Original paper

An off-line automated preconcentration system with ethylenediaminetriacetate chelating resin for the determination of trace metals in seawater by high-resolution inductively coupled plasma mass spectrometry

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ABSTRACT

A novel automated off-line preconcentration system for trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) in seawater was developed by improving a commercially available solid-phase extraction system SPE-100 (Hiranuma Sangyo). The utilized chelating resin was NOBIAS Chelate-PA1 (Hitachi High-Technologies) with ethylenediaminetriacetic acid and iminodiacetic acid functional groups. Parts of an 8-way valve made of alumina and zirconia in the original SPE-100 system were replaced with parts made of polychlorotrifluoroethylene in order to reduce contamination of trace metals. The eluent pass was altered for the back flush elution of trace metals. We optimized the cleaning procedures for the chelating resin column and flow lines of the preconcentration system, and developed a preconcentration procedure, which required less labor and led to a superior performance compared to manual preconcentration (Sohrin et al., 2008). The nine trace metals were simultaneously and quantitatively preconcentrated from ~120 g of seawater, eluted with ~15 g of 1 M HNO_3, and determined by HR-ICP-MS using the calibration curve method. The single-step preconcentration removed more than 99.998% of Na, K, Mg, Ca, and Sr from seawater. The procedural blanks and detection limits were lower than the lowest concentrations in seawater for Mn, Ni, Cu, and Pb, while they were as low as the lowest concentrations in seawater for Al, Fe, Co, Zn, and Cd. The accuracy and precision of this method were confirmed by the analysis of reference seawater samples (CASS-5, NASS-5, GEOTRACES GS, and GD) and seawater samples for vertical distribution in the western North Pacific Ocean.

Keywords:

Trace metals

Seawater

Automated preconcentration

Chelating resin

Inductively coupled plasma mass spectrometry

1. Introduction

Trace elements and their isotopes (TEIs) in the ocean are important as tracers in oceanography, micronutrients and/or toxins in biogeochemistry, and proxies in paleoceanography [1]. Recently, an international research program of the marine biogeochemical cycles of TEIs, referred to as GEOTRACES, was commenced to determine the distributions of key TEIs (such as Al, Mn, Fe, Cu, Zn, Cd, and Pb) and to clarify their sensitivity toward changing environmental conditions [2, 3]. While high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) is a powerful technique in the multi-elemental determination of trace metals, major constituents of seawater interfere with the precise determination [4]. In a previous paper, we reported a single-step and quantitative preconcentration of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb from open-ocean water, based on solid-phase extraction using a NOBIAS Chelate-PA1 resin (Hitachi High-Technologies) [5]. This resin consists of hydrophilic polyhydroxymethacrylate beads functionalized with ethylenediaminetriacetic acid and iminodiacetic acid [6]. Ethylenediaminetriacetate is an

analogue of ethylenediaminetetraacetate and a strong ligand for trace metals. In addition, NOBIAS Chelate-PA1 has certain advantages, including the effective removal of alkali and alkaline earth metals, low blanks of trace metals, and chemical and physical stability. We applied this method for oceanographic studies of trace metals in the Indian Ocean [7], the Bering Sea [8], and the Arctic Ocean [9]. The utilization of NOBIAS Chelate-PA1 is growing worldwide, not only for GEOTRACES key trace metals [10-13] but also for rare earth elements [13-17], Bi [18], Th [19], U [20], and isotopic ratios of trace metals [21-23]. Our original method was based on a manual manifold, which required skillful and uninterrupted operation. Here, we report a new automated preconcentration system with NOBIAS Chelate-PA1 for the quantitative recovery of nine trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb). Three methods using automated preconcentration systems with NOBIAS Chelate-PA1 have been reported thus far. One method was based on a seaFAST system (Elemental Scientific) for the on-line flow-injection ICP-MS determination of Mn, Fe, Co, Ni, Cu, and Zn [11]. Another method utilized a house-made, off-line preconcentration system for Mn, Co, Ni, Cu, Cd, and Pb [12]. The final method was based on a Dionex ICS3000 chromatograph for the off-line preconcentration of Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Cd, Ag, Pb, and rare earth elements [13]. While these methods utilized small volumes of seawater (9–38 mL), our system can handle a larger sample volume and can reduce the relative concentrations of blanks and interferents. In addition, while the reported methods adopted in-line pH adjustments, the sample pH in this method was adjusted off-line for a precise pH control. We utilized ~120 g of seawater, quantitatively recovered the nine metals, and realized

the lowest levels of blanks, concentrations of interferents, and detection limits.

2. Materials and methods

2.1. Reagents and materials

Deionized water (MQW) purified with a Milli-Q Integral 5 system (Millipore) was used to prepare all solutions. Ultra-high purity reagents, including HCl, HNO_3, acetic acid (HOAc), and NH_3 (Optima Acids, Fisher Scientific or TAMAPURE AA-10, Tama chemicals), were used for the solution preparation and analysis. Standard solutions of trace metals were prepared from 1000 mg L^{-1} standard solutions (Wako Pure Chemical). All solutions were prepared on a weight basis in a clean room (class 1000).

Low-density polyethylene (LDPE) bottles (Nalge Nunc) were used for sample storage and solution preparation. The bottles were cleaned in a clean hood and the operator wore polyethylene gloves (Saniment, AS ONE) to avoid contamination. The bottles and caps were soaked overnight in an alkaline detergent (5% Scat 20-X, Nacalai Tesque), rinsed with tap water, soaked overnight in 4 M HCl (reagent grade, Wako), and rinsed with MQW. The bottles were then filled with 1 M HF (Ultrapur-100, Kanto Chemical), loosely caped, sealed in a polyethylene bag, heated to ~80°C in a microwave oven, and left to stand on a bench overnight. The bottles were heated again, tightly capped, placed upside down on a bench overnight, and subsequently rinsed with MQW. Because the polypropylene caps contain some Al, it is essential to clean the inside of the caps with HF to reduce Al contamination. Subsequently, the bottles and caps were similarly cleaned with hot 1 M HNO_3 (Ultrapur-100),

and finally rinsed thoroughly with MQW in a clean room. Micropipette tips were cleaned in a similar fashion as the LDPE bottles.

