# Automated preconcentration of Fe, Zn, Cu, Ni, Cd, Pb, Co, and Mn in seawater with analysis using high-resolution sector field inductively-coupled plasma mass spectrometry

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## Abstract

A rapid, automated, high-throughput analytical method capable of simultaneous analysis of multiple elements at trace and ultratrace levels is required to investigate the biogeochemical cycle of trace metals in the ocean. Here we present an analytical approach which uses a commercially available automated preconcentration device (Sea*FAST*) with accurate volume loading and in-line pH buffering of the sample prior to loading onto a chelating resin (WAKO) and subsequent simultaneous analysis of iron (Fe), zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb), cobalt (Co) and manganese (Mn) by high-resolution inductively-coupled plasma mass spectrometry (HR-ICP-MS). Quantification of sample concentration was undertaken using isotope dilution for Fe, Zn, Cu, Ni, Cd and Pb, and standard addition for Co and Mn. The chelating resin is shown to have a high affinity for all analyzed elements, with recoveries between 83 and 100% for all elements, except Mn (60%) and Ni (48%), and showed higher recoveries for Ni, Cd, Pb, Co and Mn in direct comparison to an alternative resin (NOBIAS Chelate-PA1). The reduced recoveries for Ni and Mn using the WAKO resin did not affect the quantification accuracy. A relatively constant retention efficiency on the resin over a broad pH range (pH 5–8) was observed for the trace metals, except for Mn. Mn quantification using standard addition required accurate sample pH adjustment with optimal recoveries at pH 7.5 ± 0.3. UV digestion was necessary to increase recovery of Co and Cu in seawater by 15.6% and 11.4%, respectively, and achieved full break-down of spiked Co-containing vitamin $B_{12}$ complexes. Low blank levels and detection limits could be achieved (e.g., 0.029 nmol $L^{-1}$ for Fe and 0.028 nmol $L^{-1}$ for Zn) with the use of high purity reagents. Precision and accuracy were assessed using SAFe S, D1, and D2 reference seawaters, and results were in good agreement with available consensus values. The presented method is ideal for high throughput simultaneous analysis of trace elements in coastal and oceanic seawaters. We present a successful application of the analytical method to samples collected in June 2014 in the Northeast Atlantic Ocean.

*Keywords:*

Trace metals
Seawater
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Preconcentration
Chelating resin
ICP-MS

## 1. Introduction

A number of trace metals are essential micronutrients for phytoplankton growth and play important roles in ocean biogeochemical cycles [1, 2]. In particular iron (Fe) has been identified as a micronutrient that directly limits phytoplankton growth in high nitrate low chlorophyll regions, which constitute ~30% of the oceans surface [1], and also controlling di-nitrogen fixation in oligotrophic gyres [3]. Other trace metals such as cobalt (Co), zinc (Zn), cadmium (Cd), manganese (Mn) and copper (Cu) may also be (co-)limiting for phytoplankton growth and/or influence phytoplankton community composition [2, 4, 5]. Major sources of trace metals to the ocean include continental shelf sediments, mineral dust, river discharge, submarine hydrothermal activity, and glacial melt waters [6]. Trace metal distributions are modulated by advection and diffusion, biological uptake, solubility, scavenging, organic ligand complexation and remineralization [6]. In addition, some trace metals can be used as tracers for source inputs (e.g. Mn for lateral transport from continental margins; [7, 8], and Pb for anthropogenic inputs [9, 10]).

Due to the complexity of these processes, and a paucity of data, our understanding of the distributions and dynamics of trace metals in the ocean remains limited. In response, the international GEOTRACES program was launched to sample and measure trace metal distributions throughout all of the major ocean basins in order to resolve controls on sources, sinks, and oceanic cycling of trace elements [11]. These sampling campaigns generate large numbers of seawater samples (often >1000) that require reliable, high throughput analytical methods to determine the concentrations of a range of trace metals.

Trace metals occur typically at very low concentrations in seawater, ranging from a few pmol $L^{-1}$ to nmol $L^{-1}$ which are challenging to measure. In addition, alkali and alkaline earth elements are present at relatively high concentrations of up to several hundred mmol $L^{-1}$, and may cause challenges during ICP-MS analysis as a result of salt precipitation in parts of the instrument and isobaric interferences with the analyte of interest. Consequently, for most seawater samples preconcentration of the analytes and removal of the salt matrix is required prior to analysis. A range of preconcentration and extraction methods have been developed, including organic solvent extraction [12, 13], co-precipitation with magnesium hydroxide [14, 15], and solid phase extraction using chelating resins in columns or as a batch extraction onto suspended resin beads [16-20].

A variety of resins have been developed with different functional groups that retain trace metals over a wide range of pH conditions, with recovery using diluted acids. For example, Toyopearl AF-Chelate-650M with iminodiacetic acid (IDA) functional groups has been used in conjunction with ICP-MS detection for determination of seawater Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb [17]. A nitrilotriacetic acid (NTA)-type Superflow resin has been employed with a single batch extraction and ICPMS detection for Fe, Pb, Cd and Cu [20]. NOBIAS Chelate-PA1, containing ethylene-diaminetriacetic acid and IDA functional groups on a hydrophilic methacrylate resin, has been applied for the analysis of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb with ICP-MS detection [16, 19].

Here we present a new method for simultaneous, accurate, and precise determination of dissolved Cd, Pb, Fe, Cu, Ni, Zn, Co and Mn in seawaters using a commercially available automated preconcentration device with subsequent analysis by ICP-MS. We applied a resin with immobilized carboxymethylated pentaethylenehexamine (CM-PEHA) functional groups (WAKO; Kagaya et al., 2009). Sample quantification was undertaken using isotope dilution for all elements apart from the monoisotopic elements, Co and Mn. Accuracy and precision were examined using standard reference seawater and resin performance was extensively tested over pH ranges between 1.9 and 8.1 to assess whether this newly tested resin can achieve constant recoveries over a wider pH range than previously studied resins. Resin performance was also directly compared to an alternative resin (NOBIAS Chelate-PA1) using the same preconcentration set-up.

## 2. Experimental

### *2.1 Reagents for sample pre-concentration*

All reagents were prepared in de-ionized water (> 18.2 MΩ cm; Milli-Q, Millipore). Nitric acid (SpA, Romil) was purified by single distillation in a sub-boiling perfluoroalkoxy-polymere (PFA) distillation unit (DST-1000, Savillex). Glacial acetic acid and ammonium hydroxide (20–22%) were of the highest purity (Optima, Fisher Scientific). Ammonium acetate ($NH_4Ac$) buffer (1.5 M) was prepared in de-ionized water using 140 mL ammonium hydroxide solution and 90 mL acetic acid for 1 L buffer, and adjusted to pH 8.5 ± 0.05 using ammonium hydroxide or acetic acid. 1 M nitric acid was prepared using subboiled distilled nitric acid (d-$HNO_3$) diluted with de-ionized water. For preparation of the elution acid, 1 M d-$HNO_3$ was spiked with 250 ng $L^{-1}$ indium (In) for drift correction during ICP-MS analysis. All reagents were stored in cleaned polypropylene (PP) containers provided by Elemental Scientific Inc. (ESI). All containers and sample bottles were cleaned by soaking in 2% Decon for 1 day, 1.2 M HCl (reagent grade) for 5 days, 1.5 M $HNO_3$ (reagent grade) for 5 days and a final rinse with de-ionized water and in between the soaking steps. The buffer and diluted acid were prepared inside a fume hood within a clean laboratory (ISO 5). Further reagent handling was carried out in an ISO 3 laminar flow bench with a HEPA filter unit.

### *2.2 Spike solutions*

Quantification of samples and reference seawater was performed for Fe, Zn, Cu, Ni, Cd and Pb using isotope dilution, and for the monoisotopic elements Mn and Co using standard addition. To assess changes in recovery following resin preconcentration, which affects both naturally occurring and spiked isotope, quantification using standard addition is necessary for all elements. Therefore, we distinguished between three different spikes used during sample preparation: (1) Isotope spike, (2) multi-element spike (for standard additions) and (3) Co-Mn spike.

The employed isotope spike solution contained artificially enriched $^{57}$Fe, $^{62}$Ni, $^{65}$Cu, $^{68}$Zn, $^{111}$Cd and $^{207}$Pb. The isotopes were received in solid form (ISOFLEX USA) and were dissolved in concentrated d-$HNO_3$. After mixing in 2% $HNO_3$, concentrations were verified by ICP-optical emission spectroscopy (ICP-OES; 7500 Agilent) and by reverse isotope dilution using a multicollector ICP-MS (MC-ICP-MS; ThermoFisher Neptune). Spike ratios for $^{56}$Fe/$^{57}$Fe, $^{60}$Ni/$^{62}$Ni, $^{63}$Cu/$^{65}$Cu, $^{66}$Zn/$^{68}$Zn, $^{110}$Cd/$^{111}$Cd and $^{207}$Pb/$^{208}$Pb were determined by MC-ICP-MS. A multi-element spike for standard additions containing Cd, Pb, Mn, Co, Fe, Ni, Zn, and Cu was prepared by serial dilution of individual stock standards (CertiPur, Merck) in 0.45 M d-$HNO_3$. For lower concentrated standard additions, further dilutions were prepared in 0.045 M d-$HNO_3$. A Co-Mn spike was prepared in a similar way as the multi-element spike by serial dilution of Co and Mn stock standards in 0.045 M d-$HNO_3$.

