**Influence of organic matter on the adsorption of ^{210}Pb , ^{210}Po and ^7Be and their
fractionation on nanoparticles in seawater**

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Abstract

Improved applications of ^{210}Po , ^{210}Pb and ^7Be as geochemical proxies require more detailed understanding of their interactions with particles. Here, laboratory sorption experiments were carried out to examine the adsorption of ^{210}Po , ^{210}Pb and ^7Be and their fractionation on inorganic nanoparticles, including SiO_2 , CaCO_3 , Al_2O_3 , TiO_2 and Fe_2O_3 , in the presence or absence of macromolecular organic compounds (MOCs) that include humic acids (HA), acid polysaccharides (APS) and proteins (BSA), in natural seawater. Results showed that nanoparticle sorption was not greatly enhanced over that of microparticles as would be expected from their much higher specific surface areas, likely indicating their aggregation in seawater. It was found that synergistic interactions between inorganic nanoparticles, MOCs, and radionuclides determined the sorption, although their adsorption was particle composition-dependent. MOCs enhanced the sorption of selected nuclides on most nanoparticles. On average, in the presence of MOCs, partition coefficients (K_c) of ^{210}Po , ^{210}Pb , and ^7Be on nanoparticles increased 2.9-, 5.0- and 5.9-fold, respectively. The effect of MOCs could be explained for ^{210}Po and ^{210}Pb from their different $\log K_c$ values on inorganic nanoparticles. In addition, fractionation effects between ^{210}Po and ^{210}Pb (or between ^{210}Pb and ^7Be) could be quantified from their relative $\log K_c$ values on end-member sorbent components. Applications of both ^{210}Po - ^{210}Pb and ^7Be - ^{210}Pb pairs as particle dynamics tracers could be more quantitative when the nature of the organic coatings is taken into account.

Keywords: adsorption; radionuclide scavenging; natural organic matter; nanoparticles; polonium; lead; beryllium

1. Introduction

^{210}Pb ($T_{1/2} = 22.3$ yr), ^{210}Po ($T_{1/2} = 138$ d) and ^7Be ($T_{1/2} = 53$ d) are used in numerous applications in environmental science, geochemistry, and oceanography (e.g., [Santschi and Honeyman, 1989](#); [Krishnaswami and Cochran, 2008](#)). Both ^{210}Pb and ^{210}Po are particle-reactive radionuclides, resulting in their quick removal from seawater. Owing to the much shorter resident timescale compared to the time required for reaching equilibrium, the deficit of ^{210}Po to ^{210}Pb is ubiquitous in the upper ocean ([Bacon et al., 1976](#); [Nozaki et al., 1997, 1998](#); [Kim, 2001](#)). Furthermore, the extent of the deficit of ^{210}Po (over that expected from ^{210}Pb decay) is expected to quantitatively relate to the particle removal rate from the upper ocean. Hence, the ^{210}Po - ^{210}Pb pair has been used to track the export of particulate organic carbon ([Shimmiel et al., 1995](#); [Friedrich and Rutgers van der Loeff, 2002](#); [Murray et al., 2005](#); [Stewart et al., 2007a, 2010](#); [Buesseler et al., 2008](#); [Verdeny et al., 2008, 2009](#); [Yang et al., 2009, 2010](#); [Wei et al., 2011](#)), biogenic silica ([Friedrich and Rutgers van der Loeff, 2002](#)), particulate nitrogen ([Shimmiel et al., 1995](#); [Yang et al., 2011a](#)) and inorganic particles ([Yang et al., 2010](#)) from the euphotic zone in both coastal water and open ocean. Theoretically, there should be direct or indirect relations between the scavenging of ^{210}Po (and ^{210}Pb) and particulate components being tracked. However, the molecular mechanisms behind the application of ^{210}Po - ^{210}Pb as a particle cycling proxy have hardly been tested. Although the ^{210}Po - ^{210}Pb pair has been increasingly used in recent years, specific particle type and functionalities that are being tracked by this proxy are still unclear. For example, field observations revealed close relationships between ^{210}Po and particulate organic matter ([Murray et al., 2005](#); [Stewart et al., 2007b](#)) or Chl-*a* ([Nozaki et al., 1997](#)). Laboratory experiments also reported significant influence of selected organic carrier phases on ^{210}Po and ^{210}Pb sorption (e.g., [Quigley et al., 2002](#); [Chuang et al., 2013, 2015](#); [Yang et al., 2013](#)). Other investigations, on the other hand, found close relationships between ^{210}Po (and ^{210}Pb) and inorganic particles or mineral content ([Nozaki et al., 1998](#); [Yang et al., 2010](#)). Clearly, these different results pointed to a greater need to improve our understanding of the role of particulate

components in the scavenging of ^{210}Po and ^{210}Pb in order to better use the ^{210}Po - ^{210}Pb pair as an oceanic tracer. Yang et al. (2013) speculated that colloidal, i.e., nano-sized, particles might play a crucial role in the scavenging of ^{210}Po and ^{210}Pb . Baskaran and Santschi (1993) first reported colloidal ^{210}Pb and ^7Be abundance in coastal seawater, accounting for 16.8% and 8.3%, respectively, of their bulk dissolved pools. Yang et al. (2003) found that colloidal ^{210}Po ranged from 23% to 42% in estuarine waters. Kim et al. (2012) determined the colloidal residence time using ^{210}Po - ^{210}Pb pair in the Japan Sea. Together, these studies seemed to support their colloidal associations. Nevertheless, very few studies have reported to date on the interactions between these nuclides and colloids or nanoparticles.

