

2018-01-20

# Impact of surface ocean conditions and aerosol provenance on the dissolution of aerosol manganese, cobalt, nickel and lead in seawater

Fishwick, MP

<http://hdl.handle.net/10026.1/10450>

---

10.1016/j.marchem.2017.11.003

Marine Chemistry

Elsevier

---

*All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.*

# **Impact of surface ocean conditions and aerosol provenance on the dissolution of aerosol manganese, cobalt, nickel and lead in seawater**

Matthew P. Fishwick, School of Geography, Earth and Environmental Sciences, University of Plymouth, UK

Simon J. Ussher, School of Geography, Earth and Environmental Sciences, University of Plymouth, UK

Peter N. Sedwick, Ocean, Earth & Atmospheric Sciences, Old Dominion University, Virginia, USA

Maeve C. Lohan, University of Plymouth, UK; Present address: Ocean and Earth Sciences, National Oceanography Centre, University of Southampton, UK

Paul J. Worsfold, School of Geography, Earth and Environmental Sciences, University of Plymouth, UK

Kristen N. Buck, Bermuda Institute of Ocean Sciences, Bermuda; Present address: College of Marine Science, University of South Florida, Florida, USA

Thomas M. Church, College of Earth, Ocean, and Environment, University of Delaware, Delaware, USA

Corresponding author: Simon J. Ussher, School of Geography, Earth and Environmental Sciences, B519 Portland Square, University of Plymouth, Plymouth, PL4 8AA, UK (sussher@plymouth.ac.uk)

## Highlights

- Simulated ocean warming, ocean acidification and anoxia had little impact on the dissolution of aerosol Co, Mn, Ni and Pb in surface seawater
- Aerosol provenance and chemical speciation exerted the greatest control on Co and Pb dissolution, with combustion-associated processes (indicated by trace metal enrichment factors), enhancing solubility
- Linear relationships between enrichment factors and fractional solubility were found, which are useful in estimating solubility of Fe, Co and Pb in global data sets
- Size fractionation of seawater leaches showed that aerosol derived dissolved Pb was mostly colloidal (0.02-0.4  $\mu\text{m}$ ), dissolved Mn and Co were mostly soluble ( $< 0.02 \mu\text{m}$ ), and dissolved Ni displayed a mixed size distribution

## Keywords

Trace metals; manganese iron; cobalt; nickel; lead; aerosols; Sargasso Sea; fractional solubility; dissolution; global environmental change; anthropogenic aerosols; mineral dust

## Abstract

Atmospheric deposition is an important pathway by which bioactive trace metals are delivered to the surface ocean. The proportions of total aerosol trace metals that dissolve in seawater, and thus become available to biota, are not well constrained and are therefore a key uncertainty when estimating atmospheric fluxes of these elements to surface waters. The aim of this study was to elucidate the main physico-chemical controls on the dissolution of the bioactive trace metals manganese (Mn), cobalt (Co), nickel (Ni) and lead (Pb). To this end, aerosol and surface seawater samples were collected in the Sargasso Sea and subsequently used in sequential seawater leach dissolution experiments to assess the role of aerosol source, seawater temperature, pH, and concentrations of dissolved oxygen and organic ligands, on aerosol trace metal dissolution.

Results reveal that changes in key physico-chemical parameters in seawater leaches had little effect on the proportions of Mn, Co, Ni and Pb released from aerosols, although organic ligand amendments impacted the size distribution of aerosol-derived Mn in solution. Conversely, aerosol source and composition had the most significant effect on the dissolution of aerosol Co and Pb, with the most 'anthropogenic' aerosol samples displaying the highest fractional solubilities in seawater (up to 58% for Co and 112% for Pb).

Fractional solubilities over the range of samples and conditions tested were in the range of 50-104% for Mn, 29-58% for Co, 40-85% for Ni and 67-112% for Pb. A large proportion (36-100%, median 89%) of the total dMn, dCo, dNi and dPb was mobilised rapidly during the first leaching step (5 min), with less dTM being released in leaches 2 through 4. Furthermore, investigation of the size distribution of the aerosol-derived trace metals in seawater showed that dissolved Pb was mostly

colloidal (0.02-0.4  $\mu\text{m}$ ), dissolved Mn and Co were mostly soluble ( $< 0.02 \mu\text{m}$ ), and dissolved Ni displayed a mixed size distribution. Good empirical relationships were observed between enrichment factors for aerosol antimony (Sb) and the fractional solubilities of aerosol Fe, Co and Pb, suggesting total aerosol Sb can be useful in estimating and modelling the fractional solubility of these metals using total aerosol trace metal concentrations from historical data.

## Introduction

The past few decades have seen extensive research on the marine biogeochemistry of iron (Fe), due to its importance in controlling phytoplankton processes (Boyd et al., 2000; Coale et al., 1996; Martin et al., 1994; Takeda and Tsuda, 2005). Much less attention has been afforded to the biogeochemistry of other bioactive trace metals, such as manganese (Mn), cobalt (Co) and nickel (Ni), despite them being essential for a range of biochemical functions of marine primary producers, including photosynthesis (Raven, 1990), protein assimilation (Rees and Bekheet, 1982), carbon uptake (Price and Morel, 1990) and nitrogen fixation (Ho, 2013). Such is the importance of Co that it may co-limit marine cyanobacteria growth in a number of ocean regions (Bertrand et al., 2007; Saito et al., 2005; Saito and Goepfert, 2008). Conversely, some trace metals such as lead (Pb) are toxic to marine phytoplankton when present in sufficient concentrations (Rivkin, 1979). However, decreasing Pb concentrations are observed in open ocean surface waters since the global phase-out of leaded gasoline, which began in the late 1970s (Kelly et al., 2009).

Atmospheric deposition of mineral dust and anthropogenic aerosols is an important pathway by which trace metal micronutrients and toxicants are delivered to the surface ocean (Duce, 1986; Jickells et al., 2005). In this context, the Sargasso

Sea near Bermuda is a well-studied area that receives high annual aerosol fluxes, which can dominate the input of a number of trace metals to surface waters (Jickells et al., 2005). This oligotrophic ocean region is situated in the western North Atlantic subtropical gyre, and experiences a pronounced seasonal contrast in the origin and composition of aerosols (Sedwick et al., 2007). During the summer and autumn months, air masses typically deliver mineral dust transported from arid regions of North Africa such as the Sahara or Sahel, whereas during winter and spring the air masses are more likely to carry anthropogenically influenced aerosols carried from North America (Anderson et al., 1996; Sedwick et al., 2007; Sholkovitz et al., 2009). The seasonal delivery of North African dust to the subtropical North Atlantic has been suggested to relieve phosphorus and trace metal co-limitation (Mills et al., 2004). Moreover, observations reported by Moore et al. (2006) suggest that the initiation, duration and magnitude of the spring bloom in the North Atlantic may be modulated by aerosol Fe deposition. Given the biological importance of other atmospherically derived micronutrients and toxicants to marine phytoplankton, it is likely that these trace elements may also influence spring bloom dynamics in the subtropical Sargasso Sea, and thus primary production and carbon export in the region.

It is generally understood that trace metals are most biologically available to marine phytoplankton in their dissolved form (Morel et al., 1991; Shaked and Lis, 2012). Only a fraction of the total mass of trace metal contained within aerosols deposited to the ocean surface will dissolve in seawater. This proportion is quantified as per cent fractional solubility (% $TM_s$ ), and these values have been shown to vary considerably (Buck et al., 2013; Chance et al., 2015; Chester et al., 1993; Hsu et al., 2005; Mackey et al., 2015; Shelley et al., 2012). For example, Shelley et al. (2012) reported % $Co_s$  values in the range of 8-100% in the Sargasso Sea, and Hsu et al.

(2005) reported %Mn<sub>s</sub> and %Ni<sub>s</sub> values in the range of 4-74% and 1-86% in the East China Sea, respectively. The observed wide ranges in %TM<sub>s</sub> values demands an understanding of the key factors constraining the dissolution of bioactive trace elements from aerosols into seawater. A number of studies report the tendency for the %TM<sub>s</sub> of trace metals (e.g., Mn, Co, and Ni) in anthropogenically influenced emissions or combustion aerosols (e.g., fuel combustion products, biomass burning emissions) to be much higher in comparison to corresponding values for mineral dust (Desboeufs et al., 2005; Hsu et al., 2010, 2005; Kocak et al., 2007). Results of these investigations led researchers to postulate that chemical processing during atmospheric transport and/or the source and composition of aerosols are the principal parameters controlling %TM<sub>s</sub> of aerosol trace metals (Baker and Croot, 2010; Shelley et al., 2015).

Whilst numerous studies have examined the relationship between %TM<sub>s</sub> and the physical and chemical properties of aerosols, relatively few studies have focussed on the impact of post-depositional conditions on the dissolution of aerosol trace metals (e.g., Aguilar-Islas et al., 2010; Biscombe, 2004; Bressac and Guieu, 2013; Fishwick et al., 2014; Mackey et al., 2015; Mendez et al., 2010). However, physico-chemical parameters such as temperature, pH and dissolved oxygen (O<sub>2</sub>) concentration impact the speciation and concentration of trace metals in solution (Byrne et al., 1988; Millero, 2013), and therefore influence aerosol trace metal dissolution in seawater. For example, Biscombe (2004) reported increasing Pb solubility with increasing temperature (10.8-25.2°C), and Millero et al. (2009) modelled the speciation and associated solubility changes with pH for Mn, Co, Ni and Pb in seawater. Dissolved O<sub>2</sub> also effects solubility, for example, deoxygenated seawater is known to reduce the

oxidation rates of Mn(II), thereby inhibiting its loss from solution via precipitation (Murray and Tebo, 1991).

The presence and nature of organic ligands is another variable that may impact on the dissolution of aerosol trace metals in seawater. Indeed, the majority (> 90%) of dissolved Co is thought to be bound by organic ligands in surface waters (Bruland, 1989; Buck and Bruland, 2005; Ellwood and van den Berg, 2001) with a substantial proportion of dissolved Mn, Ni and Pb exhibiting complexation (Achterberg and Van Den Berg, 1997; Capodaglio et al., 1990; Donat et al., 1994; Nimmo et al., 1989; Oldham et al., 2015; Saito et al., 2004). Metal-binding organic ligands can be divided into classes ('L<sub>1</sub>', 'L<sub>2</sub>', 'L<sub>3</sub>', etc.) based on conditional stability constants ( $\log K_{ML_i, M'}^{cond}$ , where  $i$  denotes ligand class and  $M'$  denotes all free species of a trace metal). These classifications differ between trace metals; for example, the  $\log K_{ML_1, M'}^{cond}$  for the strongest dominant class of ligands (L<sub>1</sub> ligands) have been defined as having values > 12 for Fe (Gledhill and Buck, 2012), > 16 for Co (Ellwood and van den Berg, 2001) and > 17 for Ni (Donat et al., 1994). Changes in physico-chemical seawater parameters such as temperature and pH may affect the chelation properties of organic ligands (Millero et al., 2009), although relatively few studies have investigated this (Louis et al., 2009; Shi et al., 2010; Xu et al., 2012).

The experimental study described here aims to elucidate the main controls on the dissolution of important trace metal micronutrients (Mn and Co), toxicants (Pb) and metals with both nutritional and toxicological properties (Ni) from aerosols in surface waters of the Sargasso Sea, and to critically compare these findings with those for aerosol Fe dissolution, which was examined in the same experimental study (Fishwick et al., 2014). The process of trace metal dissolution following dry deposition was simulated using representative aerosol and seawater samples, with manipulation of

key post-depositional parameters, specifically: surface seawater temperature, pH, dissolved O<sub>2</sub> concentration and organic ligand content. These parameters are all expected to be impacted by anthropogenic greenhouse gas emissions (IPCC, 2007; Orr et al., 2005; Stramma et al., 2008; Whitney et al., 2007) and, in the case of trace-metal-binding ligands, by anthropogenic aerosol emissions (Heintzenberg, 1989; Wozniak et al., 2013). In addition, the influence of aerosol source and composition on trace metal dissolution was assessed through experiments using aerosol samples collected from the Bermuda region over a full annual cycle. This experimental framework allowed insight into the dissolution kinetics and the size-distribution of aerosol-derived trace metals in seawater, as well as information on dissolution mechanisms.

## Methods

### *Seawater and aerosol sampling*

In order to avoid trace metal contamination, all plastic labware was cleaned following the GEOTRACES protocols detailed by Cutter et al. (2010), and all stages of sample and reagent handling were carried out under a Class-5 laminar flow hood (ISO 14644-1:1999, Bassaire or AirClean units). Ultra high purity (UHP,  $\geq 18.2$  M $\Omega$  cm) deionised (DI) water from Milli-Q (Millipore) or Nanopure (Barnstead) systems was used throughout the work presented here.

Seawater used for aerosol leaches was collected at the Bermuda Atlantic Time-series Study (BATS) site in the Sargasso Sea (31°40' N, 64°10' W) during the spring and summer (April 2010 – July 2011) on three separate cruises on board *R/V Atlantic Explorer* using polyvinylchloride (PVC) 10 L Teflon-lined, external-closure Niskin-type bottles (Ocean Test Equipment). Sampling took place within the subsurface

chlorophyll maximum (~ 60-120 m depth), where concentrations of biologically important trace metals such as Fe are typically lowest (Sedwick et al., 2005). It was necessary to ensure that the trace metal concentrations in collected seawater used in aerosol leaches were as low as possible to allow observation of subtle concentration differences caused by leach conditions. Collected seawater was subsequently filtered through 0.45 µm polytetrafluoroethylene (PTFE) Osmonics membrane capsules (GE Water Systems) via gravity filtration and stored in darkness in an acid cleaned polyethylene carboy under ambient clean room laboratory conditions for no longer than three months before being used in the leaching experiments.

Four aerosol samples were collected from the Tudor Hill atmospheric observatory on the southwest coast of Bermuda (32°15.95' N, 64°52.65' W) from 13 July-20 August 2009 (sample AER 1), 27 September-11 October 2010 (sample AER 2), 22 February-10 May 2010 (sample AER 3), and 11 October-13 December 2010 (sample AER 4). The total volume of air sampled for AER 1, AER 2, AER 3 and AER 4 over these sampling periods was 8,620 m<sup>3</sup>, 10,519 m<sup>3</sup>, 35,356 m<sup>3</sup> and 24,243 m<sup>3</sup>, respectively. The samples were collected using a high volume aerosol sampler, on 8" x 10" sheets of 2.2 µm pore size quartz microfiber (QMA) Whatman filters (GE Healthcare), which were previously acid-washed following Morton et al. (2013). The aerosol sampler was located on top of a 23 m high aluminium scaffolding tower, approximately 50 m above sea level. To ensure only marine air was sampled, pumps were switched off when the wind direction was not in the onshore sector (210-315°), or if the wind speed was less than 1 m s<sup>-1</sup>. For a procedural field blank, an aerosol filter was loaded in the aerosol sampler (with pumps off) and then removed after 5 min. After collection, aerosol samples were transferred into zip-lock bags and stored frozen at -20°C for 6-24 months before use.

QMA filters were chosen as high aerosol loading was needed to allow the filter to be subsampled multiple times for replicate leaching experiments. QMA filters are also less susceptible to tearing and clogging when deployed for long periods (i.e. weeks). We note that QMA blanks for total concentrations of some trace metals can be relatively high compared to typical aerosol loadings (Morton et al., 2013). To mitigate for this blank contribution, sampling was conducted over long periods of time (14 – 63 days) resulting in high loading of these metals. In the worst cases, procedural field blanks contributed to ~ 70% Cr and ~ 58% Al of the total concentrations of trace metals in aerosol samples. However, the relative standard deviation (RSD) on mean total concentrations of replicate blank subsamples for these metals was low (< 2%,  $n = 3$ ). For Mn, Fe, Co, Ni and Pb, procedural field blank contributions to total concentrations in aerosol samples were lower: ~ 17%, ~ 9%, ~ 19%, ~ 38% and ~ 26%, respectively. Table S1 (Supplementary Material) provides the contribution of procedural field blanks to aerosol samples AER 1 – 4 for all total trace metal determinations.

