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Fractional Solubility of Aerosol Iron: Synthesis of a Global-Scale Data Set

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Abstract

Aerosol deposition provides a major input of the essential micronutrient iron to the open ocean. A critical parameter with respect to biological availability is the proportion of aerosol iron that enters the oceanic dissolved iron pool – the so-called fractional solubility of aerosol iron (%Fe_S). Here we present a global-scale compilation of total aerosol iron loading (Fe_T) and estimated %Fe_S values for ~1100 samples collected over the open ocean, the coastal ocean, and some continental sites, including a new data set from the Atlantic Ocean. Despite the wide variety of methods that have been used to define 'soluble' aerosol iron, our global-scale compilation reveals a remarkably consistent trend in the fractional solubility of aerosol iron as a function of total aerosol iron loading, with the great bulk of the data defining an hyperbolic trend. The hyperbolic trends that we observe for both global- and regional-scale data are adequately described by a simple two-component mixing model, whereby the fractional solubility of iron in the bulk aerosol reflects the conservative mixing of 'lithogenic' mineral dust (high Fe_T and low %Fe_S) and non-lithogenic 'combustion' aerosols (low Fe_T and high %Fe_S). An increasing body of empirical and model-based evidence points to anthropogenic fuel combustion as the major source of these non-lithogenic 'combustion' aerosols, implying that human emissions are a major determinant of the fractional solubility of iron in marine aerosols. The robust global-scale relationship between %Fe_S and Fe_T provides a simple heuristic method for estimating aerosol iron solubility at the regional to global scale.

1. INTRODUCTION

Iron (Fe) is a limiting nutrient for phytoplankton growth in many regions of the world's ocean. The atmosphere represents a major source of particulate and dissolved iron to the open-ocean, via the dry and wet deposition of aerosols (Duce and Tindale, 1991; Duce et al., 1991; Jickells and Spokes, 2001; Ussher et al., 2004; Jickells et al., 2005; Mahowald et al., 2009; Baker and Croot, 2010; Breitbarth et al., 2010; Raiswell and Canfield, 2012). The atmospheric transport and deposition of mineral dust from arid regions of Africa, Asia, South America and Australia is thought to provide a major source of 'new' soluble iron to the upper ocean, where soluble iron is defined as that which contributes to the dissolved iron inventory of surface seawater. In evaluating the atmospheric input of soluble iron to the ocean, a critical parameter is the so-called fractional solubility of aerosol iron, $\%Fe_S$, which is defined in this paper as $Fe_S/Fe_T \times 100$, where Fe_S and Fe_T are the atmospheric loadings of soluble aerosol Fe and total aerosol Fe, respectively. The largest contributor to iron-bearing aerosols that enter the ocean is thought to be continental soils, for which the fractional solubility of Fe is typically ~1% or less (Jickells and Spokes, 2001; Jickells et al., 2005; Mahowald et al., 2009). However, numerous studies have reported much higher values for the fractional solubility of iron in natural aerosols, which have variously been ascribed to chemical alteration of lithogenic dust during atmospheric transport, and/or an inherently higher solubility of iron in aerosols derived from natural and anthropogenic combustion processes (Zhuang et al., 1990, 1992b; Chester et al., 1993; Zhu et al., 1993; Siefert et al., 1996; Jickells and Spokes, 2001; Chen and Siefert, 2004; Desboeufs et al., 2005; Guieu et al., 2005; Hsu et al., 2005; Baker et al., 2006a; Buck et al., 2006, 2010a; Sedwick et al., 2007; Aguilar-Islas et al., 2010; Kumar and Sarin, 2010; Mori et al., 2011; Theodosi et al., 2010a; Trapp et al., 2010; and Supplementary Tables S1 and S2).

In this paper, we present a new and extensive compilation of aerosol iron solubility estimates for samples collected around the globe, and use these data to argue that the fractional solubility of aerosol iron entering the ocean can be significantly higher than the values of ~1% that are typical of lithogenic soil dust, due largely to contributions from anthropogenic combustion emissions. Two previous studies provide the foundation for this paper. The first is the report of Chuang et al. (2005), who show that the water soluble fraction of iron in aerosols collected in the Asian continental outflow increases from ~0.1% to ~10% in direct proportion to the aerosol concentration of black carbon, which led them to conclude that the solubility of aerosol iron was related to anthropogenic emissions, as traced by elemental carbon. Second is the study by Sedwick et al. (2007) in the Sargasso Sea, who report that the fractional solubility of iron in aerosols carried in North American air masses (up to 19%) greatly exceeds that of Saharan dust that is transported from North Africa (~0.5%), and conclude that the fractional solubility of iron in the bulk aerosol is controlled by the relative proportions of lithogenic mineral dust and anthropogenic aerosols. The conclusions of these two empirical studies are supported by the results of subsequent modeling studies, which suggest that combustion emissions contribute a significant fraction of the total aeolian input of soluble iron to the surface ocean, although the model results are strongly dependent on the values assigned for the fractional solubility of iron in lithogenic and combustion aerosols (Sedwick et al., 2007; Luo et al., 2008; Mahowald et al., 2009; Sholkovitz et al., 2009).

We have compiled data from the literature to provide estimates of the fractional solubility of iron in aerosols collected from open-ocean and coastal environments, as well as from several continental sites (see Supplementary Table S1). This compilation provides access to a large set of data on the fractional solubility of aerosol iron and total aerosol iron loading for a diverse range of oceanic regions (Figs. 1 and 2). Despite the range of different methods that have been used to estimate $\%Fe_S$ values, the combined data set reveals a remarkable systematic trend in $\%Fe_S$ vs. Fe_T, which should prove useful for modelers who seek to incorporate the atmospheric deposition of soluble iron into numerical models of ocean biogeochemistry and ecology (e.g., Fung et al., 2000; Hand et al., 2004; Moore et al., 2004; Parekh et al., 2004; Luo et al., 2005, 2008; Mahowald et al., 2005, 2009, 2011, Meskhidze et al., 2005; Fan et al., 2006; Moore and Doney, 2007; Moore and Braucher, 2008; Krishnamurthy et al., 2009; Tagliabue et al., 2009; Luo and Gao, 2010, Okin et al., 2011).

2. COMPENDIUM OF DATA FOR ATMOSPHERIC LOADING AND FRACTIONAL SOLUBILITY OF AEROSOL IRON

Supplementary material for this paper is archived and freely available at *http://dx.doi.org/10.1575/1912/5104* in the Woods Hole Open Access Server (WHOAS). This material consists of three tables (S1, S2 and S3), and a 'Readme' file that provides a detailed description of the contents of these tables. Table S1 is a compilation of ~ 1100 *paired data* for total aerosol iron loading (Fe_T) and the fractional solubility of aerosol iron ($\%Fe_S$) for aerosols collected at oceanic sites around the globe (Figs. 1 and 2). Figures 3-9 use the data in Table S1. Table S1 and the Readme file include information on sample locations, collection dates, and methods of collection and **storage,** as well as the leaching protocols that were used to define 'soluble' aerosol iron (Fe_S) in each of the 26 studies. Table S1 also contains two relatively large sets of previously unpublished data, for aerosol samples collected from: (1) Bermuda and the adjacent Sargasso Sea during 2007 and 2008 (93 samples; T.M. Church, P.N. Sedwick and E.R. Sholkovitz, unpublished data); and (2) the North and South Atlantic Ocean during 2003-2008 (291 samples; A.R. Baker and C.F. Powell, unpublished data). Previous overviews of the fractional solubility of iron in marine aerosols (and in rain water in some cases) have been provided by Jickells and Spokes (2001), Hand et al. (2004), Mahowald et al. (2005), Fan et al. (2006), Aguilar-Islas et al. (2010), Moxim et al. (2011) and Srinivas et al. (2011). These publications only present the range of $\%Fe_S$ values reported in the literature.

