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Source-age dynamics of estuarine particulate organic matter using fatty acid $\delta^{13}C$ and $\Delta^{14}C$ composition

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Abstract

This study used a multiproxy approach to elucidate the source and age composition of estuarine particulate organic matter (POM) using bulk stable isotopes ($\delta^{13}C_{POC}$), fatty acid (FA) biomarkers, and compound specific isotopic analyses in surface waters along the Delaware River and Bay (Delaware Estuary, hereafter). $\delta^{13}C$ values of FA ($\delta^{13}C_{FA}$) ranged more widely (−30.9‰ to −21.8‰) than $\delta^{13}C_{POC}$ (−27.5‰ to −23.5‰), providing greater insight about POM sources along the estuary. $\delta^{13}C$ values of $C_{16:0}$ phospholipid FA (primarily, aquatic sources) increased along the salinity gradient (−29.8‰ to −23.4‰), while $\delta^{13}C_{FA}$ values of long-chain neutral fatty acid (terrestrial sources) decreased (−28.6‰ to −30.9‰). $\delta^{13}C_{FA}$ values for $C_{18's}$ FA indicated the importance of marsh-derived organic matter within Delaware Estuary. Compound specific radiocarbon analysis showed the heterogeneous age structure of FA associated with POM (FA_{POM}). ^{14}C ages of FA ranged from modern (postbomb) to 1790 BP; aged FA (120 BP to 1700 BP) derived primarily from the watershed, whereas modern FA were produced within Delaware Estuary. ^{14}C ages of short-chain FA (aquatic sources) reflected differences in the age of dissolved inorganic carbon along the estuary and had older ^{14}C ages at the river endmember. ^{14}C ages of FA from terrigenous sources were older than water and sediment residence times indicating this source derived from the watershed. This study is the first to document the complex age distribution of FA_{POM} along the estuarine salinity gradient and shows that inorganic carbon sources, watershed inputs and autochthonous production contribute to variation in the ages of POM.

Estuaries are challenging environments in which to study the origins, pathways and fates of organic matter (OM) because of the complex sources and processes influencing its composition and distribution. Sources of OM to estuaries include, but are not limited to, terrigenous materials (soils and plant detritus), contributions from anthropogenic activities (sewage effluent, urban runoff), as well as aquatic and marine primary production (phytoplankton, benthic microalgae, and marsh and aquatic plants). Rivers and estuaries are not passive transporters of OM. Instead, OM is transformed along the river-estuarine gradient by biotic (e.g., bacterial) and abiotic (e.g., photochemical) processes resulting in selective losses of "younger," more labile OM and removal of more refractory components through burial along the estuarine gradient and export to the coastal ocean (McCallister et al. 2005, 2006; Bianchi and Allison 2009). This complexity suggests the need for studies focused on understanding the magnitude and reactivity of OM of different sources and ages and the need to identify the signatures of organic carbon (OC) exported from estuarine environments to better understand the coastal ocean carbon cycle.

Biological markers or "biomarkers," with their source specificity and ability to persist in the environment, have been widely used for determining source composition of estuarine OM (Canuel et al. 1997; Mannino and Harvey 1999). Lipid biomarkers have been used to distinguish contributions from terrestrial, marine, bacterial, and anthropogenic OM sources. Fatty acids (FA) are a class of lipid biomarkers; they make up a majority of the lipid biochemical class and are used for examining contributions from allochthonous and autochthonous OM sources. Short-chain (SC) FA ($C_{12:0}$, $C_{14:0}$), for example, are typically attributed to algal and bacterial sources, while long-chain (LC) FA ($> C_{24:0}$) are ascribed to terrigenous sources such as soils and higher plants (Parkes and Taylor 1983; Volkman et al. 1989; Meyers 1997 and references therein).

In addition to lipid biomarker composition, stable carbon isotopes ($\delta^{13}C$) and radiocarbon ($\Delta^{14}C$) have been used to delineate OM sources (Raymond and Bauer 2001). Particulate organic matter (POM) is a complex, heterogeneous mixture

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with biochemical components that range in radiocarbon ages reflecting different levels of lability and residence times (Wang et al. 1998). $\Delta^{14}C$ analyses of biochemical classes have shown lipid components to be the oldest biochemical class in both dissolved organic matter (DOM) and POM (Hwang et al. 2006). In the Delaware Estuary, for example, ^{14}C age of the lipid associated with ultrafiltered DOM (0.1 μm–1 kDa, 23,300 years before present [BP]) was considerably older than total dissolved organic carbon (DOC; 120 BP), as well as other biochemical classes (Wang et al. 2006). Results from the Delaware and other estuaries in the U.S.A. indicate that the lipid fraction was older than other biochemical classes (i.e., carbohydrates, amino acids, and the acid insoluble fraction) and its age was older than the water residence times of the study systems (Wang et al. 2006).

To understand what components contribute to the "age" of total lipid extracts (TLE), individual compounds can be separated for compound specific radiocarbon analysis (CSRA) (Eglinton et al. 1996). The advent of CSRA augments the source information of biomarkers with the age information of radiocarbon (^{14}C) and has proven useful for deconvoluting OM sources in complex and heterogeneous matrices (Eglinton et al. 1996; Pearson et al. 2001). CSRA analyses of lipid biomarker compounds (e.g., *n*-alkanes and FA), polycyclic aromatic hydrocarbons (PAHs), and lignin have been used to provide source (e.g., plankton, vascular plants, anthropogenic) and age information (Pearson et al. 2001; Reddy et al. 2002; Feng et al. 2013). The combination of compound-specific $\delta^{13}C$ and $\Delta^{14}C$ analyses with biomarker identification provides a powerful approach for elucidating sources of OM and their residence times within terrestrial, estuarine, and marine systems (Pearson and Eglinton 2000).

Over the past 20 yr, CSRA has been used in marine systems but for the most part in sediments [i.e., Santa Monica Basin, CA (Pearson et al. 2001), Beaufort Sea (Drenzek et al. 2007), Ross Sea (Ohkouchi et al. 2003), and the Washington margin (Feng et al. 2013)]. A few studies have also examined components of POM such as biomarkers derived from deep-sea archaea associated with POM (>0.2 μm) (Ingalls et al. 2006; Shah and Pearson 2007). However, to the best of our knowledge, previous studies have not used CSRA to analyze POM within an estuarine system.

A combination of bulk properties ($\delta^{13}C$, POC), FA composition, and compound specific isotopic analyses of FA were used in this study to better understand POM source variations along the estuarine salinity gradient and how these variations influence the OM age distribution. Source composition and $\delta^{13}C$ and $\Delta^{14}C$ values for individual phospholipid-linked fatty acids (PLFA) and neutral fatty acids (NFA) from surface water POM collected along the salinity gradient of Delaware River and Bay were analyzed (see Table 1 for abbreviations). This study presents the first compound specific isotope measurements of both PLFA and NFA associated with POM along an estuarine gradient at physically and biologically important locations (i.e., river, estuary turbidity maximum [ETM], and chlorophyll *a* [chl *a*] maximum).

Table 1. Commonly used terms and their abbreviations.

Abbreviation	Lipid and Fatty Acid Terms
FA	Fatty acid
FAME	Fatty acid methyl ester
FA_{POM}	Fatty acids associated with particulate organic matter
LCFA	Long chain fatty acid ($C_{24:0}+C_{26:0}+C_{28:0}$)
MCFA	Mid chain fatty acid ($C_{16:0}+C_{18's}$)
NFA	Neutral fatty acid
PLFA	Phosopholipid-linked fatty acid
SCFA	Short-chain fatty acid ($C_{12:0}+ C_{14:0}$)
TLE	Total lipid extract
TLE-N	Neutral total lipid extract
TLE-P	Polar total lipid extract
Fatty Acid Nomenclature	
$C_{X:Y}$	X=number of carbon atoms,
	Y=number of double bonds

The Delaware River-Bay system is a temperate, coastal plain estuary located in the mid-Atlantic region of the U.S.A. (Fig. 1). The Delaware River and Bay, hereafter Delaware Estuary, provides a model system for studying the sources and "ages" of OC along the salinity gradient because it is dominated by one freshwater tributary (Delaware River, 60% of the freshwater input to Delaware Bay) allowing the ability to trace terrigenous materials along the salinity gradient. The Delaware Estuary is both highly urbanized with the Delaware River running through Trenton NJ, Philadelphia PA, and Wilmington DE and has extensive undeveloped fringing freshwater and salt marshes (Fig. 1). Tidal influence is measured 215 km from the bay mouth and there is a broad ETM, around the zone of salt intrusion (0.2 salinity), located 60 km to 100 km from the bay mouth (Biggs et al. 1983; Sommerfield and Wong 2011). Primary production within Delaware Bay is light, not nutrient, limited and is highest in the region downstream of the ETM during spring (Pennock 1985; Pennock and Sharp 1986). POM composition along the Delaware Estuary has a terrigenous signature in the river and takes on a marine/estuarine character along the estuary with marsh sources strongly influencing the OM in the turbid region of the estuary (Cifuentes et al. 1988; Mannino and Harvey 1999; Hermes 2013).

Methods

Water collection

Surface water (1 m or 2 m) samples were collected in late March/early April 2011 along the salinity gradient of the Delaware Estuary aboard the R/V *Hugh R. Sharp* (Fig. 1 and Table 2). Large volumes of surface water (650 to 1200 L per site) were collected into organic solvent rinsed stainless steel canisters using a peristaltic pump with precleaned

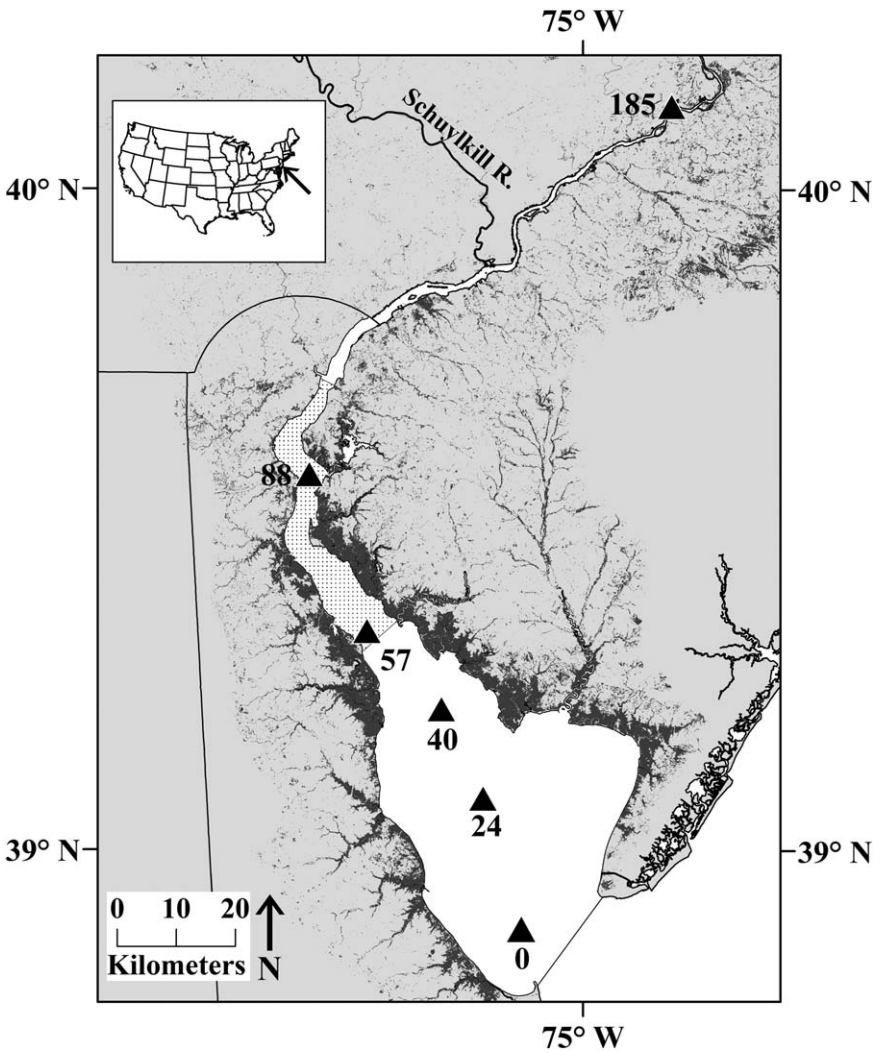

Fig. 1. Study area and sampling locations in late March-early April 2011. The Delaware Estuary is located on the mid-Atlantic coast of the U.S.A., shown in the map inlay. Sampling locations are labeled by their distance in km upstream from the Bay mouth site at 0 km. Large volumes of POM for lipid composition, $\delta^{13}C$ and/or $\Delta^{14}C$ analyses were collected at the 185 km (River), 88 km (ETM), and 40 km (Chl *a* maximum) sites. The shaded area between ~55 km to ~100 km identifies the ETM zone as identified by Sommerfield and Wong (2011). Dark gray shading indicates the extent of fringing fresh and saltwater marshes.

