

1 Distinct basin-scale-distributions of aluminum, manganese, cobalt, and lead in the North  
2 Pacific Ocean

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15 Abstract

16 Aluminum (Al), manganese (Mn), cobalt (Co), and lead (Pb) are key trace elements  
17 in seawater and thus significant in chemical oceanography research. However, although all of  
18 these elements are highly scavenged in the ocean, only a few studies focus on the  
19 intercomparison of their distributions. Here, we report the basin-scale and full-depth sectional  
20 distributions of these elements observed during three GEOTRACES Japan cruises in the  
21 North Pacific. We confirmed that a surface maximum of the dissolved (d) species is not a  
22 common feature for the four elements and that the d species have the lowest concentrations in  
23 the Pacific Deep Water (PDW) as compared to other oceans. The elements showed different  
24 speciations and distributions. The fraction of labile particulate (lp) species was calculated as  
25 the difference between the total dissolvable (td) species and d species. The lpM/tdM ratio,  
26 where M refers to an element, is highest for Al, at  $0.66 \pm 0.31$  (average  $\pm$  sd,  $n = 489$ ), and  
27 lowest for Pb, at  $0.02 \pm 0.08$  ( $n = 575$ ). Further, the distribution of each element is uniquely  
28 related to ocean circulation. The tdAl concentration is high in the Equatorial Under Current  
29 (EUC), the North Equatorial Current (NEC), and the Lower Circumpolar Deep Water

30 (LCDW). Manganese is supplied from reductive sources such as sediments on the continental  
31 shelves around the northern boundary. Cobalt is concentrated in the North Pacific  
32 Intermediate Water (NPIW) and in the Equatorial Pacific Intermediate Water (EqPIW) owing  
33 to the combined effects of supply from the continental shelves, biogeochemical cycling, and  
34 scavenging. Lead shows a subsurface maximum centered at  $\sim 35^\circ\text{N}$  and  $\sim 200$  m depth,  
35 implying an association with the formation of the Subtropical Mode Water (SMW) and the  
36 Central Mode Water (CMW). Although the subsurface Pb maximum in the Atlantic has  
37 diminished over the last three decades owing to the ban on leaded gasoline use, it has been  
38 sustained in the North Pacific through the growth of other anthropogenic sources in Asia and  
39 Russia. We propose that the enrichment factor of dM, defined as  $EF(dM) =$   
40  $(dM/dAl)_{\text{seawater}} / (M/Al)_{\text{upper crust}}$ , where  $(M/Al)_{\text{upper crust}}$  is the molar ratio in upper crustal  
41 abundance, can be a good parameter for the sources. The median is  $1.3 \times 10^2$  ( $n = 436$ ) for  
42  $EF(dMn)$ ,  $3.2 \times 10^2$  ( $n = 430$ ) for  $EF(dCo)$ , and  $1.2 \times 10^3$  ( $n = 413$ ) for  $EF(dPb)$ . The  
43  $EF(dPb)$  found in this study is on the same order of magnitude as the  $EF$  values for aerosols  
44 found in the literature, suggesting that the deposition of aerosols is a major source for dPb.  
45 Because  $EF(dMn)$  and  $EF(dCo)$  are ten to hundred times higher than the  $EF$  for aerosols,  
46 sources other than the aerosol deposition are more significant contributors to the  
47 concentrations of Mn and Co.

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49 Keywords: GEOTRACES; Trace metals; Ocean sections; Scavenging; Biogeochemical  
50 cycling; Anthropogenic pollution

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## 53 1. INTRODUCTION

54 Elements in seawater have been divided into conservative, nutrient (or recycled),  
55 and scavenged groups based on their dissolved (d) concentration–depth profiles (Bruland and  
56 Lohan, 2003; Chester, 2000). Scavenged group elements are adsorbed on particles and  
57 removed from the ocean with a short residence time of  $\sim 10^2$ – $10^3$  years, resulting in high  
58 concentrations near the sources. In a broad sense, aluminum (Al), manganese (Mn), cobalt

59 (Co), and lead (Pb) are classified as the scavenged elements.

60 Aluminum is supplied to the ocean surface via the deposition of atmospheric dust  
61 (Hydes, 1979; Maring and Duce, 1987). The surface dAl concentration in the Pacific is as low  
62 as a tenth of that in the tropical and subtropical North Atlantic, because the Pacific receives  
63 less dust per unit area (Bruland et al., 1994; Measures et al., 2005; Measures and Vink, 2000;  
64 Orians and Bruland, 1986). Another important **transporter** of Al is currents, particularly in the  
65 equatorial Pacific (Kaupp et al., 2011; Slemons et al., 2012). Dissolved and particulate Al are  
66 transported eastward by the Equatorial Under Current (EUC) from the northeastern coastal  
67 margins of New Guinea and New Ireland (Kaupp et al., 2011; Slemons et al., 2012). Supply  
68 of Al by tropical and subtropical currents is also observed in the Indian Ocean (Vu and Sohrin,  
69 2013). **Other examples would be dAl in Mediterranean Outflow Water (MOW) (Kramer et al.,**  
70 **2004) and in North Atlantic Deep Water (NADW) (Middag et al., 2015).** Dissolved Al is  
71 removed from the water column by passive adsorption onto particles or active uptake (e.g.  
72 diatoms) (Mackenzie et al., 1978; Moran and Moore, 1988). Gehlen et al. (2002) reported  
73 direct evidence for the structural association of Al and silicon (Si) in biogenic silica. The  
74 vertical profiles of dAl in the ocean often exhibit a mid-depth minimum and increasing  
75 concentrations towards the sediment-water interface, which is caused by the advection of  
76 Al-rich deep water or by the diffusion of Al from sediment pore water (Bruland et al., 1994;  
77 Orians and Bruland, 1985, 1986; Zheng et al., 2017). Suspended particulate Al (pAl) in  
78 seawater decreases with distance from the North American continent and increases closer to  
79 the bottom due to the resuspension of sediments (Orians and Bruland, 1986). As a result of  
80 scavenging, the deep-water dAl concentration in the North Pacific is ~40-fold lower than that  
81 in the North Atlantic (Orians and Bruland, 1986). Recent GEOTRACES studies have  
82 revealed wide variations in the concentration of **dAl and pAl** in both the intra- and inter-basin  
83 scales in the Atlantic Ocean (Barrett et al., 2015; Measures et al., 2015; Middag et al., 2015),  
84 the **Southern** Ocean (Middag et al., 2011b), and the Mediterranean Sea (Rolison et al., 2015).

85 The dMn commonly has a maximum concentration at the surface and in the oxygen  
86 minimum layer, where O<sub>2</sub> falls below 100 μmol kg<sup>-1</sup> (Boyle et al., 2005; Bruland et al., 1994;  
87 Fujishima et al., 2001; Klinkhammer and Bender, 1980; Landing and Bruland, 1980; Martin

88 and Knauer, 1980; Zheng et al., 2017). Manganese maxima also occur in hydrothermal  
89 plumes in deep water (Boyle et al., 2005; Coale et al., 1991; Klinkhammer, 1980) and in  
90 bottom water at the continental margins (Biller and Bruland, 2013; Chase et al., 2005;  
91 Minakawa et al., 1998; Slemons et al., 2012). These dMn maxima are related to reductions of  
92 Mn(IV) or Mn(III) to soluble Mn(II). Manganese(IV) is reduced via photoreduction in surface  
93 water (Sunda and Huntsman, 1988), by microorganisms in sediments (Froelich et al., 1979),  
94 and by seawater–basalt interaction during hydrothermal circulation (Von Damm and Bischoff,  
95 1987). Horizontal sections off of North America indicate that Mn is actively remobilized from  
96 anoxic sediments on the continental shelves and slopes, diffused into the overlying seawater,  
97 and transported by lateral advection (Jones and Murray, 1985; Martin and Knauer, 1984;  
98 Martin et al., 1985). Oxidation of Mn(II) is microbially catalyzed, resulting in fast scavenging  
99 from a water column (Cowen et al., 1990; Mandernack et al., 1995; Moffett and Ho, 1996).  
100 Recent GEOTRACES investigations revealed sectional distributions of Mn in the Atlantic  
101 Ocean (Noble et al., 2012; van Hulst et al., 2017), in the Southern Ocean (Middag et al.,  
102 2011a), and in the Indian Ocean (Vu and Sohrin, 2013).

103         The profile of dCo was first observed off central California, showing a surface  
104 maximum and a strong correlation with dMn (Knauer et al., 1982). Subsequent observations  
105 revealed a subsurface dCo maximum at 50–700 m depths (Ezoe et al., 2004; Fujishima et al.,  
106 2001; Noble et al., 2008; Zheng et al., 2017). Cobalt is microbially co-oxidized with Mn  
107 (Moffett and Ho, 1996), concentrated in manganese oxides, and released into water through  
108 manganese reduction (Biller and Bruland, 2013). Recent studies have indicated the correlation  
109 between dCo and phosphate in the upper water column, concluding that dCo is affected by  
110 both nutrient cycling and scavenging onto manganese oxides (Hawco et al., 2018; Noble et al.,  
111 2008; Saito et al., 2017). The latter process concentrates Co in pelagic sediments, manganese  
112 nodules, and manganese crusts, resulting in a small d inventory in deep waters.

113         Nozaki et al. (1976) reported that radioactive  $^{210}\text{Pb}$  ( $t_{1/2} = 22.3$  y) in the Pacific  
114 surface water has a maximum concentration at  $\sim 35^\circ\text{N}$  and  $170^\circ\text{E}$ . They explained  $^{210}\text{Pb}$   
115 distribution by dust deposition from the atmosphere and scavenging in the water column,  
116 estimating the residence time of Pb in surface water to be 1.7 years in the North Pacific

117 subtropical gyre. Then, Nozaki et al. (1997) evaluated the residence time of  $^{210}\text{Pb}$  in the  
118 Pacific Deep Water (PDW) to be > 200 years in the central gyre and 50–100 years at the  
119 margins. For stable Pb, Schaule and Patterson (1981) studied the concentration of total  
120 dissolvable Pb (tdPb) in seawater between Hawaii and California, revealing the first reliable  
121 vertical profile of stable Pb in 1976. Lead is supplied to the North Pacific mainly via the  
122 atmosphere at a rate of  $\sim 50 \text{ ng cm}^{-2} \text{ y}^{-1}$ , which exceeds the prehistoric output flux of  
123 authigenic Pb recorded in pelagic sediments by  $\sim 170$  times (Flegal and Patterson, 1983). Both  
124 the  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$  ratios in seawater fitted between the isotopic ratios of  
125 Australian and North American leads (Flegal et al., 1984). Boyle et al. (2005) reported a tdPb  
126 profile at the Hawaii Ocean Time-series (HOT)-A Long-Term Oligotrophic Habitat  
127 Assessment (ALOHA) station (22.75°N, 158°W) in 1999 and found an insignificant change  
128 in the subsurface maximum concentration from that in 1976. They attributed the remaining Pb  
129 in the Pacific water to Asian emissions by high-temperature processes such as coal burning,  
130 although leaded gasoline had been abolished in the United States, Canada, and Japan. They  
131 also observed a time-series in the mixed layer near the Hawaii Air-Sea Logging Experiment  
132 (HALE)-ALOHA mooring site and reported the presence of an annual cycle in the Pb  
133 concentration in which it is  $\sim 20\%$  higher in the winter months owing to the downward mixing  
134 of the winter mixed layer. Wu et al. (2010) reported that the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in the North  
135 Pacific abyssal water is substantially lower than the pre-industrial value, suggesting that  
136 anthropogenic Pb has invaded and become the predominant Pb source there. Recently,  
137 comprehensive data on Pb isotopes in seawater have been reported from the western North  
138 Pacific (Gallon et al., 2011; Zurbrick et al., 2017). It was concluded that only three  
139 countries—China, Russia, and Japan—have aerosol Pb isotope composition similar to that of  
140 seawater and these occupy about 74% of the industrial input to the western North Pacific. The  
141 latest data on the distribution of Pb in seawater were obtained from the Philippine Sea (Chien  
142 et al., 2017), near the Juan de Fuca Ridge (Zheng et al., 2017), and from the eastern equatorial  
143 Pacific (Pinedo-González et al., 2018). Sectional distributions of Pb have been reported in the  
144 Atlantic Ocean (Bridgestock et al., 2018; Bridgestock et al., 2016; Noble et al., 2015; Rigaud  
145 et al., 2015; Rusiecka et al., 2018; Zurbrick et al., 2018) and the Indian Ocean (Echegoyen et

146 al., 2014; Lee et al., 2015; Vu and Sohrin, 2013).

