1	Size-fractionated labile trace elements in the Northwest Pacific and Southern
2	Oceans.
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28 ABSTRACT

29 Photosynthesis by marine phytoplankton requires bioavailable forms of several trace 30 elements that are found in extremely low concentrations in the open ocean. We have 31 compared the concentration, lability and size distribution (< 1 nm and < 10 nm) of a suite 32 of trace elements that are thought to be limiting to primary productivity as well as a toxic 33 element (Pb) in two High Nutrient Low Chlorophyll (HNLC) regions using a new 34 dynamic speciation technique, Diffusive Gradients in Thin-film (DGT). The labile 35 species trapped within the DGT probes have a size that is smaller or similar than the pore 36 size of algal cell walls and thus present a proxy for bioavailable species. 37 Total Dissolvable trace element concentrations (TD concentration) varied between 0.05 nM (Co) and 4.0 nM (Ni) at K2 (Northwest Pacific Ocean) and between 0.026 nM (Co) 38 39 and 4.7 nM (Ni) in the Southern Ocean. The smallest size fractionated labile 40 concentrations (< 1 nm) observed at Southern Ocean sampling stations ranged between 41 0.002 nM (Co) and 2.1 nM (Ni). Moreover, large differences in bioavailable fractions 42 (ratio of labile to TD concentration) were observed between the trace elements. In the 43 Northwest Pacific Ocean Fe, Cu and Mn had lower labile fractions (between 10 and 44%) 44 than Co, Cd, Ni and Pb (between 80 and 100%). In the Southern Ocean a similar trend 45 was observed, and in addition: (1) Co, Cd, Ni and Pb have lower labile fractions in the 46 Southern Ocean than in the Northwest Pacific and (2) the ratios of <1nm to dissolvable 47 element concentrations at some Southern Ocean stations were very low and varied between 4 and 16 %. 48 49 50 51 52 53 54 Keywords: trace elements, speciation, bioavailability, Pacific Ocean, Southern Ocean 55 56

57 INTRODUCTION

58 In the contemporary ocean, photosynthetic carbon fixation by marine phytoplankton 59 leads to formation of \sim 45 gigatons of organic carbon (C) per annum, of which \sim 11 60 gigatons are exported to the ocean interior (Laws et al., 2000). To sustain this C flux 61 through marine ecosystems, essential elements must be supplied in a ratio reflecting the 62 composition of marine phytoplankton species. The role of some of these essential trace 63 elements has been summarized by Morel et al. (2003) and Morel and Price (2003) for 64 example, of Co, Cd and Zn in carbon dioxide acquisition, Fe and Mn in carbon fixation, 65 Zn, Cd and Se in silica uptake, Fe and Mo in fixation and Fe, Cu and Ni in organic N 66 utilization. 67 In most areas of the oceans, the concentrations of essential trace elements are 68 extremely low. Moreover, these elements are present in different chemical forms such as 69 free ionic, labile bound and strongly bound to organic ligands, and different sizes, such as 70 truly soluble through colloidal (nominally >1000 kDa to $<0.2 \mu m$) to particulate (>0.2 71 μm). Not all of these forms are accessible to phytoplankton. To cross the phytoplankton 72 cell membrane they need to be small (Carpita et al., 1979; Zhang and Davision, 2000; 73 Zemke-White et al., 2000) and in free ionic or labile bound forms (Davison and Zhang, 74 1994; Morel and Price, 2003). It is thus important to assess the small and labile fraction 75 of those essential trace elements in the dissolved phase because they are the most 76 bioavailable. 77 Techniques which enable estimation of the labile metal fraction in the ocean are 78 DGT, electrochemical stripping techniques such as ASV, CSV and chronopotentiometry

79 or ion exchange methods (e.g. Buckley and van den Berg, 1986; Davison and Zhang,

80 1994; Zhang and Davison, 2000; Twiss and Moffett, 2002). The DGT device consists of a 81 double layer system, with the diffusive gel layer (controlling the mass transport) on top of 82 a Chelex-100 resin gel layer (acting as a sink for metals). According to Zhang and 83 Davison (2000) and Twiss and Moffett (2002), the difference between DGT and Anodic 84 Stripping Voltammetry is that DGT contains a thicker diffusion layer allowing more 85 dissociation of labile complexes and also allowing the choice of an appropriate sampling 86 time scale. DGT devices are also easier to handle and more robust at sea than 87 voltammetric instruments.