### *2.3 Seawater sample preparation*

Sample preparation was performed in a laminar flow bench. All low-density polyethylene (LDPE) and fluorinated ethylene propylene (FEP) bottles used for sample preparation and standard solutions, were acid washed according to protocols for washing of sample bottles described above [21]. After each use the FEP bottles were rinsed with de-ionized water, filled with 0.35 M hydrochloric acid (HCl), and stored for a minimum of 4 days before next usage. Prior to use, the FEP-bottles were rinsed 5 times with de-ionized water and once with a few mL of the sample. Pipette tips were rinsed three times with 3 M HCl (Trace Metal Grade, Fisher) and 3 times with de-ionized water.

Method tests were made using filtered (0.2 µm Sartobran capsule filter, Sartorius) North Pacific (Cruise NH1417, 2014, 25 m depth) and Southern Ocean seawater (Cruise JR271, 2012, surface water), as specified. Seawater was sub-sampled from 25 L carboys into 1 L LDPE bottles (Nalgene) and acidified to pH 1.9 using concentrated HCl (UpA, Romil). 15 mL aliquots of acidified seawater were transferred into 30 mL FEP bottles (Nalgene). Seawater and reference seawater samples (SAFe

S1, D1 and D2) were spiked with 125 µL of diluted isotope-spike. To determine Co and Mn concentrations in these samples, standard additions using the Co-Mn spike were performed on several (n = 4–7) 15 mL aliquots of North Pacific seawater covering a concentration range of 0.005–0.4 nmol $L^{-1}$ for Co and 0.25–20 nmol $L^{-1}$ for Mn. Prior to preconcentration, samples were UV-digested by placing the filled FEP-bottles into a homemade UV light box equipped with four low pressure mercury vapor lamps (25 Watt, Philips) [17]. Sample bottles were UV irradiated for 4 hours (unless stated differently). For tests on efficiency of UV digestion and recovery, no isotope-spike was added to the seawater and standard addition (n=7) was performed for all elements using the multi-element spike.

### *2.4 Pre-concentration set-up*

An automated system (SC-4 DX Sea*FAST* pico; ESI) with online pH buffering was used for sample preconcentration and seawater matrix removal. The preconcentration device (Fig. 1) was equipped as recommended by the manufacturer. The autosampler (4DX *FAST*ready) was equipped with a sample probe with 1.0 mm inner diameter (ID), a vacuum pump for sample aspiration and two independent rinse pumps supplying the rinsing station with 1 M d-$HNO_3$ from 4 L reservoirs. The reagents were distributed by a syringe system (S400V) consisting of an ethylene chlorotrifluoroethylene (CTFE) valve with PFA rotor and four syringes: one 12 mL CTFE/polytetrafluoroethylene (PTFE) syringe (S1), and three 3 mL quartz/PFA syringes (S2, 3 and 4). The reagent flow paths were controlled by a valve module (*FAST* DX 3) with two 11-port CTFE valves (V1 and V2) and one 5-port CTFE valve (V3), all three with a PFA rotor. The sample coil utilized in this study had a volume of 10 mL. All tubing connecting the valves was made of PFA. Valve 3 was connected to pressurized air for sample elution. The pressurized air was pre-filtered (ReZist Syringe Filter, PTFE, 5.0 µm, Whatman) in order to minimize any particle introduction. The buffer was cleaned in-line before mixing with the sample by a clean-up column (Nobias, ESI). Samples were eluted into 4 mL PP scintillation vials (Novodirect). The PP scintillation vials were cleaned in 2% Decon for 1 day, rinsed with tap water followed by de-ionized water, soaked 1 day in 1 M HCl heated to 45 °C, rinsed with de-ionized water, soaked 1 day in 1.5 M $HNO_3$ heated to 45 °C, rinsed 5 times with de-ionized water, and dried in a laminar flow bench.

### *2.5 Resins for pre-concentration*

Trace elements were preconcentrated with a WAKO chelate resin (similar to Presep® PolyChelate, Wako Pure Chemical Industries, Japan) with immobilized carboxymethylated pentaethylenehexamine (CM-PEHA) functional groups [22]. The resin material was obtained from Wako Pure Chemical Industries via S. Kagaya (University of Toyama, Japan) and showed the same characteristics for trace metal recovery as Presep® PolyChelate which is commercially available as a packed resin [22, 23]. The performance of the WAKO resin was compared to the NOBIAS Chelate-PA1 chelating resin (Sigma Aldrich) in tests on recovery and sample carry-over. Both resin columns were prepared in 2 cm tapered mini columns with an internal volume of 27 µL (Global FIA) by filling approximately half the column with resin material (10–15µL). The packed resins were cleaned by flushing for at least 4 h with 1 M d-$HNO_3$.

### *2.6 Pre-concentration and extraction*

The ESI SC-Autosampler and preconcentration device was controlled using a modified protocol of the ESI Software Version 2.9.0.82c. The preconcentration procedure (Table 1) includes loading of the sample into a coil (Fig. 1A), loading the sample onto the resin and rinsing off the seawater matrix using de-ionized water (Fig. 1B), rinsing the sample introduction parts with 1 M d-$HNO_3$, eluting the sample using elution acid (Fig. 1C), cleaning the sample and buffer clean-up resins using elution acid and 1 M d-$HNO_3$ (Fig. 1C, with change in position of valve 3), final rinsing of sample introduction/elution parts using 1 M d-$HNO_3$ and pre-conditioning of the preconcentration resin using the 1.5 M $NH_4Ac$ buffer and de-ionized water (Fig. 1D). In the utilized set-up, up to 63 samples (including samples for standard addition and reference samples) can be preconcentrated in one batch with a throughput of ca. 4 samples $h^{-1}$ which is similar to less automated methods [16, 17] but in the absence of an analyst.

### *2.7 Blanks*

Blank contributions were determined as two separate parts, the manifold blank and the $NH_4Ac$ buffer blank. The manifold blank accounted for contributions from the elution acid, any component of the preconcentration procedure (except buffer contributions) and manifold, as well as from the analysis on ICP-MS. The manifold blank was determined using the preconcentration method on the preconcentration device with modifications to the first three steps. Step 1 (Loading of sample on coil) and step 2 (Loading sample onto resin) were omitted and in step 3, a smaller amount (2500 µL) of de-ionized water was used for matrix removal. Elution, column cleaning and pre-conditioning steps remained the same as during seawater sample preconcentration. The $NH_4Ac$ buffer blank was determined using two batches of diluted North Pacific seawater (1:10 dilution with de-ionized water), one batch acidified with 1200 µL HCL $L^{-1}$ and the other batch acidified with 2400 µL HCl $L^{-1}$. The seawater was diluted in order to reduce the concentrations of trace metals in the solutions. Fe concentrations in undiluted North Pacific seawater were 0.747 ± 0.060 nmol $L^{-1}$ with analytical standard deviations exceeding buffer blank values. Both dilutions were treated the same as regular samples and analyzed in replicates (n=5) for each set of buffer. The buffer added in an automated manner during preconcentration was adjusted to obtain a similar pH (6.4 ± 0.2) for both dilutions. Buffer contributions were then calculated as the difference between the mean metal concentrations for the two buffer and acid volumes. This approach will also account for any contribution from the acid used for acidification. However the contribution of the high purity acid should be minimal in comparison to the buffer. The buffer contributions were also determined as the difference between obtained concentrations in the acidified (1200 µL HCL $L^{-1}$) diluted seawater and the concentration calculated using the mean value of repeated measurements of the undiluted North Pacific seawater divided by 10 (dilution factor). As final buffer blank, the mean value of the two different approaches was applied.

### *2.9 ICP-MS*

Preconcentrated samples were analyzed using an Element-XR high resolution sector field inductively coupled plasma mass spectrometer (Thermo Fisher Scientific) in low resolution (R=300) for $^{110}$Cd, $^{111}$Cd, $^{207}$Pb, $^{208}$Pb, $^{95}$Mo, $^{96}$Mo and $^{115}$In and in medium resolution (R=4000) for $^{56}$Fe, $^{57}$Fe, $^{60}$Ni, $^{62}$Ni, $^{63}$Cu, $^{65}$Cu, $^{66}$Zn, $^{68}$Zn, $^{59}$Co and $^{55}$Mn allowing isobaric interferences (e.g. $^{40}$Ar$^{16}$O on $^{56}$Fe) to be resolved. Specification of autosampler, sample introduction system, gas flow rates and RF Power are listed in Table 2.