Similar to ^{210}Po and ^{210}Pb , ^7Be and ^{10}Be ($T_{1/2} = 1.5 \times 10^6$ yr) derived mainly from atmospheric deposition, have also been widely used to constrain particle transport (Kumar et al., 1995; Feng et al., 1999a, b, c; Baskaran et al., 2007; Cámara-Mor et al., 2011; Huang et al., 2013), atmospheric deposition of trace elements, and vertical mixing of water masses (Kadko et al., 1996, 2011, 2015). However, the specific key particulate components that are responsible for the removal of Be isotopes from seawater remain unclear. Some studies reported that lithogenic particles were the strongest sorbent for Be (Luo and Ku, 2004), while others conclude that biogenic silica was the strongest sorbent (Chase and Anderson et al., 2002). Rigorous sorption experiments by Chuang et al. (2014) recently demonstrated the role of specific diatom associated biopolymers in diatoms as the responsible carrier phase for ^7Be . Regardless of particle types, the role of organic matter and its interactions with particle surfaces cannot be ignored (Li, 2005; Lin et al., 2015). To eliminate the particle composition influence on Be scavenging, different tracer pairs such as ^7Be - ^{210}Pb and ^7Be - ^{234}Th instead of Be alone have been used in some studies (e.g., Baskaran et al., 1997; Feng et al., 1999b; Matisoff et al., 2005; Masqué et al., 2007). Nevertheless, particle composition could have a significant influence on the isotopic fractionation between ^7Be and ^{210}Pb (e.g., Yang et al., 2013), thus complicating the use of these tracer pairs.

Since inorganic particles always co-exist with organic matter in the ocean, the role of natural organic matter in the scavenging and fractionation of particle-reactive radionuclides can be maximized, especially through organic coatings on particles, or specific organic compounds formed on surfaces/inner structure during the formation of cell exoskeletons, such as silica and carbonate (Li, 2005; Chuang et al., 2014). Thus, understanding the interactions between radionuclides and particles in the presence of natural organic matter is likely at the heart of a better understanding of particle adsorption and fractionation of these nuclides.

For this purpose, laboratory experiments were carried out to examine the adsorption of ^{210}Po , ^{210}Pb and ^7Be on both inorganic nanoparticles, including biogenic SiO_2 and CaCO_3 , terrestrial Al_2O_3 , TiO_2 and Fe_2O_3 and model macromolecular organic compounds (MOCs), including humic acids (HA), acid polysaccharides (APS) and proteins (bovine serum albumin, BSA) in natural seawater. Contrasting experimental systems were used to examine the interactions between nuclides (^{210}Po , ^{210}Pb and ^7Be) and inorganic nanoparticles and the role of natural organic matter in regulating the scavenging and fractionation among these nuclides. Furthermore, results from nanoparticle experiments were also compared to those of microparticles reported recently (Yang et al., 2013).

2. Materials and methods

2.1. Nanoparticles and model organic compounds used

Five inorganic nanoparticles, including SiO_2 , CaCO_3 , Al_2O_3 , TiO_2 , and Fe_2O_3 and three macromolecular organic compounds (MOCs) including humic acids (HA), acid polysaccharides (APS, carrageenan type V), and bovine serum albumin (BSA) were adopted for the sorption experiments. SiO_2 and CaCO_3 were selected since biogenic silica ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$) and carbonate were two important biogenic particulate components in the ocean. Al_2O_3 , TiO_2 and Fe_2O_3 were used to represent lithogenic particles and iron oxide, respectively. HA, APS, and BSA represent humic substances, carbohydrates and proteins, respectively, in natural waters, as were used in previous studies (Guo et al., 2002; Quigley et al., 2002; Yang et al., 2013; Lin et al., 2015).

Inorganic particles were purchased from Nachen Inc. China, with a nominal size of 20 nm. MOCs were purchased from Sigma/Aldrich as shown in Yang et al. (2013). Sizes of MOCs are variable, with humic acids at ~1-4 nm (Balnois et al., 1999), APS at 10 nm to several μm (Santschi et al., 1998), and proteins at ~2 nm - <100 nm (Ju-Nam et al., 2008). Given that 1 nm is approximately equivalent to 1-2 kDa (Guo and Santschi, 2007), one can expect that a 1 kDa ultrafilter will retain most of these colloiddally sized MOCs, even though the polydispersity of HA (as well as others) might allow for some fraction of HA to be smaller than 1 kDa (Ishiwatari, 1971; Guo and Santschi, 2007), and thus, pass a 1 kDa ultrafilter.

2.2 Sorption experiments

Natural seawater was used in all experiments as described in Yang et al. (2013). Briefly, seawater from the Gulf of Mexico with a salinity of 35.0 was filtered and ultrafiltered sequentially through a 0.4 μm cartridge (GE-Osmonics) and a 1 kDa ultrafiltration membrane (Millipore-Amicon), to remove suspended particles and colloidal matter (Guo et al., 1995). ^{210}Po and ^{210}Pb (in equilibrium) in 1 N HNO_3 -2 N HCl were purchased from Eckert & Ziegler Isotopes Products. ^7Be tracer was produced at the Paul Scherrer Institute, Switzerland and preserved in 0.5 N HCl (Schumann et al., 2010). All experiments were conducted in a constant temperature laboratory to avoid the influence of changing temperature.

