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# The influence of particle concentration and composition on the fractionation of $^{210}\text{Po}$ and $^{210}\text{Pb}$ along the North Atlantic GEOTRACES transect GA03

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1 **The influence of particle concentration and composition on the fractionation of  $^{210}\text{Po}$  and**  
2  **$^{210}\text{Pb}$  along the North Atlantic GEOTRACES transect GA03**

3  
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14  
15 **Abstract**

16 The disequilibrium between  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  has been used as a proxy for the particle flux  
17 from the upper ocean. The particle concentration and composition effect on the partitioning  
18 behavior of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  is, however, still unclear. Here, we investigate this association by  
19 comparing dissolved ( $< 0.45 \mu\text{m}$ ) and particulate (small:  $1\text{-}51 \mu\text{m}$ ; large:  $> 51 \mu\text{m}$ )  $^{210}\text{Po}$  and  
20  $^{210}\text{Pb}$  activity with size-fractionated major particle concentration and composition data from  
21 the US GEOTRACES GA03 zonal transect cruises. We observed inverse relationships  
22 between partition coefficients ( $K_d$ ) for the radionuclides and the concentration of suspended  
23 particulate matter (SPM) in the water column, known as the “particle concentration effect.”  
24 We examined the relationships between  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ , and particle composition in the top  
25 500m by using Pearson pairwise correlations for individual phases and principal components  
26 analysis (PCA) for variations among multiple phases. In addition to these analyses, an end-  
27 member mixing model was developed to estimate  $K_d$  for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in the small  
28 particulate size fraction from the compositional phases. The model predicted the range of  
29 observed  $K_d(\text{Pb})$  well, but was unable to predict the observed  $K_d(\text{Po})$  as consistently, possibly  
30 because of the bio-reactive nature of  $^{210}\text{Po}$ . Despite this, we found a strong relationship  
31 between  $^{210}\text{Po}$  and both  $\text{CaCO}_3$  and POM, as well as between  $^{210}\text{Pb}$  and both opal and

32 lithogenic phases. All of our analyses demonstrated that the fractionation of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$   
33 differed between the coast and open ocean along the GA03 transect.

34  
35 **Keywords:**  $^{210}\text{Po}$ ;  $^{210}\text{Pb}$ ; GEOTRACES; North Atlantic Ocean; particle concentration; particle  
36 composition

## 37 38 **1. Introduction**

39  $^{210}\text{Po}$  ( $T_{1/2} = 138.4$  d) and  $^{210}\text{Pb}$  ( $T_{1/2} = 22.3$  y) are particle-reactive radionuclides in the  
40  $^{238}\text{U}$  decay series, produced through the decay of  $^{222}\text{Rn}$  ( $T_{1/2} = 3.8$  d). The disequilibrium  
41 between  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  has been used in many studies to determine particle export from the  
42 upper ocean (e.g. Buesseler et al., 2008; Friedrich and Rutgers van der Loeff, 2002; Murray  
43 et al., 2005; Shimmield et al., 1995; Stewart et al., 2007a; Verdeny et al., 2008), in a similar  
44 application to the more commonly used  $^{234}\text{Th}/^{238}\text{U}$  system (e.g. Buesseler et al., 1992;  
45 Charette et al., 2001; Cochran, 2003). However, the fluxes of particulate organic carbon  
46 (POC) derived from these two techniques are often inconsistent and even contradictory  
47 (Buesseler et al., 2008; Friedrich and Rutgers van der Loeff, 2002; Le Moigne et al., 2013;  
48 Stewart et al., 2007a; Verdeny et al., 2008). For example, the POC fluxes derived from  $^{234}\text{Th}$   
49 were higher than those derived from  $^{210}\text{Po}$  in the Polar Front region, where diatoms were  
50 dominant in the phytoplankton (Friedrich and Rutgers van der Loeff, 2002), while  $^{210}\text{Po}$ -POC  
51 flux was greater than the  $^{234}\text{Th}$ -POC flux in the Sargasso Sea where small phytoplankton  
52 such as *Prochlorococcus* and *Synechococcus* dominated the community (Bibby et al., 2008;  
53 Buesseler et al., 2008). In addition, POC fluxes derived from  $^{210}\text{Po}$  were usually higher than  
54  $^{234}\text{Th}$ -derived estimates in the middle of gyres (e.g., Sargasso Sea, and Hawaii), whereas the  
55 opposite was generally true near the margins (Stewart et al., 2007a; Verdeny et al., 2009).

56 The greatest inherent differences between  $^{210}\text{Po}/^{210}\text{Pb}$  and  $^{234}\text{Th}/^{238}\text{U}$  have been  
57 interpreted as a result of the different half-lives of  $^{210}\text{Po}$  and  $^{234}\text{Th}$ , and the different particle  
58 affinities of the three particle-reactive radionuclides ( $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ ,  $^{234}\text{Th}$ ) (e.g. Murray et al.,  
59 2005; Verdeny et al., 2009). In particular, for the  $^{234}\text{Th}/^{238}\text{U}$  pair, only  $^{234}\text{Th}$  is particle-  
60 reactive while  $^{238}\text{U}$  is highly soluble in seawater (Djogic et al., 1986). In contrast, in the  
61  $^{210}\text{Po}/^{210}\text{Pb}$  technique, both radionuclides are particle-reactive although they have different  
62 chemical behaviors:  $^{210}\text{Po}$  generally has a higher affinity for particles than  $^{210}\text{Pb}$  (Heyraud et

63 al., 1976; Kharkar et al., 1976). Furthermore,  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  have different binding  
64 preferences, with  $^{210}\text{Po}$  associated with proteins and sulfur-containing compounds (Carvalho,  
65 2011; Fisher et al., 1983; Larock et al., 1996; Stewart et al., 2007b; Stewart and Fisher,  
66 2003), while  $^{210}\text{Pb}$  is adsorbed onto particle surfaces and is associated with biogenic silica  
67 and lithogenic particles (Bacon et al., 1976; Friedrich and Rutgers van der Loeff, 2002;  
68 Shannon et al., 1970; Stewart et al., 2005).

69 Several studies have used field collected marine material to simulate the binding behavior  
70 of Pb and Po radionuclides in the natural environment in the laboratory (Chuang et al., 2013;  
71 2014; 2015; Yang et al., 2013). Evidence from these laboratory experiments suggests that  
72 each radionuclide binds to specific biopolymeric functional groups, with enhanced  
73 adsorption of  $^{210}\text{Po}$  by proteins, while polysaccharides enhance the binding of  $^{210}\text{Pb}$  (Quigley  
74 et al., 2002; Yang et al., 2013), suggesting that  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  could be fractionated by  
75 specific organic and/or inorganic compounds during their sorption onto particles.

76 In this paper, we combined the measurements of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in the dissolved and  
77 particulate phases, and the major phase components of suspended particulate matter (SPM)  
78 from the U.S. GEOTRACES North Atlantic transect. With these measurements, we  
79 examined the role of particle concentration and composition in the scavenging and  
80 fractionation of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ . The inter-correlations among the radionuclides and major  
81 particle components have also been investigated, followed by principal component analysis  
82 (PCA) aiming to reduce the number of variables to only those that are most significant in  
83 describing the variability of the data set. We also applied end member mixing analysis  
84 (EMMA (Li, 2005)) to estimate the scavenging intensities of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  for particles  
85 with different compositions.

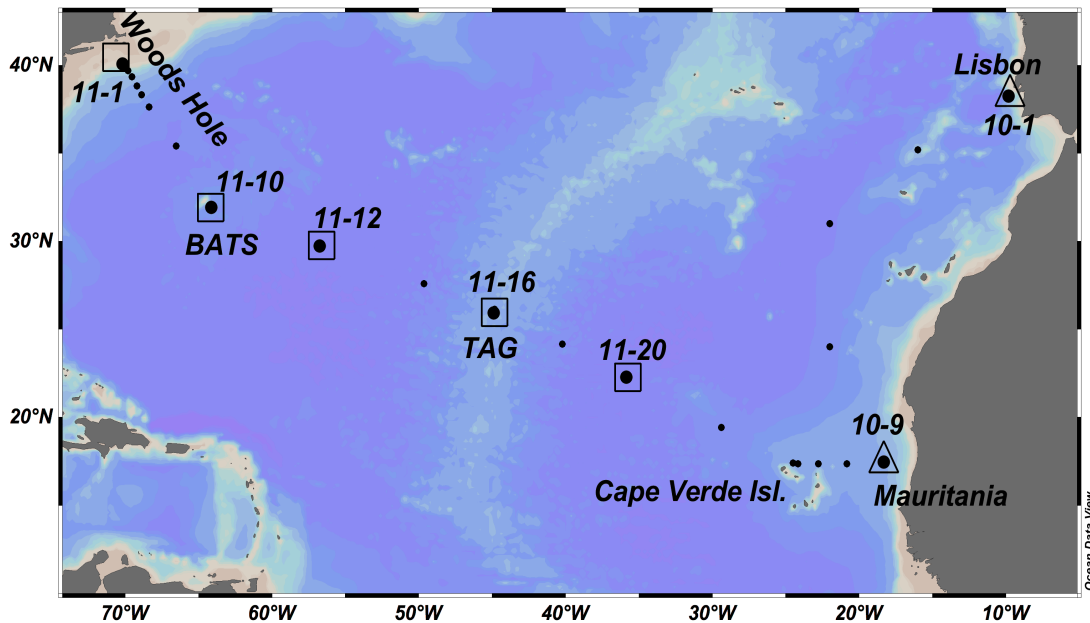
## 86 **2. Methods**

### 87 **2.1. Sampling and analysis**

88 Seawater samples were collected at 7 “super” stations (with extra casts to provide large-  
89 volume samples) from the R/V Knorr during the US GEOTRACES North Atlantic zonal  
90 transect (NAZT), cruises KN199-04 and KN204-1. Cruise KN199-04 departed from Lisbon,  
91 Portugal in October 2010 and ended in Cape Verde in November 2010. Cruise KN204-1  
92 departed from Woods Hole, MA in October 2011 and ended in Cape Verde in December  
93 2011 (Fig. 1). The super stations sampled included the three stations nearest to the coasts:

94 stn.10-1 off Lisbon and within the influence of the Mediterranean outflow, stn.10-9 located  
95 just west of the Mauritanian shelf break, and stn.11-1 off the New England continental shelf.  
96 The other four open ocean stations were mainly located in the North Atlantic subtropical  
97 gyre, including key stations 11-10 at the BATS site, and 11-16 at the TAG hydrothermal site.

98 Seawater samples (~ 20 L) were collected for dissolved  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  analysis  
99 throughout the water column at each station (12-16 depths/station) by using 30 L Niskin  
100 bottles mounted on a standard CTD rosette sampler. Particulate  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  samples were  
101 collected using McLane in situ pumps that had been modified to accommodate two filter  
102 heads (Cutter et al., 2010; Lam et al., 2015). The paired 51  $\mu\text{m}$  polyester prefilters and 1  $\mu\text{m}$   
103 quartz fiber filters (Whatman QMA) were designed to simultaneously collect large size  
104 fraction (LSF, > 51  $\mu\text{m}$ ) and small size fraction (SSF, 1-51  $\mu\text{m}$ ) particles, respectively.  
105 Details on collection and analysis of water samples and particulate matter (both small and  
106 large particulate matter) for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are given in Rigaud et al. (2015). The dissolved  
107 and particulate  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  data is available at <http://www.bco-dmo.org/dataset/3914> and  
108 <http://www.bco-dmo.org/dataset/3917>, respectively.



110 Fig. 1. Map showing stations along the US GEOTRACES GA03 North Atlantic zonal transect, from which  
111 samples were analyzed. Triangles and squares indicate stations from 2010 and 2011, respectively. BATS is the  
112 Bermuda Atlantic Time-series Site and TAG is the TAG hydrothermal site.  
113

## 115 **2.2.Size-fractionated particle composition and concentrations**

116 The concentrations of six major particle compositional components (POC, CaCO<sub>3</sub>, opal,  
117 lithogenic matter, iron, and manganese) in both the LSF and SSF at all seven stations along  
118 the transect were collected as part of the GEOTRACES NAZT project, along with basic  
119 physical and chemical parameters. The details on particle sampling and particle composition  
120 determination are described in Lam et al. (2015) and Ohnemus and Lam (2015). In addition,  
121 the mass of suspended particulate matter (SPM) was estimated as the sum of the chemical  
122 dry weight of the major particulate phases.

## 123 **2.3.Composition correlation and PCA**

124 The full dataset includes the activity of <sup>210</sup>Po and <sup>210</sup>Pb, and the concentration of six  
125 major phase particle components including POC, CaCO<sub>3</sub>, opal, lithogenic matter, Fe, and Mn  
126 (Lam et al., 2015) in both SSF and LSF from the 7 "super" stations. The data matrix is  
127 grouped into 2 major areas: near the continental margins ("coastal" stns.10-1, 10-9 and 11-1),  
128 and in the open ocean (stns.11-10, 11-12, 11-16 and 11-20). Here we focus on the samples  
129 collected from the upper 500 m depth where biological activity and aerosol deposition play  
130 the most important roles in the fractionation of <sup>210</sup>Po and <sup>210</sup>Pb.

