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

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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 (Billler 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

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upgraded with novel PVDF samplers (de Baar et al., 2012) as described in the companion article (Rijkenberg et al., in press) 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., in press).

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., in press).

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., in press). 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 gravimetric 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.

2.2.1. Reagents

The reagents used for the trace metal analyses are the same as those described by [Biller and Bruland \(2012\)](#), with the exception of a lutetium (Lu)–indium (In) spike and the use of hydrofluoric acid (HF) as described below. A 4000 nM stock of Lu and In was made in 0.024 M nitric acid (HNO₃) (triple quartz distilled) from dilutions of the respective 1000 µg g⁻¹ SPEX standards. 2.4 M and 1.2 M working solutions of HF were made by diluting concentrated HF (50%, Optima grade, Fisher Scientific). The HF addition was found to increase the recovery of notably Ti (see the [Modified multi-element standard addition ICP-MS method](#) section). A short outline of the method is given below that mainly focuses on the differences with the method described by [Biller and Bruland \(2012\)](#). For more details on the method and method verification in general, the reader is referred to [Biller and Bruland \(2012\)](#). The method uses Nobias-chelate PA1 resin to extract the metals from the seawater. The metals are subsequently eluted with 1 M nitric acid and the extracts are run on a sector field ICP-MS. The 1 M nitric acid used in this method contains 0.6 mM HF in addition to the 10 ng g⁻¹ Rh in the original method.

2.2.2. Calibration

A multi-element stock standard with natural isotopic abundances of Mn, Fe, Co, Ni, Cu, Zn, Cd, Y, La, Ti, Ga and Pb, in 0.024 M HNO₃ was used to make standard additions to natural seawater with low concentrations of metals for calibration. Five standard additions were used for calibration in this method, and every sample and standard were spiked with Lu and In to obtain a concentration of 5 nM for both elements. In addition to the seawater standard additions, 5 standards were made up in the acid used to elute the metals from the pre-concentration columns (elution acid standards). These standards (also spiked with Lu–In) and the extracted seawater standards were analysed on each run.

The resin recovery for the modified multi-element ICP-MS method was monitored as described by [Biller and Bruland \(2012\)](#). Briefly, the slope of the relationship between the ICP-MS signal and metal standard additions to seawater is compared with the slope of the relationship between the ICP-MS signal and metal additions to elution acid that was not passed through the extraction system. This was done for every set of samples that were extracted and analysed by ICP-MS. The recovery for all elements with the exception of Ga and Ti is quantitative (recovery >98%) and agrees with previous results for this resin ([Biller and Bruland, 2012](#); [Sohrin et al., 2008](#)).

Lutetium and In are two trace metals, naturally existing at sub pM concentrations ([Alibo et al., 1999](#); [Alibo and Nozaki, 1999](#); [Amakawa et al., 1996](#); [Greaves et al., 1991](#)), that are quantitatively concentrated by the extraction procedure (recovery >98%). The 5 nM spike overwhelms the natural concentration in the samples. This Lu–In spiking, when done to an exact volume (see the [Pre-concentration and analysis](#) section) of seawater, serves as an internal standard or, analogous to isotope dilution, as an ‘element dilution’ calibration technique. This is in addition to the standard additions to a seawater sample; the standard additions serve to determine the calibration sensitivity for each metal (i.e. the signal per unit of metal) while the Lu–In spike represents the concentration factor of each sample due to the extraction method. The Lu:‘metal of interest’ or In:‘metal of interest’ ratio does not change after addition of the spike to the sample and will be the same in the sample and the eluent when recoveries are quantitative. Additionally, after addition of the Lu–In spike to the seawater samples, any evaporation of the seawater samples or the eluents after extraction is irrelevant as that does not change the ratios. If the recovery of a metal is not quantitative, the method will only work if the recovery is stable, i.e. does not vary between samples and standards. In this case the calibration sensitivity will be relatively low, but the non-quantitative recovery will be accounted for in this calibration sensitivity.

By dividing the ICP-MS signal for every metal by the signal for Lu, the signal is normalized with respect to the concentration factor as

the Lu signal is proportional to the amount of sample loaded and the amount of elution acid used. Similarly, the signal for every metal can be (separately) divided by the In signal to have 2 independent determinations of the concentration factor with the added benefit that a ‘failed’ extraction shows up in large deviations of the resulting concentrations or Lu/In ratios. The Lu and In signals were determined in both medium and low resolution, and were applied appropriately to metals measured in medium resolution (⁴⁷Ti, ⁵⁵Mn, ⁵⁶Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁶⁹Ga) or low resolution (⁸⁹Y, ¹¹¹Cd, ¹³⁹La and ²⁰⁸Pb). The Rh spike to the elution acid served to quickly highlight any aspiration problems or drifts in sensitivity on the ICP-MS for the original gravimetric method. The data presented here was determined by the gravimetric method based upon the sensitivity of the standard additions to the seawater. The Lu–In element dilution method was tested versus the gravimetric method (see the [Modified multi-element standard addition ICP-MS method](#) section).

2.2.3. Pre-concentration and analysis

The off-line pre-concentration set-up and procedures are as described by [Biller and Bruland \(2012\)](#) with some small but essential differences. Most importantly, to 40 ml of seawater, 20 µl of the 1.2 M HF was added (resulting in a 0.6 mM fluoride ion concentration), followed by a 50 µl addition of the Lu–In spike. This 40 ml was taken using a 10 ml pipette from a slightly larger volume of seawater. This seawater was UV oxidised to destroy organic metal binding ligands for dissolved Co and Cu concentration determinations (this was found to be particularly important for obtaining accurate dissolved Co concentrations and significant for obtaining accurate dissolved Cu concentrations ([Biller and Bruland, 2012](#))). The overall imprecision of the pipetting the 40 ml of water was determined gravimetrically and found to be ~0.9%. The accuracy of the pipette was monitored and no drift was observed over the course of 2 months.

Samples were capped and vigorously shaken (5 s) and left overnight (14 h) to homogenise after the spiking. Immediately prior to extraction, the pH of the samples was adjusted to 5.8 ± 0.2 with ~500 µl of a 3.7 M NH₄Ac solution. About 35 ml of the sample was loaded onto the columns in ~45 min (the exact amount of the sample loaded was gravimetrically determined ([Biller and Bruland, 2012](#))). The leftover 5 ml was used to retro-actively verify that the correct pH was achieved. The columns were rinsed with a 0.05 M NH₄Ac rinse/conditioning solution for 1 and 2 min, respectively, before and after sample loading to condition the columns at the correct pH, and remove interfering sea salt before elution. Samples were eluted with ~2 ml of the elution acid in ~5 min (the exact amount of the elution acid was gravimetrically determined), resulting in a concentration factor close to 17.5. Using 8 columns in this off-line manifold allowed the simultaneous extraction of 8 samples.

Samples were analysed on a Thermo Element XR Magnetic Sector ICP-MS at the Institute of Marine Science at UCSC with nickel sample and skimmer cones (Spectron) and an ESI-PC3 Peltier cooled spray chamber (4 °C). The sample gas rate was 0.75 ml min⁻¹, and the additional gas rate was optimised every run (usually around 0.2 ml min⁻¹). The sample was pumped into the instrument at a rate of 120 µl min⁻¹. Molybdenum (⁹⁵Mo) was measured to correct for molybdenum oxide interferences on the Cd signal ([Biller and Bruland, 2012](#)) that became significant at low surface water concentrations of dissolved Cd.

Unused (i.e. not passed through the extraction set-up) elution acid was used to track the baseline associated with the acid and ICP-MS instrument and was subtracted from the raw signals. An elution acid standard (elution acid with added metals) served as a drift standard to track the sensitivity of the ICP-MS during a run even though the Rh (gravimetric method) and the Lu–In spikes (‘element dilution’ method) are used to correct for any change in sensitivity. System blanks were determined by performing the normal extraction procedure, but loading a low metal concentration seawater sample (the same as used

for the standard additions) onto the column for only 30 s versus ~45 min for an ordinary sample. This way the column is loaded with sea salts, but only minimally with metals. A system blank was determined for every column, but consistency between the blanks indicated no noticeable difference between columns. A reagent blank was determined by adding double the normal amount of HCl, buffer, HF and Lu–In spike to a sample of the same seawater used for the standard additions. The resulting concentration was compared to the ‘zero addition’ point of the calibration that only had normal amounts of reagents added. No noticeable reagent blank could be determined for the metals except a small Pb blank of 1.2 pmol kg⁻¹. Blanks and limit of detection (LOD, defined as three times the standard deviation of the system blank) are shown in Table 2. SAFe and GEOTRACES reference samples were analysed in every run (Table 3).

