# Size-fractionated labile trace elements in the Northwest Pacific and Southern Oceans

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## A R T I C L E   I N F O

## A B S T R A C T

Photosynthesis by marine phytoplankton requires bioavailable forms of several trace elements that are found in extremely low concentrations in the open ocean. We have compared the concentration, lability and size distribution (<1 nm and <10 nm) of a suite of trace elements that are thought to be limiting to primary productivity as well as a toxic element (Pb) in two High Nutrient Low Chlorophyll (HNLC) regions using a new dynamic speciation technique, Diffusive Gradients in Thin-film (DGT). The labile species trapped within the DGT probes have a size that is smaller or similar than the pore size of algal cell walls and thus present a proxy for bioavailable species.

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) and 4.7 nM (Ni) in the Southern Ocean. The smallest size fractionated labile concentrations (<1 nm) observed at Southern Ocean sampling stations ranged between 0.002 nM (Co) and 2.1 nM (Ni). Moreover, large differences in bioavailable fractions (ratio of labile to TD concentration) were observed between the trace elements. In the Northwest Pacific Ocean Fe, Cu and Mn had lower labile fractions (between 10 and 44%) than Co, Cd, Ni and Pb (between 80 and 100%). In the Southern Ocean a similar trend was observed, and in addition: (1) Co, Cd, Ni and Pb have lower labile fractions in the Southern Ocean than in the Northwest Pacific and (2) the ratios of <1 nm to dissolvable element concentrations at some Southern Ocean stations were very low and varied between 4 and 16%.

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## 1. Introduction

In the contemporary ocean, photosynthetic carbon fixation by marine phytoplankton leads to formation of ~45 gigatons of organic carbon (C) per annum, of which ~11 gigatons are exported to the ocean interior (Laws et al., 2000). To sustain this C flux through marine ecosystems, essential elements must be supplied in a ratio reflecting the composition of marine phytoplankton species. The role of some of these essential trace elements has been summarized by Morel et al. (2003) and Morel and Price (2003) for example, of Co, Cd and Zn in carbon dioxide acquisition, Fe and Mn in carbon fixation, Zn, Cd and Se in silica uptake, Fe and Mo in $N_2$ fixation and Fe, Cu and Ni in organic N utilization.

In most areas of the oceans, the concentrations of essential trace elements are extremely low. Moreover, these elements are present in different chemical forms such as free ionic, labile bound and strongly bound to organic ligands, and different sizes, such as truly soluble through colloidal (nominally >1000 kDa to <0.2 μm) to particulate (>0.2 μm). Not all of these forms are accessible to phytoplankton. To cross the phytoplankton cell membrane they need to be small (Carpita et al., 1979; Zhang and Davison, 2000; Zemke-White et al., 2000) and in free ionic or labile bound forms (Davison and Zhang, 1994; Morel and Price, 2003). It is thus important to assess the small and labile fraction of those essential trace elements in the dissolved phase because they are the most bioavailable.

Techniques which enable estimation of the labile metal fraction in the ocean are DGT, electrochemical stripping techniques such as ASV, CSV and chronopotentiometry or ion exchange methods (e.g. Buckley and van den Berg, 1986; Davison and Zhang, 1994; Zhang and Davison, 2000; Twiss and Moffett, 2002). The DGT device consists of a double layer system, with the diffusive gel layer (controlling the mass transport) on top of a Chelex-100 resin gel layer (acting as a sink for metals). According to Zhang and Davison (2000) and Twiss and Moffett (2002), the difference between DGT and Anodic Stripping Voltammetry is that DGT contains a thicker diffusion layer allowing more dissociation of labile complexes and also allowing the choice of an appropriate sampling time scale. DGT devices are also easier to handle and more robust at sea than voltammetric instruments.

