18.98	81 21.75	2.2	18.2	6.1	4 + 58
G	31 18.91	81 19.67	8.7	18.3	12.7	4 + 116
H	31 18.93	81 18.12	11.1	18.2	6.7	4 + 116
I	31 18.61	81 15.32	23.0	18.0	17.0	6 + 350
SB	31 21.13	81 11.03	33.6	15.0	33.6	0
2	31 21.23	81 07.10	31.4	15.1	35.0	388
3	31 22.03	81 01.59	32.4	15.1	40.0	388
4	31 24.90	80 56.50	32.5	15.2	53.0	388
SAB	31 15.15	80 23.15			115.0	
Oct., 2006						
A	31 18.97	81 26.51	6.2	20	16.0	4
B	31 18.81	81 26.15	6.8	20	15.0	4
C	31 18.54	81 24.20	7.7	19.8	8.0	4
D	31 18.26	81 24.07	8.9	19.7	10.0	4
E	31 18.80	81 23.20	8.5	19.3	15.0	4
F	31 18.93	81 21.96	8.4	19.2	8.0	4
G	31 18.93	81 19.95	25.1	19.1	11.0	4
H	31 19.37	81 17.30	26.4	20.5	29.0	4
M1	31 20.32	81 19.60	29.5	20.6	3.0	4
M2	31 20.80	81 19.62	30.3	20.5	10.0	4
M3	31 21.45	81 20.22	30.9	20.4	3.0	4
M4	31 22.04	81 18.62	30	21.2	8.0	4
M5	31 22.01	81 18.16	31.1	21.2	12.0	4
M5A	31 22.01	81 18.16	31.1	21.2	12.0	4
M6	31 22.15	81 17.62	31.3	21.2	4.0	4
M7	31 23.08	81 19.88	31.4	20.2	9.0	4
M8	31 23.79	81 16.81			0.0	0
Mar., 2007						
1	31 18.95	81 17.81			10.4	
2	31 18.96	81 18.07			5.7	
3	31 19.00	81 17.86			18.6	
4	31 18.97	81 18.22			7.0	
5	31 19.02	81 18.28			12.0	
6	31 19.35	81 18.18			10.3	
7	31 19.37	81 17.74			8.6	
8	31 19.39	81 17.65			6.4	
9	31 19.35	81 17.87			7.4	
10	31 19.32	81 17.96			15.2	
11	31 19.30	81 18.02			19.0	
12	31 19.20	81 18.03			27.6	
13	31 19.17	81 17.72			17.0	
14	31 19.27	81 17.94			26.0	
15	31 19.25	81 18.12			24.0	
Hatch	31 56.46	82 22.44			3.0	

Table 2. Bulk Sediment TOC, TN, C/N, $\delta^{13}C$ and $\delta^{15}N$ Analysis

March, 2002									
Station	del13C	SD	%C	SD	del15N	SD	%N	SD	C/N
A	-24.94	0.01	4.87	0.06	4.56	0.37	0.31	0.01	15.52
B	-23.65	0.04	6.41	0.18	4.42	0.16	0.47	0.01	13.78
C	-22.44	0.06	4.21	0.03	4.84	0.04	0.31	0.01	13.75
D	-23.63	0.07	2.85	0.02	4.63	0.35	0.18	0.01	16.22
E	-22.37	0.25	4.48	0.01	5.23	0.07	0.39	0.01	11.60
F	-22.17	0.23	0.85	0.03	5.90	0.38	0.08	0.01	11.27
G	-21.82	0.12	2.46	0.06	5.89	0.10	0.17	0.01	14.19
H	-21.34	0.06	2.55	0.43	5.58	0.11	0.22	0.04	11.50
I	-23.90	0.35	0.16	0.01	6.13	3.51	0.02	0.01	10.22
November, 2002									
Station	del13C	SD	%C	SD	del15N	SD	%N	SD	C/N
A	-24.98	0.06	4.44	0.17	6.45	0.51	0.26	0.00	16.76
B	-24.21	0.07	5.67	0.46	5.78	0.34	0.36	0.02	15.75
C	-23.42	0.17	5.63	0.05	5.46	0.08	0.39	0.02	14.49
D	-15.82	0.68	2.11	0.02	5.66	0.33	0.12	0.00	17.62
E	-20.63	0.01	3.45	0.01	7.08	0.17	0.30	0.00	11.58
F	-20.42	0.30	3.01	0.07	6.70	0.03	0.26	0.01	11.40
G	-20.71	0.13	4.23	0.04	5.93	0.17	0.37	0.01	11.44
H	-23.93	0.02	0.03	0.01	3.97	2.68	0.01	0.00	3.65
I	-25.25	0.33	0.06	0.00	4.91	0.40	0.01	0.00	5.83
November, 2005									
Station	del13C	SD	%C	SD	del15N	SD	%N	SD	C/N
A	-27.85	0.14	0.03	0.00	5.74	1.80	0.01	0.00	4.16
C	-23.64	0.30	6.18	0.06	3.52	1.07	0.29	0.01	21.03
D	-23.53	0.19	4.86	0.05	3.92	0.19	0.36	0.01	13.48
E	-21.53	0.54	2.39	0.77	4.40	0.69	0.17	0.05	14.29
F	-22.01	0.32	2.28	0.94	4.63	0.17	0.16	0.04	14.63
G	-23.83	1.58	1.58	0.15	2.18	1.00	0.13	0.01	12.31
H	-24.15	0.73	0.52	0.01	6.63	1.47	0.05	0.00	10.46
I	-21.00	0.10	1.14	0.01	7.19	0.08	0.10	0.00	11.62
March, 2006									
Station	del13C	SD	%C	SD	del15N	SD	%N	SD	C/N
A	-25.89	0.08	3.49	0.42	5.76	0.17	0.19	0.02	18.44
B	-26.24	0.33	10.19	0.06	2.42	0.01	0.50	0.00	20.33
C	-23.53	0.16	5.47	0.07	5.65	0.11	0.41	0.00	13.49
D	-23.79	0.01	4.26	0.07	4.99	0.01	0.36	0.01	11.92
E	-21.98	0.06	2.06	0.07	6.22	0.16	0.19	0.01	10.72
F	-23.18	0.12	4.14	0.01	5.58	0.02	0.28	0.00	14.71
G	-21.91	0.03	1.44	0.02	5.63	0.41	0.10	0.00	14.01
H	-23.98	0.12	0.05	0.00	4.84	0.80	0.01	0.00	5.11
I	-21.19	0.02	0.95	0.01	7.05	0.32	0.09	0.00	10.72
SB	-21.41	0.03	0.83	0.12	6.67	0.25	0.09	0.01	9.15
2	-24.62	0.40	0.04	0.00	4.07	0.39	0.01	0.00	4.03
3	-21.96	0.29	0.03	0.01	3.64	0.01	0.01	0.00	4.19
4	-18.99	0.34	0.03	0.00	6.96	1.34	0.01	0.00	3.32
SAB	-21.86	0.64	0.01	0.00	5.28	0.14	0.01	0.00	1.38
October, 2006									
Station	del13C	SD	%C	SD	del15N	SD	%N	SD	C/N
B	-24.83		0.80		4.49		0.07		11.38
D	-21.57		3.29		4.83		0.28		11.72
E	-23.22		0.85		4.40		0.08		10.07
F	-24.17		0.65		4.03		0.06		10.89
G	-22.15		3.21		4.79		0.32		9.97
H	-20.30		3.52		4.61		0.30		11.62
M1	-21.03		4.38		4.98		0.42		10.36
M2	-21.59		4.35		4.63		0.37		11.67
M3	-21.30		4.05		4.56		0.37		10.92
M4	-21.46		1.53		3.54		0.11		13.68
M5	-22.87		0.87		4.18		0.07		12.60
M6	-24.67		0.39		4.02		0.05		8.73
M7	-17.27		4.94		3.31		0.23		21.48

Table 3. Lignin Oxidation Products and Mass Identification Parameters

Chemical Name (text abbreviation)	Formula	M.W.	Mass Fragment Ions (Parent)
para-hydroxy Benzaldehyde (pBl)	$C_7H_6O_2$	122	151, 179, (194)
para-hydroxy Acetophenone (pBn)	$C_8H_8O_2$	136	193, (208)
para-hydroxy Benzoic acid (pBd)	$C_7H_6O_3$	138	193, 223, 267, (282)
Vanillin (Vl)	$C_8H_8O_3$	152	152, 194, 209, (224)
Acetovanillone (Vn)	$C_9H_{10}O_3$	166	193, 208, 223, (238)
Vanillic acid (Vd)	$C_8H_8O_4$	168	223, 253, 267, 282, (312)
Syringaldehyde (Sl)	$C_9H_{10}O_4$	182	224, 239, (254)
Acetosyringone (Sn)	$C_{10}H_{12}O_4$	196	223, 238, 253, (268)
Syringic acid (Sd)	$C_9H_{10}O_5$	198	253, 283, 297, 312, (342)
para-Coumaric acid (Cd)	$C_9H_8O_3$	164	219, 249, 293, (308)
Ferulic acid (Fd)	$C_{10}H_{10}O_4$	194	249, 293, 308, 323, (338)
trans-Cinnamic acid (tCa)	$C_9H_8O_2$	148	103, 131, 161, 205, (220)
Ethyl Vanillin (EV)	$C_9H_{10}O_3$	166	195, 223, (238)

Table 4. Organic Carbon and Lignin Oxidation Product (mg/100mg OC) from Sediment, Particulate Organic Matter and Core D

March, 2002 Sediment

Station	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A	4.87	0.39	0.10	0.13	2.87	0.87	0.73	2.65	0.74	0.61	0.54	0.60
B	6.41	0.28	0.07	0.09	1.68	0.52	0.46	2.12	0.55	0.62	0.60	0.92
C	4.21	0.35	0.09	0.12	1.72	0.49	0.39	2.08	0.66	0.45	0.62	0.49
D	2.85	0.34	0.09	0.12	1.71	0.43	0.39	1.85	0.52	0.41	0.46	0.33
E	4.48	0.26	0.06	0.10	1.37	0.44	0.33	1.61	0.65	0.37	0.42	0.45
F	0.85	0.36		0.17	1.94	0.45	0.49	1.96	0.78	0.51	0.46	0.34
G	2.46	0.34	0.07	0.13	2.27	0.53	0.46	2.55	0.63	0.44	0.45	0.34
H	2.55	0.35	0.07	0.11	1.73	0.41	0.37	2.21	0.56	0.45	0.61	0.49

November, 2002 Sediment

Station	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A	4.44	0.15	0.03	0.07	1.22	0.45	0.34	1.57	0.39	0.34	0.34	0.61
B	5.67	0.12	0.03	0.04	1.36	0.31	0.24	1.14	0.28	0.29	0.34	0.62
C	5.63	0.17	0.03	0.04	3.25	0.22	0.20	0.91	0.22	0.26	0.30	0.53
D	5.63	0.08	0.03	1.05	0.20	0.06	0.08	0.26	0.05	0.06	0.09	0.05
E	3.45	0.27	0.07	0.09	1.46	0.45	0.42	1.84	0.48	0.56	0.48	0.69
F	3.01	0.31	0.08	0.11	1.43	0.45	0.35	1.79	0.46	0.38	0.46	0.41
G	4.23	0.30	0.08	0.10	1.38	0.47	0.40	1.95	0.54	0.60	0.60	0.85

November, 2005 Sediment

Station	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
C	6.18	0.25	0.07	0.11	1.96	0.74	0.69	2.27	0.57	0.86	0.52	2.08
D	4.86	0.08	0.02	0.03	0.42	0.12	0.09	0.64	0.11	0.11	0.13	0.10
E	2.39	0.26	0.08	0.11	1.22	0.35	0.36	1.76	0.44	0.37	0.36	0.26
F	2.28	0.17	0.05	0.07	1.22	0.29	0.29	1.39	0.28	0.28	0.19	0.09
G	1.58	0.24	0.04	0.09	1.35	0.36	0.35	1.59	0.36	0.23	0.28	0.13
H	0.54	0.21		0.11	1.27	0.28	0.34	1.49	0.25	0.26	0.15	
1	1.14	0.19	0.05	0.06	1.02	0.38	0.32	1.49	0.37	0.46	0.43	0.81

November, 2005 Particulate Organic Matter

Station	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A	5.91	0.07		0.05	0.22	0.07	0.11	0.05	0.04	0.05	0.03	
B	4.40	0.15	0.03	0.08	0.63	0.19	0.25	0.68	0.17	0.23	0.15	0.13
C	4.44	0.11	0.02	0.06	0.44	0.14	0.18	0.45	0.12	0.14	0.07	0.06
D	4.88			0.06	0.35	0.13	0.15	0.48	0.12		0.06	
E	4.54			0.05	0.33	0.11	0.13	0.45	0.11			
F	4.13	0.26		0.14	1.10	0.33	0.41	1.16	0.28	0.33	0.19	
G	4.24	0.26	0.06	0.11	1.30	0.42	0.41	1.52	0.43	0.41	0.32	0.31
H	3.11	0.27		0.12	1.20	0.37	0.41	1.32	0.33	0.37	0.23	
1	4*	0.29	0.04	0.11	0.36	0.15	0.13	0.63	0.17	0.17	0.14	0.21
2	4*	0.30	0.03	0.12	0.11	0.05	0.05	0.21	0.05	0.07	0.05	0.15

Table 4. Organic Carbon and Lignin Oxidation Product (mg/100mg OC)
from Sediment, Particulate Organic Matter and Core D (cont.)

November, 2005 Station D Core

(mm)	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
0-20	3.93	0.13	0.03	0.31	0.62	0.39	1.45	0.99	0.25	1.55	0.37	0.35
20-40	3.66	0.32	0.06	0.15	1.62	0.68	0.39	2.32	0.73	0.73	0.86	0.92
40-60	3.17	0.32	0.07	0.10	1.50	0.45	0.53	2.52	0.54	0.87	0.84	1.49
60-80	2.95	0.30	0.08	0.16	1.38	0.54	0.46	1.91	0.52	0.70	0.70	0.66
80-100	3.17	0.23	0.06	0.07	1.40	0.52	0.08	2.10	0.40	0.51	0.50	0.52
100-120	2.95	0.22	0.05	0.07	1.27	0.45	0.37	1.92	0.45	0.47	0.44	0.47
120-140	2.80	0.35	0.12	0.18	1.47	0.72	0.66	1.50	0.38	0.89	0.50	0.42
140-160	2.93	0.24	0.06	0.07	1.53	0.52	0.08	2.15	0.43	0.54	0.57	0.55
160-180	3.11	0.31	0.09	0.15	1.47	0.63	0.34	2.01	0.70	0.65	0.82	0.91
180-200	2.93	0.24	0.06	0.08	1.24	0.48	0.44	2.00	0.52	0.66	0.64	1.13

March, 2006 Sediment

Station	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A	3.49	0.11	0.03	0.05		0.14	0.15	0.45	0.15	0.11	0.11	0.07
B	10.19	0.51	0.15	0.20	1.68	0.65	0.59	2.67	0.77	0.73	1.25	1.83
C	5.47	0.28	0.05	0.11	1.38	0.57	0.50	1.81	0.60	0.66	0.57	1.03
D	4.26	0.34	0.03	0.15	1.72	0.34	0.45	1.44	0.19	0.35	0.27	0.10
E	2.06	0.22	0.05	0.09	0.81	0.19	0.21	0.89	0.28	0.19	0.21	0.13
F	4.14	0.33	0.08	0.13	1.98	0.62	0.60	2.27	0.63	0.69	0.66	0.66
G	1.44	0.17	0.02	0.10	1.04	0.25	0.32	0.57	0.16	0.15	0.13	
1	0.95	0.17	0.04	0.08	0.86	0.23	0.23	1.34	0.33	0.18	0.27	0.11
SB	0.83	0.16	0.03	0.08	0.48	0.15	0.16	0.77	0.18	0.13	0.20	0.08
SAB	1.00	0.45	0.13	0.17	2.38	0.94	0.76	3.40	0.94	1.03	1.03	1.89

March, 2006 Particulate Organic Matter

Station	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
C	4*	0.11		0.04	0.49	0.10	0.17	0.64	0.09	0.16	0.08	
E	4*	0.32		0.13	0.90	0.36	0.39	1.45	0.42	0.42	0.19	
F	4*	0.25		0.10	0.72	0.32	0.29	1.18	0.36	0.30	0.20	0.18
I	4*			0.13	0.50		0.26	1.02	0.25	0.22	0.15	

October, 2006 Sediment.

Station	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
B	0.80	0.23		0.09	1.19	0.30	0.38	1.48	0.25	0.17	0.37	
D	3.29	0.24	0.06	0.08	1.28	0.37	0.40	1.89	0.40	0.58	0.54	0.69
E	0.85	0.29		0.11	1.19	0.30	0.41	1.40	0.24	0.20	0.39	
F	0.65	0.47	0.07	0.15	2.25	0.49	0.64	3.67	0.62	0.62	0.97	0.59
G	3.21	0.23	0.03	0.08	0.97	0.23	0.34	1.66	0.32	0.70	0.56	0.82
H	3.52	0.27	0.07	0.13	1.26	0.39	0.56	2.94	0.67	0.94	1.16	1.81
M1	3.52	0.24	0.08	0.08	0.66	0.34	0.25	0.96	0.44	0.26	0.40	0.28
M2	4.35	0.21	0.04	0.07	1.04	0.32	0.36	1.99	0.43	0.67	0.83	1.43
M3	4.05	0.28	0.10	0.10	0.85	0.42	0.29	1.21	0.56	0.29	0.45	0.19
M4	1.53	0.38	0.12	0.11	1.57	0.55	0.36	1.81	0.79	0.37	0.54	0.30
M5A	0.87	0.51	0.15	0.14	2.14	0.72	0.46	2.55	1.07	0.49	1.09	0.69
M6	0.39	0.46		0.16	1.58	0.45	0.42	2.06	0.78	0.48	0.67	0.39
M7	4.94	0.47	0.22	0.15	1.23	0.69	0.36	2.13	1.15	0.48	1.03	0.56

Table 4. Organic Carbon and Lignin Oxidation Product (mg/100mg OC) from Sediment, Particulate Organic Matter and Core D (cont.)