2.3. Comparing profiles with analytical uncertainty

To compare datasets, traditionally paired two-tailed t-tests or 95% confidence intervals (CIs; expressed as 2 × standard deviation) have been used as well as the root-mean-square (RMS) deviations of the reported values from the mean values (Bowie et al., 2003; Landing et al., 1995). The t-tests have the disadvantage that analytical uncertainty is ignored, for example Bowie et al. (2003) reported significant differences (at the 0.05 significance level) between different analytical techniques based on paired two-tailed t-tests, whereas 95% CIs were often overlapping. In addition, a t-test assumes a normal distribution of the data which is rarely the case for an oceanographic profile. Indeed, the distribution of the data is generally skewed towards higher or lower concentrations in the shape of the vertical profile of the chemical species. Solely looking at 95% CIs or RMS deviations, on the other hand, does not give a quantitative measure of comparability for an entire profile.

In order to objectively and reproducibly assess the comparability of analytical methods or sampling systems while acknowledging that there is analytical uncertainty, another approach is needed. Here we describe a relatively straight forward test that can be done in a spreadsheet or statistical programme. This approach, however, is limited to comparing analytical techniques based on results from the same samples or subsamples thereof. It is less suited to compare oceanographic samples collected at different occasions since samples will have been collected at (slightly) different depths for which another test was developed (see the Different sample approach section).

2.3.1. Same sample approach

To compare analytical results from the same samples (or subsamples thereof) first a standard paired two-tailed t-test ($\alpha = 0.05$) was done as described by Bowie et al. (2003). As an example, in case of an oceanographic profile of 24 samples analysed by two different

analytical techniques in triplicate, the test compares the 24 analytical result pairs. If this does not result in a statistical difference, the results of the two methods are not significantly different regardless of analytical uncertainty. As mentioned above, this paired two-tailed t-test assumes a normal distribution of the data. This constitutes a potential caveat for this approach. A statistical programme such as SigmaPlot 13.0 as used in this paper, will test for normality of the data when performing a t-test and, if assumptions are violated, an alternative non-parametric test such as a Wilcoxon signed-rank test can be performed instead. The test outlined here is for the comparison of 2 datasets, for multiple datasets the t-test and signed rank test can be replaced by an ANOVA or a Friedman Repeated Measures Analysis of Variance on Ranks, with a Tukey post hoc test to identify differences. If the t-test or signed-rank test does give a significant difference, the results of the two methods are subsequently assessed with consideration of the analytical uncertainty. For this, the absolute difference between results of method 1 and method 2 was calculated for each sample. Subsequently the standard deviation of the difference was calculated using Eq. (1):

$$\sigma_d = \sqrt{\sigma_1^2 + \sigma_2^2} \quad (1)$$

where σ_d is the standard deviation of the difference between the analytical method 1 and analytical method 2, and σ_1 and σ_2 are the standard deviations of the results for method 1 and method 2 respectively. The latter standard deviation is calculated based on repeat measurements of subsamples of the same sample and can also be referred to as the standard error of the mean. If no standard deviation can be calculated for one of the methods (e.g. because no multiple subsamples were analysed) the analytical uncertainty needs to be assessed by other means. Notably for ICP-MS methods, often a single sample is analysed by the instrument a number of times and the average and standard deviation of those measurements is reported. This standard deviation divided by $n^{0.5}$, where n is the number of measurements (instrument scans), is the ‘internal’ standard error for the measurement (instrument variability). It is known that this ‘internal’ standard error of one sample analysis approximates the standard deviation of replicate analysis of subsamples (standard error of the mean). However, this does not hold in case of techniques, such as the standard addition ICP-MS method, where a considerable amount of variation is not due to instrument variability, but due to variation in extractions on resin, difference in sample bottles or other non-instrument related variability. This shows in an ‘internal’ standard error for the measurement of one subsample that is smaller than the standard deviation of replicate analysis of multiple subsamples (standard error of the mean). The best determination of the standard deviation (standard error of the mean) is to analyse subsamples of the same samples an infinite number of times. The best approximation of this in a practical sense is probably the analyses of reference samples/standards that are analysed with every run. In this paper standard deviation will be denoted with the symbol σ and is based on repeat measurements of separately extracted subsamples of the same sample (standard error of the mean).

In the case of the double spike ICP-MS method where no multiple subsamples of the same seawater samples were analysed for the whole profile, the analytical uncertainty was estimated to be 2% (Conway et al., 2013) and these estimates were used as the σ . The σ_d and absolute difference were calculated for every pair of results; in the case of an oceanographic profile of 24 samples analysed by two different analytical techniques, this results in 24 absolute differences and 24 associated standard deviations of the difference. Subsequently a one-tailed paired t-test or signed-rank test can be performed to assess whether σ_d is larger than the absolute difference for the entire profile. If this is the case, it is concluded the analytical results of the two methods are not statistically different within uncertainty as the

Table 2

Blanks and limit of detection (LOD) defined as three times the standard deviation of the blank (average for the 8 different columns).

Element	Unit	Blank	LOD
Y	pmol kg ⁻¹	0.36	0.21
Cd	pmol kg ⁻¹	0.11	0.10
La	pmol kg ⁻¹	0.06	0.08
Pb	pmol kg ⁻¹	0.94	0.16
Ti	pmol kg ⁻¹	4.22	3.97
Mn	nmol kg ⁻¹	0.03	0.02
Fe	nmol kg ⁻¹	0.01	0.02
Co	pmol kg ⁻¹	0.52	0.22
Ni	nmol kg ⁻¹	0.07	0.01
Cu	nmol kg ⁻¹	0.01	0.01
Zn	nmol kg ⁻¹	0.03	0.02
Ga	pmol kg ⁻¹	1.57	1.19

Table 3

SAFE and GEOTRACES reference sample results (n = 4) and consensus values. Errors denoted one σ standard deviation.

Metal	Safe S1 91		Safe D2 492		Geotraces S 138		Geotraces D 146	
	Meas.	Cons.	Meas.	Cons.	Meas.	Cons.	Meas.	Cons.
Y pmol kg ⁻¹	62 ± 1		198 ± 2		130 ± 2		138 ± 2	
Cd pmol kg ⁻¹	1.3 ± 0.3	1.1 ± 0.3	977 ± 15	986 ± 23	2.2 ± 0.3	2.1 ± 0.6	262 ± 5	272 ± 6
La pmol kg ⁻¹	4.5 ± 0.1		30.6 ± 0.5		13.3 ± 0.3	14.7 ± 1.1 ^a	22.0 ± 0.5	23.6 ± 1.4 ^a
Pb pmol kg ⁻¹	48.3 ± 1.1	48.0 ± 2.2	27.7 ± 0.5	27.7 ± 1.5	28.7 ± 0.5	28.7 ± 0.8	42.1 ± 1.3	42.3 ± 1.3
Ti pmol kg ⁻¹	23 ± 8	48 ± 14 ^b	140 ± 32	127 ± 33 ^b	66 ± 19	75 ± 12 ^b	221 ± 61	202 ± 18 ^b
Mn nmol kg ⁻¹	0.82 ± 0.02	0.79 ± 0.06	0.36 ± 0.02	0.35 ± 0.06	1.53 ± 0.04	1.50 ± 0.11	0.20 ± 0.01	0.21 ± 0.03
Mn SB nmol kg ⁻¹			0.33 ± 0.01		1.47 ± 0.03		0.18 ± 0.01	
Fe nmol kg ⁻¹	0.10 ± 0.01	0.093 ± 0.008	0.97 ± 0.04	0.933 ± 0.023	0.53 ± 0.04	0.546 ± 0.046	0.94 ± 0.04	1.00 ± 0.10
Fe SB nmol kg ⁻¹			0.89 ± 0.03					
Co pmol kg ⁻¹	3.9 ± 0.3	4.9 ± 1.5	46.9 ± 1	45.8 ± 3.0	32.4 ± 1	31.8 ± 1.3	64.0 ± 0.9	64.5 ± 1.8
Ni nmol kg ⁻¹	2.21 ± 0.09	2.29 ± 0.08	8.50 ± 0.17	8.59 ± 0.28	2.05 ± 0.06	2.09 ± 0.05	4.04 ± 0.07	3.97 ± 0.07
Cu nmol kg ⁻¹	0.5 ± 0.02	0.53 ± 0.05	2.2 ± 0.1	2.32 ± 0.16	0.8 ± 0.1	0.83 ± 0.08	1.5 ± 0.1	1.55 ± 0.13
Zn nmol kg ⁻¹	0.07 ± 0.03	0.068 ± 0.010	7.50 ± 0.20	7.47 ± 0.27	0.04 ± 0.02	0.042 ± 0.008	1.76 ± 0.06	1.73 ± 0.09
Ga pmol kg ⁻¹	11.1 ± 0.8		7.0 ± 0.4		41.4 ± 2		29.0 ± 1.5	
Al SB NL nmol kg ⁻¹					27.4 ± 0.3	27.5 ± 0.2	17.5 ± 0.3	17.7 ± 0.2
Al SB US ^c nmol kg ⁻¹					27.4 ± 0.5		17.8 ± 0.3	

SB denotes shipboard data.