131 First, we used a Pearson pairwise correlation matrix to investigate how the size  
132 fractionated particulate <sup>210</sup>Po, <sup>210</sup>Pb related to the 6 major particle components. The  
133 significance of correlation coefficients, and strength of linear relationships between each pair  
134 of variables was determined by 2-tailed *t*-test at  $p < 0.05$ . To evaluate the correlation  
135 coefficient (*r*), we arbitrarily assign a "weak" correlation with correlation coefficient  $|r| = 0.4$ -  
136 0.49, a "moderate" correlation with  $|r| = 0.5$ -0.59, and a "strong" correlation with  $|r| \geq 0.6$  in  
137 the following discussion.

138 We next analyzed interrelationships between particle composition measurements in the  
139 SSF and LSF using a principal component analysis (PCA) for the eight variables. We applied  
140 a transformation to the sample data prior to PCA by performing centering (mean subtraction)  
141 and scaling (dividing the centered columns by their standard deviations). While we examined  
142 the first three principal components of the PCA, the first two principal components alone  
143 captured > 65% of the total variance in each dataset so the results were further visualized  
144 using a biplot, which can provide inter-unit distance and indicate clustering of observations  
145 as well as display variances and correlations of the variables (Kohler and Luniak, 2005).

146 Third, we examined the information contained in the first three principal components by  
147 regression of the principal component (PC) score of each observation against the  
148 concentration of SPM, apparent oxygen utilization (AOU), and depth. If there was a  
149 statistical relationship between PC scores and any of these parameters, we concluded that the  
150 PC was reflective of that parameter regardless of the nature of the relationship. Because the  
151 signs of PC scores are arbitrary and the data has been transformed, whether the relationship is  
152 positive or negative, linear or non-linear has no significance to our interpretation.

#### 153 **2.4. Partition Coefficients Analyses**

154 The partition coefficients ( $K_d$ ) of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are useful for describing their affinity to  
155 marine particles (Bacon et al., 1976; Baskaran and Santschi, 1993; Wei and Murray, 1994).  
156 The interpretation of the  $K_d(\text{Po})$  is complicated because while  $^{210}\text{Pb}$  only adsorbs to the  
157 surface of particles,  $^{210}\text{Po}$  is both sorbed to surfaces and also taken up into the cytoplasm of  
158 phytoplankton cells and bioaccumulated through food chains (see Discussion for further  
159 explanation). Even though the interactions of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  with particles are not the same,  
160 we will use “adsorption” or “sorption” for both  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  to describe their particle  
161 association in this paper.

162  $K_d$  ( $\text{L kg}^{-1}$ ) is defined as:

$$163 \quad K_d = \frac{A_p}{A_d} \times \frac{1}{SPM} \quad (1)$$

164 where  $A_p$  and  $A_d$  represent the nuclide activities in the particulate and the dissolved phases  
165 ( $\text{dpm } 100\text{L}^{-1}$ ), respectively, and SPM is the suspended particulate matter concentration ( $\mu\text{g L}^{-1}$ ).  
166  $K_d$  provides a measure of the partitioning of radionuclides between the dissolved and  
167 particulate phases. The conceptualized scavenging models consider chemical interactions  
168 between radionuclides either (1) in the dissolved and total particulate phases (two-box  
169 model) or (2) in the dissolved – small – large particulate phases (three-box model) or (3) in  
170 the truly dissolved – colloidal – small – large particulate phases (Baskaran et al., 1992; Clegg  
171 and Whitfield, 1991; 1990; Rigaud et al., 2015; Savoye et al., 2006). We calculated the  
172 coefficients of the bulk partitioning between the dissolved and small particulate phases  
173 ( $K_{d\_SSF}$ ), and between the dissolved and total particulate phases ( $K_{d\_TOT}$ ) without  
174 considering colloidal phase due to lack of data. However, in our samples over 90% of the  
175 total particulate radionuclide activity was in the small size fraction, and therefore these  $K_d$   
176 values were very similar. We will only present the  $K_{d\_SSF}$  in this paper.

177 Next, we examined the degree to which  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are fractionated during sorption.  
 178 The fractionation factor ( $F$ ), a ratio of the corresponding bulk  $K_d$ 's (Chase et al., 2002;  
 179 Murray et al., 2005; Nozaki et al., 1998),

$$180 \quad F(\text{Po}/\text{Pb}) = K_d(\text{Po})/K_d(\text{Pb}) \quad (2)$$

181 was used to investigate the preferential sorption of  $^{210}\text{Po}$  relative to  $^{210}\text{Pb}$ .

182 Furthermore, in order to interpret the relationship between particle composition and the  
 183 bulk partition coefficients, a six-end-member mixing model was developed here similar to  
 184 the one published by Hayes et al. (2015) for thorium isotopes.

$$185 \quad K_d = \sum_1^6 (K_d)_i \cdot f_i = (K_d)_1 \cdot f_1 + (K_d)_2 \cdot f_2 + (K_d)_3 \cdot f_3 + (K_d)_4 \cdot f_4 + (K_d)_5 \cdot f_5 + \\ 186 \quad (K_d)_6 \cdot f_6 \quad (3)$$

187 where  $K_d$  is the observed bulk partition coefficient of a given nuclide,  $(K_d)_i$  is the partition  
 188 coefficient for pure end member  $i$ ,  $f_i$  is the proportion of end member  $i$  of the total mass of a  
 189 particle sample, where  $i = 1$  (POM), 2 ( $\text{CaCO}_3$ ), 3 (opal), 4 (lithogenic material), 5 (Fe), 6  
 190 (Mn). Eq. (1) and (3) were formatted for each particle sample, and therefore for a set of given  
 191  $i = n$  samples,  $f_i$  ( $n \times 6$  matrix) and  $K_d^i$  ( $n \times 1$  matrix) are all known. The unknown  $(K_d)_i$   
 192 ( $6 \times 1$  matrix) can be solved by Eq. (4) using non-negative least squares regression (since the  
 193 negative  $K_d$  has no physical meaning).

$$194 \quad \begin{bmatrix} f_1^1 & f_2^1 & f_3^1 & f_4^1 & f_5^1 & f_6^1 \\ f_1^2 & f_2^2 & f_3^2 & f_4^2 & f_5^2 & f_6^2 \\ f_1^3 & f_2^3 & f_3^3 & f_4^3 & f_5^3 & f_6^3 \\ \dots & \dots & \dots & \dots & \dots & \dots \end{bmatrix} \times \begin{bmatrix} (K_d)_1 \\ (K_d)_2 \\ (K_d)_3 \\ (K_d)_4 \\ (K_d)_5 \\ (K_d)_6 \end{bmatrix} = \begin{bmatrix} k_d^1 \\ k_d^2 \\ k_d^3 \\ \dots \end{bmatrix} \quad (4)$$

195 We estimated the standard error of the derived end-member  $K_d$  values using the jackknife  
 196 resampling technique (Efron and Stein, 1981). Finally, the derived end-member fractionation  
 197 factors,  $F(\text{Po}/\text{Pb})$ , were calculated from Eq. (2) for each compositional component.

### 198 **3. Results**

#### 199 **3.1. Correlations**

200 In the open ocean,  $^{210}\text{Po}$  activity was strongly correlated with POC and moderately  
 201 correlated with  $\text{CaCO}_3$  in the small particles, and  $^{210}\text{Po}$  activity in the large particles was  
 202 strongly correlated with  $\text{CaCO}_3$ , moderately correlated with opal, and weakly correlated with  
 203 POC (Table 1).  $^{210}\text{Pb}$  activity in the open ocean, in contrast, was moderately correlated with



204 CaCO<sub>3</sub>, opal, and Mn in the large particles but there were no significant correlations with  
 205 <sup>210</sup>Pb activity in the small particles. In the coastal waters, both <sup>210</sup>Po and <sup>210</sup>Pb activities in the  
 206 large particles were strongly correlated with POC, CaCO<sub>3</sub>, and opal. <sup>210</sup>Po and <sup>210</sup>Pb activities  
 207 in the small particles near the coasts, however, had different relationships with the 6  
 208 particulate components relative to those in large particles. For instance, <sup>210</sup>Pb activity  
 209 strongly correlated with opal and Mn, and moderately correlated with lithogenic matter and  
 210 Fe near the coasts whereas <sup>210</sup>Po activity was found to be strongly correlated with lithogenic  
 211 matter and Fe.

212  
 213 Table 1. Pairwise Pearson Correlation Coefficients, *r*, within size-fractionated principal particle compositions in  
 214 the top 500 m at coastal (stns.10-1, 10-9 and 11-1) and open ocean (stns.11-10, -12, -16 and -20) stations. Bold  
 215 values with \* and \*\* denote moderate and strong correlation with *p* < 0.05 by *t*-test, respectively.

|                   | Coasts            |                   |                   |                   | Open Ocean        |                   |                   |                   |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|                   | SSF (n = 19)      |                   | LSF (n = 18)      |                   | SSF (n = 20)      |                   | LSF (n = 19)      |                   |
|                   | <sup>210</sup> Po | <sup>210</sup> Pb | <sup>210</sup> Po | <sup>210</sup> Pb | <sup>210</sup> Po | <sup>210</sup> Pb | <sup>210</sup> Po | <sup>210</sup> Pb |
| POC               | 0.05              | 0.07              | <b>0.68**</b>     | <b>0.60**</b>     | <b>0.68**</b>     | 0.30              | 0.45              | 0.18              |
| CaCO <sub>3</sub> | 0.25              | 0.44              | <b>0.72**</b>     | <b>0.65**</b>     | <b>0.59*</b>      | 0.42              | <b>0.71**</b>     | <b>0.59*</b>      |
| Opal              | -0.01             | <b>0.64**</b>     | <b>0.76**</b>     | <b>0.70**</b>     | 0.18              | -0.14             | <b>0.53*</b>      | <b>0.50*</b>      |
| Litho             | <b>0.75**</b>     | <b>0.54*</b>      | 0.07              | 0.05              | -0.06             | -0.01             | 0.34              | 0.10              |
| Fe                | <b>0.74**</b>     | <b>0.56*</b>      | 0.08              | 0.07              | -0.03             | 0.00              | 0.15              | -0.05             |
| Mn                | 0.36              | <b>0.84**</b>     | 0.43              | 0.42              | -0.47             | -0.11             | 0.34              | <b>0.58*</b>      |

216  
 217 Overall, the correlations between the particle components and <sup>210</sup>Po and <sup>210</sup>Pb activity in  
 218 the large particles were reasonably consistent between coastal and open ocean samples,  
 219 whereas the corresponding correlations in the small particles varied between those two  
 220 oceanic provinces.

### 221 3.2. Principal Component Analysis

222 Principal component analysis (PCA) was applied to all eight measured variables to  
 223 identify a new set of fewer, uncorrelated variables that can explain a substantial portion of  
 224 the variation of the original variables. The new set of variables, also called the principal  
 225 components (PC), will result in a lower dimensional space that explains most of the variation.  
 226 We analyzed all the SSF data and all the LSF data as two datasets, and PCA results were  
 227 summarized in Table 2, including the loadings of the first three principal components (total 8  
 228 principal components) and their contribution in explaining of the total variance. In the SSF

229 dataset (Table 2, SSF), the first three principal components contained 76.9% of the variation  
 230 of the eight original variables, with 49.8% explained by PC1, 14.8% explained by PC2, and  
 231 12.3% explained by PC3. The highest loadings of PC1 were from Mn, Fe, CaCO<sub>3</sub> and  
 232 lithogenic matter, PC2's highest loadings were <sup>210</sup>Po and POC, whereas lithogenic matter and  
 233 Fe were most important to PC3 (Table 2, Fig. 2).

234

235 Table 2. The first three principal component loadings, percentage of variance explained by each principal  
 236 component, and their cumulative percentage of total variance in the small size fraction (SSF) and the large size  
 237 fraction (LSF) of the particles. The numbers in bold font indicate the absolute loadings that are higher than 0.4.

