

Trace element and isotope deposition across the air–sea interface: progress and research needs

Shi, Zongbo

DOI:

[10.1098/rsta.2016.0190](https://doi.org/10.1098/rsta.2016.0190)

License:

Creative Commons: Attribution (CC BY)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Shi, Z 2016, 'Trace element and isotope deposition across the air–sea interface: progress and research needs', *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 374, no. 2081. <https://doi.org/10.1098/rsta.2016.0190>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Eligibility for repository: Checked on 9/12/2016

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

PHILOSOPHICAL TRANSACTIONS A

Trace Element and Isotope Deposition across the Air – Sea Interface: Progress and Research Needs

Journal:	<i>Philosophical Transactions A</i>
Manuscript ID	RSTA-2016-0190.R1
Article Type:	Review
Date Submitted by the Author:	n/a
Complete List of Authors:	Baker, Alex; University of East Anglia, School of Environmental Sciences Landing, William; Florida State University, Department of Earth, Ocean and Atmospheric Sciences Bucciarelli, Eva; Laboratoire des Sciences de l'Environnement Marin Cheize, Marie; Laboratoire des Sciences de l'Environnement Marin Fietz, Susanne; Stellenbosch University Hayes, Christopher; University of Southern Mississippi, Department of Marine Science Kadko, David; Florida International University, Applied Research Center Morton, Peter; Florida State University, Department of Earth, Ocean and Atmospheric Sciences Rogan, Nicolas; Helmholtz-Zentrum für Ozeanforschung Kiel Sarhou, Geraldine; Laboratoire des Sciences de l'Environnement Marin, Shelley, Rachel; Ifremer Centre de Bretagne, LEMAR/UMR CNRS 6539/IUEM Shi, Zongbo; University of Birmingham Shiller, Alan M.; University of Southern Mississippi, Department of Marine Science van Hulst, Marco; Laboratoire des sciences du climat et de l'environnement
Issue Code: Click http://rsta.royalsocietypublishing.org/site/misc/issue-codes.xhtml target=_new>here to find the code for your issue.:	DM1215
Subject:	Biogeochemistry < EARTH SCIENCES
Keywords:	Air – Sea Exchange, Atmospheric Deposition, Trace Element Solubility, Biogeochemical

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

	Impacts, Mineral dust, Anthropogenic aerosols

SCHOLARONE™
Manuscripts

For Review Only

1
2
3 **1 Trace Element and Isotope Deposition across the Air – Sea Interface: Progress and Research Needs**
4

5 2 A.R. Baker *1, W.M. Landing *2, E. Bucciarelli 3, M. Cheize 3, S. Fietz 4, C.T. Hayes 5, D. Kadko 6, P.L.
6

7 3 Morton 2, N. Rogan 7, G. Sarthou 3, R.U. Shelley 3, Z. Shi 8, A. Shiller 5, M.M.P. van Hulten 9
8

9 4 1 – Centre for Ocean and Atmospheric Science, School of Environmental Sciences, University of East
10 Anglia, Norwich, NR4 7TJ, UK.
11

12 6 2 – Department of Earth, Ocean & Atmospheric Science, Florida State University, Tallahassee, FL
13 32306, USA.
14

15 8 3 - LEMAR/IUEM, UMR 6539 CNRS-UBO-IRD-IFREMER, Place Nicolas Copernic, Technopôle Brest
16 Iroise, F-29280 Plouzané, France.
17

18 10 4 – Department of Earth Sciences, Stellenbosch University, 7600 Stellenbosch, South Africa.
19

20 11 5 – Department of Marine Science, University of Southern Mississippi, Stennis Space Center, MS
21 39529, USA.
22

23 13 6 – Florida International University, Applied Research Center, 10555 West Flagler St., Engineering
24 Center Suite 2100, Miami FL, 33174, USA.
25

26 15 7 – GEOMAR, Helmholtz Centre for Ocean Research Kiel, 1-3 Wischhofstrasse, Kiel 24148, Germany.
27

28 16 8 – School of Geography Earth and Environmental Sciences, University of Birmingham, UK.
29

30 17 9 – Laboratoire des Sciences du Climat et de l'Environnement (LSCE), IPSL, CEA–Orme des Merisiers,
31 91191 Gif-sur-Yvette, France.
32

33 19 * - Lead author (ARB: alex.baker@uea.ac.uk, WML: wlanding@fsu.edu)
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 20 Abstract
4

5 21 The importance of the atmospheric deposition of biologically-essential trace elements,
6 22 especially iron, is widely recognized, as are the difficulties of accurately quantifying the rates of trace
7 23 element wet and dry deposition and their fractional solubility. This paper summarises some of the
8 24 recent progress in this field, particularly that driven by the GEOTRACES, and other, international
9 25 research programmes. The utility and limitations of models used to estimate atmospheric deposition
10 26 flux, for example from the surface ocean distribution of tracers such as dissolved aluminium, are
11 27 discussed and a relatively new technique for quantifying atmospheric deposition using the short-
12 28 lived radionuclide beryllium-7 is highlighted. It is proposed that this field will advance more rapidly
13 29 by using a multi-tracer approach, and that aerosol deposition models should be ground-truthed
14 30 against observed aerosol concentration data. It is also important to improve our understanding of
15 31 the mechanisms and rates that control the fractional solubility of these tracers. Aerosol provenance
16 32 and chemistry (humidity, acidity and organic ligand characteristics) play important roles in governing
17 33 tracer solubility. Many of these factors are likely to be influenced by changes in atmospheric
18 34 composition in the future. Intercalibration exercises for aerosol chemistry and fractional solubility
19 35 are an essential component of the GEOTRACES programme.
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

38 Keywords

39 Air – Sea Exchange
40 Atmospheric Deposition
41 Trace Element Solubility
42 Biogeochemical Impacts
43 Mineral dust
44 Anthropogenic aerosols

1
2
3 45 Introduction
4

5 46 A great deal of research activity has focussed on addition of material to the ocean across the
6
7 47 air – sea interface since the realisations that iron (Fe) plays a key role as a limiting nutrient for
8
9 48 primary productivity or biological nitrogen fixation in large areas of the global ocean [1-3] and that
10
11 49 the deposition of mineral dust from the atmosphere was a major source of Fe to the remote ocean
12
13 50 [4]. That research has led to huge advances in the understanding of the impact of Fe
14
15 51 biogeochemistry on the marine carbon cycle [5], the sources and composition of Fe-bearing material
16
17 52 to the atmosphere [6, 7] and the chemical and physical processing of that material during
18
19 53 transportation through the atmosphere [8]. Alongside those advances has come the understanding
20
21 54 that a number of other trace elements (TEs) that are deposited across the air – sea interface (e.g.
22
23 55 manganese (Mn), cobalt (Co), zinc (Zn), nickel (Ni), cadmium (Cd), copper (Cu) [9]) have
24
25 56 micronutrient functions for marine microbial organisms or have potentially toxic effects (e.g. Cu
26
27 57 [10]).

28
29 58 In that context, one of the goals of the international GEOTRACES programme is to extend
30
31 59 knowledge of the exchange across the air – sea interface, based on the understanding that mineral
32
33 60 dust constitutes a vector for a wider range of important trace elements and their isotopes (TEI) than
34
35 61 Fe alone and that the sources of TEI in atmospheric deposition to the ocean are not limited to
36
37 62 mineral dust [7, 11].

38
39 63 This paper aims to highlight recent progress in this field, with a focus on research driven by
40
41 64 the international GEOTRACES programme, and identify topics for which further effort is still
42
43 65 required. Two long-standing problems – the difficulties in making accurate estimates of the
44
45 66 atmospheric flux of material to the ocean and in determining the fraction of the atmospheric flux of
46
47 67 bioactive substances that is available to marine biota – continue to challenge our understanding. The
48
49 68 extent to which anthropogenic emissions contribute to the atmospheric flux to the oceans and their
50
51 69 biogeochemical response to that flux is also of increasing interest.

52
53 70 Highlights of recent progress
54

55
56 71 *Estimation of Deposition Flux*
57

58
59 72 Atmospheric deposition is an important source of biologically-essential trace elements to the
60
61 73 open ocean. Knowledge of these fluxes helps us understand and model ocean productivity, yet these
62
63 74 fluxes are extremely difficult to measure. Although autonomous buoys capable of collecting aerosol
64
65 75 samples over extended periods have been developed and deployed at remote ocean sites [12], long-
66
67 76 term monitoring of the composition of aerosols and rainfall over the vast majority of the remote
68
69 77 ocean is effectively impossible due to limitations associated with the lack of suitable island sampling

1
2
3 78 locations and the expense of ship deployment to areas where island sites are not available. In a few
4 79 regions, where long-term records from island sampling sites exist [e.g. 13] or where specific ocean
5 80 areas are subject to relatively intense research ship activity [14-17], flux estimates based on direct
6 81 atmospheric sampling can be made. By combining observations of aerosol and rainwater chemistry
7 82 made during 28 research cruises of the GEOTRACES and other research programmes (such as the
8 83 Atlantic Meridional Transect (AMT) and the Surface Ocean Lower Atmosphere Study (SOLAS)),
9 84 Powell et al. [16] were able to estimate seasonally-resolved 10-year average atmospheric fluxes for
10 85 NO_3^- and NH_4^+ and soluble and total Fe, aluminium (Al) and Mn, for the eastern tropical North
11 86 Atlantic. However, the uncertainties associated with such deposition estimates are considerable [14-
12 87 16]. Aerosol dry deposition to the ocean surface cannot be directly measured, necessitating the use
13 88 of highly uncertain dry deposition velocities to convert measured aerosol concentrations into dry
14 89 deposition flux. Direct measurement of wet deposition fluxes are hampered by either biases in
15 90 rainfall patterns (compared to the open ocean) at island sites, or the difficulty in measuring
16 91 precipitation rates and the collection of sufficient rainfall samples to represent the wet deposition
17 92 flux effectively from ships.

18
19
20
21
22
23
24
25
26
27
28 93 With trace metals that partially solubilise from mineral dust, such as Al, titanium (Ti), gallium,
29 94 or thorium (Th), one can indirectly estimate dust deposition using the dissolved distribution of these
30 95 metals in seawater. The use of stable (non-radioactive) tracers to estimate dust fluxes often relies on
31 96 variations in Equation 1 (where dissolved Al is used as an example). The concentration of dissolved
32 97 Al in the surface ocean has been widely used as a dust deposition proxy because Al is abundant in
33 98 dust (about 8% by mass) and is not biologically essential (e.g. [18-22] Anderson et al., this volume).

$$99 \quad d[\text{Al}]/dt = (F_{\text{dust}} f(\text{Al}_{\text{dust}}) f(\text{Al}_{\text{sol}})/\text{MLD}) - ([\text{Al}]/\tau) - \nabla \cdot (\mathbf{v} [\text{Al}]) + \nabla \cdot (\mathbf{K} \cdot \nabla [\text{Al}]) \quad (1)$$

100 where:

101 $[\text{Al}]$ = dissolved Al concentration (g/m^3) in the surface ocean mixed layer

102 F_{dust} = flux of dust ($\text{g}/\text{m}^2/\text{d}$)

103 $f(\text{Al}_{\text{dust}})$ = fraction of Al in dust (typically ~ 0.08 g total Al/g dust)

104 $f(\text{Al}_{\text{sol}})$ = fraction of soluble Al in dust (variable (see below), but typically assumed to be ~ 0.03
105 g soluble Al/g total Al)

106 MLD = Mixed Layer Depth (m)

107 τ = residence time of dissolved Al in the MLD (typically on the order of 5 years)

108 $\nabla \cdot (\mathbf{v} [\text{Al}])$ = effects of advection (in x, y, and z) on the concentration of dissolved Al.