The instrument was tuned before each run to obtain maximum sensitivity and stability. For tuning, a solution of In and Uranium (U) was used and standard deviations of both elements were below 1.5%. As a result of the use of Ni cones, a relatively high Ni background signal was obtained. The Ni background signal could be reduced by running the instrument with diluted tap water (1:10 in de-ionized water) for 2–4 h in order to plate the cones. Afterwards, the instrument was run with 1 M d-$HNO_3$ to clean the tubing and instrument from remaining metals from the diluted tap water. Interferences of $MoO^+$ on $^{110}$Cd and $^{111}$Cd were corrected as described by Wu and Boyle [14]. Briefly, Mo standards were prepared by serial dilution of a Mo stock solution (Inorganic Ventures) in 1 M d-$HNO_3$ with concentrations between 2 and 200 nmol $L^{-1}$ and were measured at the beginning and end of each analytical run. The isotope $^{95}$Mo was measured on all samples and the slopes from the linear regression of $^{95}$Mo/$^{110}$Cd and $^{95}$Mo/$^{111}$Cd obtained from the Mo standards was used to correct for $MoO^+$ interference on $^{110}$Cd and $^{111}$Cd counts of the samples.

A diluted multi-element solution, diluted isotope spike solution, and 1 M d-$HNO_3$ were analyzed after every 10th sample during each ICP-MS run. This was done in order to correct for an instrumental mass bias producing slightly different isotopic ratios than the true naturally occurring isotope ratios in the multi-element solution and the artificial isotope ratios of the isotope spike solution used during sample preparation. The multi-element solution was prepared from individual stock standards

(CertiPur, Merck) in 1 M d-$HNO_3$. The isotope spike solution was also diluted in 1 M d-$HNO_3$. The 1 M d-$HNO_3$ used for preparation of the dilutions was from the same batch as the acid analyzed on the ICP-MS in order to allow correction of the count rates for contribution from the 1 M d-$HNO_3$.

### *2.10 Calculation of elemental concentration and uncertainties*

Isotope ratios of Cd, Pb, Fe, Ni, Cu and Zn of the samples were calculated after subtracting mean counts of three manifold blanks. The concentrations of these elements were then calculated as described by de Jong et al. [24]. Isotope ratios of the multi-element and isotope spike solutions obtained using the ICP-MS analyses were used instead of the stated isotope ratios of these solutions. Concentrations of Co and Mn calculated using standard addition were based on linear regressions of the sequentially-spiked sample. Standard additions were performed after every 10th sample and the mean slope from one standard addition run before and one after the sample was used for sample concentration calculation. Sensitivity changes of the mass spectrometer were corrected for using ratios of Co and Mn count rates to indium count rates for standard additions and samples.

Measurement uncertainties were calculated after the Nordtest approach [25] incorporating uncertainties of within-lab reproducibility and uncertainties derived from the bias of determined reference materials to the certified or nominal values of the reference materials. This approach creates higher uncertainties (between 13% and 25% in our study) than previously published uncertainties for oceanic trace metal measurements but is accounting for random as well as systematic effects and consequently provides a more reliable and realistic estimation of uncertainties. Uncertainties of the measurement itself using only standard deviations in count rates and isotope ratios or standard addition slopes typically revealed uncertainties between 1% and 10%.

We applied the square root of the square sum of two separately determined uncertainties to obtain the combined uncertainty $u_c$ (Eq. 1).

$$u_c = \sqrt{u(Rw)^2 + u(bias)^2} \qquad (Eq. 1)$$

With $u(R_w)$ being the within lab reproducibility and *u(bias)* being the method and laboratory bias.

The within lab reproducibility was accounted for as the uncertainty obtained for multiple measurements of the same sample or reference material over a time period of several months. Here the pooled relative standard deviation of repeated measurements of the reference seawaters SAFe S, D1 and D2, and North Pacific seawater was applied. *U(bias)* was calculated as described in [25] after Equation 2.

$$u(bias) = \sqrt{{RMS_{bias}}^2 + u(Cref)^2} \qquad (Eq. 2)$$

Where $RMS_{bias}$ is the root mean square of the bias value (as % difference from the consensus value) (Eq. 3) and *u(Cref)* is the uncertainty of the consensus value (Eq. 4).

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}} \qquad (Eq. 3)$$

$$u(Cref) = \sqrt{\frac{\sum u(Cref_i)^2}{n}} \qquad (Eq. 4)$$

With $bias_i$ being the difference between determined mean concentration of reference materials and the reported consensus values, *n* being the number of different reference materials used and $u(Cref)_i$ being the reported uncertainties in consensus values. Final uncertainties (*U*) were determined as $u_c \times 2$.

### *2.11 Reference Material*

To assess the accuracy of our analytical procedure, we analyzed reference seawater and compared our results to the available consensus values. Reference seawater standards collected as part of the SAFe inter-comparison projects S (surface, ~10 m), D1 and D2 (deep, 1000 m) were used [26].

## **3. Results and Discussion**

### *3.1 UV-digestion*

Previous studies using chelating resins for trace element preconcentration in seawater samples have shown that trace element recovery, particularly for Co and Cu, can be reduced by the presence of strong, metal-binding ligands that prevent full preconcentration by the resin [16, 17, 27]. UV-digestion of the samples has been shown to be effective in breaking down organic complexes and achieving full recovery for Co and Cu [16, 17, 27, 28]. The acidification of the seawater samples to pH 1.9 following collection, with consequent dissociation of organic-metal complexes, appears to facilitate efficient preconcentration of other trace metals [16, 17].

Efficiency of UV-digestion was tested by determination of Cu and Co concentrations after different time periods of UV exposure (10 min to 4 h) of acidified (pH 1.9) Southern Ocean seawater in FEP bottles (Fig. 2). The strength and concentrations of Co and Cu binding ligands in the Southern Ocean seawater were unknown and may have influenced the outcome of this experiment. In order to better constrain the efficiency of the UV-treatment, we also performed this test using the same seawater, spiked with a known amount (0.1 nmol $L^{-1}$) of vitamin $B_{12}$ (added Co concentration determined separately by ICP-MS = 0.086 ± 0.001 nmol $L^{-1}$). Vitamin $B_{12}$ is a Co complex known to be present at concentrations up to a few pmol $L^{-1}$ in open ocean seawater and a few tens pmol $L^{-1}$ in coastal seawater [29, 30]. In addition, a UV digestion was performed for 250 min using quartz glass cuvettes rather than FEP bottles to investigate whether UV light transparency was sufficient for the FEP bottles. Efficiency of lamps was tested with old lamps (>4000 h operation; recommended lifetime of lamps is 9000 h) and with new lamps (<100 h operation). The tests using old and new lamps have been performed on the same sample of seawater but have been carried out after different durations samples have been acidified, with 5 days for tests using old lamps and 4 weeks for tests using new lamps.

Co and Cu concentrations increased by 15.6% and 11.4%, respectively, between non UV-treated Southern Ocean seawater samples (Co: 0.117 ± 0.003 nmol $L^{-1}$, Cu: 0.678 ± 0.034 nmol $L^{-1}$) and samples UV treated for 30 min. After 30 min, no further significant increase was observed (t-test, $p>0.05$). The Co concentration in vitamin $B_{12}$ spiked seawater with no UV treatment was only slightly higher by 0.006 nmol $L^{-1}$ (0.123 ± 0.003 nmol $L^{-1}$) to the original seawater concentration. After 20 min of UV exposure, Co added as the $B_{12}$ complex was quantitatively recovered. Total measured Co concentration was 0.223 ± 0.012 nmol $L^{-1}$. This demonstrates that Co in the vitamin $B_{12}$ molecule was not retained on the resin, and after about 10–20 minutes of UV exposure, all Co was released from the vitamin $B_{12}$ and quantitatively recovered on the resin. We did not observe any significant difference between used and new UV lamps (t-test, $p>0.05$), indicating that after >4000 h operation, the UV lamps were still efficiently degrading organic compounds that complexed Co and Cu. In all tests, Cu and Co concentrations obtained after 250 min of UV exposure in quartz cuvettes were indistinguishable (t-test, $p>0.05$) from those in FEP bottles, indicating the FEP bottles are as suitable as quartz cuvettes for UV treatment. Cu and Co concentrations in seawater without UV treatment increased by 7.3% and 8.2%, respectively, with increased duration of storage from 5 days to 4 weeks of the acidified samples prior to preconcentration. Hence, it is possible that after 4 weeks of storage a fraction of the Cu and Co-complexes was broken down under acidic conditions, increasing the recovery. Co concentrations in vitamin $B_{12}$ spiked seawater increased only slightly in comparison to the concentration obtained after UV digestion. This indicates Co-vitamin $B_{12}$ complexes, do not significantly dissociate by acidification to pH 1.9 for a period of less than 4 weeks.