147           These results suggest that Al, Mn, Co, and Pb are strongly controlled by scavenging.  
148 However, each element has specific effects such as supply from reductive sources for Mn and  
149 Co, nutrient cycling for Co, and anthropogenic contamination for Pb. Simultaneous  
150 observation of these elements will serve to understand these specific effects. Studies  
151 conducting such observations are, however, limited, owing to challenges to analysis (Zheng et  
152 al., 2017). Here, we report the basin-scale and full-depth sectional distributions of Al, Mn, Co,  
153 and Pb in the North Pacific for the first time. We observed the distributions of both td and d  
154 species of these elements using a multielement analytical method (Minami et al., 2015)  
155 without ultraviolet (UV) irradiation during three GEOTRACES Japan cruises. The difference  
156 between td and d concentrations is defined as the labile particulate (lp) concentration. The lp  
157 species are liberated from particulate phases during sample storage at pH ~2 with added HCl  
158 and at room temperature for more than one year. On the basis of the comprehensive dataset,  
159 we systematically discuss the biogeochemical cycling of the scavenged elements in the North  
160 Pacific.

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## 163 2. METHODS

### 164 2.1. Hydrographic background of the study site

165           This study was conducted on the following cruises of R/V *Hakuho Maru*: KH-05-2  
166 from August to September 2005, KH-11-7 in July 2011, and KH-12-4 from August to  
167 September 2012 (Fig. 1). The map and a number of figures in this paper were prepared using  
168 the Ocean Data View software (Schlitzer, 2018). The KH-05-2 cruise was a reconnaissance  
169 study by GEOTRACES Japan. KH-11-7 and KH-12-4 were formal studies by GEOTRACES  
170 Japan, occupying GEOTRACES sections GP18 (165°E) and GP02 (47°N), respectively.  
171 Figure 2 shows the full-depth sectional distributions of salinity, O<sub>2</sub>, silicate, phosphate, and  
172 tdM along 160°W longitude. The data from 165°E and 47°N are shown in Supplementary  
173 Figs. 1 and 2, respectively. Supplementary Figs. 3 and 4 show the sectional distributions of  
174 salinity, potential temperature, O<sub>2</sub>, silicate, and phosphate at depths of 0–1000 m along

175 160°W and 165°E, respectively.

176 In the tropical Pacific, three major zonal surface currents exist (Fig. 1): the  
177 westward-flowing South Equatorial Current (SEC) between about 20°S and 3°N (ST01–03),  
178 the narrow eastward-flowing North Equatorial Counter Current (NECC) centered at about  
179 5°N (ST04, 05), and the westward-flowing North Equatorial Current (NEC) between about  
180 8°N and 20°N (ST06, 07) (Wyrcki and Kilonsky, 1984). The EUC is fed by the saline New  
181 Guinea Coastal Under Current and flows eastward just below the SEC within a pycnocline at  
182 about 200 m depth at ST03 (Supplementary Fig. 3a).

183 The westward-flowing NEC forms the southern side of the anticyclonic North  
184 Pacific subtropical gyre (Fig. 1), splitting into northward and southward boundary currents  
185 known as the Kuroshio and Mindanao Currents, respectively. The Kuroshio turns to follow  
186 the south coast of Japan and flows eastward at about 35°N to become the Kuroshio Extension  
187 (KE), which forms the northern side of the subtropical gyre (Fig. 1). The KE region is  
188 between about 30°N and 40°N (TR07–09), where surface water is characterized by high  
189 salinity > 34.3 and high temperature > 15°C. Water masses beneath the surface water include  
190 the Subtropical Mode Water (STMW) and the Central Mode Water (CMW) with potential  
191 density anomaly ( $\sigma_\theta$ ) values of 25.2–25.8 and 26.0–26.4, respectively (Yasuda, 2003)  
192 (Supplementary Fig. 4a). The formation region of the STMW is located at 32–35°N,  
193 140–180°E, and the formation region of CMW is located at 36–43°N, 150°E–160°W. The  
194 region between the Kuroshio and the Oyashio is referred to as the Transition Region (TR11,  
195 ST11, 12; Fig. 1). The broad eastward flow of this region, known as the North Pacific Current  
196 (NPC), includes both the northern side of the subtropical gyre and the southern side of the  
197 cyclonic subarctic gyre. At the eastern boundary, the NPC feeds into the southward-flowing  
198 California Current (BD17–18) and the northward-flowing Alaska Current.

199 The western boundary current for the North Pacific subpolar gyre is the  
200 Oyashio/East Kamchatka Current (EKC; Fig. 1). The Oyashio separates from the western  
201 boundary at about 42°N and flows northeastward as the Oyashio Extension (OE), where  
202 surface water is characterized by salinity of 32.7–33.8 and temperature of 0.9–11.1°C (TR13).  
203 The subsurface water is the Okhotsk Sea Mode Water (OSMW), at 26.6–27.0  $\sigma_\theta$ , which

204 originates in the Sea of Okhotsk and flows out to the Pacific through the Kuril Straits (Yasuda,  
205 1997). The OSMW is observed at a depth of about 200 m at TR16/BD07 (Supplementary Fig.  
206 4a). A number of northern stations in this study (TR15, 16, BD07–16, ST13) are located  
207 within the subpolar gyre (Fig. 1). The northern side of the gyre is the westward-flowing  
208 Alaskan Stream (AS; ST14).

209           The North Pacific Intermediate Water (NPIW) and the Antarctic Intermediate Water  
210 (AAIW) are well-known intermediate water masses in the Pacific Ocean (Talley et al., 2011).  
211 Recently, a third main water type at intermediate depths was proposed: the Equatorial Pacific  
212 Intermediate Water (EqPIW) (Bostock et al., 2010). The NPIW, which is characterized by a  
213 salinity minimum of 33.8, low O<sub>2</sub> at 50–150 μmol kg<sup>-1</sup>, and low density of 26.4–27.2 σ<sub>θ</sub>,  
214 averaging 26.8 σ<sub>θ</sub>, originates from the OSMW (Yasuda, 1997). The NPIW spreads over the  
215 subtropical gyre at a depth range of 400–800 m, bounded by the subarctic front to the north at  
216 ~40°N (ST11) and a steep potential vorticity gradient to the south at 15–20°N (ST07; Fig. 2a  
217 and Supplementary Fig. 3a). The AAIW is a distinct water mass with high O<sub>2</sub> concentrations  
218 of 200–250 μmol kg<sup>-1</sup>, salinity minima of 34.3–34.5, and a temperature range of 3.5–10°C,  
219 resulting in an average density of 27.1 σ<sub>θ</sub>. The AAIW forms below the subantarctic front and  
220 is then subducted along an isopycnal surface at depths of 600–1300 m. The EqPIW is  
221 characterized by low O<sub>2</sub> on the 26.8–27.2 σ<sub>θ</sub> isopycnals (ST01–06; Fig. 2a and  
222 Supplementary Fig. 3a). The geochemistry of the EqPIW suggests that it is composed  
223 primarily of a combination of AAIW and upwelled PDW (Bostock et al., 2010).

224           In the deep ocean, the Lower and Upper Circumpolar Deep Waters (LCDW and  
225 UCDW, respectively) are transported to the North Pacific from the Antarctic Circumpolar  
226 Current (Fig. 2c). The LCDW is characterized by a temperature range of 1–2°C, salinity of  
227 34.7, density of 27.8 σ<sub>θ</sub>, and the salinity maximum (Talley et al., 2011). The UCDW is  
228 characterized by a temperature of 2.5°C, salinity of 34.6, density of 27.6 σ<sub>θ</sub>, and the O<sub>2</sub>  
229 minimum. The LCDW enters the Central Pacific Basin through the Samoan Passage,  
230 proceeds farther north, and reaches the Northeast Pacific Basin (Kawabe and Fujio, 2010)  
231 (Fig. 4a). The major branch flows anticyclonically along the Japan, Kuril–Kamchatka, and  
232 Aleutian Trenches. The LCDW finally upwells and is transformed into the PDW, which is



233 internally formed entirely in the Pacific from the upwelling and diffusion of the LCDW. The  
234 PDW has physical properties similar to those of the UCDW but is enriched with nutrients. It  
235 shifts southward in the upper deep layer and is modified by mixing with the UCDW around  
236 the Hawaiian Islands (Fig. 2c).

237

## 238 2.2. Sampling and analysis

239 Seawater samples were collected during the three GEOTRACES Japan cruises  
240 (KH-05-2, KH-11-7, and KH-12-4) using a clean sampling system (Sohrin and Bruland,  
241 2011). The system was based on a Carousel Water Sampler Frame (SBE-32, Sea-Bird  
242 Scientific, USA) that was finished with epoxy paint and equipped with conductivity,  
243 temperature, and depth (CTD) sensors (SBE-9-plus, Sea-Bird) and Niskin-X bottles (General  
244 Oceanics, USA). The insides of the Niskin bottles were coated with Teflon and were cleaned  
245 with 1% detergent, 0.1 mol kg<sup>-1</sup> hydrochloric acid, and deionized water prepared with a  
246 Milli-Q system (MQW; Merck Millipore, Germany) at the beginning of the cruises. The clean  
247 sampling system was deployed using a titanium-armored cable. Seawater temperature was  
248 measured with the CTD sensor. Salinity reported in this paper was determined using a bench  
249 salinometer that was standardized on the basis of the IAPSO standard seawater; the O<sub>2</sub>  
250 content was measured using the Winkler method; and nutrient concentrations were  
251 determined by spectrophotometry using an automated analyzer onboard the vessel. These  
252 measurements were in accordance with the protocols for JGOFS (Knap et al., 1996). Nutrient  
253 data were checked using seawater reference nutrient material (KANSO, Japan).

254 During KH-05-2, seawater was transferred from the sampler to precleaned Nalgene  
255 low-density polyethylene (LDPE) bottles (Thermo Fisher Scientific, USA) on deck using a  
256 silicon tube and filling bell to avoid contamination by airborne particles. The samples were  
257 immediately transferred into a cleanroom laboratory (class 100) on the vessel. A portion of  
258 the seawater for **dissolved metal (dM)** species was passed through a polycarbonate Nuclepore  
259 filter with a pore size of 0.2 μm and a diameter of 47 mm (Whatman, UK) using a closed  
260 filtration system. The filter was precleaned with mixtures of HCl–H<sub>2</sub>O<sub>2</sub> and HCl–HNO<sub>3</sub>–HF  
261 (Nakatsuka et al., 2007). The filtered seawater was acidified to pH 2.2 with ultrapure HCl

262 (Tampure AA-10, Tama Chemicals, Japan). The portion of the seawater for **total dissolvable**  
263 **metal (tdM)** species analysis was acidified without filtration. These samples were stored at  
264 ambient temperature for ~10 years before analysis.

265 During KH-11-7 and KH-12-4, the Niskin bottles were carried into a clean bubble  
266 upon retrieval of the CTD sampling system, and the seawater samples were transferred from  
267 the Niskin bottles to precleaned LDPE bottles. During KH-11-7, filtration was conducted  
268 using a Nuclepore filter in a manner similar to that used during KH-05-2. During KH-12-4,  
269 filtration was conducted using an AcroPak capsule filter with a pore size of 0.2  $\mu\text{m}$  (Pall,  
270 USA), which was directly attached to the Niskin bottle. The seawater samples for both d and  
271 td species analyses were immediately acidified in a manner similar to that used during  
272 KH-05-2 and were stored at ambient temperature for at least one year before analysis.

273 An off-line automated solid-phase extraction system (SPE-100, Hiranuma Sangyo,  
274 Japan) equipped with a column of Nobias Chelate-PA1 resin (Hitachi High Technologies,  
275 Japan) was used for the preconcentration of Al, Mn, iron (Fe), Co, nickel (Ni), copper (Cu),  
276 zinc (Zn), cadmium (Cd), and Pb from the seawater (Minami et al., 2015). The seawater  
277 samples were adjusted to  $\text{pH } 6.00 \pm 0.05$  just before preconcentration by adding  
278  $\text{HAcO-NH}_4\text{AcO}$  buffer solution prepared from ultrapure HAcO and  $\text{NH}_3$  (TAMAPURE  
279 AA-10 or Optima Acids, Thermo Fisher Scientific). When preconcentrating the tdM species,  
280 unfiltered samples were first passed through a Millex syringe filter with a pore size of 0.45  
281  $\mu\text{m}$  (Merck Millipore, Germany) and then introduced into the SPE-100. The nine metals were  
282 eluted with  $1.0 \text{ mol kg}^{-1} \text{ HNO}_3$  (Optima Acids) and determined with a high-resolution  
283 inductively coupled plasma mass spectrometer (HR-ICP-MS, Element 2, Thermo Fisher  
284 Scientific) using a calibration curve.