Table S2 contains additional data on the fractional solubility of Fe in aerosols and soils derived from 28 published papers: Hodge et al. (1978); Crecelius (1980); Hardy and Crecelius (1981); Breslin and Duedall (1987); Zhen et al., (1992); Chester et al. (1993); Spokes et al., (1994); Spokes and Jickells (1996); Jickells (1999); Jickells and Spokes (2001); Bonnet and Guieu (2004); Desboeufs et al. (2005); Mackie et al., (2006); Cwiertny et al. (2008); Duvall et al. (2008); Journet et al., (2008); Wagener et al. (2008); Schroth et al. (2009); Hsu et al. (2010); Ooki et al. (2009); Buck et al. (2010b); Mendez et al. (2010); Oakes et al. (2010); Paris et al. (2010); Theodosi et al. (2010a); Mori et al. (2011); Shi et al. (2011); Upadhyay et al. (2011). Table S2 differs from Table S1 in that the majority of papers included in Table S2 report data for the fractional solubility of aerosol iron ($\%Fe_S$), but not for total aerosol iron loading (Fe_T). Table S2 also provides information on collection dates, locations, and sample types, as well as the protocols that were used to define soluble aerosol iron. Lastly, Table S3 presents details of the two end-member mixing model and the model results for eight case studies in which we have calculated $\%Fe_S$ as a function of Fe_T for various mixtures of possible aerosol end-members (see Fig. 10A).

3. AEROSOL COLLECTION AND SOLUBILITY PROTOCOLS

When comparing data on aerosol iron solubility derived from studies carried out around the globe, it is important to note that there are significant differences in the dates of aerosol collection, in collection and storage methods, and in leaching techniques and leaching solutions that have been used to define 'soluble' aerosol iron. Hence, we might expect that a global-scale comparison of aerosol iron solubility vs. total aerosol iron loading would be fraught with problems, as a result of the wide range of sampling and sample processing protocols that have been employed. However, as will be shown in this paper, the combined data reveal a remarkable systematic trend over regional and global scales that appears to dominate any effects due to methodological differences.

The paired $\%Fe_S$ and Fe_T data in our compilation correspond to aerosol samples that were collected during different seasons over a period of more than two decades. The majority of samples were collected between 1991 and 2008 on ships at sea, as well as at several island and continental sites. Both high- and low-volume vacuum filtration systems were employed, using filters that include a range of different materials, dimensions and pore sizes. In some of the studies, the aerosol samples were leached within hours of collection, whereas in other cases, the aerosol-laden filters were frozen and transported back to the home laboratories for leaching. The former include nine studies (sites 3, 4, 12, 18-22, and 26 in Fig. 1), and latter include twelve studies (sites 1, 2, 9-11, 13-17, 24 and 25). In five studies, it is not clear how the samples were stored prior to leaching (sites 5-8 and 23).

The leaching procedures also include a wide range of different techniques and solutions. Three main leaching techniques have been employed: 'batch' leaching, 'flow-through' leaching, and a combination of these two methods. The most frequently used technique is batch leaching, wherein a section of aerosol-laden filter is placed in a container containing the leaching solution for some fixed period of time, after which the solution is filtered for subsequent analysis of the operationally-defined 'soluble Fe' in the filtrate. Some studies have used ultrasonic agitation in the batch leaching method. In the flow-through method, the aerosol-laden filter is typically mounted in a filtration tower, or placed above a secondary filter membrane, and the leaching solution is then added and drawn through the filter using either gas overpressure or vacuum.

Wu et al. (2007) and Aguilar-Islas et al. (2010) have applied a 'semi-continuous leaching method', which combines features of the batch and flow-through methods: an aerosol-laden filter is placed in a filtration tower above a secondary filter membrane, and several successive aliquots of leaching solution are added and filtered after some given dissolution period. Buck et al. (2006) and Wu et al. (2007) have argued that the flow-through leaching protocol (compared with the batch-wise leaching method) alleviates the potential for precipitation of iron oxyhydroxides prior to collection of the leachate (filtrate) solution, because aerosol particles are continuously exposed to added ‘fresh’ solution during the leaching process, thus it is unlikely that the leachate solution reaches saturation with respect to iron oxyhydroxides prior to passing through the filter membrane. For all three leaching techniques, the mass of aerosol that is leached varies considerably. Both the leaching times and the particle:leach solution mass ratios are also highly variable between the batch methods used by different groups. Likewise, there are significant differences in the aerosol sample masses, and the volumes and flow rates of the leaching solutions used in the flow-through methods. In addition, different types of filters have been used to filter the leach solutions that are collected for the measurement of the thus-defined soluble iron.

Four types of leaching solutions have been most commonly used. Ultrapure deionized water (Milli-Q or similar, pH ~5.5, resistivity $\geq$ 18 MΩ cm) was used by Chuang et al. (2005), Chen et al. (2006), Hsu et al., (2009), Kumar and Sarin (2010) and Kumar et al. (2010) with the batch-leaching method, and by Buck et al. (2006, 2010a), Sedwick et al. (2007), Aguilar-Islas et al. (2010) and Church et al. (unpublished data in this paper) with the flow-through leaching method. Filtered seawater (ambient pH ~8) was used by Chen et al. (2006) and Hsu et al. (2009) with the batch-leaching method, by Buck et al. (2006, 2010a) with the flow-through leaching method, and by Wu et al. (2007) and Aguilar-Islas et al. (2010) with the combined batch and flow-through leaching method. Six studies (Siefert et al., 1996, 1999; Johansen et al., 2000; Johansen and Hoffman, 2003; Chen, 2004; Chen and Siefert, 2004) have made use of a pH 4.2-4.5 buffered solution of formate with the batch-leaching method (details in Chen and Siefert, 2003). A large data set from the University of East Anglia researchers was obtained using a pH 4.7 buffered solution of ammonium acetate with the batch-leaching method

(Baker et al., 2006a, 2006b; Witt et al., 2006, 2010; Powell and Baker, unpublished data in this paper).

Finally, four studies have employed mild to moderately strong mineral acids with the batch leaching method (Zhuang et al., 1992a; Zhu et al., 1997; Witt et al., 2006, 2010; Cwiertny et al., 2008). In general, and not unexpectedly, the results of these few studies yielded %Fe_S values that are significantly higher than values reported by other groups that have used less acidic leaching solutions. For example, Cwiertny et al. (2008) report unusually high %Fe_S values (4-16%) for desert and loess soils of Africa and Asia when using a batch leaching method with pH 1 leach solutions of HCl, HNO_3 and H_2SO_4 (Table S2). Such relatively acidic leach solutions are likely to solubilize some of the lattice-bound iron contained in clay minerals in the aerosols.

Deionized water was used as a leaching solution with a flow-through aerosol leaching method by Buck et al. (2006) and Sedwick et al. (2007), who have argued that such high-purity water provides a consistent and reproducible leaching solution, thus facilitating comparison between the results of different field studies and different investigators. Buck et al. (2010a) have further suggested that leaching aerosols with deionized water at a pH of ~ 5.5 mimics the dissolution of aerosol iron in wet deposition. Similarly, numerous studies have performed aerosol leaches using either formate- or acetate-based buffer solutions with pH ~ 4.2-4.7, with the rationale that such solutions simulate the conditions of marine precipitation. The use of seawater as an aerosol leaching solution has been relatively limited (Hsu et al., 2005; Buck et al., 2006, 2010a,b; Chen et al., 2006; Wu et al., 2007; Aguilar-Islas et al., 2010). A major concern in using seawater is that natural variations in the nature and concentration of dissolved Fe and Febinding organic ligands may lead to inconsistent and irreproducible results (Mendez et al., 2010). In contrast to the most commonly used mildly acidic leach solutions, seawater is mildly basic (pH ~ 8) and has high ionic strength (~0.7 M). In this regard, the use of seawater as a leach solution does not mimic the dissolution of aerosol iron in rainwater, although seawater leaches may provide the closest analog for the dissolution of dry aerosols in the surface ocean.