^a Not actual consensus data but results reported by van de Flierdt et al. (2012).^b Not actual consensus data but results reported by Croot (2011).^c Measured during the 2008 US occupation.

uncertainty is larger than the difference. Otherwise the conclusion is that the two methods do not give comparable results.

This analytical uncertainty assessment can be repeated using a 2 σ -based analytical uncertainty or 95% CIs, but for this paper the more conservative approach of 1 σ was chosen. Assuming a normal distribution, the 95% CI denotes the interval that contains the actual mean with 95% probability. This can be calculated by multiplying the standard error (standard error = $\sigma \times n^{-0.5}$; note this is *not* equivalent to the standard error of the mean defined above) with the critical t-value for the applicable number of degrees of freedom and chosen significance level. For large numbers of replicates ($n > 20$) the critical t-value at $\alpha = 0.05$ is ~ 2 , making the 95% CI about 2 standard errors whereas for $n = 3$ the critical t-value equals 4.3. In other words, the 95% CI is a measure of certainty about the mean reported value and this certainty increases with a larger number of replicates (smaller 95% CI). Additionally, for a normal distribution and a large number of replicates, 95% of the results lie within $\sim 2\sigma$ of the mean, which confusingly is sometimes also referred to as the 95% CI. This number of 2 σ is a measure of the spread around the mean and can therefore be considered more appropriate as a measure of analytical uncertainty. However, commonly samples are analysed in triplicate for shipboard flow injection methods, or single sample extracts are analysed for ICP-MS methods, making the estimation of the 95% CI less reliable or impossible due to the lack of degrees of freedom. Similarly, the assumption of 2 σ encompassing 95% of the variation around the mean is not valid with a small number of replicates and we opted to use 1 σ as the most reliable measure of analytical uncertainty.

Additional information can be gained by dividing the difference between result pairs (either positive or negative) by the σ_d after John and Adkins (2010; their Eq. (18)), resulting in values that are basically individual t-values for each pair of results. Subsequently the additive inverse ($-t$) of each t-value is added to the list of t-values, giving a collection of t-values with an average that equals zero. The standard deviation of this collection of t-values can be used to differentiate between intra-lab and inter-lab variability. If the standard deviation is ≤ 1 , all differences can be related to intra-lab variability (i.e. the analytical uncertainties). If the standard deviation is ≥ 1 , the number indicates how much greater the actual observed differences are than expected based on intra-lab variability, e.g. if the standard deviation is 1.3 or 4, it means that the inter-lab variability is 30% or 300% greater than expected based on intra-lab variability, respectively. A standard deviation greater or smaller than 1, however, does not indicate statistical significance at the 95% significance level as this test just predicts differences based on the reported analytical uncertainty and does not test for differences. For the latter, the above or below described tests are to be used.

2.3.2. Different sample approach

As stated above, the above approach is limited to comparing results from the same sample or subsamples thereof and is not suited to compare oceanographic samples collected by different sampling systems or at different times, as samples will have been collected at (slightly) different depths and/or locations. Therefore a script was developed in the freeware programme R (R Core Team, 2013) that interpolates oceanographic profiles and the analytical uncertainty and

subsequently tests the shape of two profiles within a prescribed depth interval. The interpolation allows comparison of a sampled depth on one profile with an interpolated value in the other profile. Additionally, errors in interpolation on mean concentrations and standard deviation of each profile are used to determine the standard deviation of the interpolated values assuming a 95%-significance confidence interval. This interpolation is based on depth, but since water masses might occupy different depths between sampling events, conservative tracers such as potential or neutral density, salinity or potential temperature might be better suited. However, for the surface ocean, salinities, temperatures and densities observed in the US BATS occupation were not observed in the NL BATS occupation, making interpolation based on these parameters unfeasible. For the sake of clarity we used depth, as in the deep ocean where comparison is feasible (see section [Intercomparison between the different sampling systems](#)), depth and density matched very well between the two occupations. Given that deep water masses generally occupy a significant depth range while density differences become smaller, using depth makes comparison between two profiles easier, notably in graphs. After interpolation, the shape of the two profiles is compared simultaneously using two statistical approaches. The first approach consists of comparing samples between each other across depth using a simple T-based distribution relying on a pooled variance assumption as follows:

$$t_z = \frac{\bar{m}_1 - \bar{m}_2}{\sqrt{(n_1\sigma_1^2 + n_2\sigma_2^2) \frac{1}{n_1 + n_2 - 1}}} \sim T_{n_1+n_2-1}$$

where \bar{m}_i and σ_i represent respectively the mean concentration at a given z depth of the profile i and the standard deviation relative to the number of samples, n_i , analysed at this depth. This gives a p -value for the comparison at each individual depth that is compared and thus gives a p -value profile, a profile of p -values which provides insight into where the largest discrepancies and the best agreements are along the depth profile.

The second approach aims at comparing the shape of the two profiles within a depth interval using a Fisher-based test. This test consists of computing both the cumulative sum of the Welch's t_z^2 (Welch, 1947) and the cumulative sum of the randomly generated Fisher distribution F_{1,n_1+n_2-2} . A chosen number of random simulations (usually 100,000) of the Fisher F_{1,n_1+n_2-2} distribution are used to estimate the distribution of the cumulative Fisher law. This distribution is then used to compute an 'integrated' p -value which represents an objective metric to determine how far the two profiles are consistent between each other within the depth interval. The script is provided in the Supplementary material with this paper.

The use of both these approaches ensures a good understanding of the profile's consistency. The 'integrated' p -value quantifies the match between profiles with one metric, i.e. whether or not there is a significant difference, while the T-based p -value profiles ensures to decipher the reason for a good or poor match between profiles.

That said, the computation of the 'integrated' p -value is sensitive to the number of samples and to the resolution of sampling over depth, i.e. if the sampling resolution is low in one profile, the interpolation will inherently miss fine scale gradients if present. The 'integrated' p -value estimated from the F or a χ^2 test can differ by about 10 to 20% due to the sensitivity on the number of samples on the computed confidence intervals. Therefore this approach cannot be considered alone without a proper analysis of profiles miss-match based on the p -value profiles. In the following, the 'integrated' p -value will be noted as 'i- p -value' and reports the analysis that is based on computation over the profiles (deeper than 1000 m depth, see the [Intercomparison between the different sampling systems](#) section).

3. Results and discussion

3.1. Modified multi-element standard addition ICP-MS method

The recovery for Mn, Fe, Co, Ni, Cu, Zn, Cd, Y, La, and Pb was quantitative (>98%) at pH 5.8. Two elements demonstrated non-quantitative recovery; Ga (75%; $\sigma = 4\%$) and Ti (50% $\sigma = 5\%$). The recovery was assessed over a range of pH and this showed that most metals were quantitatively recovered over a pH range of 4.5 to 9, but the recovery of Mn is not quantitative below pH 5.5 and Ga has its optimum recovery around a pH of 5.5. The recovery of Ti, zirconium and scandium benefited from the addition of fluoride (see Supplementary material for details). The highest recovery for Ti (75% with 0.6 mM HF) was at pH 4.5 and the recovery of Ti was relatively constant around 50% at a pH of 5.8, but multiple analyses of reference samples indicated modest precision ($\sigma \sim 10\%$).

The recovery of zirconium and scandium was unstable, resulting in concentrations with low accuracy. Further development needs to be carried out for these elements and they are currently not included in the method. The fluoride addition had a perceived positive effect on the analysis of Fe and Ga. This was mainly visible in the increased 'smoothness' of oceanic profiles (i.e. rather than meandering the profiles showed uniform trends with increasing depth) and the reproducibility of reference samples. Before addition of HF, occasionally values were measured for the reference samples that were a lot lower than expected (outside the consensus range), whereas after addition of HF this was no longer observed. The improvement of the visual appearance of the profiles and more consistent reference samples results might possibly be due to hindering of precipitation after pH adjustment in the presence of HF, but increased operator experience cannot be excluded either. The effect of fluoride addition to the seawater on the recovery was assessed at concentrations up to 10 mM fluoride and it appeared that there is an optimum of about 0.6 mM fluoride for the recovery of Ti. It is hypothesised that the addition of fluoride has an advantageous effect for the elements that form hydrolysis complexes in seawater. Potentially, the formation of metal-fluoride complexes diminishes precipitation and wall adsorption after pH adjustment to pH 5.8, leading to an improved recovery. Alternatively, the formation of metal-fluoride complexes results in an increased lability of the metal-water complexes, leading to a greater chance for the resin to form a complex with the metal. For example in the case of Fe, at the analytical loading pH (5.8) the $\text{Fe}(\text{OH})_2^+$ complex would dominate (Glasby and Schulz, 1999) and this is relatively slow with respect to water exchange (Hudson et al., 1992). The increased lability of the metal-water complexes could increase the recovery on the resin as the chelating resin is competing for the metals with the complex forming agents in the seawater. The only exception was Al; recovery of Al at pH 5.8 was about 25% without fluoride and after the fluoride addition this decreased to near 0%, indicating that the Al-fluoride complex is stronger than the Al-resin complex or kinetically inert on the time scale of its passage through the resin. Overall, the pH of 5.8 \pm 0.2 and an addition of 0.6 mM fluoride to the samples resulted in the best recovery for most elements.

