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Estimation of iron solubility from observations and a global aerosol model

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[1] Mineral aerosol deposition is the dominant source of iron to the open ocean. Soil iron is typically insoluble and understanding the atmospheric processes that convert insoluble iron to the more soluble forms observed over the oceans is crucial. In this paper, we model several proposed processes for the conversion of Fe(III) to Fe(II), and compare with cruise observations. The comparisons show that the model results in similar averaged magnitudes of iron solubility as measured during 8 cruises in 2001–2003. Comparisons show that results of cases including cloud, SO₂ and hematite processing are better than the other approaches used using the reaction rates we assume in this paper; unfortunately the reaction rates are not well known, and this hampers our ability to conclusively show one process is more likely than another. The total soluble iron deposited to the global ocean is estimated by the model to range from 0.36 to 1.6 Tg y⁻¹, with 0.88 Tg y⁻¹ being the mean estimate; however there are large uncertainties in these estimates. Comparison shows that the regions with largest differences between the model simulations and observations of iron solubility are in the Southern Atlantic near South America coast and North Atlantic near Spain coast. More observations in these areas or in the South Pacific will help us identify the most important processes. Additionally, laboratory experiments that constrain the reaction rates of different compounds that will result in a net solubilization of iron in aerosols are required to better constrain iron processing in the atmosphere. Additionally, knowing what forms of iron are most bioavailable will assist atmospheric scientists in providing better budgets of iron deposited to the ocean surfaces.

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1. Introduction

[2] Iron is a critical nutrient for organisms in the ocean because of its role in primary productivity [Zhuang *et al.*, 1990]. Iron has been hypothesized to limit phytoplankton productivity in high nitrate low-chlorophyll (HNLC) ocean regions [Martin *et al.*, 1991]. In these regions, chlorophyll levels are lower than expected because low concentrations of iron restrict the growth of phytoplankton and limit primary production [Martin *et al.*, 1991]. Deposition of

iron to these regions has important implications for the CO₂ budget, as increases in iron to the oceans may result in a decrease of CO₂ in the atmosphere on glacial time scales [Watson *et al.*, 1994; Cooper *et al.*, 1996; Lefevre and Waterson, 1999]. Additionally, nitrogen fixing organisms (diazotrophs) in the ocean are thought to have higher iron requirements than most ocean biota, and the high iron inputs to the North Atlantic may be related to the high nitrogen fixation in that ocean basin [Falkowski *et al.*, 1998]. It also has been proposed that iron in marine aerosols may affect the sulfur cycle through oxidation reactions [Zhuang *et al.*, 1992] and in turn the climate feedback loop through dimethyl sulfide (DMS) oxidation and cloud condensation nuclei formation [Charlson *et al.*, 1987; Turner *et al.*, 1996].

[3] The biogeochemical processes involving iron in the ocean are thought to be dependent upon the solubility of iron, which is a function of the oxidation state of iron along with its mineralogy. On average, desert dust aerosols contain 3.5% iron [Duce and Tindale, 1991], primarily as ferric iron (Fe(III)) in aluminosilicate form [Zhu *et al.*, 1997]. This form of Fe is insoluble in high pH solutions such as seawater [Stumm and Morgan, 1981; Zhu *et al.*,

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1992]; although some studies have suggested that ocean biota can use Fe(III) [Barbeau *et al.*, 2001]. Studies of the solubility of soils suggest that, iron solubility is on average $\sim 0.6\%$ (extracted at a pH of 4.65) [Fung *et al.*, 2000; Sillanpaa, 1982], while observations show much higher iron solubilities in aerosols over the ocean [e.g., Zhu *et al.*, 1992, 1997], implying that atmospheric processing of mineral aerosols is important for increasing iron availability. Photochemical processes reducing iron to a more soluble state (Fe(II)) have been the focus of several experimental studies [Zuo and Hoigne, 1992; Pehkonen *et al.*, 1993; Siefert *et al.*, 1994; Zuo, 1995; Saydam and Senyuva, 2002]. The steady-state concentrations of Fe(II) are strongly depending on the pH of solution and the available solar radiation [Zuo and Hoigne, 1992]. The enhanced levels of Fe(II) in the fine mode as observed by Siefert *et al.* [1999] and Johansen *et al.* [2000] suggest that atmospheric transport may play a role in the size segregation of Fe(II), as large particles are selectively removed due to gravitational settling [Hand *et al.*, 2004]. It is important to note that it is not well known what forms of iron are bioavailable, and here we assume that bioavailable iron is soluble Fe(II) iron, and we show also labile Fe(II) and Fe(III) distributions.

