1 Particulate organic matter has higher concentrations and a higher proportion of terrestrial
2 sources in bottom relative to surface waters in the Delaware Estuary, U.S.A.

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16 **Graphical Abstract**

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Abstract

The pathway and fate of land-derived suspended particulate organic matter (POM) as it passes through estuaries remains a poorly constrained component of coastal carbon dynamics. The $\delta^{13}\text{C}$ of bulk POC (particulate organic carbon; $\delta^{13}\text{C}$ -POC) and *n*-alkane biomarkers were used to assess the proportion of algal- and land- (vascular plant) derived POM through the Delaware Estuary, on five cruises in 2010-2011. We found that POC was highly correlated with suspended sediment concentrations (SSC). Higher SSC was present in bottom waters, causing bottom waters to have consistently higher concentrations of POC than surface waters, with the bottom waters of the estuarine turbidity maximum (ETM) exhibiting maximum POC concentrations for all seasons and flow regimes. Algal-derived POM seasonally affected the $\delta^{13}\text{C}$ -POC and *n*-alkane geochemical signatures of surface waters, whereas bottom waters were dominated by vascular plant-derived POM. $\delta^{13}\text{C}$ -POC results suggested a gradual loss in vascular plant-derived POM between the riverine and marine endmember stations. In contrast, *n*-alkane concentrations peaked in bottom waters of the ETM at 2-5 times surface water concentrations. Indices of the relative proportions of *n*-alkanes and *n*-alkanes as a proportion of total POC had their levels decrease considerably downstream of the ETM. These biomarker analyses suggest enhanced loss of land-derived material across the ETM and that the ETM acts as a geochemical filter for vascular plant-derived POM in a classic well mixed estuary.

1 Introduction

“The destination of material eroded is eventually the great world ocean, although there are pauses in the journey” (Judson, 1968). Estuaries are the link between land and sea carbon cycles. Land-derived sediment and particulate organic carbon (POC) is delivered to estuaries, wherein physical, biological, and chemical processes regulate the quantity and quality of material reaching the marine environment such that only half of the land-derived organic carbon delivered to estuaries escapes to the coastal ocean (Bauer et al., 2013; Bianchi, 2011; Ludwig et al., 1996; Meybeck, 1982; Schlesinger and Melack, 1981; Schlünz and Schneider, 2000). Despite much work examining organic carbon sources and loss processes in estuaries (Abril et al., 2002; Canuel and Zimmerman, 2006; Cifuentes et al., 1988; Etcheber et al., 2007; Mannino and Harvey, 2000), there is still significant uncertainty in our understanding of estuaries role in processing land-derived organic carbon en route to the ocean (e.g. Bauer et al., 2013; Benner, 2004; Blair and Aller, 2012). With estuaries having been found to be net heterotrophic, this suggests that substantial land-derived organic carbon may be being respired to CO₂ (Abril et al., 2002; Bauer et al., 2013; Cai, 2011; Frankignoulle et al., 1998). An important component of understanding what drives the net heterotrophy of estuaries is determining if land-derived POC is lost or transported through these systems.

Estuarine POC is intricately linked to sediment dynamics (e.g. Bianchi and Bauer, 2012; Blair and Aller, 2012; Blair et al., 2004). The sources of POC in estuaries vary spatially and seasonally. Physical controls, such as seasonal and event-driven changes in discharge and tidal spring/neap variability influence sediment residence time, transport, resuspension, and concentrations (e.g. Blair and Aller, 2012; Frankignoulle et al., 1998; Sommerfield and Wong, 2011). Upper estuaries are typically zones of organic matter (OM) loss and transformation through biotic processes of microbial degradation and heterotrophic respiration (see review in Bauer et al., 2013). Downstream, the estuarine turbidity maximum (ETM) is a zone of flocculation and resuspension, actively mixing, recycling, and remineralizing both algal- and land-derived organic carbon (Abril et al., 2002; del Giorgio and Pace, 2008; McCallister et al., 2006). Throughout estuaries, these processes combine with *in situ* production by phytoplankton seasonally varying autochthonous POM (Canuel and Zimmerman, 2006; Cifuentes et al., 1988; Mannino and Harvey, 1999).

A number of tracers have been employed to ascertain the source and the change in proportion of land versus aquatic organic matter along an estuary. The stable carbon isotopic

composition of POM ($\delta^{13}\text{C}$ -POC) is a useful tool for distinguishing algal- from land-derived sources of OM in coastal environments, because algal and vascular plants have distinct isotopic signatures (Jaffé et al., 2001; Kennicutt II et al., 1987; Raymond and Bauer, 2000). Combining biomarkers with bulk $\delta^{13}\text{C}$ -POC analyses has improved the ability to differentiate sources in these complex environments (e.g. Jaffé et al., 2001; Sikes et al., 2009). Whereas $\delta^{13}\text{C}$ -POC has shown a gradual dilution or disappearance of land-derived OM along-estuary (e.g. Benner, 2004; Cifuentes and Eldridge, 1998; Raymond and Bauer, 2000), biomarkers have revealed the persistence of land-derived POM throughout estuaries (e.g. Bianchi and Bauer, 2012; Bianchi, 2011; Goñi et al., 1998; Otero et al., 2000; Sikes et al., 2009). Resistant to degradation, *n*-alkanes are straight-chain hydrocarbon lipid biomarkers, synthesized by all plants. *N*-alkane carbon chain length distributions differ between marine and vascular plant-derived sources, with vascular plants having longer chain lengths of 25-35 carbon atoms and an odd-over-even chain length preference, whereas algae have shorter chain lengths of 14-24 carbon atoms (Eglinton and Hamilton, 1967). Because *n*-alkanes have multiple sources with differing characteristics they provide a direct, and quantitative tracer of both vascular plant- and algal-derived POM in environments with multiple sources such as estuarine and coastal marine environments (e.g. Medeiros et al., 2012; Sikes et al., 2009).

