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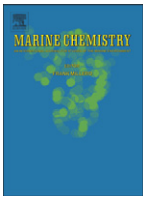

Binding of Th, Pa, Pb, Po and Be radionuclides to marine colloidal macromolecular organic matter

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ABSTRACT

To study the binding mechanisms of radionuclides to organic moieties in colloidal organic matter (COM), marine colloids (1 kDa–0.2 μm) were isolated by cross-flow ultrafiltration from seawater of the west Pacific Ocean and the northern Gulf of Mexico. For the same purpose, exopolymeric substances (EPS) produced by laboratory-cultured diatoms were collected as well. In our study areas, colloidal organic carbon (COC) concentrations ranged from 6.5 to 202 μg-C/L in the Pacific Ocean, and were 808 μg-C/L in the Gulf of Mexico. The COM compositions (organic carbon, organic nitrogen, proteins, total hydrolysable amino acids, total polysaccharides, uronic acids, hydroxamate siderophores, hydroquinone) were quantified to examine the relationships between partition coefficients (K_c) of five different radionuclides, ^{234}Th, ^{233}Pa, ^{210}Pb, ^{210}Po and ^{7}Be, and concentration ratios to COC of individual chelating biomolecules that could potentially act as a chelating moiety. The range of partition coefficients (K_c, reported as logK_c) of radionuclides between water and the different colloidal materials was 5.12 to 5.85 for ^{234}Th, 5.19 to 6.01 for ^{233}Pa, 4.21 to 4.85 for ^{210}Pb, 4.87 to 5.68 for ^{210}Po, and 4.49 to 4.92 for ^{7}Be, similar to values previously reported for lab and field determinations under different particle concentrations. While any relationship obtained between K_c and abundance of specific moieties could not be taken as proving the existence of colloidal organic binding ligands for the different radionuclides, it could suggest possible organic moieties involved in the scavenging of these natural radionuclides. Together with results from isoelectric focusing of radiolabeled COM, we conclude that binding to different biomolecules is nuclide-specific, with colloidal hydroxamate siderophoric moieties being important for the binding of Th and Pa radionuclides. Hydroquinones/quinone (HQ/Q) facilitated redox and chelation reactions seem to be involved in the binding of Pa and Be. However, the actual mechanisms are not clear. Individual amino acids, proteins, total polysaccharides and uronic acids did not yield significant relationships with logK_c values of the different radionuclides. Nonetheless, our results provide new insights into the relative importance of different potential ligand moieties in COM in the binding and possible scavenging of specific radionuclides in the ocean.

1. Introduction

A major fraction, 10–67%, of global dissolved organic carbon (DOC) exists in colloidal substances in seawater (Guo and Santschi, 2007 and the references therein). The change in the bulk composition of these colloidal substances from estuarine to shelf and offshore waters is a progressive increase in relative organic proportion and decrease in mineralogical content, e.g., clays and metal oxyhydroxides (Sigleo and Means, 1990; Santschi et al., 1995, 1998; Guo et al., 2000). The main organic carbon compositions are reactive substances categorized broadly as proteins, polysaccharides and lipids, as well as humic substances. Due to their amphiphilic (or amphipathic) nature, colloids not only have uncharged (hydrophobic) and charged groups, some of the charged groups can also provide strong chelating binding sites for trace metals and radionuclides. Binding sites include –COOH, –OH, –O═POOO–, –CONHO–, R–N–R and R–S–R groups; A type (or hard) metals (in this study: Th, Pa, and Be) prefer O over N and S binding sites, and B type (or soft) metals

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(e.g., Pb, in this study) prefer S (or N) over O binding sites; Po, in this study, as a metalloid, would have an intermediate position (Stumm and Morgan, 1996; Santschi, 2005 and references therein).

