SPATIAL AND SEASONAL PARTICULATE ORGANIC CARBON CYCLING WITHIN THE DELAWARE ESTUARY, ASSESSED USING BIOMARKER AND STABLE CARBON ISOTOPIC APPROACHES

By

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ABSTRACT OF THE THESIS

Spatial and seasonal particulate organic carbon cycling within the Delaware estuary, assessed using biomarker and stable carbon isotopic approaches

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The fate of terrestrial-derived organic matter (OM) in estuaries is poorly characterized, obscuring the link between carbon cycles of land and sea. This study characterized sources of OM in the Delaware Estuary using multiple organic geochemical analyses: bulk and compound-specific stable carbon isotopes, and *n*-alkane and phospholipid fatty acid (PLFA) biomarkers. The spatial and temporal variations in particulate organic matter (POM) character in both surface and bottom waters were evaluated for 5 seasonal cruises in 2010-2011. Axial transects were from a marine to a riverine endmember, and geochemical analyses additionally emphasized the estuarine turbidity maxima (ETM), and chlorophyll maxima.

POM characteristics were consistent with previous studies. POM was generally <10% organic carbon (OC) and the $\delta^{13}C$ signature of POM became progressively enriched moving downstream, from -26.5 ± 2.3‰ at the riverine endmember to -22.0 ± 1.9‰ at the marine endmember. Yet, mixing of sources in the ETM and spring

phytoplankton bloom signatures in Delaware Bay masked the pathway of terrestrial sources.

In contrast, *n*-alkane and PLFA biomarkers showed the proportion of algal- and terrestrial-derived OM to be comparable in surface waters throughout the estuary and bottom waters were substantially higher in terrestrial and marsh inputs. Bottom water particulates in the ETM comprise the largest suspended OC pool in the estuary, which has a significant terrestrial component and was previously uncharacterized. Biomarker results from this study suggest that the ETM is an effective trap of terrestrial POM.

The $\delta^{13}C$ of long chain *n*-alkanes (C_{23}-C_{33}) confirmed substantial inputs from C4 marsh plant material in both September 2010 (-29.3 ± 0.9‰), and in March 2011 (-31.0 ± 2.1‰). The presence of marsh-derived OM in the main axis of the estuary and ETM suggests that lateral processes are important for OM cycling in estuaries and that the vascular plant derived OM reaching the ocean may not be sourced from upland drainage basins, but from more local inputs such as fringing wetlands. The role of marsh-derived OM in the marine OC cycle demands further attention to fully constrain its reactivity and fate in the marine environment.

ACKNOWLEDGEMENTS

I used to joke that the Institute of Marine and Coastal Sciences, "didn't trust the New Mexican with blue water research," hence, this thesis work in the muddied waters of the Delaware Estuary. Indeed, I was not initially keen on tackling, 1) organic chemistry, and 2) estuarine dynamics, for the scope of a Master's project.

Yet, throughout the past few years I have developed a profound familiarity with and fondness for the blue-to-brown waters of the Delaware: envisioning its gravitational circulation while taking the Patco from Camden, NJ to Philadelphia, PA across the bright blue emblematic Ben Franklin Bridge, reminiscing our founding fathers' relationships with the very same body of water as they pondered the inner workings of our young government, scrutinizing wetland sources of carbon while overhearing modern dramas on the Riverline rumbling towards Trenton, and getting back in touch with the moon to better understand spring and neap tidal variability. Furthermore, the eight cruises aboard the R/V *Sharp* were fundamental in my growth as a student, teacher, and scientist, and being on the water will always be considered a second home during my Master's work.

I am deeply appreciative to those that provided the opportunity for me to build a relationship with this body of water that is so vitally important to millions of others in the Northeast. Thank you for believing in me as a young scientist and adult; you have changed my life in more ways than you can imagine. In this, I firstly thank my advisor Liz Sikes, as well as my committee members Bob Chant, and Liz Canuel and also Chris Sommerfield. Thanks, too, to Rutgers, and the Institute of Marine and Coastal Sciences for the continual support of my education and opportunities. Dr. Katherine Freeman and her lab members at Penn State University were generous in their assistance with

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I also thank my friends and coworkers that have supported me in times of curiosity, excitement, adventure, boredom, frustration, and homelessness: Kat Esswein, Aurora Elmore, Matt Yergey, Julie Kalansky, Ben Schiraldi, Indrani Chatterjee, Alan Lazare, Travis Miles, Cat Beck, Talia Young, Mikaela Provost, Maria Aristizabal, Natalie Howe, Tali Babila, T.R. and Audrey Morley, Becca Barnes, Michelle Hardee, Silke Severmann, Esther Ruskin, and all of those that shared moments of tired stupor slicing and dicing sediment cores at 3AM!

Above all, I thank my family and Alex for keeping me grounded during this experience and reminding me of how lovely the world is outside of my closet office at Rutgers, but how lovelier it is with the knowledge that I have earned and the questions that I have learned to ask.

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I. INTRODUCTION

"The destination of material eroded is eventually the great world ocean, although there are pauses in the journey," (Judson, 1968).

1.1 Terrestrial-derived organic matter through estuaries

Estuaries link land and sea; yet, the fate of terrestrial-derived organic matter remains an open question in coastal organic geochemical cycling (e.g. Hedges et al., 1997; Benner, 2004). Rivers deliver ~800-1000 Tg of organic carbon annually to coastal waterways and estuaries but only half, ~400-500 Tg, reaches the global ocean (Schlesinger and Melack, 1981; Meybeck, 1982; Ludwig et al., 1996; Schlunz and Schneider, 2000; Bianchi, 2011). Particulate OM (POM) is a reactive pool of OM in estuaries, intricately linked to sediment dynamics (e.g. Blair et al., 2004; Blair and Aller, 2012). Within estuaries, terrestrial POM from diverse sources and histories mixes with locally sourced OM (e.g. phytoplankton, grazer inputs, bacterial production; Figure 1-1a). This POM from diverse sources encounters precipitous changes in physical, biological, and chemical conditions *en route* to the sea. As geochemical filters, estuaries are thought to modify the identity and reactivity of terrestrial-derived OM (Hedges et al., 1997).

With different reactivities, organic carbon from differing sources may have disparate fates, including carbon burial, remineralization back to CO_2, or export to the ocean (Figure 1-1b). The fate of terrestrial-derived OM in estuaries and its reactivity in the global ocean play a role in long-term carbon cycle balances because although estuaries are a small proportion of open water surface area, they have a net positive CO_2 flux, in contrast to the open ocean and continental shelves (e.g. Cai, 2011). Yet, tracing terrestrial OM through estuaries is geochemically challenging because sources have

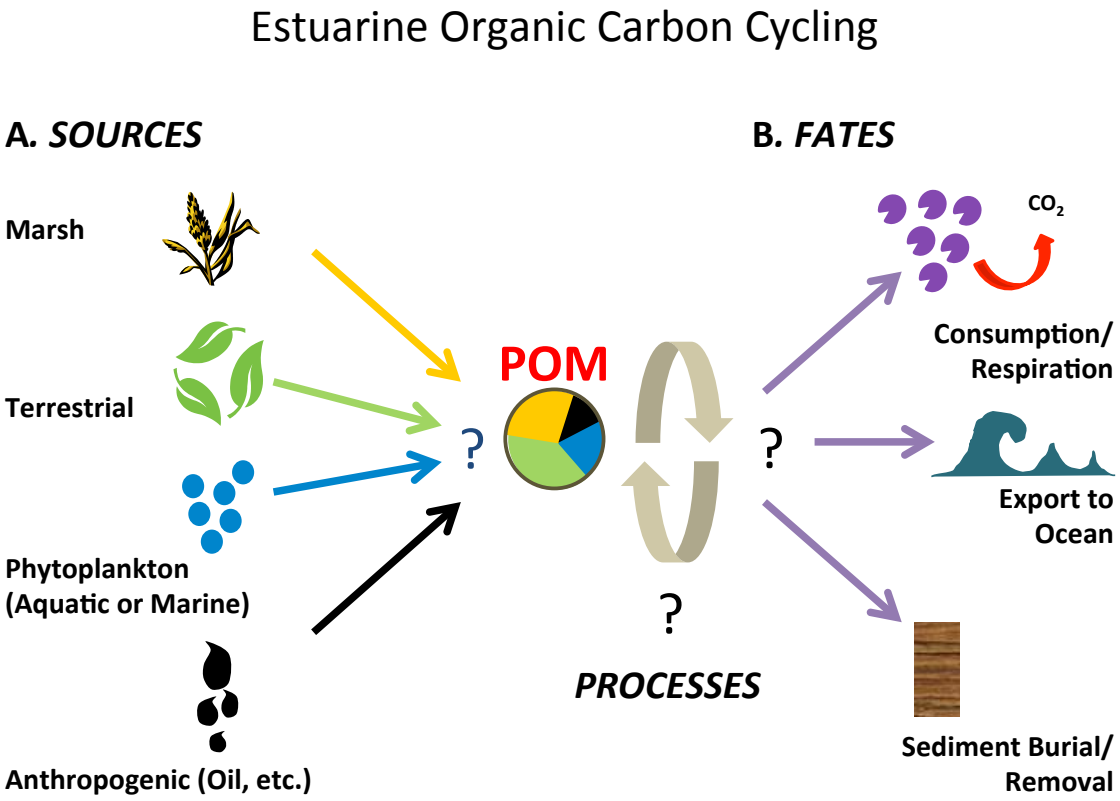


Figure 1-1. Estuarine organic carbon cyling. A) Several sources of organic matter comprise particulate organic matter (POM) in estuaries, including allochthonous sources (e.g. wetland, anthropogenic, and terrestrial), and autochthonous sources (e.g. phytoplankton). Estuarine biological, physical, and chemical processes control the proportions of sources in the POM pool and also control the different fates of individual sources. B) Fates for OM in estuaries include consumption or bacterial remineralization back to CO_2, export to the oceanic organic matter cycle, or burial. Question marks represent: What are the sources of OM that comprise estuarine POM? What are the processes by which OM is modified in estuaries, and how do these processes result in different fates for the different sources of OM?

overlapping geochemical signatures, and bulk methods average sources (e.g. Sikes et al., 2009; Mannino and Harvey, 1999).

The Delaware Estuary is a temperate coastal plain estuary on the east coast of the United States and is a model system for assessing the sources and fates of OM in estuaries (Figure 1-2). Extensive shipboard surveys through the Delaware Estuary began in the late 1970's by researchers at the University of Delaware, providing physical, chemical, and biological perspectives of the estuary (e.g. Sharp et al., 1982; Coffin and Sharp, 1987; Pennock and Sharp, 1986; Cifuentes et al., 1988; for review, Sharp et al., 2009). More recent work has focused on defining the mechanisms of sediment transport and trapping, organic matter sources, and microbial ecology (e.g. Cook et al., 2007; Sommerfield and Wong, 2011; Harvey and Maninno, 2001; Ziervogel and Arnosti, 2009; Kirchman et al., 2005). Collectively, these studies provide context for this thesis.

1.2 Delaware Estuary circulation and sediment transport processes

The discharge rate of the Delaware River and the pumping of tides primarily control the physical dynamics of the Delaware Estuary (Sharp et al., 1986). The Delaware River discharge is the primary source of freshwater to the Delaware Estuary (330 m^3/s), with smaller contributions from the Schuylkill (77 m^3/s) and Christina (19 m^3/s) rivers, which collectively account for over 80% of the freshwater to the estuary (Sommerfield and Wong, 2011; Cook et al., 2007). These rivers also deliver over 70% of sediments to the Delaware Estuary (approximately 50, 19, and 7.5%, respectively; Mansue and Commings, 1974). Pioneering work in the Delaware Estuary determined that it is generally well mixed, but stratification in Delaware Bay occurs on seasonal and tidal time scales (Sharp et al., 1986). The tidal influence extends ~215 km from the mouth of

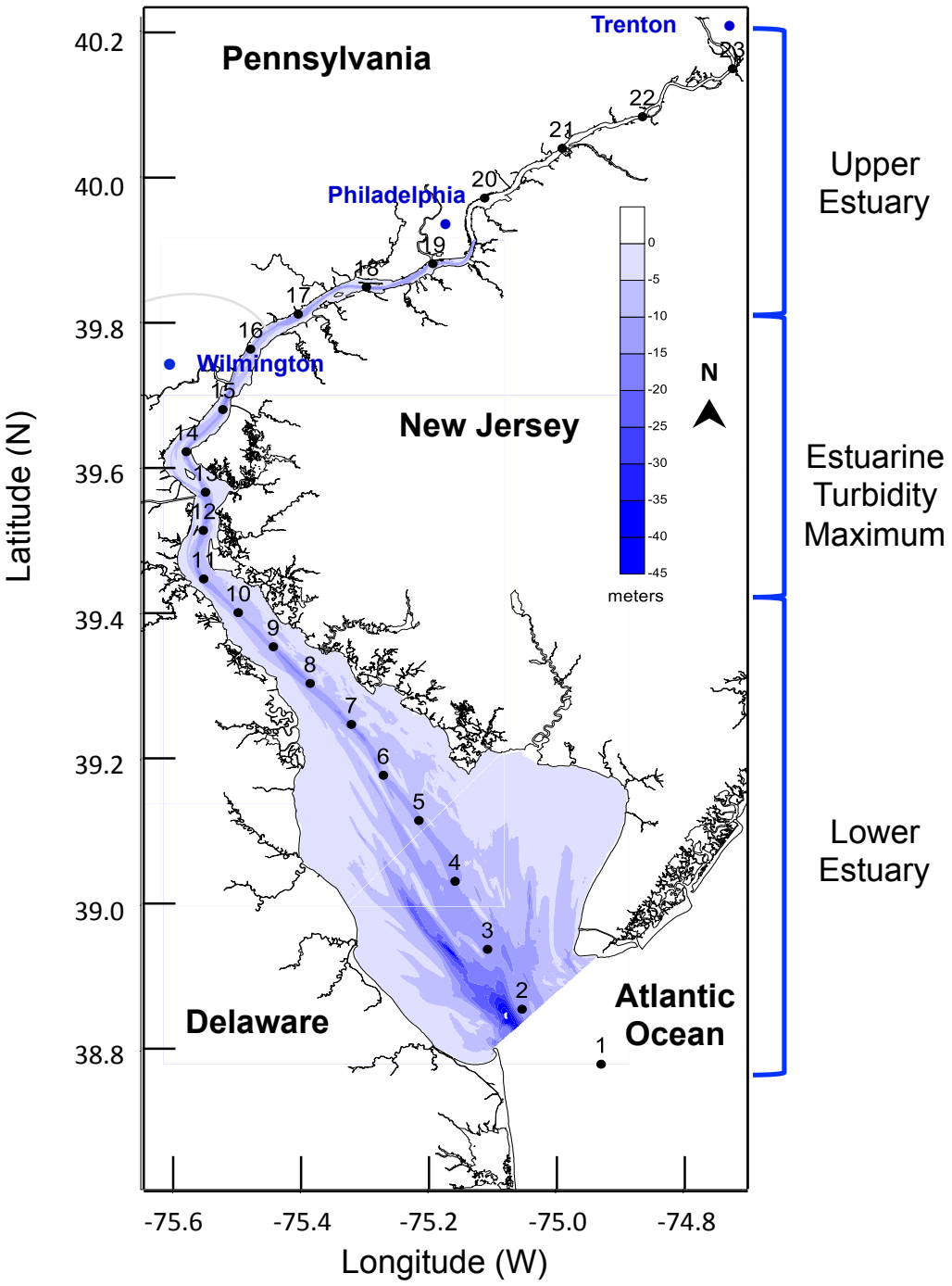


Figure 1-2. The Delaware Estuary. Water sampling stations are numbered 1-23. The scale bar indicates depth (meters).

Delaware Bay to Trenton, NJ, and tidal discharge at the Bay mouth is substantially higher than the mean annual river discharge into the estuary (1.5×10^5 m^3/s and 650 m^3/s, respectively; Garvine et al., 1992). This suggests that riverine material is substantially diluted prior to its export from the Estuary.

The funnel-shaped morphology of the Delaware Estuary plays a large role in its circulation, salt fluxes, and sediment transport. First, the Coriolis force has a significant impact on water transport because the width of Delaware Bay allows set-up of a barotropic pressure gradient, and resultant compensatory lateral flow changes directions during flood and ebb tide (e.g. Lerczak and Geyer, 2004). Second, the channel morphology of Delaware Bay drives differential advection, in which frictional differences between the shallow flanks and deeper main channel set up cross-channel density gradients and result in lateral circulation (Figure 1-3; Lerczak and Geyer, 2004; MacCready and Geyer, 2010). Although lateral transport processes in Delaware Bay have been observed for some time (e.g. Wong, 1994), the effect of these physical processes on sediment and OM exchange between fringing marshes and the main channel remains unconstrained.

Sediment dynamics in the Delaware Estuary control the mixing and transport of POM in the estuary. 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). A broad and sometimes double estuarine turbidity maximum (ETM) occurs mid-estuary (Biggs et al., 1983). Gravitational circulation and tidal pumping maintain the ETM (Sommerfield and Wong, 2011). In Delaware Bay, a net up-estuary sediment flux

A. B.

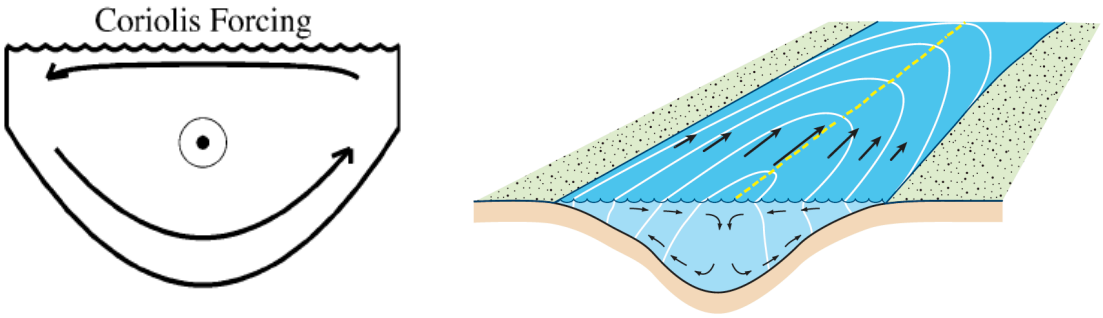


Figure 1-3. Estuarine lateral transport processes (Figure after Lerczak and Geyer, 2004; MacCready and Geyer, 2010). A) Rotational transport. The Coriolis force drives a barotropic pressure gradient, and resultant flow is across-estuary. B) Estuarine differential advection. Lateral density gradients result from frictional differences between deep and shallow bathymetry. The lateral density gradients give rise to cross-estuary circulation, manifested as two cells (small black arrows), which switch directions on flood and ebb tide. Along-estuary velocities (black arrows), salinity contours (white lines).

prevents particle escape from the ETM, resulting in an immense capability of the estuary to trap sediment in this zone (Sommerfield and Wong, 2011). The ETM can hold as much as 1-2 years of river-delivered sediment, and much of its volume is from intra-estuarine sources of material from previously deposited and subsequently remobilized sediment (Cook et al., 2007). Even during storm events that flood the estuary with freshwater and sediment, export of sediment from the ETM is buffered by increased vertical sheer in the lower estuary caused by the greater freshwater inputs, which reinforces gravitational circulation, and hence, sediment trapping (Sommerfield and Wong, 2011). Consequently, the ETM receives particles from both the upper and lower estuary, resulting in mixed sources of POM with various histories.

1.3 Estuarine sources, processing, and fates of organic matter

The sources, processing, and fates of OM are unique to every estuary, as each has varied physical dynamics, watersheds, and anthropogenic impacts that separately influence the sources and geochemical cycling of OM. However, overall controls on OM in estuaries can be constrained by examining bulk organic matter characteristics such as total organic carbon content and total nitrogen content, or the isotopic makeup of the organic carbon pool (e.g. Middelburg and Herman, 2007; Hopkinson et al., 1998). Multivariate statistical approaches also elucidate patterns in OM pathways and processing using complex data sets with biomarker, environmental, and bulk compositional data (e.g. Canuel, 2001).

1.3.1 Sources of organic matter in estuaries

Vascular plant-derived OM predominates in upper estuaries, delivered by freshwater inflow, and algal-derived OM predominates downstream with seasonal

estuarine phytoplankton blooms (e.g. Countway et al., 2007; Jaffe et al., 2001; Goni et al., 2003; Hopkinson et al., 1998). Studies using bulk geochemical techniques such as bulk stable isotopes or C:N ratios to estimate source distributions report the "disappearance" of terrestrial-derived OM in lower estuaries (e.g. Mannino and Harvey, 1999), which is ascribed to the dilution of terrestrial signatures by algal material. Studies tracing OM with biomarkers have revealed the persistence of vascular plant-derived OM where bulk measurements have not (e.g. Bianchi and Canuel, 2011; Bianchi and Bauer, 2012), and have also assisted in distinguishing terrestrial or wetland-derived vascular plant OM (e.g. Ficken et al., 2000). Nevertheless, in complex estuarine environments, overlapping biomarker source signatures complicate source apportionment, whereas compound-specific isotopic analyses can improve tracing sources of OM through coastal systems (e.g. Bull et al., 1999; Sikes et al., 2009; Tanner et al., 2010; Bianchi et al, 2011; Ahad et al, 2011).

Sources of OM specific to the Delaware Estuary include autochthonous phytoplankton production, riverine delivered terrestrial OM, anthropogenic inputs such as wastewater and petroleum OM, and wetland material (e.g. Cifuentes, 1988; Cifuentes, 1991; Mannino and Harvey 1999). Previous studies determined that the upper Delaware Estuary is dominated by degraded terrestrial vascular plant OM, with some additional inputs from sewage (Cifuentes et al., 1988; Cifuentes, 1991; Mannino and Harvey, 1999; Harvey and Mannino 2001). A seasonal cycle of phytoplankton productivity is well characterized throughout the estuary, and this imprints OM with algal geochemical signatures. Typically, high sediment loads in Delaware Bay limit light, restricting primary production despite ample nutrient availability (Pennock, 1985). Nonetheless,

elevated river discharge during spring freshets stratifies Delaware Bay, which suppresses sediment resuspension high into the water column and allows an extensive annual diatom bloom (Pennock and Sharp, 1986). Grazing, bacterial remineralization, and resuspension of sediments dampen the diatom bloom towards summer (Coffin and Sharp 1987; Pennock and Sharp 1986). Freshwater productivity blooms in the upper estuary as summer unfolds, and in late summer a second bloom dominated by nanoflagellate phytoplankton commonly develops in Delaware Bay (Pennock and Sharp 1986).

Wetlands are a distinctive feature of the Delaware Estuary, fringing nearly its entire tidal extent. Tidal freshwater wetlands border the main channel of the Delaware River and are significant throughout the small tributaries that drain into the upper estuary. The tidal freshwater wetlands are diverse, but are predominantly composed of *Peltandra virginica* (arrow arum), *Pontederia cordata* (pickerelweed), *Nuphar lutea* (yellow pond lily), *Typha sp.,* (cattails)*,* and *Zizania sp*. (wild rice; Weston et al., 2011; Kreeger et al., 2012). Saltwater marshes fringe the tributaries and coastline of Delaware Bay and are dominated by *Spartina alterniflora* (smooth cordgrass; Kreeger et a., 2012). Throughout the Delaware Estuary, the invasive species, *Phragmites australis* (common reed) is widespread (e.g. Bushaw-Newton et al., 2008).

Previous studies have indicated that marsh-derived OM is not a substantial source of OM to the Delaware estuary (Cifuentes, 1991; Mannino and Harvey, 1999). However, significant wetland erosion throughout the estuary has been observed for decades (e.g. Phillips, 1986; Kearney et al., 2002). The exchange of POM and dissolved OM (DOM) between wetlands and waterways is dependent on hydrology, which determines the residence time of materials, and regulates material degradation (Bianchi and Bauer,

2012). Lateral transport processes in Delaware Bay may link fringing and axial organic carbon exchange. For example, imported estuarine phytoplankton OM has been shown to support food webs in Canary Creek, a tributary near Lewes, DE, whereas it has been demonstrated that other salt marshes export POM to the main Estuary (Roman and Daiber, 1989; Huang et al., 2003). In light of recent hypotheses that cross-estuary exchange of carbon between wetlands and the main estuarine channel impact CO_2 fluxes in estuaries (e.g. Cai, 2011), the fate of wetland OM within the greater Delaware Estuary demands further attention.

1.3.2 Estuarine processing and the fate of terrestrial-derived OM

The fate of terrestrial-derived OM through estuaries may be bacterial remineralization, burial, or export to the marine carbon cycle. Net heterotrophy is commonly observed in estuaries and implies that allochthonous OM must be substantially remineralized (Raymond et al., 2000; Frankignoulle et al., 1998; Cai, 2011). Bacterial remineralization of detrital OM requires the 'right' combination of bacterial assemblage, extracellular enzymatic diversity, physical association between OM and bacteria, and redox conditions (Arnosti 2004, e.g. Schmidt et al., 2009). Misalignment in these ecosystem properties results in 'speed bumps' and 'barricades' for OM remineralization, and causes preferential consumption of certain constituents of the OM pool, or partial remineralization of OM (Arnosti, 2004).

Labile OM 'priming' and oscillatory redox conditions increase the remineralization rate of more recalcitrant sources of OM. The 'priming' hypothesis is derived from soil geochemistry, and suggests that inputs of labile OM increase the remineralization rate of recalcitrant OM (for review, Guenet et al., 2010). Seasonal

autochthonous productivity in estuaries provides labile OM for enhanced remineralization of recalcitrant allochthonous OM, but this process in aquatic and marine environments is understudied (Bianchi, 2011). Redox conditions also affect OM degradation. Generally, a greater proportion of OM is degraded and degraded more swiftly in oxic than anoxic environments in coastal zones and estuaries (e.g. Aller, 1998; Sun et al., 2002; Lehman et al., 2002; Arzayus and Canuel, 2004), but degradation is believed to be source specific (e.g. Lehman et al., 2002; Kristensen et al., 1995). Oscillation between oxic and anoxic conditions increases degradation rates also, suggesting oxygen exposure time may be as important for degradation as the composition of the material itself (e.g. Sun et al., 2002; Aller, 1998).

Processing of OM in estuaries has a fundamental seasonal and time variant component. Seasonal changes in runoff, such as spring freshets or punctuated storm-events, influence the amount of terrestrial OM delivered to and exported from estuaries (e.g. Countway et al., 2007; Townsend-Small et al., 2008; Medeiros et al., 2012). Additionally, seasonal changes in primary productivity impact geochemical signatures (e.g. Canuel, 2001). Bacterial uptake of OM also depends on seasonal source availability. For example, in the York River Estuary, phytoplankton material supported bacterial production during spring blooms, but marsh-derived OM supported bacterial production in the fall (McCallister et al., 2004). Shorter time scale processes such as tidal sediment resuspension can also impact the fluxes and partitioning of OM sources (Goni et al., 2005).

The ways in which terrestrial-derived OM is remineralized vary with the different zones of an estuary. The ETM is a critical reactor for OM processing with rapid changes

in redox conditions, transfer between OM size class pools (e.g. Mannino and Harvey, 1999), mixing of sources (Goni et al., 2005), and increased bacterial enzyme activities (Ziervogel and Arnosti, 2009; Revilla et al., 2000). Sources are also spatially segregated due to different settling velocities (Bianchi and Bauer, 2012, and references therein). Lower estuaries support seasonal pulses of autochthonous phytoplankton production for priming of terrestrial-derived OM (e.g. Bianchi, 2011), and lateral transport processes in this region are thought to link OM cycling in fringing wetlands with the main estuarine channel (e.g. Cai, 2011).

Processing within estuaries impacts the composition and reactivity of OM in the marine environment (e.g. McCallister et al., 2004). Some terrestrial OM must escape the estuarine geochemical sieve because signatures of terrestrial OM are commonly detected in the coastal and open ocean (e.g. Blair and Aller, 2012; Goni et al., 2008). Exported OM can be preferentially aged within coastal waterways (Blair et al., 2004; Blair and Aller, 2012; Raymond and Bauer, 2001; Raymond et al., 2004), and may be size-partitioned with terrestrial POM selectively retained and dissolved OM exported (McCallister et al., 2006). Offshore, hydrodynamic sorting results in differential delivery of terrestrial OM and the concentration of terrestrial OM in offshore "depocenters" (e.g. Tesi et al., 2007; Schmidt et al., 2009; Sikes et al., 2009). Although coastal shelves are considered "reactors" for terrestrial OM remineralization (e.g. Aller et al., 2008), a fraction of terrestrial-derived OM evades remineralization and remains diffusely suspended throughout the global ocean (e.g. Opsahl and Benner, 1997).

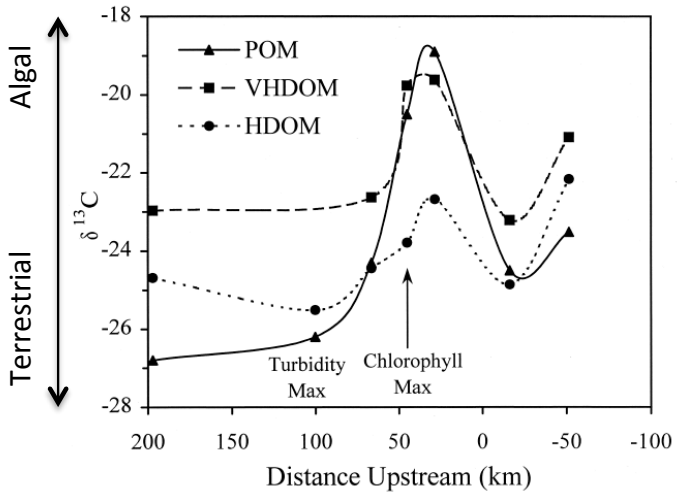
In the Delaware Estuary, the fate of riverine delivered terrestrial material is unresolved. That the upper Delaware Estuary is net heterotrophic, whereas the lower

Delaware Estuary is net autotrophic (Sharp et al., 1982; Hoch and Kirchman, 1993; Preen and Kirchman, 2004), suggests that there is substantial remineralization of terrestrial OM in the upper estuary. However, terrestrial-derived geochemical signatures dominate sediments in the upper Delaware Estuary and other estuaries (Cifuentes, 1991; Zimmerman and Canuel, 2001), suggesting that some constituents of terrestrial-derived OM exhibit a degree of recalcitrance to degradation and are selectively buried. Terrestrial-derived OM buried in the upper Delaware Estuary has a second chance at remineralization upon resuspension and advection down-estuary to the ETM (e.g. Cook et al., 2007). Disappearance of terrestrial derived OM signatures across the ETM in the Delaware Estuary indicates this region is important for terrestrial OM processing. Alternatively, terrestrial signatures may be diluted as Delaware Bay widens or are masked by algal OM signatures (Figure 1-4; Cifuentes, 1991; Mannino and Harvey, 2000). Nevertheless, it was suggested that 2×10^{10} g OC $year^{-1}$ of dissolved terrestrial OM is exported from the Delaware Estuary (Mannino and Harvey, 2000). Thus, the source and fate of terrestrial POM in the Delaware Estuary requires further investigation.

1.3.3 Anthropogenic impacts

The origin and fate of OM in estuaries is affected by policies and management practices, as anthropogenic influences substantially change OM production, delivery, and preservation via land use and land cover within the watershed. This affects nutrient delivery to coastal systems, with known consequences such as eutrophication (e.g. Zimmerman and Canuel, 2000; Kalas et al., 2009; Belmont et al., 2011). Further, the conversion of landscapes from forests to crops and construction activities alter the amount and age of erosional material delivered to estuaries (e.g. Judson, 1968; Belmont

A.



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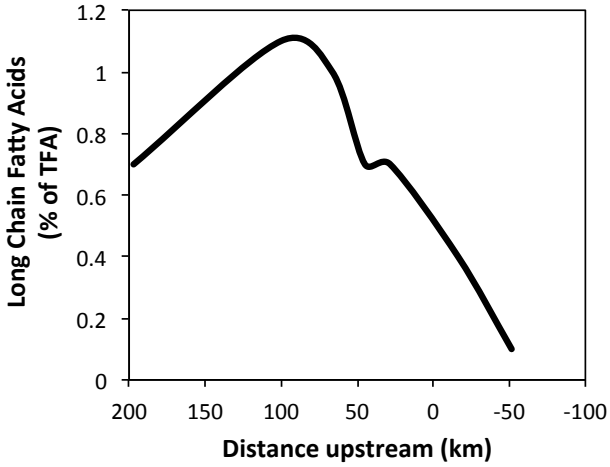


Figure 1-4. The "disappearance" of terrestrial-derived OM in the Delaware Estuary, redrafted after Mannino and Harvey (1999). A) The bulk stable carbon isotope composition of POM and very high and high molecular weight dissolved OM pools (VHDOM and HDOM) through the Delaware Estuary, Spring 1996. B) Terrestrial-derived biomarkers through the Delaware Estuary: the sum of long, straight-chain fatty acids with 24 and 26 carbon atoms as a percentage of total fatty acids (TFA).

et al., 2011; Canuel et al., 2009). Wastewater and urban OM substantially influence geochemical signatures in many impacted estuaries (e.g. Ahad et al., 2011; Griffith and Raymond, 2011).

Anthropogenic uses of the Delaware Estuary are of tremendous economic value to the U.S., and are weighed against ecosystem sustainability goals such as wetland and fisheries protection and management (e.g. Partnership for the Delaware Estuary, 2012). The Delaware River provides drinking water for 5% of the U.S. population (Sharp et al., 2009) and Delaware River ports are collectively the 5th and 20th largest in the U.S. for imports and exports, respectively (Kauffman, 2011). In addition, as much as 70% of the oil shipped to the Atlantic coast of the U.S. moves through the Delaware Estuary, and wastewater discharge into the Delaware River Basin can be as much as 16% of the mean annual Delaware River discharge (52 m^3/s and 332 m^3/s, respectively), 44% of which is from Philadelphia (Kauffman, 2011). Shipping demands require continual dredging of the main channel of the estuary by the U.S. Army Corps of Engineers since the late 1800's. As one would expect, these anthropogenic activities affect the biogeochemistry of the Estuary, including alteration to nutrient loadings and OM inputs (e.g. Sharp et al., 2009; Mannino and Harvey, 1999).

1.4 Summary and Research Objectives

Terrestrial OM delivered to estuaries is substantially processed prior to export to the world's oceans (Hedges et al., 1997; Bianchi, 2011). Net heterotrophy in upper estuaries suggests substantial remineralization of terrestrial OM (e.g. Cai, 2011; Raymond et al., 2000), but direct remineralization of terrestrial OM is difficult to constrain (e.g. McCallister et al., 2004). Processing of terrestrial OM is likely heightened within the estuarine turbidity maximum zone, with rapid sediment resuspension invoking increased bacterial enzymatic activities, changes in redox conditions, and seasonal mixing of labile and recalcitrant OM. Lateral transport processes in lower estuaries may enhance communication between fringing and axial OM pools (e.g. Cai, 2011). Constraining the source of terrestrial OM in estuaries is important for defining its reactivity through estuarine processes and into the marine environment (Bianchi, 2011).

This thesis addresses the sources and fate of terrestrial OM in the Delaware Estuary. The well-studied Delaware Estuary is a model system as it receives terrestrial OM primarily from the Delaware River, supports seasonal phytoplankton productivity throughout the estuary, and traps sediment within its ETM (Sharp et al., 2009; Cifuentes et al., 1988; Cifuentes, 1991; Mannino and Harvey, 1999; Sommerfield and Wong, 2011). Previous studies have shown that terrestrial-derived OM dominates surface water and sediments in the upper Delaware Estuary, but largely disappears across the ETM and within Delaware Bay (Cifuentes et al., 1988; Cifuentes, 1991; Mannino and Harvey, 1999; Harvey and Mannino, 2001).

Objectives of this research:

1) Characterize spatial and seasonal sources of OM through the Delaware Estuary.

Approach: One year of seasonal axial transects through the estuary address spatial changes across seasons. Bulk stable carbon isotopes and biomarkers characterize OM sources in surface and bottom water POM.

Motivation: Previous studies in the estuary addressed organic matter sources in surface water and sediments through the Delaware Estuary. Terrestrial OM was shown to decrease between the upper estuary, ETM, and Delaware Bay (Cifuentes, 1991; Mannino and Harvey, 2000). Assessing bottom water samples spatially and seasonally will determine whether terrestrial-derived sources of OM in surface and bottom water are different and if they change with changes in flow and temperature. Given that stratification plays a role in inducing phytoplankton blooms (e.g. Pennock and Sharp, 1986), and this varies with seasonally discharge, this may impact OM cycling within the estuary by restricting communication between surface and bottom water sediment pools or limiting the mixing of different OM sources. The inclusion of bottom water analyses in the present study will contribute an additional perspective to OM cycling within the Delaware Estuary.

2) Determine the contribution of wetland organic matter to the Delaware Estuary OM pool.

Approach: Biomarker and CSIA approaches characterize source*s.* Alkane biomarkers for dominant wetland plants in the Delaware in addition to riverine and marine endmembers were assessed. Compound-specific stable carbon isotopic analysis of alkanes targeting

chain lengths associated with wetland sources differentiate between C3 upland sources of vascular plant OM and C4 wetland sources of OM.

Motivation: The mismatch between previous geochemical studies suggesting wetland OM is not substantial within the Delaware Estuary (Cifuentes, 1991; Mannino and Harvey, 1999) and the evidence for substantial wetland erosion throughout the Estuary (e.g. Kearney et al., 2002) implies that wetland OM may be under-represented in previous geochemical analyses.

3) Examine the fate of terrestrial-derived OM, emphasizing the ETM as a processing zone within the Delaware Estuary.

Approach: Sources of OM in sediments and POM spanning the ETM were compared. Sources of OM at the marine endmember determine OM exported from the estuary.

Motivation: Previous work showed terrestrial OM burial in the upper Delaware Estuary (Cifuentes, 1991), but did not address the role of the ETM in this process. Decreased terrestrial OM signatures in surface water POM across the ETM in the Delaware Estuary (Mannino and Harvey, 1999) suggests that terrestrial OM is processed across this zone.

II. RELEVANT GEOCHEMICAL TOOLS FOR CHARACTERIZING SOURCES AND SINKS OF ORGANIC MATTER

Many studies of carbon cycling through coastal systems have applied geochemical methods in combination to characterize the sources and sinks of OM (see for review, Bianchi and Canuel, 2011). Biomarker distributions and abundances as well as compound-specific isotope techniques provide better source information than bulk organic matter analyses (e.g. total organic carbon and total nitrogen). The trade-off is that a smaller fraction of the total organic pool can be assessed (Bianchi and Canuel, 2011).

2.1 Bulk properties of organic matter as source tracers

The C:N (molar or atomic; $C:N_a$) ratio of particulate OM is indicative of algal- vs. vascular plant-derived OM. Algae, rich in protein, typically have a low C:N (~6-7), whereas vascular plants, with a high percentage of cellulose, have C:N from ~20 to 100 (Bianchi and Canuel, 2011). An advantage of using C:N ratios is that it reflects the total organic matter composition. However, C:N is not entirely diagnostic of OM source due to intra-species variability, seasonal changes in the C:N of plants, and overlap in the ranges of C:N for terrestrial plants, aquatic and marine algae, and bacteria (e.g. Cloern et al., 2002). Additionally, preferential loss of N during decomposition and diagenesis increases the C:N, altering the original source signature.

Both the biochemical pathway used in photosynthetic organic carbon fixation and the isotopic composition of the inorganic carbon used in carbon fixation determine the carbon isotopic composition of organic matter. The enzyme ribulose 1,5-bisphosphate carboxylase (RuBisCO) selectively discriminates against heavier $^{13}CO_2$ in the C3 carbon fixation pathway, which imprints the fixed organic material with a ^{13}C-depleted carbon

isotopic signature (~ -23 to -35‰; Farquhar et al., 1989; Cerling et al., 1993). Terrestrial and aquatic plants in estuarine watersheds that use the C3 pathway include trees, shrubs, wheat, mangroves, and freshwater marsh plants (e.g. *Typha latifolia*). The enzyme used in the C4 carbon fixation pathway, phosphoenolpyruvate (PEP) carboxylase, is less discriminating than RuBisCO, resulting in more enriched organic matter (~ -10 to -14‰; Farquhar et al., 1989; Cerling et al., 1993). C4 plants in estuarine watersheds include corn crops and a number of saltwater marsh plants (e.g. *Spartina alterniflora*). Carbon concentrating mechanisms for carbon fixation in phytoplankton overcome diffusion limitation in an aqueous environment and result in intermediate isotopic signatures to C3 and C4 material (~ -18 to -24 ‰; Fry and Sherr, 1984).

Enzymatic specificity dominates isotopic fractionation in plants, but inorganic carbon source and supply also have an isotopic effect. Terrestrial C3 plants use atmospheric CO_2 as the source of inorganic carbon for fixation, but aquatic C3 plants such as phytoplankton use dissolved CO_2, which is slightly enriched due to diffusion across the air-water interface. A limited supply of inorganic carbon also increases isotopic fractionation, resulting in a gradual depletion of ^{13}C OM signatures. This is relevant because as a phytoplankton bloom evolves, it becomes gradually depleted (e.g. Fogel et al., 1992), and an OM sample entirely comprised of phytoplankton with a depleted signature could be misinterpreted as an increase in the proportion of depleted C3 OM.

Bulk isotopic signatures are the average of all OM contributions, which effectively masks inputs from smaller contributors to the overall pool (e.g. Cloern et al., 2002; Cifuentes et al., 1988; Mannino and Harvey, 1999; Sikes et al., 2009).

Furthermore, overlapping isotopic signatures confound source identification because a mix of terrestrial C3- and C4- derived carbon yields the same isotopic signature as marine plankton. Although bulk analyses such as these provide a primary assessment of broad OM source distributions, tracing sources through coastal systems requires more specific source information.

2.2 Biomarkers

> " 'Life is a continual battle to maintain a state of order in a Universe that runs towards disorder. Living systems keep climbing the entropy gradient by obtaining energy from sunlight and food: Life 1, Second Law of Thermodynamics 0….except that the game goes into extra time and the Law gets everything in the end' (Foster and Kreitzman, 2005; Rhythms of Life, p. 97). Ah! Yes,…..but some of it spends a very long time getting there. A few hardy biomolecules remain in the sedimentary record-persistent ghosts of past life-these provide our biomarker or molecular proxies for paleoclimatology! Like radionuclides, they are often present as mere vestiges of former glory-but still with information to give," (Eglinton and Eglinton, 2008).

Biomarkers are compounds that are biosynthesized by a specific organism or class of organisms and persist so they can be traced through an environment. Compound classes of differing reactivities (e.g. amino acid, carbohydrate, and lipid classes) examine the source and fate of OM in a variety of aquatic environments (e.g. Uhle et al., 2007; Mannino and Harvey 2000; McCallister et al., 2006). Biomarkers need to be source-associated, and the "shelf-life" of a biomarker should reflect the process of interest (e.g. Volkman et al., 1998). Biomarker based investigations provide information regarding the origins and fate of OM through coastal systems when and where bulk methods are insufficient (e.g. Mannino and Harvey, 1999).

Two lipid classes of biomarkers of differing reactivities were assessed for this thesis work: *n*-alkanes (alkanes) and phospholipid-linked fatty acids (PLFAs). Resistant to degradation, alkane lipid biomarkers provide a direct tracer of OM pathways through

the environment. In contrast, PLFAs break down within days of cell death, providing a snapshot of viable OM in space and time (Eglinton and Eglinton, 2008; Boschker and Middelburg, 2002).

2.2.1 Alkanes and source indices

Alkanes are straight-chain hydrocarbon lipids synthesized by all plants, but their carbon chain length distributions differ among sources (Figure 2-1a). Using compounds from a single homologous series of alkanes allows direct comparison of terrestrial and algal inputs. Strong covalent bonds between the carbon and hydrogen atoms require specific enzyme activities for breakdown (Eglinton and Eglinton, 2008), making this class of biomarkers useful for tracing sources through coastal environments.

Algal and vascular plant alkanes are distinct in their chain length distributions, but other sources of OC have intermediate or overlapping alkane signatures (Figure 2-1b). Alkanes in terrestrial plants are epicuticular leaf waxes (e.g. Eglinton and Hamilton, 1967) and are biosynthesized by decarboxylation of even-numbered long carboxylic acids ($> C_{24}$, where the subscript designates the number of carbon atoms), resulting in a distinctive odd-chain-length carbon preference in terrestrial plants (Bianchi and Canuel, 2011). In contrast, algal alkanes are shorter ($C_{15\text{-}25}$), and lack an odd-over-even preference. Macrophytes have mid-chain length alkanes with an odd-over-even chain length preference ($C_{23\text{-}29}$; Ficken et al., 2000; Mead et al., 2005) and petroleum-derived alkanes are mid-chain-length without an odd-over-even preference.

Alkane summary indices take advantage of the differences in the chain lengths preferentially made by different plant types to estimate sources. The Average Chain Length (ACL) is the numerical average of chain length distributions between 16 and 34

A.

B.

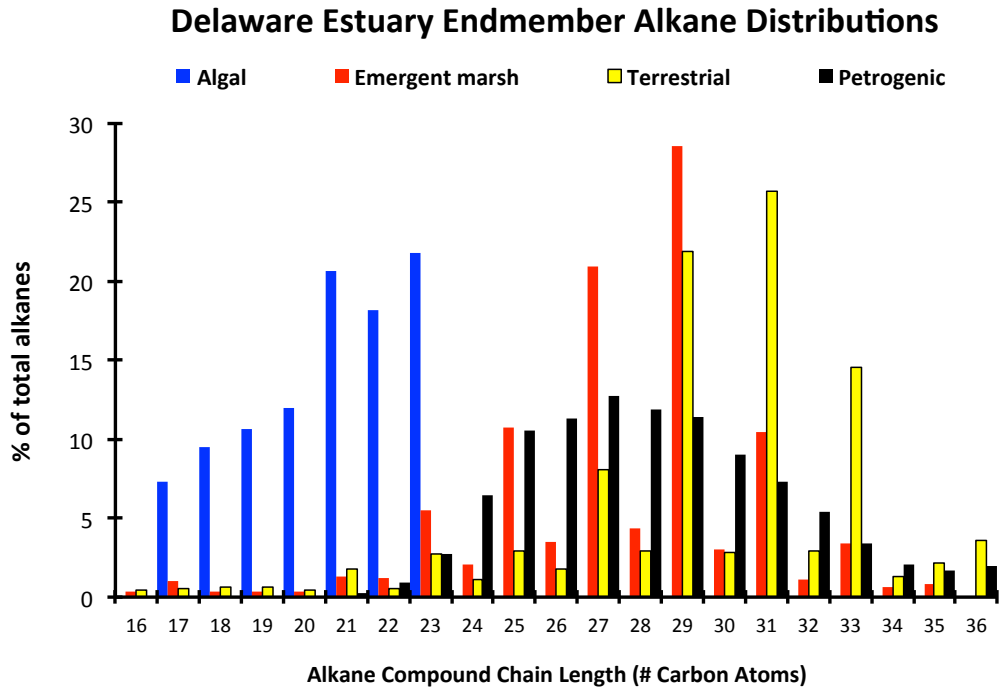


Figure 2-1. *N*-alkane (alkane) biomarkers are source-specific. A) An epicuticular terrestrial plant wax alkane, nonacosane (C_{29}; Eglinton and Hamilton, 1967). B) Delaware Estuary alkanes from different sources to illustrate endmember distributions. Alkanes were normalized for inter-comparison: microalgal (algal) alkanes are from the Delaware Bay phytoplankton bloom in June 2010 (blue), terrestrial vascular plant material is represented by alkanes from the riverine endmember in December 2010 (yellow), emergent marsh alkanes are represented by alkanes from *Phragmites australis* (red), and petroleum-derived alkanes are from a contaminated laboratory blank sample (black).

of a sample's alkanes. Higher ACL indicates a larger proportion of long alkane chain lengths, indicative of vascular (terrestrial) plant sources, and lower ACL indicates more algal OM. The Carbon Preference Index (CPI) is the numerical measure of the of odd-over-even chain alkane in a sample. Although vascular plant material has an odd-over-even chain length predominance, whereas algal and petrogenic sources do not. A CPI over 2 has been widely used to characterize terrestrial-derived OM (e.g. Chikaraishi and Naraoka, 2003; Tipple and Pagani, 2010; Sikes et al., 2009).

