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The impact of changing surface ocean conditions on the dissolution of aerosol iron

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Key points

• Aerosol source and composition have the greatest effect on iron dissolution
• Ocean warming and acidification may not impact aerosol iron dissolution
• Strong ligands draw most of the labile aerosol iron into the soluble fraction

Index terms and key words
Index terms: ‘Trace elements; aerosols; chemical speciation and complexation; biogeochemical cycles, processes, and modeling’ (in ‘oceanography: biological and chemical').

Key words: iron; biogeochemistry; marine aerosol; climate change; ligands; colloids.

Abstract

The proportion of aerosol iron (Fe) that dissolves in seawater varies greatly and is dependent on aerosol composition and the physicochemical conditions of seawater, which may change depending on location or be altered by global environmental change. Aerosol and surface seawater samples were collected in the Sargasso Sea and used to investigate the impact of these changing conditions on aerosol Fe dissolution in seawater. Our data show that seawater temperature, pH and oxygen concentration, within the range of current and projected future values, had no significant effect on the dissolution of aerosol Fe. However, the source and composition of aerosols had the most significant effect on the aerosol Fe solubility, with the most anthropogenically influenced samples having the highest fractional solubility (up to 3.2%). The impact of ocean warming and acidification on aerosol Fe dissolution is therefore unlikely to be as important as changes in land usage and fossil fuel combustion. Our experimental results also reveal important changes in the size distribution of soluble aerosol Fe in solution, depending on the chemical conditions of seawater. Under typical conditions, the majority (77 – 100%) of Fe released from aerosols into ambient seawater existed in the colloidal (0.02 – 0.4 µm) size fraction. However, in the presence of a sufficient concentration of strong Fe-binding organic ligands (10 nM) most of the aerosol-derived colloidal Fe was converted to soluble Fe (< 0.02 µm). This finding highlights the potential importance of organic ligands in retaining aerosol Fe in a biologically available form in the surface ocean.
1. **Introduction**

During the past twenty years, extensive investigations of the marine biogeochemistry of iron (Fe) have demonstrated that this micronutrient limits primary production in vast areas of the world ocean [e.g., Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Takeda and Tsuda, 2005]. In particular, the supply of Fe controls phytoplankton growth in high nutrient, low chlorophyll (HNLC) waters, where the macronutrients nitrate and phosphate are replete. In these regions, there is the potential for increased primary production, carbon export to the deep ocean and associated atmospheric carbon dioxide (CO₂) drawdown to be realized by increased inputs of Fe [Martin, 1990; Kohfeld and Ridgwell, 2009].

Atmospheric deposition of aerosols is an important pathway by which Fe is introduced into surface waters of the open ocean [Duce, 1986; Martin and Gordon, 1988; Jickells et al., 2005]. The percentage of total Fe contained within aerosols that dissolves in seawater, known as the fractional solubility of aerosol Fe (%Feₐ), is known to vary substantially, depending on a number of factors. A review by Sholkovitz et al. [2012] notes that empirical estimates of the %Feₐ range from < 0.1% to > 95% (for ~1100 published values). Factors affecting the dissolution of aerosol Fe have been discussed by Baker and Croot [2010] and include the source and composition of the aerosols [Bonnet and Guieu, 2004], the particle size [Baker and Jickells, 2006], the concentration of particles deposited at the ocean surface [Zhuang et al., 1990] and atmospheric conditioning [Zhu et al., 1997]. It is therefore important to consider differences in aerosol dissolution when constructing global biogeochemical models that include Fe input to the ocean. However, most global models
have thus far assumed a constant value for the %Fe$_s$ [e.g., Aumont et al., 2003; Moore et al., 2004; Parekh et al., 2005; Tagliabue et al., 2009].

A number of studies have considered the effect of aerosol source on aerosol Fe dissolution in the marine environment, and concluded that anthropogenic or combustion aerosols (e.g., unrefined fuel combustion products, biomass burning) contain Fe with a significantly higher %Fe$_s$ compared to mineral aerosols [e.g., Sedwick et al., 2007; Aguilar-Islas et al., 2010]. Therefore, the potential increase in anthropogenic aerosol emissions due to rising global population and the industrialization of developing nations [International Energy Agency, 2009] may be expected to increase the aeolian input of dissolved Fe (dFe) to the world ocean.

Following deposition, the physicochemical conditions of seawater, including temperature, pH and dissolved oxygen (O$_2$) concentration, will impact on the dissolution of aerosol Fe and the subsequent solution speciation of aeolian Fe [Millero et al., 2009]. Inorganic Fe(III) species have an extremely low solubility limit in seawater (< 80 pM) above which they can precipitate as ferric oxyhydroxides [Liu and Millero, 2002]. The solubility of Fe(III) species is known to increase with decreasing pH, although this trend is not strong for seawater over the pH range of 7.5 – 9 [Kuma et al., 1996; Liu and Millero, 2002]. The effect of seawater temperature and dissolved O$_2$ concentration on Fe solubility in seawater is less clear. Liu and Millero [2002] report a higher solubility value for Fe(III) in 5 °C seawater (0.5 nM) than in 25 °C seawater (0.35 nM) and 50 °C seawater (0.34 nM). However, Kuma et al. [1996] observed no change in the solubility of Fe(III) from 10 °C to 20 °C. In addition, the oxidation rate of the more soluble redox species Fe(II) is known to decrease with decreasing temperature, pH and O$_2$ concentration [Millero et al., 1987; Croot et al., 2001; Hopkinson and Barbeau, 2007; Breitbarth et al., 2010].
Iron-binding ligands in seawater play a major role in Fe biogeochemistry. By keeping Fe in solution, ligands reduce the precipitation of ferric oxyhydroxides and thus the ultimate loss of dFe from surface waters via particle scavenging and export [Boyd and Ellwood, 2010]. Two classes of Fe-binding ligands have been characterized: strong ligands (‘L1’), which occur mainly near the surface, and weak ligands (‘L2’), which are more abundant and occur throughout the water column [Rue and Bruland, 1995; Hunter and Boyd, 2007], with conditional stability constants (log $K_{Fe_{Li}Fe}^{cond}$, where $i$ denotes ligand class) of 11.1 – 13.9 and 9.7 – 11.95, respectively [Gledhill and Buck, 2012]. Numerous studies have shown that complexation by dissolved organic matter (DOM) such as saccharides [Hassler et al., 2011], humic substances [Laglera and van den Berg, 2009] and other species that make up the L1 ligands [Rue and Bruland, 1995] allow Fe to exist at concentrations well in excess of the solubility of inorganic Fe(III).

Anthropogenic greenhouse gas emissions are thought to be responsible for observed increases in surface seawater temperature (SST) [IPCC, 2013] and reductions in surface seawater pH [Orr et al., 2005]. As a consequence of increased SST, the upper ocean is expected to become more stratified and less oxygenated [Whitney et al., 2007; Stramma et al., 2008]. Furthermore, the likely increase in anthropogenic aerosol emissions may result in an increase in the delivery of organic matter to surface waters, which may potentially contain Fe-binding ligands [Wozniak et al., 2013]. These changing environmental parameters clearly have potential consequences for aerosol Fe dissolution, but the nature and magnitude of these effects are uncertain.

The experimental study described here aims to elucidate the main controls on aerosol Fe dissolution, by manipulating key parameters that are likely to be affected by future environmental change; namely, surface seawater temperature, pH, dissolved O$_2$ concentration and Fe-binding ligand concentration. Filtration using different pore size filters (0.4 µm and
0.02 µm) provided insight into the size-distribution of aerosol-derived dFe in seawater leachate, as well as possible dissolution mechanisms under the range of different physicochemical conditions. In addition, experiments using bulk aerosol samples collected over a full annual cycle allowed us to assess the impact of differing aerosol sources on aerosol Fe dissolution, in relation to differing physicochemical conditions in surface seawater.

2. Methods

2.1. Seawater and aerosol sampling

All handling of samples and reagents was carried out under a Class-5 laminar flow hood (ISO 14644-1:1999, Bassaire or AirClean units). Ultra high purity (UHP, ≥ 18.2 MΩ cm) deionized water from Milli-Q (Millipore) or Nanopure (Barnstead) systems was used throughout this work. All plastic labware was cleaned following GEOTRACES cleaning protocols detailed in Cutter et al. [2010].

