Biogeochemical characteristics of settling particulate organic matter in Lake Superior: A seasonal comparison

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ABSTRACT

To assess settling particulate organic matter (POM) seasonality and its availability to the benthic community, settling particulate matter was studied in terms of mass fluxes and main biogeochemical characteristics (including organic carbon (OC), nitrogen, and stable carbon and nitrogen isotopic values) at two Lake Superior offshore sites over the course of a year. Fourier transform infrared spectroscopy (FTIR) and hydrolysis, extraction, and derivatization were used to provide further compositional information. Carbon and nitrogen content, isotopic and wet chemical data, and FTIR spectra show that summer particulate material is mainly autochthonous, with higher proportions of amide and carbohydrate. FTIR shows that spring particulate material contains relatively high proportions of clay minerals, indicating major sources from sediment resuspension and/or spring runoff. Distinct amino acid distributions at the two sites, revealed by principal component analysis (PCA) based on amino acid mol% composition, possibly result from differences in OM sources and the degree of degradation occurring at the two sites. Carbohydrate (PCHO), total hydrolyzable amino acid (THAA) and FTIR data suggest that the nutritional value of bulk POM to benthic heterotrophs should be lower in spring than summer-fall, although both periods exhibited high sinking fluxes of total mass and OC. Due to sediment resuspension events and an oxic water column, organic matter eventually buried in Lake Superior's sediments has probably experienced extensive alteration due to several cycles through the water column and the bacterially-active sediment-water interface.

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1. Introduction

Particulate organic matter (POM) in aquatic ecosystems plays significant roles in the global carbon cycle by serving as a food source for heterotrophic organisms and by transporting organic matter produced in the euphotic zone to the sediments. During its transport, POM undergoes biogeochemical changes such as uptake by biota, remineralization and exchange with dissolved organic matter (DOM), so only a portion of the surface production eventually reaches the surface sediments (Wakeham et al., 1997; Hedges et al., 2000; Burdige, 2007). POM, by its innate composition and its reactivity, affects the cycles of global carbon, nutrients, and trace metals as well as anthropogenic pollutants (Eppley and Peterson, 1979; Sholkovitz and Copland, 1981; Baker and Eisenreich, 1989; Baker et al., 1991). Knowledge of the POM molecular level composition, fluxes and contribution

to total particulate fluxes as well as its variations is necessary not only for investigating the source and dynamics of POM but also for a better understanding of degradation and selective preservation of the macromolecules in POM. For benthic ecosystems, which are mainly fueled by settling POM, different components of the POM pool are of different nutritive values. For example, just in terms of energy equivalents, average particulate protein has been estimated to contain 24.0 J/mg as compared to an average particulate carbohydrate value of 17.5 J/mg and an average lipid value of 39.5 J/mg (Gnaiger, 1983; Navarro and Thompson, 1995). The relative contributions of energetically variable, bioavailable and nutrient-containing organic matter can fluctuate seasonally (Pusceddu et al., 1996). Studies of temporal and spatial changes in the biochemical composition of sinking particles can therefore help us assess the nutritional quality of this material, which impacts the dynamics of benthic communities. Although detailed characterization of POM is important, it is difficult because POM is heterogeneous, consisting of living and dead cells, fecal pellets, aggregates, organically coated mineral grains and other materials.

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Carbohydrate and protein are among the major biochemicals produced by photosynthetic processes in the euphotic zone and are generally considered bioavailable for aquatic organisms. They represent a significant component of the particulate organic matter in the water column (Lee and Cronin, 1982, 1984; Pakulski and Benner, 1992) and in sedimentary material. Particulate carbohydrates (PCHOs) comprise 5–20% of the total particulate organic carbon (POC) in marine sediments (Cowie and Hedges, 1992; Burdige et al., 2000). Amino acids, the building blocks of protein molecules, comprise from < 1% to as much as 67% of the organic carbon (OC), and 10–100% of the organic nitrogen in open-ocean net plankton, water column POM and sediments (Lee and Cronin, 1984; Lee, 1988; Wakeham et al., 1997). The distribution of carbohydrates and amino acids in POM mainly depends on the source of the organic matter, the depositional rate, the water depth and local hydrological factors. It primarily reflects the balance between biological production and biological consumption through the journey of those compounds to the bottom of the ocean or lake. Understanding the temporal and spatial changes in quantity and quality of particulate organic matter, including its carbohydrate and amino acid components, is important to the study of benthic heterotrophic activities by microbes and macroorganisms. Wet chemical extraction and detection methods have been developed and applied as classical ways to quantify carbohydrates and amino acids in marine and freshwater POM samples (Johnson and Sieburth, 1977; Lindroth and Mopper, 1979).