### *3.2 Recovery and pH*

The chelation of metals by the functional groups on the resin is influenced by pH, and consequently the recovery of the trace metal depends on the pH of the sample. Therefore it is necessary to buffer the acidified sample to a pH where best recoveries are achieved. However, trace metal colloids can be formed after acidified samples are buffered to a pH higher than 2 and may alter the retention of trace metal on the resin [31, 32]. In this study, pH is adjusted online prior to loading onto the resin, minimizing the time trace metal colloids can be formed and increasing the reproducibility by eliminating changes in time periods samples have been buffered before loading on the resin. To assess the optimal pH for the chelating resin used in this study, we tested the recoveries for Fe, Zn, Cu, Ni, Cd, Pb, Co, and Mn in the range of pH 1.9 and 8.1. To reduce analytical variability at low concentrations we spiked North Pacific seawater with the multi-element spike (final concentrations: 5.35 nmol Fe $L^{-1}$, 5.76 nmol Zn $L^{-1}$, 7.14 nmol Ni $L^{-1}$, 4.77 nmol Cu $L^{-1}$, 0.98 nmol Co $L^{-1}$, 2.45 nmol Cd $L^{-1}$, 0.68 nmol Pb $L^{-1}$, 6.14 nmol Mn $L^{-1}$). Modifications to seawater pH were achieved by addition of different amounts of buffer to the sample prior to loading onto the WAKO resin. Figure 3 displays the count rates (exact recoveries were only quantified at pH 6.2 and 7.0; see Table 3) obtained for the different elements and isotopes from the same seawater sample buffered to different pH values. Count rates were not corrected for blank contributions and isobaric interferences. Hence, a slight increase in count rates for some metals could have been achieved by an increased buffer contribution with increasing amounts of buffer added. But these contributions were very low (<1% at pH 6.4) compared to the concentrations in the utilized seawater (see section '3.5 *Procedural blanks and detection limits*').

All elements apart from Cu showed significantly lower recoveries at the lowest pH of 1.9 and recovery typically increased with increasing pH. Cu recoveries were remarkably constant over the entire pH range tested with slightly lower recoveries at pH 1.9. Recoveries of Cd, Pb, Fe, Zn and Mn showed a decrease at the highest pH of 8.1. Between pH 5 and 7.9 most elements (Cd, Pb, Cu, Zn and Co) showed a relatively constant recovery, whereas Mn and Ni showed an increase in count rates up to pH 7.1. The recovery of Fe showed a maximum between pH 5.6 and 7.4. Good recoveries for all elements apart from Mn at pH 5–8 are very similar to previously observed pH ranges for Toyopearl [17] and NOBIAS [16] resins. Mn recoveries at pH 5 were about 50% of the maximum recovery achieved at pH 7.5 ± 0.3 (Fig. 3), whereas a low retention of Mn (less than 10% of maximum recovery) was obtained at pH 5.0 for the Toyopearl resin [17]. Nevertheless, Mn recoveries still increased significantly up to pH 6.2.

Isotopic ratios for Pb, Fe, Ni, Cu and Zn were constant over the entire range of pH investigated (Fig. 4), which shows that calculations of concentrations of these elements by isotope dilution is possible over a wide range of pH without any significant bias to one isotope, provided recovery does not drop sufficiently to alter quantification accuracy. However, Cd showed a decrease of $^{110}Cd/^{111}Cd$ ratio with decreasing pH, which can be contributed to $MoO^+$ interferences for both $^{111}Cd$ and $^{110}Cd$, with stronger interference for $^{111}Cd$ due to the natural isotope ratio of $^{96}Mo/^{95}Mo$ of 1.73 (we observed

1.7 times larger interference for $^{111}$Cd than for $^{110}$Cd). The significance of $MoO^+$ interferences increases with decreasing pH due to the decrease in Cd recovery, whereas best recovery for Mo on the WAKO resin was between pH 2 and 4.5 [22]. Thus, for Cd analysis it is important to operate at a buffered pH higher than pH 5 in order to minimize potential $MoO^+$ interferences. During a typical analytical run with Cd concentrations ranging from 0.011 to 1.089 nmol $L^{-1}$, observed $MoO^+$ interferences resulted in an overestimation of Cd concentrations of 3–9 pmol $L^{-1}$, compared to $MoO^+$ corrected concentrations. This level of interference is negligible at deep water Cd concentrations, but contributes a large fraction to surface seawater Cd concentrations, which are typically below 10 pmol $L^{-1}$ [33].

For optimal recovery for all eight trace metals using the WAKO resin, a pH range between 6 and 7.5 appears suitable. Preconcentration at the lower end of this pH range is preferential to keep the volume addition of buffer, and consequently the buffer trace element contribution, to a minimum. Recoveries were quantified for all elements using the WAKO resin at pH 6.2 and 7.0, and compared to the NOBIAS resin at pH 6.1 (optimal pH range: 6.2 ± 0.3 [16]). To quantify trace metal recovery from the chelating resin, standard additions using multi-element spike were performed in triplicate (duplicate for WAKO at pH 7.0) in North Pacific seawater. Exact preconcentration factors (loaded sample volume divided by volume of eluate) were determined by mass in the preconcentrated samples and used to determine the added concentrations in the eluate. Recoveries were determined as the ratio of the slopes obtained from the preconcentrated standard additions in seawater to the slopes of calibration curves prepared directly in the elution acid. Table 3 summarizes the obtained recoveries for the most abundant isotope for each element.

Excellent recoveries of >95%, for pH 6.2 and 7.0 using the WAKO resin were obtained for Cd, Pb, Cu and Zn. Recoveries for Fe and Co were slightly lower, between 80 and 90%, but were very similar for pH 6.2 and 7.0. For Ni and Mn, however, recoveries at pH 6.2 were below 50%. Increasing the pH to pH 7.0 improved the recovery for Mn from 41 to 60%, but no significant increase of the recovery for Ni was observed. Highest count rates for Mn and Ni were observed around pH 7, which implies that the curves in Figure 3 do not reach 100% recovery for all elements. Previous reports using a WAKO resin found Ni recovery of 100% (Mn was not analyzed) at pH 4.0 using surface seawater and 3 M $HNO_3$ elution acid [22]. Our observed recovery of 60% for Mn was similar to Mn recovery obtained using a Toyopearl resin at pH 6.3–6.8 [17]. Recoveries of Fe, Cu and Zn using the NOBIAS resin at pH 6.1 were similar to the WAKO resin at both pH tested. All other elements showed lower recoveries, especially Ni (below 38.5%) and Mn (24.1%). The recoveries for Ni and Mn are again lower than previous studies which indicated recoveries of >96% for all elements using a NOBIAS resin and 1 M $HNO_3$ elution acid [16, 19].In a direct comparison between Nobias and the Presep® PolyChelate resin using artificial seawater, recovery characteristics were very similar for both resins apart from highest Mn recovery for Nobias being observed at pH 8, suggesting that the here tested pH of 6.1 was not sufficiently high to achieve best recoveries [23]. Recoveries can vary for the same resin as individual laboratory practices (such as length of storage time of resins, flow rates for sample loading, and resin volume) may have an impact on resin performance. It is thus important to assess recoveries for each approach. Here, we utilized a smaller resin volume (15 µL) than Kagaya et al. [22] (their resin volume was 6 mL) with similar flow rates (3 mL $min^{-1}$) which might have impacted the recovery of Mn and Ni. The level of recovery does not affect the final quantified sample concentration, as this is accounted for in the isotope dilution and standard addition approaches. However, low recoveries may increase detection limits, since these will reduce overall element concentrations in eluted samples and therefore reduce total count rates. Here, despite the reduced recoveries for Ni and Mn, a strong correlation ($R^2$ typically >0.99) was obtained for standard additions for all elements over a broad range of naturally occurring concentrations in coastal and open-ocean seawater. However, due to the differing recoveries of Mn with changing pH, it is crucial to perform standard addition in seawater with the same pH as sample pH and to assure that samples are buffered to the same pH to guarantee accurate Mn determination.

### *3.3 Sample carry-over*

The recovery experiments showed that we often do not obtain 100% recovery. Whereas this does not seem to cause a problem for metal quantification of single samples, problems could occur for the analysis of the following sample if metals were not fully eluted from the resin (during elution and cleaning step) and carried over to the next sample. To assess this risk, we measured five manifold blanks after the preconcentration of North Pacific seawater which was spiked to increase concentrations of trace metals (Fe: 51 nmol $L^{-1}$, Zn: 43 nmol $L^{-1}$, Ni: 48 nmol $L^{-1}$, Cu: 45 nmol $L^{-1}$, Co: 5 nmol $L^{-1}$, Cd: 25 nmol $L^{-1}$, Pb: 7 nmol $L^{-1}$, Mn: 51 nmol $L^{-1}$). This has been performed for both, WAKO and NOBIAS resin. The obtained carry-over was negligible for all elements except Fe and Ni (Fig. 5). Carry-over of Fe was 0.5% for both resins and was entirely washed out after the third manifold blank. Carry-over of Ni was 0.3% using the NOBIAS resin and dropped to background level at the second manifold blank. Carry-over of Ni using the WAKO resin was 1.3% and needed two manifold blanks before decreasing to less than 0.5%. Sample carry-over of 0.5–1.3% for Fe and Ni should not cause a problem if the concentration of preconcentrated samples are within the same order of magnitude, but caution needs to be applied if samples with very low concentrations are preconcentrated directly after samples containing Fe or Ni concentrations that are an order of magnitude or higher. To monitor the sample carry-over during preconcentration of a batch of samples, we recommend running two manifold blanks after every 10th sample.

