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1 Regional trends in the fractional solubility of Fe and other metals from 2 North Atlantic aerosols (GEOTRACES cruises GA01 and GA03) 3 following a two-stage leach

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16 **Abstract.** The fractional solubility of aerosol-derived trace elements deposited to the ocean surface is
17 a key parameter of many marine biogeochemical models. Yet, it is currently poorly constrained, in
18 part due to the complex interplay between the various processes that govern the solubilisation of
19 aerosol trace elements. In this study, we used a sequential two-stage leach to investigate the regional
20 variability in fractional solubility of a suite of aerosol trace elements (Al, Ti, Fe, Mn, Co, Ni, Cu, Zn,
21 Cd and Pb) from samples collected during three GEOTRACES cruises to the North Atlantic Ocean
22 (GA01, GA03-2010 and GA03-2011). We present aerosol trace element solubility data from two
23 sequential leaches that provide a “solubility window”, covering a conservative, lower limit to an upper
24 limit, the maximum potentially soluble fraction and discuss why this upper limit of solubility could be
25 used as a proxy for the bioavailable fraction in some regions.

26 Regardless of the leaching solution used in this study (mild versus strong leach), the most heavily
27 loaded samples generally had the lowest solubility. However, there were exceptions. Manganese
28 fractional solubility was relatively uniform across the full range of atmospheric loading (32 ± 13 %
29 and 49 ± 13 % for ultra-high purity water and 25 % acetic acid leaches, respectively). This is
30 consistent with other marine aerosol studies. Zinc and Cd fractional solubility also appeared to be
31 independent of atmospheric loading. Although the average fractional solubilities of Zn and Cd (Zn: 37
32 ± 28 % and 55 ± 30 %, Cd: 39 ± 23 % and 58 ± 26 % for ultra-high purity water and 25 % acetic acid
33 leaches, respectively) were similar to Mn, the range was greater, with several samples being 100%
34 soluble after the second leach. Finally, as the objective of this study was to investigate the regional
35 variability in TE solubility, the samples were grouped according to air mass back trajectories
36 (AMBTs). However, we conclude that AMBTs are not sufficiently discriminating to identify the
37 aerosol sources or the potential atmospheric processing effects that affect the physico-chemical
38 composition and solubility of the aerosols.

39 **1. Introduction**

40 Aerosol trace element (TE) solubility is a key parameter of many biogeochemical models, but it is
41 poorly constrained, e.g. Fe solubility estimates range from 0.001-90 % (Aguilar-Islas et al., 2010;
42 Baker et al., 2016). The fractional solubility (herein referred to as “solubility”) of aerosol TEs is
43 defined in terms of the amount of a TE in solution from any given leach that passes through a filter
44 (usually < 0.45 or 0.2 μm), expressed as a percentage of the total (Baker and Croot, 2010; Baker et al.,
45 2016; Jickells et al., 2016). While this operational definition accounts for some of the variability in
46 published values, it does not account for all of it. A number of factors impact aerosol TE solubility,
47 such as: (1) the choice of leaching protocol, and (2) the aerosol source, which in turn is impacted by a
48 combination of factors such as the mineralogy of the particles, atmospheric processing during
49 transport, and the presence/absence of emissions from e.g. vehicles, industry and agricultural
50 practices. Several studies have concluded that the most significant effects on aerosol Fe solubility
51 result from the source/composition of the aerosols, rather than changes in physico-chemical
52 parameters, such as temperature, pH and oxygen concentration of the leach medium, or the choice of
53 batch versus flow-through techniques (e.g. Aguilar-Islas et al., 2010; Fishwick et al., 2014).

54 There have been a number of studies that have focused on the role of aerosol TEs on biogeochemical
55 cycles in the North Atlantic (e.g. Sarthou et al., 2003; Baker et al., 2013; Buck et al., 2010; Ussher et
56 al., 2013; Powell et al., 2015). More recently, the GEOTRACES programme has produced a number
57 of aerosol datasets, which has stimulated further discussion on the use of this data to look for trends
58 that link TE solubility and aerosol source (e.g. Baker et al., 2016; Jickells et al., 2016). Elemental
59 ratios, enrichment factors and air mass back trajectory simulations have long been used as a first
60 approximation of aerosol source, and there are many studies that employ multivariate statistical
61 analyses for aerosol source apportionment (e.g. Chueinta et al., 2000; Laing et al., 2015). In addition,
62 more studies are making use of stable isotope ratios to investigate aerosol provenance. Some of these
63 methods are well-established and have a relatively long history of use in this purpose, such as Pb
64 isotopes (e.g. Maring et al., 1987), and Sr and Nd isotopes (e.g. Skonieczny et al., 2011; Scheuven et
65 al., 2013 and references therein), and data from investigations of novel isotope systems are increasing.
66 For example, Fe isotopes show promise as a way to differentiate between anthropogenic and mineral
67 dust aerosols (Conway et al., submitted). In contrast, Cd isotopes may not be a suitable tool for aerosol
68 source apportionment (Bridgestock et al., 2017).

69 As the soluble fraction of aerosol TEs are thought to be the most-readily bioavailable form of (Shaked
70 and Lis, 2009), the leachable (soluble) fraction is used as a first approximation of the bioavailable
71 fraction. Therefore, experimental conditions should mimic natural conditions as closely as possible,
72 while yielding reproducible results. Ideally, the leach protocol used fits both these criteria. However,
73 that is not always strictly possible for reasons such as access to the leach medium of choice,

74 availability of analytical instrumentation, and cost. Currently, however, there is no standardised
75 aerosol leaching protocol, but it is recognised that this should be a priority for future studies (Baker et
76 al., 2016). Some commonly-used leach media are ultra-high purity (UHP) water (18.2 MΩ.cm),
77 seawater, weak acids (e.g. 1% HCl, 25 % acetic acid), or ammonium acetate buffer (e.g. Buck et al.,
78 2006, Baker et al., 2006b; Berger et al., 2008).

79 To investigate the regional variation in the solubility of key TEs in North Atlantic, aerosol samples
80 were collected during the US-GEOTRACES GA03 campaigns in 2010 and 2011, and the French
81 GEOTRACES GA01 campaign in 2014 (www.geotraces.org). The focus of this paper is Fe and the
82 GEOTRACES “key” trace elements, Al, Cd, Cu, Mn, Pb, Zn, plus Co, Ni, and Ti (GEOTRACES
83 Planning Group, 2006). This suite of TEs includes bioactive elements, tracers of atmospheric
84 deposition, and elements characteristic of anthropogenic aerosols. Some TEs fit into more than one of
85 these categories. Here, we use the term ‘trace element’ in the context of open ocean water column
86 concentrations, thus acknowledging that elements such as Al, Fe and Ti are not present in trace
87 abundances in aerosol source material. Aerosol concentrations for a suite of other elements (Li, Na,
88 Mg, P, Sc, V, As, Se, Rb, Sr, Sn, Sb, Cs, Ba, La, Ce, Nd, Th, U) were also determined, but will not be
89 discussed further here. However, these data are available at BCO-DMO (GA03; www.bco-dmo.org/)
90 and LEFE-CYBER (GA01; (www.obsvlfr.fr/proof/php/GEOVIDE/GEOVIDE.php), and on request
91 from the lead author.

92 In this study a two-stage leach protocol was followed. the first leach employed was the
93 “instantaneous” leach described by Buck et al. (2006) which is a flow-through method where the leach
94 medium is in contact with the aerosols for 10 - 30 s. It can be conducted using UHP water or seawater.
95 The advantages of using UHP water are that UHP water is a reproducible medium (allowing for inter-
96 lab comparisons) that can easily be analysed by ICP-MS for many elements simultaneously without
97 the need for time-consuming sample handling steps such as separation techniques and drying down
98 then re-dissolving the residue. Leaches with UHP water can be conducted at sea, or in the home
99 laboratory. If fresh sea water is used the leaches must be undertaken at sea.

100 Given that UHP water and rain water have broadly similar pH (~ pH 5.6), UHP water is used as an
101 analogue for rain/wet deposition, as wet deposition is thought to dominate the supply of many TEs, at
102 least at some regional and local scales (Helmers and Shremms, 1995; Kim et al., 1999; Powell et al.,
103 2015). However, the extremely low ionic strength of UHP water, and the absence of the metal binding
104 ligands naturally present in rain water and seawater (e.g. Chieze et al., 2012; Wozniak et al., 2014),
105 means that UHP water is not a perfect analogue for oceanic receiving waters. As such, freshly-
106 collected, filtered (< 0.2 μm) seawater likely produces a better estimate of the fractional solubility of
107 TEs on first contact with oceanic receiving waters. For Fe, leaches using UHP water (~ pH 5.6)

108 typically produce higher solubility estimates than leaches conducted with natural seawater (~ pH 8.2)
109 due to the pH sensitivity of dissolution and the higher ionic strength of sea water. On occasions where
110 higher solubility in seawater is observed, complexation by Fe binding ligands is likely the cause.
111 Regardless of whether UHP water or seawater is used, the instantaneous leach likely yields
112 conservative lower limit estimates of TE solubility due to the short contact time between the aerosols
113 and leach medium, and reports that aerosol solubility has a bi-modal behaviour for many TEs (initial
114 fast release, followed by a slower sustained release with time; e.g. Desboeufs et al. 2005; Kocak et al.,
115 2007; Mackey et al., 2015).

116 The second, sequential leach was employed in order to estimate an upper limit of TE solubility, and
117 provide a “solubility window”, but also as an estimate of the maximum bioavailable fraction during
118 the residence time of aerosol particles in the euphotic zone. We used the 25 % acetic acid leach with
119 hydroxylamine hydrochloride described by Berger et al. (2008). The pH of this leach (pH 2.1) is just
120 below that of zooplankton or fish digestive tracts and the reducing agent mimics the low oxygen
121 environments inside faecal pellets and marine snow aggregates. Indeed, Schmidt et al. (2016) have
122 demonstrated that lithogenic Fe is mobilised in the gut passage of krill resulting in threefold higher Fe
123 content in the muscle, and fivefold higher Fe content of the faecal pellets of specimens close to
124 lithogenic source material compared to those from offshore.