285 It has been reported that UV irradiation prior to preconcentration is necessary for  
286 analysis of total dCo (Biller and Bruland, 2012; Milne et al., 2010; Saito and Moffett, 2001).  
287 The UV irradiation is adopted in the Sampling and Sample-handling Protocols for the  
288 GEOTRACES Cruises. However, we refrained from using UV irradiation to minimize  
289 contamination of the nine metals and to avoid unknown effects of UV irradiation on the  
290 determination of the nine metals. **So far, we have done two runs of experiment to investigate**

291 the effect of UV irradiation on the determination of the nine metals. A portion of the surface  
292 seawater sample collected from the North Pacific was taken in a PFA jar with a quartz  
293 window and exposed to a 20 mW cm<sup>-2</sup> lamp for 2–24 h. We found that the concentration of  
294 Al and Fe sometimes decreased due to unknown effects of UV irradiation. Recently, Wuttig et  
295 al. (2019) studied the effect of UV irradiation and suggested that it should not be performed  
296 on samples in which multiple elements are to be determined in order to avoid unnecessary  
297 container leaching or contamination. Thus, it should be noted that our Co data are operational  
298 results.

299 We evaluated the procedure blanks by using MQW as a sample. The MQW was  
300 initially acidified with HCl and then adjusted to pH 6.00 for preconcentration, which is a  
301 process similar to that used for seawater samples. We detected contamination during the  
302 filtration using a Nuclepore filter for KH-05-2 and KH-11-7. To eliminate this effect, a  
303 filtration method similar to that used for seawater was applied to MQW for evaluation of the  
304 procedure blanks for dM. We defined the detection limits for tdM and dM as three times the  
305 standard deviation (sd) of the procedure blank. The lpM concentrations were obtained by  
306 taking the difference between tdM and dM. Because the relative standard deviation (rsd) was  
307 ~5% for both tdM and dM, the detection limit of lpM was defined by using the following  
308 equation considering the propagation of uncertainty:  $2 \times \sqrt{2} \times 0.05 \times C_{ave}$ , where  $C_{ave}$   
309 represents the average concentration of each dM in this study. The procedure blanks and  
310 detection limits are summarized in Supplementary Table 1. We measured the certified  
311 reference materials for the trace metals, CASS-5 and NASS-6 (National Research Council  
312 Canada), and GEOTRACES open-ocean reference samples SAFe-D2, GS, and GD at an early  
313 point in the study (Minami et al., 2015). We participated in the intercalibration campaign of  
314 new reference materials of CASS-6 and NASS-7, contributing to the establishment of  
315 certified values at a late point in the study (Yang et al., 2018). Recently, we measured new  
316 GEOTRACES reference samples, GSP and GSC1. All of these data ensured the accuracy of  
317 the trace metal data collected in this study (Supplementary Table 2). A part of our data (dMn  
318 and dPb from GP02 and GP18) has been accepted for the GEOTRACES Intermediate Data  
319 Product 2017 (Schlitzer et al., 2018). The data on Fe, Ni, Cu, Zn, and Cd will be reported in

320 forthcoming papers.

321

322

### 323 3. RESULTS

324 The seawater data are summarized in Supplementary Table 3. At stations ST01 and  
325 02 of KH-05-2 and TR 07, 11, 13, and 15 of KH-11-7, the vertical profiles of dAl showed  
326 abnormal maxima higher than  $1 \text{ nmol kg}^{-1}$  at intermediate depths, suggesting that  
327 contamination from the filtration system occurred at the beginning of each cruise. The dPb  
328 data at TR07 were also questionable due to the contamination. Some samples showed  
329 abnormally high values of both tdM and dM concentrations, particularly for Pb, suggesting  
330 that contamination occurred during sampling. These questionable data have been removed  
331 from the discussion. The summary of the seawater data is presented in Table 1. Figure 2 and  
332 Supplementary Figs. 1 and 2 show the full-depth sectional distributions of salinity,  $\text{O}_2$ , silicate,  
333 phosphate, and tdM along  $160^\circ\text{W}$ ,  $165^\circ\text{E}$  (GEOTRACES section GP18), and  $47^\circ\text{N}$  (GP02),  
334 respectively. Figure 3 and Supplementary Figs. 5 and 6 show sectional distributions of dM  
335 and lpM for depths of 0–1000 m. The local distributions around the Juan de Fuca Ridge have  
336 been reported in a previous paper (Zheng et al., 2017).

337

#### 338 3.1. Aluminum

339 The tdAl concentration was as low as about  $1 \text{ nmol kg}^{-1}$  at  $40\text{--}50^\circ\text{N}$ , at 0–4000 m  
340 depth in the  $160^\circ\text{W}$  section (Fig. 2e). It steeply increased up to  $60 \text{ nmol kg}^{-1}$  above  $50^\circ\text{N}$  due  
341 to supply from the continental shelf and slope. In the southern deep waters at  $> 4000 \text{ m}$  depths,  
342 an elevated tdAl concentration was observed with a high  $\text{O}_2$  concentration, suggesting that it  
343 was supplied by the LCDW flowing northward from the Southern Ocean. High tdAl  
344 concentrations in deep waters were also found to the north of  $40^\circ\text{N}$ , where the LCDW flows  
345 eastward (Fig. 4). In the upper section, dAl maxima near  $8 \text{ nmol kg}^{-1}$  were located at a depth  
346 of 200 m at the equator, and at the surface at  $15\text{--}20^\circ\text{N}$  (Fig. 3a). They correspond to the EUC  
347 and NEC, respectively. In contrast, the supply from the northern boundary was dominated by  
348 lpAl (Fig. 3e).

349 In the sections along 165°E and 47°N, tdAl was also high below the depth of 4400  
350 m (Supplementary Figs. 1e and 2e). The tdAl species was dominated by lpAl near the  
351 Kamchatka Peninsula (Figs. 7a and b), the Aleutian Islands (Fig. 6a and Supplementary Fig.  
352 7a), and the Juan de Fuca Ridge (Zheng et al., 2017).

353 Figures 4a and 4b show the horizontal distribution of tdAl and dAl, respectively, at  
354 a depth of 4500 m where the LCDW flows. Our data are not enough to cover the whole area  
355 of the North Pacific. However, it is apparent that the tdAl concentration tends to be high  
356 along the main path of LPDW. Some local sources are found near the Hawaiian Islands, off of  
357 the Kamchatka Peninsula, and off of the Aleutian Islands. In contrast, the dAl distribution  
358 shows a zonal characteristic. The dAl concentration decreases with latitude, suggesting that  
359 there are no strong local sources at high latitudes.

360

### 361 3.2. Manganese

362 The tdMn concentration was uniformly low at 0.2–0.3 nmol kg<sup>-1</sup> in deep waters  
363 along 160°W, with an increase of up to 1 nmol kg<sup>-1</sup> in the LCDW (Fig. 2f). High tdMn values  
364 of up to 12 nmol kg<sup>-1</sup> occurred near the continental shelf of the Aleutian Islands. In the upper  
365 section, surface maxima of dMn were found in surface water where the SEC and NEC flow  
366 (Fig. 3b). Dissolved Mn was as high as 8 nmol kg<sup>-1</sup> in surface water at the northernmost  
367 station ST14 in the AS, and spreaded downwards along an isopycnic surface of about 27.0  $\sigma_\theta$ .  
368 In contrast, a significant lpMn maximum was observed only in surface water at ST14 (Fig.  
369 3f).

370 Elevated tdMn and dMn concentrations also occurred in surface waters to the north  
371 of 45°N along 165°E (Supplementary Figs. 1f and 5a) and at the western and eastern ends  
372 along 47°N (Supplementary Figs. 2f and 6b), suggesting sources on the continental shelves.  
373 In addition, high tdMn and dMn concentrations occurred in bottom water at TR16 near the  
374 Kamchatka Peninsula (Supplementary Figs. 1f and 2f) and at middle depths of 1780–3700 m  
375 around the Juan de Fuca Ridge (Zheng et al., 2017). In deep waters, tdMn was dominated by  
376 lpMn and showed a similar distribution with tdAl (Supplementary Figs. 1f and 2f).

377

378 3.3. Cobalt

379 The concentrations of tdCo and dCo were remarkably high, up to 220 pmol kg<sup>-1</sup> in  
380 the AS, similar to tdMn and dMn (Figs. 2g and 3c). Cobalt spreaded much more widely than  
381 Mn in a zone of 26.5–27.0  $\sigma_\theta$ , where the NPIW and the EqPIW existed. In the upper section,  
382 dCo was depleted in surface water from 10°S to 40°N in contrast with dMn, suggesting  
383 uptake by phytoplankton (Fig. 3c). The lpCo concentration showed some surface maxima  
384 along 160°W and abrupt increase at the northern boundary (Fig. 3g).

385 The concentrations of tdCo and dCo were as high as 90 pmol kg<sup>-1</sup> in shallow water  
386 along the Kamchatka Peninsula and extended along a zone of 26.5–27.0  $\sigma_\theta$  (Supplementary  
387 Figs. 1g and 5b). Along 47°N, tdCo and dCo showed maxima in surface water at the western  
388 and eastern ends, similar to tdMn and dMn (Supplementary Figs. 2g and 6c); however, tdCo  
389 and dCo were distributed more uniformly at intermediate depths. The lpCo concentration  
390 showed bottom maxima similar to those of lpAl in the three sections, while the maximum  
391 lpCo concentration was less than 20 pmol kg<sup>-1</sup>. A high concentration of lpCo was also  
392 observed in the bottom water around the Juan de Fuca Ridge, although an increase in dCo was  
393 not observed (Zheng et al., 2017).

394 Figure 5a shows the horizontal distribution of tdCo along the isopycnal surface of  
395 26.8  $\sigma_\theta$ . It appears that tdCo has sources on continental shelves and spreads up to the  
396 equatorial Pacific. A similar figure for tdMn indicates the same continental shelf sources for  
397 tdMn as tdCo. However, the spreading of tdMn is unclear south of 40°N.

398

399 3.4. Lead

400 The tdPb concentration was uniformly low at < 24 pmol kg<sup>-1</sup> below the depth of  
401 2000 m along 160°W (Fig. 2h). This is similar to that for tdCo. However, tdPb had a unique  
402 subsurface maximum between 15°N and 50°N at 160°W. The tdPb species were dominated  
403 by dPb, and the maxima of dPb, as high as 80 pmol kg<sup>-1</sup>, occurred in surface water, the  
404 STMW, and the CMW (Fig. 3d).

405 The maxima of tdPb and dPb in surface and subsurface water were also apparent  
406 south of 42°N at 165°E, which is located above the maxima of tdCo and dCo along the NPIW

407 (Supplementary Figs. 1h and 5c). The **maxima of tdPb and dPb were** weaker in the section  
408 along 47°N (Supplementary Figs. 2h and 6d). Labile particulate Pb was usually undetectable,  
409 while it was detected in patches in surface water and in a hydrothermal plume near the Juan  
410 de Fuca Ridge (Zheng et al., 2017).

411 Figure 5b shows the horizontal distribution of the maximum tdPb concentration  
412 through the water column. The maximum tdPb concentration usually occurs at subsurface.  
413 The tdPb maximum decreases and the corresponding  $\sigma_\theta$  increases from west to east: for  
414 example, the tdPb maximum is 89.7 pmol kg<sup>-1</sup> at 25.31  $\sigma_\theta$ , TR7 (165°E), 81.6 pmol kg<sup>-1</sup> at  
415 25.97  $\sigma_\theta$ , ST10 (160°W), and 76.9 pmol kg<sup>-1</sup> at 26.26  $\sigma_\theta$ , BD17 (132.7°W).

416 Table 2 summarizes the metal concentrations in each water mass in the North  
417 Pacific Ocean. It is apparent that each metal concentration is uniquely related with the water  
418 masses.