Studies quantifying particulate organic carbon levels in estuaries have demonstrated the loss of organic carbon within estuaries but have largely been conducted in surface waters, with the underlying assumption that sources are similar throughout the water column in well-mixed estuaries (Abril et al., 2002). Likewise source determinations of studies have also concentrated on surface waters while demonstrating the loss of terrestrial signatures down estuary (e.g. Mannino and Harvey, 1999; McIntosh, 2015). However, it is well established that there are higher concentrations of suspended sediments in bottom water (e.g. Sommerfield and Wong, 2011). Nonetheless, there are few studies examining the POC present in bottom waters associated with these particles. What is needed is information about the make-up of that POC in the lower water column and what component of that organic matter is lost or transformed as particles travel through an estuary. Here we put these pieces together and examine the organic carbon content and character of both surface and bottom water along the Delaware estuary using bulk $\delta^{13}\text{C}$ -POC and *n*-alkane biomarkers, along an estuarine transect. The aim is to “map” particulate organic carbon in surface and bottom waters, as well as its sources, in order to determine when and where land-derived POM is “lost” en route to sea.

2 Study site: The Delaware Estuary

The Delaware Estuary Delaware Bay is a an archetypal, funnel-shaped, coastal plain estuary, stretching from the mouth of Delaware Bay to approximately 215 km up-river at the head-of-tides near Trenton, NJ (Figure 1). The Delaware River is the primary source of freshwater to the Delaware Estuary, delivering over 50 % of discharge (annual average, 330 m³/s), with smaller contributions from the Schuylkill (12 %; 77 m³/s) and Christina (3 %; 19 m³/s) rivers, which, collectively, account for over 65 % of the freshwater delivered to the estuary (on average, 650 m³/s Cook et al., 2007; Sommerfield and Wong, 2011). These rivers also deliver over 70 % of sediments to the Delaware Estuary (approximately 50, 19, and 7.5 %, respectively; (Mansue and Commings, 1974). Both river discharge and sediment delivery vary seasonally, with increased flow and sediment during the spring freshet period in March and April (e.g. Cook et al., 2007; Sharp et al., 1986). The Delaware Estuary is generally well-mixed, but stratification can occur on seasonal and tidal time scales (Sharp et al., 1986). The tidal prism is substantially greater than the mean annual total river discharge (1.5×10^5 m³/s and 650 m³/s, respectively (Garvine et al., 1992).

The second largest estuary on the U.S. Atlantic coast, the Delaware has been the subject of extensive shipboard surveys since the late 1970s, providing a physical, chemical, and biological characterization of the system (Cifuentes et al., 1988; Coffin and Sharp, 1987; Pennock and Sharp, 1986; Sharp et al., 1982; Sharp et al., 2009). Additionally, previous geochemical studies examined the quantity and source of organic carbon (OC) in surface waters through the estuary, both spatially and seasonally (e.g. Harvey and Mannino, 2001; Mannino and Harvey, 1999; McIntosh, 2015). Sedimentological studies have described the transport and trapping of sediment above and within the ETM and portrayed it as a trap for large quantities of sediment (e.g. Cook et al., 2007; Sommerfield and Wong, 2011). These previous studies provide context for this work, which examines the link between biogeochemical and sedimentological processes in this system.

Mixing and transport of POM in the Delaware Estuary is tied to estuarine sediment dynamics. Sediments delivered to the upper estuary by the Delaware River have a down-estuary pathway of intermittent burial, storage, and remobilization (Cook et al., 2007). Sediment concentrations typically range from 10 – 100 mg L⁻¹, peaking in a broad, and sometimes double ETM, approximately 80 – 120 km landward of the bay mouth (Figure 1; (Biggs et al., 1983). The

Delaware Estuary has an immense capability to trap sediment within the ETM, which can hold as much as 1-2 years of the river-delivered sediment load (Cook et al., 2007; Sommerfield and Wong, 2011). Much of this sediment is derived from intra-estuarine sources, previously deposited and subsequently remobilized from both the upper and lower estuary (Sommerfield et al., 2007). Thus, the ETM receives particulates with mixed sources and histories (e.g. Cifuentes et al., 1988; Mannino and Harvey, 1999). Sediment loads in Delaware Bay largely inhibit phytoplankton productivity in Delaware Bay except in spring when conditions support the development of an annual spring bloom (Pennock and Sharp, 1986; Sharp et al., 1986).

The pattern of POC and SSC concentration in the Delaware Estuary is comparable to similar estuaries worldwide; the is loss of particulates across the ETM, and higher concentrations in bottom water (Abril et al., 2002; Etcheber et al., 2007). Previous assessment of POM distributions and sources in the in Delaware Estuary have shown that terrestrial-derived POM dominates surface waters in the upper Delaware Estuary, and decreases substantially down estuary into Delaware Bay in favor of phytoplankton dominated input during spring blooms (e.g. Bianchi and Bauer, 2012; Cifuentes, 1991; Cifuentes et al., 1988; Mannino and Harvey, 1999; Mannino and Harvey, 2000; McIntosh, 2015). Although the sources of POM have been studied in surface waters of this system, our goal was to fully characterize POM by measuring surface and bottom waters both spatially and seasonally.

3 Methods

3.1 Sample collection

Suspended particulate samples were collected during five cruises aboard the RV *Hugh Sharp* through the Delaware River and Estuary. Cruises replicated an axial transect along the main channel of the estuary from a marine endmember station around 14 km from the mouth of Delaware Bay in the Atlantic Ocean (Station 1; Figure 1) to a riverine endmember station at Trenton, New Jersey (Station 22; Figure 1). The cruises were conducted on 10-11 March 2010, 3-4 June 2010, 12-13 September 2010, 13-14 December 2010, and 21-22 March 2011. A conductivity, temperature, and depth (CTD) sonde was cast at each station, and had additional sensors for optical backscatter (OBS; a proxy for sediment concentration), fluorescence (a proxy for phytoplankton biomass), and oxygen (a proxy for active productivity). These supporting measurements were used for real-time assessment of the location and magnitude of the chlorophyll maxima and ETM (see Figure S1), which informed our geochemical sampling

stations and provided context for our geochemical interpretations.