125 **2. Methods**

126 **2.1. Aerosol sample collection**

127 Aerosol samples (n = 57) were collected aboard the *R/V Knorr* during the *US-GEOTRACES GA03*
128 cruises (15 Oct – 2 Nov 2010 and 6 Nov – 9 Dec 2011, and aboard the *N/O Pourquoi Pas?* during the
129 French GEOTRACES GA01 cruise (GEOVIDE, 15 May – 30 June 2014) (Fig. 1). Both campaigns
130 took place in the North Atlantic Ocean, with GA03-2010 and GA01 departing from Lisbon, Portugal.
131 The cruise tracks were designed to traverse a wide variety of biogeochemical provinces (Longhurst,
132 2010) including; continental shelf regions, an eastern boundary current upwelling system (off West
133 Africa), the oligotrophic North Atlantic gyre, and sub-Arctic waters, and to span a large gradient in
134 atmospheric dust loading. The aerosol collections have been described previously (Wozniak et al.,
135 2013; 2014; Shelley et al., 2015; 2017). Briefly, air was simultaneously pulled through twelve acid-
136 washed 47 mm diameter Whatman 41 (W41) ashless filter discs at approximately $1.2 \text{ m}^3 \text{ min}^{-1}$ (134
137 cm s^{-1} face velocity) using a high-volume aerosol sampler (TSP model 5170V-BL, Tisch
138 Environmental). The metadata and concentration data for the aerosol leaches can be found in the
139 supplementary information (Table S1). All filters were stored frozen (-20°C) and double bagged prior
140 to processing, both on the ship and upon returning to the home laboratories.
141 To avoid contamination from the ship’s stack exhaust, aerosol sampling was controlled with respect to
142 wind sector and wind speed using an anemometer interfaced with a datalogger (CR800, Campbell

143 Scientific). The samplers were programmed to run when the wind was $\pm 60^\circ$ from the bow of the ship
144 and $> 0.5 \text{ m s}^{-1}$. When the wind failed to meet these two criteria, the motors were shut off
145 automatically and not allowed to restart until the wind met both the speed and direction criteria for 5
146 continuous minutes. In addition, the samplers were deployed on the ship's flying bridge as high off the
147 water as possible ($\sim 14 \text{ m}$ above sea level) to minimise collection of sea spray.

148

149 **2.2. Trace element determination – totals aerosol TEs**

150 The total digestion method of Morton et al. (2013) was used for the determination of total aerosol TE
151 loadings (Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb). The W41 filter discs were digested in tightly-
152 capped 15 mL Teflon-PFA vials (Savillex). Firstly, 1000 μL of ultrahigh purity (UHP) 15.8 M nitric
153 acid (Optima or Merck ultrapur) was added to each vial, heated to 150°C on a hotplate, and then taken
154 to dryness. Secondly, 500 μL of 15.8 M nitric acid (13.2 M HNO_3) and 100 μL of 28.9 M hydrofluoric
155 acid (5.8 M HF) (Optima or Merck ultrapur) was added to each vial, re-heated to 150°C on a hotplate,
156 then taken to near dryness. After the final digestion and evaporation step, the samples were re-
157 dissolved in 20 mL of 0.32 M nitric acid for analysis. All filter digestions were performed under
158 Class-100 laminar flow conditions. Total aerosol TE concentrations were determined by magnetic
159 sector field inductively coupled plasma mass spectrometry (ICP-MS; Thermo Element-2) at the
160 National High Magnetic Field Laboratory (NHMFL) at Florida State University (FSU; GA03) or Pôle
161 de Spectrométrie Océan (PSO) at the Institut Universitaire Européen de la Mer, France (IUEM;
162 GA01). Samples were introduced to a PFA-ST nebuliser (Elemental Scientific Incorporated) via a
163 modified SC-Fast introduction system consisting of an SC-2 autosampler, a six-port valve and a
164 vacuum rinsing pump. Replicate blank solutions for the acid digestions were prepared by digesting
165 W41 discs that had been deployed in the aerosol samplers for 1 h while not in operation, and the
166 resulting concentrations were subtracted from all acid-digested filter samples. Details of the blanks
167 and analytical figures of merit, including CRM recoveries, have previously been reported (Shelley et
168 al., 2015; 2017).

169

170 **2.3. Trace element determination – soluble aerosol TEs**

171 In this study, we used a two-step, sequential leach to investigate regional variation in aerosol sources,
172 TE fractional solubility and bioavailability. We discuss the results from (1) an 'instantaneous' leach
173 (Buck et al., 2006), that provides a lower limit estimate of the most labile TE fraction (analogous to
174 the initial rapid release of TEs into rain drops and the surface mixed layer of the ocean), followed by
175 (2) a more protracted leach using 25 % acetic acid (with the reducing agent, hydroxylamine
176 hydrochloride, and heat, 10 min at 90°C), which mimics the slower and sustained release from aerosol
177 particles during their residence time in the euphotic zone.

178 The first step, the “instantaneous” leach, was conducted under a Class-100 laminar flow hood. In this
179 technique, 100 mL of UHP water (> 18 MΩ.cm resistivity, pH ~5.5, Barnstead Nanopure) is rapidly
180 passed through an aerosol-laden W41 filter held in a polysulfone vacuum filtration assembly
181 (Nalgene). Operationally-defined dissolved ($\leq 0.45 \mu\text{m}$) TEs are collected in the filtrate (leachate) by
182 positioning a GN-6 Metrice backing filter (cellulose esters) below the W41 disc in the filtration
183 assembly (Buck et al., 2006). In this study, the leachate was transferred to an acid-clean low density
184 polyethylene (LDPE) bottle and acidified to 0.024 M (~ pH 1.7) with UHP HCl and double-bagged for
185 storage until analysis at FSU or IUEM. As for total elemental determinations, soluble TEs in the
186 leachate were also determined by ICP-MS. Leachate blanks were prepared by passing 100 mL of
187 deionised water through W41 filters that had been deployed in the aerosol sampler for 1 h while not in
188 operation. For example, leachate blanks for Fe represented an average of $1.6 \pm 0.4 \%$ and 15.5 ± 15.8
189 % of the Fe sample concentrations for GA03 and GA01, respectively). A subset of samples (GA03-
190 2011) were also leached using the instantaneous leach procedure with freshly collected, filtered (0.2
191 μm) seawater as the leach medium. Leachate blanks were subtracted from all leachate sample
192 concentrations, details of which can be found in Table S1 in the Supplementary Material.

193
194 The fractional solubility was calculated using Eq. (1):

$$195 \frac{[element]_{leach}}{[element]_{total}} * 100 = \textit{Fractional Solubility} \quad (1)$$

196

197 Following the instantaneous UHP water leach, the filter was transferred to a 15 mL centrifuge tube,
198 and the second leach was undertaken, using 5 mL of 25 % (4.4 M) ultrapure acetic acid, with 0.02 M
199 hydroxylamine hydrochloride as the reducing agent (Berger et al., 2008). After a 10 min heating step
200 (90 °C), the leaches were left for 24 h before being centrifuged for 5 min at 3400xg. The leachate was
201 then carefully decanted into acid-clean LDPE bottles. In order to rinse any residual acetic acid from
202 the filter, 5 mL of UHP water was pipetted into the centrifuge tubes, which were then centrifuged
203 again for 5 min at 3400xg. This supernatant was then added to the acetic acid leachate in the LDPE
204 sample bottles. As this second leach aims to access a less labile fraction of the TEs of interest, without
205 significantly attacking TEs bound within the mineral matrix (Koçak et al., 2007; Berger et al., 2008), it
206 may provide an upper limit estimate for the fractional solubility of these aerosol TEs as the aerosols
207 mix down into the ocean. There is a slight risk that the heating step could begin to attack the mineral
208 matrix, resulting in a slight over-estimation of the upper limit of solubility, but this risk was shown to
209 be minimal (Berger et al., 2008). Despite this risk, the heating step was included because of the desire
210 for procedural similarity with marine particle leaches from the same cruises (e.g. Planquette et al.,
211 2016; H. Planquette and A. Gourain pers. comm.). This data has been used to show that for virtually
212 the whole GA01 transect atmospheric inputs of were not enough to sustain the water column

213 concentrations of Al, Fe and Pb (Menzel-Baraqueta et al., Tonnard et al., and Zurbrick et al., this
214 issue).

215 As all samples in this study were leached first using the UHP water instantaneous leach, followed by a
216 sequential leach with 25 % acetic acid, the overall solubility in 25% acetic acid was calculated using
217 Eq. (2):

$$218 \quad \frac{[element]_{UHP\ water\ leach}}{[element]_{total}} + \frac{[element]_{25\% \ HAc\ leach}}{[element]_{total}} * 100 = Fractional\ Solubility \quad (2)$$

219

220 **2.4. Major anion determination**

221 Before the UHP water leachate was acidified, a 10 mL aliquot was taken from each leach sample for
222 the determination of the soluble major anions. The aliquot was immediately frozen for storage. The
223 anions, Cl⁻, NO₃⁻ and SO₄²⁻, were determined by ion chromatography using either a Dionex 4500i (at
224 FSU for GA03 samples) or a Metrohm, IC850 system (at Laboratoire Interuniversitaire des Systèmes
225 Atmosphériques, Paris for GA01 samples).

226

227 **2.5. Air mass back trajectory simulations**

228 Air mass back trajectory (AMBT) simulations were generated using the publicly-available NOAA Air
229 Resources Laboratory Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model,
230 using the GDAS meteorology (Stein et al., 2015; Rolph, 2017). The 5-day AMBT simulations were
231 used to describe five regional categories, based on the predominant trajectories for the air masses. The
232 simulations and further details of these categories can be found in Wozniak et al., (2013; 2014) and
233 Shelley et al., (2015; 2017). Briefly, for cruise GA03 air masses were characterised as European,
234 North American, North African, or Marine (no or minimal interaction with major continental land
235 masses within the 5-day simulation period). For cruise GA01, all the samples were classified as High
236 Latitude dust (originating north of 50°N; Bullard et al., 2016). The classifications are shown in Table
237 S1, and the AMBT simulations from Shelley et al. (2015; 2017) have been reproduced and can be
238 found in the Supplementary Material (Fig. S1). The simulations use arrival heights of 50, 500 and
239 1500 m, so that at least one height was located in the marine boundary layer.