Seawater was collected at the Bermuda Atlantic Time-series Study (BATS) site in the Sargasso Sea (31°40'N, 64°10'W) on three cruises during the spring and summer period (April 2010 – July 2011) on board the R/V Atlantic Explorer. Polyvinylchloride (PVC) 10 L Teflon-lined, external-closure Niskin-type bottles (Ocean Test Equipment) were used to collect seawater samples at the deep chlorophyll maximum (~60 – 120 m depth), where Fe concentrations are typically lowest [Sedwick et al., 2005]. Upon recovery, samples were immediately transferred from the Niskin bottles into acid-washed 50 L low density polyethylene (LDPE) carboys (Nalgene) inside a polyethylene-walled ‘clean bubble’ under positive pressure. The seawater was subsequently filtered through 0.45 µm polytetrafluoroethylene (PTFE) Osmonics membrane capsules (GE Water Systems) via gravity filtration into 25 L LDPE carboys (Nalgene) and stored in the dark under ambient
clean room laboratory conditions for no longer than three months before being used in
leaching experiments. L₁-type Fe-binding ligands in ambient seawater samples, as
determined by competitive ligand exchange-adsorptive cathodic stripping voltammetry
(CLE-CSV) prior to leaching experiments were found to be subnanomolar (~0.8 nM; n = 5)
with a log \( K_{FeL,Fe'}^{cond} \) of ~12 (data not shown).

Four aerosol samples were collected from the Tudor Hill atmospheric observatory
on the southwest coast of Bermuda (32°15.95′N, 64°52.65′W) from 13 July to 20 August 2009
(AER 1, 38 days sampling), 27 September to 11 October 2010 (AER 2, 14 days sampling),
22 February to 8 March 2010 (AER 3, 14 days sampling) and 11 October to 13 December
2010 (AER 4, 63 days sampling). A high volume aerosol sampler drew air through 8 x 10
inch sheets of 2.2 µm pore size quartz microfiber Whatman QMA filters (GE Healthcare).
The total volume of air sampled for AER 1, AER 2, AER 3 and AER 4 over these sampling
periods was 8,620 m³, 10,519 m³, 11,719 m³ and 24,243 m³, respectively. The aerosol filters
were previously acid-washed following a method described by Morton et al. [2013]. The
aerosol sampler was located approximately 50 m above sea level on top of a 23 m high
aluminum scaffolding tower. To avoid local aerosol sources and ensure only marine air was
sampled, pumps were switched off when the wind direction was not in the onshore sector
(210° – 315°), or if the wind speed was less than 1 m s⁻¹. A procedural field blank was taken
by loading an aerosol filter into the aerosol sampler, leaving it in the sampler (with pumps
off) for 5 min and removing. Aerosol samples were removed and placed in zip-lock bags and
stored frozen at –20 °C for between 6 – 24 months.

2.2. Seawater preconditioning

Separate 1 L aliquots of the 0.45 µm-filtered BATS seawater were preconditioned
before use in the leaching experiments. Filtered seawater aliquots used in the variable
temperature experiments were equilibrated to 4 °C and 25 °C, using a fridge and temperature controlled laboratory, respectively. Filtered seawater aliquots used in the variable seawater pH experiments were preconditioned by sparging with filtered air/CO₂ mixtures using mass flow controllers until a stable pH was reached (between 48 – 72 h) [de Putron et al., 2011]. The sparging gas mixtures simulated equilibrium with atmospheric CO₂ concentrations of 400 ppm CO₂ (present-day conditions) and 1250 ppm CO₂ (possible future conditions), resulting in seawater pH values of 8.0 (‘ambient seawater’) and 7.6 (‘acidified seawater’), respectively (‘total scale’ pH calculated using measured values of total dissolved inorganic carbon and alkalinity using ‘CO₂sys’). Similarly, anoxic conditions (< 0.1% O₂) were created by purging dissolved O₂ from filtered seawater by sparging with filtered nitrogen (N₂) gas (for leaches 3 and 4 only). Filtered seawater aliquots used in organic ligand amendment experiments were preconditioned through the addition of a strong siderophore L₁-type ligand (either 10 nM of aerobactin [EMC Microcollections] or desferrioxamine-B [Sigma-Aldrich]) or weaker L₂-type ligands (either 10 nM of protoporphyrin-IX [Sigma-Aldrich] or 1 µM of glucuronic acid [Sigma-Aldrich]). These ligands were intended to simulate the range of iron-binding ligands that exist in open ocean waters and were added in concentrations in excess (~1 order of magnitude) of typical open ocean surface water concentrations in the eastern North Atlantic [Cullen et al., 2006] in order to observe a clear response in aerosol Fe complexation.

2.3. Aerosol leaching experiments

Aerosol leaching experiments were designed to replicate the process of dry deposition in the open ocean as closely as possible within the laboratory. Leaches were performed using an acid-washed filtration tower (Savillex) comprising a 47 mm perfluoroalkoxy (PFA) filter assembly clamp, 250 mL evacuated Teflon collection vessel and
0.25 inch diameter PTFE tubing. The PTFE tubing connected the collection vessel to a vacuum pump (GAST) via a 0.2 µm Acrovent air filter (Pall Corporation) and water trap. Acid-washed 0.4 µm pore size, 47 mm polycarbonate track-etched membrane filters (Nucleopore, GE Healthcare) were used to separate ‘dissolved Fe’ in the aerosol leachate solutions. Triplicate subsamples from each aerosol filter sample were taken using a 20 mm diameter polished steel arch punch (Osborne) and allowed to thaw at room temperature before being used for each different treatment in the aerosol leaching experiments.

The leaching process (Figure 1) involved four sequential leaches to test different equilibration times (leach 1 = 0 – 5 min, leach 2 = 5 – 10 min, leach 3 = 10 min – 48 h, and leach 4 = 48 h – 30 days). These leaching times were chosen to represent the typical temporal range of aerosol particles in the upper surface ocean. For leach 1, a 20 mm diameter aerosol-filter subsample was placed on a polycarbonate filter mounted within the filtration tower (under vacuum). Then 250 mL of preconditioned filtered seawater was poured over the aerosol filter in a continuous leaching process, lasting 5 min, with the resulting leachate collected. This process was repeated for leach 2 using the same aerosol subsample used in leach 1. Leaches 3 and 4 were batch leaches where the same aerosol subsample and polycarbonate filters used in leaches 1 and 2 were placed in fluorinated polyethylene (FPE, Nalgene) bottles with 500 mL of preconditioned filtered seawater for 48 h and 30 days for leaches 3 and 4, respectively (Figure 1). Previous studies employing an aerosol batch leach methodology have observed only negligible adsorption of dFe to bottle walls when fluorinated polymer bottles are used [Séguret et al., 2011]. To further minimize the effect of wall adsorption of dFe the FPE bottles were first preconditioned for 24 - 72 h with BATS seawater before batch leaches took place. To minimize the influence of ultraviolet light on Fe dissolution, leaches 1 and 2 were carried out under artificial light only, whereas leaches 3 and 4 were stored in darkness. The seawater leachate solutions that passed through the 0.4 µm
filter membrane in each sequential leach were subsequently decanted into acid-washed 125 mL LDPE bottles (Nalgene). The entire leaching process was conducted in triplicate for every experimental treatment.

To determine 'colloidal Fe' (cFe) and 'soluble Fe' (sFe), 125 mL of seawater leachate samples were filtered through 0.02 µm pore size, 25 mm diameter aluminum oxide Whatman Anotop syringe filters (GE Healthcare) and collected in acid-washed 60 mL LDPE bottles (Nalgene) (Figure 1). In this study, following the definitions of Wu et al. [2001], dFe is defined as the < 0.4 µm fraction and sFe is defined as the < 0.02 µm fraction. Colloidal Fe is thus inferred from the difference between dFe and sFe, representing the 0.02 – 0.4 µm size fraction (i.e., cFe = dFe – sFe). The Anotop filters used for ultrafiltration of aerosol leachate were set-up and conditioned following the inline filtration method detailed by Ussher et al. [2010]. Following aerosol leaches, all seawater leachate samples (including blanks) were acidified to pH ~1.7 using HCl (Romil, UpA) and stored for > 1 year before analysis. In addition to leachate samples, process blanks were prepared by passing ambient filtered seawater over a procedural field blank subsample (Section 2.1) and a 47 mm polycarbonate filter. Following analysis, the Fe concentrations of the relevant process blanks were subtracted from Fe concentrations of all leachate samples. The dFe concentrations of the process blanks were typically < 0.1 nM.

