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Particulate organic matter higher concentrations, terrestrial sources and losses in bottom waters of the turbidity maximum, Delaware Estuary, U.S.A.

Anna L. Hermes [1], Elisabeth L. Sikes*

Institute of Marine and Coastal Sciences, Rutgers University, 71 Dudley Rd., New Brunswick, NJ, 08901, USA

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ABSTRACT

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

1. Introduction

"The destination of material eroded is eventually the great world ocean, although there are pauses in the journey" (Judson, 1968). Estuaries are the link between land and sea carbon cycles. Land-derived sediment and particulate organic carbon (POC) is delivered to estuaries, wherein physical, biological, and chemical processes regulate the quantity and quality of material reaching the marine environment such that only half of the land-derived organic carbon delivered to estuaries escapes to the coastal ocean (Bauer et al., 2013; Bianchi, 2011; Ludwig et al., 1996; Meybeck, 1982; Schlesinger and Melack, 1981; Schlünz and Schneider, 2000). Despite much work examining organic carbon sources and loss processes in estuaries (Abril et al., 2002; Canuel and Zimmerman, 2006; Cifuentes et al., 1988; Etcheber et al., 2007; Mannino and Harvey, 2000), there is still significant uncertainty in our understanding of estuaries' role in processing land-derived organic carbon en route to the ocean (e.g. Bauer et al., 2013; Benner, 2004; Blair and Aller, 2012). With estuaries having been found to be net heterotrophic, this suggests that substantial land-derived organic carbon may be being respired to CO_2 (Abril et al., 2002; Bauer et al., 2013; Cai, 2011; Frankignoulle et al., 1998). An important component of understanding what drives the net heterotrophy of estuaries is determining if land-derived POC is lost or transported through these systems.

Estuarine POC is intricately linked to sediment dynamics (e.g. Bianchi and Bauer, 2012; Blair and Aller, 2012; Blair et al., 2004). The sources of POC in estuaries vary spatially and seasonally. Physical controls, such as seasonal and event-driven changes in discharge and tidal spring/neap variability, influence sediment residence time, transport, resuspension, and concentrations (e.g. Blair and Aller, 2012; Frankignoulle et al., 1998; Sommerfield and

* Corresponding author.
E-mail address: sikes@marine.rutgers.edu (E.L. Sikes).
[1] Present address: Philadelphia Water Department, 1101 Market St. 4th, Floor, Philadelphia, PA, 19107, USA.

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Wong, 2011). Upper estuaries are typically zones of organic matter (OM) loss and transformation through biotic processes of microbial degradation and heterotrophic respiration (see review in Bauer et al., 2013). Downstream, the estuarine turbidity maximum (ETM) is a zone of flocculation and resuspension, actively mixing, recycling, and remineralizing both algal- and land-derived organic carbon (Abril et al., 2002; del Giorgio and Pace, 2008; McCallister et al., 2006). Throughout estuaries, these processes combine with *in situ* production by phytoplankton seasonally varying autochthonous POM inputs (Canuel and Zimmerman, 2006; Cifuentes et al., 1988; Mannino and Harvey, 1999).

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

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

2. Study site: The Delaware Estuary

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

The second largest estuary on the U.S. Atlantic coast, the Delaware has been the subject of extensive shipboard surveys since the late 1970s, providing a physical, chemical, and biological characterization of the system (Cifuentes et al., 1988; Coffin and Sharp, 1987; Pennock and Sharp, 1986; Sharp et al., 1982, 2009). Additionally, previous geochemical studies examined the quantity and source of organic carbon (OC) in surface waters through the estuary, both spatially and seasonally (e.g. Harvey and Mannino, 2001;

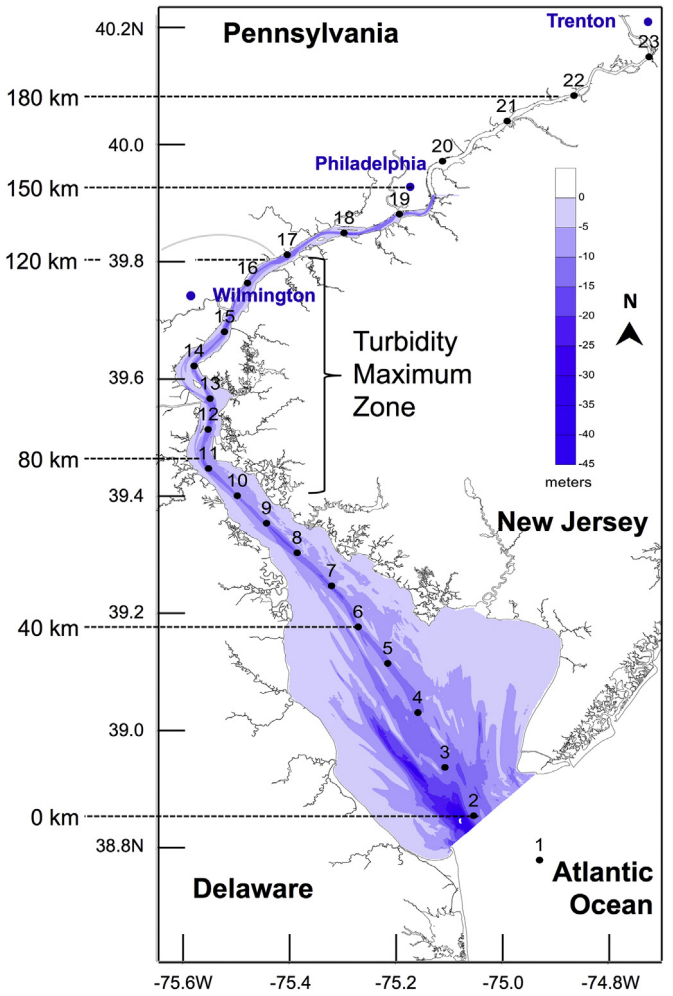

Fig. 1. The Delaware Estuary, East Coast, U.S.A. Sampling stations are numbered 1–23 and shading indicates water depth (meters). The turbidity maximum zone is typically observed between 80 and 120 km.