### *Seawater preconditioning*

Aliquots of 0.45  $\mu\text{m}$ -filtered BATS seawater were preconditioned before being used in the leaching experiments. Filtered seawater aliquots used in the temperature experiments were preconditioned by equilibrating to 25°C and 4°C, using a temperature controlled laboratory and a thermostatically regulated refrigerator, respectively. Filtered seawater aliquots used in the seawater pH experiments were preconditioned by sparging with filtered air/CO<sub>2</sub> produced mixtures using mass flow controllers (Aalborg) for 48-72 h until a stable pH was reached, following the method described by de Putron et al. (2011). This preconditioning simulated atmospheric CO<sub>2</sub>

concentrations of 400 ppm CO<sub>2</sub> (present-day conditions) and 1,250 ppm CO<sub>2</sub> (possible future scenario), with seawater pH values of 8.0 ('ambient seawater') and 7.6 ('acidified seawater'), respectively, calculated using the total pH scale from dissolved inorganic carbon and alkalinity with the software CO<sub>2</sub>sys (Pierrot et al., 2006). Similarly, anoxic conditions (< 0.1% O<sub>2</sub> saturation) were achieved by sparging filtered seawater with filtered nitrogen (N<sub>2</sub>) gas (for leaches 3 and 4 only). Anoxic experiments were only conducted in the 3<sup>rd</sup> and 4<sup>th</sup> leaches of a sequence to mimic particles falling through oxic surface water into suboxic waters beneath. For the organic ligand amendment experiments, filtered seawater aliquots used for leaches were preconditioned through the addition of a strong siderophore L<sub>1</sub>-type Fe-binding ligand, using 10 nM of either aerobactin (EMC Microcollections) or desferrioxamine-B (Sigma-Aldrich); or weaker less specific ligands, using either 10 nM protoporphyrin-IX (Sigma-Aldrich) or 1 μM glucuronic acid (Sigma-Aldrich). Conditional stability constants for these organic ligands with respect to trace metal complexation are presented in Table 1.

### *Aerosol leaching experiments*

Aerosol leaching experiments were designed to replicate the process of dry deposition in the open ocean as closely as possible within the laboratory. Triplicate subsamples from each aerosol filter sample were taken using a 20 mm diameter polished steel arch punch (Osborne) and allowed to thaw at room temperature before being used for each different seawater treatment in the aerosol leaching experiments. Leaches were performed on these triplicate subsamples from each of the four aerosol filter samples, for each seawater treatment, using an acid-washed PFA filtration tower (Savillex). This comprised a 47 mm perfluoroalkoxy (PFA) filter assembly clamp, 250

mL evacuated Teflon collection vessel and 0.25 inch diameter PTFE tubing. The PTFE tubing was used to connect the collection vessel to a vacuum pump (GAST) via a 0.2  $\mu\text{m}$  Acrovent air filter (Pall Corporation) and water trap. Acid-washed 0.4  $\mu\text{m}$  pore size, 47 mm polycarbonate track-etched membrane filters (Nucleopore, GE Healthcare) were used to separate 'dissolved trace metals' in the aerosol leachate solutions.

The aerosol leaching process involved four sequential leaches to test different equilibration times (leach 1 = 0-5 min, leach 2 = 5-10 min, leach 3 = 10 min-48 h, and leach 4 = 48 h-30 d). These leaching times were chosen to represent the range of time that aerosol particles typically reside in the upper surface ocean. For leach 1, a 20 mm diameter aerosol-filter subsample was placed on the 0.4  $\mu\text{m}$  pore size polycarbonate filter mounted within the filtration tower (under vacuum) and 250 mL of preconditioned filtered seawater was poured over the aerosol filter in a continuous (5 min) leaching process, with the resulting leachate collected.

The process for leach 1 was repeated for leach 2 using the same aerosol subsample used in leach 1. Leaches 3 and 4 were batch leaches where the same aerosol subsample and polycarbonate filters used in leaches 1 and 2 were placed in fluorinated polyethylene (FPE, Nalgene) bottles along with 500 mL of preconditioned filtered seawater and left for 48 h and 30 days, for leaches 3 and 4, respectively. Only negligible adsorption of dissolved trace metals to bottle walls was observed in previous studies employing an aerosol batch leach methodology where fluorinated polymer bottles were used (Séguret et al., 2011). Before batch leaches took place FPE bottles were first preconditioned for 24 - 72 h with filtered BATS seawater to further minimize the effect of wall adsorption of dissolved trace metals. The seawater leachate solutions that passed through acid-washed 0.4  $\mu\text{m}$  pore size polycarbonate filters in

each sequential leach were subsequently decanted into acid-washed 125 mL LDPE bottles (Nalgene). The entire leaching process was conducted in triplicate for every experimental treatment.

To determine 'colloidal trace metals' and 'soluble trace metals' (cTM and sTM, respectively, where 'TM' is Mn, Co, Ni or Pb), 125 mL of seawater leachate samples were filtered through 0.02  $\mu\text{m}$  pore size, 25 mm diameter aluminium oxide Whatman Anotop syringe filters (GE Healthcare) and the filtrate collected in acid-washed 60 mL LDPE bottles (Nalgene). Briefly, this inline filtration method involved transferring dTM seawater leachate samples from 125 mL to 60 mL LDPE bottles at 1 mL  $\text{min}^{-1}$  via 0.8 mm internal diameter PFA manifold tubing (Cole Palmer Instruments) attached to Anotop filters using a six-channel peristaltic pump (MiniPuls3, Gilson) and 2-bridge accurate PVC peristaltic pump tubing [Elkay, Tyco Healthcare]. Anotop filters were set-up, cleaned and conditioned following the method described in Ussher et al. (2010). In the study presented here, following the definitions of Wu et al. (2001), 'dissolved trace metals' (dTM) are defined as those contained in the  $< 0.4 \mu\text{m}$  filtrate, and sTM are defined as those contained in the  $< 0.02 \mu\text{m}$  filtrate. Colloidal trace metals were then calculated as the difference between dTM and sTM concentrations (i.e.,  $\text{cTM} = \text{dTM} - \text{sTM}$ ), thus representing the 0.02-0.4  $\mu\text{m}$  size fraction.

Following aerosol leaches, all seawater leachate samples and blanks were acidified to  $\text{pH} \sim 1.6$  using concentrated hydrochloric acid (Romil, Ultra-pure Acid, UpA) and stored for  $> 1$  year before analysis. Process blanks were defined as the contribution of all sample handling as well as the original concentration of metals in the seawater used. These were performed in triplicate and prepared by passing the same ambient filtered seawater used for a particular leach over an aerosol filter field blank subsample and an acid-washed 47 mm PCTE filter. The concentrations of dMn,

dCo, dNi and dPb in process blanks were typically < 0.78 nM, < 0.022 nM, < 2.1 nM and < 0.037 nM, respectively. Following analysis, the dTM concentrations of the relevant process blanks were subtracted from respective dTM concentrations of all leachate samples.

#### *Dissolved trace metal determinations*

Concentrations of the dissolved and soluble size fraction of Mn, Co, Ni and Pb in aerosol leaches were determined using flow injection inductively coupled plasma-mass spectrometry (FI-ICP-MS) inside a class 5 clean room (ISO 14644-1), based on the method described by Clough et al. (2015). The method involved passing seawater leachate samples over a chelating column containing Toyopearl AF-Chelate-650 M iminodiacetate resin (IDA, Tosoh Bioscience) for 5 min at 1.5 mL min<sup>-1</sup> in order to remove the seawater matrix and preconcentrate the analytes. Prior to loading on the chelating column, the pH of each acidified sample was adjusted to pH 6.2 by spiking with 2 M ammonium acetate (Romil, Super-pure grade, SpA), which was undertaken off-line immediately before analysis to avoid precipitation of metals from solution. High recovery rates (> 90%) of a number of trace metals (Fe, Co, Ni and Pb) concentrated from seawater on to Toyopearl-AF-Chelate-650M IDA resin at pH 6.4 have been reported (Milne et al., 2010). Whilst lower recovery rates for Mn (~60%) at this pH are reported, reproducible extraction can be achieved with careful control of sample pH (Milne et al., 2010).

Following column loading, major seawater matrix cations were removed using a pH 6.2, 0.05 M ammonium acetate (Romil, SpA) rinse for 1 min. Finally, chelated trace metals were eluted from the column using 1 M nitric acid (Romil, SpA) for 2 min, which was directly injected directly into an X-Series 2 ICP-MS (Thermo Fisher) in time

resolved analysis mode (Clough et al., 2015). To account for instrumental drift, a mid-range concentration calibration standard was analysed after every ten samples and any change in sensitivity was applied to the previous ten samples equally. In addition, the 1 M nitric acid eluent was spiked with a rhodium internal standard (Romil) to a final concentration of  $10 \mu\text{g L}^{-1}$ , and counts of this element were monitored throughout the analysis. Following elution, the chelating column was washed with a pH 6.2, 0.05 M ammonium acetate solution for 15 s to condition the resin to this higher pH before loading the next sample. To minimise polyatomic interferences, a collision cell with a helium gas flow rate of  $3.5 \text{ mL min}^{-1}$  was used, which gave cerium oxide to cerium ratios ( $^{140}\text{Ce}^{16}\text{O}:^{140}\text{Ce}$ ) of  $< 0.1\%$ .

Trace metal concentrations were quantified using the method of standard additions of a multi-element standard to low trace metal concentration seawater, which was subsampled from the original filtered seawater sample used for leaches. The multi-element standard was prepared in a solution of 0.024 M hydrochloric acid (HCl) by serial dilution of individual standards of Mn, Co, Ni and Pb (Romil). A number of concentration ranges of each element were used to span the range of concentrations anticipated in seawater leachates, based on the results of previous ICP-MS analysis of aerosol leaches using UHP DI water (data not shown). Each day at least one sample was analysed in triplicate, to estimate overall analytical precision for that day (i.e., analytical and extraction precision combined). This precision was typically better than  $\pm 5\%$  relative standard deviation (RSD,  $n = 3$ ). The accuracy of the FI-ICP-MS method was regularly assessed by analysing SAFe and GEOTRACES reference seawater and comparing measured concentrations with the published consensus values (K. Bruland, unpublished data, 2008, available at <http://es.ucsc.edu/~kbruland/GeotracesSaFe/kwbGeotracesSaFe.html>). Measured

concentrations were typically within the range of the consensus values, when the analytical precision of the measured and consensus values are considered (Supplementary Material - Table S2). The exception was Co, for which measured concentrations were often lower (10 – 30%) than the consensus values, which likely reflects organically complexed Co. Natural seawater samples are known to require UV irradiation in order to free all complexed Co (Milne et al., 2010; Shelley et al., 2010), which was undertaken for the consensus values. However, this treatment was not performed on leachate samples in this study, due to concerns of contamination. Accuracy of Co determination was not critical to enable conclusions to be drawn from comparative results of this study, however, it should be noted that fractional solubility values for Co presented here are likely to be underestimated.

#### *Total aerosol trace metal determinations*

Triplicate 20 mm diameter subsamples of AER 1-4 and filter blanks were subjected to a three-step acid digestion using concentrated hydrofluoric acid (28.9 M, Seastar, Baseline), concentrated nitric acid (15.8 M, Seastar, Baseline) and heat (Morton et al., 2013), at the University of Delaware. As the process of acid digestion destroys the subsamples, it was necessary to use different subsamples of each aerosol sample in the aerosol leaching experiments and use the mean total amount of each trace metal in fractional solubility calculations. Total elemental determinations were subsequently performed for the digest solutions at Old Dominion University using an Element2 (Thermo Finnegan) ICP-MS in medium resolution mode. Calibration standards were prepared by serial dilution of a multi-elemental standard (QC Standard 4, PlasmaCal, containing aluminium [Al], titanium [Ti], manganese [Mn], vanadium [V], chromium [Cr], Fe, cobalt [Co], nickel [Ni], copper [Cu], zinc [Zn], cadmium [Cd],

antimony [Sb] and lead [Pb]) in the same 2% (v/v) HNO<sub>3</sub> matrix as the aerosol digest solutions. All samples and standards were spiked with indium as an internal standard.

## Results and discussion

### *Aerosol source and composition*

Aerosol samples used in this study were collected in the summer (13 July to 20 August 2009, AER 1), summer/autumn (27 September to 11 October 2010, AER 2), spring (22 February to 10 May 2010, AER 3) and winter (11 October to 13 December 2010, AER 4), thus representing integrated bulk samples for a full seasonal cycle. Daily air mass back trajectories for these samples are presented by Fishwick et al. (2014), and indicate that air masses mostly travelled from east to west during the sampling of AER 1 and AER 2, and from the northwest during the sampling of AER 3 and AER 4. A seasonal shift between air masses carried from North Africa in summer and from North America in winter has been clearly established for the Bermuda region (Anderson et al., 1996; Chen and Duce, 1983; Church et al., 1990; Duce and Hoffman, 1976; Sedwick et al., 2007; Sholkovitz et al., 2009). Therefore, it is likely that the summer samples (AER 1 and AER 2) were dominated by soil dust entrained from the Sahara or Sahel regions, whereas the winter samples (AER 3 and AER 4) contained a greater proportion of aerosols entrained from North America, including anthropogenic combustion emissions.

Total element determinations in subsamples of AER 1-4 allowed an examination of differences in aerosol compositions relative to presumed source regions. The total mass of each element in these aerosols was normalised to aluminium (Al), a well-known lithogenic aerosol tracer (Chester et al., 1993; Shelley et al., 2015), and bulk element-to-aluminium ratios were compared with those of average upper continental

crust taken from Taylor and McLennan (1995) to calculate enrichment factors and hence infer non-crustal, 'anthropogenic' contributions (Figure 1 and Table 2). Enrichment factors greater than 10 for metals such as vanadium (V), Ni, copper (Cu), cadmium (Cd), antimony (Sb) and Pb are indicative of anthropogenic activities such as fossil fuel combustion, metal smelting and mining operations (Chester et al., 1999; Csavina et al., 2012; Grousset et al., 1995; Prospero, 2002). Consistent with air-mass back trajectory analysis, sample AER 4, collected in the winter, was far more enriched with anthropogenic trace metals (i.e., V, Ni, Cu, Cd, Sb and Pb) compared with aerosol samples collected in the summer (AER 1 and AER 2; Figure 1 and Table 2). For example, Sb was enriched by an order of magnitude in AER 4 vs AER 1 ( $660 \pm 20$  vs  $66 \pm 7$ , respectively), and there was also nearly an order of magnitude difference between the Cd enrichment in these aerosol samples ( $230 \pm 40$  for AER 4 vs  $26 \pm 4$  for AER 1).

Atmospheric trace metal loadings were calculated using the total elemental determinations for AER 1-4 and corresponding volumes of filtered air. Summer atmospheric loadings of Al, titanium (Ti) and Fe were consistently higher than those estimated from the winter aerosol samples, as expected for air masses dominated with mineral aerosols (Baker et al., 2006a; Buck et al., 2010a; Séguret et al., 2011; Shelley et al., 2015), and consistent with back trajectory analyses. The results presented here suggest that the aerosol samples collected at Tudor Hill contain a greater proportion of anthropogenic material and a lesser proportion of lithogenic material in the winter relative to the summer, in accord with previous work (Sedwick et al., 2007). Visual inspection of aerosol samples also supports this observation, with winter samples displaying a distinctive dark grey colouration, indicative of pollution components, whereas summer samples were orange-brown in colour, indicating the presence of

North African soil dust. Thus the sample nomenclature of AER 1-4 reflects the relative proportion of anthropogenic components, with AER 1 representing aerosols rich in mineral dust, and AER 4 representing a higher proportion of anthropogenic materials.