The polyacrylamide gels used in DGT devices allow free diffusion of metal ions and metal-ligand complexes, but the latter are limited by

their size. The pore size of the gels is not exactly known, but the diffusion of metal complexes with fulvic and humic acid indicates nominal pore sizes for Open-Pored DGT gels of ~10 nm and for Restricted-Pored DGT gels of ~1 nm. In both cases, inorganic and organic metal complexes which are less stable than the metal-Chelex bond dissociate during their transport in the gel, and are bound by the Chelex resin (Fig. 1). The fact that (1) the dimensions of the species measured by the DGT are smaller than or equal to the pore sizes of the cell walls of algae (Carpita et al., 1979; Zhang and Davison, 2000; Zemke-White et al., 2000) and (2) that only labile species were measured (Davison and Zhang, 1994) gives confidence that these species are most probable bioavailable species to algae. In fact, an in depth study by Zhang and Davison (2000) showed that if a measurement is made with an open-pored gel (in our paper indicated as <10 nm pore size), both inorganic and organic labile complexes are measured. When membrane transport is slow, the concentration of the free ion in solution determines the rate of uptake (Campbell, 1995). However, with fast membrane transport, uptake is governed by the product of the concentration of each species and their diffusion coefficient. This is exactly what DGT measures directly with the open-pored gel, as it is a physical surrogate of fast membrane transport. This type of DGT measurement therefore provides, directly, the effective bioavailable metal concentration for the worst possible biological situation of fast membrane transport. A measurement with a restricted gel (in our paper indicated as <1 nm pore size) provides a reasonable estimate of the inorganic labile species concentration.

In this work the DGT results were compared to the Total Dissolvabled (TD) element fraction in an unfiltered, acidified sample (1 mL nitric acid to 500 mL sample), following extraction with diethyldithiocarbamate in freon at a pH of 5, and analysed by inductively coupled plasma – mass spectrometry (ICP-MS). This TD fraction also includes labile trace metals associated with particulates.

## 2. Methods and materials

### 2.1. Sampling

Trace elements were sampled with ultra clean techniques following GEOTRACES guidelines recommended for the International Polar Year as closely as possible (Bowie and Lohan, 2009). All sampling processing was carried out under an ISO class 5 trace-metal-clean laminar flow bench in a clean container. For the VERTIGO-K2 cruise (Fig. 2) in the North Pacific (K2 coordinates: 47°N, 160°E), pre-cleaned
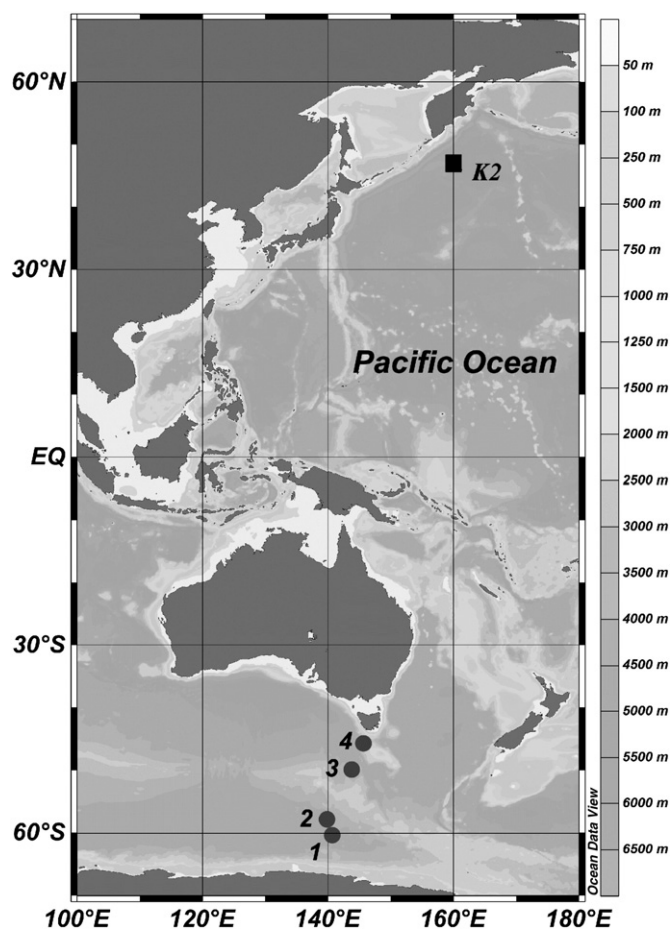


Fig. 2. Map of the sampling station K2 (Northwest Pacific) and stations 1 to 4 in the Southern Ocean.