1
2
3 109 $\nabla \cdot (\mathbf{K} \cdot \nabla[\text{Al}]) =$ effects of turbulent mixing (in x, y, and z) on the concentration of dissolved
4
5 110 Al.

6
7 111 The dust flux term is assumed to dominate the input of the tracer. The residence time can be
8
9 112 separated into components influenced by multiple removal processes such as particle adsorption
10
11 113 (scavenging removal) or incorporation into biogenic particles (biological uptake). The removal rates
12
13 114 are modelled as first-order with respect to dissolved Al. For tracers with short residence times,
14
15 115 advection and mixing are often thought to be small and therefore insignificant (the implications of
16
17 116 this simplification are discussed below). Assuming steady-state conditions, and neglecting physical
18
19 117 mixing and advection, Eqn (1) resolves to:

20
21 118 $F_{\text{dust}} = ([\text{Al}] \text{MLD}) / (\tau f(\text{Al}_{\text{dust}}) f(\text{Al}_{\text{sol}}))$ (2)

22
23 119 Equation (2) represents the MADCOW model [23] where the numerator is the inventory of the
24
25 120 tracer in the mixed layer. A comparison between this model (applied to dissolved Al and dissolved
26
27 121 ^{232}Th) and other methods for estimating dust deposition is presented in Anderson *et al.* [this
28
29 122 volume]. This intercomparison also demonstrates very dramatically how different methods for
30
31 123 measuring aerosol TEI solubility have a significant influence on the dust flux estimates.

32
33 124 Whenever possible, it is preferable to make use of the full equation (Eqn. 1) and to make
34
35 125 measurements that are relevant for the region and time of year. Rates of particle scavenging and
36
37 126 uptake into biogenic material can vary from regime to regime and season to season. The depth of
38
39 127 tracer penetration can also vary in space and time, as can the sources and chemical nature of the
40
41 128 aerosols. The physical transport terms (particularly horizontal advection) may not be insignificant.
42
43 129 Van Hulst *et al.* [24, 25] showed how important this can be, using a general ocean circulation
44
45 130 model to take into account the effects of particle scavenging, biogenic particle uptake, and physical
46
47 131 transport. These authors compare the timescales (residence times) for dissolved Al in the upper
48
49 132 water column with respect to advection and particle scavenging:

50
51 133 $Y = \tau_{\text{adv}} / \tau_{\text{scav}}$ (3)

52
53 134 and use this ratio to recommend where one-dimensional models, like MADCOW, might be applied
54
55 135 with confidence (when $Y \gg 1$, e.g. the North Pacific Ocean and Mediterranean Sea) and where not
56
57 136 (when $Y < 1$, e.g. the equatorial Atlantic Ocean), see Fig. 1.

58
59 137 Because the fractional solubility of aerosol Al exhibits significant variability [e.g. 26, 27-29] and
60
138 because dissolved Al has a somewhat complicated behaviour in the upper ocean (with respect to
139 abiotic and biotic scavenging; e.g. [30]), it has been suggested to use dissolved Ti as an alternative
140 dust input proxy [31].

1
2
3 141 A tracer that shows promise as a way to estimate atmospheric deposition is the natural
4 142 radionuclide beryllium-7 (${}^7\text{Be}$: half-life 53.3 days – comparable to the life-time of particles in the
5 143 surface ocean [32]; gamma energy 0.4776 MeV). It is produced in the upper atmosphere from
6 144 cosmic ray spallation, quickly attaches to aerosol particles, and is transported to the lower
7
8 145 troposphere by atmospheric circulation processes. Because it is associated with sub-micron aerosols,
9 146 the deposition of aerosol ${}^7\text{Be}$ is dominated by rainfall scavenging [33, 34]. Given the relatively short
10 147 half-life of ${}^7\text{Be}$, at steady state the input flux of ${}^7\text{Be}$ (atoms $\text{m}^{-2} \text{min}^{-1}$) is balanced by the ${}^7\text{Be}$
11 148 inventory, or decay rate, integrated over the upper water column (dpm m^{-2}). The important point is
12 149 that the ability to derive the atmospheric flux of ${}^7\text{Be}$ from its ocean inventory provides a key linkage
13 150 between the atmospheric concentration of chemical species and their deposition to the ocean [33,
14 151 34].

15 152 The flux (F_i) of an aerosol element into the ocean can be described as the sum of wet and dry
16 153 deposition processes, respectively:

$$17 154 F_i = C_{a_i} R S \rho + C_{a_i} V_d = C_{a_i} [R S \rho + V_d] \quad (4)$$

18 155 Where:

19 156 F_i = flux to the oceans ($\mu\text{g}/\text{m}^2/\text{d}$),

20 157 C_{a_i} = aerosol concentration ($\mu\text{g}/\text{m}^3_{\text{air}}$),

21 158 R = precipitation rate ($\text{m}_{\text{rain}}/\text{d}$),

22 159 S = washout ratio ($\text{kg}_{\text{air}}/\text{kg}_{\text{rain}}$; i.e. the concentration in rain ($\mu\text{g}/\text{kg}_{\text{rain}}$) divided by the aerosol
23 160 concentration ($\mu\text{g}/\text{kg}_{\text{air}}$)),

24 161 ρ = the ratio of the densities of water and air ($(\sim 1000 \text{ kg}_{\text{rain}}/\text{m}^3_{\text{rain}})/(\sim 1.2 \text{ kg}_{\text{air}}/\text{m}^3_{\text{air}}) = \sim 833$
25 162 $(\text{kg}_{\text{rain}} \text{ m}^3_{\text{air}})/(\text{m}^3_{\text{rain}} \text{ kg}_{\text{air}})$),

26 163 V_d = aerosol dry deposition velocity (m/d).

27 164 The bracketed term on the right in Eqn. 4 represents the effective “bulk deposition velocity”,
28 165 combining wet and dry deposition.

29 166 The aerosol dry deposition velocity (V_d) to the ocean surface is a function of humidity, wind
30 167 speed, and particle size and has been estimated to vary by a factor of 3 for sub-micron aerosol
31 168 particles [35]. There are also large uncertainties associated with wet deposition estimates [36]. The
32 169 rain rate over the ocean is very difficult to constrain as direct measurement of patchy and episodic
33 170 rain events over vast, remote areas is impractical. Remote determinations from, for example,
34 171 Microwave Imager (TMI) and precipitation radar (PR) suffer in accuracy [e.g. 37]. However, we can

172 use the known flux of ^7Be (calculated from the ocean ^7Be decay inventory) to avoid the pitfalls
 173 associated with determination of these parameters.

174 The ratio of the atmospheric flux of any aerosol component to that of ^7Be is:

$$175 \quad F_i / F_{7\text{Be}} = C_{a_i} [R S \rho + Vd]_i / C_{a_{\text{Be}}} [R S \rho + Vd]_{7\text{Be}} \quad (5)$$

176 Assuming that the right-hand terms in brackets roughly cancel:

$$177 \quad F_i \cong F_{7\text{Be}} C_{a_i} / C_{a_{\text{Be}}} \quad (6)$$

178 such that the flux of any aerosol component can be estimated by multiplying the ^7Be flux by the ratio
 179 of that component to ^7Be in aerosols. For many ocean areas [33], this formulation works well
 180 because seasonal variation in the aerosol ^7Be concentrations and the resulting ocean inventory of
 181 ^7Be are small. In regions where there is large seasonal variability in the ^7Be aerosol concentrations,
 182 such as the Arctic Ocean, the expected ^7Be inventory resulting from the input and decay of aerosol
 183 ^7Be can be described by Eqn. 7 [38]:

$$184 \quad \lambda \text{ Inventory}_{7\text{Be}} = \sum [C_{a_{\text{Be},n}}^7 + C_{a_{\text{Be},n-1}}^7 e^{-\lambda}] (R S \rho + Vd) \quad (7)$$

185 Where:

186 λ is the ^7Be decay constant (0.013 d^{-1}),

187 $\text{Inventory}_{7\text{Be}}$ is the predicted ^7Be inventory to the depth of ^7Be penetration (100-200 m;
 188 dpm/m^2),

189 $C_{a_{\text{Be},n}}^7$ is ^7Be aerosol concentration on day "n" ($\text{dpm/m}^3_{\text{air}}$),

190 $C_{a_{\text{Be},n-1}}^7 e^{-\lambda}$ is the ^7Be aerosol concentration on the previous day corrected for radioactive
 191 decay ($\text{dpm/m}^3_{\text{air}}$).

192 As in Eqn. 4, the right-hand terms in parentheses represent the effective bulk deposition
 193 velocity (m/d) that combines precipitation plus dry deposition.

194 This approach has been used in the central Arctic Ocean, yielding a bulk deposition velocity of
 195 $\sim 1350 \text{ m/d}$ [38]. For the subtropical North Atlantic, using Eqn. 6, a bulk deposition velocity of ~ 2400
 196 m/d was derived [33]. In both cases, the estimated bulk deposition velocity is higher than the dry
 197 deposition velocity that is often used to estimate mineral aerosol dry deposition ($1 \text{ cm/s} = 864 \text{ m/d}$);
 198 this is consistent with the conclusion that ^7Be deposition is dominated by wet deposition. These bulk
 199 deposition velocities from a given region of the ocean can then be used to estimate the flux of any
 200 other aerosol component, despite the complication that larger mineral dust aerosols may have
 201 higher dry deposition velocities and lower rainfall scavenging ratios. Considering Fe in mineral dust

1
2
3 202 for example, one might use $V_d = 1000$ m/d and a rainfall scavenging ratio (S) of 200 [35], while for
4 203 ^7Be one might use $V_d = 86$ m/d and $S = 500$ [39]. Using these estimates (and Eqn. 5), for a rainfall
5 204 rate of 4 mm/d, the bulk deposition velocity for aerosol Fe would only be 5% lower than that for ^7Be
6 205 [33]. The higher proportions of larger mineral dust particles immediately downwind of sources like
7 206 the Sahara may impact on the choice of deposition velocities and scavenging ratios for modelling
8 207 deposition in those regions.

208 *Trace Element Solubility*

209 Understanding the fraction of the atmospheric flux of bioactive substances that is available to
210 marine biota is a key part of assessing the biogeochemical impact of that atmospheric flux. Defining
211 the bioavailable fraction is extremely complex, but in many cases the soluble fraction of trace
212 element deposition constitutes a major part of the bioavailable fraction [40, 41].