Different techniques have been applied to heterogeneous POM for the identification and characterization of its chemical components such as flow cytometry in conjunction with fluorochromes (Moreira-Turcq and Martin, 1998; Kerner et al., 2003), flow cytometry in conjunction with pyrolysis mass spectrometry (Minor et al., 1998; Minor and Eglinton, 1999), nuclear magnetic resonance (NMR) spectroscopy (Hedges et al., 2000), and Fourier transform infrared (FTIR) spectrometry (Bruns et al., 2010; Tremblay et al., 2011). Among these, FTIR is inexpensive, non-labor intensive and can quickly provide an overview of compound class or functional group composition in complex mixtures of organic matter based upon analysis of a small amount (~1 mg) of raw dried sample (Abdulla et al., 2010). FTIR analysis is based on the fact that vibrations of different covalent bonds absorb infrared radiation at different wavenumbers resulting in an IR spectrum that can be used for structural characterization. However, as happens with DOM samples, the heterogeneity of POM samples acts to simplify their FTIR spectra, which exhibit broad bands resulting from overlap of multiple functional groups (Li et al., 2013). This feature is complicated further by the fact that POM is often intimately associated with clays and other inorganic components that also contain covalent bonds absorbing in the infrared range. Thus, this study applies classical wet extraction and derivative molecular techniques for the analysis of carbohydrates and amino acids, and stable isotope analyses, along with FTIR characterization of sinking POM. Our main aims were to investigate the origin and biochemical composition of settling POM in the open-water region of Lake Superior over seasonal scales and to estimate POM's nutritional value for benthic consumers.

2. Material and methods

2.1. Study site and sampling details

Lake Superior is the Earth's largest lake by surface area (82,100 km^2), with a maximum depth of over 400 m, mean depth of 150 m, water residence time of 180 years, and is dimictic, mixing twice annually, once in late spring-early summer (usually April to June) and once in late fall-early winter (December to January) (Herdendorf, 1982; Urban et al., 2005; Austin and Colman, 2008). Largely affected by the mixing events, sediment resuspension occurs several times a year in the lake during the unstratified periods and estimates of its contribution to settling fluxes of OC range from 10–30% in offshore sites (Urban et al., 2004). In general, Lake Superior has biogeochemical similarities to many open ocean systems such as low water column primary production (~200–350 mgC/m^2/d, Sterner et al., 2004), low dissolved OC (89–208 μM) and particulate organic carbon (POC) (2.3–16.5 μM) concentrations (Zigah et al., 2012), small terrestrial impact, and the dominance of a microbial food web (Cotner et al., 2004). Thus the study of Lake Superior and comparisons with both lakes and oceanic systems can provide valuable information for a broad audience. The OC deposition in Lake Superior sediments is about 0.48 × 10^{12} gC/yr (McManus et al., 2003) to 1.5 × 10^{12} gC/yr (Johnson et al., 1982; Klump et al., 1989). Surface sediment at open lake sites has OC contents ranging 1.5–4.3% (Li et al., 2013). Dominant signals from clay minerals/biogenic silica along with carbohydrate, carboxylic acid, aliphatic/acetyl ester, amide/protein and phenol/lignin have been identified using FTIR in the Lake Superior surface sediments (Li et al., 2013).

To obtain settling POM samples in the hypolimnion, McLane Parflux 21 cup sequential sediment traps with a diameter of 0.92 m^2 were deployed with moorings located in the eastern (EM, 150 m, total water depth 240 m) and western (WM, 150 m, total water depth 180 m) arms of the lake, as shown in Fig. 1, from October 2009 to June 2010. (Note: our site EM, which is the same as in Zigah et al. (2012), is considerably farther east, and actually within the eastern basin of the lake, as compared to the sampling location EM in Sterner et al. (2004)). On the same moorings, temperature and pressure loggers were deployed at a variety of depths from the surface to 150–200 m. The upper part of the WM mooring failed in December 2009, and the remainder was recovered and the mooring rebuilt in June 2010 at 125 m depth to continue to collect summer samples. The deep sediment trap sample collecting portion of the WM mooring remained intact through winter 2009/2010 as indicated by mooring design (location of floats, sensors, and the trap) and pressure sensor data. The EM trap was recovered and reset in June 2010 at 125 m depth to collect samples until September 2010. Physical data presented here for onset of mixing and stratification are from the EM mooring; for onset of summer stratification, site EM generally lags site WM by 1–2 weeks (J. Austin, personal communication). For both WM and EM, sample cups were programmed to rotate and collect descending particulate matter for 10/11 days during winter and 3/4 days during summer over an entire year. Because splits of these samples were used for DNA and RNA analyses on a separate project, only deionized water was added to each cup and no preservative was used. Material captured in the sediment traps was then equally split into 10 fractions with a McLane sediment trap splitter. Fractions of the captured material were freeze dried and homogenized prior to further analysis. For summer trap samples, every 3 or 4 continuous trap samples, which represent settling POM of 10 or 11 days in total, were mixed and measured as one sample. The middle day of the entire 10–11 days is used in the discussion and figures that follow to represent each collection of sample.

2.2. Elemental and isotopic analyses

Acid fumigation (Harris et al., 2001) was used to remove carbonate carbon before elemental analysis (EA) and isotope ratio mass spectrometry (IR-MS). Weighed aliquots of sample were placed in clean Ag capsules and 50 μL MilliQ water was added to each aliquot. The samples were then fumed over 12 M HCl (6–8 h), oven dried (60 °C, 4 h) and cooled. Each sample (in the Ag capsule) was enclosed within a Sn capsule before analyzing