The chelating resin column used in this study was Nobias Chelate-PA1 L (Hitachi High-Technologies). The resin of 300 mg was sandwiched with frits of high-density polyethylene (FILDUS Type F, Mitsubishi Plastics), and was sealed in a cartridge of polypropylene (NOVATEC-PP, Japan Polypropylene). Prior to use, the column was successively cleaned with 25 mL each of acetone (reagent grade), methanol (reagent grade), MQW, 1 M HCl-0.01 M H_2O_2 (reagent grade), 1 M HF (Ultrapur-100), MQW, 0.5 M NH_3 (Ultrapur-100), and MQW by sending the solutions through the column at a flow rate of ~5 mL/min using a polypropylene syringe.

2.2. Automated preconcentration system

An automated solid-phase extraction system (SPE-100, Hiranuma Sangyo) was modified for the application to open ocean seawater majorly in the following two points. The schematic configuration of the modified system is shown in Fig. 1. (1) The original system utilized alumina and zirconia parts in the 8-way valve, which led to the contamination of trace metals in preliminary experiments. According to our request, Hiranuma Sangyo prepared new parts made of polychlorotrifluoroethylene. These parts were initially cleaned with an alkaline detergent and 4 M HCl and were installed in the system. (2) The flow line of the eluent was also modified for the back flush elution of the trace metals, which effectively reduced the amount and concentration of the eluent.

The flow line was primarily composed of polytetrafluoroethylene-based materials, while a potential source of contamination was the sending unit, which has a double plunger pump composed of glass and a 4-way valve composed of alumina and zirconia (Fig. 1). Only waste solutions flowed through the sending unit during conditioning and sample loading (Table 1). The solution must not remain in the line between the column and the 4-way valve in order to avoid contamination from the sending unit. The eluent and eluate never reached the sending unit, because the eluent was sucked into a coil tube made of polytetrafluoroethylene and flowed backward through the column by sending air with the double plunger pump. The Nobias Chelate-PA1 L column was attached to the line with the TYGON SE-200 tubing (Saint-Gobain). The system was installed in a clean hood with a HEPA filtration unit (Class 100, Pure Space 01, Hokuto Soken).

The flow line was initially cleaned without attaching the column using 25 mL of each of the following reagents: (1) methanol (reagent grade) at 5 mL min^{-1} successively from the six ports of the 8-way valve and from the eluent port; (2) air from the six ports and eluent port; (3) 1 M HCl-0.01 M H_2O_2 (reagent grade) from the six ports; (4) air from the six ports; (5) 1 M HCl-0.01 M H_2O_2 (reagent grade) from the eluent port, with which the line was filed overnight; (6) air from the eluent port; (7) 1 M HNO_3 (Ultrapur-100) from the six ports; (8) air from the six ports; (9) 1 M HNO_3 (Ultrapur-100) from the eluent port, with which the line was filed overnight; and (10) air from the eluent port. After attaching the precleaned column, the flow line was cleaned using the following reagents: (1) 25 mL 0.1 M HCl（TAMAPURE AA-10 or Optima Acids）at 1 mL min^{-1} successively from the six ports of the 8-way valve;

(2) 25 mL of MQW at 5 mL min^{-1} from the six ports; (3) 25 mL of air from the six ports; (4) 80 mL of 1 M HNO_3 (TAMAPURE AA-10 or Optima Acids) at 1 mL min^{-1} from the eluent port; (5) 25 mL of air from the eluent port. The elution blank was examined by determining the concentrations of trace metals in the eluent and eluate. The procedural blank was examined by using 120 g of MQW as a sample (Supplementary data). When the measured values of the blanks were not low enough, the cleaning procedure was repeated.

2.3. Preconcentration procedure

In order to simultaneously preconcentrate the nine metals, the sample pH must be adjusted to 6.00±0.05. Although previous studies using automated systems adopted in-line mixing of the buffer and pH adjustments [11-13], it was not optimal because a slight variation in the concentration of the added acid for sample preservation causes a significant change in the pH. Therefore, we adjusted the sample pH off-line in a clean room. The HAcO-NH_4AcO buffer (3.6 M) was prepared by mixing 30 g of glacial acetic acid（Optima Acids）, 70 g of MQW, and 50 g of 20% NH_3（TAMAPURE AA-10 or Optima Acids）. A 2 g aliquot of the buffer was added to 120 g seawater containing HCl or HNO_3. The total concentration of acetic acid after mixing was ~0.06 M. The sample pH was carefully adjusted to 6.00±0.05 with 5 M NH_3 and 1 M HCl. The pH-adjusted sample was used for the preconcentration as soon as possible. The sample should not be transferred into another bottle to prevent contamination and the adsorption of trace metals on the bottle wall.

The optimized preconcentration procedure is shown in Table 1. The sample loading

volume was set to 140 mL to load ~120 g of sample and to clean up the line by following ~20 mL of air. During the elution process, the eluent volume was set to 18 mL, which resulted in ~15 g of eluate owing to dead space in the elution line. Thus, the concentration factor was ~8. The exact concentration factor was calculated based on the weights of the loaded sample and eluate. When a preconcentration cycle was carried out, the system was ready for another cycle. When a series of preconcentrations were finished, cleaning and 1–3 steps of the conditioning process were carried out to clean the line and empty it for suspension. To resume preconcentration after the suspension, the program was started from the cleaning process and MQW was used as a sample to validate the procedural blank. While some contamination was often observed in the first run, the blank became sufficiently low and stable since the second run.