213 In laboratory studies a positive relationship has been reported between the solubility of
214 aerosol Fe (and other TEs) and aerosol acidity [e.g. 42, 43]. These studies were undertaken, in part,
215 to simulate pH changes that occur when aerosol particles cycle through clouds (a process that can
216 also affect other factors that influence solubility, such as aerosol constituent mixing). Despite these
217 results, and there being a general consensus in the community that aerosol chemistry is a key
218 control on aerosol TE solubility, field observations have failed to convincingly reproduce this
219 relationship for the most part. In the Atlantic Ocean, no relationship between acid species, such as
220 non-sea salt sulphate (nss-SO_4^{2-}) and nitrate (NO_3^-), or net potential acidity (i.e., the difference
221 between total acid species concentrations and total alkaline species concentrations) and fractional
222 Fe solubility has been observed [29, 44]. In contrast, in the Pacific Ocean, a significant relationship
223 between aerosol acid species, but not oxalate concentration, and soluble aerosol Fe has been
224 observed [e.g. 26]. Similar observations were made of the relationships between aerosol Al solubility
225 and acid species concentrations at Hawaii [45]. This led Buck *et al.* [26] to conclude that aerosol
226 provenance was the dominant control on TE solubility.

227 There are a number of theories suggested to explain why field data generally fail to capture a
228 relationship between aerosol TE solubility and aerosol acidity. For example, the large buffering
229 capacity of CaCO_3 means that mineral dust particles do not easily become acidic. The pH of the
230 aqueous solution surrounding dust aerosols is controlled by the ionic balance between acidic species
231 (e.g., sulphate, nitrate, chloride anions) and basic species, including ammonium and components of
232 mineral dust itself, i.e. calcite (CaCO_3). Before Fe can be effectively mobilized from the particle
233 through proton-promoted dissolution processes [46], the concentration of acidic species must be
234 sufficiently high to overcome the alkalinity of mineral dust (which will vary according to the source

1
2
3 235 and composition of the dust), and decrease the pH of the aqueous solution surrounding the dust
4 236 particle. Alternatively, part of the problem in linking aerosol acidity and TE solubility may lie in the
5 237 difficulty of determining the acidity of aerosol particles directly, and therefore proxies are frequently
6 238 used [47]. Hennigan *et al.* [47] found from their model study that approaches that combined aerosol
7 239 and gas inputs showed the best agreement with the aerosol pH predicted from the phase
8 240 partitioning of ammonia, and that ionic balance or molar ratio approaches failed to accurately
9 241 predict aerosol pH. The highly complex nature of atmospheric aerosol suspensions, in which aerosol
10 242 components may be fully externally mixed (present in the same volume of air but in different
11 243 particles), fully internally mixed (present within the same particles within that air volume) or at some
12 244 point on a continuum between these two extremes, also makes a complete understanding of field
13 245 observations of TE solubility very challenging. At present it is not possible to acquire measurements
14 246 of TE solubility on individual aerosol particles and hence it is not possible to distinguish between
15 247 observations for which acid species are externally mixed with TE-containing particles and those for
16 248 which internal mixing might lead to increased solubility.

17
18
19
20
21
22
23
24
25
26 249 In the future, in contrast to the ocean, the atmosphere is predicted to become more basic
27 250 [48]. Emissions of SO₂ and NO_x are expected to continue to decline as a result of stricter and/or
28 251 more commonplace regulation and technological advances, whereas global ammonia emissions (the
29 252 majority, ~80%, of which come from the agriculture sector) are difficult to control and are relatively
30 253 unchecked [49]. Gaseous ammonia is the most abundant alkaline gas in the atmosphere, and global
31 254 emissions have increased over the last few decades. A more basic atmosphere might be expected to
32 255 reduce aerosol TE solubility.

33
34
35
36
37
38 256 Recent work has highlighted the impact of organic matter on TE speciation and solubility in
39 257 aerosols and rainfall. Aerosol particles and rainwater are known to contain Fe-binding organic
40 258 ligands such as formate, acetate and oxalate [50]. These ligands facilitate the dissolution of Fe in
41 259 aerosol and stabilise soluble Fe [51-56]. Kieber *et al.* [57] estimated that 69% to 100% of Fe(III) in
42 260 rainwater was organically complexed. The concentrations of the Fe organic ligands and their
43 261 conditional stability constants have been directly measured in rainwater only very recently with a
44 262 new sensitive method using Competitive Ligand Exchange-Adsorptive Cathodic Stripping
45 263 Voltammetry (CLE-ACSV) [58]. Ligand concentrations in the first measured samples of coastal
46 264 rainwater were as high as 336 ± 19 nM, with log K'_{Fe3+L} around 21.1-22.8 at pH=5.45 [58]. These
47 265 K'_{Fe3+L} values correspond to the strong ligand class in seawater [59] and imply that 80 % to 100 % of
48 266 Fe in rainwater is organically complexed [58], confirming the estimation of Kieber *et al.* [57]. The
49 267 presence in rainwater of ligands capable of complexing other TEs, e.g. Cu [60], has also been
50
51
52
53
54
55
56
57
58
59
60

1
2
3 268 demonstrated. However, the exact nature and origin of these atmospheric ligands are still largely
4 269 unknown.

5
6
7 270 The molar ratios of Fe/water soluble organic carbon (WSOC) in aerosols collected during two
8 271 GEOTRACES cruises were found to be anti-correlated with Fe solubility (Fig. 2), suggesting a possible
9 272 role of organic ligands in enhancing Fe solubility [61, 62]. Using a global chemical transport model
10 273 that considered the oxalate-promoted Fe dissolution in aerosols, Ito and Shi [52] successfully
11 274 reproduced the inverse relationship of Fe solubility and Fe/WSOC ratio over the cruise tracks (Fig. 2).
12 275 The process-based modelling by Ito and Shi [52] suggested that proton- and oxalate-promoted Fe
13 276 dissolution in the aerosol aqueous phase and mixing with combustion aerosols are the main
14 277 mechanisms to cause the high Fe solubility at low Fe loading in the North Atlantic. This is consistent
15 278 with observations [e.g. 63, 64] and previous modelling [65].

16
17
18 279 Primary biological aerosol particles, also called bioaerosols, include fungi, pollen, spores, plant
19 280 debris, epithelial cells, algae, protozoa, viruses, and bacteria. They are ubiquitous in the atmosphere
20 281 [66, 67] and cover a very large size range from viruses (about 1 nm diameter) to pollen (up to 300
21 282 μm diameter) [68]. A recent campaign over the Caribbean Sea revealed that viable bacterial cells
22 283 represented on average 20% of the total particles in the 0.25-1 μm diameter range and were at least
23 284 one order of magnitude more abundant than fungal cells, suggesting that bacteria represented an
24 285 important and underestimated fraction of micrometer-sized atmospheric aerosols [69]. Bacteria
25 286 could directly influence the atmospheric chemistry of TEs, for example through the degradation TE-
26 287 complexing carboxylic compounds [70, 71] and the release of metabolic compounds, such as
27 288 siderophores [72]. Despite these advances, airborne microorganisms above the oceans remain
28 289 essentially uncharacterized, as most work to date is restricted to samples taken close to the
29 290 continents.

30
31
32 291 Other atmospheric compounds that could complex Fe are humic-like substances (HULIS) [73,
33 292 74] and/or sugars. These have been detected in rainwater samples and in the water soluble fraction
34 293 of aerosol particles [e.g. 54] and have been shown to bind Fe, at least in the ocean [75].

35
36
37 294 The expanded range of TEs studied under the GEOTRACES programme not only provides
38 295 information about additional micronutrients (Zn, Co, Cd, Cu, Ni, etc.) but has also allowed further
39 296 progress in understanding the solubility behaviour of Fe through the synergies with elements with
40 297 similar sources or chemistry. For instance, over the spatial scale of the North and South Atlantic
41 298 Ocean the variation in fractional solubility with total element aerosol concentration of Fe, Al and
42 299 silicon (Si) has been found to be very similar [76], suggesting that redox processes and
43 300 anthropogenic inputs are relatively minor controls of aerosol Fe solubility over that spatial scale.

1
2
3 301 *Biogeochemical Impact of Trace Element Deposition*
4

5 302 Ultimately, the biogeochemical impact of TEs that enter the ocean via the air – sea interface is
6
7 303 dependent on the characteristics of the marine waters into which they are deposited, in addition to
8
9 304 the characteristics of the TEs at the point of deposition [77]. The combination of atmospheric and
10
11 305 marine influences on solubility has been discussed for Fe by Baker and Croot [8], who suggested a
12
13 306 conceptual model of aerosol iron solubility controls in which the various competing and inter-related
14
15 307 processes that influence (Fe) solubility in the atmosphere and seawater are likened to electrical
16
17 308 resistors connected in parallel in each compartment. In Fig. 3 we revisit that conceptual model,
18
19 309 adding (Fe-) binding ligands in the atmosphere and revising it to describe TE dissolution in general.
20
21 310 Whether these newly-considered organic ligands result from atmospheric biological activity or have
22
23 311 a significant impact on TE solubility in seawater still needs further investigation.

24
25 312 The combined effects of atmospheric and seawater influences on TE dissolution have been
26
27 313 studied by addition of mineral dust to natural seawater at scales ranging from bottle incubations to
28
29 314 mini- and meso-cosm experiments. For example, an initial addition of dust during the DUNE
30
31 315 mesocosm experiment led to decreased dissolved Fe concentrations due to adsorption [78, 79]. A
32
33 316 second addition of dust to the DUNE mesocosms produced a very different response, with increased
34
35 317 dissolved Fe concentrations facilitated by higher Fe-binding ligand concentrations [79]. The
36
37 318 percentage of dust Fe released into seawater can be dependent on season and related to surface
38
39 319 water dissolved organic matter concentrations and character [80]. The DUNE experiments, involving
40
41 320 the addition of controlled amounts of well characterised dust to large volumes of isolated *in situ*
42
43 321 seawater, have provided the opportunity to study the fate and impact of deposited dust in a manner
44
45 322 not possible through either laboratory or field experiments.

46
47 323 The biological response of oceanic waters to dust or ambient aerosol addition has been
48
49 324 studied in a number of short-term bottle incubation experiments [81-84]. In many of these
50
51 325 experiments, responses to dust addition were different from the systems' responses to the addition
52
53 326 of macronutrients (nitrogen (N) and phosphorus (P)) and Fe, or additions of combinations of these. It
54
55 327 is apparent that a multi-element approach to such studies is necessary in order to interpret their
56
57 328 results [84].