Although useful, these indices do not adequately account for sources of OM when marsh inputs are significant. More recently, a new index, $P_{mar\text{-}aq}$ assesses the relative contributions of wetland and terrestrial sources of OM, such that low values (<0.1) are from terrestrial OM, mid-values are from emergent macrophytes (0.1-0.4), and higher values (0.4-1) are from submerged/floating macrophytes (Ficken et al., 2000; Sikes et al., 2009). In combination, indices such as these can use the distinguishing features of an alkane homologous series to detect and the proportion of sources comprising a sample.

2.2.2 Phospholipid-linked fatty acids

Phospholipid-derived fatty acids (hereafter PLFAs) are constituents of cellular membranes and are comprised of a phosphate and glycerol "head," ester linked to fatty acid tails (Figure 2-2). In contrast to the persistence of alkane covalent bonds in the environment, the ester linkage between the PLFA hydrophilic head and fatty acid tails is rapidly turned over within cells, and degrades quickly upon cell death. Due to the rapid degradation and loss of these fatty acids, they reflect recent or current processes in the water column or sediments, and act as markers of viable biomass (Boschker and Middelburg, 2002).

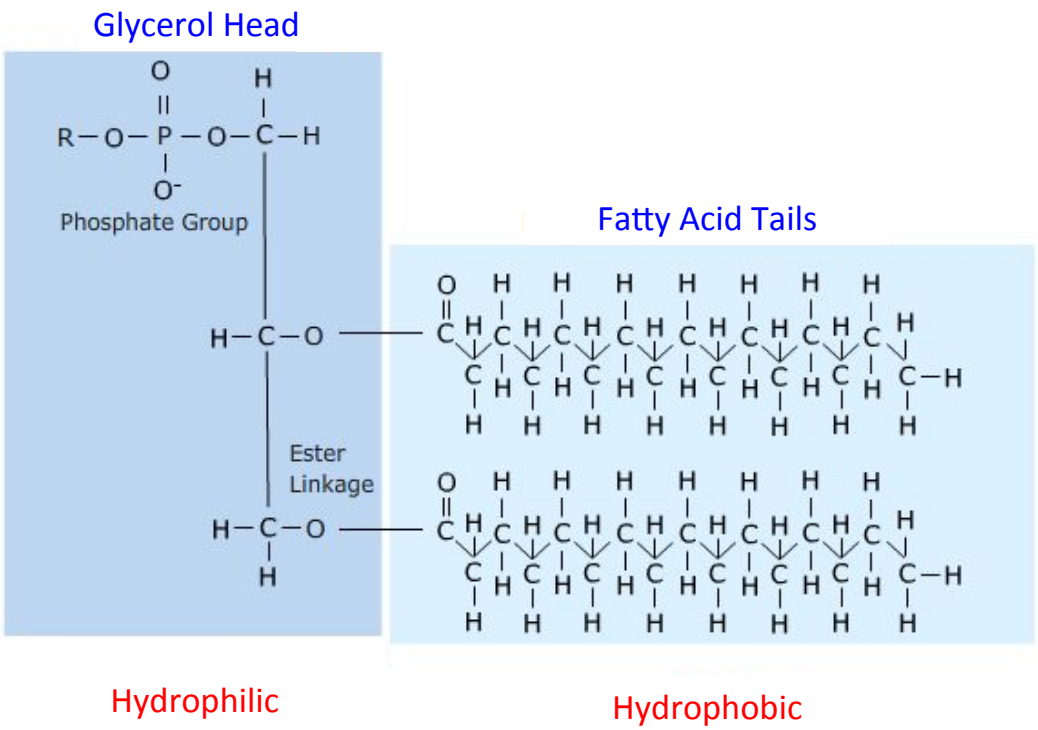


Figure 2-2. Generalized structure of phospholipid fatty acid. The glycerol head is hydrophilic, whereas the phospholipid-linked fatty acid tails are hydrophobic. Saponification frees ester linked fatty acid tails for phospholipid-linked fatty acid (PLFA) biomarker analyses.
(Figure redrafted from: http://telstar.ote.cmu.edu/biology/MembranePage/index2.html).

Similar to *n*-alkanes, PLFAs have source-specific characteristics. These are: the degree and placement of fatty acid unsaturation, the number and placement of side chain branches, and carbon chain length (Table 2-1). Assessing the relative proportions of PLFAs with source specificity provides information about the viable organic matter source at a given location and time (Bianchi and Canuel, 2011; e.g. Dijkman and Kromkamp, 2006; Zimmerman and Canuel, 2001).

2.3 Compound-specific isotope analysis (CSIA)

Overlapping source signatures dull the usefulness of bulk isotope measurements and alkane biomarker distributions to determine OM sources in coastal environments (e.g. Figure 2-1b). Compound-specific stable carbon isotopic analysis (δ^{13}C-CSIA) provides additional specificity to estimate the sources, processing, and fate of OM (e.g. Sikes et al., 2009; Uhle et al., 2007; Bianchi et al., 2011). δ^{13}C-CSIA detects the relative proportion of carbon isotopes in single compounds (Hayes et al., 1989), and the isotopic composition of an individual compound reflects its dominant source of origin. Using two-endmember mass-balance mixing models, the relative proportions of sources can be calculated, and this method is especially useful for tracing the relative proportions of C3 and C4 plant material in coastal systems. For example, Bianchi et al. (2011) used the isotopic composition of plant-derived lignin biomarkers to reveal the relative proportions of C3 riverine- and C4 marsh-derived terrestrial OM in the Gulf of Mexico, and Tanner et al. (2007) used CSIA of alkanes to trace marsh migrations as a result of sea-level change from the late Holocene to the present. As with other geochemical methods, alkane CSIA requires endmember evaluation to best characterize endmember values for mixing models (e.g. Canuel et al., 1997; Chikaraishi and Naraoka, 2003).

Table 2-1. Sources of organic matter relevant to this study and their respective phospholipid-linked fatty acids (PLFAs). PLFA nomenclature is such that the first number reflects the number of carbon atoms, followed by the number of double bonds in the fatty acid. The "*ω*" describes the position of the double bond from the aliphatic end of the fatty acid; "*c*" and "*t*" refer to *cis*- and *trans*- double bonds, respectively; "*i*" and "*a*" refer to *iso*- and *anteiso*- branched fatty acids, respectively, "*n*" refers to saturated straight chain fatty acids, with "C" number of carbon atoms.

General Source	Group	PLFA
Bacterial	Mainly *Cytophaga-Flavobacteria* and Gram positive[2]	i14:0, i15:0, a15:0, i16:0
	Mainly Gram-negative *Proteobacteria*[2]	18:1ω7*c*
	General bacteria indicator[3]	∑ branched PLFAs
Algal	Green algae (*Chlorophycaea*)[2]	18:2ω6, 18:3ω3, 18:4ω3
	Diatoms[1,2]	16:1ω7; 16:0, 14:0, 20:5ω3, 22:5ω3
	Dinoflagellates[1]	16:0, 18:5ω3, 22:6ω3
	Labile 'fresh' organic matter[3]	∑ polyunsaturated PLFA (PUFA)
Animal[1]	Non-specific	16:0, 18:0, 18:1ω9
Terrestrial[1]	Non-specific	> *n*-C_{20}

1- Canuel et al., 1995; Table 3
2- Boschker et al., 2005; Table 1
3- Zimmerman and Canuel, 2001; Table 2

III. METHODS

3.1 Sample collection in the Delaware Estuary

Eight 3-day cruises aboard the RV *Hugh Sharp* were conducted on the Delaware River and Estuary as part of an NSF-funded project to examine sediment sources, transport, and fluxes, co-PI'ed by Drs. Robert Chant (Rutgers University) and Chris Sommerfield (University of Delaware). The cruises consisted of a replicated axial transect in the main channel of the estuary from a marine endmember station (~14 km from the mouth of Delaware Bay in the Atlantic Ocean; Station 1) to a riverine endmember station (approximately Trenton, New Jersey; Station 22; Figure 1-2; Table 3-1). This thesis work examined five of the eight cruises, spanning one annual cycle: March 10-11, 2010, June 3-4, 2010, September 12-13, 2010, December 13-14, 2010, and March 21-22, 2011 (Appendix 1).

As part of the sediment transport project, *in situ* CTD casts at each station measured depth profiles of conductivity, temperature, pressure, pressure, fluorescence, optical backscatter, and on most cruises, nitrate and oxygen saturation. *In situ* measurements mapped 2-dimensional axial "snapshots" of the estuary and provided context for the collection of samples for parallel geochemical analyses. Water column samples for geochemical analyses were collected at ~11 of the 22 stations, and of these, samples for biomarker analyses included the geographically fixed marine and riverine endmembers (Stations 1 and 22, respectively) and locations of chemical interest mapped by the *in situ* CTD casts: the chlorophyll maximum, turbidity maxima, and/or locations with high salinity stratification. After the axial transect was conducted on each cruise, sediment cores were collected spanning the estuarine turbidity maximum.

Table 3-1. Delaware Estuary sampling stations, replicated each cruise. * - Landmark notated by C. Sommerfield (University of Delaware).

CTD/Water sampling station	Latitude (N)	Longitude (W)	Distance from Estuary Mouth (km)	Landmark
1	38.7820	-74.9286	-14	FB Buoy*
2	38.8575	-75.0526	0	Delaware Bay mouth
3	38.9398	-75.1066	10	10 Buoy*
4	39.0330	-75.1575	22	widest cross-section of Delaware Bay
5	39.1165	-75.2142	32	25 Buoy*
6	39.1786	-75.2698	40	6R Buoy*
7	39.2484	-75.3200	48	Bombay Hook
8	39.3047	-75.3846	57	Ship John Shoal*, Cohansey R.
9	39.3550	-75.4423	65	6L Buoy*
10	39.4018	-75.4973	72	Cedar Swamp
11	39.4481	-75.5515	78	Below Artificial Isl.
12	39.5147	-75.5521	86	Above Artificial Isl., Reedy Isl.
13	39.5671	-75.5486	92	C&D Canal
14	39.6227	-75.5787	98	Killcohook Confined Disposal Facility (CDF)
15	39.6806	-75.5214	107	near DE Mem. Br.*, below Christina R.
16	39.7635	-75.4781	116	Pedricktown CDF, Oldmans Creek
17	39.8116	-75.4034	125	Marcus Hook Range*, Commodore Barry Br.
18	39.8486	-75.2965	135	3T Buoy*, Tinicum Isl.
19	39.8808	-75.1923	145	Schuylkill R.*
20	39.9709	-75.1112	157	Petty Island*
21	40.0391	-74.9896	169	Rancocas R.*
22	40.0826	-74.8638	181	Rt. 276 Bridge*
23	40.1484	-74.7225	195	Crosswicks Creek near Trenton*

At the ~11 stations for geochemical analyses, water column samples were collected from approximately 1m below the surface and ~1 meter above the bottom at with an *in situ* pump. Large volumes of surface and bottom water (6-60 L) were filtered through multiple precombusted (500°C for 4-5 hours) 47mm Whatman GF/Fs (0.7μm) to collect particulate organic matter (POM) for biomarker analyses. Lower sample volumes were filtered at stations with high particle loads and higher sample volumes were filtered at the marine and riverine endmembers to ensure sufficient recovery of the target compounds. Subsamples (~50-1000 mL) of the large volume samples were filtered through 0.7μm GF/Fs for bulk geochemical analyses. All filters were stored in precombusted aluminum foil, and then frozen at -20°C until analyses.

Shipboard scientists from the University of Delaware collected samples for suspended solid content (SSC) measurements. Water samples (100-400mL) for SSC were filtered through pre-weighed Whatman Nuclepore Polycarbonate 1.0 μm filters (Fisher), dried for ~24 hours, and then re-weighed. The pre-weight was subtracted from the post-weight, and then was divided by the filtered volume to calculate SSC (mg/L).

In addition to the water samples collected, ~5 sediment cores were collected on each cruise (except June 2010) in the upper- to mid-estuary. Sediments were cored using a KC Denmark HAPS Bottom Corer, which maintains the sediment-water interface. Sediment cores were brought on board and sampled immediately by first collecting floc with a syringe, and then extruding 1cm core increments and slicing with spatulas. Sediment samples were stored in precombusted glass jars and frozen at -20°C until analyses. Three cores from three cruises (March and September, 2010 and March, 2011) were selected for analyses (Table 3-2). Where possible, sediments were selected for this

Table 3-2. Delaware Estuary sediment cores analyzed for this thesis.

Season (Cruise)	**Core (Water Station)**	**Latitude (N)**	**Longitude (W)**	**Time**	**Core-top Description**
March 2010 (100310)	8H-B (15)	39.6641	-75.5392	10:50 EST	dark brown mud
	13H (12)	39.5093	-75.5495	13:50 EST	sand to mud
	20H-B (9)	39.3668	-75.4792	16:00 EST	dense dark mud
September 2010 (100912)	23H-B (17)	39.8072	-75.3995	22:05 EDT	substantial floc, sandy
	25H-B (15)	39.6738	-75.5307	00:17 EDT	soft mud
	26H-B (12)	39.5427	-75.5353	02:05 EDT	sandy/course
March 2011 (110321)	32A (17)	39.8065	-75.4005	02:05 EDT	sandy/firm/to clay
	34B (15)	39.6745	-75.5288	02:05 EDT	lots of particulate matter, dense crumbly surface, quick transition to rust color
	35A (9)	39.3538	-75.4568	02:05 EDT	light brown mud to dark grey/black

study by the following characteristics: position relative to the ETM, sites that were revisited repeatedly throughout the study period, and observed transition zones down-core.

3.2 Bulk POM measurements

Water column subsamples were analyzed for bulk POM analyses including total organic carbon, total nitrogen, and bulk-$\delta^{13}C$ on a continuous flow isotope ratio mass spectrometer (GVI Isoprime coupled to a Eurovector EA). Prior to analysis, filters were freeze-dried, weighed, and acidified by fuming with concentrated HCl for at least 24 hours. Acidified samples were ventilated for at least 24 hours before drying overnight at 40-60°C after which filters were homogenized using a mortar and pestle, and 1 – 20 mg of sample was loaded into tin capsules for analysis. Blank filters and blank capsules were subtracted as background from samples.

Total organic carbon and total nitrogen concentrations were calculated based on acetanilide standard curves, which were generated for each sample run (CN Standard, CAS No. 103-84-4). Sample reproducibility was determined by running sample replicates on each analysis day, as well as between analysis days, and was ± 7.94% and ± 9.40% for total organic carbon and total nitrogen, respectivley (average coefficient of variation).

The stable carbon isotope composition of POM was reported in delta-notation (δ; in per-mil, or parts per thousand, ‰) with respect to a standard reference material using the following equation:

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

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, *standard* refers to the ratio of a reference gas. More positive delta-values are "enriched" in the heavy isotope, while more negative delta-values are "depleted" in the heavy isotope. Samples were related to Pee Dee Belemnite (PDB) using NIST Standard 8539 NBS22 (oil) as follows:

$$\delta^{13}C = \delta^{13}C_{sample} - (\delta^{13}C_{oil} + 30.03)$$

Instrument variability (average standard deviation) was assessed using a laboratory reference standard, Taughannock Light, and was 0.06‰. Sample reproducibility for $\delta^{13}C$-POM was ± 1.44% (average coefficient of variation).

3.3 Biomarker extraction and separation

Solvent extraction and wet-laboratory chemical clean-up methods isolated biomarkers from selected POM and sediment samples (Figure 3-1). POM and sediment samples were prepared for solvent extraction using an Accelerated Solvent Extractor (ASE) by first freeze-drying, after which sediments were homogenized using a mortar and pestle whereas POM filters were torn into small pieces. Samples were loaded into *Dionex* ASE cells in the following order from the base of the cells: 0.7µm GF/F filter (25mm), ~500mg CN sorbent (Supelco Discovery SPE normal CN phase), 0.7µm GF/F, ~1 cm Ottawa sand (Fisher Scientific), sample (sediment, or filter pieces), internal recovery standard (nonadecanone). Remaining top space was filled with Ottawa sand.

Alkane and phospholipid fatty acid lipid biomarker classes were ASE extracted using a two-step extraction method modified after Poerschmann and Carlson (2006). Samples in ASE cells were extracted first with hexane (50°C, 800-1000psi) to target

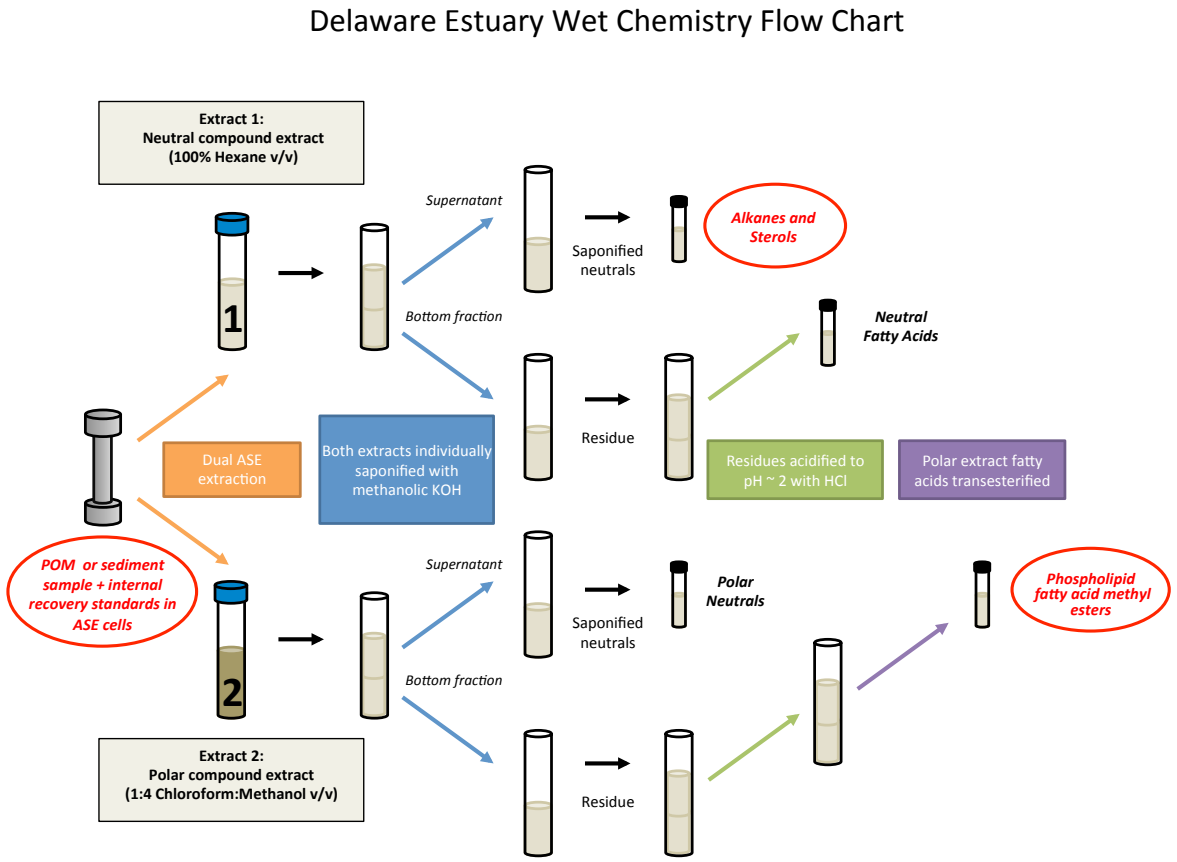


Figure 3-1. Delaware Estuary POM and sediment sample wet chemistry flow chart for biomarker extraction and separation. Steps are color-coordinated with arrows as follows: orange – dual-ASE extraction, blue – extract saponification separating neutral and polar lipids, green – acidification of residue fatty acids for both extracts, purple – transesterification of polar extract fatty acids for resultant phospholipid fatty acid methyl esters.

nonpolar alkanes (Extract 1), and then were re-extracted with chloroform-methanol (1:4 v/v; 110°C, 800-1000psi) to target phosopholipid-linked fatty acids (Extract 2). Both extractions had two ten-minute static cycles. The extraction protocol above was used for all samples except for March and June 2010 POM samples, which were extracted by an ASE method modified after Sikes et al. (2009). These samples were first extracted in hexane, and then were re-extracted with chloroform-methanol (3:1 v/v; 150°C, 1000psi), and both extractions had three ten-minute static cycles. For all samples, half of each total lipid extract was archived.

After lipid extraction, a series of wet chemical techniques separated compound classes of interest for identification and quantification (Figure 3-1). First, half of each total lipid extract (1 and 2) was saponified to separate neutral compounds (including alkanes) from fatty acids, following the methods of Sikes and Volkman (1993). Briefly, both extracts were dried, brought up in 5% KOH in methanol-water (80:20 v/v), and incubated at 80°C for two hours. The reaction was quenched with Milli-Q water, and then the neutral fraction was partitioned into hexane-dichloromethane (4:1 v/v) with 3 washes. The neutral fraction from Extract 1 was retained for alkane biomarker analysis. The remaining total fatty acids of both extracts were acidified to pH ≈ 2 using concentrated HCl and then were drawn off three times in hexane-dichloromethane (4:1 v/v). The polar phospholipid fatty acids from Extract 2 were subsequently transesterified to fatty acid methyl esters (FAMEs) using methanol-HCl-dichloromethane (10:1:1 v/v) of a known carbon isotope composition and heated at 80°C for two hours. The reactions were quenched with Milli-Q water and FAMEs were extracted with hexane-dichloromethane

(4:1 v/v). Sulfur containing compounds were removed from sediment lipid extracts by adding granular copper to samples and incubating at room temperature >15 min.

3.4 Organic biomarker identification and quantification

Biomarkers were identified and quantified on a Shimadzu GC-2010 gas chromatograph coupled to a Shimadzu GCMS-QP2010 mass spectrometer using helium as the carrier gas. Samples were injected onto a Shimadzu SHR5XLB 30 m column with a 0.25 mm internal diameter and 0.25μm thickness. For all biomarker analyses, the GCMS injector was at 300°C, the MS ion source was set to 240°C, and injection was in splitless mode for one minute before a split ratio of 4 was applied.

Neutral fractions (Extract 1, saponified neutrals) were run with a temperature program of 45°C held isothermal for 0.5 min at injection, then 30°C/min to 140°C and then 3°C/min to 320°C and held isothermal for 10 min. The GC column flow was set to 1.70 mL/min. A homologous series of alkane biomarkers were identified based on relative retention times compared to an external aliphatic hydrocarbon standard (DRH007S PAK, AccuStandard), and mass spectrum analysis of the mass 85-ion fragment, the molecular ion, and other major ion fragments. Phospholipid fatty acids (PLFAs) were run on the GCMS with a temperature program of 100°C held isothermal at injection, then 30°C/min to 110°C, and then 3°C/min to 280°C and held isothermal for 10 min. The GC column flow was set to 1.61mL/min. PLFA biomarkers were identified based on relative retention times compared to an external Supelco 37 Component FAME mix standard (47885-U) as well as mass spectrum analysis of major ion fragments.

Alkanes were quantified using both external and internal standards. External standard curves using an aliphatic hydrocarbon standard (DRH007S PAK, AccuStandard)

were run periodically throughout the analysis period to account for instrument response variability. Since the instrument response was not linear across the aliphatic hydrocarbon homologous series, response slopes were calculated for each alkane (Figure 3-2). Responses for alkanes not in the aliphatic hydrocarbon series (red points in Figure 3-2) were calculated based on either an average of the two nearest alkanes (i.e. C_{21} was calculated as the average between C_{20} and C_{22}), or by a linear fit between C_{30} and C_{36} alkanes. The percent recovery of each compound was calculated comparing the peak area of the nonadecanone internal recovery standard in a run to the known concentration of standard added to the sample prior to extraction. PLFA fractions lacked an IRS for percent recovery calculations. Instead, FAMEs abundances were reported as a percentage of the total FAMEs in each sample.

3.5 Biomarker indices

Alkane indices were calculated for each sample, and included the carbon preference index (CPI), average chain-length (ACL), and $P_{mar\text{-}aq}$. The CPI is a measure of the predominance of odd- vs. even-numbered carbon chain lengths, and was calculated after Sikes et al. (2009) using the following equation:

$$CPI = \frac{\sum odd\ chain\ length\ alkanes\ (C_{16} - C_{34})}{\sum even\ chain\ length\ alkanes\ (C_{17} - C_{35})}$$

A CPI greater than 2 was considered "terrestrial-derived," as CPI approaches 1, material reflects more marine or petrogenic sources.

The ACL was calculated modified after Sikes et al. (2009) using the following equation:

$$ACL = \frac{\sum[C_i]\times i}{\sum[C_i]}$$

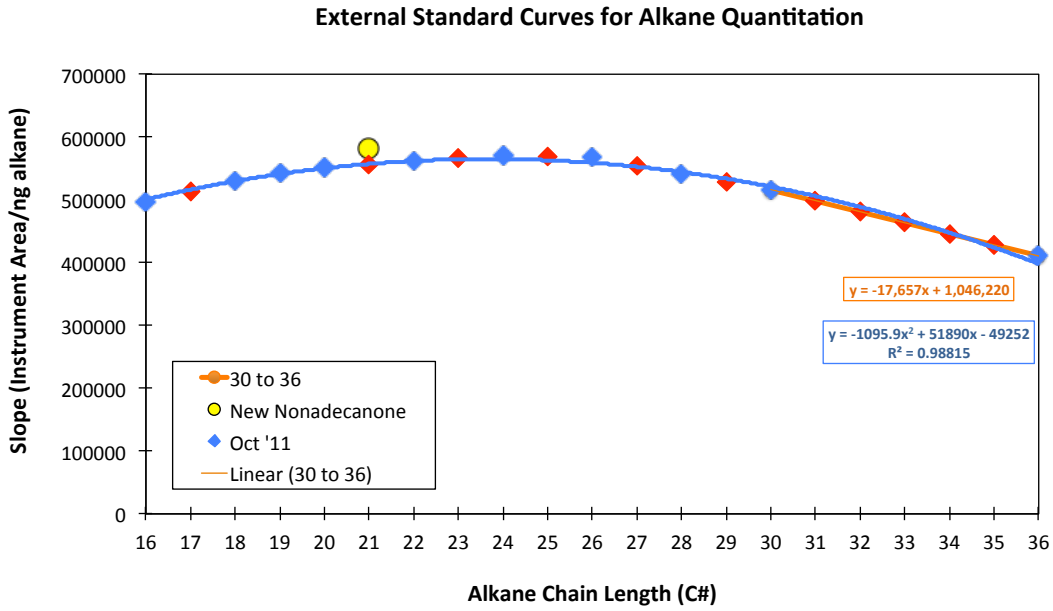


Figure 3-2. The GCMS instrument response per ng alkane for each alkane chain length in the homologous series used in this study (C# C_{16}-C_{36}). External standard curves were generated using an aliphatic hydrocarbon standard throughout the period of study (October 2011 shown in blue). As the standard mix does not include all alkanes between C_{16}-C_{36}, responses for the red points were calculated using an average of nearest points, or the linear equation depicted in orange between C_{30}-C_{36}. The yellow circle is the response for an external nonadecanone standard curve measured in March 2012 and shows similar instrument response across the period of study.

where *i* is the carbon numbers 16 – 34 and C_i is the concentration of each alkane. Using this series of alkanes, the average carbon chain length was C_{26}. Thus, ACL greater than 26 indicated predominance of "terrestrial-derived" material, and ACL less than 26 indicated predominance of marine or petrogenic material.

Lastly, the $P_{mar\text{-}aq}$ index signifies the relative influence of terrestrial, emergent macrophyte, and submerged/floating macrophyte sources. The $P_{mar\text{-}aq}$ was calculated after Sikes et al. (2009) as follows:

$$P_{mar-aq} = \frac{C_{23} + C_{25}}{C_{23} + C_{25} + C_{29} + C_{31}}$$

A $P_{mar\text{-}aq} < 0.1$ signifies terrestrial plant inputs, while 0.1 – 0.4 is characteristic of emergent macrophytes, and 0.4-1, submerged/floating macrophytes (Ficken et al., 2000; Sikes et al., 2009).

PLFA indices determined the relative proportions of labile OM, vascular plant-derived OM, and bacterial OM. The sum of polyunsaturated PLFAs (PUFAs) with chain lengths C_{16}, C_{18}, C_{20}, C_{22} is indicative of the relative proportion of labile algal OM (Palomo and Canuel, 2010). This index, hereafter called the 'Fresh' PLFA index, was modified by subtracting the $C_{18:2}$ and $C_{18:3}$ PUFAs from the total PUFAs because these compounds are detected in a high proportion in wetland plants (Canuel et al., 1997). The sum of even saturated long chain PLFAs is indicative of higher plant OM (C_{24} –C_{28}; Palomo and Canuel 2010), and is hereafter called the 'Terr' PLFA index. The sum of branched C_{15} and C_{17} PLFAs is indicative of the relative proportion of general bacterial biomass (Zimmerman and Canuel, 2001; Arzayus and Canuel, 2004), and is hereafter called the 'Bac' PLFA index. The TAR_{FA} index is the ratio of terrestrial and algal-derived PLFAs and is the sum of even numbered saturated long chain PLFAs over the sum of

even numbered saturated short chain PLFAs (Meyers, 1997; Waterson and Canuel, 2008):

$$TAR_{FA} = \frac{C_{24} + C_{26} + C_{28}}{C_{12} + C_{14} + C_{16}}$$

3.6 Compound-specific isotope analysis of n-*alkanes*

Additional clean-up methods were necessary to isolate alkanes for CSIA analysis. Isolation of alkanes in the neutral fraction from Extract 1 used in-cell sequential ASE extraction elution after Magill and Freeman (*submitted*, 2012). Chromatography columns were constructed within *Dionex* ASE extraction cells, and then compounds of interest were sequentially eluted using 3 solvent mixtures. The first two extractions (hexane-DCM 95:5 and 72:25, v/v) were conducted with three 5-min static cycles at 50°C and 500psi. The ASE cells were manually flipped, and then the third extraction (DCM-methanol 50:50, v/v) was conducted with three 5-min static cycles at 100°C and 500psi. A homologous series of *n*-alkane biomarkers elutes in the first extract of this scheme. GCMS runs alkane isolation and abundances prior to compound-specific isotope analysis.

Compound-specific stable carbon isotope analysis (CSIA) of *n*-alkanes was conducted at Pennsylvania State University in Dr. Kate Freeman's laboratory. Samples were run on a *Finnigan* MAT 252 stable-isotope-ratio mass spectrometer equipped with a dual inlet, multiple collector assemblies, and a Varian model 3400 GC combustion interface. Compound separation on the GC was in splitless mode using helium as the carrier gas and a fused silica column (Agilent J&W DB-5; 30 m x 0.32 mm i.d., 0.25 μm film thickness). The GC injector was initially at 319°C for 1.5 min and then was held isothermal at 320°C. The GC program was as follows: 60°C for 1.5 min, 60-200°C at

15°C per minute, and then 200-320°C at 6°C per minute and held for an additional 1 min. After separation, compounds were combusted over nickel and platinum with oxygen in helium at 1000°C and the resulting CO_2 was passed on to the *Finnigan* MAT 252 for carbon isotopic composition determination. Samples were run in duplicate and isotopic values were reported in delta notation relative to Vienna Pee Dee Belemnite (VPDB) as determined for bulk carbon isotopes.

Samples were run in duplicate were reported in delta notation relative to Vienna Pee Dee Belemnite (VPDB). Low abundances of some compounds in samples prevented duplicate analysis, but otherwise, CSIA values were reported as the average of duplicate runs. Samples were related to VPDB using an external laboratory standard mixture of 15 alkanes (Mix A) with known $\delta^{13}C$ values relative to the standard determined by Arndt Schimmelman (Indiana University) via offline pyrolysis and dual-inlet analysis. Mix A was run in triplicate prior to and after samples to account for any drift during a given period of sample runs. A linear regression between the actual Mix A values and the measured Mix A values corrected measured sample values. Precision in isotope determinations for alkanes was ±0.19‰ (average of Mix A standard deviations). Duplicate sample runs had ±1.5% variation (average coefficient of variation).

3.7 Statistical data analysis

A two-tailed, two-sample unequal variance t-test was performed in *Excel* to test for significant spatial or seasonal differences in geochemical parameters. P-values less than 0.05 were considered significant.

IV. RESULTS

4.1 Physical parameters in the Delaware Estuary

The 5 cruises presented in this thesis sampled the estuary across one annual cycle (March, June, September, December 2010 and March 2011). The cruises exhibited a wide range of conditions from hydrologic discharge, suspended solid content, salinity, temperatures, and phytoplankton blooms, against which to assess the spatial and seasonal variation of POM sources and fates.

4.1.1 Delaware River discharge

Discharge from the Delaware River controls sediment delivery and mixing within the Estuary (e.g. Sharp et al., 1986; Sommerfield and Wong, 2011). To assess the effect of this on carbon content, Delaware River discharge for 2010 and 2011 was compared to the interquartile range of Delaware River discharge from 1913 through 2011 (Figure 4-1). Discharge in 2010 was low to average from May to October, whereas fall and winter discharge was near the long-term average, punctuated by storm-driven flows (maximum 2,568 m^3/s, October 2, 2010). In contrast, Delaware River discharge in 2011 was consistently higher than the seasonal median, except during January and February. The highest discharge in 2011 was 4,870 m^3/s, which followed Hurricane Irene (August 24-30, 2011) and Tropical Storm Lee (September 2-5, 2011). This discharge was in fact one of the top 10 discharge events since 1913. The contrast in Delaware River hydrographs between 2010 and 2011 suggests the geochemical results of this study assessed normal to dry conditions of the estuary in 2010 and wet conditions in 2011.

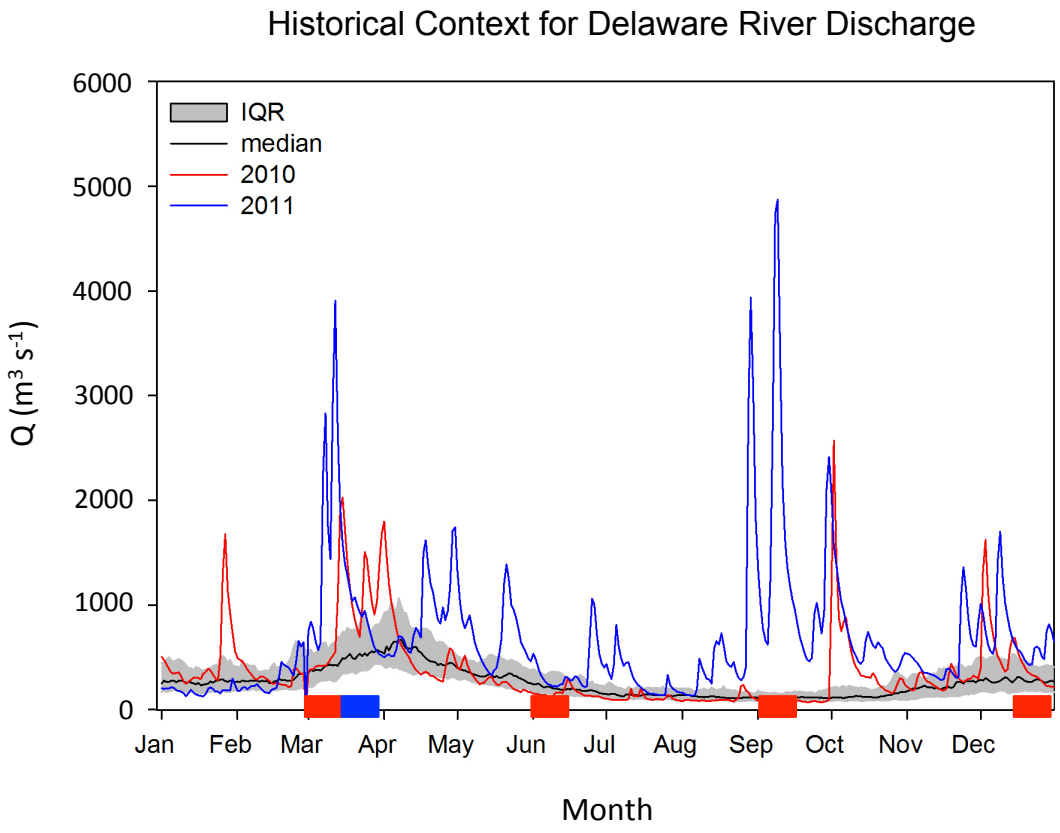


Figure 4-1. Historical context for Delaware River discharge during this study. The interquartile range (IQR; 25th- 75th percentiles) was calculated using Delaware River discharge data (Q) from 1913 – 2011 (USGS). Discharge for 2010 is in red, while 2011 is in blue. Cruises included in this thesis are indicated with colored bars on the x-axis that are color-coordinated to discharge years. Note the average to low discharge during 2010 and high discharge of 2011. Figure courtesy of R. Barnes.

The five cruises sampled occurred at a range of discharges. Discharge was averaged for the week prior to the first day of each cruise and ranged from 82 m^3/s for the September 2010 cruise to 1,303 m^3/s for the March 2011 cruise (Figure 4-2). March 2010 sampling was at the beginning of the spring freshet and was followed by a very dry summer ending with a storm event in early October. The December 2010 cruise followed a winter storm event, and the March 2011 cruise occurred after another storm event at the beginning of the spring freshet and had the highest discharge rate of the sampling cruises. March 2010 and March 2011 cruises thus sampled highly contrasting spring flow regimes.

4.1.2 Salinity, chlorophyll, and turbidity

Salinity stratification in the estuary varied with river discharge. Saltwater intrusion generally reached ~125 km up-estuary, however, some saltwater intrusion was detected 145 km up-estuary during the September 2010 cruise after low summer discharge (Figure 4-3, Appendix 2). The greatest freshwater extent and lowest salinity in the estuary was observed during the March 2011 cruise. Maximum stratification observed was during the December 2010 cruise, which had a difference in salinity between bottom and surface water of 11.7 PSU in Delaware Bay. Otherwise, Delaware Bay was well mixed in September 2010 and March 2011, and was moderately stratified (~7.5 PSU) in March and June 2010 (Figure 4-3).

In situ CTD casts at each of the 23 sampling stations along the estuary measured fluorescence and oxygen saturation, proxies for phytoplankton productivity. High fluorescence and oxygen saturation in Delaware Bay during March 2010, March 2011 and June 2010 cruises indicated active phytoplankton productivity (Figures 4-4 to 4-7).

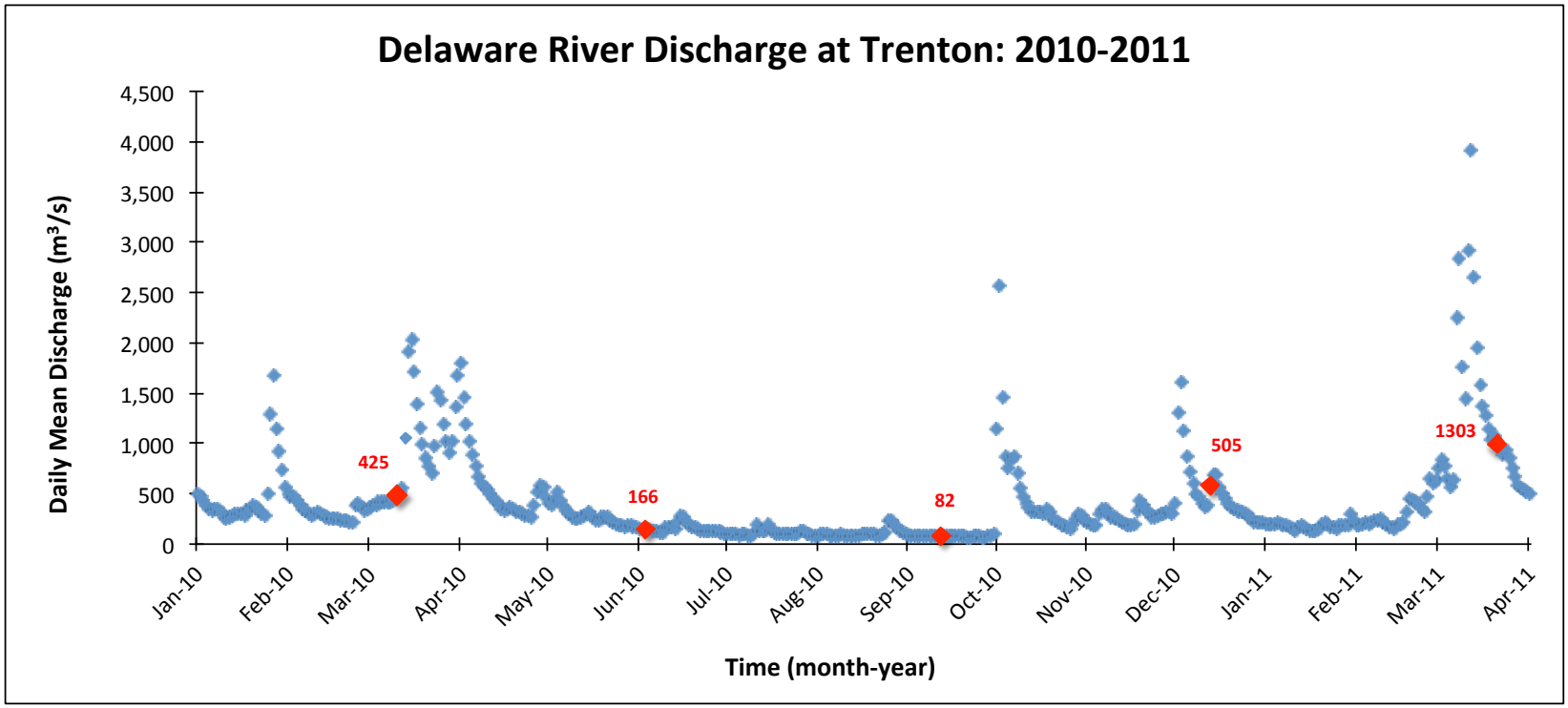


Figure 4-2. Delaware River discharge measured at Trenton, NJ during the study period. Red diamonds indicate the first day of each cruise included in this thesis, and red numbers are the average discharge (m^3/s) for the week prior to each cruise. Data is from USGS.

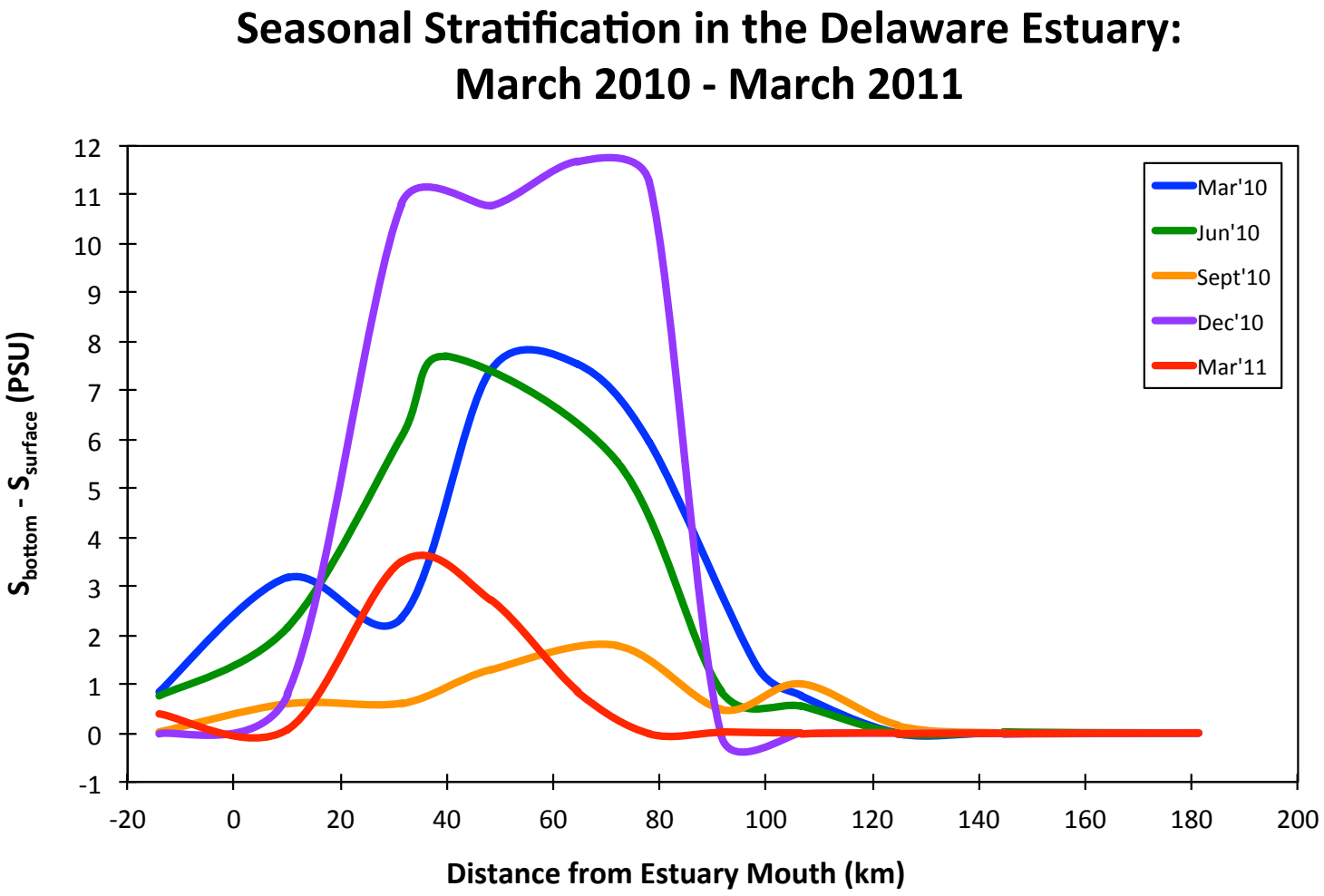


Figure 4-3. Salinity stratification for each cruise of this study (salinity of surface water, $S_{surface}$ subtracted from the salinity of bottom water, S_{bottom}).