Table 2. Physical characteristics for sampling locations along the Delaware Estuary in late March-early April 2011.

Station	Site description	Distance from Bay Mouth (km)	Date(s) sampled	Salinity*	Temperature (°C)*
1	River	185	29 March–30 March	0.10	5.91
2	ETM	88	31 March–1 April	1.41	7.52
3	High turbidity	57	1 April	11.0	7.33
4	Chl *a* Max (2 m)	40	27 March–29 March	10.6	7.25
5	High chl *a*	24	1 April	21.7	7.02

*Salinity and Surface Temperature are from the first CTD cast at each site.

polyurethane tubing. The canisters were filled multiple times over a 24 h to 38 h period to obtain large enough samples for the analyses. Samples were filtered under N_2 and POM was retained on combusted filters (142 mm, Whatman GF/F, 0.7 μm pore size). POM filters were frozen at −80°C until lipid analysis at the Virginia Institute of Marine Science.

Bulk environmental parameters

Surface water was collected concurrently along the salinity gradient for bulk environmental measurements and vacuum filtered through 25 mm glass fiber filters (Whatman GF/F, 0.7 μm pore size). These samples were collected each time the canisters were filled. chl *a* extraction was done using a solution of 45:45:10:0.1 acetone : dimethyl sulfide : deionized water : diethyl amine (Shoaf and Lium 1976; Arar and Collins 1997). Measurements of the solvent extract were made using a fluorometer (10-Au Turner Designs) to quantify chl *a* concentrations and samples were subsequently acidified to quantify pheophytin (pheo) concentrations (Arar and Collins 1997). Particulate organic carbon (POC) and particulate nitrogen (PN) were measured on acidified filters using an elemental analyzer (Flash EA 1112 Series, Thermo Electron Corporation) following the methods of Hedges and Stern (1984). POC stable carbon isotope ($\delta^{13}C_{POC}$) values were measured on acidified filters using isotope ratio-mass spectrometry. $\delta^{13}C_{POC}$ values were measured using a Costech ECS 4010 CHNSO Analyzer interfaced with a Delta V Advantage Isotope Ratio Mass Spectrometer with the Conflo IV Interface at the Virginia Institute of Marine Science and are presented relative to Vienna Pee Dee Belemnite. Analytical precision of $\delta^{13}C_{POC}$ measurements was within 0.2‰. Total suspended sediment (TSS) was collected on preweighed 47 mm polycarbonate membrane filters (Whatman, 1.0 μm pore size) and rinsed with milli-Q water to remove salts. TSS was measured gravimetrically after drying to a constant weight ($\pm$ 0.5 mg) at 105 $\pm$ 5°C.

Lipid extraction and analysis

TLE were isolated from POM samples using an accelerated solvent extraction (Dionex ASE 200) method adapted from Poerschmann and Carlson (2006). Lipids of neutral polarity (TLE-N) were extracted first (hexane : acetone, 9:1 v:v, 50°C), followed by extraction of polar lipids (TLE-P; methanol : chloroform, 4:1 v:v, 80°C) (see Table 1 for abbreviations).

Subsamples of TLE-N and TLE-P were prepared for FA analyses using previously published methods (Palomo and Canuel 2010). TLE-N and TLE-P from each site were processed using one (2 mg) aliquot of TLE for FA compositional analysis and between two and twenty aliquots of TLE (5 mg each) for CSRA. Aliquots of TLE were saponified separately using 1 N KOH in aqueous methanol. Saponified neutral lipids (SAP-N) and acidic lipids (SAP-A) were partitioned into hexane following Canuel and Martens (1993). SAP-A lipids from neutral and polar TLE were derivatized to fatty acid methyl esters (FAME) yielding neutral FAMEs (NFA) and PLFA methyl esters, respectively. Aliquots for FA compositional analysis were methylated using 3% BF_3 in methanol at 85°C on a heating block for 1 h under a headspace of N_2. After cooling, NFA and PLFA were extracted into hexane. Aliquots used for CSRA were derivatized with 5% HCl in methanol ($\delta^{13}C = -37.23$‰, Fraction modern (Fm) = 0.0023) at 50°C on a heating block for three hours under a N_2 headspace.

FAMEs were purified by adsorptive column chromatography (5% deactivated SiO_2 gel, 70–230 mesh, Sigma-Aldrich) using solvent solutions of increasing polarity. FAMEs were eluted in the third (5% ethyl acetate in hexane) and fourth (10% ethyl acetate in hexane) fractions following column elution by 100% hexane and 25% toluene in hexane. Purified FAMEs were dried under N_2 and dissolved in pure hexane for analysis.

Gas chromatography and gas chromatography-mass spectrometry

FA composition of NFA and PLFA was determined by gas chromatography (GC) using a 60 m $\times$ 0.32 mm DB-23 (dimethylphenylsilicone) fused silica capillary column (Agilent J&W Scientific) on a Hewlett Packard 5890 Series II GC with a flame ionization detector (FID) as described in McIntosh (2013). Quantification was done using methyl heneicosanoate ($C_{21:0}$) as an internal standard added before GC analysis. FA were identified initially by comparison to relative retention times of a mixture of FA standards and confirmed using gas chromatography-mass spectrometry (GC-MS) analysis equipped with a 30 $\times$ 0.25 mm HP-5MS column (Agilent Technologies). All GC-MS analyses were done on a 7890A GC system (Agilent Technologies) coupled with a 5975 C inert XL EI/CI MSD with triple axis detector (EI ionization mode, mass range 50 amu to 700 amu, Agilent Technologies).

Preparatory capillary–GC

Individual and groups of NFA and PLFA were isolated by preparatory capillary-gas chromatography (PC-GC) at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) at the Woods Hole Oceanographic Institution (WHOI) (Eglinton et al. 1996). The PC-GC system consisted of an Agilent 6890 GC with a FID and a 7683 Series autoinjector, combined with a cooled injection system (CIS4, Gerstel), and a preparative fraction collector operated at 320°C (PFC, Gerstel). The GC had a 60-m MXT-5 "megabore" column (Restek; 0.53 mm i.d; film thickness, 0.25 μm). The oven temperature program used was: 60°C for two minutes, then 15°C min^{-1} to 320°C, and isothermal for up to five minutes for a total run time of 28 min. Samples were dissolved in high purity hexane, and an injection volume of 4 μL was used. Approximately 1% of the column eluate was diverted to a FID detector and the remaining 99% went to the PFC.

Peaks of interest were collected in four traps (cleaned by combusting at 450°C for five hours) and the remaining peaks were collected in a fifth trap. Computer controlled trapping time windows were approximately two seconds before and two seconds after each compound peak to avoid ^{14}C or ^{13}C isotope fractionation (Zencak et al. 2007). Isolated FA were rinsed out of the U-tubes using hexane (5 $\times$ 200 μL). High

Table 3. Individual and groups of FA isolated by PC-GC for compound specific stable carbon and radiocarbon analyses from Delaware Estuary POM.

Sample name	Target compound	Expected source*	No. of injections	Collected CO_2 (μmol C)	Analyses performed
NFA					
River site	12:0+14:0	Algae, bacteria	50	0.38	No Data Collected
	16:0	Mixed‡	—	No Data	No Data Collected
	18:0+18:1+18:2+18:3	Algae, marsh plants	50	5.09	$\delta^{13}C$, $\Delta^{14}C$
	24:0+26:0+28:0	Higher terrestrial plants	72†	0.445	$\delta^{13}C$ Only
ETM site	12:0+14:0	Algae, bacteria	29	0.122	No Data Collected
	16:0	Mixed‡	29	0.229	$\delta^{13}C$ Only
	18:0+18:1+18:2+18:3	Algae, marsh plants	29	0.239	$\delta^{13}C$ Only
	24:0+26:0+28:0	Higher terrestrial plants	29	0.211	$\delta^{13}C$ Only
Chl *a* max site	12:0+14:0	Algae, bacteria	44	0.184	$\delta^{13}C$ Only
	16:0	Mixed‡	44	0.389	$\delta^{13}C$ Only
	18:0+18:1+18:2+18:3	Algae, marsh plants	44	1.10	$\Delta^{14}C$ Only
	24:0+26:0+28:0	Higher terrestrial plants	44	0.251	$\delta^{13}C$ Only
PLFA					
River Site	12:0+14:0	Algae, bacteria	97†	1.18	$\Delta^{14}C$ Only
	16:0	Mixed‡	62	6.60	$\delta^{13}C$, $\Delta^{14}C$
	18:0+18:1+18:2+18:3	Algae, marsh plants	62	11.9	$\delta^{13}C$, $\Delta^{14}C$
	24:0+26:0+28:0	Higher terrestrial plants	97†	1.28	$\Delta^{14}C$ Only
ETM site	12:0+14:0	Algae, bacteria	119	7.05	$\delta^{13}C$, $\Delta^{14}C$
	16:0	Mixed‡	159†	23.7	$\delta^{13}C$, $\Delta^{14}C$
	18:0+18:1+18:2+18:3	Algae, marsh plants	119	33.0	$\delta^{13}C$, $\Delta^{14}C$
	24:0+26:0+28:0	Higher terrestrial plants	119	6.42	$\delta^{13}C$, $\Delta^{14}C$
Chl *a* max site	12:0+14:0	Algae, bacteria	117	3.66	$\delta^{13}C$, $\Delta^{14}C$
	16:0	Mixed‡	117	26.3	$\delta^{13}C$, $\Delta^{14}C$
	18:0+18:1+18:2+18:3	Algae, marsh plants	117	28.2	$\delta^{13}C$, $\Delta^{14}C$
	24:0+26:0+28:0	Higher terrestrial plants	117	3.16	$\delta^{13}C$, $\Delta^{14}C$

*Literature references: Canuel et al., 1997; Dalsgaard et al., 2003; Meyers 1997; Parkes and Taylor, 1983; Volkman et al., 1989 and references therein.
†Sample had impurities after first run through PC-GC. Ran through a second time to purify isolated compounds. Second set of injections were fewer than first set.
‡Mixed sources for $C_{16:0}$ include algae, bacteria, and zooplankton sources.

recovery rates (72–77%) demonstrate that the PC-GC system collected the majority of the compounds of interest (H.A. McIntosh, L. Xu unpubl.). Column bleed was removed using adsorptive column chromatography in 500 mg combusted silica columns (0.5 mm i.d., 100–200 mesh) eluted with 3% ethyl acetate in hexane (Pearson et al. 2001). Three fractions were collected; fractions one (2 mL) and three (1 mL) were analyzed by GC to verify that the purified compounds of interest were only isolated in fraction two (2 mL). Fraction two was transferred to a 9 mm precombusted quartz combustion tube (950°C for five hours, 20 cm × 9 mm o.d.) using 3:1 pentane : dichloromethane and the sample was dried under a light stream of N_2.

About 10 mg Ag powder and CuO wires (~50 mg) were added to each quartz tube. The quartz tubes were cooled cryogenically (isopropanol/ dry ice mixture at −78°C) and evacuated on a vacuum line (10^{-3} Torr), flame sealed, and combusted (900°C, three hours). The resulting CO_2 was isolated and purified from other gases using two isopropanol and dry ice slush traps and quantified manometrically. CO_2 was split for normal (> 25 μmol C) and small (3–25 μmol C) samples for stable carbon analysis (10%) on a VG PRISM series II Mass Spectrometer and graphite reduction (90%) at NOSAMS. Analytical precision of the compound specific stable carbon analyses was ± 0.1‰.

