

1 **Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch**  
2 **Nitilotriacetate resin extraction and isotope dilution inductively coupled plasma**  
3 **mass spectrometry**

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14

15 **Abstract**

16 A simple and accurate low-blank method has been developed for the analysis of total  
17 dissolved copper, cadmium, lead, and iron in a small volume (1.3-1.5ml per element) of  
18 seawater. Pre-concentration and salt-separation of a stable isotope spiked sample is  
19 achieved by single batch extraction onto nitrilotriacetate (NTA)-type Superflow®  
20 chelating resin beads (100-2400 beads depending on the element). Metals are released  
21 into 0.1-0.5M HNO<sub>3</sub>, and trace metal isotope ratios are determined by ICPMS. The  
22 benefit of this method compared to our previous Mg(OH)<sub>2</sub> coprecipitation method is that  
23 the final matrix is very dilute so cone-clogging and matrix sensitivity suppression are  
24 minimal, while still retaining the high accuracy of the isotope dilution technique.  
25 Recovery efficiencies are sensitive to sample pH, number of resin beads added, and the  
26 length of time allowed for sample-resin binding and elution; these factors are optimized  
27 for each element to yield the highest recovery. The method has a low procedural blank  
28 and high sensitivity sufficient for the analysis of pM-nM open-ocean trace metal  
29 concentrations. Application of this method to samples from the Bermuda Atlantic Time-  
30 Series Study station provides oceanographically consistent Cu, Cd, Pb, and Fe profiles  
31 that are in good agreement with other reliable data for this site. In addition, the method  
32 can potentially be modified for the simultaneous analysis of multiple elements, which  
33 will be beneficial for the analysis of large number of samples.

34

## 35 **1. Introduction**

36 It has been widely recognized that trace metals play important roles in the ocean.  
37 Trace metals such as iron, copper, and cadmium are essential for the growth of marine  
38 phytoplankton [1-5]; for instance, iron is known to be used in chlorophyll production and  
39 nitrogen fixation [3, 6], thereby regulating primary productivity and marine  
40 biogeochemical cycles [7-8], and copper and cadmium can be toxic under some  
41 conditions [9-10]. Other trace elements, such as lead, document the impact of  
42 anthropogenic trace metal inputs to the ocean for the past two centuries [11-12].

43 In spite of their importance, however, global-scale trace metal data are sparse  
44 because of difficulties in sampling and analysis. Because of their extremely low  
45 concentrations ( $10^{-9}$ ~ $10^{-12}$  mol l<sup>-1</sup>) compared to the high-salt matrix in seawater, analysis  
46 of trace metals requires pre-concentration and purification before detection, which  
47 includes solvent extraction [13-15] and extraction onto chelating resin columns (e.g.  
48 Chelex-100, 8-HQ chelating resin) [14, 16-17] followed by trace metal quantification  
49 using graphite furnace atomic absorption spectrometry (GFAAS) or inductively coupled  
50 plasma mass spectrometry (ICPMS). Trace metal concentrations can be also measured  
51 electrochemically (e.g. anodic stripping voltammetry), where pre-concentration is  
52 achieved by long deposition times [18-19]. However, these methods are relatively labor-  
53 intensive (i.e. reagent purification and sample processing) and time-consuming as they  
54 require large sample volumes (hundreds milliliter to liter scale).

55 In the last decade, various methods have been developed to allow trace metal  
56 analysis with a simpler procedure and a smaller sample volume. One of these is the  
57 Mg(OH)<sub>2</sub> co-precipitation method coupled with isotope dilution ICPMS [20-22]. This

58 method uses small volumes (1.5 to 50ml) of seawater and reagents and has good  
59 sensitivity with low procedural blanks. However, the resulting sample matrix contains  
60 high  $Mg^{2+}$  and seasalt occluded in the precipitates that can clog the nebulizer and leave  
61 deposits on the ICPMS cones, which limits runs to a few hours, suppresses ICPMS signal  
62 strength, and requires frequent cleaning of the nebulizer and cones. Thus, this method is  
63 not ideal for the routine measurement of many samples.

64 Other approaches that have been employed are on-line column extraction methods  
65 using recently developed chelating resins that have higher affinity for metal ions [23-25].  
66 For instance, Lohan et al. [23] used on-line preconcentration by nitriloacetic acid (NTA)-  
67 type chelating resin columns coupled to flow injection analysis by ICPMS. This study  
68 demonstrated that dissolved  $Fe^{3+}$  and  $Cu^{2+}$  can be quantitatively recovered at pH below 2  
69 after oxidization of  $Fe^{2+}$  to  $Fe^{3+}$  by addition of trace  $H_2O_2$ , which is extremely  
70 advantageous in that samples can be processed without further pH adjustment (trace  
71 metal samples are routinely acidified and stored at pH 1.7-2.0 to preserve metal ions in  
72 soluble inorganic form). However, because these on-line column extraction methods  
73 assign trace metal concentrations by external standardization, accuracies are affected by  
74 sample matrix and recovery variation during pre-concentration. In cases where the  
75 sample pH needs to be adjusted to a higher pH (e.g., EDTA-type resin, or NTA resin for  
76 other trace metals except Fe and Cu), recovery efficiencies may also vary during pH  
77 adjustment because metal ions may be lost by re-complexation with organic ligands or  
78 binding to bottle walls. A very recently developed method tackles this problem by using  
79 isotope dilution and standard additions prior to on-line column extraction to analyze  
80 multiple elements simultaneously [26]. However, on-line column extraction methods

81 generally have low ICPMS throughput because sample analysis rate is limited by sample  
82 uptake and elution times, and they are also relatively sample consuming as large sample  
83 volumes are used to rinse the entire system and precondition the resin column.

84 In this study, we utilized the same resin as in Lohan et al.'s method, but modified  
85 the method by using 1) isotope dilution to avoid recovery efficiency and sensitivity issues  
86 and 2) offline batch extraction from 100-2400 resin beads to keep blanks low and  
87 improve ICPMS throughput. This method requires relatively little analyst time and  
88 minimal volume of sample (only 1.3-1.5ml), which is beneficial under circumstances  
89 when sample volume is limited. In addition, the use of small amounts of resin lowers the  
90 Fe procedural blank in particular by reducing the Fe released from the NTA resin (see  
91 section 3.2.). With this method we were able to analyze dissolved Cu, Cd, Pb, and Fe in  
92 seawater samples to demonstrate oceanographically consistent profiles near Bermuda.

93

## 94 **2. Experimental**

### 95 *2.1. Reagents*

96 All reagent and sample preparations were carried out in a Class 100 clean laminar  
97 flow bench or recirculating fume hood in a positive-pressure clean lab. High purity H<sub>2</sub>O  
98 was prepared by redistillation of “ultrapure” deionized water in a Corning “Mega-Pure”  
99 Vycor®/borosilicate still. Nitric acid was prepared by distilling reagent-grade HNO<sub>3</sub> four  
100 times in a Vycor still and diluting with high-purity water to make 0.1M or 0.5M HNO<sub>3</sub>.  
101 Clean Suprapur® hydrogen peroxide (30% solution, EMD chemicals) was diluted to  
102 0.75% with high purity H<sub>2</sub>O. Acetic acid (HAc) was prepared by Vycor-distilling  
103 reagent-grade acetic acid, and clean ammonium hydroxide (NH<sub>4</sub>OH) was purchased

104 (Optima® grade, Fisher Scientific) or alternatively made by purifying reagent-grade  
105 NH<sub>4</sub>OH by vapor-distillation.

106 Ammonium acetate buffer solution was prepared by mixing clean NH<sub>4</sub>OH and  
107 HAc. The mixing ratio was determined empirically to keep the pH of the buffer between  
108 7.9-7.98 because at pH higher than 8.0, Mg(OH)<sub>2</sub> can be precipitated when buffer meets  
109 the sample, potentially resulting in the loss of metals. The buffer was used without further  
110 dilution to minimize the volume of buffer added to the samples. Because ammonia gas is  
111 lost relatively rapidly through plastic bottle walls, the buffer was refrigerated when not in  
112 use to reduce buffer weakening.