240

241 **3. Results and Discussion**

242 **3.1. Identifying aerosol provenance**

243 Air mass back trajectory (AMBT) simulations are frequently used to identify the origin and/or flow
244 path of air masses, from which a first approximation of marine aerosol provenance (e.g. deserts, urban
245 regions, or biomass burning) are made. While a useful tool in oceanographic studies, AMBTs used

246 alone do have limitations. Perhaps the most significant of these is that they are unable to quantify the
247 contribution of different aerosol types or the amount of entrainment of particles emitted along the flow
248 path of the air mass. Indeed, within the five categories described in this study multiple sources are
249 likely to have contributed to the composition of the bulk aerosol of each category. This study is likely
250 to be particularly sensitive to this as the sampling site was not static (i.e. sampling occurred along
251 three different transects), and air masses can, and do, take different pathways within a general wind
252 direction. Consequently, AMBTs are not adequately discriminating for aerosol source apportionment.
253 However, we have organised the data using the AMBT categories as the objective of this study was to
254 look for trends in solubility at a regional level, and also for consistency with our earlier published
255 work from the North Atlantic (Wozniak et al., 2013; 2014; Shelley et al., 2015; 2017).

256 More powerful approaches for aerosol source apportionment consider the physico-chemical
257 composition of the aerosols, either as the bulk aerosol or individual particles. There have been a
258 number of field campaigns (e.g. DABEX, DODO, SAMUM and AMMA) and individual studies
259 which have provided a wealth of information about the physico-chemical composition of African dust
260 before, during and after long-range transport (e.g. Johansen et al., 2000; Johnson et al., 2008;
261 McConnell et al., 2008; Petzold et al., 2009; Marticorena et al., 2010; Trapp et al., 2010; Formenti et
262 al., 2011). These studies, and satellite data have identified the key dust source regions in North Africa
263 (Prospero et al., 2002). Chemical composition data for other aerosol end members which supply
264 aerosols to the North Atlantic is not as extensive, but some examples of individual studies and field
265 campaigns can be found in Table S2. In addition, campaigns in the Atlantic Ocean which have
266 sampled marine aerosols (e.g. Atlantic Meridional Transect, CLIVAR, GEOTRACES) have identified
267 aerosol sources from characteristic groups of elements and elemental ratios (e.g. high concentrations
268 of lithogenic elements are characteristic of a mineral dust, K is a tracer of biomass burning, and
269 correlations between V and Ni are diagnostic of emissions from marine shipping; Baker et al., 2006a;
270 Sippula et al., 2014; Baker and Jickells, 2017), organic composition (e.g. Wozniak et al., 2013; 2014,
271 2015), and/or stable isotopic signatures (Scheuvens et al., 2013 and references therein).

272 Although atmospheric inputs to the ocean are episodic and exhibit a seasonality in the tropical and
273 subtropical North Atlantic that is largely driven by the migration of the intertropical convergence zone
274 (Prospero et al., 1981; Adams et al., 2012; Doherty et al., 2014), North African/Saharan mineral dust
275 dominated aerosol composition in the GA03 study region (Conway and John, 2014; Shelley et al.,
276 2015; Conway et al., submitted). Other aerosol sources in Europe and North America and sea salt also
277 contributed to the bulk aerosol to varying extents. In contrast to GA03, the GA01 transect was located
278 north of the extent of the Saharan dust plume ($\sim 25^\circ$ N in summer, Ben-Ami et al., 2009), and was
279 thus influenced by a mixture of high latitude dust sources (Prospero et al., 2012; Shelley et al., 2017),
280 which also have a seasonal cycle. As a result, a large dynamic range of aerosol loading was observed

281 (Fe = 0.185–5650 ng m⁻³; Al = 0.761- 7490 ng m⁻³) during these two campaigns, with the highest Fe
282 and Al loadings associated with the North African samples (GA03), lower loadings with the Marine
283 samples (GA03), and the lowest loadings observed in the samples collected in the Labrador Sea
284 (GA01).

285 Total Fe and Al were strongly correlated ($r^2 = 0.999$, Pearson's ρ $P < 0.01$), demonstrating that the two
286 metals have common lithogenic source(s) (Fig. 2). However, this correlation was largely driven by the
287 heavily-loaded North African samples ($r^2 = 0.997$, $P < 0.01$). For each of the other source categories,
288 simple linear regression of the data resulted in r^2 values of: 0.879 ($P < 0.01$) for High Latitude dust
289 (GA01), 0.890 ($P = 0.057$) for European samples (GA03), 0.983 ($P 0.34$) for N. American samples
290 (GA03) and 0.751 ($P = 0.70$) for Marine samples (GA03) (Fig. 2b). Further discussion of sub-regional
291 differences in the Fe/Al ratio are addressed later in the Discussion. For the other TEs, strong
292 correlations for the combined GA01 and GA03 datasets were found between Ti/Al ($r^2 = 0.999$, $P <$
293 0.01), Mn/Al ($r^2 = 0.994$, $P < 0.01$) and Co/Al ($r^2 = 0.996$, $P < 0.01$), in accord with previous
294 observations in this region owing to the primarily lithogenic sources of these elements (e.g. Jickells et
295 al., 2016). The correlations between Al and the primarily anthropogenic TEs, Ni, Cu, Zn, Cd, and Pb,
296 were also significant at the 99% confidence level : Ni/Al ($r^2 = 0.884$), Cu/Al ($r^2 = 0.652$), Pb/Al ($r^2 =$
297 0.478), Zn/Al ($r^2 = 0.321$), Cd/Al ($r^2 = 0.303$) due the presence of the heavily-loaded North African
298 samples , which accounted for between 88 % and 30 % of the statistical variance for Ni and Cd,
299 respectively. Sources other than mineral dust (e.g. metal smelting emissions, fly ash, vehicle
300 emissions, volcanic ash, proglacial till) are presumably responsible for the residual variance.
301 Establishing the contribution of these other sources and the impact on TE solubility is a research
302 priority.

303 As the aerosol source has a direct bearing on the type and composition of aerosols, determining the
304 source could provide useful data that might be used to predict the fractional solubility of aerosol TEs.
305 As positive matrix factorisation (PMF) can be used for source apportionment, we used the USA
306 Environmental Protection Agency EPA PMF model (v. 5.0) with the total TE concentration data to
307 look for trends in the data. However, the GA01 and GA03 dataset is relatively small ($n = 57$) and the
308 model was not stable with more than two factors. The two factors were a mineral dust factor (high
309 contributions from lithogenic TEs, in particular Al, Ti, Fe and Zr) and a pollution/anthropogenic factor
310 (with high contributions from Zn and Pb) (Fig. S2a, Supplementary Material). As anticipated, the
311 mineral dust factor dominated where North African aerosols were sampled, and the pollution factor
312 was relatively more important closer to the European and North American continents (Fig. S2b). This
313 is in accord with the samples from North Africa having elemental mass ratios that are consistently the
314 closest to the UCC elemental ratios compared to aerosols from the other source regions (Fig. 3). In
315 the High Latitude samples, the pollution factor and the mineral dust factor were of approximately

316 equal dominance. Interestingly, the North African aerosols also contained a relatively strong pollution
317 component, consistent with a northeast flow into North Africa from Europe, followed by entrainment
318 of mineral dust during passage over the Sahara (Baker and Jickells, 2017). Given that the PMF
319 indicates that 100 % of the variability in the Cd concentrations was explained by the pollution factor,
320 this suggests that Cd in North African aerosols is not sourced from mineral dust, which would explain
321 why no fractionation was observed in Cd isotopes from North African and European aerosols
322 (Bridgestock et al., 2017). Further, it also suggests that even the relatively homogeneous aerosols from
323 North Africa do not represent a ‘pure’ end-member. However, the PMF analysis was not sensitive
324 enough to identify the full complement of aerosol sources contributing to the samples collected during
325 GA01 and GA03.

326 **3.2. Elemental mass ratios and aerosol source**

327 Elemental mass ratios from the ten most heavily loaded GA03 North African aerosols were averaged
328 to derive a value for the ‘North African’ ratio depicted by the dashed horizontal line in Figures 3(a-i).
329 Aluminium was used to normalise the data (Fig. 3; Table S2) and was chosen instead of Ti, another
330 proxy for mineral dust, due to the presence of some anomalously high Ti/Al ratios in some of the
331 Marine samples during GA03 (Fig. 3a; Shelley et al., 2015). We have previously reported a mass ratio
332 of 0.76 for Fe/Al for the North African end-member aerosols (Shelley et al., 2015; Fig. 2a), which is
333 significantly higher than the mean upper continental crustal (UCC) ratio of 0.47 (Rudnick and Gao,
334 2003) but entirely consistent other studies of Saharan soils and dust (e.g. Chiapello et al., 1997; Guieu
335 et al., 2002; Lafon et al., 2006; Baker et al., 2013).

336 For North African dust there does not appear to be a discernible source dependent trend in Fe/Al ratios
337 due to a natural variability in Fe-bearing minerals in soils in dust source regions (Lafon et al., 2006;
338 Scheuven et al., 2013), but it might be possible to use Fe/Al ratios for some of the other aerosol
339 groups to suggest different sources. For example, the European samples ($n = 4$) fall into two sub-
340 groups: two samples have low Fe/Al ratios (Fig. 2; E3 = 0.48, E4 = 0.10 and Fig. 3c), whereas the
341 other two samples (E1 = 0.95 and E2 = 0.78) have Fe/Al ratios within the range of the North American
342 samples (Fe/Al 1.1 ± 0.22 , range 0.86-1.42) and all but one of the Marine samples (Fe/Al, excluding
343 M12, 0.93 ± 0.33 , range 0.59-1.61; M12, collected closest to the North African samples, Fe/Al =
344 0.43).

345 Aerosols from the more northerly section, GA01, were largely outside the influence of the Saharan
346 dust plume (Shelley et al., 2017), and are all classified as High Latitude in this study (Fig. 3). For this
347 group of samples, there were also sub-groups of Fe/Al ratios. During the first half of the cruise (Fig.
348 1), there was a group of samples (G1-6, G8 and G10) with Fe/Al ratios of 0.58 ± 0.05 ; Fig.3c). This is
349 intermediate between the UCC ratio (0.48 ± 0.07) and the North African mineral dust ratio ($0.78 \pm$

0.03; Fig. 3c). For these samples, the wind direction was predominantly from the north/north west (Shelley et al., 2017), so it is unlikely that the observed ratios reflect a mixture of North African mineral dust and European aerosols. Rather, it is more likely comes from high latitude sources, as dust supplied by proglacial till from Iceland and Greenland peaks in spring/early summer, and can be deposited over the Atlantic Ocean (Prospero et al., 2012; Bullard et al., 2016), although the extensive cloud cover experienced during the GA01 cruise (May/June 2014) prevented the use of satellite observations (e.g. <http://worldview.earthdata.nasa.gov>) which would have confirmed the presence of dust from these sources. The elemental ratios calculated from TE concentrations from volcanic ash sampled during the eruption of the Eyjafjallajökull volcano in 2010 (Achterberg et al., 2013) offers some limited support for this argument, as our range of elemental ratios encompasses this end-member (Icelandic soils are almost exclusively volcanic in origin; Arnalds 2004). However, although Icelandic sands (Baratoux et al., 2011) and tephra (Oladottir et al., 2011) have Mn/Al ratios that overlap the GA01 samples, Fe/Al is generally lower in our High Latitude dust samples (Table S2).