2.4. Determination of iron in seawater leachates using flow injection with chemiluminescence

The concentrations of dFe and sFe in seawater leachate solutions were determined using flow injection with chemiluminescence detection (FI-CL) inside a Class-100 clean room (ISO 9001:2008), based on the method described by Obata et al. [1993]. Briefly, seawater leachate samples were buffered in-line to pH 3.5 with 0.35 M ammonium acetate (Romil, SpA) then loaded on a chelating column containing Toyopearl AF-Chelate-650M
iminodiacetate resin (IDA, Tosoh Bioscience). The seawater matrix major cations were removed using a 0.012 M HCl (Romil, SpA) rinse, then Fe was eluted from the column using 0.23 M HCl (Romil, SpA). The acid/analyte eluent was then mixed with 0.25 mM luminol, 0.5 M ammonium hydroxide and 0.3 M hydrogen peroxide to initiate the oxidation of luminol [Rose and Waite, 2001], which produced a chemiluminescence signal detected by a photomultiplier tube (PMT, Hamamatsu).

Iron concentrations were quantified using the method of standard additions to low-Fe seawater (< 0.35 nM dFe), subsampled from the original filtered seawater used for leaches (four sets of concentration ranges were used: 0.6 – 12 nM, 0.6 – 5 nM, 0.6 – 2.4 nM, 0.2 – 1.4 nM, n = 6). All standards and samples were analyzed in triplicate. Accuracy of the method was checked daily by analyzing samples of SAFe and GEOTRACES reference seawater and comparing determined concentrations with consensus values: SAFe S = 0.091 ± 0.008 nM (n = 29), SAFe D2 = 0.910 ± 0.022 nM (n = 29) and GEOTRACES GD = 0.98 ± 0.10 nM (n = 22). (K. Bruland, unpublished data, 2008, available from the Bruland Research Laboratory at http://es.ucsc.edu/~kbruland/GeotracesSaFe/kwbGeotracesSaFe.html).

Concentrations of Fe in reference seawater determined using this FI-CL system were consistently within the range of the consensus values (SAFe S = 0.10 – 0.10 nM [n = 3], SAFe D2 = 0.85 – 0.91 nM [n = 4] and GEOTRACES GD = 0.83 – 0.99 nM [n = 8]). Analytical precision was typically better than ± 5% relative standard deviation for all standards, reference seawater and samples.

2.5. Total trace metal determination by inductively coupled plasma mass spectrometry

Triplicate subsamples of AER 1 – 4 and blanks were completely digested using concentrated hydrofluoric acid (28.9 M HF, Seastar, Baseline), concentrated nitric acid (15.8 M HNO₃, Seastar, Baseline) and heat [Morton et al., 2013] at the University of Delaware. As
acid digestion is a destructive process, it was necessary to use different subsamples of each aerosol sample in the aerosol leaching experiments and use the mean total Fe amount in fractional solubility calculations. Total element determinations were subsequently performed on the digests at Old Dominion University using an Element2 (Thermo Fisher) inductively coupled plasma-mass spectrometer (ICP-MS) in medium resolution mode. Samples were spiked with indium ($^{115}$In) as an internal standard. Calibration standards were made up using a multi-elemental standard (QC Standard 4, PlasmaCal containing aluminum [Al], titanium [Ti], manganese [Mn], vanadium [V], chromium [Cr], Fe, cobalt [Co], nickel [Ni], copper [Cu], zinc [Zn], cadmium [Cd], antimony [Sb] and lead [Pb]) in the same 2% ($v/v$) HNO$_3$ matrix as the aerosol digest solutions.

2.6. Air mass back trajectory analysis

Air mass back trajectories were simulated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by the U.S. National Oceanic and Atmospheric Administration (NOAA, available for download at http://ready.arl.noaa.gov/hyreg/HYSPLIT_pchysplit.php). Ten-day back trajectories at altitudes of 50 m, 500 m and 2000 m were performed for each day within the period over which aerosol samples were collected. Daily back trajectories were used in the cluster analysis function of HYSPLIT to generate ten mean back trajectories for each aerosol sampling period.

3. Results and Discussion

3.1. Aerosol sample characterization

The aerosol samples collected at Tudor Hill represent a seasonal-scale time series comprising a summer sample (AER 1), an autumn sample (AER 2), a spring sample (AER 3),
and a winter sample (AER 4). Daily 500 m elevation 10-day air mass back trajectories for each day of the collection period of each aerosol sample are provided in Figure 2. Air mass back trajectories modeled at 50 m and 2000 m elevation (not shown) were similar to those modeled at 500 m. The back trajectories for AER 1 (Figure 2A), collected between July and August 2009, suggest that the air had predominately travelled from the east, likely entraining soil dust from North Africa, as is typical for aerosols in the Bermuda region during summer [Sedwick et al., 2007]. The back trajectories for AER 2 (Figure 2B), collected between September to October 2010 and AER 3 (Figure 2C), collected February to March 2010 suggest a mixture of air masses that may have delivered aerosols from both North Africa and North America. The back trajectories for AER 4 (Figure 2D), collected between October and December 2010, suggest that the air had predominately travelled from the northwest, entraining aerosols from North America. These results are consistent with time-series aerosol observations from Bermuda over a number of decades [Duce and Hoffman, 1976; Chen and Duce, 1983; Anderson et al., 1996; Sholkovitz et al., 2009].

To gain an appreciation of the relative contributions of anthropogenic versus crustal materials to the aerosols, total masses of Fe, V, Ni, Cu, Pb and Sb in the aerosol samples (Table 1) were normalized to the mass of Al, and the resulting ratios compared to those of average continental crust [Taylor and McLennan, 1995] to calculate enrichment factors (Table 2). Samples collected in the winter (i.e., AER 4) were more enriched (enrichment factors > 10) in V, Ni, Cu, Pb and Sb relative to aerosols collected in the summer (i.e., AER 1 and AER 2). These results are consistent with the back trajectory models (Figure 2), and agree with the suggestion by Sedwick et al. [2007] that marine air over the Sargasso Sea contains a greater proportion of anthropogenic combustion products (relative to continental soil dust) in the winter. Summer Fe and Al atmospheric loadings were higher than those determined in the winter (Table 1), consistent with previous work that has shown high
Fe and Al loadings in air masses dominated by lithogenic aerosols, relative to anthropogenic materials [Baker et al., 2006; Buck et al., 2010a; Séguret et al., 2011].

3.2. Effect of seawater temperature, pH and de-oxygenation on aerosol iron dissolution

Total dFe leached from aerosols into preconditioned seawater samples of different temperature, pH and O₂ concentration were calculated from the process-blank-corrected dFe concentrations and volumes of seawater leachate (Figure 3). An alternative representation of these results, as fractional solubilities of aerosol Fe (total dFe released into solution divided by total aerosol Fe), are shown in Figure 4.

The mean total dFe leached from each aerosol sample (AER 1 – AER 4) into 4 °C and 25 °C seawater is shown in Figure 3A. The mean total dFe is the sum of all dFe released into seawater during all four sequential leaches and ranged from 0.7 ± 0.2 nmol to 4 ± 2 nmol for AER 1 – AER 4. The uncertainty was dominated by differences between replicate leaches of subsamples of the same aerosol sample, with a relative standard deviation (RSD) of 13 – 45%, rather than replicate Fe analyses of the same leachate solution, with an RSD of 5 – 6%, in accord with results of other studies [e.g. Morton et al., 2013]. Most of the aerosol Fe was released into solution during the first leach, with progressively less Fe released in the subsequent sequential leach steps. It is clear that the dissolution of Fe from aerosols occurred rapidly; the majority (84 – 94%) of the aerosol-derived dFe was released within the first 10 minutes of contact with seawater. Similar kinetics were observed for all leaches assessed in this study and in other studies of aerosol Fe solubility [e.g., Buck et al., 2006; Wu et al., 2007]. Importantly, the differences in the mean total dFe released into 4 °C versus 25 °C seawater were not statistically significant (two-tailed t test, p > 0.05) for any of the aerosol samples, suggesting seawater temperature does not exert a major control on the dissolution of aerosol Fe.
The mean total sFe (< 0.02 µm) leached from each aerosol sample (AER 1 – AER 4) into 4 °C and 25 °C seawater is shown in Table 3. The mean total sFe is the sum of all sFe released during all four sequential leaches and ranged from 0.04 nmol to 0.41 nmol for AER 1 – AER. The colloidal Fe size fraction (cFe, 0.02 – 0.4 µm) can be inferred by comparing the dFe and sFe in the seawater leachate. For all leaches, the majority (77 – 97%) of dFe released from the aerosols into the seawater leachate resided in the cFe size fraction (Table 3). It should be noted that these data represent the size distribution of dFe in solution following leaching from aerosols, not the amount of sFe and cFe that has been directly leached from the aerosols. The differences in mean total sFe in the leachate using 4 °C seawater versus 25 °C seawater were not statistically significant (two-tailed t test, p > 0.05) when the differences in dFe for replicate leaches is taken into account, suggesting that seawater temperature does not exert a major control on the size distribution (sFe versus cFe) of dFe in the aerosol leachate solutions.