Water column samples were collected with an *in situ* pump at approximately 1 m below the surface and 1 m above the sediment-water interface (hereafter, “surface” and “bottom” water, respectively). Surface and bottom water samples for suspended solid content (SSC; 400-500 mL each) and particulate organic carbon properties (POC concentration and $\delta^{13}\text{C}$ -POC; ~ 1-3 L each) were collected at alternating stations (~ 11 of the 22 stations). SSC were filtered shipboard through pre-weighed Whatman Nuclepore Polycarbonate 1.0 μm filters. POC and biomarker samples were filtered onto pre-combusted (500 °C for 4-5 hours) 47 mm Whatman 0.7 μm GF/Fs, placed in pre-combusted aluminum foil and frozen at -20 °C until analysis. Large volumes of surface and bottom water (6-60 L) were collected for *n*-alkane biomarker analysis at geographically fixed marine and riverine endmembers (Stations 1 and 22, respectively) and 2 – 4 additional stations of geochemical interest, as determined by the CTD casts to define the ETM and chlorophyll maximum, which varied geographically between cruises. Three sites were analyzed for the September 2010 ETM, and two sites were analyzed for the March 2011 ETM to constrain the dual-ETM observed.

3.2 Bulk particulate analyses

Suspended sediment concentrations were provided by Dr. Chris Sommerfield (University of Delaware). Samples were oven dried for ~24 hours and re-weighed, and results were reported in mg SSC L⁻¹. POC and $\delta^{13}\text{C}$ -POC filters were freeze-dried and weighed, and inorganic carbon was removed by fuming with concentrated HCl (≥ 24 hours). Filters were homogenized using a mortar and pestle, and a subsample was loaded into tin capsules for analysis on a continuous flow isotope ratio mass spectrometer (GVI Isoprime coupled to a Eurovector elemental analyzer) at Rutgers University.

Particulate organic carbon concentrations (mg/L) were calculated based on acetanilide standard curves generated for each sample run using a CN Standard (CAS No. 103-84-4). Blank filters and blank capsules were analyzed in tandem with the Delaware Estuary samples and subtracted from sample measurements as background. Analytical reproducibility for a given sample was determined by running replicates of filter subsamples on each analysis day, as well as between analysis days, and was $\pm 7.94\%$ for POC (average coefficient of variation).

The stable carbon isotopic composition of POC, $\delta^{13}\text{C}$, was reported in delta-notation (δ ; in per-mil, ‰), with respect to a standard reference material using the following equation:

$$\delta^{13}\text{C}_{\text{sample}} = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}] \times 1000$$

where R is the ratio of the heavy to the light stable isotope (^{13}C and ^{12}C , respectively), *sample* refers to the ratio of the sample, and *standard* refers to the isotopic ratio of a reference gas. Samples were related to Vienna Pee-Dee Belemnite (V-PDB) using NIST Standard 8539 NBS22. Sample reproducibility for $\delta^{13}\text{C}$ -POC was $\pm 1.44\%$ (average coefficient of variation). Instrument variability (average standard deviation) was assessed using a laboratory reference standard, Taughannock Light, and was 0.06% . $\delta^{13}\text{C}$ -POC provides a relative measure of algal- versus vascular plant-derived OM sources. Values of $\sim -27\%$ are typical of a C_3 terrestrial endmember, and of $\sim -19\%$ are typical for a marine (algal) endmember (e.g. Bianchi, 2011; Cifuentes et al.).

3.3 *N*-alkane lipid biomarker analysis

Filters for *n*-alkane biomarker analysis were freeze-dried, and then solvent-extracted with hexane using accelerated solvent extraction (ASE 200, Dionex) at $50\text{ }^\circ\text{C}$ and 800-1000 psi for three static cycles (Poerschmann and Carlson, 2006; Sikes and Volkman, 1993). After extraction, total lipid extracts were saponified to separate neutral compounds (including *n*-alkanes) from fatty acids, following the methods of Sikes and Volkman (1993). Briefly, extracts were dried, re-dissolved in 5% KOH in methanol-water (80:20 v/v), and incubated at $80\text{ }^\circ\text{C}$ for two hours. Reactions were quenched with Milli-Q water, and the neutral fraction was partitioned into hexane-dichloromethane (4:1 v/v) with 3 washes and retained for *n*-alkane biomarker analysis.

N-alkanes were identified and quantified on a Shimadzu GC-2010 gas chromatograph coupled to a Shimadzu GCMS-QP2010 mass spectrometer using helium carrier gas at Rutgers University. Samples were injected in splitless mode onto a Shimadzu SHR5XLB column ($30\text{ m} \times 0.25\text{ mm i.d.}$). Samples were run with a temperature program of $45\text{ }^\circ\text{C}$ held isothermal for 0.5 min at injection, then ramped at $30\text{ }^\circ\text{C/min}$ to $140\text{ }^\circ\text{C}$ and then $3\text{ }^\circ\text{C/min}$ to $320\text{ }^\circ\text{C}$ and held isothermal for 10 min. Homologous series of *n*-alkanes ($\text{C}_{16} - \text{C}_{38}$) were identified based on relative retention times and mass fragments compared to an external aliphatic hydrocarbon standard (DRH007S PAK, AccuStandard). Biomarkers were quantified by peak area using an internal nonadecanone standard and external aliphatic hydrocarbon standard curves.