113

## 114 *2.2. Materials*

115 All the 1.5ml polyethylene vials (Eppendorf AG or Molecular BioProducts, Inc.  
116 with o-rings removed) and bottles were acid-leached for one day at 60°C with 10%  
117 reagent-grade HCl. The vials and bottles were then rinsed 3-5 times with pure distilled  
118 water, filled with high-purity 0.06M HCl, and then leached for another day at 60°C. The  
119 dilute HCl was left in the vials until just before use. Pipette tips were rinsed with dilute  
120 HCl and high purity H<sub>2</sub>O immediately before use. Before sample preparation, 1.5ml-size  
121 vials from different companies were tested for their Fe blank by adding 150µl of clean  
122 0.5M HNO<sub>3</sub> to acid-cleaned, empty vials and measuring Fe concentrations in the acid  
123 after 5-days of leaching. The Fe detected herein represents the Fe blank coming from the  
124 vial walls since during sample preparation Fe is eluted from the resin beads in the same  
125 way (i.e., store 150µl of 0.5M HNO<sub>3</sub> in resin-containing vials for five days). We also  
126 conducted the same test while the vials were kept upside-down to check for potential

127 contamination from vial caps. Eppendorf vials (no longer commercially available; reused  
128 repeatedly) were found to be cleaner for Fe compared to the other brands tested, so only  
129 these vials were used for Fe analysis, although different lots of vials resulted in variable  
130 Fe blanks (Table 1). We also found that vial caps are the largest contributor to Fe blanks  
131 even after they are cleaned by the acid-leaching steps described above, so vials were kept  
132 upright during sample preparation, and every effort was made to avoid contact between  
133 acidic sample solution and caps. Cu, Cd, and Pb blanks were low regardless of what  
134 brand vials were used, and vials from Eppendorf AG and Molecular BioProducts, Inc.  
135 were both used for these elements.

136

### 137 *2.3. Standards*

138 Cu, Cd, and Pb standards with natural isotope abundance were prepared by  
139 diluting ULTRA grade ICP standards (ULTRA Scientific, North Kingstown, RI) with  
140 0.1M HNO<sub>3</sub>. For the natural isotope abundance Fe standard, 99.99% pure Fe metal was  
141 dissolved in 1% (V/V) HNO<sub>3</sub> and further diluted with 0.5M HNO<sub>3</sub>. Scarcer-stable-  
142 isotope-enriched spikes (<sup>65</sup>Cu, <sup>110</sup>Cd, and <sup>204</sup>Pb) were made by dissolution of CuO, CdO  
143 and PbCO<sub>3</sub> (Oak Ridge National Laboratories) in 1% HNO<sub>3</sub>, and working isotope spikes  
144 were made by subsequent dilution with 0.1M HNO<sub>3</sub>. A <sup>54</sup>Fe-<sup>57</sup>Fe enriched isotope spike  
145 was shared with us from the laboratory of Dan Schrag (Harvard Univ., Cambridge, MA,  
146 USA). The concentrations of these working isotope spikes were adjusted to minimize  
147 error propagation of the isotope dilution method, i.e. to match approximately the isotope  
148 ratio of the sample-spike mixture with the geometric mean of the isotope ratios of the  
149 isotope spike and the natural sample, and not too far from 1:1 to minimize blank errors

150 [27-28]. The exact concentrations of Cu, Cd, Pb, and Fe in the isotope spikes were  
151 determined by isotope dilution calibration against the natural abundance standard of each  
152 element.

153

#### 154 *2.4. NTA resin*

155 We have used NTA Superflow® resin (Qiagen Inc., Valencia, CA) supplied in  
156 both Ni<sup>2+</sup> and non-Ni<sup>2+</sup> forms, although the non-Ni<sup>2+</sup> form was preferred. The resin was  
157 cleaned by multiple rinsing steps in acid-cleaned polypropylene centrifuge tubes. When  
158 not being used or cleaned, the resin was kept refrigerated. The resin was first washed  
159 several times with high purity H<sub>2</sub>O, then multiple times with high purity 1.5M HCl, and  
160 then again multiple times with high purity H<sub>2</sub>O until the pH was higher than 3. Then the  
161 resin was rinsed several times with high purity 0.5M HNO<sub>3</sub>; for the first washes, it was  
162 left on a shaker table for several hours, and then left overnight for the final wash. Finally,  
163 the resin was rinsed with high purity H<sub>2</sub>O several times until the pH was higher than 3.  
164 After each wash, the resin was centrifuged down and the supernatant was discarded.  
165 Cleaned NTA resin was then diluted with high purity H<sub>2</sub>O so the resin suspension  
166 contained ~100-400 resin beads per 25µl, and was stored in a refrigerator. The resin  
167 blank was checked by leaching the resin beads in 0.5M HNO<sub>3</sub> and measuring trace metal  
168 concentrations (see section 3.4.); if the blank was higher than expected, we repeated the  
169 0.5M HNO<sub>3</sub> and high purity H<sub>2</sub>O rinsing steps. Cleaning the resin is particularly  
170 important for Fe. It seems that Fe within the beads diffuses to the surface of the beads  
171 where it can be dissolved into the samples, so even after the resin is cleaned once,  
172 significant amounts of Fe are slowly released from the resin beads over time. We found a



173 high resin blank for Fe (up to ~2.5nM) when the resin was stored for a long time (a few  
174 months), and it decreased to the normal level (<0.2nM) after re-cleaning the resin.

175

#### 176 *2.5. Seawater for method calibration*

177 Two seawater samples, SAFe MIT “A” and SAFe D2, were used as reference  
178 samples in this study. They were collected from the surface and 1000m depth at 30°N  
179 140°W in the North Pacific during the SAFe program in 2004 [29]. This program  
180 provides reference samples (SAFe S for surface seawater and SAFe D2 for deep water)  
181 from a homogenized large volume tank, filtered and acidified (pH 1.7.) in a uniform way.  
182 The SAFe MIT “A” was taken at the surface at the same station during the same cruise  
183 using a towed fish sampler and thus should have comparable concentration to the  
184 “official” SAFe S. The SAFe MIT “A” was filtered through clean 0.2µm Osmonics  
185 capsule filters and acidified to pH 2.0.

186 Samples for an oceanographic profile were collected at the Bermuda Atlantic  
187 Time-Series Study station (BATS, 31°40’N, 64°10’W) in June 2008 during  
188 GEOTRACES IC1 intercalibration cruise. The samples used for Cu, Cd, and Pb profiles  
189 were taken using a Moored In-situ Trace Element Serial Sampler (MITESS) or with a  
190 single MITESS “ATE” (Automated Trace Element) [30-31]. Soon after sample collection  
191 (within 24 hours), the samples were filtered through acid-cleaned 0.4µm Nuclepore filters  
192 in a class 100 laminar flow bench. The samples used for Fe were collected by the  
193 GEOTRACES GOFlo rosette system, filtered through 0.2µm Osmonics capsule filters.  
194 All samples were acidified to pH 2.0 with 4x vycor-distilled 6N HCl (except SAFe D2  
195 that was acidified to pH 1.7 with sub-boiling distilled 6N HCl).

196

197 *2.6. Instrumentation*

198 A Quadrupole ICPMS (VG PlasmaQuad 2+) was used for Cu, Cd, and Pb  
199 analysis. Measured isotopes were  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  for Cu;  $^{95}\text{Mo}$ ,  $^{110}\text{Cd}$ ,  $^{114}\text{Cd}$  and  $^{118}\text{Sn}$  for  
200 Cd; and  $^{202}\text{Hg}$ ,  $^{204}\text{Pb}$ , and  $^{208}\text{Pb}$  for Pb. The sensitivity of the instrument was  $\sim 100,000$   
201 counts per second for 1 ppb Indium when a nominal  $50\ \mu\text{l}\ \text{min}^{-1}$  MicroMist® concentric  
202 nebulizer (Glass Expansion, measured flow rate of  $70\ \mu\text{l}\ \text{min}^{-1}$ ) was used in conjunction  
203 with a water-cooled Scott double by-pass spray chamber and a Fassel quartz torch (Glass  
204 Expansion). Free-aspiration was used for sample uptake, and a frit filter was used at the  
205 tip of the sipper tubing to prevent clogging from the resin beads. The operating details are  
206 listed in Table 2a. Isobaric interferences on  $^{110}\text{Cd}$  ( $^{94}\text{Mo}^{16}\text{O}$ ) and  $^{114}\text{Cd}$  ( $^{98}\text{Mo}^{16}\text{O}$ ) were  
207 corrected using  $^{95}\text{Mo}$  counts of each sample and the  $\text{MoO}/^{95}\text{Mo}$  of a Mo standard, and the  
208 magnitude of this correction was negligibly small ( $<0.1\%$ ). The  $^{114}\text{Sn}$  interference on  
209  $^{114}\text{Cd}$  and  $^{204}\text{Hg}$  interference on  $^{204}\text{Pb}$  were corrected by monitoring  $^{118}\text{Sn}$  and  $^{202}\text{Hg}$ .