### *3.4 Linearity*

To verify the concentration range over which the recovery from the resin is linear and to investigate whether there is a potential of full saturation of the resin (with the used resin volume of approximately 15 µL) at certain threshold concentrations, standard additions were made to seawater solutions. For Ni, Cu, Zn and Co no decrease in recovery was observed over the entire concentration range tested in this experiment as shown in Fig. 6. All data points lie in close proximity to the regression line obtained excluding the two highest concentrations of the standard additions. $R^2$ values for the regression lines were >0.997 for all standard additions. For Cd, Pb, and Fe a slight decrease in recovery could be observed at concentrations higher than 100 nmol Cd $L^{-1}$, 30 nmol Pb $L^{-1}$ and 200 nmol Fe $L^{-1}$. Data points at higher concentrations lie below the regression line obtained excluding those data points. As these concentrations are much higher than typically observed natural seawater concentrations, the resin volume and sample volume used in this study can be applied over a wide range of seawater environments (coastal, deep sea). However in anoxic near sediment samples these concentrations can be exceeded for Fe [34], in which case adjustment of sample or resin volume should be considered.

### *3.5 Procedural blanks and detection limits*

At very low concentrations of trace metals in seawater it is crucial to accurately determine the contributions of reagents, the preconcentration device (i.e. resin, tubing) and ICP-MS to the observed sample concentration. We separately analyzed the contributions of the buffer ($NH_4Ac$ buffer blank) and combined background counts of the preconcentration procedure, including the elution acid, chelating resin, manifold, PP-vials and the analysis by ICP-MS (manifold blank). Buffer blanks were minimized by an additional buffer clean-up column, and especially for Zn buffer blanks were much lower than previously reported [17, 18]. The obtained values for manifold and buffer blank, the combined (procedural) blank, and the resulting detection limits are summarized in Table 4, and reveal similar values to previously reported detection limits of comparable methods [16-18, 20].

### *3.6 Precision and accuracy*

The precision and accuracy of the method was evaluated by analysis of SAFe reference seawater S, D1 and D2. The results from multiple measurements of different analytical runs and the available consensus values for all measured elements are listed in Table 5. The calculated mean values include several measurements from the same bottle of D2, two different bottles of S1 and three different bottles of D1. Relative standard deviations were between 1.8% and 7.3% for concentrations >0.1 nmol $L^{-1}$, between 4.7% and 9.7% for concentrations of 25–100 pmol $L^{-1}$ and increased at very low concentrations to 62.6% for 3 pmol $L^{-1}$ of Cd. Precisions vary largely for different elements and between different concentration ranges and may also be affected by the use of different bottles of reference seawater. However, observed relative standard deviations did not differ significantly from previously reported precisions for S and D2 obtained using similar methods [16-19]. The results for S and D1 were in good agreement with the consensus values. We note that concentrations of the reference seawater D2 for Cd, Fe, Mn and Ni are slightly (<10%) higher than the reported consensus values. As measurements of S and D1 for these elements were in good agreement, we assume that our measurements were accurate, but that the bottle of SAFe D2 utilized here, likely contained somewhat higher concentrations of those elements.

### *3.7 Environmental Application— vertical oceanic profiles*

Vertical profiles of seawater samples were collected using trace metal clean GEOTRACES protocols in June 2014 in the tropical Northeast Atlantic as part of the cruise Meteor 107. The samples were filtered on board using 0.2 µm pore size cartridge filters (Acropak 500, Pall) and acidified to pH 1.9 and subsequently analyzed in our laboratory for eight trace metals. The sampling location (18°15'N, 16°75'W) was 76 km (41 nm) off the Mauritanian coast and within an oxygen minimum zone with oxygen levels reduced to below 50 µmol $kg^{-1}$ at depths between 50 and 70 m, and between 420 and 450 m. Dissolved Cd, Ni, Cu and Zn (Fig. 7) showed a nutrient-like profile with lowest concentrations in the surface waters and increasing concentrations with depth due to remineralization of sinking organic matter [35]. In contrast, dissolved Mn concentrations were enhanced in the surface waters and decreased with depth. The high dissolved Mn concentrations in the surface waters are maintained by photo-reduction of Mn(IV)-oxides to the soluble Mn(II) [36], whereas Mn in subsurface waters is affected by particle scavenging [7]. Dissolved Pb profiles showed very low concentrations in surface waters, with a slight increase with depth, and were consistent with other observations in this area [37]. Dissolved Fe and Co showed typical hybrid-type depth distributions, with low concentrations in the surface waters due to microbial uptake. At depth, Fe and Co showed increases in the low oxygen regions as a result of release from organic matter during remineralization, with lower concentration at other depths as a result of scavenging processes of the elements onto sinking particles [38, 39].

## 4. Conclusion

Here we present a method for the simultaneous analysis of Cd, Pb, Fe, Cu, Ni, Zn, Mn and Co concentrations in seawater using an automated preconcentration device. The approach uses a sample volume of only 10 mL for preconcentration using syringe injection, thereby avoiding the need for large sample volumes. Samples are pH buffered inline reducing the sample preparation time and analytical artefacts by colloid forming trace metals at pH higher than 2. The blank contribution of the buffer is minimized via a separate additional buffer clean-up column. Isotope-dilution is used for determination of all elements except Mn and Co, eliminating sensitivity to variations in recovery and preconcentration factor. However, minimal variability in automated sample loading or elution volumes allows accurate quantification via standard addition which is particularly important for the monoisotopic elements Co and Mn. Observed concentrations of reference seawater are in good agreement with available consensus values, confirming the high levels of accuracy. Full recovery of Co and Cu were achieved only after UV digestion of samples. Collectively, best recoveries for the suite of elements studied here were between pH 6–7.5 for the WAKO resin. This was mainly determined by low recoveries of Mn and increased $MoO^+$ interferences on Cd at lower pH. In direct comparison, of the WAKO to the NOBIAS resin, we could achieve better recoveries for most elements using the WAKO resin which is particularly important at very low concentrations of trace metals such as <10 pmol $L^{-1}$ for Cd and Co in surface waters. Further improvement in time efficiency and sensitivity might be achieved by on-line coupling of the preconcentration system directly to ICP-MS.

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Table 1: Steps of the preconcentration procedure

| Step | Valve (V) positions | Syringe (S) action (flow rate – total volume) | Action |
|---|---|---|---|
| (1) Load sample on coil | V1: Load<br>V2: Load<br>V3: Load | | Probe moves into sample, integrated vacuum pump turns on (28 s) and aspires sample into 10 mL sample coil |
| (2) Load sample on resin | V1: Load<br>V2: Inject<br>V3: Load | S1: 2500 µL min$^{-1}$ – 11000 µL<br>S2: Adjusted for each sample set * | The 10 mL sample is pushed over preconcentration resin at same time as pH buffer |
| (3) Rinse matrix | V1: Load<br>V2: Inject<br>V3: Load | S1: 2500 µL min$^{-1}$ – 7500 µL | Salt matrix is removed from the resin using de-ionized water |
| | | | Probe moves to rinsing station and sample loop and sample introduction system are flushed with 1 M d-$HNO_3$ |
| (4) Elution | V1: Inject<br>V2: Load<br>V3: Inject | S2: 1000 µL min$^{-1}$ – 1050 µL | Preconcentrated metals are eluted using elution acid into 4 mL vials using pressurized air (0.3–0.5 bar) |
| (5) Clean Columns | V1: Inject<br>V2: Load<br>V3: Load | S3: 2000 µL min$^{-1}$ – 3000 µL<br>S4: 2000 µL min$^{-1}$ – 3000 µL | Cleaning of preconcentration resin and buffer clean-up resin with elution acid and 1 M d-$HNO_3$ |
| (6) Condition Columns | V1: Load<br>V2: Load<br>V3: Load | S1: 2500 µL min$^{-1}$ – 4500 µL<br>S2: 550 µL min$^{-1}$ – 1000 µL | Buffer and de-ionized water are pushed over the preconcentration resin in order to condition it for the next sample. |
| | | | Probe moves back to rinsing station and sample loop and sample introduction system are flushed with 1 M d-$HNO_3$ |

* Depending on the sample pH and the desired pH for sample loading. For a sample acidified to pH 1.9 and a desired pH of 6.4 the required amount of buffer added was typically between 1188 µL (270 µL min$^{-1}$) and 1320 µL (300 µL min$^{-1}$).