2.4. ICP-MS measurements

A high-resolution ICP mass spectrometer equipped with a magnetic sector mass spectrometer (ELEMENT2, Thermo Fisher Scientific) was used for the determination of trace metals in the eluate. The measurement conditions are shown in Table 2. Isotopes typically used for the determination were ^{27}Al, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{111}Cd, and ^{208}Pb. Other isotopes were measured for cross checking, with the exception of mono-isotopes. Al, Mn, Fe, Co, Ni, Cu, and Zn were measured in the medium-resolution mode, while Co, Cd, and Pb were measured in the low-resolution mode. Polyatomic interferences such as those by ^{40}Ca^{16}O for ^{56}Fe were negligible in this method. Significant interference was observed for

both ^{111}Cd and ^{114}Cd owing to MoO, which cannot be dissolved even at medium resolution. This interference was corrected by calculation based on the measured intensities of Mo in sample solution and those of MoO and Mo in the Mo standard solution [10, 24]. Also there is a potential interference for ^{114}Cd by ^{114}Sn. However, significant difference was not observed in data determined with ^{111}Cd and ^{114}Cd. We observed a small peak, possibly of ^{43}Ca^{16}O, near the peak of ^{59}Co. Although the interference was not obvious for the measurement of ^{59}Co at low resolution in this work, it may be better to use medium resolution for ^{59}Co. The concentrations of trace metals were calibrated using external standard solutions prepared with 1 M HNO_3 (TAMAPURE AA-10 or Optima Acids). Further matrix matching was not necessary. The standard solutions were measured before and after every few samples to correct drifts of the background and the slope of the calibration curve.

The concentrations of alkali and alkaline earth metals in eluate were determined using an ICP-atomic emission spectrometer (ICP-AES, SPECTROBLUE, SPECTRO Analytical Instruments) and a quadrupole ICP-MS (Q-ICP-MS, ELAN DRC II, Perkin Elmer) by the calibration curve method.

2.5. Seawater samples

Certified reference materials of nearshore seawater for trace metals, CASS-5 and NASS-6, were obtained from the National Research Council, Canada. CASS-5 was collected from Halifax Harbor and NASS-6 was collected from Sandy Cove, Nova Scotia. The seawater was filtered through a 0.45-μm filter, acidified to pH ~1.6 with HNO_3, refiltered

through a 0.2-μm filter, and gamma irradiated. Certified values for Mn, Fe, Ni, Cu, Zn, Cd, and Pb exist, while only an information value is reported for Co and no data is available for Al.

GEOTRACES open-ocean water reference materials were obtained from US GEOTRACES. The used samples were collected at the Bermuda Atlantic Time-Series Study station (64.05°W, 31.46°N) in the western North Atlantic Ocean. GEOTRACES GS was surface water, while GEOTRACES GD was collected at a depth of 2000 m. These samples were filtered through a 0.2-μm filter and acidified with HCl to pH ~1.8 onboard the ship. Consensus values for the nine elements are open to the public (http://www.geotraces.org/science/intercalibration/322-standards-and-reference-materials).

Seawater samples for a vertical profile were collected from station TR 16 (160.05°E, 47.01°N; bottom depth 5224 m) in the North Pacific Ocean during R/V Hakuho Maru KH-11-7 cruises using the GEOTRACES Japan clean sampling system [4]. Each seawater sample was filtered through a 0.2-μm pore Nuclepore filter (Whatman), acidified with HCl to pH ~2.2, and stored in an LDPE bottle at room temperature.

3. Results and discussion

3.1. Optimization of preconcentration procedure

The basic properties of Nobias Chelate-PA1 and its application in a manual preconcentration system were reported previously [5]. Because the adsorption capacity of Nobias Chelate-PA1 for Cu(II) is 0.16±0.01 mmol g^{-1}, the capacity of the Nobias

Chelate-PA1 L column is 48 μmol. This value is a measure of the amount of available ligands, since Cu has the strongest affinity to these ligands among divalent metal ions. For the target metals, namely Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb, the total concentration is less than 100 nmol kg^{-1} in seawater, and the total amount is less than 12 nmol in a seawater sample of 120 g. Thus the capacity of the column is four thousands times larger than the amount of the target metals.

In the previous study, we examined the retention percentage in a pH range of 1–9 using 20 mL of MQW sample solutions added with a single element or plural elements of ~20 μmol kg^{-1} [5]. All the target metals were quantitatively collected at pH values between 6 and 7. The retention percentage of Al sharply decreased when pH became lower than 6, while the collection percentage of alkaline earth metals increased with pH particularly above pH6. In this study, we examined the effect of pH on the retention percentage, using 120 g of MQW sample solutions that have been added with the target metals as much as the highest concentration in seawater (90 pmol kg^{-1}–14 nmol kg^{-1}) and adjusted at pH 5.5–6.6. The results are shown in Fig. 2. The nine trace metals were quantitatively collected at pH values between 5.5 and 6.2. The collection percentage of Fe decreased above pH 6.2. While these results appear to be inconsistent with the previous results, it is likely that the decrease in retention of Al under the high concentration and low pH condition is caused by kinetic limitation in chelate formation, and the decrease in retention of Fe under the low concentration and high pH condition is caused by adsorption of Fe onto surfaces of the bottle and concentration system. Thus, we selected an optimum pH of 6.00±0.05 for the quantitative

recovery of the nine trace metals and the effective removal of the major cations. Quéroué et al. [12] selected pH 6.2 for the preconcentration of trace metals to minimize the recovery of Mo that causes interference of MoO on Cd. In this work, the interference of MoO was corrected by calculation (Section 2.4.).