A second group of GA01 samples (G7, G9, G11 and G12) had Fe/Al ratios of 0.34 ± 0.01 , but no obvious link in terms of the AMBTs. The Greenland shelf and Labrador Sea samples, except G15, had low Fe/Al (0.16 ± 0.04), and were distinct from those collected on the Canadian shelf (0.48 ± 0.02). These trends strongly suggest that the High Latitude dust is made up of at least four aerosol sources.

While there is evidence for anthropogenic source(s) of aerosol Fe to the North Atlantic (Conway et al., submitted), which is more soluble than Fe associated with mineral dust (Sedwick et al., 2007; Sholkovitz et al., 2009; 2012), North African mineral dust dominates the supply of Fe to much of the study region (Baker et al., 2013; Shelley et al., 2015; 2017; Conway et al., submitted). In addition to the samples classified as European and North American, elevated Fe/Al ratios were also observed in the Marine samples (Fig. 2b). In addition to aerosols derived from continental sources (meaning either mineral dust or anthropogenic emissions), sea spray aerosols could make a relatively higher contribution to the bulk aerosol in remote oceanic locations (de Leeuw et al., 2014). However, this would have the opposite effect as the ratio of Fe/Al in surface seawater (0.017 – 0.024 in the North Atlantic gyre, 0.019 European continental shelf, and 0.030 – 0.031 in the Mauritanian upwelling zone; Hatta et al., 2015) is two orders of magnitude lower than the crustal ratio. Hence the contribution of sea spray aerosols appears to have a negligible impact on the Fe/Al ratios in the bulk Marine aerosols.

The Marine, and the High Latitude samples had the widest range in Fe/Al ratios and were also collected in the most remote locations. These groups also had the greatest difference in the Fe/Al ratio between the total and soluble fractions, and also contained the samples with the lowest ratios of Fe/Al in the soluble fraction (minimum Fe/Al = 0.15, samples G9-GA01 and M3-GA03; Fig. 3c), suggesting that even though aerosol Fe is altered towards more soluble forms during atmospheric transport

384 (Longo et al., 2016), atmospheric processing renders Al even more soluble relative to. However,
385 although the soluble ratio of Fe/Al was the same for samples G9-GA01 and M3-GA03, the fractional
386 solubility for Fe differed from 20 % for G9-GA01 to 0.8 % for M3-GA03. We suggest North African
387 mineral dust was contributing to the composition of M3-GA03, resulting in the low solubility of Fe
388 compared to G9-GA01. This suggestion is supported by isotopic evidence (Conway et al., submitted).

389 For the anthropogenically-derived TEs, Ni, Cu, Zn, Cd and Pb (Figs. 3e-i) and for at least some of
390 samples of the mixed-source TEs (i.e. having crustal and pollution sources; e.g. Mn and Co in Figs. 3b
391 and d), there is some degree of source-dependence in the elemental ratios, with some significant
392 increases from the UCC mass ratios in the total (Shelley et al., 2015) and UHP water soluble fractions
393 (Fig. 3). The higher ratios of the UHP water soluble fraction compared to the total indicates that these
394 TEs are more labile than Al. In addition, studies that have investigated the size distribution of aerosols
395 have found that anthropogenically-derived TEs tend to be associated with fine mode aerosols (< 1 μm
396 diameter), which are more soluble than coarse mode aerosols due to the larger surface area to volume
397 ratio (Duce et al., 1991; Baker and Jickells 2006; Baker and Jickells, 2017). Size fractionated samples
398 were collected during the GA03 cruise, and the smaller size fractions were indeed more soluble than
399 the larger (Landing and Shelley, 2013). Enrichment of TEs with predominantly anthropogenic sources
400 accords with other studies in the North Atlantic, and is most striking for aerosols that did not originate
401 from the sparsely-populated, arid regions of North Africa (e.g. Buck et al., 2010; Gelado-Cabellero et
402 al., 2012; Patey et al., 2015; Shelley et al., 2015).

403

404 **3.3. Aerosol solubility**

405 **3.3.1. Solubility of aerosol TEs as a function of total concentration: UHP water (instantaneous)** 406 **compared to 25 % acetic acid leaches**

407 The UHP water soluble fraction of aerosol Fe and Al determined for all the North Atlantic GA01 and
408 GA03 samples varied by two orders of magnitude (Fig. 4a: Fe = 0.14 - 21 %, median 2.2 %; Al = 0.34
409 - 28 %, median 2.7%). Although a broader range of Fe and Al solubility was observed in this study,
410 both these results and those reported by Buck et al. (2010) using the same approach (Fe = 2.9 - 47%,
411 median = 14%, and Al = 3.7 - 50%, median = 9.5%) broadly agree that the median UHP water soluble
412 fractions of Fe compared to Al in the North Atlantic are similar. While there was considerable overlap
413 in the ranges of fractional solubility of TEs in aerosols from the different regions (e.g. Fe: European
414 1.9 – 21 %; N. American 0.84 – 8.8 %; Marine 1.7 – 18 %; High Latitude dust 1.9 – 20 %), the North
415 African samples, identified by their orange colour, high Fe and Al loadings, and definitive AMBTs)
416 formed a distinct cluster of very poorly soluble Fe, or Al (< 1%; Fig. 4a). However, the solubility of
417 the North African ('Saharan') aerosol Fe was 1 – 2 orders of magnitude lower in this study (0.14 –
418 0.57 %) than during the Buck et al. (2010) study (2.9 – 19 %). This supports the hypothesis that TEs

419 from North African aerosols sampled with a higher frequency, closer to source (as in this study) are
420 less soluble as a result of a lesser degree of atmospheric processing and/or larger particle sizes (Baker
421 and Jickells, 2006; Longo et al., 2016).

422 The inverse relationship between total aerosol loading and fractional solubility has previously been
423 reported for Fe (Sholkovitz et al., 2009; 2012; Jickells et al., 2016) and Al (Jickells et al., 2016).
424 Jickells et al. (2016) compiled solubility data from the North Atlantic and found that the general trend
425 between Fe and Al solubility and atmospheric loading was robust over the range of atmospheric
426 loadings found in the North Atlantic, regardless of the leach protocol employed. In this study, both the
427 UHP soluble, and 25 % acetic acid soluble fractions of Fe and Al (Figs 4a and b) were related to
428 atmospheric loading, i.e. the highest loaded North African samples had the lowest solubility. The
429 possible exception to this trend is the fraction of Al that dissolved from North African aerosols
430 following the 25 % acetic acid leach (Fig. 4b). However, it could simply be that we are observing
431 scatter in our data, which is smoothed out in the larger dataset ($n > 2000$) examined by Jickells et al.
432 (2016). Although, we cannot rule out that this effect is the result of the heating step in the 25 % acetic
433 acid leach attacking the alumino-silicate matrix. Further experimentation with and without the heating
434 step would help to resolve this issue.

435 For most of the other TEs investigated here (Ti, Co, Ni, Cu, Zn, Cd and Pb; Fig. 4a), the same general
436 trend as Fe and Al was observed following the UHP water leach. For the 25 % acetic acid leaches
437 (Fig. 4b), Ti, Ni, Cu and Pb solubility decreased with an increase in atmospheric loading, but the trend
438 was less clear for Co. For Co the inverse relationship between UHP water solubility and loading was
439 not observed when using the 25 % acetic acid leach, most likely because Co may be associated with
440 the Mn and Fe oxides that are easily reduced using this leach. In contrast, Mn, Zn and Cd did not
441 display the same inverse relationship as Fe and Al after either leaching step (Figs. 4a and b). This has
442 previously been noted for Mn (Jickells et al., 2016). Although the average fractional solubilities of Zn
443 and Cd (Zn: 37 ± 28 % and 55 ± 30 %, Cd: 39 ± 23 % and 58 ± 26 % for ultra-high purity water and
444 25 % acetic acid leaches, respectively) were similar to Mn (32 ± 13 % and 49 ± 13 % for ultra-high
445 purity water and 25 % acetic acid leaches, respectively), the range was greater, with several samples
446 from different regions (although not North Africa) being 100% soluble after the second leach.

447 **3.3.2. Solubility of TEs: UHP water (instantaneous) compared to 25 % acetic acid leaches**

448 All ten TEs from the five different provenances were less soluble in UHP water than 25 % acetic acid
449 (Fig. 5). This is not a surprising finding given the lower pH of acetic acid compared with UHP water,
450 that acetate is a bidentate ligand, and the longer contact time of the aerosols with the leach solution in
451 the 25 % acetic acid leach procedure. In addition, there is some degree of source-dependent variability
452 in the relative proportions of each TE that is released by the two leaches. In general, as with the

453 leaches with UHP water, the North African aerosols were distinctly less soluble than aerosols from the
454 other source regions (Fig. 5). Figure 5 highlights the distinction between the lithogenic elements, Al,
455 Fe and Ti (universally low solubility in UHP water, mostly < 20 %, and extremely low solubility of
456 North African aerosols, < 1 %), and the anthropogenic, pollution-dominated elements, Ni, Cu, Zn, Cd
457 and Pb (solubility up to 100 %). Manganese (Mn) and Co have both lithogenic and anthropogenic
458 sources, so are classified as “mixed-source”, and have intermediate solubilities. Like all the TEs
459 reported here, Mn solubility in UHP water was significantly less ($p < 0.01$, two-tailed, homoscedastic
460 t-test) in North African aerosols (median solubility = 19 %) than in the non-North African samples
461 (median = 38%), which seems to contrast somewhat with the findings of Baker et al. (2006b) and
462 Jickells et al. (2016). However, in common with these earlier studies (Baker et al., 2006b; Jickells et
463 al., 2016), there was no significant source-dependent difference in Mn solubility in 25 % acetic acid
464 (non-North African samples: $49 \pm 15\%$, North African samples: $49 \pm 6.4\%$).