419

420

## 421 4. DISCUSSION

### 422 4.1. Comparison at crossover stations and with previously published data

423 In the GEOTRACES program, a crossover station is a location where the track of  
424 one cruise overlaps with that of another cruise, although the research vessels do not have to be  
425 at the same location simultaneously (<http://www.geotraces.org>). Concentrations of dM in the  
426 deep ocean are not expected to change significantly on the time scale between cruises; thus,  
427 comparing results from crossover stations provides a measure of internal consistency. There  
428 are no strict crossover stations between cruises KH-05-2 and KH-12-4. However, stations  
429 ST13 and 14 of KH-05-2 are located at about 100 km and 300 km from BD15 of KH-12-4  
430 (160°W, 50.8°N), respectively. Thus, we can use the vertical profiles at these stations for  
431 intracomparison. Figure 6 and Supplementary Fig. 7 show the vertical profiles of tdM and dM,  
432 respectively, at these stations. For Mn and Co, the vertical profiles of tdM and dM were  
433 mostly consistent between stations ST13 and BD15. Both tdM and dM showed good linearity  
434 with a slope close to unity (Supplementary Fig. 8). These results indicate that no significant  
435 changes occurred in the vertical profiles and that the analytical data of KH-05-2 and KH-12-4

436 are consistent for Mn and Co. At ST14, significantly higher concentrations of Mn and Co  
437 were observed. ST14 is located about 80 km off the shelf break and above the Aleutian  
438 Trench. The high concentrations of Mn and Co in the surface water are supplied by the AS  
439 from reductive sources in continental shelf sediments. In deep water of 500–4000 m, Mn and  
440 Co are supplied from the continental slope by resuspension of sediments. The distance effect  
441 on concentration was most apparent for tdAl (Fig. 6a). A large amount of Al, mostly in lpAl,  
442 is supplied from the continental shelf and slope to ST14. Although most of the Al is removed  
443 from the water column between ST14 and BD15 by boundary scavenging, the tdAl  
444 concentration is still higher at BD15 than at ST13. In contrast, the distance effect was minor  
445 for dAl (Supplementary Fig. 7a). A distinct trend was observed for Pb. In deep water,  
446 insignificant differences were noted among the three stations in tdPb and dPb concentrations  
447 (Fig. 6d and Supplementary Fig. 7d). The concentrations in the surface water increased from  
448 the north station to the south station, suggesting that lithogenic and reductive sources have a  
449 negligible effect on Pb. In addition, no distance effect was noted on the Pb concentrations in  
450 the subsurface maximum at 100–200 m depths. Rather, the subsurface Pb concentrations are  
451 dependent on time, decreasing by about  $13 \text{ pmol kg}^{-1}$  from 2005 to 2012.

452 For KH-11-7 and KH-12-4, stations TR16 and BD07 are occupied at the same  
453 position ( $160^\circ\text{E}$ ,  $47^\circ\text{N}$ ) as a crossover station. Figure 7 and Supplementary Fig. 9 show the  
454 vertical profiles of tdM and dM at these stations. Supplementary Fig. 10 shows the  
455 relationship of metal concentrations between TR16 and BD07. For Mn, Co, and Pb, the  
456 vertical profiles were consistent between the two stations except that the Mn concentrations in  
457 the bottom water were higher in 2012 than in 2011. In contrast, both tdAl and dAl were  
458 higher in 2011 than in 2012. The same trend was observed for tdFe, which will be reported in  
459 the forthcoming paper. We propose a hypothesis that these temporal changes were caused by  
460 the earthquake and tsunami. Stations TR16 and BD07 are located about 280 km southeast of  
461 the Kuril–Kamchatka Trench, where the Pacific Plate is subducting under the North American  
462 Plate and seismic activity is high. The lower maps in Fig. 7 show the distribution of  
463 earthquakes with magnitude  $> 5$  that occurred for five months prior to the sampling dates  
464 during 2011 and 2012 (data taken from <https://earthquake.usgs.gov/>). No significant



465 difference is noted in the seismic activity around the Kuril–Kamchatka Trench between the  
466 two periods. A clear difference is the March 11, 2011, earthquake off the Pacific coast of  
467 Tohoku, Japan, magnitude 9.1, that occurred at 38.297°N, 142.373°E and its aftershocks. The  
468 resulting tsunami inundated a total area of 561 km<sup>2</sup> in Japan (data from Geospatial  
469 Information Authority in Japan: <http://www.gsi.go.jp/common/000059939.pdf>). The tsunami  
470 generated turbidity currents, one of which was observed with bottom sensors (Arai et al.,  
471 2013). Thirty-six days after the earthquake, observation on the continental slope below the  
472 hypocenter revealed increases in the light transmission anomaly and in the Mn concentrations  
473 of up to 15–24 nmol kg<sup>-1</sup> in the bottom water at depths of 3500–5700 m (Kawagucci et al.,  
474 2012). Four months after the earthquake, observations in the Japan Trench revealed nepheloid  
475 layers extending ~30–50 m above the sea bed and <sup>134</sup>Ce from the Fukushima Daiichi nuclear  
476 disaster on the sediment surface (Oguri et al., 2013). Because the distance between the  
477 seismic center and TR16 is about 1730 km, the effect might have reached TR16 prior to  
478 sampling. The high Mn concentrations in 2012 can be explained by a supply from a temporal  
479 reductive source that developed on the bottom sediments where a large amount of organic  
480 detritus was transported by the tsunami and the following processes. The detailed explanation  
481 of the transportation mechanism is a challenge for future research. Increased marine sediment  
482 suspension and fluxes following an earthquake have also been observed at other locations  
483 (Thunell et al., 1999).

484 We also compared our data with the literature and found general consistency for  
485 each metal; an example is shown in Supplementary Fig. 11. On the basis of these results, we  
486 deduced the following four conclusions. First, the preservation period of the samples had no  
487 significant effects on the data. Both unfiltered and filtered seawater samples were acidified to  
488 pH 2.2 with HCl and were stored at room temperature from one to ten years prior to analyses.  
489 No effect of the storage period was found for either tdM and dM at all crossover stations. In  
490 addition, a number of samples were analyzed in duplicate without significant changes,  
491 depending on the storage period. Thus, we can conclude that both the unfiltered and filtered  
492 seawater samples at pH 2.2 are stable for the determination of the trace metals from one to ten  
493 years.

494           Second, although we did not apply UV irradiation prior to the preconcentration, our  
495 data on tdCo and dCo are highly reproducible. It has been proposed that UV irradiation prior  
496 to preconcentration is necessary to determine the total dCo (Biller and Bruland, 2012; Milne  
497 et al., 2010; Saito and Moffett, 2001). Actually, it appears that our dCo concentrations were  
498 significantly lower than those for samples collected near the Hawaii Islands, which were  
499 subjected to UV irradiation (Supplementary Fig. 11a) (Noble et al., 2008). We applied UV  
500 irradiation to a mixed sample of North Pacific surface water and found an increase in dCo  
501 concentration by ~20%. The analytical data for the reference seawater samples also show  
502 similar results (Supplementary Table 2). Thus, it should be noted that our Co data are  
503 **operational** and may be lower than those with UV irradiation. **Some studies reported that the**  
504 **difference between UV irradiated and non-UV irradiated values varies throughout a water**  
505 **column (Noble et al., 2017; Shelley et al., 2010).** However, both the tdCo and dCo are  
506 reproducible and show systematic trends as described below. The difference caused by UV  
507 irradiation will not **qualitatively** affect the major points of our discussion, such as those on the  
508 basis of the enrichment factor (section 4.4) and the Co/Mn ratio (section 4.5). In addition, the  
509 non-labile Co that can be detected after UV irradiation has not been identified yet. It is  
510 probable that future comparison between Co data with and without UV will contribute to the  
511 characterization of non-labile Co. Therefore, we think our Co data will be informative for the  
512 community of chemical oceanography research.

513           Third, it appears that no significant change occurred in the subsurface Pb maximum  
514 from 1977 to the present time in the North Pacific. As an example, the vertical profiles of  
515 tdPb in 20°N–35°N, 145°W–160°W from 1976 to 2005 are compared in Supplementary Fig.  
516 11b. Because the tdPb concentration depends on the location, it is not easy to extract the  
517 temporal change from these data. However, we can say the subsurface tdPb maximum has  
518 been maintained at 63–82 pmol kg<sup>-1</sup> for 30 years in this area. This is an important  
519 characteristic in the North Pacific Ocean. In contrast, a substantial decrease in the subsurface  
520 Pb maximum has been observed in the North Atlantic. A decrease of ~150 pmol kg<sup>-1</sup> during  
521 1979–2011 was found near Bermuda, which is attributed to the phase-out of leaded gasoline  
522 in the United States and in Europe (Lee et al., 2011). The decline in the Pb concentration in

523 the Atlantic has also been found along the transect GEOTRACES GA-01 (Zurbrick et al.,  
524 2018). In the North Pacific, it has been reported that the decreasing supply from gasoline has  
525 been canceled out by the growing supply from coal combustion, metal smelting, and  
526 municipal solid waste incineration mainly from China, Russia, and Japan (Zurbrick et al.,  
527 2017). The same trend has been shown for ice core data (Gross et al., 2012).

528 Finally, our data suggest that crossover stations near the continental shelves, such as  
529 TR16 and BD07, are not ideal for intercomparison of scavenged trace metals. These metals  
530 are affected by temporal and spatial variations in the ocean boundary environment. Therefore,  
531 for unambiguous intercomparison, a crossover station should be located far from the  
532 continental shelves and the offshore side of the boundary scavenging zone.

533

#### 534 4.2. Labile particulate and dissolved fractions

535 The lpM concentration is operationally defined as the difference in concentrations  
536 between tdM and dM. Data of particulate concentrations are scarce in the North Pacific. In  
537 this study, we compared our dM and lpM data from ST09 (30.007°N, 159.996°W) with the  
538 dM and particulate M (pM) data from the Vertex IV site (28°N, 155°W) (Bruland et al., 1994).  
539 The authors collected particulate samples on a Nuclepore filter with a pore size of 0.3  $\mu\text{m}$ ,  
540 and analyzed them for the trace metal content of both the 25% acetic acid leachate and the  
541 residual refractory fraction that was treated with HCl–HNO<sub>3</sub>–HF. Figure 8b shows the results  
542 of pAl, which were mostly in the refractory fraction. Our lpAl concentration at ST09 was  
543 similar to or higher than the total pAl concentration at Vertex IV. Because ST09 is located  
544 about 800 km from the Hawaiian Seamount Chain, it is possible that the total pAl  
545 concentration is elevated compared with Vertex IV. This is consistent with the dAl  
546 concentration at depths of 2000–3000 m is higher at ST09 than that at Vertex IV (Fig. 8a).  
547 Thus, we can expect that lpAl **represents a major fraction of** total pAl. Supplementary Fig. 12  
548 shows the results for dMn and pMn. Although some of the lpMn concentration at ST09 was  
549 less than the detection limit, the general trend was similar between lpMn at ST09 and total  
550 pMn at Vertex IV, suggesting that lpMn is a good measure of total pMn. The same results  
551 were also observed for Fe, which is reported in the forthcoming paper. No data from the

552 literature are available for comparison of pCo and pPb in this area. Around the Juan de Fuca  
553 Ridge, we found that the lpFe/lpAl, lpMn/lpAl, lpCo/lpAl, and lpPb/lpAl ratios in the bottom  
554 water are close to the ratios of total concentrations in the bottom sediments (Zheng et al.,  
555 2017). On the basis of these results, we suggest that lpM represents a major fraction of total  
556 pM. We think lpM includes metals desorbed or released from aluminosilicates, metal oxides,  
557 and the degradation of phytoplankton and bacteria.

558         Supplementary Fig. 13 shows histograms of the lpM/tdM ratio for each metal in the  
559 North Pacific Ocean. It is apparent that the four metals are classified in the scavenged group  
560 but have very different speciations among d and p species. The lpAl/tdAl ratio is  $0.66 \pm 0.31$   
561 (average  $\pm$  sd,  $n = 489$ ), the lpMn/tdMn ratio is  $0.24 \pm 0.24$  ( $n = 628$ ), the lpCo/tdCo ratio is  
562  $0.12 \pm 0.18$  ( $n = 620$ ), and the lpPb/tdPb ratio is  $0.02 \pm 0.08$  ( $n = 575$ ). Because Al is the  
563 major element in the upper crust, a large amount of lpAl is supplied from the lithosphere to  
564 the ocean. Another major factor controlling the lpM/tdM ratio should be adsorption in the  
565 ocean. The adsorption is explained by the surface complexation model (Li, 1981). Inorganic  
566 minerals such as aluminosilicates and iron hydroxides have surface hydroxide groups that  
567 form surface complexes with metal ions. The stability of the surface complex has a linear  
568 relationship with the first hydrolysis constant for the metal ion. Because Al forms a trivalent  
569 cation in seawater, it has the highest hydrolysis constant, resulting in the highest lpM/tdM  
570 ratio. Although the hydrolysis constant of Pb(II) is higher than that of Mn(II) and Co(II) (Li,  
571 1981), Mn(II) is most readily oxidized to Mn(III) or Mn(IV) (Mandernack et al., 1995;  
572 Moffett and Ho, 1996), resulting in a higher lpM/tdM ratio. Moreover, it is likely that Co(II)  
573 is more readily oxidized to Co(III) than Pb(II) is oxidized to Pb(IV), because Co(II) is  
574 co-oxidized with Mn(II) via a common microbially catalyzed pathway (Moffett and Ho,  
575 1996).

