

1 **Comparison of particulate trace element concentrations in the North Atlantic Ocean as**  
2 **determined with discrete bottle sampling and in situ pumping**

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16 cruises

17 ABSTRACT

18 The oceanic geochemical cycles of many metals are controlled, at least in part, by interactions  
19 with particulate matter, and measurements of particulate trace metals are a core component of the  
20 international GEOTRACES program. Particles can be collected by several methods, including  
21 in-line filtration from sample bottles and in situ pumping. Both approaches were used to collect  
22 particles from the water column on the U.S. GEOTRACES North Atlantic Zonal Transect  
23 cruises. Statistical comparison of 91 paired samples collected at matching stations and depths  
24 indicate mean concentrations within 5% for Fe and Ti, within 10% for Cd, Mn and Co, and  
25 within 15% for Al. Particulate concentrations were higher in bottle samples for Cd, Mn and Co  
26 but lower in bottle samples for Fe, Al and Ti, suggesting that large lithogenic particles may be  
27 undersampled by bottles in near-shelf environments. In contrast, P was 58% higher on average  
28 in bottle samples. This is likely due to a combination of analytical offsets between lab groups,  
29 differences in filter pore size, and potential loss of labile P from pump samples following misting  
30 with deionized water. Comparable depth profiles were produced by the methods across a range  
31 of conditions in the North Atlantic.

32

33 1. INTRODUCTION

34

35 Trace metals play many critical roles in the biogeochemical functioning of the ocean. Many  
36 transition metals are required for the proper function of metalloproteins in phytoplankton (Sunda,  
37 1988/1989). Other metals such as Hg and Pb can be toxic to marine organisms and their  
38 consumers (Mason et al., 2012). Metals can also serve as elemental signatures for specific types  
39 of particulate matter; for example Ti is found in the ocean primarily associated with lithogenic  
40 crustal material while V is enriched in fossil fuel combustion particles (Desboeufs et al., 2005).

41

42 Trace metals can be operationally partitioned into dissolved and particulate fractions, with the  
43 latter typically collected onto filters with pore sizes of 0.2 or 0.4  $\mu\text{m}$ . Particulate material is  
44 comprised of a variety of materials including plankton cells, lithogenic and authigenic minerals,  
45 detrital particles and suspended sediments. Particles can serve both as a source (through  
46 dissolution or remineralization) or sink (through uptake or scavenging) for dissolved metals and  
47 therefore can have a significant impact on metal cycling and fate in the ocean (Goldberg, 1954;  
48 Turekian, 1977). In settings where the particle assemblage is dominated by plankton biomass,  
49 particulate metal concentrations can provide information on the physiology and potentially even  
50 the ecology of the community (Twining and Baines, 2013).

51

52 Measurements of particulate trace metals require close attention to sampling methodology.  
53 Particles are commonly collected onto membrane filters directly from Niskin-X or GO-FLO  
54 bottles (Cullen and Sherrell, 1999; Twining et al., 2011) or via submerged in situ pumps (Bishop  
55 et al., 2012; Ohnemus and Lam, 2014; Sherrell, 1991), while larger sinking particles may also be  
56 collected with sediment traps (Frew et al., 2006; Twining et al., 2014) or deckboard sieves (Ho et  
57 al., 2007). Both approaches have benefits and disadvantages. Rosette-mounted bottles are  
58 commonly available and may be more rapidly deployed, however filtration volumes are typically  
59 10 L or perhaps 30 L at most, limiting absolute sensitivity for low abundance elements such as  
60 Ti. In situ pumps can pass several thousand liters through larger filters but are expensive, labor-  
61 intensive to operate and deploy, and require significantly more wire time to achieve a sampling  
62 resolution similar to bottles.

63

64 Methodological approaches to the digestion, solubilization, and analysis of particulate materials  
65 following collection vary widely and can impact the resulting particulate metal concentrations.  
66 There are numerous formulations of digest solutions using concentrated acids (Bowie et al.,  
67 2010; Cullen and Sherrell, 1999; Eggimann and Betzer, 1976), as well as leaches that use more  
68 dilute acid treatment (Berger et al., 2008; Chester and Hughes, 1967; Lam and Bishop, 2007).  
69 The Supor filter membrane itself provides a digestion challenge (although recent digest  
70 methodology with sulfuric acid may be helping with this (Ohnemus et al., 2014)). Particulate  
71 samples can also bear substantial loads of organic matter and residual seasalt that introduce  
72 matrix effects during element analyses.

73

74 The U.S. GEOTRACES program conducted zonal transect cruises across the North Atlantic in  
75 2010 and 2011. Particulate samples were collected from the full water column via GO-FLO  
76 bottles at 34 stations. In situ pumps were also used to collect particles at 19 of these stations.  
77 Here we compare the concentrations of seven key trace elements in marine particles collected  
78 with both GO-FLO bottles and in situ pumps. Samples were collected at the same depths and  
79 stations but collection times were separated by up to 19 hours, with different collection  
80 platforms, filter membranes, digestion protocols and analytical procedures. We find that  
81 particulate concentrations of most elements were largely consistent between treatments.

82

## 83 2. MATERIALS AND METHODS

84

85 Samples were collected during two US GEOTRACES North Atlantic Zonal Transect (NAZT)  
86 cruises in 2010 and 2011 (Fig. 1). The 2010 cruise sampled from the Mediterranean outflow to  
87 the upwelling system off west Africa to the Cape Verde Islands during late October. The 2011  
88 cruise sampled from the North American shelf to the Cape Verde Islands from November to  
89 early December. Particulate samples were collected from GO-FLO bottles at all 34 stations, and  
90 pump samples were collected at 22 stations.

