

Compound specific radiocarbon content of lignin oxidation products from the Altamaha river and Coastal Georgia

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ABSTRACT

Compound-specific isotope analysis (CSIA) is a powerful tool in organic geochemistry by providing detailed information about an individual organic compound's history with regard to its source and process of formation. Most CSIA involves measurement of the stable isotope ratio of carbon ($^{13}\text{C}/^{12}\text{C}$) and hydrogen (D/H) following separation by gas or liquid chromatography. New applications are being developed using compound-specific radiocarbon (^{14}C) content for delineating age of materials, rates of decomposition and residence time in various environments. This paper details the isotopic work on specific lignin monomers derived from terrestrial plants transported and deposited within the Altamaha River, estuary and off-shore Georgia in the Atlantic Ocean. By using gas chromatographic separation and identification of selected lignin oxidation products (LOP), the harvesting of these compounds using preparative fraction collection, and measurement of their ^{14}C content using accelerator mass spectrometry, details of the age and presence of specific biomarkers unique to a given terrestrial source are revealed. Radiocarbon ages determined from water-column particulate organic carbon and sediment LOPs indicate a range of ages from modern to well over 5,000 years for the former and latter respectively. Transport mechanisms and particle size associations on mineral grains may play a significant role in ^{14}C distribution in estuary and near-shore coastal environments. This data indicates higher than modern ^{14}C activities in large particle-size sediment fractions in contrast to older LOP ^{14}C ages found associated with the same coarse grain sediments. Individual LOP ages substantiate older terrestrial materials persist in the off-shore environment even though in the presence of modern marine ^{14}C sources.

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1. Introduction

Terrestrial organic carbon, in the form of terrestrial biota and soil, accounts for a significant amount of the global carbon budget and represents an important component of global carbon cycling. The major carbon reservoirs, other than oceanic carbonates and fossil fuel, are atmospheric carbon, ocean surface carbon, terrestrial biota, soil and detritus carbon. The first three of which contain roughly $0.5\text{--}0.7 \times 10^{18}$ g each of carbon and soil and detritus carbon contain roughly 1.2×10^{18} g carbon. Approximately 0.4×10^{15} g carbon is delivered from land to estuaries annually [1]. Approximately half of this carbon is in the form of dissolved organic matter and half as particulate organic matter suspended, deposited and re-suspended within the water column [2]. Of this organic matter within the oceans, nearly 90% is deposited within deltaic and shelf environments [3,4]. Those derived exclusively from the terrestrial environment - terrestrial biota and soil carbon - can be evaluated for their source and distribution by applying isotopic techniques to targeted

biomarkers such as lignin phenols [5]. Lignin is a biopolymer, unique to vascular plants including hardwoods, softwoods and grasses, refractory in nature and second only to cellulose as the most abundant organic compound in the terrestrial environment [6]. Lignin, in its natural form, is composed of an assortment of specific lignin monomers, or substituted phenolic rings, with up to three functional groups attached. Lignin phenols, derived from the oxidation of the biopolymer lignin, are unique and specific to their source material in the terrestrial environment. Fig. 1 displays the lignin oxidation product (LOP) groups, individual compounds and associated plant groups used to determine plant source material within the terrestrial environment [7,8].

As part of a larger long-term study, of the elemental and isotopic content of lignin oxidation products from the Altamaha River and estuary and South Atlantic Bight off the coast of Georgia in the Southeastern United States, this paper describes the measurement of ^{14}C in specific lignin phenol compounds after identification, separation, collection and analysis by AMS [9]. ^{14}C content was also determined in different particle size fractions as part of this study to determine mineralogical association and transport mechanism of organic matter in both sediment and surface partic-

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Oxidation Products	Individual Compounds	Plant Group			
		G	g	A	a
p-hydroxyl phenol Group	p-hydroxy benzaldehyde	x	x		x
	p-hydroxy acetophenone	x	x		x
	p-hydroxy benzoic acid	x	x		x
Vanillyl (V) (All plants) Group	Vanillin	x	x	x	x
	Acetovanillone	x	x	x	x
	Vanillic acid	x	x	x	x
Syringyl (S) (Angiosperms) Group	Syringaldehyde			x	x
	Acetosyringone			x	x
	Syringic acid			x	x
Cinnamyl (C) non-woody Group	p-Coumaric acid		x		x
	Ferulic acid		x		x

Fig. 1. Lignin oxidation product groups, individual compounds and associated plant groups. The ratio S/V indicates the relative amount of angiosperm, C/V indicates the relative amount of non-woody tissue, and acid/aldehyde (Vd/VI) and (Sd/SI) measures the degradation rate. G and g indicates gymnosperms woody and non-woody. A and a indicates angiosperms woody and non-woody.

ulates, and their relationship to bulk sediment and lignin. Sediment samples were taken from near shore to offshore from Sapelo Island to Gray's Reef and the inner shelf of the South Atlantic Bight. ^{14}C age determination from both total organic carbon and LOPs from sediment samples indicate a large diversion between bulk organic carbon ages and those associated with lignin.