A.

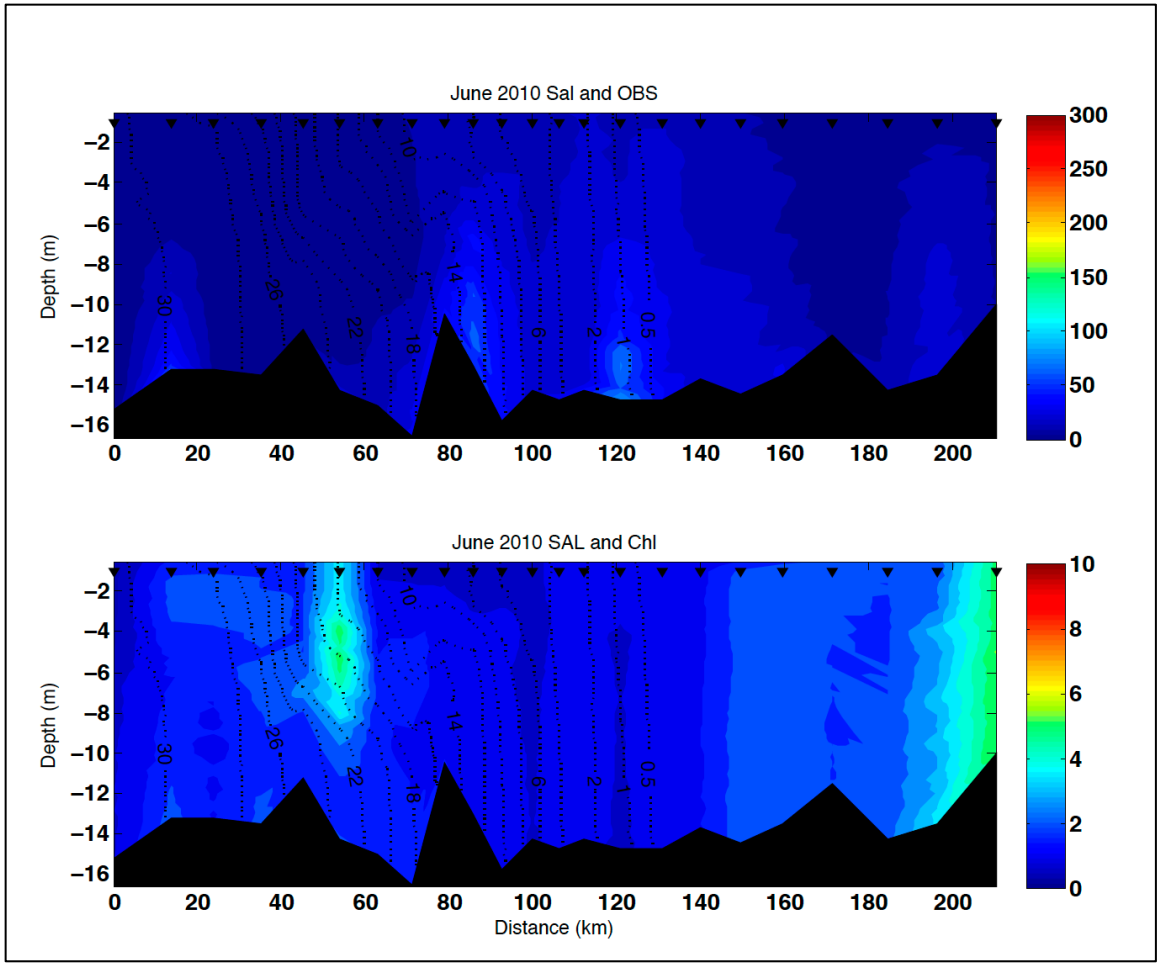


Figure 4-4a. Delaware Estuary *in situ* measurements from axial CTD casts for June 2010. The top panel color scale is for OBS (turbidity), and the bottom panel shows fluorescence (Chl - chlorophyll). Dotted lines indicate salinity and distance is measured from Station 1.

B.

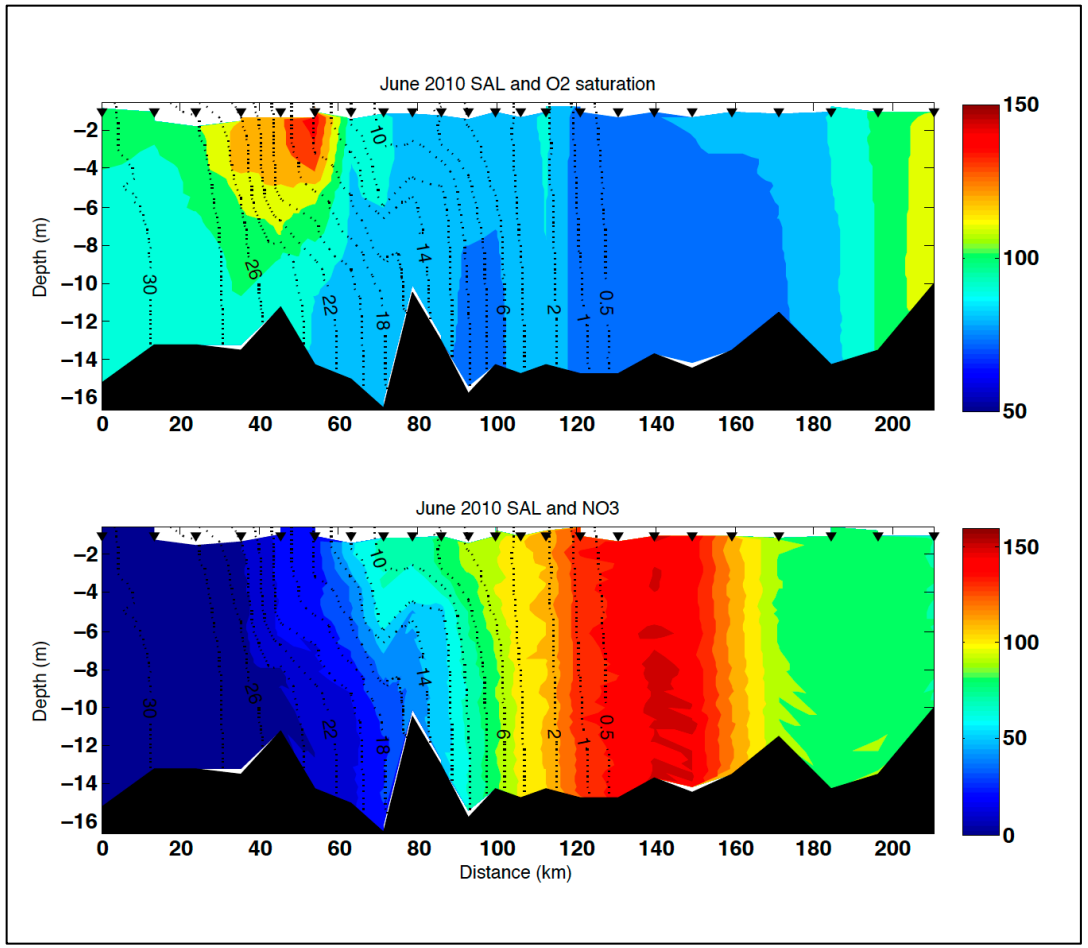


Figure 4-4b. Delaware Estuary *in situ* measurements from axial CTD casts for June 2010. The top panel color scale is for oxygen saturation (O2), and the bottom panel shows nitrate (NO3). Dotted lines indicate salinity and distance is measured from Station 1.

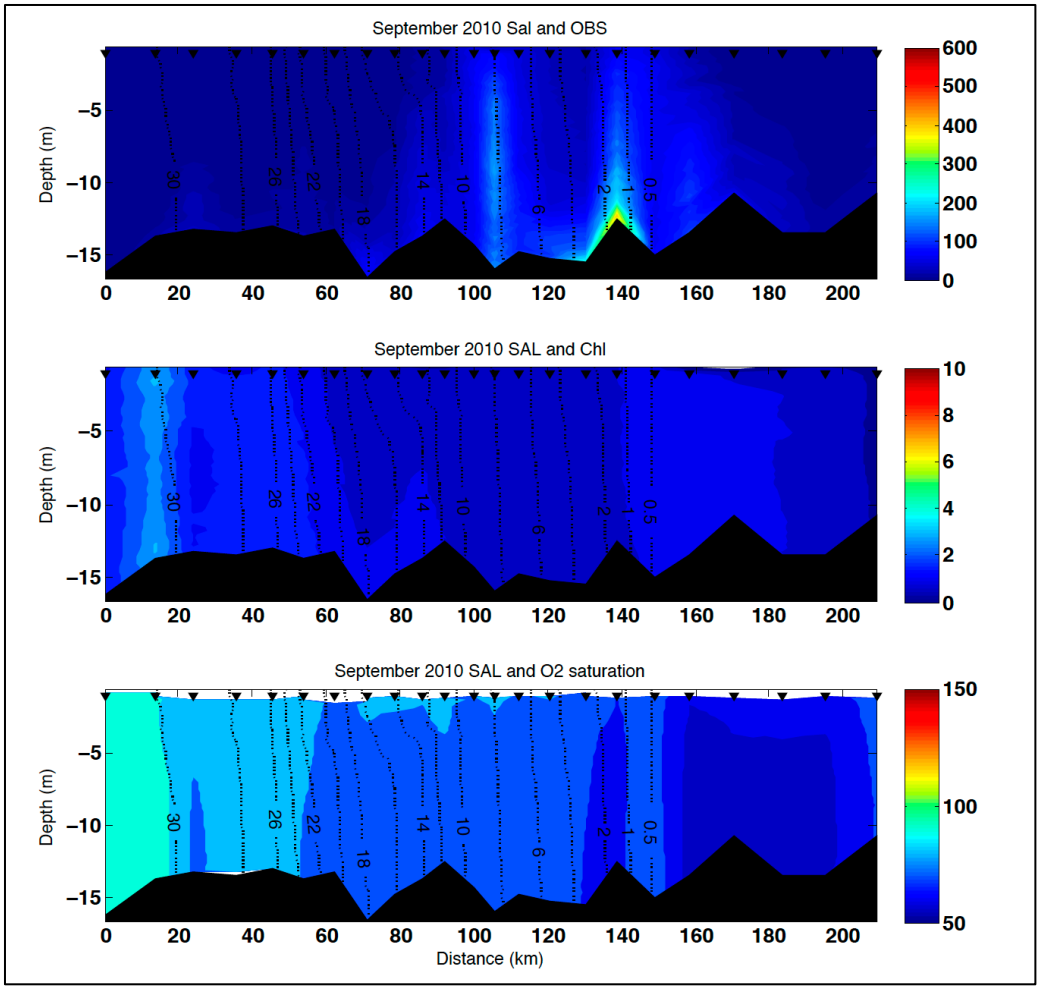


Figure 4-5. Delaware Estuary *in situ* measurements from axial CTD casts for September 2010. The top panel color scale is for OBS (turbidity), the middle panel shows fluorescence (Chl - chlorophyll), and the bottom panel is for oxygen saturation (O2). Dotted lines indicate salinity and distance is measured from Station 1.

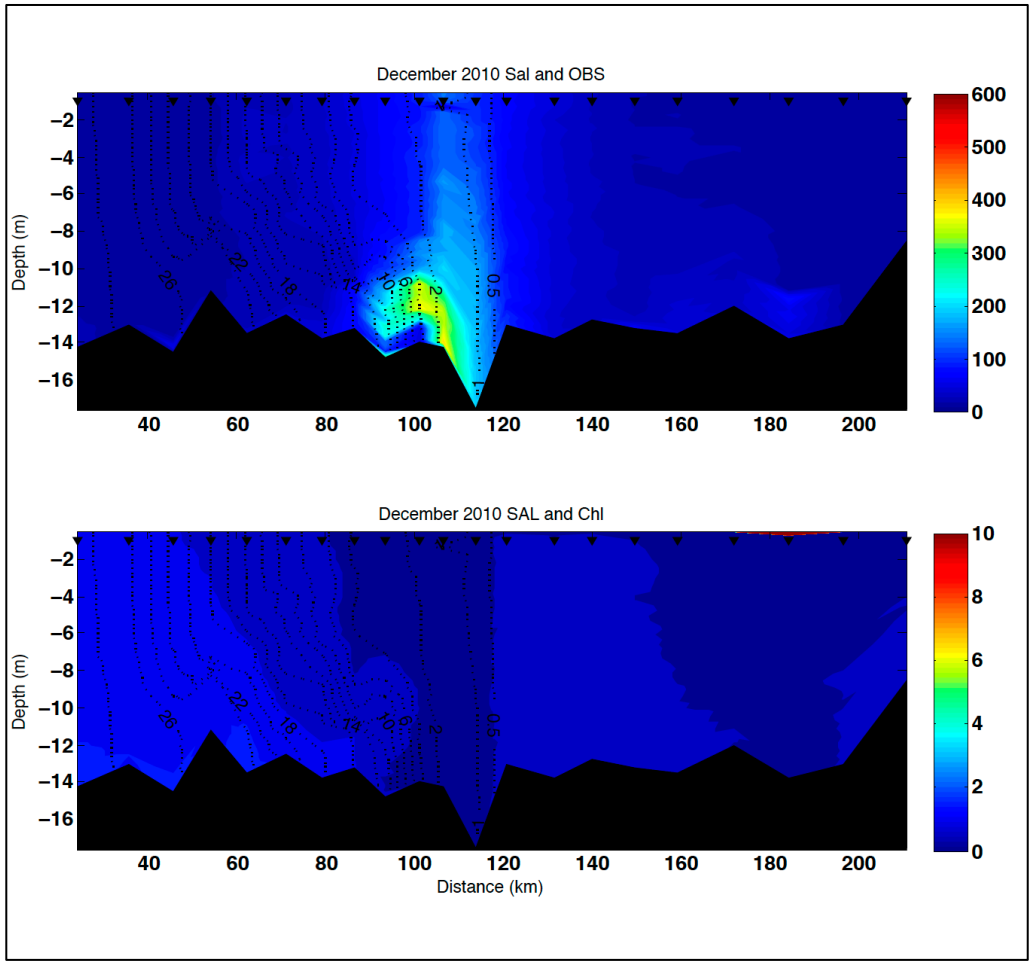


Figure 4-6. Delaware Estuary *in situ* measurements from axial CTD casts for December 2010. The top panel color scale is for OBS (turbidity), and the bottom panel shows fluorescence (Chl - chlorophyll). Dotted lines indicate salinity and distance is measured from Station 1. A problem with the shipboard CTD cage prevented measurements at Stations 1 and 2 on this cruise.

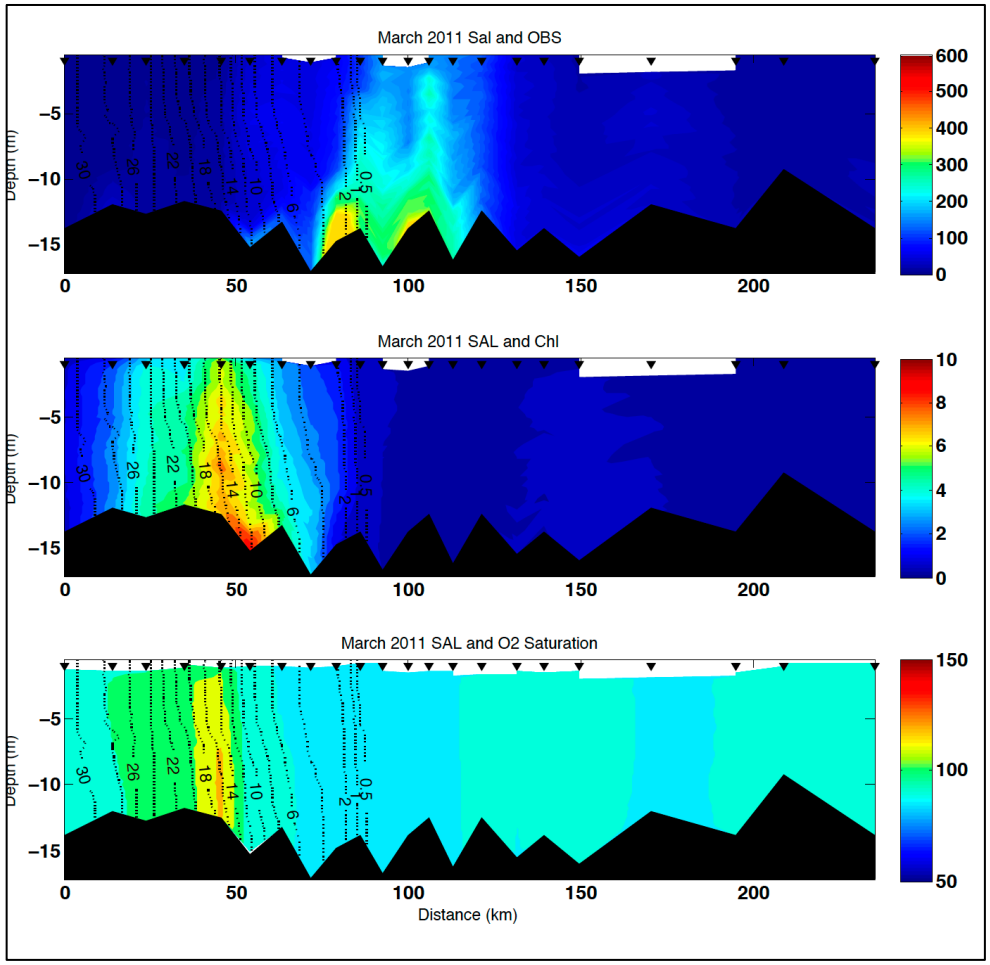


Figure 4-7. Delaware Estuary *in situ* measurements from axial CTD casts for March 2011. The top panel color scale is for OBS (turbidity), the middle panel shows fluorescence (Chl - chlorophyll), and the bottom panel is for oxygen saturation (O2). Dotted lines indicate salinity and distance is measured from Station 1.

This is characteristic of the seasonal phytoplankton blooms in the Delaware Estuary as observed in previous studies (e.g. Pennock and Sharp, 1986). While fluorescence was observed throughout the water column during the March 2011 cruise (Figure 4-7), depth profiles of fluorescence were not available for the March 2010 cruise. In contrast to the bloom that was observed in March 2011, productivity during the June 2010 cruise was restricted to surface water, and fluorescence in the upper estuary indicated additional inputs from freshwater productivity (Figure 4-4a). September 2010 had low fluorescence throughout most of the estuary, but marine productivity was indicated by fluorescence near the mouth of the Delaware Bay (Figure 4-5). Not surprisingly, December 2010 had negligible fluorescence throughout the estuary (Figure 4-6).

Surface (~1 m depth) and bottom (~1 m above the bottom) water suspended solid content (SSC) results largely paralleled *in situ* optical backscatter distributions (OBS; Figures 4-4 through 4-8). SSC and OBS consistently peaked mid-estuary, defined as the estuarine turbidity maximum (ETM). Over the course of the 5 cruises, SSC results showed that particle concentrations were on average 3 fold higher in bottom water than surface water (77 ± 113 mg/L and 25 ± 34 mg/L, respectively) and were ~8 times higher in bottom waters than surface waters of the ETM (399 ± 193 mg/L and 52 ± 29 mg/L, respectively, Figure 4-8, Appendix 2). Seasonal differences in the structure of ETM were well illustrated by SSC and OBS measurements: March and June 2010 had relatively low SSC and broad ETM, September 2010 had dual-ETM which were the farthest up-estuary of any cruise, December 2010 had a single ETM with high SSC concentrations, and March 2011 had dual-ETM with the greatest SSC observed overall.

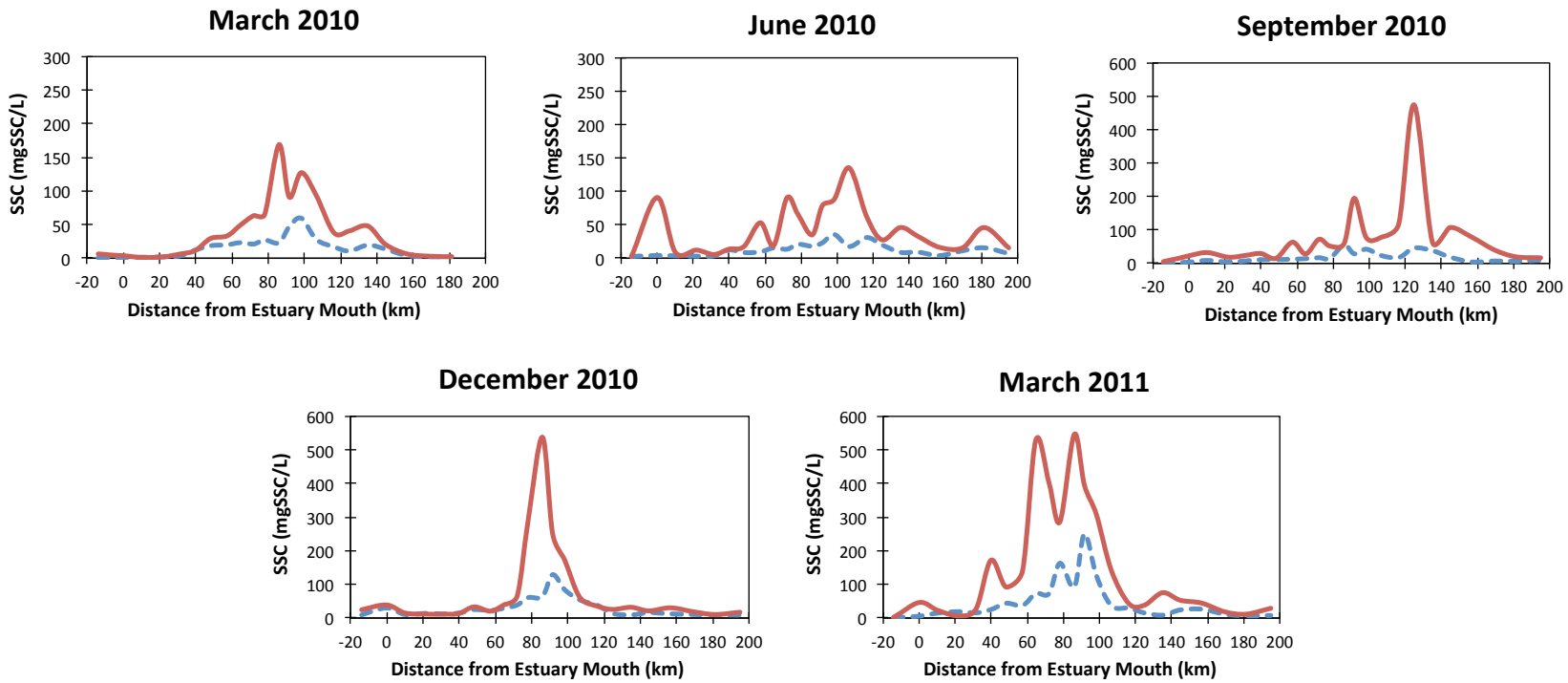


Figure 4-8. Suspended solid content (SSC) for al cruises in this study. Red solid lines are bottom water and blue dashed lines are surface water. Note the y-axis scale varies between graphs. SSC data are courtesy of the University of Delaware.

4.2 Bulk particulate organic matter

4.2.1 Particulate organic carbon and C:N ratios

The total particulate organic carbon (POC) content of surface and bottom waters was measured at ~11 of 23 the stations on each of the 5 cruises (Figure 4-9, Appendix 2). POC ranged from 22 μM OC at the marine endmember in March 2011 to 1079 μM OC in bottom water of the ETM in September 2010. Bottom water POC was on average ~ 2 times greater than surface water POC (273 μM OC and 131 μM OC, respectively), and POC was positively linearly related to SSC (Figure 4-10). Organic carbon content of surface and bottom water was 3.6% (R^2 = 0.91) and 2.5% (R^2 = 0.80) of SSC, respectively, which suggested that surface water had fewer, high OC particles and bottom water had more, low OC particles to result in overall greater POC in bottom waters.

Organic carbon content normalized to SSC showed spatial variation in the %OC of POM through the estuary (Appendix 2). Organic carbon content was consistently <10% in the ETM for all seasons (Figure 4-11). In contrast, organic content was variable in Delaware Bay and in the upper estuary (4-47% and 3-22% OC, respectively; Figure 4-11). Seasonal OC increases above 10% OC in Delaware Bay and the upper estuary were concurrent with increased *in situ* fluorescence, suggesting that phytoplankton comprised a high proportion of POM.

The ratio of total organic carbon to total nitrogen (C:N) of POM in the Delaware Estuary ranged between 6-14 throughout the estuary for the 5 cruises (Figure 4-12, Appendix 2). Generally, C:N of POM higher at the riverine endmember than the marine endmember, which suggested that terrestrial OM decreased down-estuary. Throughout the estuary, comparable C:N ratios were observed between surface and bottom water

(9.1 ± 2.0 and 9.4 ± 2.0, respectively), but where different, bottom water was generally higher than surface water (e.g. June 2010, September 2010), suggesting a higher proportion of vascular-plant derived OM was in bottom water than surface water.

4.2.2 The bulk stable carbon isotope composition of POC

The bulk stable carbon isotopic values for POM (δ^{13}C-POC) for all cruises generally increased downstream towards the marine endmember (Figure 4-13, Appendix 2). Values ranged from -26.5 ± 2.3‰ at the riverine endmember to -22.0 ± 1.9‰ at the marine endmember. Seasonal peaks in δ^{13}C-POC in Delaware Bay coincided with the *in situ* fluorescence maxima, but the absolute maximum δ^{13}C-POC varied between cruises. The highest values, -17.6‰, -18.8‰, and -20.3‰, were observed in March 2010, June 2010, and March 2011, respectively, and generally occurred not at the marine endmember, but in the fluorescence maximum (Figures 4-4, 4-7, 4-13). Likewise, not all of the δ^{13}C-POC values were lowest at the riverine endmember, which ranged from -21.7‰ to -29.5‰). With the exception of the March 2010 cruise, the riverine endmember values were within the isotopic range of C3 vascular plant material. Surface and bottom water δ^{13}C-POC were generally within 2‰ of one another.

Salinity was used to calculate δ^{13}C-POC mixing lines between the marine and freshwater (<1 PSU) endmembers to test for conservative mixing of endmember carbon sources (Figure 4-13). Endmembers for each cruise were the δ^{13}C-POC of the marine endmember, and the δ^{13}C-POC where observed salinity was <1 PSU. This freshwater endmember varied spatially in the estuary for each cruise (e.g. Figure 4-3). In March and June 2010 and March 2011, relative to the salinity models, measured δ^{13}C-POC in surface and bottom water was depleted by 10-15% in the upper estuary and enriched by

15-25% in Delaware Bay. In contrast, near-conservative mixing was observed in September and December 2010, which suggested a gradual loss or dilution of material with low δ^{13}C-POC values from the river to the sea. For all seasons, intermediate isotopic values were observed across the ETM (-23.1 ± 1.5‰).

4.2.3 Summary

Transects of physical and chemical *in situ* depth profiles through the Delaware Estuary captured distributions of suspended solids and active phytoplankton productivity across one seasonal cycle and varied predictably with discharge and season. These observations also agreed with previous studies in the Delaware Estuary (e.g. Pennock and Sharp, 1986; Sharp et al., 1982). Importantly, POC results from this study that included comprehensive bottom water sampling showed that despite overall lower organic content of particles in bottom water relative to surface water, the higher particulate concentrations, especially within the ETM, meant that greater amounts of POC were measured in bottom waters for every cruise (e.g. Figure 4-9).

The stable carbon isotope composition of POM identified the seasonal phytoplankton productivity in Delaware Bay and C3 terrestrial-derived POM in the upper estuary. At all times, the terrestrial signature of OM was lost across the ETM, suggesting that inputs of primary productivity or enriched C4 terrestrial sources, such as marsh-derived OM, were incorporated into the carbon pool downstream in a conservative mixing fashion. However, bulk measurements cannot distinguish C4 terrestrial from phytoplankton inputs without additional data.

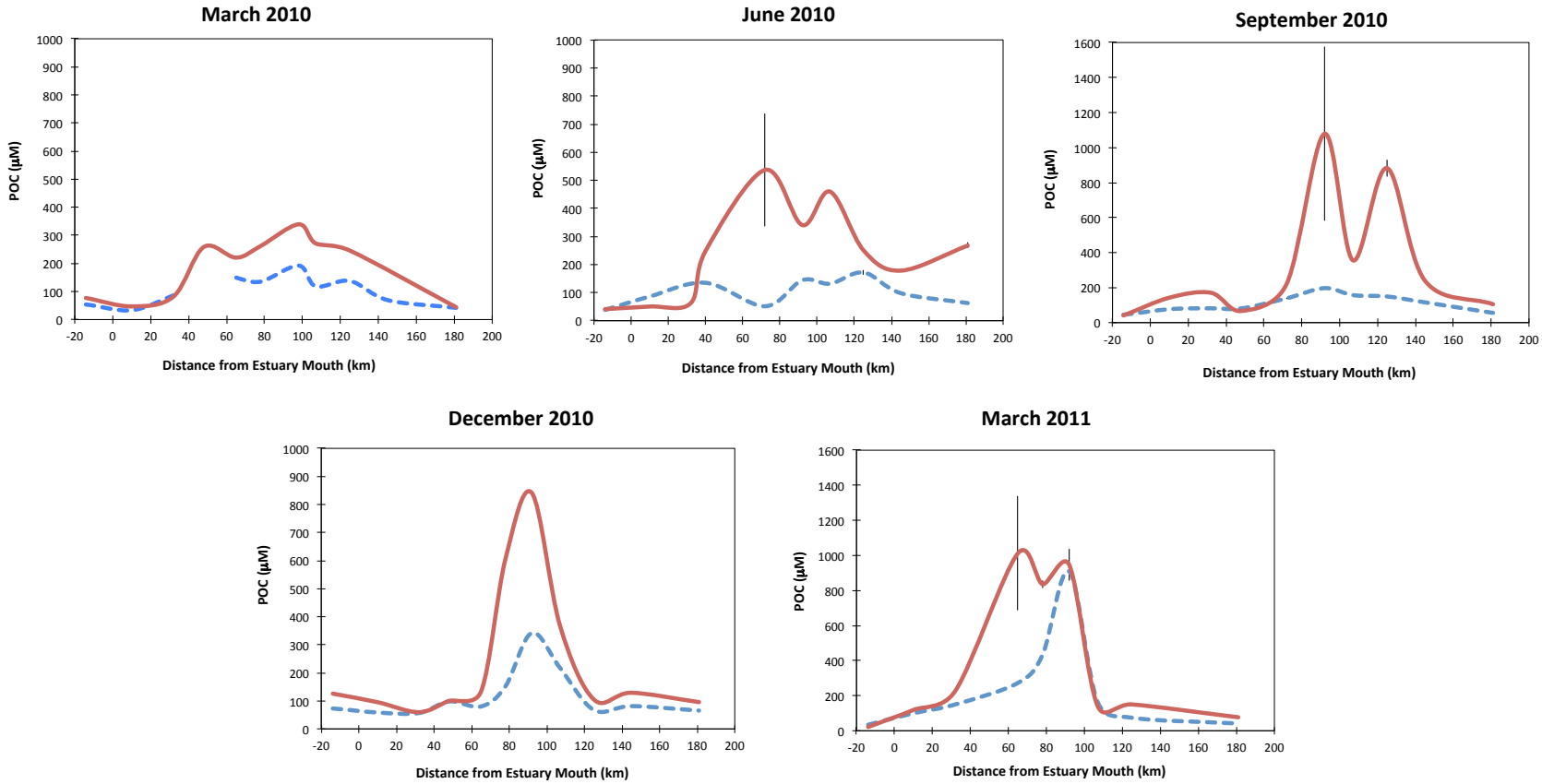


Figure 4-9. Concentrations of particulate organic carbon (POC) in the Delaware Estuary for each cruise. Red solid lines are bottom water while blue dashed lines are surface water. Error bars are the standard deviation between duplicate sample runs. Note the different scale of the y-axis for the September 2010 and March 2011 cruises.

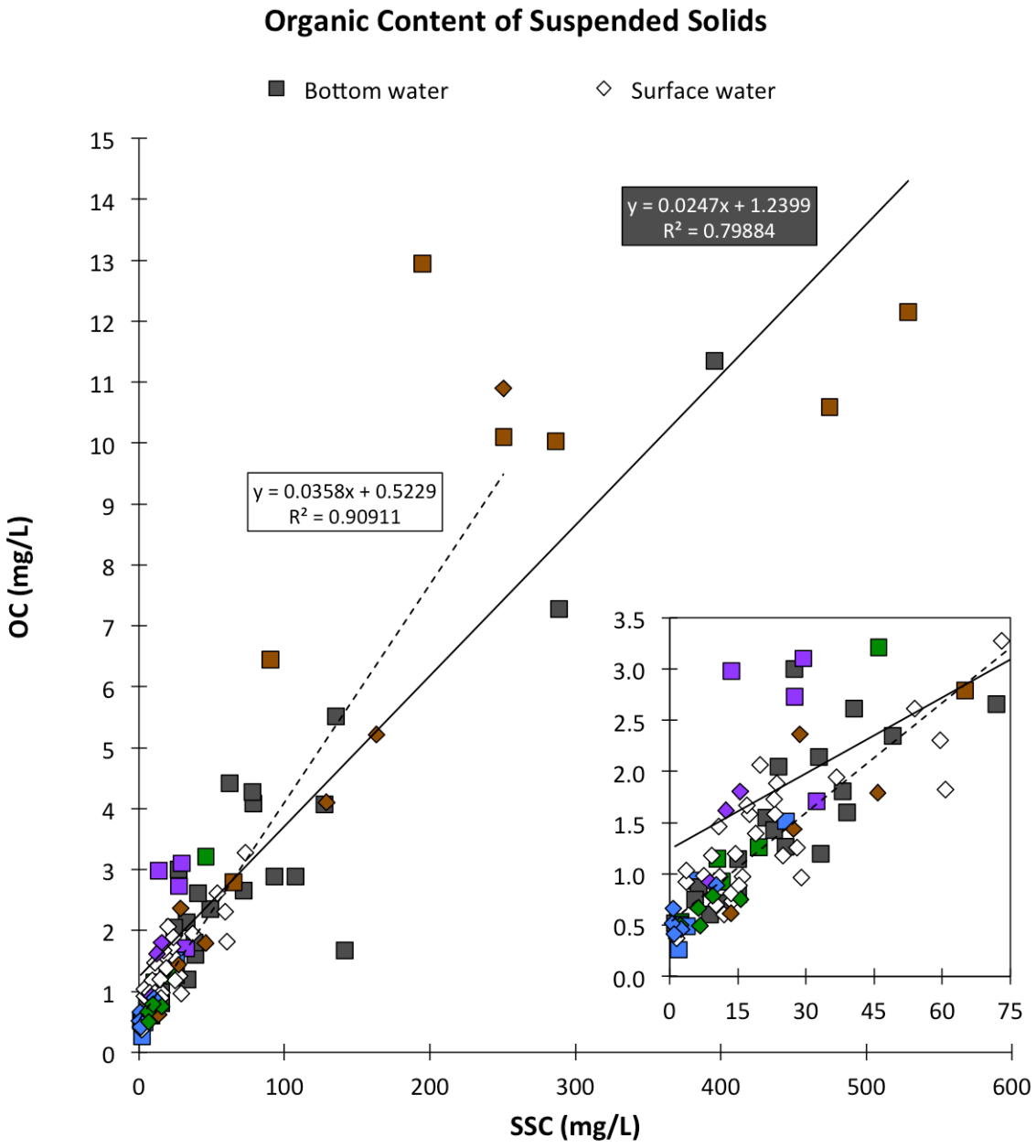


Figure 4-10. The organic carbon content (OC) of suspended solids (SSC) in the Delaware Estuary. Filled squares are bottom water, and open diamonds are surface water. Colored symbols refer to sites in the estuary: blue – marine endmember, purple – chlorophyll maxima, brown – ETM, and green – riverine 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.

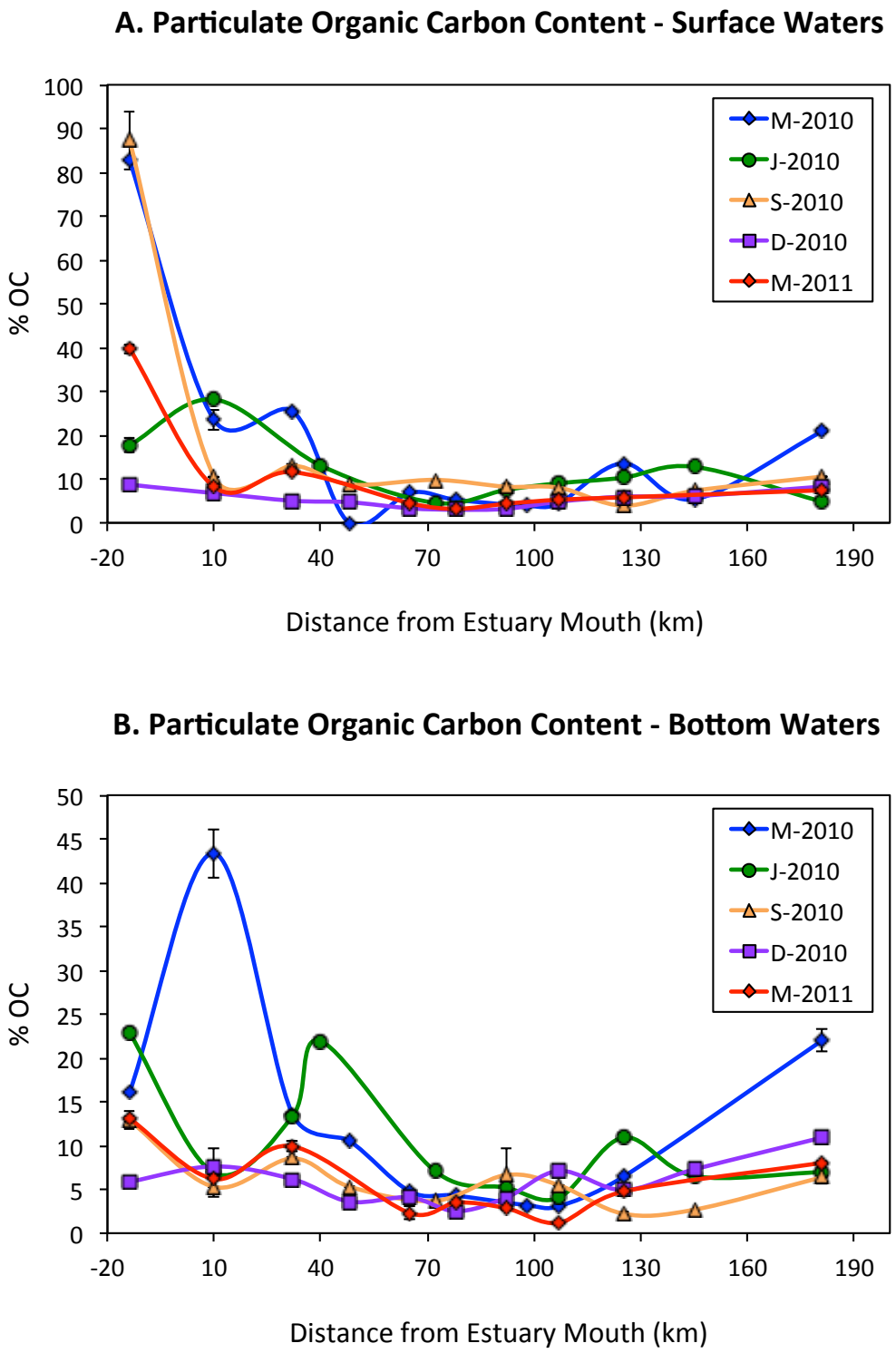


Figure 4-11. Organic carbon content of suspended solids in the Delaware Estuary in surface waters (A) and bottom waters (B). Cruises are as follows: M- March, J- June, S- September, D- December. Error bars are one standard deviation.

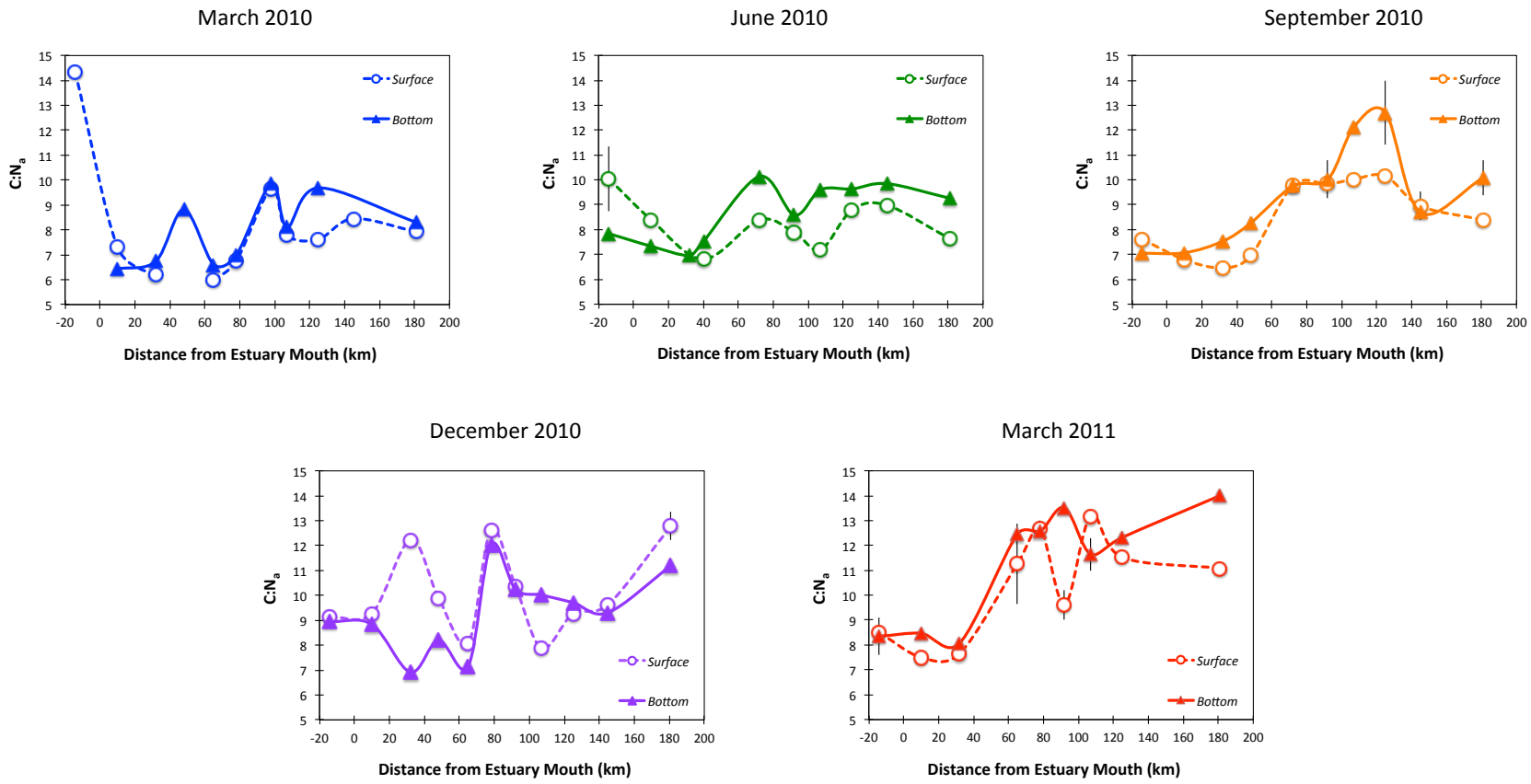


Figure 4-12. The ratio of total organic carbon (TOC) to total nitrogen (C:N, atomic-weight) in the Delaware Estuary. Bottom water – solid lines and filled trianges; surface water – dashed lines and empty circles. Error bars are the standard deviation between sample duplicates.

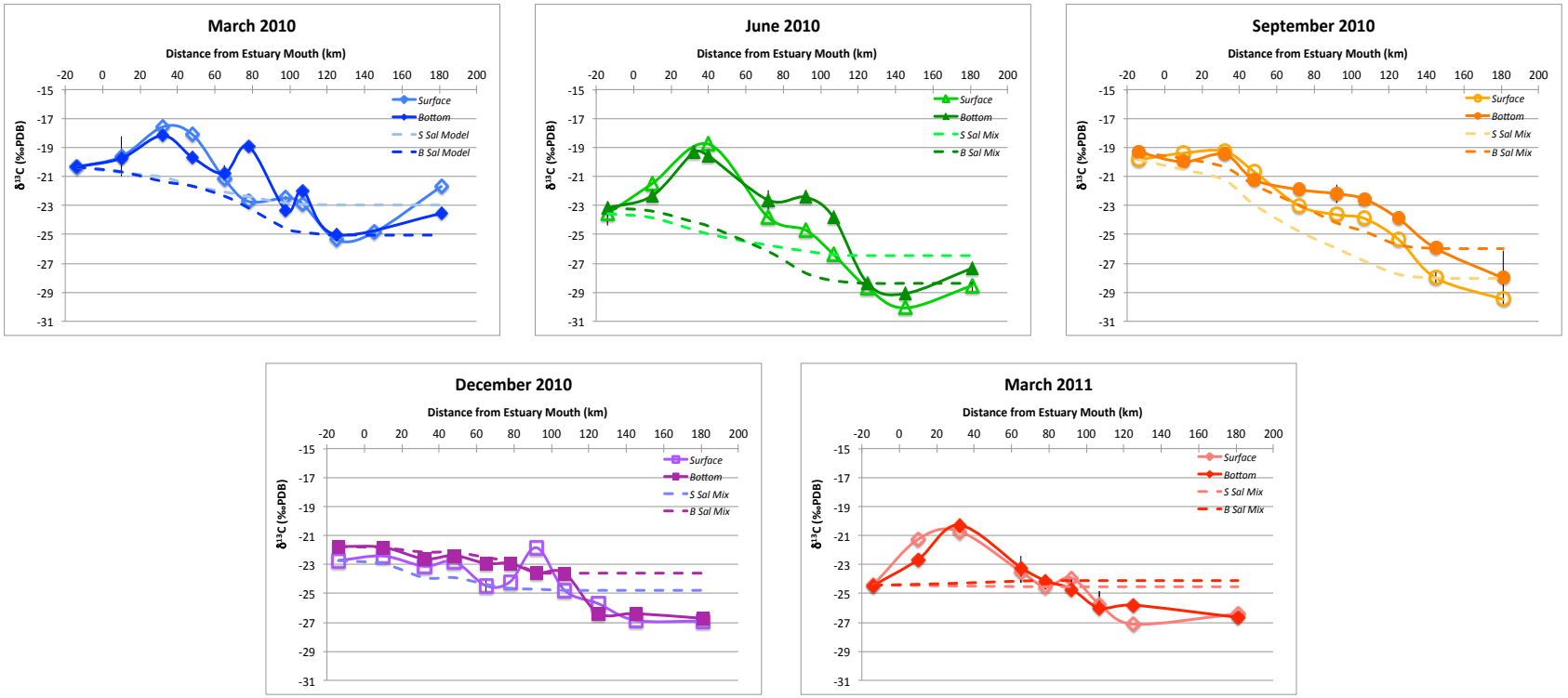


Figure 4-13. Particulate organic matter stable carbon isotopic compositions. Light colors and open symbols are surface water, dark colors and closed symbols are bottom water. Dotted lines are the calculated conservative mixing lines between the geographically fixed marine endmember and the freshwater endmember, which was set to the location where observed salinity was <1PSU on each cruise.