The mean total quantities of dFe leached from each aerosol sample (AER 1 – AER 4) into ‘ambient seawater’ (25 °C, pH 8.0, oxygenated), ‘acidified seawater’ (pH 7.6, sparged with air/CO2 mixture, 1250 ppm CO2) and ‘anoxic seawater’ (sparged with N2 for leaches 3 and 4) are shown in Figure 3B. The mean total dFe is the sum of all dFe released during all leaches and ranged from 0.6 ± 0.2 nmol to 5 ± 2 nmol for AER 1 – AER 4. Our results show that the total dFe released into acidified and anoxic seawater was not statistically different (two-tailed t test, p > 0.05) from the total dFe released into ambient seawater for all aerosol samples.

The mean total sFe in the seawater leached from each aerosol sample (AER 1 – AER 4) into ambient, acidified and anoxic seawater is shown in Table 3. The mean total sFe is the sum of all sFe released during all four sequential leaches and ranged from 0.02 nmol to 0.16 nmol for AER 1 – AER 4. In all cases, the majority (92 – 98%) of dFe in the seawater
leachate solutions resided in the cFe size fraction (Table 3). There were some differences observed between samples, however, similar to the dFe results, the differences in the mean total sFe in the various seawater leachate samples were not statistically significant (two-tailed t test, p > 0.05) when the differences in dFe for replicate leaching experiments is taken into account.

Thus our experimental results suggest that seawater temperature, pH (as controlled by pCO$_2$) and O$_2$ concentration did not exert a major control on the dissolution of aerosol Fe, nor on the size distribution of aerosol-derived dFe in seawater, within the experimental uncertainties and ranges of the parameters examined. These observations are in accord with those of Kuma et al. [1996], who reported no difference in the solubility of inorganic Fe(III) in seawater at 10 °C versus 20 °C. In contrast, however, Liu and Millero [2002] reported higher solubility of Fe(III) seawater at 5 °C versus 25 °C (0.5 ± 0.07 nM for 5 °C seawater and 0.35 ± 0.06 nM for 25 °C seawater). Other studies have demonstrated an increase in the solubility of inorganic Fe with decreasing pH [Byrne and Kester, 1976; Kuma et al., 1996; Liu and Millero, 2002]. However, Liu and Millero [2002] report that Fe solubility does not change in the pH range of 7.5 – 9, due to the dominance of the neutrally charged species Fe(OH)$_3$$^+$ [Liu and Millero, 1999]. It should be noted that in the case of Liu and Millero [2002] and Byrne and Kester [1976] equilibrium conditions were represented, whereas our leach experiments are not likely to represent equilibrium conditions. Data from our study also agree with empirical data that suggest little difference in the dissolution of aerosol Fe in seawater (pH ~8) versus UHP (≥ 18.2 MΩ cm, pH 5.6) deionized water [Aguilar-Islas et al., 2010; Buck et al., 2013].

Given the year 2100 projections for average sea surface temperatures to increase by 1 °C [Meehl et al., 2007], seawater pH to decrease by 0.25 [Caldeira and Wickett, 2003], and oceanic oxygen minimum zones (OMZs) to expand [Shaffer et al., 2009], our data
suggest that such changes will not significantly impact on aerosol Fe dissolution in surface ocean waters. However, it should be stressed that the combined effect of such changes, or the impact of such changes on other factors that impact aerosol Fe dissolution, cannot be ruled out. Our findings have important implications for modeling the impact of future changes in aerosol input to the global cycling of Fe and carbon, as well as phytoplankton growth and community structure. Specifically, our experimental results suggest that, to a first approximation, models do not need to consider that aerosol Fe dissolution will vary as a function of projected variations in seawater temperature, pH or oxygen saturation. Whilst seawater temperature, pH and O\textsubscript{2} concentration had no significant effect on aerosol Fe dissolution, we observed pronounced differences in aerosol Fe solubilities for aerosols from different source regions with different bulk compositions.

3.3. Effect of aerosol source and composition on aerosol iron dissolution

Seawater leaching of aerosol samples of different source and composition resulted in different fractional solubilities of aerosol Fe under all conditions (Figure 4). Indeed, there is nearly an order of magnitude difference in the %Fe\textsubscript{s} for the more ‘anthropogenic’ type aerosol (AER 4) relative to the ‘mineral dust’ type aerosol (AER 1). The operationally-defined %Fe\textsubscript{s} for aerosol AER 1 was consistently lower (0.3 ± 0.1% to 0.5 ± 0.2%) than that for aerosol AER 4 (2.5 ± 0.8% to 3.2 ± 0.8%), under all physicochemical conditions of the seawater leaching experiments. The dependence of aerosol Fe solubility on aerosol type and source has been noted in previous studies [Sedwick et al., 2007; Sholkovitz et al., 2009; Buck et al., 2010b; Séguret et al., 2011; Shelley et al., 2012; Baker et al., 2013; Wozniak et al., 2013]. It has been suggested that the elevated %Fe\textsubscript{s} in anthropogenically influenced aerosols reflects acidic processing at the particle surface [Meskhidze et al., 2005; Hsu et al., 2010], the presence of labile Fe sulfates and other soluble Fe phases [Oakes et al., 2012], and the
tendency for anthropogenic aerosols to be smaller than mineral dust particles [Chen and Siefert, 2004; Jang et al., 2007]. Conversely, mineral aerosol particles tend to be larger, with much of the Fe contained in refractory minerals [Desboeufs et al., 2005].

Sholkovitz et al. [2009] show a linear relationship between the %Fe, and the V/Al mass ratio of bulk aerosol samples collected over the Sargasso Sea. That linear relationship and the V/Al mass ratios of bulk aerosol samples collected in this study were used to predict fractional solubilities in ambient seawater; these predictions were then compared to empirically determined fractional solubilities. Whilst absolute values of the predicted and determined fractional solubilities differed (predicted values of 1.4%, 2.0%, 2.7% and 3.8%, for AER 1, AER 2 and AER 3 and AER 4, respectively, versus observed values of 0.5%, 1.2%, 1.3% and 2.8%, for AER 1, AER 2 and AER 3 and AER 4, respectively), the predicted trend of increasing solubility with increasing V/Al mass ratio matched the empirical values. Thus, our results indicate greater %Fe, in aerosols containing a larger proportion of anthropogenic material.

Whilst this study is unable to provide insight into the mechanism of enhanced Fe solubility in non-soil dust aerosols, the results add to the existing evidence that Fe in anthropogenic aerosols is more soluble than Fe in soil-derived mineral dust and that this variability dominates over potential changes in the fundamental parameters of temperature, pH and O₂ concentration of the seawater in which aerosols are deposited. These results suggest that the potential for an increase in anthropogenic aerosol emissions accompanying rising global population and the industrialization of developing nations [International Energy Agency, 2009] could conceivably increase the atmospheric flux of dFe to the global ocean, although soil dust is likely to continue to dominate the total aerosol Fe deposition and therefore the global importance of anthropogenic aerosol Fe input is likely to remain marginal. These results reinforce the idea that modeling efforts must consider the source of
aerosols deposited in different ocean regions, as well as the potential for future changes in the composition of aerosols entering the ocean.

