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Phospholipids as a component of the oceanic phosphorus cycle

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ABSTRACT

We characterize the distribution of oceanic phosphorus-containing lipids (PL) in the Northeast Atlantic by Iatroscan thin layer chromatography and high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Phospholipids are a small but significant fraction of oceanic particulate organic carbon (POC) (1.5%). We describe the distribution of 1862 PL compounds in total, of which only ~27% have elemental compositions that match those found in the Nature Lipidomics Gateway database (e.g., phosphatidylglycerol (PG), phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidic acid (PA), phosphatidyl serine (PS), and phosphatidylinositol (PI)). The highest phospholipid concentration is found in the epipelagic, which reflects primary production in that depth horizon. Depth-related PL removal was the strongest for PL signals that match database-reported (known) lipids and was lower for saturated non-database (novel) matched PL. The transformation of known PL is marked by depth-related increase in saturation with PA that is assumed to be generated as the earliest transformation product of PL. Novel unsaturated P-lipids likely originate from both PL transformation processes and in-situ biological production at the surface layer. Novel PL are dominated by unsaturated compounds for which unsaturation increased between the epipelagic (average molecular double bond equivalents, DBE = 5) and the abyssopelagic (average DBE = 6.7) zones. Additionally, those compounds increase in both average molecular weight and contribution to all lipid content with increasing depth, likely from cross-linking of unsaturated compounds. Our data indicate that novel PL are selectively preserved with depth and therefore are P and C carriers to the deep Atlantic. We demonstrate that a full appreciation of phosphorus cycling requires additional data on phospholipid composition and especially the ecological role and depth-related molecular change of these compounds.

1. Introduction

Phosphorous (P) is an essential nutrient for phytoplankton growth and in places limits oceanic primary production (Moore et al., 2013; Wu et al., 2000; Yoshimura et al., 2007). Phosphorus is a component of key molecules such as nucleic acids, phospholipids, ATP and complex carbohydrates. Unlike nitrogen, which can be supplied by nitrogen fixation in the euphotic zone, the supply of phosphorus is dominated by deep mixing and upwelling (Dugdale and Goering, 1967), and also depends on continental input, mainly by river runoff (Baturin, 2003). There is no atmospheric reservoir of phosphorus. The phosphorus budget of the ocean is unbalanced since the accumulation of phosphorus in marine sediments exceeds the continental input of particulate and dissolved phosphorus (Wallmann, 2010).

Various chemical forms of P participate in numerous abiotic and biotic processes collectively referred to as the P cycle, which is strongly connected to the carbon cycle and therefore to the capability of oceans for climate change mitigation due to their capacity to sequester carbon from the atmosphere. A crucial process in this is the generation of carbon-rich material in the upper ocean. The particles export a fraction of the primary production out of the euphotic zone (i.e. the “biological carbon pump”). Export flux of POC is < 5–10% of total primary production in the ocean (Buesseler, 1998). Any organic carbon that escapes mineralization in this environment is liable to be sequestered for millennia, ultimately representing the sequestration of atmospheric CO_2 (Lampitt et al., 2008). Microorganisms are primarily responsible for

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carbon (Azam, 1998) and P (Karl, 2014) assimilation and remineralization in the ocean.

Lipids are a major biochemical class in seawater along with carbohydrates and proteins. They are carbon rich, with a high energetic value, and thus represent important metabolic fuels. Phosphorus containing lipids (i.e. phospholipids) are a major component of cell membranes that provide structure and protection to cells. Membrane lipids generally contribute to 15 to 25% of the carbon in planktonic cells (Wakeham et al., 1997). The synthesis of phospholipids consumes 18–28% of the PO_4^{3-} taken up by the total planktonic community in the North Pacific subtropical gyre (Van Mooy et al., 2006). The proportion of PL in phytoplankton varies widely from a few percent to as much as half of the total lipid content (Guschina and Harwood, 2009). Nutrient conditions affect the composition of cellular lipid composition in phytoplankton; diatoms grown under nutrient replete conditions exhibit high proportions of PL, while in P-depleted conditions PL content is dramatically reduced (Geider and La Roche, 2002; Martin et al., 2011a). Phospholipids comprise a significant proportion of cellular phosphorus (e.g., 36% and 15–20% of cellular P of the freshwater phytoplankton *Ankistrodesmus folcatus* (Geider and La Roche, 2002) and marine bacteria (Dobbs and Findlay, 1993) respectively. On average, PL account for 4 ± 1% and 7.1 ± 2.5% of the total particulate phosphorus in the eastern subtropical South Pacific and in the Medditerranean, respectively (Van Mooy and Fredricks, 2010; Popendorf et al., 2011). Dominant phospholipid molecules vary by plankton species. Heterotrophic bacteria are the dominant sources of phosphatidylglycerol (PG) and phosphatidylethanolamine (PE), while PC phosphatidylcholines (PC) are derived primarily from eukaryotic phytoplankton (Van Mooy and Fredricks, 2010).