SAFE and GEOTRACES reference samples were analysed in every run and the results are in line (1σ intervals overlap) with consensus values for the metals that have those (Table 3). Currently there are no consensus values for Ti on reference samples, but Croot (2011) published results for his analysis of Ti on the reference samples (Table 3). The results for the higher concentrations agree reasonably well (1σ intervals overlap), but there appears to be more discrepancy for the lower concentrations, most notably for SAFE S. However, it should be noted that for one of the SAFE S samples (SAFE S 474) analysed by Croot (2011) the result were in range with our results for SAFE S. This indicates the analysis of Ti is challenging and more method development needs to be done in order to attain reliable data on the distribution of Ti in the open ocean. In this case the method should benefit from

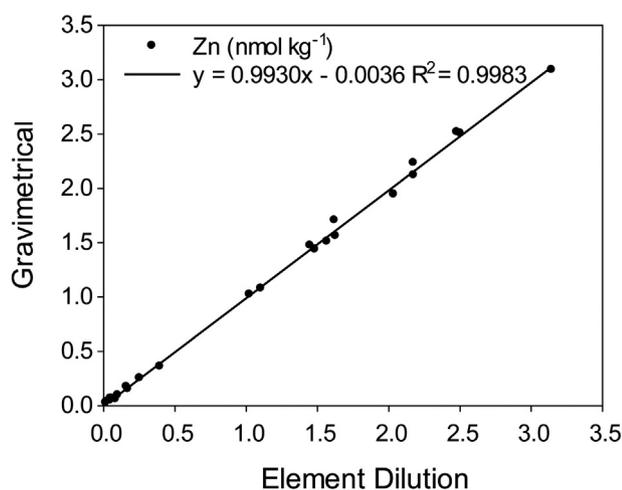


Fig. 1. Results of the element dilution calibration vs the gravimetric calibration for the 24 samples of the Netherlands BATS occupation for dissolved Zn concentration, by standard addition ICP-MS.

using isotope dilution to account for the non-quantitative and potentially variable recovery on the resin. For Y, La and Ga there are currently no consensus values either, and the obtained vertical profiles at BATS are compared to published data below (see the [Intercomparison between the different sampling systems](#) section) to assess the method's accuracy. There is data on reference samples for La (Hatje et al., 2014; van de Flierdt et al., 2012) that agrees (1σ intervals overlap) with the here reported values (Table 3).

To accurately measure the sub-pM concentrations of Lu and In the concentration factor would need to be increased, i.e. much more seawater would need to be pre-concentrated on the resin. Therefore we opted instead to use these two elements as an internal standard (see the [Calibration](#) section). This 'element dilution' calibration technique was assessed by comparing the resulting values versus the gravimetric method as described by Biller and Bruland (2012). No discernible difference was observed between the 'element dilution' and gravimetric method (Fig. 1), either with a two-tailed paired t-test ($p = 0.20$) or the script for profile comparison that includes analytical uncertainty ($p = 0.97$). The benefit of the element dilution calibration technique is that the gravimetric determination of the

pre-concentration factor is no longer necessary, making it possible to do the time consuming extractions at sea. The results presented in this paper are based on extractions done in the shore based lab, but meanwhile the extractions for the subsequent Netherlands Mediterranean GEOTRACES expedition were carried out aboard RV Pelagia by the Middag group and analysed at the University of California Santa Cruz during a visit to the Bruland lab. These results are written up separately, but the results for the GEOTRACES reference samples that were extracted shipboard are included in Table 4 and are not distinguishable from the results for the here reported samples ($p > 0.05$ in all cases; two-tailed homoscedastic t-test). The good agreement between the reference samples and the comparison of the gravimetric and the element dilution method shows the off-line extractions are no longer required to be carried out in the home laboratory and can also be done at sea, where gravimetric measurements are not possible. After returning with the extracted samples to the home laboratory all samples can be run in 1 long ICP-MS run (150 h for the Mediterranean data where a total of roughly 2100 profile samples, reference samples, standards and blanks were analysed) creating the possibility to produce the data shortly after return. We believe that this is a significant improvement over the shore-based extractions that often take many months to complete. Taking back-up seawater samples to return to the shore laboratory is always recommended in case (i) some extractions fail, or (ii) there is inadvertent contamination of some samples, or (iii) if a future interest arises in other trace elements that require different extraction techniques.

3.2. Intercomparison between the different sampling systems

The BATS intercomparison or cross-over station ($31^{\circ}45.92'N$, $64^{\circ}04.95'W$) was used to compare the sampling systems used by the Netherlands and US GEOTRACES programmes for 12 dissolved trace elements. The data of all trace elements are attached in the Supplementary material. Since a different number of samples were collected at different depths between the occupations, the R script is used to interpolate the profiles and assess the differences. Only data below the main thermocline was used (deeper than 1000 m) to avoid temporal variation between the two occupations that were over a year apart and had a negative and positive sea surface height anomaly during the Netherlands and US occupation, respectively, indicative of an up- and down-welling eddy (this was determined using the Colorado center

Table 4

SAFE reference sample results for samples that were extracted shipboard during the Mediterranean GEOTRACES expedition and analysed using the 'element dilution' technique ($n = 4$). Results are compared with the results in Table 3 that were obtained using standard gravimetric techniques.

Metal unit	Safe S1 564	2-Tailed paired t-test vs results accompanying BATS	Safe D2 54	2-Tailed paired t-test vs results accompanying BATS
Y pmol kg ⁻¹	63 ± 1	0.16	197 ± 2	0.71
Cd pmol kg ⁻¹	1.5 ± 0.1	0.21	976 ± 12	0.91
La pmol kg ⁻¹	4.7 ± 0.1	0.07	31.4 ± 0.4	0.07
Pb pmol kg ⁻¹	49.1 ± 0.2	0.2	27.4 ± 0.2	0.31
Ti pmol kg ⁻¹	16 ± 1	0.14	116 ± 7	0.20
Mn nmol kg ⁻¹	0.81 ± 0.01	0.60	0.38 ± 0.01	0.09
Fe nmol kg ⁻¹	0.10 ± 0.02	0.73	0.94 ± 0.01	0.06
Ni nmol kg ⁻¹	2.28 ± 0.02	0.17	8.62 ± 0.18	0.40
Zn nmol kg ⁻¹	0.08 ± 0.02	0.80	7.44 ± 0.07	0.53
Ga pmol kg ⁻¹	11.2 ± 0.9	0.91	8.5 ± 1.2	0.06

for astrodynamics research SSH data viewer at http://eddy.colorado.edu/ccar/ssh/nrt_global_grid_viewer.

Of the first row transition metal elements, Mn, Fe, Co, Ni, Cu, and Zn (in order of increasing atomic number (25–30)) are all essential for every living organism (de Baar and La Roche, 2003). Within the group 12 elements, the second row element Cd is akin to the first row element Zn, and thus Cd may substitute for Zn in phytoplankton, while an intrinsic Cd-carbonic anhydrase also is found in certain diatoms (Xu et al., 2008). Next, transition metal group 3 is represented by second row Y and third row La, and transition metal group 4 by its first row Ti that serves as a geochemical source tracer of mineral dust (Dammshaeuser et al., 2011) as well as the construction material of the Netherlands sampling frame. The non-transition group 13 is represented by Al and Ga with a similar ocean chemistry (Orians and Bruland, 1988), and Al is the construction material of the US sampling frame. Aluminium is discussed last as it is not measured with the ICP-MS method. Finally,

group 14 is represented by Pb, a decadal time scale tracer at BATS (Lee et al., 2011) due to the earlier use of, and subsequent phasing out, of Pb in gasoline for automobiles.

Dissolved Mn is an element that in the open ocean usually shows a strong surface enrichment due to atmospheric input (Baker et al., 2006; Landing and Bruland, 1980) and photo reduction of Mn oxides (Sunda et al., 1983). Below the surface layer, Mn concentrations are generally low and quite uniform due to (microbially mediated) removal by scavenging (Landing and Bruland, 1980; Statham et al., 1998). The Mn profile at BATS largely follows the classical profile (Fig. 2a). There are some discrepancies in the deep water at the low concentrations that are visible in the *p*-value profile, but overall the results are not statistically different within analytical uncertainty (*i-p*-value = 0.32).

Dissolved Fe is arguably one of the most analytically challenging elements to determine in the open ocean and considerable effort has been put in intercalibration in the past (e.g. Johnson et al., 2007).