88 The polyacrylamide gels used in DGT devices allow free diffusion of metal ions 89 and metal-ligand complexes, but the latter are limited by their size. The pore size of the 90 gels is not exactly known, but the diffusion of metal complexes with fulvic and humic 91 acid indicates nominal pore sizes for Open-Pored DGT gels of ~10 nm and for 92 Restricted-Pored DGT gels of ~1 nm. In both cases, inorganic and organic metal 93 complexes which are less stable than the metal-Chelex bond dissociate during their 94 transport in the gel, and are bound by the Chelex resin (Figure 2). The fact that (1) the 95 dimensions of the species measured by the DGT are smaller than or equal to the pore 96 sizes of the cell walls of algae (Carpita et al., 1979; Zhang and Davision, 2000; Zemke-97 White et al., 2000) and (2) that only labile species were measured (Davison and Zhang, 98 1994) gives confidence that these species are most probable bioavailable species to algae. 99 In fact, an in depth study by Zhang and Davison (2000) showed that if a measurement is 100 made with an open-pored gel (in our paper indicated as < 10 nm pore size), both 101 inorganic and organic labile complexes are measured. When membrane transport is slow, 102 the concentration of the free ion in solution determines the rate of uptake (Campbell,

103	1995). However, with fast membrane transport, uptake is governed by the product of the
104	concentration of each species and their diffusion coefficient. This is exactly what DGT
105	measures directly with the open-pored gel, as it is a physical surrogate of fast membrane
106	transport. This type of DGT measurement therefore provides, directly, the effective
107	bioavailable metal concentration for the worst possible biological situation of fast
108	membrane transport. A measurement with a restricted gel (in our paper indicated as < 1
109	nm pore size) provides a reasonable estimate of the inorganic labile species
110	concentration.
111	In this work the DGT results were compared to the Total Dissolvabled (TD)
112	element fraction in an unfiltered, acidified sample (1 mL nitric acid to 500 mL sample),
113	following extraction with diethyldithiocarbamate in freon at a pH of 5, and analysed by
114	inductively coupled plasma - mass spectrometry (ICP-MS). This TD fraction also
115	includes labile trace metals associated with particulates.
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117 118	METHODS AND MATERIALS. SAMPLING.
119	Trace elements were sampled with ultra clean techniques following GEOTRACES
120	guidelines recommended for the International Polar Year as closely as possible (Bowie
121	and Lohan, 2009). All sampling processing was carried out under an ISO class 5 trace-
122	metal-clean laminar flow bench in a clean container. For the VERTIGO-K2 cruise
123	(Figure 1) in the North Pacific (K2 coordinates: 47°N, 160°E), pre-cleaned Teflon-lined
124	Niskin bottles (10 L) deployed off a Kevlar cable were used to collect surface sea water,
125	up to a depth of 50 m. Additional surface samples were collected from an inflatable raft
126	upstream from the ship, using clean sampling procedures. Sampling from the vessel

127	occurred on $02/08/2005$ and $13/08/2005$, with sampling from the raft on $14/08/2005$. On
128	02/08/2005, a 15 L sample was directly poured into a pre-cleaned high density polymer
129	vessel (20 L) containing 5 DGT devices (Open Pored DGTs) and two 0.5 L aliquots
130	(unfiltered seawater) were taken from the container and stored in Teflon bottles (pH<3)
131	for later analysis of TD trace metal concentrations. The 20 L container was stored
132	between 5 and 10°C and the seawater was frequently homogenized by gentle shaking the
133	container. On 13/08/2005, two 0.5 L aliquots (unfiltered seawater) were also taken from
134	the container and stored in Teflon bottles (pH<3) for later analysis of TD trace metal
135	concentrations, before the seawater in the container was refreshed with a new 15 L
136	sample. On 24/08/2005, again two 0.5 L aliquots (unfiltered seawater) were taken from
137	the container and stored in Teflon bottles (pH<3) for TD analyses. The DGT probes were
138	then recovered, stored in sealed double layered plastic bags and kept at 4°C, together with
139	2 blank DGT probes.
140	For the SR3-GEOTRACES cruise in the Southern Ocean (Figure 1), samples were
141	collected using externally-closing, Teflon-lined Niskin-1010X bottles (5 L) deployed on
142	an autonomous 1018 intelligent rosette system specially adapted for trace metal work
143	(General Oceanics, USA) and suspended on Kevlar rope. Sampling occurred on
144	26/03/2008 at station #1 (60.4, 140.7), on $4/04/2008$ at station #2 (57.9, 139.9), on
145	11/04/2008 at station #3 (49.9, 143.8), and on $14/04/2008$ at station #4 (45.7, 145.67).
146	The DGT experiments (Open-Pored and Restricted-Pored DGTs) were run in the same
147	way as during the VERTIGO-K2 cruise, except that they lasted for 7 weeks (i.e., DGTs
148	remained in the sample solution for 7 weeks) and at a temperature of 4 °C. At the end of
149	each DGT experiment, two 0.5 L aliquots (unfiltered seawater) were also taken from the

