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# 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.

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## 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  $\mu\text{m}$ . 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 Niskin-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, 2015; 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). Each approach has 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

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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 can help 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 h, with different collection platforms, filter membranes, digestion protocols and analytical procedures. We find that particulate concentrations of most elements were largely consistent between approaches.

## 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 34 stations, and pump samples were collected at 22 stations.

### 2.1. 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- $\mu\text{m}$  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- $\mu\text{m}$  polyethersulfone filters mounted in Swinnex polypropylene filter holders. Supor filters were cleaned in 1 M reagent-grade HCl at 60 °C for 24 h and then rinsed copiously with ultrapure water (> 18 M $\Omega$ ; 'DI water') prior to use (Cutter et al., 2010). Filtration was continued until the entire bottle was empty or 2 h 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 -20 °C 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 (Saville). 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 min and then allowed to cool to room temperature. The filter was in contact with the acetic acid leach solution for a total of 2 h. 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 min 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<sub>3</sub> was added (100  $\mu\text{L}$ ) to the 7-mL digestion vial, which was subsequently heated uncapped at 110 °C to near dryness. Vial contents were redissolved in 5 mL 2% HNO<sub>3</sub> (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 4 M HCl, 4 M HNO<sub>3</sub>, and 4 M HF (all Optima grade) was added, and the vial was tightly capped and heated to 110 °C for 4 h. 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

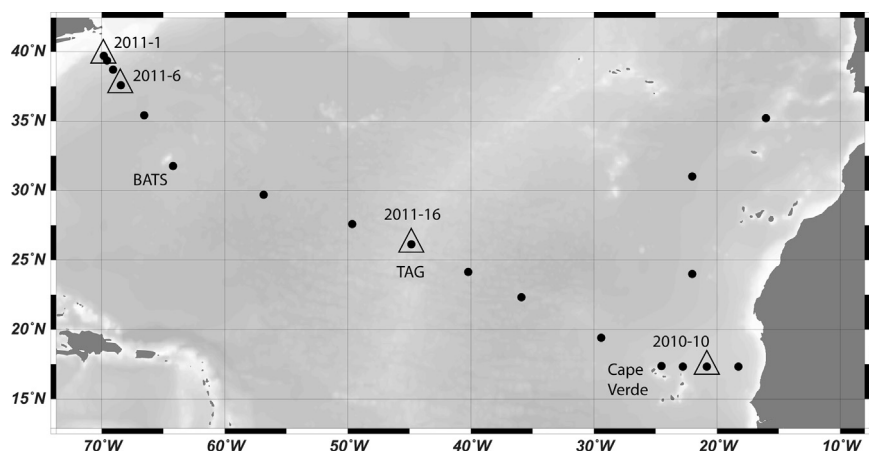


Fig. 1. Map showing cruise stations for which data are compared. Triangles indicate stations for which profiles are shown in Fig. 3. The locations of the Bermuda Atlantic Timeseries (BATS), TAG hydrothermal vent, and Cape Verde Island stations are indicated.

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