91

### 92 *Collection and analysis of GO-FLO bottle particle samples*

93 Bottle samples were collected using the GEOTRACES rosette equipped with 24 12-L GO-FLO  
94 bottles (Cutter and Bruland, 2012). Bottles were transported into a clean van and pressurized to

95 <8 psi with 0.2- $\mu$ m filtered air. Prior to filtration each bottle was gently mixed by manually  
96 inverting the bottle several times after removal of unfiltered salt samples to provide some  
97 headspace. Particles were collected onto 25-mm diameter Supor 0.45- $\mu$ m polyethersulfone  
98 filters mounted in Swinnex polypropylene filter holders. Supor filters were cleaned in 1M  
99 reagent-grade HCl at 60°C for 24 hrs and then rinsed copiously with ultrapure water (>18 M $\Omega$ ;  
100 'DI water') prior to use (Cutter et al., 2010). Filtration was continued until the entire bottle was  
101 empty or two hours had elapsed. Filtrate was collected in a container to enable measurement of  
102 filtration volume. An average of 6.5-L of seawater was filtered through each filter. Filter  
103 holders were removed from the GO-Flo bottles and a vacuum applied to remove residual  
104 seawater. Filters were then folded, stored in acid-washed centrifuge tubes, and frozen at -20°C  
105 until digestion and analysis on shore.

106  
107 Digestion and analysis of particles was performed under Class-100 conditions. Filters were  
108 digested in rigorously cleaned 22-mL PFA digestions vials (Savillex). A subset of filters  
109 collected from the shallowest GO-FLO bottle and the deep chlorophyll maximum (DCM) bottle  
110 were first digested in a 1-mL solution of 25% Optima-grade acetic acid and 0.02 M  
111 hydroxylamine hydrochloride following the protocol of Berger et al. (2008). The solution was  
112 heated to 95°C in a water bath for 10 minutes and then allowed to cool to room temperature. The  
113 filter was in contact with the acetic acid leach solution for a total of two hours. The filter was  
114 removed to a separate acid-cleaned PFA vial and was later digested using the mixture of  
115 concentrated acids described below to recover the refractory elements. The acetic  
116 acid/hydroxylamine leachate was centrifuged at 14,000 rpm for 10 minutes to sediment any  
117 remaining particles. Without disturbing particles on the bottom of the tube, approximately 0.8-  
118 mL of leachate was transferred into a 7-mL PFA digestion vial. Optima-grade HNO<sub>3</sub> was added  
119 (100  $\mu$ L) to the 7-mL digestion vial, which was subsequently heated uncapped at 110°C to near  
120 dryness. Vial contents were redissolved in 5 mL 2% HNO<sub>3</sub> (Optima grade).

121  
122 A mixture of concentrated acids was used to digest the refractory particulate fraction, following a  
123 procedure developed by Drs. Peter Morton and Michael Bizimis. Following the labile digest, the  
124 filter and any remaining leachate was transferred to a 22-mL PFA vial, 2-mL of a solution of 4M  
125 HCl, 4M HNO<sub>3</sub>, and 4M HF (all Optima grade) was added, and the vial was tightly capped and

126 heated to 110°C for 4 hours. This procedure solubilizes biogenic and mineral particles, giving  
127 90-113% recoveries for a range of elements (Table 1), while allowing the Supor filter to remain  
128 largely intact (Ohnemus et al., 2014). Following heating, the acid solution in the vial was poured  
129 into a second PFA vial. This step was required due to the brittle nature of Supor filters following  
130 the hot acid step. The filter cannot be removed from the vial without it partially degrading.  
131 Removing the digest acid without disturbing the filter ensures that no filter pieces are present for  
132 the drydown step. To ensure complete transfer of acid, the vials were thoroughly rinsed with 3 ×  
133 0.5-mL aliquots of ultrapure water that were also poured into the secondary vial. The secondary  
134 vial was then heated to dryness and the contents re-dissolved with 2 mL of a 50% Optima-grade  
135 HNO<sub>3</sub> + 15% (v/v) Optima-grade H<sub>2</sub>O<sub>2</sub> solution. This solution was again dried down and the  
136 contents re-dissolved in 5 mL 2% HNO<sub>3</sub>. Filter samples not from the shallowest bottle or DCM  
137 bottle were digested only in the HCl/HNO<sub>3</sub>/HF solution to provide the total particulate metal  
138 fraction. Spikes of Sc-45 and Y-89 were added to digestion vials in order to check recoveries of  
139 analytes through the entire digestion and analysis procedure; overall mean recoveries were 102 ±  
140 20% and 93 ± 17% for Sc-45 and Y-89, respectively, for the entire bottle dataset.

141  
142 All bottle sample digests were analyzed using a Finnegan-MAT Element2 magnetic sector ICP-  
143 MS at the University of Maine following the protocols outlined in Twining et al. (2011). The  
144 instrument is equipped with an ESI Apex desolvation nebulizer, an autosampler contained in a  
145 clean bench, and nickel cones. Cd-111 was analyzed in low-resolution mode, and the remaining  
146 isotopes were analyzed in medium-resolution mode. Multiple isotopes were analyzed for some  
147 elements (e.g., Fe-56, Fe-57); concentrations were within 4%, on average, for both Fe isotopes.  
148 Concentrations of Fe-56 are reported here. Quantification was performed by three-point  
149 standard additions, and In-115 was used as an internal standard to correct for variations in  
150 instrumental sensitivity during analyses.