4.3 Delaware Estuary particulate organic matter biomarkers

Biomarkers were analyzed from a subset of POM samples, chosen to target the geographically defined marine and riverine endmembers (stations 1 and 22, respectively), and physically defined fluorescence maxima and turbidity maxima. Fluorescence and turbidity maxima were spatially determined from the *in situ* chemical and physical measurements from each cruise and varied in distance up-estuary from cruise to cruise. Algal and vascular plant-derived sources of OM were traced in surface and bottom water POM using n-alkane (alkane) biomarkers, which are resistant to degradation. Readily degradable phospholipid fatty acids (PLFAs), which reflect *in situ* viable OM, were targeted to assess microbial uptake and processing.

4.3.1 Alkanes of POM in the Delaware Estuary

Alkane chain lengths are widely used to distinguish marine (predominantly short chains) from vascular plant (predominantly long chains) sources of OM. Alkanes with carbon chain lengths of 16 through 38 were detected in the Delaware POM samples (Figures 4-14, 4-15; Appendix 3). Chain lengths greater than C_{38} were detected only in ETM bottom waters of the March 2011 cruise. Individual alkane concentrations ranged from 1.4 – 725.0 μg alkane/gOC. The lowest detected concentration of an individual alkane was the C_{32} alkane in surface water of the ETM in September 2010, and the maximum detected concentration was the C_{31} alkane in bottom water at the riverine endmember in March 2011 (Appendix 3).

Total alkane concentrations were calculated by summing the concentration of all alkanes per sample, and total alkanes varied by cruise and spatially through the estuary. Both March cruises had higher average total alkanes than the other cruises and the

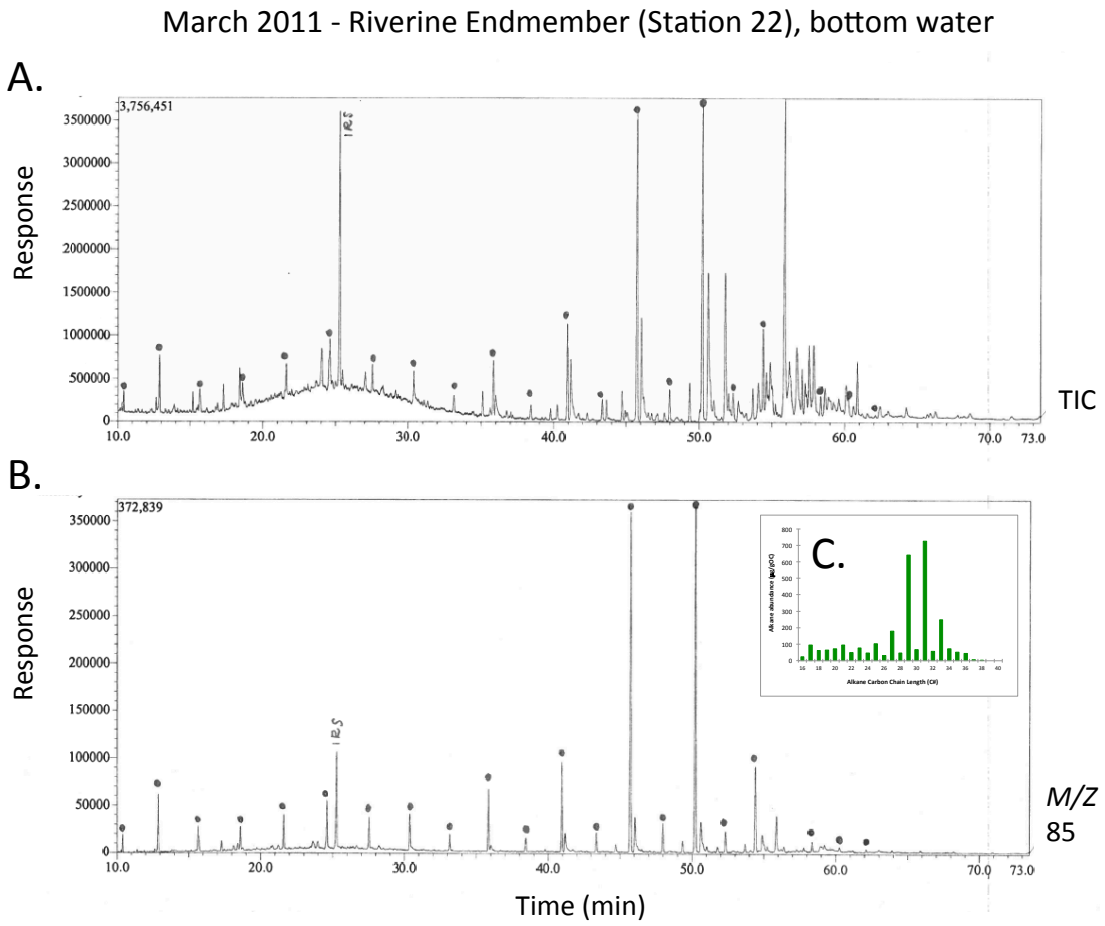


Figure 4-14. A typical GC trace for riverine endmember POM samples in the Delaware Estuary. Dotted compounds denote the homologous series of alkane compounds from carbon chain lengths 16 to 37. The internal recovery standard, nonadecanone, is indicated as 'IRS.'A) Total ion chromatogram (TIC) of the POM saponified neutral extract. B) The mass to charge ratio (M/Z) 85 for the TIC in A), showing predominantly long chain alkanes. C) Inset depicts the carbon-normalized alkane distribution resulting from the chromatogram.

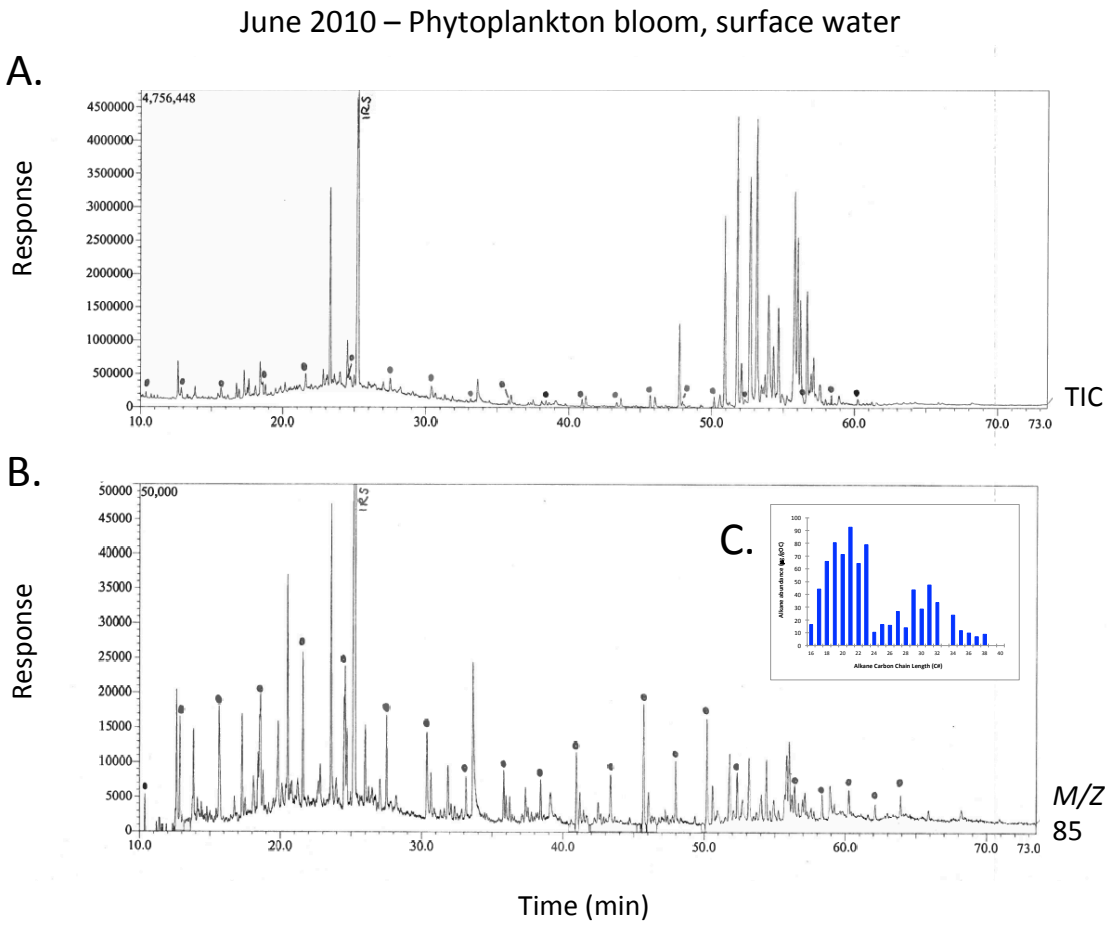


Figure 4-15. A typical GC trace for an algal-dominated POM sample in the Delaware Estuary. Dotted compounds denote the homologous series of alkane compounds from carbon chain lengths 16 to 36 (A) or 38 (B). The internal recovery standard, nonadecanone, is indicated as 'IRS.'A) Total ion chromatogram (TIC) of the POM saponified neutral extract. B) The mass to charge ratio (M/Z) 85 for the TIC in A), showing predominantly short chain alkanes. C) Inset depicts the carbon-normalized alkane distribution resulting from the chromatogram.

September cruise had the lowest average total alkanes (Table 4-1). March 2011 and December 2010 cruises had the greatest variation in total alkanes (106 – 15,928 ng total alkanes/L and 421-7,747 ng total alkanes/L, respectively). Surface and bottom water total alkanes were not significantly different ($p > 0.05$) throughout the estuary, except in the ETM in which bottom waters had greater total alkanes than surface waters (normalized to volume, $p = 0.042$; Table 4-2). Normalized to volume, the concentration of total alkanes peaked in the ETM, but normalized to organic carbon content, alkanes decreased linearly down-estuary from 1,556 ± 650 μg/gOC to 407 ± 85 μg/gOC in surface waters and from 1,438 ± 828 μg/gOC to 565 ± 312 μg/gOC in bottom waters (Table 4-2).

Alkane distributions differed along estuary, but were similar between cruises in the different geochemical regions of the estuary (Figure 4-16). Long chain alkanes dominated the riverine endmember and ETM. The most abundant alkane chain length (C_{max}) in the riverine endmembers was C_{31} 70% of the time and was otherwise C_{29}. C_{max} in ETM samples was C_{29} (Appendix 3), consistent with a shift between the riverine endmember and ETM from terrestrial to marsh or increasing marine inputs, as suggested by bulk δ^{13}C-POM.

While bottom water alkane distributions were remarkably similar across seasons at the riverine endmember and ETM, surface waters exhibited more variable alkane distributions in two ways. First, seasonal increases in short chain alkanes (June 2010 and March 2011) indicated enhanced freshwater productivity in the upper estuary, and confirmed algal inputs to the ETM. Second, in March and September 2010, surface water POM had distinctive mid-chain-length homologues predominating (C_{max} of C_{25} and C_{19},

Table 4-1. Summary statistics for the total sum of alkanes per sample for each cruise.

Cruise	Minimum	Maximum	Average	Standard deviation	Coefficient of variation (%)
ng alkanes / L					
March 2010	323	5,679	2,462	2,218	90
June 2010	519	3,353	1,868	1,096	59
September 2010	173	5,745	1,437	1,690	118
December 2010	421	7,747	1,610	2,499	155
March 2011	106	15,928	4,246	5,394	127
µg alkanes / gOC					
March 2010	488	1,594	1,101	513	47
June 2010	484	1,988	1,090	499	46
September 2010	165	1,225	514	285	56
December 2010	354	1,356	705	397	56
March 2011	138	2,863	1,109	891	80

Table 4-2. Total alkanes for each site analyzed in the Delaware Estuary for surface and bottom water. ME – marine endmember; DB – Delaware Bay; ETM – estuarine turbidity maxima; RE – riverine endmember. P-values are reported for a two-tailed t-test between surface and bottom water total alkanes at each site. $P < 0.050$ indicated surface and bottom water were significantly different.

	Site	Minimum	Maximum	Average	Standard deviation	Coefficient of variation (%)	P-value
Alkanes (ng/L)	*Surface waters*						
	ME	137	421	264	132	50	0.525
	DB	360	1,314	666	437	66	0.209
	ETM	391	6,797	2,473	2,279	92	0.042
	RE	485	1,497	1,029	415	40	0.220
	Bottom waters						
	ME	106	568	353	226	64	---
	DB	376	2,372	1,000	937	94	---
	ETM	1,463	15,928	6,761	4,689	69	---
	RE	751	3,353	1,795	1,141	64	---
Alkanes (µg / gOC)	*Surface waters*						
	ME	332	488	407	85	21	0.392
	DB	200	811	491	251	51	0.932
	ETM	165	1,594	986	565	57	0.505
	RE	728	2,151	1,556	650	42	0.819
	Bottom waters						
	ME	375	1,031	565	312	55	---
	DB	138	796	476	249	52	---
	ETM	284	1,395	812	447	55	---
	RE	776	2,863	1,438	828	58	---

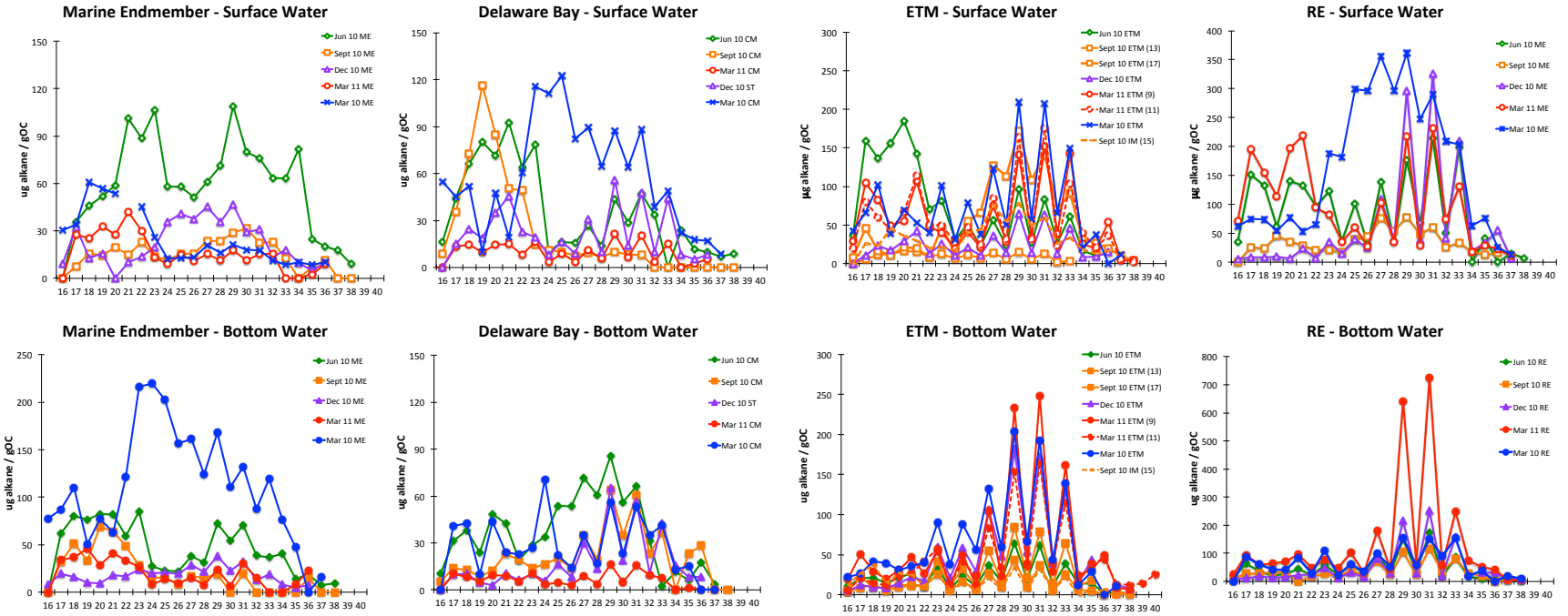


Figure 4-16. Alkane biomarker abundances from Delaware Estuary water column POM. Numbers on x-axes represent alkane chain lengths (C16-C40) and alkane abundances are reported in µg alkane per g OC. Colors represent each cruise, and open symbols are surface water whereas closed symbols are bottom water. From left to right, panels are from: the marine endmember (Station 1), Delaware Bay (fluorescence maxima in March, June, September 2010 and March 2011), the estuarine turbidity maximum zone (ETM), and the riverine endmember (Station 22). Note the different y-axes for the different regions of the estuary.

respectively). The dual-ETM sampled in September 2010 and March 2011 had similar alkane distributions for each season, but alkane abundances varied (Figure 4-16).

Alkane distributions were more variable in Delaware Bay and at the marine endmember (Figure 4-16). Long chain alkanes in all samples revealed the presence of terrestrial-derived OM, although δ^{13}C-POM for these samples was strongly algal. In Delaware Bay, bottom waters generally had C_{max} of C_{29}, as did surface water, except during algal blooms (March 2010, June 2010, September 2010), which caused $C_{max} < C_{25}$ (Appendix 3). Alkane distributions in Delaware Bay did not appear to be affected by changes in stratification. The marine endmember C_{max} varied between cruises.

The sum of long (LC, C_{24}-C_{33}) and short chain (SC, C_{16}-C_{23}) alkanes traced the relative abundances of vascular plant and algal OM through the estuary. The concentrations of LC and SC alkanes in surface waters were comparable through the estuary normalized to volume (Figure 4-17). In contrast, bottom waters had LC alkanes that were considerably higher than SC alkanes in the upper estuary and ETM relative to downstream. LC alkanes markedly decreased between the ETM and Delaware Bay by as much as 50-fold in March 2011.

The average of all LC and SC alkanes was used to calculate residuals for LC and SC alkanes at each site (Figure 4-18). Normalized to volume, LC and SC alkane residuals confirmed distributions as observed in Figure 4-17 with LC and SC tracking together in surface waters, but LC dominating bottom waters. Normalized to organic carbon content, LC and SC alkanes generally were comparable and decreased down-estuary in surface waters, and LC were generally greater than SC in bottom waters, especially in the upper estuary and ETM (Figure 4-18).

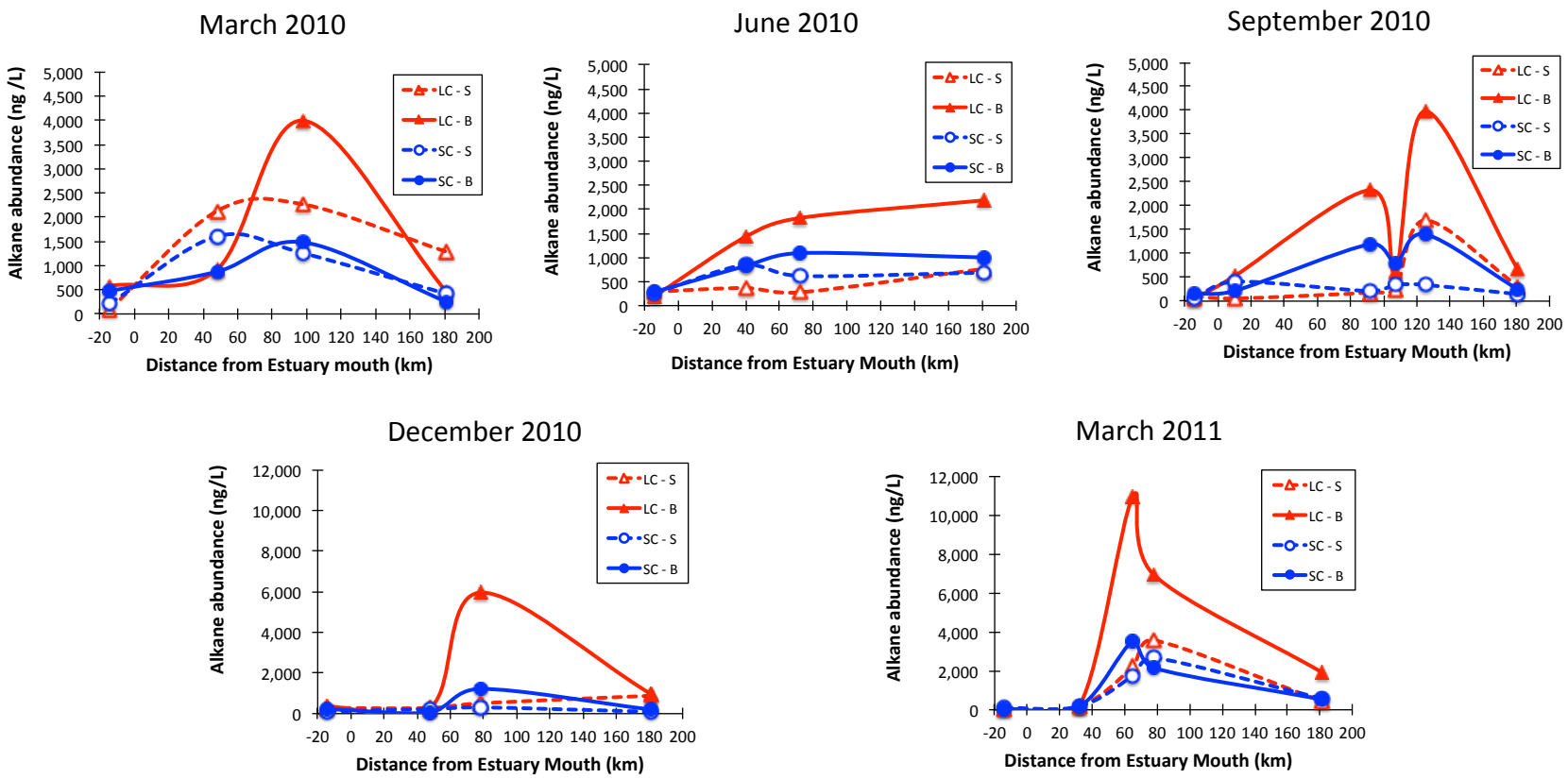


Figure 4-17. Algal- and terrestrial-derived alkanes in surface and bottom water POM of the Delaware Estuary. Terrestrial-derived alkanes have long chain lengths (LC; C_{24}-C_{33}), whereas algal-derived alkanes have short chain lengths (SC; C_{16}-C_{23}). LC alkanes are in red and SC alkanes are in blue. Open symbols indicate surface water (S) samples and closed symbols indicate bottom water (B) samples. Note the y-axis scale change for December 2010 and March 2011.

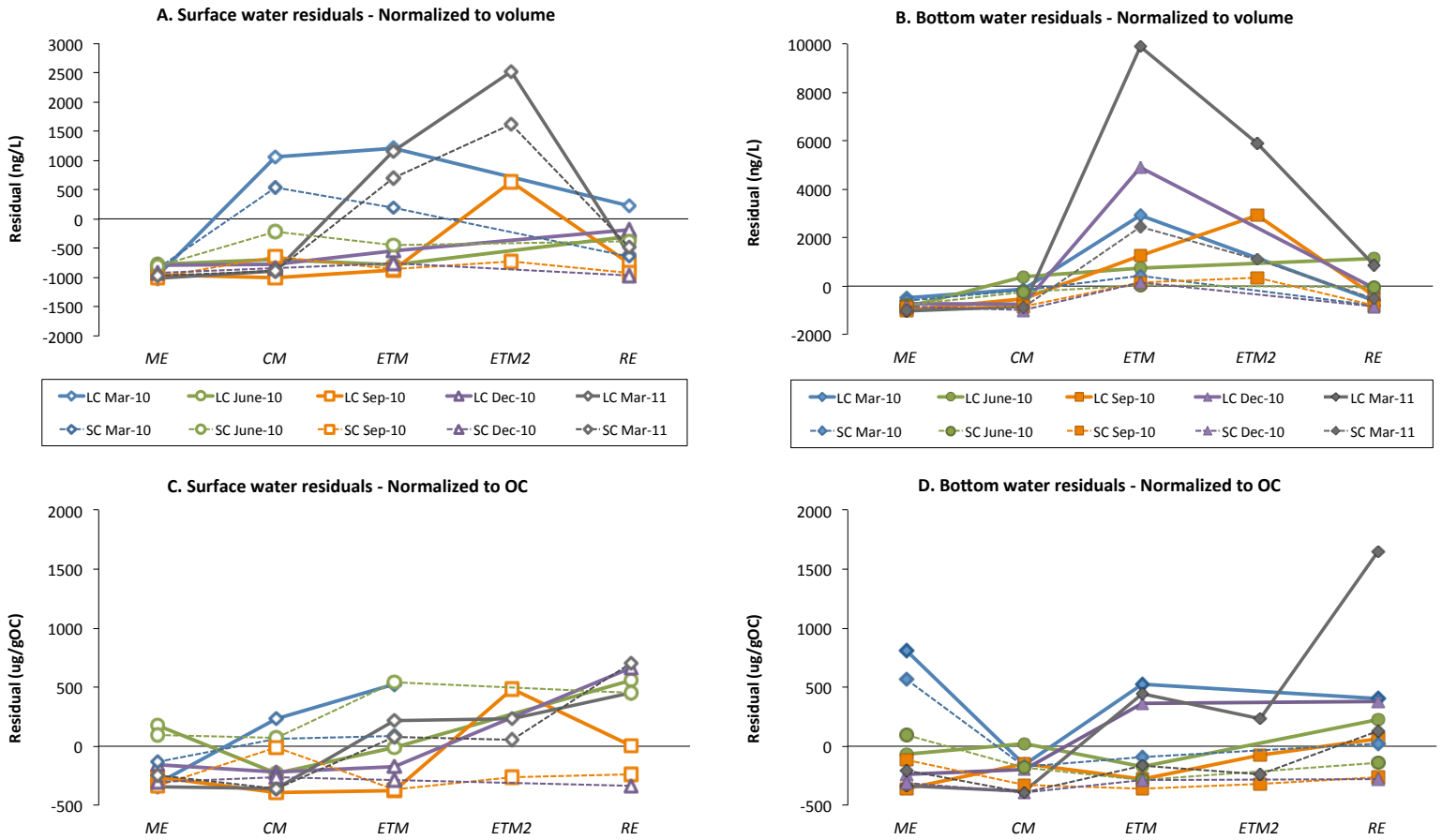


Figure 4-18. Residuals for long and short chain (LC and SC, respectively) alkanes (the difference between LC and SC alkanes and the average of all LC and SC alkanes for all sites and seasons). Alkanes are normalized to volume in surface waters (A) and bottom waters (B) and normalized to total organic carbon for surface waters (C) and bottom waters (D). SC are in dashed lines, LC are in solid lines. Cruises are differentiated by colors. Sites in the estuary are as follows: ME – Marine endmember, CM- chlorophyll maxima (or Delaware Bay for December 2010), ETM – estuarine turbidity maximum, ETM2 – second turbidity maximum up-estuary from the primary ETM, RE – riverine endmember. See text for interpretation.

Seasonal changes in the concentrations of SC and LC alkanes were related to phytoplankton productivity and river discharge, respectively. Surface water SC alkane concentrations were related to phytoplankton productivity observed in the estuary. For example, SC alkanes were higher in Delaware Bay in March, June, and September 2010 than in December 2010. Interestingly, though a bloom was observed in March 2011, SC alkanes in Delaware Bay were not elevated. Instead, SC alkanes were higher in the upper estuary and ETM than in Delaware Bay in March 2011. June and December 2010 had low SC alkanes throughout the rest of the estuary compared to the other cruises. SC alkanes were less variable in bottom waters. LC alkanes were highest in bottom waters of the upper estuary during seasons with elevated river discharge, including March and December 2010, and March 2011.

Traditional alkane indices were used to further evaluate the relative proportions of algal and vascular plant OM in the Delaware Estuary (Table 4-3). The average chain length of alkanes (ACL) is a measure of the relative proportion of short and long chain alkanes. The ACL calculated for this study used alkanes with carbon chain lengths of C_{16}-C_{36}. The ACL of this homologous series is 26; therefore, ACL < 26 indicates a greater proportion of algal input, whereas ACL >26, a greater proportion of vascular plant input. The ACL of POM in the Delaware ranged from 20.6 to 29.7, validating the wide range of sources in the Delaware Estuary (Table 4-3). The calculated ACL returned results similar to the bulk stable carbon isotopic composition of POM in that ACL was high at the riverine endmember, lowest within algal blooms, and intermediate at the marine endmember (Figure 4-19a). Bottom water POM ACL was significantly higher than surface water ACL (26.58 ± 1.68 and 25.39 ± 1.95, respectively; $p = 0.033$).

Table 4-3. Delaware Estuary water column POM alkane indices for each cruise: CPI – carbon preference index; ACL – average chain length; ME – marine endmember, CM – chlorophyll maxima; ETM – estuarine turbidity maxima – RE – riverine endmember. See Methods for index formulas and interpretations.

Cruise	Site	CPI - S	CPI - B	ACL - S	ACL - B	Pmar-aq - S	Pmar-aq - B
March 2010	ME *(1)*	0.76	1.07	23.04	25.61	0.501	0.582
	CM *(7)*	1.08	1.15	25.60	25.73	0.576	0.310
	ETM *(14)*	2.06	2.38	26.43	27.19	0.302	0.310
	RE *(22)*	1.25	2.41	27.16	26.73	0.428	0.355
June 2010	ME *(1)*	1.14	1.28	26.29	24.82	0.470	0.430
	CM *(6)*	1.29	1.13	23.56	25.86	0.511	0.351
	ETM *(10)*	1.57	2.36	22.81	26.48	0.425	0.317
	RE *(22)*	2.13	2.95	25.24	26.70	0.365	0.271
September 2010	ME *(1)*	0.98	1.10	26.41	22.36	0.363	0.531
	CM *(3)*	1.02	1.90	20.62	27.84	0.573	0.215
	ETM *(13)*	1.59	2.53	24.12	26.64	0.457	0.347
	IM *(15)*	1.59	1.84	24.05	24.28	0.406	0.378
	ETM *(17)*	1.62	3.46	28.13	27.62	0.246	0.311
	RE *(22)*	1.47	2.20	26.57	27.39	0.306	0.233
December 2010	ME *(1)*	1.34	1.38	26.16	26.07	0.439	0.387
	ST *(7)*	2.13	2.75	25.98	28.54	0.257	0.178
	ETM *(11)*	2.49	3.18	26.75	28.54	0.263	0.249
	RE *(22)*	5.30	4.84	29.68	28.87	0.107	0.143
March 2011	ME *(1)*	1.29	1.66	23.48	23.88	0.462	0.427
	CM *(5)*	2.21	1.87	25.30	25.43	0.377	0.325
	ETM *(9)*	2.27	4.05	26.08	28.12	0.217	0.177
	ETM *(11)*	2.35	2.91	26.19	28.41	0.222	0.237
	RE *(22)*	1.88	4.32	24.39	28.14	0.241	0.116

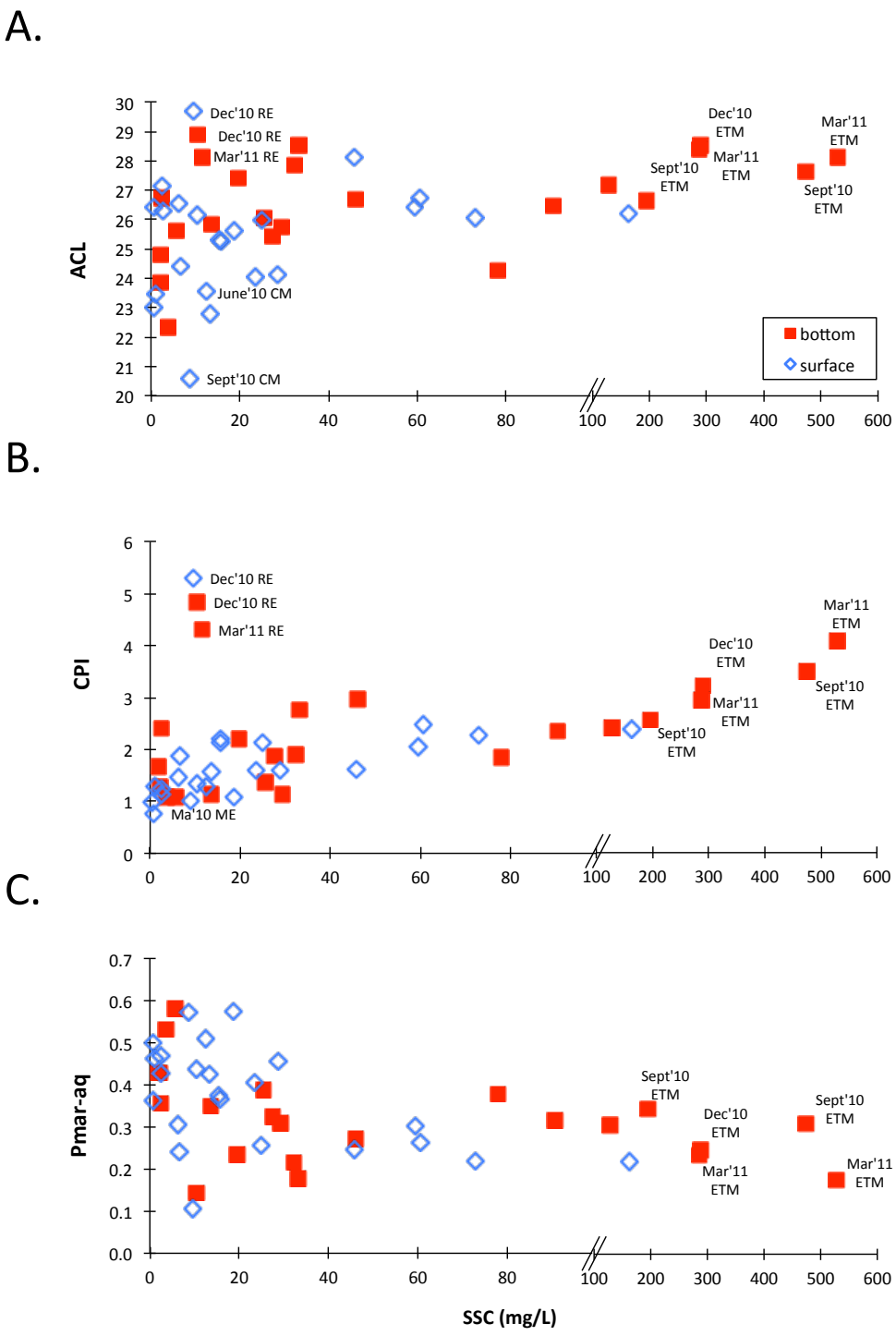


Figure 4-19. Alkane biomarker indices for Delaware Estuary POM. Surface water is in open blue diamonds, whereas bottom water is in filled red squares. A) ACL – average chain length; B) CPI – carbon preference index; and C) Pmar-aq – emergent/non-emergent plant index (see text for definitions and discussion of the indices). Note the change in x-axis scale at 100 mg/L SSC.

Bottom water ACL within the ETM (27.57 ± 0.83) was to the riverine endmember (27.57 ± 0.93), and both were consistently in the range for predominance by vascular plant OM (Table 4-4).

The carbon preference index (CPI) measures the odd or even alkane-chain-length predominance and is commonly used to distinguish vascular plant and algal material because vascular plant material alkanes exhibit a strong odd-over-even chain length preference. CPI greater than 2 indicates terrestrial-inputs, whereas algal and petroleum-derived inputs have low CPI (~1; Killops and Killops, 1993). The CPI of POM alkanes in the Delaware Estuary ranged from 0.76 at the marine endmember in March 2010 to 5.30 at the riverine endmember in December 2010 (Table 4-3). Similar to ACL, CPI of Delaware Estuary POM decreased from the riverine endmember to the marine endmember (Figure 4-19b). The CPI of the riverine endmember varied widely between seasons (2.40 ± 1.66 and 3.35 ± 1.17 for surface and bottom water, respectively; Table 4-4), reflecting the influence of seasonal freshwater productivity. In contrast, the marine endmember had relatively consistent CPI among seasons and depths (1.1 ± 0.24 and 1.30 ± 0.24 for surface and bottom water, respectively; Table 4-4), implying the OM exported from the estuary was seasonally consistent. March 2011 had the highest CPI at the marine endmember, which coincided with the highest river discharge sampled and indicated high vascular plant OM export. Surface water CPI was significantly less than bottom water CPI (1.77 ± 0.91 and 2.38 ± 1.07, respectively; $p = 0.045$).

In bottom waters, the CPI was higher at the riverine endmember than the ETM (Table 4-4). This may have resulted from mixing of algal and vascular plant OM within the ETM, but could also be driven by additional contributions of marsh OM with mid-

Table 4-4. Summary statistics (average ± standard deviation) for Delaware Estuary water column POM alkane indices for each region of the estuary across all cruises sampled: CPI – carbon preference index; ACL – average chain length; ME – marine endmember, CM – chlorophyll maxima; ETM – estuarine turbidity maxima – RE – riverine endmember. See Methods for index formulas and interpretations.

Site	CPI - S	CPI - B	ACL - S	ACL - B	Pmar-aq - S	Pmar-aq - B
ME	1.10 ± 0.24	1.30 ± 0.24	25.07 ± 1.67	24.55 ± 1.48	0.447 ± 0.052	0.472 ± 0.082
CM	1.54 ± 0.58	1.76 ± 0.67	24.21 ± 2.21	26.68 ± 1.41	0.459 ± 0.139	0.276 ± 0.075
ETM	1.99 ± 0.40	2.98 ± 0.63	25.79 ± 1.77	27.57 ± 0.83	0.304 ± 0.098	0.278 ± 0.059
RE	2.40 ± 1.66	3.35 ± 1.17	26.61 ± 2.03	27.57 ± 0.93	0.289 ± 0.123	0.224 ± 0.097

chain-lengths to the ETM. The P_{mar-aq} index has been used to evaluate inputs mid-chain-length alkanes from marshes, and does not include algal alkanes in its formula (Ficken et al., 2000). A $P_{mar-aq} < 0.1$ indicates a predominance of terrestrial plant OM, values of 0.1-0.4, emergent macrophytes, and 0.4-1, submerged/floating macrophytes (Ficken et al., 2000, Sikes et al., 2009). Delaware Estuary POM P_{mar-aq} values ranged from 0.12 - 0.58 (Table 4-3, Figure 4-19c), indicating inputs from mixed sources of OM including terrestrial and emergent and submerged/floating macrophyte sources. On average, P_{mar-aq} was lower in bottom water than surface water (0.31 and 0.37, respectively), but the difference was not significant ($p = 0.109$). P_{mar-aq} within ETM bottom water was slightly greater than at the riverine endmember (0.278 ± 0.059 and 0.224 ± 0.097, respectively) suggesting emergent wetland macrophytes were an additional source of OM within the Delaware Estuary ETM.

Outliers in alkane distributions indicated potential petroleum contamination of POM samples (Figure 4-16). Several samples (March 2010 marine endmember bottom water, Delaware Bay surface water, and riverine endmember surface water, and June 2010 marine endmember surface and bottom water, and Delaware Bay bottom water) exhibited high mid-chain-length abundances with minimal carbon chain length preference. Additionally, these outliers had skewed alkane indices, with low CPI and depressed ACL (Table 4-3). The presence of unresolved complex mixtures in chromatograms, an indicator of petroleum inputs, as well as frequently observed coprostanol, a biomarker often used for wastewater (Bianchi and Canuel, 2011), suggests anthropogenic OM is widespread in the Delaware Estuary. These biomarkers have been

previously observed in the estuary (e.g. Mannino and Harvey, 1999), but identifying and quantifying anthropogenic OM is outside of the scope of this thesis work.

4.3.2 PLFAs of POM in the Delaware Estuary

PLFAs biomarkers were analyzed for 3 of the 5 cruises (September and December 2010, and March 2011; Appendix 5). PLFAs for all samples were dominated by saturated fatty acids, which ranged from 41.1 – 68.5% of the PLFAs detected. PLFA indices were used to compare the relative contributions of sources, including the 'Fresh,' 'Bac,' 'Terr,' and TAR_{FA} indices (see methods for index formulas). 'Terr' and 'Fresh' PLFAs were more variable than 'Bac' PLFAs across sites and seasons (8.2 ± 6.6, 7.7 ± 5.7, and 4.9 ± 2.6, respectively). POM 'Fresh' PLFAs were seasonally elevated from autochthonous productivity in Delaware Bay (~11-19%), but were low in the upper river and ETM (4.6 ± 3.4%), corroborating alkane results (e.g. March 2011, Figure 4-20). However, the relatively high proportion of 'Fresh' PLFAs in the lower estuary in December 2010 was surprising considering the lack of productivity during this cruise (~8-14%). The abundance of 'Fresh' PLFAs was not significantly different between surface and bottom water samples ($p = 0.807$).

Whereas 'Fresh' PLFAs were high in the lower estuary and low in the upper estuary, 'Bac' and 'Terr' PLFAs had the inverse distribution (Figure 4-20). In March 2011, 'Bac' PLFAs peaked in the ETM, but in December 2010, 'Bac' PLFAs decreased down-estuary. 'Bac' PLFAs were overall uniform through the ETM in September 2010. Across the three cruises, surface and bottom water 'Bac' PLFAs were not significantly different. 'Terr' PLFAs were approximately <10% total PLFAs at the riverine

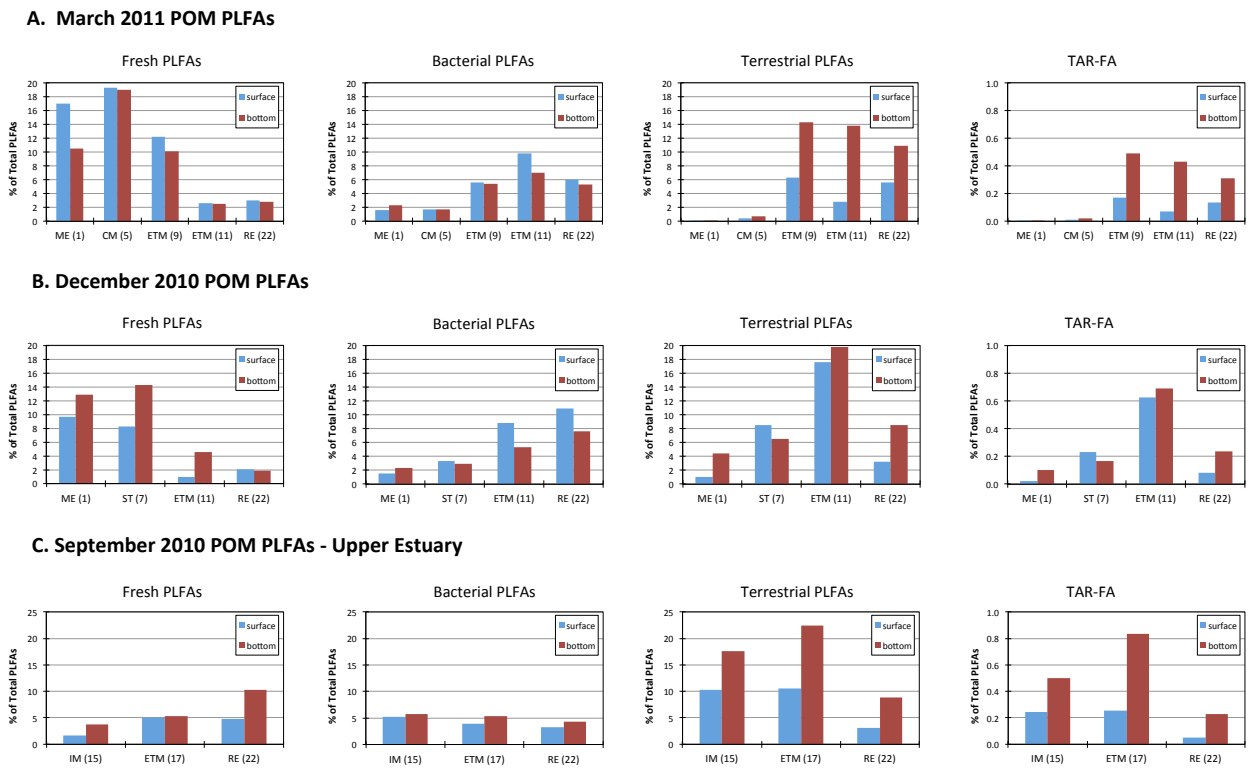


Figure 4-20. Particulate organic matter (POM) phospholipid-linked fatty acids (PLFAs) from A) March 2011, B) December 2010, and C) September 2010. PLFAs were not available for the lower estuary in September 2010 due to an instrument malfunction in the lipid extraction process. "Fresh" PLFAs are the sum of polyunsaturated PLFAs, “bacterial” PLFAs are the sum of branched C15 and C17 PLFAs, and “terrestrial” PLFAs are the sum of even saturated C24-C32 PLFAs. Surface water POM is in blue and bottom water POM results are in red. Locations in the estuary are notated as *region (site)*, with region abbreviations as follows: Ocean – Marine endmember; Bay – Delaware Bay; ETM – Estuarine turbidity maximum; River – Riverine endmember; IM – Intermediate site between dual-ETM.

endmember in all seasons, but peaked in the ETM. 'Terr' PLFAs were as much as 22% in bottom water in the ETM, but surface water varied seasonally from ~3-18%. 'Terr' PLFAs in Delaware Bay and the riverine endmember were <1% in March 2011, and <10% in December 2010. Bottom water 'Terr' PLFAs were significantly greater than surface water in the ETM and river sites ($p = 0.01$). Results from the TARFA index corroborated the distribution of 'Terr' PLFAs through the estuary and seasonally, with higher values in the upper estuary and ETM and lower values in Delaware Bay and the marine endmember (Figure 4-20, Appendix 5).