#### *Effect of seawater temperature, pH and de-oxygenation on aerosol trace metal dissolution*

The experimental simulations of trace metal dissolution following dry deposition to the ocean provide insight into the proportion of each trace metal contained in aerosols that dissolved in seawater under different physico-chemical conditions. The total amount of dTM leached from each aerosol sample (AER 1-4) into preconditioned seawater samples at different temperature, pH and O<sub>2</sub> concentrations was calculated by multiplying the blank-corrected dTM concentrations determined by FI-ICP-MS by the volume of seawater used for each sequential leaching step (250 mL for leaches 1 and 2, and 500 mL for leaches 3 and 4). The mean total amount of dissolved manganese (dMn), cobalt (dCo), nickel (dNi) and lead (dPb) leached from each aerosol sample (AER 1-4) with 4°C and 25°C seawater is shown in Figure 2, where the mean totals represent the sum of all dMn (Figure 2A), dCo (Figure 2C), dNi (Figure 2E) or dPb (Figure 2G) released during the four sequential leaches. The mean total dTM leached under these seawater conditions ranged from 1.8-6 nmol for Mn, 0.015-0.05 nmol for Co, 0.11-0.7 nmol for Ni, and 0.07-0.7 nmol for Pb. Figure 2 also shows the mean total dMn (Figure 2B), dCo (Figure 2D), dNi (Figure 2F) or dPb (Figure 2H) leached from each aerosol sample using ambient seawater (25°C, pH 8.0, oxygenated), acidified seawater (pH 7.6, sparged with air/CO<sub>2</sub> mixture, 1,250 ppm CO<sub>2</sub>), and anoxic seawater (sparged with N<sub>2</sub> for leaches 3 and 4). The mean total dTM leached under these seawater conditions ranged from 2.0-7 nmol for Mn, 0.021-

0.06 nmol for Co, 0.18-0.8 nmol for Ni, and 0.06-0.8 nmol for Pb. Despite the temperature and dissolved gas amendment experiments being undertaken separately, the mean quantities of dTM leached from the same aerosol sample were similar. Most importantly, the differences in mean total dMn, dCo, dNi and dPb released into seawater under the different conditions of temperature, pH and dissolved oxygen saturation were not significantly different (two-tailed *t* test, *p* > 0.05) for any of the aerosol samples (Figure 2), which was also the case for dFe (Fishwick et al., 2014).

The total standard deviation from the total mean amount of trace metal leached from aerosols (shown in Figure 3, Figure 4A and Figure 5) was calculated using the Equation 1, where  $sd_i$  is the standard deviation from the mean of each sequential leach (leaches 1 – 4) and *tsd* is the total standard deviation from the total mean amount of leached aerosol trace metal.

$$tsd = \sqrt{(\sum sd_{leach\ 1}^2, sd_{leach\ 2}^2, sd_{leach\ 3}^2, sd_{leach\ 4}^2)} \quad \text{Equation 1}$$

The relative standard deviation (RSD) of dTM in replicate leaches of subsamples from the same aerosol sample was high in some cases (RSD = 8-57%, Figure 2), which has also been observed in other studies (e.g., Morton et al., 2013). This, rather than analytical uncertainties, dominated the overall uncertainties in the mean total dTM leached from the aerosol samples; analytical uncertainties were comparatively low, with RSD values typically < 5% (*n* = 3). Differences in dTM leached from subsamples of the same sample may therefore reflect heterogeneity in trace metal penetration, speciation or particle size across each individual 8" x 10" aerosol-laden filter. Owing to the porous micro-irregular structure of the Whatman QMA filter, smaller aerosol particles, such as those produced by combustion, may penetrate the surface of some

areas of the filter more than others, and thus be protected from aqueous dissolution. The observed variability in dTM between replicate leaches is not explained by heterogeneity of particle loading as the total amount of Mn, Co, Ni and Pb contained on the aerosol filter. RSD values on the mean total Mn, Co, Ni and Pb for fully digested subsamples of a single aerosol sample were typically < 5% ( $n = 3$ , data not shown). When each mean %TM<sub>s</sub> is applied to the standard deviation on each mean amount of total trace metal this represents < 17%, < 11%, < 13% and < 24% of mean amount of leached dMn, dCo, dNi and dPb leached, respectively, for each aerosol sample. These observations demonstrate that replicate leaches of multiple subsamples of an aerosol filter are essential for comparative aerosol dissolution experiments.

The results of sequential aerosol leaches over 0-5 min, 5-10 min, 10 min-48 h, and 48 h-30 days provide information on the dissolution kinetics of aerosol trace metals. Generally, a large proportion (36-100%, median 89%) of the total dMn, dCo, dNi and dPb was mobilised during the first leaching step (5 min), with less dTM being released in leaches 2 through 4 (Figure 2, associated standard deviation was also highest for leach 1 and lowest for leach 4). Mn and Pb displayed the fastest leaching kinetics, with 82-98% of the dMn (median 92%) and 74-95% of the dPb (median 91%) released from aerosol samples during the first leaching step. For comparison, the leaching of dFe from these same aerosol samples in the same experiments described here, revealed that the majority (65-97%, median 89%) was also released during the initial leaching step (Fishwick et al., 2014). In contrast, Co and Ni showed more variable leaching kinetics with 55-100% of dCo (median 84%) and 36-100% of dNi (median 80%) released during the initial 5 minute leaching step. Mackey et al. (2015) reported that aerosol trace metals exhibited a continuum of dissolution, from gradual to rapid leaching, in general accord with results of this study. In their study Ni also

exhibited slower and more variable dissolution kinetics than Fe and Pb. However, their results suggest that Mn was solubilised more slowly than either Fe or Pb, which contrasts with the findings of this study and those reported by Fishwick et al. (2014). The slower leaching of Mn reported in Mackey et al. (2015) might reflect adsorption to bottle walls during the batch leaches used in their experiments, as has been observed with aerosol Fe (Wu et al., 2007), which was minimised by the continuous leach protocol used in leaches 1 and 2 of this study.

It is also possible that differences in leaching kinetics between different studies and samples reflect differences in the chemical speciation of trace metals in aerosols. For example, aerosol Mn may exist as soluble Mn(II) and as less soluble Mn(III) and Mn(IV) forms (Mendez et al., 2010). Similarly, aerosol Pb may exist as both highly soluble metal halides and less soluble oxides and carbonates (Maring and Duce, 1990; Sobanska et al., 1999). Therefore, it is likely that during the 'instantaneous' (< 5 min) leaching of aerosol Mn and Pb, the more soluble forms of these metals were released first, with an additional slow release of less soluble species. Furthermore, Co and Ni in crustal and anthropogenic aerosols are known to exist in a variety of forms, including carbonates, oxides and sulfides, which exhibit different solubilities at pH 8.1 (Caldeira and Wickett, 2003; Crundwell et al., 2011; Millero et al., 2009). The large variability observed in the leaching kinetics of Co and Ni between aerosol samples and between replicate leaches of the same sample into different seawater conditions may thus reflect heterogeneity in trace metal speciation across individual aerosol filters. However, despite these differences in leaching kinetics, the total mean dTM released from each aerosol sample into seawater was similar after 30 days leaching, suggesting a consistent seawater-leachable fraction for each metal over the timescale of a particle in the mixed layer.

The dissolved trace metals ( $< 0.4 \mu\text{m}$ ) released from aerosols into seawater will reside in either the colloidal (cTM) or soluble (sTM) size fractions, operationally defined in this study as  $0.02\text{-}0.4 \mu\text{m}$  and  $< 0.02 \mu\text{m}$ , respectively. The total amount of sTM leached from each aerosol sample (AER 1-4) with  $4^\circ\text{C}$  and  $25^\circ\text{C}$  seawater and ambient, acidified and anoxic seawater ranged from 1-5 nmol for Mn, 0.01-0.05 nmol for Co, 0.05-0.6 nmol for Ni and 0.001-0.03 nmol for Pb. Whilst there were differences in the amounts of sTM leached under different seawater conditions, for example the amount of sCo leached from AER 1 into 'acidified seawater' was higher than that leached into ambient seawater and the amount of sPb leached from AER 3 into ambient seawater was higher than that leached into 'acidified seawater', these differences were not consistent between samples. Moreover, when the differences in dTM for replicate leaching experiments are applied to sTM data (i.e., mean RSD from dTM leaches assumed as an RSD value for sTM leaches) the differences in amounts of sMn, sCo, sNi or sPb leached under different seawater conditions were not significantly different (two-tailed  $t$  test,  $p > 0.05$ ) in the majority of cases, as was observed for the dissolved metals. Table 3 presents the total mean dTM, cTM and sTM leached from each aerosol sample into ambient seawater ( $25^\circ\text{C}$ , pH 8.0, oxygenated). The lack of significant differences in dTM (Figure 2) and sTM leached under the various seawater conditions suggests that seawater temperature, pH and oxygenation did not exert a major control on the size distribution of the dissolved aerosol trace metals. The colloidal proportion of dTM ranged from  $21 \pm 16\%$  for Mn,  $31 \pm 18\%$  for Co,  $40 \pm 23\%$  for Ni and  $94 \pm 1\%$  for Pb (Table 3). We can thus characterise these elements as mostly residing in the colloidal (Pb), soluble (Mn, Co), or mixed (Ni) size fractions when released from aerosols into seawater. For comparison, most of the Fe released into seawater from aerosols is thought to reside

in the colloidal size fraction (Aguilar-Islas et al., 2010; Fishwick et al., 2014; Fitzsimmons and Boyle, 2014; Ussher et al., 2013). It should be noted that these data represent the size distribution of dTM in solution following leaching from aerosols, not the amount of sTM and cTM that has been directly leached from aerosols.

The results of this study suggest that seawater temperature, pH and O<sub>2</sub> concentration do not exert a major (i.e., statistically significant at  $p < 0.05$ ) control on the dissolution of aerosol Mn, Co, Ni or Pb, within the range of conditions tested, as was also observed for aerosol Fe (Fishwick et al., 2014). Similarly, the range of seawater conditions used in leaching experiments did not significantly impact the size distributions of these metals in the operationally defined dissolved phase. These findings imply that projected future increases in sea surface temperature or decreases in seawater pH and oxygenation driven by anthropogenic greenhouse gas emissions are unlikely to directly impact the proportions of aerosol Mn, Co, Ni and Pb that dissolve in surface ocean waters, in contrast to the results of other studies (e.g., Biscombe, 2004; Caldeira and Wickett, 2003; Millero et al., 2009; Murray and Tebo, 1991; Sunda and Huntsman, 1994). Rather, results presented in this study suggest that future changes in aerosol trace metal solubility due to changes in the physico-chemical conditions of seawater are likely to be minor relative to solubility changes that result from global shifts in aerosol source fluxes, physical and chemical changes to the atmosphere and *in situ* biological processing in surface waters.

From a methodological perspective, results presented in this study may also contribute to the debate on the most suitable aerosol leaching solution for determining trace metal solubility in seawater. In addition to being expensive and difficult to collect, trace-metal-clean seawater has long been thought to be unsuitable to be routinely-used as an aerosol leaching solution due to differences in physicochemical properties

causing inconsistent results (Mendez et al., 2010). However, results of this study suggest that key physicochemical characteristics of seawater (e.g. seawater temperature, pH and O<sub>2</sub> concentration) are unlikely to substantially affect aerosol Mn, Fe, Co, Ni and Pb solubility. Considering this, aerosol leaches using different seawaters (perhaps collected from different oceanic regions) may potentially allow for consistency between leaches, as is observed when UHP DI or ammonium acetate is used as a leaching solution (Buck et al., 2006; Chen and Siefert, 2004). However, given the influence of organic ligands on trace metal solubility and the variability between sample locations (Gledhill and Buck, 2012), it would be advisable to UV irradiate seawater samples before being used in aerosol leaching experiments where comparison between sample location is required. Whilst seawater is unlikely to offer the consistency of UHP DI or ammonium acetate, it is certainly a more representative media for determining the true solubility of aerosol trace metals.

#### *Effect of organic ligands on aerosol trace metal dissolution*

The study presented here also investigated the impact of a selection of strong organic ligand amendments on the dissolution and subsequent size distribution of aerosol trace metals in seawater. Figure 3 shows the total mean dTM leached from aerosol sample AER 1 using ambient seawater and the same seawater amended with strong L<sub>1</sub>-type ligands (the siderophores aerobactin and desferrioxamine-B; Figure 3A and Figure 3C, respectively) and with weaker L<sub>2</sub>-type ligands (protoporphyrin-IX and glucuronic acid; Figure 3E and Figure 3G, respectively). Interestingly, although these organic ligands have very different conditional stability constants for trace metal complexation (Vraspir and Butler, 2009 and Table 1), for each trace metal, the total

quantity of metal leached using the four different ligand amendments was not significantly different from that leached using unamended seawater (two-tailed  $t$  test,  $p > 0.05$ ; Figure 3).

This unexpected result may reflect the presence of sufficient concentrations of natural metal-complexing ligands in the ambient seawater (e.g., the Fe-binding ligand concentration of seawater used was  $\sim 0.8$  nM; data not shown) to complex all of the leachable aerosol metals, and/or the presence of strong organic ligands in the aerosols. However, it should also be noted that the binding strengths of the added ligands for Mn, Co, Ni and Pb are not well known, and therefore amendments with other organic ligands at higher concentrations will produce different results.

In addition to dissolved metals, the mean total soluble size fractions of Co (Figure 3D), Ni (Figure 3F) and Pb (Figure 3H) that were leached from aerosols into ligand-amended seawaters were not significantly different from each other (two-tailed  $t$  test,  $p > 0.05$ ) if differences in dissolved metals in replicate leaches are taken into account (i.e., mean RSD from dTM leaches assumed as an RSD value for sTM leaches). The size distributions of dTM leached in this experiment (Figure 3) were in accord with those observed in temperature and dissolved gas amendment experiments (Table 3), with the majority (74-97%) of dissolved Pb residing in the colloidal fraction, whilst dissolved Mn and Co were largely in the soluble size fraction (48-100% and 69-100%, respectively). The size distribution of dissolved Ni was mixed (29-81% colloidal), as seen in all other leaching experiments, which fits with the diverse chemical speciation of Ni reported in surface ocean waters (Achterberg and Van Den Berg, 1997; Donat et al., 1994; Nimmo et al., 1989; Saito et al., 2004).

Cobalt is known to form particularly strong organic complexes in seawater (Ellwood and van den Berg, 2001); thus its size distribution can be determined by the size of organic ligands present in the seawater that was used for leaching experiments. Given that there was no significant increase in dCo or sCo leached from aerosols into the ligand-amended seawaters, we suggest that Co-binding ligands were already present in the ambient seawater. Alternatively, Co-binding ligands may have been added by aerosols during leaching, however data from Mackey et al. (2015) suggest this is unlikely. Although the identity of Co-binding ligands has not been firmly established, possible candidates include vitamin B<sub>12</sub> and its metabolites (Ellwood et al., 2005; Ellwood and van den Berg, 2001; Saito et al., 2005; Saito and Moffett, 2001), and desferrioxamine-B (Duckworth et al., 2009), which are of low molecular weight (~1,000 Da) and thus likely to reside in the soluble size fraction. Complexation of leachable aerosol Co by such ligands that are present in the ambient BATS seawater or aerosols may thus explain the size distribution of dCo in the seawater leachate solutions.

The predominance of colloidal-sized aerosol Pb in the leachate is likely due to its extremely particle-reactive nature (e.g., Helmers and Rutgers van der Loeff, 1993). These experimental results suggest that following deposition and initial dissolution in surface seawater, dissolved aerosol Pb is rapidly adsorbed by colloidal material, and thus exists primarily in the colloidal phase. Alternately, leachable aerosol Pb could be associated with colloidal phases prior to deposition (Capodaglio et al., 1990). Results presented here indicate that addition of organic ligands to seawater did not alter the size distribution of dissolved aerosol Pb (i.e. cPb vs sPb), and therefore it is likely that this colloidal-sized aerosol Pb will be rapidly removed from surface waters via particle

aggregation and scavenging. Indeed, dissolved Pb is known to have a short residence time (~2 years) in the surface ocean (Wu and Boyle, 1997).

Dissolved Mn is also known to be particle-reactive and adsorbed by colloidal material in surface seawater (Sunda and Huntsman, 1994), although in this study aerosol-derived dMn was observed to reside primarily in the soluble size fraction. This might be explained by the existence of highly soluble inorganic Mn(II) in mineral aerosols (Mendez et al., 2010), combined with the well-known sluggish oxidation of Mn(II) in seawater (Stumm and Morgan, 1996). Thus a plausible mechanism for aerosol Mn dissolution in these experiments has the majority of the aerosol Mn leached during the first 10 minutes, which likely remained in the soluble size fraction as inorganic Mn(II) or was complexed by organic ligands (Oldham et al., 2015). During the subsequent third and four leaching steps (48 h-30 days), when little additional Mn was leached from the aerosols, insoluble Mn(IV) oxides may have formed and associated with colloidal material.

