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Impact of anthropogenic combustion emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso Sea

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[1] We report empirical estimates of the fractional solubility of aerosol iron over the Sargasso Sea during periods characterized by high concentrations of Saharan dust (summer 2003) and by low concentrations of aerosols in North American/maritime North Atlantic air masses (spring 2004 and early summer 2004). We observed a strong inverse relationship between the operational solubility of aerosol iron (defined using a flow-through deionized-water leaching protocol) and the total concentration of aerosol iron, whereby the operational solubility of aerosol iron was elevated when total aerosol iron loadings were low. This relationship is consistent with source-dependent differences in the solubility characteristics of our aerosol samples and can be described by a simple mixing model, wherein bulk aerosols represent a conservative mixture of two air mass end-members that carry different aerosol types: “Saharan air,” which contains a relatively high loading of aerosol iron ($27.8 \text{ nmol Fe m}^{-3}$) that has a low fractional solubility (0.44%), and “North American air,” which contains a relatively low concentration of aerosol iron ($0.5 \text{ nmol Fe m}^{-3}$) that has a high fractional solubility (19%). Historical data for aerosols collected on Bermuda indicate that the low iron loadings associated with North American air masses are typically accompanied by elevated V/Al, Fe/Al, and V/Mn mass ratios in the bulk aerosol, relative to Saharan dust, which are indicative of anthropogenic fuel-combustion products. The identification of similar compositional trends in our Sargasso Sea aerosol samples leads us to suggest that the elevated solubility of iron in the aerosols associated with North American air masses reflects the presence of anthropogenic combustion products, which contain iron that is readily soluble relative to iron in Saharan soil dust. We thus propose that the source-dependent composition of aerosol particles (specifically, the relative proportion of anthropogenic combustion products) is a primary determinant for the fractional solubility of aerosol iron over the Sargasso Sea. This hypothesis implies that anthropogenic combustion emissions could play a significant role in determining the atmospheric input of soluble iron to the surface ocean.

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Theme: Eolian Dust as a Player and Recorder of Environmental Change

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1. Introduction

[2] The availability of iron regulates the growth, biomass and species composition of phytoplankton over large areas of the surface ocean [Coale *et al.*, 1996, 2004; Behrenfeld and Kolber, 1999; Boyd *et al.*, 2000, 2004; Gervais *et al.*, 2002; Tsuda *et al.*, 2003; de Baar *et al.*, 2005]. Iron is also believed to regulate nitrogen fixation by marine autotrophs such as *Trichodesmium*, which are thought to represent an important component of new production in the subtropical and tropical oceans [Capone *et al.*, 1997, 2005; Karl *et al.*, 2002; Deutsch *et al.*, 2001; Lenos *et al.*, 2001; Moore *et al.*, 2006]. Thus the global biogeochemical cycles of iron, carbon and the nutrient elements are tightly coupled: the supply of iron to ocean surface waters regulates the formation of organic matter by phytoplankton, and, presumably, the export of organic matter from the surface to the deep ocean [de Baar and Boyd, 2000; Buesseler *et al.*, 2005; de Baar *et al.*, 2005]. This mandates the inclusion of iron in conceptual and numerical models of the marine ecosystem and ocean biogeochemistry, an imperative that is hindered by our limited understanding of the sources and sinks of biologically available iron in the surface ocean [Doney *et al.*, 2001; Johnson *et al.*, 2002; Moore *et al.*, 2004; Parekh *et al.*, 2004; Jickells *et al.*, 2005].

[3] The deposition of iron-bearing aerosols, primarily continental soil dust, is generally believed to provide the major source of “new” iron to the surface ocean [Duce and Tindale, 1991; Fung *et al.*, 2000; Mahowald *et al.*, 2005; Baker *et al.*, 2006a]. Although the total eolian flux of iron to the sea surface is reasonably well constrained [Prospero *et al.*, 2002; Jickells *et al.*, 2005; Mahowald *et al.*, 2005], the fraction of this aerosol iron that subsequently dissolves in surface seawater, which presumably determines the fraction of eolian iron available to phytoplankton, is poorly understood. Recent global-scale biogeochemical models have

assumed that the fractional solubility of aerosol iron is around 1–2% in the surface ocean [Archer and Johnson, 2000; Fung *et al.*, 2000; Aumont *et al.*, 2003; Gregg *et al.*, 2003; Moore *et al.*, 2004, 2006; Parekh *et al.*, 2004]. However, observations of temporal changes in the concentration of dissolved iron in ocean surface waters in relation to estimated dust inputs suggest that the fractional solubility of aerosol iron in the surface ocean is significantly higher than 1–2%. On the basis of changes in the distribution of iron in surface waters of the subtropical North Pacific Ocean and regional-scale estimates of aerosol iron deposition, Johnson *et al.* [2003] and Boyle *et al.* [2005] have argued that the “effective solubility” of aerosol iron must be $\geq 10\%$ and 10–40%, respectively. Similarly, by comparing measurements of dissolved iron in surface waters of the Sargasso Sea with concurrent measurements of atmospheric iron loadings, Sedwick *et al.* [2005] estimated a fractional solubility of 3–30% for aerosol iron.

[4] Direct measurements of aerosol iron solubility have been made using a variety of aerosol leaching protocols, which yield solubilities ranging from less than 1% to as much as 90% [e.g., Zhuang *et al.*, 1990; Spokes and Jickells, 1995; Zhu *et al.*, 1997; Edwards and Sedwick, 2001; Bonnet and Guieu, 2004; Chen and Siefert, 2004; Hand *et al.*, 2004; Baker *et al.*, 2006a, 2006b; Desboeufs *et al.*, 2005; Buck *et al.*, 2006; Chen *et al.*, 2006]. The wide range of these empirical estimates is not surprising, given the numerous different leaching protocols employed and the potential effects of solution pH, solution/particle mass ratio, leaching time and organic complexation on the dissolution of iron that is contained in soil dust and other particulate materials [Zhuang *et al.*, 1990; Zhu *et al.*, 1992; Spokes *et al.*, 1994; Kuma *et al.*, 1996; Desboeufs *et al.*, 1999; Jickells and Spokes, 2001; Bonnet and Guieu, 2004; Kraemer, 2004; Mackie *et al.*, 2005; Baker *et al.*, 2006a; Buck *et al.*, 2006]. Indeed, it is important to understand that such

operationally defined aerosol solubility measurements, even those that have employed continuous or multiple leaches over periods of hours to days [e.g., *Desboeufs et al.*, 1999, 2005; *Wu et al.*, 2002; *Boyle et al.*, 2005], are unlikely to reproduce the range of conditions experienced by aerosol particles deposited in the surface ocean, where effective solution/particle mass ratios are probably much larger than can be achieved in the laboratory, and reaction times may extend over periods of weeks to months. Hence these operationally defined solubility measurements are expected to yield information on the relative solubility of iron in aerosols, rather than the true or “effective” fractional solubility of aerosol iron in the surface ocean.

[5] It has long been argued that the fractional solubility of aerosol iron increases during long-range transport, due to the chemical processing of aerosol particles in the atmosphere. This “atmospheric chemical processing” is generally thought to involve the reduction of Fe(III) to Fe(II), mediated by the presence of acidic inorganic and organic species (particularly anthropogenic SO₂ and its oxidation products) and/or sunlight, during cycles of cloudwater condensation and evaporation [*Zhuang et al.*, 1992; *Pehkonen et al.*, 1993; *Spokes et al.*, 1994; *Zhu et al.*, 1993, 1997; *Johansen et al.*, 2000; *Jickells and Spokes*, 2001; *Meskhidze et al.*, 2003; *Fan et al.*, 2004; *Jickells et al.*, 2005; *Mahowald et al.*, 2005; *Buck et al.*, 2006; *Johansen and Key*, 2006]. At present, there is no consensus on the relative importance of suggested reaction mechanisms, and the argument for atmospheric chemical processing as a primary determinant for aerosol iron solubility rests largely on extrapolations from laboratory studies and numerical model simulations [*Mahowald et al.*, 2005]. Indeed, recent field studies have failed to demonstrate a consistent relationship between the operational solubility of aerosol iron and the aerosol concentrations of non-sea-salt sulfate, oxalate and nitrate, or aerosol acidity, or distance from the aerosol source [*Chen and Siefert*, 2004; *Chuang et al.*, 2005; *Mahowald et al.*, 2005; *Baker et al.*, 2006a, 2006b; *Buck et al.*, 2006]. Moreover, model predictions of aerosol iron solubility as a function of atmospheric chemical processing show significant deviations from reported field measurements [*Hand et al.*, 2004; *Luo et al.*, 2005; *Fan et al.*, 2006], or suggest relatively small increases in solubility (<1%) during basin-scale atmospheric transport [*Meskhidze et al.*, 2005].

[6] However, the results of numerous field studies indicate that the fractional solubility of aerosol iron is elevated in fine-mode aerosols and/or when total aerosol iron concentrations are relatively low [*Siefert et al.*, 1999; *Edwards and Sedwick*, 2001; *Chen and Siefert*, 2004; *Hand et al.*, 2004; *Chuang et al.*, 2005; *Baker et al.*, 2006a; *Buck et al.*, 2006; *Baker and Jickells*, 2006]. One hypothesis that is consistent with these observed trends is that the solubility of aerosol iron is influenced by the initial composition of the aerosol source materials, an idea which finds support in the results of laboratory experiments that have examined the fractional solubility of iron in various potential aerosol source materials [e.g., *Visser et al.*, 2003; *Bonnet and Guieu*, 2004; *Desboeufs et al.*, 2005]. In this regard, the results of a number of laboratory and field studies point toward an elevated solubility of iron in aerosols produced by the combustion of fossil fuels and biomass [*Spokes and Jickells*, 1995; *Veranth et al.*, 2000; *Bonnet and Guieu*, 2004; *Chuang et al.*, 2005; *Desboeufs et al.*, 2005; *Guieu et al.*, 2005; *Hsu et al.*, 2005; *Baker et al.*, 2006a, 2006b; *Chen et al.*, 2006]. Alternately, *Baker and Jickells* [2006] have recently argued that the solubility of aerosol iron is primarily controlled by a decrease in the size (hence an increase in the ratio of surface area to volume) of aerosol particles during long-range atmospheric transport, rather than differences in the composition of aerosol materials.