151  
152 Recoveries and accuracy were assessed by each lab with digestions of the certified reference  
153 materials BCR-414 (plankton, Community Bureau of Reference, Commission of the European  
154 Communities) and PACS-2 (marine sediment, National Research Council of Canada) alongside  
155 sample digestions in order to assess accuracy. These samples were not subject to the same salt  
156 matrix interferences as the pump and bottle samples and were quantified via external standard

157 curves during the same analytical runs as the NAZT samples. Recoveries were typically within  
158 10% of the certified values and within the error of the data, taken from replicate measurements  
159 (Table 1).

160  
161 Precision was determined through replicate analyses of digests of three different particle-laden  
162 filters collected by Lam. These filters were distributed to US GEOTRACES investigators  
163 working on particulate trace element analyses. Each filter was digested, and the digestion  
164 solutions were separately diluted and analyzed during analytical runs in February, November and  
165 December 2012 and July 2013. Coefficients of variation (CV) across laboratories were  
166 calculated from the four analyses for each element (Ohnemus et al., 2014). Mean precision was  
167 generally 10-15% for most elements.

168  
169 *Collection and analysis of in situ pump particle samples*

170 The collection and analysis of size-fractionated particles collected with pumps for total  
171 particulate trace metals are described in Ohnemus and Lam (2014). Here, we briefly highlight  
172 some details that are important for the comparison with the GO-FLO particles. Nominal pump  
173 sampling depths based on wire out targeted the same sample depths as the GEOTRACES rosette  
174 and were corrected for wire angle using a self-recording Seabird 19plus CTD that was deployed  
175 at the end of the pump line. On the second cruise, additional pressure loggers attached to three  
176 pumps further helped to correct for actual depths. Corrections were generally small except along  
177 line W (including stations 2011-1, 2011-6), where strong western boundary currents caused  
178 significant wire angles requiring correction. In situ pump particles were collected using battery-  
179 operated in situ pumps (McLane Research, Inc. WTS-LV) that were modified for dual-flow  
180 collection: the “QMA-side” consisted of a 51  $\mu\text{m}$  polyester prefilter followed by paired quartz  
181 fiber filters (Whatman QMA); the “Supor-side” consisted of a 51  $\mu\text{m}$  polyester prefilter followed  
182 by paired 0.8  $\mu\text{m}$  polyethersulfone (Supor800) filters. Subsamples of the QMA-side prefilter and  
183 the top 0.8  $\mu\text{m}$  Supor filter were used for analysis of the  $>51\mu\text{m}$  and 0.8-51 $\mu\text{m}$  particulate trace  
184 metal size fractions, respectively.

185  
186 Although the 0.8  $\mu\text{m}$  pore size is larger than typical 0.2  $\mu\text{m}$  or 0.45  $\mu\text{m}$  operational cut-offs for  
187 particle collection, this larger pore size was chosen specifically to address requirements unique to

188 in situ pumping (Bishop et al., 2012). These include the requirement for even particle  
189 distribution on the filter for distribution of subsamples to multiple investigators, and the  
190 requirement for adequate volume throughput for the analysis of low abundance radiogenic  
191 isotopes such as  $^{230}\text{Th}$  and Nd isotopes.

192  
193 Upon recovery, filters were lightly misted ( $\sim 100\ \mu\text{L}$ ) with ultrapure water using an acid-leached  
194 metal-free aerosol spray bottle (Nalgene) under vacuum to remove salt. This reduces the matrix  
195 effect corrections needed for the ICP-MS data analysis. A 1/8 subsection of the 51  $\mu\text{m}$  QMA-  
196 side prefilter, representing ca. 145 L, was rinsed at sea using trace-metal clean filtered (0.2  $\mu\text{m}$ )  
197 seawater from the polyester prefilter onto a 25 mm 0.8  $\mu\text{m}$  Supor filter, dried in a laminar flow  
198 bench and stored dried in an acid-clean petrislide until analysis of the large particulate size  
199 fraction. Supor filters were dried in a laminar flow bench, stored in cleanroom polyethylene  
200 bags, and subsampled back on land. A 1/16 subsection of the top Supor filter, representing  $\sim 30$   
201 L, was used for the analysis of the small particulate size fraction.

202  
203 Particle samples were digested using the Piranha digestion followed by the GO-FLO filter  
204 digestion method. Piranha completely digests the Supor filter prior to digestion of the particles  
205 (Ohnemus et al., 2014; Ohnemus and Lam, 2014). Briefly, filters were first digested using a 3:1  
206 sulfuric acid and peroxide mixture (Piranha reagent) at high heat (ca.  $220^\circ\text{C}$ ) to digest particulate  
207 organic material and the Supor filter matrix, then remaining refractory material was digested  
208 using a  $\text{HCl}/\text{HNO}_3/\text{HF}$  (4N each) acid mixture, identical to the GO-FLO particle digestion  
209 cocktail, at  $135^\circ\text{C}$  for 4 hours. Because the Piranha reagent completely dissolves the filter, there  
210 was no need to transfer to a secondary vial as for the GO-FLO particle digestions. Subsequent  
211 dry down steps were as described for the GO-FLO samples, except that the final pellet was re-  
212 dissolved in 2 mL 5%  $\text{HNO}_3$ . The mass of pump particles digested was on average 3x higher  
213 compared to bottle particles. All pump sample digests were analyzed on a Thermo Scientific  
214 Element2 ICP-MS at the WHOI Plasma Facility using a quartz spray chamber introduction  
215 system following protocols described in Ohnemus et al. (2014). Quantification was via 12 multi-  
216 element external standards spanning four orders of magnitude. All samples and standards had 1  
217 ppb Indium as an internal standard for matrix and drift corrections.