N-alkane chain lengths have been widely used to assess the relative abundances of algal- and vascular plant-derived sources. A number of indices utilize the chain length differences between sources to estimate source-relative proportions. Since vascular plants synthesize longer *n*-alkane chain lengths than algae, the average chain length (ACL) indicates which is more predominant overall. ACL is calculated as: $\text{ACL} = (\sum[\text{Ci}] \times i) / (\sum[\text{Ci}])$, where i is the carbon

numbers 16–34. Vascular plants also synthesize *n*-alkanes with an odd- over even-chain length preference, which is summarized by the carbon preference index (CPI). The CPI is calculated as: $CPI = (\sum \text{odd chain-length } n\text{-alkanes from } C_{17} - C_{35}) / (\sum \text{even chain chain-length } n\text{-alkanes from } C_{16} - C_{34})$. A CPI greater than 4 is considered indicative of vascular plant-derived sources. Another proxy ratio, P_{aq} , distinguishes between terrestrial and aquatic vascular plants in lacustrine environments (Ficken et al., 2000), and was modified to suit coastal environments as P_{mar-aq} (Sikes et al., 2009). P_{mar-aq} is defined as: $P_{mar-aq} = [C_{23} + C_{25}] / [C_{23} + C_{25} + C_{29} + C_{31}]$ (Ficken et al., 2000; Sikes et al., 2009). Low values (0.01–0.25) indicate terrestrial inputs, mid values (~0.4–0.6), emergent aquatic and marsh inputs, and high values (> 0.6) indicate the dominant inputs of submerged aquatic plants and marine phytoplankton and macrophytes.

The relative range of each of these proxies calculated for the Delaware POM proved informative, but the absolute ranges were limited (see Figure S5, Table S1, Table S2, and results). This has been previously observed in coastal settings (Sikes et al., 2009). These indices also only provide a measure of relative sources among the alkanes present and do not relate back to bulk POC. Consequently, we chose to look at the simple sums of long-chain (LC; C_{24} – C_{33}) and short-chain (SC; C_{16} – C_{23}) *n*-alkanes to broadly differentiate between vascular plant-derived “terrestrial” OM and algal OM sources within the entire POC pool. *N*-alkane chain lengths for the SC proxy were selected as typical for algal-derived OM (e.g. Blumer et al., 1971; Meyers and Ishiwatari, 1993). *N*-alkane chain lengths for the LC proxy are typical for terrestrial derived vascular plant-derived OM (e.g. Eglinton and Hamilton, 1967). Although mid-length *n*-alkanes are found in both algal and vascular plant-derived OM including marsh plants (Bianchi, 2011; Chikaraishi and Naraoka, 2003), the SC and LC used here have been shown to broadly illustrate the relative predominance of marine and terrestrial sources (Mead et al., 2005; Meyers and Ishiwatari, 1993). LC and SC results were calculated relative to water volume and were additionally normalized to POC, and SSC (Figure S6).

4 Results

4.1 Cruise characteristics

The five cruises sampled a wide range in discharge, capturing typical seasonal flow characteristics for the estuary. The average annual pattern in flow was obtained by calculating the interquartile range (IQR) of daily averaged Delaware plus Schuylkill River discharges (D+S; 1913–2011). The average discharge for the seven days prior to the first day of each cruise was compared to the D+S IQR, and showed that the March 2010 cruise sampled the beginning of

spring freshet, June and September 2010 captured low summer discharge, December 2010 had elevated flow following a winter storm event, and March 2011 sampled during the spring freshet (Figure 2). Saltwater intrusion in Delaware Bay varied inversely with Delaware River discharge ($R^2 = 0.91$), and ranged between 65-125 km up-estuary (Figure S1A – S1E). The five cruises also sampled spring and neap tide conditions as follows: March, June, December 2010 neap tides; September 2010 and March 2011 spring tides. Stratification in Delaware Bay was more related to the spring-neap tidal cycle than discharge, with neap tides being more stratified (Figure S1A – S1E).

Along-estuary *in situ* OBS profiles and SSC measurements mapped the distribution and concentration of suspended particulates for each cruise, and identified the location of the ETM. The ETM sat between 86 – 125 km from the mouth of Delaware Bay and its location varied in response to changes in D+S discharge (Figure S1F – S1J and Figure S4A – S4E). Cruises that sampled during spring tides had significantly higher ETM SSC concentrations (September 2010 and March 2011; maximum SSC 475 mg/L and 528 mg/L, respectively; Figure S4) than cruises that sampled during neap tides (March 2010, June 2010, December 2010; Figure S4). Spring tides also had dual ETM. Overall, SSC was on average ~ 3 times higher in bottom water than surface water (82 ± 121 mg/L and 28 ± 44 mg/L, respectively), but within the ETM, SSC was as much as ~ 7-10 times higher in bottom water than surface water (e.g. June 2010, September 2010, and March 2011, Figure S4A – S4E, see also Table S1).

Seasonal primary production was captured via *in situ* fluorescence measurements, indicating the presence of phytoplankton biomass (Figure S1K – S1O). Fluorescence was observed during each cruise except December 2010. Both March cruises captured a spring bloom in Delaware Bay, typical for this system. June 2010 had high fluorescence in Delaware Bay, as well as in the tidal freshwater region of the estuary, and September 2010 had fluorescence near the mouth of the estuary.

4.2 Bulk POC properties

Particulate organic carbon (mg/l) was positively linearly correlated with SSC across all cruises in both surface and bottom water ($R^2 = 0.91$ and $R^2 = 0.80$, respectively; Figure 3) with the result being that SSC and POC had similar along-estuary distributions (compare Figure S4A – S4E with Figure S4F – S4J). Organic carbon as a percentage of SSC (%OC; organic carbon content) was generally low (~ 10%), except in Delaware Bay and near the mouth of the estuary, where %OC increased to as much as 82% coincident with fluorescence maxima (Figure 3, purple

symbols, Figure S2, Figure S4K – S4O, Table S1). In the ETM, %OC was always less than 10% (Figure S4K – S4O, Table S1). Overall, %OC was marginally higher in surface waters relative to the corresponding bottom water. Consequently, surface and bottom waters had similar values along the estuary (Figure 3, Figure S4K – S4O, Table S1).