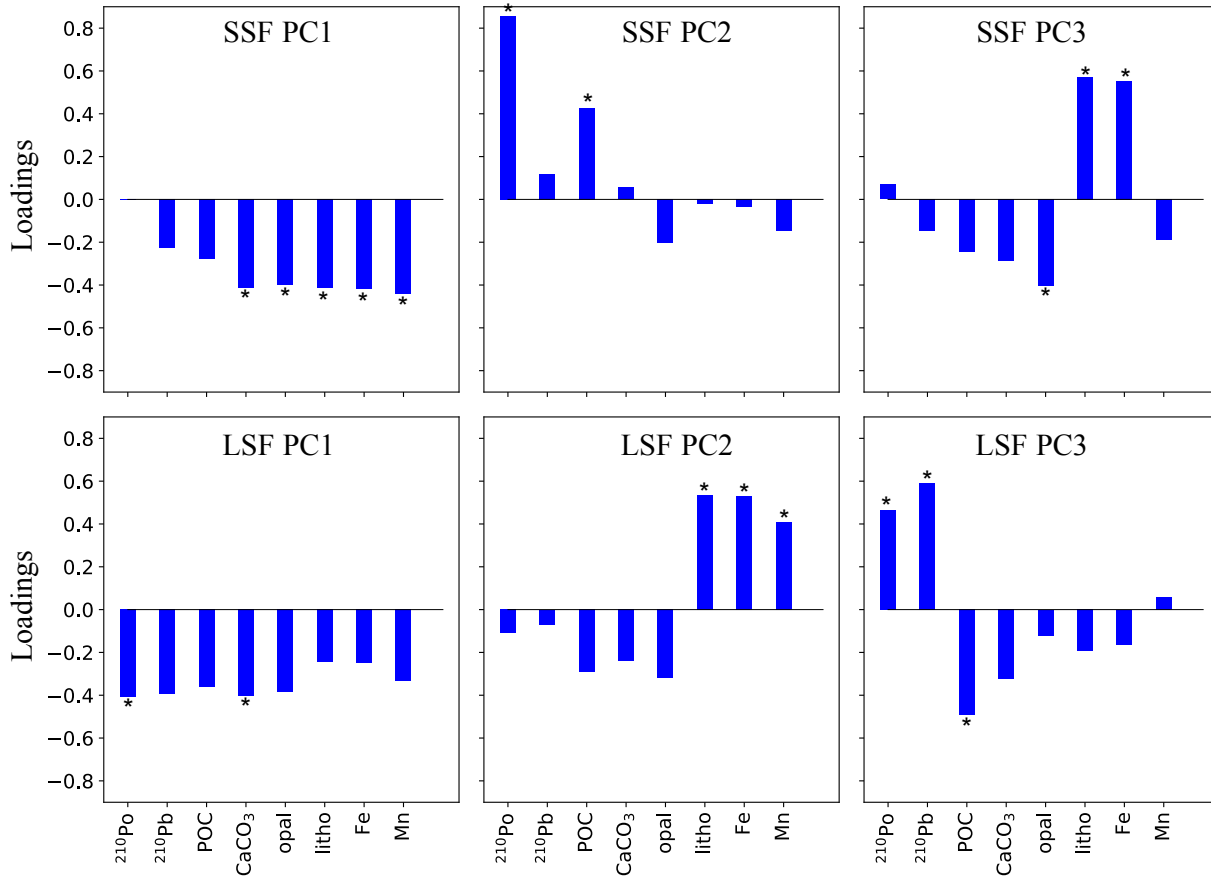
|                     | Variables         | PC1           | PC2          | PC3           |
|---------------------|-------------------|---------------|--------------|---------------|
| <b>SSF</b>          |                   |               |              |               |
| <b>(1-51 μm)</b>    | <sup>210</sup> Po | -0.001        | <b>0.858</b> | 0.070         |
|                     | <sup>210</sup> Pb | -0.226        | 0.118        | -0.149        |
|                     | POC               | -0.279        | <b>0.427</b> | -0.245        |
|                     | CaCO <sub>3</sub> | <b>-0.414</b> | 0.056        | -0.286        |
|                     | Opal              | <b>-0.401</b> | -0.205       | <b>-0.406</b> |
|                     | Litho             | <b>-0.412</b> | -0.023       | <b>0.570</b>  |
|                     | Fe                | <b>-0.417</b> | -0.034       | <b>0.553</b>  |
|                     | Mn                | <b>-0.441</b> | -0.146       | -0.187        |
|                     | % of Variance     | 49.8          | 14.8         | 12.3          |
|                     | Cumulative %      | 49.8          | 64.6         | 76.9          |
| <b>LSF</b>          |                   |               |              |               |
| <b>(&gt; 51 μm)</b> | <sup>210</sup> Po | <b>-0.408</b> | -0.110       | <b>0.466</b>  |
|                     | <sup>210</sup> Pb | -0.396        | -0.070       | <b>0.593</b>  |
|                     | POC               | -0.362        | -0.292       | <b>-0.493</b> |
|                     | CaCO <sub>3</sub> | <b>-0.405</b> | -0.239       | -0.324        |
|                     | Opal              | -0.386        | -0.321       | -0.121        |
|                     | Litho             | -0.243        | <b>0.536</b> | -0.195        |
|                     | Fe                | -0.249        | <b>0.532</b> | -0.163        |
|                     | Mn                | -0.334        | <b>0.409</b> | 0.058         |
|                     | % of Variance     | 59.9          | 29.8         | 7.4           |
|                     | Cumulative %      | 59.9          | 89.7         | 97.1          |

238

239 In contrast, the first three components of the LSF dataset explained 97.1% of the total  
 240 variance, in which PC1 explained 59.9%, PC2 explained 29.8%, and PC3 explained 7.4%  
 241 (Table 2, LSF). We observed that the highest PC1 loadings came from <sup>210</sup>Po and CaCO<sub>3</sub>,

242 PC2's highest loadings were from lithogenic matter, Fe, and Mn, and PC3 loadings were  
 243 mainly from  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$  and POC (Table 2, Fig. 2).

244



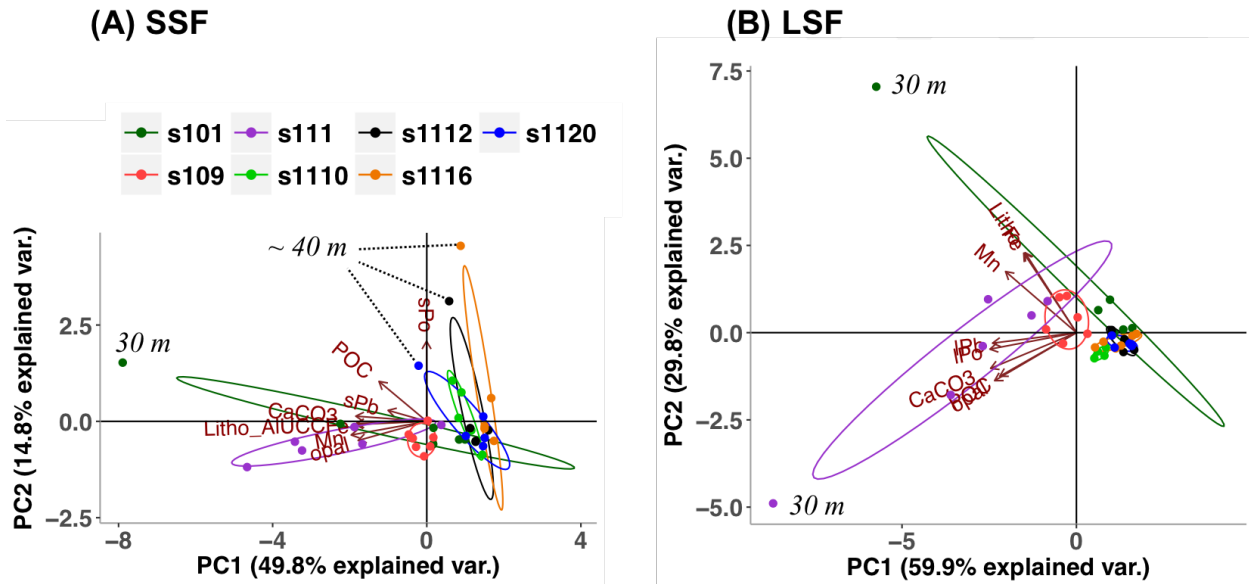
245 Fig. 2. The first three principal component loadings with respect to each variable in the small size fraction (SSF)  
 246 and the large size fraction (LSF) of the particles. The symbol “\*” indicates the absolute loadings that are higher  
 247 than 0.4.  
 248

249

250 Further, PC1 and PC2 scores of the observations for each station were examined and  
 251 visualized using biplots (Fig. 3). In the SSF dataset, the observations in the open ocean  
 252 stations generally scored high and positive on PC1, whereas the SSF at coastal station 11-1  
 253 scored high on PC1 but with negative values. The observations at stn.10-9, on the other hand,  
 254 had little loading from PC1, but had some variability along PC2, with generally negative  
 255 scores. Three of the very shallow (~ 40 m) open ocean observations scored relatively high  
 256 and positive on PC2 (stn.11-12, 11-16, and 11-20) (Fig. 3A). Most observations at stn.10-1  
 257 scored rather equally on PC1 and PC2, except for one observation (30 m) with significant

258 negative scores on PC1, suggesting this observation was overwhelmingly explained by this  
 259 component.

260



261  
 262 Fig. 3. Biplots of principal component (PC1 and PC2) scores based on observations for each station. A: small  
 263 size fraction (SSF); B: large size fraction (LSF). PC1: first principal component, PC2: second principal  
 264 component. The color of each point indicates samples from a particular station number, and ovals denote the  
 265 clustering of those samples. Note that the scales of A and B are different and the depths of the extreme points  
 266 are annotated (see section 3.2 for detailed description).

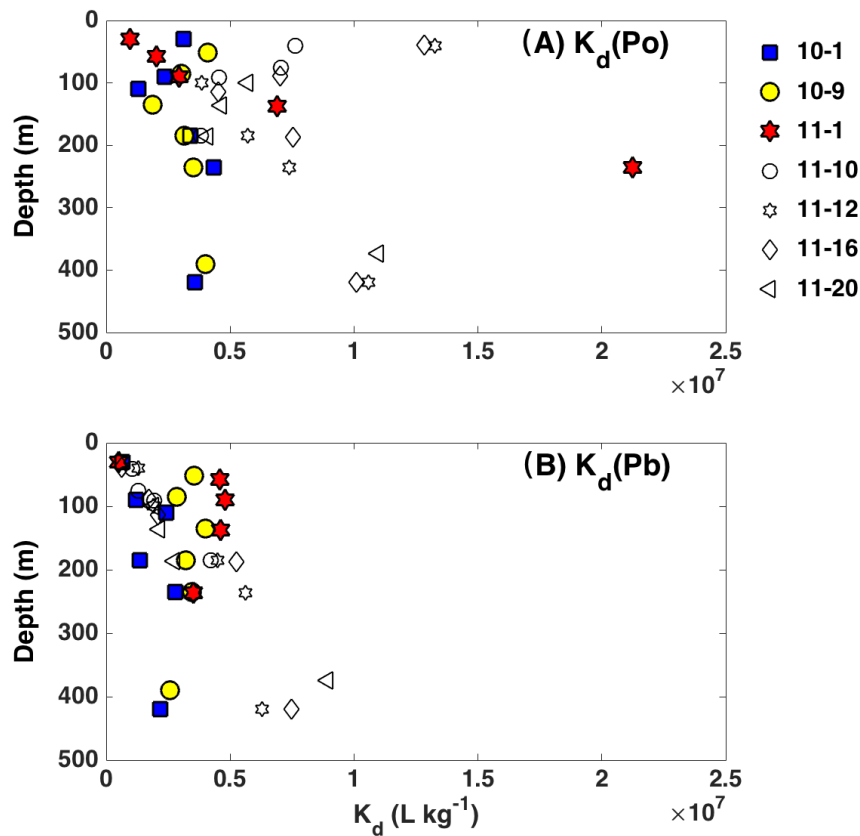
267  
 268 In the LSF dataset, the observations in the open ocean stations mostly scored highly  
 269 positive on PC1 (Fig. 3B). The PC1 scores for the observations at stn.10-1 were generally  
 270 higher than PC2 scores (positive), except from the observation at 30 m, which was the only  
 271 observation from this station to have a strongly negative PC1 score and also had a much  
 272 higher (positive) score on PC2 compared to the rest of the samples at this station. At stn.10-9,  
 273 the surface observations had generally negative scores on PC1, and the observations below  
 274 the surface layer had generally positive scores on PC2. The observations at stn.11-1, on the  
 275 other hand, scored highly negative on PC1, especially the observation at 30 m.

276 Looking at each biplot (SSF and LSF separately), component scores for the four open  
 277 ocean stations in both plots displayed a clustered pattern, whereas the observations for the  
 278 three coastal stations were more varied along PC1 and PC2. Despite the fact that the principal  
 279 components may represent different causes of variability between SSF and LSF, this suggests

280 more uniform open ocean particle characteristics within each size fraction, but more diverse  
 281 particle characteristics at the coasts. Additionally, we observed several extremely high scores  
 282 in a few surface samples (samples annotated on Fig. 3), indicating those observations were  
 283 overwhelmingly explained by a single component.

284 **3.3. The bulk partition coefficients of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$**

285 The  $K_d$  values for  $^{210}\text{Po}$  in the SSF varied between  $0.10$  and  $2.12 \times 10^7 \text{ L kg}^{-1}$  (median:  
 286  $0.43 \times 10^7 \text{ L kg}^{-1}$ ). In contrast, the  $K_d$  values for  $^{210}\text{Pb}$  ranged from  $0.05$  to  $0.89 \times 10^7 \text{ L kg}^{-1}$ ,  
 287 with a median value half as large as that of  $^{210}\text{Po}$  in the SSF (Fig. 4). We also noticed  
 288 different regional patterns in  $K_d$  for both  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  between the coasts and open ocean.  
 289 For instance,  $K_d$  for  $^{210}\text{Po}$  in the SSF in the three stations nearest to the coasts (filled markers)  
 290 were 2-times lower than those in the remote regions of the ocean (open markers) (Fig. 4A).  
 291 The  $K_d(\text{Pb})$  values, on the other hand, showed higher values between 50 and 150 m near the  
 292 coastal margins than in the interior ocean (Fig. 4B).  
 293



294  
 295 Fig. 4. Partition coefficient ( $K_d$  in the unit of  $\text{L kg}^{-1}$ ) of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  with marine suspended particulate  
 296 matter (SPM) in the upper 500 m along the NAZT GA03 transect. (A):  $K_d$  of  $^{210}\text{Po}$  in the small size

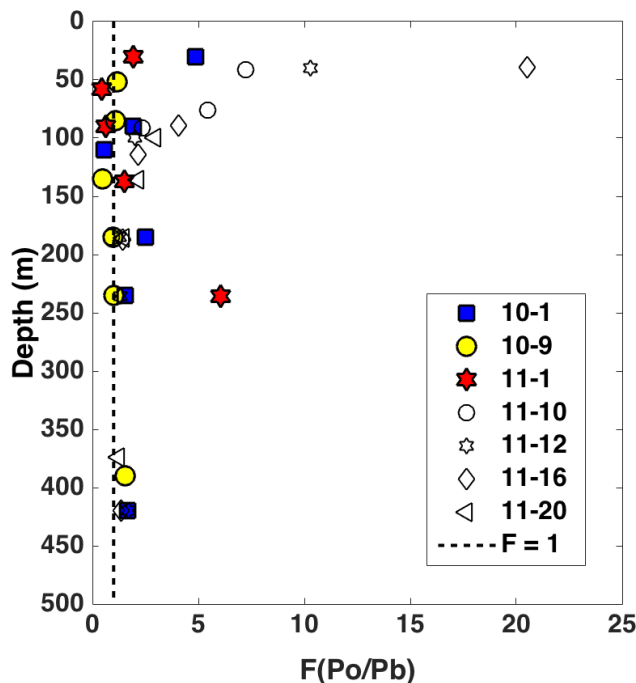
297 fraction (1-51  $\mu\text{m}$ ). (B):  $K_d$  of  $^{210}\text{Pb}$  in the small size fraction. The filled markers indicate the three stations  
 298 nearest to the margins (stns.10-1, 10-9, 11-1) and the open markers indicate the four open ocean stations  
 299 (stns.11-10, -12, -16, -20).