Purified CO_2 was reduced to graphite using standard procedures for normal and small samples depending on the amount of CO_2 (Table 3, McNichol et al. 1992; Shah and Pearson 2007). Ultramicroscale CO_2 (1–3 μmol C) samples were converted to graphite manually using ultramicroscale reactors (0.7 mL volume) (Shah et al. in press). Fe catalyst was prereduced and baked under vacuum to remove extraneous carbon. Vertical water traps were kept at −78°C in an isopropanol/ dry ice mixture. Graphite formation was done

for ultramicroscale samples on Fe catalyst with ~2.5 times the amount of H_2 as CO_2 at 625°C.

The resulting mixtures of graphite and Fe were pressed into aluminum targets with 1.0-mm diameter holes. Sample targets were loaded onto AMS sample wheels with a combination of blanks, PC-GC standards, primary OxI standards and secondary standards (von Reden et al. 1998). Radiocarbon data are reported as fraction modern (Fm), $\Delta^{14}C$ (‰), and ^{14}C age using standard conventions (Stuiver and Polach 1977).

Data analysis for CSRA

Samples prepared for CSRA went through a number of procedures and a cumulative process blank was determined. The process blank considered the entire process of sample preparation. Individual combusted filters ($n = 5$) were put through the same process as sample filters (lipid extraction by ASE, saponification, methylation, column chromatography). The methylated blank extracts were combined and then run as one sample through the PC-GC analysis (inclusive of sample trapping, transfer to a combustion tube, and combustion to CO_2). Only the isolated $C_{18's}$ FA in the process blank were large enough for reduction to graphite (inclusive of CO_2 reduction and target pressing). The processing blank ^{14}C values for the $C_{18's}$ are inclusive of all sample processing steps. The amount of carbon in the process blanks for the $C_{12:0+14:0}$, $C_{16:0}$, and $C_{24:0+26:0+28:0}$ isolated FA was insignificant. These FAs were corrected using a PC-GC analysis processing blank determined for the NOSAMS facility that included contributions of carbon during sample trapping, combustion, graphitization, and target processing. All process blank correction was done by mass-balance and error was propagated according to standard procedures (McNichol et al. 1992; Shah et al. in press).

Derivatization of FA for GC separation and analysis added one methyl group to each FA molecule. The measured $\delta^{13}C$ and $\Delta^{14}C$ (‰) values for the isolated FA were for the derivatized compounds, which included both the parent FA carbon atoms and the carbon atom added during methylation. An isotopic mass balance approach was used to determine $\delta^{13}C$ and $\Delta^{14}C$ (‰) values for the original, parent FA compounds (Eglinton et al. 1996).

Results

Particulate matter composition

The ETM was located in the mid Delaware Estuary (~88 km upstream of the bay mouth) during sample collection in late March-early April 2011 (Fig. 2A). The highest TSS concentrations in the Delaware Estuary are generally located near the salinity intrusion point (Biggs et al. 1983). However, in late March-early April 2011, TSS concentrations were elevated at both low (e.g., $S = 1.41$; 88 km upstream of the bay mouth) and moderate salinities (e.g., $S = 11.0$; 57 km upstream). The ETM site exhibited high variability in TSS concentrations during the 2-day sampling likely due to tidal fluctuations (Fig. 2A).

Similar to TSS distributions, POC and PN concentrations were lower in the Delaware River and Bay regions than in the mid-estuary (Fig. 2B). POC concentrations ranged from $37.8 \pm 5.4\ \mu mol\ L^{-1}$ to $265 \pm 10\ \mu mol\ L^{-1}$. PN concentrations ranged from $3.45 \pm 0.47\ \mu mol\ L^{-1}$ to $27.4 \pm 1.8\ \mu mol\ L^{-1}$. POC and PN were strongly correlated in the Delaware Estuary ($R^2 = 0.95$, $p = 0.004$).

Surface water concentrations of chl *a* ranged from $1.3 \pm 0.2\ \mu g\ L^{-1}$ to $12.0 \pm 0.9\ \mu g\ L^{-1}$ and pheo ranged from $0.9 \pm 0.2\ \mu g\ L^{-1}$ to $7.3 \pm 2.0\ \mu g\ L^{-1}$ (Fig. 2C). The highest concentrations of chl *a* were observed downstream of the ETM (i.e., $11.8\ \mu g\ L^{-1}$ at the high chl *a* site). The pheo concentration was highest at the ETM site but similar to concentrations measured at the high turbidity and chl *a* max sites (Fig. 2C). Stable carbon isotope values for POC ($\delta^{13}C_{POC}$) ranged from -27.5 ± 0.3‰ to -21.0 ± 0.3‰ and increased down the estuary with the lowest values measured at the river site and the highest measured at the high chl *a* site (Fig. 2D).

FA molecular distribution

Total FA concentrations associated with POM (FA_{POM}) were higher in TLE-P than in TLE-N for the same sites on both a volume-normalized (Student's paired *t*-test *p*-value = 0.038) and an OC-normalized basis (Student's paired *t*-test *p*-value = 0.039) (Table 4). Total FA_{POM} concentrations normalized to volume of water filtered were lower at the river location than at the ETM and chl *a* max sites for NFA and PLFA. Total FA_{POM} concentrations normalized to OC were lowest at the ETM site for both NFA and PLFA (Table 4). This is where POC (and TSS) concentrations were highest suggesting dilution of FA by mineral particles and other classes of OM.

Saturated FA dominated both the NFA and PLFA composition (Table 4, mean = 61.4 ± 2.3% and 62.0 ± 8.3% of total NFA and PLFA, respectively). Specifically, $C_{16:0}$ and $C_{18:0}$ made up the majority of both the saturated FA_{POM} and total FA_{POM} composition (Fig. 3). Monounsaturated FA_{POM} comprised a smaller portion of NFA (mean = 28.8 ± 4.9%) and PLFA (mean = 25.0 ± 7.7%) with $C_{16:1}$ and $C_{18:1}$ making up the majority of the monounsaturated FA_{POM}. On average, polyunsaturated FA_{POM} were less abundant than saturated FA and monounsaturated FA as a proportion of total FA_{POM} (mean = 8.4 ± 2.5% and 11.0 ± 0.4% for NFA and PLFA, respectively). Branched FA_{POM} made-up the smallest proportion (< 2%) of both NFA and PLFA.

$C_{16:0}$ FA was the most abundant compound in both the NFA and PLFA fractions and concentrations of other FAs decreased with carbon numbers both greater than and lower than $C_{16:0}$ (Fig. 3). $C_{18:0}$ was more prevalent than $C_{14:0}$ for NFA at the river and ETM sites whereas $C_{14:0}$ was more abundant than $C_{18:0}$ at the chl *a* max site. Relative to $C_{16:0}$, $C_{18:0}$ was more prevalent than $C_{14:0}$ in the PLFA for all of the sites

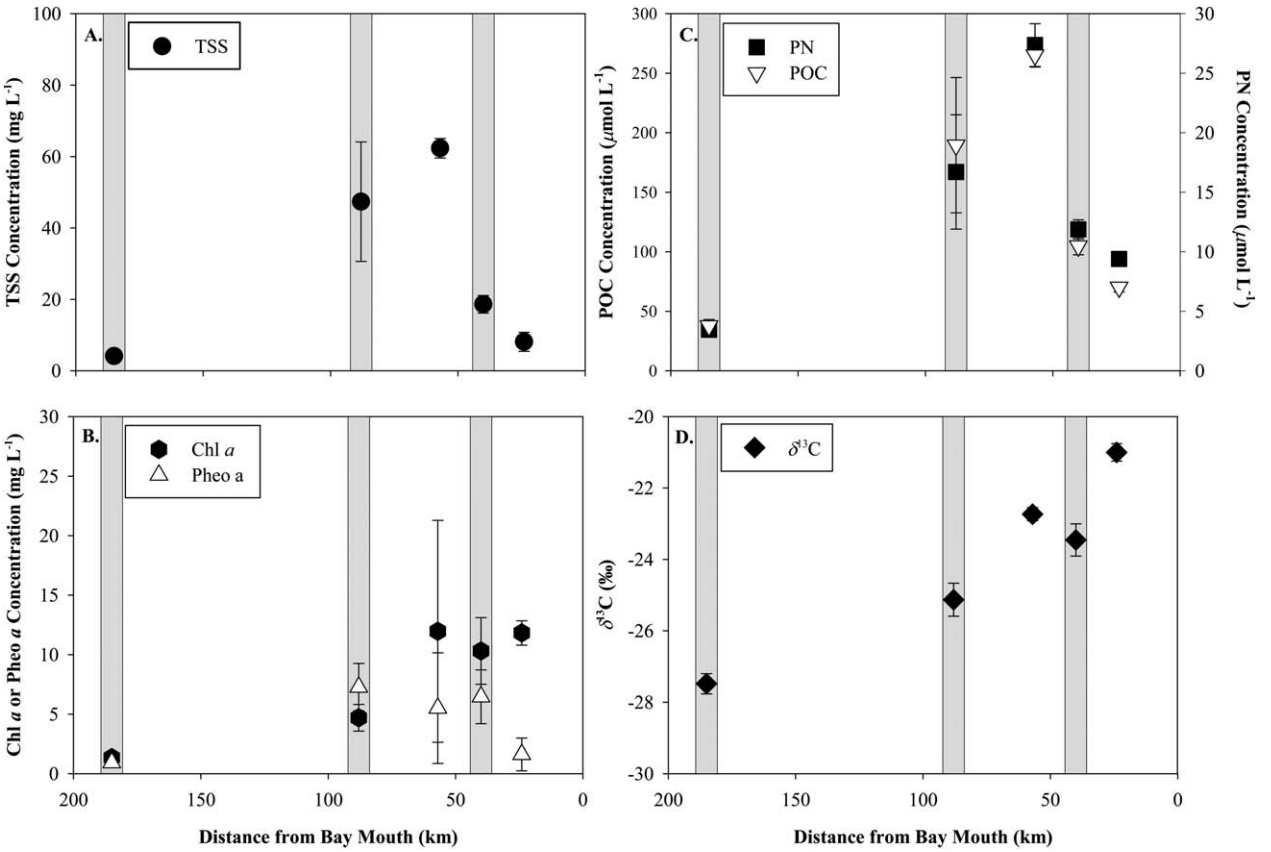

Fig. 2. Bulk suspended particulate matter properties measured along the Delaware Estuary in late March- early April 2011 (A) TSS, (B) POC and PN, (C) chl *a* and pheo, and (D) $\delta^{13}C_{POC}$ values. Gray bars indicate the three sites where large volumes of POM were collected for lipid composition and compound specific isotopic analyses. Error bars represent ± standard deviation from the mean of multiple samplings during the 24 h to 38 h samplings.

(Fig. 3). The unsaturated $C_{18:0}$ FA, $C_{18:1}$, $C_{18:2}$, and $C_{18:3}$, were typically < 20% the amount of $C_{16:0}$ except for $C_{18:1}$ in NFA and PLFA at the river site which were 20% and 40%, respectively. Relative to $C_{16:0}$, LC FA decreased in abundance with increasing chain length and LC FA had lower abundances in the NFA than in the PLFA.

POM individual FA biomarker $\delta^{13}C$ and $\Delta^{14}C$ Data

Stable carbon isotope values of FA ($\delta^{13}C_{FA}$)

Individual and groups of NFA and PLFA had $\delta^{13}C_{FA}$ ranging from −30.9‰ to −21.8‰ (Fig. 4), which was a broader range than observed for $\delta^{13}C_{POC}$ (−27.5‰ to −23.5‰; Fig. 2D). $\delta^{13}C_{FA}$ values for NFA and PLFA at the chl *a* max showed the greatest variability with values ranging from −30.9‰ to −21.8‰. Most FA had lower $\delta^{13}C_{FA}$ values than $\delta^{13}C_{POC}$ (Table 5). The difference between the $\delta^{13}C_{POC}$ and $\delta^{13}C_{FA}$ for samples from the same location was calculated as $\Delta\ \delta^{13}C$ FA : POC (i.e., $\Delta\ \delta^{13}C$ FA : POC = $\delta^{13}C_{POC}$–$\delta^{13}C_{FA}$). Only the $C_{18's}$ PLFA at the ETM and chl *a* max sites had higher $\delta^{13}C_{FA}$ values relative to POC at those sites ($\Delta\ \delta^{13}C$ FA : POC = −1.6‰ and −0.6‰, respectively; Table 5).