210 For Fe analysis,  $^{52}\text{Cr}$ ,  $^{54}\text{Fe}$ , and  $^{56}\text{Fe}$  were determined simultaneously with Faraday  
211 cups using static mode on a multi-collector magnetic sector ICPMS (GV/Micromass  
212 IsoProbe) with a hexapole collision cell using Ar and  $\text{H}_2$  collision gases to minimize  
213  $^{40}\text{Ar}^{14}\text{N}^+$  and  $^{40}\text{Ar}^{16}\text{O}^+$  interferences and thermalize the ion beam. The same nominal  $50$   
214  $\mu\text{l}\ \text{min}^{-1}$  MicroMist® concentric nebulizer was used along with an APEX Q inlet system  
215 (Elemental Scientific, Inc.) with a passive desolvating membrane and a Fassel quartz  
216 torch (Glass Expansion). A frit filter was placed on the tip of the sipper tube to avoid  
217 clogging by resin beads. This instrument provides very precise Fe data at high sensitivity  
218 because  $^{40}\text{Ar}^{16}\text{O}^+$  and  $^{40}\text{Ar}^{14}\text{N}^+$  interferences on  $^{56}\text{Fe}$  and  $^{54}\text{Fe}$  are eliminated by the

219 hexapole collision cell and the instrument can be run in low resolution mode. The Cr  
220 interference on mass 54 was corrected by monitoring  $^{52}\text{Cr}$ , but was negligibly small  
221 because the resin does not take up Cr at the analytical pH range. The operating details for  
222 the IsoProbe are listed in Table 2b.

223 Dilute nitric acid (the same acid used as for eluates, i.e. 0.1M  $\text{HNO}_3$  for Cu, Cd,  
224 and Pb and 0.5M  $\text{HNO}_3$  for Fe) was measured at appropriate intervals (“on-peak zero”,  
225 OPZ) to correct for changes in instrumental background. Instrumental mass bias was  
226 corrected by running the “natural” isotope standards of each element (spiked gravimetric  
227 standards for Pb) at the beginning and end of the sample run each day. The average of  
228 these two values was used for the correction, and a linear % per amu model was used to  
229 correct for instrumental mass bias.

230

### 231 *2.7. General procedure*

232 Because we have found that optimal conditions vary slightly for Cu-Cd, Pb, and  
233 Fe, we generally perform these analyses separately, although because of isotope dilution  
234 calibration, it is possible to do all simultaneously at pH~5 so long as the isotope spikes do  
235 not have contamination for the other elements.

236 The samples were prepared by the following procedure. Initially, an acid-leached  
237 1.5ml vial was rinsed with a small volume (~0.5ml) of the acidified seawater sample (pH  
238 1.7-2.0), and then 1.3-1.5ml of the sample was poured into the vials. The vial was  
239 weighed before and after pouring the sample, and the exact sample volume was  
240 determined by converting the weight of sample to volume using the density of seawater.  
241 Alternatively, for Cu, Cd, and Pb analysis where constant volume of sample is desirable

242 for easier pH adjustment (because the volume of buffer added to samples can be fixed),  
243 we poured the sample into the vial and pipetted out exactly 1.3ml of the sample using a  
244 clean pipette tip. The 1.3ml sample in the pipette tip was pipetted back into the same vial  
245 after quickly emptying the vial. Then, the sample was spiked with 25 $\mu$ l of stable isotope  
246 spikes (enriched in  $^{65}\text{Cu}$ ,  $^{110}\text{Cd}$ ,  $^{204}\text{Pb}$ , and  $^{54}\text{Fe}$ ) and left for a few minutes after vortex  
247 mixing to establish isotopic equilibrium. At this pH (<1.7), two minutes were proven to  
248 be sufficient to reach isotope equilibrium [20]. Then, for Cu, Cd, and Pb analysis, the pH  
249 of the sample was adjusted to pH>5 using ammonium acetate solution (80-200  $\mu$ l,  
250 depending on the initial sample pH and target pH). Buffer was not added for Fe analysis  
251 samples, but 10 $\mu$ l of 0.75%  $\text{H}_2\text{O}_2$  was added to oxidize Fe(II) to Fe(III). After the  
252 addition of buffer or  $\text{H}_2\text{O}_2$ , sample vials were vortexed again for a few seconds. Finally,  
253 25-150 $\mu$ l of the NTA resin suspension (100-2400 beads) was added to the vial, vortexed  
254 again, and then the sample vial was shaken on an orbital table for >24 hrs to allow the  
255 trace metals and resin to bind. After 1-4 days, the sample vial was centrifuged (for 45  
256 seconds at 14,500 rpm) and the overlying seawater was siphoned off carefully, leaving  
257 the resin beads at the bottom. The resin beads were then rinsed three times with high  
258 purity  $\text{H}_2\text{O}$  to remove seasalt; in each rinse, the vial was filled with high purity  $\text{H}_2\text{O}$ ,  
259 centrifuged down, and the supernatant was siphoned off. After rinsing, the 150  $\mu$ l of  
260 0.5M  $\text{HNO}_3$  (Fe) or 0.1M  $\text{HNO}_3$  (Cu, Cd, Pb) was added to the vial, and the trace metals  
261 were allowed one to five days (five days for Fe) to be released into solution. The final  
262 solution was then brought to the ICPMS, and the isotope ratios ( $^{56}\text{Fe}/^{54}\text{Fe}$ ,  $^{63}\text{Cu}/^{65}\text{Cu}$ ,  
263  $^{114}\text{Cd}/^{110}\text{Cd}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$ ) of this solution (after OPZ blank correction) were measured  
264 to calculate the concentration of each element.

265 Procedural blanks for Cu, Cd, and Fe were determined by processing small  
266 volumes (0.1-0.3 ml) of the SAFe MIT “A” seawater in the same way as samples because  
267 their concentrations in this water is small (although a correction for this contribution is  
268 made nonetheless). For Pb, 0.3ml of low-Pb seawater was used to determine Pb  
269 procedure blank, made by removal of Pb in seawater (taken from BATS, 1997) using  
270  $Mg(OH)_2$  coprecipitation followed by filtration through clean 0.4 $\mu$ m Nuclepore filters. In  
271 order to estimate accurate procedural blanks, the trace metal contents that were initially  
272 included in the SAFe MIT “A” seawater or low-Pb seawater were established by running  
273 3-6 replicates of this seawater as a sample in every sample run.

274

### 275 **3. Results and Discussion**

276 Because this method uses isotope dilution, recovery efficiency is not as critical as  
277 in flow-injection methods or other methods based on external standardization. However,  
278 a sufficient amount of trace metals should be recovered from the resin to ensure that the  
279 ICPMS signals from the sample are well above (order of magnitude at least) instrumental  
280 background, especially when trace metal concentrations are very low. The sample  
281 preparation procedure was optimized by testing various factors that may affect recovery  
282 efficiencies of Cu, Cd, Pb, and Fe from NTA resin beads, such as sample pH, resin  
283 volume, and the length of time allowed for sample-resin binding and elution from the  
284 resin. The accuracy of the method was evaluated by measuring SAFe seawaters, and the  
285 method was applied to determine vertical profiles of total dissolved Cu, Cd, Pb, and Fe  
286 concentrations in samples collected from the BATS station.

287

288 *3.1. Sample pH*

289 A previous study showed that pH is critical for trace metal recoveries from the  
290 NTA resin [23]. In Lohan et al.'s study, where a resin column and flow-injection system  
291 were used, recovery efficiency of Cu was ~50% at pH<2, ~90% at pH 2-3, and near  
292 100% at pH>3.5. Cd was recovered only at a pH higher than 5.5, with ~80% recovery  
293 efficiency. In the case of Fe(III), ~80% of Fe(III) was recovered at pH 1.5 and Fe(III) was  
294 almost fully recovered at pH higher than 2. The relationship between pH and Pb recovery  
295 from NTA resin was not investigated in Lohan et al.'s study.

296 Based on this previous study, we tested the effect of pH on recovery efficiencies  
297 of Cu, Cd, and Pb in our batch-extraction method. Fe was not studied here because Fe is  
298 recovered well (50-75%) at a typical sample pH (1.7-2.0) without pH adjustment. We  
299 added 50µl of isotope spike to 1.3ml of the acidified seawater samples (pH 1.7-2.0), and  
300 then adjusted the pH of samples using ammonium acetate buffer. The Cu and Cd  
301 recoveries were tested for pH values ranging from 5.0-6.7, and Pb was tested from pH 2.0  
302 to 6.7. The amount of buffer added to the sample was empirically determined in each test  
303 depending on the target pH. Finally, 50µl of NTA resin (~200 beads) were added to the  
304 samples, and the samples were processed following the general procedure described in  
305 section 2.4. The recovery efficiency of each element was calculated by comparing the  
306 count rates of <sup>65</sup>Cu, <sup>110</sup>Cd, and <sup>204</sup>Pb in the enriched isotope spike to those in the final  
307 sample solution.