58
59 329 *Non-dust Sources of TEIs*
60

61
62 330 Although mineral dust probably constitutes the major atmospheric source of TEIs to the ocean
63
64 331 on a global scale, other sources, including volcanic ash [85, 86], ship exhaust [87] and land-based
65
66 332 anthropogenic emissions [7, 88, 89] can also be significant on smaller scales. In a similar manner to
67
68 333 the behaviour of mineral dust, the deposition of volcanic ash has the potential to decrease surface

1
2
3 334 water Fe concentrations through scavenging, as well as acting as a source of dissolved Fe [90].
4
5 335 Anthropogenic sources of Fe have been found to be significantly more soluble than mineral dust Fe
6
7 336 [e.g. 91, 92]. Gas phase emissions from ship exhaust include CO₂, NO_x and SO₂ [87], with the latter
8
9 337 two being precursors of atmospheric acidity. Particulate emissions from shipping have been found to
10
11 338 contain a number of TEIs including Ni, vanadium (V), lead (Pb), Fe and Zn [e.g. 93, 94, 95]. In general,
12
13 339 little is known about whether such emissions might have a significant effect on the aeolian delivery
14
15 340 of TEIs to the ocean around major shipping routes. However, global ship traffic is projected to
16
17 341 increase over the coming decades and one modelling study has indicated that ship emissions might
18
19 342 constitute a significant source of soluble Fe to some ocean regions by 2100 [96].

20
21 343 Isotopic data on aerosol trace elements may also be useful in distinguishing sources, such as
22
23 344 between biomass burning or mineral dust for Fe [11], between anthropogenic emissions or mineral
24
25 345 dust for Zn [97] or between combustion aerosols from different regions with Pb isotopes (e.g. [98])

26 346 *Value of Coordinated International Research Programmes*

27
28 347 The large amount of new observational data acquired through work by the GEOTRACES and
29
30 348 other international research programmes are useful for validation of numerical models and serve to
31
32 349 enhance our understanding of TE air – sea interactions. These studies have highlighted the
33
34 350 importance of atmospheric transport regimes and deposition modes in determining the overall air –
35
36 351 sea flux of TEIs and their impacts on marine biogeochemistry. GEOTRACES data is particularly
37
38 352 valuable in this context because the programme’s sampling strategy aims to produce a co-collected,
39
40 353 corresponding set of TEI data for surface waters.

41
42 354 The collection of a coherent set of TEI data for aerosols through the GEOTRACES programme
43
44 355 has been underpinned by the successful aerosol intercalibration / intercomparison exercise [99].
45
46 356 GEOTRACES standardization and intercalibration protocols for oceanic samples generally entail
47
48 357 sharing of replicate samples among various labs/analysts and sampling at common locations
49
50 358 (crossover stations). For atmospheric aerosols, air mass origin and aerosol composition are highly
51
52 359 variable, so the applicability of crossover stations is problematic and the best options for aerosol
53
54 360 intercalibration are a readily available reference material and/or plentiful marine aerosol sample
55
56 361 replicates. During the 2008 GEOTRACES aerosol intercalibration [99], a set of replicate aerosol
57
58 362 samples consisting of a mixture of marine, lithogenic, and anthropogenic components was
59
60 363 successfully analysed for many total element and soluble ion concentrations. It was recommended
364 that digestions for “total” TEI concentrations should utilize nitric acid, hydrofluoric acid, heat and
365 pressure to achieve total dissolution of aerosol material. The exercise also revealed discrepancies in

1
2
3 366 the measurement of soluble aerosol TEI concentrations, most importantly Fe, a key parameter in
4 367 many observational and modelling studies.

5
6
7 368 Recommendations for further research

8
9 369 *Analytical Issues*

10
11 370 The continuation and expansion of intercalibration / intercomparison exercises will be
12 371 necessary to provide coherent datasets for future work. Because aerosols may be analysed for a
13 372 broad spectrum of trace elements and isotopes and soluble species (e.g. chloride, nitrate, sulphate
14 373 and soluble organic compounds), a substantial amount of aerosol material for intercalibration is
15 374 required. A suitable "reference" material is required to facilitate this intercalibration work. It should
16 375 be very fine-grained (to mimic aerosol particle sizes), homogeneous at small scales (less than 20 mg)
17 376 and be readily available at low cost.

- 18
19
20
21
22
23 377 • To address the lack of a suitable aerosol certified reference material (CRM), the Arizona Test
24 378 Dust (ATD) produced by Powder Technology, Inc. is currently being evaluated. ATD is a dry
25 379 aerosol powder that has been oven dried and sieved, but has not been subjected to washing
26 380 or leaching. ATD is available in several different size ranges, including A1 Ultrafine (PN
27 381 12103-1) whose particle size distribution shows ~70% less than 5.5 μm and ~98% less than 11
28 382 μm . It has a composition very similar to mineral (desert) dust:
29 383 <http://www.powdertechinc.com/product/iso-12103-1-a1-ultrafine-test-dust/>. A large
30 384 quantity has been purchased and our preliminary tests show that it is homogeneous at
31 385 subsample masses of 10-20 mg.
- 32 386 • A second round of intercalibration tests has begun in 2016; subsamples of the A1 Ultrafine
33 387 ATD have already been sent to a number of international labs to measure total TEI and
34 388 soluble TEI concentrations, and we hope to recruit additional collaborators for this effort. As
35 389 part of this intercalibration effort, we also want to encourage the use of ATD for
36 390 intercomparison of various aerosol solubilisation schemes. Our goal is to avoid the cost and
37 391 time delays needed to produce a true CRM or SRM, and to use the ATD material to
38 392 intercalibrate analysis of aerosol TEIs in much the same way that the SAFe and GT seawater
39 393 samples have been used to intercalibrate the sampling and analysis for TEIs in seawater.
40 394 Subsamples of our large batch of the A1 Ultrafine ATD are freely available (contact William
41 395 Landing wlanding@fsu.edu or Peter Morton pmorton@fsu.edu).
- 42 396 • Finally, we are also investigating the availability of replicate aerosol samples collected during
43 397 research cruises to further advance aerosol intercalibration. Members of the international
44 398 aerosol community are encouraged to facilitate this intercalibration by communicating and

399 collaborating; discussion is underway regarding establishment of a SCOR Working Group on
400 aerosol chemistry and solubility.

401 *Deposition*

- 402 • A multi-tracer approach shows promise in reducing the uncertainties associated with
403 quantifying dust deposition fluxes to the ocean [Anderson et al., this volume]. GEOTRACES
404 products are likely to expand the range of tracers and isotopes that can be used for this
405 purpose which should lead to further reduction of this key uncertainty.
- 406 • Modelling of dust and TEI deposition to the oceans is an essential part of the study of the
407 Earth System, since it allows estimation of TEI fluxes over spatial and temporal scales which
408 will never be accessible through direct observation. Modelling activities of this nature are
409 inherently uncertain however, because they inevitably involve the simplification of highly
410 complex systems that are themselves incompletely understood. The modelling community
411 conducts occasional intercomparison exercises [100, 101] in order to assess the variability
412 between models and to aid in model development. Since the ultimate product of these
413 models is the deposition flux of TEIs to the ocean, it makes sense for the intercomparison
414 exercises to report comparisons of deposition flux. We note however, that comparison to
415 observations is also an important part of validation and development of models. We would
416 therefore suggest that future model intercomparisons should also report model mean
417 aerosol surface level concentrations, since these are directly available from observations
418 whereas deposition fluxes to the ocean are not.

419 *Solubility*

420 Ultimately we wish to provide the modelling community with sufficient information to include
421 realistic descriptions of TE solubilisation in numerical models in the most computationally efficient
422 manner possible. In order to do this we need to clarify several outstanding issues:

- 423 • To what extent do anthropogenic emissions influence the solubility of TEI in aerosols? (How
424 significant, on global and regional scales, are direct anthropogenic emissions of TEIs in
425 determining the overall deposition of soluble forms of those TEIs to the ocean. What is the
426 indirect impact of anthropogenic emissions of acidic (NO_x, SO₂) and alkaline (NH₃)
427 substances on the evolution of aerosol TEI solubility during atmospheric transport?)
- 428 • Further improvement in our understanding of the influence of organic matter and
429 bioaerosols on TEI solubility in aerosols and in seawater after deposition, as well as their
430 potential impact on bioavailability, is required.

- 1
2
3 431 • Deposition of aerosol particles and rainfall to the surface ocean requires the transfer of
4 432 material across the sea surface microlayer (SSM), a region whose biogeochemical
5 433 characteristics are quite distinct from the properties of bulk seawater [102]. In all probability
6 434 the SSM has a significant influence on TEI solubility, but our understanding of the extent of
7 435 this influence is still in its infancy.
- 8 436 • Similarly, conditions in bulk seawater will also have a significant (perhaps dominant for Fe)
9 437 influence on TE solubility. We still need to improve our understanding of TEI dissolution
10 438 “length scales” and kinetics in relation to particle residence times in the ocean. Some of that
11 439 understanding may only be accessible via process studies or meso-scale oceanic enrichment
12 440 experiments.

13 441 *Anthropogenic impacts*

- 14 442 • There has been much recent interest in the role played by anthropogenic emissions in
15 443 introducing TEIs into the atmosphere (e.g. for soluble Fe, as stated above). Characterisation
16 444 of exemplar source end-members for these emissions will be required in order for them to
17 445 be incorporated into numerical models. Emissions from shipping are of particular interest in
18 446 this context as shipping has seen rapid growth in recent decades and this growth is
19 447 projected to increase further into the near future. Elements such as Ni and V are of
20 448 particular concern with regard to ship emissions, as are acid precursors (NO_x and SO₂),
21 449 although changes in regulations relating to ship emissions may influence this [103, 104].
- 22 450 • The introduction of routine sampling for black carbon (QMA filters) into GEOTRACES
23 451 protocols will help to link aerosol TEI concentrations to anthropogenic emissions and will
24 452 also aid in the validation of anthropogenic emissions and transport in numerical models.

25 453 Although our manuscript has focussed primarily on studies conducted under the international
26 454 GEOTRACES programme, we note that other international scientific programmes (e.g. SOLAS) share
27 455 many of the goals of GEOTRACES. We encourage the development of links between these
28 456 programmes through the sharing of data and expertise. For example, the SOLAS Aerosol and
29 457 Rainwater Chemistry database
30 458 (http://www.bodc.ac.uk/solas_integration/implementation_products/group1/aerosol_rain/
31 459) contains a large amount of GEOTRACES-relevant data and open access to results obtained by both
32 460 programmes is of clear benefit to both communities.

33 461

34 462 Competing Interests

1
2
3 463 We have no competing interests.

4
5 464 Authors' Contributions

6
7 465 Initial discussions were chaired by WML and ARB and involved all authors (other than EB). All
8
9 466 authors contributed text. The final manuscript was edited by ARB and WML and commented on by
10
11 467 all authors.

12
13 468

14
15 469 Acknowledgments

16
17 470 We thank Jan-Berend Stuut and an anonymous reviewer for their constructive comments on the
18
19 471 manuscript. GS, EB and MC would like to thank Dr Anne-Claire Baudoux, Prof. Peter Croot, Dr Anne-
20
21 472 Marie Delort and Dr Gilles Maihlot for their helpful discussions and collaboration on the Fe organic
22
23 473 speciation in the atmosphere and the potential links with bioaerosols.