[4] Hand *et al.* [2004] made a first attempt to model iron solubility using simple cloud processing and radiative processing schemes using a subset of the observations we use in this paper. Here we repeat the same cloud and radiative processes experiments, but also add in processing by sulfate and organic acid aerosols. Iron solubility from the model is compared with measurements of fine and coarse mode aerosol measured on-board cruise in the Atlantic and Pacific Oceans during 2001–2003.

[5] This paper is organized in five sections. Section 2 briefly describes the observations used in this study. Section 3 describes global aerosols transport model, and iron solubility model. Section 4 includes results and discussion and section 5 summarizes the results of the study.

2. Observations of Iron Solubility

[6] Measurements of iron solubility have been taken in several different ocean basins in recent years. We focus here on using eight cruises occurring between 2001 and 2003 in the Atlantic and Pacific Oceans [Chen and Siefert, 2003, 2004] for which we conduct a modeling study, but also show results from an Indian Ocean cruise from 1997, an Atlantic cruise from 1996 [Johansen *et al.*, 2000] and two Atlantic cruises from 2000 and 2001 [Baker *et al.*, 2003; Baker, 2004].

[7] For the MP01–MP09 cruises (Atlantic and Pacific cruises in 2001, 2002 and 2003) and the 1996 Atlantic cruise and 1997 Indian Ocean cruise, aerosol measurements were performed on-board using size resolved samplers to separate fine (diameter, $D_p < 3 \mu\text{m}$) and coarse ($D_p > 3 \mu\text{m}$) aerosol composition, following the method outlined in Siefert *et al.* [1999], Chen and Siefert [2004], and Johansen *et al.* [2000]. The labile Fe(II), in both the fine and coarse particles collected on the two filters, were determined by a sequential extraction procedure. These measurements were initiated immediately (within 1 hour) after sample collection in order to minimize any changes in Fe oxidation state due to possible redox reactions occurring during sample

storage. Three labile fractions of Fe were quantified using the procedure: (1) aqueous-labile-Fe(II) (Fe(II)aq,labile), (2) 5-min Ferrozine-labile-Fe(II) (Fe(II)FZ,5min), and (3) 22-hour ferrozine-labile-Fe(II) (Fe(II)FZ,22h,labile). Total labile iron Fe(II) (Fe(II) total,labile) is defined as the sum of these three fractions. Fe(II) concentrations were determined colorimetrically by complexation with ferrozine [Stookey, 1970] and subsequent absorption measurements using a portable spectrophotometer. Total Fe concentrations were measured in both the coarse and fine fractions of the atmospheric aerosol (using the filters from the HVDVI (High Volume Dichotomous virtual Impact). The method included a strong acid digestion of the aerosol samples, and subsequent analysis using inductively coupled plasma mass spectrometry (ICP-MS) with a Hewlett-Packard 4500 instrument. The same samples were also analyzed on a Perkin Elmer/Sciex 6000 ICP-MS for Fe for quality control [Siefert *et al.*, 1999].

[8] For the James Clark Ross (JCR) and Polarstern cruises in the Atlantic in 2000 and 2001, the soluble iron was measured following [Sarhou *et al.*, 2003]. The aerosol samplers were collected using high volume ($1 \text{ m}^3/\text{min}$) aerosol collectors [Baker *et al.*, 2003]. Two collectors were used to provide paired samples for trace metal (TM) and major iron (MI) analysis. The collectors were equipped with cascade impactors for size segregation of the aerosol. Results are reported in term of a size split of $1 \mu\text{m}$ (impactor stages 3 & 4 $D_p > 1 \mu\text{m}$, backup filter $D_p < 1 \mu\text{m}$), as this represents the boundary between the so-called accumulation mode particles that are generated in the atmosphere by gas-particle conversions and the coarse material whose source is mechanical (e.g. soil-derived dust, sea-spray particles) [Raes *et al.*, 2000]. Aerosol collection substrates (slotted and backup filters) were all Whatman 41 paper. Those used for TM sampling were acid-washed before use, while MI sampling was conducted with untreated substrates.