308 Under our batch-extraction conditions, 70-100% of Cu was recovered in the pH  
309 range 5.0-6.7. Cd recoveries were very low (1~2%) at pH below 6.0 and higher at pH 6.5  
310 (Figure 1a), but even the highest recovery at pH 6.5 was only ~5%. The low recovery of

311 Cd compared to the other elements is probably because of its low binding ability with  
312 nitriloacetate (NTA) ligands [32]. Also, the much lower recovery of Cd at the same pH  
313 compared to Lohan et al.'s study is likely because we used only ~200 resin beads,  
314 whereas Lohan et al. used a column packed with  $\sim 10^5$  resin beads (inner volume of the  
315 1cm-column: 85 $\mu$ l; bead size: 60–160 $\mu$ m). Pb recoveries were low at pH<4.5, highest at  
316 pH ~5.0, and they decreased as pH increased above 5.0 (Figure 1b). In a more detailed  
317 study using a different seawater sample, the optimal pH for Pb appeared to be 5.0-5.4  
318 (Figure 1b). Another thing we noticed was that recovery efficiencies seem to be different  
319 for different samples, presumably depending on the strength of natural ligands in each  
320 sample relative to that of NTA resin. The low overall recovery efficiency of the later  
321 experiment (experiment for pH 5.0-5.6) compared to the others seems to be caused by  
322 this natural variability of the samples, and it emphasizes the importance of using the  
323 isotope dilution technique.

324

### 325 *3.2. Number of resin beads*

326 In order to test our hypothesis that the low Cd recovery is due to the low number  
327 of resin beads used for extraction, we prepared samples by adding larger numbers of  
328 beads. Recovery efficiencies of Cu and Cd increased by ~20% and ~100% by doubling  
329 the resin volume (~400 beads) (Figure 2, white squares), and Pb recovery also increased  
330 as a function of the number of resin beads added to the samples (Figure 3). Higher  
331 recovery efficiencies were achieved by further increasing the number of resin beads; for  
332 instance, we could achieve up to 80-90% Pb recovery when 2400 beads were added to the  
333 sample. Because the volume of vial is limited to 1.5 ml, in that experiment we made a

334 more concentrated NTA resin suspension (400 beads per 25 $\mu$ l) and added 150 $\mu$ l of resin  
335 suspension to the sample.

336         The concern with using larger volume of resin beads is that adding more beads  
337 may increase the procedure blank. When the resin blank was checked for each element  
338 (details in section 3.4.), it was negligibly low for Cu, Cd, and Pb, but was significant for  
339 Fe. Thus, for Fe analysis, we did not increase the resin volume (we continued to use ~100  
340 resin beads) to keep the procedural blank low.

341

### 342 *3.3. Sample-resin binding and trace metal elution times*

343         The influences of sample-resin binding time and elution time on recovery  
344 efficiency were tested with the SAFe MIT “A” seawater. In the first experiment, the  
345 samples were allowed to bind to the resin beads on a shaker table for one to four days  
346 while the rest of the procedure was kept the same. Cu recovery efficiency increased  
347 slightly when a longer time was allowed for sample-resin binding (Figure 2a), whereas  
348 Cd recovery efficiency showed no detectable difference (Figure 2b) depending on the  
349 binding time. In case of Pb, higher recovery efficiency was achieved when the samples  
350 were left with resin beads for longer than 2 days (Figure 2c). The Fe recovery was tested  
351 for 24-48 hours, and Fe recovery efficiency increased by ~25% when the samples were  
352 left for a longer time. The Fe could be optimally recovered (>75%) when the samples  
353 were left for about 36-48 hours with the resin; if left longer, chance of contamination  
354 from the vial walls/caps increased.

355         For the sample-resin binding, speed of the shaker table also affects the binding  
356 efficiency because a certain speed is necessary to keep the resin beads suspended in the



357 sample. John and Adkins [33] showed that Fe binding to the resin is achieved within a  
358 shorter time if samples are shaken vigorously. The optimal speed we found for Cu, Cd,  
359 and Pb was ~2000 rpm. For Fe, shaking samples too vigorously increased the chance of  
360 contamination from contact of the sample with the vial caps. The most favorable speed  
361 we found to minimize the Fe procedural blank was 1200-1300 rpm.

362 In the second experiment, the samples were allowed to bind to the resin for the  
363 same length of time, but different amounts of time (1 to 5 days) were provided after the  
364 addition of nitric acid, and before the ICPMS run. A longer elution time did not increase  
365 Cu, Cd, or Pb recoveries between 1-5 days, so these elements were clearly released from  
366 the resin in a relatively short time. The recovery of Fe increased significantly when a  
367 longer time was allowed for elution. However, five days was chosen as the optimal length  
368 of time for Fe elution because procedural blank also increases with time, likely because  
369 of the slow release of Fe from the NTA resin beads. When samples could not be run on  
370 the ICPMS on schedule, they were refrigerated ( $<4^{\circ}\text{C}$ ) to slow down the release of Fe  
371 from the resin beads.

372 According to our investigation, several days to a week for sample preparation  
373 yields the highest recovery efficiencies. However, because most of this process time  
374 does not involve analyst's work, actual analyst time for sample preparation is relatively  
375 small, e.g., several hours for ~100 samples. In addition, when high recovery efficiency is  
376 not critical (i.e., for samples with moderate to high trace metal concentrations), samples  
377 can be processed and run on the ICPMS within 3 days.

378

379 *3.4. Procedural blank, detection limit, and accuracy*

380 The procedural blanks and detection limits of this method are shown in Table 3.  
381 The detection limits are considered as three times the standard deviations of the  
382 procedural blanks. The potential sources of the procedural blank of this batch-extraction  
383 method are ammonium acetate buffer or H<sub>2</sub>O<sub>2</sub>, resin beads, dilute nitric acid, sample vials  
384 and contamination during handling. Here we examine the contribution of these sources to  
385 the procedural blank.

386 The Fe blank for H<sub>2</sub>O<sub>2</sub> was measured by adding 10μl of H<sub>2</sub>O<sub>2</sub> to 100μl of 0.5M  
387 HNO<sub>3</sub> and comparing the Fe counts of this solution to those of the Fe standard. The  
388 contribution of H<sub>2</sub>O<sub>2</sub> to the Fe procedural blank was small, less than 0.004 nM.

389 The Cu, Cd, and Pb concentrations of ammonium acetate buffer were determined  
390 as follows. Because organic solvents cannot be analyzed by ICPMS directly (without  
391 addition of oxygen to the nebulizer gas), 2ml of buffer solution was evaporated on a  
392 hotplate in a V-shaped clean Teflon vial, and the remaining material was re-dissolved in  
393 200μl of 0.1M HNO<sub>3</sub>. 10μl of enriched isotope spike was then added to the vial followed  
394 by a thorough mixing, and Cu, Cd, and Pb concentrations in this solution were  
395 determined by isotope dilution ICPMS. The metal content was measured in every new  
396 batch of buffer to check for contamination. In general, when 150μl of buffer was added to  
397 1.3ml sample (buffer to sample ratio used for most of our samples), it added ~0.001nM of  
398 Cu and 0.26-0.71 pM of Pb to the procedural blanks. The contribution of buffer to the Cd  
399 blank was negligible (<d.l.). The trace metal concentrations in HAc and NH<sub>4</sub>OH were  
400 also measured separately in the same manner, and HAc was found to be the dominant  
401 source of trace metals in the buffer. Purifying HAc by further distillation will lower the  
402 present buffer blank, and consequently lower the procedural blank.

403 In order to assess the trace metals coming from the resin suspension, 50µl of resin  
404 suspension (~200 beads) was added to 1.5ml Eppendorf vials. After the addition of 150µl  
405 0.1M HNO<sub>3</sub>, the resin was left for 1-5 days so any trace metals in the resin could be  
406 released. Following the addition of 10µl isotopically-enriched standard, the metal  
407 concentration in this solution was determined by isotope dilution ICPMS. The Cu, Cd,  
408 and Pb contents in the resin suspension were negligible (<d.l.), and the procedural blanks  
409 were almost the same even though the number of resin beads was increased. The resin  
410 blank for Fe was equivalent to 0.05-0.25nM for samples depending on the time since the  
411 resin was cleaned, which means that the resin is the major source of the Fe procedural  
412 blank.

413 The accuracy of the NTA resin batch-extraction method was tested in several  
414 ways. The Cu, Cd, Pb, and Fe concentrations in SAFe seawaters analyzed by this method  
415 were compared with the SAFe consensus values  
416 ([www.geotraces.org/Intercalibration.html#Standards](http://www.geotraces.org/Intercalibration.html#Standards)) (Table 3), and they agreed well.  
417 The surface Cd concentrations are below detection limit for the sample size of 1.3ml; if  
418 lower detection limits are desired, they could be attained by increasing recovery  
419 efficiency using more resin beads and concentrating Cd from a larger sample volume. In  
420 addition, the fact that the Cu, Cd and Fe data at BATS station generated by this method  
421 match those from previous studies (see section 3.7) demonstrates that the ID-NTA bead-  
422 ICPMS method can provide accurate data.