[7] Here we report empirical estimates of aerosol iron solubility based on samples collected in the Sargasso Sea south of Bermuda during periods characterized by high concentrations of North African dust (summer 2003), and by low concentrations of aerosol iron associated with North American air masses (spring and early summer 2004). Our data reveal systematic variations in the relative solubility of aerosol iron, and in the bulk composition of the aerosol samples, which together suggest a significant role for anthropogenic combustion emissions in controlling the fractional solubility of iron in the bulk marine aerosol.

2. Methods

2.1. Study Area

[8] The Bermuda region of the Sargasso Sea (western subtropical North Atlantic) is well situated for research concerning the role of aerosol sources and transport history in controlling the solubility of aerosol iron over the open ocean. Several decades

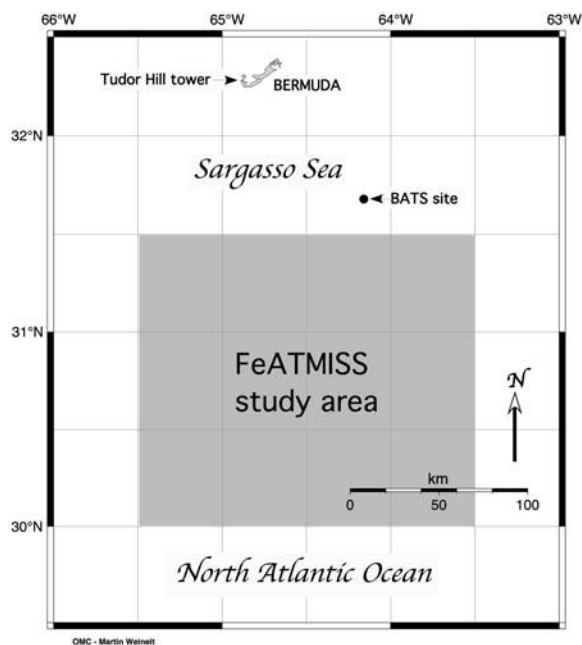


Figure 1. Location map of the FeATMISS study area (shaded box), the BATS site, and the Tudor Hill atmospheric sampling tower on Bermuda.

of time series observations have established that aerosols over Bermuda and the surrounding ocean region are typically dominated by North African (“Saharan”) dust during summer and early fall, whereas aerosols carried with air masses from North America are more important during late fall, winter and spring [e.g., *Duce and Hoffman*, 1976; *Chen and Duce*, 1983; *Arimoto et al.*, 1995, 2003; *Moody et al.*, 1995; *Huang et al.*, 1999; *Smirnov et al.*, 2002]. This seasonal dichotomy facilitates a comparison of the solubility of iron in North African dust versus aerosols derived from North America and other “non-Saharan” sources. Field studies in the Bermuda region also benefit from the legacy of data collected during past and ongoing time series programs, including the Atmosphere-Ocean Chemistry Experiment (AEROCE), the Bermuda Atlantic Time-series Study (BATS), and the Oceanic Flux Program. In this paper, we consider data from aerosol, rainwater and water column samples that were collected in 2003 and 2004 as part of the Iron Atmospheric Inputs to the Sargasso Sea (FeATMISS) project. These samples were collected during three cruises aboard R/V *Weatherbird II* in an area bounded by $\sim 30^{\circ}\text{N}$ – 31.5°N and $\sim 63.5^{\circ}\text{W}$ – 65.5°W (Figure 1), over the periods 22 July to 6 August 2003 (FeATMISS-I, “summer 2003”), 29–30 April 2004 (FeATMISS-II,

“spring 2004”), and 1–5 June 2004 (FeATMISS-III, “early summer 2004”).

2.2. Collection of Aerosol Samples

[9] Aerosol samples were collected from the marine boundary layer during the three FeATMISS cruises using methods similar to those described by *Veron and Church* [1997]. Low-volume pumps (air flow rate $\sim 2 \text{ m}^3 \text{ h}^{-1}$) were used to pull air through acid-cleaned 47-mm diameter filter membranes mounted in downward-facing filter heads under cylindrical polyethylene rain shields. Two filter types were deployed in parallel: Millipore HA filters ($0.45 \mu\text{m}$ nominal size cutoff) were used for the analysis of bulk aerosol composition, and Poretics polycarbonate membranes ($0.4 \mu\text{m}$ pore size) were used for the operational-solubility leaching procedure (described below). The rain-shielded filter heads were mounted on a 7-m high sampling tower located forward of the ship’s bridge, and samples were collected while slowly underway into the wind over periods of 9–18 hours.

2.3. Processing and Analysis of Aerosol Samples

[10] For the analysis of bulk aerosol composition, Millipore HA filter halves were treated with a 1:3 (v/v) mixture of 48% (w/w) hydrofluoric acid solution and 70% (w/w) nitric acid solution at 80°C for one day. Following the dissolution of aerosol particles, any filter residue was removed and the solution was heated to dryness, then the digestion residue was redissolved in 1N nitric acid. Total iron was determined by inductively coupled plasma optical emission spectroscopy (Jobin Yvon JY70 Plus), and total aluminum and manganese were determined by flameless atomic absorption spectrophotometry (Perkin Elmer 3300), using multielement calibration standards. The estimated analytical precision of these analyses was $\pm 5\%$, based on repeated determinations. We assume that the Fe, Al and Mn determined in the digested aerosol material accounts for essentially all of the aerosol Fe, Al and Mn, including that contained in the lattice of aluminosilicate particles. For each aerosol filter sample, the measured Fe, Al and Mn concentrations in the filter digest solution were combined with the total volume of air passed through the filter to yield corresponding “total aerosol” concentrations of iron (Fe_T), aluminum (Al_T) and manganese (Mn_T), in units of nmol m^{-3} . In addition, high-resolution inductively coupled plasma mass spectrometry (Finnegan Element-2)



was used to determine vanadium in the aerosol filter digest solutions, from which total aerosol concentrations of vanadium (V_T) were similarly calculated. For these analyses, Indium was added to both samples and standards as an internal standard, and ^{51}V and ^{115}In were measured in medium-resolution range ($R = 3,000$), with the resulting intensity data for V normalized against the signal intensity for In. Standards were prepared in 5% nitric acid from commercial standards. Calibrations based on these standards and In-normalized count rates were used to calculate V concentrations in the aerosol digest solutions. All of the bulk aerosol analyses include the analysis of a filter blank, for which a Millipore HA filter was mounted on the shipboard sampling tower, then removed and digested in the same manner as the bulk-aerosol filter samples.

[11] In this study, we estimated the operational solubility of aerosol iron using a modification of the deionized-water leaching protocol described by *Buck et al.* [2006]. In our protocol, 250 mL of deionized water (freshly produced Barnstead Nanopure, $>18\text{ M}\Omega\text{-cm}$ resistivity, $\sim\text{pH } 5.5$), was rapidly passed through an aerosol-laden polycarbonate filter membrane held in a Savillex Teflon PFA filter funnel, using a stringent trace-metal clean protocol. The leaching was performed within hours of the aerosol sample collection, and the resulting filtrate (leachate) was immediately transferred into an acid-cleaned 125 mL low-density polyethylene bottle and acidified to $\sim\text{pH } 2.2$ with Seastar Baseline ultrapure hydrochloric acid. Dissolved iron was subsequently determined in the acidified leachate by flow-injection analysis, following the procedure described by *Sedwick et al.* [2005]. Together with the aerosol leach solutions, blank solutions were prepared by passing 250 mL of deionized water over polycarbonate filter membranes that had been mounted on the shipboard sampling tower without running the pumps; iron concentrations were below detection in all of these blank solutions. The measured concentration of dissolved iron in the aerosol leachate solution is defined as the “soluble” aerosol iron, from which a corresponding soluble aerosol iron concentration (Fe_S , in units of nmol m^{-3}) was calculated using the total volume of air passed through the filter. The percent operational solubility of aerosol iron ($\%\text{Fe}_S$) was then calculated using the total aerosol iron concentration (Fe_T) as calculated from the analysis of a parallel aerosol sample (Millipore HA filter), as follows: $\%\text{Fe}_S = 100(\text{Fe}_S/\text{Fe}_T)$.

[12] As already discussed, operationally defined measurements of aerosol iron solubility are expected to provide information on the relative solubility, rather than the effective solubility, of aerosol iron in surface ocean waters. Nonetheless, such measurements may yield important qualitative information concerning the factors that control the effective solubility of aerosol iron. Our choice of a deionized-water leaching protocol to estimate the operational solubility of aerosol iron follows the rationale of *Buck et al.* [2006], who argue that high-purity deionized water provides a consistent and reproducible leaching solution, thus facilitating comparison between the results of different field studies. By contrast, the use of filtered seawater as a leaching solution may introduce significant inconsistencies due to differences in the concentrations of dissolved iron and natural iron binding ligands, which are likely to vary according to collection location and storage conditions. In addition, *Buck et al.* [2006] argue that the use of a rapid, flow-through leaching protocol (rather than a batch-wise leaching method) alleviates the potential for precipitation of iron hydroxides prior to collection of the leachate solution, because the aerosol particles are continuously exposed to added “fresh” solution during the leaching process (i.e., it is unlikely that the leaching solution reaches saturation with respect to iron hydroxides prior to passing through the filter membrane). It should be noted, however, that aerosol iron defined as “soluble” by this flow-through leaching protocol is likely to include truly dissolved iron as well as colloidal iron species that are less than $0.4\ \mu\text{m}$ in size (as does operationally defined “dissolved iron” in seawater [*Wu et al.*, 2001]). Once it has passed through the aerosol-laden filter membrane, the leachate solution was immediately mixed, transferred and acidified, in order to minimize any possible losses of iron from the solution.