300

### 301 3.4.Fractionation between $^{210}\text{Po}$ and $^{210}\text{Pb}$ in the bulk samples

302 The fractionation factor of the bulk sample,  $F(\text{Po/Pb})$ , which is the ratio of the bulk  
 303  $K_d(\text{Po})$  to bulk  $K_d(\text{Pb})$ , ranged from 0.44 to 20.5 in the small particles (Fig. 5). We observed  
 304 that the fractionation factor generally decreased with depth at nearly all stations, displaying a  
 305  $F(\text{Po/Pb})$  minimum in the subsurface zone between 100-200 m. For the particles collected  
 306 from the interior ocean,  $F(\text{Po/Pb})$  were all greater than 1 in the upper 300 m, indicating a  
 307 strong preference for scavenging of  $^{210}\text{Po}$  over  $^{210}\text{Pb}$ . In contrast,  $F(\text{Po/Pb})$  values for  
 308 particles near the coasts reveal that most were lower than or equal to unity, indicating a slight  
 309 preference for scavenging of  $^{210}\text{Pb}$  over  $^{210}\text{Po}$ , or perhaps a higher rate of  $^{210}\text{Po}$   
 310 remineralization from the particles to the seawater (Rigaud et al., 2015).

311



312

313 Fig. 5. Fractionation of  $^{210}\text{Po}$  relative to  $^{210}\text{Pb}$  ( $F(\text{Po/Pb}) = K_d(\text{Po})/K_d(\text{Pb})$ ) in the small size fraction. The  
 314 vertical dashed line is drawn for  $F = 1$ . The filled markers indicate the three stations nearest to the margins  
 315 (stns.10-1, 10-9, 11-1) and the open markers indicate the four open ocean stations (stns.11-10, -12, -16, -  
 316 20).

317

318 **4. Discussion**

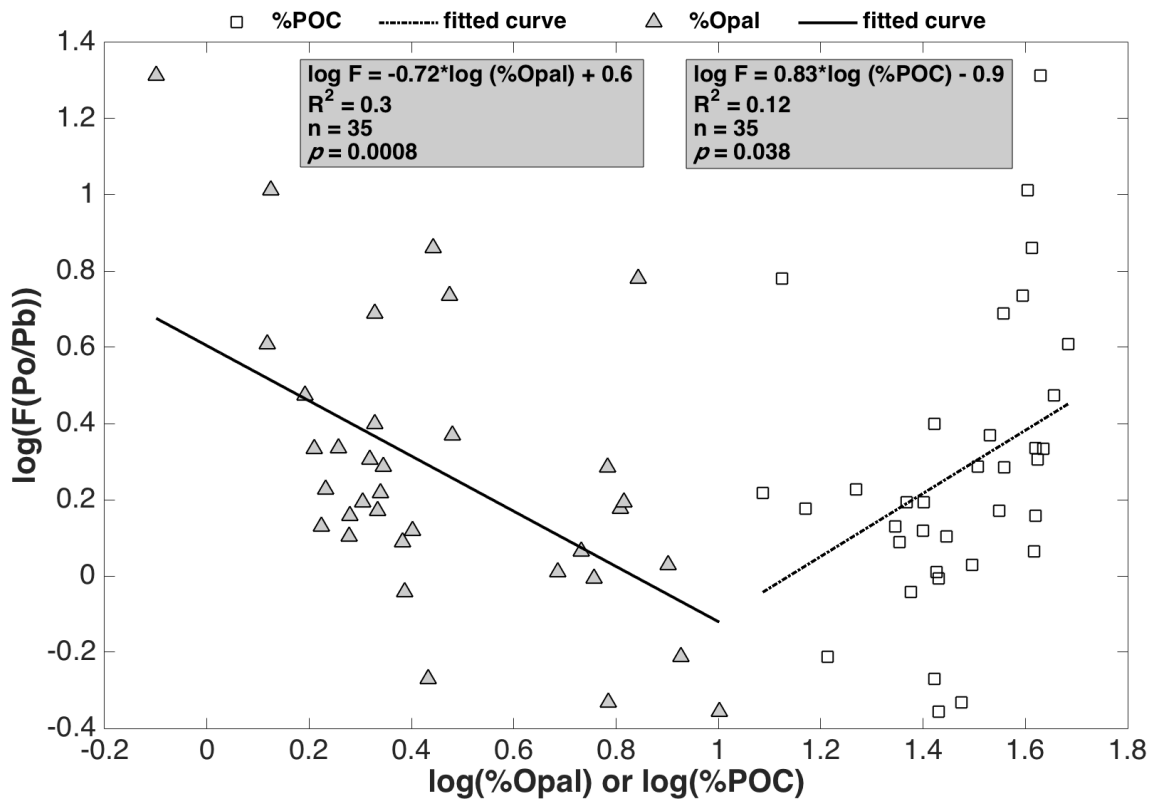
319 **4.1. Correlations of radionuclide activities to chemical composition**

320 We observed correlations between  $^{210}\text{Po}$  activity and POC in the large particles across  
321 both the coastal and open ocean stations, while similar correlations in the small particles  
322 were only found in the open ocean but not in coastal waters (Table 1). When correlations  
323 existed between  $^{210}\text{Po}$  activity and POC in the upper 500 m, there were also correlations  
324 between  $^{210}\text{Po}$  activity and  $\text{CaCO}_3$ . In our PCA results, POC and  $\text{CaCO}_3$  in the large particles  
325 had similar loadings on the first three principal components while the loadings of POC and  
326  $\text{CaCO}_3$  in small particles had similar values on PC1 and PC3, but not on PC2 (Table 2, Fig.  
327 2). These results suggest that POC and  $\text{CaCO}_3$  were more closely associated with each other  
328 and more evenly important to the components in the large particles relative to their  
329 relationship in the small particles. Indeed, correlations between POC and  $\text{CaCO}_3$  were  
330 previously observed in the large particles in the upper 2000 m in this section, but no such  
331 correlations were seen at any depth in the small particles (Lam et al., 2015). This may be due  
332 to a relationship between “ballast”  $\text{CaCO}_3$  and POC in large, sinking particles (Armstrong et  
333 al., 2001).

334 Despite these relationships in the large particles, in the small particles near the margins  
335 no correlation was found between  $^{210}\text{Po}$  and POC, while strong positive relationships were  
336 observed between  $^{210}\text{Po}$  and Fe and lithogenic material (Table 1). As these areas had the  
337 highest input of lithogenics (Lam et al., 2015), we suggest that this could reflect scavenging  
338 of  $^{210}\text{Po}$  by particles from atmospheric dust deposition or continental shelf input. This is an  
339 indication that the source of particles can influence the distribution of  $^{210}\text{Po}$ , and suggests that  
340 the radionuclide activity in the small particles near the coasts has a different relationship with  
341 Fe and lithogenic phases than the small particles and large particles in the rest of the study.

342 While large particles are often aggregates of small particles in the surface ocean, the large  
343 particles throughout the water column (top 500m) at the coasts and open ocean had different  
344 correlations between the compositional components and  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  than the small  
345 particles, implying that they are not just aggregates of smaller particles. Below the surface  
346 layer, there are many reasons to explain why various sized particle compositions could be  
347 different (explained further in 4.2).

348 It was reported by Friedrich and Rutgers van der Loeff (2002) that the fractionation of  
 349  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  on particles from the Antarctic Circumpolar Current was dependent on the  
 350 POC/opal ratio, and suggested that  $^{210}\text{Po}$  was more strongly associated with POC while  $^{210}\text{Pb}$   
 351 was more associated with opal. The Pearson correlation analysis in this study (Table 1)  
 352 revealed a stronger correlation between POC and  $^{210}\text{Po}$  than between POC and  $^{210}\text{Pb}$  in  
 353 general. The results did not show a stronger correlation between opal and  $^{210}\text{Pb}$  than between  
 354 opal and  $^{210}\text{Po}$ .  
 355



356  
 357 Fig. 6. The log-log model:  $\log F(\text{Po/Pb}) = \alpha + \beta \log(\% \text{opal})$  and  $\log F(\text{Po/Pb}) = \alpha + \beta \log(\% \text{POC})$  was  
 358 applied to study the linear relationship between the logarithmic transformed dependent and independent  
 359 variables. Open squares represent  $\log(\% \text{POC})$ , and filled triangles indicate  $\log(\% \text{opal})$ . The curves were fitted  
 360 by linear regression functions, and the fitted function and corresponding statistical information are shown in the  
 361 gray-shaded boxes.  
 362

363 To examine this further, we applied linear regression models by plotting  $\log(F(\text{Po/Pb}))$   
 364 against both  $\log(\% \text{POC})$  and  $\log(\% \text{opal})$  for small particles (Fig. 6). This was done only for  
 365 small particles because we only calculated  $K_d(\text{Po})$  and  $K_d(\text{Pb})$  for these particles. A linear



366 function fit the relationship between  $\log(F(\text{Po/Pb}))$  and  $\log(\%opal)$  reasonably well ( $R^2 =$   
367  $0.29$ ,  $n = 35$ ,  $p = 0.0008$ ), showing a 1% increase in %opal reduces  $F(\text{Po/Pb})$  by 0.7%,  
368 supporting siliceous matter's preferential affinity for  $^{210}\text{Pb}$ . The relationship between  
369  $\log(F(\text{Po/Pb}))$  and  $\log(\%POC)$ , on the other hand, was not well captured with a linear  
370 function ( $R^2 = 0.13$ ,  $n = 35$ ,  $p = 0.04$ ). Nonetheless, the relationship is still significant,  
371 suggesting a 1% increase in %POC increases  $F(\text{Po/Pb})$  by 0.8%, supporting the association  
372 of  $^{210}\text{Po}$  with POC.

373 We did, however, find lower  $F(\text{Po/Pb})$  values in surface samples from the coasts than we  
374 found in the open ocean, despite the higher POC along the margins (Figure 5). It is worth  
375 noting that the phytoplankton composition near the coasts was dominated by siliceous  
376 plankton (diatoms, higher %opal) (Twining et al., 2015a), and could result in a decrease in  
377  $F(\text{Po/Pb})$ , despite high %POC. To further assess this, we applied a multiple linear regression  
378 by using both  $\log(\%opal)$  and  $\log(\%POC)$  as predictors and  $\log(F(\text{Po/Pb}))$  as response:  
379  $\log(F(\text{Po/Pb})) = 0.0155 - 0.63733 \log(\%opal) + 0.37465 \log(\%POC)$  ( $R^2 = 0.31$ ). The results  
380 suggest that %opal has a larger negative impact and %POC had a smaller positive impact on  
381 the fractionation. When %opal and %POC are combined in the model,  $\log(\%POC)$  is no  
382 longer significant ( $p = 0.33$ ) while  $\log(\%opal)$  is ( $p = 0.005$ ). Due to this smaller  
383 fractionation between  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  near the margins, the  $^{210}\text{Po}$  deficits with respect to  
384  $^{210}\text{Pb}$  were not as significant as those in the subtropical gyre (Rigaud et al., 2015) where non-  
385 siliceous organisms like *prymnesiophytes*, *cryptophytes* and *chrysophytes* comprised 40-60%  
386 of the community (Twining et al., 2015a).