465 **3.3.3. Soluble TEs: UHP water compared to seawater instantaneous leaches**

466 Seawater leaches were conducted on a subset of samples (GA03-2011), to investigate the suitability of
467 seawater as the leach medium in the instantaneous leach (Fig. 6). During this study, Fe solubility in
468 seawater was lower than in UHP water (Fig. 6c). This phenomenon has previously been observed in
469 atmospheric aerosols from the North Atlantic Ocean (Buck et al., 2010). For Fe, only a few samples
470 of North American and Marine provenance conformed to the relationship described by the equation
471 proposed by Buck et al. (2010), with most of our data plotting above the regression line of the Buck et
472 al. (2010) study (Fig. 6c), indicating that our data was relatively more soluble in UHP water compared
473 to seawater than in this earlier study. One possibility is that the higher aerosol Fe loadings we
474 observed during GA03-2011 (this study, maximum = $5650 \text{ ng Fe m}^{-3}$), compared to the A16N-2003
475 transect (Buck et al. 2010; maximum = $1330 \text{ ng Fe m}^{-3}$), resulted in a particle concentration effect
476 (Baker and Jickells, 2006), whereby the relationship between aerosol Fe loading and fractional
477 solubility breaks down because dust on the filter can be a source of soluble Fe but can also scavenge
478 dissolved Fe from the sea water leach solution as it passes through the filter. Given that the link
479 between Fe solubility in seawater and Fe-binding ligand availability is well established (e.g. Rue and
480 Bruland, 1995; Gledhill and Buck, 2012), an alternative explanation for the difference in Fe solubility
481 is that the organic composition of the seawater used as the leach mediums differed between the two
482 studies.

483 Mn is the only TE that has a slope close to unity (0.98; Fig. 6b), suggesting that solubility estimates
484 were not impacted by the choice of leach medium used. This is consistent with other studies that have
485 found that Mn solubility is less sensitive to the choice of leach media, or to aerosol provenance than
486 other TEs (Baker et al., 2006b; Jickells et al., 2016). Due to the large variability in the data set, there
487 was no significant difference between Mn solubility in UHP water or seawater ($32 \pm 13\%$ and 24 ± 17

488 %, respectively; Fig. S3, and Tables S3 and S4, Supplementary Material). Table 1 shows which
489 regions had slopes for UHP water versus seawater fractional solubility that did not differ significantly
490 from 1.0 at the 95 % confidence level (t-statistic; Table S5). For the North American samples, the
491 slope did not differ significantly from 1.0 for Al, Mn, Co, and Zn. For the Marine samples, the same
492 was true for Al, Co and Zn, and for the North African samples this was the case for Al, Fe, Ni, Cu, Zn
493 and Cd. Pb was the only TE with slopes differing significantly from 1.0 for all regions.

494 For Co and Pb (Figs 6d and i), most of the data falls below the 1:1 line, indicating that they were
495 generally more soluble in seawater than UHP water. In contrast, the opposite trend was observed for
496 Fe and Ni (Figs 6c and e), perhaps due to differences in the availability of metal binding ligands in the
497 seawater used. A challenge of using seawater as the leach medium is that it is difficult to control for
498 natural variability in the types and concentrations of organic ligands. Consequently, it is not possible
499 to determine conclusively why contrasting trends in the fractional solubility of TEs were observed. For
500 this reason, we advocate for the use of UHP water as a common leach medium to facilitate
501 comparisons of solubility resulting from differences in aerosol composition. An additional benefit is
502 the ease of analysis of UHP water compared to seawater.

503

504 **3.4. Visualising marine aerosol sources using multivariate statistical approaches**

505 As the PMF analysis was only able to identify two significant factors accounting for the total aerosol
506 TE concentrations, another multivariate approach was taken. Hierarchical cluster analysis (Ward's
507 method, Euclidian distance) was performed using the R statistical package (v. 3.3.0; R Core Team,
508 2016) to look for trends in the data that might reveal the various aerosol sources. Hierarchical cluster
509 analysis was performed on (1) log transformed total aerosol TE plus NO_3^- concentration data (Fig. 7a),
510 and (2) log transformed TE fractional solubility plus NO_3^- concentration data (Fig. 7b). The NO_3^-
511 concentrations appear in both runs as we wanted to include TEs plus an indicator of anthropogenic
512 pollution.

513 Figure 7a shows two main branches to the dendrogram of the total TE concentration data. One branch
514 groups all the North African and European samples and two North American samples (N2 and N4)
515 together, and the other branch groups all other samples together. Samples closest to each other are the
516 most similar to each other, and those joined in the same groups share similar characteristics.
517 Therefore, in this analysis, the North African samples are grouped together, as are the High Latitude
518 samples. All but three North African samples form a distinct sub-group. The three remaining North
519 African samples (A8, A9 and A11) share more characteristics with the European samples, lending
520 support for mixing of aerosols from the two regions. Counterintuitively, the two European samples

521 with the lowest Fe/Al ratios (E3 and E4) are the ones that are most similar to the two North American
522 samples, which have relatively high Fe/Al ratios of 0.90 and 0.87. The GA01 samples (with the
523 exception of one sample, G15) form a distinct cluster, but with three sub-groups: one is the
524 Greenland/Labrador Sea samples (without G15), and the other two are related to each other but
525 distinct from the Greenland/Labrador Sea samples and are a mixture geographically of the other
526 samples. However, there is a trend, the 'middle' group is the group of samples collected closest to land,
527 the group to the right is the group of samples collected furthest from land. The other groupings are
528 made up of a mixture of North American and Marine samples. This could suggest that the Marine
529 samples are comprised predominantly of North American aerosols from more than one source. The
530 only anomaly is the two N American samples that 'look European'.

531 Although there are differences between Figures 7a (total TEs) and 7b (fractional solubility), the
532 general trend of an inverse relationship between TE atmospheric loading and fractional solubility
533 holds, as the samples with the highest concentrations appear on the left in Figure 7a, and on the right
534 in Figure 7b. In terms of fractional solubility, the N. African samples form a distinct cluster, but this
535 cluster is made up of two sub-groups: one collected during GA03-2010 and one during GA03-2011.
536 The samples from near Greenland and the Labrador Sea are also distinct from the other GA01 samples
537 (again with the exception of G15), and also distinct from all other samples. The European samples, all
538 other GA01 samples, and three North American samples form a loose cluster. The remaining North
539 American samples and all the Marine samples form another loose cluster.

540 Plotting the data this way still does not allow us to identify the aerosol sources definitively, but it does
541 allow us to visualise which samples have the most similar physico-chemical characteristics and
542 confirms the general trend of a relationship between aerosol loading and fractional solubility and, by
543 extension, bioavailability, even though we have demonstrated that this relationship is not present for
544 all TEs. This knowledge is then useful as a general rule of thumb in biogeochemical models, although
545 clearly other factors also exert controls on aerosol TE solubility. For example, during their
546 investigations of the GA03 aerosols, Wozniak et al., (2013; 2014; 2015) proposed a role for water
547 soluble organic carbon (WSOC) in controlling the solubility of Fe. Desboeufs et al. (2005) also found
548 evidence for a link between total carbon and TE solubility in regions impacted by anthropogenic
549 activity. Thus, both aerosol acidity and organic carbon content are implicated as controls on aerosol Fe
550 solubility, but the relationship is frequently not linear.

551

552 **3.5. Choice of leach protocol and modelling TE solubility**

553 Furthermore, the ability of models to replicate subtleties in aerosol TE solubility may prove critical in
554 forecasting ecosystem impacts and responses. Due to the magnitude of North African dust inputs to
555 North Atlantic region, this is a particular challenge and is compounded by additional unknowns such
556 as how aerosol acidity will be impacted by the combined effects of increasing
557 industrialisation/urbanisation, and changes in the magnitude of future mineral dust supply and biomass
558 burning (Knippertz et al., 2015; Weber et al., 2016). In other words, it is important to accurately
559 constrain aerosol trace element solubility with high quality data in order to improve the predictive
560 capacity of models. Clearly the choice of leach media and protocol impacts the measured fractional
561 solubility. This is shown in both Figures 4 and 5 and has a number of implications with regard to
562 modelling the impact of atmospheric deposition on marine biogeochemistry. For example, for
563 elements with generally low solubility, such as Fe, the difference between 1 % and 2 % solubility is an
564 increase of 100 %, meaning that only half the amount of dust is needed to yield the same amount of
565 dissolved Fe. To complicate matters further, recent research has demonstrated that some diazotrophs
566 are able to directly access particulate Fe (Rubin et al., 2011). The significance of this is that
567 *Trichodesmium* are common in the North Atlantic gyre under the influence of the Saharan plume, and
568 the North African dust samples have higher fractional solubility for Fe using the acetic acid leach. If
569 *Trichodesmium* are able to access particulate Fe, as the study indicates (Rubin et al., 2011), our data
570 suggests that twentyfold more aerosol Fe is available for uptake than is suggested from the
571 instantaneous leach. This data suggests that in regions where *Trichodesmium* proliferate, we are likely
572 to underestimate bioavailable Fe using the instantaneous approach.

573 There are implications for modelling the impact of atmospheric deposition for other TEs. Although,
574 the lack of source dependent differences in Mn solubility in these aerosols makes modelling Mn
575 solubility simpler, there was still a difference in the fractional solubility calculated from the two
576 leaches (UHP water: 32 ± 13 % and 25 % acetic acid: 49 ± 13 %). However, for Al, there was a large
577 range in solubility: 0.3 – 28 % using UHP water and 4.1 – 100 % using 25 % acetic acid. Both ranges
578 far exceed the relatively narrow range used in the MADCOW model (1.5 – 5 %), which has been used
579 to estimate atmospheric inputs based on dissolved Al concentrations in the mixed layer (Measures and
580 Brown, 1996). It is noted, however, that the median values from this study fall within the range used
581 by the MADCOW model (2.7 % and 3.3 % for UHP water and 25 % acetic acid, respectively). We
582 highlight this issue to draw attention to some of the problems inherent in modelling TE solubility and
583 its impact on the chemistry and biogeochemistry of the upper ocean.