Teflon-lined Niskin bottles (10 L) deployed off a Kevlar cable were used to collect surface sea water, up to a depth of 50 m. Additional surface samples were collected from an inflatable raft upstream from the ship, using clean sampling procedures. Sampling from the vessel occurred on 02/08/2005 and 13/08/2005, with sampling from the raft on 14/08/
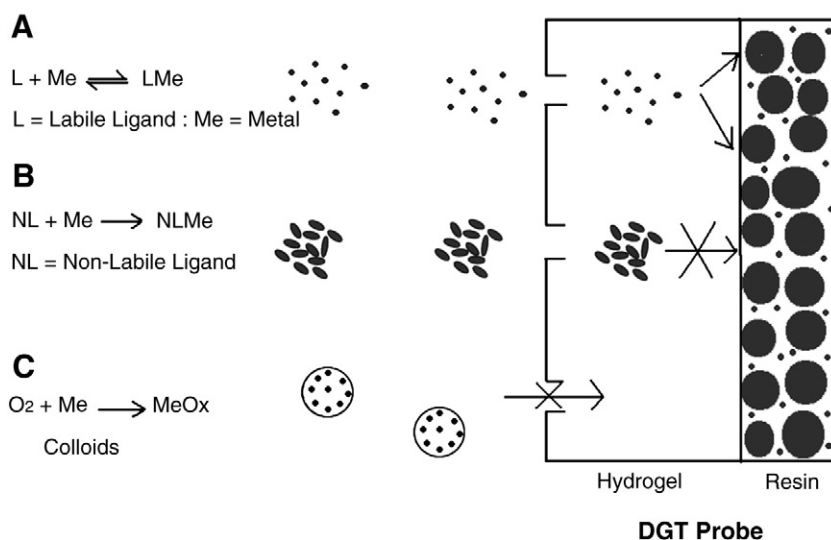


Fig. 1. Schematic view of labile and non-labile trace element compounds diffusing into a DGT probe. Pore-size is about 10 nm for Open-Pored and 1 nm for Restricted-Pored hydrogels.

2005. On 02/08/2005, a 15 L sample was directly poured into a pre-cleaned high density polymer vessel (20 L) containing 5 DGT devices (Open Pored DGTs) and two 0.5 L aliquots (unfiltered seawater) were taken from the container and stored in Teflon bottles (pH<3) for later analysis of TD trace metal concentrations. The 20 L container was stored between 5 and 10 °C and the seawater was frequently homogenized by gentle shaking the container. On 13/08/2005, two 0.5 L aliquots (unfiltered seawater) were also taken from the container and stored in Teflon bottles (pH<3) for later analysis of TD trace metal concentrations, before the seawater in the container was refreshed with a new 15 L sample. On 24/08/2005, again two 0.5 L aliquots (unfiltered seawater) were taken from the container and stored in Teflon bottles (pH<3) for TD analyses. The DGT probes were then recovered, stored in sealed double layered plastic bags and kept at 4 °C, together with 2 blank DGT probes.

For the SR3-GEOTRACES cruise in the Southern Ocean (Fig. 2), samples were collected using externally-closing, Teflon-lined Niskin-1010X bottles (5 L) deployed on an autonomous 1018 intelligent rosette system specially adapted for trace metal work (General Oceanics, USA) and suspended on Kevlar rope. Sampling occurred on 26/03/2008 at station #1 (60.4 °S, 140.7 °E), on 4/04/2008 at station #2 (57.9 °S, 139.9 °E), on 11/04/2008 at station #3 (49.9 °S, 143.8 °E), and on 14/04/2008 at station #4 (45.7 °S, 145.67 °E). The DGT experiments (Open-Pored and Restricted-Pored DGTs) were run in the same way as during the VERTIGO-K2 cruise, except that they lasted for 7 weeks (i.e., DGTs remained in the sample solution for 7 weeks) and at a temperature of 4 °C. At the end of 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.