In contrast to the other trace metals we examined, there were significant differences (two-tailed *t* test,  $p > 0.05$ ) in the quantity of sMn leached from aerosols into ligand-amended seawater. Specifically, more aerosol-derived sMn was present in the leachate solutions using seawater amended with desferrioxamine-B and glucuronic acid, relative to the ambient seawater leaches (Figure 3B). This suggests that these organic ligand amendments allowed additional cMn to be drawn into the soluble fraction, over and above that stabilised by organic ligands present in the ambient seawater or leached from the aerosols. A similar result was observed for aerosol Fe leached by desferrioxamine-B-amended seawater (Fishwick et al., 2014). Desferrioxamine-B can certainly form strong complexes with Mn as well as Fe, with a conditional stability constant measured by Duckworth et al. (2009) of  $10^{29.9}$  (for

comparison, that of desferrioxamine-B and Fe was measured as  $10^{32.0}$ ), whereas the binding affinity of glucuronic acid for Mn is not known. It should be noted, however, that in the case of the desferrioxamine-B amendment, sMn exceeded dMn in the leachate solution, indicating contamination of this sample with Mn, possibly during the ultrafiltration procedure.

Though they are not representative of the broad variety of classes of organic ligands in seawater, the results presented here suggest that an increase in the siderophore- and saccharide-type organic ligands in ambient seawater has no effect on the amounts of dissolved Co, Ni and Pb that are released from the aerosols into seawater, nor on the distributions of soluble versus colloidal size fractions of these elements in the seawater leachate. Thus *in situ* production of these types of strong ligands relating to biological processes or increases in the atmospheric deposition of similar organic ligands to the Sargasso Sea (e.g., Heintzenberg, 1989; Wozniak et al., 2013) would not be expected to affect the dissolution these trace metals from aerosols, nor their size distribution, in surface waters of the study region. In the case of Mn, however, seawater amended with glucuronic acid (and possibly desferrioxamine-B) was able to retain the majority of dMn leached from aerosols in the soluble size fraction. Thus, if sufficient concentrations of such organic ligands (and potentially others) are present in surface waters of the Sargasso Sea, aerosol Mn may be expected to be retained in the soluble size fraction, thus potentially extending its residence time and biological availability in the euphotic zone, as was suggested for aerosol Fe in Fishwick et al. (2014).

*Impact of aerosol source and composition on aerosol trace metal dissolution*

The operationally-defined fractional solubilities (%TM<sub>s</sub>) of aerosol trace metals were calculated for each aerosol sample by dividing the total dTM released into solution by the total bulk trace metal in each aerosol sample, thus allowing the comparison of the leaching characteristics of aerosols with different sources and compositions. The fractional solubilities of Mn, Co, Ni or Pb in samples AER 1-4, with respect to seawater at given temperatures, pH and O<sub>2</sub> concentrations are shown in Figure 4. Mean %TM<sub>s</sub> values ranged from 50-104% for Mn, 29-58% for Co, 40-85% for Ni, and 67-112% for Pb. The fractional solubilities of these aerosol trace metals thus followed the order Co < Ni < Mn < Pb, with at least 29% of any of these aerosol trace metals dissolving in seawater. In contrast, a smaller proportion of the total aerosol Fe in these samples dissolved in seawater, with %Fe<sub>s</sub> values ranging from 0.3 ± 0.1% to 3.2 ± 0.8% (Fishwick et al., 2014).

Results presented here are consistent with the findings of Kocak et al. (2007), who observed the speciation of Pb in aerosols to be dominated by an 'exchangeable' phase (e.g., halide species), whereas the speciation of aerosol Fe was dominated by a 'refractory' phase. Interestingly, despite exhibiting very different speciation in aerosols, both aerosol Fe and Pb tend to eventually reside in the colloidal phase when leached into seawater under these experimental conditions, owing to their high particle affinity. In addition, the fractional solubilities of Mn, Co, Ni and Pb calculated in this study are in broad agreement with the wide ranges of values reported elsewhere (Table 4): 4-92% for Mn, 8-100% for Co, 1-86% for Ni and 1-69% for Pb (Baker et al., 2006b; Buck et al., 2013, 2010b; Chester et al., 1993; Hsu et al., 2010, 2005; Shelley et al., 2012). However, these literature values, like the values reported in this work, were highly variable among aerosol samples of different provenance, with anthropogenically influenced samples generally displaying higher fractional solubility

values for these trace metals. The mean fractional solubilities of Mn, Co, Ni and Pb in the most 'anthropogenic' type aerosol (AER 4) were consistently higher than those of the 'mineral dust' type aerosol (AER 1) for all seawater leaching conditions. For example, total mean %Pb<sub>s</sub> in ambient seawater was  $100 \pm 15\%$  for AER 4 compared with  $72 \pm 18\%$  for AER 1. A relationship between aerosol composition and aerosol trace metal solubility has been reported in previous studies for Mn, Co, Ni and Pb (Desboeufs et al., 2005; Hsu et al., 2005) and for Fe (Buck et al., 2010b; Fishwick et al., 2014; Sedwick et al., 2007; Séguret et al., 2011; Sholkovitz et al., 2009). The enhanced fractional solubility in anthropogenically influenced aerosols has been attributed to acidic processing of the aerosol particles (Hsu et al., 2010), source and composition of the aerosols (Sholkovitz et al., 2009), variations in the bulk matrix with which the trace metals are associated (Desboeufs et al., 2005), and the tendency of anthropogenic aerosols to have a higher surface to volume ratio (S:V) compared with mineral dust (Baker and Jickells, 2006; Jang et al., 2007).

#### *The use of enrichment factor to predict trace metal solubility*

The mean fractional solubilities of Mn, Fe, Co, Ni and Pb from AER 1-4 for all seawater leaching conditions as a function of the enrichment factors for each of these trace metals are shown in Figure 5A. There is a significant positive correlation (Spearman's Rho correlation,  $r = 1.00$ ,  $p < 0.0001$ ) between %Pb<sub>s</sub> and enrichment factors for Pb, suggesting a higher fractional solubility of Pb in aerosols containing more anthropogenically derived Pb. There were no significant correlations between %TM<sub>s</sub> of Mn, Fe, Co or Ni and their aerosol enrichment factors. As Sb is a sensitive element to anthropogenic enrichment (Smichowski, 2008) the %TM<sub>s</sub> of the same aerosol metals for all seawater conditions were plotted as a function of aerosol

Sb enrichment and are shown in Figure 5B. Fractional solubilities of Fe, Co and Pb all show strong positive correlations with aerosol Sb enrichments (Spearman's Rho correlation,  $r = 1.00$ ,  $p < 0.0001$ ). No significant correlation was observed between %Mn<sub>s</sub> or %Ni<sub>s</sub> and aerosol Sb enrichments. There were also positive correlations (Spearman's Rho correlation,  $r = 1.00$ ,  $p < 0.0001$ ) between %Fe<sub>s</sub>, %Co<sub>s</sub> and %Pb<sub>s</sub> with aerosol enrichments in V, Ni and Cu (Table 5), which are also indicators of anthropogenic aerosol emissions (Chester et al., 1999). These empirical relationships illustrate the potential for use of aerosol V, Ni, Cu and Sb enrichments to broadly estimate the fractional solubility of aerosol Fe, Co and Pb, without the need for time consuming aerosol leaching experiments. This follows a similar approach to that described by Sholkovitz et al. (2009) for estimating %Fe<sub>s</sub> from aerosol V/Al mass ratios. Following validation with a more extensive dataset of dissolved and leachable trace metals in aerosols, estimates of Fe, Co and Pb solubility could be made using only bulk aerosol trace metal concentrations, which would be of great use to workers in this field. The linear regression equations for these empirical relationships for %Fe<sub>s</sub>, %Co<sub>s</sub> and %Pb<sub>s</sub> with Sb enrichment factor (Sb<sub>EF</sub>) are shown in Equations 2, 3 and 4, respectively. The uncertainty on Equations 2, 3 and 4 is  $3.5 \times 10^{-5}$ ,  $5.6 \times 10^{-4}$  and  $2.9 \times 10^{-4}$ , respectively.

$$\%Fe_s = (0.00003 \times Sb_{EF}) + 0.0038 \quad \text{Equation 2}$$

$$\%Co_s = (0.0003 \times Sb_{EF}) + 0.2965 \quad \text{Equation 3}$$

$$\%Pb_s = (0.0006 \times Sb_{EF}) + 0.7439 \quad \text{Equation 4}$$

Comparison of Figure 5A with Figure 5B suggest that the higher fractional solubility of Fe and Co in aerosols with greater anthropogenic influence is not driven by differences between anthropogenic and crustal chemical speciation of these metals. Rather, these differences appear to be a consequence of other properties

associated with anthropogenic activities. For example, acidic pollutants (e.g., oxides of nitrogen and sulphur) released along with anthropogenic aerosols during fossil fuel combustion can form acidic hygroscopic hydration layers on particles during condensation-evaporation cycles in clouds (Zhu et al., 1992) and increase the solubility of trace metals (Hsu et al., 2010; Zhuang et al., 1990; Zhu et al., 1997). Alternately, Fe and Co in anthropogenic aerosols, rather than being strongly bound to aluminosilicates, may exist as impurities adsorbed to carbonaceous matrices, or as sulphates or oxides, which can be released rapidly upon contact with seawater (Desboeufs et al., 2005; Fu et al., 2012).

Conversely, results presented here indicate that the enhanced solubility of Pb in more anthropogenically influenced aerosols is controlled in part by differences in Pb speciation in anthropogenic aerosols versus mineral dust. Indeed, combustion products are known to contain highly soluble metal halides, whereas Pb in mineral dust is in the form of less soluble oxides, for example PbO and PbO<sub>2</sub> (Maring and Duce, 1990). Analogous to Fe and Co, other properties attributed to anthropogenic aerosols (e.g., acidic processing, association of metals with carbonaceous matrices, smaller particle size and larger S:V) may also play a role in enhancing aerosol Pb solubility, as argued by Kocak et al. (2007), who showed a relationship between anthropogenic aerosol Pb and its solubility in both 'exchangeable' (e.g., PbCl<sup>+</sup>, PbCl<sub>2</sub> and PbCl<sub>3</sub><sup>-</sup>) and oxide/carbonate (e.g., PbO, PbO<sub>2</sub> and PbCO<sub>3</sub>) fractions, indicating enhanced solubility for contrasting Pb species.

Investigations into the influence of aerosol source and composition on aerosol trace metal dissolution in relation to differing physico-chemical seawater conditions indicates that source-driven variations in bulk aerosol composition is a dominant factor in controlling the seawater solubility of aerosol Fe, Co and Pb, but not Mn and Ni.

Thus estimates of the aeolian input of bioactive trace elements to the surface ocean need to consider aerosol source and composition, which are arguably more important than the physico-chemical conditions in surface seawater in terms of the dissolution of aerosol trace metals. The apparent source-dependent differences in aerosol Fe, Co and Pb solubility, coupled with the seasonal contrast in air mass transport to the Sargasso Sea (Sedwick et al., 2007) may impact the atmospheric input of dissolved metals to surface waters in this region, and to other analogously situated ocean regions (e.g., see Arimoto et al., 1995; Kumar et al., 2010).

## Conclusions

The results of this experimental study suggest that realistic maximum variations in the temperature, pH and dissolved O<sub>2</sub> concentration of surface seawater have little effect on the dissolution of aerosol Mn, Co, Ni and Pb. The size distribution of these trace metals released from aerosols into the dissolved pool, and the dissolution kinetics of these species, were also unaffected by such variations in seawater physico-chemical conditions. These findings imply that future ocean warming, acidification and decreases in seawater oxygenation will not significantly impact aeolian inputs of dissolved Mn, Co, Ni and Pb to surface waters of the Sargasso Sea and it is likely to apply to other ocean regions. Furthermore, results presented here demonstrate the importance of Mn-binding ligands (such as glucuronic acid and desferrioxamine-B) in stabilising aerosol Mn following leaching into surface waters, helping to retain Mn in the soluble fraction where it will remain available in the euphotic zone for uptake by phytoplankton.

Leaching experiments indicate that aerosol source and composition exert a significant control on the dissolution of aerosol Co and Pb, with the most anthropogenically influenced aerosol samples, based on enrichment of anthropogenic elements in the bulk composition, displaying the highest fractional solubilities (up to 58% for Co and 100% for Pb). The previously reported values for the fractional solubility of Fe in these same aerosol samples also indicate an elevated solubility for the more anthropogenically influenced aerosols. Further, the data suggest that the enhanced solubility of Pb in anthropogenically influenced aerosols reflects chemical speciation and, to a lesser extent, other factors associated with combustion emissions, such as acidic processing. These factors may be driving increases in the solubility of aerosol Fe and Co and thus biologically available inputs of these micronutrient elements to the surface ocean. In addition, empirical relationships were observed between the fractional solubilities of aerosol Co and Pb and the enrichment of Sb in the bulk aerosol, relative to crustal abundance, which can be used to estimate the fractional solubility of these aerosol trace metals in the Sargasso Sea and potentially other ocean regions.

### Acknowledgments

This research was supported by a European Commission Marie Curie International Outgoing Fellowship for SJU (PIOF-GA-2009-235418 SOLAIROS), a European Commission Marie Curie Career Integration Grant for SJU (PCIG-GA-2012-333143 DISCOSAT), a Natural Environment Research Council (NERC) PhD studentship for MPF (NE/J500380/1), and National Science Foundation (NSF) awards to PNS (OCE 0222053), KNB (OCE 1446327) and TMC (OCE 0222046). The authors would like to acknowledge Andrew Peters, Nicholas Bates and Samantha de Putron

(Bermuda Institute of Ocean Sciences) for all their support in this project, and thank the Bermuda Institute of Ocean Sciences for a grant-in-aid. Data to supplement this article are available directly from the corresponding author, Simon Ussher (simon.usshe@plymouth.ac.uk).

## References

- Achterberg, E.P., Van Den Berg, C.M.G., 1997. Chemical speciation of chromium and nickel in the western Mediterranean. *Deep Sea Res. Part II Top. Stud. Oceanogr.* 44, 693–720. doi:10.1016/S0967-0645(96)00086-0
- Aguilar-Islas, A.M., Wu, J., Rember, R., Johansen, A.M., Shank, L.M., 2010. Dissolution of aerosol-derived iron in seawater: Leach solution chemistry, aerosol type, and colloidal iron fraction. *Mar. Chem.* 120, 25–33. doi:10.1016/j.marchem.2009.01.011
- Anderson, J.R., Buseck, P.R., Patterson, T.L., Arimoto, R., 1996. Characterization of the Bermuda tropospheric aerosol by combined individual-particle and bulk-aerosol analysis. *Atmos. Environ.* 30, 319–338. doi:10.1016/1352-2310(95)00170-4
- Arimoto, R., Duce, R.A., Ray, B.J., Ellis, W.G., Cullen, J.D., Merrill, J.T., 1995. Trace elements in the atmosphere over the North Atlantic. *J. Geophys. Res. Atmospheres* 100, 1199–1213. doi:10.1029/94jd02618
- Baker, A.R., Croot, P.L., 2010. Atmospheric and marine controls on aerosol iron solubility in seawater. *Mar. Chem.* 120, 4–13. doi:10.1016/j.marchem.2008.09.003
- Baker, A.R., Jickells, T.D., 2006. Mineral particle size as a control on aerosol iron solubility. *Geophys. Res. Lett.* 33, L17608. doi:10.1029/2006gl026557
- Baker, A.R., Jickells, T.D., Biswas, K.F., Weston, K., French, M., 2006a. Nutrients in atmospheric aerosol particles along the Atlantic Meridional Transect. *Deep Sea Res. Part II Top. Stud. Oceanogr.* 53, 1706–1719. doi:10.1016/j.dsr2.2006.05.012
- Baker, A.R., Jickells, T.D., Witt, M., Linge, K.L., 2006b. Trends in the solubility of iron, aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean. *Mar. Chem.* 98, 43–58. doi:10.1016/j.marchem.2005.06.004
- Bertrand, E.M., Saito, M.A., Rose, J.M., Riesselman, C.R., Lohan, M.C., Noble, A.E., Lee, P.A., DiTullio, G.R., 2007. Vitamin B-12 and iron colimitation of phytoplankton growth in the Ross Sea. *Limnol. Oceanogr.* 52, 1079–1093.
- Biscombe, A., 2004. Factors influencing the seawater solubility of aerosol associated trace metals. Plymouth University, Plymouth.
- Boyd, P.W., Watson, A.J., Law, C.S., Abraham, E.R., Trull, T., Murdoch, R., Bakker, D.C.E., Bowie, A.R., Buesseler, K.O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R., Maldonado, M.T., McKay, R.M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., Zeldis, J., 2000. A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature* 407, 695–702. doi:10.1038/35037500
- Bressac, M., Guieu, C., 2013. Post-depositional processes: What really happens to new atmospheric iron in the ocean's surface? *Glob. Biogeochem. Cycles.* doi:10.1002/gbc.20076
- Bruland, K.W., 1989. Complexation of zinc by natural organic ligands in the central North Pacific. *Limnol. Oceanogr.* 34, 269–285.
- Buck, C.S., Landing, W.M., Resing, J., 2013. Pacific Ocean aerosols: Deposition and solubility of iron, aluminum, and other trace elements. *Mar. Chem.* 157, 117–130. doi:10.1016/j.marchem.2013.09.005