To reduce the concentrations of the major cations in the eluate, it was necessary to clean the column with 0.05 M HAcO-NH_4AcO buffer (pH 6.00±0.05) after sample loading (Step 2, Sample loading process, Table 1). We found that the concentrations of the major cations were substantially reduced with the flow of the first 7 mL of buffer, and gradually decreased as the amount of the buffer was increased to 40 mL. Because the buffer could be a source of contamination of trace metals, we determined the optimum setting as 30 mL at 3 mL min^{-1}.

In addition, we examined the effect of the amount of eluent (1 M HNO_3) on the recovery of the target metals. Al and Fe were quantitatively eluted with 12 g of eluent, while other trace metals were quantitatively eluted with 6 g of the eluent at a flow rate of 1 mL min^{-1}. Therefore, the optimum parameter for the elution process was set as 18 mL at 1 mL min^{-1} (Table 1), which resulted in ~15 g of eluate. After the elution was repeated more than 100 cycles, the performance of Nobias Chelate-PA1 resin did not change significantly.

3.2. Removal of major cations in seawater

Table 3 summarizes the concentrations of major cations in the eluate for the eightfold preconcentration of the trace metals from seawater. The concentrations were less

than 30 μmol kg^{-1}. The percentages of the remaining amount of major cations in the eluate against the amount in seawater were calculated by a following equation.

$$\% \text{ remaining} = \{(C_{\text{eluate}} \times V_{\text{eluate}})/(C_{\text{seawater}} \times V_{\text{seawater}})\} \times 100$$

where C_{seawater} and C_{eluate} represent concentrations in seawater and eluate, and V_{seawater} and V_{eluate} represent volumes of seawater passed through the column and of eluate, respectively. Calculated values were $\sim 1 \times 10^{-3}$ %. These results indicate that Nobias Chelate-PA1 is highly effective in separating trace metals from major cations. The remaining concentrations of major cations in this work are less than 17% of those in the manual method [5]. This improvement is probably due to the lower dead volume in the automated system.

Wang et al. [13] reported effects of Mg and Ca on the determination of trace metals by HR-ICP-MS. According to their data, Cu was the most sensitive and the signal decreased by 60–76% at Mg and Ca concentrations above 0.0025 mM. This effect was not observed with our eluate. The interference of CaO on Fe was also not significant in this work.

3.3. Blanks, detection limits, and recoveries

In order to reduce the blank values of Al and Fe, it was essential to clean the Nobias Chelate-PA1 column initially with HF and HCl-H_2O_2. The latter solution probably reduces Fe^{3+} to Fe^{2+} resulting in the effective removal of Fe from the column. Previously, a solution of HCl-ascorbic acid was used for this purpose. However, we found that some ascorbic acid remained in the column after cleaning and caused a decrease in the collection percentage, especially for Fe.

The procedural blank values were estimated using 120 g of MQW initially acidified with hydrochloric acid to achieve a final concentration of 1×10^{-2} mol kg^{-1} and then adjusted to pH 6.00±0.05 by adding buffer according to the optimized procedure. Relatively large blanks of ~0.1 nmol kg^{-1} were found for Al and Zn (Table 4 and Supplementary data). The procedural blanks were generally less than the lowest concentration in open-ocean water, with the exception of Fe and Zn. The procedural blank of Cd was less than the detection limit of HR-ICP-MS. The detection limit of this method was defined as 3 SD for the procedural blank, except for Cd. The detection limit of Cd was limited to ~0.002 nmol kg^{-1} owing to interference by MoO. The detection limits were lower than the lowest seawater concentrations for Mn, Ni, Cu, and Pb, while they were comparable or higher for Al, Fe, Co, Zn, and Cd. The blanks and detection limits are compared with those of previous studies using Nobias Chelate-PA1 in Table 4. The data suggest that the blanks and detection limits of this study are at the lowest level for all the nine metals.

The recoveries of spiked metals from seawater were 93–107%, with SDs less than 9% (Supplementary data). The recoveries usually did not change following the preconcentration of ~100 samples. However, the recoveries decreased particularly for Fe, when organic matter such as ascorbic acid and other natural organic acids were adsorbed on the resin. Researchers from Hitachi High-Technologies found that citric acid substantially decreased the recoveries of Fe and Mn (private communication). Although some organic matter was removed by passing ethanol and aqueous NH_3 through the column, thorough cleaning was difficult.

3.4. Analysis of reference materials of seawater

This method was applied to seawater reference materials for trace metals. The results are summarized in Table 5. For Mn, Fe, Ni, Cu, Zn, Cd, and Pb in the nearshore seawater reference materials of CASS-5 and NASS-6, our results agreed with the certified values within 2 SD. Our concentrations for Co were slightly lower than the information values. For reference materials of open-ocean water of GEOTRACES GS and GD, our results agreed with the consensus values within 2 SD for the most part. For Co and Cu in both samples, our results were significantly lower than the consensus values. This was probably because UV irradiated samples were used for the determination of the consensus values. It has been explained that UV oxidation decomposes natural organic ligands, permitting the complete recovery of dissolved Co and Cu [10, 12]. The average concentration for Al in GS was also significantly lower than the consensus values. The reason behind this is unclear at the moment. The RSDs in this study were generally less than 6%. The concentrations measured by plural nuclides (Table 2) were consistent within analytical errors. The Fe concentrations based on ^{54}Fe were slightly higher than those based on ^{56}Fe and ^{57}Fe, which was probably due to an isobar of ^{54}Cr. These results suggested that our method had sufficient accuracy and precision to study trace metals in seawater in a concentration range varying from 25 nmol kg^{-1} to 2 pmol kg^{-1}.