Phospholipid concentration varies between marine environments. Particulate PL concentrations in the northern Adriatic, Mediterranean, throughout a year vary in the range of 3.0 to 27.7 μg/l, with a contribution to total lipids between 17.8 and 50.3% (Frka et al., 2011; Marić et al., 2013) as measured by thin layer chromatography. PL in the oligotrophic to mesotrophic region of the east Atlantic, measured by thin layer chromatography, ranged from 1.3 to 7.8 μg/l, contributing between 11.4 and 55.0% of total lipid content (Gašparović et al., 2014). In the upper 250 m of the oceanic water column, concentrations of measured PL (PG + PE + PC) in the eastern subtropical South Pacific ranged between 130 and 1350 pmol/l (Van Mooy and Fredricks, 2010). The depth distribution of the three phospholipids (PG, PE, and PC) across the Mediterranean Sea was quite similar, each phospholipid class was approximately 200–600 pmol/l in the surface, increasing to 200–800 pmol/l at 50–75 m, then decreasing to 100–200 pmol/l at 250 m (Popendorf et al., 2011). There is a wide variability in P-related physiology among marine plankton, including the ability to acquire and utilize different organic P sources (Ivančić et al., 2012), and the substitution of PL with non-phosphorus lipids in P-limited conditions (Van Mooy et al., 2009; Sebastián et al., 2016).

The transformation processes of phosphorus-containing molecules within the water column remain poorly understood (Benitez–Nelson, 2000), particularly related to their degradation (Rontani et al., 2009; Rontani et al., 2012). To our knowledge, there are no published reports on oceanic phospholipid degradation processes, but they are clearly an essential resource for some deep ocean organisms that are unable to synthesise them (Mayor et al., 2013; Pond et al., 2014).

Given the importance of P as a major limiting nutrient, we are interested in the surface Atlantic production of phospholipids and their potential as a phosphorus and carbon carrier to the deep ocean. There is a pressing need to understand the processes involved in the early transformation of PL that are responsible for chemical change in terms of both concentration and molecular characteristics. To address this issue we performed complete phospho-lipidomic analysis by direct-infusion FT-ICR MS. Molecular formulae are derived directly from FT-ICR MS measurement and subsequently matched to a lipid database. While this approach neglects isomeric identification, it is the only measure

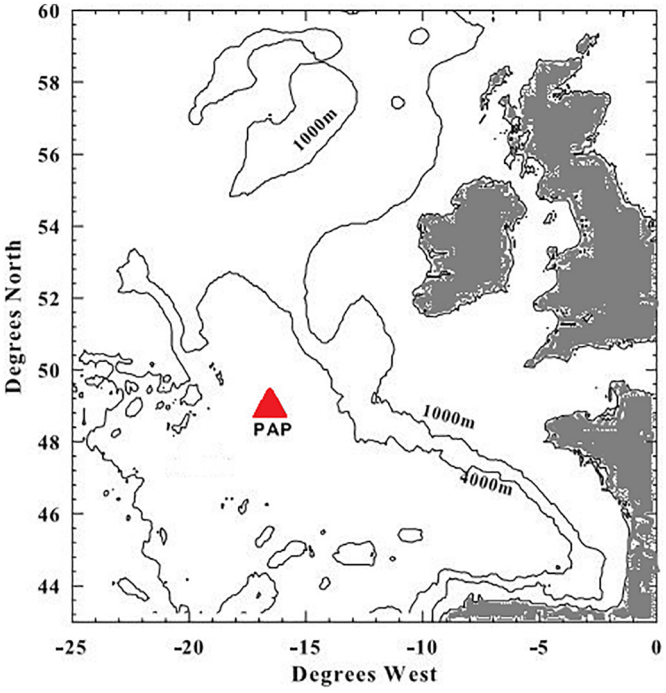

Fig. 1. PAP-SO sampling site

available that provides global description for multiple thousands of organic molecules in these environments. With these data, we characterize the nature of particulate PL, their removal and transformations through the water column. In addition we used thin–layer chromatography with flame ionization detection to quantitatively detect total lipid and bulk phospholipid to complement the FT-ICR MS analysis and illuminate the modern P cycle.

2. Methods

2.1. Location

The study site, of the Porcupine Abyssal Plain Sustained Observatory (PAP-SO) in the Northeast Atlantic (49 N, 16.5 W) (Fig. 1) has been the main focus of many studies since 1992. This region is isolated from the complexities of the continental slope and the Mid-Atlantic Ridge. A persistent feature of the North Atlantic is undersaturation of CO_2 in surface waters throughout the year, which gives rise to a perennial CO_2 sink and makes this a region of great importance in the global carbon cycle (Hartman et al., 2012). In terms of biogeographical provinces that have dynamical boundaries, it is well within the North Atlantic Drift (NADR) province (Longhurst, 2007), which is generally characterized with spring bloom that is developing from the late April, starting at the southern part of NADR and progressing northward until June. The influences of the continental shelves and slope are thought to be slight at PAP with negligible advection of particulate material (Weaver et al., 2000). Eddy activity is much lower than in many other oceanic regions (Chelton et al., 2007), and such as they are, they tend not to traverse quickly. Currents are generally weak (Lampitt et al., 2001) and lateral advection speeds are low but significant (Williams et al., 2006; Hartman et al., 2010).

2.2. Sample processing

Sampling was conducted at the PAP station from the RRS James Cook on June 14, 2013. Ocean samples were collected at 21 depths from the surface (2 m) to 4800 m (50 m above bottom) (epipelagic (0–100 m), mesopelagic (100–1000 m), bathypelagic (1000–4000 m)