- Buck, C.S., Landing, W.M., Resing, J.A., 2010a. Particle size and aerosol iron solubility: A high-resolution analysis of Atlantic aerosols. *Mar. Chem.* 120, 14–24. doi:10.1016/j.marchem.2008.11.002
- Buck, C.S., Landing, W.M., Resing, J.A., Lebon, G.T., 2006. Aerosol iron and aluminum solubility in the northwest Pacific Ocean: Results from the 2002 IOC cruise. *Geochem. Geophys. Geosystems* 7, Q04M07. doi:10.1029/2005gc000977
- Buck, C.S., Landing, W.M., Resing, J.A., Measures, C.I., 2010b. The solubility and deposition of aerosol Fe and other trace elements in the North Atlantic Ocean: Observations from the A16N CLIVAR/CO2 repeat hydrography section. *Mar. Chem.* 120, 57–70. doi:10.1016/j.marchem.2008.08.003
- Buck, K.N., Bruland, K.W., 2005. Copper speciation in San Francisco Bay: A novel approach using multiple analytical windows. *Mar. Chem.* 96, 185–198. doi:10.1016/j.marchem.2005.01.001
- Byrne, R.H., Kump, L.R., Cantrell, K.J., 1988. The influence of temperature and pH on trace metal speciation in seawater. *Mar. Chem., Inorganic Marine Chemistry* 25, 163–181. doi:10.1016/0304-4203(88)90062-X
- Caldeira, K., Wickett, M.E., 2003. Oceanography: anthropogenic carbon and ocean pH. *Nature* 425, 365–365. doi:10.1038/425365a
- Capodaglio, G., Coale, K.H., Bruland, K.W., 1990. Lead speciation in surface waters of the eastern North Pacific. *Mar. Chem.* 29, 221–233. doi:10.1016/0304-4203(90)90015-5
- Chance, R., Jickells, T.D., Baker, A.R., 2015. Atmospheric trace metal concentrations, solubility and deposition fluxes in remote marine air over the south-east Atlantic. *Mar. Chem., Biogeochemistry of trace elements and their isotopes 177, Part 1*, 45–56. doi:10.1016/j.marchem.2015.06.028
- Chen, L., Duce, R.A., 1983. The sources of sulfate, vanadium and mineral matter in aerosol particles over Bermuda. *Atmos. Environ.* 17, 2055–2064. doi:10.1016/0004-6981(83)90362-1
- Chen, Y., Siefert, R.L., 2004. Seasonal and spatial distributions and dry deposition fluxes of atmospheric total and labile iron over the tropical and subtropical North Atlantic Ocean. *J. Geophys. Res. Atmospheres* 109. doi:10.1029/2003jd003958
- Chester, R., Murphy, K.J.T., Lin, F.J., Berry, A.S., Bradshaw, G.A., Corcoran, P.A., 1993. Factors controlling the solubilities of trace metals from non-remote aerosols deposited to the sea surface by the “dry” deposition mode. *Mar. Chem.* 42, 107–126. doi:10.1016/0304-4203(93)90241-F
- Chester, R., Nimmo, M., Preston, M.R., 1999. The trace metal chemistry of atmospheric dry deposition samples collected at Cap Ferrat: a coastal site in the Western Mediterranean. *Mar. Chem.* 68, 15–30. doi:10.1016/S0304-4203(99)00062-6
- Church, T.M., Véron, A., Patterson, C.C., Settle, D., Erel, Y., Maring, H.R., Flegal, A.R., 1990. Trace elements in the North Atlantic troposphere: Shipboard results of precipitation and aerosols. *Glob. Biogeochem. Cycles* 4, 431–443. doi:10.1029/GB004i004p00431
- Clough, R., Sela, H., Milne, A., Lohan, M.C., Tokalioglu, S., Worsfold, P.J., 2015. Uncertainty contributions to the measurement of dissolved Co, Fe, Pb and V in seawater using flow injection with solid phase preconcentration and detection by collision/reaction cell—quadrupole ICP–MS. *Talanta, SI: 18TH ICFIA (2013)* 133, 162–169. doi:10.1016/j.talanta.2014.08.045

- Coale, K.H., Johnson, K.S., Fitzwater, S.E., Gordon, R.M., Tanner, S., Chavez, F.P., Ferioli, L., Sakamoto, C., Rogers, P., Millero, F., Steinberg, P., Nightingale, P., Cooper, D., Cochlan, W.P., Landry, M.R., Constantinou, J., Rollwagen, G., Trasvina, A., Kudela, R., 1996. A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. *Nature* 383, 495–501. doi:10.1038/383495a0
- Crundwell, F.K., Moats, M., Ramachandran, V., 2011. *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*. Elsevier.
- Csavina, J., Field, J., Taylor, M.P., Gao, S., Landázuri, A., Betterton, E.A., Sáez, A.E., 2012. A review on the importance of metals and metalloids in atmospheric dust and aerosol from mining operations. *Sci. Total Environ.* 433, 58–73. doi:10.1016/j.scitotenv.2012.06.013
- Cutter, G., Andersson, P., Codispoti, L., Croot, P., Francois, R., Lohan, M., Obata, H., Rutgers vd Loeff, M., 2010. *Sampling and sample-handling protocols for GEOTRACES Cruises*. GEOTRACES, Toulouse.
- de Putron, S.J., McCorkle, D.C., Cohen, A.L., Dillon, A., 2011. The impact of seawater saturation state and bicarbonate ion concentration on calcification by new recruits of two Atlantic corals. *Coral Reefs* 30, 321–328. doi:10.1007/s00338-010-0697-z
- Desboeufs, K.V., Sofikitis, A., Losno, R., Colin, J.L., Ausset, P., 2005. Dissolution and solubility of trace metals from natural and anthropogenic aerosol particulate matter. *Chemosphere* 58, 195–203. doi:10.1016/j.chemosphere.2004.02.025
- Donat, J.R., Lao, K.A., Bruland, K.W., 1994. Speciation of dissolved copper and nickel in South San Francisco Bay: a multi-method approach. *Anal. Chim. Acta* 284, 547–571. doi:10.1016/0003-2670(94)85061-5
- Duce, R., A., 1986. The Impact of Atmospheric Nitrogen, Phosphorus, and Iron Species on Marine Biological Productivity, in: *Buat-Ménard, P. (Ed.), The Role of Air-Sea Exchange in Geochemical Cycling*, NATO ASI Series. Springer Netherlands, pp. 497–529.
- Duce, R.A., Hoffman, G.L., 1976. Atmospheric vanadium transport to the ocean. *Atmospheric Environ.* 1967 10, 989–996. doi:10.1016/0004-6981(76)90207-9
- Duckworth, O.W., Bargar, J.R., Jarzecki, A.A., Oyerinde, O., Spiro, T.G., Sposito, G., 2009. The exceptionally stable cobalt(III)–desferrioxamine B complex. *Mar. Chem.* 113, 114–122. doi:10.1016/j.marchem.2009.01.003
- Ellwood, M.J., van den Berg, C.M.G., 2001. Determination of organic complexation of cobalt in seawater by cathodic stripping voltammetry. *Mar. Chem.* 75, 33–47. doi:10.1016/S0304-4203(01)00024-X
- Ellwood, M.J., van den Berg, C.M.G., Boye, M., Veldhuis, M., de Jong, J.T.M., de Baar, H.J.W., Croot, P.L., Kattner, G., 2005. Organic complexation of cobalt across the Antarctic Polar Front in the Southern Ocean. *Mar. Freshw. Res.* 56, 1069–1075.
- Fishwick, M.P., Sedwick, P.N., Lohan, M.C., Worsfold, P.J., Buck, K.N., Church, T.M., Ussher, S.J., 2014. The impact of changing surface ocean conditions on the dissolution of aerosol iron. *Glob. Biogeochem. Cycles* 2014GB004921. doi:10.1002/2014gb004921
- Fitzsimmons, Boyle, 2014. Assessment and comparison of Anopore and cross flow filtration methods for the determination of dissolved iron size fractionation into soluble and colloidal phases in seawater. *Limnol. Oceanogr.-Methods* 12, 246–263.

- Fu, H., Lin, J., Shang, G., Dong, W., Grassian, V.H., Carmichael, G.R., Li, Y., Chen, J., 2012. Solubility of Iron from Combustion Source Particles in Acidic Media Linked to Iron Speciation. *Environ. Sci. Technol.* 46, 11119–11127. doi:10.1021/es302558m
- Gledhill, M., Buck, K.N., 2012. The organic complexation of iron in the marine environment: A review. *Front. Microbiol.* 3. doi:10.3389/fmicb.2012.00069
- Grousset, F.E., Quétel, C.R., Thomas, B., Donard, O.F.X., Lambert, C.E., Guillard, F., Monaco, A., 1995. Anthropogenic vs. lithogenic origins of trace elements (As, Cd, Pb, Rb, Sb, Sc, Sn, Zn) in water column particles: northwestern Mediterranean Sea. *Mar. Chem.* 48, 291–310. doi:10.1016/0304-4203(94)00056-J
- Heintzenberg, J., 1989. Fine particles in the global troposphere A review. *Tellus B* 41B, 149–160. doi:10.1111/j.1600-0889.1989.tb00132.x
- Helmers, E., Rutgers van der Loeff, M.M., 1993. Lead and aluminum in Atlantic surface waters (50°N to 50°S) reflecting anthropogenic and natural sources in the Eolian transport. *J. Geophys. Res. Oceans* 98, 20261–20273. doi:10.1029/93jc01623
- Hernlem, B.J., Vane, L.M., Sayles, G.D., 1996. Stability constants for complexes of the siderophore desferrioxamine B with selected heavy metal cations. *Inorganica Chim. Acta* 244, 179–184. doi:10.1016/0020-1693(95)04780-8
- Ho, T.-Y., 2013. Nickel limitation of nitrogen fixation in *Trichodesmium*. *Limnol. Oceanogr.* 58, 112–120. doi:10.4319/lo.2013.58.1.0112
- Hsu, S.-C., Lin, F.-J., Jeng, W.-L., 2005. Seawater solubility of natural and anthropogenic metals within ambient aerosols collected from Taiwan coastal sites. *Atmos. Environ.* 39, 3989–4001. doi:10.1016/j.atmosenv.2005.03.033
- Hsu, S.-C., Wong, G.T.F., Gong, G.-C., Shiah, F.-K., Huang, Y.-T., Kao, S.-J., Tsai, F., Candice Lung, S.-C., Lin, F.-J., Lin, I.I., Hung, C.-C., Tseng, C.-M., 2010. Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea. *Mar. Chem.* 120, 116–127. doi:10.1016/j.marchem.2008.10.003
- IPCC, 2007. Working Group I Contribution to the IPCC Fourth Assessment Report Climate Change 2007: The Physical Science Basis, Summary for Policymakers. Intergovernmental Panel on Climate Change, Geneva.
- Jang, H.-N., Seo, Y.-C., Lee, J.-H., Hwang, K.-W., Yoo, J.-I., Sok, C.-H., Kim, S.-H., 2007. Formation of fine particles enriched by V and Ni from heavy oil combustion: Anthropogenic sources and drop-tube furnace experiments. *Atmos. Environ.* 41, 1053–1063. doi:10.1016/j.atmosenv.2006.09.011
- Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A., Kawahata, H., Kubilay, N., laRoche, J., Liss, P.S., Mahowald, N., Prospero, J.M., Ridgwell, A.J., Tegen, I., Torres, R., 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* 308, 67–71. doi:10.1126/science.1105959
- Kelly, A.E., Reuer, M.K., Goodkin, N.F., Boyle, E.A., 2009. Lead concentrations and isotopes in corals and water near Bermuda, 1780–2000. *Earth Planet. Sci. Lett.* 283, 93–100. doi:10.1016/j.epsl.2009.03.045
- Kocak, M., Kubilay, N., Herut, B., Nimmo, M., 2007. Trace metal solid state speciation in aerosols of the Northern Levantine basin, East Mediterranean. *J. Atmospheric Chem.* 56, 239–257. doi:10.1007/s10874-006-9053-7

