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Lipid and ^{13}C signatures of submicron and suspended particulate organic matter in the Eastern Tropical North Pacific: Implications for the contribution of Bacteria

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ABSTRACT

The contribution of bacterial biomass to total particulate organic matter (POM) in the ocean, including exported material, is poorly constrained. To examine potential signatures for the presence and export of bacterioplankton and their detrital remains, here we provide a detailed compound-specific ^{13}C characterization of fatty acids from membrane polar lipids obtained from a water column profile in the Eastern Tropical North Pacific. POM of submicron size (0.2–0.7 μm; "X-POM") was sampled and analyzed separately from the size class typically collected as "suspended" POM (0.7–53 μm; "L-POM"). The distributions of polar head group classes, specific fatty acid side chains, and natural ^{13}C contents all vary, both between particle size classes and with depth in the water column. In general, the polar lipids in submicron material – and by inference, lipids of bacterial origin – have higher ^{13}C content than polar lipids from larger POM and are equally abundant. Lipid signatures from the photic zone appear to be partially conserved in the suspended pool during transit down the water column. However, bacterial heterotrophy and possibly chemoautotrophy partially overprint these surface signatures. In addition, active metabolisms in the oxygen minimum zone (OMZ) appear to mediate the disaggregation of POM transported from the surface, thus adding complexity to the pathways of mid-water carbon flux and providing additional organic substrates to the OMZ and below. This "substrate injection" may provide important fuel for the denitrification and anammox reactions. Finally, examination of ^{13}C content in polar lipids provides a basis for new interpretation of depth-related variations in δ^{13}C values of bulk suspended POM.

1. Introduction

Export of organic matter from the surface ocean is a major flux of carbon into deep reservoirs, removing it from exchange with atmospheric CO_2 on short time-scales. In order to predict carbon cycle responses to global change, it is vital to accurately characterize biotic and environmental controls that affect the balance of export versus respiration. Small plankton and other slowly-settling particles – otherwise known as "suspended" POM – have been overlooked as contributors to carbon export (e.g., Richardson and Jackson, 2007; Lomas and Moran, 2011; Arístegui et al., 2009; Burd et al., 2010; Alonso-González et al., 2010). The majority of cellular biomass in the surface ocean is classified as suspended: most phytoplankton and all free-living Bacteria are smaller than the typical 53 μm cut-off often used for distinguishing "sinking" versus "suspended" POM (Kostandinov et al., 2010; Bacon et al., 1985; Wakeham and Lee, 1989). Because hydrodynamic models dependent on Stokes's Law suggest that this small (<53 μm) material should not sink passively to any extent, the downward flux of suspended POM in the water column must involve other processes.

Recent studies have explored the potential for exchange between "suspended" and "sinking" POM (Sheridan et al., 2002; Goutx et al., 2007; Abramson et al., 2010). Radioisotope tracers indicate significant exchange and hence homogenization between these two pools (Bacon and Anderson, 1982), but organic characterization reveals their compositions to be qualitatively dissimilar (Wakeham and Canuel, 1988; Abramson et al., 2010). Significantly, these previous studies did not include POM $<\sim 1$ μm in diameter ("submicron" POM). However, the majority of free-living marine Bacteria and Archaea exist within the submicron size class (e.g., Koike et al., 1990; Ingalls et al., 2012); these, along with particle-attached prokaryotes, are critical mediators of particle transformations. The biomass of living Bacteria alone comprises $>20\%$ of

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POM in the oligotrophic Pacific surface ocean (Kawasaki et al., 2011), with similar estimates in other oceanic regions (Li et al., 1983; Turley et al., 1986; Fuhrman et al., 1989; Karl et al., 1988; Cho and Azam, 1988; Koike et al., 1990). By routinely neglecting submicron POM in geochemical measurements, key stages in the production, aggregation, disaggregation, and consumption of organic matter may be missing from our conceptual and numerical models of POM export.

Here we begin to address this deficit in knowledge by comparing "submicron" POM (0.2–0.7 μm; henceforth "X" for extra-small) and a typical "suspended" class of POM (0.7–53 μm; "L" for large) from the water column of the Eastern Tropical North Pacific (ETNP). Subsurface waters in the ETNP contain one of the three most extensive oxygen minimum zones (OMZ) in the world ocean (Ward et al., 2008). Export of organic matter at this location has important implications for global productivity: OMZs are the sites of the largest discrete losses of fixed nitrogen from the world ocean (Codispoti et al., 2001). The supply of organic matter to denitrifying Bacteria in the OMZ may be the limiting factor in determining the magnitude of this nitrogen loss (Ward et al., 2008). The global strength and extent of OMZs is increasing with recent climate trends (Stramma et al., 2008), so it is vital to characterize the transformations in POM in these regions.

We focus on the upper 800 m of the water column in the ETNP, encompassing the depths over which the remineralization of exported carbon is the most intensive (Martin et al., 1987; Buesseler et al., 2007). We utilize a compound-specific approach to characterize the concentration and $\delta^{13}C$ values of fatty acids from X-POM and L-POM. Fatty acid data described here derive from two classes of intact polar lipids (IPLs), nominally distinguished as glycolipids and phospholipids. This approach is novel in allowing us to capture the isotopic characteristics of primarily in situ organisms; compound-specific $\delta^{13}C$ values rarely are reported separately for glycolipids versus phospholipids from suspended POM.