Most natural radionuclides have metal characteristics, making them susceptible to complexation by strong organic ligands, such as siderophores (Vraspir and Butler, 2009) or saccharides (Benner, 2011), which are found to be major classes of metal chelators in the aquatic environment. The direct source and nature of strong complexing ligands that control trace element speciation in seawater is still not well understood. However, it is very likely that colloidal organic ligands are released in relation to microbial and other biological activities in the ocean. A handful of marine prokaryotes are well known to release siderophores, a group of high-affinity metal-binding ligand compounds, in response to their need for soluble Fe, which is present at very low concentrations in oceanic waters (Reid et al., 1993; Neilands, 1995; Winkelmann, 2002). Exopolymeric substances (EPS) produced by bacteria and phytoplankton also form an important fraction of dissolved organic matter (Bhaskar et al., 2005) and are usually regarded as the precursors of transparent exopolymer particles (TEP) (Passow and Alldredge, 1994; Passow et al., 1994) and acid polysaccharides (Hung et al., 2003; Santschi et al., 2003), which play a decisive role in aggregation processes (Quigley et al., 2001, 2002; Bhaskar et al., 2005) and gel formation (Verdugo et al., 2004; Verdugo and Santschi, 2010; Verdugo, 2012). EPS composed mainly of polysaccharides and glycoproteins, and containing charged functional groups and amphiphilic, adsorptive and adhesive properties (Quigley et al., 2002; Arce et al., 2004), provide a substantial pool of organic carbon available to serve as a natural ligand source for many other molecules, including trace metals (Bhaskar et al., 2005; Doucet et al., 2007), nanoparticles (Chen et al., 2011; Zhang et al., 2013), and radionuclides (Zhang et al., 2008; Xu et al., 2009, 2011b; Chuang et al., 2014).

Various studies have found that colloidal organic carbon (COC) can play an important role in controlling the speciation, transport and bioavailability of natural trace elements in seawater and freshwater systems (Wilkinson and Lead, 2007 and references therein). However, the colloidal associations differ distinctly among the different radionuclides and areas of the world's oceans. Therefore, while it is clear that the colloidal fraction of any given nuclide is not necessarily coupled tightly to the abundance of bulk colloidal carbon, less is known about the specific ligands or functional groups distributed within the colloidal organic matrix. Due to the complexities in the real environments, the straightforward correlations found for model compounds (e.g., Yang et al., 2013) cannot be applied directly to predict radionuclides flux or scavenging. Hence, it is very important to use field collected marine organic material to simulate the sorption systems in the natural environment.

In this study, five particle reactive radionuclides, ^{234}Th, ^{233}Pa, ^{210}Pb, ^{210}Po and ^{7}Be, were selected to evaluate their binding to specific functional groups in marine colloidal macromolecular matter. These radionuclides have been widely used for decades as important proxies to understand oceanic processes (Broecker and Peng, 1982; Baskaran, 2011), such as boundary scavenging (^{7,10}Be, ^{234,228}Th) and paleocirculation, estimation of particle and colloid fluxes in the water column (^{231}Pa, $^{228,\,230,\,234}$Th, ^{210}Pb, ^{210}Po), as well as residence times of different water masses (^{7,10}Be, ^{234}Th, ^{210}Pb, ^{210}Po). Although the use of multiple isotopes pairs, such as ^{7}Be–^{234}Th, ^{210}Po–^{234}Th and ^{7}Be–^{210}Pb$_{xs}$, may eliminate the effects of particle composition (Feng et al., 1999a, 1999b, 1999c; Friedrich and van der Loeff, 2002; Matisoff et al., 2005), discrepancies on fractionation effects could still be observed in the field studies (Chase et al., 2002; Luo and Ku, 2004). A four-end-member mixing model (lithogenic clays, organic carbon, carbonates, and opal) clearly indicated the great importance of organic carbon to the nuclides distribution coefficients in sediment-trap materials (Li, 2005). Nonetheless, it is well observed that the bulk organic carbon content could not be a good proxy to predict the radionuclide flux (Chuang et al., 2013). It is thus reasonable to hypothesize that affinities of radionuclides vary among different organic moieties. In order to evaluate the potential radionuclide-binding phases in colloids, the compositions of marine colloids collected from the West Pacific Ocean and the Gulf of Mexico and EPS extracted from laboratory diatom cultures have been comprehensively examined, including proteins, individual amino acids, total polysaccharides, uronic acids, hydroquinones, and hydroxamate-type and catechol-type siderophores. The purpose was thus to examine their possible relationships with experimentally determined partitioning coefficients of ^{234}Th, ^{233}Pa, ^{210}Po, ^{210}Pb and ^{7}Be between colloidal (1 kDa to 0.2 μm) and dissolved phases (<1 kDa). Results from the analysis of radiolabeled colloid and EPS samples after separation by isoelectric focusing, as well as chemical relationships and statistical analyses provide further evidence of the relative importance of specific organic carrier phases in the binding and removal of specific radionuclides by marine biopolymers.