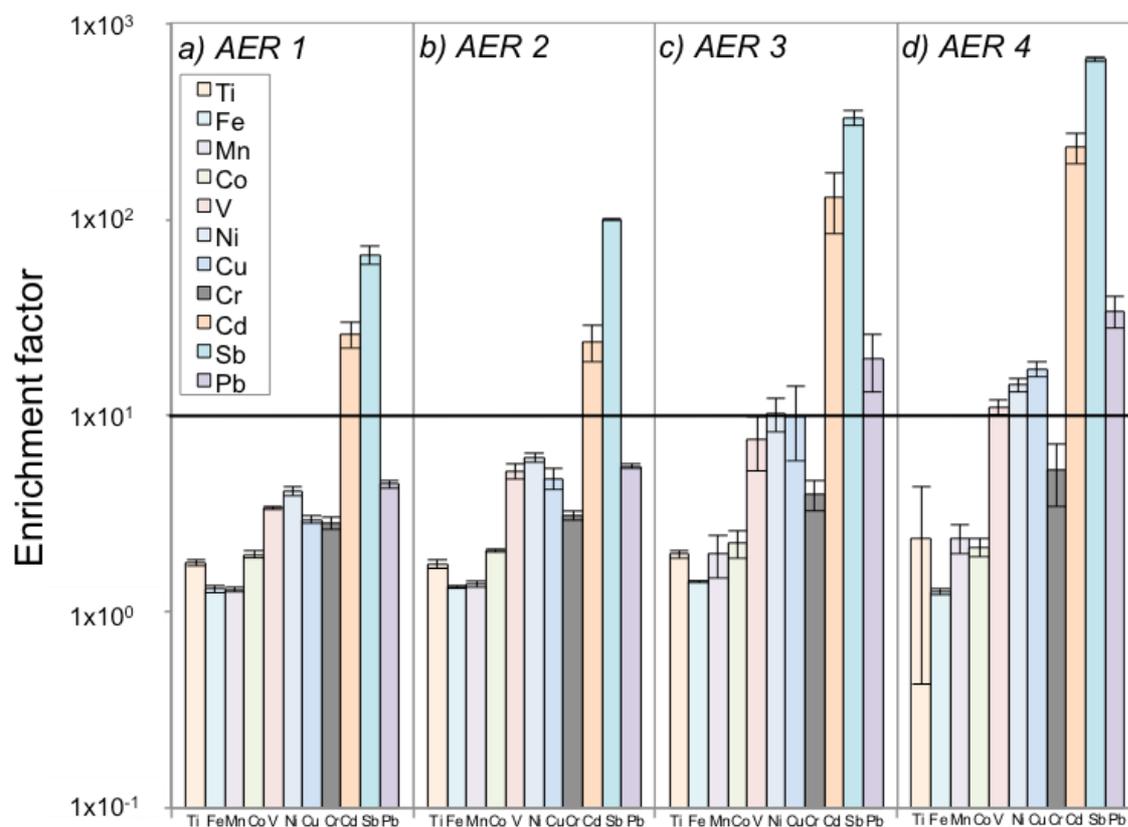
- Kumar, A., Sarin, M.M., Srinivas, B., 2010. Aerosol iron solubility over Bay of Bengal: Role of anthropogenic sources and chemical processing. *Mar. Chem.* 121, 167–175. doi:10.1016/j.marchem.2010.04.005
- Louis, Y., Garnier, C., Lenoble, V., Omanović, D., Mounier, S., Pižeta, I., 2009. Characterisation and modelling of marine dissolved organic matter interactions with major and trace cations. *Mar. Environ. Res.* 67, 100–107. doi:10.1016/j.marenvres.2008.12.002
- Mackey, K.R.M., Chien, C.-T., Post, A.F., Saito, M.A., Paytan, A., 2015. Rapid and gradual modes of aerosol trace metal dissolution in seawater. *Microbiol. Chem. Geomicrobiol.* 5, 794. doi:10.3389/fmicb.2014.00794
- Maring, H.B., Duce, R.A., 1990. The impact of atmospheric aerosols on trace metal chemistry in open ocean surface seawater: 3. Lead. *J. Geophys. Res. Oceans* 95, 5341–5347. doi:10.1029/JC095iC04p05341
- Martin, J.H., Coale, K.H., Johnson, K.S., Fitzwater, S.E., Gordon, R.M., Tanner, S.J., Hunter, C.N., Elrod, V.A., Nowicki, J.L., Coley, T.L., Barber, R.T., Lindley, S., Watson, A.J., Vanscoy, K., Law, C.S., Liddicoat, M.I., Ling, R., Stanton, T., Stockel, J., Collins, C., Anderson, A., Bidigare, R., Ondrusek, M., Latasa, M., Millero, F.J., Lee, K., Yao, W., Zhang, J.Z., Friederich, G., Sakamoto, C., Chavez, F., Buck, K., Kolber, Z., Greene, R., Falkowski, P., Chisholm, S.W., Hoge, F., Swift, R., Yungel, J., Turner, S., Nightingale, P., Hatton, A., Liss, P., Tindale, N.W., 1994. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature* 371, 123–129. doi:10.1038/371123a0
- Mendez, J., Guieu, C., Adkins, J., 2010. Atmospheric input of manganese and iron to the ocean: Seawater dissolution experiments with Saharan and North American dusts. *Mar. Chem.* 120, 34–43. doi:10.1016/j.marchem.2008.08.006
- Millero, F.J., 2013. *Chemical oceanography*, 4th ed. Taylor & Francis, Boca Raton.
- Millero, F.J., Woosley, R., DiTrollo, B., Waters, J., 2009. Effect of Ocean Acidification on the Speciation of Metals in Seawater. *Oceanography* 22, 72–85. doi:10.5670/oceanog.2009.98
- Mills, M.M., Ridame, C., Davey, M., La Roche, J., Geider, R.J., 2004. Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic. *Nature* 429, 292–294. doi:10.1038/nature02550
- Milne, A., Landing, W., Bizimis, M., Morton, P., 2010. Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Anal. Chim. Acta* 665, 200–207. doi:10.1016/j.aca.2010.03.027
- Moore, C.M., Mills, M.M., Milne, A., Langlois, R., Achterberg, E.P., Lochte, K., Geider, R.J., La Roche, J., 2006. Iron limits primary productivity during spring bloom development in the central North Atlantic. *Glob. Change Biol.* 12, 626–634. doi:10.1111/j.1365-2486.2006.01122.x
- Morel, F.M.M., Rueter, J.G., Price, N.M., 1991. Iron nutrition of phytoplankton and its possible importance in the ecology of ocean regions with high nutrient and low biomass. *Oceanography* 4, 56–61. doi:10.5670/oceanog.1991.03
- Morton, P.L., Landing, W.M., Hsu, S.-C., Milne, A., Aguilar-Islas, A.M., Baker, A.R., Bowie, A.R., Buck, C.S., Gao, Y., Gichuki, S., 2013. Methods for the sampling and analysis of marine aerosols: results from the 2008 GEOTRACES aerosol intercalibration experiment. *Limnology Oceanogr. Methods* 11, 62–78. doi:10.4319/lom.2013.11.62
- Murray, J.W., Tebo, B.M., 1991. Black Sea Oceanography: Results from the 1988 Black Sea Expedition Manganese(II) oxidation in the suboxic zone of the Black

- Sea. Deep Sea Res. Part Oceanogr. Res. Pap. 38, S883–S905.  
doi:10.1016/S0198-0149(10)80015-9
- Nimmo, M., van den Berg, C.M.G., Brown, J., 1989. The chemical speciation of dissolved nickel, copper, vanadium and iron in Liverpool Bay, Irish Sea. *Estuar. Coast. Shelf Sci.* 29, 57–74. doi:10.1016/0272-7714(89)90073-5
- Oldham, V.E., Owings, S.M., Jones, M.R., Tebo, B.M., Luther III, G.W., 2015. Evidence for the presence of strong Mn(III)-binding ligands in the water column of the Chesapeake Bay. *Mar. Chem.* 171, 58–66.  
doi:10.1016/j.marchem.2015.02.008
- Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* 437, 681–686. doi:10.1038/nature04095
- Pierrot, D., Lewis, E., Wallace, D.W.R., 2006. CO2SYS DOS Program developed for CO2 system calculations. ORNLCDIAC-105 Carbon Dioxide Inf. Anal. Cent. Oak Ridge Natl. Lab. US Dep. Energy Oak Ridge TN.
- Price, N.M., Morel, F.M.M., 1990. Cadmium and cobalt substitution for zinc in a marine diatom. *Nature* 344, 658–660. doi:10.1038/344658a0
- Prospero, J.M., 2002. The Chemical and Physical Properties of Marine Aerosols: An Introduction, in: Gianguzza, P.A., Pelizzetti, P.E., Sammartano, P.S. (Eds.), *Chemistry of Marine Water and Sediments*, Environmental Science. Springer Berlin Heidelberg, pp. 35–82.
- Raven, J.A., 1990. Predictions of Mn and Fe use efficiencies of phototrophic growth as a function of light availability for growth and of C assimilation pathway. *New Phytol.* 116, 1–18. doi:10.1111/j.1469-8137.1990.tb00505.x
- Rees, T.A.V., Bekheet, I.A., 1982. The role of nickel in urea assimilation by algae. *Planta* 156, 385–387. doi:10.1007/bf00393307
- Rivkin, R.B., 1979. Effects of lead on growth of the marine diatom *Skeletonema costatum*. *Mar. Biol.* 50, 239–247. doi:10.1007/BF00394205
- Saito, M.A., Goepfert, T.J., 2008. Zinc-cobalt colimitation of *Phaeocystis antarctica*. *Limnol. Oceanogr.* 53, 266–275. doi:10.4319/lo.2008.53.1.0266
- Saito, M.A., Moffett, J.W., 2001. Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean work. *Mar. Chem.* 75, 49–68. doi:10.1016/S0304-4203(01)00025-1
- Saito, M.A., Moffett, J.W., DiTullio, G.R., 2004. Cobalt and nickel in the Peru upwelling region: A major flux of labile cobalt utilized as a micronutrient. *Glob. Biogeochem. Cycles* 18, GB4030. doi:10.1029/2003GB002216
- Saito, M., Rocap, G., Moffett, J.W., 2005. Production of cobalt binding ligands in a *Synechococcus* feature at the Costa Rica Upwelling Dome. *Limnol. Oceanogr.* 50, 279–290.
- Sedwick, P.N., Church, T.M., Bowie, A.R., Marsay, C.M., Ussher, S.J., Achilles, K.M., Lethaby, P.J., Johnson, R.J., Sarin, M.M., McGillicuddy, D.J., 2005. Iron in the Sargasso Sea (Bermuda Atlantic Time-series Study region) during summer: Eolian imprint, spatiotemporal variability, and ecological implications. *Glob. Biogeochem. Cycles* 19, GB4006. doi:10.1029/2004gb002445
- Sedwick, P.N., Sholkovitz, E.R., Church, T.M., 2007. Impact of anthropogenic combustion emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso Sea. *Geochem. Geophys. Geosystems* 8, Q10Q06. doi:10.1029/2007gc001586

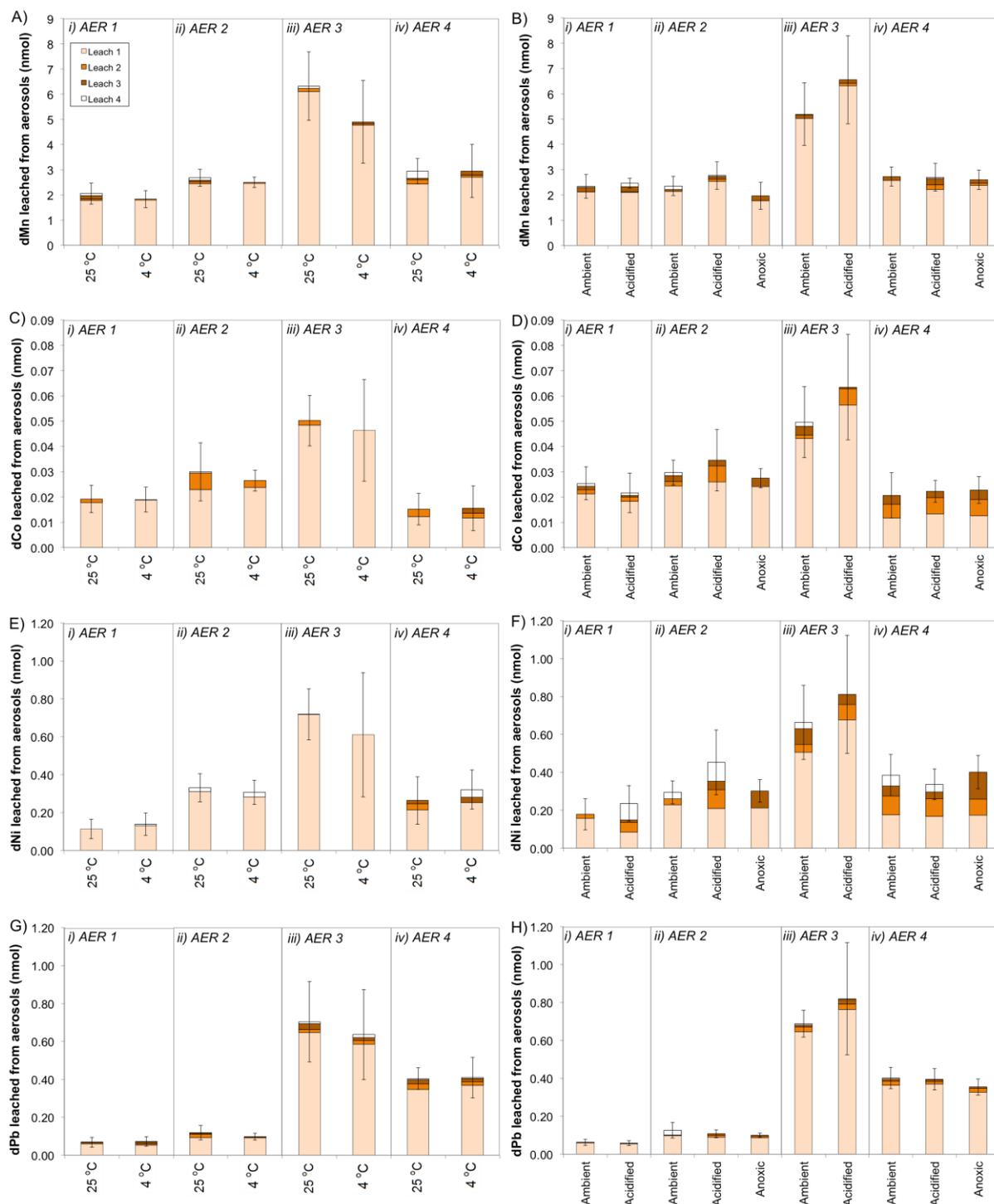
- Séguret, M.J.M., Koçak, M., Theodosi, C., Ussher, S.J., Worsfold, P.J., Herut, B., Mihalopoulos, N., Kubilay, N., Nimmo, M., 2011. Iron solubility in crustal and anthropogenic aerosols: The Eastern Mediterranean as a case study. *Mar. Chem.* 126, 229–238. doi:10.1016/j.marchem.2011.05.007
- Shaked, Y., Lis, H., 2012. Disassembling iron availability to phytoplankton. *Front. Microbiol.* 3. doi:10.3389/fmicb.2012.00123
- Shelley, R., Sedwick, P.N., Bibby, T., Cabedo Sanz, P., Church, T.M., Johnson, R.J., Macey, A., Marsay, C., Sholkovitz, E.R., Ussher, S.J., 2012. Controls on dissolved cobalt in surface waters of the Sargasso Sea: Comparisons with iron and aluminum. *Glob. Biogeochem. Cycles* 26, GB2020. doi:10.1029/2011GB004155
- Shelley, R.U., Morton, P.L., Landing, W.M., 2015. Elemental ratios and enrichment factors in aerosols from the US-GEOTRACES North Atlantic transects. *Deep Sea Res. Part II Top. Stud. Oceanogr., GEOTRACES GA-03 - The U.S. GEOTRACES North Atlantic Transect 116*, 262–272. doi:10.1016/j.dsr2.2014.12.005
- Shelley, R.U., Zachhuber, B., Sedwick, P.N., Worsfold, P.J., Lohan, M.C., 2010. Determination of total dissolved cobalt in UV-irradiated seawater using flow injection with chemiluminescence detection. *Limnol. Oceanogr. Methods* 8, 352–362. doi:10.4319/lom.2010.8.352
- Shi, D., Xu, Y., Hopkinson, B.M., Morel, F.M., 2010. Effect of ocean acidification on iron availability to marine phytoplankton. *Science* 327, 676–679. doi:10.1126/science.1183517
- Sholkovitz, E.R., Sedwick, P.N., Church, T.M., 2009. Influence of anthropogenic combustion emissions on the deposition of soluble aerosol iron to the ocean: Empirical estimates for island sites in the North Atlantic. *Geochim. Cosmochim. Acta* 73, 3981–4003. doi:10.1016/j.gca.2009.04.029
- Smichowski, P., 2008. Antimony in the environment as a global pollutant: A review on analytical methodologies for its determination in atmospheric aerosols. *Talanta* 75, 2–14. doi:10.1016/j.talanta.2007.11.005
- Sobanska, S., Ricq, N., Laboudigue, A., Guillermo, R., Brémard, C., Laureyns, J., Merlin, J.C., Wignacourt, J.P., 1999. Microchemical Investigations of Dust Emitted by a Lead Smelter. *Environ. Sci. Technol.* 33, 1334–1339. doi:10.1021/es9805270
- Stramma, L., Johnson, G.C., Sprintall, J., Mohrholz, V., 2008. Expanding oxygen-minimum zones in the tropical oceans. *Science* 320, 655–658. doi:10.1126/science.1153847
- Stumm, W., Morgan, J.J., 1996. *Aquatic chemistry: chemical equilibria and rates in natural waters*, 3rd ed, Environmental science and technology. Wiley, New York.
- Sunda, W.G., Huntsman, S.A., 1994. 12th International Symposium “Chemistry of the Mediterranean” Photoreduction of manganese oxides in seawater. *Mar. Chem.* 46, 133–152. doi:10.1016/0304-4203(94)90051-5
- Takeda, S., Tsuda, A., 2005. An in situ iron-enrichment experiment in the western subarctic Pacific (SEEDS): Introduction and summary. *Prog. Oceanogr.* 64, 95–109. doi:10.1016/j.pocean.2005.02.004
- Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental crust. *Rev. Geophys.* 33, 241–265. doi:10.1029/95rg00262
- Ussher, S.J., Achterberg, E.P., Powell, C., Baker, A.R., Jickells, T.D., Torres, R., Worsfold, P.J., 2013. Impact of atmospheric deposition on the contrasting iron