Overall, $\delta^{13}C_{FA}$ values for NFA did not have the same patterns as PLFA suggesting different sources or processes influence these FA groups (Fig. 4; Table 6). SC NFA had the highest $\delta^{13}C$ value of the isolated NFA at the chl *a* max site (−24.5‰), while $\delta^{13}C_{FA}$ values for $C_{16:0}$ and $C_{18's}$ (mid-chain [MC]) NFA were intermediate to other $\delta^{13}C_{FA}$ (∼ −28‰) (Fig. 4A). LC NFA had the lowest $\delta^{13}C_{FA}$ of the isolated NFA at each site and values decreased from the freshwater to higher salinity regions (−28.6‰, −30.0‰, and −30.9‰, respectively) (Fig. 4A).

$\delta^{13}C_{FA}$ values for the SC PLFA ($C_{12:0+14:0}$) were lower at the ETM site compared to the chl *a* max site (−27.4‰ and −24.3‰, respectively; Fig. 4B). $\delta^{13}C_{FA}$ values for $C_{16:0}$ PLFA increased along the estuary from the Delaware River site (−29.8‰) to the ETM site (−26.2‰) to the chl *a* max site (−23.4‰) suggesting different sources for this FA along the estuary. Similarly, $\delta^{13}C_{FA}$ values for $C_{18's}$ PLFA were lower at the river site (−30.5‰) than at the chl *a* max site (−21.8‰). LC PLFA ($C_{24:0+26:0+28:0}$) had the lowest $\delta^{13}C_{FA}$ values of the isolated PLFA at the ETM and chl *a* max (−29.4‰ and −29.5‰, respectively).

Table 4. NFA and PLFA concentrations (A) normalized to volume filtered, (B) normalized to POC, and (C) as % total FA for total FA, saturated FA, monounsaturated FA, polyunsaturated FA, and branched FA.

	NFA			PLFA		
	River	ETM	Chl *a* max	River	ETM	Chl *a* max
(A) Concentration ($\mu g\,L^{-1}$)						
Total FA	1.33	1.57	3.61	3.77	7.37	6.41
Saturated FA	0.82	1.01	2.14	1.99	4.89	4.43
Monounsaturated FA	0.39	0.37	1.21	1.24	1.58	1.27
Polyunsaturated FA	0.11	0.17	0.21	0.49	0.75	0.68
Branched FA	0.02	0.03	0.05	0.06	0.15	0.04
(B) Concentration (mg g^{-1} OC)						
Total FA	2.94	0.69	2.87	8.31	3.24	5.09
Saturated FA	1.80	0.44	1.70	4.37	2.15	3.52
Monounsaturated FA	0.85	0.16	0.96	2.73	0.70	1.00
Polyunsaturated FA	0.25	0.07	0.17	1.08	0.33	0.54
Branched FA	0.04	0.01	0.04	0.14	0.07	0.03
(C) % Total FA						
Total FA	100	100	100	100	100	100
Saturated FA	61	64	59	53	66	69
Monounsaturated FA	29	24	34	34	22	20
Polyunsaturated FA	9	11	6	11	10	11
Branched FA	1	2	1	2	2	1

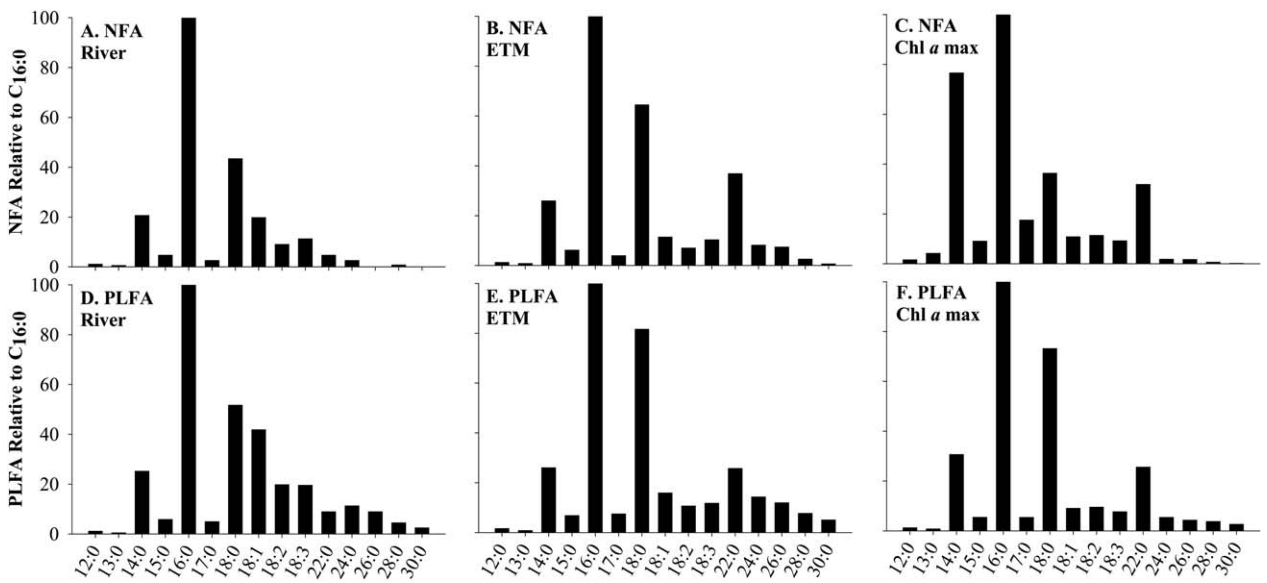

Fig. 3. Abundance of select saturated and unsaturated FA relative to $C_{16:0}$ in the NFA and phospholipid linked fatty acids (PLFA) at the River (A,D), ETM (B,E) and Chl *a* max (C,F), respectively. $C_{19:0}$ and $C_{21:0}$ were excluded because they were added as a surrogate and an internal standard, respectively.

FA radiocarbon ($\Delta^{14}C_{FA}$) composition

In addition to $\delta^{13}C$, $\Delta^{14}C$ was measured for individual and groups of FA ($\Delta^{14}C_{FA}$) when sample sizes were large enough to permit these analyses (Table 6; Fig. 5). In the NFA, only $C_{18's}$ at the river and chl *a* max sites were large enough to permit $\Delta^{14}C$ measurements (Fig. 5). $\Delta^{14}C$ values for the NFA $C_{18's}$ from the river were lower than the corresponding PLFA $C_{18's}$ by 40 ± 10‰ (difference ± propagated error). At the chl *a* max the NFA $C_{18's}$ had a lower $\Delta^{14}C$ value than the corresponding PLFA C_{18} by 35 ± 12‰, respectively.

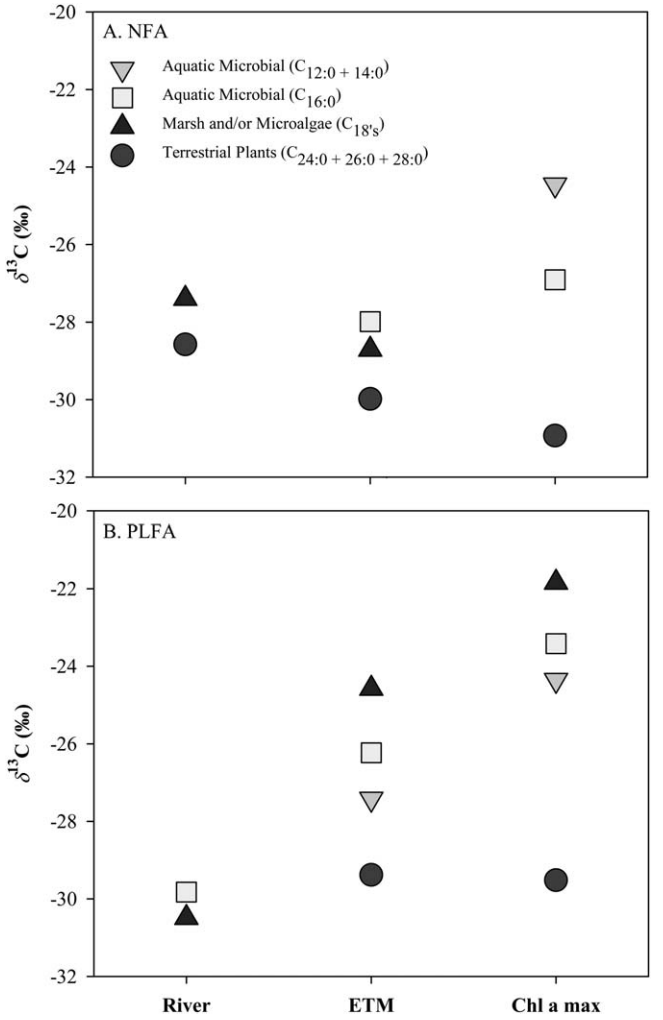

Fig. 4. $\delta^{13}C$ values for individual and groups of FA extracted from POM collected in the Delaware Estuary. $\delta^{13}C$ values for phospholipid-linked FA (PLFA) (A) are compared with $\delta^{13}C$ values for NFA (B). Error bars ($\pm$ 0.1‰) are not included because the error is smaller than the size of the symbols.

Table 5. $\Delta\ \delta^{13}C$ FA : POC ($\delta^{13}C_{POC}$ minus $\delta^{13}C_{FA}$, Canuel et al. 1997) for NFA and phospholipid-linked FA (PLFA) in ‰. Typically FA had more negative $\delta^{13}C$ values relative to POC (positive $\Delta\ \delta^{13}C$ FA : POC), but two individual or groups of FA had more positive $\delta^{13}C$ values relative to POC (negative $\Delta\ \delta^{13}C$ FA : POC) when error was taken into consideration ($\pm$ 0.2‰). Averages are for the four individual or groups of NFA or PLFA collected at each site. Dashes represent no data available.

	$\Delta\ \delta^{13}C$ FA:POC (‰)			
	River	ETM	Chl *a* max	Overall
NFA $C_{12:0+14:0}$	—	—	1.0	
NFA $C_{16:0}$	—	2.9	3.5	
NFA $C_{18's}$	−0.1	3.6	—	
NFA $C_{24:0+26:0+28:0}$	1.1	4.9	7.5	
Average	0.5	3.8	4.0	
Standard deviation	0.8	1.0	3.3	
PLFA $C_{12:0+14:0}$	—	2.3	0.9	
PLFA $C_{16:0}$	2.3	1.1	0.0	
PLFA $C_{18's}$	3.0	−0.6	−1.6	
PLFA $C_{24:0+26:0+28:0}$	—	4.3	6.1	
Average	2.7	1.8	1.3	
Standard deviation	0.5	2.0	3.3	
Total Average	1.6	2.6	2.5	**2.3**
Total Standard deviation	1.4	1.9	3.3	**2.4**

$^{14}C_{FA}$ analyses indicate that PLFA were produced within the last two millennia with ^{14}C ages of 1700 BP to modern ($\Delta^{14}C_{FA} = -194‰$ to $+57‰$). Most of the SC PLFA and MC PLFA at the ETM and chl *a* max sites had positive $\Delta^{14}C_{FA}$ values and modern ^{14}C ages (Fig. 5). These compounds contained bomb ^{14}C, but at the river and ETM sites they had more positive $\Delta^{14}C_{FA}$ values ($-83 \pm 18‰$ to $+58 \pm 4‰$, 30 BP to modern) than surface water dissolved inorganic carbon (DIC; −125‰ to −71‰ in October 2010; Table 7). SC PLFA at the chl *a* max site had lower $\Delta^{14}C_{FA}$ values ($+43 \pm 11‰$, modern) compared to surface water DIC (+51‰ and +63‰ for DIC replicates in October 2010). $\Delta^{14}C_{FA}$ values for SC PLFA and MC PLFA differed at the river site ($-83 \pm 18‰$ and $-6 \pm 5‰$, 700 BP and 50 BP, respectively) but were similar at the chl *a* max site ($43 \pm 4‰$ and $45 \pm 3‰$, modern and modern, respectively). This suggests that sources for these compounds were similar in age at the chl *a* max site in Delaware Bay. $\Delta^{14}C_{FA}$ values for SC PLFA increased along the salinity gradient of the Delaware Estuary from the river site ($-83 \pm 19‰$, 70 BP) to the chl *a* max site ($+43 \pm 11‰$, modern), while LC PLFA decreased from the river site ($-16 \pm 18‰$, 120 BP) to the chl *a* max site ($-190 \pm 11‰$, 1700 BP).