Most of the studies that we have included in our data compilation report total soluble aerosol iron (Fe_S). A smaller number of studies, particularly those that have used formate as the leaching solution, have reported soluble Fe(II), and in some cases soluble Fe(III). In reporting values for the fractional solubility of aerosol iron ($\%Fe_S$), we have chosen not to distinguish between the oxidation states of the operationally defined soluble aerosol iron. In cases where both oxidation states of iron are reported, we have summed these concentrations to calculate Fe_S and $\%Fe_S$. Where only soluble Fe(II) or total Fe(II) data are reported, we have used those data to calculate $\%Fe_S$ and Fe_T, respectively. For those papers that report Fe data for both fine and coarse aerosol fractions, we have summed the soluble and total iron in these fractions (see Supplementary Table S1; Siefert et al., 1999; Johansen et al., 2000; Johansen and Hoffman, 2003; Chen, 2004; and Chen and Siefert, 2004).

4. RESULTS

4.1. Aerosol samples: field data

Variation in the fractional solubility of aerosol iron ($\%Fe_S$) as a function of total aerosol iron loading (Fe_T) is the primary focus of this paper, with scatter plots of $\%Fe_S$ versus Fe_T from various studies constituting the core results (Figs. 3-9). We will begin with a description of the full set of the globally-distributed samples (Fig. 3), and then focus on five different regions: the Indian Ocean/coastal Asia (Fig. 4); the Atlantic Ocean (Figs. 5 and 6); the Pacific Ocean (Fig. 7); the Gulf of Aqaba (Fig. 8); and the Southern Hemisphere ocean (Fig. 9). With the exception of Figs. 7 and 9, our scatter plots include an insert showing expanded x and y scales, which allows the reader to focus on the lower end of the Fe_T range, where the greatest variation in $\%Fe_S$ is typically observed. Data from the Sargasso Sea (site 21; Sedwick et al., 2007) are used as a benchmark for comparisons with the global and regional data sets; as such, the Sargasso Sea data for $\%Fe_S$ and Fe_T are included in most of the figures. Plots of $\%Fe_S$ vs. Fe_T for individual sample sites can be found in Table S1.

The global-scale compilation reveals a consistent trend in the fractional solubility of aerosol iron as a function of total aerosol iron loading, with the great bulk of the data defining an hyperbolic trend for $\%Fe_S$ vs. Fe_T (Fig. 3A and 3B). Remarkably, this clear trend is evident despite the wide range of differences in the dates and locations of aerosol sampling, in the aerosol collection and storage methods, and in the leaching methods and solutions used to define Fe_S (as described in Section 3). In detail, the total aerosol iron loadings range from ~5 ng Fe m^{-3} to ~17,000 ng Fe m^{-3}. High Fe_T values are typically associated with 'dusty' conditions off the coasts of West Africa and South Korea, whereas the low values come from the remote regions of the Atlantic and Pacific Oceans, including the Southern Ocean south of Tasmania (Figs. 2 and 9; Bowie et al., 2009). Estimates of the fractional solubility of aerosol iron range from near zero to more than 95%, with most samples yielding $\%Fe_S$ values less than 50%. The great majority of samples with Fe_T above 500 ng m^{-3} have corresponding $\%Fe_S$ values less than 2%. The highest %FeS values are associated with low Fe_T values, although not all samples with low total loading exhibit elevated values of $\%Fe_S$. The expanded scales in Figure 3B show that much of the variability in the full global data set, namely the high $\%Fe_S$ values between Fe_T values of 100 and 1000 ng Fe m^{-3}, is associated with samples collected from three coastal regions – the Gulf of Aqaba (site 5), the East China Sea (site 7) and South Korea (site 8) – or from the continental United States (site 14). As we discuss later, this most likely reflects the highly polluted nature of air masses and aerosols in these regions.

Aerosol samples from the Indian Ocean/Asian regions (Fig. 4), the Atlantic Ocean (Figs. 5 and 6), the Pacific Ocean (Fig. 7), the Gulf of Aqaba (Fig. 8) and the Southern Hemisphere oceans (Fig. 9) are all characterized by an hyperbolic relationship between $\%Fe_S$ and Fe_T. A common feature of the Indian Ocean/Asian sampling sites, as well as the sampling sites in the continental United States (site 14) and Sargasso Sea (site 21), is that they receive both soil dust and anthropogenic pollution aerosols from strong local or regional sources. As such, aerosols from the Indian Ocean/Asian sites define a highly uniform and compact trend for $\%Fe_S$ vs. Fe_T, for which most samples with Fe_T greater than ~1000 ng Fe m^{-3} have $\%Fe_S$ values between 0.1% and 2%. As noted by Kumar et al. (2010) and Kumar and Sarin (2010), the moderate to high $\%Fe_S$ values (~20–50%) for aerosols over the Bay of Bengal and at Mt. Abu in western India appear to be associated with polluted air carried from Southeast Asia. Likewise, the aerosols with high $\%Fe_S$ values collected from Taiwan, the East China Sea and Korea are associated with aerosols that contain elevated concentrations of elemental carbon (Chuang et al., 2005) or heavy metals (Hsu et al., 2005, 2009), indicative of anthropogenic pollution emissions. These data trends are similar to those described by Sedwick et al. (2007) and Sholkovitz et al.

(2009) for aerosols over the Sargasso Sea, where high %Fe_S values were typically associated with elevated V/Al and Ni/Al mass ratios (Fig. 10C), which are tracers of fuel combustion emissions. The North Atlantic aerosol data of Buck et al. (2010a) also indicate that high %Fe_S values are often associated with V-rich aerosols.

The majority of aerosol samples from thirteen sites in the North Atlantic Ocean were collected between 10°N and 40°N. Here total aerosol iron loadings range from minimum values of ~20 ng Fe m^{-3} up to maximum values of 5,000-17,000 ng Fe m^{-3}. The latter Fe_T values were associated with desert dust-laden air off the northwest coast of Africa. The corresponding fractional solubility of aerosol iron ranges from near zero to ~50%, with most values falling below 25%. Data from and Zhu et al. (1997) and Chen and Siefert (2004) fall above the main data trend (Fig. 5B), although we note that the latter study uses an unusually acidic leach solution (pH 1) to define soluble aerosol iron (see Section 3).

Pacific Ocean aerosols are characterized by a greater scatter in the %Fe_S vs. Fe_T relationship than aerosols sampled in the Indo/Asian region and the Atlantic Ocean. Most of the Pacific samples were collected from remote open-ocean locations, thus the majority of the data lie at the low end of the Fe_T range (<200 ng Fe m^{-3}). The greater variability in the %Fe_S vs. Fe_T trend for the Pacific Ocean aerosols may reflect the relatively large geographic area that was sampled over a period of one month by Buck et al. (2006); the samples collected during these long zonal and meridional transects (site 11 in Fig. 1) likely contain mixtures of a variety of different aerosols that include mineral dust and anthropogenic aerosols from Asia and elsewhere (e.g., Duce et al., 1976, 1983; Arimoto et al., 1985; Newell and Evans, 2000). This diversity of aerosol sources could be expected to produce a relatively large range in $\%Fe_S$ values for the bulk aerosol at low total iron loadings. Nevertheless, the data trend for the Pacific Ocean aerosols is broadly consistent with those from other regions of the globe, in showing that the fractional solubility of aerosol iron increases from low values (<5%) to ~10-30% as the total aerosol iron loading decreases. Indeed, the $\%Fe_S$ vs. Fe_T data trend for the Pacific Ocean broadly follows that defined by data from the Sargasso Sea aerosols (Fig. 7).