2.4. Rainwater Sampling and Analysis

[13] In addition to aerosol samples, we collected a total of 9 rainwater samples during the FeATMISS cruises: 7 during summer 2003 and 2 during early summer 2004 (no rain events were observed during the spring 2004 cruise). Rainwater samples were collected in acid-cleaned 2 L low-density polyethylene bottles attached beneath a high-density polyethylene funnel mounted outboard on the ship’s bow. The samples were collected during short rain events while the ship headed slowly into the wind. Immediately after collection, $\sim 250\text{ mL}$ of each rainwater sample was filtered through a $0.4\ \mu\text{m}$

Table 1. Compositional Data for FeATMISS Aerosol Samples

Collection Date	Air Mass Type ^a	Fe _T , nmol m ⁻³	Al _T , nmol m ⁻³	V _T , nmol m ⁻³	Mn _T , nmol m ⁻³	%Fe _S
24 Jul 2003	MAR	1.86	7.75	0.015	0.034	2.19
25 Jul 2003	MAR	1.83	6.34	0.010	0.033	2.58
26 Jul 2003	MAR	4.57	17.9	0.024	0.068	2.26
27 Jul 2003	MAR	13.1	39.3	0.053	0.202	0.69
28 Jul 2003	MAR	14.1	44.9	0.053	0.210	0.85
1 Aug 2003	MAR	23.1	111	0.106	0.522	1.08
2 Aug 2003	MAR/SAH	14.0	54.5	0.053	0.261	1.03
3 Aug 2003	MAR/SAH	27.8	114	0.107	0.511	0.44
4 Aug 2003	MAR/SAH	8.86	26.6	0.045	0.148	1.05
5 Aug 2003	MAR/SAH	2.85	11.5	0.017	0.061	2.45
29 Apr 2004	NAM	0.75	2.45	0.008	0.030	10.7
30 Apr 2004	NAM	0.54	1.84	0.014	0.019	16.0
31 May 2004	NAM	0.50	2.31	0.055	0.014	19.0
1 Jun 2004	NAM/MAR	0.56	2.34	0.051	0.014	15.2
2 Jun 2004	NAM/MAR	0.95	3.82	0.055	0.022	10.8
3 Jun 2004	NAM/MAR	1.31	6.08	ND ^b	0.030	3.93
4 Jun 2004	MAR/NAM	1.97	6.86	0.020	0.037	7.19
5 Jun 2004	MAR/NAM	0.45	1.18	0.018	0.009	10.0

^a Air mass type (see text) inferred from 10-day air mass back-trajectory analyses: MAR, maritime North Atlantic air; SAH, Saharan air; NAM, North American air.

^b ND, not determined.

pore polycarbonate filter membrane mounted on a Savillex Teflon PFA filter funnel, and 125 mL of the resulting filtrate was acidified to \sim pH 2.2 with Seastar Baseline ultrapure hydrochloric acid in an acid-cleaned low-density polyethylene bottle. An additional 125 mL of each bulk unfiltered rainwater sample was acidified to \sim pH 1.6 with Seastar Baseline ultrapure hydrochloric acid in an acid-cleaned low-density polyethylene bottle. Dissolved iron ($d\text{Fe}_{\text{rain}}$, measured in the filtered, acidified rainwater samples) and total-dissolvable iron ($\text{TDFe}_{\text{rain}}$, measured in the unfiltered acidified rainwater samples) were determined after more than 6 months storage using flow-injection analysis, as described by *Sedwick et al.* [2005]. Total-dissolvable iron provides a measure of dissolved iron plus particulate iron that is solubilized after extended storage at pH 1.6; the latter is assumed to include most of the particulate iron present in rainwater, with the exception of iron that is bound in the most refractory aluminosilicate particles. In a manner analogous to our definition of the percent operational solubility of aerosol iron (%Fe_S), we define the percent operational solubility of rainwater iron (%Fe_{S-rain}) as follows: %Fe_{S-rain} = 100($d\text{Fe}_{\text{rain}}/\text{TDFe}_{\text{rain}}$).

2.5. Water Column Sampling and Iron Analysis

[14] In addition to the aerosol and rainwater samples that were collected during the three FeAT-

MISS cruises, we collected water column samples for the analysis of dissolved iron, using the rigorous trace-metal clean methods described by *Sedwick et al.* [2005]. In an effort to assess changes in surface water iron concentrations in relation to atmospheric deposition, our water column sampling followed a quasi-Lagrangian design, whereby our sampling stations were located in the core of mesoscale cyclonic eddies during each of the three cruises. Water column samples were processed at sea, and dissolved iron (operationally defined by filtration through a 0.4 μm pore polycarbonate filter membrane) was subsequently determined in the filtered, acidified samples using flow injection analysis with in-line preconcentration on resin-immobilized 8-hydroxyquinoline, following established protocols [*Sedwick et al.*, 2005; *Johnson et al.*, 2007].

3. Results and Discussion

[15] Table 1 presents data for the FeATMISS aerosol samples, including collection dates, air mass types inferred from back-trajectory analyses, total aerosol concentrations of iron (Fe_T), aluminum (Al_T), vanadium (V_T) and manganese (Mn_T), and the percent operational solubility of aerosol iron (%Fe_S).

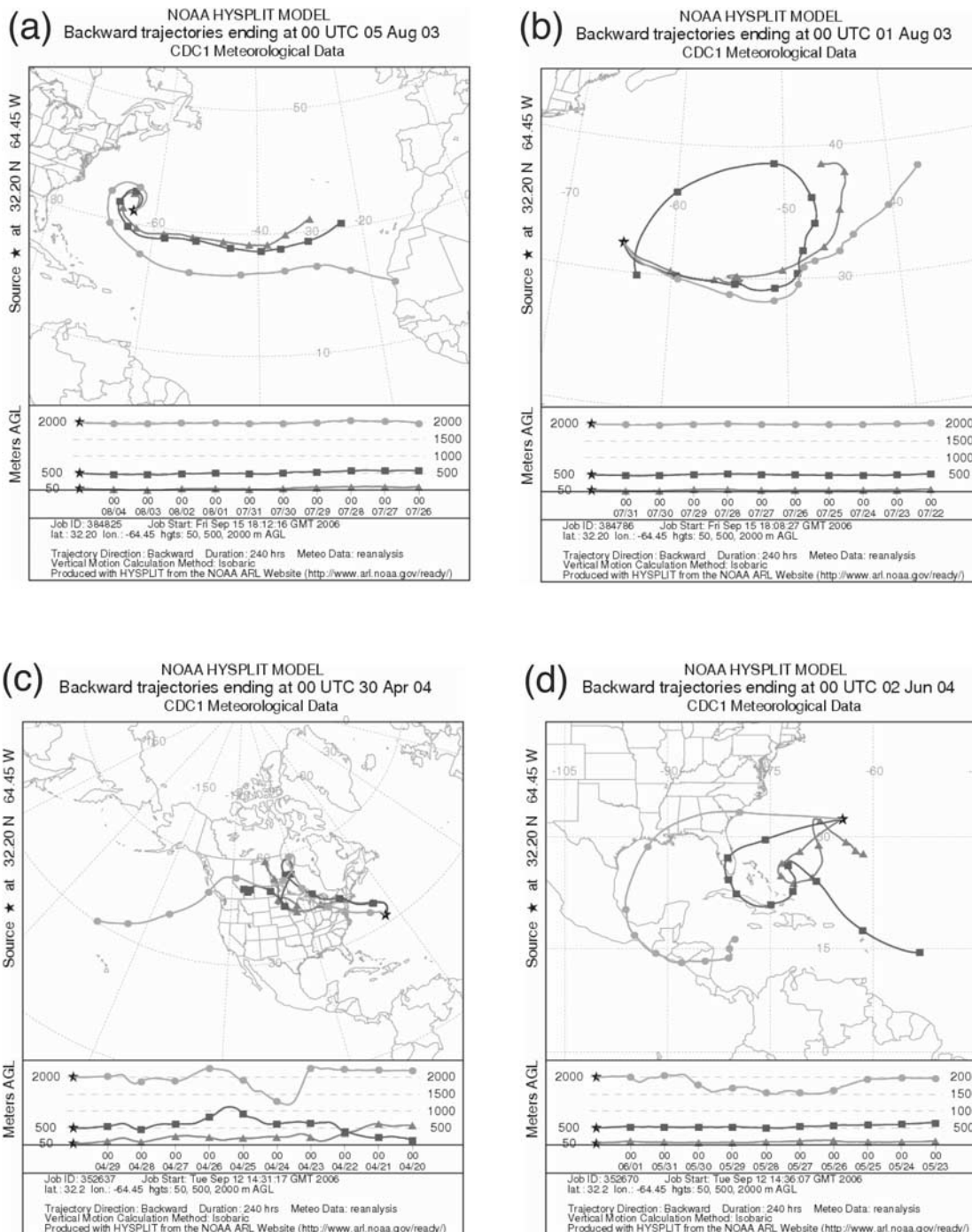


Figure 2. Representative 10-day air mass back trajectory analyses (HYSPLIT model) for the Bermuda area during the FeATMISS cruises (a) 5 August 2003 (summer 2003 cruise): “Saharan air”; (b) 1 August 2003 (summer 2003 cruise): “maritime North Atlantic air”; (c) 30 April 2004 (spring 2004 cruise): “North American air”; and (d) 2 June 2004 (early summer 2004 cruise): “North American/maritime North Atlantic air.”

