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

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ABSTRACT

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

1. INTRODUCTION

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

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

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

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

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

2. MATERIALS AND METHODS

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

Collection and analysis of GO-FLO bottle particle samples

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

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

Digestion and analysis of particles was performed under Class-100 conditions. Filters were digested in rigorously cleaned 22-mL PFA digestions vials (Savillex). A subset of filters collected from the shallowest GO-FLO bottle and the deep chlorophyll maximum (DCM) bottle were first digested in a 1-mL solution of 25% Optima-grade acetic acid and 0.02 M hydroxylamine hydrochloride following the protocol of Berger et al. (2008). The solution was heated to 95°C in a water bath for 10 minutes and then allowed to cool to room temperature. The filter was in contact with the acetic acid leach solution for a total of two hours. The filter was removed to a separate acid-cleaned PFA vial and was later digested using the mixture of concentrated acids described below to recover the refractory elements. The acetic acid/hydroxylamine leachate was centrifuged at 14,000 rpm for 10 minutes to sediment any remaining particles. Without disturbing particles on the bottom of the tube, approximately 0.8-mL of leachate was transferred into a 7-mL PFA digestion vial. Optima-grade HNO_3 was added (100 µL) to the 7-mL digestion vial, which was subsequently heated uncapped at 110ºC to near dryness. Vial contents were redissolved in 5 mL 2% HNO_3 (Optima grade).

A mixture of concentrated acids was used to digest the refractory particulate fraction, following a procedure developed by Drs. Peter Morton and Michael Bizimis. Following the labile digest, the filter and any remaining leachate was transferred to a 22-mL PFA vial, 2-mL of a solution of 4M HCl, 4M HNO_3, and 4M HF (all Optima grade) was added, and the vial was tightly capped and

heated to 110°C for 4 hours. This procedure solubilizes biogenic and mineral particles, giving 90-113% recoveries for a range of elements (Table 1), while allowing the Supor filter to remain largely intact (Ohnemus et al., 2014). Following heating, the acid solution in the vial was poured into a second PFA vial. This step was required due to the brittle nature of Supor filters following the hot acid step. The filter cannot be removed from the vial without it partially degrading. Removing the digest acid without disturbing the filter ensures that no filter pieces are present for the drydown step. To ensure complete transfer of acid, the vials were thoroughly rinsed with 3 × 0.5-mL aliquots of ultrapure water that were also poured into the secondary vial. The secondary vial was then heated to dryness and the contents re-dissolved with 2 mL of a 50% Optima-grade HNO_3 + 15% (v/v) Optima-grade H_2O_2 solution. This solution was again dried down and the contents re-dissolved in 5 mL 2% HNO_3. Filter samples not from the shallowest bottle or DCM bottle were digested only in the HCl/HNO_3/HF solution to provide the total particulate metal fraction. Spikes of Sc-45 and Y-89 were added to digestion vials in order to check recoveries of analytes through the entire digestion and analysis procedure; overall mean recoveries were 102 ± 20% and 93 ± 17% for Sc-45 and Y-89, respectively, for the entire bottle dataset.

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

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

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

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

Collection and analysis of in situ pump particle samples

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

Although the 0.8 µm pore size is larger than typical 0.2 µm or 0.45 µm operational cut-offs for 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}Th and Nd isotopes.
192
193 Upon recovery, filters were lightly misted (~100 µL) 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 µm QMA-
196 side prefilter, representing ca. 145 L, was rinsed at sea using trace-metal clean filtered (0.2 µm)
197 seawater from the polyester prefilter onto a 25 mm 0.8 µm 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 ~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°C) to digest particulate
207 organic material and the Supor filter matrix, then remaining refractory material was digested
208 using a HCl/HNO_3/HF (4N each) acid mixture, identical to the GO-FLO particle digestion
209 cocktail, at 135˚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% 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

3. RESULTS and DISCUSSION

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

Digest and process blanks

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

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

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

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

Vertical profiles

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

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

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

Offsets between bottles and pumps

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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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 ± 1 SD, when available.

	n	P	Cd	Mn	Co	Fe	Al	Ti
BCR-414								
Bottle	14	[113 ± 18]	94 ± 30	93 ± 6	[92 ± 17]	[100 ± 11]	[102 ± 14]	--
Pump	4-6	[128 ± 21]	96 ± 16	102 ± 13	[126 ± 25]	[114 ± 14]	[116 ± 17]	--
PACS-2								
Bottle	8	103 ± 15	90 ± 11	95 ± 8	90 ± 9	96 ± 9	95 ± 14	90 ± 10
Pump	5	101 ± 6	106 ± 11	96 ± 6	106 ± 17	99 ± 8	97 ± 10	95 ± 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-µm 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 ± 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
Digest blank (pmol/vial)							
Bottle	113 ± 120	0.01 ± 0.02	0.8 ± 0.5	0.11 ± 0.14	25 ± 9	145 ± 139	44 ± 53
Pump	154	0.12	6.7	0.54	144	570	83
Process blank (pmol/cm^2)							
Bottle	358 ± 261	0.018 ± 0.008	2.0 ± 1.5	0.051 ± 0.024	64 ± 27	558 ± 316	47 ± 35
Pump	145 ± 47	0.035 ± 0.016	2.1 ± 0.72	0.053 ± 0.078	49 ± 27	131 ± 56	29 ± 28
Limit of detection (pmol/cm^2)							
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
Bottle (n=239-252)							
Median	5.3	2.2	1.2	1.1	3.6	10.4	19.0
Mean ± SD	6.8 ± 5.2	3.6 ± 3.8	2.1 ± 2.7	1.3 ± 0.9	5.4 ± 5.1	15.3 ± 15.1	23.2 ± 16.3
Range	0.97-30	0.024-25	0.17-15	0.079-6	0.041-29	0.74-85	2.8-84
Pump (n=320-334)							
Median	4.5	3.8	0.7	1.3	1.4	1.2	6.8
Mean	6.3 ± 5.8	9.3 ± 12.9	0.9 ± 1.0	1.4 ± 0.9	2.6 ± 3.3	2.8 ± 4.3	13 ± 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 (± 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 ± 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
	± 0.021	± 0.033	± 0.024	± 0.018	± 0.029	± 0.036	± 0.041
p-value	**<0.0001**	0.2685	**0.0212**	**0.0023**	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
	± 0.06	± 0.10	± 0.05	± 0.08	± 0.05	± 0.06	± 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 (± 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 μm) 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.