3.5. Application to vertical distributions in the ocean

Observation of the vertical profiles in the ocean is the best way to evaluate the performance of analytical methods for marine geochemistry of trace metals. Using this method, the vertical profiles of dissolved trace metals were observed at a station in the western North Pacific Ocean (160.05°E, 47.01°N; bottom depth 5224 m). Each sample was analyzed in duplicate. The results are shown in Fig. 3. The average RSDs were less than 4% for Mn, Ni, Cu, Zn, Cd, and Pb; 5.8% for Fe; 7.4% for Co; and 11.5% for Al. This represents the first full-depth and simultaneous profiles of the nine metals in the Pacific Ocean. These profiles are oceanographically consistent. Also, fine structures seemed to be well detected. For example, both Mn and Pb showed surface maxima, subsurface minima at 100-m depth, and broad maxima at ~300-m depth. Both Al and Fe showed maxima at 500- and 790-m depths, probably owing to advection of the North Pacific Intermediate Water.

4. Conclusions

A simple and precise determination method of GEOTRACES key trace metals in seawater was developed using a new automated preconcentration system with NOBIAS Chelate-PA1 chelating resin. The automated system substantially relieved operators' load. The remaining concentrations of major seawater cations in the eluate were decreased compared with the manual system [5], leading to reduction of interferences in the determination by HR-ICP-MS. The blank and detection limits were as low as those with the manual system. This method was successfully applied to the determination of trace metals in reference seawater and vertical samples from the western North Pacific. The RSD was

typically less than 6%. Because this preconcentration system is suited to handle a large amount of sample, it can be used in further studies for determining not only the concentrations of ultra-trace metals but also the isotopic ratios of stable trace metal isotopes.

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Figure captions

Fig. 1. Manifold schematic of the modified automated concentration system. The sending unit, a possible source of contamination, is shown in the box with the broken line.

Fig. 2. Effect of pH on the retention percentage of trace metals. The error bars show ±SD.

Fig. 3. Vertical profiles of dissolved trace metals in the western North Pacific Ocean (160.05°E, 47.01°N). The error bars show ±SD.

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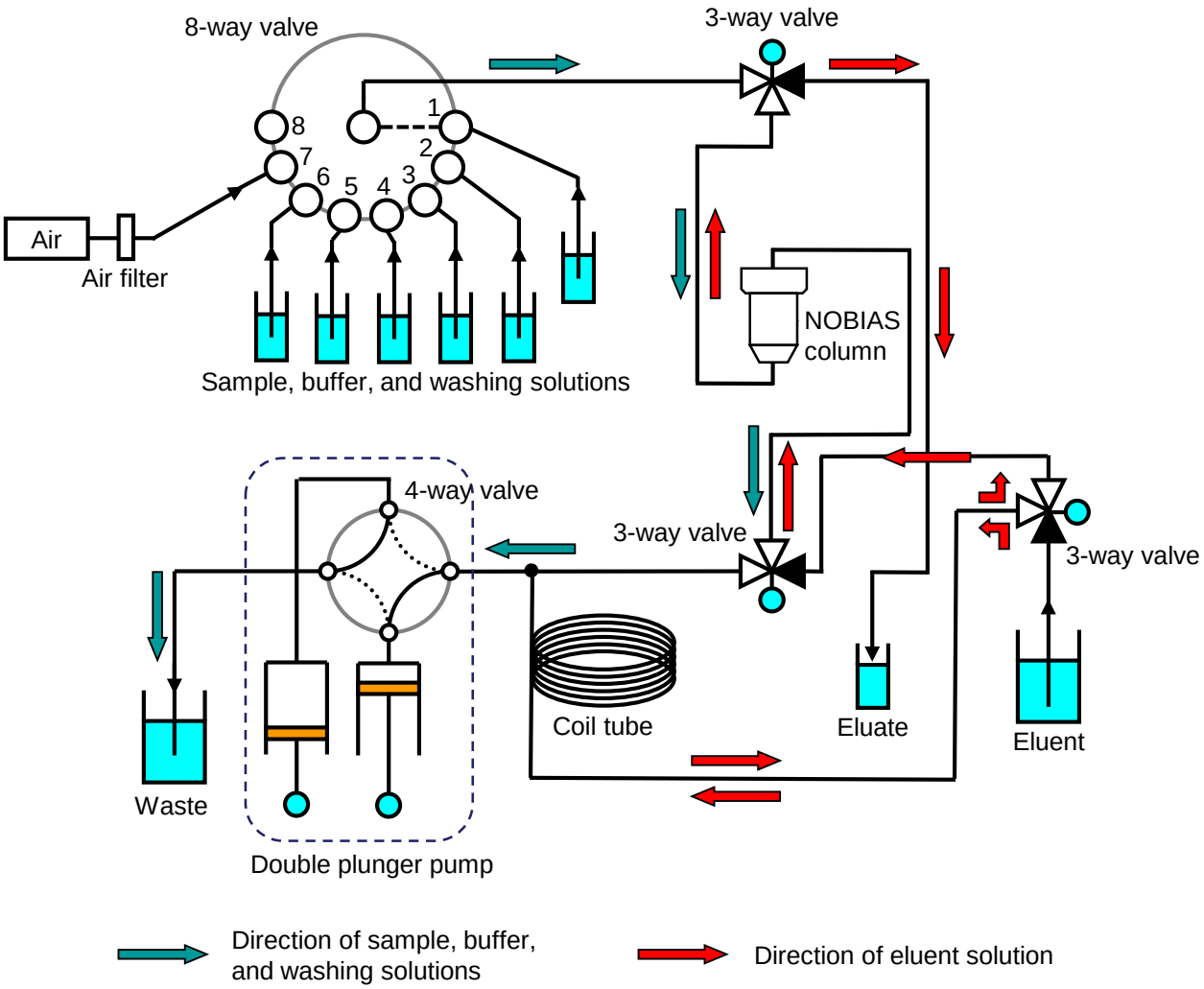
8-way valve
3-way valve
8
1
2
7
6
5
4
3
Air
Air filter
Sample, buffer, and washing solutions
NOBIAS
column
4-way valve
3-way valve
3-way valve
Coil tube
Eluate
Eluent
Waste
Double plunger pump
Direction of sample, buffer,
and washing solutions
Direction of eluent solution