Discussion

Particulate composition

The Delaware Estuary is a light-limited estuary and TSS concentrations along the estuary exert an important control on where marine primary production occurs (Pennock 1985). TSS concentrations in late March-early April 2011 were elevated in the mid-estuary but did not reach the highest concentrations previously measured of approximately 150 mg L^{-1} (Sharp et al. 2009). TSS concentrations were well correlated with POC concentrations ($R^2 = 0.99$, $p < 0.001$). Fluxes and concentrations of OM, especially from terrestrial sources, generally increase in the Delaware Estuary following the spring freshet and with increased river discharge (Sharp et al. 1986; Raymond and Oh 2007). The late March-early April 2011 sampling occurred 2–3 weeks after the spring freshet in the Delaware estuary, which peaked at a daily average of 3900 m^3 s^{-1} on 12 March 2011 (USGS 2012). An

Table 6. Compound specific stable carbon and radiocarbon isotope values for FA associated with POM in the Delaware Estuary. All values presented are for the derivative corrected parent FA compounds and errors presented for Fraction modern were propagated for instrument and procedural blanks.

Sample name	Target compound	$\delta^{13}C$ (‰)*	Fraction modern (Fm)	^{14}C age (BP)
NFA				
River site	12:0 + 14:0	—	—	—
	16:0	—	—	—
	18:0 + 18:1 + 18:2 + 18:3	−27.4	0.954 (0.008)	380 (70)
	24:0 + 26:0 + 28:0	−28.6	—	—
ETM site	12:0 + 14:0	—	—	—
	16:0	−28.0	—	—
	18:0 + 18:1 + 18:2 + 18:3	−28.7	—	—
	24:0 + 26:0 + 28:0	−30.0	—	—
Chl *a* max site	12:0 + 14:0	−24.5	—	—
	16:0	−26.9	—	—
	18:0 + 18:1 + 18:2 + 18:3	—	1.009 (0.011)	Modern
	24:0 + 26:0 + 28:0	−30.9	—	—
PLFA				
River Site	12:0 + 14:0	—	0.917 (0.019)	700 (160)
	16:0	−29.8	0.985 (0.007)	120 (60)
	18:0 + 18:1 + 18:2 + 18:3	−30.5	0.994 (0.005)	50 (40)
	24:0 + 26:0 + 28:0	—	0.984 (0.018)	130 (130)
ETM site	12:0 + 14:0	−27.4	0.996 (0.005)	30 (30)
	16:0	−26.2	1.058 (0.004)	Modern
	18:0 + 18:1 + 18:2 + 18:3	−24.6	1.043 (0.004)	Modern
	24:0 + 26:0 + 28:0	−29.4	0.821 (0.007)	1600 (100)
Chl *a* max site	12:0 + 14:0	−24.4	1.043 (0.011)	Modern
	16:0	−23.4	1.043 (0.004)	Modern
	18:0 + 18:1 + 18:2 + 18:3	−21.8	1.045 (0.003)	Modern
	24:0 + 26:0 + 28:0	−29.5	0.809 (0.011)	1700 (100)
NFA Blank	18:0 + 18:1 + 18:2 + 18:3	—	0.946 (0.029)	440 (250)
PLFA Blank	18:0 + 18:1 + 18:2 + 18:3	—	0.965 (0.030)	290 (250)

*Error associated with $\delta^{13}C$ measurements is 0.1‰.
Values in parentheses provide the error in Fm or ^{14}C age that was propagated from instrument variability and sample blanks
- No Data Available

initial pulse of terrestrial OM flushing out of the watershed was likely captured during this sampling. All of the terrestrial OM from the spring freshet would not have made its way through the Delaware Estuary due to its 80 d to 100 d flushing time (Ketchum 1952).

Environmental variables, especially TSS (4.1 mg L^{-1} to 62.3 mg L^{-1}) and POC (37.8 μmol L^{-1} to 265 μmol L^{-1}), were similar to previous studies of the system in June of 1996 (Mannino and Harvey 1999) and routine research cruises between 1978 and 2003 (Sharp et al. 2009). TSS fell within the concentration range of 4.3 mg L^{-1} to 92 mg L^{-1} collected by Mannino and Harvey (1999), but bracketed the 25-year range for TSS of 6.5 mg L^{-1} to 45.9 mg L^{-1} (Sharp et al. 2009). POC was lower in the river than seen by Mannino and Harvey (1999), likely due to differences in discharge between the two studies. Similarities between suspended sediment concentrations and POC in this and previous studies suggests this was a representative sampling of estuarine OM for this system.

Chl *a* and pheo concentrations were used as a proxies for live and dead phytoplankton biomass, respectively. Chl *a* concentrations increased gradually from the mid-estuary to the Delaware Bay, downstream of the turbid section of the estuary (Fig. 2C). The chl *a* concentrations suggest low phytoplankton abundance ($< 20\,\mu g\,L^{-1}$ chl *a*), consistent with findings by Pennock (1985) for the central axis of the Delaware River and Bay. The late March-early April sampling likely preceded the larger spring phytoplankton blooms (50–$60\,\mu g\,L^{-1}$ chl *a*) that are seen from March to May depending on the timing of peak freshwater discharge (Pennock 1985;

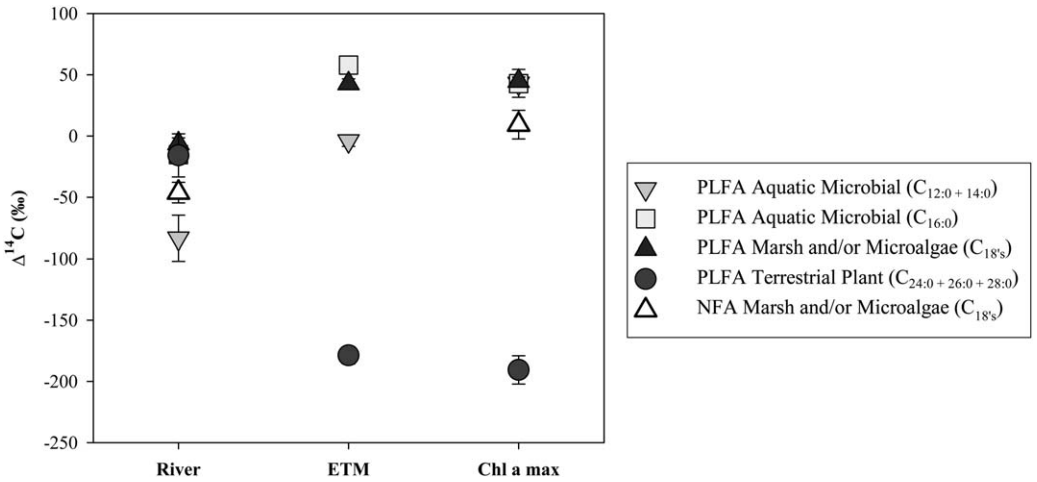

Fig. 5. $\Delta^{14}C$ values for individual and groups of FA biomarkers extracted from POM collected in the Delaware Estuary. Isotope values for PLFA biomarkers are represented by filled symbols and values for neutral FA (NFA) biomarkers are represented by open symbols. Error bars representing blank correction error propagation are visible outside the symbols for small and ultrasmall samples.

Table 7. Dissolved inorganic carbon stable carbon and radiocarbon isotopic values measured from the Delaware Estuary in October 2010.

Station	Site description		Distance from Bay Mouth (km)	DIC		
				$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	^{14}C Age (BP)
1	River		185	−9.0	−124.6 ± 0.6	1070
2	ETM	Rep 1	92	−9.2	−70.5 ± 0.3	590
		Rep 2	92	−9.6	−75.5 ± 0.3	630
5	Chl *a* Max	Rep 1	24	−0.5	50.5 ± 0.2	Modern
		Rep 2	24	−0.4	62.9 ± 0.3	Modern
6	Bay Mouth	Rep 1	0	0.2	52.8 ± 0.2	Modern
		Rep 2	0	0.3	53.2 ± 0.2	Modern

Pennock and Sharp 1986). Pheo concentrations were lower than chl *a* at all sites except the ETM. The ETM in the Delaware Estuary is characterized by high sediment trapping where fresh OM, such as phytoplankton, can decompose before being resuspended and dispersed downstream into the Delaware Bay during high discharge events (Sommerfield and Wong 2011). Overall, live and dead phytoplankton abundances were typical for the estuary since the sampling occurred prior to the spring bloom.

$\delta^{13}C_{POC}$ distributions

$\delta^{13}C_{POC}$ isotopic composition changed from values typical of terrigenous sources at the river location to aquatic sources downstream of the turbid mid-estuary. In the Delaware River and upper estuary sites, the values of $\delta^{13}C_{POC}$ indicate that the dominant source was terrigenous OM from the watershed (Fig. 2D) (Fry and Sherr 1984; Meyers 1997). The $\delta^{13}C_{POC}$ value in the river (−27.5‰) was more negative than the often-quoted $\delta^{13}C$ value of −26‰ for terrestrial OM (Fry and Sherr 1984) and lower than the value measured in the upper estuary (−25.8‰) in late spring 1984 (Cifuentes et al. 1988). In Delaware Bay, $\delta^{13}C_{POC}$ values were −23.5‰ at the chl *a* max site (40 km from bay mouth) and −21.0‰ at the high chl *a* site (24 km from bay mouth). These values are slightly more negative than seen previously in the Delaware Bay (Cifuentes et al. 1988; Mannino and Harvey 1999). Over the period from 1984 to 1985, $\delta^{13}C$ values in Delaware Bay between 0 km to 40 km from the Bay Mouth, ranged from approximately −22‰ to −16.6‰ (Cifuentes et al. 1988). Low chl *a* concentrations measured in our study relative to other samplings during spring, suggests lower phytoplankton biomass in the estuary and lower aerial primary production rates (Pennock and Sharp 1986). The more positive $\delta^{13}C$ values previously measured by Cifuentes et al. (1988) were attributed to high rates of aerial primary production. Because our sampling missed the spring phytoplankton bloom, $\delta^{13}C_{POC}$ values in the bay were lower than if we had captured the bloom and high rates of phytoplankton production.

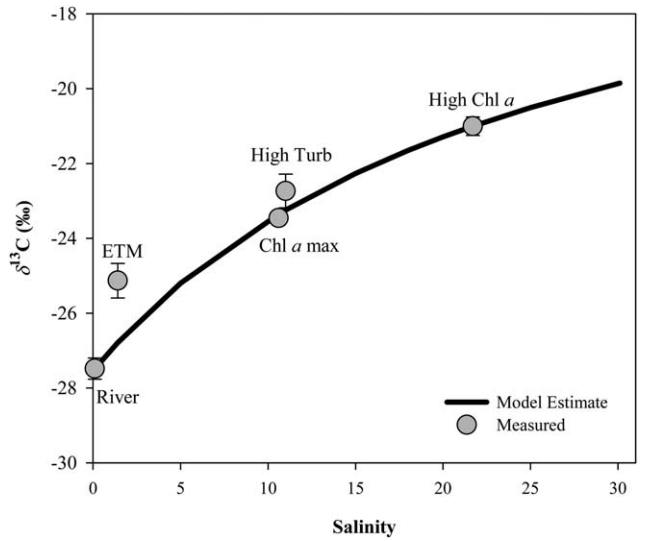

Fig. 6. Isotopic mixing curve and measured isotopic data for $\delta^{13}C_{POC}$. The mixing curve was based on Raymond and Bauer (2001) and used $\delta^{13}C$ values of $-27.5‰$ for the riverine end-member and $-21.0‰$ for the marine end-member.

