Intercomparison of dissolved trace elements at the Bermuda Atlantic Time Series station

R. Middag [a,b,c,*], R. Séférian [d], T.M. Conway [e,f], S.G. John [e,g], K.W. Bruland [b], H.J.W. de Baar [c]

[a] Department of Chemistry, University of Otago, Dunedin, Otago, New Zealand
[b] Department of Ocean Sciences & Institute of Marine Sciences, University of California Santa Cruz, CA 95064, USA
[c] Royal Netherlands Institute for Sea Research (Royal NIOZ), Den Burg, Texel, The Netherlands
[d] CNRM-GAME, Centre National de Recherche Météorologique-Groupe d'Etude de l'Atmosphère Météorologique, Météo-France/CNRS, 42 Avenue Gaspard Coriolis, 31100 Toulouse, France
[e] Department of Earth and Ocean Sciences, University of South Carolina, SC 29208, USA
[f] Department of Earth Sciences, ETH Zürich, 8092 Zürich, Switzerland
[g] Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089, USA

ABSTRACT

The international GEOTRACES programme is emphasising the use of the GEOTRACES reference sample programme and the importance of cross-over or baseline stations where all aspects of sample collection, filtration, processing and analytical methods can be compared. These intercomparison efforts are of crucial importance to merge or link data from different origins together. The occupation of the Bermuda Atlantic Time Series (BATS) station (31°45.92′N, 64°04.95′W) by the Netherlands GEOTRACES (GA02; 13 June 2010) as well as US GEOTRACES (GA03; 19–21 November 2011) Atlantic section expeditions provided an intercomparison opportunity to confirm the compatibility of the 2 different sampling systems as well as different analytical techniques used. In order to compare the data from different sampling systems or analytical techniques, a new statistical approach was developed to include the analytical uncertainty. Furthermore, modifications to an existing multi-element technique (Biller and Bruland, 2012) were made that increased the number of elements analysed and that allows the time consuming extractions to be done shipboard. Overall, we show excellent agreement between data generated by different sampling systems and analytical techniques. However, while both sampling systems are capable of collecting uncontaminated samples for all the GEOTRACES key elements, some apparent outliers are present. The intercomparison between the different analytical techniques also reveals subtle differences that would have gone unnoticed if only reference samples would have been used, underlining the importance and power of intercomparison stations. The results show that cross-over station data can be used to assess consistency between datasets if these stations have been carefully planned and analysed in combination with (internal) seawater reference samples to assure intra-dataset consistency.

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1. Introduction

The GEOTRACES programme is an international study which aims to improve the understanding of the global marine biogeochemical cycles and large-scale distribution of trace elements and their isotopes. As GEOTRACES is an international effort with scientists from approximately 30 nations participating, the emerging datasets are produced using differing sampling systems and analytical methods. These datasets are merged in the Intermediate Data Product (The GEOTRACES group, 2015). To assure consistency between datasets, the international programme is emphasising the concurrent analysis of reference samples from the GEOTRACES reference sample programme for concentrations of 9 key dissolved trace elements, as well as the planning of cross-over or baseline stations where all aspects of sample collection, filtration, processing and analytical methods can be compared. The intercomparison of data for the Intermediate Data Product has been carried out by the GEOTRACES Standards and Intercalibration committee, which shares the results only with contributors to encourage participation. This paper, independently of the findings of that committee, describes the comparison of 2 sampling systems and four analytical techniques, as well as statistical methods to compare trace metal profiles.

The US and Netherlands designed new trace metal clean sampling systems specifically for their respective GEOTRACES programmes to obtain accurate values of the distributions of key trace metal elements and isotopes along full depth sections. These are the Titan sampling system of the Netherlands (De Baar et al., 2008) that was recently

* Corresponding author at: Department of Chemistry, University of Otago, Dunedin, Otago, New Zealand.
E-mail addresses: rob.middag@otago.ac.nz (R. Middag), rseferian.cnrm@gmail.com (R. Séférian), conway.tm@gmail.com (T.M. Conway), sjohn@geol.sc.edu (S.G. John), bruland@ucsc.edu (K.W. Bruland), Hein.de.Baar@nioz.nl (H.J.W. de Baar).

upgraded with novel PVDF samplers (de Baar et al., 2012) as described in the companion article (Rijkenberg et al., 2015) and the US GEOTRACES carousel (Cutter and Bruland, 2012). Both systems utilise a conducting cable with a CTD instrument as part of the sampling system and can collect 24 samples, but they differ in the materials used and the procedures of recovery and deployment. For example, the whole Titan system with its 24.4 litre PVDF samplers goes into its own cleanroom van for sub-sampling whereas the 12 litre, Teflon-coated, GO-FLO sampling bottles are removed from the US GEOTRACES carousel and are brought into a dedicated cleanroom van for filtration and sub-sampling (for more details see Cutter and Bruland, 2012; De Baar et al., 2008; Rijkenberg et al., 2015).

Besides the development of new sampling equipment, considerable progress has also been made in the development of new multi-element methods (e.g. Biller and Bruland, 2012; Lee et al., 2011; Milne et al., 2010; Sohrin et al., 2008) using chelating resins for off-line extraction, with subsequent detection with a high-resolution, magnetic sector, inductively coupled plasma mass spectrometer (ICP-MS). Most of the data presented in this paper has been analysed using a modified version of the Biller and Bruland (2012) method that will be described here.