4.4 Biomarkers from sediments in the Delaware Estuary

4.4.1 Alkanes of sediments in the Delaware Estuary

Sediment samples from the upper estuary and through the ETM were evaluated to assess the source of OM deposited across this geochemical transition zone. Three sediment cores from three cruises were analyzed for biomarker distributions (Table 3-2). Floc samples were taken from the water directly above the sediment surface of the cores, when available, to estimate how sources of OM differed across the sediment-water interface. Although short and long chain alkanes were detected in all POM samples, all floc layer and sediment samples were strongly skewed to long and odd chain alkanes (Figure 4-21). In all seasons and samples, C_{max} in was either C_{29} or C_{31} (Appendix 4).

Alkane indices in the sediments revealed subtle seasonal differences in OM sources with respect to bottom water POM (Table 4-5). For all sediments, indices for core-top alkanes from below the ETM were similar to ETM bottom water POM. Otherwise, sediments up- and down-estuary from the ETM were more seasonally variable. Sediments in March 2011 had an ACL that was less than that of the POM (26.6-

27.4 vs. 28.1-28.4), and P_{mar-aq} greater than POM (0.260-0.290 vs. 0.120-0.240). In contrast, sediments in March 2010 had ACL that was greater than POM (27.4-28.2 vs. 26.7-27.2) and P_{mar-aq} less than POM (0.216-0.245 vs. 0.310-0.355). September 2010 sediments had no less consistent pattern relative to POM, but September sediment ACL increased down-estuary, as did P_{mar-aq} decreased down-estuary.

4.4.2 PLFAs of sediments in the Delaware Estuary

September 2010 and March 2011 sediments were selected for PLFA analysis to compare sources of OM during low and high river discharge, and low and high estuarine productivity, respectively. In all sediment samples, 'Terr' PLFAs were a greater proportion of PLFAs than 'Bac' or 'Fresh' PLFAs (Figure 4-22, Appendix 6). The core-top at Station 15 in March 2011 had the greatest measured proportion of 'Terr' PLFAs of any sample in the sediments or in POM (~50% of total PLFAs). 'Fresh' PLFAs in the sediments were less than or similar to POM samples in the upper estuary, but surprisingly, the March 2011 floc layers did not have any 'Fresh' PLFAs. 'Bac' PLFAs were generally consistent between all samples and seasons in upper estuary POM and sediments (<10%).

4.5 Compound specific isotope analysis of alkanes

The compound specific stable carbon isotopic composition (δ^{13}C-CSIA) of alkanes from a subset of POM and sediment samples was analyzed for September 2010 and March 2011 to determine the inputs through the estuary across differing estuarine conditions. The δ^{13}C-CSIA of mid-to-long chain alkanes (C_{23}-C_{33}) was substantially different between September 2010 and March 2011 POM (Figure 4-23). The September long chain alkane δ^{13}C-CSIA of the POM had a narrow range, from -30.7‰ to -27.5‰.

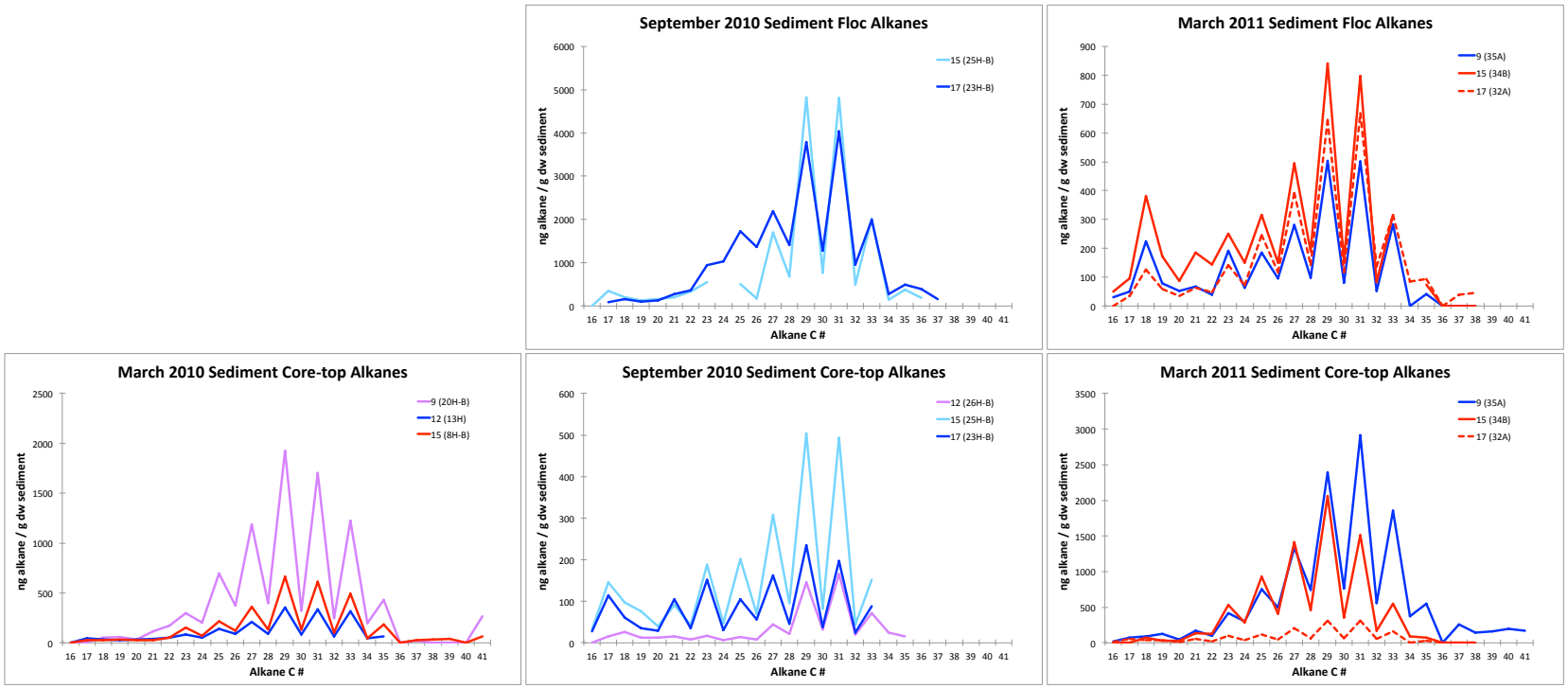
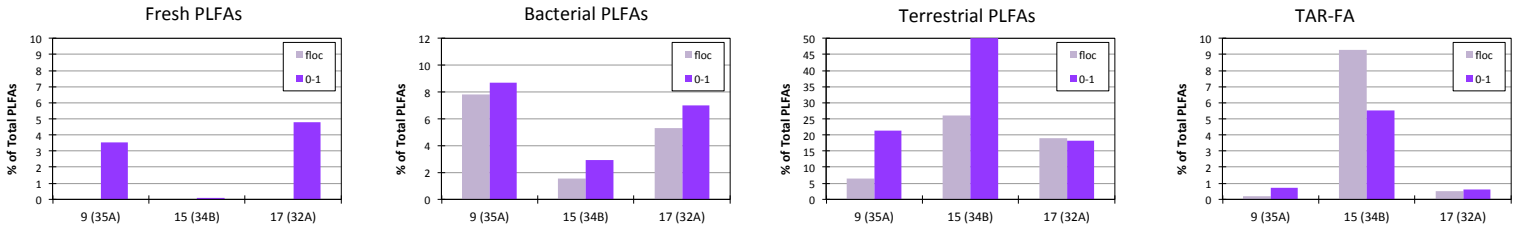


Figure 4-21. Delaware Estuary sediment alkanes. Colors indicate relation to the ETM as follows: purple – down-estuary from the ETM; blue – beneath the ETM; red – up-estuary from the ETM; light blue – between a dual-ETM. March 2010 flocs were not available for analysis.

A. March 2011 Sediment PLFAs



B. September 2010 Sediment PLFAs

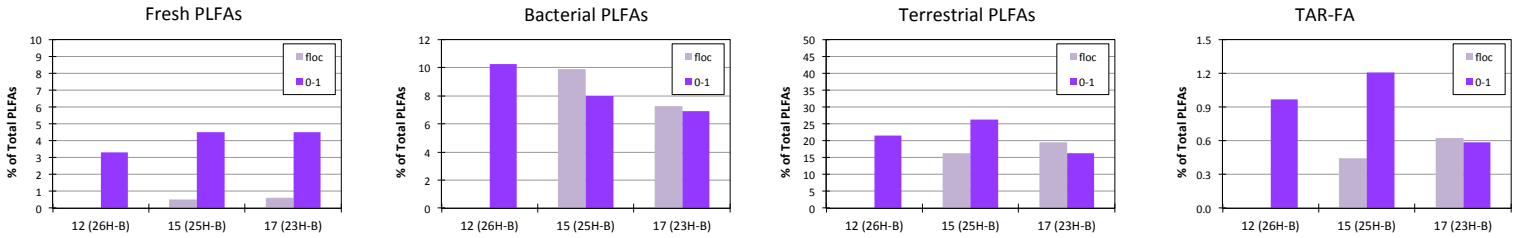


Figure 4-22. Sediment core phospholipid-linked fatty acids (PLFAs) from A) March 2011, and B) September 2010. "Fresh" PLFAs are the sum of polyunsaturated PLFAs, “bacterial” PLFAs are the sum of branched C15 and C17 PLFAs, and “terrestrial” PLFAs are the sum of even saturated C24-C32 PLFAs. PLFAs from floc are in light purple and core tops (0-1cm) are in dark purple. Sediments are notated by core number and corresponding water sampling station.

Table 4-5. Delaware Estuary sediment alkane indices for floc and core-top (0-1cm) samples. Relation to the ETM is as follows: 'down' – down-estuary of the ETM; 'in' – within the ETM; 'up' in the upper estuary from the ETM.

Cruise	Site *(Core)*	Relation to ETM	CPI		ACL		Pmar-aq		ACL-long		CPI-long	
			floc	0-1cm	floc	0-1cm	floc	0-1cm	floc	0-1cm	floc	0-1cm
March 2010	9 *(20H-B)*	down	N/A	3.81	N/A	28.15	N/A	0.216	N/A	29.37	N/A	4.27
	12 *(13H)*	in	N/A	2.96	N/A	27.41	N/A	0.245	N/A	29.38	N/A	3.50
	15 *(8H-B)*	up	N/A	3.92	N/A	28.02	N/A	0.225	N/A	29.49	N/A	4.45
September 2010	12 *(26H-B)*	down	N/A	3.28	N/A	27.60	N/A	0.091	N/A	30.03	N/A	4.24
	15 *(25H-B)*	in	5.19	3.93	28.20	26.03	0.099	0.281	29.83	28.41	6.03	5.47
	17 *(23H-B)*	in	2.26	3.42	27.23	25.08	0.254	0.373	28.98	27.97	2.27	4.78
March 2011	9 *(35A)*	in	2.97	3.03	26.33	27.95	0.273	0.180	28.77	29.66	5.09	3.16
	15 *(34B)*	up	2.54	3.61	25.95	27.42	0.257	0.290	28.63	28.34	4.21	3.99
	17 *(32A)*	up	3.02	4.00	26.93	26.58	0.228	0.259	29.20	28.88	3.73	4.80

In contrast, long chain alkanes in March 2011 POM had a wider range of isotope values from -37.2‰ to -28.6‰, with the lowest values at the riverine endmember. The $\delta^{13}C$ of alkanes in March 2011 increased from the riverine endmember down-estuary to bottom waters of Delaware Bay, which were similar to values in surface and bottom waters of the ETM.

The $\delta^{13}C$ of surface sediment alkanes did not exhibit a consistent $\delta^{13}C$-CSIA trend down-estuary unlike the POM. Instead, they had a narrow range in isotopic values for both seasons (~ -27‰ to -32‰, Figure 4-24). In September 2010, the sediment $\delta^{13}C$-CSIA was comparable to that of the POM, but in March 2011, the sediment $\delta^{13}C$ of alkanes was similar to POM in the ETM rather than the riverine endmember. The $\delta^{13}C$-CSIA results supported alkane biomarker distribution results in that sediments and bottom waters of the ETM were largely derived from vascular plant OM, but the change in $\delta^{13}C$-CSIA between the riverine endmember and ETM in March 2011 suggested that the source of vascular plant material is more enriched in the ETM.

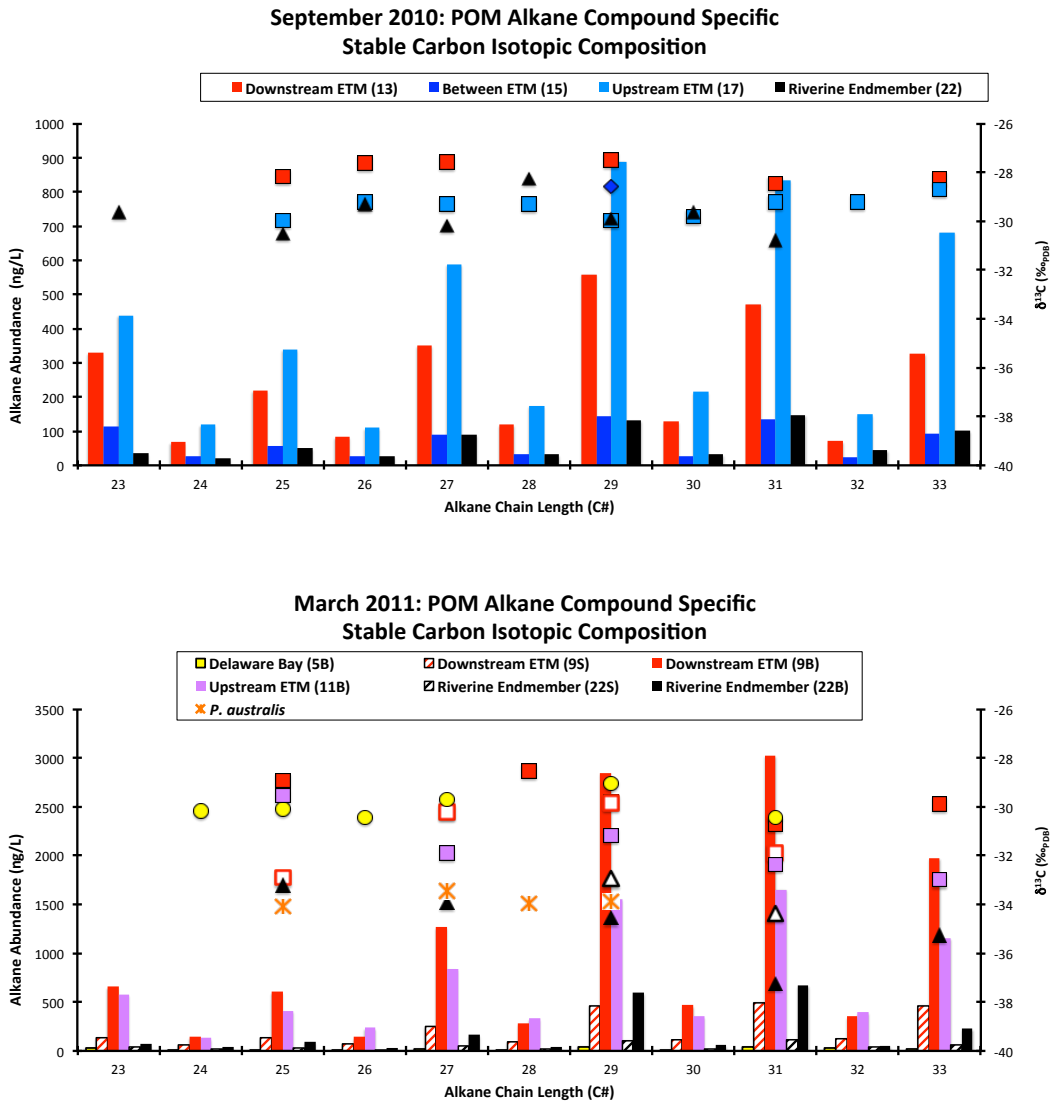


Figure 4-23. POM alkane compound specific stable carbon isotopic composition for (a) September 2010 and (b) March 2011. Bar graphs show alkane abundances while symbols indicate the individual alkane isotopic composition ($\delta^{13}C$). Symbol colors coordinate with bars and shapes represent sites: riverine endmember bottom water – solid black triangles; riverine endmember surface water – white and black triangles; upstream ETM bottom water – solid light purple squares; intermediate site between ETMs – solid dark blue diamond; downstream ETM bottom water – solid red squares; downstream ETM surface water – white and red squares; Delaware Bay bottom water – solid yellow circles. The isotopic composition of *P. australis* leaf alkanes is in orange stars as a representative C3 marsh endmember.

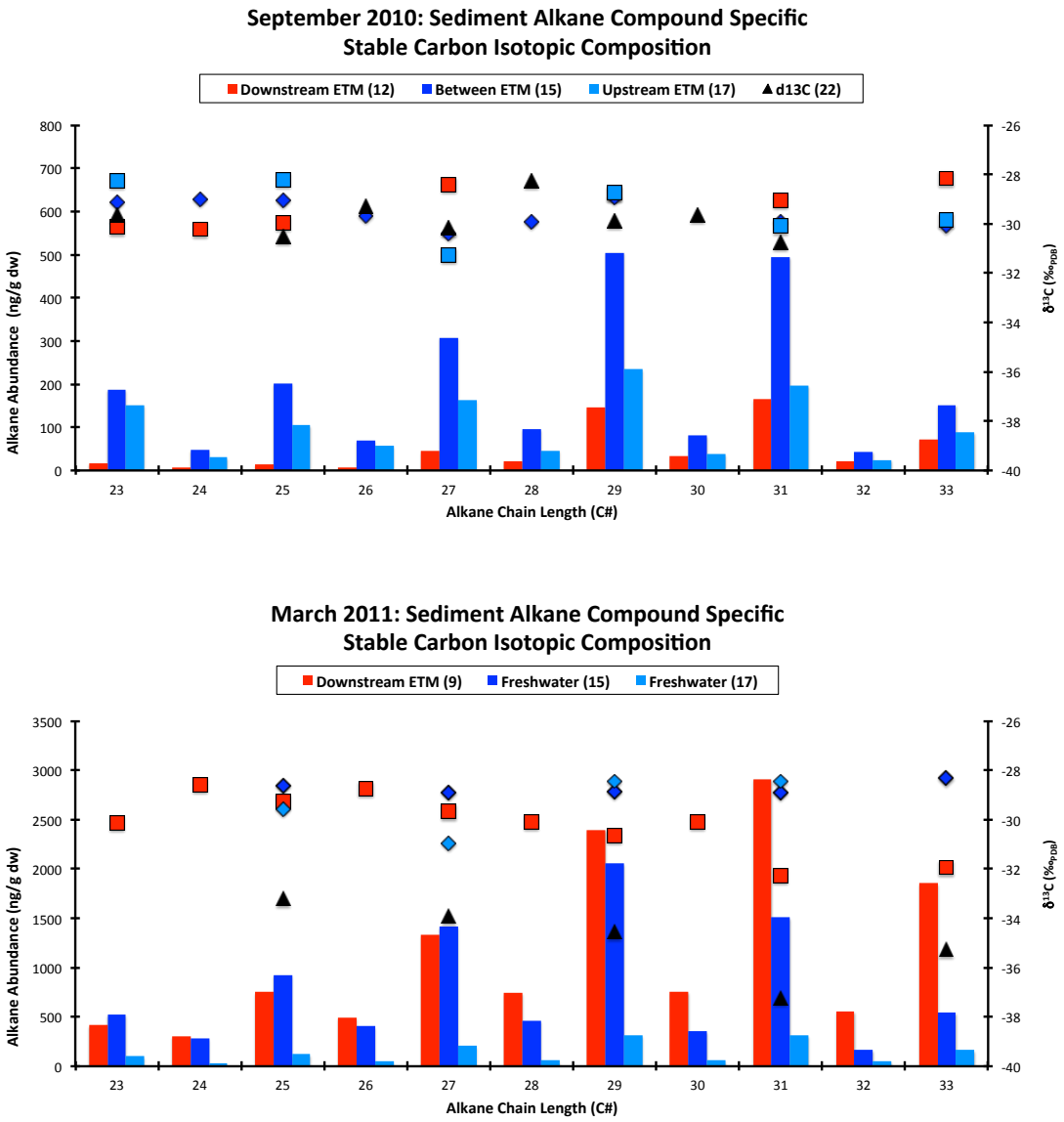


Figure 4-24. Sediment (0-1cm) alkane compound specific stable carbon isotopic composition for (a) September 2010 and (b) March 2011. Bar graphs show alkane abundances while symbols indicate the individual alkane isotopic composition ($\delta^{13}C$). As a reference, riverine endmember POM isotopic composition is retained in black trianges. Symbol colors coordinate with bars and shapes represent sites: Station 17 core – solid light blue squares or diamonds; Station 15 core – solid dark blue squares or diamonds; downstream ETM – solid red squares.

V. DISCUSSION

5.1 Bulk properties of particulate organic matter

5.1.1 Bulk organic content

The organic carbon content of particulates in both surface and bottom waters of the Delaware Estuary was seasonally affected by phytoplankton productivity. Particulates were typically <10% OC in the absence of phytoplankton production, however, seasonal productivity such as observed Delaware Bay in March and June 2010 elevated the OC content to as much as 29% and 47% in surface and bottom waters, respectively (e.g. Figure 4-11). As Delaware Bay sediments have <1% OC (Cifuentes, 1991), elevated bottom water OC could not be sourced only from sediment pools of OC, but instead must have sourced from surface waters. Two mechanisms may have caused increased OC in bottom waters under differing conditions. In June 2010, *in situ* fluorescence was restricted to surface waters (Figure 4-4); high OC in bottom waters (22%) suggests that decayed bloom material or grazer inputs contributed to the increased OC in bottom waters. In contrast, in March 2011, vertically homogeneous *in situ* fluorescence and oxygen saturation observations suggest that a vertically mixed active bloom was sampled, resulting in similar OC in surface and bottom waters (12% and 10%, respectively; Figure 4-11). Seasonally elevated OC in the tidal freshwater reaches of the estuary were also concurrent with observed *in situ* fluorescence, suggesting phytoplankton were the primary source of OC here as well.

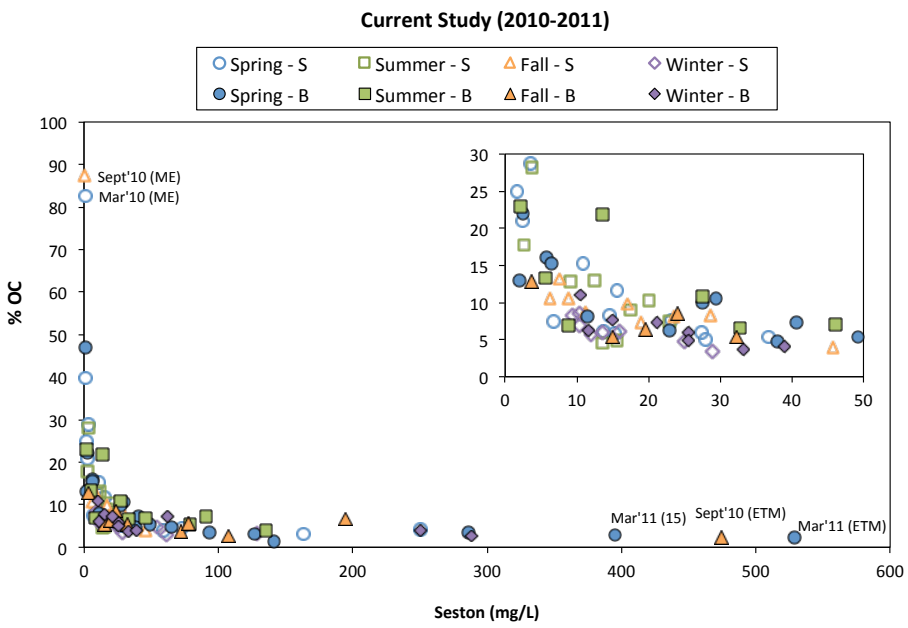
The ETM had seasonally consistent OC content, whereas the marine endmember had the most variable OC content observed in the estuary. Surface and bottom waters in

the ETM always had organic content below 10%. Low OC in the ETM has been attributed to the dilution of suspended particulates with low OC sediments (Cifuentes, 1991). Despite low %OC of particulates in the ETM, the fact that the ETM bottom waters had the maximum particle densities in the estuary resulted in the highest concentration of POC there under all conditions and seasons (Figures 4-9, 4-10). Highly variable OC has been observed at the marine endmember in previous studies (Table 5-1). This variability has been attributed to seasonal coastal marine productivity, and productivity in the lower Delaware Bay, as observed during the September 2010 cruise (Pennock and Sharp, 1986). Overall, surface water OC content measured in this study for each region of the estuary largely agreed with previous work in the Delaware Estuary (Table 5-1).

An inverse relationship between organic carbon content and suspended sediment concentration was observed for particulate samples collected in this study, and the relationship is consistent with previous observations in the Delaware Estuary (Figure 5-1; e.g. Cifuentes, 1991; Harvey and Mannino, 2001; Sharp et al., 2009). Such inverse relationships are common to estuaries and rivers worldwide, and demonstrate a trade off between suspended sediment loads and primary productivity, such that when sediment concentrations are above a certain concentration, productivity is light limited (Bianchi and Bauer, 2012). Results from this study suggest that primary productivity is light-limited when sediment concentrations are over ~ 20 mg/L in the Delaware Estuary (Figure 5-1).

The highest suspended solid concentrations measured in the Delaware Estuary were generally measured in the ETM during spring and fall in this and previous studies (Figure 5-1). Two mechanisms can explain the increase in suspended solids in the ETM

A.



B.

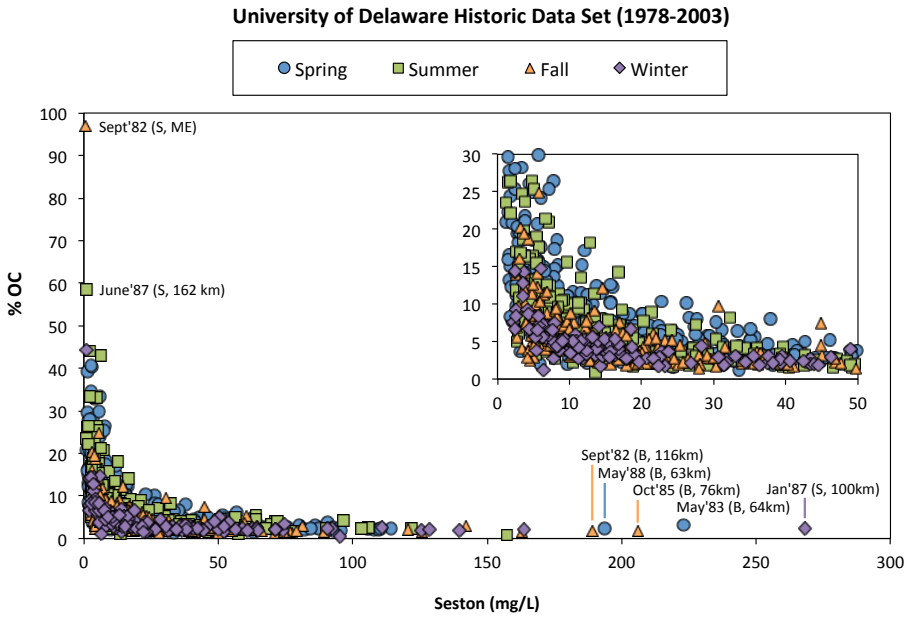


Figure 5-1. Organic carbon content of total suspended solids (seston) in the Delaware Estuary from A) this study and B) a historical data set from 1978-2003 (Sharp et al., 2009). Blue diamonds – Spring (March, April, May); Green square – Summer (June, July, August); Orange triangles – Fall (September, October, November); Purple diamonds – Winter (December, January, February). In A: bottom water - filled symbols; surface water - open symbols. Outliers are labeled by month and year: distance (km) is from the mouth of the estuary; ME – Marine endmember; ETM – estuarine turbidity maximum, 15 – Station 15. Note the difference in x-axes between panels and that the level of suspended solids measured in bottom waters can be as much as 2-3 times that in surface water, as measured by the current study.

Table 5-1. Organic carbon content of Delaware Estuary POM (% OC) for the different regions of the estuary. Previous studies examined surface water, and this study added bottom water.

Region	Biggs et al. (1983)	Cifuentes (1991)	Mannino and Harvey (2001)	This study - Surface Water	This study - Bottom Water
River	3-4.5%	1-14%	8-15%	5-21%	3-22%
ETM	2.5-3%		3-6%	3-10%	1-7%
Delaware Bay	3.5-9.5%	1-30%	12-43%	5-29%	4-47%
Coastal Ocean	N/A	N/A	16-47%	9-87%	6-23%

with contrasting river discharge (e.g. Figure 4-1). Spring freshet increases sediment delivery to the estuary, whereas low river discharge in fall enhances tidal mixing of the water column and extensive sediment resuspension. The September 2010 cruise of this study sampled after a long period of low river discharge and just after a spring tide. This combination of forces led to enhanced mixing of the water column and particle resuspension (e.g. Sommerfield and Wong, 2011). Although studies of physical processes within the estuary have recorded total particle concentrations in bottom water similar to the present work (~500mg/L SSC; Cook et al., 2007), notably, the maximum particle associated organic carbon concentrations measured in the present work was nearly 2 fold higher than the concentrations observed in a long term data set from the University of Delaware (529 mg/L and 278 mg/L, respectively; Figure 5-1). This discrepancy can be attributed to the fact that previous organic carbon studies in the Delaware Estuary only sampled surface water POM, and the sheer volume of TSS in bottom waters increases the OC content of those waters. This demonstrates that a large fraction of the organic carbon pool in the Delaware Estuary was previously uncharacterized (e.g. Cifuentes, 1991; Mannino and Harvey, 1999; Sharp et al., 2009).

The C:N ratio of POM determined in this study (~6-14) agree with previous work in the Delaware and other estuaries (Figure 4-12; e.g. Sharp et al., 2009, Mannino and Harvey, 2000; Countway et al., 2007). As a first approximation of OM sources through the estuary, the C:N ratio of POM confirmed terrestrial sources in the upper estuary, especially during high flow seasons (December 2010 and March 2011). Algal C:N ratios dominated in Delaware Bay and the coastal ocean, except during the December 2010 cruise for which intermediate C:N ratios were observed and fluorescence indicated no

productivity. The relatively narrow range of C:N ratios in estuaries has been attributed to OM degradation, because degradation of terrestrial OM decreases C:N ratios and conversely increases algal C:N ratios (Middelburg and Herman, 2007).

5.1.2 Bulk stable carbon isotopic composition

The bulk $\delta^{13}C$ signature of POM measured in this study was consistent with values that have been measured in the Delaware Estuary for decades. Depleted signatures dominate the upper estuary, characteristic of C3 terrestrial-derived material from the upper drainage basin of the Delaware River, and enriched algal-derived signatures seasonally dominate the lower estuary while the ETM has a mixed signature (Figure 5-2; e.g. Cifuentes, 1991; Mannino and Harvey, 1999; Fogel et al., 1988). Despite the general consistency of this pattern of $\delta^{13}C$-POm through the estuary, inter-annual and inter-seasonal variability between studies are largely driven by changes in river discharge and primary productivity.

The $\delta^{13}C$-POM signatures in spring were controlled by spring freshet river discharge and the development of the spring phytoplankton bloom, resulting in inter-annual differences of 2-3‰. For example, the March 2010 cruise in this study was sampled at the onset of the spring freshet before peak flow occurred (Figure 4-1), and $\delta^{13}C$-enriched POM in Delaware Bay was associated with an early and active phytoplankton bloom. In contrast, the March 2011 cruise occurred after a high discharge event at the beginning of the spring freshet (Figure 4-1). During this cruise, the upper estuary was more depleted than observed in March 2010 because of newly delivered terrestrial-derived OM. The more depleted phytoplankton bloom signature observed in March 2011, relative to the year before, can be attributed to CO_2 limitation in an evolved

bloom (Cifuentes et al., 1988). Similar differences in sampling time of the spring cruises with respect spring bloom evolution are invoked to describe δ^{13}C-POM distributions from previous studies (Cifuentes et al., 1988; Fogel et al., 1988).

The δ^{13}C signature of POM in other seasons was influenced by microalgal productivity in the upper estuary and lower Delaware Bay. For example, the June 2010 cruise had highly depleted material upriver from the ETM, which co-occurred with elevated levels of fluorescence and reflected freshwater algal production. Freshwater algal production can have an isotopic composition as low as -32‰ due to utilization of isotopically light CO_2 from microbial respiration (Cloern et al., 2002; Cifuentes et al., 1988). The summer observations from Fogel et al. (1988) also had strong depletion in the same location as the June 2010 cruise of this study. Summer phytoplankton productivity in Delaware Bay had a very consistent isotopic signature between studies (Figure 5-2).

The phytoplankton bloom observed near the mouth of Delaware Bay during the September 2010 cruise was likely marine productivity and had an isotopic composition consistent with of Mid-Atlantic Bight primary productivity (~ -20‰; Pennock and Sharp, 1985; Bauer et al., 2002). The lack of a mid-estuary peak in δ^{13}C-POM and a steep decrease in δ^{13}C-POM up-estuary suggests conservative mixing between the marine productivity and riverine-delivered material. Winter profiles with intermediate values and flat profiles suggest that mixed inputs are throughout the estuary, and not surprisingly, little to no productivity.

Conservative mixing lines for δ^{13}C-POM results from this study highlight blooms as the source of enriched OM in Delaware Bay and freshwater algae and terrestrial OM as the source of depleted OM in the upper estuary (Figure 4-13). In spring and summer,

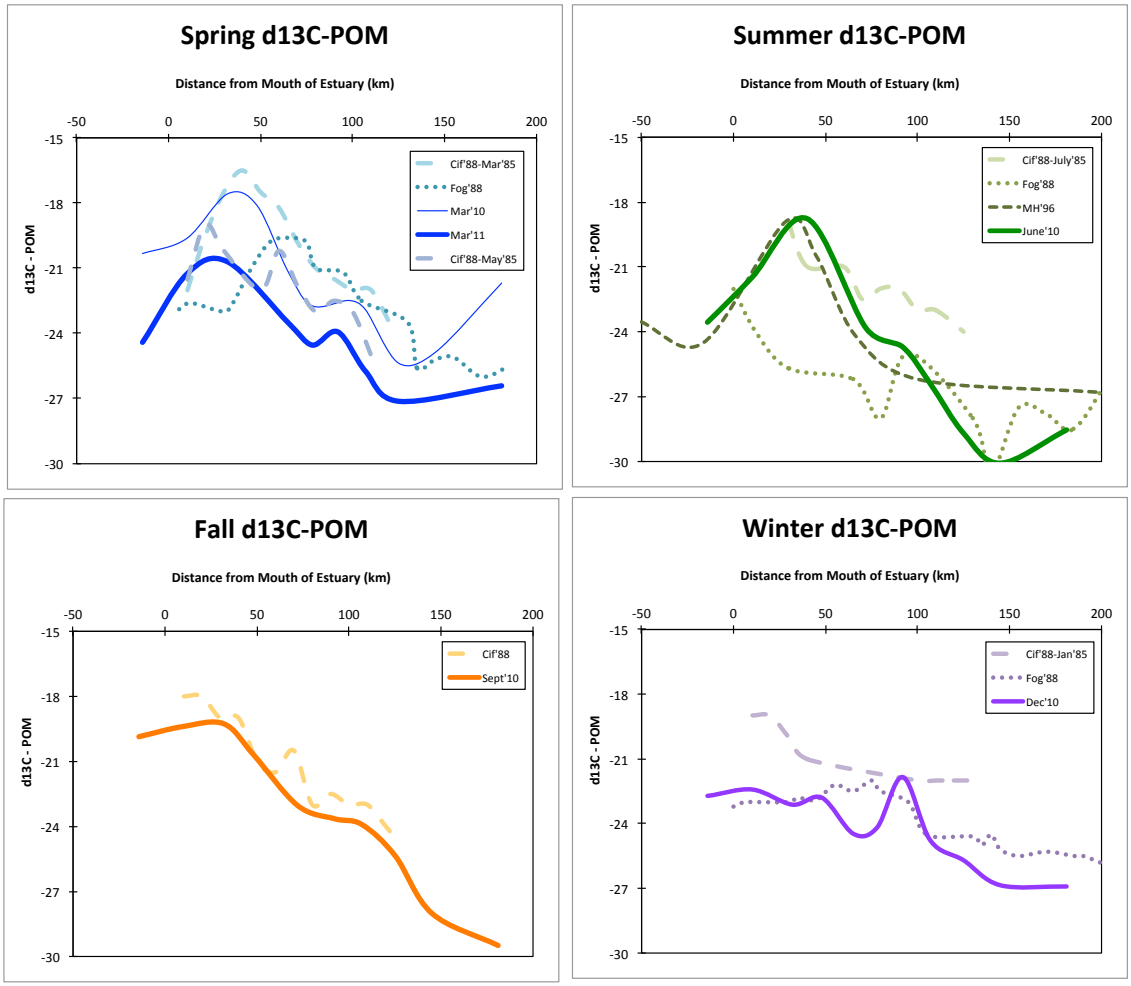


Figure 5-2. Historical comparison of the bulk stable carbon isotopic composition of surface water POM in the Delaware Estuary for winter (purple), spring (blue), summer (green), and fall (orange). Dotted and dashed lines are from past studies: Cif'91 – Cifuentes (1991); Cif'88 – Cifuentes et al. (1988); Fog'88 – reproduced from Bianchi and Bauer (2012) which was data from Fogel et al. (1988); MH'96 – Mannino and Harvey (1999). Solid lines are from the current study.

the depleted signature of terrestrial-derived OM was masked by mixing with algal bloom material in the ETM, but near conservative mixing of δ^{13}C-POM was observed in fall and winter cruises. Near conservative mixing suggests that when there is a lack of autochthonous carbon inputs, terrestrial-derived OM is gradually lost from the riverine endmember to the marine endmember.

5.1.3 Summary

The overall character of POM in the Delaware Estuary is similar to that found in other functionally turbid, sediment-trapping estuaries, wherein primary productivity is primarily light-limited and particles have long residence times that foster geochemical alteration (e.g. Middelburg and Herman, 2007; Hopkinson et al., 1998). Mixing of sources and homogenization of POM was especially pronounced in the ETM, with consistent C:N ratios and bulk stable carbon isotopes regardless of season (Figures 4-12, 4-13). Although the organic carbon content was consistently low in the ETM, maximum particle concentrations in bottom waters produced the highest concentrations of POC in the estuary during all seasons (Figures 4- 9, 4-10). Importantly, bottom water measurements in this study address a large fraction of the carbon pool that was previously geochemically uncharacterized (e.g. Cifuentes, 1991; Mannino and Harvey, 1999; Sharp et al., 2009).

Overall the bulk δ^{13}C-POM and C:N ratios results reflected source signatures and patterns consistent with previous work in the Delaware Estuary. Consistency between this study and previous work for surface water POM suggests there have not been major shifts in the sources or amounts of OM in the Delaware Estuary for several decades. As previously observed, seasonal changes in river discharge and primary productivity

controlled the geochemical signatures of bulk OM through the estuary. However, the pathway of terrestrial-derived OM through the estuary was obscured mid-estuary by mixing in the ETM and dilution with phytoplankton signatures in Delaware Bay.

5.2 Sources of OM in the Delaware Estuary

5.2.1 Algal and vascular plant-derived OM in the Delaware Estuary

Biomarkers revealed mixed sources of OM throughout the Delaware estuary in contrast to the bulk parameters of POM, which suggested primarily vascular plant OM in the upper estuary and algal sources in the lower estuary. Long chain alkanes and PLFAs in Delaware Bay and at the marine endmember showed the presence of vascular plant material throughout the Delaware Estuary in all seasons, despite overwhelmingly algal bulk signatures in the lower estuary. Alkane and PLFA biomarker results agreed through the estuary, and showed that POM was comprised of similar proportions of vascular plant and algal OM throughout the estuary in surface waters, but vascular plant OM was typically higher than algal OM in the upper estuary and vice-versa in the lower estuary (Figure 4-17, 4-20). This pattern of sources confirmed previous observations in the Delaware Estuary (Mannino and Harvey, 1999; Cifuentes, 1991), and also the pattern of POM sources in estuaries generally (e.g. Canuel, 2001; Fernandes et al., 1997; Countway et al., 2007; Medeiros et al., 2012).

The bulk $\delta^{13}C$ signature of POM combined with the alkane average chain lengths (ACL) clarified source differences between surface and bottom waters (Figure 5-3). Surface water POM was seasonally imprinted by algal productivity throughout the estuary resulting in a greater distribution of the ACL and wider spread of bulk isotopic compositions. In ETM surface waters, reduced ACL compared to the riverine

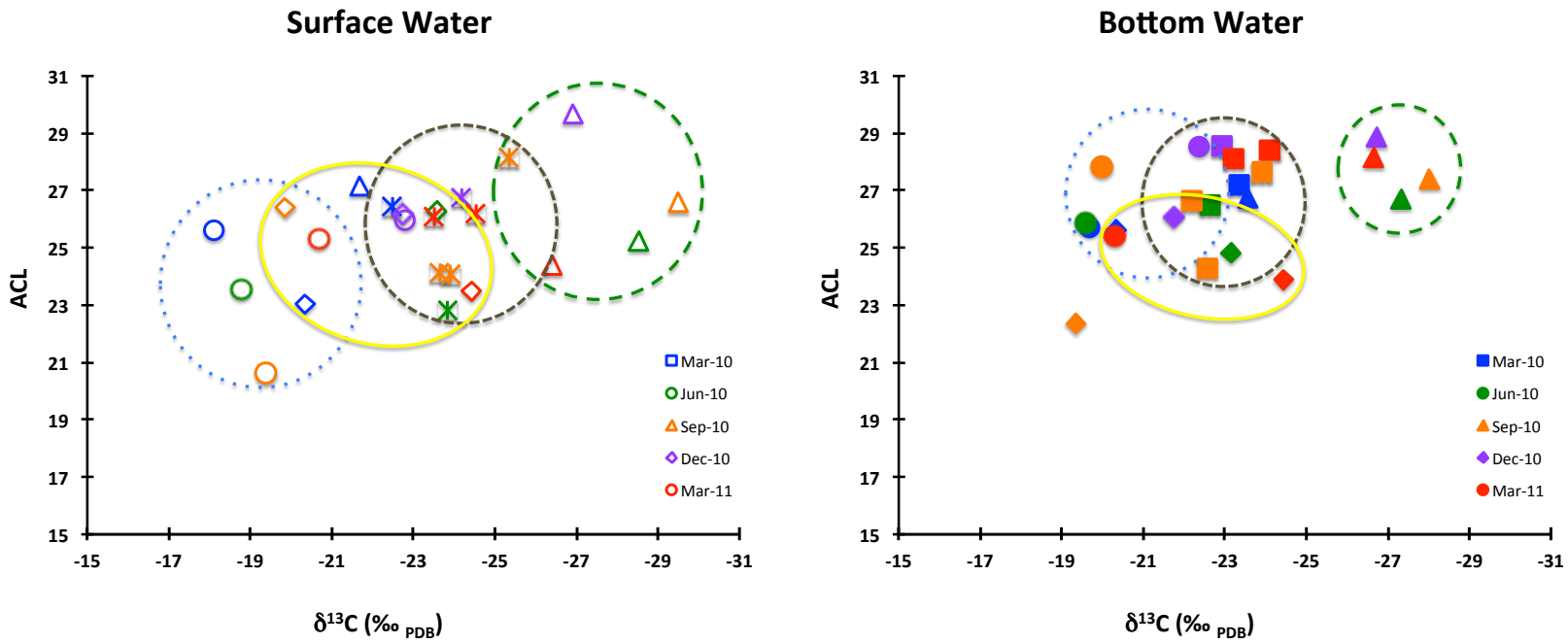


Figure 5-3. Delaware Estuary POM average chain length (ACL) vs. bulk stable carbon isotopes. Surface water and bottom water samples are divided and are empty and filled symbols, respectively. Seasons are notated by colors of symbols: March 2010 – blue; June 2010 – green; September 2010 – orange; December 2010- purple; March 2011- red. Region of the estuary is notated by symbol shape: Riverine endmember- triangles; ETM- squares and asterisks; Delaware Bay- circles; marine endmember- diamonds. Large circles outline the four estuary regions: green dash – riverine; black small dash- ETM; yellow oval- marine endmember; blue dots- Delaware Bay.

endmember, as well as the presence of algal PLFAs, suggested that algal inputs to the ETM were delivered by estuarine circulation since sediment concentrations are known to limit productivity in the ETM (e.g. Figures 5-3, 4-20; Pennock and Sharp, 1986). The geochemical composition of OM in surface waters show a clear but gradual shift from riverine to the marine endmember, suggesting, similar to bulk measurements alone, that terrestrial material was gradually lost through the estuary.

In direct contrast to the mixed sources of POM in surface water throughout the Delaware Estuary, bottom waters had more vascular plant derived signatures consistently (Figure 5-3). Bottom water exhibited a narrow range in geochemical signatures, especially within the ETM. The trapping of vascular plant OM in bottom waters of the ETM, as evidenced by both biomarker classes, constrasted directly with the bulk measurements that suggest near-conservative mixing through the estuary (e.g. Figures 5-3, 4-20, 4-13). Taken together, bulk and biomarker results suggest that the terrestrial OM pool in the Delaware Estuary is concentrated in bottom waters, and analysis of surface waters alone imprints the estuary with a much more “algal” appearance overall.

Seasonally, there was a bimodal pattern to the alkane distributions, with high levels of vascular plant compounds in both winter to spring and fall (Figure 4-17). Samples from the September 2010 cruise were predominantly vascular plant-derived, supporting observations of high terrestrial OM in the fall (Cifuentes, 1991). High levels of vascular plant material were also observed in the March 2011 and December 2010 cruises, suggesting river discharge in the winter and spring delivers material with higher concentrations of terrestrial material to the estuary. Thus, high flow delivers vascular plant OM to the estuary and low flow conditions enhance resuspension of vascular plant

OM into the water column. Otero et al. (2000) also determined that greater terrestrial inputs occurred during periods of low production and higher flushing.

5.2.2 The ETM traps vascular plant material

Unlike bulk analyses, biomarker results illustrate that vascular plant-derived OM collects in the ETM, especially in bottom waters, and dramatically decreases downstream of the ETM under most conditions (Figure 4-17). These results reinforce mechanisms determined from sedimentological studies in the Delaware Estuary, which show that particles in the ETM have a large intra-estuary source from sites of persistent of sediment deposition in the upper tidal freshwater river (Cook et al., 2007). Also, minimal particulate material escapes the ETM outside of transient down-estuary fluxes during perigeanal spring tides and storm-driven high discharge events (Sommerfield and Wong, 2011). Results from the present study suggest that the material trapped in the ETM is largely derived from the land, but seasonally mixes with primary productivity sourced from the upper river or Delaware Bay. Trapping of vascular plant derived OM in surface waters of the ETM was previously documented in the Delaware Estuary (e.g. Mannino and Harvey, 1999; Harvey and Mannino, 2000; Cifuentes, 1991), and in other estuaries such as the York River Estuary (Countway et al., 2007), but the present study highlights the importance of ETM bottom water, especially, as a trap for vascular-plant derived OM.