#### 387 **4.2. Interpretation of PCA**

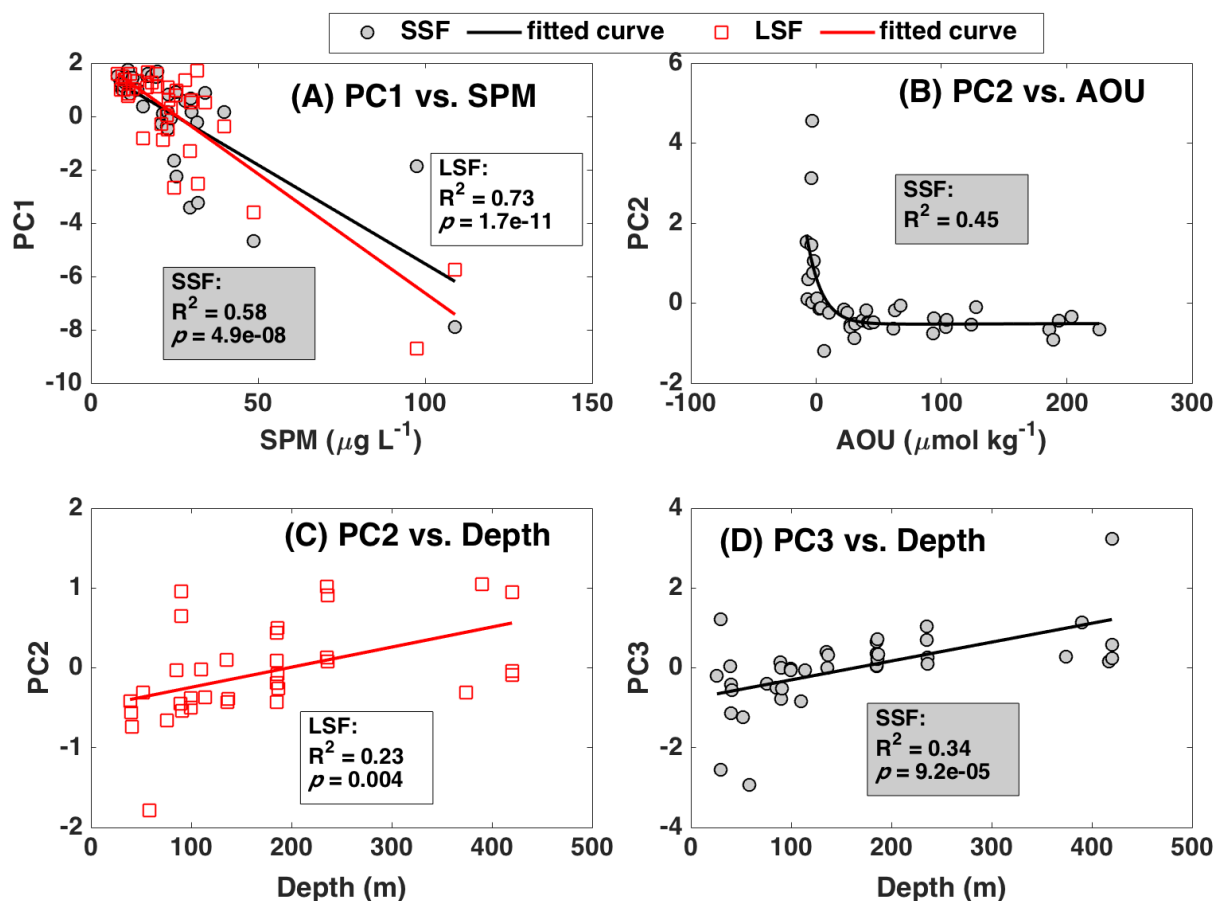
388 According to the PCA loadings (Fig. 2) and scores in the biplots (Fig. 3), the first  
389 principle component (PC1) for both the SSF and the LSF was characterized by similar  
390 loadings of the compositional components (all negative) as well as a clear geographic split in  
391 sample scores; samples from the open ocean had positive scores, samples from the coastal  
392 stations had generally negative scores, and samples from station 10-9 had a unique  
393 distribution with both negative and positive scores. Both of these observations suggest a  
394 similar interpretation for PC1 for both size fractions. In contrast, the loadings and scores for  
395 PC2 were distributed quite differently between SSF and LSF samples, suggesting a different  
396 interpretation for this PC in the SSF vs. LSF. In addition, the loadings and scores (data not

397 shown) for PC3 were also distinct between the two size fractions, but there were some  
398 similarities between the loadings of PC3 in the SSF and PC2 in the LSF. The loadings for  
399 PC2 in the SSF and PC3 in the LSF were relatively distinct from all the other loading  
400 patterns.

401 To attempt to interpret the “meaning” of the first three principle components in each size  
402 fraction, we plotted the scores of all the samples against physical and chemical characteristics  
403 of the samples from the GEOTRACES database. For example, because the scores on PC1 of  
404 both size fractions seemed to be related to geographic distribution, but the loadings of all the  
405 variables were similar/negative, we expected that some trend other than particulate  
406 composition was driving this component from the coast to the open ocean. We hypothesized  
407 that this could be related to total suspended particle load (SPM), which tends to be higher at  
408 margin stations. Along the transect, between 52 and 99% of the mass of SPM was  
409 determined by three biogenic phases: POM (which is  $1.88 \times \text{POC}$ ), opal, and  $\text{CaCO}_3$  (data  
410 not shown), which all are generated by phytoplankton production. Thus, SPM could be used  
411 as an indicator of production, with a gradient from the coast to the center of the gyre. Indeed,  
412 we observed a strong and significant linear relationship between PC1 scores and the  
413 concentration of SPM in both the small and large size fractions (SSF:  $R^2 = 0.66$ ; LSF:  $R^2 =$   
414  $0.73$ ) (Fig. 7A), suggesting a similar interpretation (“production”) for PC1 in both size  
415 fractions. However, no general pattern was found using SPM as an explanatory variable for  
416 the variations in PC2 or PC3 in both size fractions.

417 PC2 has strong positive loadings for both  $^{210}\text{Po}$  and POC in the SSF (Table 2, Fig. 2) and  
418 we hypothesized that this PC was related to some biogeochemical processes that affected  
419  $^{210}\text{Po}$  and POC in a similar manner in the SSF. We did in fact find a strong relationship by  
420 using a two-term exponential model ( $R^2 = 0.45$ ) between PC2 in the SSF and apparent  
421 oxygen utilization (AOU) (Fig. 7B), while none of the other PCs had a significant relationship  
422 with AOU. AOU is defined as the difference between the saturation oxygen concentration  
423 and the observed oxygen concentration. Dissolved oxygen in the seawater is consumed by  
424 microorganisms for the oxidation of organic matter, and therefore AOU can be used as a  
425 measure of respiration/remineralization in the oceans (Duteil et al., 2013; Ito et al., 2004).  
426 Besides reflecting local respiration/remineralization, AOU is also related to water mass age  
427 and the ventilation age of the water (Stanley et al., 2012). This relationship between PC2 in

428 small particles, which has the highest loadings from  $^{210}\text{Po}$  activity, and AOU suggests that  
 429 recent and past remineralization and respiration affect the  $^{210}\text{Po}$  distribution in small particles  
 430 more than large particles.  
 431



432  
 433 Fig. 7. Relationships between the scores on the first three principal components and the concentration of  
 434 suspended particulate matter (SPM), apparent oxygen utilization (AOU), and depth. There were a total 9  
 435 relationships in each size fraction: PC (1, 2, 3) vs. SPM, PC (1, 2, 3) vs. AOU, and PC (1, 2, 3) vs. Depth. Only  
 436 the graphs with significant relationships are displayed in this figure: (A) PC1 score vs. SPM (SSF and LSF); (B)  
 437 PC2 score vs. AOU (SSF); (C) PC2 score vs. Depth (LSF); (D) PC3 score vs. Depth (SSF). The filled gray  
 438 circles represent the SSF and open red squares represent the LSF. The statistical regression lines (solid line) and  
 439 the R-squared statistic ( $R^2$ ) are shown in all the plots. The  $p$ -value is annotated only for linear regressions (A, C,  
 440 D) but not for the two-term exponential model (B).  
 441

442 Looking at the loadings further (Table 2, Fig. 2), it seems that SSF PC3 (12.3% variation  
 443 explained) and LSF PC2 (29.8% variation explained) could be driven by similar variables,

444 and appear to reflect a gradient from biogenic particle phases (POC, CaCO<sub>3</sub>, opal), which  
445 have negative loadings, towards abiotic particle phases (litho, Fe, Mn), which have positive  
446 loadings. This transition from biogenic material towards inorganic mineral phases tends to  
447 occur as freshly-produced particles sink from the surface and degrade with depth. Indeed,  
448 when the scores along these principle components were plotted vs. depth, the relationship for  
449 both was linear and significant (Fig. 7C and 7D). There were no significant relationships  
450 between PC3 and any of the variables we examined in the large size fraction.

451 The different relationships between principle components and production and  
452 remineralization suggests a decoupling of the driving forces that determine composition and  
453 <sup>210</sup>Po and <sup>210</sup>Pb activity in the two size fractions, suggesting both different sources and  
454 possibly different residence times between the SSF and the LSF in the top 500m. For  
455 example, the source of LSF may reflect production in the surface ocean, especially at the  
456 margins where large diatoms, foraminifera, and pteropods could be predominating. The  
457 source of SSF in the surface, on the other hand, is probably composed of small diatoms and  
458 flagellates. Further differences between the particle characteristics may reflect differences in  
459 the residence times of large (faster sinking) and small (slower sinking) particles, especially  
460 below the euphotic zone. While there is evidence that large particles are often aggregates of  
461 small particles in the surface (Ohnemus and Lam, 2015), there is no reason to expect their  
462 compositions will be identical, especially as particles leave the euphotic zone. Small particles  
463 at depth may be derived from the disaggregation of larger particles, and may spend several  
464 months in the water column as they sink slowly. In contrast, large particles at the same  
465 depths could represent fast-sinking material that left the surface within the past several days-  
466 weeks, and so may be “fresher” than the small particles in this study due to differences in the  
467 extent of degradation and remineralization (Abramson et al., 2010; Wakeham and Canuel,  
468 1988).

469 Stewart et al. (2007b) applied principal component analysis to explore the connection  
470 between <sup>210</sup>Po and organic matter within sediment trap particles at 200m in the northwestern  
471 Mediterranean. They suggested that degradation contributed the most to the variability in the  
472 composition of those sinking particles. While we find remineralization (low AOU as a proxy  
473 for “freshness”) was an important driver of variation in the small particles, it was not  
474 significant for the large particles. The difference in our results, specifically the lack of

475 correlation between AOU and PC scores for large particles, may be caused by differences  
476 between the particulate material collected by sediment traps and those collected by in situ  
477 pumps (Abramson et al., 2010; Lepore et al., 2009). This concept, however, that degradation  
478 and sinking speed can cause some variation of composition within the small and large  
479 particles, was confirmed by our result that the depth of the sample is correlated to the  
480 distribution along PC2 in the large fraction (which explains 30% of the variation in the  
481 particle composition), and along PC3 in the small fraction (12 % of the variation). Thus  
482 differences between our results and those of Stewart et al. (2007b) could also be explained by  
483 the range of depths of our samples (0-500 m) as opposed to the single depth (200 m) of the  
484 sediment trap.

#### 485 **4.3. Particle concentration effect**

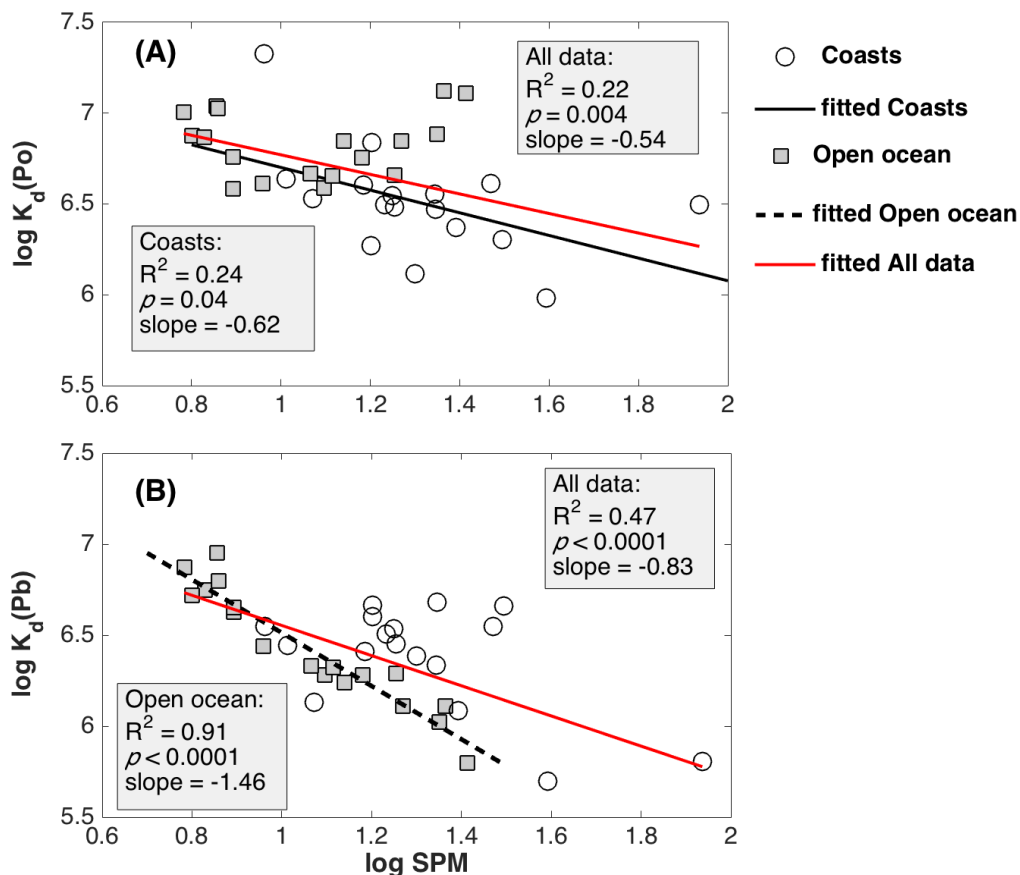
486 The  $K_d$  values suggest that  $^{210}\text{Po}$  has a higher affinity for particles than  $^{210}\text{Pb}$ , as its  $K_d$   
487 ranged between  $10^{6.0}$  and  $10^{7.3}$   $\text{L kg}^{-1}$  while the  $K_d$  values for  $^{210}\text{Pb}$  ranged from  $10^{5.7}$  to  $10^{7.0}$   $\text{L}$   
488  $\text{kg}^{-1}$ . These  $K_d$  values are higher and span a wider range compared to previous values in the  
489 nearshore waters off western Taiwan ( $10^{5.53}$ - $10^{5.56}$  and  $10^{5.38}$ - $10^{5.87}$   $\text{L kg}^{-1}$ , Wei et al., 2012),  
490 in surface waters of the northwestern Mediterranean Sea ( $10^{5.80}$ - $10^{5.97}$  and  $10^{4.90}$ - $10^{5.08}$   $\text{L kg}^{-1}$ ,  
491 Masqué et al., 2002), and in the turbid waters of the Yellow Sea ( $10^{4.59}$ - $10^{6.51}$  and  $10^{5.23}$ -  
492  $10^{5.86}$   $\text{L kg}^{-1}$ , Hong et al., 1999). All the samples collected in these previous studies were  
493 either from surface waters or coastal, turbid environments. The samples evaluated in our  
494 study, in contrast, were collected from the surface to 500 m depth, and from the coast to the  
495 open ocean, covering a wider range in SPM concentration and more diverse particle  
496 composition. Indeed, an even wider range of  $K_d(\text{Po})$  values ( $10^{4.7}$ - $10^{7.2}$   $\text{L kg}^{-1}$ ) and  $K_d(\text{Pb})$   
497 values ( $10^{5.0}$ - $10^{6.8}$   $\text{L kg}^{-1}$ ) was observed in a 4000-m water column study in the northern  
498 South China Sea (Wei et al., 2014).