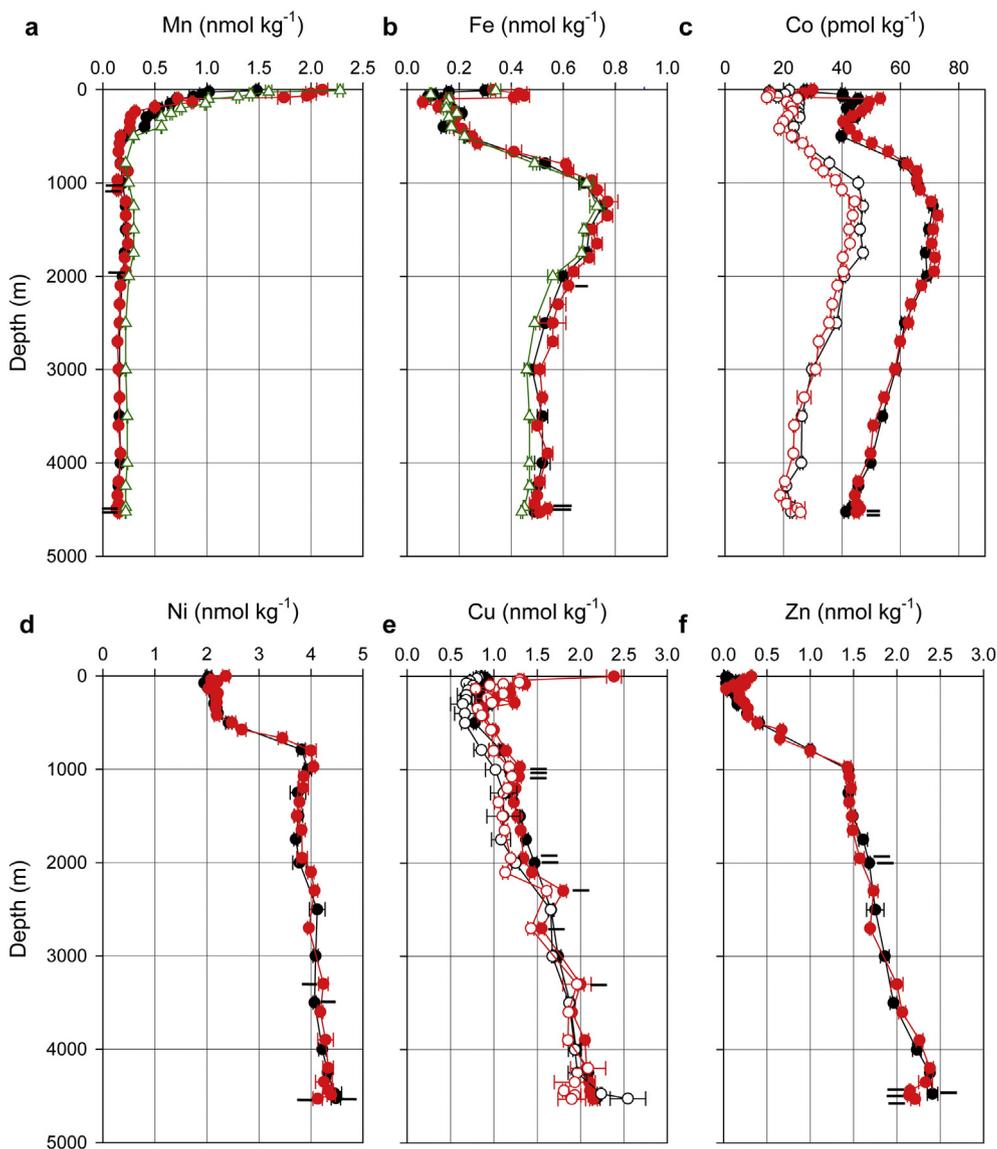


Fig. 2. Concentrations of dissolved trace metals (by standard addition ICP-MS) for the Netherlands (black circles) and US (red circles) occupations of the BATS station for A) Mn (nmol kg^{-1}); B) Fe (nmol kg^{-1}); C) Co (pmol kg^{-1}) with and without UV oxidation; D) Ni (nmol kg^{-1}); E) Cu (nmol kg^{-1}) with and without UV oxidation; and F) Zn (nmol kg^{-1}). Shipboard data are denoted by green triangles for Fe and Mn. Open symbols denote no UV oxidation for Co and Cu. On each graph, a black horizontal bar indicates a significant difference ($p < 0.05$) between samples at individual depths (deeper than 1000 m) between the US and Netherlands' profiles (UV oxidised in the case of Co and Cu) observed in the *p*-value profile (see the Different sample approach section for calculation and the supplementary material for the *p*-value profiles). Note that the integrated *p*-value (*i-p*-value) reported in the text is based on the profiles deeper than 1000 m depth and does not equal the average of the *p*-values at individual depths (see the Different sample approach section). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Dissolved Fe displays characteristics of both a nutrient-type element and a scavenged-type element in the open ocean which is also visible at the BATS station (Fig. 2b). Surface concentrations are elevated, most likely due to recent dust input, but decrease to $\sim 0.1 \text{ nmol kg}^{-1}$ around 100 m depth due to biological uptake. Dissolved Fe concentrations are relatively constant close to 0.5 nmol kg^{-1} in the deep ocean, indicating equilibrium between input and scavenging removal. The profiles for dissolved Fe (Fig. 2b) are not statistically different within analytical uncertainty (i - p -value = 0.50).

Dissolved Co, like Fe, displays characteristics of both a scavenged-type as well as a nutrient-type element. The latter is due to the nutritional requirement of phytoplankton for Co (e.g. Saito and Goepfert, 2008). For Co, the UV oxidation step is of utmost importance, as can be seen by the difference between the data from samples with and without UV oxidation (Fig. 2c). Only one replicate was analysed for the UV oxidised samples and thus the analytical uncertainty was conservatively estimated at 2%. The Fisher law in the R script cannot be run when only one replicate measurement is available for both profiles. To allow comparison, two replicates for each data point were assumed (note that increasing the number of replicates makes the test harsher). With this assumed error, the profiles are not statistically different within analytical uncertainty (i - p -value = 0.93).

Dissolved Ni is another nutrient-type element (Fig. 2d) as it is used in the breakdown of urea (Price and Morel, 1991) and by nitrogen fixers (e.g. Ho, 2013). The general agreement between the data of the Netherlands and US occupation is good, but the data from the US occupation showed four outliers (3000, 2500, 1800 and 874 m depth). Outliers were defined as described by Middag et al. (2011), where a linear regression was determined between the data above and below the suspect data point and a deviation of more than 10% from the predicted value was used as the rejection criterion. The samples contaminated for Ni were also contaminated for Cu and Zn at a roughly constant ratio of Ni:Cu:Zn but were not contaminated for these metals in profiles analysed by a different PI in the US GEOTRACES programme (Jingfeng Wu, pers. com.), so it does not appear to be a problem with the GO-FLO samplers. Additionally, the Zn samples analysed with the double spike ICP-MS method were not contaminated either. When excluding those four outliers, the profiles are not statistically different within analytical uncertainty (i - p -value = 0.77) for Ni, further confirming that the US sampling system is not the source of contamination. Either these four subsampling bottles were contaminated for Ni, Cu and Zn or the contamination was introduced during subsequent sample handling. The samples of these four coinciding outliers have been excluded from the profiles for Ni, Cu and Zn.

Dissolved Cu has a hybrid type profile (Fig. 2e) with slightly depleted surface concentrations as there is a biological requirement for Cu (e.g. Annett et al., 2008; Peers and Price, 2006), and relatively uniform deep concentrations. For Cu, the UV oxidation step is also of importance as can be seen by the difference between the data from samples with and without UV oxidation (Fig. 2e). As for Co, only one replicate was analysed for the UV oxidised samples and thus the error was conservatively estimated at 2% and the number of replicate analyses was set at 2. With this assumed error, the profiles are not statistically different within analytical uncertainty (i - p -value = 0.46). There are two additional outliers (6 in total) for Cu at 666 and 500 m depth in the upper ocean of the US profile (not considered in the comparison), implying a contamination issue for Cu of unknown origin. This is further corroborated by the relatively modest agreement between the 2 profiles and further research is required to resolve this, but currently any discrepancies do not seem related to the sampling systems.

Dissolved Zn is a nutrient type element due to its biological requirement by phytoplankton, most notably in the carbonic anhydrase enzyme to acquire CO_2 for photosynthesis (Morel et al., 1994). Dissolved Zn is one of the most contamination prone elements and each profile has one outlier (US at 2100 m and NL at 4525 m), in addition to the four excluded samples from the US occupation. This

demonstrates that the utmost care needs to be taken during sample handling. The profiles for dissolved Zn (Fig. 2f) are not statistically different within analytical uncertainty (i - p -value = 0.08). Towards the seafloor (deeper than 4200 m), the US samples trend to lower values, whereas the Netherlands remain similar, resulting in lower p -values in the p -value profile (see Supplementary material). These decreasing p -values near the seafloor are also seen for Mn, Fe and Co, indicating natural variation. This variation might be related to the thick benthic nepheloid layer that has been observed at the BATS station during the US occupation (Lam et al., 2015).