3.4. Effect of organic ligands on aerosol iron dissolution

Figure 5A shows the mean total dFe leached from aerosol sample AER 1 into ambient seawater and into seawater samples amended with various organic ligands. Despite the added ligands having very different conditional stability constants with respect to Fe complexation, the mean total dFe leached from aerosols following all leaches (including a control using seawater with no added ligands) fell in the narrow range of 0.8 ± 0.1 nmol to 1.2 ± 0.5 nmol. Interestingly, there was no statistical difference between the mean total dFe leached into each ligand-amended seawater sample and that leached into unamended ambient seawater (two-tailed t test, p > 0.05), which contrasts with the results of previous work by Aguilar-Islas et al. [2010]. However, this earlier study did not include replicate leaches using subsamples of a single aerosol sample. Our study has shown that the RSD associated with replicate leaches can exceed 50%, and whilst the mean total amounts of dFe leached into ligand-amended seawater appeared to differ from that leached into ambient seawater, these differences were not statistically significant. The majority of the variation in dFe leached from sub-samples of a single aerosol filter reflects either the inherent variability of the leaching process (i.e. the leaching mechanism or variability in the Fe species or particle character) or heterogeneity of Fe species with different fractional solubilities across the aerosol filter. Bulk analysis of an extended suite of aerosol digest solutions (data not shown) suggests that heterogeneity in total Fe contained on the aerosol filter is unlikely to be responsible for the observed variability in dFe between replicate leaches (RSD on mean of total Fe in subsamples of a single aerosol sample is < 3%).
In stark contrast, there were pronounced differences in the mean total sFe in leachate solutions after leaching with unamended ambient seawater versus seawater amended with the L₁-type ligands aerobactin and desferrioxamine-B (Figure 5B). The mean total sFe leached into ambient seawater leachate was 0.02 nmol, whereas leachate from seawater amended with aerobactin and desferrioxamine-B contained 1.3 nmol and 1.1 nmol sFe, respectively. This large impact observed with L₁-type ligand amended seawater was not seen with the weaker organic ligands glucuronic acid and protoporphyrin-IX, for which leachate solutions contained 0.10 nmol and 0.16 nmol sFe, respectively.

In comparing the dFe and sFe in the seawater leachate solutions, it is apparent that the majority (100%) of the dFe in ambient seawater leachate existed as cFe. The same was true for all of the seawater leachate solutions from the temperature, pH and dissolved O₂ experiments. This observation is consistent with the results of previous laboratory studies and field observations [Wu et al., 2001; Bergquist et al., 2007; Aguilar-Islas et al., 2010; Ussher et al., 2013; Fitzsimmons and Boyle, 2014; S. J. Ussher, manuscript in preparation, 2014]. Conversely, for aerosols leached with seawater amended with the L₁-type ligands aerobactin and desferrioxamine-B, the majority of dFe in the leachate (77 – 98%) resided in the sFe fraction. However, for leaches with seawater amended with the weaker ligands; glucuronic acid and protoporphyrin-IX, there was only a small increase in the proportion of sFe in the leachate compared with the control experiment using ambient conditions (sFe accounted for 11 – 21% of dFe). This observation suggests that the stronger L₁-type ligands may play an important role in the dissolution of aerosol Fe in the surface ocean.

Based on the results of this study, we hypothesize a two-stage mechanism for the dissolution of aerosol Fe in seawater (Figure 6). First, upon deposition of aerosols at the ocean surface, labile inorganic Fe(II) and Fe(III) is released into seawater, whereupon it is rapidly forms colloidal-sized ferric oxyhydroxides [following oxidation, if Fe(II)], or is
adsorbed or complexed by colloidal-sized organic matter (e.g., saccharides [Hassler et al., 2011], amino acids [Benner, 2011] and humic substances [Laglera and van den Berg, 2009]).

After this first stage, the dissolved aerosol Fe exists predominantly in the cFe size fraction, as observed in the majority of our experimental leachate solutions. During the second stage of our hypothesized mechanism, strong L₁-type ligands, such as siderophores, if present uncomplexed in sufficient concentration, form strong Fe-ligand complexes, whereby there is a transfer of dissolved aerosol Fe from the colloidal to the soluble size fraction, as low molecular weight (~300 – 1000 Da) Fe-ligand complexes [Macrellis et al., 2001]. The fact that not all Fe is ‘solubilized’ by L₁-type ligands, despite seawater being amended with large excess concentrations (10 nM) in our experiments, may reflect the physical or chemical association of some L₁-type ligands with colloidal material present in the seawater.

An alternative hypothesis is that upon deposition at the surface seawater, aerosols may release colloidal-sized organic matter or inorganic phases with which Fe is already associated [Raiswell and Canfield, 2012; Paris and Desboeufs, 2013]. In seawater, L₁-type ligands can then draw the aeolian cFe into the soluble fraction, as described above. If this is the case, it suggests ligands associated with aerosols are weak and colloidal, contrary to findings of Wozniak et al. [2013]. However, we suggest it is more likely that dFe released from aerosols enters the colloidal size fraction in seawater. This conclusion is based on results for the leaching of aerosols using seawater preconditioned by filtration (< 0.4 µm) and ultrafiltration (< 0.02 µm), which show lower dFe concentrations in leachate derived using ultrafiltered seawater [Ussher, 2005]. In addition, Dammshäuser and Croot [2012] showed that aerosol Al and titanium (Ti) colloidal associations are very low following dissolution into seawater, potentially indicating low input of colloidal matter from aerosols. An important factor that determines whether colloidal Fe is delivered by aerosols or forms in seawater following deposition maybe the particle size of deposited aerosols, which is related
to aerosol composition (i.e., mineral dust versus combustion products). Certainty, a higher proportion of colloidal Fe has been observed in regions of fine mode aerosol deposition in comparison to coarse mode aerosol deposition, and this fine size fraction results in higher fractional solubilities of Fe [Buck et al., 2010b; Ussher et al., 2013].

In summary, from our experimental results, it seems clear that stronger organic Fe-binding ligands play an important role in the dissolution of aerosol Fe. This observation has important implications for our understanding of the biogeochemical role of organic ligands with regard to the cycling of Fe. In the absence of such organic ligands, aerosol-derived dFe will remain largely in the colloidal size fraction in seawater, in which case it is expected to be more rapidly lost from surface ocean waters over a period of weeks to months [Moran and Buesseler, 1992; Boyd et al., 2010]. In the presence of sufficient concentrations of strong ligands, however, aerosol-derived dFe may be transferred from the colloidal to the soluble size fraction, where it may be expected to have a longer residence time in the euphotic zone [Boyd and Ellwood, 2010] and thus have greater biological availability to phytoplankton. It is important to note that the role that biological organisms play in aerosol Fe dissolution has not been considered in this study and should be included when attempting to understand the complete aerosol Fe dissolution mechanism.

4. Conclusions

The results of this experimental study suggest that plausible future variations in the temperature, pH and O₂ concentration of seawater will have a minor impact on the dissolution of aerosol Fe. However, in accord with other studies, our data indicate that aerosol composition has the most significant effect on the dissolution of aerosol Fe, with North Atlantic aerosol samples with the greatest ‘anthropogenic’ components having the highest fractional solubility. Hence, we surmise that future increases in the proportion of
combustion aerosols, relative to mineral dust, are likely to be the most important driver of changes in the atmospheric flux of dFe to the surface ocean. Therefore, it is reasonable for modelers not to prioritize the inclusion of seawater temperature, pH and O$_2$ concentration effects on aerosol Fe dissolution, but instead focus attention on the regional differences in the original source of deposition aerosols.

Furthermore, our results highlight the likely importance of strong Fe-binding organic ligands in regulating the size distribution of aerosol-derived dFe in surface ocean waters; specifically, in increasing the residence time and biological availability of aerosol-derived Fe in the surface ocean. A conceptual model of aerosol Fe dissolution is proposed in which strong Fe-binding organic ligands play a key role. The proposed two-stage mechanism highlights the significance of the colloidal phase and the strong L$_1$-type ligands in retaining biologically-available aerosol Fe in surface ocean waters following deposition of aerosols.

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Table 1. Total trace metal masses\(^a\) contained in aerosol subsamples and atmospheric loading of trace metals in sampled air\(^b\).

| Aerosol sample | Sample period      | Total mass of trace metal in aerosol subsample (ng) | Concentration of trace metal in sampled air (pmol m\(^{-3}\)) |
|----------------|--------------------|----------------------------------------------------|---------------------------------------------------------------|
| AER 1          | 13 Jul. to 20 Aug. 2009 | 16,200 ± 700, 9,180 ± 300, 41.0 ± 0.4, 17.0 ± 0.6, 14.8 ± 0.4, 18.0 ± 0.6, 2.65 ± 0.2, 8,800 ± 400 | 2,400 ± 70, 12 ± 0.1, 4.3 ± 0.2, 3.4 ± 0.1, 1.3 ± 0.4, 0.32 ± 0.04, 8,800 ± 400 |
| AER 2          | 27 Sept. to 11 Oct. 2010 | 21,000 ± 500, 12,300 ± 100, 82.0 ± 5, 32.0 ± 1, 31.1 ± 3, 28.8 ± 0.5, 5.21 ± 0.01, 9,400 ± 200 | 2,700 ± 30, 19 ± 1, 6.6 ± 0.2, 5.9 ± 0.5, 1.7 ± 0.03, 0.52 ± 0.001 |
| AER 3          | 22 Feb. to 8 Mar. 2010 | 30,000 ± 500, 18,600 ± 200, 169 ± 40, 76.0 ± 10, 92.9 ± 30, 146 ± 30, 24.6 ± 1, 12,000 ± 400 | 3,600 ± 80, 36 ± 8, 14 ± 2, 16 ± 4, 7.6 ± 2, 2.2 |
| AER 4          | 11 Oct. to 13 Dec. 2010 | 8,840 ± 500, 4,870 ± 100, 73.0 ± 4, 31.0 ± 1, 47.5 ± 3, 75.0 ± 9, 14.4 ± 0.3, 1,700 ± 200 | 460 ± 10, 7.5 ± 0.4, 2.8 ± 0.1, 3.9 ± 0.2, 1.9 ± 0.2, 0.62 ± 0.01 |

\(^a\)Total mean masses (ng) of aluminum (Al), iron (Fe), vanadium (V), nickel (Ni), copper (Cu), lead (Pb) and antimony (Sb) in triplicate subsamples of each aerosol sample.