Another useful comparison is provided by the large range of $\%Fe_S$ values for aerosols collected over the continental United States (Fig. 3; site 14 in Fig. 1; Siefert et al., 1996). Here the aerosol samples with highest $\%Fe_S$ (40-78%) and lowest Fe_T values were collected in Pasadena, California and Whiteface Mountain, New York. The latter site is downwind of the highly industrialized U.S. Midwest, whereas the former, located in the Los Angeles basin, is impacted by both pollution emissions and desert dust. Notably, for the Los Angeles samples, total aerosol iron loading increases by ~10-fold and $\%Fe_S$ drops from 11-22% to 1-4% when strong Santa Ana winds transport mineral dust from the deserts of California to Pasadena, suggesting that $\%Fe_S$ reflects the relative proportions of desert soils and anthropogenic emissions in the bulk aerosol.

The previously published data of Baker et al. (2006a,b) and Sedwick et al. (2007), together with unpublished data from the authors of this paper, are presented in Figure 6. The previously unpublished results add 384 data points to the compilation in Table S1. These new data define a clear hyperbolic relationship between $\%Fe_S$ and Fe_T for aerosols collected over the Atlantic Ocean. There is a pronounced increase in the fractional solubility of aerosol iron when Fe_T values are less than ~100 ng Fe m^{-3}, whereas most samples with Fe_T >400 ng Fe m^{-3} have $\%Fe_S$ values between 0.1% and 2%. The aerosols collected on the Bermuda Tudor Hill tower have %Fe_S values that consistently fall below those of the ship-collected aerosols (~ 0.5% vs. 1-2%), which may reflect differences in the aerosol collection and processing procedures, or inherent differences in the aerosols, which were sampled over a relatively large area of the subtropical and tropical North Atlantic (Fig. 1).

The Gulf of Aqaba data of Chen et al. (2006) indicate that batch-wise leaching of aerosols with pH 5.6 deionized water yields %Fe_S values that are, on average, 9-fold higher than values obtained when pH 8.16 seawater is used as a leaching solution (Fig. 8). Nevertheless, the data from both leaching protocols define clear hyperbolic relationships between %Fe_S and Fe_T. In the absence of evidence that differences in the ionic strength of the leach solution (seawater vs. deionized water) lead to large differences in the extent of dissolution of aerosol iron, the results of Chen et al. (2006) most likely reflect an enhanced solubility of iron-containing minerals and iron oxides at mildly acidic pH values (Stumm and Morgan, 1996; Desboeufs et al., 1999; Liu and Millero, 2002). Early studies show that pH is a key parameter for the iron solubility of marine aerosols (Zhuang et al., 1990, 1992). This interpretation is consistent with the results of Witt et al. (2010), who report %Fe_S values that are 2-5 times higher for marine aerosol samples that were leached batch-wise using pH 1 vs. pH 4.5 leach solutions, as well the results of experimental work involving batch leaching of Saharan soils and urban aerosols (Spokes et al., 1994, Spokes and Jickells, 1996). In this regard, empirical estimates of %Fe_S appear to be more sensitive to leach solution pH when batch leaching methods are used. Indeed, Buck et al. (2006, 2010a) and Aguilar-Islas et al. (2010) report much smaller differences in %Fe_S estimates obtained using deionized water vs. seawater as leach solutions, when employing flow-through and semi-continuous leaching methods, respectively. In fact, Aguilar-Islas et al. (2010) estimate slightly higher $\%Fe_S$ values when seawater was used as the leaching solution, which they attribute to the presence of natural iron-binding organic ligands in the seawater.

The Southern Hemisphere samples, 57 of which provide unpublished data for the South Atlantic Ocean (Fig. 2), are characterized by extremely low aerosol iron loadings (5-150 ng Fe m^{-3} air), and the familiar hyperbolic relationship between $\%Fe_S$ and Fe_T (Fig. 9). With the exception of one high value (48%), $\%Fe_S$ estimates range from 0.5% to 22%. Around a quarter of the Southern Hemisphere samples have $\%Fe_S$ values less than 2%, which is similar to $\%Fe_S$ estimates for aerosols in other regions of the globe that are impacted by soil dust (Figs. 3-8). Some forty percent of the samples have $\%Fe_S$ values >5% , while fourteen percent have $\%Fe_S$ values >10%. A large proportion of the samples with high $\%Fe_S$ (>5%) and low Fe_T values were collected on cruises Z-D and BGH, which covered the most remote areas of the South Atlantic Ocean (Fig. 2). By way of comparison, the more elevated $\%Fe_S$ values for the Sargasso Sea aerosol samples correspond to Fe_T values < 60 ng Fe m^{-3} air, which are thought to be associated with an increased proportion of anthropogenic combustion aerosols carried from North America and Europe (Sedwick et al., 2007).

It is difficult to explain the elevated $\%Fe_S$ values in our data compilation based on the solubility of iron in aerosols derived from natural sources. The fractional solubility of iron in arid continental soils (< 0.1-0.5% and in some cases < 0.01%) are less than the values of 0.5-2% that are typically associated with marine aerosols carried from Africa and Asia (Fig. 3 and Table S2; Desboeufs et al., 1999; Journet et al., 2008; Schroth et al., 2009; Paris et al., 2010, 2011; Srinivas et al., 2011). This difference may reflect chemical and mineralogical variations in the dust source materials, as well as chemical and/or physical processing of soil dust after emission to the atmosphere (Journet et al., 2008; Paris et al., 2010). Furthermore, estimates of the fractional solubility of iron in aerosols produced from natural biomass burning are not particularly high: Guieu et al. (2005) and Paris et al. (2010) report $\%Fe_S$ values of ~2% for samples collected off Africa and southern France.

4.2. Modeling results

The pervasive curvilinear trend in $\%Fe_S$ vs. Fe_T that is described in the preceding section resembles the mixing hyperbola that is produced by the conservative mixing of two geochemical end members (e.g., see Faure and Mensing, 2005). To examine whether this simple conceptual model can adequately describe the $\%Fe_S$ vs. Fe_T trend that is defined by the global-scale data set shown in Fig. 3, we have modeled the trend that would result from the conservative mixing of two aerosol end-member populations, A and B, each characterized by distinct atmospheric concentrations of soluble aerosol iron (Fe'_A and Fe'_B, respectively) and total aerosol iron (Fe_A and Fe_B, respectively). This yields the following expressions for the soluble aerosol iron loading (Fe'_M) and total aerosol iron loading (Fe_M) of resulting aerosol mixtures (Faure and Mensing, 2005):

$$Fe'_M = Fe'_A f_A + Fe'_B(1 - f_A) \qquad (1)$$

$$Fe_M = Fe_A f_A + Fe_B(1 - f_A) \qquad (2)$$

where f_A and f_B are the fractions of aerosols A and B, respectively, in the aerosol mixture. The percent fractional solubility for the aerosol iron in the mixture (bulk aerosol) is then given by:

$$\%Fe_S = 100(Fe'_M / Fe_M) = 100[Fe'_A f_A + Fe'_B(1 - f_A)]/[Fe_A f_A + Fe_B(1 - f_A)] \quad (3)$$