423

424 *3.5. Multi-element analysis*

425 This method has the potential to detect multi-element concentrations from a single  
426 1.3ml-size sample. The sample can be spiked with a multi-isotope standard (a mixture of  
427 the enriched isotope standard of each element), and the isotope ratios of the multiple  
428 elements in the sample can be detected concurrently on the ICPMS. In order to achieve  
429 this goal, each scarcer-isotope-enriched spike should be clean with respect to the other  
430 elements to yield low procedural blank for all analyzed elements. When  $^{65}\text{Cu}$ -,  $^{110}\text{Cd}$ -,  
431 and  $^{204}\text{Pb}$ -enriched isotope spikes were checked for Cu, Cd, and Pb concentrations (Table  
432 4), they were relatively clean for each other except the  $^{65}\text{Cu}$  isotope spike, which was  
433 slightly contaminated with Pb probably during storage and handling (this  $^{65}\text{Cu}$  spike  
434 solution was more than 10yrs old). Spiking 25 $\mu\text{l}$  of this  $^{65}\text{Cu}$  spike to samples will  
435 increase the Pb procedural blank by 0.28pM; however, this is still acceptable considering  
436 typical Pb concentrations in the ocean. Cross-contamination was not investigated for Fe  
437 because we measure Fe on a different instrument (IsoProbe) from the other elements  
438 (PQ2+). Because mixing the  $^{65}\text{Cu}$ ,  $^{114}\text{Cd}$ , and  $^{204}\text{Pb}$  isotope spikes will slightly change the  
439 fraction of each isotope and isotope ratios (contamination from the other isotope spikes),  
440 they should be precisely measured before use. Also, the accuracy of this multi-element  
441 analysis can be improved by adjusting the mixing ratio and concentrations of each  
442 isotope standard to minimize error propagation. The Cu and Cd concentrations in SAFe  
443 seawaters were assessed simultaneously by spiking the samples with  $^{65}\text{Cu}$ - and  $^{114}\text{Cd}$ -  
444 enriched isotope spike, and the result agreed well with the SAFe consensus value,  
445 affirming that multiple elements can be analyzed simultaneously using this method.

446

447 *3.6. Cu, Cd, Pb, and Fe concentrations from open ocean (BATS) samples*

448 This new method was applied to the open ocean seawater samples taken from the  
449 BATS site during June 2008 GEOTRACES IC1 cruise (Figure 4). The Cu, Cd, and Pb  
450 data shown here are from the samples collected by MITESS samplers, and Fe is from  
451 GEOTRACES GoFlo samplers (GPrI Isotope cast).

452 The Cu profile generated by this method agrees well with the previous data  
453 obtained in the Sargasso Sea (Figure 4a) [34-35]. Dissolved Cu is low in the upper layer  
454 and it increases almost linearly with increasing depth. This characteristic feature of Cu  
455 has been observed in other studies [20, 34-37], and is attributed to the combination of  
456 biological uptake and remineralization, scavenging onto particles, and the release of Cu  
457 from surface sediments. Otherwise, the profile might be maintained by a relatively  
458 uniform supply of Cu from decomposing organic particles at depth combined with a rapid  
459 exchange of dissolved Cu with sinking particulate Cu by analogy to  $^{230}\text{Th}$  and  $^{231}\text{Pa}$   
460 profiles [38].

461 The vertical distribution of Cd is characterized by extremely low values in the  
462 surface waters and an intermediate maximum at ~1000 m (Figure 4b), the result of  
463 biological removal at the surface and regeneration at depth. The concentrations of Cd are  
464 close to the results of the previous studies carried out in the similar region [35, 39]. The  
465 station lying at the northwest of the BATS (35°40'N, 71°53'W; BATS: 31°40'N,  
466 64°10'W) has slightly lower Cd concentrations in deep sea, but all these stations show a  
467 consistent Cd-P relationship (Figure 5).

468 The comparison of this Pb data with the previous data in the NW Atlantic [11, 20,  
469 40] shows the continuing decline in oceanic Pb due to the phase-out of leaded gasoline in  
470 the United States and Europe (Figure 4c). The Fe data show low values below the

471 seasonal mixed layer increasing to a maximum in deep waters because of biological  
472 uptake at surface and regeneration at depth (Figure 4d). These data are consistent with  
473 published Fe data from the same cruise [26] although there is an offset in the upper ocean  
474 (<500m). The samples used for Milne et al.'s work are from a different sampling system  
475 (CLIVAR rosette) on a different day, and the offset in the shallow water could be caused  
476 by a natural variation in Fe with time. Strong eddy activity observed in T-S profiles  
477 supports this possibility. The Fe profile also shows a similar trend to that from a nearby  
478 station (34.8°N, 57.8°W) [41].

479

#### 480 **4. Conclusion**

481 This paper describes a simple analytical method for measuring total dissolved Cu,  
482 Cd, Pb, and Fe in seawater using batch-extraction of metals onto NTA Superflow resin  
483 beads and isotope dilution ICPMS. The method uses only 1.3-1.5 ml of seawater per  
484 element and small volume of reagents that can be purified easily, removes salt effectively,  
485 and has low procedural blanks and a low detection limit. In addition, accuracy and  
486 precision is ensured regardless of sample matrix (e.g. organic ligands in samples) because  
487 isotope dilution is used. This study also demonstrates the potential of the simultaneous  
488 analysis of multi-elements by spiking a sample with a multi-isotope enriched standard.  
489 The method was applied to measure total dissolved Cu, Cd, Pb, and Fe in open ocean  
490 seawaters and the results showed excellent agreement with SAFe reference values and the  
491 data from previous studies. This method will be beneficial for the analysis of a large  
492 number of samples, as planned in GEOTRACES program, because multiple elements can

493 be measured from a small volume of sample, which will make sample collection, storage  
494 and handling much easier.

495

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497

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506

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569  
570

**Table 1.** Fe released from various vials with different positions. The Fe concentrations were measured in 0.5M HNO<sub>3</sub> after 150µl of the 0.5M HNO<sub>3</sub> was stored in empty vials for five days, which corresponds to the Fe procedural blank coming from the vials. Eppendorf A and B are from different lots.

<b>Vials</b>	<b>Position</b>	<b>Fe (nM)</b>
Eppendorf A	Right-side up	0.004
	Upside-down	0.021
Eppendorf B	Right-side up	0.005
	Upside-down	0.043
Molecular BioProduct	Right-side up	0.041
	Upside-down	0.030

**Table 2a.** Typical PQ2+ operating conditions for Cu, Cd, and Pb analysis.

<b>Instrumental Parameter</b>	<b>Set point</b>
Forward power	1450 W
Reflected power	<3 W
Plasma Ar gas flow	15.1 l min <sup>-1</sup>
Carrier Ar gas flow	1.18 l min <sup>-1</sup>
Auxiliary Ar gas flow	1.14 l min <sup>-1</sup>
Acquisition method	Peak jump mode
Channels per mass	3
Channel spacing	0.02
Number of sweeps	200
Dwell time	10 ms/peak
Data acquisition time	73 sec