The concentration of suspended POC in bottom waters was on average twice as much as surface waters (3.28 ± 3.34 mg/l versus 1.57 ± 1.65 mg/l; see also Table S1), indicating that bottom waters held the majority of the total suspended POC pool in the estuary. The highest POC concentrations were always found in bottom waters of the ETM, owing to the high concentration of a large number of low %OC particulates. The lowest POC concentrations were typically found at the marine endmember (Figure 4, Figure S4, Table S1). Similar to SSC results, the concentration of POC in the ETM was highest during spring tides (September 2010 and March 2011; Figure 4 and Figure S4), but was also elevated during a neap tidal phase in December 2010 following a storm event (Figure 2). On average, concentrations fell 5-9 fold for SSC and 2-4 fold for POC between the ETM and Delaware Bay (Figure S4A – S4E, Figure 4A – 4E, Table S1).

The $\delta^{13}\text{C}$ -POC was used as a measure of the average source of POM along estuary. The $\delta^{13}\text{C}$ -POC values at the riverine end member (Station 22) were consistently in the range for C3 terrestrial plant material (~ -26 ‰), and the marine endmember was consistently more enriched, with values typical of marine phytoplankton (~ -22 ‰; Figure 4F – 4J, Table S1). For all cruises the $\delta^{13}\text{C}$ -POC in the ETM was between riverine and marine endmembers (~ -24 ‰). Generally, $\delta^{13}\text{C}$ -POC showed a gradual change from riverine to marine endmember values mimicking a conservative mixing curve, especially in September and December 2010 (Figure 4H – 4I). Where phytoplankton biomass was observed from *in situ* florescence (Figure S1), $\delta^{13}\text{C}$ -POC deviated noticeably from conservative mixing between endmembers and coincided with maximum *in situ* florescence (compare Figure S1K – S1O and Figure 4F – 4J). In both March cruises and the June and September 2010 cruise, $\delta^{13}\text{C}$ -POC was enriched to -16.6 to -22 ‰ in Delaware Bay, values typical for the estuary and nearby coastal regions (Bauer et al., 2001; Cifuentes et al., 1988; Pennock and Sharp, 1986). Corresponding with fluorescence upstream in the tidal freshwater river in June 2010 was the most depleted $\delta^{13}\text{C}$ -POC observed anywhere (~ -30 ‰; Figure 4G, Figure S1L), which has been recorded in a similar location previously, and can be attributed to freshwater algal production preferentially using CO_2 versus HCO_3^- as a carbon source (Fogel et al., 1988).

4.3 *N*-alkane biomarkers

$\delta^{13}\text{C}$ -POC records the average source of OM, whereas *n*-alkane biomarkers trace the relative abundances of algal- vs. vascular plant-derived OM. *N*-alkane abundances were used to calculate several source indices, the average chain length (ACL), the carbon preference index (CPI), and the $P_{\text{mar-aq}}$. The overall range in these parameters was limited as is typical in coastal environments (e.g. Sikes et al., 2009), but all indices showed a decrease in the proportion of terrestrial-derived OM between riverine and marine endmembers (Figure S5, Table S2). In most instances, the indices showed a more pronounced step change of source across the ETM, and a greater difference between surface and bottom waters than $\delta^{13}\text{C}$ -POC. In contrast to the $\delta^{13}\text{C}$ -POC results, surface and bottom water indices were substantially different, and this was most clearly seen in ACL and CPI (compare Figure 4F – 4J and Figure 5A – 5E, Figure S5, Table S1).

Although the *N*-alkane indices discussed above can provide a quantitative and internally consistent measure of the relative abundance of *n*-alkanes, we wished to relate biomarker sources to POC. Consequently we assessed the concentrations of short- and long-chain alkanes (SC and LC alkanes, respectively) to examine the absolute concentration (μg alkane/l), and observe sources as a proportion of the total SSC and POC pools ($\mu\text{g/g}$ SSC and $\mu\text{g/g}$ OC, respectively; Figure S6, Figure 5F – 5J, Table S1). Notably, regardless of how SC and LC alkanes were normalized, LC alkanes were almost always greater than SC alkanes in bottom waters, even when well-mixed, spring tidal conditions were sampled such as in September 2010 (Figure 5F – 5J, closed symbols versus open symbols, Figure S6, Table S1).

Short chain and LC concentrations by volume had similar concentrations in surface water (0.58 ± 0.65 $\mu\text{g/l}$ and 0.80 ± 0.94 $\mu\text{g/l}$, respectively; Figure S6A - S6E, dashed lines, see also Table S1) In contrast, bottom waters had on average 2.6 times more LC than SC (0.08 ± 0.81 $\mu\text{g/l}$ and 2.06 ± 2.71 $\mu\text{g/l}$ respectively; Figure S6A – S6E, solid lines, see also Table S1 for individual cruise results). Both SC and LC alkane concentrations were elevated in the ETM, with LC concentrations in ETM bottom waters the highest of anywhere in the estuary (Figure S6A – S6E, Table S1). Similar to % OC and $\delta^{13}\text{C}$ -POC results, seasonal algal inputs increased SC *n*-alkanes (e.g. Figure S6A - S6C, open symbols in Delaware Bay).