For sorption experiments, 49 ml of the <1 kDa ultrafiltrate of seawater in a stirred-cell unit was added with 1 ml of non-complexing Tris-HCl buffer solution to maintain a constant pH of 8.1 and to prevent formation of pseudo-colloids during the addition of spikes (Roberts et al., 2008, 2009). For the single-sorbent experiments, 2 mg of inorganic particles was added into the solution while stirring, corresponding to a particle concentration of about 40 mg/l, falling in the concentration range of particles in coastal seawater (Chuang et al., 2013; Yang et al., 2013), but somewhat higher than that in open seawater (Guo et al., 1997). Successively, a total of 0.2 ml of ^{210}Pb , ^{210}Pb and ^7Be spikes, with the activities of 100 Bq, 100 Bq and 150 Bq respectively, were added drop by drop while stirring. The pH value was checked after adding spikes and found to

be 8.1, supporting that colloid formation and particle dissolution are unlikely because changes in pH were negligible. For the single MOC experiments, procedures were the same as described above. The final concentration of HA, APS or BSA was at 1 mg/l, which was within the concentration range of natural organic matter in marine environments (Guo et al., 1995).

In the present study, an equilibrium time of 2 h was consistently used in all experiments. After 2 h, the particulate or colloidal phases were separated through ultrafiltration using a 1 kDa membrane (Amicon YM1). The >1 kDa retentate (final volume of ~4 ml) and aliquot of the <1 kDa ultrafiltrate or permeate solutions (10 ml) were transferred into a counting vial for γ -counting.

Equilibrium times from hours to days have been used for laboratory adsorption experiments of other particle-reactive nuclides. Overall, it was a tradeoff between sorption lost and equilibrium. We used short equilibrium time because the same equilibrium time (2 h) has been used for the sorption experiments of Th(IV) and Pa(IV,V) (e.g., Guo et al., 2002; Quigley et al., 2002; Lin et al., 2014, 2015) as well as ^{210}Po , ^{210}Pb and ^7Be (Yang et al., 2013). In addition, short equilibrium time could reduce possible changes in redox and pH conditions resulting from bacterial growth (Nyffeler et al., 1984). Furthermore, the use of a consistent equilibrium time should allow comparisons between different studies.

For the binary-sorbent experiments, macromolecular organic matter was added after the inorganic nanoparticles. The experimental solution was then stirred for 30 min to allow inorganic particles to interact with MOCs. After that, spikes were added. Other experimental procedures were the same as the single-sorbent experiments. While this procedure assures that the majority of the MOCs are retained by the 1 kDa membrane, it does not assure that the original size distribution is maintained during the experiments. On the contrary, one would expect that these experimental procedures do not prevent possible aggregation of nanoparticles or coating and occlusion of MOCs (if present) because nanoparticles have very high surface energy, which may cause them to aggregate.

2.3. Measurements of ^{210}Pb , ^{210}Pb and ^7Be activities

Retentate (containing nanoparticles) and permeate (< 1 kDa dissolved) samples were measured for ^{210}Pb and ^7Be by non-destructive gamma counting using a Canberra ultra-high purity germanium well detector. The counting efficiencies at different sample geometries (1-10 ml) at 46.5 keV for ^{210}Pb and 477.6 keV for ^7Be were calibrated using tracers with certified activities.

The activities of ^{210}Po in samples were measured using α -spectrometry (Kim and Church, 2001). For the permeate samples, 5 ml of permeate was acidified to pH <1.5 with HCl, then 4 Bq ^{209}Po was added, followed by ascorbic acid powder, 1 ml of hydroxylamine hydrochloride (20%) and 1 ml of sodium citrate (25%). Finally, the mixed solution was adjusted to a pH of 1.5. Polonium isotopes, including ^{209}Po and ^{210}Po , were plated on a silver disc at 90°C for 4 h under stirring. Procedures for the retentate samples were the same, except that the retentate was digested with mixed acids in a manner similar to the digestion used for particulate samples (Church et al., 2012; Baskaran et al., 2013). Then, the solution was dried to near dryness.

Activities of ^{209}Po and ^{210}Po on silver disc were counted by a Canberra alpha analyst system (Yang et al., 2013). The procedural efficiencies of Po isotopes were determined by the measured ^{209}Po and initially added ^{209}Po activities. The strategies proposed by Rigaud et al. (2013), including reducing uncertainties and improving calculations, were used to calculate the activities of ^{210}Po .

2.4. Partition coefficients

Partition of ^{210}Po , ^{210}Pb and ^7Be can be expressed by the partition coefficient of K_c (Honeyman and Santschi, 1989; Guo et al., 1997), which can be calculated by the following equation,

$$K_c = \frac{A_c}{A_p \times C_c} \quad (1)$$

where A_c and A_p represent the activities (in Bq/l) of each nuclide in nanoparticles (>1 kDa) and the <1 kDa permeate solution, respectively. C_c denotes the concentration of nanoparticles or colloidal organic matter in seawater (in g/ml or kg/l). The K_c values (ml/g or l/kg) are presented in a logarithmic form. For the binary system, one can assume that the observed K_c would contain terms for MOCs and nanoparticles, i.e.,

$$K_c(\text{obs}) = K_c(\text{nano}) \times (1 - C_{\text{MOC}}/C_c) + K_c(\text{MOCs}) \times C_{\text{MOC}}/C_c \quad (2)$$

where $C_{\text{MOC}}/C_c = 0.0244$.

3. Results

For all experiments, recoveries were 75-89% for ^{210}Po , 80-96% for ^{210}Pb , and 87-108% for ^7Be , with a mean of $82 \pm 4\%$, $88 \pm 5\%$ and $92 \pm 5\%$, respectively (Fig. 1). On average, 8-18% of these nuclides could adsorb on equipment walls and ultrafiltration filters. For a specific nuclide, the presence of MOCs seemed to increase the adsorption of nuclides on filter and equipment walls, probably through a “MOC-bridge” effect. For the three nuclides, loss of ^{210}Po was the highest compared to ^{210}Pb and ^7Be . Thus, the interactions of MOCs with nuclides could be MOC-specific or nuclide-specific. Since the fraction adsorbed on filter/walls was irreversibly lost and did not participate in the reactions between nuclides and particles (Roberts et al., 2009) they were not included in calculating the partition coefficients.