3.1. Aerosol Iron Solubility in Relation to Aerosol Sources and Loadings

[16] In terms of the sources and total atmospheric loadings of aerosols during our FeATMISS cruises,

there are significant differences between the summer 2003 cruise and the spring and early summer 2004 cruises. The summer 2003 cruise coincided with the transport of significant plumes of North

African soil dust over our study region, particularly later in the cruise period, as revealed by satellite images, air mass back-trajectory analyses using the HYSPLIT model (<http://www.arl.noaa.gov/ready.html>; see Figures 2a and 2b), and aerosol-transport simulations by the NAAPS model (<http://www.nrlmry.navy.mil/aerosol/>). Relatively high aerosol iron concentrations (mean $\text{Fe}_T = 11 \text{ nmol m}^{-3}$) and high surface water dissolved iron concentrations ($\sim 1\text{--}2 \text{ nM}$) were observed in association with this “Saharan dust event” [Sedwick *et al.*, 2005]. In contrast, the spring 2004 and early summer 2004 cruises were characterized by relatively low aerosol iron loadings (mean $\text{Fe}_T = 0.64 \text{ nmol m}^{-3}$ and 0.96 nmol m^{-3} , respectively) associated with air masses that had previously passed over or near the North American continent (Figures 2c and 2d). The NAAPS model simulations for the spring and early summer 2004 cruise periods suggest that these air masses were carried from areas impacted by both Asian soil dust (which had crossed the Pacific and North America) and North American sulfate aerosols. Differences in the color of aerosols sampled during our cruises are consistent with these inferred source regions: aerosols collected during summer 2003 were orange-brown in color, as is typical of North African soil dust, whereas the spring and early summer 2004 samples were gray-brown in color, as is typical of North American and/or Asian aerosols [Arimoto *et al.*, 2003; Tomza *et al.*, 2001].

[17] A striking result of our aerosol iron solubility measurements is the apparent hyperbolic relationship between the percent operational solubility of aerosol iron and the total aerosol iron concentration. The trend defined by the $\% \text{Fe}_S$ versus Fe_T data (Figure 3a) resembles a rectangular hyperbola of the form $y = k/x$, and there is a significant linear correlation between $\% \text{Fe}_S$ and $1/\text{Fe}_T$ ($r^2 = 0.85$, Figure 3b). Calculated $\% \text{Fe}_S$ values range from 0.44% to 19% (Table 1), and the $\% \text{Fe}_S$ values decrease sharply from 19% to 2% at the low end of the observed aerosol iron loadings, as the Fe_T values increase from $\sim 0.5 \text{ nmol m}^{-3}$ to $\sim 5 \text{ nmol m}^{-3}$ (Figure 3a). Hence the operational solubility of aerosol iron was highest when total aerosol iron loadings were low, as is the case for the aerosol samples collected in spring 2004 and early summer 2004, whereas the aerosol samples collected during summer 2003 had $\% \text{Fe}_S$ values of less than 3%. To some extent, these results might reflect an enhanced dissolution of aerosol iron under conditions where the mass ratio of leach solution to aerosol particles is relatively high [Zhuang *et al.*, 1990;

Bonnet and Guieu, 2004] (the so-called “particle-concentration effect” [Baker *et al.*, 2006a]) as a result of low aerosol filter loadings. This seems unlikely, however, given our use of a flow-through leaching protocol in which the aerosol particles are continuously exposed to fresh leach solution [Buck *et al.*, 2006]. Instead, the fact that the highest $\% \text{Fe}_S$ values ($>3\%$) are associated with non-Saharan air masses suggests that the observed range of $\% \text{Fe}_S$ values reflects real, innate differences in the fractional solubility of iron in our aerosol samples, rather than artifacts of the aerosol leaching protocol. This interpretation implies that the fractional solubility of iron in aerosols associated with North American air masses (spring 2004 and early summer 2004 samples) was significantly elevated relative to the fractional solubility of iron in Saharan dust (summer 2003 samples).

[18] The data presented by Baker *et al.* [2006a] and Buck *et al.* [2006] for aerosols collected over the Atlantic and North Pacific, respectively, define trends that are qualitatively consistent with our FeATMISS results; that is, elevated aerosol iron solubility tends to be associated with low aerosol iron loadings. Importantly, Baker *et al.* [2006a] performed experiments in which they leached several different-sized portions of individual aerosol samples, thereby demonstrating that observed differences in operational iron solubility were the result of differences in the character of the aerosol samples, rather than artifacts of their leaching procedure. This and a lack of correlation between operational iron solubility and either acid species concentration or net potential acidity of their aerosol samples led Baker *et al.* [2006a] to conclude that differences in the relative solubility of iron in aerosols over the Atlantic Ocean are primarily controlled by the source and chemical nature of the aerosols, rather than the effects of atmospheric chemical processing. More recently, however, Baker and Jickells [2006] have argued that aerosol iron solubility is controlled by size-sorting of mineral aerosols during atmospheric transport (“atmospheric physical processing”) rather than aerosol composition, based on a reexamination of the data presented by Baker *et al.* [2006a, 2006b].

[19] Qualitatively, the observed relationship between $\% \text{Fe}_S$ and Fe_T for the FeATMISS aerosol samples (Figure 3a) is not inconsistent with the control of aerosol iron solubility via atmospheric chemical processing and/or atmospheric physical processing of the aerosol particles. However, in the following sections we will argue that our results are more

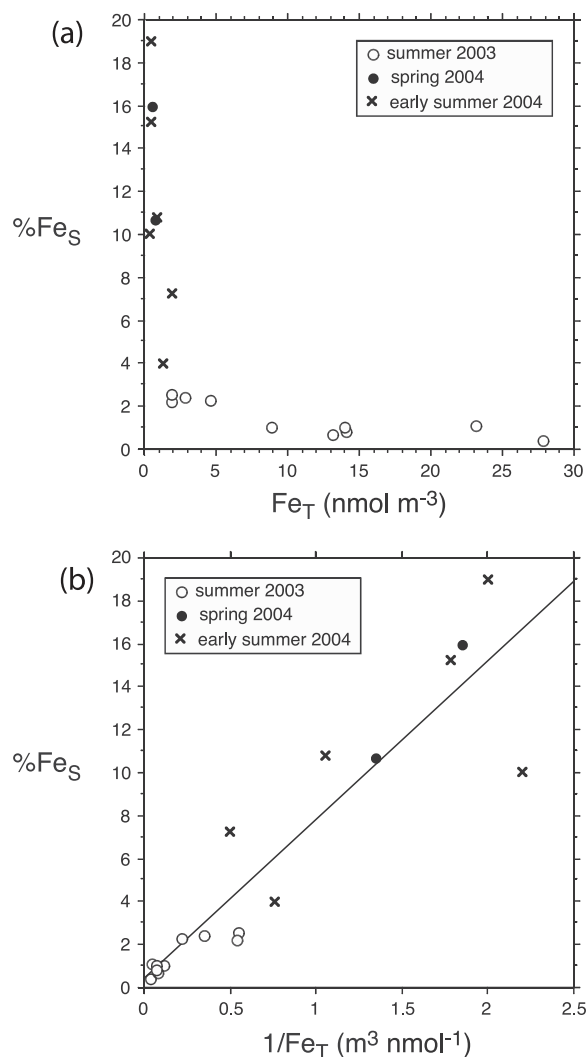


Figure 3. (a) Operational solubility of aerosol iron ($\%Fe_S$) versus total aerosol iron concentration (Fe_T) for FeATMISS aerosol samples; (b) $\%Fe_S$ versus $1/Fe_T$ for the same samples, showing best fit linear regression ($r^2 = 0.85$). Open circles, summer 2003 cruise; filled circles, spring 2004 cruise; crosses, early summer 2004 cruise.

compatible with an alternate hypothesis; namely, that the fractional solubility of iron in aerosols over the Sargasso Sea is primarily controlled by the origin and composition of the aerosol particles, rather than the effects of atmospheric processing.

3.2. Solubility of Aerosol Iron Over the Sargasso Sea: A Simple Mixing Model

[20] A simple interpretation of the $\%Fe_S$ versus Fe_T trend shown in Figure 3a is that it represents a

mixing line between two air masses characterized by significant differences in Fe_T and $\%Fe_S$. On the basis of this assumption, we have modeled the operational solubility and total concentration of aerosol iron that would result from conservative mixtures of two air mass end-members, “Saharan air” and “North American air,” which are distinguished by differences in the relative solubility of iron and the total concentration of iron in their respective aerosol burdens. Here we introduce terms to distinguish the relative solubility of iron in aerosols carried by these two air masses, as is suggested by the data presented in the preceding section: the Saharan air end-member carries “fresh aerosol minerals” (FAM), primarily North African soil dust, for which the fractional solubility of iron is relatively low; whereas the North American air end-member carries “weathered and anthropogenic aerosol minerals” (WAAM), a mixture of soil dust and anthropogenic aerosols, for which the fractional solubility of iron is relatively high. Here the terms “fresh” and “weathered” refer to the effects of atmospheric processing (chemical and/or physical) on the solubility of aerosol iron prior to the mixing of the two air mass end-members. Our choice of the terms FAM and WAAM implies that the fractional solubility of iron in these two aerosol “types” may be controlled by the origin and/or atmospheric processing of aerosol particles, although we will later argue that source-dependent composition is the most important factor controlling the fractional solubility of iron in WAAM-type aerosols.