**Table 2b.** Typical Isoprobe operating conditions for Fe analysis.

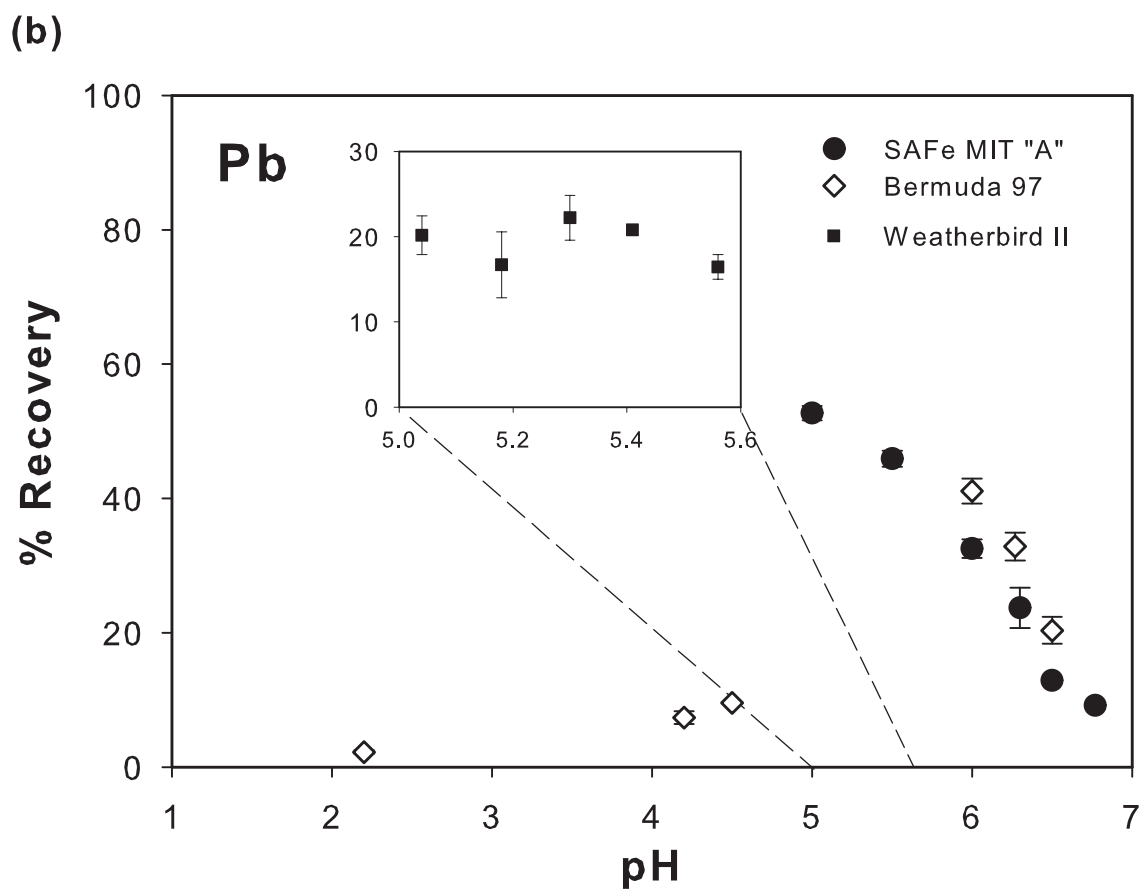
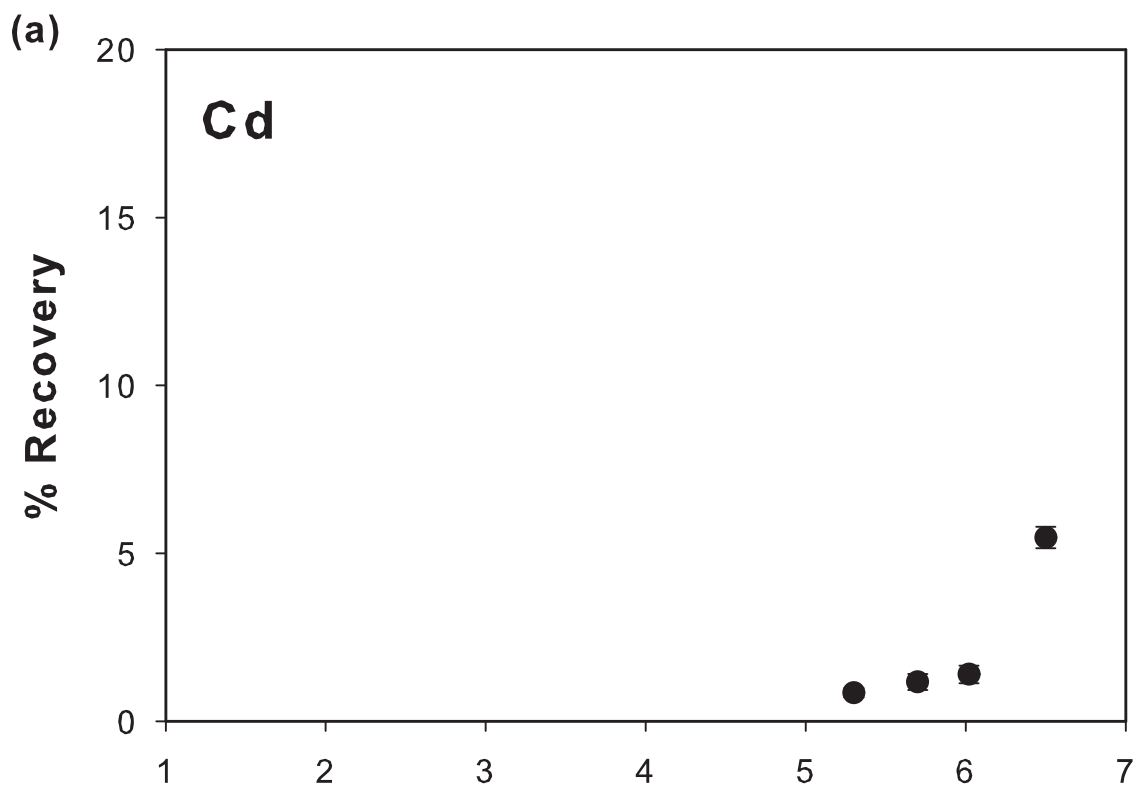
<b>Instrumental Parameter</b>	<b>Set point</b>
Forward power	1350 W
Reflected power	<1 W
Hexapole Ar gas flow	1.8 ml min <sup>-1</sup>
Hexapole H <sub>2</sub> gas flow	2.5 ml min <sup>-1</sup>
Expansion pressure	3x10 <sup>-1</sup> mbar
Hexapole pressure	4x10 <sup>-4</sup> mbar
Analyzer pressure	2x10 <sup>-7</sup> mbar
Nebulizer gas flow	0.8 l min <sup>-1</sup>
Cool gas flow	14 l min <sup>-1</sup>
Aux. gas flow	1.0 l min <sup>-1</sup>
Data acquisition time	24 sec

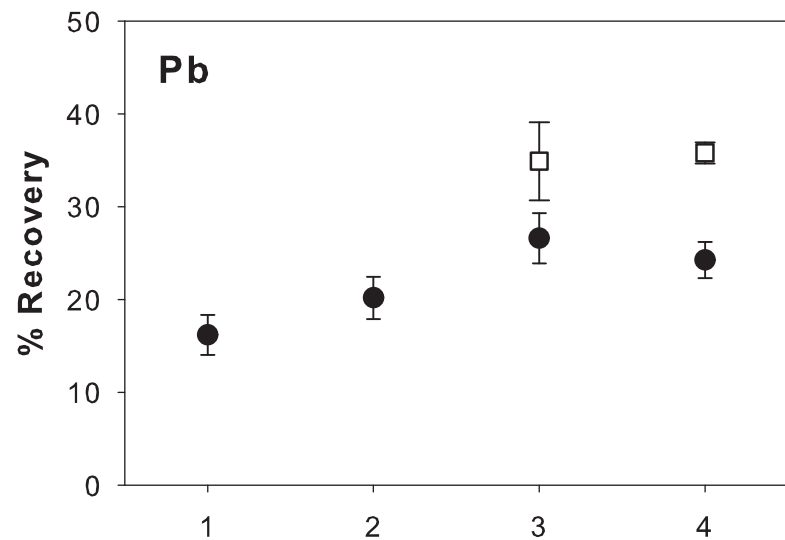
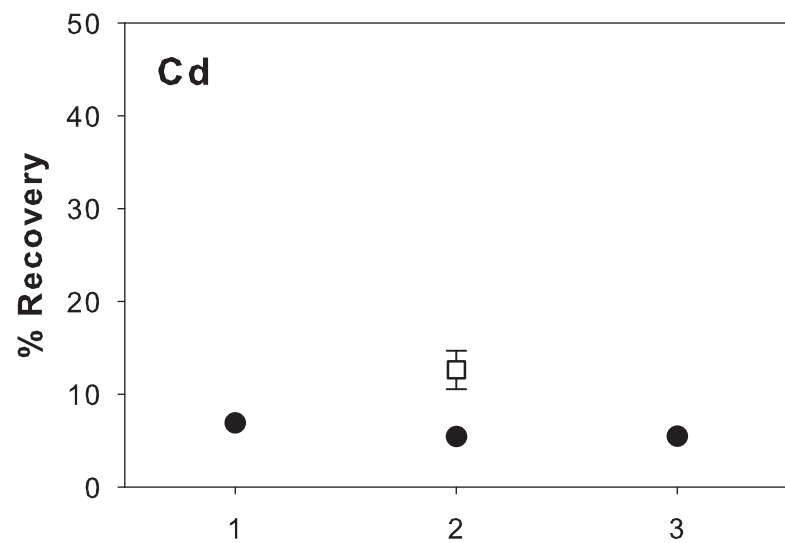
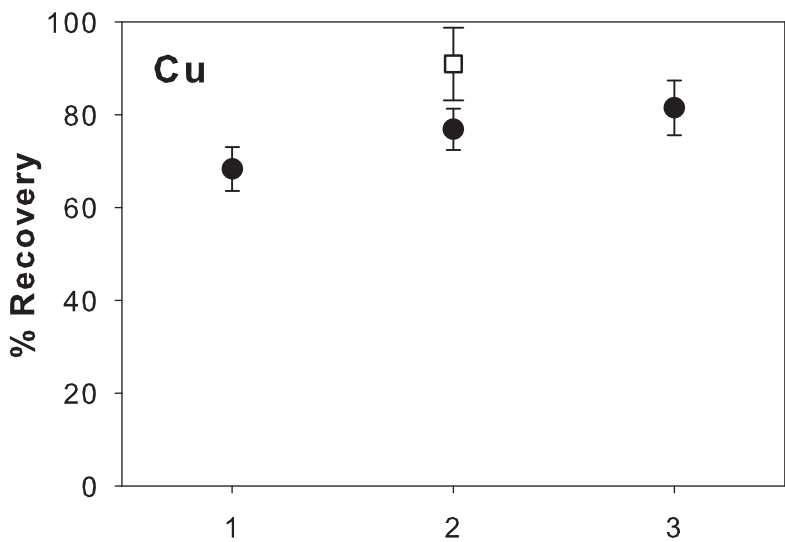
**Table 3.** Procedural blank and detection limit of this method ( $\pm 1\sigma$ ) and comparison of the SAFe consensus Cu, Cd, Pb, and Fe values with those determined by this method.