Table 2: ICP-MS instrumentation and settings

| **Instrument** | **Element XR, Thermo Fisher Scientific** |
|---|---|
| Autosampler | 4DX *FAST*ready , ESI |
| Nebulizer | 200 µL PFA nebulizer, AHF |
| Nebulizer uptake rate | 180 µL min$^{-1}$ |
| Sampler Cone | Ni, ICP-MS Cones LTD |
| Skimmer Cone | Ni 'H', ICP-MS Cones LTD |
| Spray Chamber | PFA Scott-Spray Chamber, AHF |
| Injector | Sapphire injector, AHF |
| Cool gas flow (L min$^{-1}$) | 14.5–15.32 |
| Sample gas flow (L min$^{-1}$) | 1.174–1.210 |
| Auxiliary gas flow (L min$^{-1}$) | 0.70–0.73 |
| RF Power (W) | 1110–1117 |

Table 3: Recoveries obtained for Cd, Pb, Fe, Ni, Cu, Zn, Co and Mn using a WAKO resin with sample preconcentration pH 6.2 and 7.0 and a NOBIAS resin at pH 6.1.

| | **$^{110}$Cd (%)** | **$^{208}$Pb (%)** | **$^{56}$Fe (%)** | **$^{60}$Ni (%)** | **$^{63}$Cu (%)** | **$^{66}$Zn (%)** | **$^{59}$Co (%)** | **$^{55}$Mn (%)** |
|---|---|---|---|---|---|---|---|---|
| **WAKO pH 6.2** | 97.1 ± 2.6 | 96.4 ± 2.8 | 80.3 ± 2.6 | 46.2 ± 1.1 | 99.3 ± 2.7 | 99.0 ± 2.8 | 87.8 ± 3.1 | 41.0 ± 0.9 |
| **WAKO pH 7.0** | 98.4 ± 0.5 | 96.5 ± 2.5 | 83.2 ± 0.9 | 48.0 ± 0.4 | 100.8 ± 1.2 | 99.9 ± 1.4 | 83.3 ± 1.2 | 59.6 ± 2.4 |
| **NOBIAS pH 6.1** | 85.5 ± 3.1 | 88.5 ± 1.6 | 83.1 ± 2.6 | 38.5 ± 1.4 | 102.7 ± 3.4 | 95.0 ± 3.4 | 73.1 ± 3.2 | 24.1 ± 0.2 |

Table 4: Values for manifold and buffer blanks (± 1 standard deviation of repeated measurements) as well as combined blank with resulting detection limits (three times the standard deviation of the blank: 3×SD)

| | Manifold blank (pmol $L^{-1}$) | Buffer blank (pmol $L^{-1}$) | Procedural blank (pmol $L^{-1}$) | Detection limit (3×SD) (pmol $L^{-1}$) |
|---|---|---|---|---|
| Cd | 0.7 ± 0.2 | 1.5 ± 0.2 | 2.2 ± 0.3 | 0.8 |
| Fe | 33.4 ± 4.4 | 34.0 ± 8.6 | 67.6 ± 9.6 | 28.8 |
| Ni | 111.6 ± 19.5 | 0.1 ± 0.2 | 111.7 ± 19.5 | 58.5 |
| Cu | 11.1 ± 2.3 | 3.1 ± 2.1 | 14.2 ± 3.1 | 9.3 |
| Zn | 4.7 ± 1.6 | 25.3 ± 9.2 | 30.0 ± 9.4 | 28.1 |
| Mn | 2.3 ± 1.6 | 11.2 ± 5.4 | 13.5 ± 5.6 | 16.9 |
| Co | 2.1 ± 0.7 | 0.6 ± 0.3 | 2.7 ± 0.8 | 2.5 |
| Pb | 0.084 ± 0.003 | 0.3 ± 0.2 | 0.4 ± 0.2 | 0.6 |

Table 5: Analyzed reference seawater. Mean values and standard deviation in nmol $L^{-1}$ for Cd, Pb, Fe, Ni, Cu, Zn, Mn and Co and available consensus values in nmol $L^{-1}$ (± 1 standard deviation), n = number of measurements.

| | SAFe S n=11 | SAFe S consensus value | SAFe D1 n=13 | SAFe D1 consensus value | SAFe D2 n=7 | SAFe D2 consensus value |
|---|---|---|---|---|---|---|
| Cd | 0.003 ± 0.002 | 0.001 | 1.015 ± 0.020 | 1.016 ± 0.032 | 1.089 ± 0.043 | 1.011 ± 0.024 |
| Pb | 0.050 ± 0.003 | 0.049 ± 0.002 | 0.025 ± 0.003 | 0.029 ± 0.003 | 0.028 ± 0.001 | 0.029 ± 0.002 |
| Fe | 0.091 ± 0.009 | 0.095 ± 0.008 | 0.645 ± 0.037 | 0.69 ± 0.04 | 1.029 ± 0.038 | 0.956 ± 0.024 |
| Ni | 2.415 ± 0.086 | 2.34 ± 0.09 | 8.693 ± 0.197 | 8.79 ± 0.27 | 9.625 ± 0.175 | 8.85 ± 0.26 |
| Cu | 0.514 ± 0.037 | 0.53 ± 0.05 | 2.216 ± 0.087 | 2.33 ± 0.11 | 2.176 ± 0.152 | 2.34 ± 0.15 |
| Zn | 0.070 ± 0.005 | 0.071 ± 0.010 | 7.327 ± 0.277 | 7.59 ± 0.36 | 7.433 ± 0.216 | 7.62 ± 0.26 |
| Co | 0.005 ± 0.001 | 0.005 ± 0.001 | 0.048 ± 0.003 | 0.046 ± 0.005 | 0.048 ± 0.003 | 0.047 ± 0.003 |
| Mn | 0.814 ± 0.033 | 0.810 ± 0.062 | 0.365 ± 0.017 | - | 0.437 ± 0.029 | 0.36 ± 0.05 |

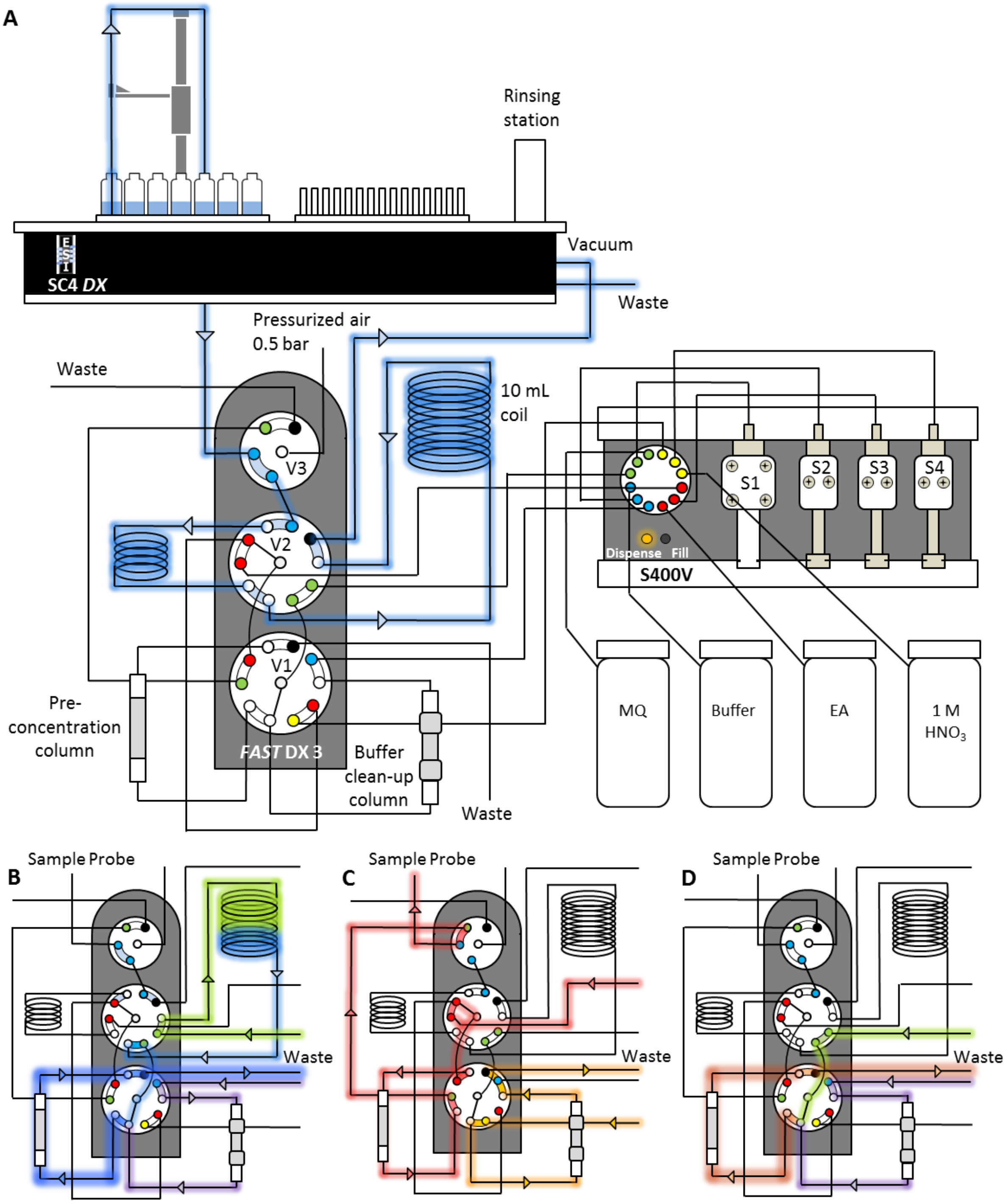

Figure 1: Schematic set-up of Sea*FAST* system and valve positions. A) Entire set-up including autosampler unit (SC4 DX), syringe system (S400V) and valve module (*FAST* DX 3) with the three valves in position for sample loading on coil (V1: Valve 1, V2: Valve 2, V3: Valve 3), blue line contours indicate sample flow path. B) Valve module in position for sample loading on resin and matrix rinsing. Line contours indicate sample and reagent flow (blue: sample, green: de-ionized water, purple: buffer, dark blue: sample-buffer mix). C) Valve module in position for elution. Line contours (red:

elution acid (EA), orange: 1 M $HNO_3$). D) Valve module in position for column conditioning. Line contours (green: de-ionized water, purple: buffer, brown: de-ionized water-buffer mix).