The accumulation of long chain alkanes and a high proportion of PLFAs in ETM bottom waters suggest that bottom water particulates are primarily derived from vascular plant OM (Figures 4-17, 4-20). In contrast, δ^{13}C-POM signatures in the ETM for all seasons were enriched relative to the riverine endmember (Figure 5-3). The discrepancy between strongly terrestrial biomarkers and enriched δ^{13}C-POM signatures relative to the

riverine endmember in the ETM is not easily attributed to the mixing of depleted material from the upper estuary with enriched algal material, especially since the enriched signature in the ETM occurs even during seasons without observed phytoplankton productivity (e.g. December 2010). The more likely geochemical cause of this inconsistency is that an additional source of OM is more prevalent in bottom than surface waters and has a 'vascular plant' biomarker signature, but enriched isotopic signature. This suggests that marsh-derived OM may be a significant input of OM to the ETM.

5.2.3 Marsh-derived vascular plant OM in the Delaware Estuary

An additional source of OM is necessary to describe the geochemical signatures of bottom water OM in the Delaware Estuary, especially within the ETM. The Delaware River watershed primarily drains forest and agricultural land, which is dominated by C3 plants. In contrast, the lower estuary drainage basins include a higher proportion of wetlands (~23% vs 15%; Fry et al., 2011), which contain a high proportion of C4 plants. Wetland erosion throughout the Delaware Estuary has been documented for decades (e.g. Kearney et al., 2002), which would imply that wetland OM is a likely source of OM to the estuary. Yet, differentiating this source of OM from traditional terrestrial endmembers, such as the forest-dominated upper drainage basin, is difficult due to overlapping source signatures in alkane chain lengths (e.g. Figure 2-1). Nevertheless, salt marsh OM from the lower estuary has a distinct isotopic geochemical signature that can assist in clarifying the sources of OM where there are mixtures of sources, such as the bottom waters of the ETM. Although salt marshes have terrestrial-appearing biomarker signatures, their biomarkers have enriched isotopic signatures (Canuel et al, 1997; Tanner

et al., 2007). By employing both biomarker distributions and their isotopic signatures, wetland contributions to the Delaware Estuary OM pool were assessed.

5.2.3.1 Biomarker approach

Delaware salt marshes are predominantly comprised of *P. australis* and *S. alterniflora* (Bushaw-Nelson et al., 2008; Kreeger et al., 2012). *P. australis* alkanes were analyzed for this thesis work using a variety of plant samples collected from Delaware Bay in May and October 2010 (Figure 5-4). Alkanes of *P. australis* had a predominance of C_{25}, C_{27}, and C_{29} alkanes, with C_{max} consistently being the C_{29} alkane. The alkane signature of *P. australis* was very similar to that of *S. alterniflora,* (Canuel et al., 1997; Wang et al, 2003). As alkane distributions for both dominant marsh plants were similar, *P. australis* alkanes were used as a representative endmember for marsh OM.

Representative distributions for algal, terrestrial, and marsh OM were mathematically mixed in varying proportions to examine the influence of three source endmembers on alkane distributions (Figure 5-5). Alkanes from the June 2010 phytoplankton bloom in Delaware Bay were modified for a 'pure' algal endmember by removing alkanes greater than C_{23} from the distribution. The alkane distribution of the December 2010 riverine endmember was selected to represent a composite of terrestrial OM delivered to the estuary from the Delaware River. The marsh endmember was the composite of stem, root, flower, and leaf *P. australis* alkanes, calculated by averaging the normalized alkanes of these plant parts (Figure 5-4). Notably, the integration of wetland OM into alkane distributions increased the proportion of mid-chain-length (C_{25}, C_{27}) alkanes relative to long-chain-lengths (C_{31}, C_{33}; Figure 5-5).

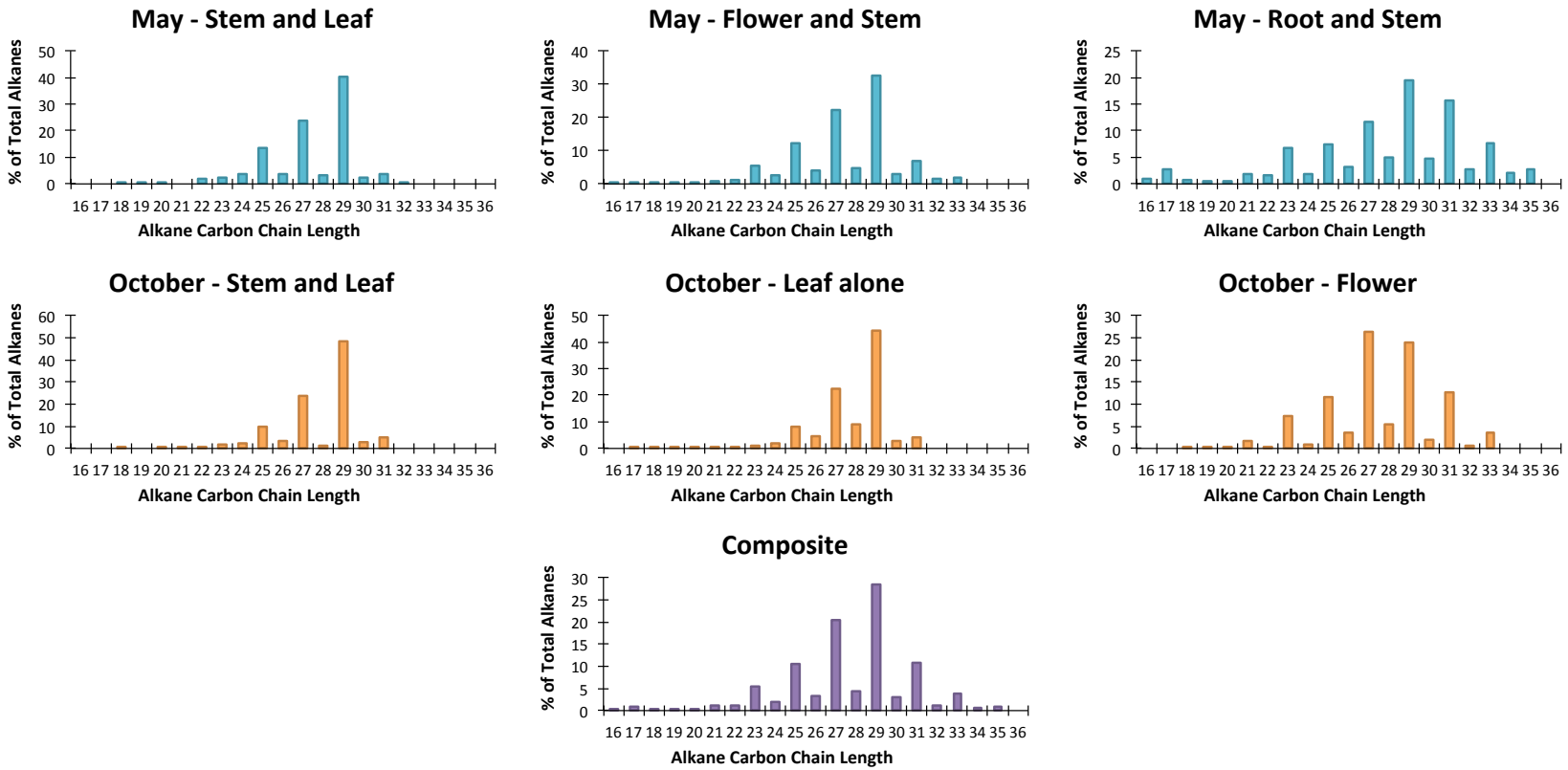


Figure 5-4. *N*-alkanes from *Phragmites australis* plant material, collected in May and October 2010 on the New Jersey shore of Delaware Bay (Haskins Shelfish Research Station, Shellpile, NJ). Alkanes are shown normalized to the total concentration of alkanes for each sample. The composite sample is the average of the normalized October flower, March root and stem, and the average of all stem and leaf samples.

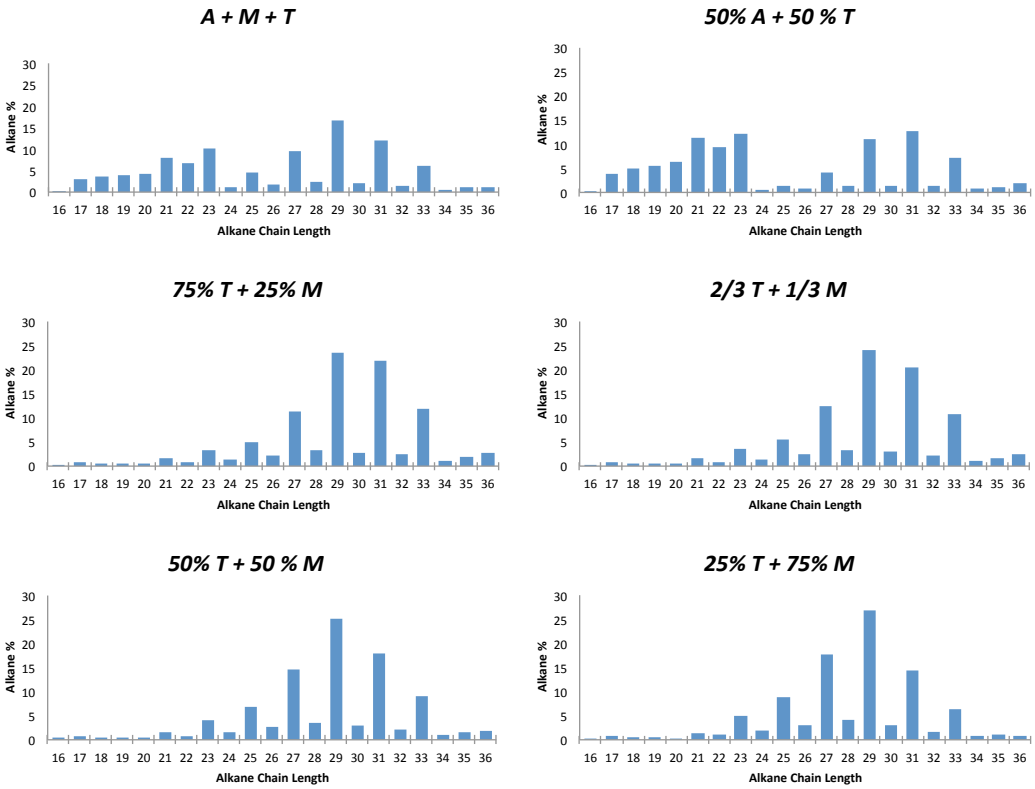


Figure 5-5. Delaware Estuary OM endmembers mathematically mixed by adding the endmembers in various proportions. A – Algal (June 2010 phytoplankton bloom POM), M – Marsh (*P. australis* composite), and T – Terrestrial (December 2010 riverine endmember POM).

Alkane indices were calculated from the mixing models of alkane distributions and were compared to Delaware Estuary POM alkane indices (Table 5-2). However, POM ACL and CPI were confounded by overlapping sources in the Delaware Estuary because marsh inputs with significant mid-chain-lengths shifted these indices towards an intermediate mixture of algal and vascular plant OM. The $P_{mar\text{-}aq}$ index, developed to differentiate wetland macrophytes and terrestrial sources of OM in aquatic environments (e.g. Ficken et al., 2000; Mead et al., 2005), was also insensitive in the Delaware Estuary because all POM samples had $P_{mar\text{-}aq}$ within the terrestrial-emergent range (<0.6; Table 4-3). This range for $P_{mar\text{-}aq}$ can arise from mixed terrestrial and emergent sources of OM instead of indicating one source or the other (Ficken et al., 2000).

An index was needed to differentiate laterally delivered marsh OM and axially delivered terrestrial OM in the Delaware Estuary. As with the $P_{mar\text{-}aq}$ index, the index had to eliminate algal contributions to alkane distributions, but additionally needed to distinguish the diagnostic chain lengths of salt marsh and terrestrial long chain alkanes. Capitalizing on the subtle differences in the abundances of mid- and long- chain lengths, the marsh-terrestrial index (MTI) was defined as:

$$MTI = \frac{C_{25} + C_{27}}{C_{31} + C_{33}}$$

The C_{29} and C_{23} alkanes were not included in the equation because the C_{29} alkane is highly abundant in both marsh and terrestrial sources of OM, and the C_{23} alkane is frequently derived from macroalgae (e.g. Chikaraishi and Naraoka, 2003). Applying the MTI to the mixing model distributions of marsh and terrestrial alkanes, alkane

Table 5-2. Alkane indices calculated from the hypothetical endmember mixes as in Figure 38. A – Algal endmember; T – Terrestrial (riverine) endmember; M – Marsh endmember. LC – long chain indices calculated using only alkane chain lengths C_{25}-C_{34}.

Index	A+M+T	A+T	50%M + 50%T	75%T+ 25%M	75%M+ 25%T	33%M+ 66%T
ACL	25.97	25.15	28.61	29.11	28.11	28.94
ACL-LC	28.45	28.81	29.07	29.61	28.54	29.43
Pmar-aq	0.335	0.366	0.202	0.154	0.249	0.170
CPI	3.14	2.59	5.15	5.27	5.03	5.23
CPI-LC	5.77	6.04	5.07	4.89	5.27	4.95
MTI	0.788	0.272	0.788	0.479	1.295	0.568

distributions with greater marsh inputs have an MTI greater than 1, whereas greater terrestrial inputs displayed an MTI less than 1 (Table 5-2). This allowed the influence of marsh inputs to be distinguished in samples with mixed algal, vascular plant, and marsh inputs.

Although MTI was able to differentiate between terrestrial and mash inputs in the estuary, highly degraded or petroleum inputs contribute mid- to long-chain alkanes in some samples. The CPI readily detects these inputs, since terrestrial and marsh OM have an odd carbon chain length preference, but long chain alkanes from degraded or petroleum sources have no odd-even chain length preference. The CPI for just the long chain alkanes (CPI-LC; C_{25}-C_{34}) was calculated to focus in on the same compounds as the MTI as well as remove influences from algal inputs with short chain alkanes.

In combination, MTI and CPI-LC of Delaware Estuary POM and sediments were able to distinguish degraded and/or petroleum inputs, and likewise distinguish marsh and terrestrial inputs (Figure 5-6). CPI-LC lower than 2 suggested long chain alkanes were highly degraded or petroleum derived, and samples with a low CPI-LC also had highly variable MTI (~0.5 – 2.5). Samples with low CPI-LC (~1-2) and variable MTI were primarily found in surface waters at the marine endmember (open diamonds) and Delaware Bay (open circles; Figure 5-6). This is consistent with the highly degraded nature of vascular plant material exported from the estuary and in surface waters in Delaware Bay. In contrast, POM from the riverine endmember, ETM, and bottom waters of Delaware Bay all had MTI < 1 and CPI-LC > 2, suggesting the relative influence of terrestrial and marsh vascular plant OM could be determined.

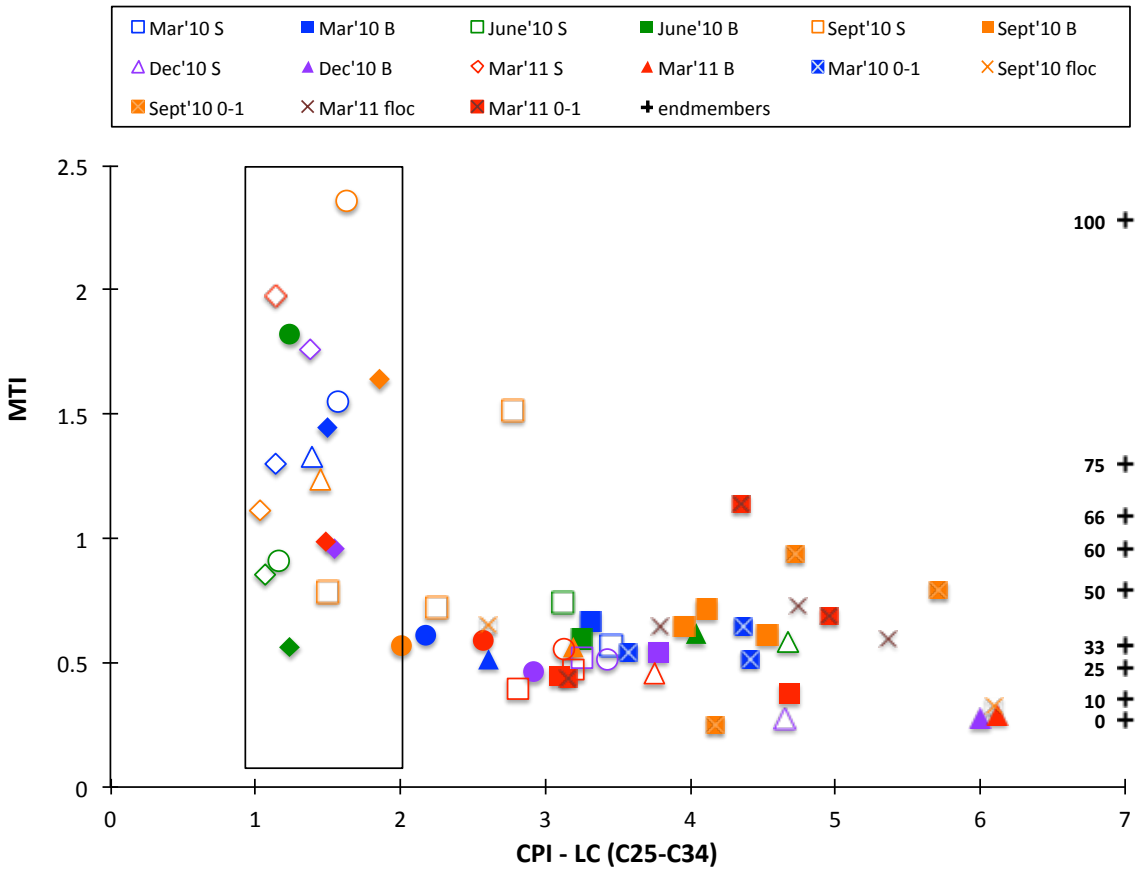


Figure 5-6. Delaware Estuary POM and sediment CPI – LC (long chain carbon preference index) vs. MTI. S – Surface water POM (open symbols); B – Bottom water POM (closed symbols); 0-1 – Core-top sediments (closed 'X'); floc – sediment-water interface (open 'X'). Symbol shape indicates region of the estuary: Riverine endmember- triangles; ETM- squares; Delaware Bay- circles; marine endmember- diamonds. Crosses indicate MTI values for hypothetical endmembers as depicted in the previous figure, with percent marsh indicated next to each cross. The black box from 1-2 CPI-LC indicates degraded or petroleum-derived OM. Note that samples in the ETM and in most Delaware Bay bottom waters have a CPI-LC greater than 2 and a CPI that indicate marsh inputs are between 25-50% of the total vascular plant material.

Within this range of CPI-LC and MTI, the average MTI for bottom water POM consistently increased from the riverine endmember through the ETM, into Delaware Bay (0.45, 0.57, and 0.81, respectively; Figure 5-6), indicating that the proportion of marsh OM contributing to the vascular plant OM pool increased down-estuary. ETM and Delaware Bay bottom waters had MTI values that equated to having ~15-45% marsh contributions (minimum and maximum values were in the March 2011 ETM and September 2010 ETM, respectively). The lower CPI-LC observed in the ETM and Delaware Bay than observed at the riverine endmember is attributed to the degradation of vascular plant POM down-estuary, supporting other geochemical characteristics of POM in the Delaware Estuary. Therefore, the MTI index successfully demonstrated that there are substantial marsh OM inputs in Delaware Bay and the ETM, relative to the riverine endmember.

5.2.3.2 Compound-specific stable carbon isotopic approach

Alkane biomarker signatures in this study did provide evidence for appreciable marsh inputs to Delaware Estuary particulate carbon, nonetheless, results from the traditional indices and even the march targeting index, MTI were all fairly equivocal. However, the $\delta^{13}C$ of POM long chain alkanes from the September 2010 and March 2011 cruises (low and high flow, respectively) were able to further resolve marsh and terrestrial sources and changes in their relative inputs along the estuary with differing estuarine conditions. In September 2010, long chain alkanes exhibited roughly half the isotopic range of March 2011 (-27.6‰ to -31.3‰ and -28.5‰ to -37.2‰, respectively; Figure 4-23), and the March 2011 riverine endmember had C3 values (-33.0‰ to

-37.2‰), whereas the September 2010 riverine endmember had values consistent with inputs from enriched freshwater wetland plants (-31.1‰ to -28.2‰; e.g. Ficken et al., 2000). This is likely owing to the fact that tidal mud flats near the riverine endmember are often seasonally coated with submerged/floating macrophytes (Leck and Leck, 2005), and signatures from this source may be more enhanced during periods of low river discharge, such as was present during September 2010. Overall, the narrow range in alkane isotopic composition in September 2010 suggests POM was generally more homogenized than in March 2011, due to both low river discharge and enhanced particle mixing. In both seasons, $\delta^{13}C$ of long chain alkanes gradually became more positive moving down-estuary, indicating progressively increasing marsh inputs down-estuary (Figure 4-23).

The isotopic composition of POM long chain alkanes in both seasons was sufficiently enriched that it required a source such as C4 plant OM from lower estuary salt marshes. The proportion of C4 material necessary to obtain observed values was calculated from a two-endmember mass balance model, modified after Sikes et al. (2009) and Bianchi et al. (2011):

$$f_{marsh} = \frac{\delta^{13}C_{alkane} - \delta^{13}C_{terr}}{\delta^{13}C_{marsh} - \delta^{13}C_{terr}}$$

$$f_{terr} = 1 - f_{marsh}$$

where f_{terr} and f_{marsh}, were the fractions of terrestrial and marsh OM, respectively, and $\delta^{13}C_{alkane}$, $\delta^{13}C_{terr}$, and $\delta^{13}C_{marsh}$ were the carbon isotopic composition of the sample alkane, terrestrial endmember alkane, and marsh endmember alkane, respectively. The isotopic composition of March 2011 alkanes were used for the $\delta^{13}C_{terr}$ endmember for

both cruises, because they were in the range typical for C3 plants (e.g. Tipple and Pagani, 2010, Table 5-3) and were representative of the upper Delaware drainage basin (Fry et al., 2011). *S. alterniflora* alkane CSIA values were used as a representative C4 marsh plant $\delta^{13}C_{marsh}$ endmember (Table 5-3).

Source apportionments were calculated using the C_{27}, C_{29}, and C_{31} alkanes, and results were averaged (Table 5-4). For March 2011 POM, C4 salt marsh inputs were calculated to be 26 – 42% of the long chain vascular plant derived OM. In September 2010, C4 marsh inputs were 42 – 57% of the long chain vascular plant derived OM. Consistent with down-estuary enrichment of alkanes, the calculated proportion of marsh OM increased incrementally down-estuary for both seasons. The proportion of marsh input from CSIA was consistently greater than that determined by the MTI by 10-20%., which is attributed to the greater specificity of CSIA to identify sources in a complex mixture. Nonetheless, both analyses suggest that salt marsh OM is substantial in Delaware Bay and ETM bottom waters and that the proportion of marsh inputs may be as high as nearly half of the vascular plant derived OM in these pools. The fraction of marsh OM becomes an especially considerable proportion of mass in the ETM since ETM bottom waters hold the greatest amount of OC in the Delaware Estuary.

Isotopic mixing model results from this thesis work likely underestimate marsh contributions to the Delaware Estuary. The dominant grass species in Delaware Estuary salt marshes (*P. australis* and *S. alterniflora*) have only slightly different alkane distributions despite having very different isotopic signatures. Thus, the source apportionment derived from alkane indices cannot distinguish between these marsh inputs. Mixing model results from the $\delta^{13}C$ of alkane biomarkers were based on a C4

Table 5-3. Relevant geochemical signatures of potential OM endmembers in the Delaware Estuary. References and data are as follows: * - this study, @ - Church et al. (2006), ~ - Tanner et al. (2007; 2010), ^ - Wainright et al. (2000), # - Kemp et al. (2011), % - Canuel et al. (1997), $ - Tipple and Pagani (2010). If two references are reported, the value is an average. The shaded values were calculated using the same fractionation factor between bulk $\delta^{13}C$ and alkane- $\delta^{13}C$ of *S. alterniflora* plant material.

Endmembers:	**Freshwater wetlands**	***P. australis* plant**	***P. australis* sediments**			***S. alterniflora* plant**	***S. alterniflora* sediments**			**C4 - general**	**C3 - general**
Signatures:	**Avg ± Stdev**	**Avg ± Stdev**	**Min**	**Max**	**Avg**	**Avg ± Stdev**	**Min**	**Max**	**Avg**	**Avg ± Stdev**	**Avg ± Stdev**
bulk $\delta^{13}C$	-25.63 ± 1.26[@]	-25.91 ± 0.77^#	-27^#	-22^#		-12.85 ± 0.54^#	-18.9#	-15.4#	-18.6#	-13.8 ± 1.9[$]	-27.8 ± 2.3[$]
C:N	25.96 ± 4.35[@]					50.00#			16.71#		
alkane ACL	29.46 ± 0.49[~]	*27.68* ± 0.21*			*27.93**	28.70[~]			29#		
alkane CPI	>3.5[~]	*5.42* ± 1.86*			*3.30**	3.80#			4#		
alkane CPI-LC		*6.81* ± 2.89*			*3.67**						
MTI		*5.15* ± 3.38*			*0.82**						
$\delta^{13}C$-C_{27}		*-33.47* ± 0.08*				-20.85[%~]			-26.605	All alkane Avg ± Stdev	
$\delta^{13}C$-C_{29}		*-33.86* ± 0.03*				-22.45[%~]			-28.205	-21.7 ± 2.4[$]	-33.1 ± 2.3[$]
$\delta^{13}C$-C_{31}						-23.40[%]			-29.155		

Table 5-4. Two-endmember mixing model results from compound specific isotope analysis of alkanes for March 2011 and September 2010. Two-endmember mixing models were used to calculate the fractions of C4 marsh (*S. alterniflora*) vs. riverine endmember OM (f_{marsh} and f_{terr}, respectively). POM are as follows: CHL MAX – chlorophyll maximum; ETM – estuarine turbidity maximum zone; IM – intermediate site between ETM; RE – riverine endmember, and SW – surface water; BW – bottom water. Sediments are labeled as core (water sampling site) and were all the 0-1cm core-top sample.

March 2011									
Sample Type:	**POM**						**Surface Sediments (0-1cm)**		
SAMPLE:	***CHL MAX - BW***	***ETM (9)- SW***	***ETM (9)- BW***	***ETM (11)- BW***	***RE - SW***	***RE- BW***	***35A (9)***	***34B (15)***	***32A (17)***
USING C27									
Fmar	*0.32*	*0.28*	*0.28*	*0.16*	*N/A*	*0.00*	*0.32*	*0.38*	*0.23*
% Marsh	32.30	28.26	28.21	15.52		0.00	32.46	38.20	22.62
Fterr	*0.68*	*0.72*	*0.72*	*0.84*		*1.00*	*0.68*	*0.62*	*0.77*
% Terr	67.70	71.74	71.79	84.48		100.00	67.54	61.80	77.38
USING C29									
Fmar	*0.46*	*0.39*	*0.39*	*0.28*	*0.13*	*0.00*	*0.32*	*0.47*	*0.50*
% Marsh	45.53	38.85	39.23	27.60	13.11	0.00	32.28	46.90	50.17
Fterr	*0.54*	*0.61*	*0.61*	*0.72*	*0.87*	*1.00*	*0.68*	*0.53*	*0.50*
% Terr	54.47	61.15	60.77	72.40	86.89	100.00	67.72	53.10	49.83
USING C31									
Fmar	*0.49*	*0.39*	*0.47*	*0.35*	*0.21*	*0.00*	*0.36*	*0.60*	*0.63*
% Marsh	49.25	38.66	47.19	35.39	20.77	0.00	35.96	60.10	63.35
Fterr	*0.51*	*0.61*	*0.53*	*0.65*	*0.79*	*1.00*	*0.64*	*0.40*	*0.37*
% Terr	50.75	61.34	52.81	64.61	79.23	100.00	64.04	39.90	36.65
AVERAGE OF C27, C29, C31									
% Marsh	42.36	35.26	38.21	26.17	16.94	N/A	33.57	48.40	45.38
% Terr	57.64	64.74	61.79	73.83	83.06	N/A	66.43	51.60	54.62
St. Dev. (±)	8.91	6.06	9.53	10.01	5.41	N/A	2.07	11.03	20.78

Table 5-4 (cont).

September 2010									
Sample Type:	**POM**						**Surface Sediments (0-1cm)**		
SAMPLE:	***ETM (13)-BW***	***IM (15)-BW***	***ETM (17)-SW***	***ETM (17)-BW***	***RE-SW***	***RE-BW***	***26HB (12)***	***25HB (15)***	***23HB (17)***
USING C27									
Fmar	*0.48*	*N/A*	*0.35*	*N/A*	*0.29*	*N/A*	*0.42*	*0.27*	*0.20*
% Marsh	48.43		35.29		28.56		42.28	26.90	20.17
Fterr	*0.52*		*0.65*		*0.71*		*0.58*	*0.73*	*0.80*
% Terr	51.57		64.71		71.44		57.72	73.10	79.83
USING C29									
Fmar	*0.58*	*0.49*	*0.38*	*0.42*	*0.39*	*N/A*	*0.48*	*0.46*	*0.48*
% Marsh	58.26	49.40	37.75	42.10	38.67		47.86	46.43	47.89
Fterr	*0.42*	*0.51*	*0.62*	*0.58*	*0.61*		*0.52*	*0.54*	*0.52*
% Terr	41.74	50.60	62.25	57.90	61.33		52.14	53.57	52.11
USING C31									
Fmar	*0.64*	*N/A*	*0.58*	*N/A*	*0.47*	*N/A*	*0.59*	*0.53*	*0.52*
% Marsh	63.50		58.16		46.82		59.32	52.90	51.62
Fterr	*0.36*		*0.42*		*0.53*		*0.41*	*0.47*	*0.48*
% Terr	36.50		41.84		53.18		40.68	47.10	48.38
AVERAGE OF C27, C29, C31									
% Marsh	56.73	49.40	43.73	42.10	38.02	*N/A*	49.82	42.08	39.89
% Terr	43.27	50.60	56.27	57.90	61.98		50.18	57.92	60.11
St. Dev. (±)	7.65	*N/A*	12.56	*N/A*	9.15	*N/A*	8.69	13.54	17.18

marsh plant endmember, although *P. australis* is a C3 plant. Therefore, additional C3 inputs of *P. australis,* which are very similar to fully terrestrial plants such as trees, would not be considered in the proportions from these mixing model calculations. Also, the tidal freshwater reaches of the Delaware Estuary have diverse wetlands with C3 marsh plants that are not well characterized using the geochemical methods employed in this study. These marsh inputs were not considered in this study, but would act as additional sources of marsh-derived OM to the estuary.

5.2.3.3 Mechanisms for wetland organic matter input to the Delaware Estuary

The combination of biomarker and compound-specific isotope analyses employed in this investigation showed that wetland OM is an important fraction of the vascular plant material in the Delaware Estuary. This stands in contrast to previous work in the Delaware Estuary (Cifuentes, 1991). This discrepancy may have been caused by an increase in the delivery of marsh material to the axial OM pool over the last 20 years, but it is more likely that marsh material has previously evaded geochemical characterization in previous studies.

Evidence for wetland erosion in Delaware Bay has been documented for decades, even during the period that the previous geochemical work in the Delaware Estuary was conducted (Phillips, 1986; Cifuentes,1991; Mannino and Harvey, 1999). More than 3,300 acres of salt marsh wetlands were lost between 1996-2006, most of which was fringing Delaware Bay (Partnership for the Delaware Estuary, 2012). The rate of wetland erosion for some regions of the Delaware Estuary increased between 1996-2001 and 2001-2006, but greater rates of change were calculated for the upper estuary than the lower estuary (Partnership for the Delaware Estuary, 2012). Since the bulk parameters of POM, such as

%OC, C:N ratios, and δ^{13}C-POM, were consistent between this work and previous studies in the estuary, changes in circulation and sediment dynamics of the estuary are unlikely to have altered the delivery of eroded wetland material to the axial channel.

Without evidence for substantial alteration to the delivery of wetland material to the Delaware Estuary since previous work, it appears that wetland OM was not detected by the techniques used in previous studies. Cifuentes (1991) used lignin biomarkers, bulk stable carbon isotopes and C:N ratios and concluded that *S. alterniflora* inputs to Delaware Bay were minimal. In that study, a mismatch in the salt marsh endmember (the Broadkill Estuary) and observed lignin biomarker ratios was ascribed to dilution by other non-woody plants from local drainage basins or algal productivity (Cifuentes, 1991). However, more recent studies have demonstrated that lignin biomarkers degrade in *S. alterniflora* beds (Haddad et al., 1992; Benner et al., 1991), which implies that lignin may not be useful for tracing salt marsh inputs. Mannino and Harvey (1999) used lipids to examine OM sources and also reported minimal wetland influence in Delaware Estuary POM, but because their study focused on surface waters they 'missed' the significant pool of wetland OM predominantly in bottom waters, detected in this study.

The classic portrait of axial estuarine gravitational circulation is reinforced by the predominance of marsh-derived POM in bottom waters of the ETM, with less influence in ETM surface waters (Table 5-4). However, the presence of marsh-derived OM anywhere in the main channel of the estuary requires lateral transport of OM from fringing wetlands. Past drifter studies and sediment transport observations have demonstrated that there are considerable lateral transport processes in Delaware Bay (Wong, 1994; Sommerfield and Wong, 2011), and provide a mechanism for transport of

wetland OM into the axial OM pool. Lateral transport processes are currently under investigation for the Delaware Estuary, but preliminary results from a three-dimensional numerical model show strong across-estuary transport throughout the lower estuary (Aristizabal, pers. comm.). On the flood tide, water is transported laterally out onto the shallow flanks of the estuary, and the marsh flats are filled; this reverses pulling water and suspended OM into the axial channel on ebb tide. Particles in the shallow flanks of the estuary are injected into bottom water of the estuary during ebb tide, and become trapped in bottom waters unless strong spring tides enhance sediment resuspension high into the water column. The agreement between geochemical results from this study that suggest marsh OM is present in the Delaware Estuary with that of the recent studies of physical transport processes in the lower estuary, confirm that lateral processes are important for sediment and OM cycling in the Delaware Estuary.

5.3 The fate of terrestrial OM in the Delaware Estuary

5.3.1 Vascular plant derived OM is sedimented in the upper estuary

Biomarker analyses were determined on surface sediments from cores taken at sites of consistent mud accumulation (Sommerfield and Madsen, 2004). Cores from two opposing flow regimes were selected to determine the source of OM preferentially deposited in the upper estuary (sitting between water sampling stations 15 and 17, Figure 1-2). Core sites were generally landward of the ETM during periods of high discharge (March 2010 and 2011), but were within the ETM during periods of low river discharge (September 2010). Additional sediment cores within the ETM and down-estuary of the ETM were examined to assess changes in burial across the ETM interface (Table 3-2).

Biomarker distributions in the flocs and surficial sediments showed that the OM was primarily derived from vascular plants (Figures 4-21, 4-22, 5-7). Alkane distributions in sediments had minimal short chain alkanes, high CPI (~3-4) and ACL (25-28), and the PLFAs had a greater proportion 'Terr' than 'Fresh' PLFAs (6-50% and 0-5%, respectively, Figure 4-22, Appendix 6). The results from the present study agree with previous work in the Delaware and other estuaries that have documented the deposition of vascular plant OM in the ETM and upper estuary using both biomarkers (lignin and fatty acids) and bulk isotopes (e.g. Cifuentes, 1991; Shi et al., 2001; Middelburg and Nieuwenhuize, 1998). Present results also corroborate sedimentological work in the Delaware Estuary that suggested riverine-delivered sediments have patchy pathways of deposition and resuspension down-estuary (Cook et al., 2007). This provides a mechanism for vascular plant signatures in sites of persistent sediment deposition.

In sediments associated with the ETM, labile vascular plant derived OM was preferentially deposited over algal derived OM as indicated by the PLFA distributions. The proportion of vascular plant PLFAs increased step-wise between surface water (3-6% and 3-11%, respectively), bottom water (11-14% and 9-22%, respectively), and core-top sediments (18-50% and 16-26%, respectively; Figure 5-8). This process can be driven by density partitioning of sources, or by biogeochemical processing in the water column. Differentiating these processes is outside the scope of this thesis work, but previous studies in the Delaware Estuary have also suggested that substantial remineralization of algal material in the water column of the estuary results in the preferential consumption of algal POM and residual sedimentation of vascular plant derived OM (Cifuentes, 1991). Biogeochemical processing of organic matter was also evidenced by the sequential

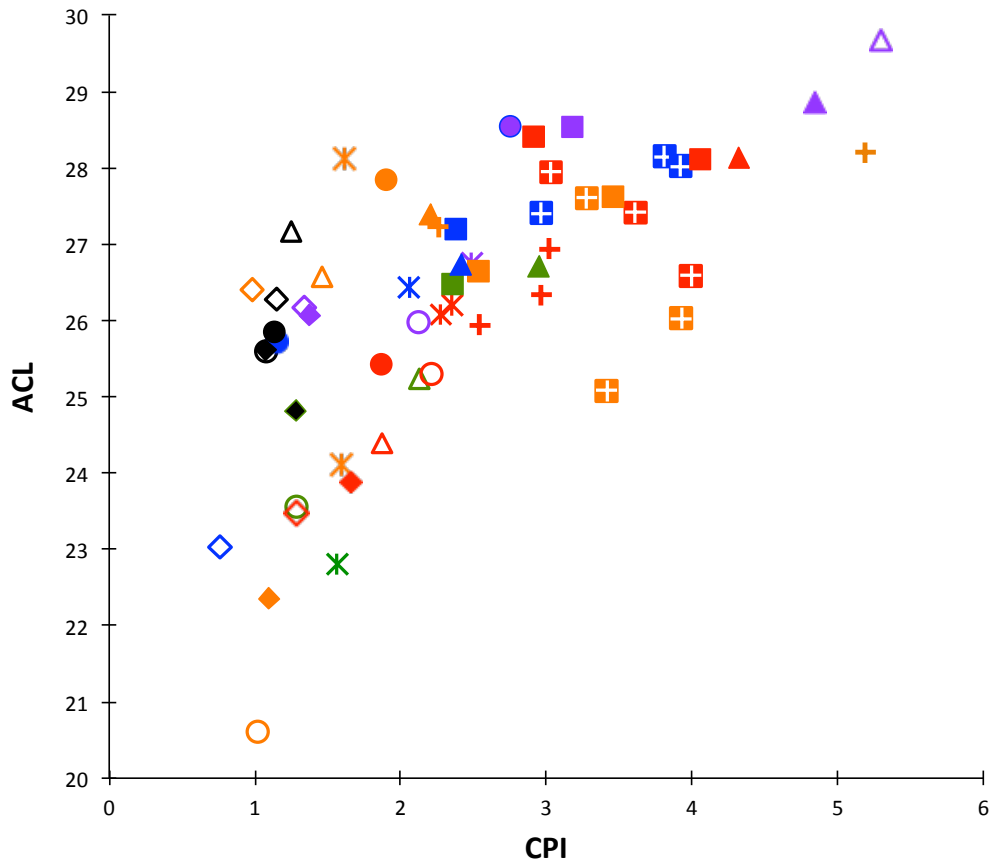


Figure 5-7. Delaware Estuary POM and sediment alkane biomarker ACL (average chain length; C16-C33) and CPI (carbon preference index; C16-C33). Surface water and bottom water POM are empty and filled symbols, respectively. Regions of the estuary are notated by symbol shape: Riverine endmember- triangles; ETM- squares and asterisks; Delaware Bay- circles; marine endmember- diamonds. Sediment floc layers are empty crosses, whereas core-tops are filled crosses. Seasons are notated by symbol color: March 2010 – blue; June 2010 – green; September 2010 – orange; December 2010- purple; March 2011- red. Black symbols were potentially contaminated by petroleum OM.

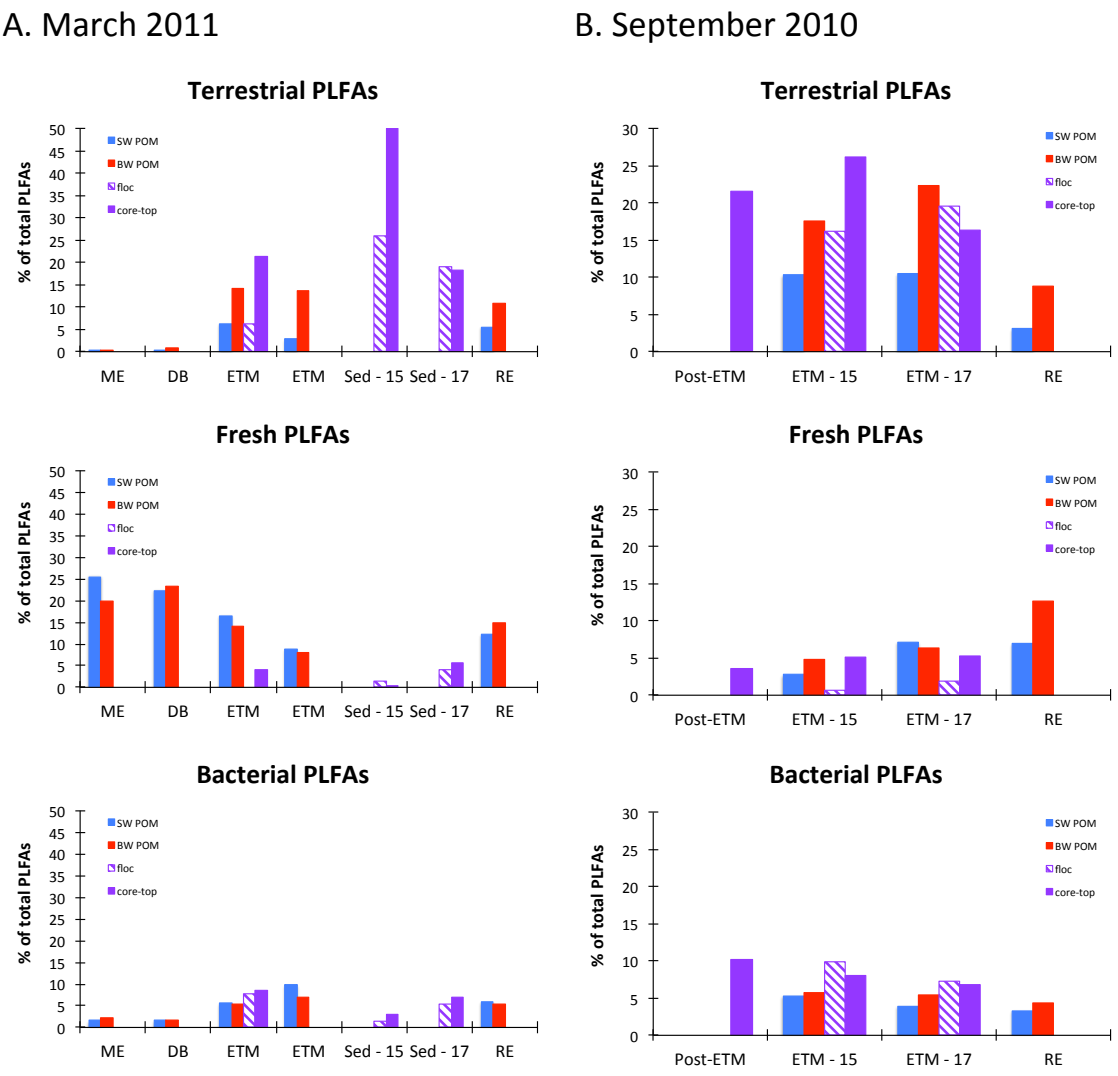


Figure 5-8. Delaware Estuary POM and sediment PLFA biomarkers for A) March 2011 and B) September 2010. Terrestrial PLFAs are the sum of even long chain PLFAs (C24-C28); Fresh PLFAs are the sum of even short chain poly-unsaturated PLFAs (C16-C22); Bacterial PLFAs are the sum of C15 and C17 branched PLFAs. SW POM – Surface water POM (blue); BW POM – Bottom water POM (red). Sites are labeled as follows: ME – marine endmember; DB – Delaware Bay; ETM – estuarine turbidity maximum; Post-ETM – site down-estuary of the ETM; Sed-15 – Sediment core at water station 15; Sed- 17 – Sediment core at water station 17; RE – riverine endmember.

decrease in other labile biomarkers from surface waters to surficial sediments. For example, whereas sterols were abundant in surface water samples, minimal to no sterols were detected in surficial sediments (*data not shown*).

Both the alkane MTI and the $\delta^{13}C$ signature of long chain alkanes in the sediments demonstrated that marsh OM was a substantial fraction of the vascular plant derived OM that sedimented in the estuary (Figure 5-6, Table 5-4). In both September 2010 and March 2011, cores from water stations 15 and 17 had unique alkane index values, with depressed ACL and high MTI in sediments compared to POM (with ACL values of 25-27 vs. 26.5-28.5 and MTI of 0.68-1.14 vs. 0.38-0.70, respectively; Figures 5-6, 5-7). The average MTI for sediments equates to marsh OM being 40-50% of the vascular plant OM. In addition, the $\delta^{13}C$ signature of alkanes corroborated MTI results, suggesting 34-50% of the vascular plant material was derived from C4 salt marshes (Table 5-4). These results indicated that deposition sites in the Delaware Estuary have mixed sources, with approximately half of the deposited vascular plant material delivered from the upper estuary, and the other half derived form marsh OM deposited in the ETM.

The deposition of vascular plant material in the upper estuary has implications for Delaware Estuary management strategies. Dredging in the Delaware Estuary removes 3,300,583 m^3/yr of sediment from the estuary annually (U.S. Army Core of Engineers, 2011). The preferential retention of terrestrial and marsh OM over algal OM in sediments implies that vascular plant derived OM is removed from the system during dredging. Dredged material is deposited at confined deposit facilities, and future dredged materials will be deposited at wetland restoration sites. Anthropogenic activities such as dredging

may short-circuit the carbon pathway between land and sea in the modern Delaware Estuary.

5.3.2 Terrestrial OM is preferentially remineralized over marsh OM

Remineralization of OM was not directly measured in this study, but changes in the relative abundances of biomarkers and their isotopic compositions between the riverine endmember and ETM was used to infer remineralization of terrestrial OM through the estuary. CSIA results for March 2011, showed an enrichment of ~4-6‰ for individual alkanes between the riverine endmember and ETM. The source apportionment calculations indicated that ~38% of terrestrial material at the riverine endmember was replaced by salt marsh OM in ETM bottom waters (Table 5-4). Two mechanisms could account for this. Either the enriched signature of marsh OM in the ETM diluted the depleted signature of terrestrial OM, or a significant proportion of depleted terrestrial OM from the riverine endmember was remineralized before the ETM.