[21] In our mixing model, the Saharan air end-member contains a relatively high concentration of FAM (and no WAAM), whereas the North American air end-member contains a relatively low concentration of WAAM (and no FAM). End-member air masses are defined by the maximum and minimum values of $\%Fe_S$ and Fe_T observed for our FeATMISS aerosol samples (Table 1): North American air contains only WAAM, with an operational iron solubility ($\%Fe_{S-WAAM}$) of 19% and a total aerosol iron concentration (Fe_{T-WAAM}) of 0.5 nmol m^{-3} , whereas Saharan air contains only FAM, with an operational solubility ($\%Fe_{S-FAM}$) of 0.44% and a total aerosol iron concentration (Fe_{T-FAM}) of 27.8 nmol m^{-3} . The $\%Fe_S$ versus Fe_T relationship resulting from a conservative mixture of these two end-member air masses is shown in Figure 4 (solid curve), together with the data for our FeATMISS aerosol samples (open symbols). This simple mixing model is quite successful in simulating the hyperbolic relationship between

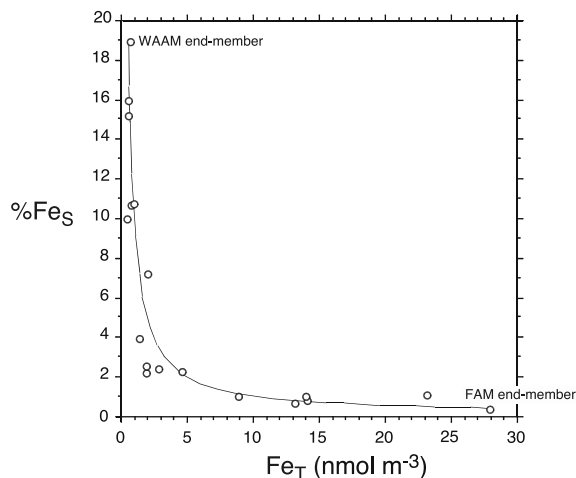


Figure 4. Modeled %Fe_S versus Fe_T relationship defined by a conservative mixture of “Saharan” and “North American” air masses (solid curve; refer to text for details), together with data for the FeATMISS aerosol samples (open symbols).

%Fe_S and Fe_T defined by our FeATMISS aerosol data. The %Fe_S data tend to be slightly lower than the model predictions at the low end of the Fe_T range (~1–3 nmol m⁻³), however, model calculations using different end-member conditions (results not shown) indicate that the curvature of the mixing line at low Fe_T values (i.e., the sharp decrease in %Fe_S with increasing Fe_T) is highly sensitive to our choice of values for %Fe_{S-WAAM} and Fe_{T-WAAM}.

[22] Strictly speaking, our mixing model describes a single mixing event, whereas the data points plotted in Figure 3a and Figure 4 represent discrete aerosol samples that were collected over time periods ranging from days to months. Our model thus constitutes a gross simplification of the mixing of air masses and their constituent aerosols over the Sargasso Sea, in that it ignores changes in both the concentration and composition of aerosols in Saharan and North American air masses, as well as likely aerosol contributions from other source regions, such as Europe and Central America. Nonetheless, the success of this simple model in simulating our field data lends support to our basic premise; namely, that the fractional solubility of iron in bulk aerosols over the Sargasso Sea is determined by the relative proportions of iron associated with two distinct aerosol types: a FAM-type material for which the fractional solubility of iron is relatively low, and a WAAM-type

material for which the fractional solubility of iron is relatively high.

3.3. Anthropogenic Combustion Aerosols: Geochemical Signature and Influence on the Solubility of Aerosol Iron

[23] The apparent seasonal differences in the operational solubility of iron in aerosols over the Sargasso Sea point to the existence of two distinct aerosol “types,” WAAM and FAM, associated with air masses arriving from North America and North Africa, respectively. In this section, we will show that the WAAM-type aerosols display a characteristic geochemical signature, owing to the presence of fossil-fuel combustion products, and we will argue that these anthropogenic emissions account for the enhanced solubility of iron in WAAM-type aerosols, relative to Saharan dust.

[24] Seasonal to interannual variations in the concentration and composition of aerosols over the Sargasso Sea are well documented as a result of the AEROCE program, for which daily aerosol samples were collected at Tudor Hill, Bermuda between 1988 and 1997. These samples were collected atop a 23-m high tower, on Whatman 41 cellulose filters, using a wind-sector controlled high-volume vacuum filtration system, and were subsequently analyzed using neutron activation analysis [Arimoto *et al.*, 1992, 1995, 2003; Huang *et al.*, 1999; S. Huang, personal communication,

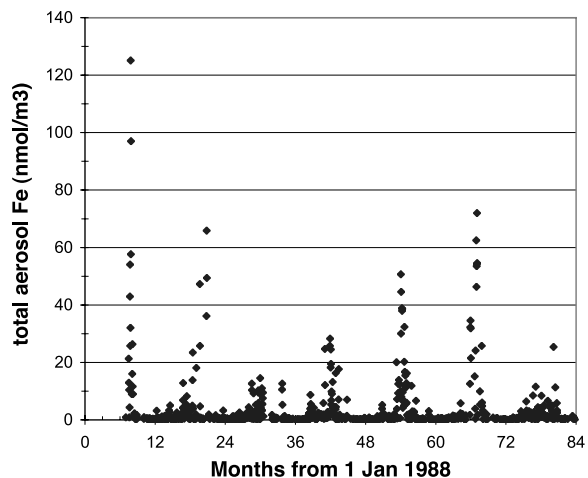


Figure 5. Time series record of total aerosol iron concentrations at Tudor Hill, Bermuda, for the period 1988–1994 (data provided by S. Huang). The summertime concentration maxima are typically associated with the transport of North African (“Saharan”) dust to the Bermuda region.

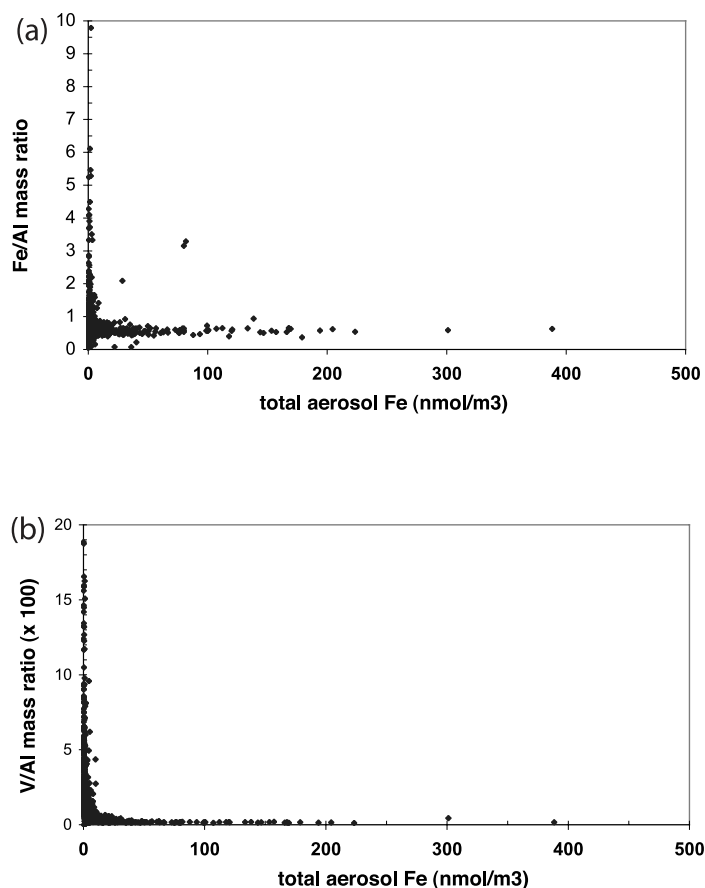


Figure 6. Aerosol mass ratios of (a) Fe/Al and (b) V/Al plotted against total aerosol iron concentration for samples collected on Bermuda during the AEROCE program between 1988 and 1994 (data provided by S. Huang). Samples with unusually high ratios of Fe/Al (>10) and V/Al (>0.20) are omitted from the figure.

2005]. The data from the Bermuda AEROCE samples demonstrate pronounced seasonal-scale variations in aerosol iron loadings (Figure 5), whereby maxima in total aerosol iron concentrations are typically associated with the transport of Saharan dust to the Bermuda region during mid to late summer [Arimoto *et al.*, 1995; Huang *et al.*, 1999], as we also observed during the FeATMISS-I cruise.

[25] The Bermuda AEROCE data also reveal significant, seasonal-scale variations in the bulk composition of aerosols over the Sargasso Sea. Here we focus our attention on the Fe/Al and V/Al mass ratios of the AEROCE aerosol samples, which are plotted against total aerosol iron concentrations in Figure 6. The data plotted in this figure represent around 800 bulk aerosol samples that were collected at Tudor Hill during all seasons between 1988 and 1994 (S. Huang, personal communication, 2005), although a small number of samples with extremely high Fe/Al and V/Al ratios (4 samples with Fe/Al $>$

10, and 15 samples with V/Al > 0.20) are omitted from the figure for the sake of clarity in scaling the figure. For total aerosol iron concentrations greater than $\sim 10 \text{ nmol m}^{-3}$, most of the AEROCE samples have Fe/Al and V/Al mass ratios in the ranges of 0.4–0.7 and 0.001–0.003, respectively. These mass ratios are similar to those reported for soil dust from North Africa [Chen and Duce, 1983; Chiapello *et al.*, 1997; Prospero *et al.*, 2001; Eglinton *et al.*, 2002; Arimoto *et al.*, 2003; Formenti *et al.*, 2003; Desboeufs *et al.*, 2005; Stuut *et al.*, 2005] and for the upper continental crust [Taylor and McLennan, 1985; Wedepohl, 1995; Li, 2000]. However, for total aerosol iron loadings below $\sim 5\text{--}10 \text{ nmol m}^{-3}$, the Fe/Al and V/Al mass ratios increase sharply to values above 1 and 0.05, respectively.