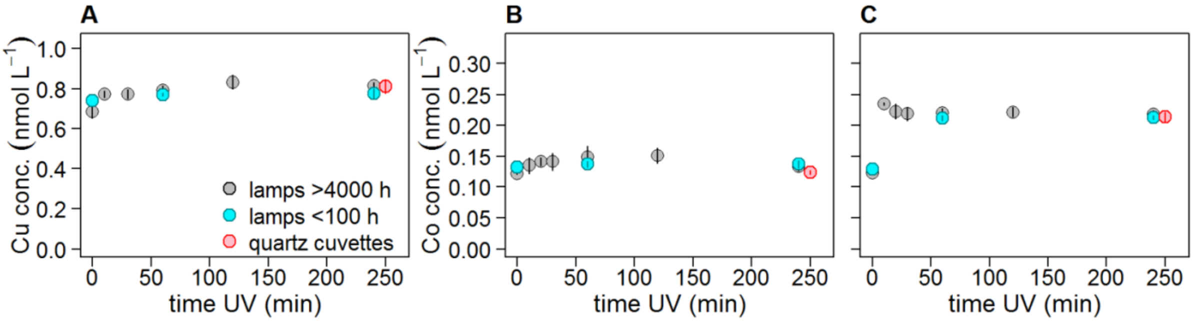

Figure 2: UV digestion efficiency experiment for Co and Cu with Southern Ocean water. A) Cu concentrations (in nmol $L^{-1}$) determined after UV exposure of up to 240 min with old UV lamps >4000 h and new UV lamps <100 h, and using quartz glass cuvettes rather than FEP bottles. Error bars show the standard deviation of three repeated samples. B) The same as A for Co. C) The same as B after spiking the seawater with vitamin $B_{12}$. The Co concentration after 10 min of UV treatment was higher than at any other time points, indicating possible contamination.

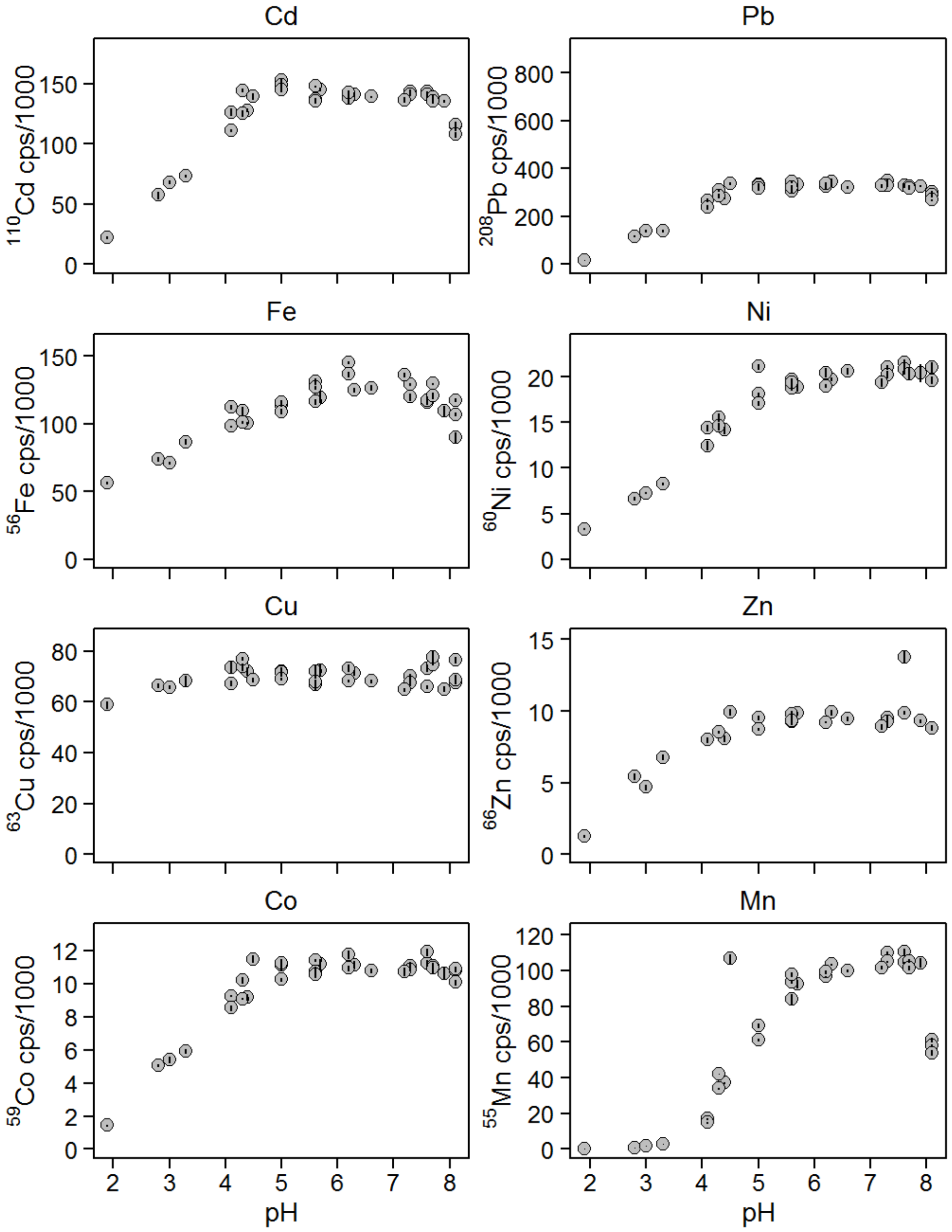

Figure 3: Count rates (cps) for the most abundant isotope of Cd, Pb, Fe, Ni, Cu, Zn, Co and Mn in North Pacific seawater with added spikes of trace metals over a pH range between 1.9 and 8.1. Displayed count rates are not corrected for blank contributions and isobaric interferences and were obtained in one analytical session.

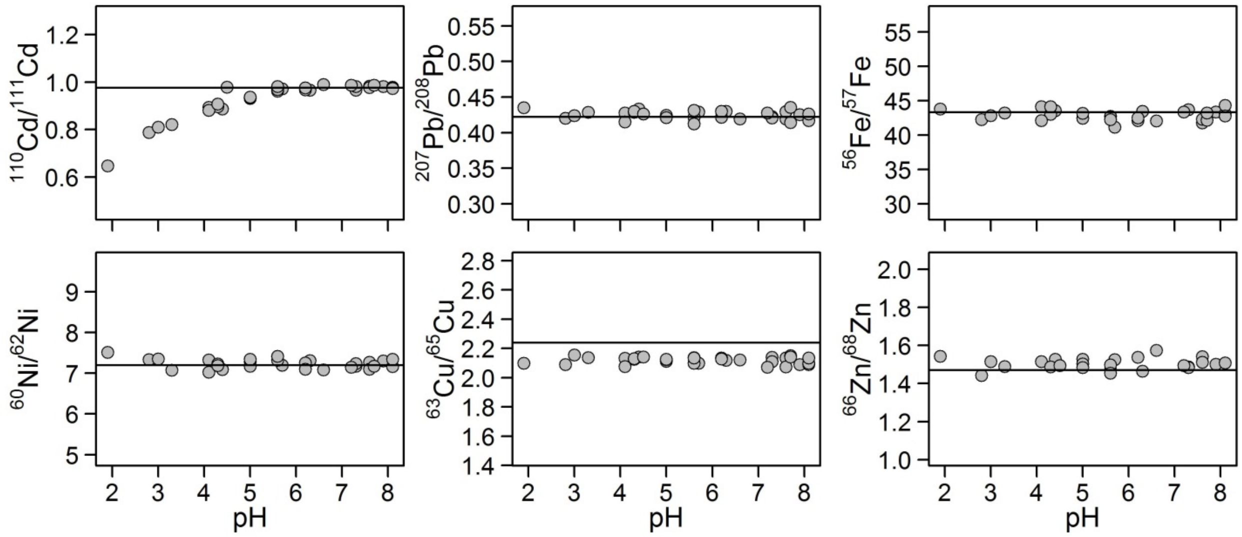

Figure 4: Isotope ratios obtained for Cd, Pb, Fe, Ni, Cu and Zn (natural isotopic composition) over a pH range employed during preconcentration of between 1.9 and 8.1 in North Pacific seawater. Ratios were not corrected for $MoO^+$ interferences and instrumental mass bias. Horizontal lines indicate the natural isotopic ratios.