In the single-sorbent experiments, the K_c values of ^{210}Po spanned 1 to 2 orders of magnitude, with $\log K_c$ values ranging from 3.63 to 5.35 (Fig. 2). MOCs were the strongest sorbents, with an average $\log K_c$ of 5.27 ± 0.05 . CaCO_3 , SiO_2 and Al_2O_3 had the lowest, and comparable, $\log K_c$ values for ^{210}Po , averaging 3.68 ± 0.05 (Fig. 2). The addition of MOCs resulted in an increase in the $\log K_c$ values of ^{210}Po on almost all inorganic nanoparticles. For example, the average $\log K_c$ value increased to 4.28 ± 0.09 , 4.27 ± 0.10 , and 4.58 ± 0.10 in the presence of HA, APS and BSA respectively, which were higher than 3.92 ± 0.10 on pure inorganic nanoparticles.

The $\log K_c$ values of ^{210}Pb varied from 3.68 to 6.53 in the single-sorbent experiments, following the order of $\text{Fe}_2\text{O}_3 > \text{TiO}_2 \geq \text{HA} > \text{BSA} > \text{Al}_2\text{O}_3 = \text{APS} > \text{CaCO}_3 \geq \text{SiO}_2$ (Fig. 2). Fe_2O_3

and TiO₂ were the strongest sorbents for ²¹⁰Pb (Fig. 2). In the presence of MOCs, TiO₂ had the highest logK_c value for ²¹⁰Pb, followed by Fe₂O₃. In contrast, the logK_c values of ²¹⁰Pb on CaCO₃, SiO₂ and Al₂O₃ remained the lowest, although they also increased after the addition of MOCs.

For ⁷Be, its logK_c values ranged between 3.03 and 5.98, with an average of 4.66±0.02 for the pure inorganic nanoparticles (Fig. 2). The highest and lowest logK_c values of ⁷Be sorbing on pure nanoparticles were observed on Fe₂O₃ and CaCO₃, respectively. Among the three MOCs, HA had the highest logK_c value for ⁷Be, followed by BSA and then APS, which was similar to the case of ²¹⁰Pb. MOCs promoted the sorption of ⁷Be on all inorganic particles except for Fe₂O₃, yielding the highest values for BSA on SiO₂ and CaCO₃.

4. Discussion

4.1. Influence of particle size on sorption of ²¹⁰Po, ²¹⁰Pb and ⁷Be

Frequently, geochemists use specific surface area normalizations. It is thus interesting to compare the results from this work using nanoparticles with those of Yang et al. (2013) where 2.5-4 μm microparticles were used. The 20 nm SiO₂ nanoparticles should nominally have a specific surface area of about 120 m²/g, based on geometrical considerations (area/volume ratio should be 3/r) and particle density (2.5 g/cm³), which is close to that provided by the manufacturer, i.e., 103 m²/g. For 2.5-4 μm SiO₂ microparticles, that specific surface area should be 0.6 m²/g, i.e., a factor of up to 200 lower for 4 μm vs. 20 nm particles. Since the specific surface site concentration is proportional to the specific surface area, the surface site concentration ratio should also be a factor of up to 200 higher for nanoparticles, and the K_c values, which should be directly proportional to the specific surface site concentration, should also be a factor of up to 200 higher than the K_d values reported by Yang et al. (2013) for microparticles. Usually, K_d and K_c values are used to describe micro-particles and nanoparticles (or colloids), respectively, in order to differentiate particle size. However, the K_c and K_d values

are often only a factor of 3-4 apart. It is likely then that a higher particle aggregation state of the nanoparticles (than the microparticles) might decrease the difference between K_c and K_d values.

4.2. Effect of MOCs on the partitioning of ^{210}Po on nanoparticles

As shown in Fig. 2, MOCs enhanced the adsorption of ^{210}Po on all nanoparticles to a varying degree. One-way ANOVA analysis was used to test the significance of differences in the $\log K_c$ values of ^{210}Po on the three particle types (i.e. SiO_2 , CaCO_3 and Al_2O_3) between the single- and binary-sorbent experiments. Clearly, the mean square difference between groups accounts for the majority of the total mean square at the 0.05 significance level (Table 1), indicating that the $\log K_c$ values in the presence of MOCs were significantly different from those in pure inorganic nanoparticle experiments. Hence, adsorption of ^{210}Po in natural seawater was indeed enhanced by organic compounds. In the presence of MOCs, the $\log K_c$ values of ^{210}Po (3.86-5.26) fell in the range of published field values ranging from 3.84 to 7.06, as compiled in Yang et al. (2013). The $\log K_c$ value on SiO_2 in the presence of MOCs was slightly lower than the value obtained from the diatom particles (Chuang et al., 2014). Since biominerals (e.g., calcite and biogenic silica) in natural seawater are usually biogenic and contain protein and acid polysaccharide matrixes (Chuang et al., 2014), and/or coated by MOCs, even after the death of the organisms, these results provide direct evidence of organic matter influence on ^{210}Po distribution observed in sinking particles (Stewart et al., 2007b) and suspended particles (Yang et al., 2011b).