499 We examined the effect of particle concentration on the solid/solution partitioning for  $^{210}\text{Po}$   
500 and  $^{210}\text{Pb}$  by focusing on the uptake of radioactivity from the water to the small particles. The  
501 values of partitioning ( $\log K_d$ ) versus particle concentration ( $\log \text{SPM}$ ) in the small particles  
502 are shown in Fig. 8. Over a range of more than two orders of magnitude of SPM  
503 concentrations, an inverse correlation between  $\log K_d$  and  $\log \text{SPM}$  was observed for both  
504  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in this study. Such negative correlation, known as the “particle concentration  
505 effect”, has been commonly found in field and laboratory observations for  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ , and

506 other particle-reactive radionuclides such as  $^{230}\text{Th}$ ,  $^{234}\text{Th}$ ,  $^{231}\text{Pa}$ , and  $^7\text{Be}$  (Hayes et al., 2015;  
507 Wei and Murray, 1994). Although a number of hypotheses have been proposed to explain  
508 this observation, the presence of colloidal material which scavenges radionuclides is widely  
509 accepted as the factor that results in the particle concentration effect (Honeyman et al., 1988;  
510 Honeyman and Santschi, 1989). The colloids provide sorption sites available for particle-  
511 reactive species within the operationally defined “dissolved” phase. Increases in particle  
512 concentration are associated with increases in the amount of colloidal radionuclides (Benoit  
513 and Rozan, 1999). The colloidal radionuclide passes through the 0.45  $\mu\text{m}$  filters and will  
514 result in an overestimate of the dissolved radionuclide fraction ( $A_d$ ) in the water column (Li,  
515 2005) as well as lower  $K_d$  and hence the inverse relationship between  $\log K_d$  and  $\log \text{SPM}$ .  
516 Recent work on the kinetics of thorium scavenging has suggested that the particle  
517 concentration effect could also be explained by a dependency of the loss of thorium from the  
518 particle phase (e.g., by desorption and/or remineralization) on particle concentration (Lerner  
519 et al., 2017) but it is unknown whether this would also apply to  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ . The  
520 slope of the  $\log K_d$  vs.  $\log \text{SPM}$  plot observed for the entire dataset was  $-0.54$  ( $R^2 = 0.22$ ,  $p =$   
521  $0.004$ ,  $n = 35$ ) for  $^{210}\text{Po}$  and  $-0.83$  for  $^{210}\text{Pb}$  ( $R^2 = 0.47$ ,  $p < 0.0001$ ,  $n = 35$ ). This finding is  
522 comparable with the slope of  $-0.79$  for  $^{210}\text{Po}$  and  $-0.78$  for  $^{210}\text{Pb}$  in the East China Sea (Su et  
523 al., 2016), but the slopes of the regression lines are flatter than the values reported in the  
524 water column at Kuala Selangor, Malaysia ( $-1.05$  for  $^{210}\text{Po}$  and  $-1.20$  for  $^{210}\text{Pb}$ ) (Theng and  
525 Mohamed, 2005).

526 This relationship was further examined for coastal and open ocean stations respectively,  
527 and the results show some regional differences. We found a significant negative relationship  
528 between  $\log K_d(\text{Po})$  and  $\log \text{SPM}$  in the coastal waters ( $R^2 = 0.24$ ,  $p = 0.04$ ), whereas no  
529 significant linear correlation was observed in the open ocean (Fig. 8A). In contrast,  $\log$   
530  $K_d(\text{Pb})$  was significantly correlated with  $\log \text{SPM}$  in the open ocean ( $R^2 = 0.91$ ,  $p < 0.0001$ )  
531 but not at the coastal stations (Fig. 8B). It is also worth noting that the  $\log K_d$  values for  $^{210}\text{Po}$   
532 near the coasts tended to be lower at a given particle concentration ( $\text{SPM}: \sim 10\text{-}25 \mu\text{g L}^{-1}$ )  
533 than would have been expected based on the data from the open ocean. In contrast, most  $\log$   
534  $K_d$  values for  $^{210}\text{Pb}$  near the coasts were higher than those observed in the open ocean at the  
535 same range of particle concentration.

536



537  
 538 Fig. 8. The variation in the solid/solution partitioning ( $\log K_d$  in  $\text{L kg}^{-1}$ ) for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  with particle  
 539 concentration ( $\log \text{SPM}$  in  $\mu\text{g L}^{-1}$ ) in the small size fraction from the upper 500 m. (A):  $\log K_d(\text{Po})$  vs.  $\log \text{SPM}$ .  
 540 (B):  $\log K_d(\text{Pb})$  vs.  $\log \text{SPM}$ . The open circles indicate the field data from the three coastal stations (stn.10-1,  
 541 10-9, 11-1). The filled squares represent the data from the four open ocean stations (stn.11-10, -12, -16, -20).  
 542 The black solid line represents the fit to the coastal data, the black dashed line represents the fit to the open  
 543 ocean data, and the red solid line represents the fit to all data. All slopes shown are significant ( $p < 0.05$ ).  
 544

545 These results suggest that the available binding sites for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  for a given  
 546 particle concentration may be different between the coasts and open ocean along the transect,  
 547 probably related to particle size, composition, and origin (Balls, 1989; Honeyman et al.,  
 548 1988). This supports our previous findings in section 4.1, for example, that  $^{210}\text{Po}$  and  
 549 lithogenics were correlated at the coasts but not in the open ocean. Further, the clustering of  
 550 our PCA scores in Fig. 3 suggests a more homogeneous particle composition in the open  
 551 ocean and a more heterogeneous particle composition at the coasts, and the relationships  
 552 between the principal components and proxies for production (SPM) and remineralization  
 553 (AOU, depth) suggest different drivers for the composition of the particles.

#### 4.4. End-member mixing model evaluation: Observed vs. Predicted

Based on our analyses thus far which indicates a significant difference in the drivers of particle composition along our transect, we separated our proportional composition and bulk  $K_d$  (SSF) dataset into coastal ( $n = 17$ ) and open ocean ( $n = 14$ ) stations in order to calculate the partition coefficient for each end-member via non-negative least squares regression (Eq. 4). The significant  $(K_d)_i$  values for each compositional component obtained from the regression for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are listed in Table 3.

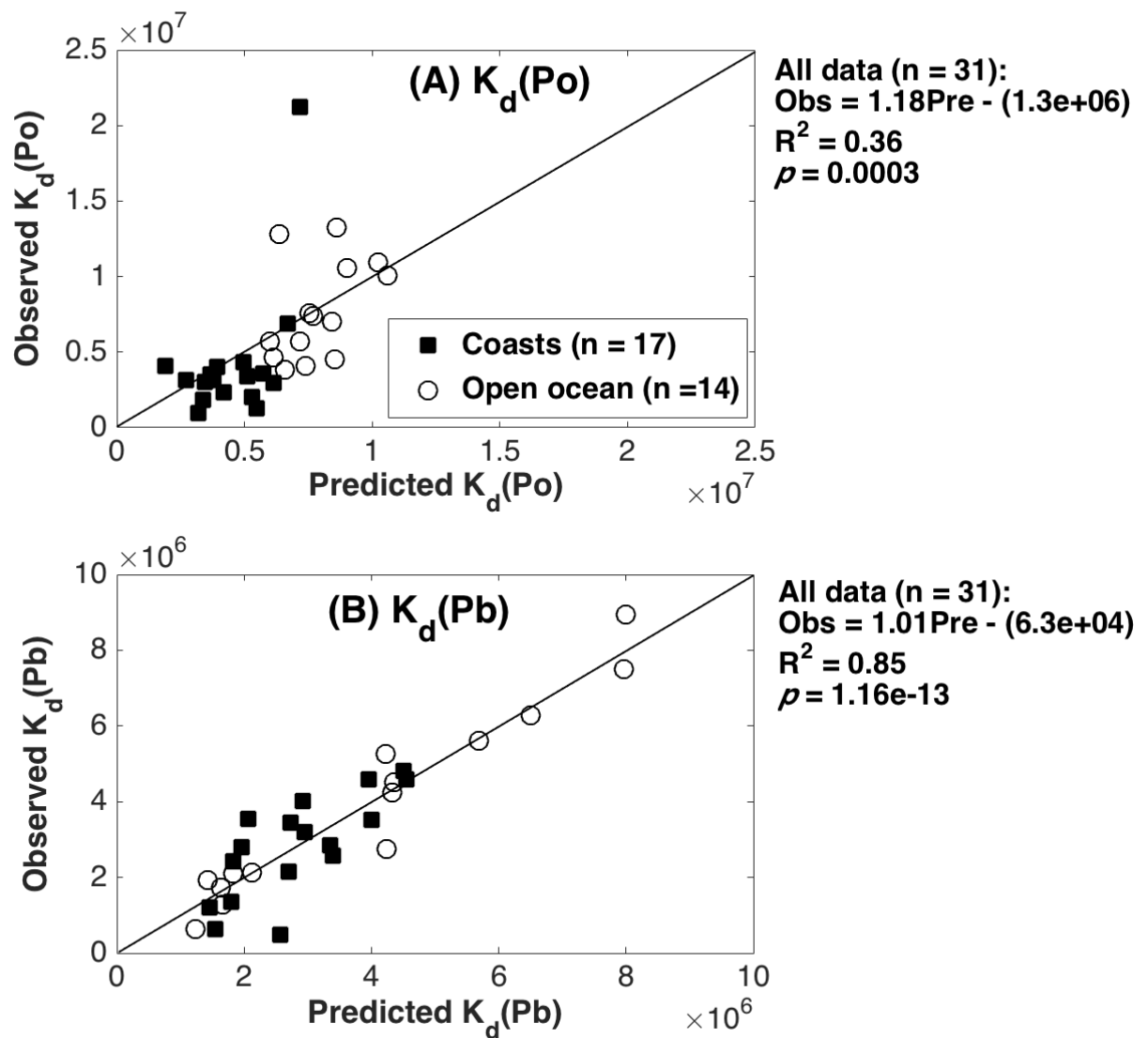
Table 3. Model-predicted distribution coefficients ( $\text{L kg}^{-1}$ ) for  $^{210}\text{Po}$  ( $K_d(\text{Po})_i$ ) and  $^{210}\text{Pb}$  ( $K_d(\text{Pb})_i$ ) for six end members of particulate materials in the small size fraction (SSF) and their associated fraction factors,  $F(\text{Po/Pb}) = K_d(\text{Po})/K_d(\text{Pb})$ .

|                                 | Components        | $K_d(\text{Po})$<br>$\times 10^7$ | $\pm$ | $K_d(\text{Pb})$<br>$\times 10^7$ | $\pm$ | $F(\text{Po/Pb})$ | $\pm$ |
|---------------------------------|-------------------|-----------------------------------|-------|-----------------------------------|-------|-------------------|-------|
|                                 | POM               | -                                 | -     | -                                 | -     | -                 | -     |
| SSF, Coasts<br>( $n = 17$ )     | CaCO <sub>3</sub> | 1.14                              | 0.29  | 0.18                              | 0.05  | 6.3               | 2.4   |
|                                 | Opal              | -                                 | -     | 3.24                              | 0.35  | -                 | -     |
|                                 | Litho             | 0.52                              | 0.18  | 0.3                               | 0.05  | 1.7               | 0.7   |
|                                 | Fe                | -                                 | -     | -                                 | -     | -                 | -     |
|                                 | Mn                | 46.9                              | 45.9  | 18.3                              | 12.3  | 2.6               | 3.0   |
| SSF, Open Ocean<br>( $n = 14$ ) | POM               | 0.6                               | 0.08  | -                                 | -     | -                 | -     |
|                                 | CaCO <sub>3</sub> | 0.5                               | 0.18  | -                                 | -     | -                 | -     |
|                                 | Opal              | -                                 | -     | 6.3                               | 1.86  | -                 | -     |
|                                 | Litho             | 3.7                               | 0.45  | 3.85                              | 0.16  | 1.0               | 0.1   |
|                                 | Fe                | 2173.6                            | 910.1 | 322.2                             | 119.1 | 6.7               | 3.8   |
|                                 | Mn                | -                                 | -     | 87.3                              | 33.2  | -                 | -     |