218



219 3. RESULTS and DISCUSSION

220  
221 The full water column at each station compared herein was sampled using both methods, but  
222 analyses of bottle-collected samples were performed only on samples from the upper water  
223 column (<1,000 m), primarily the upper 500 m. Target sampling depths for the pumps (8 depths  
224 per cast) were matched with bottle depths (12 depths per cast), but in some cases exact sampled  
225 depths varied due to wire angle and subsurface currents, especially near the North American  
226 margin. Higher sampling resolution by bottles resulted in unmatched depths at some stations.  
227 We limit our pairwise comparisons to bottle and pump samples collected within 5 m of each  
228 other, resulting in a dataset of 91 samples across the transect. The dataset includes only four  
229 paired samples collected from 500-1,000 m.

230  
231 *Digest and process blanks*

232 The sensitivity of particulate trace element measurements is typically limited by the signal  
233 associated with the filters used to collect the samples (Cullen and Sherrell, 1999). Both bottle  
234 and pump sampling programs used Pall Supor polyethersulfone (PES) filters, but bottle  
235 collection utilized 0.45- $\mu\text{m}$  nominal pore-size filters and pump collection utilized 0.8- $\mu\text{m}$  pore-  
236 size filters. Different digestion methods were also used on the bottle and pump samples.  
237 Resulting digest blanks for the two digest methods were similar for P and Ti but 4- to 10-fold  
238 higher in the Piranha digest for Cd, Mn, Co, Fe and Al (Table 2). However it is the median  
239 *process* blank (a filter exposed to particle-free seawater prior to digestion as a sample) that is  
240 subtracted from each sample, and process blanks for the two digest methods were similar after  
241 normalization to filter area (Table 2, Fig. 2). The largest differences were seen in P and Al,  
242 which were 2- to 4-fold higher in bottle process blanks.

243  
244 Process blanks were prepared differently for bottle and pump measurements. Bottle process  
245 blank filters each had 2 L of 0.2- $\mu\text{m}$  filtered water passed through them, while pump process  
246 blank filters were sandwiched within 1- $\mu\text{m}$  polyester mesh in a perforated polypropylene  
247 container and submerged with the pumps, exposing the blank filters to 1  $\mu\text{m}$ -filtered ambient  
248 seawater without actively passing seawater through the filter pores. While this distinction  
249 between exposure vs. active flow likely does not matter for most elements, some elements (e.g.,

250 Al onto quartz fiber filters and Cu onto Supor filters (Planquette and Sherrell, 2012)) may have  
251 flow-dependent adsorption of dissolved species. For example, P concentrations in the bottom  
252 0.8- $\mu\text{m}$  Supor filters (which are only exposed to  $<0.8\mu\text{m}$ -filtered water) from pump deployments  
253 on the U.S. GEOTRACES intercalibration cruises were positively related to filtration volumes  
254 (P.J. Lam and J.K.B Bishop unpublished data). Such an adsorption effect would suggest that P  
255 could be underestimated in process blanks, since neither approach passed a volume of water  
256 equal to the samples through the blank filters. Potential underestimation would be larger for  
257 pump blanks due to the lack of any active flow, however this would not explain the lower pump-  
258 measured P (see below), which would need to be explained by an *overcorrection* for P in pump  
259 process blanks.

260  
261 Although process blanks from both sampling approaches were generally similar on a filter area-  
262 normalized basis, pump-collected filters were loaded with approximately 2.4-fold more particles  
263 than bottle-collected filters. Approximately 6.5 L was passed through most bottle filters, while  
264 ca. 485 L was passed through the average pump filter. This equates to  $3.1 \text{ L cm}^{-2}$  for pump  
265 samples and  $1.3 \text{ L cm}^{-2}$  for bottle samples. Process blank corrections represent a  
266 correspondingly smaller correction for pump than bottle samples for some elements, primarily  
267 the lithogenics. As shown in Table 3, median and mean process blank percent corrections for P,  
268 Cd, Mn, and Co were similar for bottle and pumps. However, lower bottle sample loading  
269 resulted in consistently higher process-blank percent corrections for Fe, Al, and Ti. In both  
270 datasets the samples with larger Fe, Al, and Ti corrections (approaching and even exceeding  
271 50%) were those collected at the DCM, where packaging and vertical export appears to lower  
272 lithogenic particle concentrations while elevated biomass reduces filtration volumes. By  
273 comparison, the largest P corrections (20-30%) were seen in deep ( $>500 \text{ m}$ ) samples with very  
274 low plankton biomass. The process blank corrections for bottle filters are somewhat higher (ca.  
275 2-5 fold for P, Mn, Fe and Al) than those reported for SAFe station by Planquette and Sherrell  
276 (2012). This may result from use of filtered deep water for process blanks by Planquette and  
277 Sherrell (2012), whereas water from shallow, deep and mid-water depths was used in this study.  
278 Additionally, dissolved Mn, Fe and Al are higher in Atlantic waters than in Pacific waters, which  
279 likely contribute to somewhat higher process blanks.

280

281 *Vertical profiles*

282 The two particle sampling approaches produced similar element profiles at both near-shore and  
283 open-ocean stations. At station 2011-1, located in 2,100 m of water at the edge of the North  
284 American shelf (Fig. 1), biogenic elements P and Cd were elevated in the upper 60 m in both  
285 datasets, although bottle samples present >2-fold higher concentrations (Fig. 3a) Particulate Mn  
286 concentrations were highest in the DCM (58 m). The primarily lithogenic elements Al, Fe and  
287 Ti presented a sub-surface maximum from 90 to 180 m. Cobalt, which often presents a hybrid  
288 distribution between biogenic and lithogenic elements (Saito and Moffett, 2002), is slightly  
289 elevated in sub-surface waters between 90 and 180 m like Al, Fe and Ti, but the highest  
290 concentration is at the surface like P and Cd. With the exception of Mn and Co concentrations at  
291 the uppermost depth, the bottle and pump datasets present very similar biogeochemical stories.