October, 2006 Particulate Organic Matter

Station	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A	4*	0.35	0.11	0.30	1.06	0.52	0.58	0.59	0.12	0.29	0.36	0.12
B	4*	0.41	0.10	0.40	0.89	0.41	0.56			0.17	0.33	
C	4*	0.41	0.12	0.45	0.83	0.47	0.66	0.32	0.12	0.29	0.41	0.15
D	4*	0.38	0.12	0.44	0.82	0.54	0.71	0.31	0.15	0.34	0.45	0.17
E	4*	0.34	0.06	0.19	0.87	0.38	0.36	1.08	0.35	0.34	0.34	0.19
F	4*	0.38	0.07	0.21	0.84	0.46	0.45	1.40	0.54	0.47	0.47	0.32
G	4*	0.39	0.09	0.47	0.71	0.31	0.38	0.07	0.05	0.14	0.29	
H	4*	0.47	0.12	0.61	0.66	0.25	0.50	0.09		0.14	0.34	

March, 2007 Sediment and Particulate Organic Matter

Station	%OC	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
Sediment												
1	4*	0.12	0.08	0.14	0.43	0.42	0.33	0.50	0.35	0.38	0.38	0.24
Hatch	0.4	0.09		0.08	0.87	0.28	0.33	0.72	0.23	0.25	0.05	
Particulate Organic Matter												
1	4*	0.15	0.05	0.11	0.57	0.27	0.23	0.55	0.20	0.20	0.23	0.12
12	4*	0.17	0.07	0.15	0.68	0.38	0.31	0.65	0.27	0.28	0.32	0.15
Hatch	4*	0.15		0.09	0.74	0.27	0.34	0.92	0.24	0.33	0.06	

Abbreviations: %OC: percent organic carbon, pBl: para-hydroxy Benzaldehyde, pBn: para-hydroxy acetophenone, pBd: para-hydroxy Benzoic acid, Vl: Vanillin, Vn: Acetovanillone, Vd: Vanillic acid, Sl: Syringaldehyde, Sn: Acetosyringone, Sd: Syringic acid, Cd: para-Coumaric acid and Fd: Ferulic acid,
*average value used due to small sample.

Table 5. Lignin Oxidation Product (mg/100mg OC), Sums and Ratios of Major Groups from Sediment, Particulate Organic Matter and Core D

March, 2002 Sediment

Station	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
A	4.47	4.00	1.14	8.47	9.61	0.89	0.25	0.26	0.23
B	2.65	3.29	1.52	5.94	7.46	1.24	0.57	0.27	0.29
C	2.60	3.19	1.11	5.79	6.90	1.23	0.43	0.22	0.22
D	2.53	2.77	0.78	5.30	6.08	1.10	0.31	0.23	0.22
E	2.15	2.63	0.86	4.78	5.64	1.23	0.40	0.24	0.23
F	2.88	3.25	0.80	6.13	6.93	1.13	0.28	0.25	0.26
G	3.26	3.62	0.79	6.88	7.67	1.11	0.24	0.20	0.17
H	2.51	3.22	1.10	5.73	6.83	1.28	0.44	0.22	0.21

November, 2002 Sediment

Station	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
A	2.01	2.29	0.95	4.31	5.26	1.14	0.47	0.28	0.22
B	1.90	1.72	0.95	3.62	4.57	0.90	0.50	0.17	0.26
C	3.67	1.39	0.82	5.07	5.89	0.38	0.22	0.06	0.28
D	0.34	0.38	0.14	0.72	0.85	1.11	0.41	0.38	0.25
E	2.33	2.88	1.17	5.21	6.38	1.24	0.50	0.29	0.30
F	2.23	2.63	0.87	4.86	5.73	1.18	0.39	0.25	0.21
G	2.26	3.09	1.46	5.35	6.81	1.37	0.65	0.29	0.31

November, 2005 Sediment

Station	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
C	3.39	3.70	2.60	7.10	9.70	1.09	0.77	0.35	0.38
D	0.62	0.86	0.23	1.48	1.71	1.39	0.37	0.21	0.17
E	1.92	2.58	0.62	4.50	5.12	1.34	0.32	0.29	0.21
F	1.80	1.94	0.28	3.75	4.03	1.08	0.16	0.24	0.20
G	2.06	2.19	0.41	4.24	4.65	1.06	0.20	0.26	0.14
H	1.89	2.00	0.15	3.89	4.04	1.05	0.08	0.27	0.18
1	1.72	2.32	1.24	4.05	5.29	1.35	0.72	0.31	0.31

November, 2005 Particulate Organic Matter

Station	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
A	0.40	0.15	0.03	0.55	0.57	0.37	0.07	0.51	0.99
B	1.06	1.08	0.27	2.15	2.42	1.02	0.26	0.39	0.34
C	0.76	0.71	0.13	1.46	1.59	0.93	0.17	0.42	0.30
D	0.63	0.60	0.06	1.23	1.29	0.94	0.10	0.43	
E	0.58	0.56		1.14	1.14	0.97		0.40	
F	1.84	1.77	0.19	3.61	3.80	0.96	0.10	0.38	0.20
G	2.13	2.36	0.63	4.49	5.12	1.11	0.29	0.31	0.27
H	1.98	2.01	0.23	3.99	4.22	1.02	0.11	0.34	0.28
1	0.64	0.97	0.35	1.61	1.96	1.52	0.54	0.36	0.26
2	0.22	0.33	0.19	0.54	0.74	1.51	0.90	0.44	0.33

Table 5. Lignin Oxidation Product (mg/100mg OC), Sums and Ratios of Major Groups from Sediment, Particulate Organic Matter and Core D (cont.)

November, 2005 Sediment D Core

Depth(mm)	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
0-20	1.99	2.25	0.59	4.24	4.83	1.13	0.29	2.33	1.56
20-40	2.02	2.84	1.34	4.87	6.20	1.40	0.66	0.24	0.31
40-60	1.62	2.56	1.52	4.19	5.71	1.58	0.94	0.35	0.34
60-80	1.48	1.96	0.86	3.44	4.30	1.33	0.58	0.33	0.36
80-100	1.21	1.83	0.62	3.04	3.66	1.51	0.51	0.06	0.24
100-120	1.27	1.72	0.55	2.99	3.54	1.36	0.43	0.29	0.25
120-140	1.67	1.63	0.53	3.29	3.82	0.97	0.32	0.44	0.58
140-160	1.22	1.79	0.65	3.02	3.66	1.47	0.53	0.05	0.25
160-180	1.56	2.15	1.11	3.70	4.81	1.38	0.71	0.23	0.32
180-200	1.30	1.91	1.07	3.21	4.28	1.47	0.82	0.35	0.33

March, 2006 Sediment

Station	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
A	0.29	0.71	0.18	1.00	1.18	2.49	0.63		0.25
B	2.92	4.17	3.08	7.09	10.17	1.43	1.05	0.35	0.27
C	2.45	3.08	1.61	5.52	7.13	1.26	0.66	0.36	0.37
D	2.50	1.98	0.38	4.49	4.89	0.79	0.15	0.26	0.25
E	1.21	1.35	0.34	2.57	2.91	1.12	0.28	0.26	0.21
F	3.20	3.59	1.32	6.79	8.11	1.12	0.41	0.30	0.30
G	1.61	0.88	0.13	2.49	2.62	0.55	0.08	0.31	0.27
1	1.33	1.85	0.37	3.18	3.55	1.40	0.28	0.27	0.14
SB	0.78	1.07	0.29	1.85	2.14	1.38	0.37	0.33	0.17
SAB	4.09	5.37	2.92	9.46	12.38	1.31	0.71	0.32	0.30

March, 2006 Particulate Organic Matter

Station	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
C	0.75	0.88	0.08	1.63	1.72	1.18	0.11	0.34	0.24
E	1.65	2.29	0.19	3.95	4.14	1.39	0.12	0.43	0.29
F	1.33	1.84	0.38	3.17	3.55	1.38	0.29	0.41	0.26
I	0.76	1.48	0.15	2.24	2.39	1.96	0.20	0.51	0.21

October, 2006 Sediment

Station	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
B	1.87	1.90	0.37	3.76	4.14	1.01	0.20	0.32	0.12
D	2.05	2.87	1.22	4.92	6.15	1.40	0.60	0.31	0.31
E	1.90	1.85	0.39	3.75	4.14	0.98	0.21	0.34	0.14
F	3.39	4.91	1.56	8.30	9.86	1.45	0.46	0.29	0.17
G	1.55	2.68	1.38	4.22	5.61	1.73	0.89	0.35	0.42
H	2.20	4.54	2.97	6.74	9.71	2.07	1.35	0.44	0.32
M1	1.25	1.65	0.67	2.90	3.57	1.33	0.54	0.37	0.27
M2	1.72	3.10	2.26	4.82	7.08	1.80	1.31	0.35	0.34
M3	1.56	2.06	0.64	3.61	4.25	1.32	0.41	0.34	0.24
M4	2.48	2.97	0.84	5.45	6.29	1.20	0.34	0.23	0.20
M5	3.32	4.11	1.78	7.42	9.20	1.24	0.54	0.21	0.19
M6	2.45	3.32	1.06	5.77	6.83	1.35	0.43	0.27	0.23
M7	2.28	3.76	1.59	6.04	7.63	1.65	0.70	0.29	0.23

Table 5. Lignin Oxidation Product (mg/100mg OC), Sums and Ratios of Major Groups from Sediment, Particulate Organic Matter and Core D (cont.)

October, 2006 Particulate Organic Matter

Station	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
A	2.16	1.01	0.48	3.16	3.64	0.47	0.22	0.55	0.50
B	1.86	0.17	0.33	2.03	2.35	0.09	0.18	0.63	
C	1.96	0.74	0.55	2.70	3.25	0.38	0.28	0.79	0.91
D	2.07	0.80	0.62	2.87	3.48	0.39	0.30	0.86	1.11
E	1.61	1.78	0.54	3.38	3.92	1.11	0.33	0.42	0.31
F	1.76	2.40	0.80	4.16	4.95	1.37	0.45	0.54	0.33
G	1.41	0.26	0.29	1.67	1.96	0.19	0.21	0.54	1.91
H	1.40	0.23	0.34	1.64	1.98	0.17	0.25	0.77	1.63

March, 2007 Sediment and Particulate Organic Matter

Station	V	S	C	Λ_6	Λ_8	S/V	C/V	Vd/Vl	Sd/Sl
Sediment									
1	1.18	1.23	0.62	2.40	3.02	1.04	0.53	0.76	0.76
Hatch	1.48	1.19	0.05	2.68	2.72	0.81	0.03	0.38	0.35
POM									
1	1.07	0.95	0.35	2.02	2.36	0.89	0.33	0.41	0.37
12	1.37	1.20	0.47	2.57	3.04	0.88	0.34	0.45	0.42
Hatch	1.35	1.49	0.06	2.84	2.90	1.10	0.04	0.46	0.36

Abbreviations: V=sum of Vanillyl phenols, S=sum of Syringyl phenols, C=sum of Cinnamyl phenols, Λ_6 = sum of V + S phenols, Λ_8 = sum of V + S + C phenols,
Vd= Vanillic acid, Vl= Vanillin, Sd= Syringic acid, Sl= Syringaldehyde.

Table 6. $\delta^{13}C$ Comparison of Sediment, Lignin Oxidation Product and Particulate Organic Matter vs Station and Date

	March, 2002		November, 2002		November, 2005			March, 2006		
Station	SED	LOP	SED	LOP	SED	LOP	POM	SED	LOP	POM
A	-25.43	-27.16	-25.51	-28.57	-27.36		-26.55	-26.24		-27.23
B	-24.00	-25.67	-24.24	-26.13			-25.56	-25.98	-27.54	-26.48
C	-22.79	-23.56	-23.66	-24.96	-24.04	-25.54	-24.88	-24.10	-25.02	-26.05
D	-23.82	-25.31	-17.25	-19.48	-24.11	-26.11	-25.31	-24.28	-26.24	-26.58
E	-22.97	-24.06	-22.44	-24.00	-21.35	-22.60	-25.17	-22.42		
F	-22.81	-23.13	-21.82	-22.58	-22.74	-23.31	-24.19	-23.65	-24.82	
G			-22.51	-23.39	-22.40		-24.03	-22.48		-24.96
H					-22.94		-24.42	-23.87		-25.09
I										
2										
3								-21.92	-26.80	
4								-18.38	-27.20	

Table 7. Lignin Oxidation Products $\delta^{13}C$ by GC/IRMS in Sediment and Particulate Organic Matter

March, 2002 Sediment

Station	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A	-25.47	-22.39	-29.27	-25.50	-27.46	-22.40	-29.20	-38.17	-29.27	-21.30	-21.47
B	-24.44	-22.54	-28.15	-23.70	-26.76	-19.36	-27.17	-34.84	-27.61	-18.87	-18.28
C	-23.80	-21.36	-27.34	-22.23	-25.78	-18.38	-26.67	-32.07	-27.15	-19.79	-16.73
D	-24.30	-23.29	-29.67	-24.19	-26.23	-25.28	-29.55	-31.82	-29.77	-20.52	-18.25
E	-23.07	-21.31	-27.68	-22.22	-25.50	-23.72	-29.21	-33.29	-26.71	-16.16	-16.41
F	-18.26	-18.21	-30.04	-23.51	-27.27	-29.80	-31.03	-33.79	-35.32	-7.69	-12.98
G	-20.31	-19.73	-30.90	-22.51	-25.10	-26.04	-29.69	-32.69	-28.94	-15.18	-14.14
H	-20.60	-20.86	-27.01	-28.16	-25.32	-25.30	-29.02	-33.21	-19.90	-13.49	-13.59

Nov., 2002 Sediment

Station	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A	-23.83	-22.63	-36.15	-27.42	-30.38	-31.90	-30.85	-32.37	-32.74	-21.91	-22.80
B	-22.03	-24.04	-29.23	-24.24	-25.61	-23.41	-27.38	-29.94	-27.21	-18.90	-18.35
C	-22.71	-22.75	-28.41	-19.25	-25.50	-26.30	-26.95	-27.22	-26.08	-17.40	-15.54
D	-18.40	-19.16	-25.04	-21.54	-25.41	-22.98	-28.48	-30.32	-27.78	-12.11	-14.84
E	-23.88	-24.10	-29.79	-23.75	-27.15	-25.13	-29.78	-35.87	-29.01	-10.23	-13.34
F	-23.78	-27.28	-30.07	-22.84	-26.80	-24.91	-29.34	-35.33	-28.47	-8.04	-10.75
G	-23.39	-22.85	-25.87	-21.20	-24.52	-18.93	-25.24	-29.87	-24.14	-16.38	-16.04

Nov., 2005

Station	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
C	-20.00	-22.50	-26.97	-26.91	-24.80	-23.57	-27.43	-31.26	-29.64	-16.26	-18.08
D	-18.73	-18.53	-25.32	-19.78	-21.91	-20.28	-25.86	-33.67	-22.53	-14.00	-12.98
E	-21.90	-17.04	-26.54	-23.85	-32.09	-21.41	-37.90	-41.43	-34.44	-12.48	-10.79
F	-24.24	-16.65	-29.09	-24.88	-34.21	-25.39	-28.47	-41.72	-36.71	-13.16	-7.76
G	-24.67		-24.88	-24.26	-33.12	-27.35	-44.85	-27.89	-33.04	-8.41	-6.17
H	-25.20			-28.93		-34.89	-38.46	-38.39	-30.88		
I	-26.36	-29.78	-27.47	-23.18	-27.24	-16.27	-27.39	-38.85	-27.85	-17.52	-17.60
SAB	-34.01	-49.51	-37.12	-26.27	-32.37	-26.25	-31.85	-43.97	-33.43	-8.63	-18.69

March, 2006

Station	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A	-22.27		-29.51	-25.39	-23.17	-27.43	-27.39	-31.52	-28.51	-18.59	-17.66
B	-24.57	-26.22	-27.79	-25.42	-25.35	-20.97	-27.22	-29.91	-28.99	-20.27	-18.98
C	-19.95	-28.93	-24.43	-22.80	-22.10	-22.57	-23.51	-26.01	-24.84	-13.03	-12.25
D	-21.77	-21.89	-26.52	-22.45	-20.02	-25.02	-24.95	-27.15	-25.47	-14.93	-16.19
E	-23.88	-23.37	-17.62	-30.46	-32.16	-29.55	-25.10	-40.98	-24.76	-18.09	-9.89
F	-22.27	-22.88	-25.86	-23.09	-23.42	-23.82	-24.50	-28.62	-25.46	-15.16	-14.50
G			-26.65	-32.41	-36.15	-33.87	-24.65		-31.17	-15.50	
H			-17.02			-25.90	-26.93				-29.84
I	-16.97		-23.85	-20.77	-16.85	-19.76	-22.69	-26.03	-22.71	-14.80	-29.38
SB	-17.42		-23.72	-15.92	-16.12	-19.94	-22.54	-24.11	-17.69	-14.42	-30.58
2							-29.17				-32.11
3	-17.30						-30.64				-30.36
4	-18.86						-28.96				-31.83
SAB							-26.09				-32.69

Table 7. Lignin Oxidation Products $\delta^{13}C$ by GC/IRMS in Sediment and Particulate Organic Matter (cont.)