## 3. 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, 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.

### 3.1. Nitric acid

Ultrapure nitric acid was obtained through distillation of concentrated $HNO_3$ (Merck, Pro Analysis) using an all-Teflon sub-boiling still. Buffer: An ammonium acetate buffer was prepared by diluting a solution of 22.5 mL ammoniumhydroxide ($NH_4OH$; Merck, Suprapur) and 11.8 mL acetic acid ($CH_3COOH$; Merck, Suprapur) up to 100 mL with Milli Q water (Millipore). Complexant: 1.0 g Ammonium Pyrolidine DithioCarbamate (APDC; Merck, Pro Analysis) and 1.0 g Diethylammonium Diethyl DithioCarbamate (DDDC; Merck, Pro Analysis) were dissolved in 1 mL $NH_4OH$ (Suprapur) and diluted to 100 mL with Milli Q water. The clean up of this solution involved a three times extraction with 20 mL freon. The solution was freshly prepared every 3 days. Freon: 400 mL freon (Pro Analysis) was washed three times with 5 mL sub boiled nitric acid in a 1000 mL Teflon separatory funnel.

Between 200 and 400 g of sample or blank (Milli Q water) was weighed and brought to a pH of 4.5 to 5.0 by means of the ammonium acetate buffer, in order to obtain optimal complexation. The pH was immediately checked and if required, additional buffer was added. To the buffered solution 2.5 mL complexant (solution of 1% APDC/1% DDDC) was added. The metal complexes were then extracted in three

steps: for the first extraction, 10 mL of freon was added, the funnel shaken vigorously for 2 min, the phases separated over 5 min and the freon phase then layered off into a second separation Teflon funnel; for the second extraction, 5 mL of freon was added, with the further steps identical to that of the first extraction; the third extraction was identical to the second one. All 3 Freon layers were collected in the second separation Teflon funnel, to which 200 μL of $HNO_3$ was added, and allowed to react for 15 min. Six mL of Milli Q water was then added, the funnel shaken for 1 min, and 5 mL of the upper aqueous phase transferred to a 10 mL polypropylene tube and stored at 4 °C. These samples were analysed by high resolution inductively coupled – mass spectrometry (ICP-MS; Thermo Finnigan Element2). The NASS5 reference material (from the National Research Council, Canada) was analyzed after Freon extraction along with the samples. Agreement between reference and our measured values after Freon extraction was satisfactory (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 μL of a mixed isotope spike of 49.34 μg L$^{-1}$ of Fe (57), 54.00 μg L$^{-1}$ of Cd (111) and 62.95 μg 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 concentrations of Cd, Cu and Fe obtained with the isotope dilution method were very 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 (http://www.quasimeme.org/structure.htm).

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, 2007). Half of the eluted volume (2 mL) was analyzed after 5 times dilution, while 40 μL of the same mixed isotope spike 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.

## 4. 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 ~140°E 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 and 7 weeks in the Southern Ocean).

For each of the considered trace elements, a certain fraction of their TD pool will likely be non-bioavailable to phytoplankton (Zhang and Davison, 2000; Morel and Price, 2003). These non-available fractions of the TD pool are most pronounced for Fe, Cu and Mn, as can be seen from the percentages of each of the 3 trace element pools (0–1 nm, 1–10 nm and 10 nm-TD) averaged over all stations (Fig. 3). Although the percentages for each of the individual element pools vary between the stations (Table 1), the general trend remains the same. In the Northwest Pacific, the TD and <10 nm concentrations are very similar for several elements (Co, Cd, Ni, Pb), while for others like Fe and Cu, the concentrations in the size class <10 nm measured by
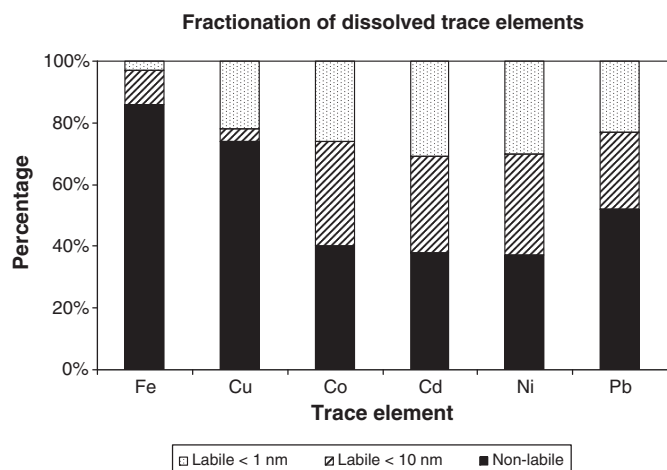
**Fractionation of dissolved trace elements**



**Fig. 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.

DGT are by far lower than the TD concentrations (Table 2). Even when we take into account the rather large uncertainties on those small to very small concentrations (on the TD concentrations, RSDs are up to 20%, see Table 2 where averages and STDs are reported, and are thus of the same magnitude as the differences found on the reference sea water sample NASS5), they had no influence on the conclusions we can draw between the 3 trace element pools (0–1 nm, 1–10 nm and 10 nm-TD). For example TD Fe is between 4 and 14 times higher than the <10 nm fraction and the latter is between 3 and 7 times higher than the <1 nm fraction.