292  
293 Bottle and pump data also show similar features at stations further offshore. At station 2011-6,  
294 located farther from the shelf in 4,500 m of water 275 km to the southwest of station 2011-1,  
295 concentrations of P and Cd were again strongly elevated in the upper 100 m, with higher  
296 concentrations in bottle samples (Fig. 3b). Although surface concentrations were at least 3-fold  
297 lower than at station 2011-1, both datasets show Al, Fe and Ti to be depleted in upper 130 m and  
298 increasing below. Again Mn presents the outlier, with diverging profile shapes and  
299 concentrations. Cobalt concentrations are in better agreement, except at 140 m, where Co may  
300 have been scavenged or co-precipitated onto Mn oxides captured by the bottle sample. At station  
301 2011-16 in the middle of the North Atlantic Ocean, plankton biomass (as indicated by particulate  
302 P concentrations) was 4- to 5-fold lower than at the other stations (Fig. 3c). Particulate P, Cd  
303 and Co all have sub-surface peaks at the DCM (90 m) in the bottle samples, but the pump  
304 samples show highest concentrations of these elements either at the surface (P and Co) or below  
305 the DCM (Cd at 137 m). Surface particulate Mn is an order of magnitude lower here than at the  
306 other two stations, but bottle and pump profiles agree fairly well. Al, Fe and Ti show matching  
307 sub-surface minima around 100 m in both datasets. There is also agreement at deeper depths.  
308 On the eastern side of the North Atlantic basin and closer to the African continent, profiles from  
309 station 2010-10 provide one of the few comparisons >500 m (Fig. 3d). Particulate P, Cd, Co and  
310 Mn concentrations are consistent >300 m, with the exception of a feature at ca. 400 m that  
311 appears to not have been sampled by bottles.

312

313 Absolute particulate element concentrations vary to some extent between bottle and pump  
314 samples taken from matching stations and depths, but such variability is not surprising given the  
315 heterogeneous and dynamic nature of particles, especially in the euphotic zone. Since bottle and  
316 pump samples were collected on different casts, separated by up to 19 h, we are generally  
317 encouraged by the consistency of trends in particle concentrations between the techniques across  
318 a range of oceanographic conditions.

319

#### 320 *Offsets between bottles and pumps*

321 The profile comparisons do suggest there may be consistent offsets in the measured  
322 concentrations of some elements (i.e., P and Cd), especially in surface waters. Such offsets were  
323 examined more rigorously through pairwise comparisons of the data. Particulate data were log-  
324 transformed to stabilize variance, as particulate element concentrations varied more than 10-fold  
325 between stations and between depths. Statistically significant differences ( $p < 0.05$ , Wilcoxon  
326 signed rank test) were observed for some of the labile elements (Table 4). Geometric mean  
327 particulate P was 58% higher in bottle samples compared to pump samples across the transect;  
328 this was the largest and most statistically significant difference ( $p < 0.0001$ ). Bottle-based  
329 concentrations of particulate Cd, Co and Mn were 7-8% higher than pump-based concentrations,  
330 and these differences were statistically significant for Co and Mn. Particulate concentrations of  
331 the lithogenic elements (Fe, Al and Ti) were 3-13% lower in bottle samples, and these  
332 differences were not significant. Thus, the elements can be grouped into three categories of  
333 common behavior: biomass elements (P), labile elements (Cd, Co and Mn), and refractory  
334 elements (Fe, Al, Ti).

335

336 Previous pump-bottle comparisons have found higher concentrations of POC in bottle samples  
337 compared to pump samples (e.g., Gardner et al., 2003; Liu et al., 2009). A variety of in situ  
338 pump filter holder designs were tested during the GEOTRACES intercalibration cruises, and it  
339 was found that the filter holder designs used in those previous studies were prone to losing large,  
340 organic-rich particles, which could explain the up to 200x lower POC on pump samples collected  
341 from highly productive regions like the Ross Sea (Bishop et al., 2012). The filter holders used

342 during the North Atlantic GEOTRACES cruise were designed to solve the problem of large  
343 particle loss, so this is unlikely to be an explanation for pump-bottle offsets observed here.

344  
345 Consistent offsets in bottle and pump particulate element concentrations, as described above,  
346 could be caused by a number of factors. First, the two systems may collect somewhat different  
347 populations of particles. Bottle samples were collected onto 0.45- $\mu\text{m}$  filters, and pump samples  
348 were collected onto 0.8- $\mu\text{m}$  filters; thus bottle samples likely collect sub-micron particles more  
349 efficiently. However it should be noted that these are nominal pore sizes, and effective filtration  
350 efficiency will also be affected by particle loading. In addition, the average time elapsed  
351 between particle collection from the bottles and from the pumps was 11 hours (range was 3-19  
352 hours). Euphotic zone particle abundance can vary by 25% diurnally at oligotrophic stations  
353 (Bishop and Wood, 2008). Additionally, pumps may collect larger lithogenic particles more  
354 efficiently, as such particles may settle in GO-FLO bottles prior to sampling. Bottles were  
355 mixed immediately prior to filtration and filtration times kept to  $<2$  h; this has been indicated to  
356 adequately sample such fast-sinking particles (Planquette and Sherrell, 2012). However the  
357 possibility for undersampling remains. Second, the collected particulate samples were handled  
358 somewhat differently. Bottle samples were stored at  $-20^{\circ}\text{C}$  without rinsing, while pump samples  
359 were misted with deionized water to minimize seasalt retention prior to drying. Third, the  
360 samples were digested using different techniques. These digest techniques have been carefully  
361 intercalibrated (Ohnemus et al., 2014), but the digests do have minor differences in the  
362 recoveries of some elements. Finally, the entire processes—sampling to handling to digest to  
363 analysis—have different blanks, and correction for these may introduce offsets. We will  
364 examine these possible causes for each category of elements.