Oct., 2006											
Station	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A	-19.89		-34.32	-25.59	-26.54	-32.59	-29.87	-33.16	-24.63	-22.08	
B	-19.66		-30.88	-23.30	-21.10	-30.23	-27.09	-30.08	-29.06	-18.36	-18.67
C											
D	-16.37	-16.06	-22.72	-17.91	-19.31	-17.74	-21.25	-25.49	-21.48	-14.16	-11.09
E	-16.96		-23.10	-20.15	-24.10	-26.20	-24.81	-26.65	-24.19	-15.58	-13.32
F	-19.18		-26.94	-21.41	-19.20	-23.91	-24.95	-27.42	-25.07	-16.71	-14.88
G	-24.35	-14.63	-27.02	-19.74	-23.87	-20.74	-24.57	-27.64	-24.49	-18.56	-16.24
H	-20.42	-19.72	-25.98	-18.09	-21.88	-19.77	-22.52	-26.51	-24.48	-15.45	-12.51
M1	-23.35	-25.03	-29.36	-22.16	-29.23	-31.82	-28.53	-29.16	-26.44	-19.70	-23.49
M2	-22.34	-16.58	-26.57	-19.46	-23.41	-20.45	-23.89	-27.21	-25.52	-15.64	-24.42
M3	-23.60	-23.74	-33.32	-24.57	-30.24	-30.64	-29.30	-29.48	-28.56	-18.35	-19.41

Oct., 2006											
Station	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A POM	-24.04	-31.48	-26.01	-20.80	-23.33	-22.33	-23.92	-29.69	-22.25	-17.24	-20.83
B POM	-24.18	-30.67	-29.08	-9.59	-31.01	-27.63	-32.47	-32.52	-22.24	-13.95	
C POM		-27.58	-28.26	-2.28	-30.27	-27.37	-32.98	-33.63	-23.70	-14.00	
D POM		-30.00	-23.28	-6.18	-30.93	-28.79	-31.26	-29.73	-26.27	-19.85	
E POM	-21.73	-21.07	-27.69	-20.83	-23.26	-22.30	-25.04	-26.03	-23.33	-13.57	-18.44
F POM	-20.60	-19.72	-26.99	-20.74	-22.34	-20.36	-24.71	-25.16	-23.20	-13.41	-17.74
G POM		-25.96	-27.23	-8.66	-30.68	-27.31	-30.66	-30.37	-18.89	-15.96	-26.08
H POM		-26.80	-27.49		-31.84	-24.63	-31.00	-28.72	-20.29	-9.50	

March, 2007											
Station	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
47 Hatch		-20.34	-33.15	-32.78	-26.47	-45.94	-31.40		-30.33		
Hatch POM	-26.10	-26.10	-30.78	-24.33	-33.39	-40.17	-31.98	-35.54	-32.80	-34.03	
1 POM	-29.00	-21.52	-27.89	-17.44	-23.80	-27.69	-25.91	-31.58	-28.10	-16.66	-13.98
12 POM	-26.19	-21.07	-23.36	-17.10	-23.58	-26.23	-25.94	-30.74	-26.59	-17.15	-17.25
15	-27.32	-21.40	-28.10	-19.69	-24.57	-28.16	-26.48	-32.11	-28.35	-15.47	-14.33
1a	-21.56	-26.83	-26.83	-24.70	-22.19	-26.97	-26.44	-34.15	-26.59	-16.55	-16.07
1b	-35.47	-24.60	-29.38	-18.37	-25.88	-24.92	-30.70	-33.35	-28.94	-20.05	-25.76

Abbreviations: pBl: para-hydroxy Benzaldehyde, pBn: para-hydroxy acetophenone, pBd: para-hydroxy Benzoic acid, Vl: Vanillin, Vn: Acetovanillone, Vd: Vanillic acid, Sl: Syringaldehyde, Sn: Acetosyringone, Sd: Syringic acid, Cd: para-Coumaric acid and Fd: Ferulic acid.

Table 8. $\delta^{13}C$ Comparison of Derivatization Algorithms for Standards

Lignin Phenol	Accepted IRMS	Measured GC/IRMS	Measured Std. Dev.	Calculated Underiv.*	Calculated TMCS	Calculated Underiv.**
pBl	-29.14	-33.56	0.61	-30.58	-43.87	-29.01
pBn	-30.28	-33.41	0.08	-30.75	-41.75	-29.37
pBd	-24.81	-32.84	0.14	-26.27	-41.68	-23.13
Vl	-27.49	-31.36	0.24	-27.93	-43.34	-26.56
Vn	-32.58	-34.50	0.27	-32.50	-40.35	-31.28
Vd	-30.12	-35.09	0.32	-31.04	-40.26	-28.29
Sl	-31.77	-33.77	0.13	-31.52	-42.20	-30.30
Sn	-35.83	-37.06	0.21	-36.03	-39.76	-34.93
Sd	-32.49	-37.38	0.46	-35.30	-41.72	-32.86
Cd	-22.02	-29.55	0.13	-22.25	-41.16	-19.81
Fd	-25.28	-30.93	0.29	-25.19	-44.72	-22.99
tCa	-32.27	-35.04	0.08	-33.22	-40.85	-31.99
EV	-27.48	-31.65	0.21	-28.70	-44.17	-27.48
				* based on meas TMCS = -40.50		** based on EV TMCS = -44.17

Table 9. $\delta^{13}C$ and ^{14}C of Sediment and POM

Sediment Mar.,2002	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	80.36	1.25	1756	-25.43	80.43	-196
B	99.28	0.48	58	-24.00	99.08	-9
C	87.46	0.44	1076	-22.79	87.08	-129
D	62.64	0.34	3758	-23.82	62.49	-375
E	98.21	0.47	145	-22.97	97.81	-22
F	96.50	0.55	286	-22.81	96.08	-39
G	82.99	0.48	1497	-23.28	82.70	-173
H	97.09	0.48	237	-21.02	96.31	-37
I	105.52	0.53	Post-Modern	-23.49	105.20	52
Nov., 2002	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	87.63	0.45	1060	-25.51	87.72	-123
B	99.59	0.50	33	-24.24	99.44	-6
C	99.86	0.49	11	-23.66	99.59	-4
D	58.04	0.33	4370	-15.82	56.97	-430
E	97.06	0.49	239	-22.44	96.57	-34
F	98.36	0.51	133	-20.42	97.45	-25
G	97.31	0.51	218	-22.51	96.83	-32
H	>200	18.43	Post-Modern	-24.54		
I	159.30	0.90	Post-Modern	-25.50	159.46	595
Nov., 2005	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	102.90	0.53	Post-Modern	-27.36	103.38	34
B	167.05	0.82	Post-Modern		167.05	671
C	101.87	0.50	Post-Modern	-24.04	101.67	17
D	100.99	0.56	Post-Modern	-24.11	100.81	8
E	79.59	0.45	1834	-21.35	79.01	-210
F	82.57	0.47	1538	-22.74	82.20	-178
G	95.65	0.52	357	-22.40	95.15	-49
H	185.52	1.00	Post-Modern	-22.94	184.75	848
I	85.71	0.50	1238	-20.38	84.92	-151
Core D	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
0-20	107.52	0.55	Post-Modern	-24.29	107.37	74
20-40	101.75	0.54	Post-Modern	-24.74	101.70	17
40-60	100.61	0.53	Post-Modern	-23.55	100.32	3
60-80	99.72	0.55		-23.62	99.44	-6
80-100	93.78	0.50		-23.64	93.52	-65
100-120	98.59	0.55		-23.55	98.30	-17
120-140	99.06	0.55		-23.49	98.76	-12
140-160	98.59	0.51		-23.28	98.25	-17
160-180	99.24	0.53		-23.38	98.92	-11
180-200	98.99	0.52		-23.29	98.65	-13

Table 9. $\delta^{13}C$ and ^{14}C of Sediment and POM (Cont.)

Sediment Mar., 2006	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	96.01	0.51	327	-26.24	96.25	-38
B	91.84	0.49	683	-25.98	92.02	-80
C	97.49	0.51	203	-24.10	97.32	-27
D	100.36	0.51	14	-24.28	100.21	2
E	86.17	0.46	1195	-22.42	85.73	-143
F	96.31	0.49	301	-23.65	96.05	-39
G	82.94	0.48	1502	-22.48	82.52	-175
H	>200	7.57	Post-Modern	-23.87		
H >20	138.37	0.62	Post-Modern	-26.47	138.78	388
H <60	95.40	0.51	378	-22.77	94.97	-50
I	85.55	0.47	1253	-21.73	84.99	-150
SB	91.18	0.49	741	-21.47	90.54	-95
2	87.55	0.47	1067	-24.53	87.47	-125
2 >20	185.69	0.83	Post-Modern	-21.41	184.36	844
2 >35	>200	1.28	Post-Modern	-14.82		
2 >60	142.80	0.68	Post-Modern	-21.60	141.83	418
2 <60	122.56	0.59	Post-Modern	-21.14	121.61	216
3	85.66	0.47	1243	-21.92	85.13	-149
3 >20	194.79	0.89	Post-Modern	-21.00	193.23	932
3 >35	196.83	0.94	Post-Modern	-21.86	195.60	956
3 >60	122.81	0.62	Post-Modern	-21.52	121.96	220
3 <60	115.78	0.60	16	-21.79	115.03	150
4	128.43	0.63	Post-Modern	-18.38	126.72	267
4 >20	76.41	0.42	2173	-23.26	76.15	-239
4 >35	93.83	0.51	526	-22.52	93.36	-66
4 >60	100.28	0.52	14	-21.47	99.57	-4
4 <60	63.64	0.39	3630	-21.13	63.14	-369
SAB	70.24	0.36	2838	-21.23	69.71	-303
Oct.,2006	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	104.07	0.45	Post-Modern	-26.23	104.32	43
B	90.48	0.40	803	-24.16	90.33	-97
D	86.63	0.39	1154	-21.82	86.07	-139
E	98.38	0.42	130	-22.79	97.95	-21
F	98.32	0.56	136	-22.92	97.91	-21
G	97.89	0.43	171	-21.86	97.27	-27
H	97.87	0.44	190	-21.47	97.18	-28
M1	99.32	0.43	55	-22.16	98.76	-12
M2	98.68	0.42	106	-22.42	98.17	-18
M3	101.51	0.43	Post-Modern	-22.02	100.91	9
M4	95.96	0.42	331	-20.94	95.18	-48
M5	95.63	0.41	359	-20.35	94.74	-53
M5A	92.63	0.40	614	-20.52	91.80	-82
M6	96.90	0.42	253	-20.70	96.07	-39
M7	70.28	0.37	2833	-18.82	69.41	-306
M8	101.28	0.43	Post-Modern	-20.57	100.38	4

Table 9. $\delta^{13}C$ and ^{14}C of Sediment and POM (Cont.)

Sediment Mar.,2007	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
1	96.43	0.44	292	-20.70	95.60	-44
2	93.64	0.61	527	-20.62	92.82	-72
3	98.62	0.46	111	-21.98	98.03	-20
4	94.83	0.47	426	-21.95	94.26	-57
5	96.77	0.46	263	-21.39	96.08	-39
6	87.62	0.43	1061	-14.46	85.77	-142
7	87.08	0.45	1111	-17.63	85.80	-142
8	88.40	0.41	990	-17.65	87.10	-129
9	94.27	0.45	473	-20.66	93.45	-65
10	96.75	0.59	265	-20.41	95.87	-41
11	98.50	0.52	121	-22.69	98.04	-20
12	86.33	0.45	1181	-22.04	85.81	-142
13	97.68	0.60	188	-23.87	97.46	-25
14	95.98	0.45	329	-23.28	95.65	-44
15A	85.05	0.45	1301	-22.11	84.56	-154
15B	94.28	0.44	473	-24.06	94.10	-59
1A	82.54	0.45	1542	-22.27	82.09	-179
1B	85.16	0.45	1290	-21.44	84.55	-155
47 Hatch	98.60	0.51	113	-27.52	99.10	-9

POM Nov., 2005	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	101.35	0.52	Post-Modern	-26.55	101.66	17
B	102.25	0.51	Post-Modern	-25.56	102.36	24
C	101.54	0.50	Post-Modern	-24.88	101.52	15
D	102.75	0.51	Post-Modern	-25.31	102.81	28
E	101.52	0.50	Post-Modern	-25.17	101.55	16
F	101.24	0.49	Post-Modern	-24.19	101.08	11
G	101.63	0.49	Post-Modern	-24.03	101.43	14
H	101.87	0.50	Post-Modern	-24.42	101.75	18
Mar., 2006	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	91.16	0.56	743	-27.23	91.57	-84
B	90.01	0.47	845	-26.48	90.28	-97
C	94.65	0.46	441	-26.05	94.85	-52
D	82.91	0.42	1505	-26.58	83.17	-168
G	97.00	0.49	244	-24.96	96.99	-30
H	97.30	0.48	219	-25.09	97.32	-27
Mar.,2007	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
15	78.57	0.41	1937	-23.59	78.35	-216
1A	80.38	0.42	1754	-23.53	80.15	-199
1B	85.64	0.44	1245	-26.58	85.91	-141
Hatch	91.30	0.46	731	-28.07	91.86	-81

Table 10. $\delta^{13}C$ and ^{14}C of Lignin Oxidation Products (LOP)

LOP Mar.,2002	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	80.10	0.41	1782	-27.16	80.45	-196
B	97.68	0.52	188	-25.67	97.81	-22
C	82.48	0.40	1548	-23.56	82.24	-178
D	60.08	0.31	4093	-25.31	60.11	-399
E	94.44	0.42	459	-24.06	94.26	-57
F	90.28	0.51	821	-23.13	89.94	-101
Nov., 2002	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	86.34	0.45	1179	-28.57	86.96	-130
B	91.44	0.46	719	-26.13	91.64	-84
C	95.73	0.50	352	-24.96	95.72	-43
D	60.31	0.36	4062	-19.48	59.64	-404
E	95.35	0.43	382	-24.00	95.16	-48
F	94.29	0.50	472	-22.58	93.83	-62
Nov., 2005	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
C	80.74	0.46	1719	-25.54	80.83	-192
D	98.89	0.53	89	-26.11	99.11	-9
E	75.97	0.43	2207	-22.60	75.61	-244
F	76.63	0.40	2140	-23.31	76.37	-236
I	80.67	0.39	1725		80.67	-193
D (0-20)	99.68	0.99	25	-23.91	99.46	-5
D (20-40)	90.12	0.41	835	-27.15	90.50	-95
D (60-80)	85.27	0.39	1279	-25.64	85.38	-146
D (120-140)	84.59	0.39	1344	-25.65	84.70	-153
D (160-180)	82.07	0.45	1587	-25.30	82.12	-179
D (180-200)	85.73	0.52	1237	-24.42	85.63	-144

Table 10. $\delta^{13}C$ and ^{14}C of Lignin Oxidation Products (LOP) (Cont.)

LOP Mar., 2006	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
B	85.83	0.40	1227	-27.54	86.27	-137
C	87.76	0.45	1049	-25.02	87.76	-122
D	89.65	0.50	877	-26.24	89.88	-101
F	88.26	0.47	1003	-24.82	88.23	-118
H >20	117.35	0.69	Post-Modern	-26.44	117.69	177
H <60	76.27	0.47	2176	-24.11	76.13	-239
2 >60	80.46	0.46	1746		80.46	-195
2 <60	73.95	0.42	2423		73.95	-260
3 >20	23.31	0.19	11698	-27.49	23.43	-766
3 >35	78.59	0.45	1935		78.59	-214
3 >60	68.22	0.40	3071		68.22	-318
3 <60	58.45	0.47	4314	-26.11	58.58	-414
4 >20	28.91	0.22	9968	-28.16	29.09	-709
4 >35	34.59	0.34	8528		34.59	-654
4 >60	65.50	0.38	3398		65.50	-345
4 <60	53.89	0.36	4966	-26.23	54.02	-460
SAB >20	18.69	0.18	13471	-28.31	18.81	-812
SAB >60	68.09	0.4	3087		68.09	-319
SAB <60	54.63	0.4	4857	-24.9	54.62	-454
Oct.,2006	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
A	74.83	0.38	2329	-28.26	75.31	-247
B	70.10	0.36	2853	-26.88	70.36	-296
C	67.02	0.39	3214		67.02	-330
D	71.57	0.41	2687	-25.06	71.58	-284
E	80.32	0.40	1760	-26.64	80.58	-194
F	80.12	0.42	1780	-27.25	80.48	-195
G	86.28	0.40	1185	-25.04	86.29	-137
H	78.13	0.37	1982	-24.67	78.08	-219
M1	81.92	0.38	1602	-24.72	81.87	-181
M2	67.61	0.35	3144	-25.41	67.67	-323
M3	86.71	0.38	1145	-23.35	86.42	-136
M4	79.26	0.34	1867	-23.57	79.03	-210
M5	91.21	0.48	738		91.21	-88
M6	64.84	0.40	3480		64.84	-352
M7	56.31	0.29	4613	-20.37	55.79	-442
M8	66.22	0.31	3311	-25.69	66.31	-337
Mar.,2007	14C (pMC)	14C 1 sig	Age (YBP)	δ13C(‰)	Corr.pMC	Δ14C(‰)
15A	78.57	0.41	1937	-23.59	78.35	-216
1A	80.38	0.42	1754	-23.53	80.15	-199
1B	85.64	0.44	1245	-26.58	85.91	-141
47 Hatch	91.30	0.46	731	-28.07	91.86	-81

Table 11. ^{14}C and $\delta^{13}C$ and Normalized Weights of Sediment Size Fractions for Sediment and Lignin Oxidation Products (LOP)