Substituting  $(K_d)_i$  values from Table 3 into Eq. 3, we can ultimately obtain the model-predicted  $K_d$  value for each sample. Observed  $K_d$  vs. predicted  $K_d$  (OP) regressions were used to evaluate the six-end member mixing model applied in this study. First, we did OP regressions for the coastal ( $n = 17$ ) and open-ocean  $K_d$  data ( $n = 14$ ) separately. The analysis of the coefficient of determination ( $R^2$ ) revealed that 27% of the total variance was explained by the regression model for  $K_d(\text{Po})$  at coasts, and 22% in the open ocean (data not shown). In contrast, 57% and 94% of coastal  $K_d(\text{Pb})$  and oceanic  $K_d(\text{Pb})$  were explained by the OP regression, respectively (data not shown). Then, we applied the OP regressions for the



574 combined data ( $n = 31$ ) from the coasts and open ocean (Fig. 9). The results show 36% of the  
575 total variance across all samples was explained by the regression model for  $K_d(\text{Po})$  (Fig. 9A),  
576 while 85% of the total variance of  $K_d(\text{Pb})$  was explained by the regression model (Fig. 9B).  
577 The regression of OP values was significant for both  $K_d(\text{Po})$  ( $p = 0.0003$ ) and  $K_d(\text{Pb})$  ( $p =$   
578  $1.16\text{e-}13$ ); the slope of OP for  $K_d(\text{Pb})$  was very close to 1 while the slope was further from 1  
579 for  $K_d(\text{Po})$ . The model overestimated observed  $K_d(\text{Po})$  at low values and underestimated it at  
580 high values. Further, the intercept was significantly different from 0 from the OP regression  
581 of  $K_d(\text{Po})$  ( $1.3\text{e}+06$ ) while the  $K_d(\text{Pb})$  intercept was almost two orders of magnitude smaller  
582 (closer to 0). By assessing  $R^2$ , the slope, and intercept of the OP regression, we think that the  
583 model captured the main characteristics of variability of the observed  $K_d(\text{Pb})$  well, while the  
584 modeled  $K_d(\text{Po})$  values were less reflective of the observed values. In other words, particle  
585 composition based on these 6 phases can explain most of the variation in the observed  
586  $K_d(\text{Pb})$ , but it does not explain variation in the  $K_d(\text{Po})$  as well, suggesting either the studied  
587 particle composition here is not an important control on  $K_d(\text{Po})$  or the model is missing one  
588 or more important scavenging end members for  $^{210}\text{Po}$ . This conclusion highlights the caution  
589 which must be taken in interpretation of the end-member partition coefficients for  $^{210}\text{Po}$  in  
590 the following discussion.



591  
 592 Fig. 9. Observed vs. Model predicted  $K_d$  in the small size fraction. (A)  $K_d(\text{Po})$ ; (B)  $K_d(\text{Pb})$ . The filled  
 593 squares and open circles represent the coastal data ( $n = 17$ ) and the open ocean data ( $n = 14$ ), respectively.  
 594 The 1:1 line was plotted in each plot, and overall the prediction captured the majority of variation in the  
 595 observed  $K_d(\text{Pb})$  while the model overestimated observed  $K_d(\text{Po})$  at low values and underestimated it at  
 596 high values. The statistical results of the regression of observed (Obs) vs. predicted (Pre)  $K_d$  values (all  
 597 data,  $n = 31$ ) are also shown in the graphs.

598

#### 599 4.5. End-member partition coefficients

600 While we found that the end-member mixing model could predict the overall  $K_d(\text{Pb})$   
 601 better than the overall  $K_d(\text{Po})$ , we nevertheless investigated the contribution of each phase's

602 partitioning strength ( $K_d$ )<sub>i</sub> to the modeled total  $K_d$ . As above, we found that the ( $K_d$ )<sub>i</sub> of each  
603 phase differed between the coast and the open ocean (e.g.  $K_d(\text{Po})_{\text{Mn}}$  for the coast was  
604 different than  $K_d(\text{Po})_{\text{Mn}}$  for the open ocean). Our results are similar to those of Li (2005)  
605 wherein the ( $K_d$ )<sub>i</sub> contribution of four measured components (lithogenic material, organic  
606 matter, carbonate, opal) for the total  $K_d$  of isotopes of Th, Pa, and Be differed between three  
607 oceanic regions. This may reflect multiple influences on ( $K_d$ )<sub>i</sub> values. The first interpretation  
608 of our results is that each measured compositional component (litho, POM, Fe, Mn, opal, and  
609  $\text{CaCO}_3$ ) is not chemically identical everywhere along the transect. We mentioned this above  
610 when we suggested that there may be different numbers of binding sites for a given  
611 composition and concentration of particles in the coast and open ocean.

612 For the lithogenic and organic (POM) components, this may reflect different elemental  
613 (e.g. Al vs. Ti vs. Fe for litho, (Ohnemus and Lam, 2015), or P content for POM (Twining et  
614 al., 2015b)) or macromolecular (e.g. differences in fatty acid or amino acid content (Stewart  
615 et al., 2007b)) composition of these *aggregated* phases from the coast to the open ocean. For  
616 the mineral phases, the measured elements (Fe, Mn, Ca, Si) may be consistent from the shore  
617 to the center of the gyre, but the organic matrices or biomolecules associated with the  
618 minerals could differ. This has been demonstrated in laboratory experiments where the  
619 organic biopolymers within mineral matrices can change the sorption nature of those  
620 minerals (Chuang et al., 2015; 2013; Yang et al., 2013).

621 Another possible explanation is that partition coefficients are affected by more than  
622 particle composition alone. This has been particularly noted in dynamic, coastal  
623 environments where physical and chemical conditions vary more than in the open ocean. For  
624 example, Turner (1996) highlights salinity affecting trace metal  $K_d$  values in multiple  
625 estuaries, while Balls (1989) asserts that in European coastal waters particle-particle  
626 interactions affect  $K_d$  values, justifying the need to include the SPM loadings in the  
627 calculation of  $K_d$ . That same paper asserts that previous work has found that multiple  
628 physiochemical parameters such as salinity and pH influence partition coefficients. These  
629 additional factors should be kept in mind as we detail the various ( $K_d$ )<sub>i</sub> values found for  $^{210}\text{Po}$   
630 and  $^{210}\text{Pb}$  below (Table 3).

631 Derived end-member  $K_d(\text{Po})_i$  for the six phases were different between the coasts and  
632 open ocean. For example, Fe was not a major scavenging phase of  $^{210}\text{Po}$  at the coasts,

633 whereas it was the most significant scavenger in the open ocean ( $10^{10.3}$  L kg<sup>-1</sup> for <sup>210</sup>Po). Mn  
634 had the opposite trend; the most significant end-member  $K_d(\text{Po})_i$  was derived from Mn at the  
635 coasts while no significant  $K_d(\text{Po})_i$  value was obtained in the open ocean. Nonetheless, the  
636  $K_d(\text{Po})_i$  values for Mn ( $10^{8.7}$  L kg<sup>-1</sup>) and Fe ( $10^{10.3}$  L kg<sup>-1</sup>) at coastal and open ocean stations,  
637 respectively, were orders of magnitude above those for the other carrier phases in their  
638 associated oceanic regime. Previous laboratory work has also found that MnO<sub>2</sub> and Fe(OH)<sub>3</sub>  
639 were important in the binding of <sup>210</sup>Po (Chuang et al., 2013; Yang et al., 2013; 2015). The  
640  $K_d(\text{Po})_i$  values for Fe and Mn reported here, though, are much larger than what has been  
641 previously reported (e.g. Fe<sub>2</sub>O<sub>3</sub>:  $10^{4.48}$  L kg<sup>-1</sup>, MnO<sub>2</sub>:  $10^{5.19}$  L kg<sup>-1</sup>) (Yang et al., 2013). The  
642 above cited studies, however, did not imply that mineral phases were more important than  
643 organic phases. Instead, Chuang et al. (2013) suggested that the direct binding of <sup>210</sup>Po to  
644 organic biopolymers may be obscured due to the close association between mineral carrier  
645 phases and associated biopolymers.

646 There was no significant  $K_d(\text{Po})_i$  value derived for POM at the coasts, while POM was a  
647 major scavenging phase of <sup>210</sup>Po ( $10^{6.8}$  L kg<sup>-1</sup>) in the open ocean. This was consistent with  
648 our previous finding from the pairwise correlations and PCA analyses that there was a  
649 significant association between particulate <sup>210</sup>Po and POM at the open ocean stations but not  
650 at coastal stations. CaCO<sub>3</sub> and lithogenics, on the other hand, did not show significant  
651 difference between coasts and open ocean, with  $K_d(\text{Po})_i$  values for both carrier phases in the  
652 range of  $10^{6.7} - 10^{7.6}$  L kg<sup>-1</sup> in the two contrasting oceanic regimes.

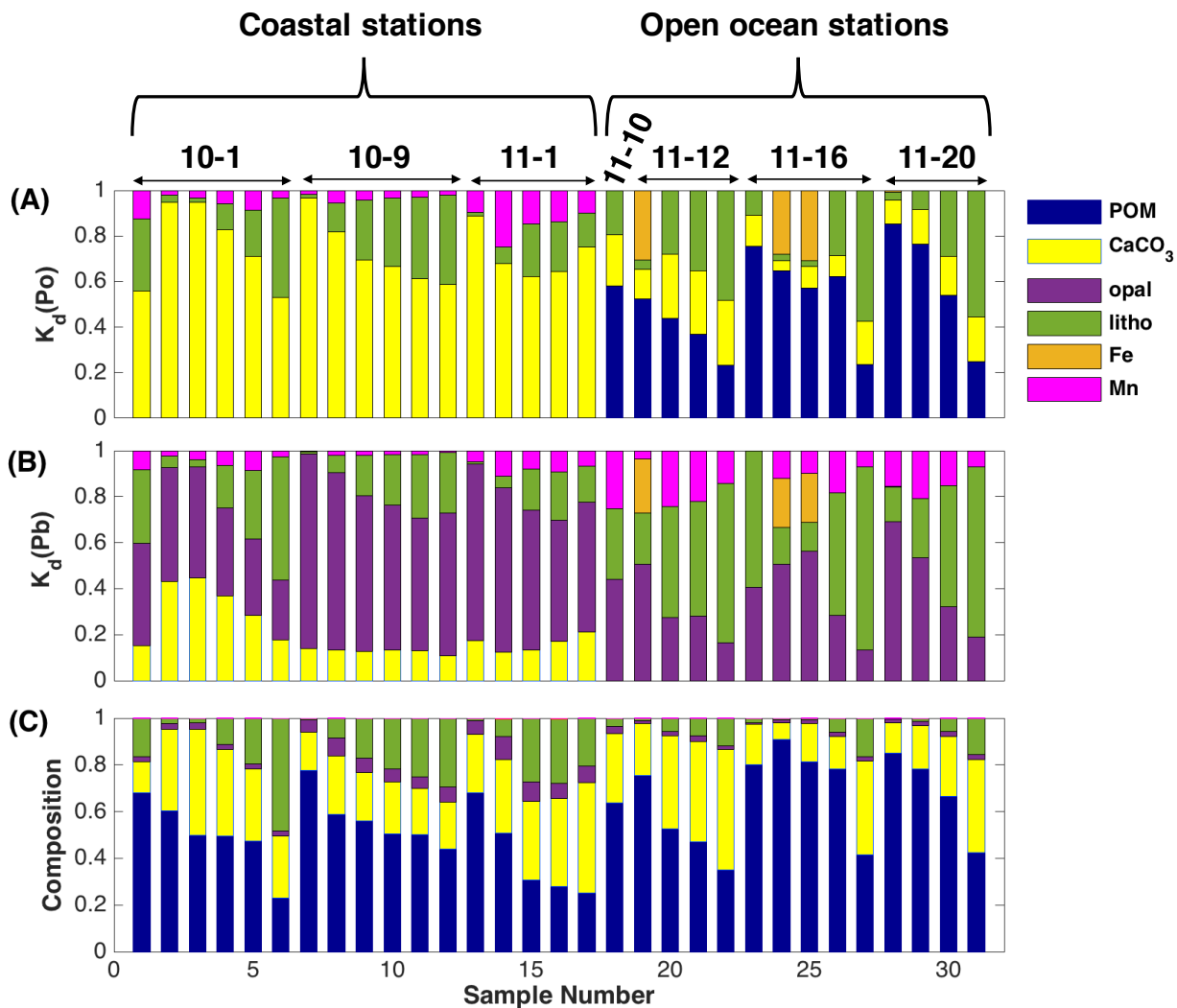
653 Derived end-member  $K_d(\text{Pb})_i$  values for MnO<sub>2</sub>, CaCO<sub>3</sub>, lithogenics, and POM spanned 2-  
654 3 orders of magnitude. We noticed the following relationships for  $K_d(\text{Pb})$  in Table 3:  $K_d$   
655 (Mn) >  $K_d$  (opal) >  $K_d$  (lithogenics) >  $K_d$  (CaCO<sub>3</sub>) ≫  $K_d$  (Fe) ≈  $K_d$  (POM) = 0 at coasts;  $K_d$   
656 (Fe) >  $K_d$  (Mn) >  $K_d$  (opal) >  $K_d$  (lithogenics) ≫  $K_d$  (CaCO<sub>3</sub>) ≈  $K_d$  (POM) = 0 in the open  
657 ocean. The enhanced intensity of scavenging by Mn is consistent with previous work  
658 (Canfield et al., 1995; Swarzenski et al., 1999). Both studies concluded that the behavior of  
659 <sup>210</sup>Pb was tightly coupled to the redox cycling of manganese oxides, but indicated a much  
660 less significant role for iron oxides on the behavior of lead. Indeed, laboratory studies  
661 showed that MnO<sub>2</sub> had one order of magnitude higher  $K_d$  values for <sup>210</sup>Pb than Fe<sub>2</sub>O<sub>3</sub> (Yang  
662 et al., 2013). Nevertheless, the  $K_d(\text{Pb})_i$  values for Fe ( $10^{9.5}$  L kg<sup>-1</sup>) and Mn ( $10^{8.3-8.9}$  L kg<sup>-1</sup>)  
663 derived here are much larger than what have been determined via experimental studies