Dissolved Cd displays nutrient type behaviour in the ocean. This was a long standing subject of debate as Cd was not previously considered a bio-essential metal (Lane and Morel, 2000). However, biological roles for Cd have now been identified, e.g. Cd can substitute Zn in carbonic anhydrase in some phytoplankton species (Xu and Morel, 2013). The profiles for dissolved Cd (Fig. 3a) are not statistically different within analytical uncertainty (i - p -value = 0.57).

Dissolved yttrium has a narrow range of concentrations at BATS, ranging between ~ 125 and 165 pmol kg^{-1} , with the highest concentrations in the deep waters (Fig. 3b). The sparse amount of data that exists for Y suggests that it has somewhat of a nutrient-type distribution in the oceans with slightly higher concentrations in the older Pacific waters (Alibo et al., 1999). Yttrium has also been reported to have higher concentrations in the Mediterranean due to the high dust input in the latter region (Alibo et al., 1999). The profiles for dissolved Y (Fig. 3b) are not statistically different within analytical uncertainty (i - p -value = 0.34).

The concentrations of dissolved Y have been reported to be tightly correlated with dissolved La (Zhang et al., 1994). At BATS, Y correlates with La with a correlation coefficient, R^2 , 0.84 ($n = 60$; not shown). The relatively modest correlation between Y and La is caused by a La maximum around 1500 m depth (Fig. 3c) that is absent in the Y profile, indicating a source to the upper North Atlantic Deep Water for La without accompanying Y. Lanthanum correlates strongly with Si with a R^2 of 0.97 ($n = 60$; not shown) over the entire water column. The profiles for dissolved La (Fig. 3c) are not statistically different within analytical uncertainty ($p = 0.42$). As part of a GEOTRACES intercalibration effort on rare earth elements (REEs), Pahnke et al. (2012) reported La at several depths at the BATS station from the US GEOTRACES intercalibration cruise in 2008 and this data agrees with the here reported data within analytical uncertainty (i - p -value = 0.43). We included La as a typical example of a light REE and Lu works well as a heavy REE, but for the latter the concentration factor needs to be increased. A recent paper has shown that this method does work well for the suite of REEs (Hatje et al., 2014).

The recovery for Ti was not quantitative at $\sim 50\%$ recovery, resulting in relatively poor precision and accuracy. The concentrations were calculated based upon the standard addition sensitivities assuming that all samples and standard additions had the same 50% recovery. Nevertheless, the vertical profiles of both occupations agree quite well (Fig. 3e), and are not statistically different within analytical uncertainty (i - p -value = 0.80). Due to the low accuracy it might not be suitable to look at the actual concentrations, but the observed trends should represent actual variation in the ocean. However, one thing that is worth noting is that the data of the Netherlands occupation is not significantly higher than the data from the US occupation, indicating that there is no noticeable contamination of Ti from the Netherlands titanium frame.

Dissolved Ga is a scavenged type element with an atmospheric source to the surface ocean (Orians and Bruland, 1988; Shiller, 1998). This is reflected at BATS in the elevated surface concentrations, followed by a decrease with depth and relatively constant concentrations in the deep waters, indicating equilibrium between input and scavenging removal (Fig. 3e). The agreement between the two occupations is remarkably good considering that the overall precision of the Ga measurements is low due to the non-quantitative recovery of Ga on the

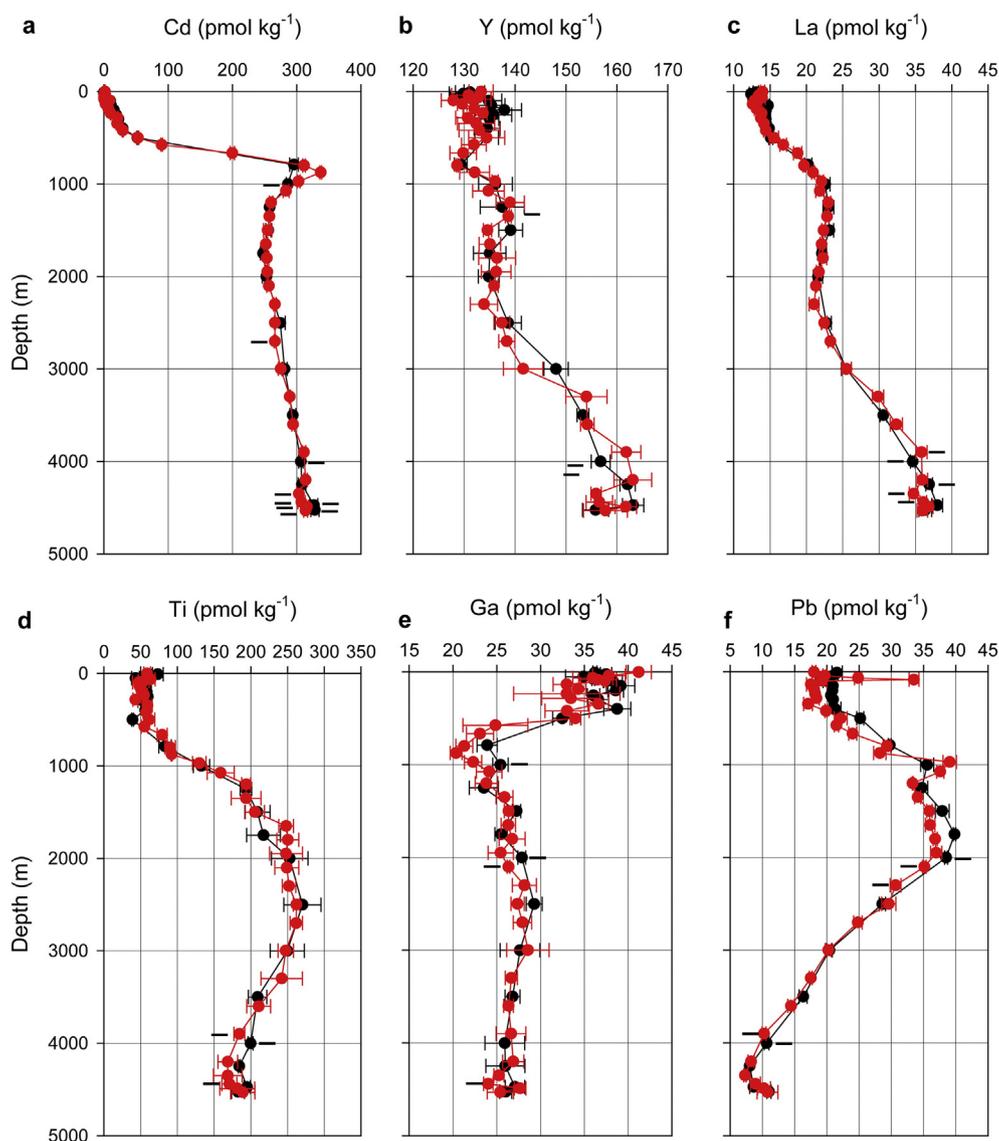


Fig. 3. Concentrations of dissolved trace metals (by standard addition ICP-MS) for the US (red circles) and Netherlands (black circles) occupations of the BATS station for A) Cd (pmol kg^{-1}); B) Y (pmol kg^{-1}); C) La (pmol kg^{-1}); D) Ti (pmol kg^{-1}); E) Ga (pmol kg^{-1}); and F) Pb (pmol kg^{-1}). On each graph, a black horizontal bar indicates a significant difference ($p < 0.05$) between samples at individual depths (deeper than 1000 m) between the US and Netherlands' profiles observed in the p -value profile (see the [Different sample approach](#) section for calculation and the supplementary material for the p -value profiles). Note that the integrated p -value (i - p -value) reported in the text is based on the profiles deeper than 1000 m depth, except for Pb for which the test was based on depths deeper than 2000 m, and this i - p -value does not equal the average of the p -values at individual depths (see the [Different sample approach](#) section). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

resin. The profiles are not statistically different within analytical uncertainty (i - p -value = 0.29). The profile shape is also consistent with previous data from the region (Shiller, 1998). Whereas these results are encouraging, non-quantitative recovery is not ideal and is likely to result in significant variability between different measurement runs and hence, relatively modest accuracy. Using isotope dilution should solve this issue. The results for Ga produced with the current method should mainly be used to assess general trends rather than putting emphasis on the actual concentrations or small differences.

Dissolved Pb is an element with a strong anthropogenic atmospheric input related to the use of leaded gasoline that peaked in the mid-1970s. Since leaded gasoline is largely phased out, the anthropogenic input to the surface oceans has been reduced and Pb concentrations in the surface and subsurface Atlantic Ocean have been declining (Lee et al., 2011), due to scavenging removal of Pb. Subsurface concentrations of Pb were about 2 pmol kg^{-1} higher during the NL 2010 occupation

than almost a year and a half later during the US occupation of the same station. Below 2000 m, the profiles (Fig. 3f) are not statistically different within analytical uncertainty (i - p -value = 0.24).