container and stored in Teflon bottles (pH<3) for later TD analysis. The DGT probes
were recovered, stored in sealed double layered plastic bags and kept at 4°C, together
with 2 blank DGT probes.

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154 ANALYSIS OF TRACE METALS.

Analyses of total dissolvable (TD) trace metal concentrations in the surface ocean waters were performed according to standard QA/QC protocols in the laboratory of Analytical and Environmental Chemistry at the Vrije Universiteit Brussel (VUB). A solvent extraction method, slightly modified from Danielsson et al. (1978 and 1982) was applied in order to preconcentrate the trace elements and to eliminate the salt matrix. Ultrapure reagents were used throughout, and where necessary, an additional purification procedure was applied, as detailed below:

162 Nitric acid: Ultrapure nitric acid was obtained through distillation of concentrated 163 (Merck, Pro Analysis) using an all-Teflon sub-boiling still. Buffer: An ammonium acetate 164 buffer was prepared by diluting a solution of 22.5 mL ammoniumhydroxide (; Merck, 165 Suprapur) and 11.8 mL acetic acid (; Merck, Suprapur) up to 100 mL with Milli Q water 166 (Millipore). Complexant: 1.0 g Ammonium Pyrolidine DithioCarbamate (APDC; Merck, 167 Pro Analysis) and 1.0 g Diethylammonium Diethyl DithioCarbamate (DDDC; Merck, 168 Pro Analysis) were dissolved in 1 mL (Suprapur) and diluted to 100 mL with Milli Q 169 water. The clean up of this solution involved a three times extraction with 20 mL freon. 170 The solution was freshly prepared every 3 days. Freon: 400 mL freon (Pro Analysis) was 171 washed three times with 5 mL sub boiled nitric acid in a 1000 mL Teflon separatory 172 funnel.

173 Between 200 and 400 g of sample or blank (Milli Q water) was weighed and brought

174 to a pH of 4.5 to 5.0 by means of the ammonium acetate buffer, in order to obtain optimal 175 complexation. The pH was immediately checked and if required, additional buffer was 176 added. To the buffered solution 2.5 mL complexant (solution of 1% APDC / 1% DDDC) 177 was added. The metal complexes were then extracted in three steps: for the first 178 extraction, 10 mL of freon was added, the funnel shaken vigorously for 2 minutes, the 179 phases separated over 5 minutes and the freon phase then layered off into a second 180 separation Teflon funnel; for the second extraction, 5 mL of freon was added, with the 181 further steps identical to that of the first extraction; the third extraction was identical to 182 the second one. All 3 Freon layers were collected in the second separation Teflon funnel, 183 to which 200 µL of was added, and allowed to react for 15 minutes. Six mL of Milli Q 184 water was then added, the funnel shaken for 1 min, and 5 mL of the upper aqueous phase 185 transferred to a 10 mL polypropylene tube and stored at 4°C. These samples were 186 analysed by high resolution inductively coupled – mass spectrometry (ICP-MS; Thermo 187 Finnigan Element2). The NASS5 reference material (from the National Research 188 Council, Canada) was analyzed after Freon extraction along with the samples. Agreement 189 between reference and our measured values after Freon extraction was satisfactory 190 (maximum of 18% deviation, see Table S1).