576         The vertical distributions of the lpM/tdM ratio are also distinct among the  
577 scavenged elements (Fig. 9). The lpAl/tdAl ratio is uniformly high at high latitudes. The ratio  
578 is lower at low latitudes, especially in surface water, probably due to supply of dAl via  
579 surface and subsurface currents from lands in the tropical zone where intense weathering  
580 occurs. The lpMn/tdMn ratio shows a generally increasing trend with depth, without a

581 significant change with the latitude. This probably reflects the effects of oxidative scavenging  
582 throughout the water column. The  $lpCo/tdCo$  ratio shows a trend that is generally increasing  
583 in deep water, similar to the  $lpMn/tdMn$  ratio, while the former is significantly lower than the  
584 latter. In addition, high values of the  $lpCo/tdCo$  ratio occur in surface water at lower latitudes  
585 due to the uptake of  $dCo$  by phytoplankton.

586

#### 587 4.3. Lithogenic effects presented by Al

588 Our data show that  $tdAl$  is a good tracer of LCDW in the North Pacific (Fig. 2e,  
589 Supplementary Figs. 1e and 2e, and Fig. 4a). In Fig. 10, the  $tdAl$  concentration is plotted on  
590 the temperature–salinity diagram. The graph indicates that waters with  $\sigma_\theta > 27.8$  are enriched  
591 with  $tdAl$ . In particular,  $tdAl$  is useful because tracking LCDW in the northern North Pacific  
592 is not easy when using conventional oceanographic parameters. Total dissolvable Al is not  
593 only supplied by the LCDW from the South Pacific but also added locally **by resuspension of**  
594 **sediments** in the North Pacific. **The relative contributions from transport via LCDW and from**  
595 **resuspension are unclear at present and would be a challenge in future study.** In contrast,  $dAl$   
596 decreases when the LCDW flows from south to north in the North Pacific (Fig. 4b).  
597 Supplementary Fig. 14 shows that the  $dAl$  concentration decreases with latitude at depths  
598 greater than 4500 m, where the LCDW flows. The LCDW is the only origin of deep water  
599  $dAl$  in the North Pacific; no other water supplies  $dAl$  to the depths. When the LCDW flows in  
600 the North Pacific,  $dAl$  is gradually adsorbed onto particles. In addition,  $lpAl$  is added to the  
601 LCDW by resuspension of bottom sediments during the track, although the supply of  $dAl$   
602 from the bottom sediments is negligible. Overall, the  $dAl$  concentration in deep waters  
603 decreases from about  $4 \text{ nmol kg}^{-1}$  around the equator to about  $1 \text{ nmol kg}^{-1}$  around  $50^\circ\text{N}$ . It  
604 takes about 100 years for the LCDW to travel from the equator to  $50^\circ\text{N}$  (Matsumoto, 2007);  
605 the apparent decreasing rate of  $dAl$  is  $0.03 \text{ nmol kg}^{-1} \text{ y}^{-1}$  in deep waters in the North Pacific  
606 Ocean.

607

#### 608 4.4. Enrichment factor

609 Here, we use stoichiometry to characterize sources for each element. The

610 enrichment factor (*EF*) of dM in seawater over the upper crust is defined in accordance with  
611 **the *EF* of M in aerosols in** the literature (Rahn, 1976) as follows:

$$612 \quad EF(dM) = (dM/dAl)_{\text{seawater}} / (M/Al)_{\text{upper crust}}$$

613 The  $(M/Al)_{\text{upper crust}}$  is calculated in moles using concentrations published in a review  
614 (Rudnick and Gao, 2005) as the following:  $4.7 \times 10^{-3}$  for Mn,  $9.7 \times 10^{-5}$  for Co, and  $2.7 \times$   
615  $10^{-5}$  for Pb. Figure 11 shows box plots of *EF*(dM). The median is  $1.3 \times 10^2$  ( $n = 436$ ) for  
616 *EF*(dMn),  $3.2 \times 10^2$  ( $n = 430$ ) for *EF*(dCo), and  $1.2 \times 10^3$  ( $n = 413$ ) for *EF*(dPb). The median  
617 of *EF*(dPb) is on the same order as that of *EF* for aerosols in the literature (Rahn, 1976),  
618 suggesting that **aerosols are** a major source of dPb. For Mn and Co, the *EF* for aerosols is  
619 usually 1–10. **Thus, *EF*(dMn) and *EF*(dCo) are ten to hundred times** higher than the *EF* for  
620 aerosols. **This would be partly due to the differences in solubility of the metals in aerosols. As**  
621 **an example, Baker et al. (2006) reported that the solubility of Mn is several to ten times**  
622 **higher than that of Al. Another important cause would be that** sources other than aerosols are  
623 more significant contributors to **Mn and Co**. Sectional distributions of *EF*(dM) and *EF*(lpM)  
624 along 160°W and 47°N are given in Supplementary Figs. 15 and 16, respectively. These  
625 figures show that the other sources of **dMn and dCo** are restricted to shallow depths near the  
626 northern boundaries of the North Pacific.

627 Figure 2 shows the sectional distributions of dM and lpM in the upper ocean along  
628 160°W. It is clear that each element has different sources and is uniquely related to the ocean  
629 circulation. The dAl concentration is high in the EUC and NEC. The transport of Al by the  
630 EUC from New Guinea and New Ireland has been reported in the literature (Kaupp et al.,  
631 2011; Slemons et al., 2012). The source of dAl in the NEC should be the Hawaiian Islands.  
632 The elevated dAl concentration near the Hawaiian Islands has been reported in the literature  
633 (Measures et al., 2005). In contrast, the dAl concentration is low in northern currents, such as  
634 the AS. Similarly, high dAl concentrations in tropical currents have been found in the Indian  
635 Ocean (Vu and Sohrin, 2013). These results are ascribed to supply of dAl **via surface and**  
636 **subsurface currents from lands in the tropical zone where intense weathering occurs**. The dMn  
637 concentration is high in the AS, suggesting the source is manganese reduction in sediments on  
638 the continental shelf. Substantially high dMn concentrations have been observed over the

639 Bering Sea shelf (Cid et al., 2011). A surface maximum of dMn occurs between 7°N and  
640 26°N, suggesting the effect of photoreduction (Sunda and Huntsman, 1988). The dCo  
641 concentration is high in the AS, suggesting the same reductive source with dMn. These results  
642 are also consistent with the observation in the Bering Sea (Cid et al., 2011). A remarkable  
643 feature of dCo is that it expands through the NPIW and EqPIW over the North Pacific. The  
644 subsurface maximum of dPb occurs between 20°N and 45°N, corresponding with the STMW  
645 and CMW in the subtropical gyre. Supplementary Figs. 5 and 6 shows the sectional  
646 distributions of dM in the upper ocean along 165°E and 47°N, respectively. These  
647 distributions also indicate that dMn and dCo are derived from the same sources on the  
648 continental shelves, which do not contribute significantly to dPb.

649 Figure 5 shows distinct horizontal distributions of tdCo and tdPb over the North  
650 Pacific. For tdCo, the concentration on an isopycnal plane of 26.8  $\sigma_\theta$  is presented. It is clear  
651 that tdCo originated from the northern shelves and spread southward. For tdPb, the highest  
652 subsurface concentration maximum is presented because the  $\sigma_\theta$  value for the tdPb maximum  
653 significantly increases from west to east. The highest tdPb occurs in the subtropical gyre and  
654 decreases from west to east. This horizontal distribution of tdPb is consistent with that of  
655 radioactive  $^{210}\text{Pb}$  in the surface water (Nozaki et al., 1976).

656

#### 657 4.5. Redox and biogeochemical control on Co

658 As discussed above, Co and Mn have a common source in the continental shelf  
659 sediments. In hydrothermal plumes around the Juan de Fuca Ridge, the concentration of Mn  
660 increases remarkably and that of Co does not. This is because the flux of Mn from  
661 hydrothermal vents is considerably higher than that of Co (Seyfried Jr et al., 2003). In  
662 addition, the solubility product is much lower for CoS than MnS (Chemical et al., 1964),  
663 although the solubility of Co increases with increasing chloride concentration (Seyfried Jr et  
664 al., 2003). Thus, Co is not transported far by hydrothermal plumes. Supplementary Fig. 17a  
665 shows the relationship between dCo and dMn in water columns above the depth of  
666 hydrothermal plumes ( $\sigma_\theta < 27.64$ ). The following overall linear relationship is present:

667 
$$\text{dCo (pmol kg}^{-1}\text{)} = 19.7 \text{ dMn (nmol kg}^{-1}\text{)} + 17.2 \quad (r = 0.656, p < 0.0001, n = 386)$$

668 This slope is nearly consistent with the ratio of  $\text{Co/Mn} = 2.1 \times 10^{-2}$  for average mole  
669 concentrations in the upper crust (Rudnick and Gao, 2005). These results imply that the  
670 ultimate source of Mn and Co in the North Pacific Ocean has a Co/Mn ratio similar to that in  
671 the upper crust. However, most data in the graph are along another line with a higher slope,  
672 which means that dCo and dMn are substantially fractionated in the North Pacific.

673 Figure 12 shows that the dCo/dMn ratio varies from zero to 0.174 in the North  
674 Pacific. Although both Mn and Co are taken up by phytoplankton as micronutrients, the  
675 concentration factor of Co in phytoplankton is much higher than that of Mn (Morel et al.,  
676 2003). As a result, the effects of biogeochemical cycles are apparent only in the distribution  
677 of Co in the ocean. The dCo concentration is low in the surface water except at stations near  
678 continental shelves (Fig. 3c and Supplementary Figs. 5b and 6c). This is ascribed to the  
679 uptake of Co by phytoplankton. Supplementary Fig. 17b shows the general relationship of  
680 dCo against phosphate in water columns above the depth of the NPIW ( $\sigma_\theta < 26.5$ ):

$$681 \quad \text{dCo (pmol kg}^{-1}\text{)} = 36.4 \text{ PO}_4 \text{ (}\mu\text{mol kg}^{-1}\text{)} + 6.4 \quad (r = 0.692, p < 0.0001, n = 176)$$

682 These results are mostly consistent with the data on total dCo in the literature (Hawco et al.,  
683 2018; Noble et al., 2008; Saito et al., 2017), which suggest that dCo is taken up by  
684 phytoplankton and is remineralized from settled particles concurrently with phosphate. The  
685 dCo/phosphate ratio tends to be higher at higher latitudes. Particularly high ratios were found  
686 in the surface water at ST14 in the AS. Biogeochemical effects are also apparent in the  
687 vertical distribution of the dCo/dMn ratio (Fig. 12). The ratio becomes lower in surface water  
688 according to the selective uptake and removal of dCo by phytoplankton and increases with  
689 depth above the NPIW with  $\sigma_\theta = 26.8$ , through remineralization. Another cause for the high  
690 dCo/dMn ratio in waters with  $\sigma_\theta > 26$  should be the microbial oxidation of dMn, which is  
691 7–10 times faster than that of dCo (Moffett and Ho, 1996), resulting in the selective  
692 transformation from dMn to lpMn. Below the NPIW, no clear relationship is apparent  
693 between the dCo and phosphate, and the dCo/dMn ratio decreases. Because the concentrations  
694 of  $\text{O}_2$  and biogenic particulate organic matter decrease below the NPIW, scavenging becomes  
695 predominant over remineralization for the distribution of dCo.

696



697 4.6. Anthropogenic control on Pb

698 In this paper, we report the basin-scale distribution of stable Pb in the North Pacific  
699 for the first time. The subsurface maximum centered at  $\sim 26 \sigma_\theta$  is a basin-scale characteristic.  
700 The maximum concentration tends to decrease from west to east. In addition,  $EF(dPb)$  is as  
701 high as  $EF$  for aerosols. These results further support the anthropogenic control on Pb in the  
702 North Pacific, which has been discussed in previous research (Boyle et al., 2005; Zurbrick et  
703 al., 2017). To summarize, anthropogenic Pb originating from China, Japan, and Russia is  
704 carried to the North Pacific as aerosols by westerlies centered at  $\sim 35^\circ N$ , deposited on the sea  
705 surface, and dissolved in the mixed layer during formation of the STMW and CMW.  
706 Although dPb is quickly scavenged from the surface water by biogenic particles, it has a  
707 longer residence time in subsurface water and spreads over the North Pacific by current  
708 systems of subtropical and subarctic gyres. This mechanism is not as important for Al, Mn,  
709 and Co because these metals are less enriched in industrial aerosols. For example, the  
710 enrichment factor of Pb was 10–100 times higher than that of Mn and Co in atmospheric  
711 deposition samples collected around Japan (Okubo et al., 2013).