[26] Most of the low aerosol iron loadings in the Bermuda AEROCE data set represent samples collected during the months of October through May, when Bermuda is typically impacted by

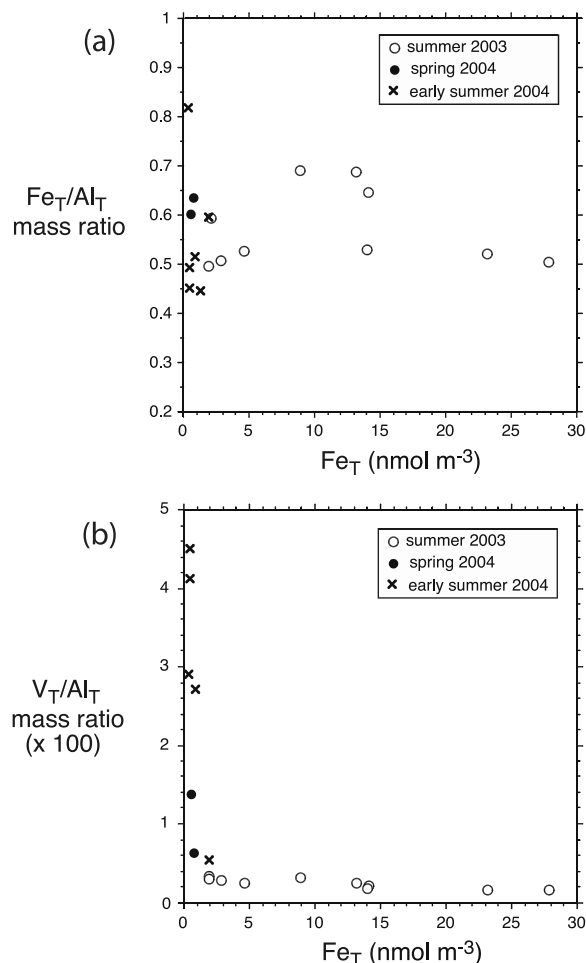


Figure 7. Mass ratios of (a) Fe_T/Al_T and (b) V_T/Al_T plotted against total iron concentration for FeATMISS aerosol samples. Open circles, summer 2003 cruise; filled circles, spring 2004 cruise; crosses, early summer 2004 cruise.

aerosols carried from North America, rather than Saharan dust [Moody *et al.*, 1995; Huang *et al.*, 1999]. Thus, in terms of the different aerosol types that we have proposed to explain the solubility of iron in our FeATMISS aerosol samples, the “WAAM-type” aerosols in North American air masses might be expected to display elevated Fe/Al and V/Al mass ratios, relative to the “FAM-type” aerosols in Saharan air masses. In Figure 7, we have plotted Fe_T/Al_T versus Fe_T and V_T/Al_T versus Fe_T for the FeATMISS aerosol samples. Although the highest Fe_T/Al_T ratios correspond to samples collected during spring 2004 and early summer 2004, when aerosol iron loadings were relatively low (Figure 7a), most of the Fe_T/Al_T ratios are within the range of values reported for North African soil dust and the upper continental crust

($\sim 0.4\text{--}0.7$). This may reflect the small number of samples in the FeATMISS data set, although it should be noted that not all of the AEROCE samples display elevated Fe/Al ratios at low total iron loadings (Figure 6a). However, the FeATMISS V_T/Al_T versus Fe_T trend closely follows that of the Bermuda AEROCE data: the V_T/Al_T ratios increase sharply when total aerosol iron loadings fall below $\sim 5 \text{ nmol m}^{-3}$, reaching values that are over ten times higher than those observed during the summer 2003 cruise (Figure 7b). Importantly, there is a striking similarity between the plots of V_T/Al_T versus Fe_T (Figure 7b) and $\% \text{Fe}_S$ versus Fe_T (Figure 3a) for the FeATMISS aerosol samples, with the highest V_T/Al_T ratios and highest $\% \text{Fe}_S$ values observed in samples collected during the spring 2004 and early summer 2004 cruises, when aerosol iron loadings were low. Indeed, there is a significant linear correlation ($r^2 = 0.73$) between $\% \text{Fe}_S$ and V_T/Al_T for the FeATMISS aerosol samples (data not shown). This observation suggests that the relatively high operational solubility of aerosol iron in North American air masses is related to the bulk composition, hence origin, of these aerosol particles, rather than the effects of atmospheric processing.

[27] What do the elevated V/Al and Fe/Al mass ratios of the WAAM-type aerosols tell us about their origin? It is well documented that elevated V/Al ratios in aerosols, relative to typical crustal values, are a robust indicator for the presence of fuel-oil combustion products, since certain crude oils and their combustion products are known to contain high concentrations of vanadium [Zoller *et al.*, 1973; Duce and Hoffman, 1976; Chen and Duce, 1983; Rahn and Lowenthal, 1984; Arimoto *et al.*, 1985, 1995, 2003; Nriagu and Pacyna, 1988; Holmes *et al.*, 1997; Hope, 1997; Huang *et al.*, 1999; Lighty *et al.*, 2000; Desboeufs *et al.*, 2005; Jang *et al.*, 2007]. Thus elevated V/Al ratios of bulk aerosols over the Sargasso Sea are almost certainly indicative of the presence of anthropogenic fossil-fuel combustion products. Similarly, elevated aerosol Fe/Al ratios may reflect the presence of fuel combustion emissions, since Fe/Al mass ratios greater than one are reported for fuel-oil fly ash, urban aerosols, and exhaust particles produced by diesel combustion [Desboeufs *et al.*, 2005; Dwivedi *et al.*, 2006], relative to Fe/Al ratios in the range of 0.4–0.7 for North African soil dust and the upper continental crust. These suggestions are further supported by the elevated V/Mn mass ratios of the FeATMISS aerosol samples from spring 2004 and early summer 2004, relative to

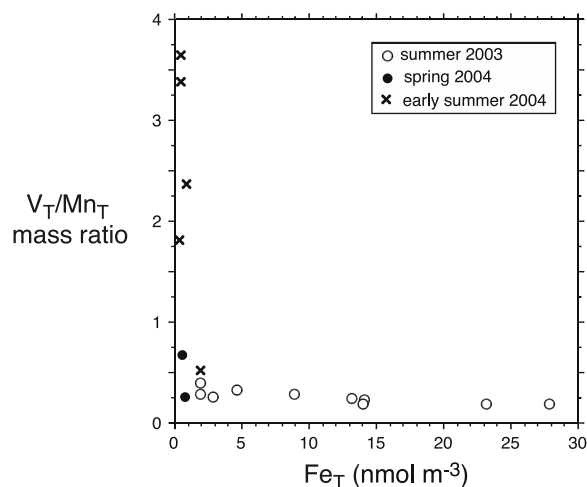


Figure 8. Mass ratio of V_T/Mn_T plotted against total iron concentration for FeATMISS aerosol samples. Open circles, summer 2003 cruise; filled circles, spring 2004 cruise; crosses, early summer 2004 cruise.

the summer 2003 samples (Figure 8), given that *Chen and Duce* [1983] have linked elevated V/Mn ratios in aerosols to “anthropogenic emissions” from North America.

[28] On the basis of the apparent correlation between the operational solubility of iron and the proportion of fuel-oil combustion products in our FeATMISS aerosol samples, we suggest that the elevated solubility of iron in WAAM-type aerosols associated with North American air masses reflects the presence of anthropogenic fuel-combustion products, which contain iron that is highly soluble relative to that contained in soil dust. We thus propose that the source-dependent composition of aerosols is a primary determinant for the solubility of aerosol iron over the Sargasso Sea, and perhaps for the solubility of aerosol iron in general. Strong support for this hypothesis is provided by the results of two recent studies. In a laboratory investigation of potential aerosol source materials, *Desboeufs et al.* [2005] found that the operational solubility of iron in both fuel-oil fly ash and urban aerosol particles was significantly higher than that for desert soils, which led them to suggest that “...in the case of regions where anthropogenic influence is particularly present, the atmospheric metals input could be significant for the marine biosphere if air masses are charged with carbonaceous matter.” Also of significance is the field-based study of *Chuang et al.* [2005], who observed that the operational solubility of aerosol iron in the east Asian atmospheric outflow was proportional to

the concentration of elemental carbon, leading them to similarly conclude that “...anthropogenic emissions, as traced by elemental carbon, appear to be strongly connected to particulate soluble Fe.” The data of *Chuang et al.* [2005] further suggest that the atmospheric concentration of soluble iron is not related to atmospheric loadings of soil dust or sulfate, thus implicating the origin of the aerosols, rather than atmospheric chemical processing, as the primary factor controlling aerosol iron solubility.

[29] As well as emissions from the burning of fuel oils, other carbonaceous combustion products are likely to contribute to the aerosol burden of soluble iron in the marine atmosphere. Chemical and toxicological studies of coal fly ash, which can contain significant proportions of iron [*Smith, 1980*], indicate that iron present in coal fly ash is more soluble, and thus more readily available to human tissues, than the iron present in soil dust [*Lighty et al., 2000; Veranth et al., 2000*]. In addition, aerosols produced by biomass burning are thought to contain iron that is more soluble than the iron present in soil dust, as demonstrated by the recent study of *Guieu et al.* [2005]. An enhanced solubility of iron in combustion aerosols, relative to soil dust, may reflect a number of factors, including the chemical association of iron with metal salts and amorphous materials rather than aluminosilicates; reactions of the aerosol particles with acidic gases produced during the combustion process; and the generally smaller size of carbonaceous combustion aerosols relative to soil dust [*Lighty et al., 2000; Veranth et al., 2000; Chuang et al., 2005; Desboeufs et al., 2005; Jang et al., 2007*]. This last point is significant because it provides a way to reconcile our hypothesis with the model of *Baker and Jickells* [2006], who posit that aerosol iron solubility is primarily determined by aerosol particle size, provided that their conceptual model is broadened to consider the role of aerosol source materials in defining the size distribution of marine aerosols.

[30] With regard to ocean biogeochemical modeling, an important implication of our hypothesis is that the wide range of aerosol iron solubility values reported in the literature may in large part be real, rather than an artifact of methodological differences. Therefore, as noted by *Baker and Jickells* [2006], discussions concerning the “correct” or “average” value for the fractional solubility of aerosol iron are moot. Instead, our results imply

that the fractional solubility of aerosol iron will vary in space and time.