Analysis	fraction-material	Station (distance from Altamaha Sound) H(0)	2(10mi)	3(14mi)	4(19mi)	SAB(47mi)
^{14}C(pMC)						
	>20-Sed	138.37	185.69	194.79	76.41	
	>35-Sed		214.10	196.83	93.83	
	>60-Sed		142.80	122.81	100.28	
	<60-Sed	95.40	122.56	115.78	63.64	
	>20-LOP	117.35		23.31	31.62	18.69
	>35-LOP			78.59		
	>60-LOP		80.46	68.22	65.50	68.09
	<60-LOP	76.27	73.95	58.45	53.89	54.63
$\delta^{13}C$(‰)						
	>20-Sed	-26.47	-21.41	-21.00	-23.26	
	>35-Sed		-14.82	-21.86	-22.52	
	>60-Sed		-21.60	-21.52	-21.47	
	<60-Sed	-22.77	-21.14	-21.79	-21.13	
	>20-LOP	-26.44		-27.49	-28.16	
	>35-LOP					
	>60-LOP					
	<60-LOP	-24.11		-26.11	-26.23	
wt.(g)						
	>20-Sed	19.82	1.97	9.54	22.62	51.53
	>35-Sed	29.92	2.96	13.24	26.82	58.79
	>60-Sed	36.80	14.29	41.73	30.11	69.19
	<60-Sed	2.92	69.92	18.61	12.02	15.62
	total wt.	89.46	89.14	83.12	91.57	195.13
Percent	>20	22.2	2.2	11.5	24.7	26.4
normalized	>35	33.4	3.3	15.9	29.3	30.1
size	>60	41.1	16.0	50.2	32.9	35.5
fractions	<60	3.3	78.4	22.4	13.1	8.0

Table 12. Standards and Solvents $\delta^{13}C$ and ^{14}C (Pre- and Post- PFC)

ID, Compound, (time or rep.)	Calculated mass (ug)	Dual-inlet Pre-PFC δ13C(‰)	GC/IRMS Post-PFC δ13C(‰)	Measured 14C (pMC)	Corrected 14C (pMC)	Accepted 14C (pMC)
20423 Vl	77	-27.05	-28.62	69.40	95.10	104.80
20423 Sl	60	-30.29	-29.98	0.04	0.05	0.02
20423 Sd	175	-32.23	-34.21	0.09	0.15	0.45
20423 Vl (+15)	84	-27.05	-28.18	72.02	98.65	104.80
20423 Sl (+15)	120	-30.29	-31.05	0.14	0.18	0.02
20423 Sd (+15)	105	-32.23	-30.54	2.42	4.02	0.45
20423 Vl (+30)	98	-27.05	-29.36	74.89	102.60	104.80
20423 Sl (+30)	86	-30.29	-29.98	0.10	0.13	0.02
20423 Sd (+30)	79	-32.23	-31.75	0.36	0.60	0.45
3 STD Vl (1)	31	-27.56	-28.66	* 73.46	100.63	107.70
3 STD Vl (2)	38	-27.56		* 79.75	109.28	107.70
3 STD Vl (3)	53	-27.56	-27.10	* 77.19	105.76	107.70
3 STD Vl (4)	77	-27.56		* 77.06	105.58	107.70
3 STD Vl (5)	108	-27.56		75.89	103.97	107.70
3 STD Vl (6)	53	-27.56	-25.68	74.32	101.82	107.70
3 STD Sl (1)	34	-30.85	-31.02	* 84.21	115.04	112.80
3 STD Sl (2)	77	-30.85		* 84.30	115.16	112.80
3 STD Sl (3)	43	-30.85		* 81.96	111.95	112.80
3 STD Sl (4)	46	-30.85	-28.02	85.34	113.45	112.80
Solvents						
Pyridine A		-29.96			0.49	
Pyridine B		-30.25			0.45	
Ethyl acetate B		-28.95			54.77	
Ethyl acetate C		-29.57			0.15	
Hexane		-30.60			0.50	
Acetone		-32.02			0.36	
BSTFA/TMCS		-40.50			0.74	

UGA AMS (error <1.5pMC ~200yr.for PFC, <0.5pMC for solvents)
* UC Irvine Keck AMS (error <0.5pMC)

Table 13. Sample $\delta^{13}C$ (Pre-PFC and Post- PFC) and ^{14}C (Post- PFC)

Date, Station, Compound	Calculated mass(ug)	Dual-inlet Pre-PFC δ13C(‰)	GC/IRMS Post-PFC δ13C(‰)	Measured 14C (pMC)	Corrected 14C (pMC)	Corrected 14C Age (YBP)
Nov.05, C, Vl	87	-26.91	-27.45	* 52.07	71.22	2726
Nov.05, C, Sl	46	-27.43		65.39	87.18	1102
Nov.05, C, Sd	53	-29.64		nd		
Nov.05, I, Vl	43	-23.18		41.65	56.89	4530
Nov.05, I, Sl	60	-27.39		nd		
Nov.05, I, Sd	46	-27.85		nd		
Mar.06, D, Vl	91	-22.45	-23.63	* 58.25	79.72	1821
Mar.06, D, Sl	74	-24.95	-20.97	* 72.61	96.48	288
Mar.06, F, Vl	41	-23.09		nd		
Mar.06, F, Sl	26	-24.50	nd	70.30	93.40	549
Mar.06, F, Sd	29	-25.46	nd	71.18	94.57	448
Mar.06, SAB, Vl	118	-26.27	-27.23	* 36.61	49.96	5574
Mar.06, SAB, Sl	96	-31.85	nd	* 57.04	76.39	2164
Mar.06, SAB, Sd	67	nd	nd	21.08	34.47	8557

UGA AMS (error <1.5pMC ~200yr.)
* UC Irvine Keck AMS (error <0.5pMC)
nd:not detn.

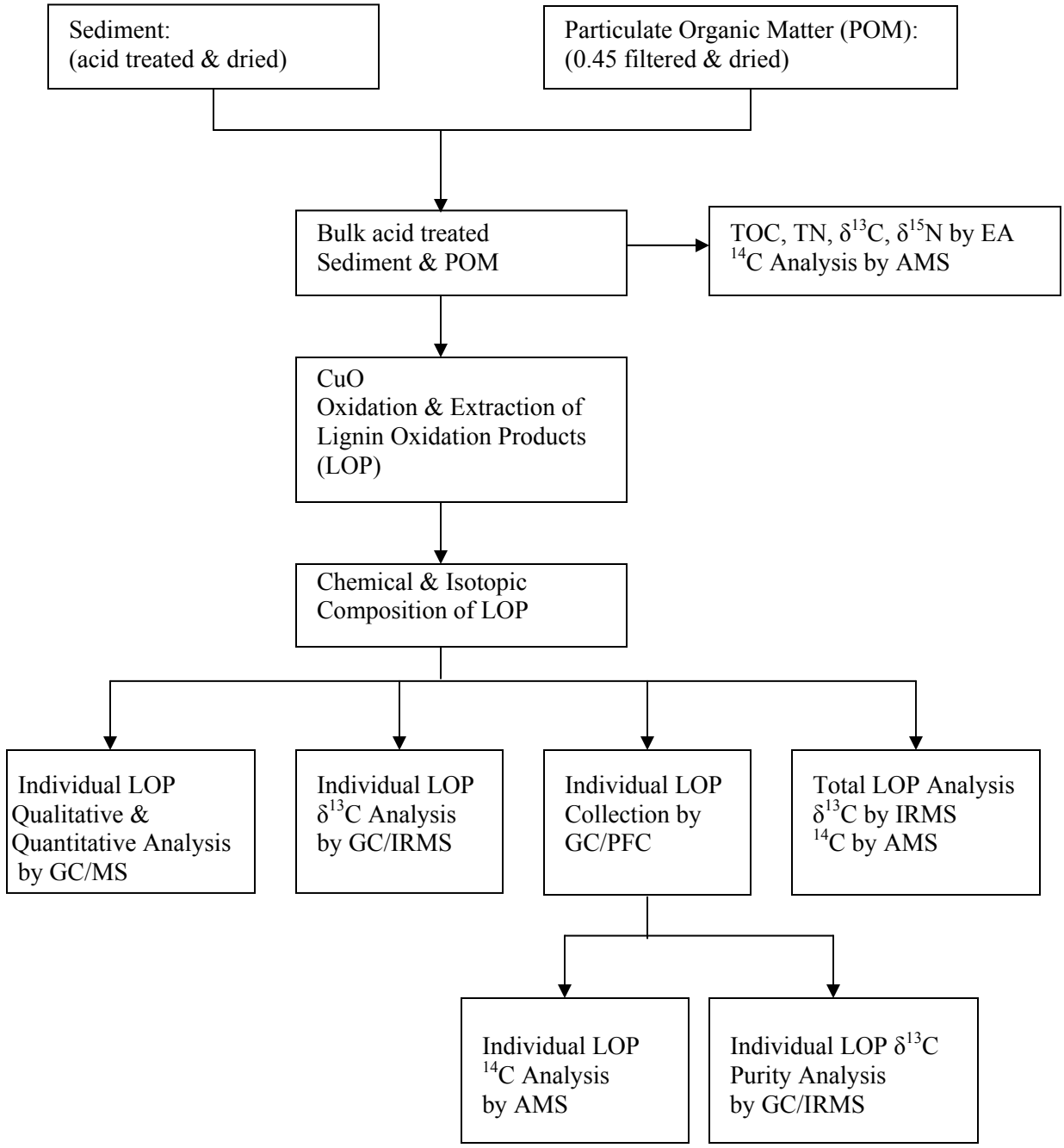
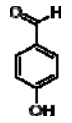
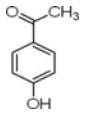
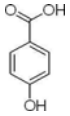
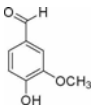
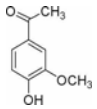
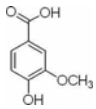
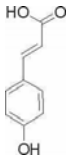
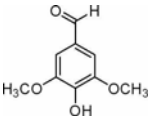
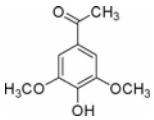
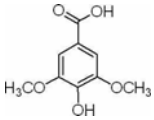
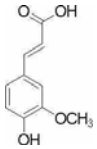
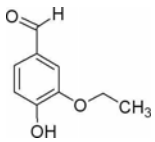
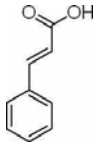


Figure 1. Chemical and Isotopic (^{14}C and $\delta^{13}C$) Analytical Approach

Aldehydes	Ketones	Carboxylic acids	
			
p-hydroxy benzaldehyde	p-hydroxy acetophenone	p-hydroxy benzoic acid	
			
Vanillin	Acetovanillone	Vanillic acid	p-Coumaric acid
			
Syringaldehyde	Acetosyringone	Syringic acid	Ferulic acid
			
	Ethyl Vanillin	t-Cinnamic acid	

Oxidation Products		Plant sources			
		G	g	A	a
p-hydroxy phenols	p-hydroxy benzaldehyde	*	*		*
	p-hydroxy acetophenone	*	*		*
	p-hydroxy benzoic acid	*	*		*
Vanillyl (V)	Vanillin	*	*	*	*
	Acetovanillone	*	*	*	*
	Vanillic acid	*	*	*	*
Syringyl (S)	Syringaldehyde			*	*
	Acetosyringone			*	*
	Syringic acid			*	*
Cinnamyl (C)	p-Coumaric acid		*		*
	Ferulic acid		*		*

S/V ≡ relative amount of angiosperm
C/V ≡ relative amount of non-woody tissue
G & g: Gymnosperm woody and non-woody, A & a: Angiosperm woody and non-woody.
Figure 2. Lignin Oxidation Products (w/ Internal Standards) and Associated Plants

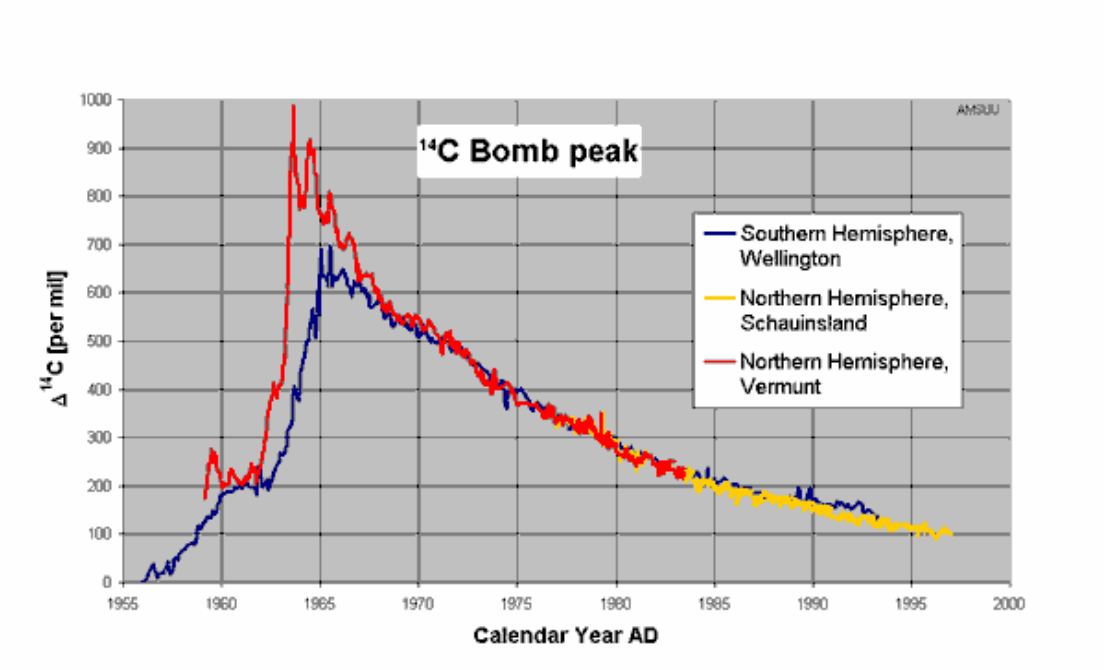


Figure 3. Atmospheric ^{14}C Record (from Manning et al., 1994, Levin et al., 1994)