Fe and Cu are known to be mainly present in the dissolved phase as colloids or as complexes that are strongly bound to ligands and thus unlikely to form labile complexes (Wells, 2002; Morel and Price, 2003). At all stations in the Southern Ocean, the trace 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 the TD. At Southern Ocean stations 3 and 4, we observe still lower concentrations (TD and labile) of almost all trace elements examined, compared to the two most southerly stations (1 and 2). The <1 nm concentrations are only assessed in the Southern Ocean: (1) at stations 1 and 2, low <1 nm/<10 nm ratios are observed for Fe and Mn, indicating that the fraction <1 nm is small compared to that between 1 and 10 nm; (2) at stations 3 and 4, despite the fact that for all elements the <10 nm/TD ratios are the lowest of all stations, we observe a further decrease from the <10 nm to the <1 nm levels for Co, Mn and Ni.

It is difficult to compare our total and labile, size fractionated trace element concentrations to the limited literature data set because: (1)

**Table 1**

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

|  | Fe | Cu | Co | Cd | Mn | Ni | Pb |
|---|---|---|---|---|---|---|---|
| *VERTIGO station K2* |  |  |  |  |  |  |  |
| % <10 nm/TD | 10 | 21 | 100 | 100 | 44 | 100 | 82 |
|  |  |  |  |  |  |  |  |
| *ANTAR Geotraces, stations # 1 & 2* |  |  |  |  |  |  |  |
| % <10 nm/TD | 27 | 35 | 47 | 61 |  | 48 | 45 |
| % <1 nm/TD | 4 | 32 | 44 | 45 | 30[a] | 44 | 38 |
|  |  |  |  |  |  |  |  |
| *ANTAR Geotraces, stations # 3 & 4* |  |  |  |  |  |  |  |
| % <10 nm/TD | 7 | 14 | 33 | 24 |  | 40 | 16 |
| % <1 nm/TD | 3 | 12 | 8 | 16 | 33[a] | 15 | 8 |

[a] For Mn the ratio <1 nm/<10 nm is presented.

our concentrations are time averages over several weeks while literature data reflect short-term conditions; (2) our samples were collected from surface to 50–100 m depth; and (3) due to heterotrophic enzymatic activity and without phytoplankton uptake in the DGT experiments, the size fractionated concentrations can increase with time by bio-degradation of macromolecules containing the trace elements. In fact, our DGT results represent the amount of trace elements that are, considered over a time period of several weeks, bioavailable to the phytoplankton community. Although it is impossible at this moment to quantify the effect of microbial activity on the size fractionated concentrations observed, we performed some additional measurements in the Northwest Pacific that allow us to get a better insight in the magnitude of that process. During the Vertigo experiment at K2, ammonium regeneration as well as bacterial mineralization rates were assessed with two different methods (Elskens et al., 2008). Both rates compared very well, with average values of 0.1 and 0.06 μM-N h$^{-1}$ for ammonium regeneration and bacterial mineralization, respectively. In terms of phosphorus by using the Redfield ratio of 16 for N/P, this means a regeneration rate of the order of 5.2 nM h$^{-1}$. In the literature we can find some ranges of Me/P ratios in phytoplankton and as a first approximation we will assume that those ratios are maintained during organic matter regeneration. We will consider two extreme cases: an element with a very low labile fraction (Fe) and one with a high labile fraction (Co), see Table 2. The Me/P ratios reported in the literature can vary a lot depending, for example, on the phytoplankton species, the way they are determined (in vitro or in situ) and for in vitro determinations even the season of sampling. Considering only open ocean diatoms and flagellates, Fe/P ratios vary from $1.1 \times 10^{-3}$ (Ho et al., 2003) to $0.63 \times 10^{-3}$ (Twining et al., 2004), while for Co/P only Ho et al. (2003) reported a value, being $0.14 \times 10^{-3}$. Due to microbial activity, the daily regeneration of Fe in these conditions ranges from 3.3 to 5.8 pM-Fe h$^{-1}$ and amounts for Co to 0.75 pM-Co h$^{-1}$. These regeneration rates are initial rates related to the consumption of the most labile DOC compounds and will only last during a limited time period. Once the most labile DOC compounds are exhausted the regeneration rates rapidly decline. Using the multi-G model of Berner, Chen and Wangersky (1996) studied the DOC decay rates for a natural phytoplankton assemblage (off the coast of Nova Scotia, Canada). If we assume similar sizes for the 4 DOC pools (11, 5.8, 13.7 and 15.5% from very labile to more refractive) and we apply the corresponding decay rates (0.12, 0.03, 7.7 10$^{-3}$ and 2.9 10$^{-3}$ d$^{-1}$) on our system, after 3 weeks 0.25 nM Fe and 0.046 nM Co are regenerated from the DOC pool. Although DOC pool sizes and their decay rates are probably different in the Northwest Pacific, it is surprising to notice that the calculated regenerated Fe and Co concentrations 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 degradation of DOC in HNLC oceanic areas.