584 Given that the different leaching approaches access different fractions of aerosol TEs (those TEs that
585 are loosely bound to surfaces and TEs that are associated with less reactive phases), that can dissolve
586 from aerosols at different rates (e.g. Kocak et al., 2007; Mackey et al., 2015), we need to conduct
587 experiments that elucidate the relationship between the soluble and bioavailable fractions. In the

588 meantime, we suggest that the 25 % acetic acid leach might be better to estimate the bioavailable
589 fraction given that Fe (and perhaps other TEs) associated with lithogenic particles are directly
590 available to micro-organisms in productive regions and regions with high dust inputs (Rubin et al.,
591 2011) and that aerosol particles can be processed by zooplankton (Schmidt et al., 2016).

592

593 **4. Conclusions**

594 Aerosol TE solubility is usually determined using operationally-defined methods, while
595 biogeochemical models require robust relationships between two or more parameters that can be used
596 to predict TE solubility in order to constrain the bioavailable fraction of aerosol TEs. In this study, we
597 used a two-stage leach (UHP water followed by 25 % acetic acid with hydroxylamine hydrochloride)
598 to investigate the fractional solubility of a suite of trace elements (Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Cd,
599 Pb) from aerosols collected in the North Atlantic during three GEOTRACES campaigns (GA03-2010,
600 GA03-2011 and GA01). Five regions were identified based on air mass back trajectory (AMBT)
601 simulations; i) North Africa, ii) Europe, iii) North America, iv) High Latitude, and v) Marine.
602 However, the AMBTs were not able to sufficiently discriminate aerosol sources within these regions.
603 Of these five categories, the North African aerosols were the most homogeneous in terms of their
604 fractional solubility and elemental ratios. In contrast, samples from the most remote locations, the
605 Marine and High Latitude aerosols, had the most spread in their fractional solubility and elemental
606 ratios. Elemental ratios were discussed rather than enrichment factors since earlier work highlighted
607 that the UCC ratios are not representative of the North African mineral dust end-member, which
608 dominates aerosol supply in much of the study area.

609 We observed an inverse relationship between the fractional solubility of Al, Ti, Fe, Ni, Cu and Pb and
610 aerosol loading for all leach media (UHP water, filtered seawater, and 25 % acetic acid). However,
611 Mn, Zn and Cd fractional solubility appears to be independent of atmospheric loading. For Co, the
612 inverse relationship between UHP water solubility and loading was not observed when using the 25 %
613 acetic acid leach, most likely because Co may be associated with the Mn and Fe oxides that are easily
614 reduced using the 25 % acetic acid leach. Further work is required to assess exactly which fraction is
615 accessed by the various leach protocols in order to understand links between the soluble and
616 bioavailable fractions.

617

618 **Data availability**

619 Data is available at BCO-DMO (GA03; www.bco-dmo.org) and LEFE-CYBER (GA01;
620 (www.obsvlfr.fr/proof/php/GEOVIDE/GEOVIDE.php), and on request from the lead author.

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636

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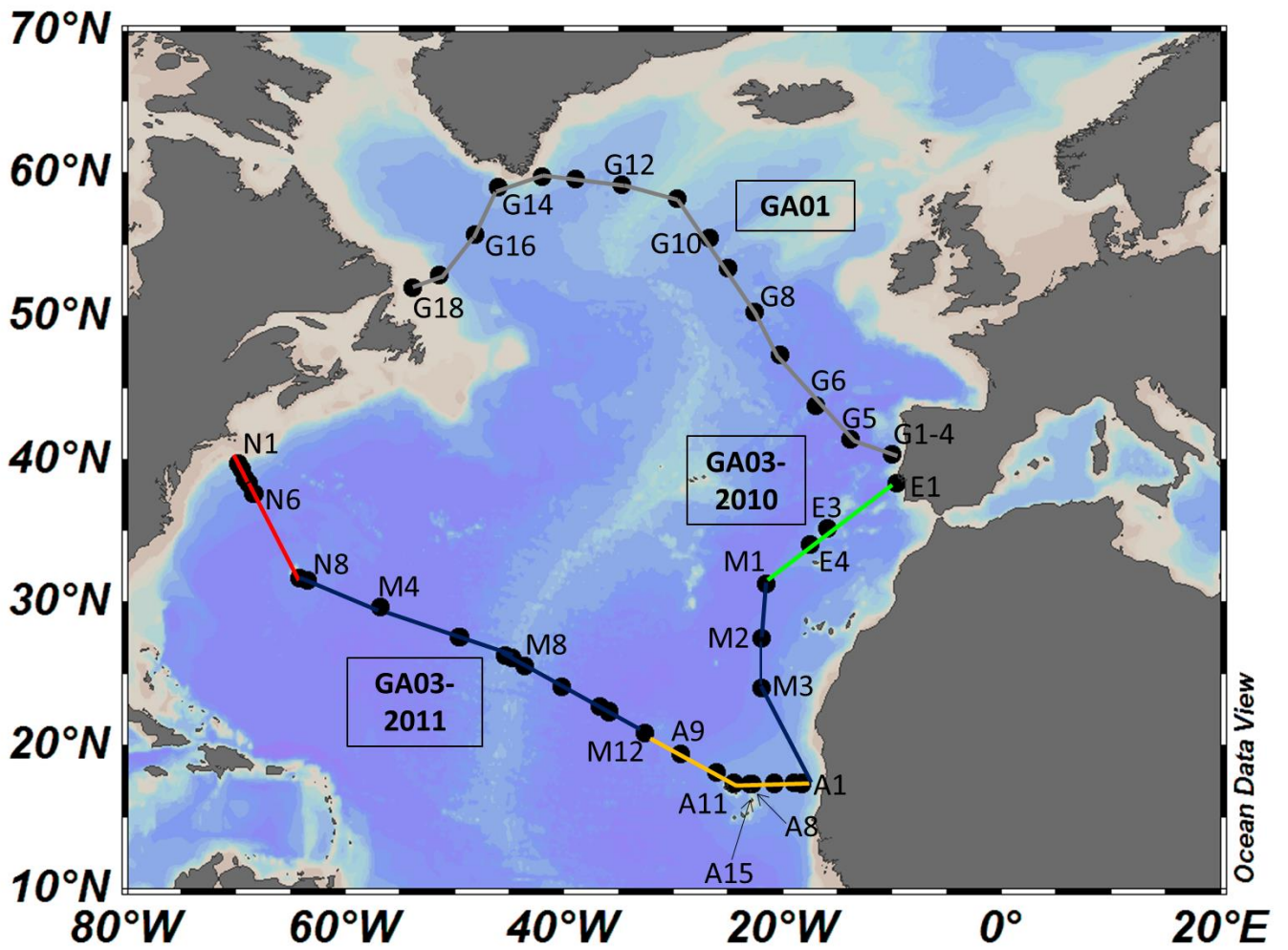
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916 **Figure 1**

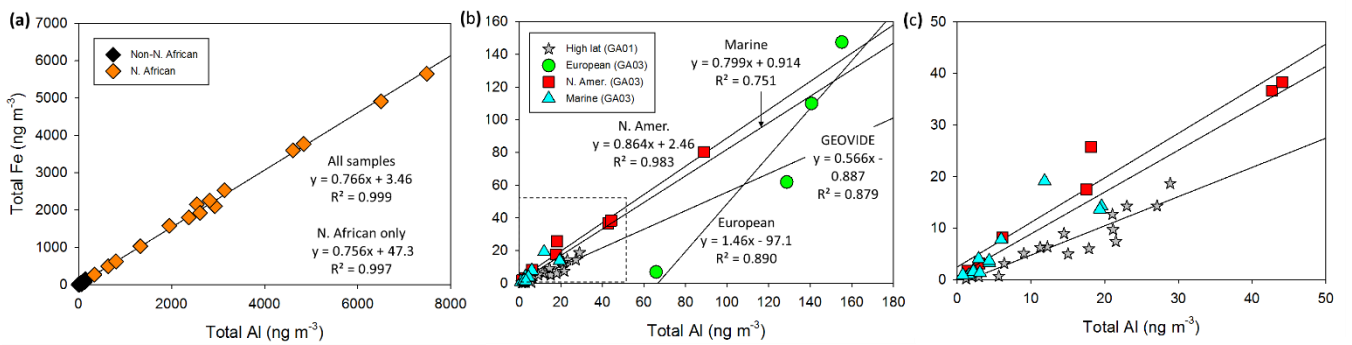
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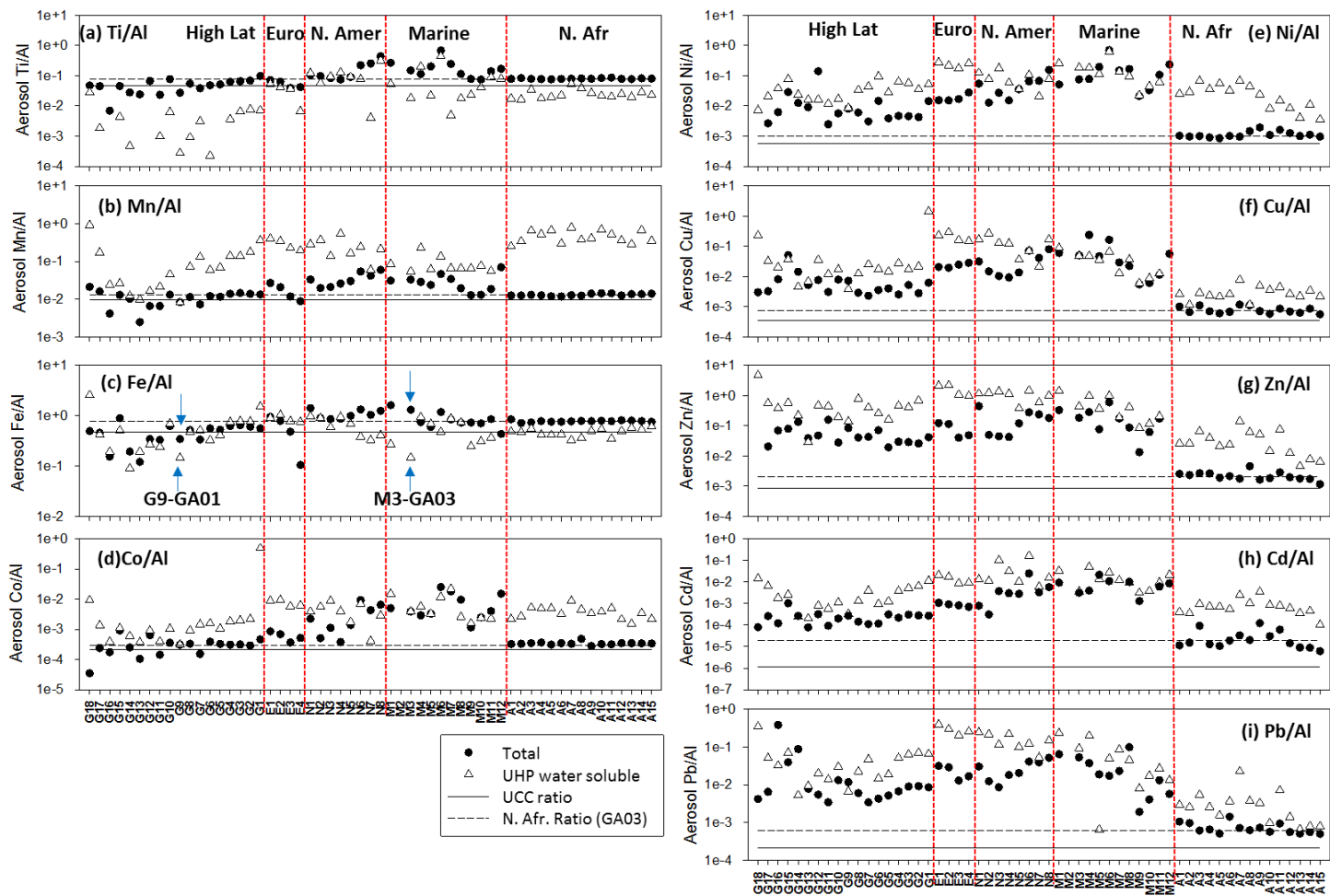