Using Eq. (3), we have calculated $\%Fe_S$ as a function of Fe_T for various combinations of plausible end-member aerosol iron loadings (Fe_A and Fe_B) and corresponding end-member fractional solubility of aerosol iron ($100Fe'_A / Fe_A$ and $100Fe'_B / Fe_B$, respectively). In this conceptual model, we follow the approach used by Sedwick et al., (2007). One of the aerosol members is characterized by relatively high aerosol iron loading (Fe_T) and relatively low fractional solubility of aerosol iron ($\%Fe_S$), as is typical of aerosols derived from arid continental soils (e.g., Saharan dust); we refer to this as the 'lithogenic' aerosol end-member. The other end-member is characterized by relatively low aerosol iron loading (Fe_T) and relatively high fractional solubility of aerosol iron ($\%Fe_S$). As discussed in Section 5, the elevated fractional solubility of iron in this end-member may reflect an inherently higher solubility of iron in aerosols derived from anthropogenic and natural combustion sources, and/or the chemical alteration of lithogenic dust by pollutants (largely combustion related) during atmospheric transport. We thus refer to this as the 'combustion' aerosol end-member. Fig. 10A shows the resulting trends for the mixtures using eight combinations of plausible aerosol end members, based on the observed $\%Fe_S$ and Fe_T values of the global data set shown in Figs. 3-9. Details of the mixing model and the results for the eight case studies are found in Table S3 of the Supplementary material (see *http://dx.doi.org/10.1575/1912/5104*).

As expected, the shape of the modeled mixing trend changes according to the values of $\%Fe_S$ and Fe_T assigned to the aerosol end-members. The eight different cases indicate that the model results are most sensitive to the Fe_T values selected for the combustion aerosol end-member (Fig. 10A). Case III, which uses aerosol end-members with total iron loadings of 10 ng m^{-3} and 2000 ng m^{-3}, and corresponding $\%Fe_S$ values of 50% and 1%, respectively, appears to adequately describe the trend for a major fraction of the global data set (black circles in Fig. 3B). In contrast, the case V end-members appear to better describe the trend defined by aerosol samples from the East China Sea, South Korea, the Gulf of Aqaba and the continental USA, all of which are distinguished by elevated $\%Fe_S$ values for total aerosol iron loadings in the range of 50-1000 ng m^{-3} (Figs. 3 and 4). The case V example uses aerosol end-members with total iron loadings of 100 and 2000 ng m^{-3}, and corresponding $\%Fe_S$ values of 50% and 1%, respectively. Hence, case V differs from case III in having a 10-fold higher aerosol iron loading for the combustion aerosol end-member, as might be expected nearer the likely source of such aerosols in Asia, Eurasia and North America. In broad terms, the $\%Fe_S$ vs. Fe_T trends defined by the global aerosol data set (Fig. 3B) are reasonably well described and constrained by the eight aerosol mixtures that we have considered, in that most of the global data fall between the mixing lines defined by the examples of cases III and V.

It should be noted that the hyperbolic relationship that we observe is not an artefact of plotting $\%Fe_S$ vs. Fe_T, which is essentially equivalent to plotting Fe_S/Fe_T vs. Fe_T. The only constraints on the two variables, Fe_S and Fe_T, are that $Fe_T \geq 0$ and that $0 \leq Fe_S \leq Fe_T$. If a set of random Fe_S and Fe_T values are selected with these constraints, then

Fe_S/Fe_T vs. Fe_T produces a random scatter plot, and not the well-defined curvilinear trend that is apparent in Fig. 3.

5. DISCUSSION AND CONCLUSIONS

5.1. Sources of iron to the atmosphere

Aerosol iron in Earth's lower atmosphere has both natural and anthropogenic sources. Soils in arid continental regions are the major sources of natural aerosol iron, in the form of clay minerals and iron oxides, which we term 'lithogenic aerosols' (Jickells and Spokes, 2001; Jickells et al., 2005; Luo et al., 2008; Mahowald et al., 2009; Baker and Croot, 2010; Raiswell and Canfield, 2012). Iron-bearing aerosols are also derived or impacted by emissions from various combustion processes, both anthropogenic and natural. As detailed by Luo et al. (2008), these include fossil fuel combustion (coal and oil used for electricity, industry, transport, heating), a variety of industrial processes, human combustion of wood, agricultural wastes and biofuels and natural biomass burning. In this paper we use the term 'combustion aerosols' to cover these forms of aerosols. As noted in Section 5.5, lithogenic aerosols that have been chemically altered by acidic species can have elevated fractional solubility of iron with respect to arid soil samples. Acidic species (SO_2 in particular), are largely derived from anthropogenic combustion processes (Hand et al., 2004; Meskhidze et al., 2005).

5.2. Aerosol iron solubility data derived from leaching procedures

Raiswell and Canfield (2012) note that iron-bearing aerosols undergo a complex series of chemical reactions and transformations in the atmosphere before reaching the ocean. These authors suggest that a common agreed aerosol leaching protocol would be an important step toward an improved understanding of aerosol iron dissolution, as would an increased focus on aerosol mineralogy and the role of colloids and nanoparticles in the interpretation of aerosol dissolution experiments. While the latter recommendation is clearly beyond the scope of this paper, we heartily concur with the suggestion that a standard aerosol leaching protocol be adopted by aerosol iron researchers. In this regard, it is important to recognize that the various leaching protocols that were used to derive the data compiled in this paper can only provide operational definitions of the fractional solubility of aerosol iron. That is, such leaching methods are unable to faithfully mimic the dissolution of aerosol iron in meteoric waters, nor the release of dissolved iron from aerosols into surface ocean waters (Sedwick et al., 2007; Aguilar Islas et al., 2010; Baker and Croot, 2010). Aerosol dissolution experiments thus provide qualitative and semi-quantitative information on the ‘effective’ solubility of iron that is delivered to the ocean via dry and wet deposition.

A robust evaluation and intercomparison of aerosol leaching protocols is also beyond the scope of this paper. Indeed, a comprehensive assessment of the impact of leaching protocols on resulting estimates of 'soluble' aerosol iron requires the application of different leaching methods to sets of identical aerosol samples, as has been attempted in the studies of Chen et al. (2006) and Aguilar-Islas et al. (2010). The data presented in Figures 3-9 do allow the comparison of $\%Fe_S$ values derived using different leaching protocols (as identified by the figure legends), although such comparisons are necessarily tenuous, given that the data for different leaching methods were derived from samples at diverse locations and dates. Fig. 13 in Sholkovitz et al. (2009) is an example of good agreement between two different storage and leaching protocols, one using frozen storage and one using immediate leaching. The most significant observation with respect to the intercomparison issue is the pronounced and consistent trend in $\%Fe_S$ vs. Fe_T that is observed for the global-scale data set (Fig. 3), this *despite* the wide variety of techniques that were used to collect, store and leach the aerosol samples. As noted by Aguilar-Islas et al. (2010), this result implies that inherent differences in the composition and source of aerosol samples are more important in determining the effective solubility of aerosol iron than differences between leaching protocols.

5.3. Fractional solubility of aerosol iron over the ocean

Our global-scale aerosol data compilation reveals a large range in the fractional solubility of aerosol iron (~0-95%), as well as a consistent hyperbolic trend in the fractional solubility of aerosol iron as a function of total aerosol iron loading (Figs. 3-9). The hyperbolic relationship in $\%Fe_S$ vs. Fe_T for the global data set essentially follows that identified for aerosols collected in the Sargasso Sea by Sedwick et al. (2007), who showed that such a trend could be explained by the conservative mixing between two aerosol end-members with (1) high Fe_T and relatively low $\%Fe_S$ (~1%) and (2) low Fe_T and relatively high $\%Fe_S$ (~20% or more), as shown in Figure 10B. Kumar and Sarin (2009) and Kumar et al. (2010) have also shown that a simple two end-member aerosol mixing model can describe the hyperbolic trend in $\%Fe_S$ vs. Fe_T observed for aerosols collected from Mt. Abu in northwest India and over the northern Indian Ocean. The model results that are presented in Figure 10A confirm that this simple mixing model, as detailed in Section 4.2, can also adequately describe the %Fe_S vs. Fe_T trend defined by the global-scale data compilation.