For 3 elements, Cd, Cu and Fe, an isotope dilution experiment was also carried out on the unfiltered sea water samples. To 250 mL of unfiltered seawater, 125 μ L of a mixed isotope spike of 49.34 μ g L⁻¹ of Fe (57), 54.00 μ g L⁻¹ of Cd (111) and 62.95 μ g L⁻¹ of Cu (65) was added. The extraction of those seawater samples was carried out in a similar way as for the non-spiked sample. Concentrations of Fe, Cd and Cu isotopes were measured by ICP-MS and calculated using the isotope dilution method. The

197 concentrations of Cd, Cu and Fe obtained with the isotope dilution method were very198 similar to the ones obtained with the non-spiked extraction procedure.

Our laboratory also regularly participates in international intercalibration exercises on trace metals in marine samples, such as the QUASIMEME Laboratory Performance studies (://www.quasimeme.org/structure.).

202 The labile metal amounts captured by the chelex resin of the DGT probe were also

analyzed with the ICP-MS instrument after acid elution (1 M nitric acid) of the metals

and their concentrations were calculated using Fick's first diffusion law (Davison and

Zhang, 1994; Davison et al., 2000; Gao et al., 2006 and 2007). Half of the eluted volume

206 (2 mL) was analyzed after 5 times dilution, while 40 µL of the same mixed isotope spike

207 of Fe (57), Cd (111) and Cu (65) used for the unfiltered seawater samples, was added to

the other half of the eluted volume. Analysis was performed using ICP-MS and for the

spiked solution, concentrations of Fe, Cu and Cd were calculated using the isotope

dilution method.

211

212 RESULTS AND DISCUSSION

The TD, labile and non-labile trace element concentrations of Fe, Mn, Co, Cu, Cd, Ni (trace elements important for phytoplankton growth) and Pb (a non-essential trace element and potential toxicant) were measured in upper mixed layer waters at the K2 (47°N, 160°E) time series station Northwest Pacific Ocean (Buesseler et al., 2007) and at 4 sampling stations along the ~ meridian in the Southern Ocean south of Australia, both HNLC regions. Our experiments were carried out at ambient seawater temperature in the dark, to avoid assimilation of the trace elements by phytoplankton, and due to the

extremely low concentrations lasted for several weeks (3 weeks in the Pacific Ocean and7 weeks in the Southern Ocean).

222 For each of the considered trace elements, a certain fraction of their TD pool will 223 likely be non-bioavailable to phytoplankton (Zhang and Davison, 2000; Morel and Price, 224 2003). These non-available fractions of the TD pool are most pronounced for Fe, Cu and 225 Mn, as can be seen from the percentages of each of the 3 trace element pools (0-1 nm, 1-226 10 nm and 10 nm-TD) averaged over all stations (Figure 3). Although the percentages for 227 each of the individual element pools vary between the stations (Table 1), the general 228 trend remains the same. In the Northwest Pacific, the TD and <10 nm concentrations are 229 very similar for several elements (Co, Cd, Ni, Pb), while for others like Fe and Cu, the 230 concentrations in the size class <10 nm measured by DGT are by far lower than the TD 231 concentrations (Table 2). Even when we take into account the rather large uncertainties 232 on those small to very small concentrations (on the TD concentrations, RSDs are up to 233 20%, see Table 2 where averages and STDs are reported, and are thus of the same 234 magnitude as the differences found on the reference sea water sample NASS5), they had 235 no influence on the conclusions we can draw between the 3 trace element pools (0-1 nm, 236 1-10 nm and 10 nm-TD). For example TD Fe is between 4 to 14 times higher than the 237 <10 nm fraction and the latter is between 3 and 7 times higher than the <1 nm fraction. 238 Fe and Cu are known to be mainly present in the dissolved phase as colloids or as 239 complexes that are strongly bound to ligands and thus unlikely to form labile complexes 240 (Wells, 20002; Morel and Price, 2003). At all stations in the Southern Ocean, the trace 241 element concentrations are lower than in the Northwest Pacific but follow the same trend vs. size. The <10 nm concentrations of Co, Cd, Ni and Pb are substantially smaller than 242