365  
366 The largest and most significant offset was observed for P, which is primarily associated with  
367 and used as a proxy for biogenic particles (i.e., plankton) in the ocean. Particulate P  
368 concentrations varied by approximately 30-fold across the section, with the highest plankton  
369 biomass observed near the North American and African margins (Fig. 4a). The slope of the  
370 regression line for scatterplot of log bottle P vs. log pump P is less than 1 ( $0.86 \pm 0.06$ , Table 4)  
371 and comes closest to the 1:1 line at higher particulate P concentrations (Fig. 4a). It is unclear  
372 what the source of this offset is. The most consistent offsets of bottle and pump data are seen in

373 samples from deeper waters with low P concentrations (Fig. 5). This suggests that blank  
374 corrections may contribute to the offsets. However higher P is observed in the bottle sample for  
375 all but approximately 6 samples, including all but 2 samples with particulate P above 10 nM.  
376 Therefore, differences in process blank corrections are unlikely to explain most of the overall  
377 offset, since process blanks represent only a small fraction of the sample signal at high  
378 particulate P loading (Table 3). More efficient collection of smaller cells (i.e.,  
379 picophytoplankton and bacteria <1µm that dominate in the sub-tropical gyres and at depth) likely  
380 explains part of the offset, as noted above. For example, at station 2011-16 a clear peak in  
381 particulate P is observed at the DCM in the bottle data (Fig. 3c) that is likely to be  
382 *Prochlorococcus* (DuRand et al., 2001). These cells have a mean cell size (0.68 µm; DuRand et  
383 al., 2001) below the pore size of the pump filters, and indeed no particulate P peak is seen in the  
384 pump data. However an offset is also observed at near-margin stations characterized by larger  
385 plankton taxa (B. Twining, unpublished data), and offsets were distributed throughout the water  
386 column and not limited to DCM depths dominated by cyanobacteria.

387  
388 Offsets between bottle and pump concentrations may be caused by a combination of inter-lab  
389 analytical and methodology differences. Both Twining and Lam laboratories achieved good  
390 recoveries for CRMs (Table 1) (Ohnemus et al., 2014), but P concentrations in the  
391 intercalibration pump samples determined by Twining lab were consistently higher ( $22 \pm 15\%$ )  
392 than concentrations determined by Lam lab. However there was a large deviation around the  
393 bottle/pump offset: pairwise differences between bottle and pump concentrations were  $46\% \pm$   
394  $41\%$  of the average of the paired measurements. So the differences are not caused by a simple  
395 calibration offset. Other differences may be caused by the effect of misting pump filters with  
396 distilled water. Particulate P has been shown to be extremely labile and prone to loss during  
397 sample handling (Collier and Edmond, 1984). Misting samples while under vacuum may cause  
398 loss of labile P compounds, however comparison of misted and un-misted QMA filters collected  
399 during the 2009 GEOTRACES intercalibration cruise did not show significant differences in P or  
400 Cd:P (Bishop, pers. comm.). Using particulate organic carbon (POC) concentrations determined  
401 with QMA filters collected in parallel on the pumps, we calculate a mean C:P= $128 \pm 48$  in the  
402 upper 300 m using pump P. This is consistent with a compilation of hundreds of C:P

403 observations from coastal and open ocean particulate matter (C:P=155 ± 53) (Sterner et al.  
404 2008), showing that the pump samples are internally consistent with expected stoichiometry.  
405

406 Particulate concentrations of the labile elements Cd, Co and Mn from the two sampling systems  
407 were within 10% of each other in the paired dataset. Cadmium concentrations were not  
408 significantly different, on average, and the slope of the bottle vs. pump scatter plot was not  
409 significantly different from 1 (Fig. 4b). The largest offsets were seen at the lowest Cd  
410 concentrations, where bottle measurements fell well below pump measurements. This may be  
411 caused by overcorrection for process blanks in bottle samples at the lowest concentrations. Even  
412 though Cd is remineralized in concert with P (Boyle et al., 1976), the loss of P but not Cd from  
413 misting is consistent with previous leaching experiments conducted on plankton tow samples that  
414 show that more P is lost to leach solutions than Cd (Collier and Edmond, 1984). Particulate Co  
415 and Mn also showed 7-8% offsets. In both cases the slope of the regression line was <1 ( $0.81 \pm$   
416  $0.5-0.8$ ; Table 4) and crossed the 1:1 line at higher concentrations (Figs. 4c-d). Thus there was  
417 good agreement between datasets at higher concentrations and slight offsets at lower  
418 concentrations, again with higher concentrations seen in the bottle data. Lower bottle process  
419 blanks for both elements may help explain this. Consistent differences in the recoveries of these  
420 elements were not seen during the digestion intercalibration (Table 1), as expected since the  
421 labile nature of Cd, Co and Mn enable complete solubilization without rigorous treatment.  
422