Dissolved aluminium is not part of the ICP-MS multi-element method due to the poor recovery of Al on the resin with the current method, especially in the presence of HF. However, it is included in the discussion here as it is the material of construction for the US sampling system and shipboard results are available. The result for Al by flow injection (FI) method from the NL 2010 occupation and the previous US 2008 occupation with the same US sampling system (Fig. 4) are not statistically different within analytical uncertainty (i - p -value = 0.16) and the accompanying reference samples are within 1 standard deviation from each other as well as the consensus values (Table 3), verifying the accuracy of the Al data. It is worth noting that the data of the Netherlands occupation is not significantly lower than the data from the US occupation, indicating that there is no noticeable contamination of Al from the US aluminium frame. The shipboard

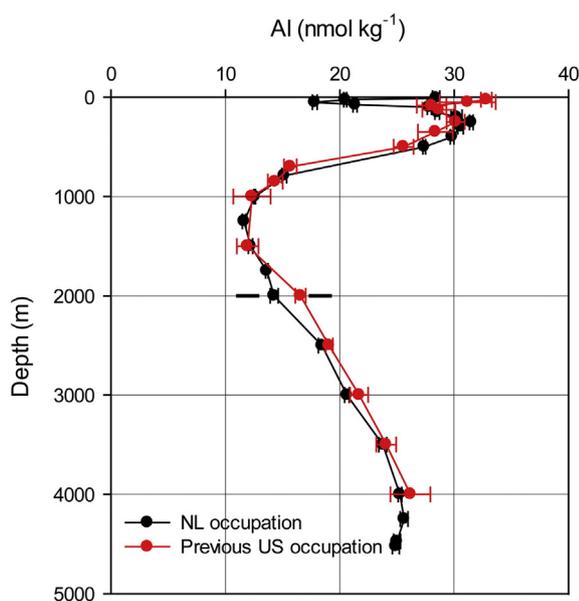


Fig. 4. Concentrations of Al (nmol kg^{-1}) from shipboard analysis during the Netherlands (black circles) and a previous (2008) US (red circles) occupation of the BATS station. The US data was analysed by Matt Brown from the University of California Santa Cruz (UCSC) and is the mean and standard deviation (error bars) of different samples filtered with different filtration systems as part of the initial Inter-calibration efforts of the GEOTRACES programme. The NL data is the mean and standard deviation (error bars) of triplicate analysis of the same sample. A black horizontal line denotes a significant difference between samples at individual depths (in the 1000 to 4000 m depth range) between the two profiles observed in the p -value profile (see the [Different sample approach](#) section for calculation and the supplementary material for the p -value profile). Note that the integrated p -value (i - p -value) reported in the text is based on the profiles between 1000 m and 4000 m depth. The excellent agreement is firm evidence by ocean crossover station approach of the accuracy of the measurements of dissolved Al in seawater by both laboratories (UCSC and NIOZ). This data was previously presented in a different form by [Cutter and Bruland \(2012\)](#). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

data for the US 2011 occupation ([Measures et al., 2015](#)) was significantly higher (i - p -value < 0.01) than the current data and the 2008 occupation. This was also noted by [Middag et al. \(2015\)](#) and the reason for the significantly higher values reported by [Measures et al. \(2015\)](#) in comparison to the 2008 and current data is currently unknown (see [Middag et al., 2015](#) for further details).

3.3. Intercomparison between methods

3.3.1. Multi-element standard addition ICP-MS versus double spike ICP-MS

The data for Fe, Zn and Cd from the US occupation of the BATS profile as well as 2 additional stations (station KN204-1-12 at 29.7°N , 56.8°W and station KN204-1-20 at 22.3°N , 35.7°W) from the two different ICP-MS methods were compared with both the t -test and the R-script. The samples were drawn from the same samplers at the same station and cast. These data are attached in the Supplementary material and are discussed in oceanographic context elsewhere ([Conway and John, 2014a, 2014b, 2015](#); [Rijkenberg et al., 2014](#)). The results of the standard addition ICP-MS method were triplicate extractions and measurements of the same sample. The standard deviation of the triplicate results was used as the analytical uncertainty. The double spike method is designed to obtain isotope ratios and uses more volume and samples were typically extracted once and analysed twice. A 2% error was used as the analytical uncertainty ([Conway et al., 2013](#)).

For Fe at the BATS station, the results ([Fig. 5a](#)) are not statistically different within analytical uncertainty when using the R-script (i - p -value = 0.09), but are significantly different when considering the analytical uncertainty using the t -test approach ([Table 5](#)). When comparing the 2 additional stations, no significant differences were observed using either test for station 12, but the t -test approach reported a significant difference for station 20 ([Table 5](#)). Thus the two ICP-MS methods produce comparable results, but the outcomes of the different tests differ. The different test results between the t -test and the R script are related to the manner of testing, where the R script is more reliable

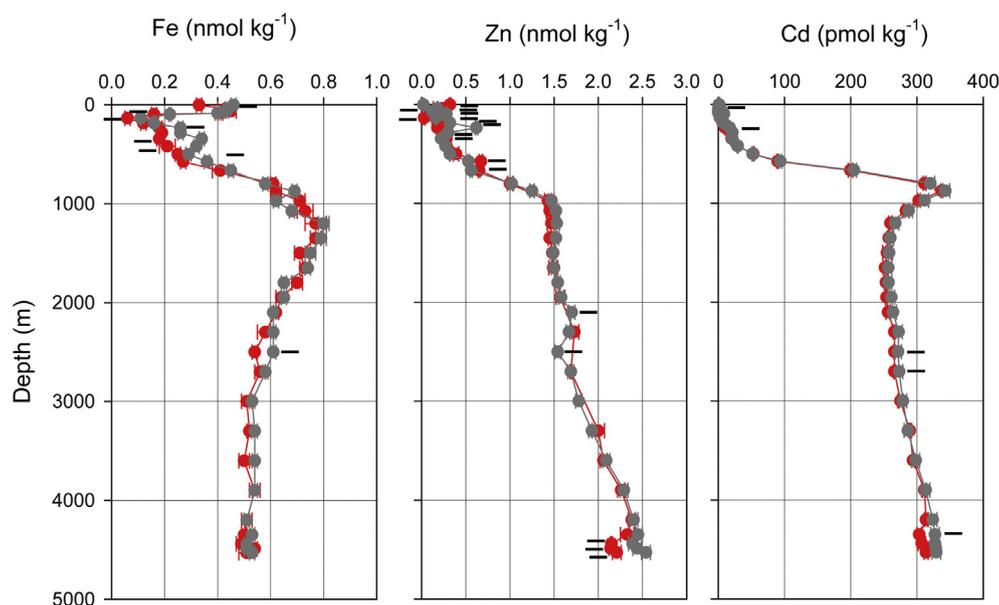


Fig. 5. Concentrations of trace metals for the standard addition ICP-MS method (red circles) and double spike isotope dilution ICP-MS method (grey circles) analyses at the US BATS station occupation for A) Cd (pmol kg^{-1}); B) Zn (nmol kg^{-1}); C) Fe (nmol kg^{-1}). A black horizontal bar indicates a significant difference ($p < 0.05$) observed in the p -value profile between samples at individual depths (whole water column) between the standard addition and double spike isotope dilution ICP-MS method profiles (p -values were calculated using the R script, see the [Different sample approach](#) section for calculation and the supplementary material for the p -value profiles). Note that the integrated p -value (i - p -value) reported in the text is based on the entire profile as these samples were collected simultaneously (i.e. the 'Different sample approach' was used for subsamples of the same sample, analysed using two analytical techniques, allowing simultaneous testing of the difference in concentration as well as the analytical uncertainty).

Table 5
Intercomparison results between subsamples of the same profiles for 3 stations in the North Atlantic Ocean using Double spike isotope dilution ICP-MS versus standard addition ICP-MS. Both statistical testing approaches were used (R script and t-test approach). Please note that for the initial t-test a $p > 0.05$ implies no significant differences between the profiles, whereas for the secondary t-test a $p < 0.05$ implies the two methods are not statistically different within uncertainty.

	Double spike					
	BATS		KN204-1-12		KN204-1-20	
	t-Test <i>p</i> -Value	R script <i>i-p</i> -Value	t-Test <i>p</i> -Value	R script <i>i-p</i> -Value	t-Test <i>p</i> -Value	R script <i>i-p</i> -Value
Standard addition Fe	0.99 ^a	0.09	0.28 ^b	0.16	0.99 ^a	0.07
Standard addition Zn	0.22 ^b	0.03	0.10 ^b	0.11	0.47 ^b	0.08
Standard addition Cd	0.11 ^a	0.30	0.02 ^c	0.75	0.41 ^b	0.10

For the R script, an *i-p*-value > 0.05 means the analytical results of the two methods are not statistically different within uncertainty.

^a t-Test result when considering the analytical uncertainty > 0.05 (σ_d not greater than absolute difference between data points and the analytical results of the two methods are statistically different when considering uncertainty).

^b Initial t-test gives no significant difference ($p > 0.05$).