243	the TD. At Southern Ocean stations 3 and 4, we observe still lower concentrations (TD
244	and labile) of almost all trace elements examined, compared to the two most southerly
245	stations (1 and 2). The <1 nm concentrations are only assessed in the Southern Ocean: (1)
246	at stations 1 and 2, low <1 nm/<10 nm ratios are observed for Fe and Mn, indicating that
247	the fraction <1 nm is small compared to that between 1 and 10 nm; (2) at stations 3 and 4,
248	despite the fact that for all elements the <10 nm/TD ratios are the lowest of all stations,
249	we observe a further decrease from the <10 nm to the <1 nm levels for Co, Mn and Ni.
250	It is difficult to compare our total and labile, size fractionated trace element
251	concentrations to the limited literature data set because: (1) our concentrations are time
252	averages over several weeks while literature data reflect short-term conditions; (2) our
253	samples were collected from surface to 50-100 m depth; and (3) due to heterotrophic
254	enzymatic activity and without phytoplankton uptake in the DGT experiments, the size
255	fractionated concentrations can increase with time by bio-degradation of macromolecules
256	containing the trace elements. In fact, our DGT results represent the amount of trace
257	elements that are, considered over a time period of several weeks, bioavailable to the
258	phytoplankton community. Although it is impossible at this moment to quantify the effect
259	of microbial activity on the size fractionated concentrations observed, we performed
260	some additional measurements in the Northwest Pacific that allow us to get a better
261	insight in the magnitude of that process. During the Vertigo experiment at K2,
262	ammonium regeneration as well as bacterial mineralization rates were assessed with two
263	different methods (Elskens et al., 2008). Both rates compared very well, with average
264	values of 0.1 and 0.06 μ M-N h ⁻¹ for ammonium regeneration and bacterial
265	mineralization, respectively. In terms of phosphorus by using the Redfield ratio of 16 for

266	N/P, this means a regeneration rate of the order of 5.2 nM h^{-1} . In the literature we can find
267	some ranges of Me/P ratios in phytoplankton and as a first approximation we will assume
268	that those ratios are maintained during organic matter regeneration. We will consider two
269	extreme cases: an element with a very low labile fraction (Fe) and one with a high labile
270	fraction (Co), see Table 2. The Me/P ratios reported in the literature can vary a lot
271	depending, for example, on the phytoplankton species, the way they are determined (in
272	vitro or in situ) and for in vitro determinations even the season of sampling. Considering
273	only open ocean diatoms and flagellates, Fe/P ratios vary from $1.1 \ge 10^{-3}$ (Ho et al, 2003)
274	to 0.63 x 10^{-3} (Twining et al., 2004), while for Co/P only Ho et al. (2003) reported a
275	value, being 0.14×10^{-3} . Due to microbial activity, the daily regeneration of Fe in these
276	conditions ranges from 3.3 to 5.8 pM-Fe h^{-1} and amounts for Co to 0.75 pM-Co h^{-1} .
277	These regeneration rates are initial rates related to the consumption of the most labile
278	DOC compounds and will only last during a limited time period. Once the most labile
279	DOC compounds are exhausted the regeneration rates rapidly decline. Using the multi-G
280	model of Berner, Chen and Wangersky (1996) studied the DOC decay rates for a natural
281	phytoplankton assemblage (off the coast of Nova Scotia, Canada). If we assume similar
282	sizes for the 4 DOC pools (11, 5.8, 13.7 and 15.5% from very labile to more refractive)
283	and we apply the corresponding decay rates (0.12, 0.03, 7.7 10^{-3} and 2.9 10^{-3} d ⁻¹) on our
284	system, after 3 weeks 0.25 nM Fe and 0.046 nM Co are regenerated from the DOC pool.
285	Although DOC pool sizes and their decay rates are probably different in the Northwest
286	Pacific, it is surprising to notice that the calculated regenerated Fe and Co concentrations
287	are very similar to their labile concentrations measured with the DGT. This observation

asks for further investigation of the release of trace elements during the bacterial

289 degradation of DOC in HNLC oceanic areas.