Clearly, our two end-member conservative mixing model simplifies the process by which aerosols with different characteristics are mixed in the marine boundary layer. In reality, the bulk marine aerosol will reflect the mixing of multiple aerosol types, both natural and anthropogenic, which are each characterized by different atmospheric loadings and %Fe_S values, depending on their sources and transport histories. A greater variability in %Fe_S might be expected for lower Fe_T values, reflecting both spatial and temporal differences in the composition, alteration and loading of the putative 'combustion' aerosols. This expectation is consistent with the greater spread of the global %Fe_S data at lower Fe_T values (Fig. 3). Indeed, the range in %Fe_S for combustion-derived aerosols is expected to be large. Iron in oil fly ash can reach fractional solubility values of 80%, based on leaching with in pH 5.5 deionized water (Schroth et al., 2009), and Desboeufs et al. (2005) have reported %Fe_S values of 0.2, 3.0 and 36% for coal fly ash, urban dust and oil fly ash, respectively.

In summary, our global data compilation is broadly consistent with the simple conceptual model whereby the fractional solubility of iron in the bulk marine aerosol is dominated by the inherently low %Fe_S values (~1%) of lithogenic aerosols (soil dust) for total aerosol iron loadings greater than ~500-1000 ng Fe m^{-3}. For Fe_T values below ~500 ng Fe m^{-3}, it appears that marine aerosols contain iron that is inherently more soluble than that carried in soil dust, resulting in high average %Fe_S values for the bulk aerosols in 'non-dusty' marine air.

5.4. Wet deposition of soluble iron

Although this paper focuses on the fractional solubility of iron in dry aerosols, and thus implicitly on the process of dry deposition, wet deposition is thought to account for a significant fraction of the input of soluble aerosol iron to the ocean (Ginoux et al., 2001; Kim and Church, 2001; Ỏzsoy and Saydam, 2001; Gao et al., 2003; Luo et al., 2003; Fan et al., 2006; Breitbarth et al., 2010; Raiswell and Canfield, 2012). Indeed, much of the iron delivered in wet deposition may enter the ocean in dissolved form (where 'dissolved' is defined by filtration). However, the magnitude of wet-deposition fluxes remains poorly constrained, owing to the small number of studies with appropriate field data, which largely reflects the patchy and episodic nature of rainfall over the open ocean (Jickells and Spokes, 2001; Jickells et al., 2005; Mahowald et al., 2005; Sedwick et al., 2005).

In addition to the aerosol samples discussed in this paper, Sedwick et al. (2007) have also reported data on the operational solubility of iron for nine rainwater samples collected in the Sargasso Sea cruises during 2003 and 2004. Here the operational solubility of iron in rainwater (%$Fe_{S\text{-}rain}$) is defined as $dFe_{rain}/TDFe_{rain}$ x 100, where dFe_{rain} is the concentration of 'dissolved iron' measured in rainwater that was immediately filtered through a 0.4 µm pore polycarbonate membrane, and $TDFe_{rain}$ is the concentration of 'total-dissolvable iron' in the unfiltered rainwater sample after it was acidified to ~pH 1.6 with hydrochloric acid and stored for >6 months. The thus determined %$Fe_{S\text{-}rain}$ values range from ~0.6% to ~12%, which lie within the range of fractional iron solubility values (%FeS) obtained for aerosols collected during the same cruises (see Fig. 10B). In most cases, %$Fe_{S\text{-}rain}$ values are remarkably similar to corresponding $\%Fe_S$ values obtained for aerosols using a pH 5.5 deionized water leach. Moreover, the rainwater iron data reveal a trend that resembles the aerosol iron solubility data (Fig. 10B), in that the highest values of $\%Fe_{S\text{-}rain}$ tend to be associated with low $TDFe_{rain}$ concentrations. These data are not inconsistent with the idea that the composition of aerosols is the primary determinant for the effective solubility of aerosol iron in both dry and wet deposition to the Sargasso Sea.

Studies of rainwater and aerosols collected in the eastern Mediterranean Sea lead to a similar conclusion. Samples collected by Theodosi et al. (2010a) indicate fractional solubility values of ~0.5% for iron in rainwater (pH ~ 8) collected during Saharan dust episodes. In contrast, their acidic (pH 4-5) polluted rainwater samples yield iron solubility values of 27%. Theodosi et al. (2010b) note that the operational solubility of iron in wet and dry deposition in the eastern Mediterranean Sea increases significantly with decreasing dust loading and decreasing pH. Séguret et al. (2011)'s study of dry deposition to this same region uses seawater leaching experiments to show that the maximum fractional solubility of iron in Saharan dust is ~ 1%; whereas values as high as 12% were obtained for aerosols associated with anthropogenic emissions. In summary, there are limited data which suggest that the effective solubility of iron in wet deposition may depend on the total iron concentration in a manner similar to that identified for dry aerosols, although there is a clear need for more field studies that focus on the effective solubility of iron in wet deposition.

5.5. Aerosol iron solubility: role of atmospheric processing vs. source

In this section we consider the elevated fractional solubility of aerosol iron when total aerosol iron loadings are low, which is a key observation that emerges from our global data compilation. As was briefly mentioned in Section 4.1, possible explanations include the chemical and/or physical processing of soil dust during long-range atmospheric transport, as well as source-dependent chemical and mineralogical variations in the iron-bearing aerosols. Size sorting of aerosol particles in the atmosphere, leading to an increase in the surface area to volume ratio for smaller particles (Baker and Jickells, 2006), has not found support in recent field studies of aerosol iron solubility (e.g., Buck et al., 2006, 2010b; Shi et al., 2011). However, aerosol iron solubility may vary as a function of source-dependent differences in aerosol particle size, such that elevated $\%Fe_S$ values are associated with small, combustion-derived aerosols (Srinivas et al., 2011).

It has long been argued that aerosol iron solubility increases during long-range transport due to the ‘atmospheric chemical processing’. This process is generally thought to include the reduction of Fe(III) to Fe(II), mediated by the presence of acidic inorganic and organic species (particularly anthropogenic SO_2, NO_X, and their oxidation products) and/or sunlight, during cycles of condensation and evaporation of meteoric water (Baker and Croot, 2010; Breitbarth et al., 2010; Bligh and Waite; 2011; Raiswell and Canfield, 2012).

Although there is little doubt that atmospheric chemical processing serves to increase the fractional solubility of iron in lithogenic aerosols, there is no clear consensus on the importance of this process. Data from a number of field studies reveal no consistent relationship between the operational solubility of aerosol iron and the concentrations of non-sea-salt sulfate (nss-sulfate), oxalate, nitrate, acidity, or distance from source (Chen and Siefert, 2004; Baker et al., 2006a,b; Buck et al., 2006, Paris et al., 2010). In contrast, Kumar et al. (2010) and Srinivas et al. (2011) suggest that acid dissolution significantly increases the $\%Fe_S$ of aerosols collected over the Bay of Bengal, based on significant correlations between $\%Fe_S$ and nss-sulfate. We note, however, that correlation between these two parameters does not necessarily imply a mechanistic relationship: it is possible that aerosols with high nss-sulfate concentrations are associated with the same emission processes that produce combustion aerosols for which the fractional solubility of iron is inherently elevated relative to lithogenic dust. Indeed, the use of field measurements to identify changes in aerosol iron solubility during atmospheric transport is inherently difficult.