- biogeochemistry of the North and South Atlantic Ocean. *Glob. Biogeochem. Cycles*. doi:10.1002/gbc.20056
- Ussher, S.J., Achterberg, E.P., Sarthou, G., Laan, P., de Baar, H.J.W., Worsfold, P.J., 2010. Distribution of size fractionated dissolved iron in the Canary Basin. *Mar. Environ. Res.* 70, 46–55. doi:10.1016/j.marenvres.2010.03.001
- Vraspir, J.M., Butler, A., 2009. Chemistry of Marine Ligands and Siderophores, in: *Annual Review of Marine Science*, Annual Review of Marine Science. Annual Reviews, Palo Alto, pp. 43–63.
- Whitney, F.A., Freeland, H.J., Robert, M., 2007. Persistently declining oxygen levels in the interior waters of the eastern subarctic Pacific. *Prog. Oceanogr.* 75, 179–199. doi:10.1016/j.pocean.2007.08.007
- Wozniak, A.S., Shelley, R.U., Sleighter, R.L., Abdulla, H.A.N., Morton, P.L., Landing, W.M., Hatcher, P.G., 2013. Relationships among aerosol water soluble organic matter, iron and aluminum in European, North African, and Marine air masses from the 2010 US GEOTRACES cruise. *Mar. Chem.* 154, 24–33. doi:10.1016/j.marchem.2013.04.011
- Wu, J., Boyle, E.A., 1997. Lead in the Western North Atlantic Ocean: Completed Response to Leaded Gasoline Phaseout. *Geochim. Cosmochim. Acta* 61. doi:10.1016/S0016-7037(97)89711-6
- Wu, J., Boyle, E., Sunda, W., Wen, L.-S., 2001. Soluble and colloidal iron in the oligotrophic North Atlantic and North Pacific. *Science* 293, 847–849. doi:10.1126/science.1059251
- Wu, J., Rember, R., Cahill, C., 2007. Dissolution of aerosol iron in the surface waters of the North Pacific and North Atlantic oceans as determined by a semicontinuous flow-through reactor method. *Glob. Biogeochem. Cycles* 21. doi:10.1029/2006gb002851
- Xu, Y., Shi, D., Aristilde, L., Morel, F.M.M., 2012. The effect of pH on the uptake of zinc and cadmium in marine phytoplankton: Possible role of weak complexes. *Limnol. Oceanogr.* 57, 293–304. doi:10.4319/lo.2012.57.1.0293
- Zhuang, G., Duce, R.A., Kester, D.R., 1990. The Dissolution of Atmospheric Iron in Surface Seawater of the Open Ocean. *J. Geophys. Res.* 95, 16207–16216. doi:10.1029/JC095iC09p16207
- Zhu, X., Prospero, J.M., Millero, F.J., Savoie, D.L., Brass, G.W., 1992. The solubility of ferric ion in marine mineral aerosol solutions at ambient relative humidities. *Mar. Chem.* 38, 91–107. doi:10.1016/0304-4203(92)90069-M
- Zhu, X.R., Prospero, J.M., Millero, F.J., 1997. Diel variability of soluble Fe(II) and soluble total Fe in North African dust in the trade winds at Barbados. *J. Geophys. Res. Atmospheres* 102, 21297–21305. doi:10.1029/97jd01313

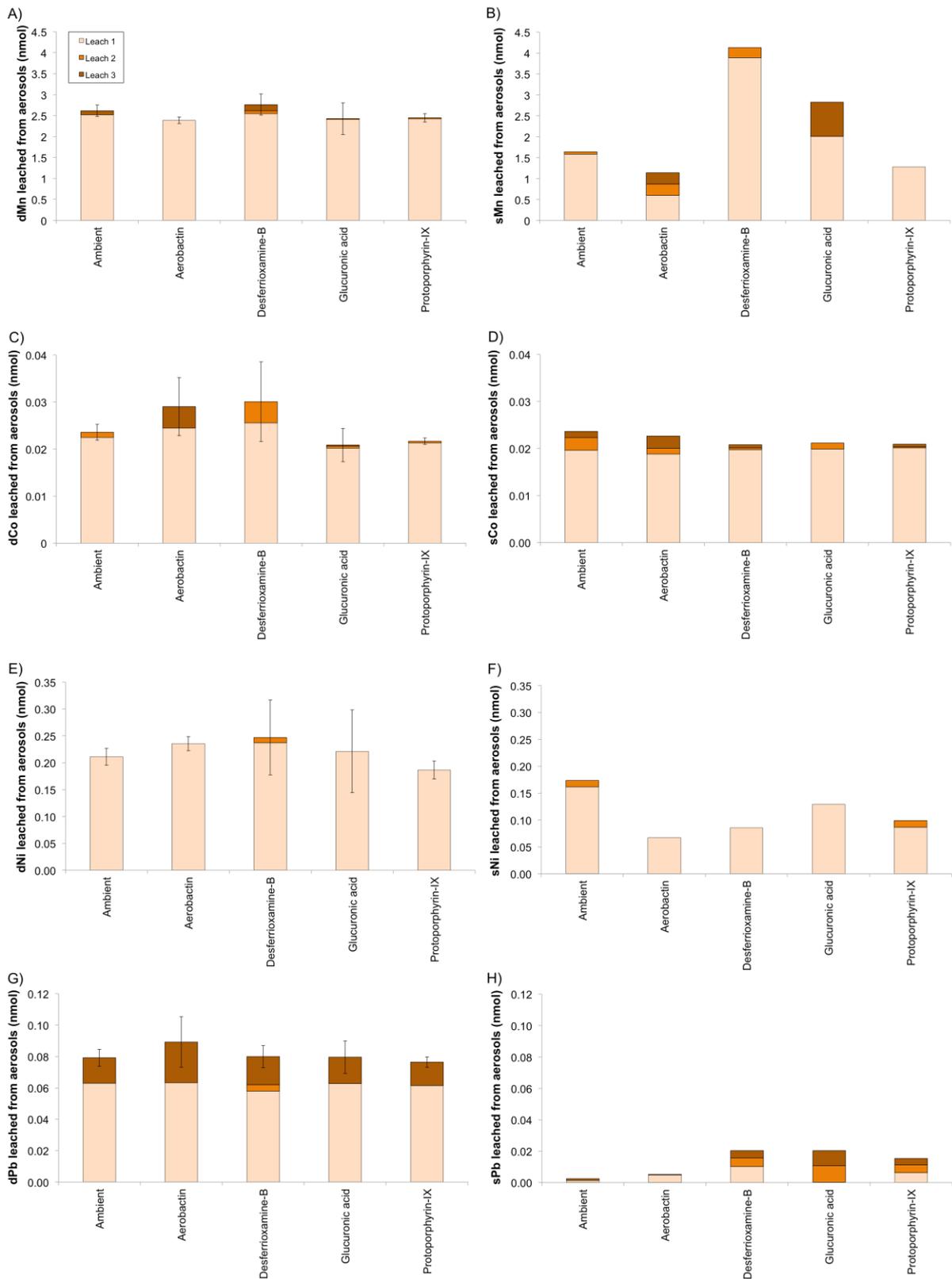
## Figures



**Figure 1. Enrichment factors for 'lithogenic' (Ti, Fe), 'mixed' (Mn, Co), and 'anthropogenic' (V, Ni, Cu, Cr, Cd, Sb, Pb) trace metals in aerosol samples AER 1, AER 2, AER 3 and AER 4, relative to crustal abundances. Enrichment factors were calculated by dividing mean trace metal/aluminium mass ratios of each aerosol sample by mean trace metal/aluminium mass ratios for the upper continental crust (Taylor and McLennan, 1995). Standard deviations on mean enrichment factors ( $\pm 1 \sigma$ ) represent the uncertainty in aerosol trace metals mean mass determinations only. The solid black line at  $1 \times 10^1$  denotes a threshold above which elemental enrichment is indicative of anthropogenic sources (Chester et al., 1999).**

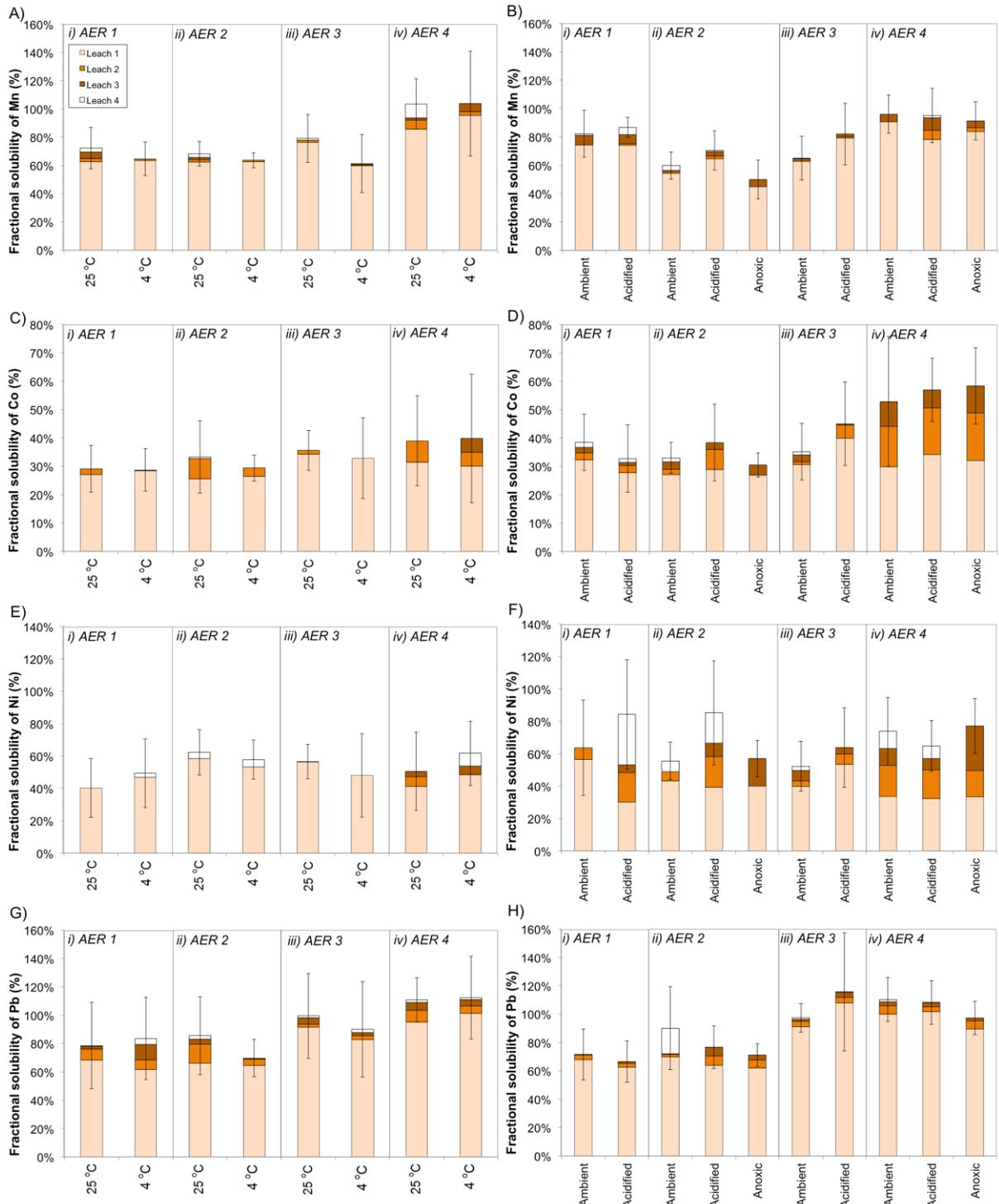


**Figure 2.** Mean nmol of dissolved manganese (dMn), cobalt (dCo), nickel (dNi) and lead (dPb) leached from aerosol samples i) AER 1, ii) AER 2, iii) AER 3 and iv) AER 4 in three replicate leaches with 4°C and 25°C seawater (A, C, E, G) and ambient seawater (25°C, pH 8.0, oxygenated), acidified seawater (25°C, pH 7.6, sparged with air enriched with carbon dioxide) and anoxic seawater (25°C, sparged with nitrogen gas for leaches 3 and 4) (B, C, F and H). Error bars represent one standard deviation ( $\pm 1\sigma$ ) on the mean dissolved trace metal (dTM) leached from replicate subsamples of a single aerosol sample. Segments of each bar show the amount of dTM leached during each sequential aerosol leach (i.e., leaches 1-4). Sequential leaches 1, 2, 3 and 4 represent the following time periods during which seawater was exposed to aerosols: 0-5 min, 5-10 min, 10 min-48 h and 48 h-30 days, respectively.

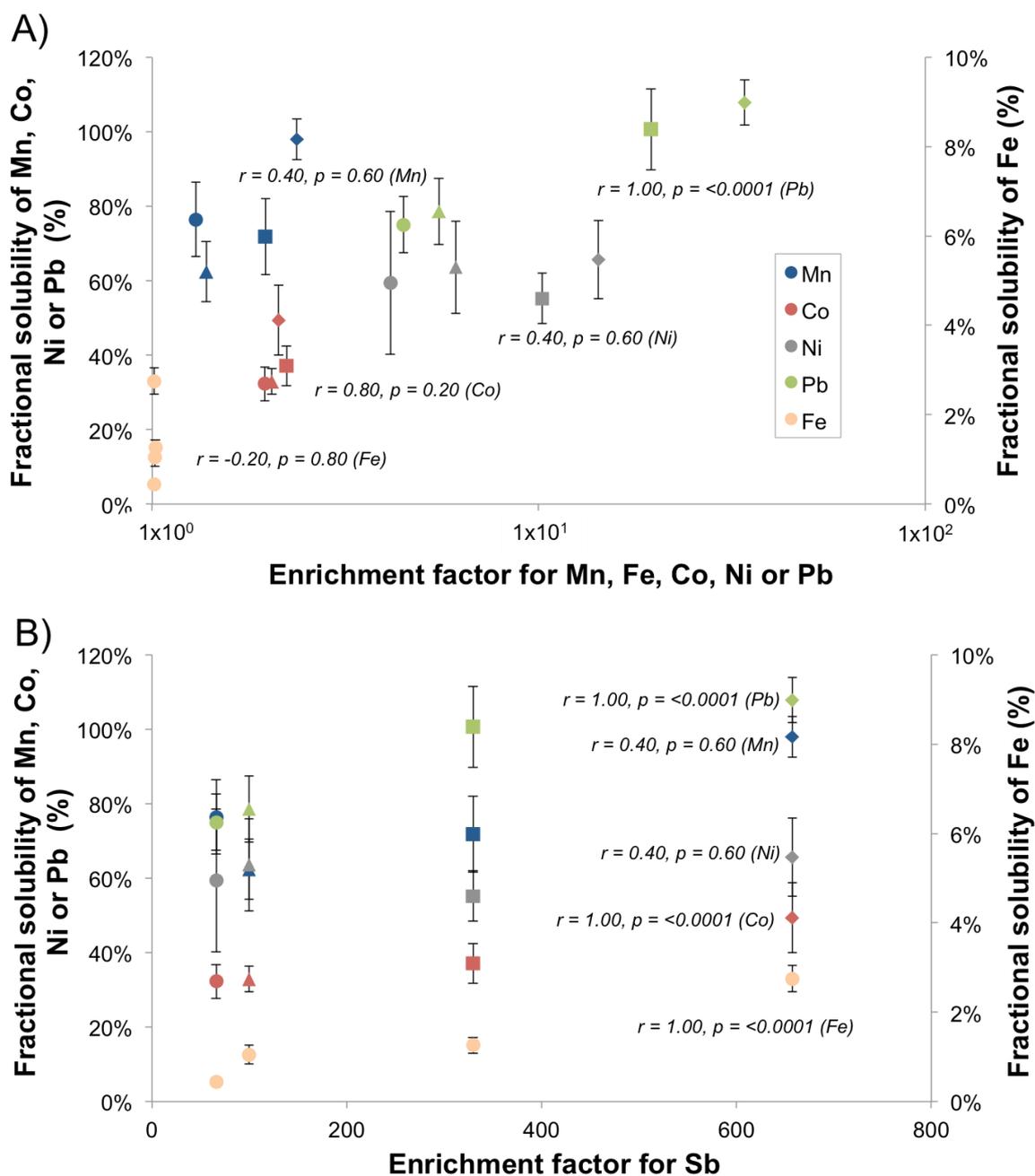


**Figure 3. Mean nmol of dissolved trace metal (dTM, < 0.4  $\mu\text{M}$ , A, C, E and G) and soluble trace metal (sTM, < 0.02  $\mu\text{M}$ , B, D, F and H) leached from aerosol sample AER 1 into ambient seawater and seawater amended with organic ligands aerobactin (10 mM), desferrioxamine-B (10 nM), glucuronic acid (1  $\mu\text{M}$ ) and protoporphyrin-IX (10 nM). A) Dissolved manganese (dMn), B) soluble manganese (sMn) C) dissolved cobalt (dCo), D) soluble cobalt (sCo), E) dissolved nickel (dNi), F) soluble nickel (sNi), G) dissolved lead (dPb), and H) soluble lead**

(sPb). Error bars represent one standard deviation ( $\pm 1 \sigma$ ) on the mean dTM leached from replicate subsamples of a single aerosol sample. No error bars are shown for sTM, as replicate leaches were not performed. For both dTM and sTM, segments of each bar show the amount of trace metal leached during each sequential aerosol leach (i.e., leaches 1-3). Sequential leaches 1, 2 and 3 represent the following time periods during which seawater was exposed to aerosols: 0-5 min, 5-10 min, and 10 min-48 h, respectively. Leach 4 was not performed in this experiment. It should be noted in the case of the desferrioxamine-B amendment (B), sMn exceeded dMn in the leachate solution, indicating contamination of this sample with Mn, possibly during the ultrafiltration procedure.