\(^b\)Mean concentrations (pmol m\(^{-3}\)) of Al, Fe, V, Ni, Cu, Pb and Sb in sampled air calculated using total mean masses of trace metals in each aerosol subsample and the total volume of air passed through each sample filter over the sampling period. Standard deviations from mean concentrations (± 1 σ) represent the uncertainly of trace metals mean mass measurements only.
Table 2. Trace metal to aluminum mass ratios\(^a\) and trace metal enrichment factors relative to upper continental crust abundances\(^b\).

| Aerosol sample | Mass ratio | Enrichment factors |
|----------------|------------|--------------------|
|                | Fe/Al      | V/Al               | Ni/Al | Cu/Al | Pb/Al | Sb/Al | Fe  | V   | Ni  | Cu  | Pb  | Sb  |
| AER 1          | 0.568 ± 0.06 | 0.00254 ± 0.00004 | 0.00105 ± 0.00006 | 0.000917 ± 0.000006 | 0.00111 ± 0.00002 | 0.00164 ± 0.0001 | 1.3 | 3.4 | 4.2 | 2.9 | 4.5 | 66  |
| AER 2          | 0.584 ± 0.01 | 0.00391 ± 0.00003 | 0.00152 ± 0.00008 | 0.00148 ± 0.00002 | 0.00137 ± 0.00003 | 0.000248 ± 0.000001 | 1.3 | 5.2 | 6.1 | 4.8 | 5.5 | 100 |
| AER 3          | 0.620 ± 0.0008 | 0.00563 ± 0.0002  | 0.00253 ± 0.00005 | 0.00310 ± 0.0001 | 0.00486 ± 0.00007 | 0.000820 ± 0.000002 | 1.4 | 7.5 | 10  | 10  | 20  | 330 |
| AER 4          | 0.551 ± 0.02 | 0.00826 ± 0.00007 | 0.00351 ± 0.0003 | 0.00537 ± 0.0002 | 0.00848 ± 0.00005 | 0.00163 ± 0.00005 | 1.3 | 11.0| 14  | 17  | 34  | 660 |

\(^a\)Iron/aluminum (Fe/Al), vanadium/aluminum (V/Al), nickel/aluminum (Ni/Al), copper/aluminum (Cu/Al), lead/aluminum (Pb/Al) and antimony/aluminum (Sb/Al) mass ratios calculated by dividing the total mean mass of each trace metal with the total mean mass of aluminum in each aerosol subsample. Standard deviations from mean mass ratios (± 1 σ) represent the uncertainty of trace metals mean mass measurements only.

\(^b\)Iron (Fe), vanadium (V), nickel (Ni), copper (Cu), lead (Pb) and antimony (Sb) enrichment factors were calculated by dividing trace metal/aluminum mass ratios of aerosol samples by trace metal/aluminum ratios found in the upper continental crust. Abundances of trace metals in the upper continental crust taken from Taylor and McLennan [1995] and used to calculate mass ratios (Fe/Al = 0.4, V/Al = 0.0007, Ni/Al = 0.0002, Cu/Al = 0.0003, Pb/Al = 0.0002 and Sb/Al = 0.000002). Standard deviations from mean enrichment factors (± 1 σ) represent the uncertainty of trace metals mean mass measurements only.
Table 3. The mean total (nmol) of dissolved iron (dFe), colloidal iron (cFe) and soluble iron (sFe) leached from aerosol samples AER 1, AER 2, AER 3 and AER 4 during three replicate leaches with seawater.

| Aerosol sample | Seawater condition | Total Fe leached from aerosols (nmol) | Colloidal proportion of dFe (%) |
|---------------|--------------------|--------------------------------------|-------------------------------|
|               |                    | dFe       | cFe   | sFe   |                               |
| AER 1         | 25 °C              | 0.9 ±0.4  | 0.7   | 0.20  | 77%                           |
| AER 1         | 4 °C               | 0.7 ±0.2  | 0.6   | 0.037 | 94%                           |
| AER 1         | Ambient (25 °C, pH 8.0, oxygenated) | 0.8 ±0.4  | 0.8   | 0.016 | 98%                           |
| AER 1         | Acidified (pH 7.6) | 0.6 ±0.2  | 0.5   | 0.043 | 92%                           |
| AER 2         | 25 °C              | 2.4 ±0.4  | 2.3   | 0.15   | 94%                           |
| AER 2         | 4 °C               | 2.8 ±0.4  | 2.3   | 0.41   | 85%                           |
| AER 2         | Ambient (25 °C, pH 8.0, oxygenated) | 2.6 ±0.3  | 2.5   | 0.09   | 97%                           |
| AER 2         | Acidified (pH 7.6) | 1.7 ±0.3  | 1.6   | 0.052 | 97%                           |
| AER 2         | Anoxic             | 2.0 ±0.3  | 1.9   | 0.060 | 97%                           |
| AER 3         | 25 °C              | 4.3 ±1.6  | 4.2   | 0.12   | 97%                           |
| AER 3         | 4 °C               | 3.3 ±1.1  | 3.1   | 0.22   | 93%                           |
| AER 3         | Ambient (25 °C, pH 8.0, oxygenated) | 4.3 ±1.3  | 4.2   | 0.16   | 96%                           |
| AER 3         | Acidified (pH 7.6) | 4.7 ±1.9  | 4.6   | 0.11   | 98%                           |
| AER 4         | 25 °C              | 2.5 ±0.5  | 2.2   | 0.23   | 91%                           |
| AER 4         | 4 °C               | 2.2 ±1.0  | 2.0   | 0.15   | 93%                           |
| AER 4         | Ambient (25 °C, pH 8.0, oxygenated) | 2.4 ±0.6  | 2.3   | 0.055 | 98%                           |
| AER 4         | Acidified (pH 7.6) | 2.2 ±0.7  | 2.1   | 0.055 | 97%                           |