24
25 474

26
27 475 Funding Statement

28
29 476 This work was supported by grants to the following authors: to ARB, UK Natural Environment
30
31 477 Research Council (NERC) (grant NE/H00548X/1); to DK and WML, Chemical Oceanography Program
32
33 478 of the National Science Foundation (grant OCE-1034746); to ZS, NERC (grants NE/I021616/1,
34
35 479 NE/K000845/1) and the Royal Society-NSFC; to MC, EB and GS, the BOA project (ANR-05-BLANC
36
37 480 0153), the BIOCAP project (ANR-13-BS06-0004), the GIS-Europôle Mer research axis 2 "Global
38
39 481 Change-Ocean-Marine Ecosystems Interactions" and a grant from the European CoOperation in
40
41 482 Science and Technology (COST) Action 735 "Tools for assessing global air-sea fluxes of climate and
42
43 483 air pollution relevant gases"; to NR, German BMBF SOPRAN project (grant FKZ03F0662A).

44
45 484

46
47 485 References

- 48 [1] Martin, J.H. 1990 Glacial-Interglacial CO₂ change: the iron hypothesis. *Paleoceanography* **5**, 1-13.
49 [2] Martin, J.H. & Fitzwater, S.E. 1988 Iron deficiency limits phytoplankton growth in the northeast
50 Pacific Subarctic. *Nature* **331**, 341-343.
51 [3] Falkowski, P.G. 1997 Evolution of the nitrogen cycle and its influence on the biological
52 sequestration of CO₂ in the ocean. *Nature* **387**, 272-275.
53 [4] Jickells, T.D., An, Z.S., Anderson, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J., Boyd, P.W.,
54 Duce, R.A., Hunter, K.A., et al. 2005 Global Iron Connections between desert dust, ocean
55 biogeochemistry and climate. *Science* **308**, 67-71.

- 1
2
3 494 [5] Boyd, P.W., Jickells, T., Law, C.S., Blain, S., Boyle, E.A., Buesseler, K.O., Coale, K.H., Cullen, J.J., de
4 495 Baar, H.J.W., Follows, M., et al. 2007 Mesoscale iron enrichment experiments 1993-2005: synthesis
5 496 and future directions. *Science* **315**, 612-617.
- 6 497 [6] Nickovic, S., Vukovic, A., Vujadinovic, M., Djurdjevic, V. & Pejanovic, G. 2012 Technical Note:
7 498 High-resolution mineralogical database of dust-productive soils for atmospheric dust modeling.
8 499 *Atmospheric Chemistry and Physics* **12**, 845-855.
- 9 500 [7] Luo, C., Mahowald, N., Bond, T., Chuang, P.Y., Artaxo, P., Siefert, R., Chen, Y. & Schauer, J. 2008
10 501 Combustion iron distribution and deposition. *Global Biogeochemical Cycles* **22**, GB1012,
11 502 doi:10.1029/2007GB002964.
- 12 503 [8] Baker, A.R. & Croot, P.L. 2010 Atmospheric and marine controls on aerosol iron solubility in
13 504 seawater. *Marine Chemistry* **120**, 4-13. (doi:10.1016/j.marchem.2008.09.003).
- 14 505 [9] Morel, F.M.M. & Price, N.M. 2003 The biogeochemical cycles of trace metals in the oceans.
15 506 *Science* **300**, 944-947.
- 16 507 [10] Paytan, A., Mackey, K.R.M., Chen, Y., Lima, I.D., Doney, S.C., Mahowald, N., Labiosa, R. & Post,
17 508 A.F. 2009 Toxicity of atmospheric aerosols on marine phytoplankton. *Proceedings of the National*
18 509 *Academy of Sciences of the United States of America* **106**, 4601-4605.
19 510 (doi:10.1073/pnas.0811486106).
- 20 511 [11] Mead, C., Herckes, P., Majestic, B.J. & Anbar, A.D. 2013 Source apportionment of aerosol iron in
21 512 the marine environment using iron isotope analysis. *Geophysical Research Letters* **40**, 5722-5727.
22 513 (doi:10.1002/2013GL057713).
- 23 514 [12] Sholkovitz, E.R. & Sedwick, P.N. 2006 Open-ocean deployment of a buoy-mounted aerosol
24 515 sampler on the Bermuda Testbed Mooring: Aerosol iron and sea salt over the Sargasso Sea. *Deep-*
25 516 *Sea Research Part I* **53**, 547-560.
- 26 517 [13] Tian, Z.L., Olliver, P., Veron, A. & Church, T.M. 2008 Atmospheric Fe deposition modes at
27 518 Bermuda and the adjacent Sargasso sea. *Geochemistry Geophysics Geosystems* **9**, Q08007,
28 519 (doi:10.1029/2007GC001868).
- 29 520 [14] Baker, A.R., Lesworth, T., Adams, C., Jickells, T.D. & Ganzeveld, L. 2010 Estimation of
30 521 atmospheric nutrient inputs to the Atlantic Ocean from 50°N to 50°S based on large-scale field
31 522 sampling: Fixed nitrogen and dry deposition of phosphorus. *Global Biogeochemical Cycles* **24**,
32 523 GB3006, (doi:10.1029/2009GB003634).
- 33 524 [15] Baker, A.R., Adams, C., Bell, T.G., Jickells, T.D. & Ganzeveld, L. 2013 Estimation of atmospheric
34 525 nutrient inputs to the Atlantic Ocean from 50°N to 50°S based on large-scale field sampling: Iron and
35 526 other dust-associated elements. *Global Biogeochemical Cycles* **27**, 755-767.
36 527 (doi:10.1002/gbc.20062).
- 37 528 [16] Powell, C.F., Baker, A.R., Jickells, T.D., Bange, H.W., Chance, R. & Yodle, C. 2015 Estimation of
38 529 the atmospheric flux of nutrients and trace metals to the eastern tropical North Atlantic Ocean.
39 530 *Journal of the Atmospheric Sciences of the American Meteorological Society* **72**, 4029-4045.
40 531 (doi:10.1175/JAS-D-15-0011.1).
- 41 532 [17] Chance, R., Jickells, T.D. & Baker, A.R. 2015 Atmospheric trace metal concentrations, solubility
42 533 and deposition fluxes in remote marine air over the south-east Atlantic. *Marine Chemistry* **177**, 45-
43 534 56. (doi:10.1016/j.marchem.2015.06.028).
- 44 535 [18] Vink, S. & Measures, C.I. 2001 The role of dust deposition in determining surface water
45 536 distributions of Al and Fe in the South West Atlantic. *Deep-Sea Research Part II-Topical Studies in*
46 537 *Oceanography* **48**, 2787-2809.
- 47 538 [19] Measures, C.I. & Vink, S. 2000 On the use of dissolved aluminum in surface waters to estimate
48 539 dust deposition to the ocean. *Global Biogeochemical Cycles* **14**, 317-327.
- 49 540 [20] Kramer, J., Laan, P., Sarthou, G., Timmermans, K.R. & de Baar, H.J.W. 2004 Distribution of
50 541 dissolved aluminium in the high atmospheric input region of the subtropical waters of the North
51 542 Atlantic Ocean. *Marine Chemistry* **88**, 85-101.

- 1
2
3 543 [21] Measures, C.I., Brown, M.T. & Vink, S. 2005 Dust deposition to the surface waters of the
4 544 western and central North Pacific inferred from surface water dissolved aluminum concentrations.
5 545 *Geochemistry, Geophysics, Geosystems* **6**, Q09M03, (doi:10.1029/2005GC000922).
6 546 [22] Middag, R., van Hulten, M.M.P., Van Aken, H.M., Rijkenberg, M.J.A., Gerringa, L.J.A., Laan, P. &
7 547 de Baar, H.J.W. 2015 Dissolved aluminium in the ocean conveyor of the West Atlantic Ocean: Effects
8 548 of the biological cycle, scavenging, sediment resuspension and hydrography. *Marine Chemistry* **177**,
9 549 69-86. (doi:10.1016/j.marchem.2015.02.015).
10 550 [23] Measures, C.I. & Brown, E.T. 1996 Estimating dust input to the Atlantic Ocean using surface
11 551 water Al concentrations. In *The impact of desert dust across the Mediterranean* (eds. S. Guerzoni &
12 552 R. Chester), pp. 301-311. Dordrecht, Kluwer.
13 553 [24] van Hulten, M.M.P., Sterl, A., Middag, R., de Baar, H.J.W., Gehlen, M., Dutay, J.C. & Tagliabue, A.
14 554 2014 On the effects of circulation, sediment resuspension and biological incorporation by diatoms in
15 555 an ocean model of aluminium. *Biogeosciences* **11**, 3757-3779. (doi:10.5194/bg-11-3757-2014).
16 556 [25] van Hulten, M.M.P., Sterl, A., Tagliabue, A., Dutay, J.C., Gehlen, M., de Baar, H.J.W. & Middag, R.
17 557 2013 Aluminium in an ocean general circulation model compared with the West Atlantic Geotraces
18 558 cruises. *Journal of Marine Systems* **126**, 3-23. (doi:10.1016/j.jmarsys.2012.05.005).
19 559 [26] Buck, C.S., Landing, W.M. & Resing, J. 2013 Pacific Ocean aerosols: Deposition and solubility of
20 560 iron, aluminum, and other trace elements. *Marine Chemistry* **157**, 117-130.
21 561 (doi:10.1016/j.marchem.2013.09.005).
22 562 [27] Buck, C.S., Landing, W.M. & Resing, J.A. 2010 Particle size and aerosol iron solubility: A high-
23 563 resolution analysis of Atlantic aerosols. *Marine Chemistry* **120**, 14-24.
24 564 [28] Buck, C.S., Landing, W.M., Resing, J.A. & Lebon, G.T. 2006 Aerosol iron and aluminum solubility
25 565 in the northwest Pacific Ocean: Results from the 2002 IOC cruise. *Geochemistry Geophysics*
26 566 *Geosystems* **7**, Q04M07, doi:10.1029/2005GC000977.
27 567 [29] Baker, A.R., Jickells, T.D., Witt, M. & Linge, K.L. 2006 Trends in the solubility of iron, aluminium,
28 568 manganese and phosphorus in aerosol collected over the Atlantic Ocean. *Marine Chemistry* **98**, 43-
29 569 58.
30 570 [30] Ohnemus, D.C. & Lam, P.J. 2015 Cycling of lithogenic marine particles in the US GEOTRACES
31 571 North Atlantic transect. *Deep Sea Research Part II: Topical Studies in Oceanography* **116**, 283-302.
32 572 (doi:10.1016/j.dsr2.2014.11.019).
33 573 [31] Damshäuser, A., Wagener, T. & Croot, P.L. 2011 Surface water dissolved aluminum and
34 574 titanium: Tracers for specific time scales of dust deposition to the Atlantic? *Geophysical Research*
35 575 *Letters* **38**, L24601, (doi:10.1029/2011GL049847).
36 576 [32] Barrett, P.M., Resing, J.A., Buck, N.J., Landing, W.M., Morton, P.L. & Shelley, R.U. 2015 Changes
37 577 in the distribution of Al and particulate Fe along A16N in the eastern North Atlantic Ocean between
38 578 2003 and 2013: Implications for changes in dust deposition. *Marine Chemistry* **177**, 57-68.
39 579 (doi:10.1016/j.marchem.2015.02.009).
40 580 [33] Kadko, D., Landing, W.M. & Shelley, R.U. 2015 A novel tracer technique to quantify the
41 581 atmospheric flux of trace elements to remote ocean regions. *J. Geophys. Res.* **120**, 848-858.
42 582 (doi:10.1002/2014JC010314).
43 583 [34] Kadko, D. & Prospero, J. 2011 Deposition of ⁷Be to Bermuda and the regional ocean:
44 584 Environmental factors affecting estimates of atmospheric flux to the ocean. *J. Geophys. Res.* **116**,
45 585 C02013, (doi:10.1029/2010JC006629).
46 586 [35] Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P., Hicks, B.B., Miller, J.M., Prospero,
47 587 J.M., Arimoto, R., Church, T.M., et al. 1991 The atmospheric input of trace species to the world
48 588 ocean. *Global Biogeochemical Cycles* **5**, 193-259. (doi:10.1029/91GB01778).
49 589 [36] Prospero, J.M., Landing, W.M. & Schulz, M. 2010 African dust deposition to Florida: Temporal
50 590 and spatial variability and comparisons to models. *J. Geophys. Res.* **115**, D13304,
51 591 (doi:10.1029/2009JD012773).