Deviations from conservative mixing were seen for $\delta^{13}C_{POC}$ values in the Delaware Estuary in March 2011 (Fig. 6). A two end-member isotopic mixing model was employed to estimate the conservative mixing of $\delta^{13}C_{POC}$ using the riverine ($-27.5‰$) and high chl *a* ($-21.0‰$) sites as end-members (Raymond and Bauer 2001). Although $\delta^{13}C_{POC}$ distributions in March 2011 generally followed conservative mixing along the estuary, values at the ETM and high turbidity sites were more positive than predicted by the two end-member isotopic mixing model. It is not surprising that POC at these sites does not behave conservatively with respect to the model, as advective processes dominate suspended sediment transport in this region of the estuary (Sommerfield and Wong 2011). Surface water samples at the ETM were likely influenced by mixing of water from the river and bay as well as resuspended sediments (Cook et al. 2007; Sommerfield and Wong 2011). The tidal river and turbid portion of the estuary can hold suspended sediments for 1–2 yr, while the river and bay sites represent pools of OM that entered or were produced within the flushing time of the estuary (Cook et al. 2007). As a result, the ETM and high turbidity sites may represent OM integrated over years while values at the other sites may be more representative of more recent (< 100 d) conditions.

Isotopic mixing models for DOC in other river-estuary systems along the East Coast of the U.S.A. such as the York River (Virginia, USA) and Parker River (Massachusetts, USA) exhibited nonconservative mixing (Raymond and Bauer 2001). Raymond and Bauer (2001) proposed that both the removal of $\delta^{13}C$-depleted riverine DOC and the addition of $\delta^{13}C$-enriched DOC from autochthonous sources accounted for the deviation from conservative mixing. An alterative explanation to the deviation of $\delta^{13}C_{POC}$ values from conservative isotopic mixing is that biotic and abiotic processes in the turbid estuary caused the deviation. Within the Delaware Estuary, abiotic processes (e.g., flocculation, adsorption/absorption, and precipitation) and/or biotic microbial processes (e.g., respiration of labile OM) at the ETM may remove terrestrial POC with more negative $\delta^{13}C$ values or incorporate DOC that is older, more degraded, and has more positive $\delta^{13}C$ into the POC pool (Sharp et al. 1984; Hwang et al. 2006).

FA composition

Along the Delaware Estuary, the overall FA molecular distributions as % of total FA were similar between sites (Fig. 3), but the total NFA and PLFA concentrations varied along the estuary normalized to volume and POC (Table 4). $C_{16:0}$ and $C_{18:0}$ FA, the dominant FA_{POM}, derive from a mixture of planktonic (bacteria, phytoplankton, and zooplankton) and higher plant sources (Volkman et al. 1989; Canuel et al. 1997; Dalsgaard et al. 2003). High amounts of $C_{16:0}$ and $C_{18:0}$ FA and their FA homologs in POM were observed previously in the Delaware (Mannino and Harvey 1999). The predominance of saturated FA, with mixed planktonic sources, has been reported in other mid-Atlantic estuaries (Harvey and Johnston 1995; Canuel 2001). The saturated FA during late March-early April 2011 were dominated by SC $C_{12:0+14:0}$ FA and MC $C_{16:0}$ and $C_{18's}$ FA from aquatic microbial, marsh, and microalgae sources and lower abundances of LC $C_{24:0+26:0+28:0}$ FA from higher plant terrestrial sources (Fig. 3 and references within Table 3).

Compared to saturated FA, polyunsaturated FA and branched FA comprised a smaller portion of both the total neutral and total polar FA_{POM} (Table 4). Polyunsaturated FA are attributed to planktonic sources, such as microalgae, especially the C_{20} and C_{22} polyunsaturated FA (Volkman et al. 1989). Branched FA are attributed to heterotrophic bacterial OM sources (Parkes and Taylor 1983). Because both classes represented small contributions to total FA_{POM}, it was not possible to perform CSRA analyses on these FA. Polyunsaturated FA and branched FA indicate that planktonic and bacterial sources contribute to surface water POM along the Delaware Estuary, respectively, but other, more abundant, FA components were used to provide ^{14}C information on planktonic and bacterial sources. Instead, SC FA were used for microbial (microalgae and bacteria) sources associated with POM (Parkes and Taylor 1983) and $C_{18's}$ FA provided information about microalgal and marsh sources (Volkman et al. 1989; Canuel et al. 1997).

Ideally individual FA with known sources would be isolated for $\delta^{13}C$ and $\Delta^{14}C$ analyses to better understand the heterogeneity of isotopic values in OM (Eglinton et al. 1996). In this case, SC FA were combined for $\delta^{13}C$ and $\Delta^{14}C$ analyses due to their low abundances and the likelihood

that both of these compounds represented microbial sources. $C_{14:0}$ also had lower abundances than $C_{16:0}$ and $C_{18:0}$ in NFA and PLFA in all samples except NFA from the chl *a* max (Fig. 3). Higher contributions from $C_{14:0}$ at the chl *a* max could be representative of greater primary production or phytoplankton contribution to OM (Meyers 1997). MC $C_{18's}$ were difficult to separate chromatographically and so were collected together to avoid preferential isotopic fractionation from the collection of only a portion of the $C_{18:0}$ peak (Eglinton et al. 1996; Zencak et al. 2007). LC FA for $\delta^{13}C$ and $\Delta^{14}C$ analyses were combined and displayed much lower concentrations than the SC FA suggesting greater planktonic contributions than higher plant terrestrial contributions to surface water POM composition (Fig. 3). Even when all LC FA were combined, there was not always enough material for both $\delta^{13}C$ and $\Delta^{14}C$ analyses (Table 3).

$C_{18's}$ FA ($C_{18:0+18:1+18:2+18:3}$) are typically ascribed to microalgae and/ or marsh sources. The mixture of sources in the $C_{18's}$ can be resolved with additional information from stable and radiocarbon isotopes. Some marsh plants are more enriched in ^{13}C compared to both terrestrial and marine OM sources to estuaries. In North Carolina, marsh plants such as *Spartina* had $\delta^{13}C$ values for total FA of −18.4‰ with prevalent FA being $C_{18:2}$ and $C_{18:3}$, both collected in the $C_{18's}$ sample (Canuel et al. 1997). Isotopic depletion in the $C_{18's}$ would indicate bacterial or marine sources (Hayes 2001). $\delta^{13}C$ analysis of $C_{18's}$ FA suggests that the marshes on the periphery of Delaware Estuary may be an important source of POM, as described further in the next section.

A comparison of $\delta^{13}C_{POC}$ and $\delta^{13}C_{FA}$

The pattern for $\delta^{13}C_{POC}$ and $\delta^{13}C_{FA}$ along the estuary was similar but the values differed. The majority of $\delta^{13}C_{FA}$ were more negative than $\delta^{13}C_{POC}$ for the same site ($\Delta\ \delta^{13}C$ FA : POC = 2.3 ± 2.4‰, Table 5). These differences are within the range expected based on isotopic fractionations during lipid biosynthesis ($\Delta\ \delta^{13}C$ FA : POC = 0‰ to 12‰) (Hayes 2001 and references therein). Only the $\delta^{13}C_{FA}$ values for the $C_{18's}$ PLFA measured at the ETM and chl *a* max were more positive than $\delta^{13}C_{POC}$. $\delta^{13}C$ values for $C_{18's}$ PLFA at the chl *a* max were more elevated compared to POC ($\Delta\ \delta^{13}C$ FA : POC = −1.6‰) than at the ETM ($\Delta\ \delta^{13}C$ FA : POC = −0.6‰; Table 5). The LC FA tended to have the lowest $\delta^{13}C_{FA}$ compared to $\delta^{13}C_{POC}$, with the largest difference at the chl *a* max site ($\Delta\ \delta^{13}C$ FA : POC = 7.5‰). Individual lipid compounds (i.e., FA, *n*-alkanes, *n*-alcohols) are usually 3‰ to 5‰ depleted relative to bulk carbon (Collister et al. 1994; Canuel et al. 1997). For instance, *n*-alkanes in plant tissues for C_3 and C_4 plants were on average between 1.9‰ and 5.9‰ lower than total carbon while *n*-alkanes from different tissues within the same plant varied up to 5‰ (Collister et al. 1994). In estuarine and marine sediments, $\delta^{13}C_{PLFA}$ were 2.2‰ to 11.4‰ lower than bulk sediment $\delta^{13}C_{TOC}$, while in terrestrial soils $\delta^{13}C_{PLFA}$ values were 0.1‰ to 2.1‰ depleted relative to soil $\delta^{13}C_{TOC}$ (Cifuentes and Salata 2001). Similarly, FA associated with POM in the Delaware Estuary typically had lower $\delta^{13}C$ compared to POC, the exception being $C_{18's}$ PLFA.

Higher $\delta^{13}C_{FA}$ values for $C_{18's}$ PLFA compared to POC at the ETM and chl *a* max sites suggest potential contributions of OM from the marshes adjacent to the Delaware Estuary that are not seen at the river site (Canuel et al. 1997). Freshwater marshes fringe the lower, tidal Delaware River, while saltmarshes border smaller tributaries, as well as, the entire Delaware Bay (Fig. 1). Hermes (2013) found marsh OM contributions to POM in the ETM and Delaware Bay made up 20–50% of the vascular plant derived POM in the estuary. As aforementioned, both $\delta^{13}C_{TOC}$ and $\delta^{13}C_{FA}$ tend to be higher in marsh plants than in phytoplankton and terrigenous sources. In our study, $\delta^{13}C$ values for $C_{18's}$ were higher than both POC and other PLFA at the ETM and chl *a* max site, consistent with contributions from marsh-derived OM. These data suggest the potential importance of marsh OM and indicate that delivery of OM by lateral exchange processes along the estuarine salinity gradient should be considered in carbon budgets for estuarine systems. Recent studies indicate that quantifying the exchange of materials at the marsh-estuary interface remains an important gap in our understanding of the coastal carbon budget (Najjar et al. 2012) and these data suggest the potential importance of inputs from the tidal marshes in the Delaware system.

FAME and PLFA $\delta^{13}C$ and $\Delta^{14}C$ distributions

The stable and radio- carbon isotopic content of individual and groups of FA changed along the Delaware Estuary (Fig. 4 and 5). SC FA primarily reflect autochthonous microbial and planktonic sources of OM, while MC FA reflect marsh and microalgae sources ($C_{18's}$). While the MC $C_{16:0}$ FA can derive from a variety of sources, $C_{16:0}$ $\delta^{13}C_{FA}$ generally tracked aquatic and microbial sources in our study. $\delta^{13}C$ values of SC and MC NFA did not vary greatly along the estuary (Fig. 4A), while $\delta^{13}C$ values of SC and MC PLFA increased along the estuary (Fig. 4B). NFA are storage lipids and can derive from viable biomass and detritus, while PLFA are membrane lipids that turnover quickly when an organism dies and likely represent viable, or recently viable, microbial sources (White et al. 1979). Primary producers in the Delaware Estuary preferentially use CO_2 ($\delta^{13}C = \sim -8‰$) rather than bicarbonate ($\delta^{13}C = -3‰$) to produce OM except during times of low CO_2 concentrations or high photosynthetic production (Fogel and Cifuentes 1993). In regions of high photosynthetic production, bicarbonate becomes an increasingly important source of DIC to plankton and microalgae (Fogel and Cifuentes 1993). As chl *a* increased along the Delaware Estuary (Fig. 2C), suggesting increased primary producers and photosynthetic production, the bicarbonate incorporation rates likely also increased along the estuary

which produced SC and MC FA with more enriched, less fractionated $\delta^{13}C$ (Fogel and Cifuentes 1993). The change in DIC source is expected to be more apparent in the $\delta^{13}C$ values of PLFA, compared to NFA, since PLFA reflect viable or recently viable biomass (White et al. 1979; Zink et al. 2008). The differences in the isotopic distributions of SC and MC NFA and PLFA likely reflect their biosynthetic origin as storage lipids or recently produced membrane lipids, respectively.

SC FA decreased in age along the estuary from a maximum age at the river site to "younger" ages at the chl *a* max (Table 6, Fig. 5). The decrease in age is consistent with DIC ages along the Delaware Estuary in October 2010 (Table 7). Differences in DIC $\Delta^{14}C$ ($\Delta^{14}C_{DIC}$) isotopic values along a river-estuary continuum reflect different DIC sources. Rock weathering and simultaneous respiration and primary production influenced $\Delta^{14}C_{DIC}$ in the river and air-sea exchange of CO_2 influenced $\Delta^{14}C_{DIC}$ in the bay end-member (Fry and Sherr 1984; Meyers 1997 and references therein; Raymond et al. 2004). Shale and sandstone are mainly found in the Delaware River watershed to the north of Trenton, NJ in the lowland Piedmont region (Mansue and Commings 1974). As old rocks weather within the Delaware River watershed, old and ^{14}C depleted carbonate species are introduced to the Delaware. Downstream, riverine DIC mixes with marine DIC, which derives from diffusion of atmospheric CO_2. This results in $\Delta^{14}C_{DIC}$ values in Delaware Bay in October 2010 ($\Delta^{14}C = +52.8$, $+53.2‰$) being similar to modern atmospheric CO_2 ($\Delta^{14}C = +40‰$ in 2010; Hua et al. 2013). The SC FA ^{14}C ages have the same trend as $^{14}C_{DIC}$ ages along the Delaware Estuary.