Notably, the $\log K_c$ value of ^{210}Po in the presence of specific MOC was larger than that on the pure inorganic particle and smaller than that on the particular MOC (Fig. 2). This pattern followed by all MOCs suggests that both coating of MOCs and enhanced adsorption of ^{210}Po on MOCs co-occurred in the presence of MOCs. Thus, MOCs-induced enhancement of ^{210}Po sorption can be ascribed to the binding mechanisms between inorganic and organic particles. Usually, nanoparticles possess considerable surface energies (e.g., Honeyman and Santschi, 1989; Feldheim et al., 2001), giving rise to a metastable state. To reduce the surface energy, inorganic

particles tend to adsorb ions from solution (Ju-Namet et al., 2008) and/or aggregate. Hence, the interaction between ^{210}Po and inorganic nanoparticles was likely through direct surface site binding aided by electrostatic effects. In contrast, the MOCs often bind metals via chemical bonds. Organic compounds possess not only abundant ligands, but also redox-active groups. For example, HA contain carboxyl ($-\text{COOH}$) and phenolic hydroxyl ($-\text{OH}$) functional groups (Hizal et al., 2006), and APS can contain carboxyl ($-\text{COOH}$) and sulfate ester ($-\text{O}-\text{SO}_3^-$) groups (Alvarado et al., 2006; Ananthi et al., 2010). BSA also contains disulfide bonds ($-\text{S}-\text{S}-$), sulfhydryl ($-\text{SH}$), and amino groups (Yan et al., 2010). These negatively charged MOCs or ligand groups could favor binding to ^{210}Po , directly or after reduction from the prevailing +IV state (Hussain et al., 1995), leading then to enhanced ^{210}Po uptake. Notably, the binary-sorbent experimental results of BSA indicated the strongest ^{210}Po sorption, except for TiO_2 (Fig. 2). The average $\log K_c$ value of ^{210}Po , in the presence of BSA, was 4.45 ± 0.25 , which was slightly higher than 3.97 ± 0.13 in the HA-containing experiments and 4.03 ± 0.25 in the APS-containing experiments (Fig. 2). Functional groups of BSA include disulfide bonds and sulfhydryl groups in BSA (Yan et al., 2010), which can be oxidized under oxic conditions, and which are less abundant in HA. Thus, BSA binding of ^{210}Po could be enhanced after reduction. Consequently, the strongest enhancement of ^{210}Po on nanoparticle sorption was observed in the presence of BSA (Fig. 2). Indeed, previous studies indicated a possible relation between proteins and ^{210}Po . For example, Po was enriched in proteins of phytoplankton and zooplankton cells (Fisher et al., 1983; Steward et al., 2003a, b). Protein-bound Po in some bacterial cells was also reported (Cherrier et al., 1995). Polonium was also assumed to act as an analog of sulfur (Harada et al., 1989), which was also supported by a similarity of volatile S and Po (Kim et al., 2000). Stewart et al. (2007b) reported a positive correlation between sulfur-containing methionine (amino acids) and the particulate ^{210}Po content in seawater. Although the molecular mechanisms are still unclear, our results clearly showed an enhanced adsorption of ^{210}Po in protein-particle mixed

systems, providing direct evidence for the role of MOCs, especially protein, in controlling the sorption of ^{210}Po on particle surfaces in the ocean.

Although the increase in the $\log K_c$ values of ^{210}Po was either MOC- or nanoparticle-specific in the presence of MOCs (Fig. 2), a significant linear correlation ($p < 0.01$) for the $\log K_c$ values of ^{210}Po between pure inorganic nanoparticle systems and binary-sorbent systems was observed. Statistically, the K_c value after the addition of MOCs was around three times higher than that for inorganic nanoparticles. This relationship along with other recent findings (Chuang et al., 2013, 2014) may allow one to roughly estimate the partitioning of ^{210}Po in seawater, although the role of biota needs also to be considered.

4.3. Effect of MOCs on the partitioning of ^{210}Pb

In the presence of MOCs, the adsorption of ^{210}Pb on inorganic nanoparticles was evidently enhanced, except for Fe_2O_3 (Fig. 2). For example, the average $\log K_c$ value of ^{210}Pb on SiO_2 was 3.68 without MOCs, but it increased to 4.75, 5.26 and 4.75 in the presence of HA, APS and BSA, respectively (Fig. 2). CaCO_3 , Al_2O_3 and TiO_2 nanoparticles also showed a similar increase in ^{210}Pb partition coefficients, with a large range of nearly two orders of magnitude. The increase introduced by APS and BSA is statistically significant (Table 1). The $\log K_c$ values of ^{210}Pb on SiO_2 with MOCs were similar to the value obtained from diatom particles (5.27 ± 0.08), including both biogenic silica and embedded MOCs (Chuang et al., 2014). Also, the average $\log K_c$ values of ^{210}Pb in the presence of MOCs (5.33) fell in the range of reported ^{210}Pb partition coefficients compiled in Yang et al. (2013).

Different from ^{210}Po , the $\log K_c$ values of ^{210}Pb were higher than those on pure inorganic particles or on pure MOCs in most cases, except for Fe_2O_3 -containing experiments (Fig. 2). Ternary surface complexes (Fein, 2002) between radioactive metal ions, MOCs, and particle surfaces can explain the, at times, contradictory observations. Such ternary complexes can shift the sorption maximum of metal ions to lower pH values, and have the tendency to solubilize the metal ions at higher pH due to the increasingly negative charge of the metal ligands. Because we

329 did not vary the pH, no quantitative evaluation of each of the shifts in radionuclide sorption is
330 possible. While the existence of ternary surface complexes is well established, most quantitative
331 work has been carried out only with low and medium molecular weight ligands, including humic
332 and fulvic acids. For Pb^{2+} and many other metal ions, ternary surface complexes have been
333 evaluated in terms of the surface complexation model (reviewed by [Fein, 2002](#)). In addition to
334 electrostatic effects, hydrophobic effects can increase the tendency of MOC sequestration by
335 particles.