423 Particulate concentrations of the lithogenic elements Fe, Al and Ti show a different trend. Paired  
424 bottle concentrations were on average slightly lower than pump concentrations, but the  
425 differences were not significant. Regression slopes were substantially less than 1 ( $0.64-0.80$ ;  
426 Table 4) and appear to be driven by higher values in the pump samples from high lithogenic  
427 samples (Figs. 4e-g). Consistent offsets were seen in the concentrations at stations 2011-1 and  
428 2011-2, both near the North American margin. Additionally, concentrations of Fe, Al and Ti in  
429 the intercalibration pump samples were 17-24% lower as determined using the Twining lab  
430 digestion procedure than as determined using the Piranha digestion in the Lam lab (Ohnemus et  
431 al., 2014), so there again appear to be minor but potentially consistent offsets between the labs.  
432 The regression data indicate rather that bottles may be undercollecting larger lithogenic particles  
433 near the shelf. The lithogenic elements in the samples with the highest concentrations are largely

434 >51 $\mu$ m (Fig. 6), and these fast-sinking particles are prone to be missed with bottle collection  
435 (Gardner, 1977). Supporting this, Planquette and Sherrell (2012) found particulate Al in the  
436 upper water column (<300 m) at near-shore stations to be most prone to particle sinking artifacts  
437 in GO-FLO bottles. Although mixing bottles immediately prior to sampling generally keeps  
438 particles suspended in bottles (Planquette and Sherrell, 2012), larger, dense, fast-sinking  
439 lithogenic particles are generally more effectively sampled with in situ pumping.

440  
441 The data presented here demonstrate that comparable particulate trace element concentrations  
442 and profiles can be obtained using either GO-FLO bottles or in situ pumps. Measurements of  
443 particulate trace elements and their isotopes are a core component of the international  
444 GEOTRACES program (GEOTRACES, 2006) and are required to obtain mass balance and  
445 understand particulate sources and sinks of trace elements. In situ pumps generate large  
446 quantities of particles that enable sharing of samples from the same cast with multiple  
447 investigators. Large quantities of rare particulate analytes such as Th and Nd and trace metal  
448 stable isotopes can also be obtained. However shiptime and resource constraints preclude pump  
449 deployments on many cruises, so it is important that comparable particulate data be collected  
450 with bottles. This study places constraints on such comparisons, finding mean concentrations to  
451 be within 10% for most elements. Particular care is needed when considering highly labile  
452 elements such as P. Rigorous analytical intercalibration is recommended, as methodological  
453 differences can result in small but significant offsets. Such intercalibration is a hallmark of the  
454 GEOTRACES program.

455  
456 If a specific particle type is the focus of study, sampling protocols can be optimized for that  
457 particle type. As noted above, large fast-sinking lithogenics are likely to be more accurately  
458 sampled by pumps. Additionally, the large volumes filtered by pumps enable more accurate  
459 determination of rarer lithogenic elements like Ti in productive coastal waters where filters are  
460 prone to clogging by biogenic particles. In such situations absolute Ti concentrations in bottle  
461 samples may be low and prone to uncertainty from blank corrections. Studies of metal cycling  
462 by biogenic particles may benefit from bottle sampling, as these samples can be precisely  
463 targeted to specific depths with CTD instrumentation and matched with complementary  
464 measurements (i.e., of community composition or nutrient concentrations) on water from the



465 same bottles. Bottles are also amenable to higher resolution sampling within the euphotic zone,  
466 as well as the use of smaller pore-size filters to capture prokaryotic plankton. In contrast, pumps  
467 can enable collection of high-volume particle samples for other complementary high-volume  
468 analyses such as radioisotopes or proteins. Thus, the choice of sampling approach will be driven  
469 by available resources and scientific questions.

470

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565  
566

TABLES

**Table 1.** Percent recoveries of several certified reference materials (CRMs) for the digest procedures used to analyze particulate filters. Recoveries are shown relative to certified or informational values (in brackets). Uncertainties for all recovered values are  $\pm 1$  SD, when available.

	n	P	Cd	Mn	Co	Fe	Al	Ti
<i>BCR-414</i>								
Bottle	14	[113 $\pm$ 18]	94 $\pm$ 30	93 $\pm$ 6	[92 $\pm$ 17]	[100 $\pm$ 11]	[102 $\pm$ 14]	--
Pump	4-6	[128 $\pm$ 21]	96 $\pm$ 16	102 $\pm$ 13	[126 $\pm$ 25]	[114 $\pm$ 14]	[116 $\pm$ 17]	--
<i>PACS-2</i>								
Bottle	8	103 $\pm$ 15	90 $\pm$ 11	95 $\pm$ 8	90 $\pm$ 9	96 $\pm$ 9	95 $\pm$ 14	90 $\pm$ 10
Pump	5	101 $\pm$ 6	106 $\pm$ 11	96 $\pm$ 6	106 $\pm$ 17	99 $\pm$ 8	97 $\pm$ 10	95 $\pm$ 5

**Table 2.** Digest blanks, process blanks, and limits of detection for bottle and pump filter analysis. Bottle process blanks have 2L of 0.2- $\mu\text{m}$  filtered seawater passed through them on ship. Pump process blanks are submerged with the pumps, but seawater is not actively passed through the filters. Values are medians  $\pm$  SD of 19 and 15 replicates for the bottle and pump process blanks, respectively. Bottle blanks are for the GO-FLO filter digestion technique.