**Figure 4. Mean fractional solubility (%) of aerosol manganese (%Mn<sub>s</sub>), cobalt (%Co<sub>s</sub>), nickel (%Ni<sub>s</sub>) and lead (%Pb<sub>s</sub>) for aerosol samples i) AER 1, ii) AER 2, iii) AER 3 and iv) AER 4 for three replicate leaches with 4°C and 25°C seawater (A, C, E, G) and ambient seawater (25°C, pH 8.0, oxygenated), acidified seawater (25°C, pH 7.6, sparged with air enriched in carbon dioxide) and anoxic seawater (25°C, sparged with nitrogen gas for leaches 3 and 4) (B, C, F and H). Error bars represent one standard deviation ( $\pm 1 \sigma$ ) on the mean fractional solubility (%TM<sub>s</sub>) of replicate subsamples from a single aerosol sample. Segments of each bar show the %TM<sub>s</sub> for each sequential aerosol leach (i.e., leaches 1-4). Sequential leaches 1, 2, 3 and 4 represent the following time periods during which seawater was exposed to aerosols: 0-5 min, 5-10 min, 10 min-48 h and 48 h-30 days, respectively.**



**Figure 5.** Mean fractional solubility (% $TM_s$ ) of aerosol manganese (Mn), iron (Fe) [data from Fishwick et al. (2014)], cobalt (Co), nickel (Ni) and lead (Pb) from aerosol samples AER 1 (circles), AER 2 (triangles), AER 3 (squares) and AER 4 (diamonds) leached with 4°C and 25°C seawater and ambient seawater (25°C, pH 8.0, oxygenated), acidified seawater (25°C, pH 7.6, sparged with air enriched in carbon dioxide) and anoxic seawater (25°C, sparged with nitrogen gas for leaches 3 and 4) as a function of A) enrichment factors for bulk aerosol Mn, Fe, Co, Ni and Pb and B) enrichment factors for bulk aerosol antimony (Sb). Error bars represent the range of mean fractional solubilities of these metals for all seawater conditions examined. Spearman's Rho correlation coefficient  $r$ -values and  $p$ -values are shown beside each series plotted.

1 Tables

2

3 **Table 1. Conditional stability constants for organic ligands added during ligand amendment**  
 4 **experiments with respect to trace metal complexation.**

5

Organic ligand added	Log conditional stability constant for trace metal complexation			
	Manganese (Mn <sup>3+</sup> )	Cobalt (Co <sup>2+</sup> )	Nickel (Ni <sup>2+</sup> )	Lead (Pb <sup>2+</sup> )
Aerobactin	nd	nd	nd	nd
Desferrioxamine-B	29.9 <sup>a</sup>	10.31 <sup>b</sup>	10.9 <sup>b</sup>	10 <sup>c</sup>
Glucuronic acid	nd	< 0 <sup>b</sup>	< 0 <sup>b</sup>	2 <sup>b</sup>
Protoporphyrin-IX	nd	nd	nd	nd

6 <sup>a</sup>Data from Duckworth et al. (2009).

7 <sup>b</sup>Data from the National Institute of Standards and Technology (NIST). NIST Standard Reference  
 8 Database 46 v8.0. NIST Critically Selected Stability Constants of Metal Complexes Database. NIST,  
 9 2004.

10 <sup>c</sup>Data from Hernlem et al. (1996).

11 nd = no data.

12 **Table 2. Aerosol trace metal enrichment factors relative to upper continental crust abundances<sup>a</sup>**  
 13

Aerosol sample	Air mass source <sup>b</sup>	Enrichment factor										
		Ti	Fe	Mn	Co	V	Ni	Cu	Cr	Cd	Sb	Pb
AER 1	Sahara	1.8 ± 0.07	1.3 ± 0.1	1.3 ± 0.04	2 ± 0.07	3.4 ± 0.05	4.2 ± 0.2	2.9 ± 0.1	2.8 ± 0.2	26 ± 4	66 ± 7	4.5 ± 0.2
AER 2	Sahara/North America	1.8 ± 0.09	1.3 ± 0.02	1.4 ± 0.05	2 ± 0.03	5.2 ± 0.5	6.1 ± 0.3	4.8 ± 0.6	3.1 ± 0.2	24 ± 5	100 ± 0.4	5.5 ± 0.1
AER 3	North America	2 ± 0.1	1.4 ± 0.02	2.0 ± 0.5	2.2 ± 0.4	7.5 ± 2	10 ± 2	10 ± 4	4 ± 0.7	130 ± 40	330 ± 30	20 ± 6
AER 4	North America	2.4 ± 2	1.3 ± 0.05	2.4 ± 0.4	2.1 ± 0.2	11 ± 1	14 ± 1	17 ± 1	5.3 ± 2	230 ± 40	660 ± 20	34 ± 6

14 <sup>a</sup>Enrichment factors for lithogenic [titanium (Ti), iron (Fe)], mixed [manganese (Mn), cobalt (Co)] and anthropogenic [vanadium (V), nickel (Ni), copper (Cu),  
 15 chromium (Cr), cadmium (Cd), antimony (Sb) and lead (Pb)] trace metals in AER 1, AER 2, AER 3 and AER 4. Enrichment factors were calculated by  
 16 dividing trace metal/aluminium mass ratios of triplicate subsamples of each aerosol sample determined by inductively coupled plasma mass spectrometry  
 17 (ICP-MS) by trace metal/aluminium ratios found in the upper continental crust. Standard deviations from mean enrichment factors ( $\pm 1 \sigma$ ) represent the  
 18 uncertainty of trace metals mean mass measurements only.

19 <sup>b</sup>Air mass source inferred from 500 m 10-day back trajectories from Tudor Hill generated using the Hybrid Single-Particle Lagrangian Integrated Trajectory  
 20 (HYSPLIT) model over each sampling period. Data shown in Fishwick et al. (2014).

21 **Table 3. Total nmol of dissolved trace metal (dTM), colloidal trace metal (cTM) and soluble**  
 22 **trace metal (sTM) leached from aerosol samples AER 1, AER 2, AER 3 and AER 4 into ambient**  
 23 **seawater (25°C, pH 8.0, oxygenated) for the first replicate leach. Data are reported here for Mn,**  
 24 **Co, Ni and Pb**

Trace Metal	Aerosol Sample	Total mean amount of trace metal leached from aerosols (nmol)			Soluble proportion of dTM (%)	Colloidal proportion of dTM (%)
		dTM	cTM	sTM		
Mn	AER 1	2.0	0.32	1.7	84%	16%
Mn	AER 2	2.2	0.0	2.4	100%	0%
Mn	AER 3	6.0	1.9	4.1	69%	31%
Mn	AER 4	3.1	1.1	2.0	65%	35%
Co	AER 1	0.021	0.0052	0.016	76%	24%
Co	AER 2	0.028	0.012	0.016	57%	43%
Co	AER 3	0.053	0.0045	0.048	91%	9%
Co	AER 4	0.030	0.014	0.015	52%	48%
Ni	AER 1	0.11	0.056	0.052	48%	52%
Ni	AER 2	0.34	0.20	0.14	42%	58%
Ni	AER 3	0.61	0.034	0.58	94%	6%
Ni	AER 4	0.45	0.21	0.25	55%	45%
Pb	AER 1	0.051	0.049	< 0.0021 <sup>a</sup>	4%	96%
Pb	AER 2	0.15	0.14	0.0086	6%	94%
Pb	AER 3	0.66	0.62	0.042	6%	94%
Pb	AER 4	0.44	0.41	0.032	7%	93%

26 <sup>a</sup>This sPb value was below the limit of detection (LOD) measured on the day of analysis and therefore  
 27 the mean LOD for the method is shown.

28  
29**Table 4. Literature values of aerosol trace metal fractional solubility.**

Aerosol sample characteristics	Fractional solubility range (%)				Reference
	Mn	Co	Ni	Pb	
AER 1 – North Africa influenced	65 – 87	29 – 38	40 – 84	67 – 84	This study
AER 4 – anthropogenically influenced	91 – 104	39 – 58	51 – 77	97 – 112	This study
North Atlantic / European influenced	45 – 92				Baker et al. (2006c)
North Atlantic influenced	13 – 75				Baker et al. (2006c)
Sahara influenced	50 – 64				Baker et al. (2006c)
Collected in the Pacific Ocean	45.1 <sup>a</sup>				Buck et al. (2013)
Anthropogenically influenced (collected in Liverpool)	20 – 52			35 – 69	Chester et al. (1993)
North Africa influenced (collected in West Africa)	11 – 20			< 1 – 1.5	Chester et al. (1993)
Anthropogenically influenced (collected in Corsica)	49 – 61			27 – 35	Chester et al. (1993)
Mixed source (collected in the North Atlantic)	31 – 37			7 – 22	Chester et al. (1993)
Mixed source (collected in the Arabian Sea)	18 – 44			11 – 37	Chester et al. (1993)
Anthropogenically influenced (collected in the Taiwan Strait)	4 – 74		1 – 86	1 – 45	Hsu et al. (2005)
Anthropogenically influenced (collected in western Taiwan)	57 – 79		74 – 91	29 – 65	Hsu et al. (2005)
Anthropogenically influenced	49 <sup>b</sup>	36 <sup>b</sup>	26 <sup>b</sup>	45 <sup>b</sup>	Hsu et al. (2010)
North Africa influenced		8 – 10			Shelley et al. (2012)
Mixed source (collected in North Atlantic)		75 – 100			Shelley et al. (2012)

30  
31<sup>a</sup>Median fractional solubility reported in Buck et al. (2013).<sup>b</sup>Mean fractional solubility reported in Hsu et al. (2010).

32 **Table 5. Spearman's Rho correlation (*r*) and significance (*p*) values for aerosol trace metal fractional solubilities<sup>a</sup> as a function of enrichment**  
 33 **factors.**

34

Trace metal	Fractional solubility of trace metals versus their enrichment factors <sup>b</sup>		Fractional solubility of trace metals versus enrichment factors for V <sup>c</sup>		Fractional solubility of trace metals versus enrichment factors for Ni <sup>c</sup>		Fractional solubility of trace metals versus enrichment factors for Cu <sup>c</sup>		Fractional solubility of trace metals versus enrichment factors for Sb <sup>c</sup>	
	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>
Mn	0.40	0.60	0.4	0.6	0.4	0.6	0.4	0.6	0.4	0.6
Fe	-0.20	0.80	1	< 0.0001	1	< 0.0001	1	< 0.0001	1	< 0.0001
Co	0.80	0.20	1	< 0.0001	1	< 0.0001	1	< 0.0001	1	< 0.0001
Ni	0.40	0.60	0.4	0.6	0.4	0.6	0.4	0.6	0.4	0.6
Pb	1.00	< 0.0001	1	< 0.0001	1	< 0.0001	1	< 0.0001	1	< 0.0001

35 <sup>a</sup>Total mean trace metal fractional solubilities of manganese (Mn), cobalt (Co), nickel (Ni), lead (Pb) and iron (Fe) [data from Fishwick et al. (2014)] from  
 36 aerosol samples AER 1 – AER 4 into 4°C and 25°C seawater and ambient seawater (25°C, pH 8.0, oxygenated), acidified seawater (25°C, pH 7.6, sparged  
 37 with air enriched in carbon dioxide) and anoxic seawater (25°C, sparged with nitrogen gas for leaches 3 and 4).

38 <sup>b</sup>Fractional solubilities of Mn, Fe, Co, Ni and Pb as a function of respective enrichment factors for these metals.

39 <sup>c</sup>Fractional solubilities of Mn, Fe, Co, Ni and Pb as a function of enrichment factors for vanadium (V), Ni, copper (Cu) and antimony (Sb).

40 Supplementary Material

41

42

43

**Table S1. Proportion of the total amount of each metal<sup>a</sup> contained in each aerosol sample (AER 1 – 4) that the procedural field blank contributes<sup>b</sup>.**

Aerosol sample	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Cd	Sb	Pb
AER 1	61%	14%	5%	79%	21%	9%	20%	57%	33%	73%	60%	46%
AER 2	54%	11%	3%	70%	16%	7%	16%	38%	19%	70%	44%	34%
AER 3	45%	7%	1%	53%	9%	4%	11%	19%	7%	24%	14%	9%
AER 4	73%	18%	3%	78%	21%	15%	30%	38%	13%	38%	22%	17%
<i>Mean for all aerosol samples</i>	<i>58%</i>	<i>13%</i>	<i>3%</i>	<i>70%</i>	<i>17%</i>	<i>9%</i>	<i>19%</i>	<i>38%</i>	<i>18%</i>	<i>51%</i>	<i>35%</i>	<i>26%</i>
<i>RSD on mean determinations of triplicate subsamples of the procedural field blank</i>	<i>1%</i>	<i>5%</i>	<i>8%</i>	<i>1%</i>	<i>3%</i>	<i>2%</i>	<i>3%</i>	<i>2%</i>	<i>3%</i>	<i>1%</i>	<i>1%</i>	<i>2%</i>

44

<sup>a</sup>Trace metals considered: aluminium (Al), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), cadmium (Cd), antimony (Sb) and lead (Pb).

45

46

<sup>b</sup>Mean of triplicate subsamples of the procedural field blank used.

47

48 **Table S2. Concentrations of dissolved manganese (dMn), cobalt (dCo), nickel (dNi) and lead (dPb) determined in reference seawater using flow**  
 49 **injection with inductively coupled plasma mass spectrometry (FI-ICP-MS) and consensus concentrations for reference seawaters.**  
 50

Reference seawater	Bottle number/s	Measured concentrations of reference seawater (nM) <sup>b</sup>					Consensus concentrations of reference seawater (nM) <sup>c</sup>			
		n <sup>a</sup>	dMn	dCo	dNi	dPb	dMn	dCo	dNi	dPb
S1	547	4	0.64 ± 0.05	0.0035 ± 0.001	2.46 ± 0.1	0.0514 ± 0.002	0.77 ± 0.06	0.0047 ± 0.0012	2.22 ± 0.09	0.0468 ± 0.0021
D1	278, 540	4	0.27 ± 0.05	0.0298 ± 0.002	8.91 ± 0.6	0.036 ± 0.01	n/a	0.0443 ± 0.0046	8.37 ± 0.25	0.027 ± 0.0025
D2	237	7	0.26 ± 0.04	0.0396 ± 0.02	8.69 ± 2	0.031 ± 0.01	0.34 ± 0.05	0.0446 ± 0.0028	8.42 ± 0.24	0.027 ± 0.0015
GS	132	3	1.23 ± 0.1	0.036 ± 0.03	2.34 ± 0.3	0.0358 ± 0.01	1.46 ± 0.11	0.031 ± 0.0011	2.03 ± 0.06	0.0279 ± 0.0098
GD	158	4	0.2 ± 0.05	0.0500 ± 0.01	4.64 ± 0.9	0.0464 ± 0.01	0.2 ± 0.03	0.0636 ± 0.0012	3.9 ± 0.098	0.0417 ± 0.0015

51 <sup>a</sup>Number of dissolved trace metal (dTM) measurements of reference seawater over different days.

52 <sup>b</sup>Mean concentration of a number of dTM measurements of reference seawater over different days. Standard deviation ( $\pm 1 \sigma$ ) of the mean dTM  
 53 concentration includes variability between repeat analyses of reference seawater on different days.

54 <sup>c</sup>Consensus concentrations of dTM in reference seawater and standard deviation of repeat analyses from K. Bruland, unpublished data, 2008, available from  
 55 the Bruland Research Laboratory available at <http://es.ucsc.edu/~kbruland/GeotracesSaFe/kwbGeotracesSaFe.html>.