Fig. 1

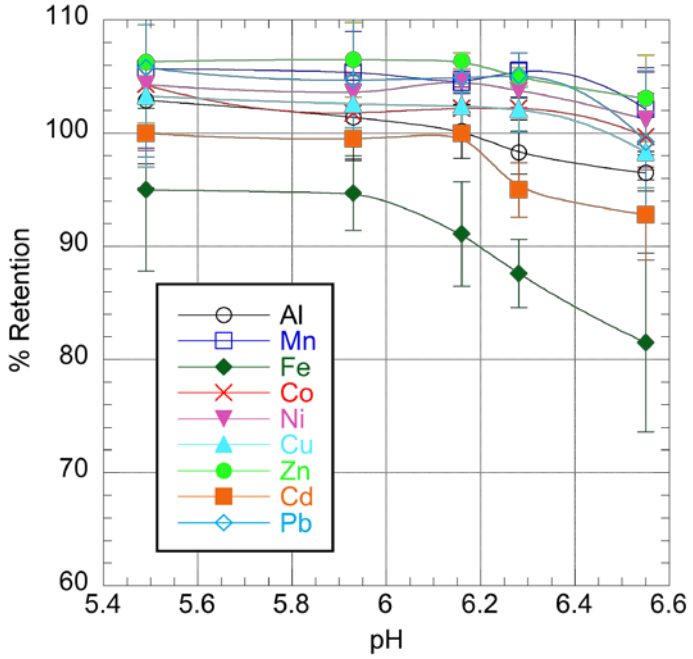
110
100
90
80
70
60
% Retention
5.4
5.6
5.8
6
6.2
6.4
6.6
pH
Al
Mn
Fe
Co
Ni
Cu
Zn
Cd
Pb

Fig. 2

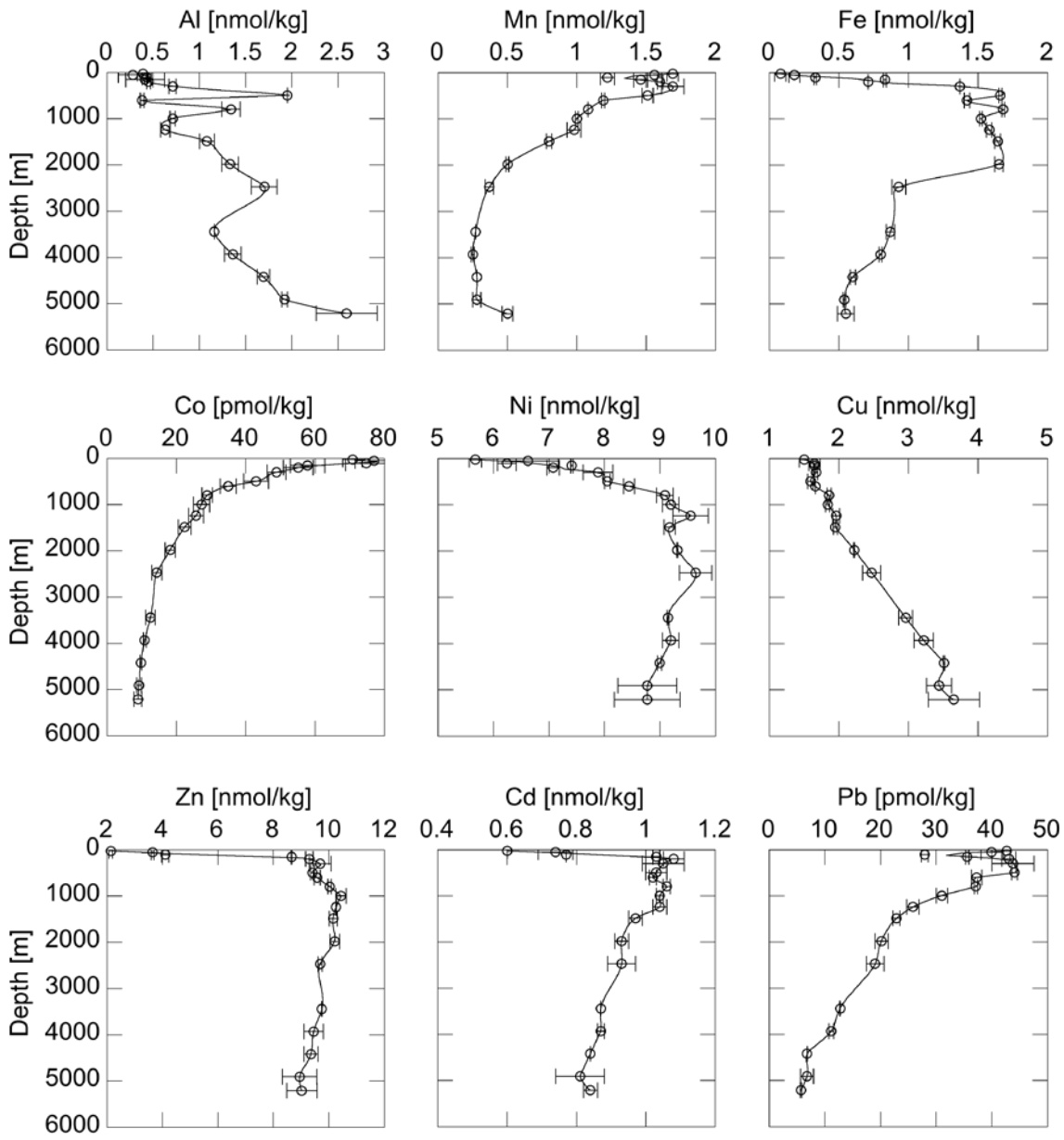
Al [nmol/kg]
0 0.5 1 1.5 2 2.5 3
Mn [nmol/kg]
0 0.5 1 1.5 2
Fe [nmol/kg]
0 0.5 1 1.5 2
Co [pmol/kg]
0 20 40 60 80
Ni [nmol/kg]
5 6 7 8 9 10
Cu [nmol/kg]
1 2 3 4 5
Zn [nmol/kg]
2 4 6 8 10 12
Cd [nmol/kg]
0.4 0.6 0.8 1 1.2
Pb [pmol/kg]
0 10 20 30 40 50
Depth [m]
0 1000 2000 3000 4000 5000 6000