- 1
2
3 592 [37] Ikai, J. & Nakamura, K. 2003 Comparison of rain rates over the ocean derived from TRMM
4 593 Microwave Imager and Precipitation radar. *Journal of Atmospheric and Oceanic Technology* **20**,
5 594 1709-1726.
- 6 595 [38] Kadko, D., Galfond, B., Landing, W.M. & Shelley, R.U. 2016 Determining the pathways, fate, and
7 596 flux of atmospherically derived trace elements in the Arctic Ocean/ice system. *Marine Chemistry*
8 597 **182**, 38-50. (doi:10.1016/j.marchem.2016.04.006).
- 9 598 [39] Akata, N., Kawabata, H., Hasegawa, H., Sato, T., Chikuchi, Y., Kondo, K., Hisamatsu, S. & Inaba, J.
10 599 2008 Total deposition velocities and scavenging ratios of ^7Be and ^{210}Pb at Rokkasho, Japan. *Journal of*
11 600 *Radioanalytical and Nuclear Chemistry* **277**, 347-355.
- 12 601 [40] Lis, H., Shaked, Y., Kranzler, C., Keren, N. & Morel, F.M.M. 2015 Iron bioavailability to
13 602 phytoplankton: an empirical approach. *The ISME Journal* **9**, 1003-1013.
14 603 (doi:10.1038/ismej.2014.199).
- 15 604 [41] Morel, F.M.M., Kustka, A.B. & Shaked, Y. 2008 The role of unchelated Fe in the iron nutrition of
16 605 phytoplankton. *Limnology and Oceanography* **53**, 400-404. (doi:10.4319/lo.2008.53.1.0400).
- 17 606 [42] Spokes, L.J. & Jickells, T.D. 1996 Factors controlling the solubility of aerosol trace metals in the
18 607 atmosphere and on mixing into seawater. *Aquatic Geochemistry* **1**, 355-374.
- 19 608 [43] Desboeufs, K.V., Losno, R., Vimeux, F. & Cholbi, S. 1999 The pH-dependent dissolution of wind-
20 609 transported Saharan dust. *Journal of Geophysical Research-Atmospheres* **104**, 21287-21299.
- 21 610 [44] Buck, C.S., Landing, W.M., Resing, J.A. & Measures, C.I. 2010 The solubility and deposition of
22 611 aerosol Fe and other trace elements in the North Atlantic Ocean: Observations from the A16N
23 612 CLIVAR/CO₂ repeat hydrography section. *Marine Chemistry* **210**, 57-70.
24 613 (doi:10.1016/j.marchem.2008.08.003).
- 25 614 [45] Measures, C.I., Sato, T., Vink, S., Howell, S. & Li, Y.H. 2010 The fractional solubility of aluminium
26 615 from mineral aerosols collected in Hawaii and implications for atmospheric deposition of
27 616 biogeochemically important trace elements. *Marine Chemistry* **120**, 144-153.
- 28 617 [46] Meskhidze, N., Chameides, W.L. & Nenes, A. 2005 Dust and pollution: A recipe for enhanced
29 618 ocean fertilization? *Journal of Geophysical Research-Atmospheres* **110**, D03301,
30 619 (doi:10.1029/2004JD005082).
- 31 620 [47] Hennigan, C.J., Izumi, J., Sullivan, A.P., Weber, R.J. & Nenes, A. 2015 A critical evaluation of
32 621 proxy methods used to estimate the acidity of atmospheric particles. *Atmospheric Chemistry and*
33 622 *Physics* **15**, 2775-2790. (doi:10.5194/acp-15-2775-2015).
- 34 623 [48] Lamarque, J.F., Dentener, F., McConnell, J., Ro, C.U., Shaw, M., Vet, R., Bergmann, D., Cameron-
35 624 Smith, P., Dalsoren, S., Doherty, R., et al. 2013 Multi-model mean nitrogen and sulfur deposition
36 625 from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP): evaluation
37 626 of historical and projected future changes. *Atmospheric Chemistry and Physics* **13**, 7997-8018.
38 627 (doi:10.5194/acp-13-7997-2013).
- 39 628 [49] Behera, S.N., Sharma, M., Aneja, V.P. & Balasubramanian, R. 2013 Ammonia in the atmosphere:
40 629 a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. *Environ.*
41 630 *Sci. Pollut. Res.* **20**, 8092-8131. (doi:10.1007/s11356-013-2051-9).
- 42 631 [50] Vet, R., Artz, R.S., Carou, S., Shaw, M., Ro, C.-U., Aas, W., Baker, A., Bowersox, V.C., Dentener, F.,
43 632 Galy-Lacaux, C., et al. 2014 A global assessment of precipitation chemistry and deposition of sulfur,
44 633 nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmospheric*
45 634 *Environment* **93**, 3-100. (doi:10.1016/j.atmosenv.2013.10.060).
- 46 635 [51] Willey, J.D., Kieber, R.J., Humphreys, J.J., Rice, B.C., Hopwood, M.J., Avery, G.B. & Mead, R.N.
47 636 2015 The role of fossil fuel combustion on the stability of dissolved iron in rainwater. *Atmospheric*
48 637 *Environment* **107**, 187-193. (doi:10.1016/j.atmosenv.2015.02.033).
- 49 638 [52] Ito, A. & Shi, Z. 2016 Delivery of anthropogenic bioavailable iron from mineral dust and
50 639 combustion aerosols to the ocean. *Atmospheric Chemistry and Physics* **16**, 85-99. (doi:10.5194/acp-
51 640 16-85-2016).
- 52 641 [53] Kieber, R.J., Williams, K., Willey, J.D., Skrabal, S. & Avery, G.B. 2001 Iron speciation in coastal
53 642 rainwater: concentration and deposition to seawater. *Marine Chemistry* **73**, 83-95.

- 1
2
3 643 [54] Willey, J.D., Kieber, R.J., Seaton, P.J. & Miller, C. 2008 Rainwater as a source of Fe(II)-stabilizing
4 644 ligands to seawater. *Limnology and Oceanography* **53**, 1678-1684.
- 5 645 [55] Paris, R. & Desboeufs, K.V. 2013 Effect of atmospheric organic complexation on iron-bearing
6 646 dust solubility. *Atmospheric Chemistry and Physics* **13**, 4895-4905. (doi:10.5194/acp-13-4895-2013).
- 7 647 [56] Paris, R., Desboeufs, K.V. & Journet, E. 2011 Variability of dust iron solubility in atmospheric
8 648 waters: Investigation of the role of oxalate organic complexation. *Atmospheric Environment* **45**,
9 649 6510-6517.
- 10 650 [57] Kieber, R.J., Skrabal, S.A., Smith, B.J. & Willey, J.D. 2005 Organic complexation of Fe(II) and its
11 651 impact on the redox cycling of iron in rain. *Environmental Science & Technology* **39**, 1576-1583.
12 652 (doi:10.1021/es040439h).
- 13 653 [58] Cheize, M., Sarthou, G., Croot, P.L., Bucciarelli, E., Baudoux, A.-C. & Baker, A.R. 2012 Iron organic
14 654 speciation determination in rainwater using cathodic stripping voltammetry. *Analytica Chimica Acta*
15 655 **736**, 45-54.
- 16 656 [59] Gledhill, M. & Buck, K.N. 2012 The organic complexation of iron in the marine environment: a
17 657 review. *Front. Microbiol.* **3**, 69-69.
- 18 658 [60] Spokes, L.J., Campos, M.L.A.M. & Jickells, T.D. 1996 The role of organic matter in controlling
19 659 copper speciation in precipitation. *Atmospheric Environment* **30**, 3959-3966.
- 20 660 [61] Wozniak, A.S., Shelley, R.U., Sleighter, R.L., Abdulla, H.A.N., Morton, P.L., Landing, W.M. &
21 661 Hatcher, P.G. 2013 Relationships among aerosol water soluble organic matter, iron and aluminum in
22 662 European, North African, and Marine air masses from the 2010 US GEOTRACES cruise. *Marine*
23 663 *Chemistry* **154**, 24-33. (doi:10.1016/j.marchem.2013.04.011).
- 24 664 [62] Wozniak, A.S., Shelley, R.U., McElhenie, S.D., Landing, W.M. & Hatcher, P.G. 2015 Aerosol water
25 665 soluble organic matter characteristics over the North Atlantic Ocean: Implications for iron-binding
26 666 ligands and iron solubility. *Marine Chemistry* **173**, 162-172. (doi:10.1016/j.marchem.2014.11.002).
- 27 667 [63] Sedwick, P.N., Sholkovitz, E.R. & Church, T.M. 2007 Impact of anthropogenic combustion
28 668 emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso Sea. *Geochemistry*
29 669 *Geophysics Geosystems* **8**, Q10Q06, doi:10.1029/2007GC001586.
- 30 670 [64] Séguret, M.J.M., Koçak, M., Theodosi, C., Ussher, S.J., Worsfold, P.J., Herut, B., Mihalopoulos, N.,
31 671 Kubilay, N. & Nimmo, M. 2011 Iron solubility in crustal and anthropogenic aerosols: The Eastern
32 672 Mediterranean as a case study. *Marine Chemistry* **126**, 229-238.
33 673 (doi:10.1016/j.marchem.2011.05.007).
- 34 674 [65] Shi, Z.B., Woodhouse, M.T., Carslaw, K.S., Krom, M.D., Mann, G.W., Baker, A.R., Savov, I., Fones,
35 675 G.R., Brooks, B., Drake, N., et al. 2011 Minor effect of physical size sorting on iron solubility of
36 676 transported mineral dust. *Atmospheric Chemistry and Physics* **11**, 8459-8469. (doi:10.5194/acp-11-
37 677 8459-2011).
- 38 678 [66] Despres, V.R., Huffman, J.A., Burrows, S.M., Hoose, C., Safatov, A.S., Buryak, G., Froehlich-
39 679 Nowoisky, J., Elbert, W., Andreae, M.O., Poeschl, U., et al. 2012 Primary biological aerosol particles in
40 680 the atmosphere: a review. *Tellus Series B-Chemical and Physical Meteorology* **64**, 15598.
41 681 (doi:10.3402/tellusb.v64i0.15598).
- 42 682 [67] Froehlich-Nowoisky, J., Burrows, S.M., Xie, Z., Engling, G., Solomon, P.A., Fraser, M.P., Mayol-
43 683 Bracero, O.L., Artaxo, P., Begerow, D., Conrad, R., et al. 2012 Biogeography in the air: fungal diversity
44 684 over land and oceans. *Biogeosciences* **9**, 1125-1136. (doi:10.5194/bg-9-1125-2012).
- 45 685 [68] Duce, R.A., Mohnen, V.A., Zimmerman, P.R., Grosjean, D., Cautreels, W., Chatfield, R., Jaenicke,
46 686 R., Ogren, J.A., Pellizzari, E.D. & Wallace, G.T. 1983 Organic material in the global troposphere.
47 687 *Reviews of Geophysics* **21**, 921-952. (doi:10.1029/RG021i004p00921).
- 48 688 [69] DeLeon-Rodriguez, N., Latham, T.L., Rodriguez-R, L.M., Barazesh, J.M., Anderson, B.E.,
49 689 Beyersdorf, A.J., Ziemba, L.D., Bergin, M., Nenes, A. & Konstantinidis, K.T. 2013 Microbiome of the
50 690 upper troposphere: Species composition and prevalence, effects of tropical storms, and atmospheric
51 691 implications. *Proceedings of the National Academy of Sciences of the United States of America* **110**,
52 692 2575-2580. (doi:10.1073/pnas.1212089110).