*25 °C seawater, 4 °C seawater, ambient seawater from the pH and de-oxygenation experiment (25 °C, pH 8.0, oxygenated), acidified seawater (pH 7.6, sparged with air enriched in carbon dioxide) and anoxic seawater (sparged with nitrogen gas for leaches 3 and 4). Standard deviations (± 1 σ) from mean total Fe leached from replicate subsamples of the same aerosol sample shown for dFe.
Figure 1. Summary of aerosol leaching method. Leach 1 and 2 were continuous leaches carried out using a Savillex filtration tower, and leach 3 and 4 were batch leaches carried out in 500 mL fluorinated polyethylene (FPE) bottles. All seawater leachate samples were filtered through 0.4 µm and 0.02 µm pore size filters to define the size distribution of dissolved iron species in solution.
Figure 2. Mean air mass back-trajectory clusters generated from daily 500 m 10 day back trajectories from Tudor Hill using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model for the following sampling periods: A) 13 July to 20 August 2009 (AER 1), B) 27 September to 11 October 2010 (AER 2), C) 22 February to 8 March 2010 (AER 3) and D) 11 October to 13 December 2010 (AER 4). Ten mean back trajectory clusters are shown for each sample with the proportion of total trajectories used in each cluster shown beside each mean back trajectory cluster. UPDATE BACK TRAJECTORY "C" AND ASSOCIATED DISCUSSION
Figure 3. The mean total dissolved iron (dFe, nmol) leached from aerosol samples AER 1, AER 2, AER 3 and AER 4 during three replicate leaches with A) 4 °C and 25 °C seawater and B) ambient seawater (25 °C, pH 8.0, oxygenated), acidified seawater (pH 7.6, sparged with air enriched in carbon dioxide) and anoxic seawater (sparged with nitrogen gas for leaches 3 and 4). Error bars represent the standard deviation (± 1 σ) on the mean total dFe leached from replicate subsamples of the same aerosol sample. Segments of each bar show the amount of dFe leached during each sequential aerosol leach (i.e., leaches 1 – 4). Sequential leaches 1, 2, 3 and 4 represent the following time periods seawater was exposed to aerosols: 0 – 5 min, 5 – 10 min, 10 min – 48 h and 48 h – 30 days, respectively.
**Figure 4.** Fractional solubility (%) of iron (Fe) from aerosol samples AER 1, AER 2, AER 3 and AER4 leached with ambient seawater (combined mean of the temperature experiment and pH and de-oxygenation experiment, 25 °C, pH 8.0, oxygenated), 4 °C seawater, acidified seawater (pH 7.6, sparged with air enriched in carbon dioxide) and anoxic seawater (sparged with nitrogen gas for leaches 3 and 4). Error bars represent the standard deviation (± 1 σ) on the mean fractional solubility of Fe leached from replicate subsamples of the same aerosol sample. Segments of each bar show the fractional solubility of each sequential aerosol leach (i.e., leaches 1 – 4). Sequential leaches 1, 2, 3 and 4 represent the following time periods seawater was exposed to aerosols: 0 – 5 min, 5 – 10 min, 10 min – 48 h and 48 h – 30 days, respectively.
Figure 5. The mean total amount (nmol) of A) dissolved iron (dFe), and B) soluble iron (sFe) leached from aerosol sample AER 1 into ambient seawater and seawater amended with various Fe-binding organic ligands (aerobactin, desferrioxamine-B, glucuronic acid and protoporphyrin-IX). Error bars of A represent the standard deviation (± 1 σ) on the mean total dFe leached from replicate subsamples of the same aerosol sample. No error bars are shown in B, as replicate leaches were not performed. In both A and B, segments of each bar show the amount of dFe leached during each sequential aerosol leach (i.e., leaches 1 – 3). Sequential leaches 1, 2 and 3 represent the following time periods seawater was exposed to aerosols: 0 – 5 min, 5 – 10 min, and 10 min – 48 h, respectively. Leach 4 was not performed in this experiment.
Figure 6. A conceptual model for the dissolution of aerosol iron (Fe) in surface ocean waters, which proposes a two-stage mechanism. Fe = refractory Fe species, Fe’ = labile Fe species, FeL1 = L1, Fe-ligand complexes.
Dear Dr. Ussher:

Thank you for your manuscript submission entitled "The impact of changing surface ocean conditions on the dissolution of aerosol iron" [Paper #2014GB004921] to Global Biogeochemical Cycles. I have now received the Associate Editor's recommendation and 3 reviews of your manuscript.

All three reviewers find that this study is potentially an important contribution to understanding aerosol iron input to the ocean and is potentially publishable in GBC. All three provide detailed comments, though most require relatively minor changes/clarifications of the text. Please respond to all of the reviewer comments in your revision.

The feedback provided in the reviewer assessments of your manuscript is important and should be taken into account as you complete your revision. I encourage you to submit a suitably revised version of your manuscript within 30 days of receipt of this letter.

Upon submission, we will need to receive the following:

1. A response to reviewer file that lists each of the comments and describes how the manuscript has/has not been modified in response to those comments.

2. A copy of the manuscript with the changes noted (e.g., highlighted, "track changes," italics or bold changes). Please upload the article with tracked/highlighted changes as a response to reviewer file.

3. A copy of the revised manuscript with the changes incorporated.

4. All files in publication-ready formats.

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I look forward to receiving your revised manuscript. If you have any questions, please contact the editor's assistant at gbc@agu.org.

Sincerely,

Susan Trumbore
Reviewer #1 (Comments to Author):

Title: Impact of changing ocean conditions on the dissolution of aerosol iron
Authors: Mathew Fishwick, Peter Sedwick, Maeve Lohan, Paul Worsfold, Kristen Buck, Tom Church, Simon Usher

The manuscript describes the influence of several seawater parameters (pH, temperature, dissolved oxygen, and organic iron-binding ligands) on the dissolution of bulk aerosol iron as observed during a series of aerosol leaching experiments conducted on samples collected in Bermuda, using seawater (amended and un-amended) collected within the deep chlorophyll maximum near BATS. These parameters were chosen and are appropriate for investigating effects of changes in ocean conditions expected in the near-future, and which have the potential to alter the dissolution of aerosol iron after deposition in surface waters. The authors' choice of experimental conditions provides insight into the effect of single variables on dissolution and size portioning of the solubilized aerosol Fe. A conceptual model describing the dissolution of aerosol Fe in seawater is also presented.

The manuscript is a well-organized and clearly written. The experimental design is logical, and results provide additional data to support previous notions regarding aerosol Fe dissolution in surface waters (e.g. aerosol type is the key aspect controlling the observed variability in the fractional aerosol Fe solubility), as well as new insight into soluble aerosol Fe species (e.g. L1-type ligands influence the size partitioning of Fe after dissolution). The authors have considerable experience studying various aspects of Fe marine biogeochemistry, and these data contribute towards understanding of atmospheric Fe input to the ocean and informs modelers of important parameters to consider when modeling this input.

I recommend the manuscript is accepted for publication at GBC. Below are suggested minor revisions that should be addressed prior to publication. Hopefully these comments will be useful.

General Comments/Suggestion

The title and abstract appropriately reflect the findings of the study.

The introduction provides a good background on the subject and places aerosol Fe dissolution into a
The Methods section is easy to follow. A few areas could use clarification/additional information (see Specific Suggestions). Results are clearly communicated, and their interpretation is reasonable. Some suggestions are provided in the specific comments below.

Given the team's expertise in Fe speciation, inclusion of redox speciation in the initial leachate would have contributed towards the conceptual model presented. Its omission, however, does not lessen the insights gained by the study.

Specific Suggestions

Line 170. Provide length of time for seawater storage. Seawater storage time (< 3 months) now added to the manuscript.

Line 172. Were the ligand characteristics determined in the freshly collected, filtered seawater, or after storage? Is the concentration of excess strong ligand in the seawater at the time of the experiments known? CSV-CLE was undertaken at the time of leaching experiments. This has been added to the manuscript.

Line 176. AER 2 and AER 3 are numbered out of chronological sampling order, but I can't see a reason for this. It might be easier for the reader if the sample collected during Feb/Aug 2010 were labeled AER2, and the sample collected during Sept/Oct 2010 were labeled AER 3. The order of samples follows the order of anthropogenic influence and we believe by ordering it in this allows for a clearer discussion of the influence of source on dissolution. The sample ordering has not been changed in the manuscript.

Line 186. Aerosol storage time can affect dissolution. Like me, others might be curious about the longest time aerosols were stored. Storage time (6 – 24 months) added now added to the manuscript.

Lines 207-209. Provide the reasoning behind the choice of excess ligand concentrations in the amended seawater. The choice of ligand concentrations by based on the concentration typically observed in surface waters of the North Atlantic. We wanted to ensure a clear response in aerosol Fe complexation and therefore amended seawater to ensure a great excess of ambient concentrations. This justification has been added to the manuscript.

Lines 229 -233. State whether wall absorption of Fe during leaches 3 and 4 was considered. If considered, how was it determined? Wall adsorption of Fe during batch leaches (leaches 3 and 4) was considered during the experimental set up. Fischer et al. (2007) identify that Fe adsorption to container material can be significant, depending on the container material. Therefore the choice of bottle material is important. Séguret et al. (2011) found that when fluorinated polymer containers were used, adsorption to the container walls was negligible. FPE is typically used for CSV-CLE analysis specifically to avoid competition for Fe between wall surfaces and ligands. Therefore, it was decided to use FPE bottles for batch leaches to minimise the effect of wall adsorption as much as possible. As a further measure, FPE bottles were first preconditioned for 24-72 h with BATS seawater in order to allow major cations to adsorb to any charged surfaces of the bottles before they were exposed to leached Fe. Moreover, previous studies (e.g. Buck et al., 2006 and Wu et al. 2007) have shown leaching of Fe from aerosols occurs rapidly (i.e. < 5 mins) and therefore it is unlikely that, following two continuous leaches, the aerosol filter was able to saturate 500 mL of seawater in the following batch leaches. In these low iron conditions, the seawater leachate will be likely ‘out compete’ container walls for iron.
Line 279. Provide FI-CL value for SAFe and GEOTRACES samples. FI-CL values for reference seawater now added to manuscript.

Lines 289-290. List relevant elements included in QC Standard 4. Elements have now been listed in the manuscript.