Remineralization likely caused the discrepancy between riverine endmember and ETM signatures. The alkane biomarker distributions did not appear overwhelmingly marsh-derived. The MTI indicated ~15-45% marsh inputs (Figure 5-6) and the CPI decreased between the riverine endmember and the ETM for not only March 2011 but also, December and June 2010, by ~0.5, 1, and 2 units, respectively (Figure 5-7). A decreased CPI is indicative of terrestrial OM degradation, as the odd-even signature is lost as the material travels down-estuary. Additionally, labile biomarkers such as sterols, alcohols and PLFAs were observed to sequentially decrease between surface water POM, bottom water POM, floc layers, and sediments (*data not shown*). This loss is an indicator of rapid remineralization of OM in the water column as well as across the sediment-water

interface. These results support observations of net heterotrophy in the upper Delaware Estuary (Sharp et al., 1982; Hoch and Kirchman, 1993; Preen and Kirchman, 2004) and suggest that riverine delivered labile terrestrial OM is preferentially remineralized both down-estuary, and vertically between the water column and sediments.

5.3.3 Degraded vascular plant OM is exported

Despite significant trapping of vascular plant OM in the ETM, long chain vascular plant derived alkane and PLFA biomarkers were detected at the marine endmember site in all seasons and both depths, demonstrating that a fraction of vascular plant derived OM was consistently exported from the estuary (e.g. Figure 4-16). Long chain alkanes at the marine endmember exhibited a slightly higher CPI in bottom than surface water in December 2010 and March 2011, suggesting vascular plant derived OM was substantially reworked and degraded in surface water, but less so in bottom water (Table 4-3). This suggested that vascular plant OM was largely exported from the estuary in bottom waters. During high discharge such as sampled in the December 2010 and March 2011 cruises, a higher proportion of terrestrial, riverine-delivered OM was exported. Significant marsh OM in the Delaware Estuary organic pool, as demonstrated by this study, suggested that marsh signatures from Delaware Bay imprint bottom water POM at the marine endmember. CSIA results in the Delaware agree with those from Gulf of Mexico sediments (Bianchi et al., 2011), in that the role of marsh OM in the marine carbon cycle may be significant and demands further attention.

River discharge is well known to be a controlling factor on the character of OM exported from estuaries (e.g. Canuel, 2001; Countway et al., 2007; Townsend-Small et al., 2008; Medeiros et al., 2012). Suppressed export of material from the ETM even

during high discharge events, as suggested by Sommerfield and Wong (2011), was observed in March 2011, which had the highest discharge and the highest concentration of long chain alkanes in the ETM (e.g. Figure 4-17). However, it had the lowest concentration of long chain alkanes in Delaware Bay and at the coastal ocean site (Figure 4-17). Vascular plant OM trapped in bottom waters of the ETM during such conditions could escape the ETM by several mechanisms: filtering laterally out into subtidal flats and marshes (e.g. Church et al., 2006), processing into the DOM pool (e.g. Mannino and Harvey, 1999), resuspension and lateral transport down-estuary during large spring tides (Sommerfield et al., 2011), or flushing with higher discharge events than were sampled by this study. The March 2011 cruise occurred just after material flushed out of the upper estuary, and as flow diminished, significant amounts of riverine-delivered material were actively trapped in the ETM as the flood waters waned.

VI. SUMMARY AND CONCLUSIONS: A NEW PERSPECTIVE OF OM CYCLING IN THE DELAWARE ESTUARY

Transects through the Delaware Estuary on five cruises spanning one seasonal cycle captured the estuary with varied phytoplankton productivity, suspended solid distributions, and Delaware River discharge. The character of POM in the Delaware Estuary was determined to be similar to other functionally turbid, sediment-trapping estuaries that have long particle residence times which foster geochemical alteration (e.g. Middelburg et al., 1998; Hopkinson et al., 1998). Surface water POM properties corroborated previous research in the estuary, showing that inputs were significantly influenced by seasonal phytoplankton productivity but outside this factor, there were similar proportions of algal and vascular plant derived OM through the estuary (Cifuentes et al., 1988; Cifuentes, 1991; Mannino and Harvey, 1999; Sharp et al., 2009). Despite low percentages of OC in bottom waters of the ETM, very high particle concentrations there resulted in the highest levels of POC measured in estuarine waters for every season sampled. This was the first study to determine carbon character and content in bottom waters in the Delaware Estuary. These results demonstrated that previous surface water surveys resulted in a more 'algal' dominated picture of the estuary and missed the largest component of the vascular plant OM pool in the estuary. The added dimension of bottom water analyses identified marsh inputs as an important piece missing from previous studies of OM cycling within the estuary.

Bottom water POM throughout the estuary was consistently predominated by vascular plant OM in all seasons. Although the ETM had all sources of OM: terrestrial and algal from upriver, and terrestrial, phytoplankton, and salt marsh from Delaware Bay,

the concentration of long chain alkanes in the ETM support observations of sediment trapping in the Delaware Estuary ETM and indicate that little terrestrial material escapes the ETM except during large spring tides and discharge events (Sommerfield and Wong, 2011). ETM bottom waters trapped OC, acting as a virtual wall for riverine-delivered vascular plant OM, diminishing its export to the ocean.

Capitalizing on subtle differences in alkane distributions from marsh and terrestrial vascular plant material, the Marsh-Terrestrial Index (MTI) was developed to differentiate these sources in this complex coastal environment. Combined with the long chain carbon preference index, MTI suggests that 20-50% of vascular plant OM in the ETM and Delaware Bay was marsh-derived. Compound specific stable carbon isotopic composition of alkane biomarkers corroborated MTI estimations and indicated that vascular plant derived alkanes gradually became more marsh-like moving downstrean from the riverine endmember through the ETM. This suggests that C4 salt marsh inputs are increasingly important in POM pools down-estuary. These marsh inputs must come from the flanks of the estuary, thus, the OM cycling of the Delaware Estuary is not driven simply by the axial mixing of marine and riverine OM, but includes lateral injection of local OM into the lower estuary. Hence, there is a distinct separation of OM pools between the upper and lower estuary across the ETM. Laterally-sourced OM must be driven by lateral transport processes across Delaware Bay, which injects OM into bottom waters of the main channel and then is subsequently subjected to classical gravitational circulation and geochemical processing and degradation.

A large fraction of terrestrial-derived OM is remineralized and sedimented in the upper estuary. The disappearance of depleted terrestrial signatures between the riverine

endmember and ETM is attributed to remineralization of terrestrial OM in the upper estuary, and replacement by marsh OM in the ETM. Remineralization of terrestrial OM in the upper Delaware Estuary supports previous determinations of net heterotrophy in the upper estuary (e.g. Preen and Kirchman, 2004). MTI and CSIA source apportionment calculations indicated the vascular plant material contributions to the sediments was ~30-45% salt marsh OM. This suggests that marsh-derived OM is transported from fringing wetlands in Delaware Bay up-estuary into the ETM where it is deposited during periods of low flow. The vascular plant OM in the coastal ocean is highly degraded, and likely sourced from the lower estuary. Although removal of sediment via dredging removes vascular plant derived OM from the system altogether, the sediment trapping nature of the Delaware Estuary results in long particle residence times. Thus, exposure to remineralization opportunities within the ETM delivers a more degraded organic component to the sea.

The results of this study provide a new perspective of particulate organic carbon cycling in estuaries. For decades, OM in estuaries has been treated as axial mixing between riverine-delivered vascular plant OM and locally produced algal material. While these sources can (and do) mix within the ETM, vascular plant OM remains trapped in bottom water and sediments. Evidence for marsh-derived OM in the Delaware Estuary requires lateral transport and exchange with fringing wetlands and the main channel of the Estuary. This fundamentally changes the perspective of OM cycling in the estuary in that lateral advection of OM may be as significant as axial advection in moving material in and out of the estuarine OM cycle. Future work in estuaries similar to the Delaware estuary should include sampling strategies that address lateral processes in addition to

axial processes. Additionally, vertical profiles of the water column will ensure large proportions of terrestrial and wetland-derived OM do not evade geochemical characterization. The ETM acts as a filter for wetland material, trapping a substantial amount of riverine delivered material, while allowing inputs from the lower estuary into bottom water by lateral and then up-estuary advection. If local marsh inputs of land-derived OM are important in lower estuaries during average flow conditions, the reactivity of land-derived OM exported to the ocean may be significantly different than previously thought.

VII. REFERENCES

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VIII. APPENDICES

APPENDIX I. Delaware Estuary cruise sampling log. Shaded samples were analyzed for biomarkers.

R/V Sharp UNOLS #100310CS March 10-13, 2010											
Date	Site #	Latitude (N)	Longitude (W)	Water Depth (m)	Surface or bottom water?	Sample Depth (m)	Sample Time (EST)	Biomarkers (total L)	Biomarkers (# filters)	Biomarkers (L/filter)	TOC (L/filter)
3/10/10	1	38.7835	-74.9295	16	B	15	15:27	42	24	1.750	1.00
3/10/10	1	38.7835	-74.9295	16	S	1	15:27	34	17	2.000	1.00
3/11/10	3	38.9392	-75.1072	14.8	B	13.8	22:57	28.4	15	1.893	1.00
3/11/10	3	38.9392	-75.1072	14.8	S	1	22:57	28	14	2.000	1.00
3/11/10	5	39.1167	-75.2127	14.9	B	13.9	1:16	18.5	11	1.682	1.00
3/11/10	5	39.1167	-75.2127	14.9	S	1	1:19	18.5	15	1.233	1.00
3/11/10	7	39.2490	-75.3207	17.9	B	16.9	3:39	12	14	0.857	1.00
3/11/10	7	39.2490	-75.3207	17.9	S	1	3:39	10	13	0.769	1.00
3/11/10	9	39.3572	-75.4438	16.5	B	15.5	5:17	12.6	15	0.840	1.00
3/11/10	9	39.3572	-75.4438	16.5	S	1	5:17	12.5	15	0.833	0.75
3/11/10	11	39.4542	-75.5585	16?	B	?15	7:07	8.75	16	0.547	0.50
3/11/10	11	39.4542	-75.5585	16?	S	1	7:07	8.5	16	0.531	0.50
3/11/10	14	39.6225	-75.5796	16.5	B	15.75	9:14	6.45	18	0.358	0.35
3/11/10	14	39.6225	-75.5796	16.5	S	1	9:14	7.25	18	0.403	0.50
3/11/10	15	39.6788	-75.5219	15.3	B	14.85	10:12	8.4	19	0.442	0.50
3/11/10	15	39.6788	-75.5219	15.3	S	1	10:12	8.2	16	0.513	0.50
3/11/10	17	39.8103	-75.4052	15.9	B	14.9	12:21	8.2	16	0.513	0.50
3/11/10	17	39.8103	-75.4052	15.9	S	1	12:21	11.05	17	0.650	0.50
3/11/10	19	39.8815	-75.1916	14.2	B	12.4	14:45	8.4	16	0.525	0.75
3/11/10	19	39.8815	-75.1999	14.2	S	1	14:45	16.05	19	0.845	0.50
3/11/10	22	40.1165	-74.8307	~13	B	~12.3	1:12??	23.8	24	0.992	1.00
3/11/10	22	40.1165	-74.8307	~13	S	1	1:12??	37.65	28	1.345	1.00

APPENDIX I (cont). Delaware Estuary cruise sampling log. Shaded samples were analyzed for biomarkers.

R/V Sharp UNOLS #100603CS June 3-5, 2010											
Date	Site #	Latitude (N)	Longitude (W)	Water Depth (m)	Surface or bottom water?	Sample Depth (m)	Sample Time (EDT)	Biomarkers (total L)	Biomarkers (# filters)	Biomarkers (L/filter)	TOC (L/filter)
6/3/10	1	38.7828	-74.9255	14	S	1	13:44	59.55	30	1.985	1
6/3/10	1	38.7828	-74.9255	14	B	13	13:44	60.20	38	1.584	1
6/3/10	3	38.9395	-75.1055	14.2	S	1	17:03	32.45	28	1.159	1
6/3/10	3	38.9395	-75.1055	14.2	B	13.2	17:03	32.55	32	1.017	1
6/3/10	5	39.1147	-75.2092	12.7	S	1	19:42	N/A	N/A	N/A	N/A
6/3/10	5	39.1147	-75.2092	12.7	B	11.7	19:42	18.70	23	0.813	1
6/3/10	6	39.1786	-75.2687	~14.25	S	1	N/A	20.05	32	0.627	0.6
6/3/10	6	39.1786	-75.2687	~14.25	B	~13.7108	N/A	20.55	34	0.604	0.50
6/4/10	9	39.3560	-75.4397	11.6	S	1	2:16	N/A	N/A	N/A	N/A
6/4/10	10	39.4033	-75.4993	~13	S	1	N/A	20.45	34	0.601	0.75
6/4/10	10	39.4033	-75.4993	~13	B	~12.5	N/A	18.60	57	0.326	0.5
6/4/10	13	39.5673	-75.5485	16.5	S	1	6:38	17.90	37	0.484	0.5
6/4/10	13	39.5673	-75.5485	16.5	B	15.5	6:38	16.60	48	0.346	0.5
6/4/10	15	39.6798	-75.5217	16.5	S	1	9:07	20.14	36	0.559	0.5
6/4/10	15	39.6798	-75.5217	16.5	B	15.5	9:07	14.20	46	0.309	0.375
6/4/10	17	39.8145	-75.3958	15.2	S	1	11:44	18.90	33	0.573	0.5
6/4/10	17	39.8145	-75.3958	15.2	B	~14	11:44	18.78	36	0.522	0.5
6/4/10	19	39.8808	-75.1862	~13.5	S	~1	N/A	N/A	N/A	N/A	1
6/4/10	19	39.8808	-75.1862	~13.5	B	~13	N/A	N/A	N/A	N/A	1
6/4/10	22	40.0858	-74.8607	15.6	S	1	18:20	36.25	44	0.824	1
6/4/10	22	40.0858	-74.8607	15.6	B	14.6	18:20	39.55	74	0.534	1

APPENDIX I (cont). Delaware Estuary cruise sampling log. Shaded samples were analyzed for biomarkers.

R/V Sharp UNOLS #100912CS September 12-15, 2010											
Date	Site #	Latitude (N)	Longitude (W)	Water Depth (m)	Surface or bottom water?	Sample Depth (m)	Sample Time (EDT)	Biomarkers (total L)	Biomarkers (# filters)	Biomarkers (L/filter)	TOC (L/filter)
9/12/2010	1	38.7818	-74.9287	16.9	S	1	12:53	59.33	34	1.745	1
9/12/2010	1	38.7818	-74.9287	16.9	B	15.9	12:43	55.175	37	1.491	1
9/12/2010	3	38.9423	-75.1068	14.2	S	1	4:50	25	28	0.893	1
9/12/2010	3	38.9423	-75.1068	14.2	B	13.2	~4:45	23	37	0.622	1
9/12/2010	5	39.1140	-75.2110	13.4	S	1.2	19:45	19	25	0.760	1
9/12/2010	5	39.1140	-75.2110	13.9	B	13.1	19:33	19	35	0.543	1
9/12/2010	7	39.2450	-75.3142	13.9	S	1	~21:55	24	32	0.750	1
9/12/2010	7	39.2450	-75.3142	13.9	B	12.5	21:42	22	30	0.733	1
9/12/2010	9	39.3553	-75.4415	16	S	N/A	N/A	N/A	N/A	N/A	N/A
9/13/2010	10	39.4067	-75.5012	14.8	S	1	~1:00	23	44	0.523	0.5
9/13/2010	10	39.4067	-75.5012	14.8	B	13.2	0:53	18	48	0.375	0.5
9/13/2010	13	39.5712	-75.5475	14	S	1	3:42	28	42	0.667	0.5
9/13/2010	13	39.5675	-75.5475	17.1	B	15.8	3:26	20	70	0.286	0.3
9/13/2010	15	39.6812	-75.5198	15.9	S	1	5:55	17	29	0.586	0.5
9/13/2010	15	39.6812	-75.5198	15.9	B	~14.9	5:45	11	24	0.458	0.5
9/13/2010	17	39.8088	-75.4075	13.3	S	1	8:45	13	21	0.619	0.75
9/13/2010	17	39.8092	-75.4070	13.2	B	12.2	8:32	10	30	0.333	0.4
9/13/2010	19	39.8812	-75.1905	14.5	S	1	11:00	7	11	0.636	0.75
9/13/2010	19	39.8812	-75.1873	14.8	B	~13.8	10:50	4	12	0.333	1
9/13/2010	22	40.0833	-74.8620	16.5	S	1	15:11	19	16	1.188	1
9/13/2010	22	40.0830	-74.8630	15.6	B	13.43	15:06	17.7	18	0.983	1

APPENDIX I (cont). Delaware Estuary cruise sampling log. Shaded samples were analyzed for biomarkers.

R/V Sharp UNOLS #101213CS December 13-15, 2010											
Date	Site #	Latitude (N)	Longitude (W)	Water Depth (m)	Surface or bottom water?	Sample Depth (m)	Sample Time (EST)	Biomarkers (total L)	Biomarkers (#filters)	Biomarkers (L/filter)	TOC (L/filter)
12/13/10	1	N/A	N/A	15.1	S	1	7:07	34.8	40	0.870	0.5
12/13/10	1	N/A	N/A	13.3	B	~12.3	9:20	23	40	0.575	0.5
12/13/10	3	38.9335	-75.1035	15.6	S	~1	15:20	31.5	39	0.808	0.5
12/13/10	3	38.9335	-75.1035	15.8	B	15.05	15:15	22	38	0.579	0.5
12/13/10	5	39.1162	-75.2100	15.2	B	~13.3	18:35	30	38	0.789	0.5
12/13/10	5	39.1162	-75.2100	15.3	S	1.5	18:45	30	40	0.750	0.5
12/13/10	7	39.2397	-75.3105	15.8	B	14.3	21:40	24	40	0.600	0.5
12/13/10	7	39.2397	-75.3105	15	S	~1.3	21:47	22	39	0.564	0.5
12/14/10	9	N/A	N/A	16.9	B	~15.9	0:00	20	38	0.526	0.5
12/14/10	9	N/A	N/A	17.1	S	1	0:07	18	33	0.545	0.5
12/14/10	11	N/A	N/A	16.1	S	1	2:11	10	42	0.238	0.345
12/14/10	11	N/A	N/A	15.5	B	~14.5	2:00	10	43	0.233	0.32
12/14/10	13	39.5663	-75.5480	16.4	B	13.9	4:50	7.48	48	0.156	0.3
12/14/10	13	39.5663	-75.5480	16	S	~1.5	5:00	8	46	0.174	0.3
12/14/10	15	39.6728	-75.5228	15.3	B	13.6	6:35	10	36	0.278	0.5
12/14/10	15	39.6728	-75.5228	10.2	S	~1.5	6:42	14	46	0.304	0.27
12/14/10	17	38.8127	-75.4020	14.8	B	13.8	8:25	15.2	38	0.400	0.5
12/14/10	17	38.8127	-75.4020	15.3	S	1	8:30	16.37	34	0.481	0.5
12/14/10	19	39.8800	-75.1928	15.7	B	~12.7	10:25	N/A	N/A	N/A	0.5 (?)
12/14/10	19	39.8800	-75.1928	15.7	S	1	N/A	N/A	N/A	N/A	0.5
12/14/10	22	N/A	N/A	15.5	S	1.5	14:45	34	44	0.773	0.5
12/14/10	22	N/A	N/A	15.6	B	~13.6(?)	14:30	37.8	49	0.771	0.5

APPENDIX I (cont). Delaware Estuary cruise sampling log. Shaded samples were analyzed for biomarkers.

R/V Sharp UNOLS #110321CS: 21-23 March, 2011												
Date	Site #	Latitude (N)	Longitude (W)	Water Depth (m)	Surface or bottom water?	Sample Depth (m)	Sample Time (EDT)	Biomarkers (total L)	Biomarkers (#filters)	Biomarkers (L/filter)	TOC 1 (L/filter)	TOC 2 (L/filter)
3/21/11	1	38.7847	-74.9227	14.6	B	12.6	12:40	58.2	27	2.156	0.5	0.5
3/21/11	1	38.7867	-74.9195	14.3	S	5.5	12:51	54	28	1.929	0.25	0.25
3/21/11	3	38.9375	-75.1060	13.7	B	11.7	16:45	32	45	0.711	0.135	0.13
3/21/11	3	28.9375	-75.1060	13.7	S	1	16:55	20	33	0.606	0.15	0.15
3/21/11	5	39.1163	-75.2122	14.2	B	13.2	22:58?	22	32	0.688	0.14	0.1
3/21/11	5	39.1163	-75.2122	14.2	S	1	22:56?	22	27	0.815	0.15	0.11
3/21/11	7	39.2503	-75.3203	14.4	B	13.4	20:37	N/A	N/A	N/A	N/A	N/A
3/21/11	7	39.2512	-75.3213	15.4	S	1	N/A	N/A	N/A	N/A	N/A	N/A
3/21/11	9	39.3557	-75.4463	16.9	B	14.9	22:20	10	52	0.192	0.17	~0.110
3/21/11	9	39.3562	-75.4473	16.4	S	1	N/A	12	57	0.211	0.04	0.09
3/21/11	11	39.4448	-75.5495	18.1	B	16.5	23:43	11.445	62	0.185	0.07	0.04
3/21/11	11	39.4452	-75.5510	18.6	S	1	23:50	10.64	59	0.180	0.08	0.04
3/22/11	13	39.5677	-75.5457	14	B	12	1:10	12	58	0.207	0.08	0.03
3/22/11	13	39.5677	-75.5457	14	S	1	1:25	10	38	0.263	0.08	0.06
3/22/11	15	39.6798	-75.5188	13	B	12	2:40	17.1	60	0.285	0.15	0.05
3/22/11	15	39.6798	-75.5188	13	S	2	2:55	20	63	0.317	0.115	0.065
3/22/11	17	39.8085	-75.4033	14.25	B	13.5	4:40	13.4	39	0.344	0.15	0.08
3/22/11	17	39.8085	-75.4020	14.5	S	1	N/A	19.5	37	0.527	0.19	0.095
3/22/11	22	40.0815	-74.8658	15.1	B	9	10:25	43.7	61	0.716	0.265	0.11
3/22/11	22	40.0815	-74.8658	15.2	S	1	10:28	36	41	0.878	0.34	0.205

APPENDIX II. Bulk parameters of Delaware Estuary POM. Values are reported as an average and standard deviation of multiple sample runs, where available. Bottom waters are shaded. *ME = marine endmember; RE = riverine endmember; CM = chlorophyll maximum; ETM = estuarine turbidity max. ~ SSC data courtesy the University of Delaware.

Cruise 100310 – March 2010										
Sample (Site-Depth)	**End-member or max?***	**Distance up-estuary (km)**	**CTD Salinity (PSU)**	**SSC~ (mg/L)**	**δ^{13}C-POM (‰ PDB)**	**mg TOC/L**	**µM OC**	**µM TN**	**%OC**	**C:N (mol:mol)**
1-1m	ME	-14	31.37	0.80	-20.35 ± 0.47	0.66	55.13	3.84	82.69	14.34
3-1m		10	26.76	1.60	-19.62 ± 1.38	0.38 ± 0.04	31.31 ± 2.98	4.28 ± 0.30	23.48 ± 2.24	7.31 ± 0.18
5-1m		32	23.10	3.60	-17.58	0.92	76.58	12.38	25.53	6.19
7-1m	CM	48	15.76	18.67	-18.11	N/A	N/A	N/A	N/A	N/A
9-1m		65	10.98	23.20	-21.17	1.58	132.01	21.97	6.83	6.01
11-1m	ETM (12)	78	6.94	27.32	-22.73	1.44	119.83	17.75	5.26	6.75
14-1m		98	1.79	59.50	-22.49 ± 0.15	2.31	192.26	19.92	3.88	9.65
15-1m		107	0.69	28.00	-22.91	1.26	104.98	13.43	4.50	7.82
17-1m		125	0.21	10.80	-25.37	1.47	122.15	16.01	13.57	7.63
19-1m		145	0.16	13.67	-24.87	0.74	61.40	7.27	5.39	8.45
22-1m	RE	181	0.11	2.40	-21.69 ± 0.01	0.50 ± 0.01	41.82 ± 0.79	5.21	20.91 ± 0.39	8.03
1-btm	ME	-14	32.23	5.80	-20.34 ± 0.17	0.933	77.74	N/A	16.08	N/A
3-14m		10	29.95	1.20	-19.74 ± 0.28	0.52 ± 0.03	43.36 ± 2.78	6.74 ± 0.17	43.36 ± 2.78	6.43 ± 0.25
5-14m		32	25.45	6.40	-18.18	0.87	72.55	10.75	13.60	6.75
7-17m	CM	48	23.17	29.41	-19.69 ± 0.08	3.10	258.53	29.33	10.55	8.81
9-16m		65	18.51	49.20	-20.78 ± 0.55	2.35 ± 0.06	195.79 ± 5.24	29.64 ± 0.56	4.78 ±m0.13	6.61 ± 0.05
11-23?	ETM (12)	78	12.89	65.00	-18.93	2.79	232.53	33.24	4.29	7.00
14-16m		98	3.14	127.33	-23.35 ± 0.23	4.07	339.16	34.38	3.20	9.87
15-15m		107	1.46	93.33	-22.03	2.89	240.59	29.67	3.09	8.11
17-15m		125	0.21	40.67	-25.02	2.62	217.91	22.50	6.43	9.69
22-btm	RE	181	0.11	2.40	-23.56 ± 0.07	0.53 ± 0.03	44.05 ± 2.63	5.08	22.02	8.67

APPENDIX II (cont).

Cruise 100603 – June 2010										
Sample (Site-Depth)	**End-member or max?***	**Distance up-estuary (km)**	**CTD Salinity (PSU)**	**SSC~ (mg/L)**	**δ^{13}C-POM (‰ PDB)**	**mg TOC/L**	**µM OC**	**µM TN**	**%OC**	**C:N (mol:mol)**
1-1m	ME	-14	30.30	2.60	-23.58 ± 0.81	0.46 ± 0.04	38.47 ± 3.45	3.72 ± 0.78	17.76 ± 1.59	10.33
3-1m		10	27.43	3.67	-21.49	1.03	86.11	10.25	28.16	8.40
6-1m	CM	40	15.81	12.40	-18.77	1.62	134.97	19.80	13.06	6.81
10-1m	ETM	72	7.59	13.50	-23.84 ± 0.06	0.62 ± 0.05	51.37 ± 4.04	5.78	4.57 ± 0.36	8.89
13-1m		92	3.45	23.00	-24.71	1.73	144.13	18.28	7.52	7.89
15-1m		107	0.70	17.50	-26.41	1.58	131.84	18.34	9.04	7.19
17-1m		125	0.16	20.00	-28.69 ± 0.13	2.06 ± 0.09	171.74 ± 7.91	19.54 ± 0.34	10.30 ± 0.47	8.79 ± 0.25
19-1m		145	0.14	9.20	-30.08	1.18	98.07	10.92	12.79	8.98
22-1m	RE	181	0.13	15.67	-28.54 ± 0.40	0.75 ± 0.05	62.78 ± 4.34	8.06 ± 0.76	4.81 ± 0.33	7.79 ± 0.27
1-13m	ME	-14	31.04	2.20	-23.15 ± 0.09	0.50 ± 0.04	41.95 ± 3.39	5.04	22.88 ± 1.85	8.32
3-13m		10	29.59	8.80	-22.33	0.61	50.51	6.89	6.89	7.33
5-12m		32	25.18	5.60	-19.35	0.75	62.25	8.94	13.34	6.96
6-btm	CM	40	23.50	13.60	-19.58	2.98	248.38	33.00	21.92	7.53
10-btm	ETM	72	13.14	90.48	-22.64 ± 0.65	6.45 ± 2.40	537.06 ± 200.33	46.35 ± 23.14	7.12 ± 2.66	11.59 ± 0.17
13-15m		92	4.31	78.50	-22.44 ± 0.40	4.09 ± 0.02	340.60 ± 1.55	39.67 ± 0.63	5.21 ± 0.02	8.59 ± 0.18
15-15m		107	1.25	135.33	-23.85	5.52	459.59	47.86	4.08	9.60
17-14m		125	0.16	27.50	-28.37	3.00	250.18	25.97	10.92	9.63
19-btm		145	0.14	32.80	-29.09	2.14	178.28	18.10	6.52	9.85
22-14m	RE	181	0.13	46.00	-27.33 ± 0.24	3.21 ± 0.12	267.56 ± 9.82	28.42 ± 0.67	6.98 ± 0.26	9.41

APPENDIX II (cont).

Cruise 100912 – September 2010										
Sample (Site-Depth)	**End-member or max?***	**Distance up-estuary (km)**	**CTD Salinity (PSU)**	**SSC~ (mg/L)**	**δ^{13}C-POM (‰ PDB)**	**mg TOC/L**	**µM OC**	**µM TN**	**%OC**	**C:N (mol:mol)**
1-1m	ME	-14	31.22	0.59	-19.85 ± 0.03	0.52 ± 0.04	42.91 ± 3.30	5.32	87.28 ± 6.72	8.06
3-1m	CM (2)	10	28.67	8.80	-19.39	0.92	76.81	11.31	10.47	6.79
5-1m		32	25.92	7.50	-19.27 ± 0.06	0.98 ± 0.02	81.81 ± 1.50	12.66 ± 0.28	13.09 ± 0.24	6.46 ± 0.02
7-1m		48	19.40	11.11	-20.68	0.97	81.00	11.64	8.75	6.96
10-1m		72	12.45	17.00	-23.03 ± 0.00	1.67 ± 0.04	138.89 ± 3.55	14.22 ± 0.49	9.80 ± 0.25	9.76 ± 0.09
13-1m	ETM	92	7.98	28.67	-23.64	2.36	196.92	20.03	8.24	9.83
15-1m		107	4.63	23.50	-23.91	1.88	156.97	15.66	8.02	10.02
17-1m	ETM	125	1.18	45.81	-25.35	1.79	149.42	14.71	3.91	10.15
19-1m		145	0.23	19.00	-28.01 ± 0.40	1.39 ± 0.06	115.83 ± 5.19	12.98 ± 1.42	7.32 ± 0.33	8.92 ± 0.58
22-1m	RE	181	0.12	6.33	-29.49	0.67	55.62	6.63	10.54	8.39
1-16m	ME	-14	31.23	3.80	-19.34 ± 0.14	0.49 ± 0.04	40.81 ± 3.11	5.47	12.89 ± 0.98	7.46
3-13m	CM (2)	10	29.28	32.33	-19.99	1.71	142.45	20.15	5.29	7.07
5-13m		32	26.52	24.00	-19.47	2.05	170.57	22.64	8.53	7.54
7-12m		48	20.69	15.00	-21.23	0.80	66.53	8.04	5.32	8.27
10-13m		72	14.24	72.00	-21.91 ± 0.12	2.66 ± 0.07	221.34 ± 5.45	22.71 ± 0.87	3.69 ± 0.09	9.75 ± 0.13
13-16m	ETM	92	8.47	195.00	-22.19 ± 0.64	12.94 ± 5.95	1078.50 ± 495.57	110.62 ± 60.34	6.64 ± 3.05	9.75 ± 0.75
15-15m		107	5.63	78.00	-22.57	4.27	355.87	29.34	5.47	12.13
17-12m	ETM	125	1.35	474.67	-23.91 ± 0.01	10.59 ± 0.58	882.40 ± 48.37	69.76 ± 4.75	2.23 ± 0.12	12.65 ± 1.30
19-14m		145	0.23	107.33	N/A	2.88	240.07	27.62	2.68	8.69
22-14m	RE	181	0.13	19.67	-28.02 ± 1.87	1.26 ± 0.01	104.88 ± 0.71	10.42 ± 0.65	6.40 ± 0.04	10.07 ± 0.70

APPENDIX II (cont). ST = site of greatest observed stratification.

Cruise 101213 – December 2010										
Sample (Site-Depth)	**End-member or max?***	**Distance up-estuary (km)**	**CTD Salinity (PSU)**	**SSC~ (mg/L)**	**δ^{13}C-POM (‰ PDB)**	**mg TOC/L**	**µM OC**	**µM TN**	**%OC**	**C:N (mol:mol)**
1-1m	ME	-14	32.04	10.33	-22.74	0.89	74.21	8.12	8.62	9.14
3-1m		10	28.70	10.33	-22.42	0.70	58.47	6.30	6.79	9.28
5-1m	ST	32	13.77	12.00	-23.12	0.61	50.39	4.12	5.04	12.23
7-1m		48	13.80	25.00	-22.80	1.18	98.10	9.90	4.71	9.91
9-1m		65	6.63	29.00	-24.47 ± 0.49	0.96 ± 0.08	80.10 ± 6.58	9.92 ± 0.61	3.31 ± 0.27	8.08 ± 0.24
11-1m		78	2.15	60.67	-24.18	1.82	151.74	12.03	3.00	12.61
13-1m	ETM	92	1.33	129.00	-21.84	4.11	342.05	32.94	3.18	10.38
15-1m		107	0.12	54.00	-24.78	2.62	217.96	27.66	4.84	7.88
17-1m		125	0.09	13.60	-25.70	0.81	67.64	7.30	5.97	9.27
19-1m		145	0.10	16.00	-26.86	0.98	81.33	8.45	6.10	9.63
22-1.5m	RE	181	0.09	9.50	-26.91 ± 0.08	0.79 ± 0.01	65.50 ± 1.14	5.12 ± 0.14	8.27 ± 0.14	12.78 ± 0.57
1-btm	ME	-14	31.24	25.60	-21.75	1.51	126.16	14.09	5.91	8.95
3-10m		10	29.49	15.00	-21.81	1.14	95.30	10.79	7.62	8.83
5-13m	ST	32	24.58	11.60	-22.61 ± 0.07	0.78 ± 0.06	59.74 ± 4.82	8.64 ± 0.63	6.18 ± 0.50	6.92 ± 0.06
7-14m		48	24.58	33.20	-22.38	1.20	99.74	12.16	3.61	8.20
9-16m		65	18.32	39.00	-22.93	1.60	133.15	18.62	4.10	7.15
11-14.5m		78	13.41	289.00	-22.93	7.27	605.89	50.40	2.52	12.02
13-14m	ETM	92	1.27	250.70	-23.58	10.10	841.53	82.06	4.03	10.26
15-btm		107	0.12	62.14	-23.60	4.42	368.49	36.80	7.12	10.01
17-14m		125	0.09	25.60	-26.36 ± 0.17	1.26 ± 0.03	105.13 ± 2.10	10.83 ± 0.13	4.93 ± 0.10	9.71 ± 0.08
19-btm		145	0.09	21.25	-26.39	1.55	129.01	13.86	7.29	9.31
22-13.6m	RE	181	0.09	10.50	-26.72	1.15	95.61	8.54	10.93	11.20

APPENDIX II (cont).

Cruise 110321 – March 2011										
Sample (Site-Depth)	**End-member or max?***	**Distance up-estuary (km)**	**CTD Salinity (PSU)**	**SSC~ (mg/L)**	**δ^{13}C-POM (‰ PDB)**	**mg TOC/L**	**µM OC**	**µM TN**	**%OC**	**C:N (mol:mol)**
1-1m	ME	-14	30.97	1.04	-24.43 ± 0.00	0.41 ± 0.01	34.43 ± 0.90	4.07 ± 0.25	39.73 ± 1.04	8.47 ± 0.75
3-1m		10	24.68	14.57	-21.26	1.20	99.93	13.33	8.23	7.50
5-1m	CM	32	13.91	15.56	-20.70	1.80	150.21	19.62	11.58	7.65
9-1m	ETM	65	1.97	73.04	-23.51	3.28	272.97	24.24	4.48	11.26
11-1m	ETM	78	0.17	163.20	-24.54	5.22	434.55	34.30	3.20	12.67
13-1m		92	0.14	250.43	-23.93	10.90	908.14	94.44	4.35	9.62
15-2m		107	0.10	36.77	-25.74 ± 0.87	1.94 ± 0.08	161.84 ± 6.53	12.29 ± 0.18	5.28 ± 0.21	13.17 ± 0.65
17-1m		125	0.10	15.33	-27.12	0.89	74.29	6.45	5.81	11.52
22-1m	RE	181	0.08	6.67	-26.41	0.50	41.35	3.73	7.44	11.08
1-14m	ME	-14	31.36	2.00	-24.44 ± 0.08	0.26 ± 0.01	21.71 ± 0.47	2.61 ± 0.03	13.03 ± 0.28	8.33 ± 0.29
3-12m		10	24.76	23.00	-22.67	1.43	118.80	14.03	6.20	8.47
5-14m	CM	32	17.42	27.50	-20.28	2.73 ± 0.15	227.32 ± 12.79	28.15 ± 1.81	9.92 ± 0.56	8.08 ± 0.07
9-15m	ETM	65	2.82	528.70	-23.22 ± 0.78	12.15 ± 3.92	1012.43 ± 326.31	81.02 ± 21.99	2.30 ± 0.74	12.50 ± 1.62
11-16m	ETM	78	0.16	286.40	-24.12 ± 0.18	10.03 ± 0.26	835.88 ± 21.43	66.54 ± 0.10	3.50 ± 0.09	12.56 ± 0.34
13-12m		92	0.15	395.45	-24.70 ± 0.32	11.35 ± 1.08	945.69 ± 89.90	69.88 ± 3.57	2.87 ± 0.27	13.53 ± 0.60
15-12m		107	0.10	141.54	-26.02	1.68	139.72	12.00	1.18	11.64
17-14m		125	0.10	38.00	-25.81	1.81	150.40	12.21	4.75	12.32
22-9m	RE	181	0.08	11.50	-26.66	0.92	76.97	5.50	8.03	14.01

APPENDIX III. Delaware Estuary POM *n*-alkane biomarkers (concentrations in ng alkane liter^{-1}). Sites are named as follows: ME – marine endmember, CM – chlorophyll maximum, ST – site of greatest stratification, ETM – estuarine turbidity maximum, IM – site between ETM, RE – riverine endmember. Surface waters are filled white and bottom waters are filled grey. The alkane with the highest concentration in each sample is in blue (C_{max}). See text for description of alkane indices.

	March 2010				**June 2010**				**September 2010**					
	Site *(Station)*				Site *(Station)*				Site *(Station)*					
Alkane C# (ng/L)	ME *(1)*	CM *(7)*	ETM *(14)*	RE *(22)*	ME *(1)*	CM *(6)*	ETM *(10)*	RE *(22)*	ME *(1)*	CM *(3)*	ETM *(13)*	IM *(15)*	ETM *(17)*	RE *(22)*
16	20	171	98	31		27	22	27		8		31	14	
	36		92			32	69	43		9	54	50	51	13
17	23	140	152	38	16	72	98	114	4	33	13	**65**	82	17
	40	127	108	46	31	93	135	201	15	24	107	115	233	37
18	**40**	162	236	37	21	107	84	100	8	67	27	52	29	16
	51	132	170	32	41	113	137	123	25	22	172	**158**	103	34
19	38	32	90	27	24	130	96	46	8	**107**	28	38	20	30
	23	31	159	22	38	71	93	62	16	15	63	64	82	44
20	35	148	159	38	27	115	**114**	105	10	78	**38**	50	38	24
	36	136	126	21	42	145	139	84	**34**	21	126	115	115	40
21		60	122	27	47	**150**	88	100	8	46	36	34	35	20
	29	74	143	44	41	127	174	148	31	39	143	103	146	0
22	30	188	92	33	41	104	43	73	12	46	21	20	14	14
	56	71	163	16	30	57	73	71	24	33	134	47	112	22
23	17	359	233	95	49	128	50	92	7	13	30	43	85	14
	100	83	366	58	**43**	84	226	190	14	24	329	113	439	35

	March 2010 cont.				June 2010 cont.				September 2010 cont.					
	Site *(Station)*				Site *(Station)*				Site *(Station)*					
Alkane C# (ng/L)	ME *(1)*	CM *(7)*	ETM *(14)*	RE *(22)*	ME *(1)*	CM *(6)*	ETM *(10)*	RE *(22)*	ME *(1)*	CM *(3)*	ETM *(13)*	IM *(15)*	ETM *(17)*	RE *(22)*
24	8	344	72	91	27	17	19	28	6	10	16	12	24	11
	101	**219**	153	12	14	101	46	77	7	28	68	27	119	22
25	8	**380**	182	150	27	26	31	76	8	9	26	21	98	27
	93	68	358	32	11	160	152	194	7	35	219	57	339	50
26	9	254	88	149	24	25	14	23	8	7	18	16	118	29
	72	44	226	19	11	158	67	92	4	24	83	28	110	27
27	14	278	285	179	28	43	35	105	12	9	32	36	229	51
	74	110	539	52	19	213	234	312	8	60	350	89	587	90
28	11	200	117	149	33	23	14	27	12	6	13	20	203	36
	57	51	241	27	16	181	105	103	7	33	119	32	175	31
29	14	271	**482**	**182**	**50**	71	59	133	15	9	35	49	**308**	**52**
	78	173	**828**	**82**	36	**255**	**419**	485	9	**109**	**559**	144	**889**	132
30	12	198	133	124	37	46	16	51	**16**	8	14	21	195	33
	51	72	270	30	27	167	121	119		59	128	28	215	32
31	12	273	479	146	35	77	52	**161**	12	7	31	44	252	40
	61	165	786	81	36	198	394	**552**	10	104	472	134	833	**148**
32	8	120	152	105	29	54	17	38	12		3	13	125	18
	40	109	178	48	19	93	77	60		39	71	23	149	44
33	6	151	345	102	29		38	149	6		7	35	164	22
	55	128	566	82	18	7	250	271		62	326	92	681	101
34	7	69	47	32	38	39	10						56	12
	35	41	48	10	20	34	86	55			81		128	36
35	6	55	87	38	11	19	7	31	4			9	48	9
	22	46	114	21	7	19	91	27		40	60	20	186	24

	March 2010 cont.				June 2010 cont.				September 2010 cont.					
	Site *(Station)*				Site *(Station)*				Site *(Station)*					
Alkane C# (ng/L)	ME *(1)*	CM *(7)*	ETM *(14)*	RE *(22)*	ME *(1)*	CM *(6)*	ETM *(10)*	RE *(22)*	ME *(1)*	CM *(3)*	ETM *(13)*	IM *(15)*	ETM *(17)*	RE *(22)*
36	7	53		13	9	16			6			16	36	11
					9	53	17	27	7	48		25		
37		26	25	6	8	11		12					18	
	7		43	10	4	12	10	29			10		36	6
38					4	14		6					7	
				5	5			28					16	9
Total alkanes (ng/L)	***323***	***3,932***	***3,679***	***1,790***	***616***	***1,314***	***908***	***1,497***	***173***	***464***	***391***	***624***	***2,197***	***485***
	1,120	***1,880***	***5,679***	***751***	***519***	***2,372***	***3,116***	***3,353***	***220***	***827***	***3,674***	***1,463***	***5,745***	***976***
CPI	0.76	1.08	2.06	1.25	1.14	1.29	1.57	2.13	0.98	1.02	1.59	1.59	1.62	1.47
	1.07	1.15	2.38	2.41	1.28	1.13	2.36	2.95	1.10	1.90	2.53	1.84	3.46	2.20
ACL	23.04	25.60	26.43	27.16	26.29	23.56	22.81	25.24	26.41	20.62	24.12	24.05	28.13	26.57
	25.61	25.73	27.19	26.73	24.82	25.86	26.48	26.70	22.36	27.84	26.64	24.28	27.62	27.39
$P_{mar\text{-}aq}$	0.50	0.58	0.30	0.43	0.47	0.51	0.42	0.36	0.36	0.57	0.46	0.41	0.25	0.31
	0.58	0.31	0.31	0.36	0.43	0.35	0.32	0.27	0.53	0.22	0.35	0.38	0.31	0.23
LC (C_{25}-C_{33})	92	2,126	2,264	1,284	293	366	276	764	101	55	180	255	1,692	308
	583	919	3,994	453	195	1,431	1,820	2,187	45	525	2,326	627	3,979	656
SC (C_{16}-C_{24})	211	1602	1254	416	253	848	616	685	62	409	211	345	341	146
	472	874	1480	252	279	824	1091	1000	167	215	1196	792	1400	245
CPI-LC (C_{25}-C_{33})	1.14	1.57	3.46	1.39	1.07	1.16	3.12	4.68	1.03	1.63	2.77	2.25	1.50	1.45
	1.50	2.17	3.31	2.61	1.24	1.24	3.25	4.04	1.86	2.01	4.12	3.96	4.53	3.19
ACL-LC (C_{23}-C_{36})	27.51	26.40	28.10	29.19	27.99	24.25	26.04	27.33	29.95	24.45	25.62	27.21	30.65	30.33
	26.56	28.01	28.21	27.92	26.78	29.58	27.91	28.15	25.48	30.18	27.00	26.33	27.86	29.39
MTI	1.30	1.55	0.57	1.33	0.86	0.91	0.74	0.58	1.11	2.36	1.52	0.72	0.79	1.24
	1.44	0.61	0.66	0.51	0.56	1.82	0.60	0.62	1.64	0.57	0.71	0.65	0.61	0.56

APPENDIX III (cont).