3.4. Relationship Between the “Operational” and “Effective” Solubility of Aerosol Iron

[31] In section 3.2 we have shown that observed variations in the operational solubility of aerosol iron over the Sargasso Sea are explained by a simple mixing model, in which the composition and solubility of iron in the bulk aerosol reflects a conservative mixture of two distinct aerosol “types” borne by air masses from North America and North Africa, respectively. The operational solubility of iron in aerosols over other ocean regions will not necessarily follow the mixing trend shown in Figure 4, since these aerosols may be derived from sources other than those that dominate the bulk aerosol in our study region. Within this conceptual framework, a multicomponent mixing model might allow global-scale estimates of the operational solubility of aerosol iron, provided that the source functions, atmospheric transport, and solubility characteristics can be constrained for relevant aerosol end-members. However, for such estimates to be useful within the context of ocean biogeochemical models, we must be able to relate *operational* measurements of aerosol iron solubility to the *effective* solubility of aerosol iron in the surface ocean. The latter is the appropriate variable for use in biogeochemical models, because it represents the fraction of aerosol iron that contributes to the biologically available pool of dissolved iron in the surface ocean.

[32] As already discussed, a wide variety of leaching/dissolution protocols have been used to estimate the fractional solubility of iron in marine aerosols. We maintain that none of these methods (including the leaching method employed in this study) are able to faithfully mimic the dissolution of aerosol iron in the surface ocean, where effective solution/particle mass ratios are large and reaction times are long, relative to conditions that are practical in the laboratory. Implicit in the discussion of our operational solubility results is the assumption that these values provide a robust indication of the *relative* solubility of aerosol iron in the surface ocean. But how do these operational solubility measurements relate to the true or “effective” solubility of aerosol iron in the surface ocean? Our aerosol leaching protocol is based on the method of *Buck et al.* [2006], who estimated the operational solubility of aerosol iron by passing

100 mL of either deionized water or filtered seawater over filters loaded with freshly collected aerosols. For aerosols collected over the North Pacific Ocean, *Buck et al.* [2006] report that the mean operational solubility of aerosol iron for samples leached with deionized water ($9 \pm 8\%$) was not significantly different from, although slightly higher than, the mean operational solubility of iron for samples leached with filtered seawater ($6 \pm 5\%$). These workers also argue that their operational solubility estimates are likely *higher* than the long-term “net” solubility (equivalent to our definition of “effective” solubility) of aerosol iron in surface seawater, a suggestion that is not supported by the results of our study, as described below.

[33] The combined aerosol and water column iron data from our FeATMISS cruises allows us to estimate the effective solubility of aerosol iron in surface waters of the Sargasso Sea (that is, the fraction of total aerosol iron that contributes to the dissolved ($<0.4 \mu\text{m}$) iron pool in surface seawater) using a simple, mass balance approach. During the summer 2003 cruise, we observed an increase of $\sim 0.6 \text{ nM}$ in the dissolved iron concentration of surface waters over a period of 13 days, which we assume to be the cumulative result of eolian iron input [*Sedwick et al.*, 2005]. This concentration change corresponds to an increase of $\sim 12 \mu\text{mol m}^{-2}$ in the inventory of dissolved iron over the $\sim 20 \text{ m}$ depth of the surface mixed layer. Over this same period, we estimate that the total dry deposition of aerosol iron was $\sim 130 \mu\text{mol m}^{-2}$, based on a time-integrated total aerosol iron concentration of $1.33 \times 10^4 \mu\text{mol m}^{-3} \text{ s}$ [*Sedwick et al.*, 2005] and assuming a deposition velocity of 0.01 m s^{-1} for iron-bearing aerosol particles [*Arimoto et al.*, 2003]. Neglecting the wet deposition of iron, these estimates require an effective aerosol iron solubility of $\sim 9\%$ during the summer 2003 cruise. This calculation implies that the mean operational solubility of aerosol iron based on deionized water leaches ($1.5 \pm 0.8\%$) was considerably *less* than the effective solubility of aerosol iron during our summer 2003 cruise, when aerosols were dominated by FAM-type Saharan dust.

[34] A similar estimate of effective aerosol iron solubility can be made with data from our FeATMISS cruises in spring 2004 and early summer 2004. During these cruises and the intervening 4-week period, air mass back-trajectory analyses and NAAPS model simulations suggest that the aerosols in our study area were mainly composed of



Asian soil dust and North American sulfate aerosols; i.e., WAAM-type materials. During both cruises, we collected water column samples from the core of a single mesoscale cyclonic eddy, which was located to the east of the BATS site on 29–30 April 2004 (spring 2004 cruise) and, subsequently, to the southwest of the BATS site on 1–5 June 2004 (early summer 2004 cruise). Analyses of surface water samples indicate a small but analytically significant increase of ~ 0.2 nM in the concentration of dissolved iron between our late April and early June cruises, which we attribute to the cumulative deposition and dissolution of aerosol iron. This concentration change equates to an increase of $\sim 4 \mu\text{mol m}^{-2}$ in the inventory of dissolved iron in the surface mixed layer, which extended to a depth of ~ 20 m during both cruises. In the period between these two cruises, a time series of weekly bulk aerosol samples was collected at Tudor Hill, Bermuda, located roughly 200 km from our shipboard sampling sites. From analysis of these aerosol samples [Sholkovitz and Sedwick, 2006], we calculate a time-integrated total aerosol iron concentration of $2.29 \times 10^3 \mu\text{mol m}^{-3} \text{ s}$ for the period 28 April to 2 June 2004, which corresponds to a time-integrated dry deposition of $\sim 23 \mu\text{mol Fe m}^{-2}$, again using a deposition velocity of 0.01 m s^{-1} for Fe-bearing aerosols [Arimoto *et al.*, 2003]. Assuming aerosol loadings at Tudor Hill to be representative of those in our shipboard study area (see discussion by Sholkovitz and Sedwick [2006]), and neglecting wet deposition of Fe, this Fe dry-deposition estimate may be directly compared with the estimated increase in the dissolved iron inventory of the surface mixed layer between late April and early June 2004 ($\sim 4 \mu\text{mol m}^{-2}$). These estimates require an effective solubility of $\sim 17\%$ for aerosol iron over this period. Thus the mean operational solubility of iron for our spring 2004 and early summer 2004 aerosol samples ($12 \pm 5\%$) is slightly less than, but not significantly different from, our estimate of the effective solubility of aerosol iron over the period between these cruises.

[35] There are several assumptions that lend uncertainty to our preceding estimates of the effective solubility of aerosol iron. We have ignored biological uptake and scavenging of dissolved iron, processes which would remove eolian dissolved iron from the mixed layer, and we have neglected wet deposition, a process which would add eolian dissolved iron to the surface mixed layer. We have also assumed a constant dry-deposition velocity of 0.01 m s^{-1} , which has an uncertainty of at least \pm a

factor of 3 [Arimoto *et al.*, 2003] and may differ for WAAM- versus FAM-type aerosol particles (although in support of this assumption, we note that Z. Tian *et al.* (Atmospheric Fe deposition modes at Bermuda and adjacent Sargasso Sea, submitted to *Geochemistry, Geophysics, Geosystems*, 2007) report empirical estimates of 0.004 – 0.012 m s^{-1} for the deposition velocity of iron-bearing aerosols in Bermuda during spring and summer). Nonetheless, our estimates suggest that the effective solubility of aerosol iron in the Sargasso Sea is generally higher than corresponding operational solubility values, particularly for periods when aerosols are dominated by FAM-type Saharan dust. Recently, Chase *et al.* [2006] have simulated seasonal changes in the distribution of iron in surface waters of the Gulf of Aqaba (northern Red Sea) using a one-dimensional model that includes eolian deposition and dissolution, scavenging, and biological uptake, constrained by water column and aerosol iron measurements. These authors concluded that an effective aerosol iron solubility of 2% provides the best agreement with their observations, a value that is considerably lower than our estimates of the effective solubility of iron in aerosols deposited to the Sargasso Sea. However, in comparing our mass balance based solubility estimates with the results of Chase *et al.* [2006], it should be noted that the Gulf of Aqaba is immediately adjacent to several major desert dust sources, thus eolian iron fluxes are likely to be dominated by relatively large soil dust particles with solubility characteristics that are quite different from aerosols over the open ocean.

[36] Clearly, an important priority for future field studies should be to obtain additional estimates of the effective solubility of aerosol iron, with the aim of examining the relationship between the effective and operational solubility of aerosol iron. If such studies can establish a consistent, quantitative relationship between these two variables, then the effective solubility of aerosol iron could be readily estimated from operational solubility measurements.

3.5. Relative Solubility of Aerosol Iron in Wet Versus Dry Deposition

[37] Wet deposition is believed to account for significant but highly variable fractions of the total and dissolved iron that enters the surface ocean [Ginoux *et al.*, 2001; Kim and Church, 2001; Gao *et al.*, 2003; Luo *et al.*, 2003; Sarthou *et al.*, 2003]. The magnitude of these wet-deposition fluxes is highly uncertain at the regional scale, owing to a

Table 2. Iron Data for FeATMISS Rainwater Samples

Collection Date	TDFe _{rain} , nM	dFe _{rain} , nM	%Fe _{S-rain}
25 Jul 2003	137	3.38	2.47
26 Jul 2003	229	8.18	3.58
27 Jul 2003	2,430	18.4	0.76
27 Jul 2003	1,470	182	12.4
1 Aug 2003	12,300	69.4	0.57
5 Aug 2003	478	6.54	1.37
5 Aug 2003	441	15.3	3.46
4 Jun 2004	1,330	26.4	1.98
4 Jun 2004	1,090	26.0	2.37

lack of 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 this context, the soluble fraction of iron in wet deposition is an important unknown. The inorganic and organic acids present in rainwater are thought to promote the reductive dissolution of aerosol iron [Zhu et al., 1993; Pehkonen et al., 1993; Siefert et al., 1994; Spokes et al., 1994; Spokes and Jickells, 1995; Kieber et al., 2003; Hand et al., 2004]. On this basis, one might predict that the fractional solubility of iron in wet deposition to the Sargasso Sea is considerably higher than that estimated for dry aerosols at any one time. However, data from the limited number of rain samples (9) collected during our FeATMISS cruises do not support this prediction.