	<b>Cu (nM)</b>	<b>Cd (pM)</b>	<b>Pb (pM)</b>	<b>Fe (nM)</b>
Blank	0.06±0.04	0±2	1.3±0.2	0.05-0.25
Detect. Lim.	0.12	6	0.5	0.07
SAFe S concensus	0.55±0.04	1	47.0±3.4	0.094±0.008
SAFe MIT “A”	0.58±0.05	1±2	47.2±2.3	0.10±0.05
SAFe D2 concensus	2.35±0.19	992±35	27.6±1.9	0.923±0.029
SAFe D2	2.49±0.10	977±25	26.5±2.0	0.99±.05

**Table 4.** Concentrations of Cu, Cd, and Pb in <sup>65</sup>Cu, <sup>110</sup>Cd, and <sup>204</sup>Pb enriched isotope spikes. When 25µl of each isotope spike is added to 1.3ml sample, it increases the procedural blank of the other elements as much as the numbers in parenthesis.

	<b>Cu (nM)</b>	<b>Cd (nM)</b>	<b>Pb (nM)</b>
<sup>65</sup> Cu spike		0.031 (<0.001)	47.15 (0.28)
<sup>110</sup> Cd spike	0.306 (0.002)		8.07 (0.05)
<sup>204</sup> Pb spike	0.976 (0.006)	0.048 (<0.001)	