- 1
2
3 693 [70] Amato, P., Demeer, F., Melaouhi, A., Fontanella, S., Martin-Biesse, A.S., Sancelme, M., Laj, P. &
4 694 Delort, A.M. 2007 A fate for organic acids, formaldehyde and methanol in cloud water: their
5 695 biotransformation by micro-organisms. *Atmospheric Chemistry and Physics* **7**, 4159-4169.
6 696 [71] Vaitilingom, M., Deguillaume, L., Vinatier, V., Sancelme, M., Amato, P., Chaumerliac, N. & Delort,
7 697 A.-M. 2013 Potential impact of microbial activity on the oxidant capacity and organic carbon budget
8 698 in clouds. *Proceedings of the National Academy of Sciences of the United States of America* **110**, 559-
9 699 564. (doi:10.1073/pnas.1205743110).
10 700 [72] Sullivan, T.S., Ramkissoon, S., Garrison, V.H., Ramsubhag, A. & Thies, J.E. 2012 Siderophore
11 701 production of African dust microorganisms over Trinidad and Tobago. *Aerobiologia* **28**, 391-401.
12 702 (doi:10.1007/s10453-011-9243-x).
13 703 [73] Graber, E.R. & Rudich, Y. 2006 Atmospheric HULIS: How humic-like are they? A comprehensive
14 704 and critical review. *Atmospheric Chemistry and Physics* **6**, 729-753.
15 705 [74] Okochi, H. & Brimblecombe, P. 2002 Potential trace metal-organic complexation in the
16 706 atmosphere *The Scientific World* **2**, 767-786. (doi:10.1100/tsw.2002.132).
17 707 [75] Hassler, C.S., Schoemann, V., Nichols, C.M., Butler, E.C.V. & Boyd, P.W. 2011 Saccharides
18 708 enhance iron bioavailability to Southern Ocean phytoplankton. *Proceedings of the National Academy*
19 709 *of Sciences of the United States of America* **108**, 1076-1081. (doi:10.1073/pnas.1010963108).
20 710 [76] Baker, A.R., Laskina, O. & Grassian, V.H. 2014 Processing and ageing in the atmosphere. In
21 711 *Mineral Dust: A key player in the Earth System* (eds. P. Knippertz & J.B. Stuut), pp. 75-92. Dordrecht,
22 712 Springer.
23 713 [77] Wagener, T., Pulido-Villena, E. & Guieu, C. 2008 Dust iron dissolution in seawater: Results from a
24 714 one-year time-series in the Mediterranean Sea. *Geophysical Research Letters* **35**, L16601,
25 715 (doi:10.1029/2008GL034581).
26 716 [78] Wagener, T., Guieu, C. & Leblond, N. 2010 Effects of dust deposition on iron cycle in the surface
27 717 Mediterranean Sea: results from a mesocosm seeding experiment. *Biogeosciences* **7**, 3769-3781.
28 718 (doi:10.5194/bg-7-3769-2010).
29 719 [79] Wuttig, K., Wagener, T., Bressac, M., Dammschaeuser, A., Streu, P., Guieu, C. & Croot, P.L. 2013
30 720 Impacts of dust deposition on dissolved trace metal concentrations (Mn, Al and Fe) during a
31 721 mesocosm experiment. *Biogeosciences* **10**, 2583-2600. (doi:10.5194/bg-10-2583-2013).
32 722 [80] Bressac, M. & Guieu, C. 2013 Post-depositional processes: What really happens to new
33 723 atmospheric iron in the ocean's surface? *Global Biogeochemical Cycles* **27**, 859-870.
34 724 (doi:10.1002/gbc.20076).
35 725 [81] Mills, M.M., Ridame, C., Davey, M., La Roche, J. & Geider, R.J. 2004 Iron and phosphorus co-limit
36 726 nitrogen fixation in the eastern tropical North Atlantic. *Nature* **429**, 292-294.
37 727 [82] Moore, C.M., Mills, M.M., Milne, A., Langlois, R., Achterberg, E.P., Lochté, K., Geider, R.J. & La
38 728 Roche, J. 2006 Iron limits primary productivity during spring bloom development in the central North
39 729 Atlantic. *Global Change Biology* **12**, 626-634. (doi:10.1111/j.1365-2486.2006.01122.x).
40 730 [83] Duarte, C.M., Dachs, J., Llabres, M., Alonso-Laita, P., Gasol, J.M., Tovar-Sanchez, A., Sanudo-
41 731 Wilhemy, S. & Agustí, S. 2006 Aerosol inputs enhance new production in the subtropical northeast
42 732 Atlantic. *Journal of Geophysical Research-Biogeosciences* **111**, G04006, doi:10.1029/2005JG000140.
43 733 [84] Mackey, K.R.M., Buck, K.N., Casey, J.R., Cid, A., Lomas, M.W., Sohrin, Y. & Paytan, A. 2012
44 734 Phytoplankton responses to atmospheric metal deposition in the coastal and open-ocean Sargasso
45 735 Sea. *Front. Microbiol.* **3**, 359, (doi:10.3389/fmicb.2012.00359).
46 736 [85] Achterberg, E.P., Moore, C.M., Henson, S.A., Steigenberger, S., Stohl, A., Eckhardt, S., Avendano,
47 737 L.C., Cassidy, M., Hembury, D., Klar, J.K., et al. 2013 Natural iron fertilization by the Eyjafjallajökull
48 738 volcanic eruption. *Geophysical Research Letters* **40**, 921-926. (doi:10.1002/grl.50221).
49 739 [86] Browning, T.J., Bouman, H.A., Henderson, G.M., Mather, T.A., Pyle, D.M., Schlosser, C.,
50 740 Woodward, E.M.S. & Moore, C.M. 2014 Strong responses of Southern Ocean phytoplankton
51 741 communities to volcanic ash. *Geophysical Research Letters* **41**, 2851-2857.
52 742 (doi:10.1002/2014gl059364).