664 (Fe<sub>2</sub>O<sub>3</sub>: 10<sup>5</sup> L kg<sup>-1</sup>, MnO<sub>2</sub>: 10<sup>6.3</sup> L kg<sup>-1</sup>) (Yang et al., 2013). This suggests that naturally  
665 formed authigenic MnO<sub>2</sub> may be more reactive in terms of adsorption than the pure phase  
666 that has been used in the laboratory studies. Further, the finding that K<sub>d</sub>(Pb)<sub>i</sub> for Mn was  
667 ~100 times greater than the compositional partition coefficients for the other components  
668 (except Fe in the open ocean) appears consistent with the behavior of <sup>230</sup>Th and <sup>231</sup>Pa (Hayes  
669 et al., 2015), and that of Hg (Lamborg et al., 2016) along the same transect, but the results in  
670 those studies were either unexpected or considered a result of methods or operational  
671 definitions. Opal appeared to be another major scavenging phase of <sup>210</sup>Pb as there were  
672 significant K<sub>d</sub>(Pb)<sub>i</sub> values (10<sup>7.5</sup> – 10<sup>7.8</sup> L kg<sup>-1</sup>) derived for opal from our data set. This  
673 finding supports previous work (Friedrich and Rutgers van der Loeff, 2002) and results of  
674 this study (Fig. 6), which both suggest an enhanced intensity of scavenging of <sup>210</sup>Pb by opal.

675 The modeled fractionation factors (F(Po/Pb)), the ratio of end-member K<sub>d</sub>(Po)<sub>i</sub> to end-  
676 member K<sub>d</sub>(Pb)<sub>i</sub>, ranged from 1 to 6.7 in the small particles (Table 3). The end-member  
677 fractionation factors could only be derived when their associated compositional K<sub>d</sub>'s were  
678 available for both <sup>210</sup>Po and <sup>210</sup>Pb. Thus, we only obtained modeled F(Po/Pb) for CaCO<sub>3</sub>,  
679 lithogenics, and Mn for coastal particles, and for lithogenics and Fe for particles in the open  
680 ocean.

681 We further did the OP regression of observed F(Po/Pb) vs. predicted F(Po/Pb) and found  
682 it was significant (R<sup>2</sup> = 0.4, p = 0.0001, data not shown). Even though the predicted K<sub>d</sub>(Po)  
683 values seemed to deviate from the observed K<sub>d</sub>(Po) values, the predicted F(Po/Pb) were  
684 relatively consistent with observed F(Po/Pb) results. We found that the strongest  
685 fractionation between <sup>210</sup>Po and <sup>210</sup>Pb was associated with coastal CaCO<sub>3</sub> (F(Po/Pb) = 6.3)  
686 and open ocean Fe (F(Po/Pb) = 6.7) showing a preference for scavenging <sup>210</sup>Po by both  
687 particulate components. The predicted fractionation factors estimated for lithogenics imply  
688 no preference for scavenging <sup>210</sup>Po over <sup>210</sup>Pb in the open ocean (F = 1), but a weak  
689 preference for <sup>210</sup>Po over <sup>210</sup>Pb at the coasts (F = 1.7).

690



691  
 692 Fig. 10. The fractional contributions of six end members to the predicted bulk distribution coefficients of  
 693 A)  $^{210}\text{Po}$  ( $K_d(\text{Po})$ ), and B)  $^{210}\text{Pb}$  ( $K_d(\text{Pb})$ ), in comparison to the weight fractions of the end members in SPM  
 694 (C) in the upper 500 m. Note that there are two models applied for each  $K_d$ : one is based on coastal data ( $n = 17$ ), the other is open-ocean data ( $n = 14$ ). The horizontal axis represents the sample number (total 31  
 695 samples), ordered from left to right: stn.10-1 ( $n = 6$ ), 10-9 ( $n = 6$ ), 11-1 ( $n = 5$ ), 11-10 ( $n = 1$ ), 11-12 ( $n =$   
 696 4), 11-16 ( $n = 5$ ), 11-20 ( $n = 4$ ) (labeled on the top of the plot).  
 697

698  
 699 Further, we calculated the percent contribution of each end-member to the bulk  
 700 distribution coefficients to assess the importance of each end-member to scavenging (end-  
 701 member  $K_d$  for phase  $i$ ,  $(K_d)_i$ , multiplied by the percent content of phase  $i$ ,  $f_i$ , divided by the  
 702 total predicted  $K_d$ ,  $\sum f_i \cdot (K_d)_i$ ). Fig. 10 summarizes the percent contribution of the six EMs  
 703 to the predicted partition coefficients of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  (Fig. 10A and B, respectively), and

704 the weight percent of each end member in SPM (Fig. 10C). At coastal stations, opal was the  
705 major contributor ( $57.1 \pm 16.1\%$ ) to the predicted  $K_d(\text{Pb})$  in the small particles, followed by  
706  $\text{CaCO}_3$  ( $20.3 \pm 11.1\%$ ), lithogenics ( $17.9 \pm 13.8\%$ ) and Mn ( $4.8 \pm 3.4\%$ ). The major carrier  
707 phases of  $^{210}\text{Pb}$  in the open ocean, in contrast, were lithogenics ( $43.5 \pm 2.0\%$ ) and opal ( $37.8 \pm$   
708  $16.8\%$ ). Further, Mn and Fe in the open ocean contributed to  $K_d(\text{Pb})$  by  $14.0 \pm 7.8\%$  and  $4.8$   
709  $\pm 9.4\%$ , respectively (Fig. 10B).

710 The contributions of the carrier phases for  $^{210}\text{Po}$  were also different between the coasts  
711 and the open ocean; the major contributor to  $K_d(\text{Po})$  was  $\text{CaCO}_3$  ( $73.3 \pm 14.2\%$ ) at coastal  
712 stations vs. POM ( $52.7 \pm 20.1\%$ ) at open ocean stations. Lithogenics contributed  $\sim 20\%$  to  
713 overall  $^{210}\text{Po}$  scavenging (Fig. 10A). Interestingly, we observed Fe contributing  $\sim 30\%$  and  $\sim$   
714  $22\%$  in 3 samples (one at stn.11-10, two at stn.11-16) for  $K_d(\text{Po})$  and  $K_d(\text{Pb})$ , respectively,  
715 despite the low Fe concentrations of these samples ( $\sim 0.011\%$ ). The predicted enhanced  
716 scavenging by Mn and Fe for both  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  is surprising due to both phases' relative  
717 scarcity (low contribution to particle mass). This may highlight a bias in the derived partition  
718 coefficients for particle composition which occurs when using weight percentage rather than  
719 reactive surface area in the end-member mixing model, as suggested by Hayes et al. (2015)  
720 for Th and Pa.

#### 721 **4.6. $^{210}\text{Po}$ vs. $^{210}\text{Pb}$**

722 We observed more significant relationships between  $^{210}\text{Po}$  and POC than between  $^{210}\text{Pb}$   
723 and POC, especially in the open ocean (Table 1). The positive correlation between  $F(\text{Po/Pb})$   
724 and %POC suggests the preference for uptake of  $^{210}\text{Po}$  over  $^{210}\text{Pb}$  by organic carbon and can  
725 be useful in identifying biotic vs. lithogenic particle composition, in the same manner as the  
726 ratio of  $^{210}\text{Po}/^{210}\text{Pb}$  proposed in Radakovitch et al. (1999). A biological signature  
727 ( $F(\text{Po/Pb}) > 1$ ) was observed in the upper 50 m at the coastal stations and upper 300 m in the  
728 open ocean. On the other hand,  $F(\text{Po/Pb})$  values close to or lower than unity at 100 m depth  
729 at stn.10-1, at 135 and 185 m at stn.10-9, and at 58 and 90 m at stn.11-1 suggests a more  
730 lithogenic composition, such as higher contribution from atmospheric dust or continental  
731 margin sediments. Moreover, our end member mixing analysis (EMMA) results show that  
732  $K_d(\text{Pb})$  for lithogenics was a factor of three higher than  $K_d(\text{Pb})$  for POM (Table 3), further  
733 highlighting the important role of lithogenic/inorganic matter in the scavenging of  $^{210}\text{Pb}$ .  
734 These results support the well documented preference for  $^{210}\text{Po}$  uptake over  $^{210}\text{Pb}$  in marine

735 organisms and that  $^{210}\text{Po}$  is both particle-reactive and bio-reactive, whereas  $^{210}\text{Pb}$  is only  
736 particle-reactive (Fisher et al., 1983; Heyraud et al., 1976; Heyraud and Cherry, 1979; Larock  
737 et al., 1996; Stewart and Fisher, 2003; Wilson et al., 2009). The known bio-reactive behavior  
738 of  $^{210}\text{Po}$  and its association with sulfur (Balistrieri et al., 1995; Cherrier et al., 1995; Harada  
739 et al., 1989), both suggest its cycling in particles is more complicated than  $^{210}\text{Pb}$  cycling and  
740 supports our hypothesis that important end-members were missing for the model of  $K_d(\text{Po})$ .  
741 The PCA results also support this conclusion because there was a closer association between  
742  $^{210}\text{Po}$  and AOU than between  $^{210}\text{Pb}$  and AOU, indicating that biological processes affect the  
743 cycling of polonium more than that of lead.

744 An alternative interpretation of the less predictive power of the EMMA for  $^{210}\text{Po}$ , the  
745 model  $K_d(\text{Po})$  values differing from the observed  $K_d(\text{Po})$  values, was suggested in the  
746 methods when we indicated that the uptake of  $^{210}\text{Po}$  by particles is not purely due to  
747 adsorption to particle surfaces as is the nature of  $^{210}\text{Pb}$  uptake.  $^{210}\text{Po}$  can be found associated  
748 with particles via three routes: 1) direct sorption of  $^{210}\text{Po}$  to particle surfaces, 2) the ingrowth  
749 of  $^{210}\text{Po}$  from previously sorbed  $^{210}\text{Pb}$ , and 3) the bioconcentration and biomagnification of  
750  $^{210}\text{Po}$  by organisms. This does not mean that  $K_d(\text{Po})$  has no significance, meaning, or use, it  
751 may, instead, explain why composition alone could not determine  $K_d(\text{Po})$  in this study. It  
752 would be nearly impossible to distinguish the relative contribution of these three pathways,  
753 but this is an avenue of research that should be pursued. While we cannot easily model the  
754 three processes listed above, together they will still result in a higher  $K_d(\text{Po})$  than  $K_d(\text{Pb})$  for  
755 most samples, especially biogenic particles, so the fractionation of the two isotopes can still  
756 be used to trace the export of particles.

## 757 **5. Conclusions**

758 From an investigation into the partitioning of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  activity between particles  
759 and solution in the upper 500 m water column across the North Atlantic basin, and an  
760 analysis of how the particle concentration and composition affect their partitioning, we draw  
761 the following conclusions:

- 762 (1) While both  $K_d(\text{Po})$  and  $K_d(\text{Pb})$  were inversely related to particle concentration, their  
763 relationships differed between the coasts and open ocean, and the particle  
764 concentration effect was strongest for  $K_d(\text{Pb})$  in the open ocean.



- 765 (2) Our correlation and PCA results indicated that the relationships between  $^{210}\text{Po}$  and  
766  $^{210}\text{Pb}$  activity and the composition of coastal and open ocean particles were different,  
767 but that particle concentration (SPM), remineralization/residence time (AOU), and  
768 depth were important drivers of variability in both small and large particles.
- 769 (3) A six-end member particle composition mixing model could accurately predict the  
770 scavenging of  $^{210}\text{Pb}$ , and indicated that opal and lithogenic phases are the major  
771 drivers of  $K_d(\text{Pb})$ . The mixing model could not predict  $K_d(\text{Po})$  with as much accuracy,  
772 indicating either that the model is missing important scavenging end members for  
773  $^{210}\text{Po}$ , (such as sulfur, protein, or another component of organic matter) or that  
774 particle composition alone is not the only driver of  $K_d(\text{Po})$  because the partitioning of  
775  $^{210}\text{Po}$  between the dissolved and particulate phase is more complicated than simple  
776 sorption.
- 777 (4) Despite the complexity of the cycling of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ , and the diversity of particle  
778 concentration and composition measured along the GEOTRACES North Atlantic  
779 Zonal Transect (GA03),  $^{210}\text{Po}$  consistently exhibited a higher affinity for POC than  
780  $^{210}\text{Pb}$ , supporting the use of  $^{210}\text{Po}$  fractionation and disequilibrium from  $^{210}\text{Pb}$ , as a  
781 tracer of the export of organic matter in the surface ocean.

782

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