Fig. 3

Table 1
Optimized preconcentration program for eightfold preconcentration.

		Port 1		Port 2		Port 3		Port 4		Port 7		Eluent port		Time
Process	Step	Sample		0.05 M HAcO-NH_4AcO (pH6)		MQW		0.1 M HCl		Air		1 M HNO_3		
		mL	mL min^{-1}	mL	mL min^{-1}	mL	mL min^{-1}	mL	mL min^{-1}	mL	mL min^{-1}	mL	mL min^{-1}	min
Cleaning	1											30	1	30
Conditioning	1							30	3					10
	2					30	3							10
	3									30	6			5
	4			30	3									10
Sample loading	1	140	3											47
	2			30	3									10
	3									30	6			5
Elution	1											18	1	18
Total time (min)														145

Table 2
Measurement conditions of HR-ICP-MS.

RF power	1200 W
Sampler cone	Ni
Skimmer cone	Ni
Nebulizer	PFA MicroFlow PFA-100
Sample take-up rate	100 μL min^{-1}
Spray chamber	PFA Teflon
Plasma gas flow rate	16 L min^{-1}
Auxiliary gas flow rate	0.8 L min^{-1}
Nebulizer gas flow rate	Daily optimized for ^{7}Li, ^{115}In, and ^{238}U
Touch position	Daily optimized for ^{7}Li, ^{115}In, and ^{238}U
Lenses	Daily optimized for ^{7}Li, ^{115}In, and ^{238}U
Isotopes	
^{27}Al	Medium resolution, R ~ 4000
^{55}Mn	Medium resolution, R ~ 4000
^{56}Fe, ^{57}Fe	Medium resolution, R ~ 4000
^{59}Co	Low resolution, R ~ 600
^{60}Ni, ^{62}Ni	Medium resolution, R ~ 4000
^{63}Cu, ^{65}Cu	Medium resolution, R ~ 4000
^{66}Zn, ^{68}Zn	Medium resolution, R ~ 4000
^{111}Cd, ^{114}Cd	Low resolution, R ~ 600
^{206}Pb, ^{208}Pb	Low resolution, R ~ 600
Search window	150 % (Low resolution), 50 % (Medium resolution)
Integration window	60 % (Low resolution), 60 % (Medium resolution)
Take-up time	50 s
Sample time	0.01 s
Sample per peak	10 (Low resolution), 20 (Medium resolution)
Pass	3
Run	3
Scan (Pass × Run)	3 × 3 = 9

Table 3
Remaining major cations in eluate for eightfold preconcentration of trace metals from seawater.

Element	Automated system method					Manual system method[a]		
	Concentration (μmol kg^{-1})			% remaining[b]		Concentration (μmol kg^{-1})		
	n	AVE	SD	AVE	SD	*n*	AVE	SD
Na	6	30.3	± 7.5	7.6E-04	± 1.9E-04	6	186	± 29
K	6	0.86	± 0.22	1.0E-03	± 2.7E-04	6	7.9	± 1.3
Mg	6	4.38	± 0.75	9.7E-04	± 1.7E-04	6	26.1	± 3.3
Ca	6	0.69	± 0.18	7.9E-04	± 2.2E-04	6	6.5	± 0.7
Sr	6	0.008	± 0.002	1.1E-03	± 2.2E-04			–

[a] Data taken from ref 7.

[b] The percentage of the remaining amount of elements in the eluate against the amount in seawater.

Table 4
Blanks and detection limits of this study and literature using Nobias Chelate-PA1.

Element	Unit	Blank					Detection limit					Concentration in open-ocean water[b]
		This study	Sohrin et al. (2008)	Lagerström et al. (2013)	Quéroué et al. (2014)	Wang et al. (2014)	This study	Sohrin et al. (2008)	Lagerström et al. (2013)	Quéroué et al. (2014)	Wang et al. (2014)	
Al	nmol kg^{-1}	0.15	0.14	n.a.[a]	n.a.	–	0.3	0.24	n.a.	n.a.	–	0.3 – 40
Mn	nmol kg^{-1}	0.001	<0.01	0.008	0.004	0.005	0.003	0.01	0.002	0.002	0.01	0.06 – 10
Fe	nmol kg^{-1}	0.032	0.033	0.065	0.25	0.07	0.09	0.04	0.014	0.090	0.19	0.03 – 3
Co	pmol kg^{-1}	0.5	<2	0.72	1.7	1	2	2	0.29	0.70	1	3 – 300
Ni	nmol kg^{-1}	0.017	<0.01	0.026	0.013	0.04	0.07	0.01	0.013	0.003	0.03	2 – 12
Cu	nmol kg^{-1}	0.017	<0.005	0.013	0.053	0.02	0.02	0.005	0.003	0.030	0.19	0.4 – 5
Zn	nmol kg^{-1}	0.12	0.071	0.115	n.a.	0.09	0.1	0.06	0.016	n.a.	0.21	0.05 – 10
Cd	nmol kg^{-1}	<0.002	<0.009	n.a.	0.00019	0.001	0.002	0.009	n.a.	0.00012	0.0005	0.001 – 1.05
Pb	pmol kg^{-1}	0.3	1.6	n.a.	0.72	1	0.9	1	n.a.	0.20	1	4 – 160

[a] Not analyzed.