712 In deep water ( $\sigma_\theta > 26.7$ ), a linear relationship between dPb and dCo is observed  
713 (Fig. 13):

$$714 \quad dPb \text{ (pmol kg}^{-1}\text{)} = 1.06 dCo \text{ (pmol kg}^{-1}\text{)} - 3.1 \quad (r = 0.868, p < 0.0001, n = 374)$$

715 which suggests the concurrent effect of scavenging. Because there are no significant sources  
716 for both metals in deep waters, a common property emerges for the scavenged elements. The  
717 dPb/dCo ratio tends to be higher at higher latitudes. This probably reflects the dependency of  
718 atmospheric aerosol deposition flux on the latitude. In shallow waters, no significant  
719 relationship is observed between dPb and dCo, which reflects different sources for these  
720 metals. Clearly, anthropogenic Pb sources contribute to high concentrations mostly in warm  
721 surface waters of the temperate zone (Fig. 3d and Supplementary Fig. 5c).

722 Interestingly, radiocesium emitted from the Fukushima Daiichi Nuclear Power Plant  
723 ( $37^\circ 25' N$ ,  $141^\circ 02' E$ ) in March 2011 presently shows a distribution similar to that of Pb in the  
724 North Pacific (Aoyama et al., 2018; Kumamoto et al., 2014; Smith et al., 2017). As an  
725 example, Kumamoto et al. (2014) measured d radiocesium at stations along  $149^\circ E$  in winter

726 2012 (Supplementary Fig. 18). In particular, they found a subsurface radiocesium maximum  
727 at a depth of ~300 m around 32°N, which is a characteristic similar to the subsurface  
728 maximum of Pb. They concluded that atmosphere-deposited radiocesium south of the KE had  
729 been transported not only eastward along with surface currents but also southward owing to  
730 the formation/subduction of the STMW within about 10 months after the accident. Smith et al.  
731 (2017) reported that the Fukushima-derived radiocesium plume was first observed in June  
732 2012 at the westernmost station on Line P, which is an oceanographic sampling line  
733 extending 1500 km westward of British Columbia, Canada. The plume spread over the  
734 Canadian continental shelf during 2013 and 2014. It is likely that anthropogenic contaminants  
735 in aerosols are entrained in the same distribution mechanism as that for Pb. Although Cs is a  
736 conservative element in oceanography, the Fukushima-derived radiocesium followed Pb in  
737 the manner of its distribution mechanism and spread over the North Pacific, at least during the  
738 first several years after the accident.

739

740

## 741 5. CONCLUSIONS

742 We observed basin-scale and full-depth sectional distributions of Al, Mn, Co, and  
743 Pb in the North Pacific using a multi-elemental determination method and without using UV  
744 irradiation. This study revealed that the speciation of the dM and pM fractions differs  
745 significantly among the four metals. Analysis based on stoichiometry revealed that Mn, Co,  
746 and Pb are dominated by different sources than those of Al and that each element is a unique  
747 tracer for distinct currents and water masses. However, despite the apparent differences, these  
748 elements should be grouped as scavenged elements. The four metals are affected by  
749 scavenging throughout the ocean, although the relative intensity of the other processes  
750 controls the distribution of each metal. As an example, Co and Pb show a strong correlation in  
751 the deep waters of the North Pacific, where no significant sources occur for these metals, and  
752 scavenging is the predominant process. In contrast, the differences between Co and Mn in  
753 terms of the oxidation rate, the enrichment by phytoplankton, and the effect of hydrothermal  
754 plumes cause substantial fractionations of dCo and dMn in the North Pacific.

755           We propose  $EF(dM)$  as a potential parameter to systematically explain inter-basin  
756 variations in the distribution of  $dM$ . Dissolved Al occurs in a wider concentration range in the  
757 world's oceans than the other metals. Because  $dAl$  concentration is normally low in the North  
758 Pacific,  $EF$  is high for  $dMn$ ,  $dCo$ , and  $dPb$ , resulting in the unique distribution of each metal.  
759 Since  $dAl$  concentration is substantially higher in the Atlantic Ocean and the Mediterranean  
760 Sea, features common with  $dAl$  may emerge for  $dMn$ ,  $dCo$ , and  $dPb$ .

761

762

### 763 ACKNOWLEDGEMENTS

764           This research was supported by The Japan Society for the Promotion of Science  
765 (JSPS) KAKENHI grants (Grant Nos. JP16204046, JP21350042, JP24241004, and  
766 JP15H0127), by grants from the Steel Foundation for Environmental Protection Technology,  
767 and by Mitsumasa Ito Memorial Research Grant from the Research Institute for  
768 Ocean chemistry Foundation. The authors thank the crew, technicians, students, and  
769 scientists onboard the KH-05-2, KH-11-7, and KH-12-4 cruises for assistance with sampling  
770 and analysis of routine data. We would like to thank Editage ([www.editage.jp](http://www.editage.jp)) for English  
771 language editing. Finally, we thank three anonymous reviewers and the associate editor Tina  
772 van de Flierdt for their helpful and constructive comments.

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774

775

776 Figure Captions

777 Fig. 1. A map showing the locations of the data collected in this study. The white lines show  
778 surface currents and the dashed line shows the subsurface current.

779

780 Fig. 2. Full-depth sectional distribution of salinity,  $O_2$ , silicate, phosphate, and tdM along  
781  $160^\circ W$ . EqPIW: Equatorial Pacific Intermediate Water; NPIW: North Pacific Intermediate  
782 Water; UCDW: Upper Circumpolar Deep Water; LCDW: Lower Circumpolar Deep Water;  
783 PDW: Pacific Deep Water; **AS: Alaskan Stream; STMW: Subtropical Mode Water.**

784

785 Fig. 3. Sectional distributions of dM and lpM at depths of 0–1000 m along  $160^\circ W$ . EUC:  
786 Equatorial Under Current; NEC: North Equatorial Current; AS: Alaskan Stream; EqPIW:  
787 Equatorial Pacific Intermediate Water; NPIW: North Pacific Intermediate Water; STMW:  
788 Subtropical Mode Water; CMW: Central Mode Water.

789

790 Fig. 4. The distributions of tdAl and dAl at a depth of 4500 m. The red line shows the major  
791 flows of the LCDW, which were taken from the literature (Kawabe and Fujio, 2010). A  
792 number in a circle shows the volume transport of the current in Sv ( $10^6 \text{ m}^3 \text{ s}^{-1}$ ). The number  
793  $4^+$  ( $4^-$ ) means a little more (less) than 4 Sv. A circle with a center point shows upwelling from  
794 this layer; its transport volume is shown by an accompanying number.

795

796 Fig. 5. (a) The horizontal distribution of tdCo on the isopycnal plane of  $26.8 \sigma_\theta$ . (b) The  
797 horizontal distribution of the maximum tdPb in the water column, which occurs in the  
798 subsurface water.

799

800 Fig. 6. Vertical profiles of tdM at ST13 (red circles), BD15 (blue squares), and ST14 (cyan  
801 diamonds).

802

803 Fig. 7. (a) and (b): The vertical profiles of tdAl and dAl at TR16 (red circles) and BD07 (blue  
804 squares). The distribution of earthquakes (magnitude  $> 5$ ) around the Kuril–Kamchatka

805 Trench from February 28 to July 28, 2011 (c), and from March 28 to August 28, 2012 (d). A  
806 black circle represents a seismic center and the diameter of such a circle represents the  
807 relative magnitudes of the earthquakes. The data were taken from <https://earthquake.usgs.gov>.

808

809 Fig. 8. Vertical profiles of dAl and particulate Al (pAl). Red triangles represent dAl and lpAl  
810 at ST09 (30.007°N, 159.996°W). Black marks represent data at the Vertex IV site (28°N,  
811 155°W) (Bruland et al., 1994). (b) Open circles, squares, and diamonds represent acetic acid  
812 leachable pAl, refractory pAl, and total pAl, respectively.

813

814 Fig. 9. Vertical distribution of the lpM/tdM ratio in the North Pacific. **The colors of the dots**  
815 **represent the latitudes.**

816

817 Fig. 10. Potential temperature–salinity diagram. The colors of the dots represent the tdAl  
818 concentrations.

819

820 Fig. 11. Box plots of  $EF(dM)$  for Mn, Co, and Pb. The middle line of the box represents the  
821 median; the top and bottom lines of the box represent the upper and lower quartiles,  
822 respectively; and circles represent potential outliers.

823

824 Fig. 12. The tdCo/tdMn ratio against the potential density anomaly in the North Pacific. The  
825 colors of the dots represent the latitudes. The black line shows the average Co/Mn mole ratio  
826 of  $2.1 \times 10^{-2}$  in the upper crust (Rudnick and Gao, 2005).

827

828 Fig. 13. The relationship between dPb and dCo in deep waters ( $\sigma_\theta > 26.7$ ). The red line  
829 represents the regression line, the equation for which is presented in the text. The colors of the  
830 dots represent the latitudes.

831

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Table 1  
Statistical summary of seawater data.

Element	Fraction	<i>n</i>				Minimum	Maximum	Median
		Total	> DL	< DL	Questionable and discarded			
Al (nmol/kg)	td	638	610	21	7	< 0.1	59.6	2.16
	d	638	438	76	124	< 0.1	8.63	0.46
	lp	638	436	75	127	< 0.2	56.7	1.13
Mn (nmol/kg)	td	638	633	0	5	0.17	12.3	0.74
	d	638	633	0	5	0.08	8.38	0.52
	lp	638	429	199	10	< 0.1	5.65	0.12
Co (pmol/kg)	td	638	631	0	7	4.5	221	24.1
	d	638	623	3	12	< 0.4	179	20.2
	lp	638	288	332	18	< 4	44.2	< 4
Pb (pmol/kg)	td	638	628	0	10	3.4	89.7	28.5
	d	638	579	0	59	2.0	85.0	28.6
	lp	638	30	545	63	< 4	14.1	< 4

Table 2  
Summary of water mass data.

Water mass	Salinity	Potential Temperature [°C]	$\sigma_\theta$ [kg/m <sup>3</sup> ]	Reference	Al [nmol/kg]			Mn [nmol/kg]			Co [pmol/kg]			Pb [pmol/kg]		
					td	d	lp	td	d	lp	td	d	lp	td	d	lp
Subtropical Mode Water (STMW)			25.2–25.8	Yasuda 2003	0.12–1.3	< 0.1–1.3	< 0.2–1.0	0.54–1.2	0.45–0.79	< 0.1–0.11	15–31	8–25	< 4–13	64–78	62–83	< 4
Central Mode Water (CMW)			26.0–26.7	Yasuda 2003	0.54–4.9	< 0.1–1.6	0.21–1.3	0.27–1.1	0.19–0.95	< 0.1–0.35	28–43	26–39	< 4–10	52–80	56–83	< 4
Okhotsk Sea Mode Water (OSMW)	33.5–33.6	1–2	26.6–27	Yasuda 1997	1.6–6.0	0.21–0.53	1.4–5.5	1.2–2.0	0.51–1.7	0.27–0.91	48–75	50–72	< 4–7	31–52	30–51	< 4
North Pacific Intermediate Water (NPIW)	33.8–34.1		26.4–27.2, averaging 26.8	Dickson et al. 2000, Bostock et al. 2010	1.0–6.8	0.18–1.1	0.63–6.1	0.32–1.1	0.22–0.74	< 0.1–0.37	34–47	30–43	< 4–9	44–71	41–63	< 4–6
Equatorial Pacific Intermediate Water (EqPIW)	34.5–34.6		27.3	Bostock et al. 2010	1.1–2.5	0.87–1.9	< 0.2–1.6	0.32–0.43	0.22–0.36	< 0.1–0.14	32–39	30–38	< 4	12–25	12–28	< 4
Upper Circumpolar Deep Water (UCDW)	34.6	2.5	27.6	Talley et al. 2012	1.2–3.0	0.73–1.6	< 0.2–1.2	0.22–0.38	0.17–0.23	< 0.1–0.16	21–30	17–29	< 4	7–12	9–14	< 4
Pacific Deep Water (PDW)	34.7	1.1–1.2	27.7	Talley et al. 2011	0.88–4.5	< 0.1–0.86	0.63–3.7	0.19–0.82	0.13–0.66	< 0.1–0.33	14–26	13–23	< 4–6	9–31	6–32	< 4–6
Lower Circumpolar Deep Water (LCDW)	34.7	1–2	27.8	Talley et al. 2013	1.5–40	0.36–4.1	0.60–37	0.16–5.7	0.08–1.3	< 0.1–4.4	12–32	8–20	< 4–20	3–16	3–16	< 4–6