336 ^{210}Pb showed the highest $\log K_c$ values in the presence of APS on all nanoparticles except for
337 Fe_2O_3 ([Fig. 2](#)). [Quigley et al. \(2002\)](#) found that marine colloidal organic matter enriched in
338 polysaccharides increased the complexation of ^{210}Pb in seawater. Though few studies on the
339 interactions between APS and inorganic particles have been reported, available studies on HA
340 may provide insights into these synergistic interactions. Humic substances can bind Pb^{2+} via
341 COO^- chelation ([Liang et al., 2011](#)), and then the HA-bound Pb could coat the inorganic particles,
342 such as Al_2O_3 , kaolinite ([Hizal et al., 2006](#); [Ra et al., 2008](#)) and SiO_2 ([Liang et al., 2011](#)). Since
343 particle surfaces might have larger adsorption capacity for HA than for Pb^{2+} , increase of the
344 particulate fraction should occur, as proposed by [Lai et al. \(2001\)](#). [Hizal et al. \(2006\)](#) also
345 pointed out that the coating of HA likely resulted in a change in the sorption of Pb(II) on
346 kaolinite surfaces from simply inorganic ion-exchange to covalent (chelation) binding. Hence,
347 changes in ^{210}Pb binding mechanisms on inorganic particles were responsible for the
348 enhancement of ^{210}Pb sorption in the presence of MOCs. Based on global *in situ* datasets, [Li](#)
349 ([2005](#)) pointed out that organic matter in regulating the partition coefficients of some particle-
350 reactive nuclides (i.e. ^{230}Th , ^{231}Pa and ^{10}Be) could not be ignored. Our new results provide some
351 direct evidence for the role of organic matter and their regulating mechanisms.

352 The contrasting effects of MOCs indicate that the sorption of ^{210}Pb in seawater depends not
353 only on the composition of particles and MOCs, but also on the synergistic interactions between

MOCs, nuclides and inorganic particles. Statistically, the $\log K_c$ values of ^{210}Pb in the presence of MOCs followed the following equation:

$$y = 2.57 + 0.61 x \quad (r^2 = 0.58, p = 0.001) \quad (3)$$

where y and x represent the $\log K_c$ values in the presence and absence of MOCs, respectively.

This relationship showed an enhancement in the sorption of ^{210}Pb in the presence of MOCs until a $\log K_c$ value of 7.8 was reached, which could be used in models for simulating the adsorption of ^{210}Pb onto particle surfaces in marine environments.

4.4. Effect of MOCs on the partitioning of ^7Be

Among the selected inorganic nanoparticles, CaCO_3 was the weakest sorbent for ^7Be . In comparison, SiO_2 had a considerably stronger affinity for ^7Be . These results are consistent with those of field observations (e.g., [Honeyman and Santschi, 1989](#); [Chase and Anderson et al., 2002, 2004](#)) and laboratory studies using marine diatoms (e.g., [Chuang et al., 2014](#)) or microparticles (e.g., [Yang et al., 2013](#)). The $\log K_c$ values of ^7Be in the presence of MOCs (4.01-6.25) were also comparable to field values (3.00 to 6.63) as compiled in [Yang et al. \(2013\)](#). Interestingly, the addition of APS and BSA appeared to eliminate the difference in the $\log K_c$ values of ^7Be between CaCO_3 and SiO_2 nanoparticles ([Fig. 2](#)). The $\log K_c$ values of ^7Be on SiO_2 (6.2) and CaCO_3 (6.0) ([Fig. 2](#)) in the presence of BSA are exceptionally high, and are another indication that proteins appear to be primary carrier molecules for ^7Be , as previously suggested by [Chuang et al. \(2014\)](#). These elevated values also appear to be similar to the extrapolated $\log K$ values for the two biogenic particulate components based on the datasets from the US JGOFS EqPac and AESOPS ([Chase and Anderson et al., 2002](#)). Even though effects of MOCs on particle surfaces and thus on the sorption of ^7Be were rarely evaluated, the $\log K_c$ values derived from our laboratory experiments resemble to a great extent those observed for ^7Be in oceanic environments.

Overall, similar to ^{210}Pb , MOCs enhanced the sorption of ^7Be on inorganic nanoparticles except for Fe_2O_3 . One-way ANOVA analysis indicated that increase in the $\log K_c$ values of ^7Be

between adsorption experiments with and without MOCs (APS and BSA at 0.1 level) was significant (Table 1). But the difference induced by HA was not statistically significant. In depth analysis illustrated that the insignificant difference probably resulted from the large variability in the $\log K_c$ values of ^7Be in pure inorganic systems, which outweighed the difference between single- and binary-sorbent experiments (Fig. 2).