Depleted $\Delta^{14}C_{DIC}$ values at the Delaware River site were likely propagated into the SC FA at that site. At the Delaware Estuary ETM, the SC FA were depleted in $\Delta^{14}C$ relative to the MC FA, but at the chl *a* max, where DIC was modern in age, the $\Delta^{14}C$ isotope values more positive for SC and MC FA. In a previous study, depleted $\Delta^{14}C_{DIC}$ ($\sim -100‰$) in the Antarctic Ocean were propagated through C_{14} FA ($-200‰$ to $-100‰$ $\Delta^{14}C$) in sediments (Ohkouchi et al. 2003). In the Antarctic Ocean, DIC is two to three times older than DIC in other ocean basins and the depleted $\Delta^{14}C$ SC FA from the region indicate the incorporation of the depleted surface water $\Delta^{14}C_{DIC}$ (Ohkouchi et al. 2003). $\Delta^{14}C_{DIC}$ was likely propagated through the SC and MC FA along the Delaware Estuary, as in other locations.

The isotopic signatures of bacterial membrane lipids (PLFA) can provide insights about the sources of OM supporting heterotrophic bacteria. In our study, bacteria-specific PLFAs (e.g., branched 15:0) were not isolated for radiocarbon analysis because of their low concentrations, but the aquatic microbial SC FA likely contained bacterial membrane components (Parkes and Taylor 1983). At the river and ETM sites, SC PLFA had lower ^{14}C values than $C_{16:0}$ ($68 \pm 20‰$ and $61 \pm 6‰$ lower, respectively) and $C_{18's}$ ($77 \pm 20‰$ and $47 \pm 5‰$ lower, respectively) MC PLFA from aquatic microbial and marsh sources, reflecting incorporation of substrates with older radiocarbon ages (Fig. 5). In contrast, bacterial and planktonic derived PLFA had overlapping $\Delta^{14}C$ values at the chl *a* max site suggesting incorporation of carbon with modern ages (Fig. 5). A previous study showed bacterial membrane PLFAs depleted in ^{14}C due to bacteria consuming fossil carbon (Wakeham et al. 2006). PLFA from marsh sediments showed bacterial membrane PLFAs (branched 15:0, 16:1, 10-methyl-16, and branched 17:0) were depleted in ^{14}C by $150‰$ to $250‰$ compared to recently produced planktonic and marsh plant derived PLFAs (14:0, 16:0, 18:0, and 18:1) (Wakeham et al. 2006). The older ages for the SC FA at the river and ETM sites likely reflect that bacteria are using "older" carbon as substrates in these regions from soils or weathered rock, or that the primary producers are using older inorganic carbon sources. Within the Delaware Estuary, the increasingly positive $\Delta^{14}C$ for SC PLFA suggests the sources of carbon supporting microbes changed along the estuarine gradient.

$\Delta^{14}C$ values for LC FA, traditionally biomarkers for terrigenous sources such as higher plants and soils, decreased (became "older") along the Delaware Estuary. The "youngest" ^{14}C age for LC PLFA was observed at the river site (130 ± 130 BP) while the "oldest" age occurred at the chl *a* max (1700 ± 100 BP) (Table 6). These data suggest "aging" of terrestrial OM or inputs of aged terrestrial OM along the estuarine gradient. In the Delaware Estuary, there was a larger difference in the age of LC PLFA between the Delaware River and ETM sites (approximately 1500 yr) than between the ETM and chl *a* max sites (100 yr). The increase in age between the river and ETM sites was more than would be expected based on estuarine sediment storage and transport alone (e.g., < 2 yr; Cook et al. 2007; Sommerfield and Wong 2011). This suggests that a source of "aged" terrestrial OM may enter the estuary between the river and ETM sites, possibly at the confluence with the Schuylkill River, the second largest source of freshwater to the estuary. Where LC FA were measured in sediments of other systems, the continental residence time for LC FA ranged from centennial (360–1200 BP; Mollenhauer and Eglinton 2007) to millennial timescales (5000–10,000 BP; Drenzek et al. 2007). The "younger" LC FA in the upper Delaware Estuary suggests that the FA either derived from recently produced vegetation or derived from the watershed with short continental residence-times. The "older" LC FA in the Delaware Bay may have spent more time in the lower watershed surrounding the Delaware Bay, such as in marsh sediments. Extensive fringing marshes may retain terrestrial OM, acting both as a source and sink for OM, prior to it entering the estuary (Couto et al. 2013; Hermes 2013). Differences in the age of LC FA along the Delaware estuary indicate multiple sources and/or processes influence terrigenous OM. Terrestrial OM may spend more time in the watershed surrounding the Schuylkill River or in

the lower watershed, such as in marshes fringing the Delaware Bay, than terrestrial OM in the upper, forested watershed.

Despite the wide range in radiocarbon ages of FA (modern to 1700 BP), none of the FA had ^{14}C ages similar to lipids previously measured in ultrafiltered dissolved organic matter (UDOM) in the Delaware Estuary (23,300 BP; Wang et al. 2006) or POC measured in the Delaware Estuary in October 2010 (940 BP; McIntosh 2013). Within standard reference material sediments, PAHs from the New York/New Jersey Waterway and urban dust were determined to have radiocarbon ages between 15,600 and 34,100 BP ($\Delta^{14}C$ of $-860‰$ to $-986‰$; Reddy et al. 2002). Like the New York/New Jersey waterway, the Delaware is influenced by several urban locations and PAH components associated with POM could be one of the contributing factors to the old age of lipids. In another highly urbanized aquatic system, fatty alcohols and aliphatic hydrocarbons were much greater in age than expected based on time of deposition in surface sediments of Lake Washington, Seattle, WA (Wakeham et al. 2004). Fatty alcohols in sediment deposited in 2000 were ~2000 BP in age ($\Delta^{14}C$ of $-457.6 \pm 2.0‰$), while aliphatic hydrocarbons in those same sediments had an age of ~11,200 BP ($\Delta^{14}C$ of $-964.9 \pm 0.8‰$) (Wakeham et al. 2004). Based on the ^{14}C ages for FA_{POM} observed in this study, other components, such as PAHs, *n*-alkanes, or *n*-alkanols likely contribute to the age of the lipids associated with POM and UDOM in the Delaware. Further exploration is needed to determine which components are contributing to the old ages of lipids associated with POM and UDOM in this and other study systems.

Overall, this study adds to the body of work on the complexity of OM in aquatic and marine environments by evaluating the composition and age distribution of FA along an estuarine salinity gradient. This is the first investigation to demonstrate a heterogeneous age distribution for FA_{POM} along the river-estuary continuum. The most abundant FA components along the Delaware Estuary were of aquatic and marine origin, with decreasing amounts of FA of terrestrial origin from the river to the Delaware Bay. Within the FA_{POM}, which are expected to reflect recently produced OM; there was a wide range in ^{14}C ages. The aged FA had sources that derived from the Delaware Estuary watershed, while the FA with modern ^{14}C ages were produced within Delaware Bay. Aged DIC was incorporated into microbial FA at the river site and modern CO_2 was incorporated into microbial FA at the chl *a* max site. Apparent aging of terrestrial OM along the estuary was due to older material entering along the estuary rather than physical or biological processes. Despite having one major riverine source, the stable carbon and radiocarbon isotopic distributions for FA_{POM} in the Delaware were complex, highlighting the many processes influencing OM composition including DIC sources, multiple inputs from the watershed along the salinity gradient, and biological and physical processes within the estuary.

References

Arar, E. J., and G. B. Collins. 1997. In vitro determination of chlorophyll a and pheophytin a in marine and freshwater algae by fluorsescence. method 445.0, Revision 1.2. National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH.

Bianchi, T. S., and M. A. Allison. 2009. Large-river delta-front estuaries as natural "recorders" of global environmental change. Proc. Natl. Acad. Sci USA. **106**: 8085–8092. doi:10.1073/pnas.0812878106

Biggs, R. B., J. H. Sharp, T. C. Church, and J. M. Tramontano. 1983. Optical properties, suspended sediments, and chemistry associated with the turbidity maxima of the Delaware Estuary. Can. J. Fish. Aquat. Sci. **40**: 172–179. doi:10.1139/f83-279

Canuel, E. A. 2001. Relations between river flow, primary production and fatty acid composition of particulate organic matter in San Francisco and Chesapeake Bays: A multivariate approach. Org. Geochem. **32**: 563–583. doi:10.1016/S0146-6380(00)00195-9

Canuel, E. A., and C. S. Martens. 1993. Seasonal variations in the sources and alteration of organic matter associated with recently-deposited sediments. Org. Geochem. **20**: 563–577. doi:10.1016/0146-6380(93)90024-6

Canuel, E. A., K. H. Freeman, and S. G. Wakeham. 1997. Isotopic compositions of lipid biomarker compounds in estuarine plants and surface sediments. Limnol. Oceanogr. **42**: 1570–1583. doi:10.4319/lo.1997.42.7.1570

Cifuentes, L. A., and G. G. Salata. 2001. Significance of carbon isotope discrimination between bulk carbon and extracted phospholipid fatty acids in selected terrestrial and marine environments. Org. Geochem. **32**: 613–621. doi:10.1016/S0146-6380(00)00198-4

Cifuentes, L. A., J. Sharp, and M. L. Fogel. 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. Limnol. Oceanogr. **33**: 1102–1115. doi:10.4319/lo.1988.33.5.1102

Collister, J. W., G. Rieley, B. Stern, G. Eglinton, and B. Fry. 1994. Compound-specific $\delta^{13}C$ analyses of leaf lipids from plants with differing carbon dioxide metabolisms. Org. Geochem. **21**: 619–627. doi:10.1016/0146-6380(94)90008-6

Cook, T. L., C. K. Sommerfield, and K. Wong. 2007. Observations of tidal and springtime sediment transport in the upper Delaware Estuary. Estuar. Coast. Shelf Sci. **72**: 235–246. doi:10.1016/j.ecss.2006.10.014

Couto, T., B. Duarte, I. Caçador, A. Baeta, and J. C. Marques. 2013. Salt marsh plants carbon storage in a temperate Atlantic estuary illustrated by a stable isotopic analysis based approach. Ecol. Ind. **32**: 305–311. doi:10.1016/j.ecolind.2013.04.004

Dalsgaard, J., M. St. John, G. Kattner, D. Muller-Navarra, and W. Hagen. 2003. Fatty acid trophic markers in the pelagic marine environment. Adv. Mar. Biol. **46**: 227–340. doi:10.1016/S0065-2881(03)46005-7

Drenzek, N. J., D. B. Montluçon, M. B. Yunker, R. W. Macdonald, and T. I. Eglinton. 2007. Constraints on the origin of sedimentary organic carbon in the Beaufort Sea from coupled molecular 13C and 14C measurements. Mar. Chem. **103**: 146–162. doi:10.1016/j.marchem.2006.06.017

Eglinton, T. I., L. I. Aluwihare, J. E. Bauer, E. R. M. Druffel, and A. P. McNichol. 1996. Gas chromatographic isolation of individual compounds from complex matrices for radiocarbon dating. Anal. Chem. **68**: 904–912. doi:10.1021/ac9508513

Feng, X., and others. 2013. ^{14}C and ^{13}C characteristics of higher plant biomarkers in Washington margin surface sediments. Geochim. Cosmochim. Acta. **105**: 14–30. doi:10.1016/j.gca.2012.11.034

Fogel, M. L., and L. A. Cifuentes. 1993. Isotope fractionation during primary production, p. 73–98. *In* M. H. Engel and S. A. Macko [eds.], Organic geochemistry. Plenum.