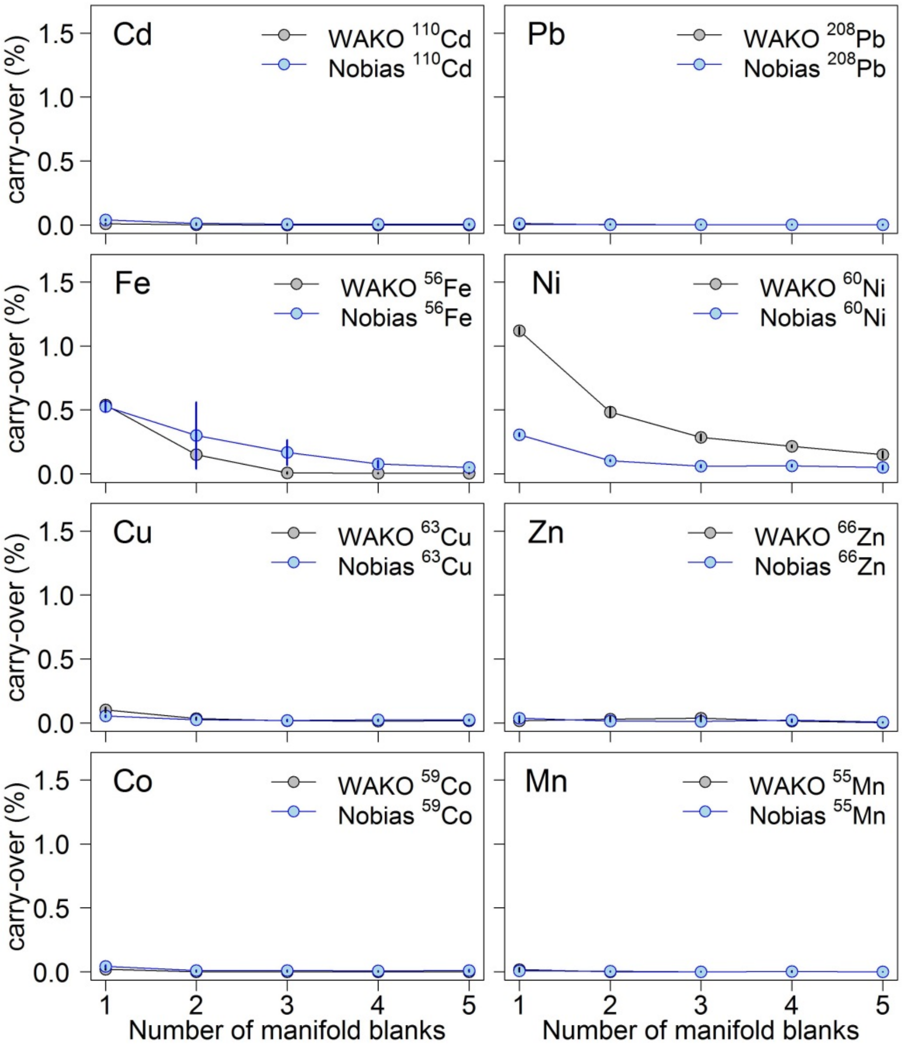

Figure 5: Carry-over of metals from an enriched North Pacific seawater sample to five following manifold blanks using a WAKO and a NOBIAS resin for preconcentration. The carry-over is given as percentage of counts of the blank to counts of the sample. This test was performed three times and error bars show standard deviations of triplicates.

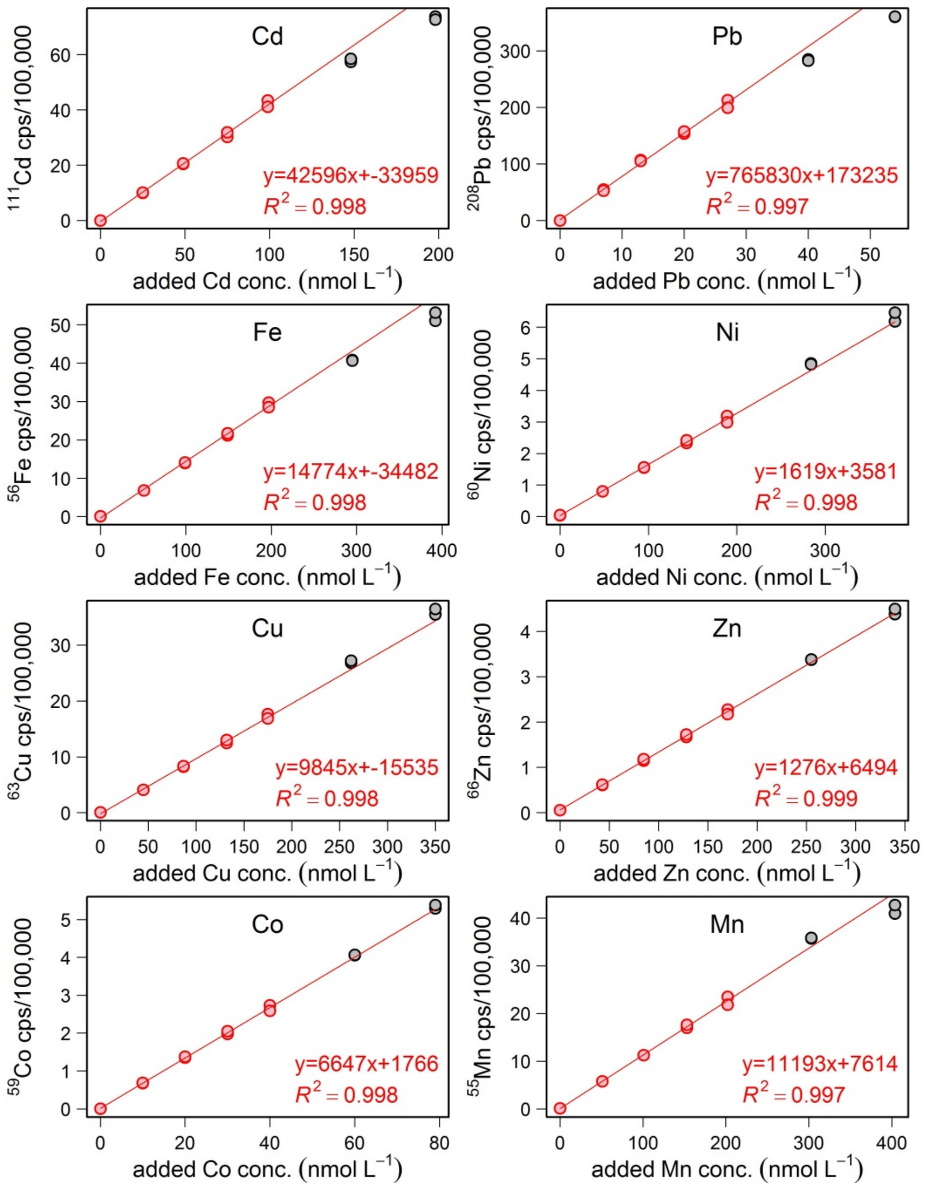

Figure 6: Linear regressions for high concentrated standard additions. Red line: regressions obtained by excluding the highest two concentrations. Red circles: data points included to calculate the linear regression. Standard deviations in count rates for each measurement were typically below 3%.

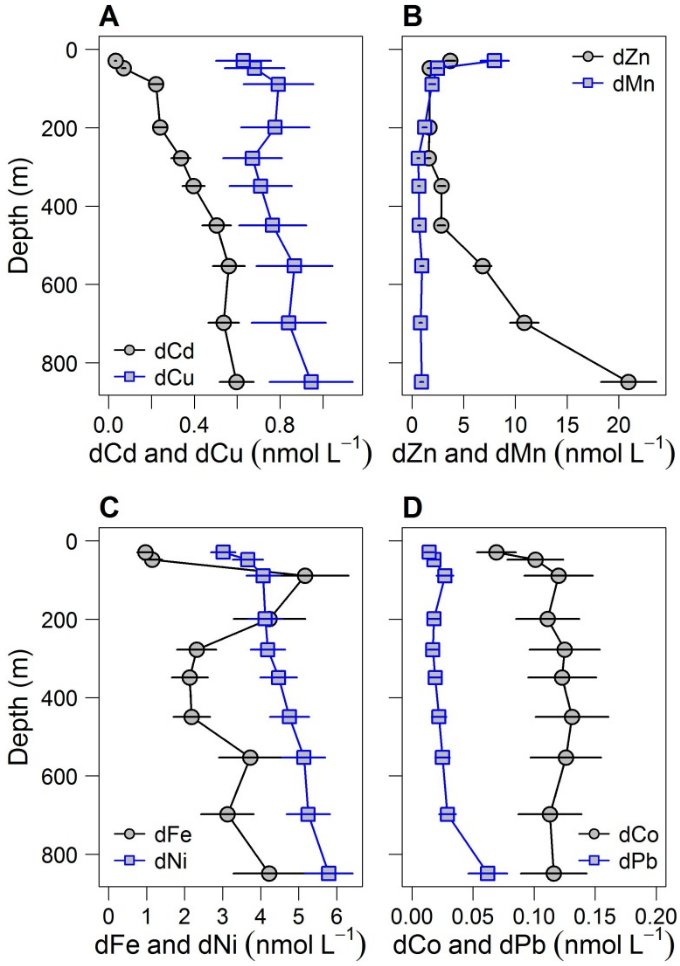

Figure 7: Depth profiles of eight trace metals. Samples were collected during cruise M107 using trace metal clean water sampler on June 12, 2014 (18°15’N, 16°75’W). Error bars indicate uncertainties calculated after the Nordtest approach.