4.5. Fractionation among ^{210}Po , ^{210}Pb and ^7Be

^{210}Po and ^{210}Pb have been used as a pair to trace particle cycling with little consideration of the fractionation between the two nuclides due to a lack of knowledge on their interactions with particle surfaces and functionalities. Based on our results, both APS and BSA tended to adsorb ^{210}Po preferentially, whereas other particles preferred ^{210}Pb over ^{210}Po , except for SiO_2 , which had similar affinities for ^{210}Po and ^{210}Pb (Table. 1). Thus, it seems that inorganic nanoparticles tend to adsorb a greater fraction of ^{210}Pb than ^{210}Po . In the presence of MOCs, the difference in the K_c values between ^{210}Po and ^{210}Pb spanned more than an order of magnitude. Apparently, the fractionation between ^{210}Po and ^{210}Pb during their adsorption onto particles cannot be neglected. These results provided valuable insights into the discriminative geochemical behavior between ^{210}Pb and ^{210}Po in marine environments though both ^{210}Pb and ^{210}Po are particle-reactive nuclides (e.g., Masqué et al., 2002; Yang et al., 2011b, c). In previous field studies, a positive correlation between the removal rate of ^{210}Po and chlorophyll-*a* (Nozaki et al., 1997, 1998) and negative correlation between particulate ^{210}Po activity and fluorescence (Masqué et al., 2002) were observed, indicating that either phytoplankton or biogenic particulate organic matter are probably responsible for the scavenging of ^{210}Po . In addition, Kim (2001) and Kim and Church (2001) reported the influence of nitrogen-fixation on the partition of ^{210}Po between particulate and dissolved phases. Higher remineralization of ^{210}Po compared to ^{210}Pb in the twilight zone (Bacon et al., 1976; Yang et al., 2009) also suggests more ^{210}Po binding to organic matter than ^{210}Pb in oceanic environments. Stewart et al. (2007b) stated that fresh phytoplankton-derived, nitrogen-rich organic matter and sulfur-containing amino acids may affect the distribution of ^{210}Po based

on statistical analyses. Together with laboratory evidence reported here, these observations all attest to the crucial role of MOCs in the scavenging of ^{210}Po .

Besides chemical composition effects, previous studies also highlighted the importance of MOCs in fractionating ^{210}Po and ^{210}Pb via biological activities. ^{210}Po was found to closely associate with proteins in cells (Fisher et al., 1983; Cherrier et al., 1995; Stewart et al., 2003b) though it may not be actively assimilated by biota (Cherrier et al., 1995). Similarly, biogenic volatile Po was also reported (Kim et al., 2000). However, ^{210}Pb appeared to associate with cell structure components, i.e. cell walls and plasmalemmae (Fisher et al., 1983), which are very different chemically from proteins. According to Fowler (2011), nearly all marine biota contained more ^{210}Po than ^{210}Pb . Bacteria-induced large deficits of ^{210}Po relative to ^{210}Pb were also observed in oligotrophic seas (Kim, 2001; Chung et al., 2005). Finally, Quigley et al. (2002) reported that polysaccharide-enriched colloids from the Gulf of Mexico showed enhanced K_c values for ^{210}Pb , but decreased values for ^{210}Po , as compared to ambient colloids. These results provide support for the different affinities of MOCs for ^{210}Po and ^{210}Pb and successive fractionation during biological activity.

As for the ^7Be - ^{210}Pb pair, the difference in their K_c values spanned nearly two orders of magnitude. Both SiO_2 and Al_2O_3 had consistently higher $\log K_c$ values of ^7Be compared to ^{210}Pb , while Fe_2O_3 and TiO_2 had higher $\log K_c$ values of ^{210}Pb in both single- and binary-sorbent experiments. Compared to ^{210}Pb , CaCO_3 adsorbed ^7Be preferentially in the presence of APS and BSA, while the opposite was true in the presence of HA (Fig. 2). These results reveal that preferential scavenging of ^7Be over ^{210}Pb is more complicated in natural seawater. For the ^7Be - ^{210}Po pair, even larger differences in their K_c values between ^7Be and ^{210}Po were observed, spanning nearly three orders of magnitude.

Previous studies have indicated that activity ratios of particle-reactive radionuclides, such as $^{231}\text{Pa}/^{230}\text{Th}$, $^{10}\text{Be}/^{230}\text{Th}$ and $^{210}\text{Po}/^{210}\text{Pb}$, could be affected by particle composition in addition to particulate fluxes (e.g., Luo and Ku, 1999; Chase and Anderson et al., 2002; Yang et al., 2013)

due to differences in particle surface affinities between radionuclides (Guo et al., 2002; Geibert et al., 2004; Kretschmer et al., 2011; Chuang et al., 2013). Differences in particle composition might complicate the relationship between particle fluxes and these proxies through fractionation effects (Luo and Ku, 1999; Narita et al., 2003). However, if the fractionation between nuclides could be well-quantified, these nuclide pairs could be better used as particle flux proxies. Our results suggest that the fractionation could be quantified statistically for both ^{210}Po - ^{210}Pb and ^7Be - ^{210}Pb pairs based on all selected particle types (Fig. 3), though the relationships vary with specific particle types. The $\log K_c$ values of ^{210}Pb significantly correlated with those of ^{210}Po ($p < 0.001$). Similar relationships also occurred between ^7Be and ^{210}Pb ($p < 0.02$), but this was not observed for the ^{210}Po - ^7Be pair. Notably, the correlation for the ^7Be - ^{210}Pb pair is poorer than that for the ^{210}Po - ^{210}Pb pair. Such difference may be related to their electron configuration and chemical properties. For example, Be has a much smaller atomic number than Pb and Po. In contrast, Po and Pb are much closer in the periodic table. Thus far, studies on the adsorption of Be onto different particle types remain scarce. Further studies are needed to provide new insights into the difference between the ^{210}Po - ^{210}Pb pair and ^{210}Pb - ^7Be pair.