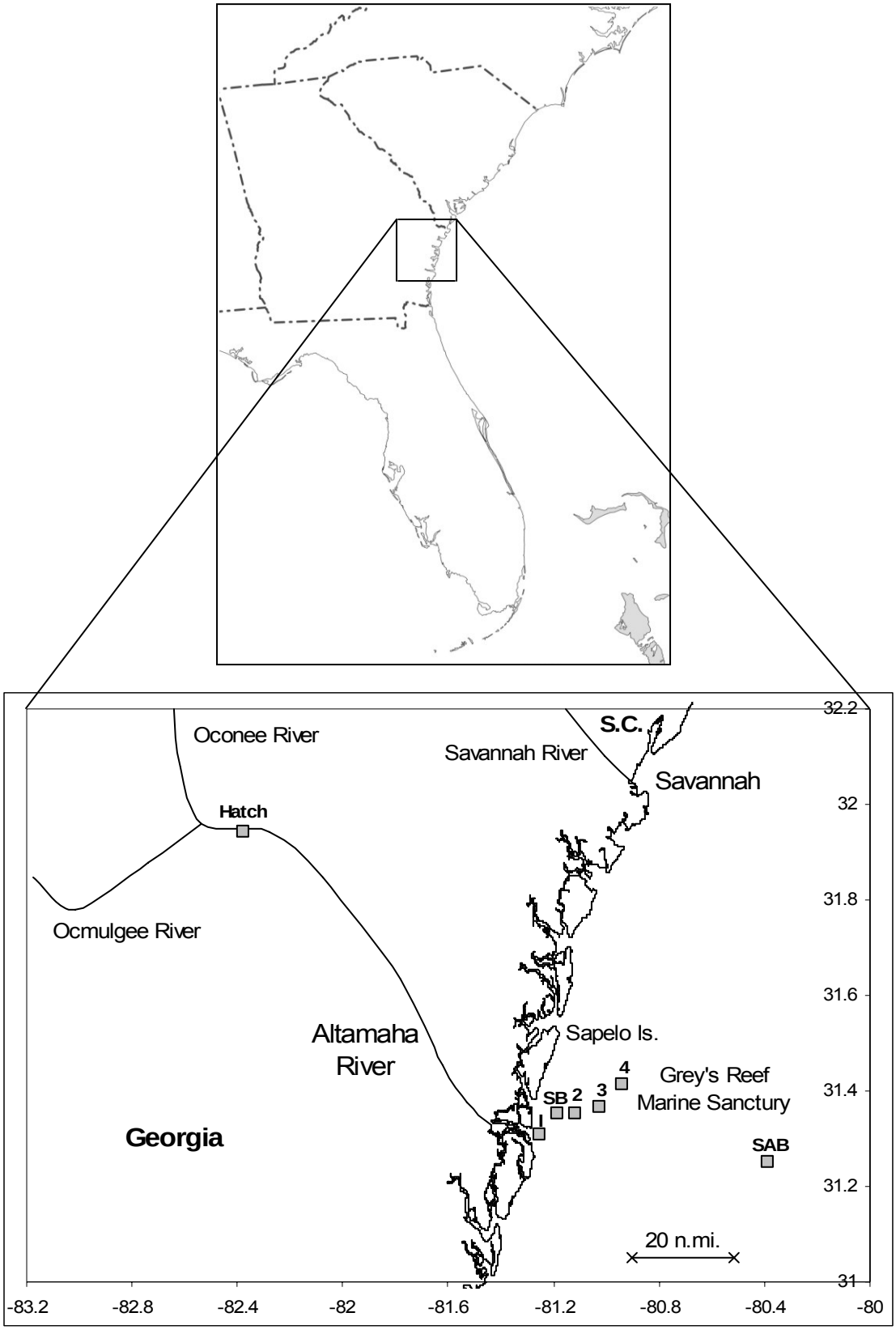


Figure 4. Altamaha River and South Atlantic Bight Sampling Stations

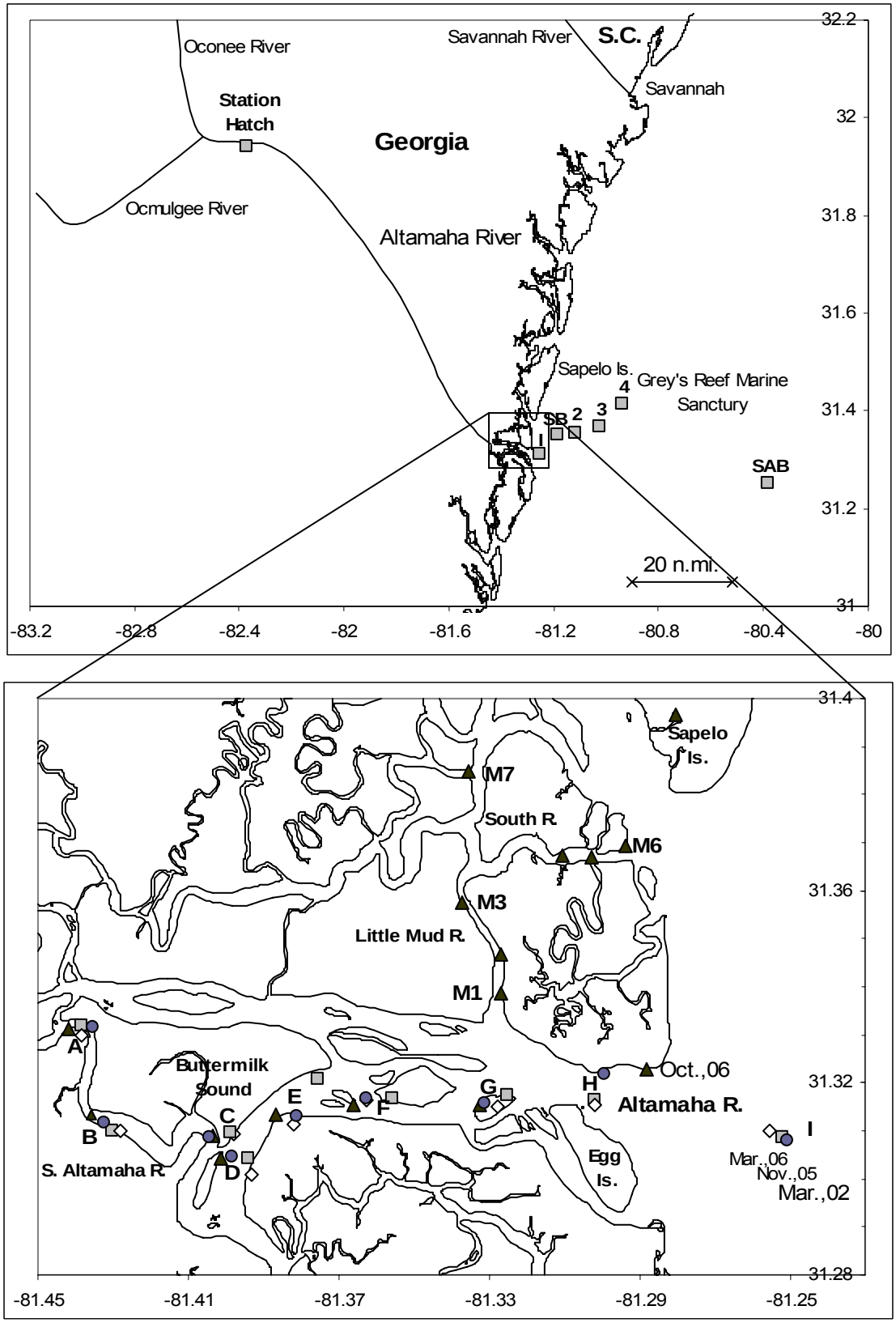


Figure 5. Altamaha River and Estuary Sampling Stations

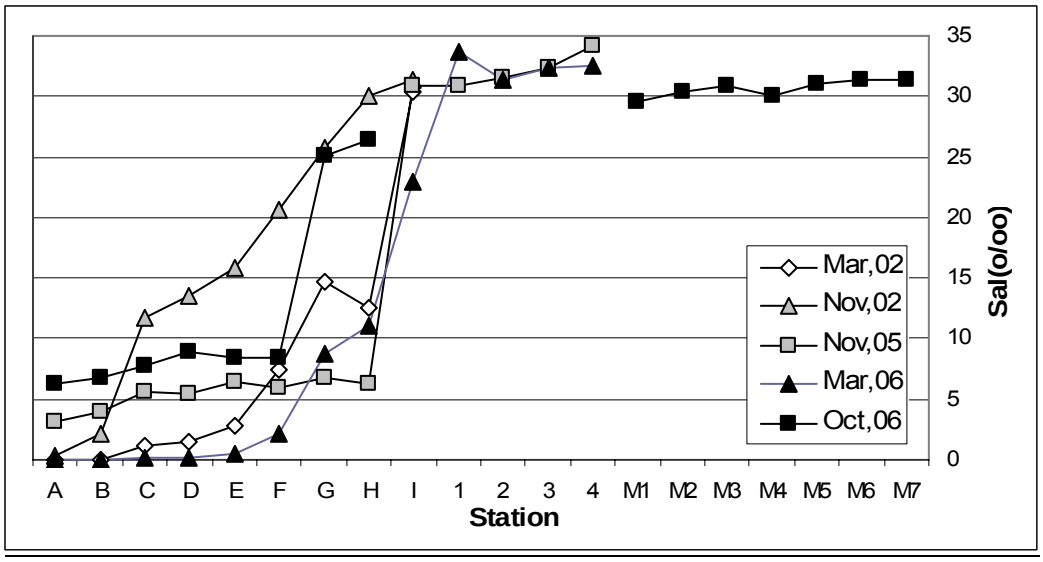


Figure 6. Surface Salinity vs Station and Date

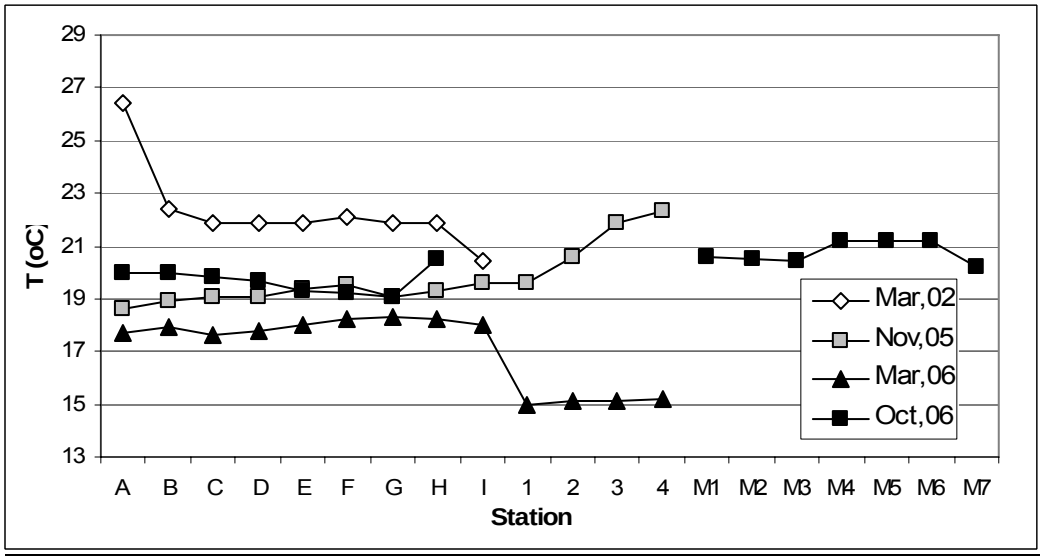


Figure 7. Surface Temperature vs Station and Date

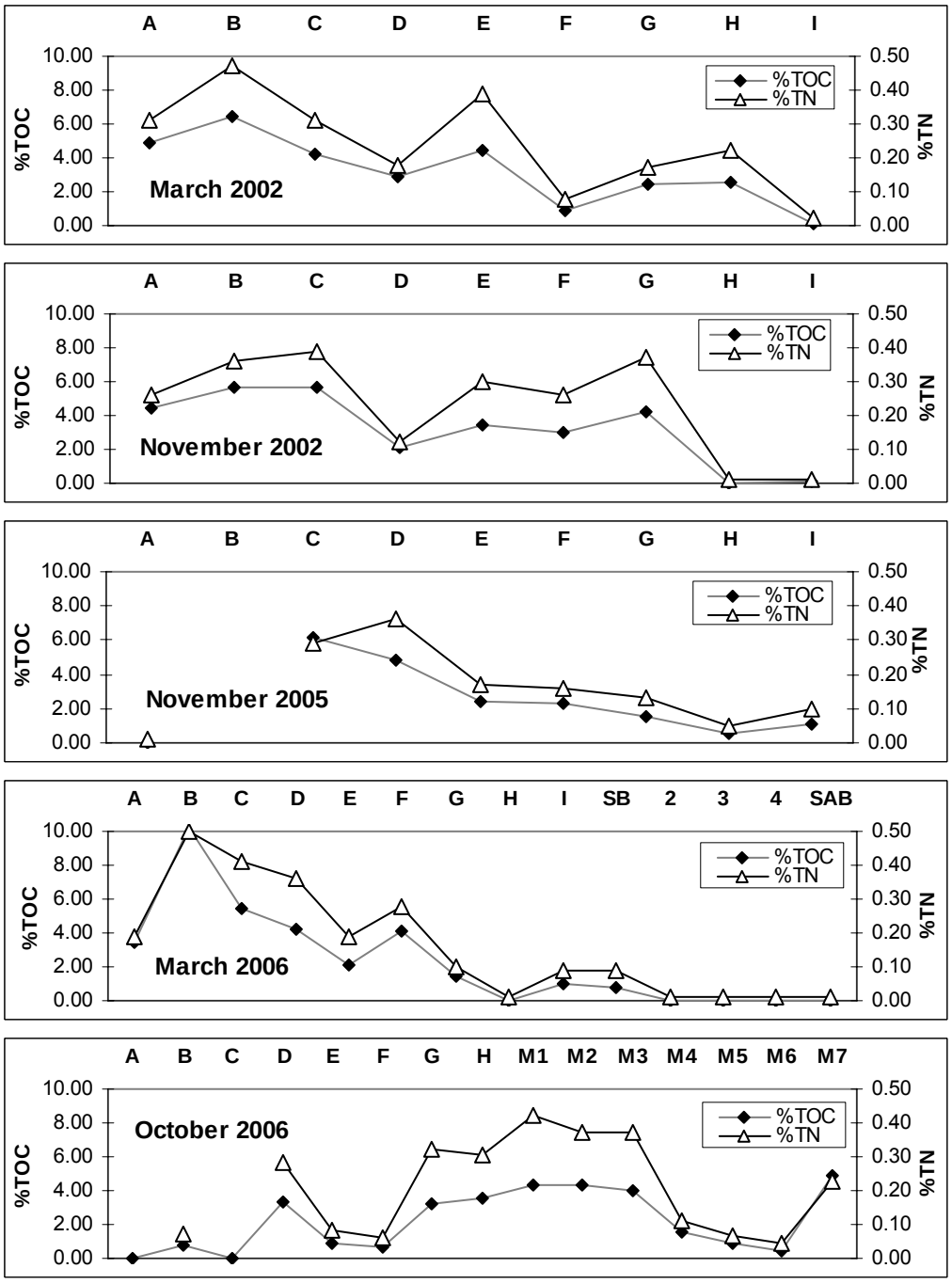


Figure 8. Sediment %TOC and %TN vs Station and Date

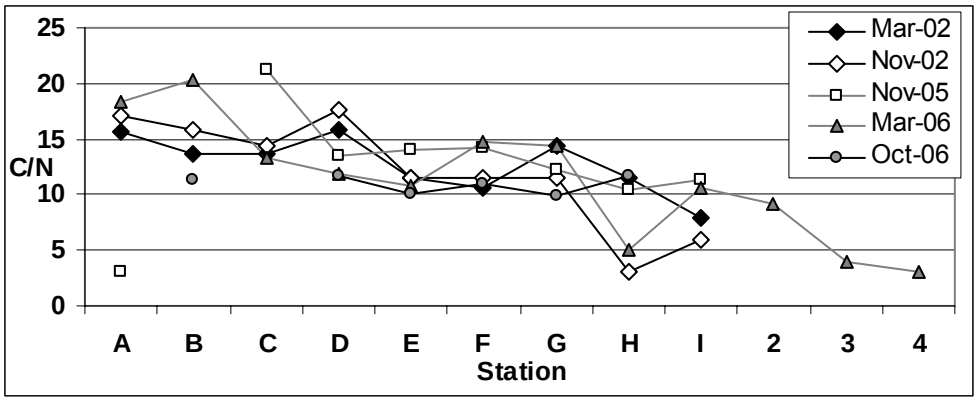


Figure 9. Sediment C/N Ratio vs Station and Date

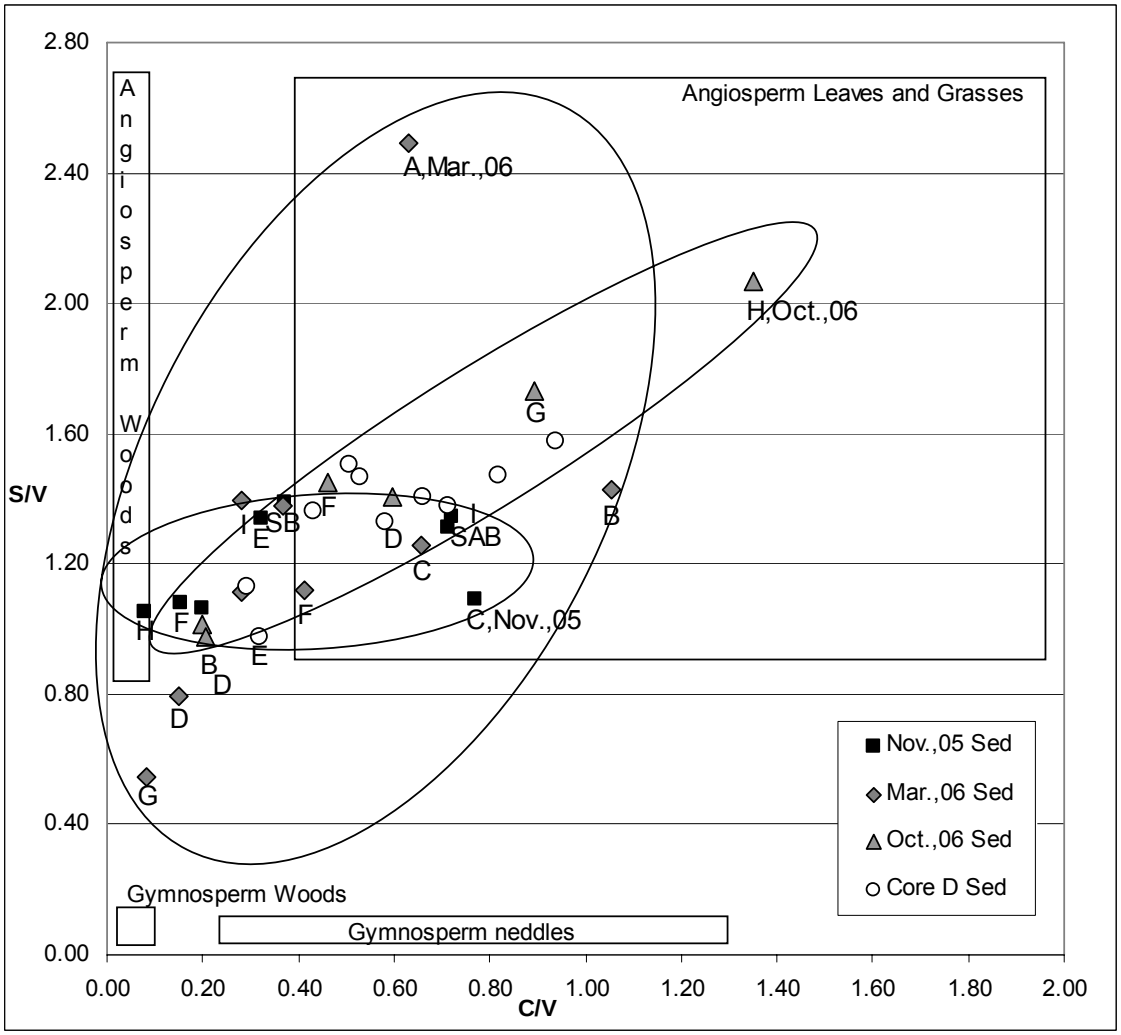


Figure 10. C/V to S/V Ratio for Surface and Core D Sediment vs Date

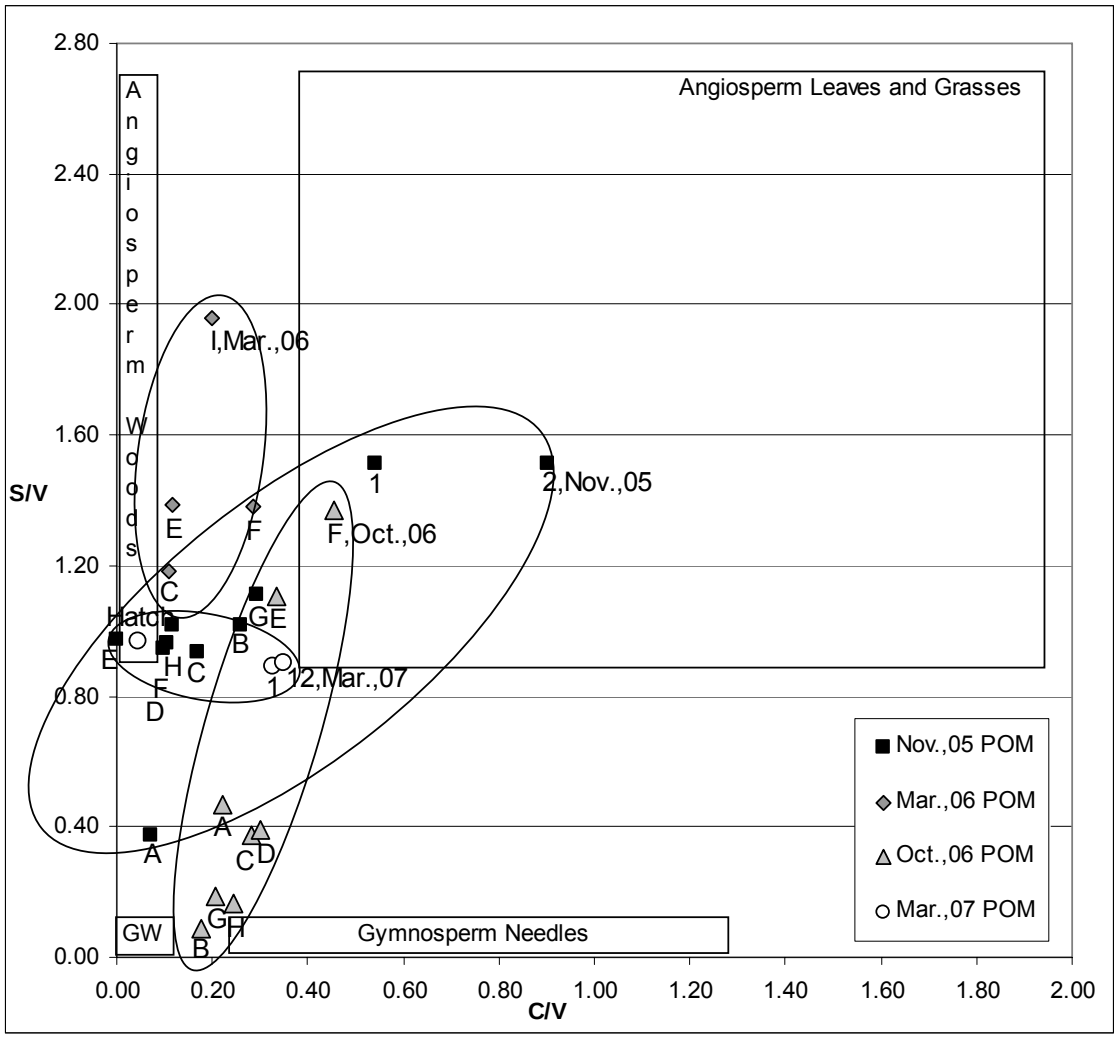


Figure 11. C/V to S/V Ratio for Particulate Organic Matter vs Date