With these sampling and processing systems, datasets of unprecedented resolution are being produced that are linked together in a global database (The GEOTRACES group, 2015). Therefore, we must be confident the sampling systems as well as different analytical techniques obtain comparable and uncontaminated samples. The occupation of the Bermuda Atlantic Time Series (BATS) station by the Netherlands GEOTRACES during a meridional section of the western Atlantic in June 2010 (GA02) and the US GEOTRACES during a zonal section of the North Atlantic in November 2011 (GA03) provided an opportunity to collect dissolved trace metal samples from two occupations of the same 'cross-over' station with different sampling systems, which were analysed for a suite of trace metals by the same analyst with the same analytical method. For Al, Fe and Mn, shipboard dissolved concentration data values are available from the June 2010 Netherlands BATS occupation allowing further intercomparison with shipboard data. Additionally, for Cd, Fe and Zn, concentration data is available from the US occupation using a double spike multi-collector ICP-MS method (Conway et al., 2013). More data is available from the US occupation as well as historic occupations of the BATS station, but for the sake of conciseness not all data and methods can be described and compared in this paper and we contrast shipboard methods and 2 recent ICP-MS methods that apply standard addition versus isotope dilution double spiking as the calibration method.

Besides comparing the results of the different sampling systems and analytical techniques (Table 1), this paper also aims to describe the modifications made to the method of Biller and Bruland (2012). In order to compare the data from different sampling systems or analytical techniques, a new statistical approach had to be developed to include the analytical uncertainty that is described in this paper. In the companion paper the new PVDF samplers are described (Rijkenberg et al., 2015).

Table 1
Overview of the comparisons made in this paper.

Comparison	Parameters
Netherlands sampling system vs US sampling system	Mn, Fe, Co, Ni, Cu, Zn, Cd, Y, La, Ti, Ga, Pb via ICP-MS (same analyst)
Netherlands sampling system vs US sampling system	Al via flow injection (different analysts)
Standard addition ICP-MS vs double spike isotope dilution ICP-MS	Fe, Zn and Cd
Standard addition ICP-MS vs shipboard flow injection	Fe and Mn

2. Methods

For the Titan sampling system and the US GEOTRACES carousel the reader is referred to the respective papers (Cutter and Bruland, 2012; De Baar et al., 2008) and the companion paper on the PVDF samplers (Rijkenberg et al., 2015). The only differences in sample treatment are the filtration and acidification. Seawater samples were acidified to a concentration of 0.024 M hydrochloric acid (HCl) which results in a pH of 1.7 to 1.8 with either Baseline® HCl (Seastar Chemicals Inc.) for the samples from the Netherlands cruises, or Q-HCl (produced at UCSC as 6 N Q-HCl with a sub-boiling quartz still) for samples from the US cruise analysed with the multi element standard addition ICP-MS method. Seawater samples from the US cruise analysed with the double spike ICP-MS method were acidified to a concentration of 0.012 M HCl (which results in a pH of 2.0) with Aristar Ultra HCl (VWR International). Any difference between these acids is accounted for in the blank determination. On the Netherlands GEOTRACES cruise, the samples were filtered using 0.2 μm pore size Sartobran capsule filters, whereas on the US GEOTRACES cruise 0.2 μm pore size Acropak capsule filters were used. The use of these different brands of filter cartridge does not result in significant differences in trace metal concentrations (Cutter and Bruland, 2012). All samples were stored in LDPE bottles that were acid washed according to the 'Sample and Sample-handling Protocols for GEOTRACES cruises' (http://www.geotraces.org).

2.1. Double spike ICP-MS and shipboard methods

The details of the double spike ICP-MS method for Fe, Zn and Cd by Thermo Neptune multicollector ICP-MS are described by Conway et al. (2013). Accuracy of the double spike method for dissolved concentrations has been previously demonstrated by agreement with the consensus values for SAFe D1, D2 and S reference standards (Conway et al., 2013), which were analysed within the same ICP-MS analytical sessions at the Center for Elemental Mass Spectrometry (University of South Carolina) as the samples presented in this intercomparison. Procedural blanks for this technique were determined as 5 pmol kg^{-1} (Fe), 1 pmol kg^{-1} for (Zn) and 35 fmol kg^{-1} for Cd (Conway et al., 2013). The details on the shipboard methods of the Netherlands occupation for Fe, Mn and Al were described by Rijkenberg et al. (2014), Middag et al. (2011) and Middag et al. (2015), respectively. Typical precisions and detection limits for shipboard Al were 3.3% for multiple measurements of a 6.5 nM sample (n = 40) and a detection limit of 0.05 nM (defined as three times the standard deviation of the lowest concentration observed) (Middag et al., 2015). For shipboard Mn these were 5.1% for a 0.45 nM sample (n = 37) and a detection limit of 0.01 nM. For shipboard Fe the precision was 4% for replicate measurements of a 0.94 nM reference sample (n = 29) and a limit of detection of 0.01 nM (Rijkenberg et al., 2014).

2.2. Multi-element standard addition ICP-MS method

This method includes the analysis of yttrium (Y), lanthanum (La), titanium (Ti) and gallium (Ga), in addition to manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb) that were determined in the original method by Biller and Bruland (2012). Moreover, we introduce a new 'element dilution' approach that can be used for extractions performed at sea that is less labour intensive than the gravimetrical method described by Biller and Bruland (2012) as the weighing of the samples has been excluded. The extraction of the samples is the process where the trace metals of interest are separated from the original seawater matrix to remove interfering ions, as well as concentrating the samples via the use of a chelating column (Nobias PA1 chelating resin in this method). This pre-concentration is necessary due to the low concentrations of trace metals in the open ocean and the high background salt matrix of seawater.