	December 2010				March 2011				
	Site *(Station)*				Site *(Station)*				
Alkane C# (ng/L)	ME *(1)*	ST *(7)*	ETM *(11)*	RE *(22)*	ME *(1)*	CM *(5)*	ETM *(9)*	ETM *(11)*	RE *(22)*
16	8			4			95	101	35
	12		33	10			245	52	23
17	29	18	19	6	11	24	343	416	97
	29	12	86	13	9	28	611	216	87
18	12	29	41	7	11	26	271	313	77
	25	12	70	21	9	23	358	140	56
19	14	22	31	7	14	17	159	227	56
	15	6	57	15	12	15	240	117	59
20		41	53	5	11	26	182	351	97
	14	4	104	18	7	26	374	226	66
21	9	54	76	18	17	27	351	598	108
	27	12	164	26	11	24	562	268	89
22	12	26	24	6	12	14	156	265	47
	25	8	124	27	9	15	319	420	45
23	18	23	46	28	6	30	132	256	41
	36	12	427	54	7	29	658	579	71
24	32	10	19	12	4	6	64	146	18
	30	7	153	17	2	10	148	134	43
25	36	19	37	30	6	16	135	248	30
	31	19	427	36	4	13	606	414	96
26	34	10	20	19	4	7	69	127	14
	30	10	212	19	2	8	141	238	29

	December 2010 cont.				March 2011 cont.				
	Site *(Station)*				Site *(Station)*				
Alkane C# (ng/L)	ME *(1)*	ST *(7)*	ETM *(11)*	RE *(22)*	ME *(1)*	CM *(5)*	ETM *(9)*	ETM *(11)*	RE *(22)*
27	40	36	66	85	6	20	247	443	51
	43	36	773	94	4	25	1268	840	167
28	32	11	26	31	5	11	94	160	17
	33	16	348	33	2	10	286	333	43
29	**42**	**66**	**118**	233	7	**39**	463	853	108
	57	**78**	**1323**	248	6	**44**	2841	1551	593
30	26	16	25	30	5	11	113	163	15
	35	22	391	35	2	14	468	357	63
31	28	57	115	**256**	6	37	**497**	**916**	**115**
	49	68	1252	**288**	8	42	**3020**	**1652**	**670**
32	12	12	22	32	6	7	129	121	36
	19	13	279	24	4	26	356	399	52
33	16	52	83	165		28	465	542	65
	28	51	956	184		21	1975	1152	229
34	9	10	15	15			84	209	9
	13	18	106				302	162	68
35	4	6	16	26	1	4	64	106	14
	7	10	316	36	2	4	371	385	47
36	9	9	26	44	4	10	176	192	11
	11	10		37	6		599	444	40
37				6			13	29	5
			91	11			103	138	6
38							12	14	
			55	5			77	121	4

	December 2010 cont.				March 2011 cont.				
	Site *(Station)*				Site *(Station)*				
Alkane C# (ng/L)	ME *(1)*	ST *(7)*	ETM *(11)*	RE *(22)*	ME *(1)*	CM *(5)*	ETM *(9)*	ETM *(11)*	RE *(22)*
39									
								142	
40									
								256	
Total alkanes (ng/L)	***421***	***527***	***876***	***1,066***	***137***	***360***	***4,312***	***6,797***	***1,067***
	568	***424***	***7,747***	***1,251***	***106***	***376***	***15,928***	***10,735***	***2,645***
CPI	1.34	2.13	2.49	5.30	1.29	2.21	2.27	2.35	1.88
	1.38	2.75	3.18	4.84	1.66	1.87	4.05	2.91	4.32
ACL	26.16	25.98	26.75	29.68	23.48	25.30	26.08	26.19	24.39
	26.07	28.54	28.54	28.87	23.88	25.43	28.12	28.41	28.14
$P_{mar\text{-}aq}$	0.44	0.26	0.26	0.11	0.46	0.38	0.22	0.22	0.24
	0.39	0.18	0.25	0.14	0.43	0.33	0.18	0.24	0.12
LC (C_{25}-C_{33})	266	279	510	881	46	175	2,211	3,574	451
	324	313	5,961	961	32	202	10,961	6,935	1,940
SC (C_{16}-C_{24})	134	223	309	94	86	171	1752	2673	576
	214	73	1218	201	66	170	3515	2152	539
CPI-LC (C_{25}-C_{33})	1.38	3.43	3.26	4.65	1.14	3.13	2.81	3.20	3.75
	1.55	2.92	3.78	6.00	1.49	2.57	4.68	3.10	6.12
ACL-LC (C_{23}-C_{36})	29.04	28.66	28.68	30.27	28.00	26.91	29.76	29.15	28.40
	28.29	30.09	29.08	29.52	26.72	26.95	29.34	29.17	29.56
MTI	1.76	0.51	0.52	0.28	1.98	0.55	0.40	0.47	0.45
	0.96	0.46	0.54	0.27	0.99	0.59	0.38	0.45	0.29

APPENDIX III (cont). Delaware Estuary POM *n*-alkane biomarkers (concentrations in µg alkane gOC^{-1}). Sites are named as follows: ME – marine endmember, CM – chlorophyll maximum, ST – site of greatest stratification, ETM – estuarine turbidity maximum, IM – site between ETM, RE – riverine endmember. Surface waters are filled white and bottom waters are filled grey. The alkane with the highest concentration in each sample is in blue for surface water and orange for bottom water (C_{max}).

Alkane C# (µg alkane gOC^{-1})	**March 2010**				**June 2010**				**September 2010**					
	Site *(Station)*				Site *(Station)*				Site *(Station)*					
	ME *(1)*	CM *(7)*	ETM *(14)*	RE *(22)*	ME *(1)*	CM *(6)*	ETM *(10)*	RE *(22)*	ME *(1)*	*CM (3)*	ETM *(13)*	IM *(15)*	ETM *(17)*	RE *(22)*
16	30	55	42	62	0	16	36	35	0	9	0	16	8	0
	78	0	22	0	0	11	11	13	0	5	4	12	5	10
17	34	45	66	75	36	44	160	151	8	36	6	**35**	45	26
	87	41	26	87	62	31	21	62	32	14	8	27	22	30
18	**61**	52	102	74	46	66	137	133	16	73	12	28	16	23
	110	43	42	61	81	38	21	38	51	13	13	**37**	10	27
19	57	10	39	54	52	80	156	61	15	**117**	12	20	11	45
	50	10	39	42	76	24	14	19	33	9	5	15	8	35
20	53	48	69	77	59	71	**185**	140	20	85	**16**	27	21	36
	77	44	31	40	83	49	22	26	**69**	12	10	27	11	31
21	0	19	53	53	101	**93**	143	133	15	50	15	18	19	29
	63	24	35	83	82	43	27	46	64	23	11	24	14	0
22	45	60	40	65	89	64	70	97	23	49	9	11	8	20
	122	23	40	30	59	19	11	22	48	19	10	11	11	18

Alkane C# (µg alkane gOC^{-1})	March 2010 cont.				June 2010 cont.				September 2010 cont.					
	Site *(Station)*				Site *(Station)*				Site *(Station)*					
	ME *(1)*	CM *(7)*	ETM *(14)*	RE *(22)*	ME *(1)*	CM *(6)*	ETM *(10)*	RE *(22)*	ME *(1)*	*CM (3)*	ETM *(13)*	IM *(15)*	ETM *(17)*	RE *(22)*
23	26	116	101	188	106	79	82	123	14	15	13	23	48	21
	216	27	90	110	**85**	28	35	59	28	14	25	26	41	28
24	13	111	31	181	58	10	31	37	12	11	7	6	13	17
	219	**71**	38	23	27	34	7	24	15	16	5	6	11	17
25	13	**123**	79	300	58	16	51	101	15	10	11	11	55	40
	202	22	88	60	23	54	24	60	15	20	17	13	32	40
26	13	82	38	296	51	16	22	31	16	8	7	9	66	44
	156	14	56	36	22	53	10	29	8	14	6	7	10	21
27	21	90	123	356	61	27	57	140	24	9	14	19	128	76
	161	35	132	99	38	71	36	97	17	35	27	21	55	72
28	16	64	51	296	71	14	23	36	24	7	5	11	113	55
	124	16	59	51	31	61	16	32	15	19	9	7	17	25
29	21	87	**209**	**362**	**109**	44	96	176	29	10	15	26	**172**	**78**
	168	56	**203**	156	72	**85**	**65**	151	19	**64**	**43**	34	**84**	105
30	18	64	58	247	80	29	27	67	**32**	8	6	11	109	49
	111	23	66	56	54	56	19	37	0	35	10	7	20	25
31	18	88	208	290	76	47	84	**214**	22	8	13	23	140	60
	132	53	193	153	71	66	61	**172**	20	61	36	31	79	**118**
32	11	39	66	209	64	34	27	51	23	0	1	7	70	26
	87	35	44	90	39	31	12	19	0	23	5	5	14	35
33	8	49	150	203	63	0	61	198	12	0	3	19	91	34
	120	41	139	**156**	37	2	39	84	0	37	25	22	64	80
34	10	22	21	63	82	24	17	0	0	0		0	31	18
	76	13	12	20	41	11	13	17	0	0	6	0	12	29

Alkane C# (µg alkane gOC^{-1})	**March 2010 cont.**				**June 2010 cont.**				**September 2010 cont.**					
	Site *(Station)*				Site *(Station)*				Site *(Station)*					
	ME *(1)*	CM *(7)*	ETM *(14)*	RE *(22)*	ME *(1)*	CM *(6)*	ETM *(10)*	RE *(22)*	ME *(1)*	*CM (3)*	ETM *(13)*	IM *(15)*	ETM *(17)*	RE *(22)*
35	9	18	38	76	25	12	11	41	7	0		5	27	13
	47	15	28	39	14	6	14	8	0	23	5	5	18	19
36	10	17	0	26	20	10		0	12	0		9	20	16
	0	0	0	0	18	18	3	8	15	28	0	6		0
37		8	11	13	18	7		15	0	0			10	
	16	0	10	19	8	4	2	9	0	0	1		3	5
38					9	9		7	0	0			4	
				9	10			9	0	0	0		2	7
Total alkanes (µg alkane/gOC)	*488*	*1267*	*1594*	*3566*	*1333*	*811*	*1474*	*1988*	*337*	*504*	*165*	*331*	*1225*	*728*
	2425	*606*	*1395*	*1419*	*1031*	*796*	*484*	*1044*	*448*	*484*	*284*	*343*	*543*	*776*
LC (C_{25}-C_{33})	*140*	*685*	*981*	*2559*	*634*	*226*	*448*	*1014*	*197*	*60*	*76*	*135*	*944*	*462*
	1262	*296*	*981*	*857*	*387*	*480*	*282*	*681*	*93*	*307*	*180*	*147*	*376*	*521*
SC (C_{16}-C_{24})	*320*	*517*	*544*	*830*	*547*	*524*	*999*	*910*	*121*	*444*	*89*	*183*	*190*	*218*
	1023	*282*	*364*	*475*	*554*	*276*	*169*	*311*	*340*	*126*	*92*	*185*	*132*	*195*

APPENDIX III (cont).

Alkane C# (µg alkane gOC^{-1})	**December 2010**				**March 2011**				
	Site *(Station)*				Site *(Station)*				
	ME *(1)*	*ST (7)*	ETM *(11)*	RE *(22)*	ME *(1)*	CM *(5)*	ETM *(9)*	ETM *(11)*	RE *(22)*
16	9	0	0	6	0	0	29	19	71
	8	0	4	9	0	0	20	5	25
17	33	15	10	8	28	13	105	80	195
	19	10	12	11	34	10	50	21	94
18	13	25	23	8	25	15	83	60	155
	16	10	10	18	36	8	29	14	61
19	16	19	17	9	33	10	49	43	114
	10	5	8	13	**46**	6	20	12	64
20	0	35	29	7	28	15	55	67	197
	9	3	14	16	28	9	31	23	72
21	10	46	42	23	**42**	15	107	115	218
	18	10	23	22	42	9	46	27	96
22	14	22	13	7	30	8	47	51	94
	17	6	17	24	33	6	26	42	49
23	20	19	25	36	13	17	40	49	82
	24	10	59	47	26	11	54	58	77
24	36	8	10	15	9	3	19	28	36
	20	6	21	15	8	4	12	13	47
25	41	17	20	39	15	9	41	48	61
	20	16	59	31	14	5	50	41	103
26	38	9	11	24	11	4	21	24	27
	20	8	29	17	9	3	12	24	31

Alkane C# (µg alkane gOC^{-1})	**December 2010 cont.**				**March 2011 cont.**				
	Site *(Station)*				Site *(Station)*				
	ME *(1)*	*ST (7)*	ETM *(11)*	RE *(22)*	ME *(1)*	CM *(5)*	ETM *(9)*	ETM *(11)*	RE *(22)*
27	45	31	36	109	15	11	75	85	103
	28	30	106	82	16	9	104	84	180
28	36	10	14	39	11	6	29	31	35
	21	13	48	29	8	4	24	33	46
29	**47**	**56**	**65**	296	18	**21**	141	164	217
	38	**65**	**182**	217	24	**16**	234	155	642
30	29	14	14	38	11	6	34	31	29
	23	19	54	30	7	5	39	36	68
31	31	48	63	**326**	15	20	**152**	**176**	**232**
	32	57	172	**251**	30	16	**249**	**165**	**725**
32	13	10	12	41	16	4	39	23	73
	13	11	38	21	15	9	29	40	56
33	18	44	45	210	0	16	142	104	130
	18	43	131	160	0	8	163	115	248
34	10	8	8	19	0	0	26	40	19
	8	15	15		0	0	25	16	73
35	5	5	9	33	2	2	19	20	29
	5	8	43	32	8	2	31	38	51
36	10	8	14	56	9	5	54	37	23
	7	8		32	23	0	49	44	44
37				8			4	5	10
			13	10			8	14	7

Alkane C# (µg alkane gOC^{-1})	**December 2010 cont.**				**March 2011 cont.**				
	Site *(Station)*				Site *(Station)*				
	ME *(1)*	*ST (7)*	ETM *(11)*	RE *(22)*	ME *(1)*	CM *(5)*	ETM *(9)*	ETM *(11)*	RE *(22)*
38							4	3	
			8	4			6	12	4
39									
								14	
40									
								25	
Total alkanes (µg alkane/gOC)	*473*	*448*	*481*	*1,356*	*332*	*200*	*1,316*	*1,303*	*2,151*
	375	*354*	*1,065*	*1,090*	*407*	*138*	*1,311*	*1,070*	*2,863*
LC (C_{25}-C_{33})	*298*	*237*	*280*	*1121*	*112*	*97*	*675*	*685*	*909*
	214	*262*	*820*	*838*	*123*	*74*	*902*	*691*	*2100*
SC (C_{16}-C_{24})	*150*	*189*	*170*	*119*	*208*	*95*	*535*	*513*	*1162*
	141	*61*	*167*	*175*	*253*	*62*	*289*	*215*	*583*

APPENDIX IV. Delaware Estuary sediment *n*-alkane biomarkers (concentrations in ng alkane per g sediment dry weight). Sites are the water column sampling stations. Floc samples are filled white and 0-1cm core-top sediments are filled grey, * indicates that March 2010 cores did not have substantial floc for analysis. Alkane indices are as defined in the text.

Alkane C# (ng/g sed. dw)	**March 2010**			**September 2010**			**March 2011**		
	Site *(Core)*			Site *(Core)*			Site *(Core)*		
	9 *(20H-B)*	12 *(13H)*	15 *(8H-B)*	12 *(26H-B)*	15 *(25H-B)*	17 *(23H-B)*	9 *(35A)*	15 *(34B)*	17 *(32A)*
16	---	---	---	---	0		31	49	0
	0	0	0	0	32	27	17	0	12
17	---	---	---	---	346	88	51	96	34
	11	45	28	16	145	114	70	0	53
18	---	---	---	---	207	155	225	381	127
	55	31	24	26	98	61	91	77	41
19	---	---	---	---	134	107	79	173	60
	61	25	35	13	76	35	129	33	38
20	---	---	---	---	164	134	53	88	34
	33	34	26	12	39	30	51	27	12
21	---	---	---	---	202	277	68	186	62
	113	41	30	15	91	104	167	132	53
22	---	---	---	---	340	356	38	143	47
	172	51	54	9	43	35	97	127	23
23	---	---	---	---	557	945	192	250	142
	301	83	155	17	187	152	417	528	99
24	---	---	---	---		1028	63	151	72
	202	50	73	6	47	30	306	284	34
25	---	---	---	---	506	1724	185	316	245
	696	142	215	14	202	104	751	928	120
26	---	---	---	---	180	1361	96	150	118
	371	93	119	8	70	57	496	404	48
27	---	---	---	---	1693	2195	281	495	393
	1185	211	358	44	308	163	1335	1415	205
28	---	---	---	---	681	1404	98	189	142
	401	93	134	21	96	46	747	464	62
29	---	---	---	---	4829	3794	503	841	644
	1923	355	663	145	504	234	2395	2056	314

Alkane C# (ng/g sed. dw)	March 2010 cont.			September 2010 cont.			March 2011 cont.		
	Site *(Core)*			Site *(Core)*			Site *(Core)*		
	9 *(20H-B)*	12 *(13H)*	15 *(8H-B)*	12 *(26H-B)*	15 *(25H-B)*	17 *(23H-B)*	9 *(35A)*	15 *(34B)*	17 *(32A)*
30	---	---	---	---	763	1272	80	160	117
	326	81	134	32	81	38	758	356	62
31	---	---	---	---	4811	4037	501	798	669
	1699	336	615	165	493	196	2912	1507	312
32	---	---	---	---	496	953	53	83	138
	245	64	101	20	44	25	559	169	53
33	---	---	---	---	2014	1988	283	316	315
	1223	314	496	72	152	88	1853	545	162
34	---	---	---	---	150	268	0		84
	199	49	44	24			370	91	0
35	---	---	---	---	379	488	42	75	94
	428	65	187	15			551	77	30
36	---	---	---	---	183	385	0	0	0
	0		0				0	0	0
37	---	---	---	---		152	0	0	38
	21		25				260	0	0
38	---	---	---	---			0	0	46
	0		31				147	0	0
39	---	---	---	---					
	0		38				164		
40	---	---	---	---					
	0		0				194		

cont.

Alkane C# (ng/g sed. dw)	March 2010 cont.			September 2010 cont.			March 2011 cont.		
	Site *(Core)*			Site *(Core)*			Site *(Core)*		
	9 *(20H-B)*	12 *(13H)*	15 *(8H-B)*	12 *(26H-B)*	15 *(25H-B)*	17 *(23H-B)*	9 *(35A)*	15 *(34B)*	17 *(32A)*
Total alkanes	N/A	N/A	N/A	N/A	*18,636*	*21,708*	*2,921*	*4,939*	*3,623*
	9,930	*2,162*	*3,651*	*675*	*2,708*	*1,539*	*15,011*	*9,220*	*1,733*
CPI	N/A	N/A	N/A	N/A	5.19	2.26	2.97	2.54	3.02
	3.81	2.96	3.92	3.28	3.93	3.42	3.03	3.61	4.00
ACL	N/A	N/A	N/A	N/A	29.06	28.56	26.91	26.49	28.18
	28.97	28.36	28.95	28.57	26.55	25.59	29.22	28.00	27.56
$P_{mar\text{-}aq}$	N/A	N/A	N/A	N/A	0.099	0.254	0.273	0.257	0.228
	0.216	0.245	0.225	0.091	0.281	0.373	0.180	0.290	0.259
LC (C_{25}-C_{33})	N/A	N/A	N/A	N/A	*15,973*	*18,728*	*2,080*	*3,348*	*2,781*
	8,070	*1,688*	*2,835*	*522*	*1,950*	*952*	*11,805*	*7,844*	*1,338*
SC (C_{16}-C_{24})	N/A	N/A	N/A	N/A	1950	3090	800	1516	579
	948	360	427	114	758	587	1347	1208	365
CPI-LC (C_{25}-C_{33})	N/A	N/A	N/A	N/A	6.10	2.61	5.37	4.75	3.79
	4.36	3.58	4.41	4.17	5.71	4.72	3.16	4.35	4.96
ACL-LC (C_{23}-C_{36})	N/A	N/A	N/A	N/A	29.83	28.98	28.77	28.63	29.20
	29.37	29.38	29.49	30.03	28.41	27.97	29.66	28.34	28.88
MTI	N/A	N/A	N/A	N/A	0.322	0.650	0.596	0.728	0.648
	0.643	0.541	0.517	0.246	0.790	0.941	0.438	1.141	0.685

APPENDIX V. POM phospholipid fatty acid methyl esters (PLFAMES). All PLFAMES are reported as a percentage of total PLFAMES per sample. Summary indices are at the bottom of the table; refer to Methods for index formulas and interpretations. Compounds are identified as follows: the first number in is the number of carbon atoms, and is followed by the number of double bonds; placement of double bonds is notated by 'w,' and is counted from the aliphatic end of the fatty acid; 'c' and 't' refer to *cis* and *trans* double bonds; 'i' and 'a' refer to *iso*- and *anteiso*- branched fatty acids; '10MeXXbr' refers to branched fatty acids at the 10^{th} carbon atom; ~ indicates the position of the double bond was not determined; * indicates co-eluting compounds.

APPENDIX V (cont).

Cruise 110321 – March 2011 POM										
Region	**Marine Endmember**		**Chlorophyll Max**		**ETM**		**ETM**		**Riverine Endmember**	
Site - Depth	**1 - S**	**1 - B**	**5 - S**	**5 - B**	**9 - S**	**9 - B**	**11 - S**	**11 - B**	**22 - S**	**22 - B**
Compound (%)										
12:0	0.20	0.32	0.11	0.25	0.42	0.66	1.39	0.77	0.92	1.23
i13	0.02	0.02	0.04	0.03	0.17	0.23	0.35	0.24	0.26	0.26
a13	0.00	0.00	0.00	0.00	0.04	0.05	0.14	0.06	0.00	0.08
13:0	0.04	0.04	0.22	0.27	0.32	0.34	0.37	0.31	0.19	0.27
i14	0.15	0.24	0.26	0.29	1.12	1.40	2.15	1.48	0.70	0.64
14:1w9~	0.08	0.13	0.07	0.03	0.00	0.24	0.00	0.23	0.00	0.00
14:1w7~	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.10	0.00	0.00
14:0	13.74	15.44	16.31	15.65	11.61	8.32	9.06	5.20	6.35	5.89
i15	0.89	1.28	0.84	0.78	2.60	2.45	4.43	3.06	2.87	2.43
a15	0.54	0.80	0.65	0.59	2.07	2.02	3.81	2.58	2.27	1.99
15:1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15:0	0.84	1.13	1.62	1.60	1.70	1.69	2.09	1.44	1.07	1.09
16:4	1.94	0.73	2.27	2.41	1.20	0.85	0.00	0.00	0.00	0.20
16:3	1.60	1.14	3.71	3.49	2.72	1.65	0.65	0.61	0.00	0.00
16:2	3.16	1.91	4.09	3.16	2.93	2.02	1.05	0.78	0.40	0.48
i16	0.00	0.00	0.00	0.00	1.21	0.93	1.26	1.38	0.61	0.75
a16	0.00	0.00	0.00	0.00	0.60	0.69	0.92	0.91	0.24	0.21
16:1w9	0.00	0.00	0.15	0.21	0.58	0.70	0.52	0.00	0.00	0.41
16:1w7	23.41	20.15	25.95	25.74	16.84	13.76	13.08	8.92	14.51	10.01
16:1w5	0.49	0.53	0.81	1.16	1.31	1.40	2.14	1.80	1.59	1.75
16:0	25.70	30.57	19.49	21.10	17.85	13.29	25.50	19.95	25.03	20.63
10Me17br	0.00	0.00	0.00	0.00	0.23	0.56	0.00	0.62	0.00	0.32
i17	0.08	0.21	0.17	0.17	0.53	0.57	0.81	0.78	0.43	0.44
a17	0.08	0.00	0.10	0.17	0.45	0.40	0.78	0.62	0.40	0.47
17:1~	0.00	0.00	0.00	0.28	0.46	0.47	0.00	0.35	0.33	0.33
17:1~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.57	0.00	0.37
17:0	0.23	0.47	0.44	0.27	0.64	0.67	0.85	0.79	0.52	0.63
18:3w6	2.85	2.57	0.60	0.60	0.00	0.00	0.00	0.00	0.00	0.00
18:4	0.00	0.00	2.86	2.52	2.35	1.10	0.00	0.00	1.62	0.72
18:2w6	1.62	1.63	0.75	1.59	1.15	1.15	1.19	1.10	1.84	4.65
18:3w3* 18:1w9c* 18:2w3*	4.09	5.23	1.74	2.29	3.19	3.33	5.05	4.28	7.38	7.56
18:1w9t	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.45
18:1w7	2.58	2.70	4.40	3.59	4.66	4.34	4.74	3.82	3.97	0.59
18:1w5	0.13	0.07	0.24	0.38	0.39	0.43	0.27	0.44	0.33	0.00
18:0	4.33	5.14	1.78	1.71	6.66	4.74	9.40	12.33	16.66	12.40
10Me19br	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19:0	0.31	0.04	0.20	0.08	0.41	0.41	0.66	0.61	0.34	0.40
20:5w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:4w6	0.12	0.05	0.20	0.31	0.22	0.39	0.00	0.12	0.00	0.12

Cruise 110321 – March 2011 POM cont.										
Region	Marine Endmember		Chlorophyll Max		ETM		ETM		Riverine Endmember	
Site - Depth	1 - S	1 - B	5 - S	5 - B	9 - S	9 - B	11 - S	11 - B	22 - S	22 - B
20:5w3	7.47	4.55	4.15	4.52	2.27	3.18	0.84	0.90	0.68	0.87
20:3w6	0.00	0.19	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:4w3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:2	0.00	0.00	0.25	0.56	0.00	0.00	0.00	0.00	0.00	0.17
20:3w3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:1w9~	0.29	0.30	0.40	0.43	0.15	0.27	0.00	0.00	0.00	0.00
20:1w7~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:1w5~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:0	0.18	0.21	0.22	0.34	1.23	4.81	2.21	3.79	0.66	1.38
21:0	0.00	0.00	0.00	0.00	0.20	0.57	0.15	0.44	0.20	0.44
22:6w6	0.00	0.00	0.00	0.00	0.51	0.00	0.00	0.00	0.00	0.00
22:6w3	2.69	1.95	1.60	2.01	0.00	0.94	0.03	0.11	0.26	0.21
22:5w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:5w3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:1w9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:1w7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:0	0.10	0.15	0.22	0.29	1.19	2.08	0.90	2.36	1.27	2.62
23:0	0.00	0.00	0.02	0.00	0.28	0.60	0.17	0.72	0.00	0.90
24:1	0.00	0.00	0.24	0.37	0.38	0.00	0.00	0.00	0.00	0.43
24:0	0.05	0.08	0.29	0.41	1.85	3.29	1.16	3.81	1.60	3.34
25:0	0.00	0.00	0.01	0.03	0.44	0.70	0.12	0.65	0.26	0.56
26:0	0.00	0.00	0.09	0.19	1.54	3.56	0.80	3.55	1.34	2.57
27:0	0.00	0.00	0.00	0.00	0.22	0.64	0.08	0.52	0.00	0.39
28:0	0.00	0.00	0.05	0.15	1.65	4.08	0.62	3.77	1.37	2.66
29:0	0.00	0.00	0.00	0.00	0.21	0.63	0.02	0.50	0.23	0.41
30:0	0.00	0.00	0.00	0.00	1.24	3.32	0.23	2.65	1.27	2.30
31:0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32:0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
% Sat FA's	45.71	53.59	41.06	42.34	49.66	54.39	55.78	64.15	59.29	60.11
% Mono Unsat	31.08	29.12	34.01	34.48	27.98	25.02	25.81	20.50	28.11	24.89
% Polyunsat	25.54	19.96	22.33	23.45	16.55	14.62	8.82	7.91	12.19	14.98
% Br FA's	1.76	2.57	2.05	2.02	8.79	8.74	14.64	11.11	7.79	7.27
% Fresh	16.98	10.53	19.24	18.96	12.20	10.14	2.57	2.52	2.97	2.77
% Terr	0.05	0.09	0.43	0.745	6.28	14.25	2.81	13.77	5.59	10.88
% Bac	1.59	2.30	1.75	1.70	5.65	5.44	9.83	7.04	5.98	5.33
TAR-FA	0.001	0.002	0.012	0.020	0.169	0.491	0.072	0.429	0.134	0.309

APPENDIX V (cont).

Cruise 101213 – December 2010 POM								
Region	**Marine Endmember**		**Delaware Bay**		**ETM**		**Riverine Endmember**	
Site - Depth	**1 - S**	**1 - B**	**7- S**	**7 - B**	**11 - S**	**11 - B**	**22 - S**	**22 - B**
Compound (%)								
12:0	0.24	0.17	0.38	0.27	0.47	0.31	0.61	0.53
i13	0.02	0.04	0.08	0.08	0.14	0.12	0.15	0.13
a13	0.00	0.00	0.00	0.01	0.00	0.03	0.04	0.03
13:0	0.10	0.10	0.09	0.09	0.20	0.11	0.19	0.18
i14	0.30	0.37	0.61	0.68	1.21	0.84	0.96	0.68
14:1w9~	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00
14:1w7~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14:0	20.95	16.21	8.60	11.66	5.49	5.01	5.17	4.41
i15	0.70	0.95	1.40	1.22	4.62	2.28	3.79	2.76
a15	0.61	0.84	1.18	1.08	2.53	1.99	5.50	3.38
15:1	0.00	0.00	0.00	0.00	1.62	1.43	1.49	0.00
15:0	1.19	1.42	1.48	1.63	0.00	0.00	0.00	1.15
16:4	1.37	1.89	1.03	1.77	0.00	0.59	0.00	0.07
16:3	0.93	1.27	2.06	2.52	0.40	0.92	0.49	0.31
16:2	1.93	1.85	1.56	2.23	0.56	1.02	0.73	0.68
i16	0.00	0.27	0.70	0.71	1.06	0.63	1.87	1.18
a16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16:1w9	0.00	0.26	0.35	0.40	0.49	0.58	0.67	0.47
16:1w7	20.67	20.64	15.39	19.49	10.56	10.61	13.37	11.07
16:1w5	3.58	2.54	0.74	0.75	1.46	1.20	1.21	1.16
16:0	24.50	20.34	20.49	20.35	17.60	17.31	25.71	22.84
10Me17br	0.00	0.21	0.24	0.18	0.00	0.83	0.34	0.40
i17	0.14	0.22	0.33	0.32	0.89	0.65	0.57	0.56
a17	0.09	0.28	0.39	0.29	0.81	0.43	1.04	0.95
17:1~	0.00	0.16	0.36	0.30	0.00	0.44	0.00	0.30
17:0	0.34	0.55	0.48	0.64	0.76	0.87	0.55	0.73
18:3w6	0.33	0.47	2.62	0.26	0.00	0.43	0.00	0.00
18:4	2.86	2.99	0.00	1.76	0.00	0.00	0.00	0.00
18:2w6	1.70	1.52	0.59	0.69	0.56	0.54	1.91	1.79
18:3w3* 18:1w9cis* 18:2w3*	4.37	3.50	3.12	2.87	5.97	2.90	8.48	7.75
18:1w9t	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18:1w7	2.92	3.02	3.53	3.78	4.73	3.95	6.44	5.88
18:1w5	0.00	0.00	0.00	0.00	0.00	0.36	0.61	0.93
18:0	5.44	5.38	14.59	7.07	8.87	7.36	11.81	14.18
10Me19br	0.00	0.00	0.00	0.00	0.00	0.15	0.26	0.46
19:0	0.25	0.50	0.83	0.71	1.41	0.69	0.32	1.04
20:5w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:4w6	0.00	0.19	0.11	0.27	0.00	0.19	0.09	0.10
20:5w3	1.90	3.43	2.91	4.51	0.00	1.61	0.77	0.65

Cruise 101213 – December 2010 POM cont.								
Region	Marine Endmember		Delaware Bay		ETM		Riverine Endmember	
Site - Depth	1 - S	1 - B	7- S	7 - B	11 - S	11 - B	22 - S	22 - B
20:3w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:4w3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:3w3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:1w9~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:1w7~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:1w5~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:0	0.50	1.30	1.74	1.47	3.25	6.60	0.41	1.02
21:0	0.00	0.11	0.18	0.14	0.38	0.70	0.05	0.22
22:6w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:6w3	0.72	1.22	0.57	1.25	0.00	0.21	0.00	0.06
22:5w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:5w3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:1w9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:1w7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:0	0.27	0.79	1.50	1.07	3.11	2.77	0.54	1.84
23:0	0.00	0.14	0.26	0.23	0.62	0.76	0.13	0.53
24:1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24:0	0.47	1.36	2.33	1.90	5.50	4.78	0.91	2.43
25:0	0.00	0.16	0.30	0.28	0.86	0.89	0.15	0.37
26:0	0.41	1.21	2.16	1.75	4.88	5.12	0.82	1.94
27:0	0.00	0.15	0.34	0.27	1.03	0.89	0.19	0.31
28:0	0.21	1.11	2.40	1.70	4.34	5.75	0.87	2.25
29:0	0.00	0.12	0.36	0.25	0.72	0.91	0.12	0.37
30:0	0.00	0.76	1.62	1.14	2.90	4.16	0.68	1.92
31:0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32:0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
% Sat FA's	54.87	51.88	60.13	52.60	62.39	65.00	49.24	58.26
% Mono Unsat	31.54	30.12	23.49	27.59	24.84	21.53	32.27	27.56
% Polyunsat	16.12	18.32	14.58	18.13	7.49	8.40	12.48	11.40
% Br FA's	1.85	2.98	4.68	4.370	11.25	6.98	13.91	9.68
% Fresh	9.71	12.83	8.25	14.31	0.96	4.53	2.09	1.86
% Terr	1.09	4.45	8.51	6.49	17.62	19.82	3.27	8.54
% Bac	1.53	2.29	3.30	2.90	8.84	5.36	10.90	7.65
TAR-FA	0.024	0.100	0.234	0.166	0.625	0.692	0.082	0.238

APPENDIX V (cont).

Cruise 100912 – September 2010 POM						
Region	**ETM**		**ETM**		**Riverine Endmember**	
Site - Depth	**15 - S**	**15 - B**	**17 - S**	**17 - B**	**22 - S**	**22 - B**
Compound (%)						
12:0	0.64	0.86	1.13	0.65	1.27	1.01
i13	0.09	0.18	0.11	0.16	0.07	0.12
a13	0.00	0.00	0.00	0.05	0.01	0.03
13:0	0.15	0.21	0.14	0.21	0.37	0.79
i14	0.69	0.85	0.62	0.85	0.84	0.96
14:1w9~	0.07	0.00	0.00	0.00	0.00	0.00
14:1w7~	0.00	0.00	0.00	0.00	0.04	0.00
14:0	8.00	7.20	7.69	5.31	12.10	9.55
i15	2.63	2.61	2.05	2.64	2.16	2.49
a15	1.86	1.96	1.13	1.69	0.72	1.12
15:1	0.00	0.00	0.00	0.00	0.00	0.00
15:0	1.83	1.65	1.38	1.37	1.79	2.21
16:4	0.00	0.16	0.55	0.41	0.12	0.28
16:3	0.50	1.23	1.65	1.23	1.79	4.44
16:2	0.92	1.19	1.50	1.39	2.11	3.25
i16	0.87	0.99	0.59	0.94	0.50	0.82
a16	0.33	0.00	0.00	0.26	0.12	0.35
16:1w9	1.44	0.64	0.00	0.54	0.00	0.62
16:1w7	9.60	8.18	9.41	6.84	16.71	14.82
16:1w5	0.70	0.89	0.95	1.67	0.96	1.82
16:0	27.40	19.98	25.79	15.85	38.87	22.41
10Me17br	0.44	0.44	0.28	0.51	0.00	0.12
i17	0.50	0.72	0.41	0.69	0.31	0.50
a17	0.27	0.41	0.31	0.38	0.12	0.21
17:1~	0.00	0.61	0.24	0.15	0.16	0.33
17:1~	0.64	1.25	0.73	0.41	0.70	0.00
17:0	1.02	0.00	0.00	0.86	0.00	0.72
18:3w6	0.50	0.64	0.84	0.24	0.67	0.81
18:4	0.00	0.00	0.00	0.73	0.00	0.00
18:2w6	0.54	0.49	1.22	0.85	1.48	1.51
18:3w3* 18:1w9cis* 18:2w3*	4.71	3.95	5.98	3.64	6.33	5.57
18:1w9t	3.55	0.00	0.00	0.00	0.00	0.00
18:1w7	0.00	3.16	2.46	2.23	2.92	2.84
18:1w5	0.00	0.59	0.22	0.33	0.80	0.00
18:0	12.00	9.11	13.97	7.63	0.00	4.78
10Me19br	0.31	0.17	0.00	0.11	0.00	0.00
19:0	1.08	0.83	1.15	0.61	0.42	0.44
20:5w6	0.30	0.00	0.00	0.00	0.00	0.00
20:4w6	0.00	0.00	0.00	0.22	0.11	0.34

Cruise 100912 – September 2010 POM cont.						
Region	**ETM**		**ETM**		**Riverine Endmember**	
Site - Depth	**15 - S**	**15 - B**	**17 - S**	**17 - B**	**22 - S**	**22 - B**
20:5w3	0.00	1.14	1.29	1.19	0.63	1.88
20:3w6	0.00	0.00	0.00	0.00	0.00	0.00
20:4w3	0.00	0.00	0.00	0.00	0.00	0.00
20:2	0.00	0.00	0.00	0.00	0.00	0.00
20:3w3	0.00	0.00	0.00	0.00	0.00	0.00
20:1w9~	0.00	0.00	0.00	0.00	0.00	0.00
20:1w7~	0.00	0.00	0.00	0.00	0.00	0.00
20:1w5~	0.00	0.00	0.00	0.26	0.00	0.00
20:0	1.73	4.02	1.86	5.67	0.36	0.70
21:0	0.26	0.44	0.24	0.00	0.17	0.00
22:6w6	0.00	0.00	0.00	0.00	0.00	0.00
22:6w3	0.00	0.00	0.10	0.18	0.00	0.10
22:5w6	0.00	0.00	0.00	0.00	0.00	0.00
22:5w3	0.00	0.00	0.00	0.00	0.00	0.00
22:2	0.00	0.00	0.00	0.00	0.00	0.00
22:1w9	0.00	0.00	0.00	0.00	0.00	0.00
22:1w7	0.00	0.00	0.00	0.00	0.00	0.00
22:0	2.37	2.75	1.78	3.49	0.73	1.64
23:0	0.43	0.68	0.42	1.03	0.15	0.44
24:1	0.00	0.00	0.00	0.22	0.00	0.00
24:0	3.35	4.65	3.24	6.12	1.17	2.70
25:0	0.49	0.79	0.50	1.16	0.13	0.34
26:0	2.57	4.46	2.74	6.01	0.82	2.34
27:0	0.44	0.77	0.44	1.04	0.09	0.32
28:0	2.79	4.97	2.80	6.09	0.79	2.47
29:0	0.37	0.66	0.36	1.00	0.06	0.26
30:0	1.61	3.50	1.73	4.14	0.31	1.35
31:0	0.00	0.00	0.00	0.00	0.00	0.00
32:0	0.00	0.00	0.00	0.00	0.00	0.00
% Sat FA's	68.55	67.53	67.36	68.25	59.61	54.47
% Mono Unsat	20.71	19.28	20.00	16.29	28.61	26.00
% Polyunsat	7.46	8.79	13.13	10.07	13.25	18.18
% Br FA's	7.250	7.73	5.23	7.64	4.86	6.60
% Fresh	1.71	3.72	5.08	5.35	4.76	10.29
% Terr	10.33	17.57	10.51	22.36	3.09	8.86
% Bac	5.27	5.71	3.90	5.39	3.31	4.32
TAR-FA	0.242	0.502	0.254	0.836	0.053	0.228

APPENDIX VI. Sediment phospholipid fatty acid methyl esters (PLFAMES). All PLFAMES are reported as a percentage of total PLFAMES per sample. Summary indices are at the bottom of the table; refer to Methods for index formulas and interpretations. Compounds are identified as follows: the first number in is the number of carbon atoms, and is followed by the number of double bonds; placement of double bonds is notated by 'w,' and is counted from the aliphatic end of the fatty acid; 'c' and 't' refer to *cis* and *trans* double bonds; 'i' and 'a' refer to *iso*- and *anteiso*- branched fatty acids; '10MeXXbr' refers to branched fatty acids at the 10^{th} carbon atom; ~ indicates the position of the double bond was not determined; * indicates co-eluting compounds.

APPENDIX VI (cont).

Cruise 110321 – March 2011 Sediment							Cruise 100912 – Sept. 2010 Sediment				
Region	**ETM (9)**		**Up-river (15)**		**Up-river (17)**		**Post-ETM (12)**	**ETM (15)**		**ETM (17)**	
Core - depth	35 floc	35 0-1	34 floc	34 0-1	32 floc	32 0-1	26 0-1	25 floc	25 0-1	23 floc	23 0-1
Compound (%)											
12:0	2.61	0.49	0.00	0.24	0.82	1.29	0.55	1.13	0.70	0.29	0.83
i13	0.00	0.26	0.00	0.06	0.00	0.14	0.16	0.14	0.23	0.05	0.16
a13	0.00	0.17	0.00	0.00	0.06	0.00	0.06	0.00	0.09	0.00	0.08
13:0	0.00	0.24	0.00	0.09	0.53	1.16	0.19	0.18	0.24	0.08	0.34
i14	1.05	1.11	0.13	0.86	0.66	0.98	0.84	1.09	1.11	0.75	0.76
14:1w9~	0.00	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14:1w7~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14:0	7.90	5.94	2.17	1.55	4.45	6.74	3.78	7.40	4.06	6.03	6.31
i15	3.42	3.45	1.03	1.02	2.53	3.16	4.24	4.97	3.58	3.74	3.44
a15	3.00	3.25	0.53	1.25	1.92	2.46	3.47	3.28	2.57	2.27	2.11
15:1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15:0	2.06	2.44	0.51	0.57	1.70	2.87	1.51	2.02	1.72	1.63	1.80
16:4	0.00	0.29	0.00	0.07	0.00	0.00	1.58	0.00	1.49	0.00	0.00
16:3	0.00	0.74	0.00	0.00	0.00	0.96	0.40	0.31	0.53	0.22	1.11
16:2	0.00	0.63	0.00	0.00	0.00	2.64	0.00	0.00	0.72	0.00	1.88
i16	1.23	1.57	0.00	0.75	0.66	1.20	0.00	1.45	0.00	1.01	0.96
a16	0.00	0.39	0.00	0.00	0.42	0.72	0.32	0.00	0.30	0.00	0.00
16:1w9	0.00	0.68	0.00	0.00	2.86	2.81	1.20	0.00	0.54	1.07	2.54
16:1w7	7.04	7.64	1.70	1.26	11.69	11.81	6.97	9.55	5.42	10.72	11.72
16:1w5	1.02	1.30	28.35	0.14	3.64	4.76	3.02	2.11	2.08	2.70	4.28
16:0	20.09	15.95	0.24	5.42	24.83	15.20	14.40	23.89	12.53	22.87	19.15
10Me17br	0.70	1.36	0.00	0.31	0.52	0.66	3.10	1.10	1.37	0.79	0.88
i17	0.67	0.90	0.00	0.34	0.53	0.77	1.26	1.12	1.06	0.80	0.82
a17	0.71	1.06	0.00	0.31	0.35	0.63	1.27	0.55	0.77	0.45	0.52
17:1~	0.39	0.53	0.00	0.00	0.23	0.50	0.00	0.00	0.22	0.00	0.54
17:1~	0.00	0.72	0.00	0.00	0.00	0.00	0.00	0.00	0.75	0.00	0.00
17:0	1.01	0.99	0.00	0.60	0.59	0.74	1.37	1.08	1.06	0.81	0.75
18:3w6	0.00	0.00	0.00	0.00	0.55	0.15	0.00	0.00	0.00	0.00	0.00
18:4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18:2w6	0.00	0.51	0.00	0.00	0.00	0.61	0.28	0.11	0.56	1.24	0.77
18:3w3* 18:1w9cis* 18:2w3*	1.11	0.00	1.51	0.00	3.46	0.81	2.94	1.63	2.62	3.26	3.59
18:1w9t	9.08	2.05	0.00	0.32	0.00	3.32	0.00	0.00	0.00	0.00	0.00
18:1w7	10.83	3.25	0.00	0.80	2.92	2.48	3.11	2.45	2.47	2.63	2.48
18:1w5	3.68	0.73	0.00	0.13	0.00	0.31	0.32	0.13	0.49	0.00	0.20
18:0	9.18	3.38	21.71	2.20	4.77	2.37	3.86	4.03	3.45	3.80	2.85
10Me19br	0.00	0.00	0.00	0.00	0.00	0.00	0.27	0.00	0.26	0.00	0.06

Cruise 110321 – March 2011 Sediment cont.							Cruise 100912 – Sept. 2010 Sediment cont.				
Region	**ETM (9)**		**Up-river (15)**		**Up-river (17)**		**Post-ETM (12)**	**ETM (15)**		**ETM (17)**	
Core - depth	35 floc	35 0-1	34 floc	34 0-1	32 floc	32 0-1	26 0-1	25 floc	25 0-1	23 floc	23 0-1
19:0	0.87	0.64	3.17	0.93	0.80	0.27	0.69	0.40	0.57	0.39	0.45
20:5w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:4w6	0.00	0.60	0.00	0.00	0.00	0.22	0.24	0.00	0.49	0.07	0.34
20:5w3	0.00	1.09	0.00	0.00	0.00	1.00	0.99	0.23	1.08	0.34	1.17
20:3w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:4w3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:3w3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:1w9~	0.00	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:1w7~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:1w5~	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20:0	4.11	6.86	7.84	15.29	3.78	3.11	9.35	8.22	8.31	6.50	5.14
21:0	0.00	0.88	0.00	1.65	0.23	0.27	0.74	0.43	1.13	0.40	0.39
22:6w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:6w3	0.00	0.17	0.00	0.00	0.00	0.00	0.10	0.00	0.20	0.00	0.00
22:5w6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:5w3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:1w9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:1w7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22:0	1.55	3.04	3.05	4.66	2.39	1.61	2.97	3.02	3.62	3.16	3.14
23:0	0.00	0.00	0.00	1.37	0.65	0.86	0.77	0.59	1.11	0.71	0.72
24:1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24:0	2.95	5.35	6.39	10.64	4.95	4.12	5.70	5.50	6.65	6.96	6.89
25:0	0.35	1.05	0.66	2.45	0.77	0.68	0.78	0.61	1.26	0.87	0.79
26:0	2.09	5.42	7.47	13.96	5.19	4.86	6.26	4.75	6.79	6.39	5.25
27:0	0.00	0.89	1.35	2.82	0.80	0.69	0.76	0.39	1.21	0.57	0.49
28:0	0.91	5.70	8.50	15.21	5.63	5.61	6.15	4.23	7.38	4.93	3.19
29:0	0.00	1.02	0.00	2.47	0.78	0.73	0.56	0.18	1.22	0.17	0.14
30:0	0.40	4.87	3.68	10.25	3.31	3.75	3.49	1.72	5.45	1.35	1.01
31:0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32:0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

cont.

Cruise 110321 – March 2011 Sediment cont.							Cruise 100912 – Sept. 2010 Sediment cont.				
Region	**ETM (9)**		**Up-river (15)**		**Up-river (17)**		**Post-ETM (12)**	**ETM (15)**		**ETM (17)**	
Core - depth	35 floc	35 0-1	34 floc	34 0-1	32 floc	32 0-1	26 0-1	25 floc	25 0-1	23 floc	23 0-1
% Sat FA's	56.07	65.15	66.74	92.37	66.99	56.92	63.87	69.78	68.47	67.92	59.61
% Monounsat	33.15	17.29	31.56	2.66	24.80	26.80	17.56	15.88	14.58	20.37	25.34
% Polyunsat	1.11	4.04	1.51	0.07	4.01	6.38	6.54	2.28	7.70	5.12	8.84
% Br FA's	10.08	12.16	1.69	4.59	7.14	10.05	11.61	12.59	9.70	9.06	8.85
% Fresh	0.00	3.53	0.00	0.07	0.00	4.82	3.31	0.54	4.52	0.63	4.49
% Terr	6.34	21.35	26.04	50.06	19.08	18.34	21.60	16.21	26.28	19.63	16.33
% Bac	7.80	8.66	1.56	2.92	5.34	7.02	10.23	9.91	7.98	7.26	6.89
TAR-FA	0.194	0.736	9.267	5.515	0.524	0.628	0.967	0.447	1.204	0.626	0.583