Fig. 2 describes the chemical and isotopic flowchart used within this study including isolation and collection of lignin phenols from sediments and particulate organic matter (POM). Total and individual LOPs are analyzed by a number of analytical techniques and instrumentation typically used for stable isotopic analysis as well as ^{14}C determinations. These instruments include Thermo-Finnigan isotope ratio mass spectrometers and National Electrostatics Corporation's accelerator mass spectrometer. The University of Georgia's Center for Applied Isotope Studies accelerator mass spectrometer is referred to as the UGAMS system [10,11]. Less common is the approach to collection of specific biomarker compounds required for AMS ^{14}C determination. A Gerstel Corporation preparative fraction collector coupled to a Hewlett Packard gas chromatograph was used for repeated collection of compounds of interest.

As the analytical approach becomes more complex and individual compounds are investigated for their isotopic composition, the potential for contamination and perturbing true values increases dramatically. As demonstrated in previous research [12,13], the challenges in compound specific radiocarbon measurement can be overcome by careful and diligent control of analytical methods. Reduction of blank ^{14}C and contamination are the most important considerations to ensure accuracy in this type of analysis. Although new techniques are currently underway for enhanced separation of individual compounds without the problems associated with derivatization to enhance volatilization [14], direct measurement of chromatographically separated and combusted individual compounds in AMS instruments are now developed. Although these newer techniques will reduce cost, preparation time and increase throughput, they may lack the ability to confirm separation efficiency or control blank additions or contamination. The use of multiple analysis before and after separation of compounds of interest, affords a quality control to sample preparation needed for unique sample types and matrices.

2. Methods

Sediment samples used for bulk and compound specific ^{14}C measurement were collected from the Altamaha River and South Atlantic Bight, offshore Sapelo Island during the winter and spring of 2005 and 2006 respectively. Location, time, date, depth, temperature and salinity were recorded at time of sampling. Samples were immediately placed on ice for transport back to the laboratory, as were particulate organic matter samples that were collected on pre-combusted silica filters. Samples followed the analytical scheme detailed in Fig. 2. Sediment samples for bulk carbon isotope analysis, as well as those for lignin extraction procedure and compound specific isotopic analysis were acid treated to remove carbonate species, dried and homogenized. Bulk carbon ^{14}C analysis was determined using AMS following combustion and graphitization of carbon dioxide. Lignin was extracted and isolated according to previous research [15] with minor modifications in extraction solvent [16]. The lignin phenols were then derivatized using *N,O* bis(trimethylsilyl)-trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) (Supelco Co.). Correction for added carbon from derivatization compound was made using Eq. (1):

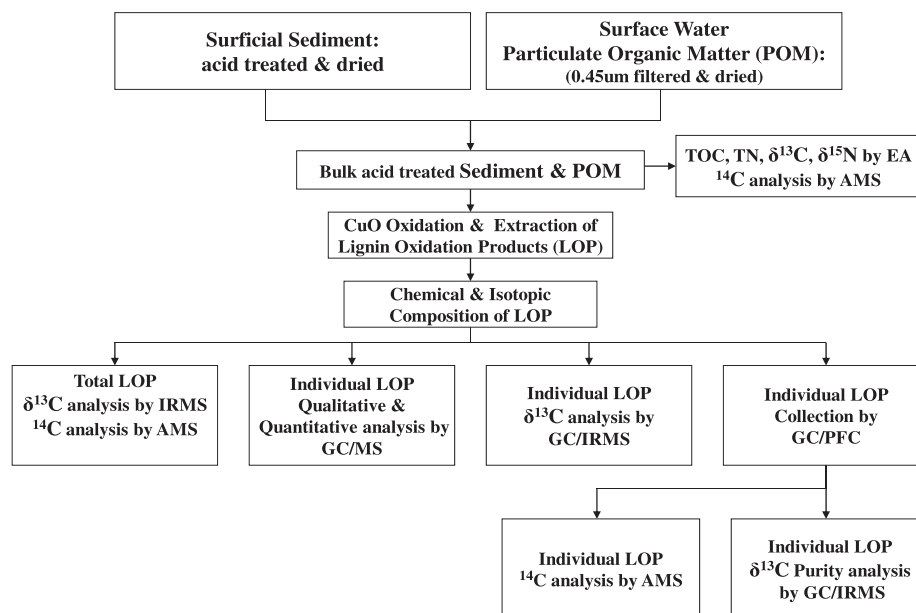


Fig. 2. Chemical and isotopic ^{14}C , $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analytical approach.

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