290 In Table 3, an overview of trace element concentrations reported in the literature 291 and unpublished Fe data from the SR3-GEOTRACES Antarctic cruise are presented. 292 Despite the differences in experimental design, sampling and analytical techniques, these 293 literature data reflect the same range of concentrations as our data. 294 Depending on the region and the season, different elements can limit primary 295 productivity of the HNLC oceans (Moore et al., 2004). Nitrogen is usually the most 296 important phytoplankton growth limiting element, including most regions of the Pacific 297 Ocean (Falkowski et al., 1998), but in HNLC regions such as the subarctic North Pacific 298 Ocean and the Southern Ocean, it has been shown that low levels of Fe are entirely or 299 partly responsible for the under-utilization of the major nutrients and the lower than 300 expected chlorophyll levels (e.g. Martin and Fitzwater, 1988; Boyd et al., 2000). 301 However, an important remaining question is whether phytoplankton primary 302 productivity is limited by the labile concentrations of trace elements other than Fe, and if 303 so, (1) which one's and (2) is this co-limitation the same in the Northwest Pacific and the 304 Southern Ocean? In prior studies of the Peru upwelling region, Co scarcity and speciation 305 was found to influence phytoplankton species composition (Saito et al., 2004) and Fe, 306 Mn, Cu and Zn were found to be co-limiting productivity in the subarctic Pacific Ocean 307 (Coale, 1991). In studies on phytoplankton cultures, several co-limitations were observed: 308 for example Peers and Price (2004) found Fe and Mn to be co-limiting. 309 Several parameters will finally determine which of the elements is limiting or co-310 limiting primary productivity in the open ocean. The cellular Me/P ratios, which reflect

311 the plankton demand of a given trace element during growth, are different when 312 considering diatoms, flagellates or coccolitophores (Ho et. al, 2003; Twining et al., 2004) 313 and will vary during the season, relative to the trace element's availability (Sunda and 314 Huntsman, 1995). For some of the trace elements there exists also a mechanism of 315 replacement by some other one in case of scarcity (Morel, 2008). But the most important 316 parameter is the pool of bioavailable trace element in the ocean's surface. To our 317 knowledge, no prior studies have directly assessed the concentration of bioavailable trace 318 element fractions (<10 nm, <1 nm), in HNLC areas. This information is very valuable in 319 studies related to limiting or co-limiting elements in such open oceanic systems.

320

321 CONCLUSION

322 In this paper, it is demonstrated that it is possible to determine the extremely low 323 bioavailable concentrations of the trace elements Cd, Co, Cd, Fe, Mn, Ni and Pb in 324 HNLC oceans such as the Northwest Pacific and Southern Oceans. In our experiments 325 the labile trace element concentrations obtained by the DGT reflect the amount that was 326 initially present in the watermass increased by the contribution from bacterial degradation 327 of DOC. Therefore, the size-fractionated labile amounts reported in this paper are a good 328 proxy of the averaged (over a time span of a few weeks) bioavailable trace element pools 329 for phytoplankton in the surface water of the Northwest Pacific and Southern Oceans, 330 without external inputs. This bioavailable fraction represents only a few percentages of 331 the total dissolvable amount for elements such as Fe, Mn and Cu while for some other 332 ones the differences between the TD and bioavailable pools are much smaller. In the 333 future, it would be interesting to assess the spatio-temporal variability of bioavailable

334	trace metal concentrations in HNLC oceans and to study their limiting effect on primary
335	productivity.
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FIGURE LEGENDS

Figure 1: Map of the sampling station K2 (Northwest Pacific) and stations 1 to 4 in the Southern Ocean.

- Figure 2: Schematic view of labile and non-labile trace element compounds diffusing into
- a DGT probe. Pore-size is about 10 nm for Open-Pored and 1 nm for Restricted-Pored hydrogels.

- Figure 3: Average percentages of non-labile, labile and <10 nm and labile and <1 nm
- dissolved trace elements in the Northwest Pacific and Southern Oceans.

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467 TABLE LEGENDS

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470	Table 1: Percentages of size-fractionated, labile to total dissolvable (TD) trace element
471	concentrations.
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- 473 Table 2: Total dissolvable (TD) and size fractionated, labile element concentrations in the
- 474 Northwest Pacific (VERTIGO) and Southern Oceans (SR3-GEOTRACES). TD = Total
- Dissolvable, <10 nm = labile fraction smaller than 10 nm, < 1 nm = labile fraction smaller than 1
 nm.

- 478 Table 3: Literature results of trace element concentrations from the same oceanic areas
- 479 (TD = Total Dissolvable).
- 480



100°E

160°E

A



DGT Probe



Table 1: Percentages of size-fractionated, labile to total dissolvable (TD) trace element concentrations.