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923 **Figure 2**

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Figure 3

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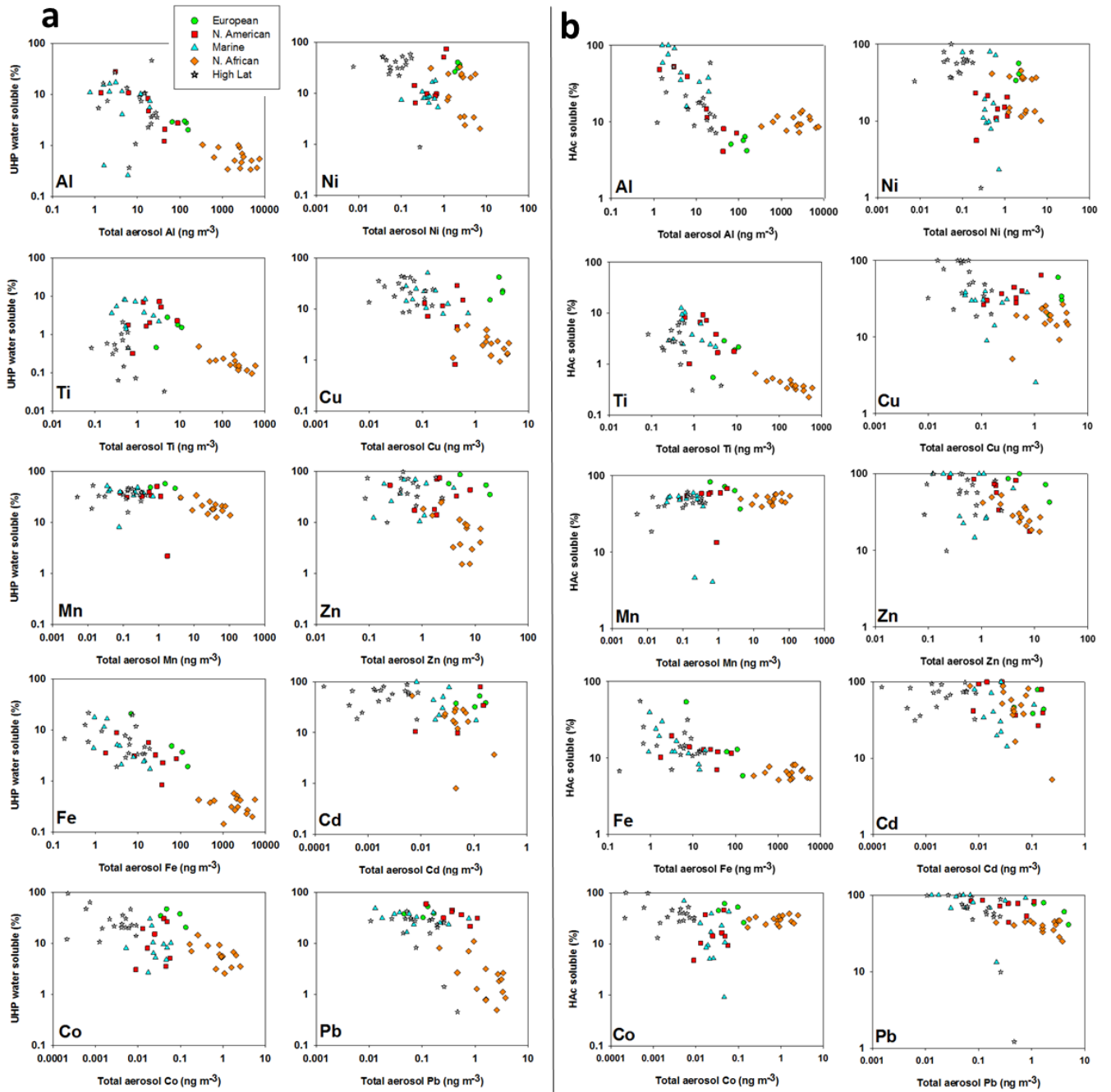
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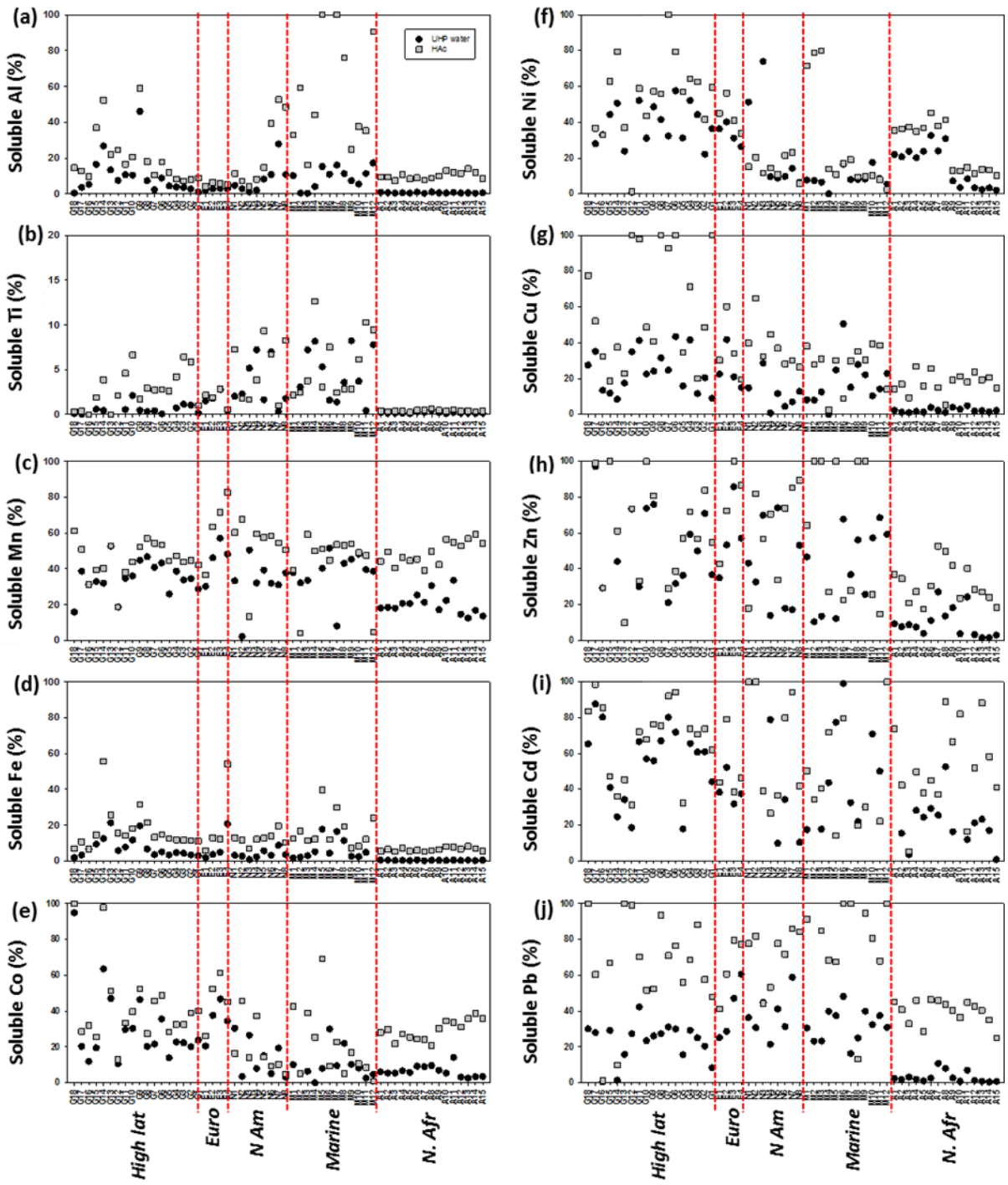
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Figure 4