Much of the evidence for the impact of atmospheric chemical processing on aerosol iron solubility comes from numerical modeling and laboratory-based studies. The modeling study of Hand et al. (2004) simulates the atmospheric transport, chemical reaction and deposition of iron-bearing aerosols. In this model, fine and coarse sized aerosols from the Atlantic and Pacific Oceans have an initial $\%Fe_S$ value of ~ 0.1%. The combination of solar radiation and cloud processing increases $\%Fe_S$ to values of 4-10%. Meskhidze et al. (2005) model the chemical reactions of lithogenic aerosols with anthropogenic acidic species and conclude that this atmospheric processing yields a relatively small increase (from 0.1% to 0.5%) increase in aerosol iron solubility during transport across the North Pacific Ocean. Using a model that includes the reactions lithogenic dust with HNO_3 and SO_2, Fan et al. (2006) estimate values of 4.6% and 17% for the global average solubility of iron in dry and wet deposition, respectively, with values exhibiting a large geographic variability. Results of a leaching experiment by

Paris et al. (2011) show that oxalic acid at pH 4.7 increases the solubility of aerosol iron in African dust from 0.003% to 0.25 %, whereas the modeling study of Luo and Gao (2010) suggests that oxalic acid increases the solubility of iron in lithogenic dust to values of 1-3%. Other model results reported by Luo and Gao (2010) similarly suggest that atmospheric chemical processing results in relatively modest increases in aerosol iron solubility, with most $\%Fe_S$ values falling between 0.5% and 5%.

Taken together, the results of the abovementioned studies provide compelling evidence that atmospheric chemical processing can increase the fractional solubility of iron in lithogenic aerosols. However, the proposed increases in $\%Fe_S$ via this process are not large, with maximum values in the range of 1-5% for most cases. In contrast, our global-scale compilation of empirical estimates of aerosol iron solubility shows a substantial portion of samples have $\%Fe_S$ values >10%. On this basis, we assert that source-dependent variations in aerosol composition - specifically, the emission of aerosols from anthropogenic and natural combustion processes – must be a major determinant of aerosol iron solubility (see Sedwick et al., 2007; Sholkovitz et al., 2009). In summary, we conclude that both atmospheric chemical processing and the emission of aerosols from combustion processes contribute to the elevated $\%Fe_S$ values observed at low aerosol iron loadings. Although the relative importance of these processes may vary on a regional basis, the latter appears to be most important at the global scale.

5.6. Mineral dust and the human perturbation of the iron cycle

The long-range atmospheric transport and deposition of natural and anthropogenic aerosols over the ocean is well documented (e.g., Duce et al., 1976, 1983; Rahn, 1981;

Rahn and Lowenthal, 1984; Arimoto et al., 1995; Prospero, 1999; Newell and Evans, 2000; Gangoiti et al., 2006; Hadley et al., 2007; Ito, 2011; Siddaway and Petelina, 2011). In the context of the atmospheric input of biologically available iron to the surface ocean, the fractional solubility of aerosol iron is a critical parameter (e.g., Jickells et al., 2005; Mahowald et al., 2005, 2009). Most global-scale biogeochemical models have assigned fixed solubility values to aerosol iron, with $\%Fe_S$ typically in the range of 1-2% (Archer and Johnson, 2000; Aumont et al., 2003; Gregg et al., 2003; Moore et al., 2004; Parekh et al., 2004; Chase et al., 2006; Moore and Doney, 2007) or 1-10% (Lefévre and Watson, 1999; Fung et al., 2000; Gao et al., 2003). As an alternative approach to this problem, our global-scale data compilation suggests that the fractional solubility of aerosol iron might be scaled to vary as a function of total aerosol iron loading, following the empirical trend defined by the data in Figure 3. However, we note that the significant range in $\%Fe_S$ values for any given Fe_T will have a large impact on the range of model-based estimates of soluble iron deposition. The global compilation shows that $\%Fe_S$ varies over roughly a factor of four, from ~0.5% and ~2%, at mid-to-high (dusty) range of Fe_T values (Fig. 3). Hence, it hard to more accurately predict the fractional solubility of Fe for lithogenic dust from the arid regions of the world that provide a major source of ‘new’ soluble iron to the ocean.

In terms of understanding the atmospheric input of biologically-available iron to the ocean, a significant conclusion that emerges from our data compilation is that combustion aerosols appear to constitute a significant source of highly soluble iron to the surface ocean. This implies that the aeolian flux of dissolved iron to the surface ocean does not necessarily scale with total aerosol iron deposition, because the soluble fraction of the total iron deposition can vary greatly according to the composition of the bulk aerosol. Despite low total aerosol iron loadings, regions receiving combustion aerosols with relatively high %Fe_S values may receive a disproportionately large aeolian flux of soluble Fe. Indeed, modeled flux estimates by Sholkovitz et al. (2009) suggest that combustion aerosols may contribute as much as 70% and 85% of the annual soluble iron input to the surface ocean near Bermuda and Ireland, respectively, implying that human activities have profoundly affected the iron budget for the North Atlantic Ocean. Continued anthropogenic emissions of iron-bearing combustion aerosols thus have the potential to influence the magnitude and spatial distribution of soluble iron input to the surface ocean, with attendant impacts on marine biota and carbon cycling (Moore et al., 2004; Moore and Doney, 2007; Krishnamurthy et al., 2009; Mahowald et al., 2009, 2011; Okin et al. 2011). As noted in the Introduction, the global-scale models of Luo et al. (2008) and Mahowald et al. (2009) suggest that combustion aerosols are currently an important , if not the dominant, source of soluble iron to the surface ocean. In these model studies, %Fe_S values of 0.45% and 4% are assigned for lithogenic and combustion aerosols, respectively. Our compilation of empirical %Fe_S data indicates that 4% is a conservative minimum value for combustion aerosols, hence these models may underestimate the importance of combustion aerosols to the ocean iron budget.

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Figure Captions

Figure 1. Site location map of the 26 studies from around the globe. Data are plotted on Figs. 3-9. References cited below are numbered to correspond to the numbers on the location map in this figure. The letters after the location numbers refer to the type of leaching methods used in each study: **B** for batch method, **F_T** for flow-through method and **B/F_T** for a combination batch and flow-through method. The second group of letters refer to type of leaching solutions used; they include Milli-Q (MQ) deionized water, other deionized water (DI), formate pH 4.5 buffer (formate), ammonium acetate pH 4.7 buffer (acetate) and seawater (SW at pH ~ 8). The next and last set of numbers refers to the number of data point in each reference. For example, "**1-B-MQ-32**" means that site 1 has batch leach data using Milli-Q water for 32 samples. Data sources are as follows:

(1-B-MQ-32) Kumur et al., 2010; (**2-B-MQ-49**) Kumar and Sarin, 2010; (**3-B-formate-26**) Johansen and Hoffmann, 2003; (**4-B-formate-16**) Siefert et al. 1999; (5**-B-MQ-31 and SW-19**) Chen et al. 2006; (**6-B-SW-28**) Hsu et al., 2005; (**7-B-MQ-40**) Hsu et al., 2009; (**8-B-MQ-26**) Chuang et al., 2005; (**9-B/F_T-MQ-8 and SW-9**) Aguilar-Islas et al, 2010; (**10-B/F_T-SW-15**) Wu et al. 2007; (**11-F_T-DI-54 and SW-54)** Buck et al., 2006. (**12-B-formate-59**) Chen, 2004; (**13-B-dilute HCl-18**) Zhuang et al. 1992; (**14-B-formate-23**) Siefert et al. 1996; (**15-F_T-DI-43 and SW-41**) Buck et al, 2010a; (**16-B-acetate-65**) Baker et al., 2006 a; (**17-B-acetate-36**) Baker et al., 2006 b. (**18-B-formate-29**) Chen and Siefert, 2004; (**19-B-formate-17**) Johansen et al., 2000; (**20-B-pH 2 NaCl-25**) Trapp et al., 2010; (**21-F_T-DI-18**) Sedwick et al. 2007**;** (**22-F_T-DI-93**) Church, Sedwick and Sholkovitz, unpublished data; (**23-B-pH 1 NaCl-25**) Zhu et al., 1997; (**24-B-pH 1 HNO_3-12)** Witt et al., 2006; (**25-B-acetate-7 and pH 1 HNO_3-7)** Witt et al. 2010; (**26-F_T-SW**-7) Bowie et al., 2009.