[38] Table 2 presents the concentrations of total-dissolvable iron (TDFe_{rain}) and dissolved iron (dFe_{rain}) in rain samples collected during the FeATMISS cruises in summer 2003 and early summer 2004, together with calculated values for the percent operational solubility of rainwater iron (%Fe_{S-rain}). The calculated %Fe_{S-rain} values range from ~0.6% to ~12%, and lie within the range of operational iron solubility estimates for aerosols collected during the FeATMISS cruises; all but one of the %Fe_{S-rain} values are less than 4% (Table 1). In Figure 9a, we compare the operational solubility of iron in rainwater with the operational solubility of iron in aerosols, for samples collected during the same 24-hour period. In most cases, the %Fe_{S-rain} values are remarkably close to corresponding %Fe_S values, with the exception of samples collected on 27 July 2003 (one rain sample has a relatively high %Fe_{S-rain} value) and 4 June 2004 (the aerosol sample has a relatively high %Fe_S value). One caveat that must be considered here is that the “total iron” concentrations of the rainwater samples (TDFe_{rain}) are unlikely to account for all of the particulate iron in these samples (see section 2.5),

therefore our calculated %Fe_{S-rain} values are likely to overestimate the relative proportion of dissolved iron in the rainwater. However, this bias is not likely to be large, since data presented by Kim et al. [1999] indicate that ~70% or more of the total iron in aerosols collected on Bermuda is solubilized after 2 weeks storage in a solution of dilute (pH 1.3) hydrochloric acid.

[39] Figure 9b shows the percent operational solubility of rainwater iron (%Fe_{S-rain}) plotted against the total-dissolvable iron concentration (TDFe_{rain}) of our rainwater samples. This figure reveals a

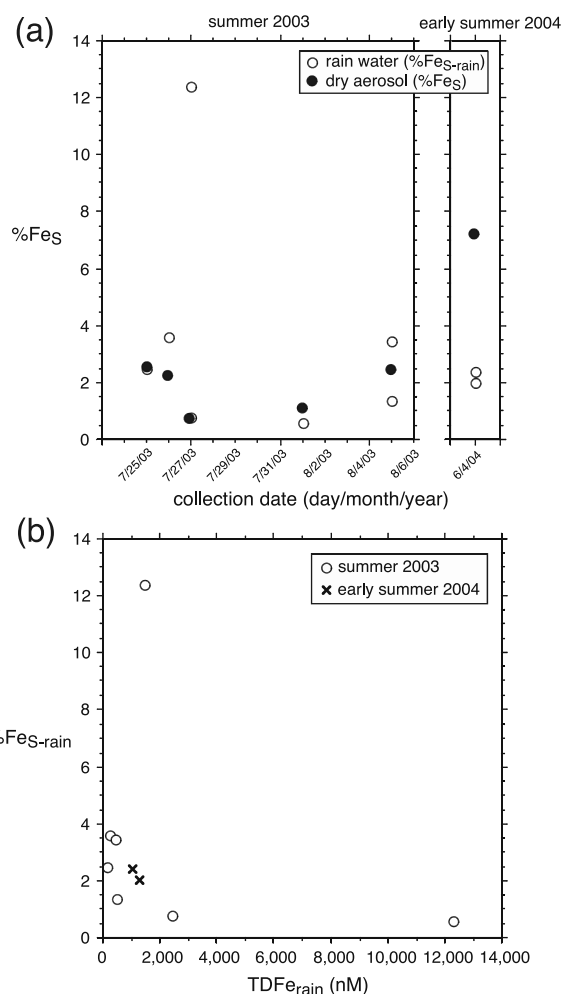


Figure 9. (a) Operational solubility of iron in rainwater (%Fe_{S-rain}) and dry aerosols (%Fe_S) collected within corresponding 24-hour periods during FeATMISS cruises. (b) Operational solubility of rainwater iron (%Fe_{S-rain}) plotted against total-dissolvable iron concentration (TDFe_{rain}) for rainwater samples collected during the FeATMISS cruises. Open circles, summer 2003 cruise; crosses, early summer 2004 cruise (no rain samples were collected during the spring 2004 cruise).

trend that resembles the operational solubility data for the FeATMISS aerosol samples (compare with Figure 3a), in that the highest %Fe_{S-rain} values tend to be associated with low TDFe_{rain} concentrations. These data suggest that aerosol composition may be the primary determinant for the solubility of aerosol iron in both dry and wet deposition to the Sargasso Sea. However, we are lacking the critical data needed to test this hypothesis, namely, estimates of %Fe_{S-rain} for rainwater associated with North American air masses. The factors controlling the solubility of iron in wet deposition thus remains an important topic for further studies.

4. Conclusions

[40] In terms of understanding the atmospheric input of biologically available iron to the surface ocean, the most significant finding of our study is a strong inverse relationship between the operational solubility of iron and the total atmospheric concentration of iron in aerosols over the Sargasso Sea. This relationship appears to reflect source-dependent differences in the solubility characteristics of aerosols carried to the Sargasso Sea, whereby the relative solubility of iron is elevated in aerosols borne by North American air masses, relative to Saharan dust. Indeed, we are able to model the operational solubility of iron in our aerosol samples as the result of a mixture of two distinct aerosol “types,” WAAM and FAM, which are associated with air masses from North America and North Africa, respectively. On the basis of compositional trends observed in historical data for aerosols collected on Bermuda and in our aerosol data from the Sargasso Sea, we infer that the elevated solubility of iron in aerosols associated with North American air masses reflects the presence of anthropogenic fuel-combustion products, which contain iron that is highly soluble relative to Saharan dust. We thus propose that the source-dependent composition of aerosol particles, specifically, the relative proportion of anthropogenic combustion aerosols, is a primary determinant for the fractional solubility of aerosol iron over the Sargasso Sea. This hypothesis implies that anthropogenic combustion emissions may play a major role in determining the fractional solubility of iron in aerosols entering the surface ocean. Noting the apparent relationship between the V/Al mass ratio and the operational solubility of iron in our aerosol samples, we are currently exploring the idea that the proportion of non-crustal V in bulk aerosols may be used to predict the relative solubility of

aerosol iron at the global scale (E. R. Sholkovitz et al., manuscript in preparation, 2007).

[41] An important corollary of our “anthropogenic iron hypothesis” is that the eolian 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 according to the source and composition of the Fe-bearing aerosols. This result is clearly illustrated by plotting the atmospheric concentration of operationally defined soluble aerosol iron (Fe_S) versus the total concentration of aerosol iron (Fe_T) for our Sargasso Sea aerosol samples (Figure 10): over a thirty-fold range in total aerosol iron concentration, there is a less than two-fold increase in the atmospheric loading of soluble iron. Such source-driven changes in the relative proportions of soluble aerosol iron might explain why the concentration of dissolved iron in Atlantic Ocean surface waters does not vary in proportion to estimated dust inputs, as noted by *Bergquist and Boyle* [2006]. *Baker et al.* [2006a] have argued that the flux of soluble iron delivered to the ocean in non-desert dust aerosols is insignificant, relative to the inputs of desert dust, which clearly dominate the total eolian iron flux to the ocean. However, this argument may need to be reconsidered in light of our data, which suggest that the relative solubility of iron in anthropogenic aerosols from North America may be more than an order of magnitude higher than that for soil dust from North Africa. If our results are generally representative of Fe-bearing aerosols at the global scale, then anthropogenic aerosols could conceivably account for a significant fraction of the eolian flux of soluble iron to the surface ocean, particularly in regions far from major soil-dust sources, such as the Southern Ocean and the South Pacific. Indeed, on the basis of their analyses of aerosols collected in southern Korea, *Chuang et al.* [2005] have argued that atmospheric loadings of water-soluble iron in the east Asian atmospheric outflow are dominated by anthropogenic aerosols over annual timescales.

[42] Interestingly, our results imply that the present-day eolian flux of soluble iron to the ocean, hence the global cycling of iron, could be quite different from conditions in preindustrial times. Anticipated increases in fossil fuel combustion during the coming decades [*International Energy Agency*, 2006] may be expected to increase the atmospheric burden of WAAM-type aerosols, whereas the transport of FAM-type soil dust to the ocean is predicted to decrease over the same period [*Mahowald and*

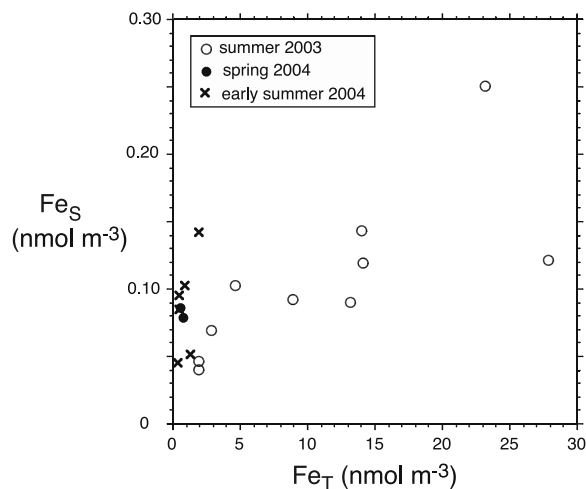


Figure 10. Atmospheric concentration of operationally defined soluble aerosol iron (Fe_S) versus total aerosol iron concentration (Fe_T) for FeATMISS aerosol samples. Open circles, summer 2003 cruise; filled circles, spring 2004 cruise; crosses, early summer 2004 cruise.

Luo, 2003; Mahowald *et al.*, 2006]. Hence continued anthropogenic fuel combustion has the potential to exert significant influences on the magnitude and spatial distribution of soluble iron fluxes to the surface ocean, with attendant impacts on oceanic biota and ocean carbon cycling.

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