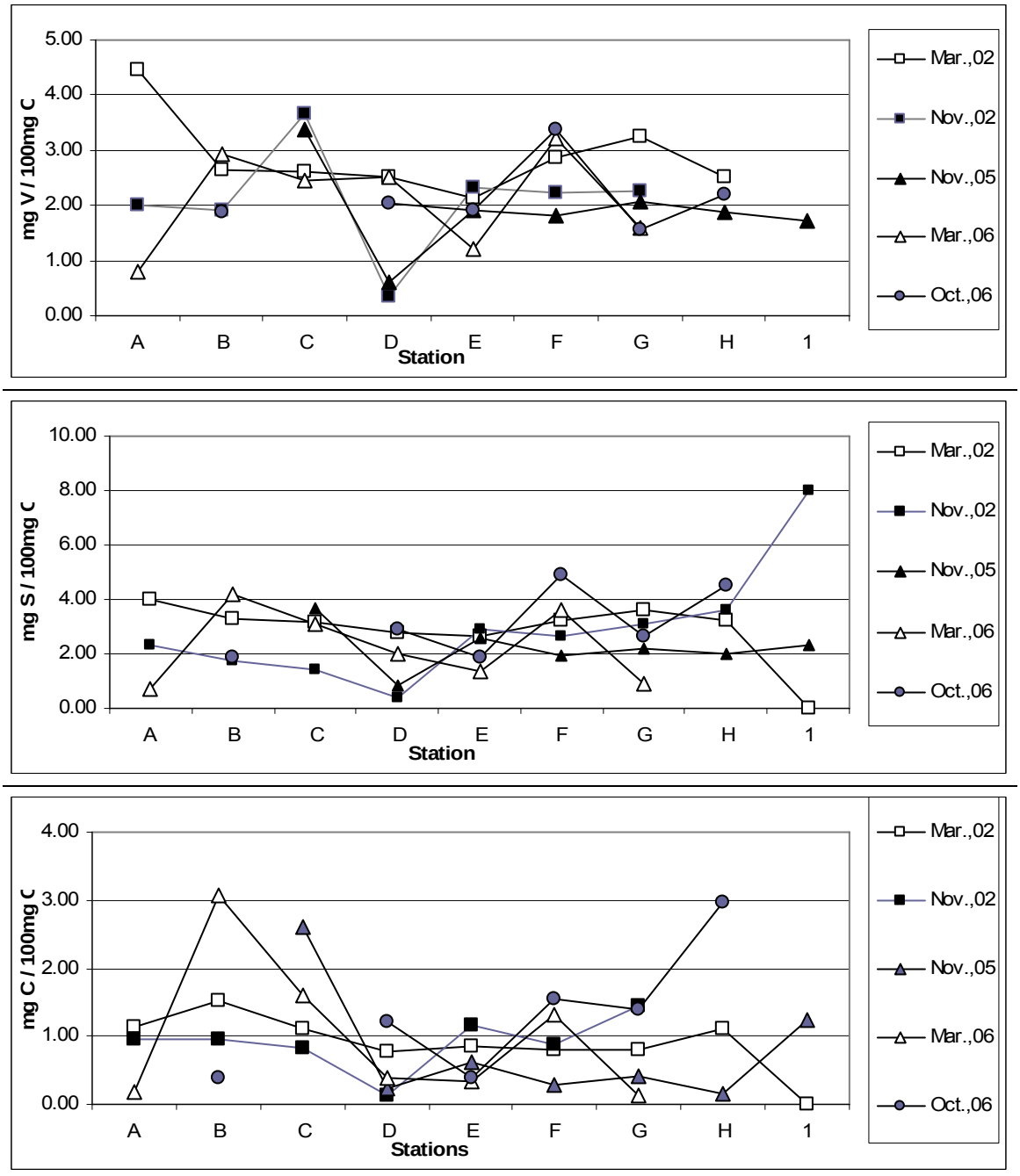


Figure 12. Vanillyl (V), Syringyl (S) and Cinnamyl (C) vs Station and Date.

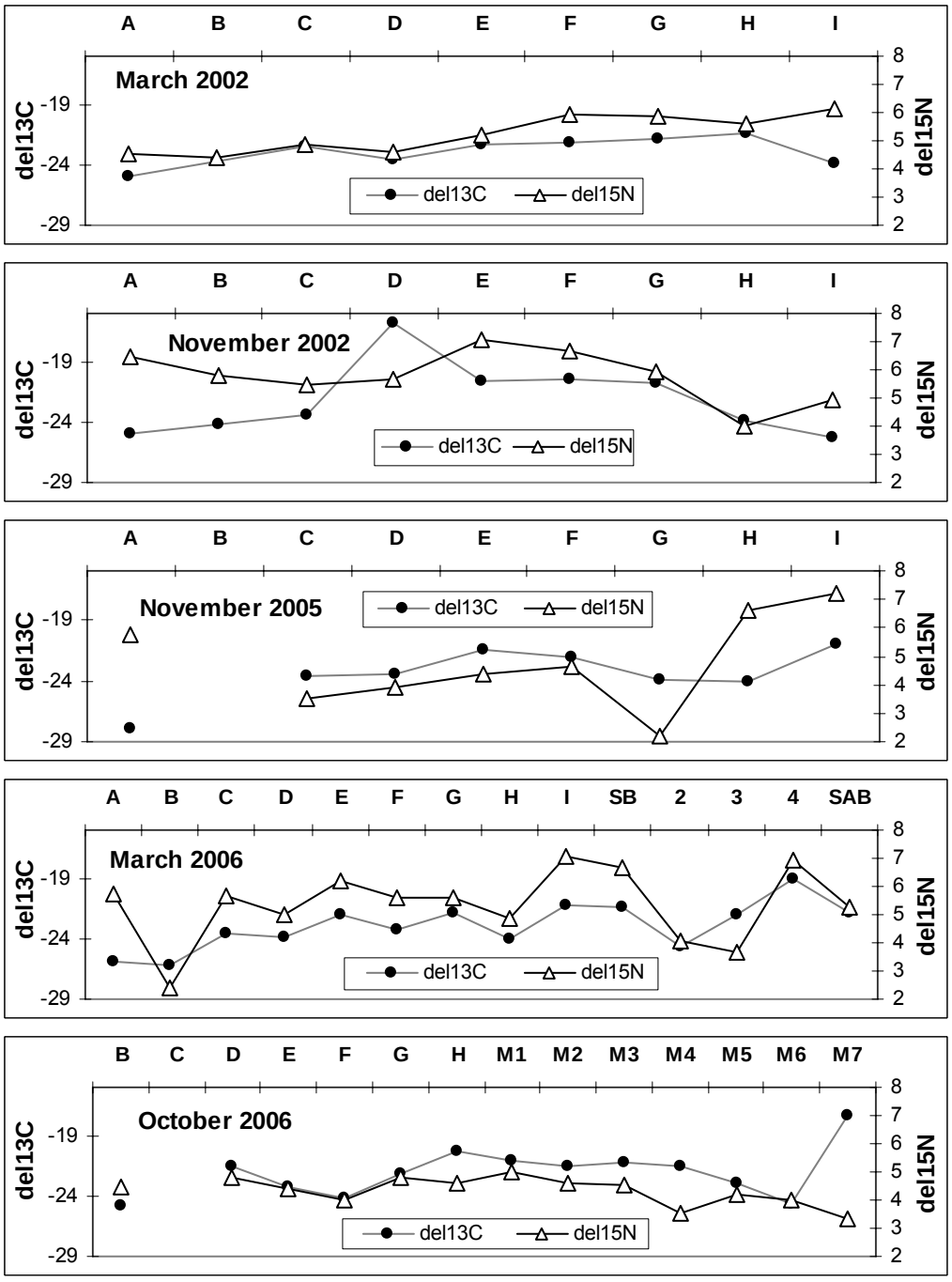


Figure 13. Sediment $\delta^{13}C$ and $\delta^{15}N$ vs Station and Date

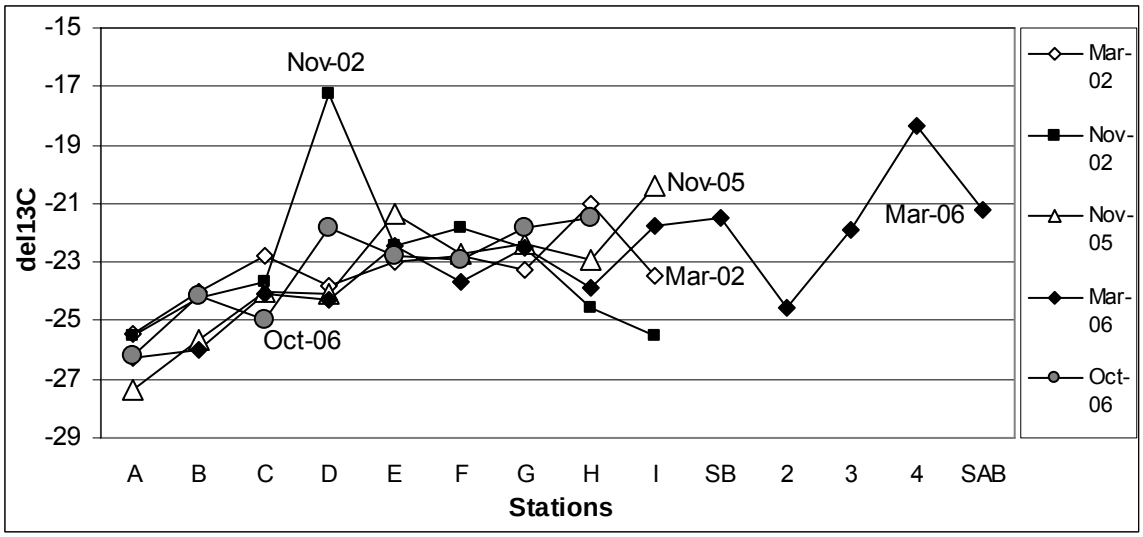


Figure 14. Sediment $\delta^{13}C$ for First Five Sampling Dates.

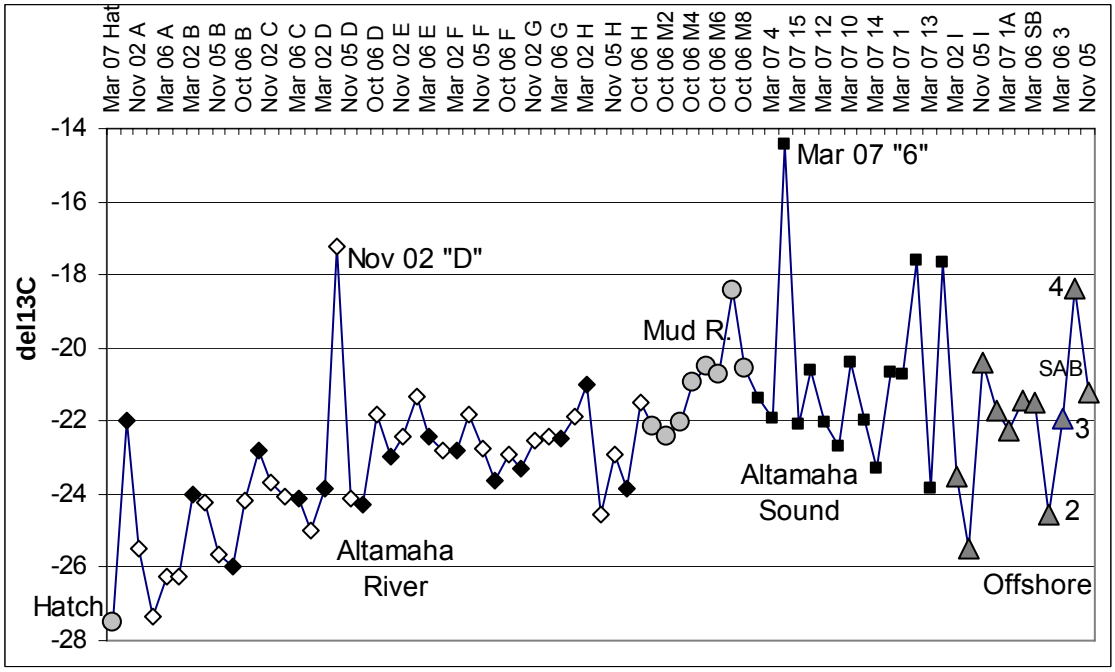


Figure 15. Sediment $\delta^{13}C$ at All Stations and Dates

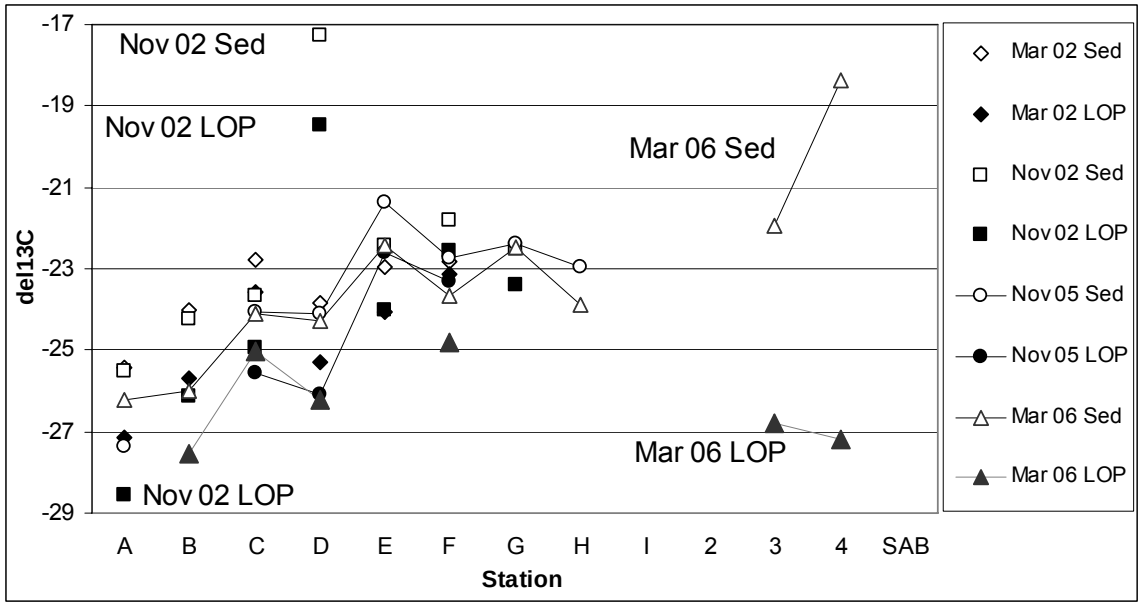


Figure 16. $\delta^{13}C$ Comparison of Sediment (open symbols) and Lignin Oxidation Products (closed symbols) vs Station and Date

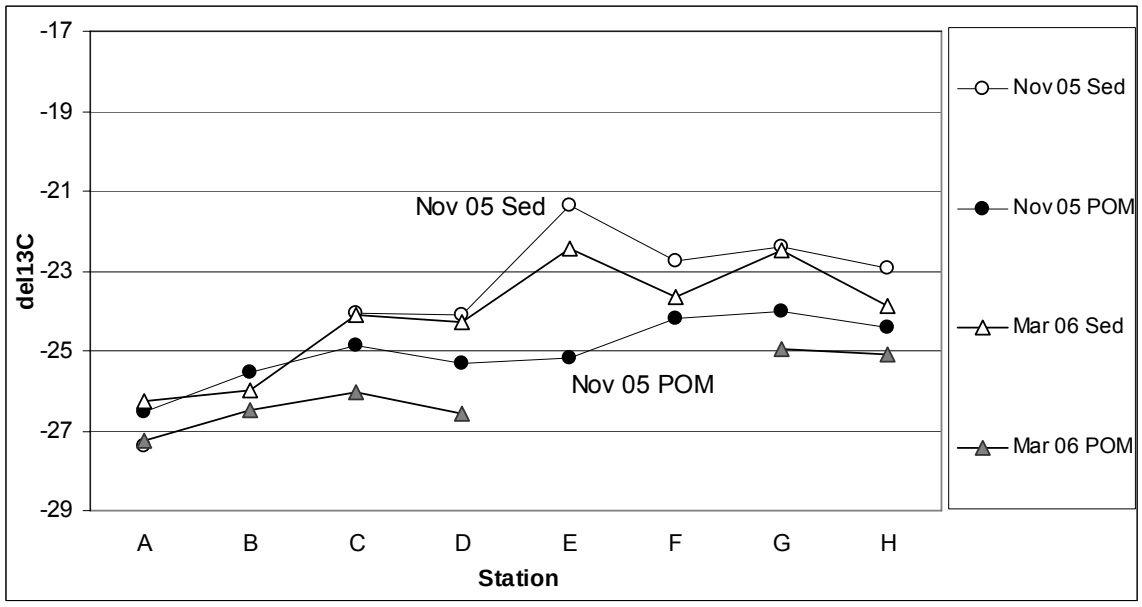


Figure 17. $\delta^{13}C$ Comparison of Sediment (open symbols) and Particulate Organic Matter (closed symbols) vs Station and Date