[b] Data taken from ref 4.

Table 5
Analytical results for the certified reference materials of nearshore sewater (CASS-5 and NASS-6) and the GEOTRACES reference samples of seawater (GS and GD).

Element	Unit	CASS-5				NASS-6				GS				GD			
		This study		Certified value		This study		Certified value		This study[a]		Consensus value		This study[b]		Consensus value	
		n	AVE SD	AVE	SD	*n*	AVE SD	AVE	SD	*n*	AVE SD	AVE	SD	*n*	AVE SD	AVE	SD
Al	nmol kg^{-1}	4	22.3 ± 1.8	–		4	12.7 ± 0.5	–		4	22.7 ± 0.7	27.5	± 0.2	4	17.0 ± 0.8	17.7	± 0.2
Mn	nmol kg^{-1}	4	41.5 ± 1.0	46.6	± 1.8	4	8.36 ± 0.21	9.39	± 0.43	4	1.62 ± 0.05	1.50	± 0.11	4	0.255 ± 0.013	0.21	± 0.03
Fe	nmol kg^{-1}	4	24.8 ± 1.6	25.1	± 1.0	4	8.14 ± 0.24	8.65	± 0.40	4	0.564 ± 0.063	0.546	± 0.046	4	1.16 ± 0.04	1.00	± 0.10
Co	pmol kg^{-1}	4	1232 ± 12	1578[c]		4	191 ± 5	255[c]		4	25.2 ± 0.9	31.8	± 1.1[d]	4	47.2 ± 2.1	65.2	± 1.2[d]
Ni	nmol kg^{-1}	4	5.87 ± 0.46	5.49	± 0.19	3	5.22 ± 0.27	5.01	± 0.21	4	2.18 ± 0.08	2.08	± 0.06	4	4.22 ± 0.10	4.00	± 0.10
Cu	nmol kg^{-1}	4	5.66 ± 0.31	5.84	± 0.22	4	3.48 ± 0.12	3.81	± 0.20	4	0.661 ± 0.019	0.84	± 0.06[d]	4	1.43 ± 0.02	1.62	± 0.07[d]
Zn	nmol kg^{-1}	4	11.6 ± 0.6	10.7	± 0.5	4	4.66 ± 0.62	3.84	± 0.15	4	0.063 ± 0.013	0.041	± 0.007	4	1.83 ± 0.03	1.71	± 0.12
Cd	nmol kg^{-1}	4	0.185 ± 0.002	0.187	± 0.008	4	0.263 ± 0.007	0.270	± 0.008	4	0.0025 ± 0.0010	0.0021	± 0.0006	4	0.276 ± 0.006	0.271	± 0.006
Pb	pmol kg^{-1}	4	49.0 ± 2.3	53.1	± 4.8	4	25.3 ± 1.0	29.0	± 4.8	4	27.2 ± 2.4	28.6	± 1.0	4	42.2 ± 1.9	42.7	± 1.5

[a] The sample number was GS-64.

[b] The sample number was GD-54.

[c] Information value.

[d] With UV irradiation.

Supplementary Table 1
Detection limits and procedural blanks.

Element	Unit	Detection limit without preconcentration[a]	Eightfold preconcentration			Concentration in open-ocean water[c]
			Procedural blank		Detection limit[b]	
			n	AVE SD		
Al	nmol kg^{-1}	0.023	15	0.15 ± 0.10	0.3	0.3 – 40
Mn	nmol kg^{-1}	0.001	15	0.001 ± 0.001	0.003	0.06 – 10
Fe	nmol kg^{-1}	0.004	15	0.032 ± 0.029	0.09	0.03 – 3
Co	pmol kg^{-1}	0.3	15	0.5 ± 0.6	2	3 – 300
Ni	nmol kg^{-1}	0.014	15	0.017 ± 0.0226	0.07	2 – 12
Cu	nmol kg^{-1}	0.003	15	0.017 ± 0.007	0.02	0.4 – 5
Zn	nmol kg^{-1}	0.007	15	0.12 ± 0.05	0.1	0.05 – 10
Cd	nmol kg^{-1}	0.004	15	n.d.[d]	0.002[e]	0.001 – 1.05
Pb	pmol kg^{-1}	0.1	15	0.3 ± 0.3	0.9	4 – 160

[a] 3 SD for 1 M HNO_3 (n = 10).

[b] 3 SD for procedural blank, with the exception of Cd.

[c] Data taken from ref 4.

[d] Not detected.

[e] Limited by interference of MoO.

Supplementary Table 2
Recovery experiments from seawater.

Element	From seawater						
	Unspiked seawater concentration (nmol kg^{-1})			Spiked average concentration (nmol kg^{-1})	% Recovery		
	n	AVE	SD		*n*	AVE	SD
Al	3	5.2	± 0.7	14.6	3	104	± 3
Mn	3	1.01	± 0.11	7.19	3	106	± 4
Fe	3	0.82	± 0.12	2.35	3	92.9	± 9.2
Co	3	0.034	± 0.005	0.0916	3	99.5	± 8.1
Ni	3	5.9	± 0.7	11.2	3	106	± 5
Cu	3	1.6	± 0.2	10.4	3	101	± 4
Zn	3	6.0	± 0.7	10.1	3	107	± 6
Cd	3	0.59	± 0.06	1.17	3	105	± 6
Pb	3	0.069	± 0.006	0.126	3	100	± 6