Fry, B., and E. B. Sherr. 1984. δ13C Measurements as indicators of carbon flow in marine and freshwater ecosystems. Contrib. Mar. Sci. **27**: 13–47. doi:10.1007/978-1-4612-3498-2_12

Harvey, H. R., and J. R. Johnston. 1995. Lipid composition and flux of sinking and size-fractionated particles in Chesapeake Bay. Org. Geochem. **23**: 751–764. doi:10.1016/0146-6380(95)00056-K

Hayes, J. M. 2001. Fractionation of carbon and hydrogen isotopes in biosynthetic processes. Rev. Mineral. Geochem. **43**: 225–277. doi:10.2138/gsrmg.43.1.225

Hedges, J. I., and J. Stern. 1984. Carbon and nitrogen determinations of carbonate-containing solids. Limnol. Oceanogr. **29**: 657–663. doi:10.4319/lo.1984.29.3.0657

Hermes, A. L. 2013. Spatial and seasonal particulate organic carbon cycling within the delaware estuary, assessed using biomarker and stable carbon isotopic approaches. M.S. thesis. Rutgers, The State University of New Jersey.

Hua, Q, M. Barbetti, and Rakowski, A. Z. 2013. Atmospheric radiocarbon for the period 1950-2010. Radiocarbon **55**: 2059–2072. doi:10.2458/azu_js_rc.v55i2.16177

Hwang, J., E. R. M. Druffel, and J. E. Bauer. 2006. Incorporation of aged dissolved organic carbon (DOC) by oceanic particulate organic carbon (POC): An experimental approach using natural carbon isotopes. Mar. Chem. **98**: 315–322. doi:10.1016/j.marchem.2005.10.008

Ingalls, A. E., S. R. Shah, R. L. Hansman, L. I. Aluwihare, G. M. Santos, E. R. M. Druffel, and A. Pearson. 2006. Quantifying archaeal community autotrophy in the mesopelagic ocean using natural radiocarbon. Proc. Natl. Acad. Sci USA. **103**: 6442–6447. doi:10.1073/pnas.0510157103

Ketchum, B. H. 1952. The distribution of salinity in the estuary of the Delaware River. Woods Hole Oceanogr. Inst. Rep.52–103. doi:10.1575/1912/5339

Mannino, A., and H. R. Harvey. 1999. Lipid composition in particulate and dissolved organic matter in the Delaware Estuary: Sources and diagenetic patterns. Geochim. Cosmochim. Acta. **63**: 2219–2235. doi:10.1016/S0016-7037(99)00128-3

Mansue, L. J., and A. B. Commings. 1974. Sediment transport by streams draining into the Delaware Estuary. Geologic Survey Water-Supply Paper. 1–18.

McCallister, S. L., J. E. Bauer, and E. A. Canuel. 2006. Bioreactivity of estuarine dissolved organic matter: A combined geochemical and microbiological approach. Limnol. Oceanogr. **51**: 94–100. doi:10.4319/lo.2006.51.1.0094

McCallister, S. L., J. E. Bauer, J. Kelly, and H. W. Ducklow. 2005. Effects of sunlight on decomposition of estuarine dissolved organic C, N and P and bacterial metabolism. Aquat. Microb. Ecol. **40**: 25–35. doi:10.3354/ame040025

McIntosh, H. A. 2013. Composition, sources, and age of dissolved and particulate organic matter in the Delaware River and estuary. M.S. thesis. College of William and Mary, School of Marine Science.

McNichol, A. P., A. R. Gagnon, G. A. Jones, and E. A. Osborne. 1992. Illumination of a black box: Analysis of gas composition during graphite target preparation. Radiocarbon **34**: 321–329. doi:10.2458/azu_js_rc.34.1471

Meyers, P. A. 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Org. Geochem. **27**: 213–250. doi:10.1016/S0146-6380(97)00049-1

Mollenhauer, G., and T. I. Eglinton. 2007. Diagenetic and sedimentological controls on the composition of organic matter preserved in California Borderland Basin sediments. Limnol. Oceanogr. **52**: 558–578. doi:10.4319/lo.2007.52.2.0558

Najjar, R. G., M. A. M. Friedrichs, and W.-J. Cai. 2012. Report of the U.S. East Coast Carbon Cycle Synthesis Workshop, January 19–20, 2012, 34 p. *In* Ocean Carbon and Biogeochemistry Program and North American Carbon Program.

Ohkouchi, N., T. I. Eglinton, and J. M. Hayes. 2003. Radiocarbon dating of individual fatty acids as a tool for refining Antarctic margin sediment chronologies. Radiocarbon **45**: 17–24. doi:10.2458/azu_js_rc.45.4155

Palomo, L., and E. A. Canuel. 2010. Sources of fatty acids in sediments of the York River Estuary: Relationships with physical and biological processes. Estuaries Coast. **33**: 585–599. doi:10.1007/s12237-010-9268-3

Parkes, R. J., and J. Taylor. 1983. The relationship between fatty acid distributions and bacterial respiratory types in contemporary marine sediments. Estuar. Coast. Shelf Sci. **16**: 173–189. doi:10.1016/0272-7714(83)90139-7

Pearson, A. and T. I. Eglinton. 2000. The origins of *n*-alkanes in Santa Monica Basin surface sediment: A model based on compound-specific $\Delta^{14}C$ and ^{13}C data. Org. Geochem. **31**: 1103–1116. doi:10.1016/S0146-6380(00)00121-2

Pearson, A., A. P. McNichol, B. Benitez-Nelson, J. M. Hayes, and T. I. Eglinton. 2001. Origins of lipid biomarkers in Santa Monica Basin surface sediment: A case study using compound-specific $\Delta^{14}C$ analysis. Geochim. Cosmochim. Acta. **65**: 3123–3137. doi:10.1016/S0016-7037(01)00657-3

Pennock, J. R. 1985. Chlorophyll distributions in the delaware estuary: Regulation by light-limitation. Estuar. Coast. Shelf Sci. **21**: 711–725. doi:10.1016/0272-7714(85)90068-X

Pennock, J. R., and J. Sharp. 1986. Phytoplankton production in the Delaware Estuary: Temporal and spatial variability. Mar. Ecol. Prog. Ser. **34**: 143–155. doi:10.3354/meps034143

Poerschmann, J., and R. Carlson. 2006. New fractionation scheme for lipid classes based on "in-cell fractionation" using sequential pressurized liquid extraction. J. Chromatogr. A. **1127**: 18–25. doi:10.1016/j.chroma.2006.07.063

Raymond, P. A., and J. E. Bauer. 2001. Use of ^{14}C and ^{13}C natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: A review and synthesis. Org. Geochem. **32**: 469–485. doi:10.1016/S0146-6380(00)00190-X

Raymond, P. A., J. E. Bauer, N. F. Caraco, J. J. Cole, B. Longworth, and S. T. Petsch. 2004. Controls on the variability of organic matter and dissolved inorganic carbon ages in northeast US rivers. Mar. Chem. **92**: 353–366. doi:10.1016/j.marchem.2004.06.036

Raymond, P. A., and N. Oh. 2007. An empirical study of climatic controls on riverine C export from three major U.S. watersheds. Global Biogeochem. Cycles. 21: GB2022. doi:10.1029/2006GB002783

Reddy, C. M., and others. 2002. Radiocarbon as a tool to apportion the sources of polycyclic aromatic hydrocarbons and black carbon in environmental samples. Environ. Sci. Technol. **36**: 1774–1782. doi:10.1021/es011343f

Shah, S. R., A. R. Gagnon, M. L. Roberts, A. P. McNichol, M. C. Lardie Gaylord, and E. Klein. In press. Ultra-small graphitization reactors for ultra-microscale radiocarbon analysis at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility. Radiocarbon.

Shah, S. R., and A. Pearson. 2007. Ultra-Microscale (5-25 μg C) analysis of individual lipids by ^{14}C AMS: Assessment and correction for sample processing blanks. Radiocarbon. **49**: 69–82. doi:10.2458/azu_js_rc.49.2900

Sharp, J., L. A. Cifuentes, R. B. Coffin, J. R. Pennock, and K. Wong. 1986. The influence of river variability on the circulation, chemistry, and microbiology of the Delaware Estuary. Estuaries Coast. **9**: 261–269. doi:10.2307/1352098

Sharp. J., J. R. Pennock, T. M. Church, J. M. Tramontano, and L. A. Cifuentes. 1984. The estuarine interaction of nutrients, organics, and metals: A case study in the Delaware Estuary. p. 241–258. *In* V. Kennedy [ed.], The estuary as a filter. Academic Press.

Sharp, J., K. Yoshiyama, A. Parker, M. Schwartz, S. Curless, A. Beauregard, J. Ossolinski, and A. Davis. 2009. A biogeochemical view of estuarine eutrophication: Seasonal and spatial trends and correlations in the delaware estuary. Estuaries Coast. **32**: 1023–1043. doi:10.1007/s12237-009-9210-8

Shoaf, W. T., and B. W. Lium. 1976. Improved extraction of chlorophyll a and b from algae using dimethyl sulfoxide. Limnol. Oceanogr. **21**: 926–928. doi:10.4319/lo.1976.21.6.0926

Sommerfield, C., and K. Wong. 2011. Mechanisms of sediment flux and turbidity maintenance in the Delaware Estuary. J. Geophys. Res. **116**: C01005 1–16. doi:10.1029/2010JC006462

Stuiver, M., and H. A. Polach. 1977. Discussion: Reporting of ^{14}C data. Radiocarbon **19**: 355–363. doi:10.2458/azu_js_rc.19.493

USGS. 2012. US Geological Survey Delaware River gauge data. Discharge data for the USGS 01463500 gauging station at Trenton, NJ. doi:http://waterdata.usgs.gov/usa/nwis/uv?01463500

von Reden, K. F., A. P. McNichol, A. Pearson, and R. J. Schneider. 1998. ^{14}C AMS measurements of $<100\,\mu$g samples with a high-current system. Radiocarbon **40**: 247–253. doi:10.2458/azu_js_rc.40.2010

Volkman, J. K., S. W. Jeffrey, P. D. Nichols, G. I. Rogers, and C. D. Garland. 1989. Fatty acid and lipid composition of 10 species of microalgae used in mariculture. J. Exp. Mar. Biol. Ecol. **128**: 219–240. doi:10.1016/0022-0981(89)90029-4

Wakeham, S. G., J. Forrest, C. A. Masiello, Y. Gélinas, C. R. Alexander, and P. R. Leavitt. 2004. Hydrocarbons in Lake Washington Sediments. A 25-Year Retrospective in an Urban Lake. Environ. Sci. Technol. **38**: 431–439. doi:10.1021/es0343149

Wakeham, S. G., A. P. McNichol, J. E. Kostka, and T. K. Pease. 2006. Natural-abundance radiocarbon as a tracer of assimilation of petroleum carbon by bacteria in salt marsh sediments. Geochim. Cosmochim. Acta. **70**: 1761–1771. doi:10.1016/j.gca.2005.12.020

Wang, X., J. Callahan, and R. F. Chen. 2006. Variability in radiocarbon ages of biochemical compound classes of high molecular weight dissolved organic matter in estuaries. Estuar. Coast. Shelf Sci. **68**: 188–194. doi:10.1016/j.ecss.2006.01.018

Wang, X., E. R. M. Druffel, S. Griffin, C. Lee, and M. Kashgarian. 1998. Radiocarbon studies of organic compound classes in plankton and sediment of the northeastern Pacific Ocean. Geochim. Cosmochim. Acta. **62**: 1365–1378. doi:10.1016/S0016-7037(98)00074-X

White, D. C., W. M. Davis, J. S. Nickels, J. D. King, and R. J. Bobbie. 1979. Determination of the sedimentary microbial biomass by extractible lipid phosphate. Oecologia **40**: 51–62. doi:10.2307/4215834.

Zencak, Z., C. M. Reddy, E. L. Teuten, L. Xu, A. P. McNichol, K. E. Gustafson, and Ö Gustafsson. 2007. Evaluation of gas chromatographic isotope fractionation and process contamination by carbon in compound-specific radiocarbon analysis. Anal. Chem. **79**: 2042–2049. doi:10.1021/ac061821a

Zink, K., K. Mangelsdorf, L. Granina, and B. Horsfield. 2008. Estimation of bacterial biomass in subsurface sediments by quantifying intact membrane phospholipids. Anal. Bioanal. Chem. **390**: 885–896. doi:10.1007/s00216-007-1732-y

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