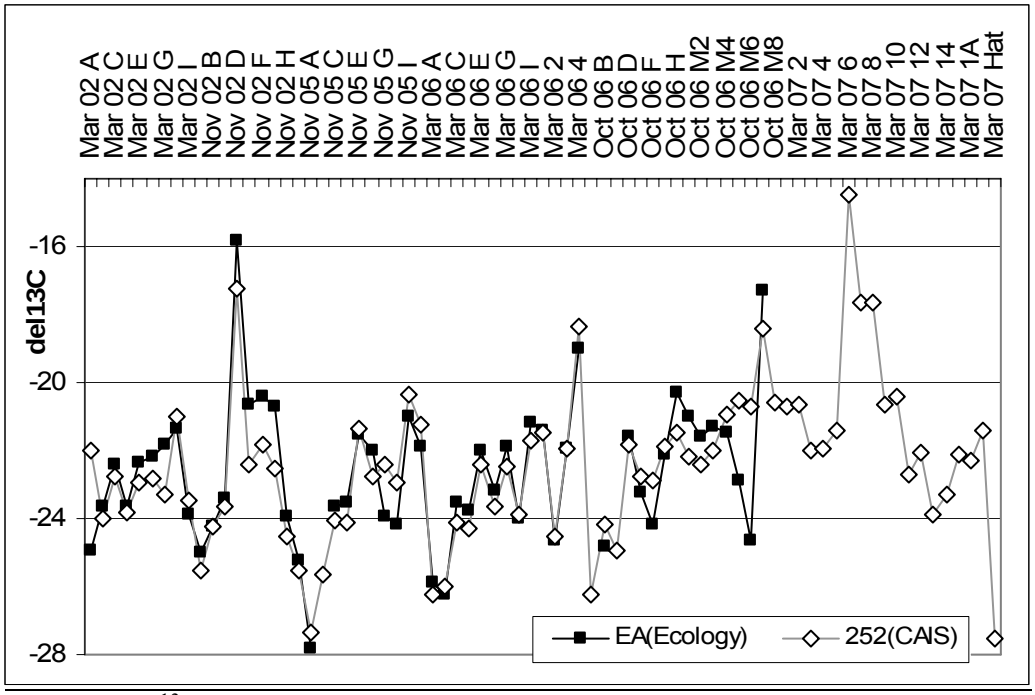


Figure 18. $\delta^{13}C$ Comparison between Continuous Flow and Dual-Inlet IRMS

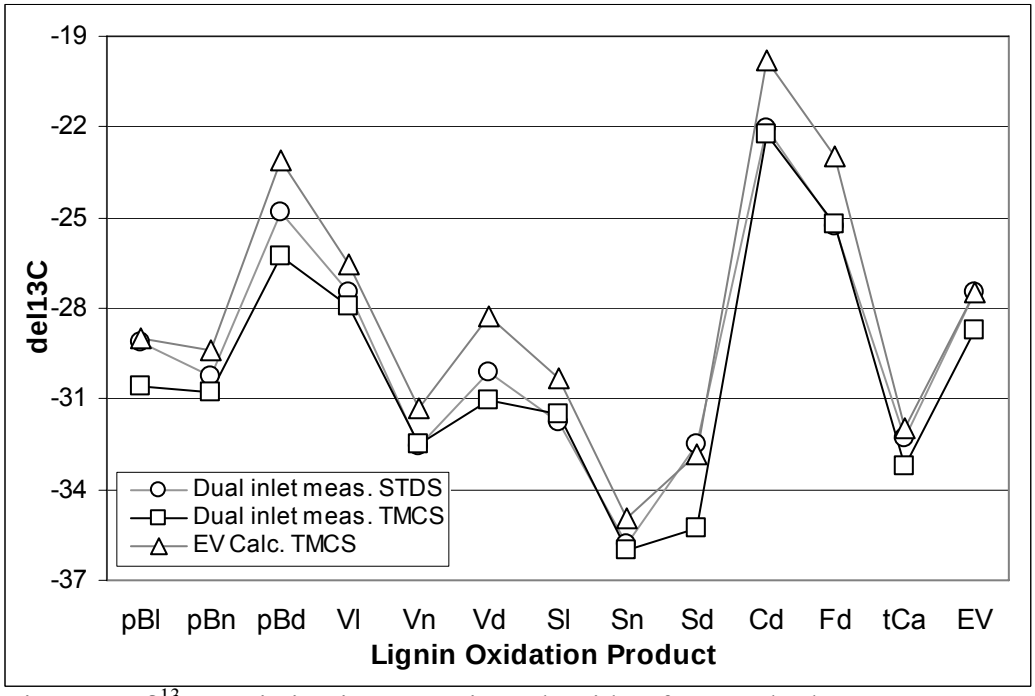


Figure 19. $\delta^{13}C$ Variation in Correction Algorithm for Standards

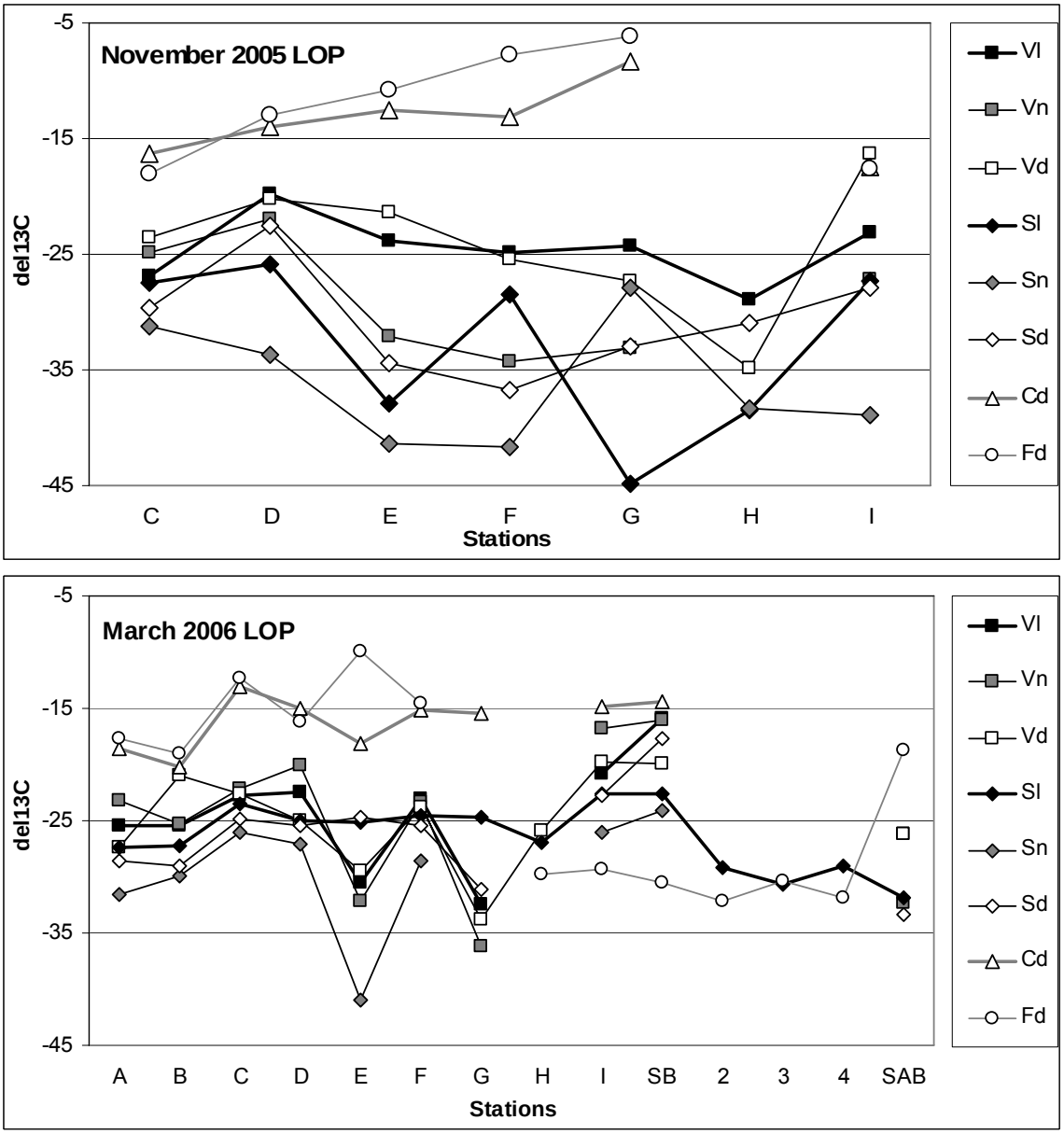


Figure 20. $\delta^{13}C$ of Lignin Oxidation Products from Sediment from Two Sampling Cruises

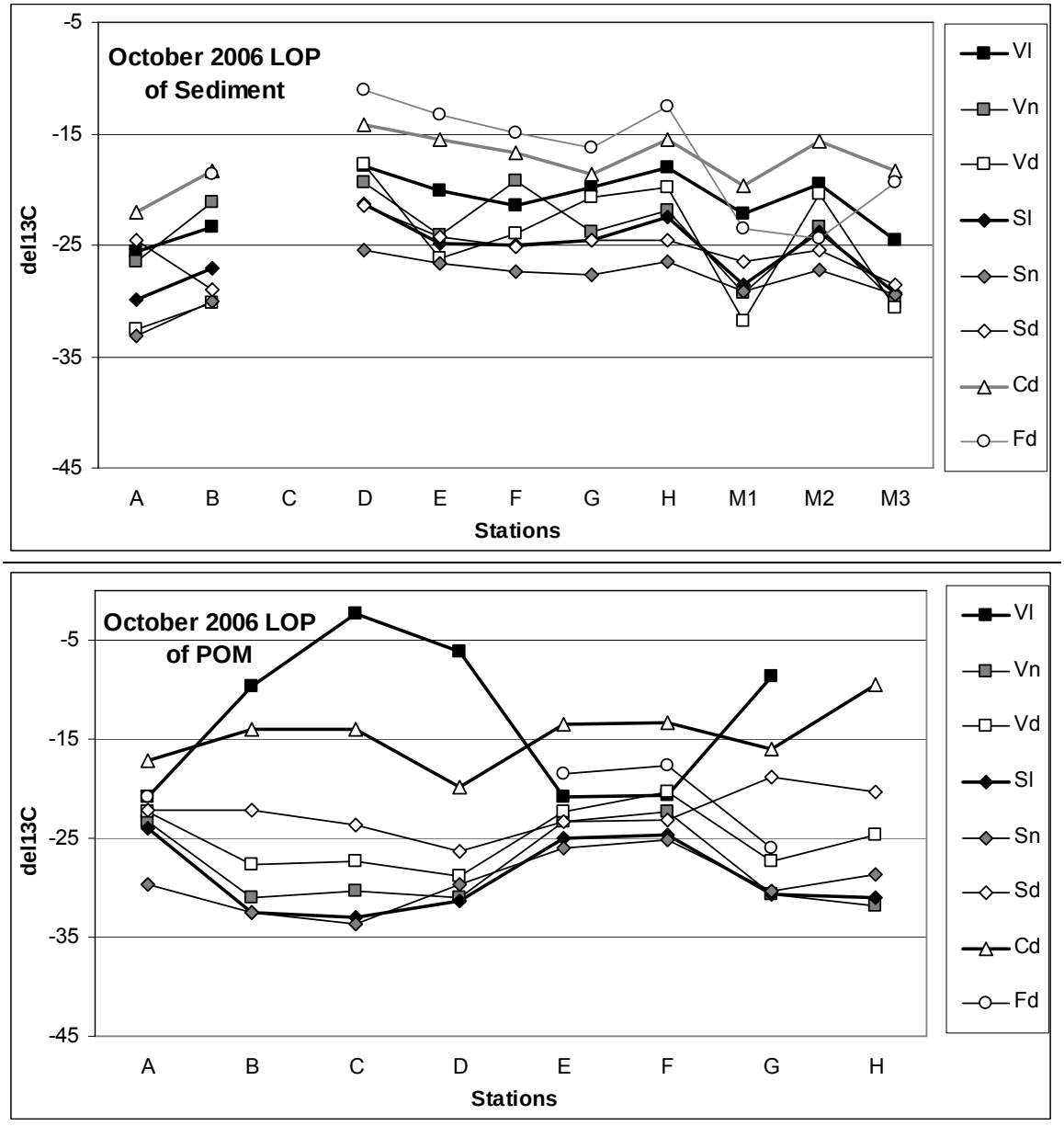


Figure 21. $\delta^{13}C$ of Lignin Oxidation Products from Sediment and POM from October 2006 Sampling Cruise

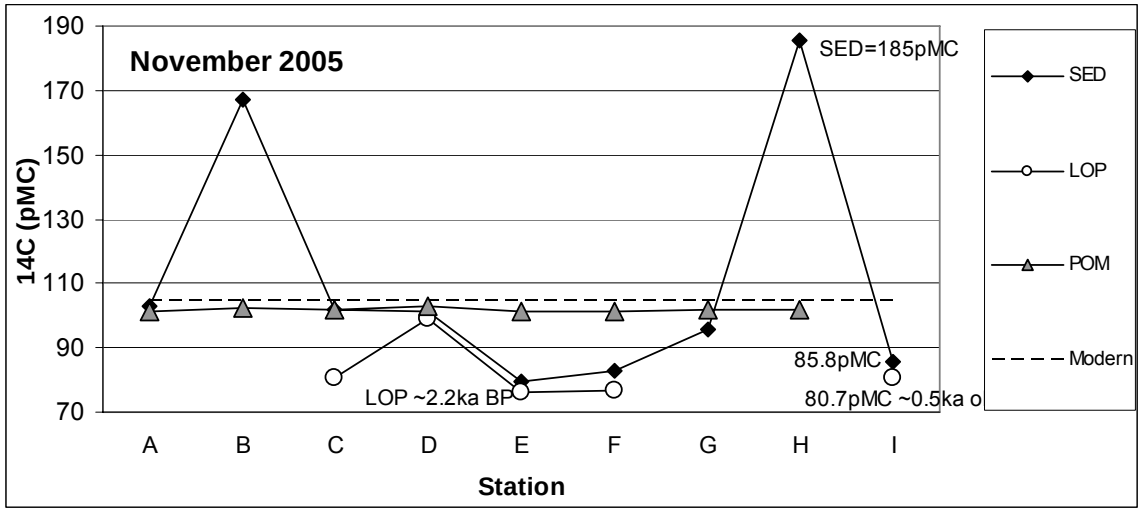


Figure 22. ^{14}C of Sediment, Lignin Oxidation Product and Particulate Organic Matter vs November 2005 Stations

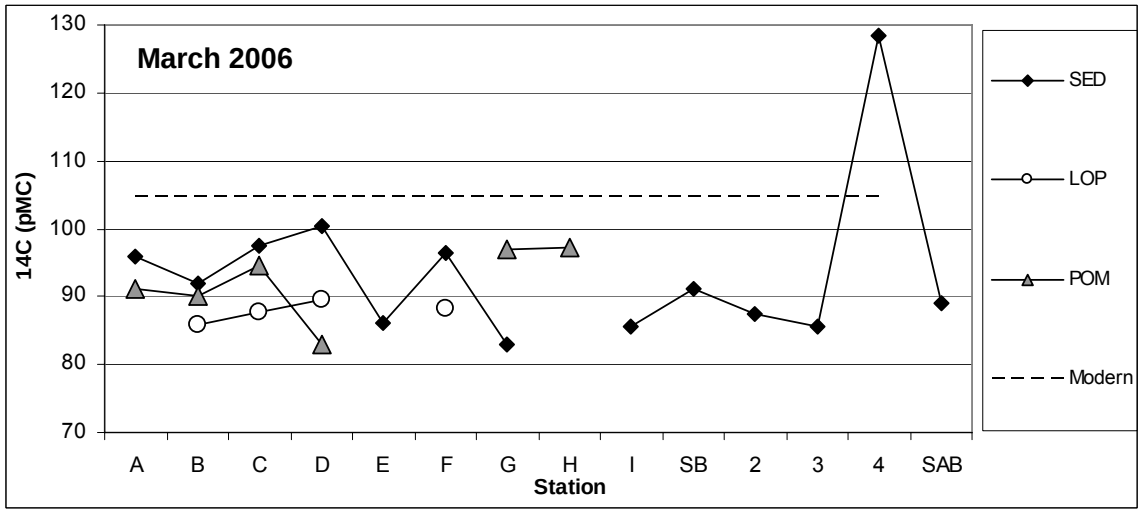


Figure 23. ^{14}C of Sediment, Lignin Oxidation Product and Particulate Organic Matter vs March 2006 Stations