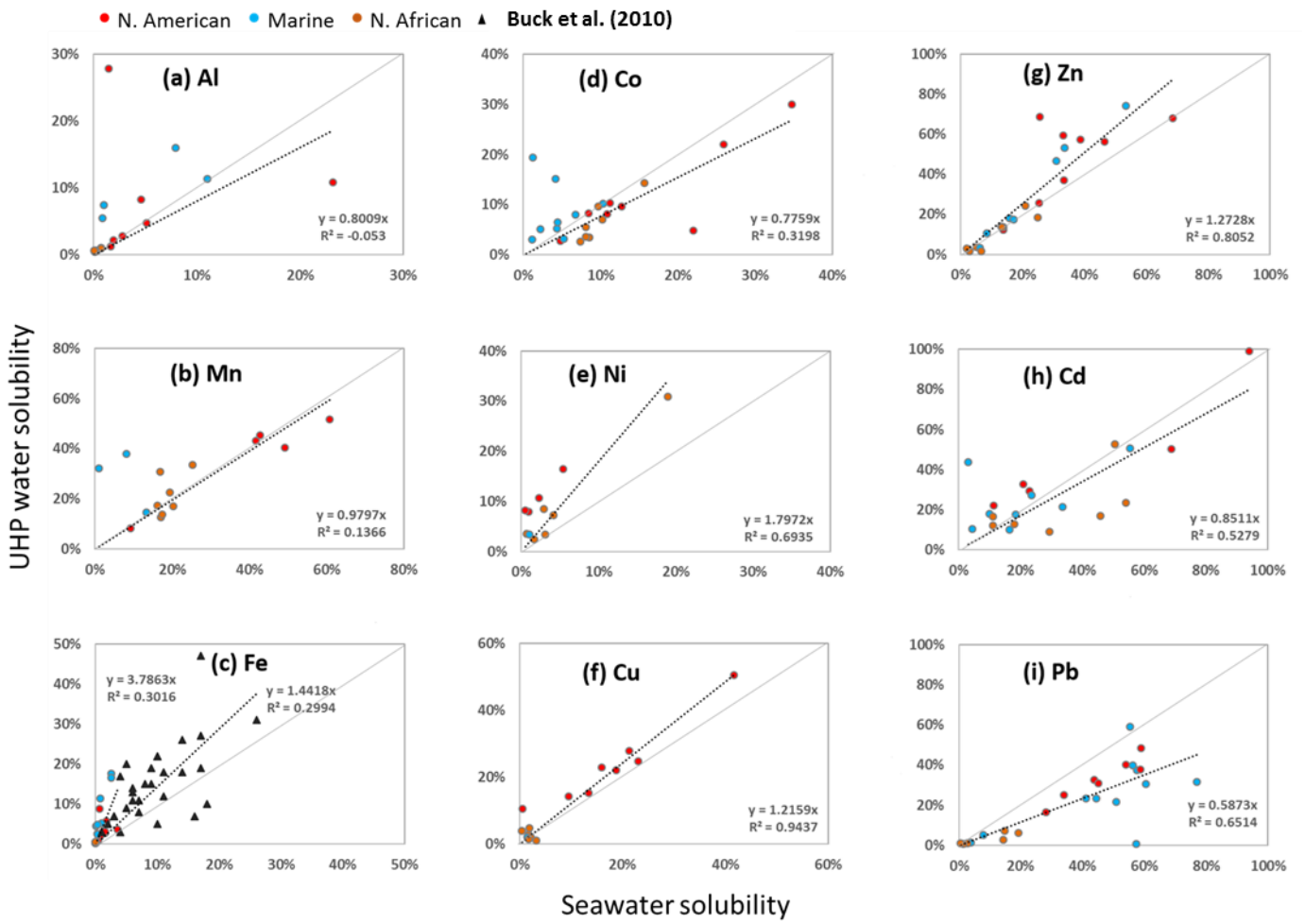
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944 **Figure 5**



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Figure 6

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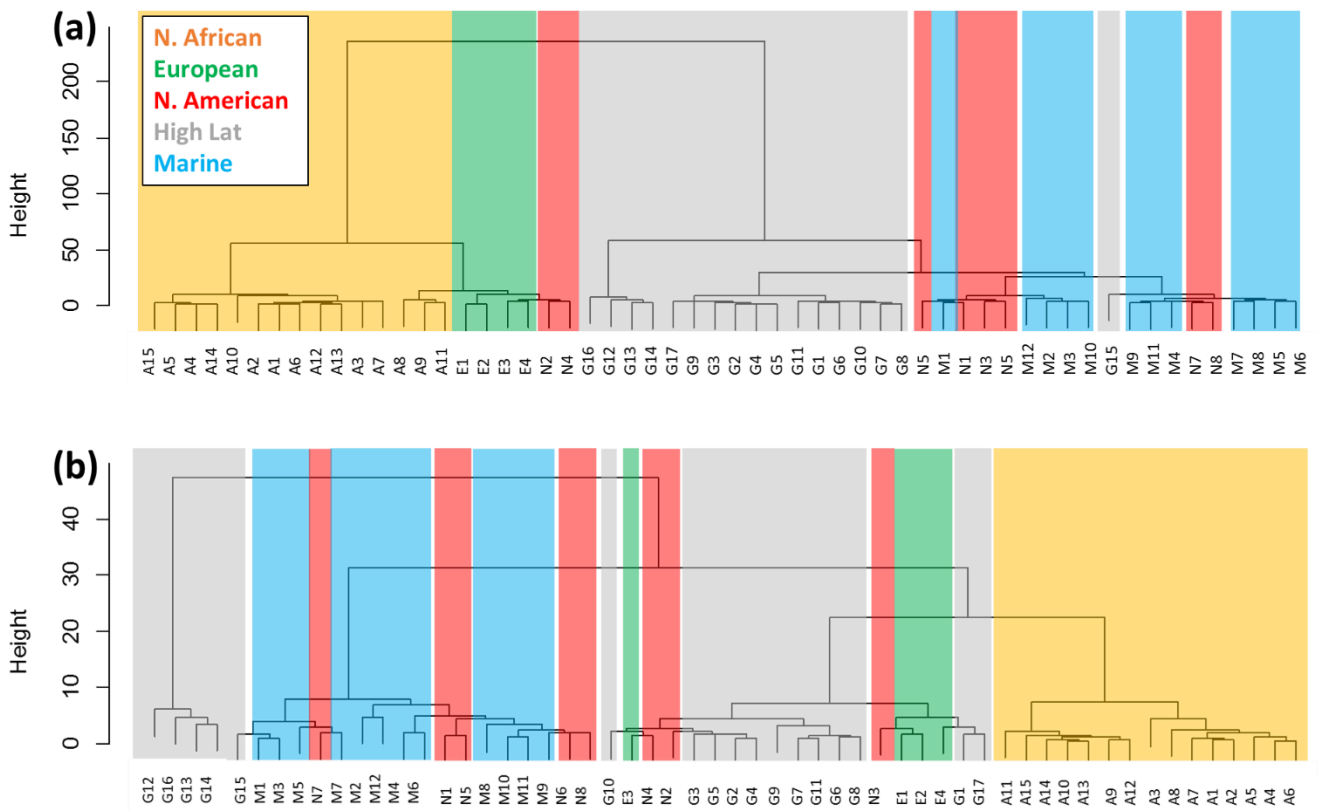
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Figure 7

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Table 1

973

	N. Amer.	Marine	N. Afr.
Al	x	x	x
Mn	x	NA	
Fe			x
Co	x	x	
Ni		NA	x
Cu		NA	x
Zn	x	x	x
Cd			x
Pb			

974

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977 **Captions: Figures**

978

979 Figure 1. The GEOTRACES GA01 and GA03 cruise tracks (GA01, GA03-2010 and GA03-2011). In total, 57
980 aerosol samples (GA01 n = 18, GA03 n = 39; black dots) were collected. The samples are grouped by aerosol
981 source region (green = European (E1-4), blue = Marine (M1-12), yellow = North African (A1-15), red = North
982 American (N1-8), and grey = High Latitude (G1-18)), identified from air mass back trajectory simulations using
983 the NOAA ARL model, HYSPLIT (Stein et al., 2015; Rolph, 2017). Note that a different labelling convention
984 was used in Shelley et al. (2017) to refer to the GA01 samples. Here we use G1-18 to refer to the samples
985 collected during GA01 (A1-18 in Shelley et al., 2017), and A1-15 to refer to the North African samples from
986 GA03.

987

988 Figure 2. Total aerosol Fe and Al (ng m^{-3}) for: (a) all aerosol samples from cruises GA01 and GA03, (b)
989 samples from sources other than North Africa (i.e. the black diamonds in Fig. 2a), and (c) the samples inside the
990 dashed box in Fig. 2b. For High Latitude dust n = 18, European samples n = 4, North American samples n = 8,
991 Marine samples n = 12, and Saharan samples n = 15. Note error bars (standard deviations shown in Table S1)
992 are not included so as not to obscure the symbols.

993

994 Figure 3. Elemental mass ratios (normalised to Al) of total (black circles) and UHP water soluble (white
995 triangles) TEs. The UCC elemental ratio (Rudnick and Gao, 2003) is indicated by the solid horizontal line, and
996 the elemental ratio in North African sourced aerosols (Shelley et al., 2015) is indicated by the dashed horizontal
997 line on each plot. The red vertical lines separate the aerosol source regions, which are labelled in panel (a).
998 Samples G9-GA01 and M3-GA03 are indicated by blue arrows in panel c (see text for details).

999

1000 Figure 4. (a) Percentage of UHP water soluble TEs versus total aerosol TE (ng m^{-3}), (b) percentage of 25 %
1001 acetic acid soluble TE versus total aerosol TE (ng m^{-3}). Data is plotted on log-log scales.

1002

1003 Figure 5. Solubility of Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb following a UHP water leach (UHP water, black
1004 circles, calculated using Eq. 1), and a sequential leach of 25 % acetic acid (HAc, grey squares, calculated using
1005 Eq. 2). The red vertical dashed lines represent the different aerosol source categories, as labelled in panel (b).
1006 Note that Ti (panel b) is highly insoluble and has a maximum value of <13%.

1007

1008

1009 Figure 6. Comparison of TE solubility following instantaneous leaches using UHP water or locally-collected,
1010 filtered seawater. The solid line is the 1:1 line. Where fewer data are observed, concentrations were below
1011 detection for one or both of the two leaches. The data for soluble aerosol Fe from within our study region from
1012 Buck et al. (2010) are plotted as black triangles in panel (c).

1013

1014 Figure 7. Hierarchical cluster analysis of (a) log transformed total TE concentration data plus NO_3^- , and (b) log
1015 transformed fractional solubility following the two-step sequential leach (fractional solubility calculated using
1016 Eq. 2). The coloured blocks correspond with the aerosol source regions shown in the legend.

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1020 **Captions: Tables**

1021

1022 Table 1. Slopes that did not differ significantly from 1.0 at the 95 % confidence levels for the UHP water versus
1023 seawater instantaneous leaches are marked with x. NA = not assessed due to the number of paired samples
1024 being ≤ 3 .