2. Methods

2.1. Sampling of marine colloidal organic matter

Since concentrations of marine colloids are very low, large-scale preconcentration using cross-flow ultrafiltration is needed (e.g., Benner et al., 1992; Buesseler et al., 1996; Wen et al., 1996; Guo and Santschi, 2007; Kruger et al., 2011). Marine colloids were concentrated from tens to hundreds liters of seawater from a coastal site in the Gulf of Mexico (Aug, 2010), and open ocean sites in the west Pacific Ocean (Mar, 2009; May, 2010) (Table 1). One GOM colloid sample was collected at a near shore station (coastal water) that was also used as reference material and can be compared to open ocean marine colloids (west Pacific waters). The laboratory-made ultrafiltration system was composed of four 1 kDa cutoff cartridges (Millipore®) with a peristaltic pump and Teflon tubing adapted from that of Wen et al. (1996). Cartridges, tubing and reservoirs were all thoroughly cleaned before sampling with detergent (Micro®), 0.01 N NaOH and 0.01 N HCl, following procedures described in Wen et al. (1996). All cartridges were checked for their integrity using vitamin B$_{12}$ (1.3 kDa). All operations were conducted carefully to avoid sample contamination. Briefly, tens to hundreds liters of seawater were prefiltered through a 0.2 μm Millipore® cartridge (in-line set-up) into an enclosed reservoir of the ultrafiltration system. After ultrafiltration, the retentate, the colloidal fraction (1 kDa–0.2 μm), of each sample was stored in the freezer. After returning to the lab, samples were defrosted for subsequent desalting via diafiltration and freeze-drying for further experiments. The freeze-drying process might cause some physicochemical alteration of natural organic matter samples, but any it has not been well documented in the literature; the fact that COM readily redissolved clearly indicates that any such alteration would have been reversible and thus minimal. More importantly, it would not have affected the aim of this study to investigate relationships between possible binding moieties in colloids and binding extent (K_c) of natural radionuclides.

The details of the eleven marine COM samples, including sampling times, depths, locations, water depths and surface water temperature, salinity, yield, and colloidal carbon concentration are given in Table 1.

2.2. Phytoplankton cultures and the separation of EPS

Marine phytoplankton, *Phaeodactylum tricornutum* (UTEX 646) and *Skeletonema costatum*, were cultivated in f/2 media (salinity of 26) at a temperature of 19 ± 1 °C with a light cycling of 14 h:10 h under a saturating irradiance of 100 μmol quanta $m^{-2}\,s^{-1}$ for EPS production. All cultures were axenic. *P. tricornutum*, unlike most diatoms, is able to grow in the absence of silicate with the biogenesis of its silicified frustules being facultative. It is well documented that EPS produced under different culture conditions (such as diatoms cultured under Si depletion conditions, considered as a stressed condition for diatoms) are different (Chuang et al., 2014 and references therein). Thus, two different kinds of EPS were collected from *P. tricornutum* cultured in f/2 and f/2