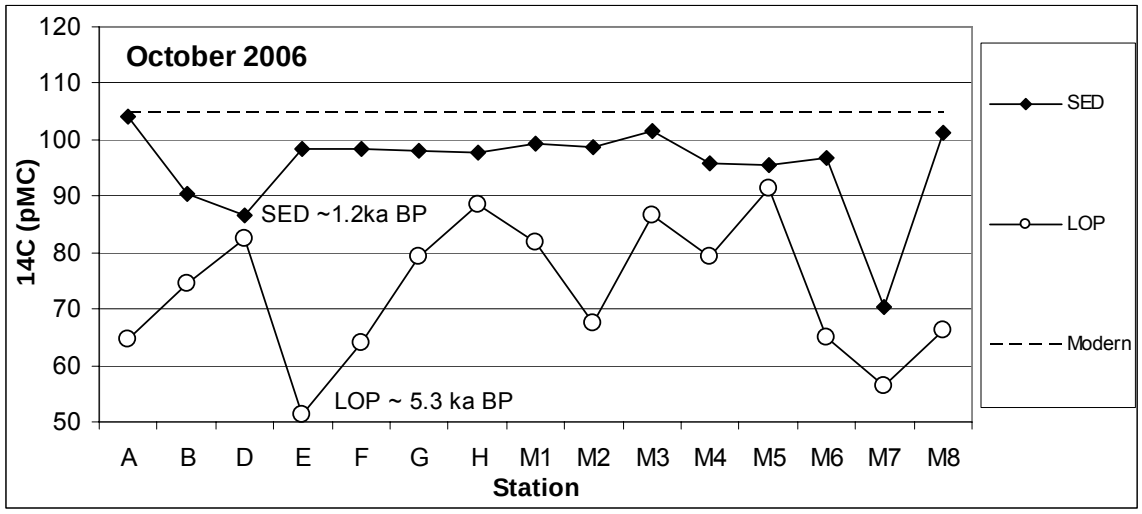


Figure 24. ^{14}C of Sediment and Lignin Oxidation Product vs October 2006 Stations

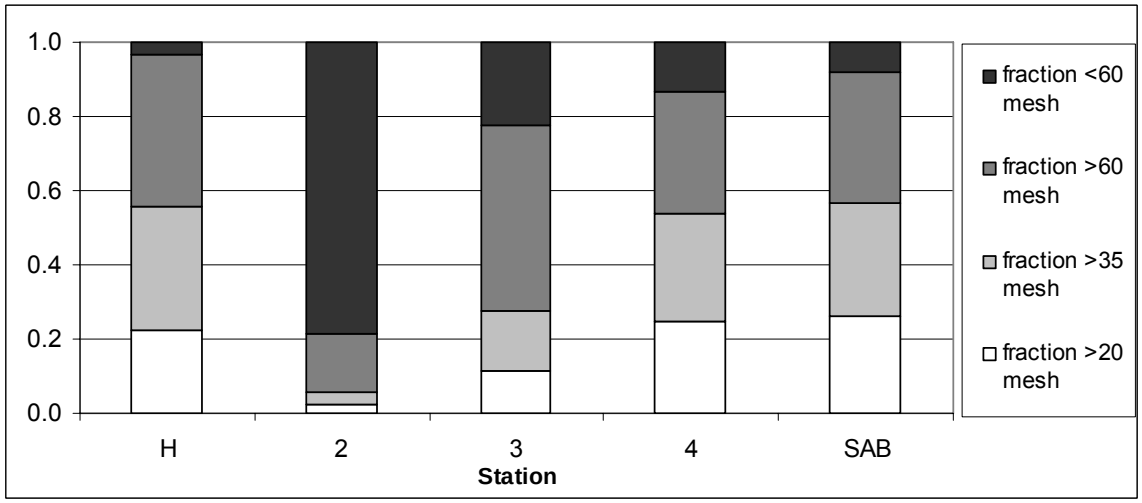


Figure 25. Normalized Particle Size Distribution for Offshore Sediments

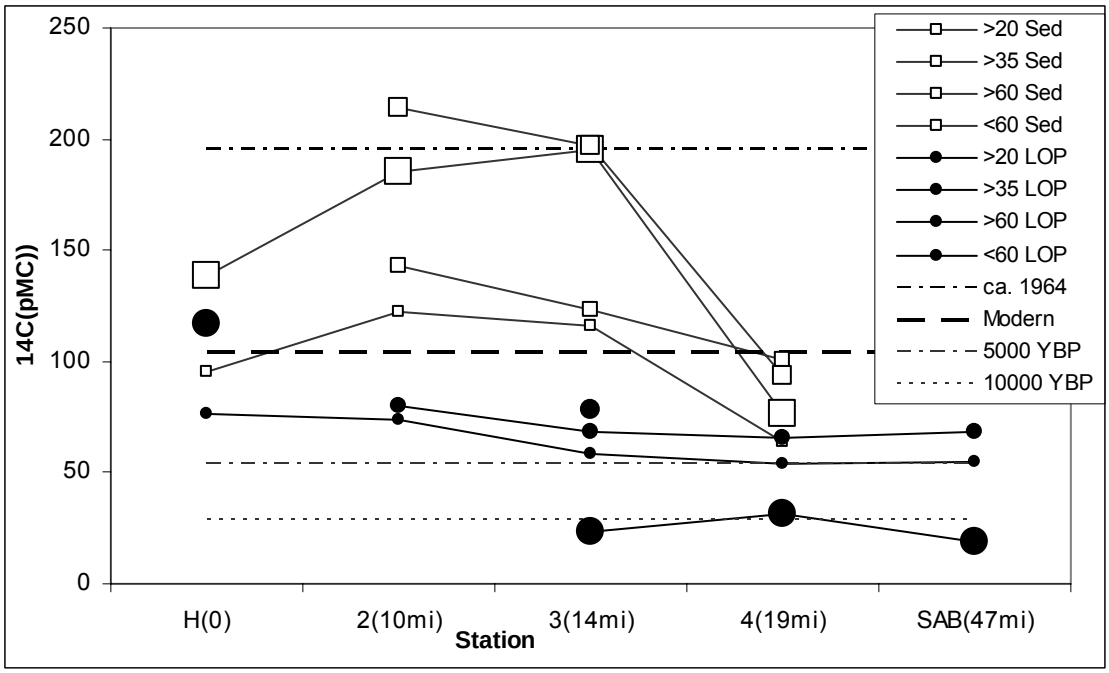


Figure 26. ^{14}C Activity in March 2006 Sediment and Lignin Oxidation Product vs Size Fraction and Station (Distance from Sound)

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8. APPENDICES:

Appendix A: GC/MS data average and standard deviation (ng/g).

March, 2002	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A SED	189	48	65	1397	425	358	1293	360	298	262	294
Std Dev.	13	3	4	79	24	17	63	17	13	13	13
B SED	178	43	57	1076	331	295	1362	351	397	384	588
Std Dev.	1	1	0	14	3	5	15	5	7	5	15
C SED	147	39	49	724	208	162	876	277	191	261	208
Std Dev.	31	9	11	143	48	36	185	64	45	61	56
D SED	97	25	36	487	123	111	526	148	116	130	93
Std Dev.	5	1	1	16	5	3	19	7	3	5	4
E SED	114	26	46	613	198	149	721	289	168	186	200
Std Dev.	53	12	22	271	45	75	345	110	80	91	104
F SED	30	0	15	165	38	42	166	67	43	39	29
Std Dev.	16	0	5	91	24	29	106	0	18	17	0
G SED	84	18	32	559	131	113	628	155	110	110	85
Std Dev.	42	8	19	271	64	65	329	83	69	68	61
H SED	90	17	27	441	104	95	562	143	116	155	124
Std Dev.	45	8	16	219	50	55	293	74	70	93	84

Nov., 2002	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A SED	67	15	32	540	201	152	696	172	150	152	271
Std Dev.	2	1	1	15	5	6	17	4	7	6	21
B SED	71	16	20	771	173	134	647	161	165	190	349
Std Dev.	5	1	1	45	12	9	40	9	14	14	37
C SED	93	15	20	1831	125	111	514	126	144	168	296
Std Dev.	1	0	0	17	2	1	7	2	3	3	5
D SED	46	14	27	114	34	43	147	28	36	48	30
Std Dev.	3	1	4	7	2	6	17	6	6	6	4
E SED	93	23	31	506	154	144	637	166	193	166	239
Std Dev.	5	1	3	31	11	12	51	21	13	13	15
F SED	95	25	33	430	135	107	537	138	115	138	124
Std Dev.	12	3	5	54	17	25	85	58	20	21	20
G SED	128	34	42	584	200	171	826	228	255	255	361
Std Dev.	5	2	2	22	8	10	37	10	16	13	33
H SED	0	0	0	0	0	0	11	0	0	0	0
Std Dev.	0	0	0	0	0	0	1	0	0	0	0

Nov., 2005	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
C SED	152	44	68	1209	457	429	1405	355	530	322	1287
Std Dev.	14	3	8	113	37	46	311	36	63	35	169
D SED	38	9	15	202	57	42	310	54	53	65	46
Std Dev.	8	2	1	47	13	4	39	18	8	9	8
E SED	63	19	26	291	84	85	421	105	88	87	62
Std Dev.	11	0	4	45	15	12	62	17	13	15	11
F SED	39	11	16	278	67	66	317	65	63	43	21
Std Dev.	13	0	5	83	23	19	90	22	20	15	0
G SED	38	7	15	213	56	56	252	57	36	44	21
Std Dev.	3	0	1	16	5	4	19	5	4	5	1
H SED	11	0	6	66	15	18	78	13	14	8	0
Std Dev.	1	0	1	9	2	3	10	2	3	1	0
I SED	22	5	7	117	44	37	170	42	53	50	92
Std Dev.	1	0	0	3	1	1	4	1	2	2	7
SAB SED	45	13	17	238	94	76	340	94	103	103	189
Std Dev.	4	1	1	17	7	4	20	6	6	6	12

Appendix A: GC/MS data average and standard deviation (ng/g).Cont.

March, 2006	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A SED	37	10	16	182	47	53	158	53	39	38	25
Std Dev.	1	0	0	4	2	0	2	2	1	1	3
B SED	516	152	200	1715	661	603	2720	787	745	1272	1864
Std Dev.	23	8	9	63	27	26	94	32	353	292	88
C SED	151	28	59	755	311	272	991	327	363	314	565
Std Dev.	3	0	1	14	6	13	30	24	11	11	24
D SED	145	13	63	733	143	190	615	80	151	116	44
Std Dev.	9	0	3	41	6	9	56	9	9	8	6
E SED	64	6	37	146	17	51	70	40	0	13	0
Std Dev.	6	0	4	28	0	0	0	0	0	0	0
F SED	143	42	50	783	257	196	797	298	190	225	212
Std Dev.	11	5	5	80	30	27	107	44	32	47	54
G SED	36	8	35	130	22	59	64	0	0	14	0
Std Dev.	21	0	22	104	0	71	0	0	0	0	0
1 SED	16	4	8	82	22	22	127	31	17	25	10
Std Dev.	1	0	0	4	1	1	6	1	0	1	1
SB SED	14	2	7	40	12	13	64	15	11	17	7
Std Dev.	2	0	1	6	2	2	10	4	2	2	1

Oct., 2006	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
B SED	18	0	7	94	24	30	118	20	14	30	0
Std Dev.	0	0	2	0	0	2	1	0	0	1	0
D SED	78	19	27	421	122	132	622	133	192	176	226
Std Dev.	1	1	6	3	1	10	2	2	3	3	4
E SED	24	0	9	101	25	35	119	21	17	33	0
Std Dev.	1	0	2	1	0	3	1	0	2	1	0
F SED	31	4	10	147	32	42	240	41	40	64	38
Std Dev.	0	0	1	1	0	2	0	0	1	1	1
G SED	73	11	25	312	74	110	534	101	223	181	263
Std Dev.	3	0	10	2	1	15	4	6	8	6	13
H SED	97	24	44	442	137	196	1036	235	329	409	636
Std Dev.	3	0	6	4	1	20	5	11	9	8	12

Nov., 2005	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A POM	30	0	87	28	20	22	44	16	22	11	0
Std Dev.	13	0	33	10	6	2	13	0	6	0	0
B POM	60	13	252	75	31	271	98	70	92	59	50
Std Dev.	4	1	7	0	1	2	4	3	3	2	1
C POM	44	9	174	55	25	182	74	46	55	28	23
Std Dev.	4	1	20	8	4	35	9	4	10	7	0
D POM	34	0	100	30	23	88	51	0	0	0	0
Std Dev.	2	0	1	2	0	1	1	0	0	0	0
E POM	49	0	139	46	31	151	72	31	39	23	0
Std Dev.	6	0	16	6	2	11	6	0	1	2	0
F POM	105	0	440	131	55	465	165	112	132	76	0
Std Dev.	4	0	12	3	1	6	4	7	3	2	0
G POM	111	27	538	177	46	642	168	177	170	135	130
Std Dev.	16	4	56	21	6	75	22	24	22	17	19
H POM	107	0	478	148	50	528	164	130	148	91	0
Std Dev.	9	0	44	12	5	42	15	10	14	7	0
1 POM	116	15	144	60	44	253	52	69	67	54	84
Std Dev.	17	1	22	8	9	49	10	12	13	10	18

Appendix A: GC/MS data average and standard deviation (ng/g).Cont.

March, 2006	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
C POM	28	3	10	99	28	37	122	28	30	15	5
Std Dev.	13	3	4	83	9	26	116	8	28	15	6
E POM	127	0	51	361	144	156	579	170	169	76	0
Std Dev.											
F POM	101	0	39	289	126	117	472	143	122	79	73
Std Dev.											
I POM	19	2	24	90	10	46	164	45	40	28	9
Std Dev.	16	3	26	96	9	49	211	46	41	28	8

Oct., 2006	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
A POM	138	43	121	425	206	232	237	48	118	145	46
Std Dev.	15	7	41	22	12	24	23	5	13	15	6
B POM	163	39	160	355	166	223	0	0	66	130	0
Std Dev.	8	2	15	0	6	0	18	0	5	6	0
C POM	162	48	181	332	190	263	129	49	118	163	58
Std Dev.	3	6	8	14	3	4	4	1	1	1	6
D POM	152	48	176	329	215	282	123	61	136	181	66
Std Dev.	8	2	13	10	7	3	11	3	5	7	6
E POM	136	0	48	344	132	111	541	174	136	115	87
Std Dev.	11	0	3	24	9	8	37	12	9	8	6
F POM	155	0	62	327	167	157	768	267	193	183	152
Std Dev.	10	0	5	17	14	9	75	12	12	11	23
G POM	158	36	188	286	126	153	29	20	55	117	0
Std Dev.	6	2	10	5	7	2	11	7	3	8	0
H POM	189	48	245	262	99	201	35	0	58	138	0
Std Dev.	12	0	15	41	14	2	11	0	5	9	0

Nov., 2005 Core	pBl	pBn	pBd	Vl	Vn	Vd	Sl	Sn	Sd	Cd	Fd
0-20mm	50	11	18	305	197	18	940	98	607	146	139
Std Dev.	2	0	3	2	5	4	19	1	15	3	12
20-40mm	115	23	56	594	247	144	850	267	266	314	336
Std Dev.											
40-60mm	101	21	33	477	144	169	800	172	275	267	473
Std Dev.											
60-80mm	89	23	46	406	158	137	564	153	207	208	195
Std Dev.	28	15	25	92	76	155	22	20	134	5	27
80-100mm	73	18	24	445	164	25	665	127	163	158	164
Std Dev.											
100-120mm	66	15	20	375	132	110	566	134	139	129	138
Std Dev.											
120-140mm	99	33	49	412	202	184	420	107	249	140	118
Std Dev.	21	18	54	21	120	245	20	122	224	198	166
140-160mm	70	16	22	448	152	23	631	125	157	167	162
Std Dev.											
160-180mm	95	28	46	457	195	105	626	217	201	255	284
Std Dev.	16	13	27	46	63	56	58	87	29	101	65
180-200mm	70	17	24	363	142	128	585	152	194	187	331

Appendix B: $\delta^{13}C$ by Elemental Analyzer and Dual-Inlet IRMS

Mar-02	EA	252
A	-24.94	-22.00
B	-23.65	-24.00
C	-22.44	-22.79
D	-23.63	-23.82
E	-22.37	-22.97
F	-22.17	-22.81
G	-21.82	-23.28
H	-21.34	-21.02
I	-23.90	-23.49
Nov-02		
A	-24.98	-25.51
B	-24.21	-24.24
C	-23.42	-23.66
D	-15.82	-17.25
E	-20.63	-22.44
F	-20.42	-21.82
G	-20.71	-22.51
H	-23.93	-24.54
I	-25.25	-25.50
Nov-05		
A	-27.85	-27.36
B		-25.67
C	-23.64	-24.04
D	-23.53	-24.11
E	-21.53	-21.35
F	-22.01	-22.74
G	-23.93	-22.40
H	-24.15	-22.94
I	-21.00	-20.38

Mar-06	EA	252
A	-25.89	-26.24
B	-26.24	-25.98
C	-23.53	-24.10
D	-23.79	-24.28
E	-21.98	-22.42
F	-23.18	-23.65
G	-21.91	-22.48
H	-23.98	-23.87
I	-21.19	-21.73
SB	-21.41	-21.47
2	-24.62	-24.53
3	-21.96	-21.92
4	-18.99	-18.38
SAB	-21.86	-21.23
Oct-06		
A		-26.23
B	-24.83	-24.16
C		-24.97
D	-21.57	-21.82
E	-23.22	-22.79
F	-24.17	-22.91
G	-22.15	-21.86
H	-20.30	-21.47
M1	-21.03	-22.15
M2	-21.59	-22.42
M3	-21.30	-22.02
M4	-21.46	-20.94
M5	-22.87	-20.52
M6	-24.67	-20.70
M7	-17.27	-18.43

Mar-07	252
1	-20.70
2	-20.62
3	-21.98
4	-21.95
5	-21.39
6	-14.46
7	-17.63
8	-17.65
9	-20.66
10	-20.41
11	-22.69
12	-22.04
13	-23.87
14	-23.28
15	-22.11
1A	-22.27
1B	-21.44
Hatch	-27.52