Long chain *n*-alkanes normalized to both SSC and POC ($\mu\text{g/g}$ SSC and $\mu\text{g/g}$ OC, respectively) were clearly influenced by the ETM. LC $\mu\text{g/g}$ OC and LC $\mu\text{g/g}$ SSC generally decreased between the riverine endmember and the ETM, and then dramatically across the ETM (Figure 5F – 5J, Figure S6F – S6O, closed symbols). This occurred even when LC's were

somewhat elevated again downstream in Delaware Bay (e.g. June 2010 and September 2010; Figure 5G – 5H). Unlike the LC, the proportion of SC normalized to POC and SSC ($\mu\text{g/g OC}$ and $\mu\text{g/g SSC}$), with few exceptions, remained the same or increased along the estuary in both surface and bottom waters (Figure 5F – 5J and Figure S6, open symbols). This pattern contrasts strongly with SC and LC concentrations by volume, described above, which had a clear ETM pattern of always being elevated within the ETM (Figure S6A – S6E). The SC and LC alkanes as a proportion of SSC mimicked well the %OC values, which were sampled at more stations, suggesting that the total concentration of alkanes were indicative of overall OC content (compare Figure S4K – S4O with Figure S6K – S6O).

5 Discussion

5.1 *Physical and biological controls on seasonal SSC and POC concentrations*

Suspended solid content and POC distributions were always dominated by the ETM, and seasonal patterns in SSC and POC concentrations within the ETM were influenced by both river discharge and spring/neap tidal phase. In surface waters, SSC and POC concentrations in the ETM appeared to be predominantly controlled by discharge; December 2010 and March 2011 had the highest discharge and highest SSC and POC concentrations overall (Figure 2, Figure 4A – 4E, Figure S4). However, bottom waters seemed to respond to both tidal phase and discharge (Figure 4A – 4E, Figure S4). For example, concentrations in ETM bottom waters were elevated during a low flow-spring tide (September 2010), a high flow-neap tide (December 2010), and a high flow-spring tide (March 2011), which had the highest concentrations recorded in this study (Figure 2, Figure S4). When increased flow coincided with spring tidal phase, concentrations were elevated in both surface and bottom waters. These results agree with the fact that, as in most rivers, increased discharge delivers increased concentrations of particulate material to estuaries (Mansue and Commings, 1974; Sharp et al., 2009), and with the well-established understanding that concentrations of particles in the ETM respond to spring-neap tidal variability. The response to these forcings has recently been quantified for the Delaware (McSweeney et al., 2016). Here, there is a pattern of sediment export in spring, especially in bottom waters, when flows are persistently higher due to freshet which becomes laterally variable in the summer with low flows, owing to intermittent burial, resuspension, and advection, reinforcing the conclusion that the Delaware Estuary can trap tremendous amounts of sediment in the ETM (Cook et al., 2007; McSweeney et al., 2016; Sommerfield and Wong, 2011). While sediment transport processes throughout the water column have been documented in physical

and sedimentological studies, our results show that although SSC and POC are strongly correlated, their differing concentrations between surface and bottom waters means that differing mechanisms may influence POC transport in surface and bottom waters in estuaries.

On average, particulates in the Delaware River had relatively low organic content (~ 10% OC), which is comparable to European estuarine systems (Abril et al., 2002; Middelburg and Herman, 2007), squarely placing the Delaware as typical among functionally turbid, sediment-trapping systems. The systematically low organic content of particulates within the ETM formed the basis of the strong correlation between SSC and POC ($R^2 = 0.91$ and $R^2 = 0.80$ for surface and bottom waters, respectively; Figure 3 and Figure S4). The organic carbon content of particulates decreased between the riverine endmember and the ETM, with an average difference of 4.5% in surface waters and 6.3% in bottom waters (Table S1). Assuming that this loss is entirely due to microbial remineralization (Abril et al., 2002), we can use the decrease in % OC between the riverine endmember and the ETM to calculate the amount of riverine POC being remineralized in the ETM. Following Abril et al. (2002), the POC loss is the average riverine endmember concentration of SSC multiplied by the change in %OC between the riverine endmember and the ETM (%OC riverine endmember minus %OC ETM). This calculation suggests an average loss of 8.1 mg/l POC in surface water and 18.0 mg/l POC in bottom waters across the varying conditions sampled. The surface water estimate of POC loss is 2-4 times higher than that found in European estuaries with comparable POC and SSC concentrations (Abril et al., 2002). The loss in bottom waters was approximately double that in the surface, suggesting that a significant amount of remineralization and loss of terrestrial organic matter is missed by exclusively surveying surface waters. The intermittent burial and resuspension of particles in bottom waters of the ETM would increase oxygen exposure time (Aller, 1994; Sun et al., 2002) and in combination with the enhanced microbial enzyme activity there (Ziervogel and Arnosti, 2009) this provides a plausible mechanism for enhanced remineralization in bottom waters. It remains an open question whether CO_2 evolved from remineralization would remain trapped in bottom waters or, if with lateral pumping and mixing, it degasses within the estuary.

5.2 *Suspended POC sources in the Delaware Estuary*

We used a combination of bulk $\delta^{13}\text{C}$ -POC to infer the average source of algal- and vascular plant-derived POM and *n*-alkane biomarkers to trace the pathway of land-derived POM through the estuary. The $\delta^{13}\text{C}$ -POC in surface and bottom waters along-estuary generally approximated a theoretical conservative mixing line between the riverine (~ -27‰) and marine