Figure 2. Site location map for the unpublished data of Baker and Powell. Data come from 291 samples from twelve cruises in the eastern North Atlantic Ocean and South Atlantic Ocean between 2003 and 2008. Batch leaching with pH 4.7 ammonium acetate buffer solution was employed.

Figure 3. (A) Full-scale plot of fractional solubility of aerosol iron (%Fe_S) versus total aerosol iron loading (Fe_T) for the global set of 1091 samples from sites shown in Figures 1 and 2. **(B)** Expanded x- and y-scale plot of same data as in part (A). The majority of samples are plotted as 'closed circles". Different and distinct symbols are used to highlight four sites (5, 7, 8 and 14) that show %Fe_S values that lie above the main set of data points. The deionized water leach data from the Sargasso Sea are plotted with a distinct 'open circle' symbol; data from this site (21) will be used as '*benchmark*' set of data for Figures 3 to 7 and 9. With respect to the x-axis, a Fe_T value of 1000 ng/m^3 equates to a dust load of ~28 μg/m^3; this assumes that the aerosol is 3.5% Fe, a value that is typical of the upper continental crust and mineral dust from the desert regions. All the data from the twenty-six studies in Fig. 1 and from the 16 cruises to the Atlantic Ocean in Fig. 2 can be found in Table S1 in the supplemental material at http://dx.doi.org/10.1575/1912/5104. Three studies contain Fe solubility data for the same samples using both deionized water and seawater leaches (Chen et al., 2006; Buck

et al., 2006, 2010); only the deionized water leach data are presented in this figure. Data from a study that only used a seawater leach are plotted in this figure (site 6, Hsu et al., 2005). Some data in the compilation have been excluded from parts (A) and (B). These include data from Zhuang et al. (1992) (site 13), because their use of strong mineral acid yields %Fe_S values that are significantly higher than the data from the other studies. The seven data points from Bowie et al. (2011) for site 26 are not plotted.

Figure 4 Plot of %Fe_S vs. Fe_T for the eight coastal studies in the Middle East/Indian Ocean/Asia region. Sites (1-8) range from the Gulf of Aqaba to South Korea. **(A)** Full-scale plot of the whole data set which consists of ~ 217 data points from sites 1-8 in Fig. 1 (see Fig. 1 caption for corresponding references). The deionized water leach data of the Sargasso Sea plot are shown as a 'benchmark' set of data. Data from sites 14 in the continental United States (formate leach, gray squares) are shown for comparison. **(B)** Expanded x- and y-axis scales of Part (A) with symbols and leaching information for each site. Key refers to part B only.

Figure 5. Plot of %Fe_S vs. Fe_T for all the studies in the open Atlantic Ocean. **(A).** full scale plot of the whole data set which consists of ~706 data points from sites 10, 12, 15,17, 18, 19, 21, 22 and 23 in figure 1 and all the sites in Fig. 2. Sites in Fig. 2 yield ~291 unpublished data points of Baker and Powell. One data point in Part (A) at x = 9.5 and y = 95 is not plotted. **(B).** Expanded x- and y-axis scales of Part (A). Distinct symbols are used for the three sites (15, 18 and 23) that show %Fe_S values that lie above the main set of points. The deionized water leach data of the Sargasso Sea plot are shown

as a ‘benchmark’ set of data. Unpublished data of Baker and Powell are highlighted with their own symbol (gray circle).

Figure 6. Plot of $\%Fe_S$ vs. Fe_T vs. for unpublished Atlantic Ocean data of Baker and Powell (291 samples, batch leaching with acetate buffer) and unpublished data of Church, Sedwick and Sholkovitz (93 samples; flow-through leaching with deionized water). The latter samples were collected in the Sargasso Sea and at the Tudor Hill atmospheric tower in Bermuda. Published data from the same authors are also plotted (Baker et al., 2006 a,b; Sedwick et al., 2007). (A) full-scale plot of all the data. (B) Expanded x- and y-axis scales of Part (A). The deionized water leach data of the Sargasso Sea (site 21) are shown as a ‘benchmark’ set of data.

Figure 7. Plot of Fe_T vs. $\%Fe_S$ for all the North Pacific open ocean studies. The whole data set consists of 132 data points from sites 9-13 in Fig. 1. The deionized water leach data for the Sargasso Sea (site 21) are shown as a ‘benchmark’ set of data

Figure 8. Plot of Fe_T vs. $\%Fe_S$ for samples from the Gulf of Aqaba (Chen et al., 2006) **(A).** Comparison of data from pH 5.5 deionized water leach and pH 8.16 seawater leach. **(B).** Expanded x and y scale of the seawater data.

Figure 9. Plot of Fe_T vs. $\%Fe_S$ for 84 samples from Southern Hemisphere (SH) ocean and equator. The deionized water leach data of the Sargasso Sea (site 21) are shown as a ‘benchmark’ set of data. Cruise tracks are in Figure 2. The majority of the SH samples

come from the unpublished data of Baker and Powell in Table S1. Data points from site 26 (Bowie et al., 2011) were inadvertently left off. Five of seven data points fall between x values of 5 and 11 and y values of 0.2 and 2.5.

Figure 10. (A). Results of two end-member conservative mixing model derived from equation (3) in section 4.2 of the text (see supplemental material for details). Eight case studies are shown, each with different end-member values for total aerosol iron loading (Fe_T) and fractional solubility of aerosol iron (%Fe_S). Cases I –VIII have the following end-member values of Fe_T (ng m^{-3} air) for the anthropogenic and mineral dust end-members respectively: I (50, 1000), II (50, 500), III (10, 2000), IV (50, 2000), V (100, 2000), VI (50, 2000), VII (50, 2000) and VIII (50, 500). Cases I–VIII have the following end-member values for %Fe_S for the 'combustion' and 'lithogenic' end-members respectively: I (50, 1), II (50, 1), III (50, 1), IV (50, 1), V (50, 1), VI (60, 1), VII (60, 0.5) and VIII (30, 0.5). Note that case V differs from case III in having a 10-fold higher aerosol iron loading for the combustion end-member (100 vs.10 ng m^{-3} air). The other cases have Fe_T = 50 ng m^{-3} air for the combustion end-members. **(B).** The fractional solubility of iron (%Fe_S) vs. total atmospheric iron loading (Fe_T) for shipboard aerosol samples collected near Bermuda in the Sargasso Sea. The data and the two end-member mixing model trend are from Sedwick et al. (2007). Samples were collected in July-August 2003 (open squares), April 2004 (open circles), and June 2004 (filled triangles). **(C).** Total atmospheric iron loading (Fe_T) versus the mass ratios of V/Al (x100) and Ni/Al (x100) of same total bulk aerosol samples as in part B (from Sholkovitz et al.,

2009). Flow-through leaching with pH ~ 5.5 deionized water was employed for all samples in parts B and C.