Figure1  
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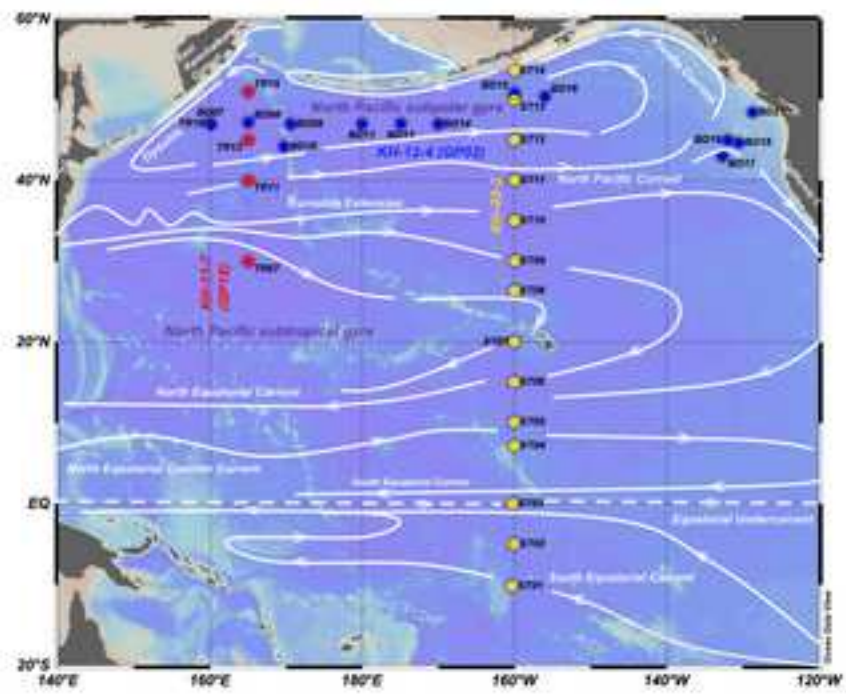


Figure 1

Figure2

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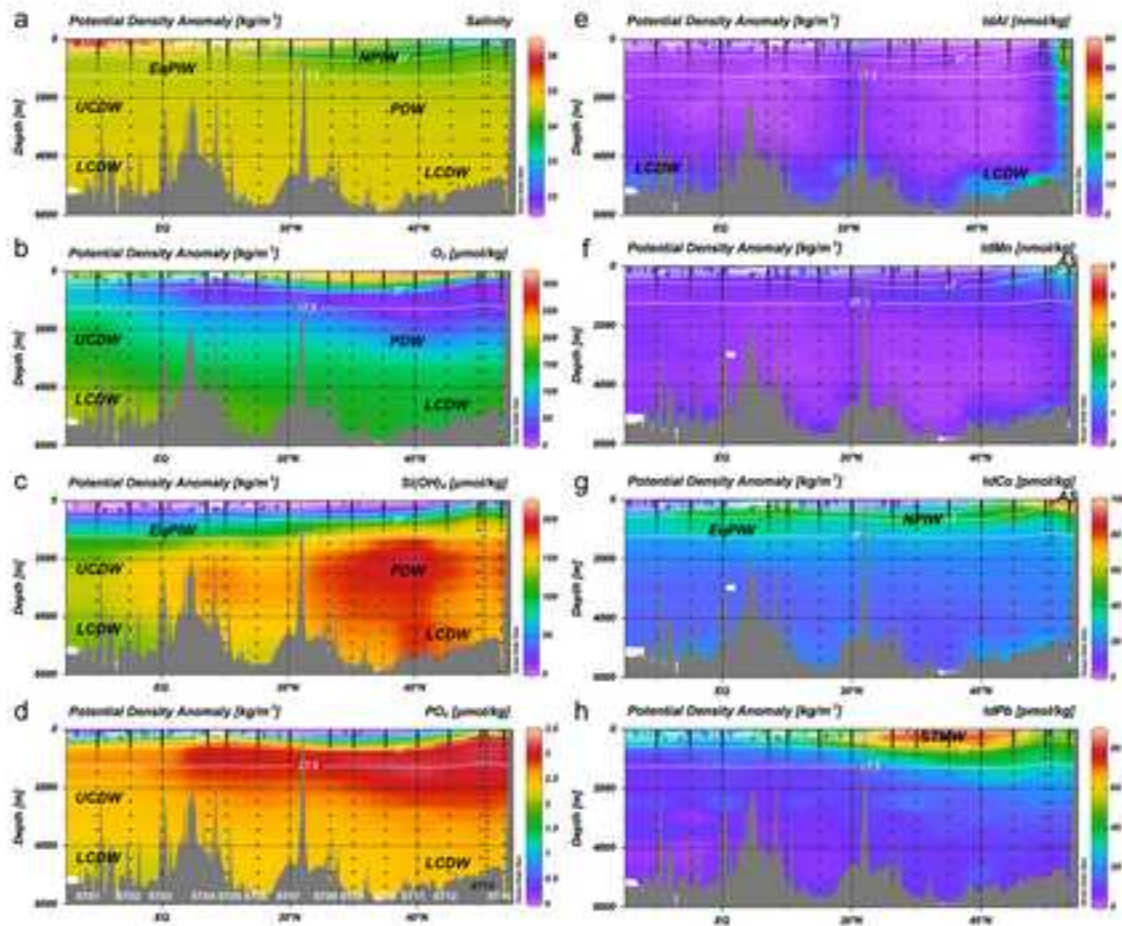


Figure 2



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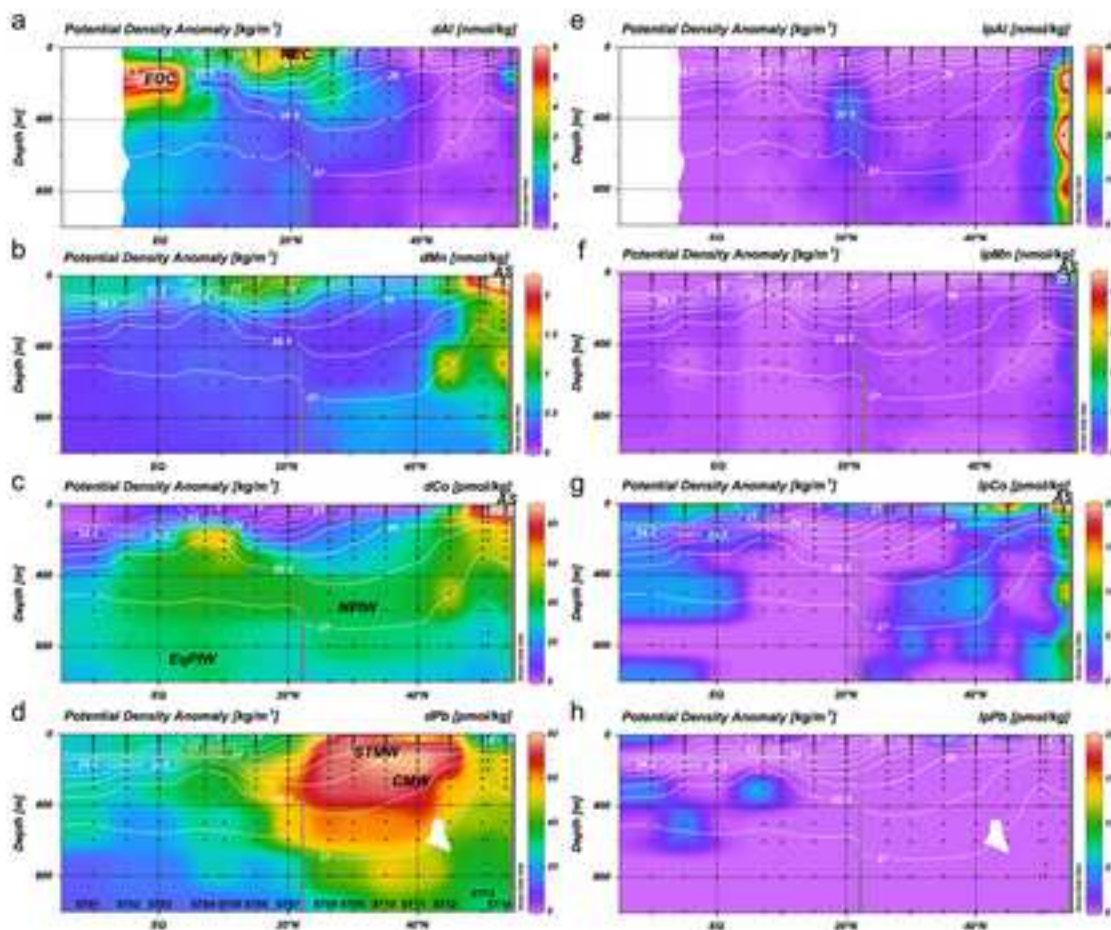


Figure 3

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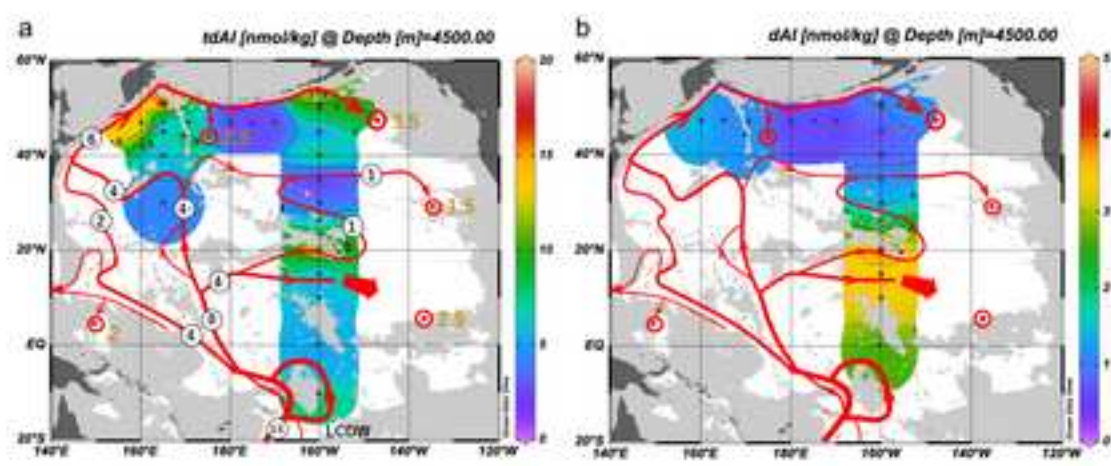