	P	Cd	Mn	Co	Fe	Al	Ti
<i>Digest blank</i>							
<i>(pmol/vial)</i>							
Bottle	113 $\pm$ 120	0.01 $\pm$ 0.02	0.8 $\pm$ 0.5	0.11 $\pm$ 0.14	25 $\pm$ 9	145 $\pm$ 139	44 $\pm$ 53
Pump	154	0.12	6.7	0.54	144	570	83
<i>Process blank</i>							
<i>(pmol/cm<sup>2</sup>)</i>							
Bottle	358 $\pm$ 261	0.018 $\pm$ 0.008	2.0 $\pm$ 1.5	0.051 $\pm$ 0.024	64 $\pm$ 27	558 $\pm$ 316	47 $\pm$ 35
Pump	145 $\pm$ 47	0.035 $\pm$ 0.016	2.1 $\pm$ 0.72	0.053 $\pm$ 0.078	49 $\pm$ 27	131 $\pm$ 56	29 $\pm$ 28
<i>Limit of detection</i>							
<i>(pmol/cm<sup>2</sup>)</i>							
Bottle	780	0.024	4.6	0.073	81	950	104
Pump	290	0.048	2.2	0.23	81	170	28

**Table 3.** Process blank corrections as a percentage of the uncorrected sample (calculated as digest blank-corrected process blank/digest blank-corrected sample). Data are for all total digests.

	P	Cd	Mn	Co	Fe	Al	Ti
<i>Bottle (n=239-252)</i>							
Median	5.3	2.2	1.2	1.1	3.6	10.4	19.0
Mean $\pm$ SD	6.8 $\pm$ 5.2	3.6 $\pm$ 3.8	2.1 $\pm$ 2.7	1.3 $\pm$ 0.9	5.4 $\pm$ 5.1	15.3 $\pm$ 15.1	23.2 $\pm$ 16.3
Range	0.97-30	0.024-25	0.17-15	0.079-6	0.041-29	0.74-85	2.8-84
<i>Pump (n=320-334)</i>							
Median	4.5	3.8	0.7	1.3	1.4	1.2	6.8
Mean	6.3 $\pm$ 5.8	9.3 $\pm$ 12.9	0.9 $\pm$ 1.0	1.4 $\pm$ 0.9	2.6 $\pm$ 3.3	2.8 $\pm$ 4.3	13 $\pm$ 18
Range	0.31-22	0.085-41	0.004-9	0.009-6	0.004-20	0.003-24	0.019-50

**Table 4.** Pair-wise comparisons of pump and bottle data. Mean ( $\pm$  SE) differences between logged pump and logged bottle concentrations (bottle – pump) are shown in the first row. Statistical significance of these differences was tested with the non-parametric Wilcoxon signed rank test, and  $p$ -values are presented below the mean differences ( $p$ -values  $< 0.05$  in bold). Geometric mean ratios of bottle to pump data are shown in row 3. The bottom row presents the slope  $\pm$  SE of linear fit to log-log plot (log bottle on y-axis, log pump on x-axis).  $n = 83-91$ .

	P	Cd	Mn	Co	Fe	Al	Ti
Mean difference between pairs	0.199	0.029	0.031	0.033	-0.020	-0.06	-0.013
	$\pm 0.021$	$\pm 0.033$	$\pm 0.024$	$\pm 0.018$	$\pm 0.029$	$\pm 0.036$	$\pm 0.041$
$p$ -value	<b>&lt;0.0001</b>	0.2685	<b>0.0212</b>	<b>0.0023</b>	0.9080	0.4647	0.9799
Mean bottle/pump ratio	1.58	1.07	1.07	1.08	0.95	0.87	0.97
Slope of log-log plot	0.86	1.04	0.81	0.81	0.74	0.80	0.64
	$\pm 0.06$	$\pm 0.10$	$\pm 0.05$	$\pm 0.08$	$\pm 0.05$	$\pm 0.06$	$\pm 0.06$

## FIGURE CAPTIONS

**Fig. 1.** Map showing cruise stations for which data are compared. Triangles indicate stations for which profiles are shown in Fig. 3. The locations of the Bermuda Atlantic Timeseries (BATS), TAG hydrothermal vent, and Cape Verde Island stations are indicated.

**Fig. 2.** Mean ( $\pm$  SD) process blanks for bottle and pump samples.

**Fig. 3.** Depth profiles of particulate trace metals in the North Atlantic Ocean as determined using GO-FLO bottles or in situ pumps. The stations span an onshore-offshore gradient, with Station 2011-1 (A) located at the edge of the continental shelf 200 km from land, Station 2011-6 (B) located in between Cape Cod and Bermuda 475 km from land, and Station 2011-16 (C) located in the middle of the North Atlantic basin nearly 3,000 km from a continental landmass. Station 2010-10 (D) is located between the African continent and Cape Verde Islands. The dashed line in each figure shows the depth of the sub-surface chlorophyll maximum.

**Fig. 4.** Scatterplots of particulate (A) P, (B) Cd, (C) Co, (D) Mn, (E) Fe, (F) Al, and (G) Ti concentrations as determined using GO-FLO bottles or in situ pumps across all stations. Each datapoint corresponds to a specific station and depth from which both bottle and pump values were determined within 5m of each other. Axes present particulate concentrations on a logarithmic scale. Symbol color indicates the distance of the station from the beginning of the transect (approx. the North American continental shelf). The black line indicates a 1:1 relationship between the bottle and pump concentrations. The red line is the fit of a linear regression to the log-transformed data.

**Fig. 5.** Scatterplot of particulate P concentrations as determined using GO-FLO bottles or in situ pumps across all stations, with symbol color indicating the depth from which the samples were collected. Axes present particulate concentrations on a logarithmic scale.

**Fig. 6.** Scatterplot of particulate Fe concentrations in the sinking fraction ( $>51 \mu\text{m}$ ) plotted against total particulate Fe concentrations. All concentrations determined using in situ pumps. Symbol color indicates the distance of the station from the beginning of the transect. Axes present particulate concentrations on a logarithmic scale.