VERTIGO station K2

	Fe	Cu	Со	Cd	Mn	Ni	Pb
% <10 nm/TD	10	21	100	100	44	100	82
		ANTAR	Geotraces, s	tations # 1 &	z 2		
	Fe	Cu	Со	Cd	Mn	Ni	Pb
% <10 nm/TD	27	35	47	61		48	45
% < 1 nm/TD	4	32	44	45	30*	44	38
		ANTAR (Geotraces, s	tations # 3 &	: 4		
	Fe	Cu	Со	Cd	Mn	Ni	Pb
% <10 nm/TD	7	14	33	24		40	16
% < 1 nm/TD	3	12	8	16	33*	15	8

* For Mn the ratio <1 nm/<10 nm is presented

Table 2: Total dissolvable (TD) and size fractionated, labile element concentrations in the Northwest Pacific (VERTIGO) and Southern Oceans (SR3-GEOTRACES). TD = Total Dissolvable, <10 nm = labile fraction smaller than 10 nm, <1 nm = labile fraction smaller than 1 nm.

Element concentrations in nM (VERTIGO)

	Р	Fe	Cu	Со	Cd	Mn	Ni	Pb
TD average	2000	3.1	1.5	0.050	0.41	1.69	4.02	0.056
STD		± 0.5	±0.3	± 0.008	±0.05	±0.23	±0.76	±0.012
< 10 nm average STD		0.30 ±0.08	0.31 ±0.03	0.056 ± 0.005	0.40 ±0.03	0.74 ±0.08	4.04 ±0.32	0.046 ±0.005

Element concentrations in nM (SR3-GEOTRACES, stations # 1 & 2)

	Р	Fe	Cu	Со	Cd	Mn	Ni	Pb
TD average	500-1700	2.5	1.03	0.0285	0.24		4.7	0.088
STD		±0.4	±0.15	± 0.0045	± 0.04		±0.7	±0.012
< 10 nm average		0.68	0.36	0.0135	0.147	0.28	2.30	0.040
STD		±0.09	±0.05	±0.0020	±0.023	±0.05	±0.35	±0.009
< 1 nm average		0.10	0.325	0.0125	0.11	0.085	2.1	0.033
STD		±0.02	±0.043	±0.0019	±0.02	± 0.006	±0.3	± 0.008

Element concentrations in nM (SR3-GEOTRACES, stations # 3 & 4)

	Р	Fe	Cu	Со	Cd	Mn	Ni	Pb
TD average	500-1700	2.4	0.80	0.0255	0.112		2.91	0.085
STD		±0.4	± 0.08	±0.0040	±0.015		±0.29	±0.014
< 10 nm average		0.165	0.11	0.0085	0.0265	0.23	1.17	0.014
STD		±0.025	±0.02	±0.0010	±0.0040	±0.04	±0.17	±0.002
< 1 nm average		0.06	0.095	0.002	0.0175	0.075	0.44	0.007
STD		± 0.01	±0.015	± 0.001	± 0.0030	±0.010	±0.06	±0.001

Table 3: Literature results of trace element concentrations from the same oceanic areas (TD = Total Dissolvable).

	Element concentrations (nM) around K2							
	Р	Fe	Cu	Со	Cd	Mn	Ni	Pb
TD (Brown et al., 2005) <0.2 μm dissolved (idem)		1.33-3.16 0.27-0.46						
<0.2 µm dissolved (Fujishima et al., 2001)				0.03-0.05		1.53-1.85	4.8-5.3	
	Element concentrations (nM) in the Southern Ocean (southern latitudes)							
	Р	Fe	Cu	Co	Cd	Mn	Ni	Pb
<0.2 µm dissolved (SR3-GEOTRACES cruise, unpublished results)		0.03						
	Element concentrations (nM) in the Southern Ocean (northern latitudes)							
<0.2 µm dissolved (Ellwood, 2008)	Р	Fe	Cu 0.5-1.2	Со	Cd 0.012-0.35	Mn	Ni 3.0-5.0	Pb 0.012-0.022
<0.2 µm dissolved (SR3-GEOTRACES cruise, unpublished results)		0.08						