^c t-Test result when considering the analytical uncertainty < 0.05 (σ_d is greater than the absolute difference between data points and the analytical results of the two methods are not statistically different within uncertainty).

due to the simultaneous testing of both differences and analytical uncertainty as detailed for Zn below.

For Zn at the BATS station, the results (Fig. 5b) are not statistically different using the t-test approach ($p = 0.21$), but the results are different within analytical uncertainty when using the R-script (*i-p*-value = 0.03) (Table 5). The *p*-value profile shows that the main discrepancy is in the upper 200 m where the Zn concentrations are low (Fig. 5b and Supplementary material). When excluding these data points (first 8 of 37), the results are not statistically different within analytical uncertainty (*i-p*-value = 0.19). This implies that there is an issue with accuracy for the low Zn numbers, but small differences due to low level contamination cannot be excluded either. The differing results between the t-test and R script, like for Fe, are related to the manner of testing. The initial t-test does not consider analytical error and will give an insignificant difference if the 2 profiles are 'snaking' around each other even if individual differences are relatively large, hence the passing of the test for Zn. The secondary test is only performed if the initial test fails (e.g. in case of Fe) and only considers the analytical error and with respect to the absolute difference without regard for the directionality of the difference. In contrast, the R script considers both factors simultaneously. When comparing the 2 additional stations for Zn, no significant differences were observed using either test (Table 5).

The low *p*-values in the *p*-value profile in the surface (Fig. 5b) were also observed for Fe (Fig. 5a and Supplementary material) and might be attributed to lower analytical reproducibility for the lower concentrations, for example because of a greater contribution from analytical blanks or lower signal/noise ratio during analysis, or to low level contamination of the original samples, or to a combination of both factors. For the standard addition ICP-MS method, the standard deviations were higher for the lowest concentrations of Fe and Zn, confirming the lower reproducibility for the lower concentrations. Low level contamination might arise from the used sample bottles or during filtrations, e.g. due to metals leaching from the filter or particulates caught on the filter. More research is needed to verify or exclude the latter hypothesis.

For Cd at the BATS station the results (Fig. 5c) are not statistically different within analytical uncertainty when using the R-script (*i-p*-value = 0.30), but are significantly different within analytical uncertainty when using the t-test approach (Table 5). However, when excluding the most deviation data points (more than 30% or 10 pmol/kg; 6 out of 37 data points) the σ_d is significantly larger than the absolute difference for the entire profile and thus are not different within analytical uncertainty (Table 5). When comparing the 2 additional stations, no significant differences were observed using either test (Table 5). Thus the two ICP-MS methods produce very comparable results, but some individual data points do differ. The R script is less sensitive to these individual 'outliers' than the t-test approach.

Overall, the two ICP-MS based methods give results that are not statistically different for Fe, Zn and Cd. The *p*-value profiles (Fig. 5 and

Supplementary material) show that for the low surface ocean concentrations (closer to the LOD), there is more deviation between the two methods. Additionally, the intercomparison shows that the manner of testing is very important and the R-script gives results that are more reliable due to the simultaneous testing of the difference in concentration as well as the analytical uncertainty. The agreement between profiles does differ between the different stations (Table 5) indicating that a single cross-over station might not be representative. Multiple cross-over stations between transects will often be unpractical, but repeat sampling at a cross-over station and independent analyses (e.g. in different runs some weeks apart) could provide more representative intercomparisons.

3.3.2. Multi-element standard addition ICP-MS versus shipboard flow injection methods

The metals Mn and Fe were also analysed shipboard using flow injection methods. Both methods are based on chemiluminescence produced by the reaction between hydrogen peroxide and luminol which is catalyzed by Fe or Mn (see Klunder et al. (2011) and Middag et al. (2011) for details). The vertical profiles, at first sight, demonstrate agreement between the shipboard methods and the standard addition ICP-MS method (Fig. 2a, b), but for both metals there is a small discrepancy. For Mn, the profiles are not significantly different within analytical uncertainty using the R script (*i-p*-value = 0.05) but the t-test approach does give a significant difference within analytical uncertainty. The shipboard data is about ~ 0.03 nmol kg⁻¹ lower at all depths. A similar offset was observed for the analysed reference samples (Table 3), but results for both methods were within the consensus range. For the shipboard data the blank was undeterminable, so no blank was subtracted. For the ICP-MS data a small blank of 0.04 nmol kg⁻¹ was determined and subtracted from the data. Perhaps this blank is an underestimation, but that does not seem very likely since Mn is not a contamination sensitive element. Adjusting either dataset for the observed offset makes them undistinguishable when considering the analytical error using either test (*i-p*-value = 0.83 and $p = 0.91$ for the R script and t-test approach, respectively), implying that this indeed is an absolute offset. However, given that the offset is just insignificant based on the R-script, the deviation between the profiles roughly equals the analytical uncertainty.

For Fe, the profiles are also not significantly different within analytical uncertainty using the R-script (*i-p*-value = 0.06), but the t-test approach does give a significant difference within analytical uncertainty. The results for reference samples for both methods were within the consensus range, but showed a similar discrepancy as observed for the profiles with the ICP-MS data being $\sim 5\%$ higher. Since the same relative offset is observed at high and low concentrations, this discrepancy appears related to a difference in calibration. For the sake of argument we adjusted the shipboard data towards the ICP-MS data based on the

~5% difference observed in the reference samples. This results in the profiles being no longer distinguishable using the t-test approach either (*i*-*p*-value = 0.18 and *p* = 0.82 for the R script and t-test approach, respectively). As for Mn the deviation between the profiles is just smaller than the overall analytical uncertainty.

It should be realised that the consensus values for the reference samples have a range and therefore have limited suitability to be able to distinguish small differences. Similarly, when comparing to previously published data, there is inherent variation due to discrepancies in the sampling depths as well as truly natural spatial and temporal variations that can mask small differences between methods. Both the ICP-MS and shipboard data included reference sample analysis and these agreed within the consensus range. When looking in detail, it is noticed that there appears to be a small discrepancy between the vertical profiles (ICP-MS vs shipboard) of dissolved Fe and Mn that is also represented between the reference samples, but usually this would have been ignored as both were within the range of reproducibility and accuracy. The small difference observed between the shipboard and ICP-MS methods is just insignificant, but does warrant monitoring.

4. Conclusion

The intercomparison of the different Netherlands and US sampling system by analysing samples from the BATS cross-over station with the same method and analyst demonstrated that both sampling systems are capable of collecting uncontaminated samples for all the GEOTRACES key elements. Nevertheless, at all times throughout the procedure, utmost care must be taken to avoid inadvertent contamination. All results for reference samples are in agreement with the current consensus values for those elements that have a consensus value available. Moreover, the data reported here for trace metal profiles obtained with different analytical methods are consistent, demonstrating comparability between techniques. This implies the analytical ICP-MS methods and the shipboard FI methods are functioning as expected and produce accurate data that can be reliably compared between cruises, with the caveat of Ga and Ti profiles, for which we did not yet achieve quantitative recovery.

Despite the strong consistency between collection and analytical techniques presented here, ultimately it is realised that all measurements have an uncertainty associated with them. Comparison of results from the exact same station i.e. measuring sub-samples from the same sample with different techniques allowed us to discern small differences between the shipboard measurements and the ICP-MS measurements. We were fortunate enough to run sub-samples from the same sample on the different methods, but these comparisons should also be possible from cross-over station as long as that station is sampled at common depths and in a relatively short timeframe to minimize natural variation, highlighting the importance of cross-over stations to the GEOTRACES programme.

4.1. Comments and recommendations

For the design of future crossover stations it is advisable to optimise the coordination of sampling depths, or preferably common neutral density horizons. This would greatly benefit the intercomparison, but might not aid intercomparison in the surface ocean if large variations occur between occupations. For comparisons between analytical techniques or sampling systems the deep ocean is simply best suited to make these comparisons. Comparison in the surface ocean is inherently less accurate due to variation in biological processes as well as the larger interpolation necessary along steep gradients and the fact that some processes (such as sinking and remineralising particles) are a function of depth as well as density.

In order to merge or link data from different cruises, investigators and nations into a coherent global dataset, cross-over stations will be an invaluable tool. This has been done for example by the CARINA

programme for ocean CO₂ and ancillary measurements (Olsen et al., 2009). It should be realised though, that one cross-over station in a long section is not a definitive answer to resolve potential differences. It will only work if every dataset is also validated by regular measurements of the international reference samples to ensure consistency within the international community and merged database.

A remark here with respect to the reference samples is that these should not only be analysed, but the results also need to be submitted to the reference sample coordinator (K.W. Bruland; bruland@ucsc.edu) in order to have the most representative updated consensus values available to the community. Furthermore, since the consensus values are not certified or constant, no corrections should be made to datasets based on analyses of reference standards; the values should just be part of the metadata. Internal seawater reference samples are most useful to identify any intra-dataset variability (i.e. variation between analyses performed on different days). The routine use of an internal seawater reference samples to be analysed far more frequently than the international reference samples is recommended, simply due to the scarcity of the international reference samples.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2015.06.014>.

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