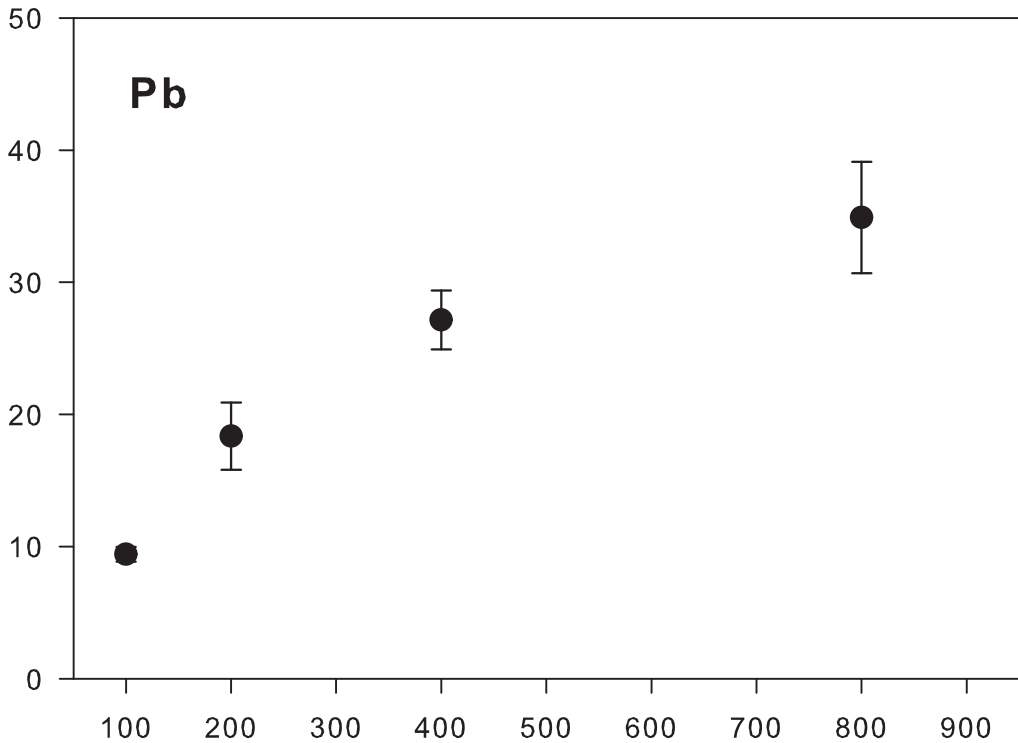




days allowed for sample-resin binding

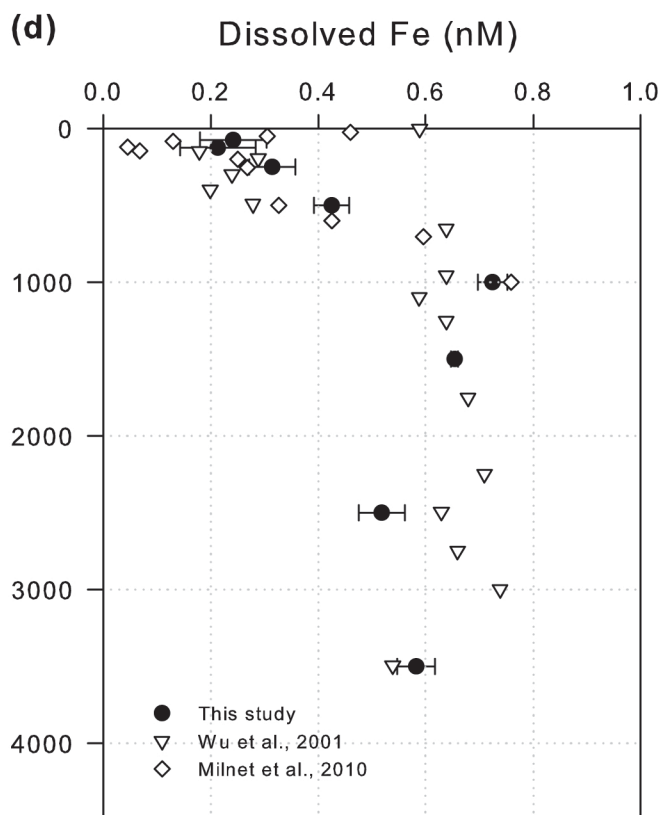
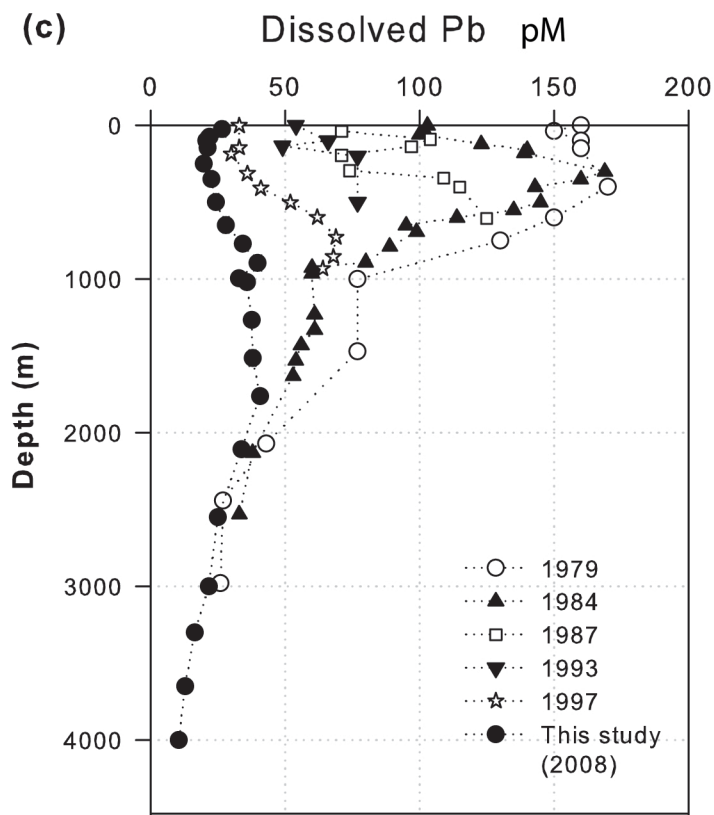
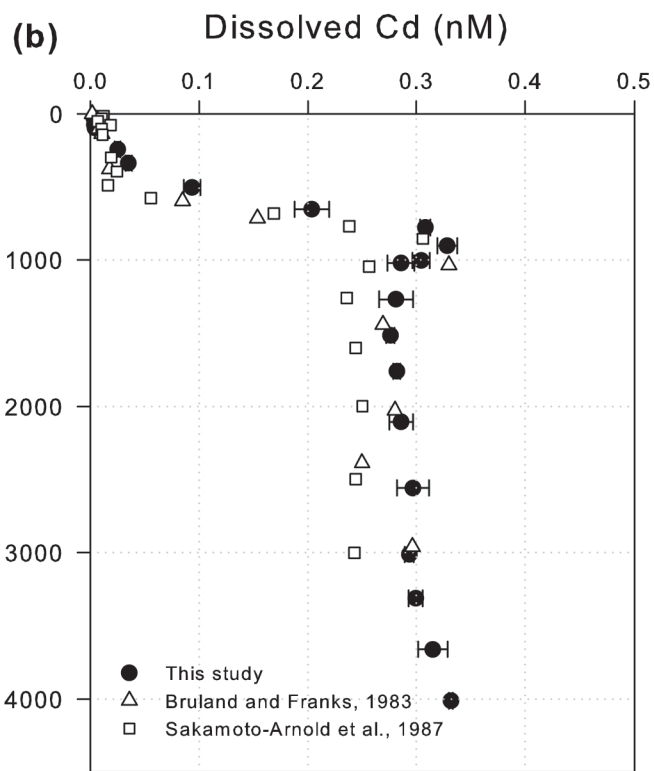
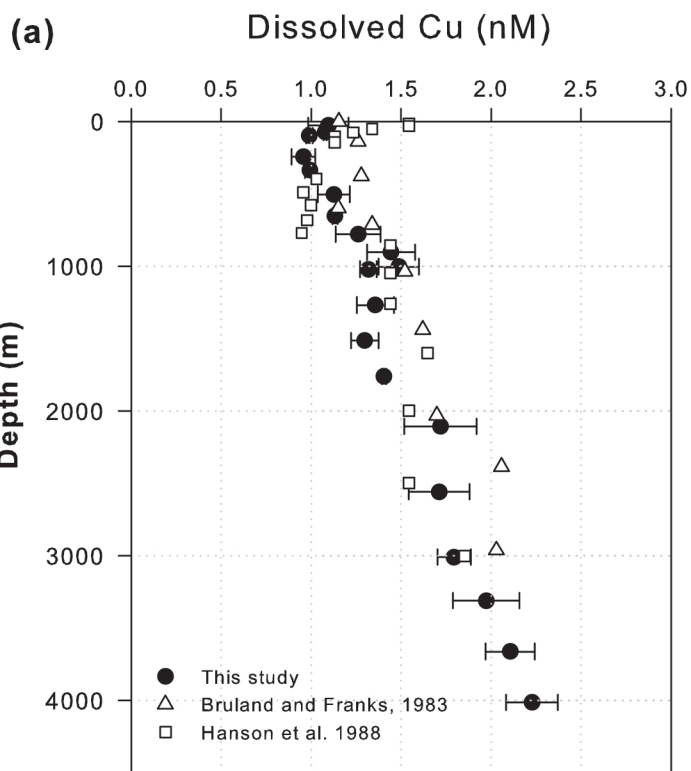
**% Recovery**

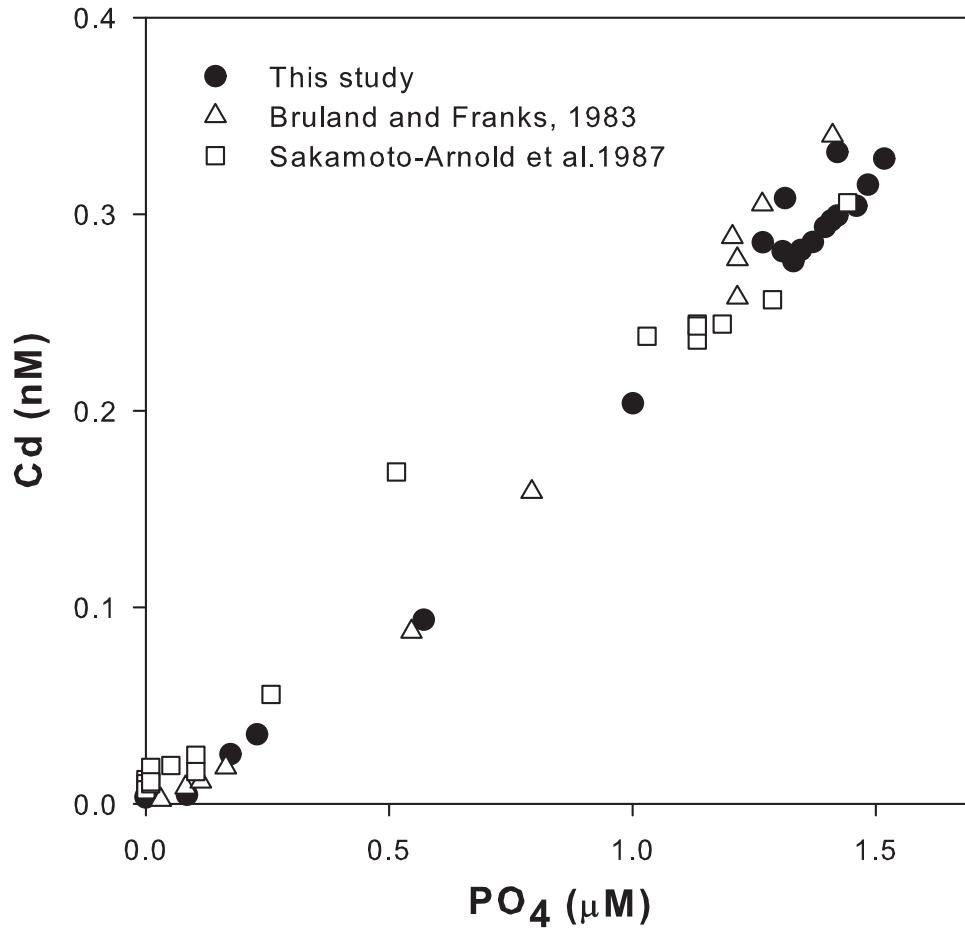
**Pb**



**number of resin beads added**







## Figure captions

**Figure 1.** Relationships between the percent recovery of Cd and Pb and the sample pH when ~200 resin beads were added to 1.3ml of sample. Notice the difference in scales on the vertical axes. Various seawater samples were used for Pb experiments; Pb recovery efficiencies also varied with the nature of the samples.

**Figure 2.** Relationships between percent recovery of Cu, Cd, and Pb and the number of days allowed for sample-resin binding. Samples were prepared at pH 6.5 for Cu and Cd and at pH 5.3 for Pb, and ~200 beads were added to the samples (■). The percent recoveries shown as white squares (□) are when ~400 resin beads were added to the samples.

**Figure 3.** Relationships between percent recovery of Pb and the number of NTA resin beads added to the sample. The samples were prepared in pH 5.0-5.3 and three days were allowed for sample-resin binding. Pb was released from the resin for 2-3 days. In another study using different seawater, Pb recovery up to 80-90% could be achieved by adding 2400 beads to the samples.

**Figure 4.** Profiles of Cu, Cd, Pb, and Fe at BATS analyzed by the ID-NTA bead-ICPMS method and comparison with the data from nearby stations in Sargasso Sea. The Cu and Cd profiles are from Bruland and Franks, 1987 (34°06'N, 66°07'W), Hanson et al., 1988 and Sakamoto-Arnold et al., 1987(35°40'N, 71°53'W). The Pb profiles are from Schaule and Patterson, 1983 (sampled in 1979), Boyle et al., 1986 (sampled in 1984), Wu and Boyle, 1997 (sampled in 1993), and others are unpublished data. The Fe profiles are from Wu et al., 2001 (34.8°N, 57.8°W) and Milne et al., 2010 (same cruise, different cast with different sampling device).

**Figure 5.** Cd-P relationship in the GEOTRACES-BATS station (this study) compared with that from nearby stations. The phosphate data were generated using an Astoria-Pacific rapid flow analyzer and standard chemistry based on molybdenum blue method.