Lines 313-318. Move description of AER 4 back trajectories after description of AER 3. If AER 2 and AER 3 labels are switch, switch description here accordingly. This has now been moved.

Line 328. "Cu" is listed twice. This has now been amended in manuscript.

Line 344. Replace "the four different aerosol samples" with "AER 1 - AER 4". This makes it clear that the sentence is referring to the four samples and not to subsamples in the four leaches. This has now been amended in manuscript and made clearer to understand.

Line 345. To clarify, replace "four sequential leaches" with "four sets of sequential leaches". The four sequential leaches refers to leach 1 (0-5 min), leach 2 (5-10 min), leach 3 (10 min to 48 hr) and leach 4 (48 hr to 30 day) rather than the four aerosols. We have clarified this in the text of the manuscript now.

Line 355. "Wu, 2007" could be added to reference. Reference added to manuscript.

Lines 359-360: Replace "the four different aerosol samples" with "AER 1 - AER 4". This has now been amended in manuscript and made clearer to understand.

Lines 374-375: Replace "the four different aerosol samples" with "AER 1 - AER 4" This has now been amended in manuscript and made clearer to understand.

Line 406: "Aguilar-Islas et al., 2010" could be added to reference. Reference added to manuscript.

Lines 476 - 501. These 2 paragraphs might be better integrated. They seem a bit repetitive. Paragraph starting on line 481 describes the total sFe concentrations of seawater amended with ligands and leads quite nicely onto paragraph starting on 501 deals, which goes on to describe the size partitioning of Fe in solution.

Line 510: Specify "un-complexed" before "in sufficient" This has now been amended in manuscript.

Lines 522-528: I would suggest that aerosol type (soil dust vs. combustion) would also play a role in whether colloids form after dissolution or are deposited. Aerosols Fe in the colloidal size class is likely being deposited on surface water from combustion sources, since this type of aerosols exits mostly in the fine size fraction. Buck et al., 2010 showed considerable DI soluble Fe coming from the smaller size fractions of aerosols collected with their impactor when anthropogenic aerosols were
present in the sample. Although the impactor does not separate particles based on their geometric
diameter, the smaller aerodynamic diameter of fine aerosols they collected were 0.098 and 0.056
um, and could potentially contain Fe colloids. A paragraph has been added to the manuscript to
consider aerosol composition and size as a factor in determining whether colloidal Fe is delivered by
aerosols or forms in seawater following deposition.

Tables & Figures:
Table 3: For improved readability add lines between AER # sets of samples Tables are formatted
according to the GBC guidelines, which does not have any horizontal lines between rows.
Figures 2-5: Switch AER 2 and AER 3 labels are switched in the text. Not amended in manuscript. See
above.
Figure 6: Add to Stage 1 text "is deposited as," before "forms or attaches...". Text added to figure.
Reviewer #2 (Comments to Author):
Excellent, yet brief review of aerosol inputs, solubility and iron binding ligands in seawater. The
introduction does a very good job putting all the pieces of a complex interaction together in an
appropriately referenced and clearly written section.

Line 198... dissolved (not dissolve). This has now been amended in manuscript.
Line 205, consider re-wording... These ligands were intended to simulate the range of iron-binding
ligands that exist in open ocean waters. Omit the reference to use by phytoplankton, etc... This has
now been amended in manuscript.
The manuscript is satisfyingly replete with analytical methods... I appreciate this, yet it could be
shortened somewhat in this section if necessary.
The discussion and conclusion sections are well anchored in the results of this experiment and the
conceptual model is believable, yet, as the authors point out, there are alternatives that seem
plausible as well.
One potential weakness of the manuscript is the assignment of anthropogenic influence over the elemental composition of the aerosols. I understand the argument of enrichment of anthropogenic elements as being an indicator, but there are also strong variations in elemental composition from one weathering basin to another. A simple crustal abundance approach is appealing but simplistic. The paragraph on enrichment factors (line 340) has been re-worded slightly to stress that enrichment factors only an indicator of anthropogenic influence.

In brief, I believe this paper will make an important contribution and point the way towards some interesting studies that will help modelers to forecast a more accurate assessment of changing land/ocean conditions as influenced by anthropogenic forcing.

Reviewer #3 (Comments to Author):

This is a very nice paper that describes some very thorough and illuminating studies of the controls on iron solubility at Bermuda. The analytical work reported appears to be of a very high standard, from and excellent research group. I have no doubt the paper should be published and I have only some minor suggestions.

The Bermuda site is particularly useful because it is subject to quite a significant change in aerosol type between anthropogenic and crustal sources, allowing the effect of this difference to be evaluated. However, as the authors do note on line 548, the importance of anthropogenic iron as a global source of iron to the ocean is probably dwarfed by dust sources, although this does require further study. Thus while the statement on line 103 is probably correct, the environmental significance of such an increase is unclear. Text added to the manuscript to stress that any increase in combustion sources is not likely to significant in the global context, considering the likely continued dominance of mineral aerosols.

The issue of the controls on solubility of iron has been reviewed rather well by Baker and Croot 2010 and the authors here might use this as a source to help rationalise their experiments which elegantly test some of the mechanisms Baker and Croot consider. This importance reference has now been added to the manuscript.

In the abstract (line 59) and later in the text the authors use the phrase "size distribution of soluble aerosol iron" and I was tripped up by this each time I read it because of the large amount of work done on aerosol size distribution, whereas the authors mean the colloidal/dissolved split of aerosol iron after it has dissolved in seawater. They might want to rephrase this to avoid confusing others. This phrase has been re-worded to include mention of size distribution in seawater or solution.

P7 It is not clear how long aerosol samples were collected for. I think based on what is written later
there are actually only 4 samples collected each over a period of a week to 10 days, but when I first read the paragraph line 174-186 I assumed they had daily samples. Assuming that there are only 4 samples used for the experiments, then some caution about the representativeness of the results might be appropriate. The filters were left on the sampler for the entire periods of sampling (ranging from 14 to 63 days). The number of days has now been added to the manuscript, along with volume of air sampled.

Line 222-226. I would suggest that the authors might justify their choice of leaching times in terms of the lifetime of particles in the surface ocean and other biogeochemical processes. I don't disagree at all with the timescales they have used, but they can indicate that the longest time is about how long an aerosol particle spends in the surface ocean. Justification for these leach times has now been added to the manuscript.

Line 248-253. Whenever I have contemplated experiments such as these I have worried that the surface area of the filter may produce adsorption effects. The way blanks have been conducted here I think does allow the authors to confirm that there appears to be no blank effect revealed either as an increase or decrease in iron concentration.

Line 325-329. Conventionally small enrichment factors have often been considered uncertain given the variability of crustal concentration, so perhaps the authors should be cautious about EF values less than 10. Sentence stating the all samples were enriched in Fe, V, Ni, Cu, Pb and Sb removed from the manuscript.

P14 There seems to be some repetition lines 355- 358 and 370-373. The first discusses dFe and the second leads on to discuss sFe and size distribution. There is some repetition in the wording but we feel it is important to be clear in the description what mean total Fe is and therefore have kept the working similar to avoid confusion.

A second point on this page and later (e.g. line 387-390) the authors several times comment on differences (here between 4 and 25oC) and then say the differences are not significant. If the differences are not significant I don't think you can usefully really note the differences at all. The commentary on differences has now been removed from the manuscript.

Line 378-380 The anoxic experiment is useful but I suspect on this time scale this is effectively an inorganic experiment and describes the lack of impact of lower oxygen on the inorganic conversion of FeIII to FeII. Probably more relevant to the global iron cycle is the bacterial reduction of iron which is probably precluded here. At a more general level too, while the experiments described here are very impressive and useful, they do not consider the role of the bacterial and planktonic community in solubilising iron from aerosol particles. I think this latter point needs to be acknowledged in the discussion of the mechanism of aerosol iron solubility on p20. It has been acknowledged in the manuscript that the mechanism is missing biological interactions. I think the proposed mechanism is OK as a hypothesis but it needs to be clear that it is that. It had been made clear in the manuscript that it is a hypothesis. Aggregation and disaggregation of colloidal ligands may play a role (line 500). More generally it seems to me that as iron dissolves from aerosol there is a complex (and time varying) competition between different sinks for that iron including complexation by ligands, inorganic precipitation and biological uptake. Clearly the authors demonstrate that ligands play a key role, but we do know that from the higher solubility of iron in the real ocean compared to its inorganic solubility. The value of the work reported here is to emphasise again that this interaction is key and that the role of temperature, pH and oxygen is minor.