endmembers ($\sim -20\%$), suggesting simple dilution down estuary of the riverine-delivered POM with autochthonous phytoplankton inputs. This pattern was most evident during higher discharge and/or spring tidal phases, such as observed in September 2010, December 2010, and March 2011 (Figure 4H – 4J). Seasonal phytoplankton biomass, not only increased the %OC of particulates, but also caused substantial deviations from a simple mixing line. Our surface water $\delta^{13}\text{C}$ -POC results were remarkably similar to previous measurements in the estuary (e.g. Cifuentes et al., 1988; Mannino and Harvey, 1999). Seasonal phytoplankton production not only increased the organic carbon content of particulates as described above, but also enriched the stable isotopic composition of that particulate organic carbon causing the $\delta^{13}\text{C}$ -POC profile to deviate from a simple mixing curve. Under the varying conditions sampled in this study, the greatest deviation from conservative mixing in the $\delta^{13}\text{C}$ -POC profile occurred when elevated productivity coincided with the low discharge. This resulted in bottom water $\delta^{13}\text{C}$ -POC being more enriched than overlying surface waters (March, June, and September 2010, Figure 4). We infer from this pattern a higher proportion of algal matter in ETM bottom waters during these conditions. We suggest that up-estuary transport of freshly produced algal matter could have been a component of the landward transport of suspended solids observed in bottom waters during low discharge (McSweeney et al., 2016).

Comparing the two March cruises illuminated biogeochemical processes that influenced $\delta^{13}\text{C}$ -POC signatures. These two cruises exhibited an inter-annual difference of 2-3‰ (compare Figure 4A and 4J). The March 2010 cruise sampled a neap tidal phase prior to the onset of peak spring freshet flow, whereas the March 2011 cruise occurred during a spring tidal phase following peak discharge as the spring freshet began to taper off (Figure 2). Peak $\delta^{13}\text{C}$ -POC values of $\sim -18\%$ in Delaware Bay in March 2010 are suggestive of an active phytoplankton bloom and were similar to values measured in Delaware Bay in March 1985 which had high rates of primary production (Figure 4A); (Cifuentes et al., 1988). The $\delta^{13}\text{C}$ -POC at the location of the fluorescence maximum in March 2011 was more depleted relative to the year before (-21% ; Figure 4J), which we ascribe to higher discharge and spring tides that increased re-suspension and delivery of riverine-derived particulates throughout the estuary, and depleted $\delta^{13}\text{C}$ -POC values with a larger proportion of C3 vascular plant-derived OM. Contrasts between March cruises suggest that the timing and magnitude of discharge, spring/neap phase, and the development of the spring phytoplankton bloom influence inter-annual differences in $\delta^{13}\text{C}$ -POC in Delaware Bay.

Although the *n*-alkane indices differed somewhat in the detail of their along-estuary profiles, CPI, ACL and $P_{\text{mar-aq}}$, had a consistent pattern showing the loss of vascular plant-derived alkanes across the ETM (Figures 5 and Figure S5). Moreover, LC and SC concentrations revealed consistent patterns in sources across the conditions sampled in this study. These biomarker-based results mimicked along-estuary patterns $\delta^{13}\text{C}$ -POC in surface, but not bottom waters. In surface waters, alkane indices showed a similar proportion of algal- and vascular plant-derived *n*-alkanes, with vascular plant-derived POM predominance in the upper estuary and algal-derived POM seasonally predominant in the lower estuary (Figure S5, Figure S6, dashed lines). This is a pattern that has been previously observed in the Delaware Estuary (Mannino and Harvey, 1999; Mannino and Harvey, 2000; McIntosh, 2015). In contrast, the larger pool of POC in bottom waters, was nearly always dominated by vascular plant-derived LC *n*-alkanes compared to surface waters, even when well-mixed, spring-tidal conditions were sampled, such as in September 2010 (Figure 5, Figure S5, Figure S6, solid lines; Table S1). These results reveal that bottom waters are important in the transport and processing of vascular plant-derived OM between land and sea, especially within the ETM. The difference in sources between surface and bottom water have not been documented previously in the composition of estuarine POM.

Similar to our calculation that POC is lost between the riverine endmember and the ETM, our *n*-alkane indices normalized to SSC and POC all had a consistent pattern showing the loss of vascular plant-derived alkanes across the ETM (Figures 5, Figure S6). This suggests that a substantial fraction of the “lost” POC is vascular plant-derived. Loss of vascular plant-derived POM appeared to be more enhanced in bottom waters and at higher discharge (e.g. December 2010 and March 2011, Figure S6N and S6O), which is consistent with previous work in the nearby Mullica River-Estuary, in which discharge was found to be a strong control on the transport and processing of terrestrial-derived material (Medeiros et al., 2012). This loss of vascular plant-derived OM across the ETM is not evident in the gradual dilution of bulk $\delta^{13}\text{C}$ -POC signatures down-estuary, reinforcing the use of a multi-proxy approach combining bulk and biomarker methodologies as a useful technique for examining source pathways and processing of organic matter in complex coastal environments. The change in character and loss of vascular plant-derived POM across the ETM is likely due to the entrapment and/or remineralization during resuspension of POM with higher levels of vascular plant-derived in the ETM. Loss of vascular plant-derived POM above or within the ETM is also supported by evidence that the

upper Delaware and ETM are heterotrophic (Joesoef et al., 2015; Preen and Kirchman, 2004). Thus, we suggest that bottom waters make an important contribution to the net loss of land-derived POM above and within the ETM.