- 1
2
3 743 [87] Eyring, V., Isaksen, I.S.A., Berntsen, T., Collins, W.J., Corbett, J.J., Endresen, O., Grainger, R.G.,
4 744 Moldanova, J., Schlager, H. & Stevenson, D.S. 2010 Transport impacts on atmosphere and climate:
5 745 Shipping. *Atmospheric Environment* **44**, 4735-4771. (doi:10.1016/j.atmosenv.2009.04.059).
6 746 [88] Chuang, P.Y., Duvall, R.M., Shafer, M.M. & Schauer, J.J. 2005 The origin of water soluble
7 747 particulate iron in the Asian atmospheric outflow. *Geophysical Research Letters* **32**, L07813,
8 748 doi:10.1029/2004GL021946.
9 749 [89] Baker, A.R., Thomas, M., Bange, H.W. & Plasencia Sánchez, E. 2016 Soluble trace metals in
10 750 aerosols over the tropical south-east Pacific offshore of Peru. *Biogeosciences* **13**, 817-825.
11 751 (doi:10.5194/bg-13-817-2016).
12 752 [90] Rogan, N., Achterberg, E.P., Le Moigne, F.A.C., Marsay, C.M., Tagliabue, A. & Williams, R.G. 2016
13 753 Volcanic ash as an oceanic iron source and sink. *Geophysical Research Letters* **43**, 2732-2740.
14 754 (doi:10.1002/2016GL067905).
15 755 [91] Desboeufs, K.V., Sofikitis, A., Losno, R., Colin, J.L. & Ausset, P. 2005 Dissolution and solubility of
16 756 trace metals from natural and anthropogenic aerosol particulate matter. *Chemosphere* **58**, 195-203.
17 757 (doi:10.1016/j.chemosphere.2004.02.025).
18 758 [92] Oakes, M., Ingall, E.D., Lai, B., Shafer, M.M., Hays, M.D., Liu, Z.G., Russell, A.G. & Weber, R.J.
19 759 2012 Iron solubility related to particle sulfur content in source emission and ambient fine particles.
20 760 *Environmental Science & Technology* **46**, 6637-6644. (doi:10.1021/es300701c).
21 761 [93] Viana, M., Hammingh, P., Colette, A., Querol, X., Degraeuwe, B., de Vlieger, I. & van Aardenne, J.
22 762 2014 Impact of maritime transport emissions on coastal air quality in Europe. *Atmospheric*
23 763 *Environment* **90**, 96-105. (doi:10.1016/j.atmosenv.2014.03.046).
24 764 [94] Isakson, J., Persson, T.A. & Lindgren, E.S. 2001 Identification and assessment of ship emissions
25 765 and their effects in the harbour of Goteborg, Sweden. *Atmospheric Environment* **35**, 3659-3666.
26 766 (doi:10.1016/s1352-2310(00)00528-8).
27 767 [95] Becagli, S., Sferlazzo, D.M., Pace, G., di Sarra, A., Bommarito, C., Calzolari, G., Ghedini, C.,
28 768 Lucarelli, F., Meloni, D., Monteleone, F., et al. 2012 Evidence for heavy fuel oil combustion aerosols
29 769 from chemical analyses at the island of Lampedusa: a possible large role of ships emissions in the
30 770 Mediterranean. *Atmospheric Chemistry and Physics* **12**, 3479-3492. (doi:10.5194/acp-12-3479-2012).
31 771 [96] Ito, A. 2013 Global modeling study of potentially bioavailable iron input from shipboard aerosol
32 772 sources to the ocean. *Global Biogeochemical Cycles* **27**, 1-10. (doi:10.1029/2012GB004378).
33 773 [97] Dong, S., Weiss, D.J., Strekopytov, S., Kreissig, K., Sun, Y., Baker, A.R. & Formenti, P. 2013 Stable
34 774 isotope ratio measurements of Cu and Zn in mineral dust (bulk and size fractions) from the
35 775 Taklimakan Desert and the Sahel and in aerosols from the eastern tropical North Atlantic Ocean.
36 776 *Talanta* **114**, 103-109. (doi:10.1016/j.talanta.2013.03.062).
37 777 [98] Sen, I.S., Bizimis, M., Tripathi, S.N. & Paul, D. 2016 Lead isotopic fingerprinting of aerosols to
38 778 characterize the sources of atmospheric lead in an industrial city of India. *Atmospheric Environment*
39 779 **129**, 27-33. (doi:10.1016/j.atmosenv.2016.01.005).
40 780 [99] Morton, P., Landing, W.M., Hsu, S.C., Milne, A., Aguilar-Islas, A.M., Baker, A.R., Bowie, A.R.,
41 781 Buck, C.S., Gao, Y., Gichuki, S., et al. 2013 Methods for sampling and analysis of marine aerosols:
42 782 results from the 2008 GEOTRACES aerosol intercalibration experiment. *Limnology and*
43 783 *Oceanography-Methods* **11**, 62-78. (doi:10.4319/lom.2013.11.62).
44 784 [100] Lamarque, J.F., Shindell, D.T., Josse, B., Young, P.J., Cionni, I., Eyring, V., Bergmann, D.,
45 785 Cameron-Smith, P., Collins, W.J., Doherty, R., et al. 2013 The Atmospheric Chemistry and Climate
46 786 Model Intercomparison Project (ACCMIP): overview and description of models, simulations and
47 787 climate diagnostics. *Geosci. Model Dev.* **6**, 179-206. (doi:10.5194/gmd-6-179-2013).
48 788 [101] Huneus, N., Schulz, M., Balkanski, Y., Griesfeller, J., Prospero, J., Kinne, S., Bauer, S., Boucher,
49 789 O., Chin, M., Dentener, F., et al. 2011 Global dust model intercomparison in AeroCom phase I.
50 790 *Atmospheric Chemistry and Physics* **11**, 7781-7816. (doi:10.5194/acp-11-7781-2011).
51 791 [102] Tovar-Sanchez, A., Duarte, C.M., Arrieta, J.M. & Sanudo-Wilhelmy, S. 2014 Spatial gradients in
52 792 trace metal concentrations in the surface microlayer of the Mediterranean Sea. *Frontiers in Marine*
53 793 *Science* **1**. (doi:10.3389/fmars.2014.00079).

- 1
2
3 794 [103] Tao, L., Fairley, D., Kleeman, M.J. & Harley, R.A. 2013 Effects of switching to lower sulfur
4 795 marine fuel oil on air quality in the San Francisco Bay Area. *Environmental Science & Technology* **47**,
5 796 10171-10178. (doi:10.1021/es401049x).
6 797 [104] Moldanova, J., Fridell, E., Winnes, H., Holmin-Fridell, S., Boman, J., Jedynska, A., Tishkova, V.,
7 798 Demirdjian, B., Joulie, S., Bladt, H., et al. 2013 Physical and chemical characterisation of PM
8 799 emissions from two ships operating in European Emission Control Areas. *Atmospheric Measurement*
9 800 *Techniques* **6**, 3577-3596. (doi:10.5194/amt-6-3577-2013).

11 801

13 802

14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Review Only

803 Figure Captions

804 Fig. 1 Distribution of the ratio of advection to scavenging timescales (Y) for Al in the global ocean
805 (after [25]). This is a measure of the relative importance of scavenging versus advection for Al
806 export. Regions where Y is higher than one are scavenging-driven, those where Y is smaller than one
807 are advection-driven. Where advection dominates (blue) the one-dimensional MADCOW model is
808 predicted to be unreliable.

809 Fig. 2 Fe solubility as a function of Fe/WSOC molar ratio for model estimates (red squares) and
810 measurements (black circles, from [61, 62]) of aerosol samples collected over the Atlantic Ocean.
811 Reproduced from [52].

812

813 Fig. 3: Conceptual model of aerosol TEI solubility controls proposed (for Fe) by Baker and Croot [8],
814 with the addition of a new control factor in the atmosphere: Ligand complexation, which may be
815 linked to bioaerosols (see text for more details).

816

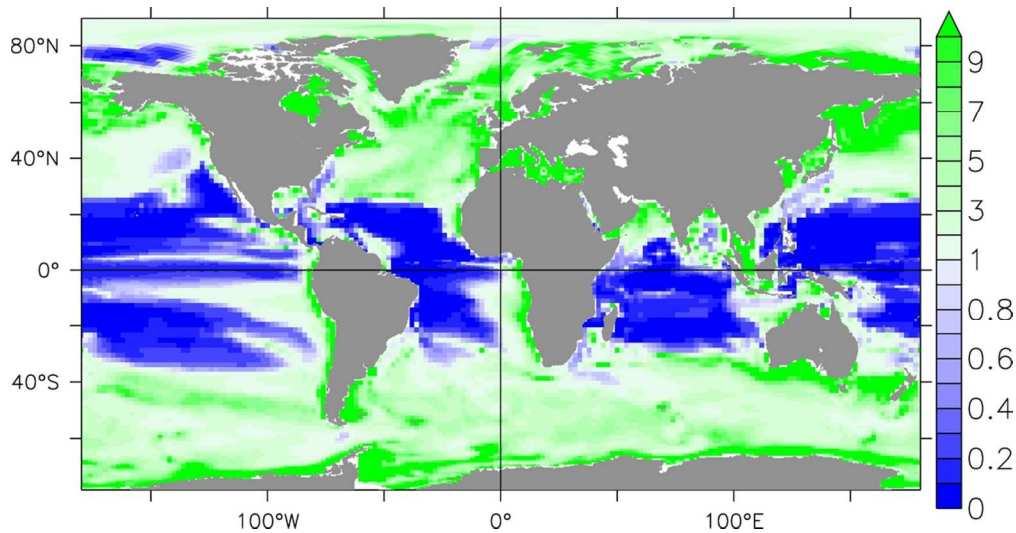
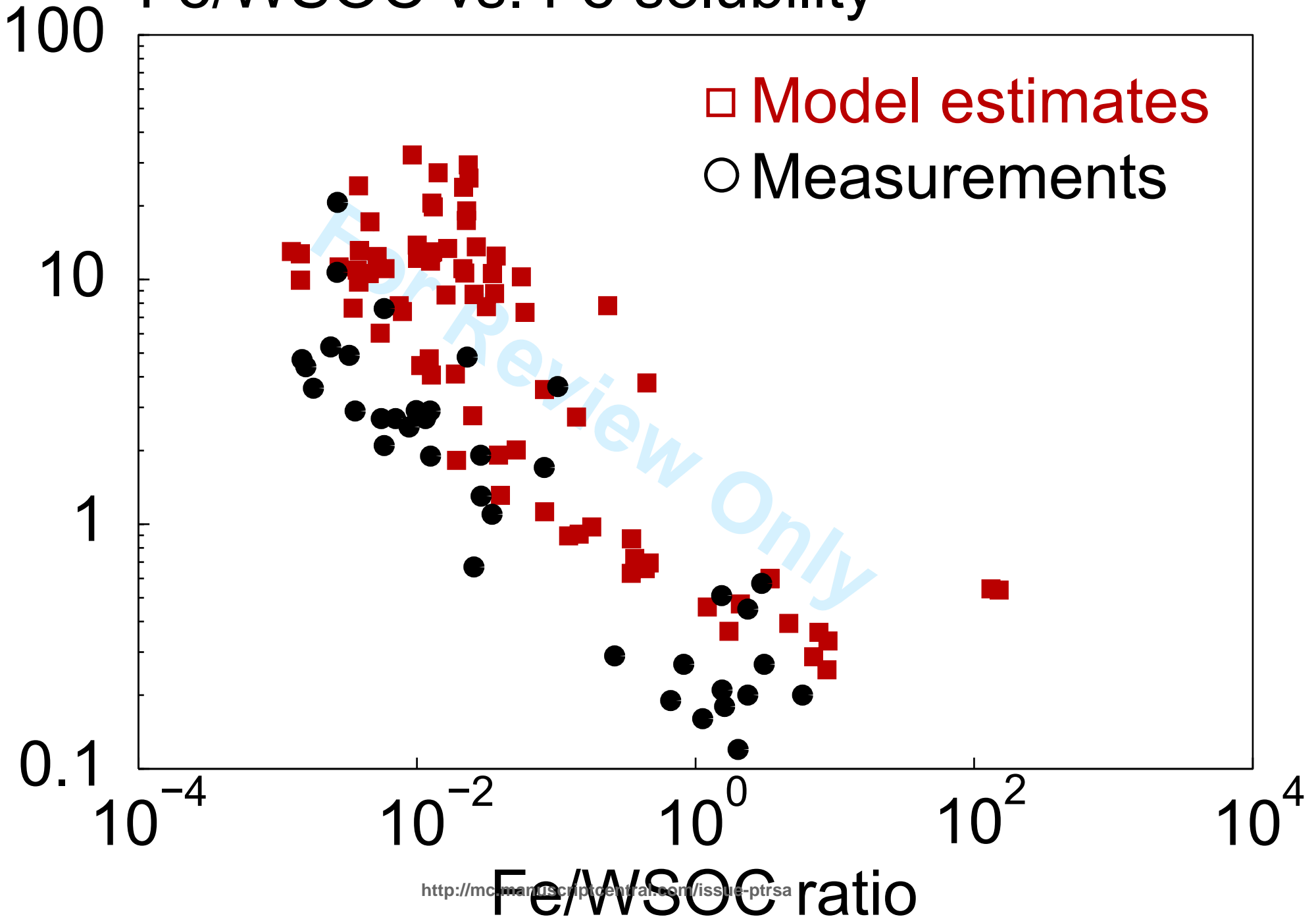


Fig. 1 Distribution of the ratio of advection to scavenging timescales (Y) for AI in the global ocean (after [25]). This is a measure of the relative importance of scavenging versus advection for AI export. Regions where Y is higher than one are scavenging-driven, those where Y is smaller than one are advection-driven. Where advection dominates (blue) the one-dimensional MADCOW model is predicted to be unreliable.

101x52mm (300 x 300 DPI)

Fe/WSOC vs. Fe solubility

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