The results indicate that *de novo* production by autotrophs and heterotrophs, sinking, and particle dynamics such as aggregation/disaggregation all likely influence the lipid and isotopic content of submicron and larger suspended size classes of POM throughout the water column. Specifically, we show that (i) X-POM and L-POM contain approximately equal concentrations of IPLs; (ii) there is wide heterogeneity in $\delta^{13}C$ values of individual compounds, both within and between samples; (iii) X-POM is enriched in ^{13}C, potentially a bacterial signature; and (iv) there are unique processes and $\delta^{13}C$ signatures associated with the strong OMZ in this region.

2. Methods

Oceanographic stations in the Eastern Tropical North Pacific were defined during a 2007 field season (Cass et al., 2011; Rush et al., 2012; Podlaska et al., 2012). Samples for this investigation were collected from aboard the R/V *Knorr* in December 2008–January 2009 from 13°N 105°W (Station 1, "Tehuantepec Bowl"; 3235 m total depth) and 9°N 90°W (Station 8, "Costa Rica Dome"; 3525 m total depth; Fig. 1).

2.1. In situ filtration.

Seawater was sequentially filtered in situ via submersible pumps (WTS-LV 08 upright: McLane Research Laboratories, Inc.), with total collected volumes of 200–1890 L per depth. Six to seven depths were sampled at each station, targeting the surface; upper and lower fluorescence maxima; upper oxycline; upper, middle, and lower OMZ; and lower oxycline, as defined by a Seabird CTD package (Fig. 2). Most pumps were equipped with three filter tiers, each 142-mm in diameter. The first tier was fitted with an acid-cleaned 53 μm-mesh Nitex screen, the second with one or two (stacked) glass fiber filters (GF/F; 0.7 μm pore-size), and the last with a polyethersulfone filter (Pall Supor; 0.2 μm pore-size). Overall lipid yields for X-POM versus L-POM were similar regardless of the use of one (Station 1) or two (Station 8) GF/Fs on the middle tier, suggesting that filters retained structural integrity and separated particle size classes roughly uniformly across samples. For several depths at Station 1, pumps were equipped with only two filter tiers, and only Nitex and GF/F filters were used. Average flow rates were 2.1–3.6 L min^{-1} when Supor filters were used and 5.3–7.0 L min^{-1} when Supor filters were not used. Each filter was wetted with sterile-filtered deionized water before tiers were assembled for deployment. Pumps equilibrated with water at the sampling depths for 20–30 min before pumping commenced. Upon recovery, pumps were activated briefly to remove excess

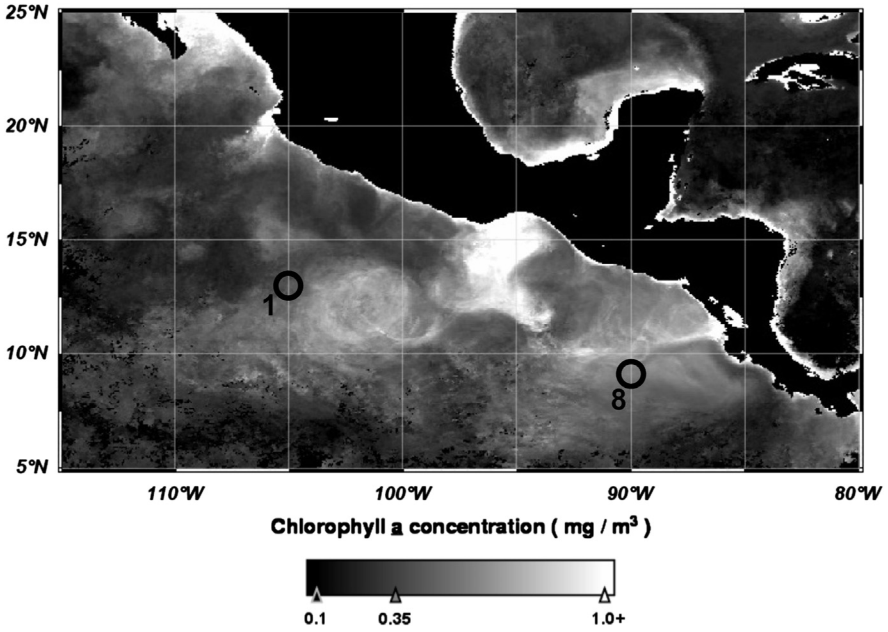

Fig. 1. Study sites in the Eastern Tropical North Pacific: Station 1, 13°N 105°W; Station 8, 9°N 90°W, and mean chlorophyll-*a* concentration from remote sensing by Aqua MODIS (Moderate-resolution Imaging Spectroradiometer) between 10 Dec 2008 and 10 Jan 2009 (Feldman and McClain, accessed 2013; edited in SeaDAS).