In Table 3, an overview of trace element concentrations reported in the literature and unpublished Fe data from the SR3-GEOTRACES Antarctic cruise are presented. Despite the differences in experimental design, sampling and analytical techniques, these literature data reflect the same range of concentrations as our data.

Depending on the region and the season, different elements can limit primary productivity of the HNLC oceans (Moore et al., 2004). Nitrogen is usually the most important phytoplankton growth limiting element, including most regions of the Pacific Ocean (Falkowski et al., 1998), but in HNLC regions such as the subarctic North Pacific Ocean and the Southern Ocean, it has been shown that low levels of Fe are entirely or partly responsible for the under-utilization of the major nutrients and the lower than expected chlorophyll levels (e.g. Martin and Fitzwater, 1988; Boyd et al., 2000). However, an important remaining question is whether phytoplankton primary productivity is limited by the labile concentrations of trace elements other than Fe, and if so, (1) which one's and (2) is this co-limitation the same in the Northwest Pacific and the Southern Ocean? In prior studies of the Peru upwelling region, Co

**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.

|  | P | Fe | Cu | Co | Cd | Mn | Ni | Pb |
|---|---|---|---|---|---|---|---|---|
| *Element concentrations in nM (VERTIGO)* | | | | | | | | |
| 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 |  | 0.30 | 0.31 | 0.056 | 0.40 | 0.74 | 4.04 | 0.046 |
| STD |  | ±0.08 | ±0.03 | ±0.005 | ±0.03 | ±0.08 | ±0.32 | ±0.005 |
| *Element concentrations in nM (SR3-GEOTRACES, stations # 1 & 2)* | | | | | | | | |
| 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)* | | | | | | | | |
| 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 |

scarcity and speciation was found to influence phytoplankton species composition (Saito et al., 2004) and Fe, Mn, Cu and Zn were found to be co-limiting productivity in the subarctic Pacific Ocean (Coale, 1991). In studies on phytoplankton cultures, several co-limitations were observed: for example Peers and Price (2004) found Fe and Mn to be co-limiting.

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

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

|  | P | Fe | Cu | Co | Cd | Mn | Ni | Pb |
|---|---|---|---|---|---|---|---|---|
| *Element concentrations (nM) around K2* | | | | | | | | |
| TD (Brown et al., 2005) |  | 1.33–3.16 |  |  |  |  |  |  |
| <0.2 µm dissolved (idem) |  | 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)* | | | | | | | | |
| <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) |  |  | 0.5–1.2 |  | 0.012–0.35 |  | 3.0–5.0 | 0.012–0.022 |
| <0.2 µm dissolved (SR3-GEOTRACES cruise, unpublished results) |  | 0.08 |  |  |  |  |  |  |

## 5. Conclusion

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

Supplementary materials related to this article can be found online at doi:10.1016/j.marchem.2011.04.004.

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