Additional insight into the sources of POM in the Delaware Estuary was gained by examining $\delta^{13}\text{C}$ -POC and the ACL of *n*-alkane biomarker relative to one another (Figure 6). In surface waters, ACL and $\delta^{13}\text{C}$ -POC decreased proportionally across the different geochemical zones of the estuary. In contrast, ACL in bottom waters remained unchanged through the estuary, with only the marine endmember showing a decrease in ACL, indicative of increased marine influence at the mouth of the estuary. If the intermediate $\delta^{13}\text{C}$ -POC signatures in bottom waters of the ETM were caused by along-channel mixing of depleted terrestrial material from the upper estuary with enriched algal material from the lower estuary, we would expect the biomarkers to reflect a higher proportion of “algal” sources. Instead, ACL values in bottom waters generally indicated a greater proportion of vascular plant-derived OM than algal-derived OM (ACL > 26). Additionally, the enriched signature in the ETM was measured even during seasons without observed phytoplankton productivity (e.g. December 2010). One explanation for this discrepancy between different source determinations is that an additional local source of vascular plant-derived POM is being delivered to bottom waters of the lower estuary. The Delaware Estuary has substantial fringing saltwater marshes (e.g. Kreeger et al., 2012), and the predominant marsh grass species, *Spartina alterniflora*, has an alkane signature of vascular land plants, but an enriched $\delta^{13}\text{C}$ isotopic signature (Canuel et al., 1997). Contributions from this source to the lower estuary and ETM could potentially resolve the difference between the bulk $\delta^{13}\text{C}$ -POC and alkane source information (Hermes, 2013; McIntosh, 2015). Possible mechanisms for the addition of wetland sources to bottom waters of the ETM include the net landward sediment flux in Delaware Bay during low flows (Sommerfield and Wong, 2011) working in concert with lateral transport processes (Aristizabal and Chant, 2014; Chant and Stoner, 2001; Church and Sommerfield, 2006; McSweeney et al., 2016; Sommerfield and Wong, 2011).

6 Conclusions

Seasonal transects through the Delaware Estuary sampled a range of freshwater discharge, tidal phases, and phytoplankton biomass, which influenced the distribution and composition of suspended particulate organic carbon in the estuary. We sampled both surface and bottom waters throughout the estuary and characterized the source of particulate organic

matter using both bulk and tracer compound geochemical techniques. Significant findings of our multi-proxy study are:

- We demonstrated that bottom waters hold the majority of the POC throughout the estuary, but especially within the ETM. POC concentrations in bottom waters were as much as double that in surface waters, and ETM bottom waters had the highest POC concentrations overall. Prior organic geochemical work in the Delaware Estuary largely focusing on surface waters may have underestimated POC transport and remineralization.
- The $\delta^{13}\text{C}$ -POC in surface and bottom waters estimated the average source of algal- and vascular plant-derived POM. Surface and bottom signatures were generally similar using this technique. Along-estuary $\delta^{13}\text{C}$ -POC generally approximated a theoretical conservative mixing line suggesting gradual dilution of terrestrial material down estuary, except where phytoplankton productivity overwhelmed the signal.
- *N*-alkane biomarkers showed that the source of POM in bottom waters was dominated by vascular plant-derived OM, whereas surface waters were more strongly influenced by seasonal algal productivity. This suggests that even in classically well-mixed estuaries, studies emphasizing surface waters alone may miss a large fraction of the land-derived POM in the system.
- *N*-alkane biomarker indices revealed that land-derived POM decreased dramatically across the geochemical barrier of the ETM. The large concentration of land-derived POM within estuarine bottom waters and the change in composition across the ETM suggests that this zone is an important loss point for land-derived POM *en route* to sea.

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Figure captions:

Figure 1. The Delaware Estuary, East Coast, U.S.A. Sampling stations are numbered 1-23 and shading indicates water depth (meters). The turbidity maximum zone is typically observed between 80-120 km.

Figure 2. River discharge during the study period. Delaware and Schuylkill River discharges were summed as the primary sources of freshwater to the Delaware River ($\text{m}^3 \text{s}^{-1}$; data from USGS gauges 01463500 and 01474500 for the Delaware and Schuylkill Rivers, respectively). The black line is Delaware plus Schuylkill River discharge ($D + S$) for 2010, and the dashed line is $D + S$ for the first three months of 2011. $D + S$ during the study period was compared to the daily average interquartile range (IQR; 25th- 75th percentiles; grey shading) and median (grey line) from 1913 – 2011. The 7-day average discharge prior to each cruise is indicated above the graph with arrows, and cruises are indicated with boxes on the x-axis, with neap tide cruises in black and spring tide cruises in grey. Note that the March 2010 and 2011 cruises occurred prior to and after discharge events, respectively, June and September captured typical low summer discharge, and December sampled after a winter storm event.

Figure 3. The relationship between SSC and POC in the Delaware Estuary. Squares are bottom water and circles are surface water. Colored symbols refer to sites in the estuary: blue – marine endmember, purple – chlorophyll maxima, brown – ETM, and green – riverine endmember. The dashed line is the linear fit to all surface water data and the solid line is the linear fit for all bottom water data. The bottom water linear fit holds even excluding high SSC values in the ETM. Inset: same graph with zoomed in axes.

Figure 4. Delaware Estuary surface (dashed lines with open circles) and bottom water (solid lines with filled squares) A – E) particulate organic carbon (POC, mg/L) and F – J) the stable carbon isotopic signature of POC ($\delta^{13}\text{C}$ -POC, ‰ PDB). Error bars are the standard deviation of sample duplicates.

Figure 5. *N*-alkane biomarker distributions. Open (short-chain; SC) and closed (long-chain; LC) circles with dashed lines are in surface water, and open (SC) and closed (LC) squares with solid lines are in bottom water. SC and LC *n*-alkanes are normalized to: A – E) water volume; F – J) particulate organic carbon; and K – O) suspended solid content. Note the changes in scale for the y-axes in each panel.

Figure 6. Delaware Estuary POM average chain length (ACL) vs. $\delta^{13}\text{C}$ -POC (‰ PDB) for A) surface water and B) bottom water. Cruises are notated by symbol color as follows: March 2010 – blue; June 2010 – green; September 2010 – orange; December 2010- purple; March 2011- red. Symbol shape indicates region of the estuary: Riverine endmember- triangles; ETM- squares and asterisks; Delaware Bay- circles; marine endmember- diamonds. Large circles were hand drawn to outline

592 the four estuary regions: green dash – riverine; black small dash- ETM; yellow oval- marine
593 endmember; blue dots- Delaware Bay.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6