4.6. Implications for using ^{210}Po - ^{210}Pb and ^7Be - ^{210}Pb pairs as geochemical proxies

Our results indicate that macromolecular organic compounds are important in regulating the adsorption of ^{210}Po , ^{210}Pb and ^7Be onto inorganic particles. However, it seems that the fractionation between ^{210}Po and ^{210}Pb or between ^{210}Pb and ^7Be can be statistically quantified (Fig. 3). Chemically, these observations lend support to the better use of ^{210}Po - ^{210}Pb and ^7Be - ^{210}Pb pairs to trace organic compound cycling in oceanic environments as long as their fractionation can be quantified. Since most organic compounds are derived from biota, including phytoplankton, zooplankton and bacteria, the adsorption of ^{210}Po , ^{210}Pb and ^7Be should be regulated, to a different extent, by biological activities in the ocean. This is especially true for ^{210}Po , as bacteria-induced deficiency of ^{210}Po (with respect to equilibrium with ^{210}Pb) in the water column has been observed in oligotrophic seas (e.g., Kim, 2001; Chung et al., 2005)

although its mechanisms are still unclear. A few studies also indicated the influence of plankton on the removal of ^{210}Po either via active or passive uptake (e.g., [Cherry et al., 1975](#); [Stewart et al., 2003a, 2003b](#)). Thus, further studies are needed to examine the interactions between radionuclides (e.g., ^{210}Po , ^{210}Pb and ^7Be) and biota (e.g., plankton and bacteria) and organic substances produced from biota (e.g., [Chuang et al., 2014](#)).

5. Conclusions

Controlled laboratory experiments provided valuable information for better understanding the adsorption of ^{210}Po , ^{210}Pb , and ^7Be on nanoparticles in the presence of MOCs. Statistically, the addition of MOCs resulted in an increase in the $\log K_c$ values of ^{210}Po , ^{210}Pb and ^7Be over those of inorganic nanoparticles alone, consistent with previous findings of the importance of major organic carrier phases for these radionuclides. For example, the results by [Chuang et al. \(2014\)](#) on ^7Be sorption to diatoms indicated that proteins are important in the binding of ^7Be , and the results by [Quigley et al. \(2002\)](#) indicated that APS were the major carrier phases for ^{210}Pb . The increase in the $\log K_c$ values appeared, statistically, to be quantifiable for ^{210}Po or ^{210}Pb based on the relationship between their $\log K_c$ values in the presence or absence of MOCs. There was a significant correlation between the $\log K_c$ values of ^{210}Po and those of ^{210}Pb in the presence of MOCs, even though the $\log K_c$ values of ^{210}Po were not greatly elevated over those of inorganic nanoparticles. Correlations also occurred between ^{210}Pb and ^7Be . MOCs, especially proteins, tended to preferentially adsorb ^7Be and ^{210}Po , while inorganic nanoparticles (especially Fe_2O_3) exhibited stronger affinities for ^{210}Pb than when MOCs were present. Thus, sorption fractionation between radionuclides during their interactions with different organic ligands and inorganic surfaces could be controlled by the partitioning of the organic phases. These results provide insights and better understanding of the mechanisms controlling the adsorption and fractionation of ^{210}Po , ^{210}Pb and ^7Be isotopes onto nanoparticles. Further studies are needed to examine the adsorption of these nuclides onto natural mixed particle regimes including bacterial systems.

Acknowledgements

We gratefully acknowledge the assistance from Zhengzhen Zhou, Huijun He and Hailong Huang in seawater sampling and processing. We also thank the Editor, Jean Lynch-Stieglitz, and two anonymous reviewers who provided constructive comments that improved the manuscript. This work was supported in part by grants from the NSF (OCE#0850957 to L.G. and OCE#08511191 to P.H.S.), NSFC (41476061 to W.Y.), and the University of Wisconsin-Milwaukee.

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Table 1

One-way ANOVA analysis of the $\log K_c$ values for each nuclide (^{210}Po , ^{210}Pb and ^7Be) on SiO_2 , CaCO_3 and Al_2O_3 for difference discrimination between the single- (inorganic nanoparticles only) and binary-component experiments (inorganic nanoparticle plus one MOC).

Nuclides	Single/binary system pairs	Mean square		<i>F</i> value	Significance level <i>p</i>
		Between groups	Within groups		
^{210}Po	HA system	0.132	0.009	14.70	0.019
	APS system	0.187	0.012	15.20	0.018
	BSA system	0.889	0.032	27.72	0.006
^{210}Pb	HA system	0.443	0.122	3.63	0.130
	APS system	2.077	0.100	20.86	0.010
	BSA system	1.162	0.136	8.56	0.043
^7Be	HA system	0.123	0.642	0.19	0.684
	APS system	3.053	0.588	5.19	0.085
	BSA system	4.717	0.576	8.19	0.046

Figure captions

- Fig. 1.** Statistical analysis of ^{210}Po , ^{210}Pb and ^7Be recoveries in various group experiments. In the diagram, the horizontal line within the box is the median of the sample. Notations for the x -axis: Po, Pb and Be represent the single-sorbent (i.e. one type of nanoparticle) experiments; Po-, Pb- and Be-suffix denote the binary-sorbent experiments including inorganic nanoparticle and the “suffix” organic compound, including humic acids (HA), acid polysaccharides (APS) and proteins (bovine serum albumin, BSA); Po-, Pb- and Be-T represent the datasets of all Po, Pb and Be experiments.
- Fig. 2.** Comparisons in the $\log K_c$ values of ^{210}Po , ^{210}Pb and ^7Be onto different nanoparticles in the presence or absence of macromolecular organic compounds (MOCs). Notations for the legends: sorbent represents the single-sorbent experiment; sorbent-suffix represent the binary-sorbent experiments including one type of inorganic nanoparticle and one organic compound.
- Fig. 3.** Relations (a) between the $\log K_c$ values of ^{210}Pb and ^{210}Po , and (b) between the $\log K_c$ values of ^7Be and ^{210}Pb .

Fig. 1.

Fig. 2.

Fig. 3.