Figure 4

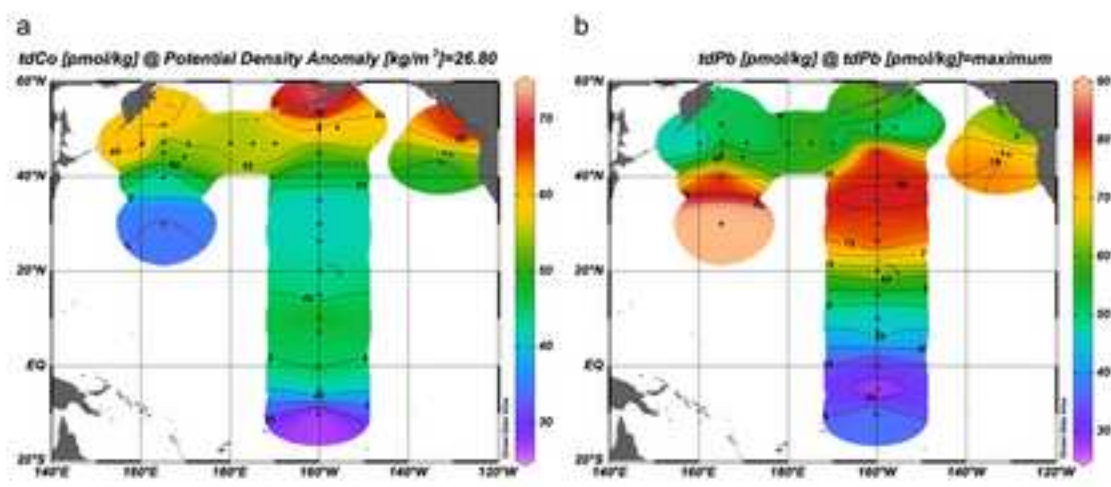


Figure 5

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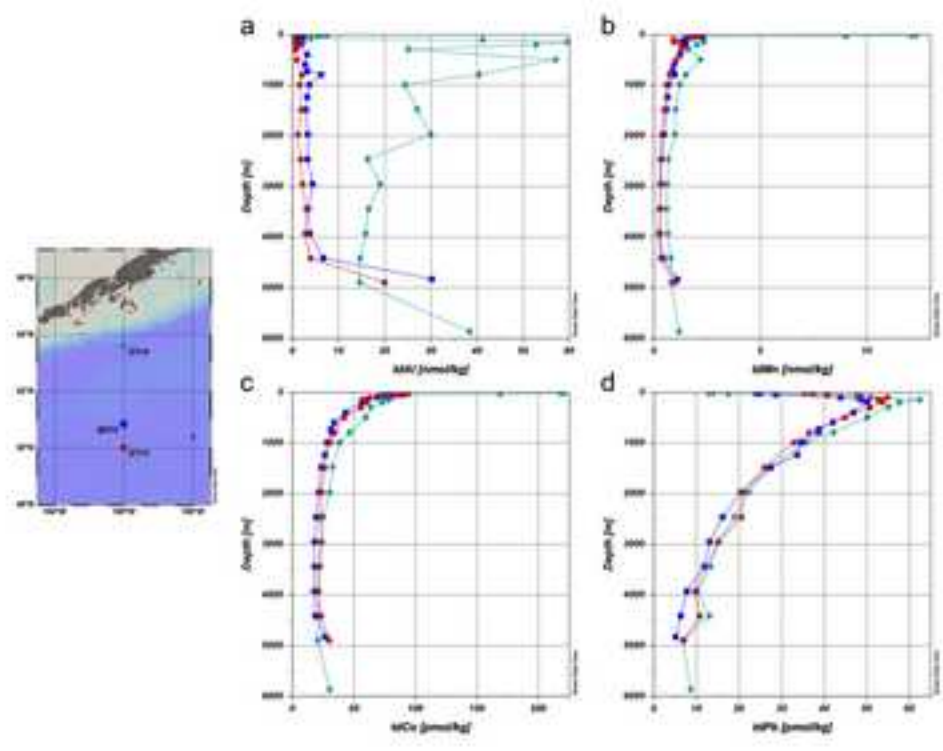


Figure 6

Figure7

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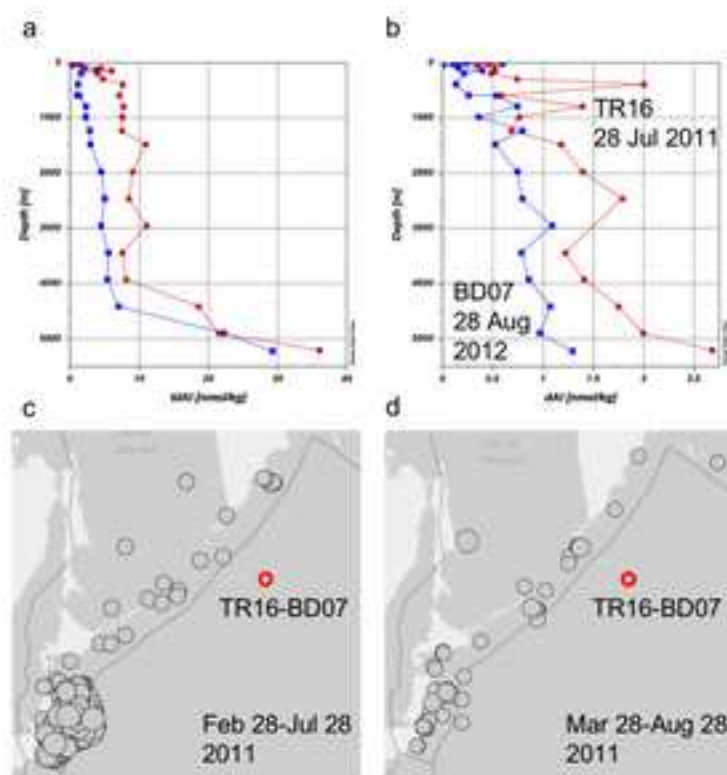


Figure 7

Figure8

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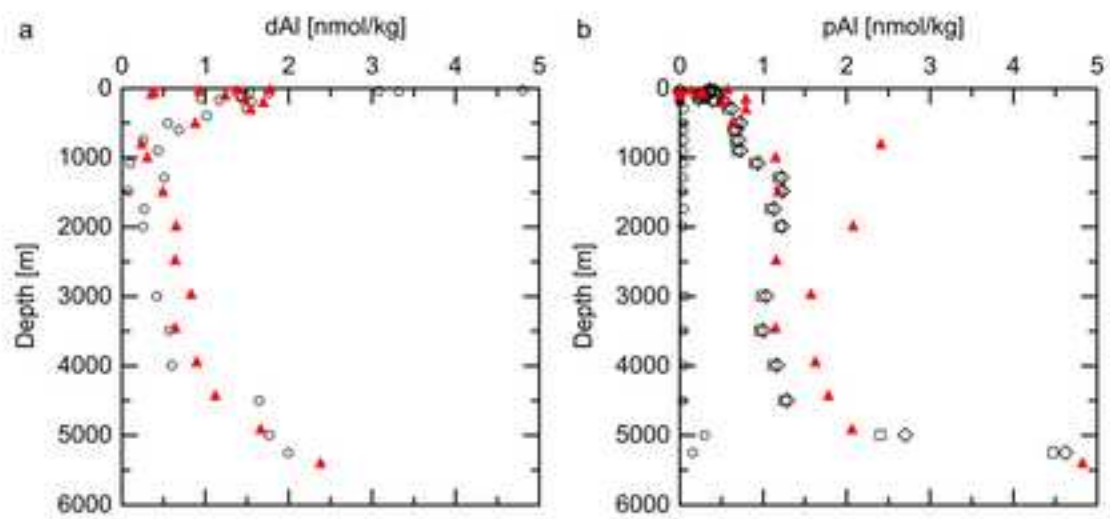


Figure 8

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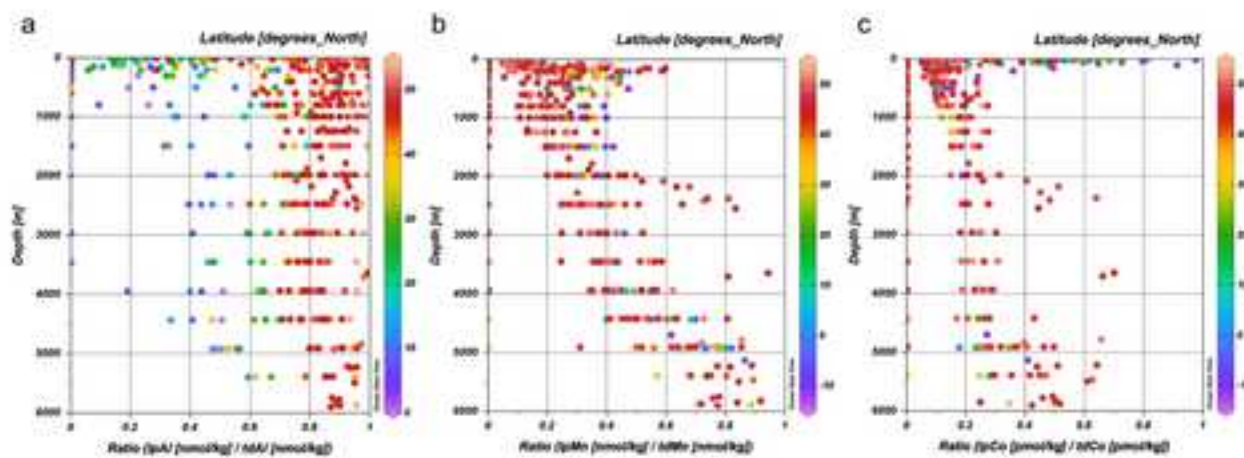


Figure 9

Figure10  
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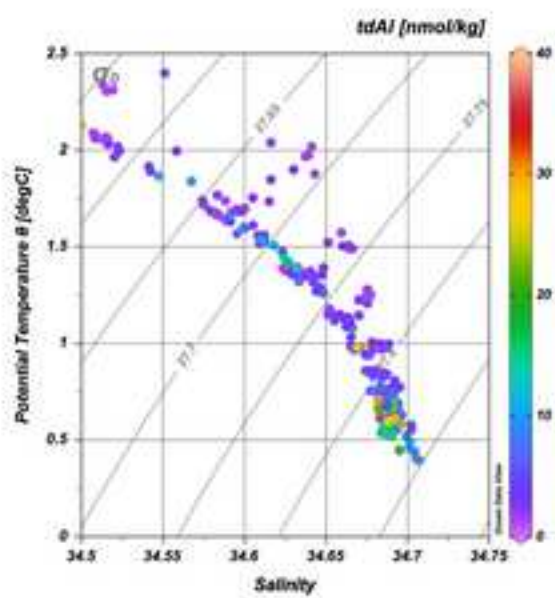


Figure 10



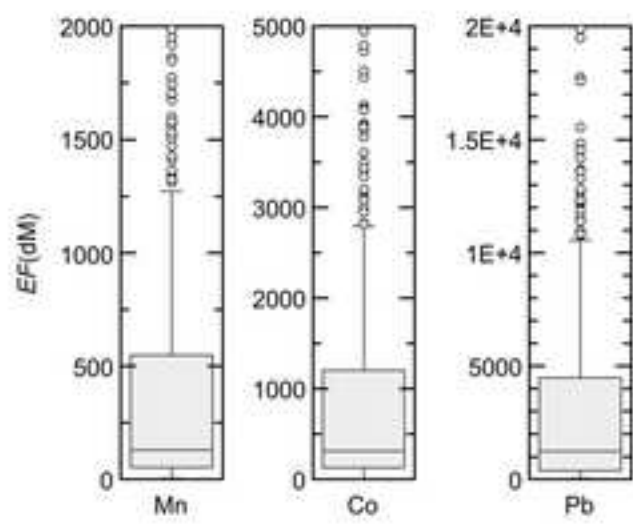


Figure 11

Figure12  
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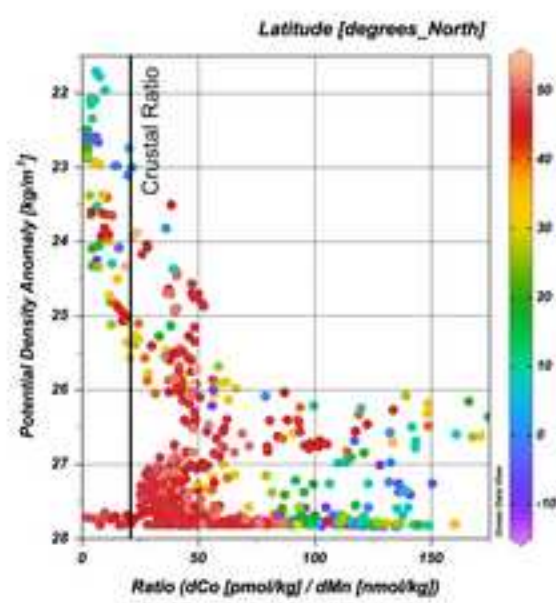


Figure 12

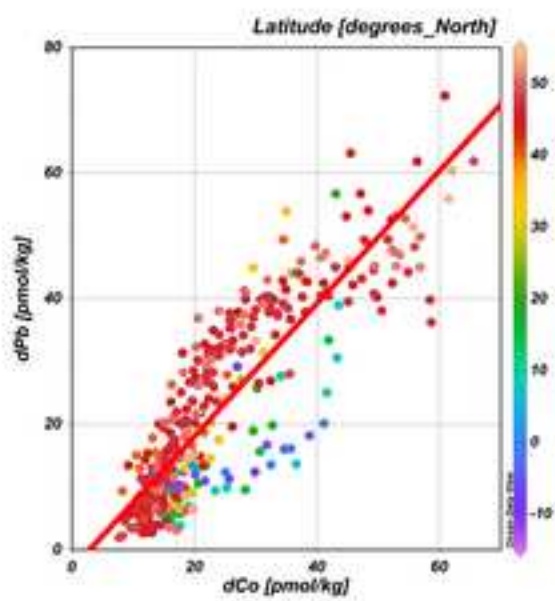


Figure 13

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