[9] Total and soluble Fe were extracted from fractions of the TM aerosol samples. Soluble Fe was extracted using an ammonium acetate leach at pH 4.7 for 1–2 hours [Sarhou *et al.*, 2003], and determined by graphite furnace atomic absorption spectroscopy (GFAAS). A strong acid (HNO_3/HF) digestion procedure followed by inductively coupled plasma – optical emission spectrometry analysis was used to determine total Fe. Major ions (including Na^+ and SO_4^{2-}) were determined by ion chromatography after extraction of a quarter of the MI filters in ultra pure water with one hour of ultrasonic agitation. Full analytical details for all these procedures can be found elsewhere [Baker, 2004]. Na^+ data were used to calculate the component of aerosol SO_4^{2-} concentrations arising from non-seasalt (nss SO_4) sources by assuming that aerosol Na^+ was derived exclusively from sea spray [see Baker, 2004].

[10] More detailed information about the methodology for measuring iron and other constituents are found in the data description papers for each cruise [Chen and Siefert, 2003, 2004; Baker *et al.*, 2005; Johansen *et al.*, 2000]. Labile iron (II and III) is operationally defined as the portion of iron, which is released after 4.2 pH leaching and after 22 hours of ferrozine addition for most of the data (except the JCR and Polarstern cruises) [Siefert *et al.*, 1999]. For the JCR and Polarstern cruises, we assume the ‘soluble Fe’ fraction is similar to the labile iron (II and III) measurement

from the other cruises. Note that these different measurement techniques may not be completely consistent. For most of our analysis, we use the consistent measurements taken during 2001–2003 of Fe(II) [Chen and Siefert, 2003, 2004].

[11] Figure 1 shows the spatial distribution of percentage iron solubility in the fine and coarse mode as observed in these limited observations, where we define iron solubility as both Fe(II)/Fe * 100 (Figures 1a and 1b) and as labile Fe (II and III)/Fe * 100 (Figures 1c and 1d). The observations show that fine mode iron solubility is higher than coarse mode solubility [e.g., Siefert *et al.*, 1999; Johansen *et al.*, 2000; Baker *et al.*, 2005]. Additionally, there is some tendency for the largest solubilities to occur far from the source areas (e.g. western tropical Atlantic, mid-latitude North and South Atlantic), consistent with atmospheric processing of the iron, or alternatively with anthropogenic sources of iron. For this study, we will assume the iron is dominantly from desert dust, similar to other studies [Mahowald *et al.*, 2005].

[12] These observations suggest high iron solubilities in regions with relatively little pollution (e.g. South Atlantic). The average percents of labile Fe solubilities (labile Fe/Fe * 100) are 10.3%, 1.34% and 7.68% for fine mode aerosols in the Atlantic, Indian and Pacific oceans respectively, and average percents of labile Fe solubility are 5.45%, 0.20% and 15.9% for coarse mode in Atlantic, Indian and Pacific ocean basin respectively for the data shown on Figure 1. Using only one consistent dataset of MP01–MP09 observed in Atlantic and Pacific Basins, the average percents of Fe(II) solubility (Fe(II)/Fe * 100) are 3.72%, and 4.50% for fine mode in Atlantic and Pacific, and 1.90% and 4.45% for coarse mode in the Atlantic and Pacific ocean basins, respectively. Observations of iron in seawater have suggested larger iron solubilities in the Pacific than the tropical Atlantic [Boyle *et al.*, 2005]. It is unclear from the aerosol data presented here whether the aerosols in the tropical Atlantic or Pacific have greater iron solubilities. Additionally, more work is necessary to deduce how the iron solubility as measured in the atmosphere (either Fe(II) or labile Fe fraction) relates to the fraction that dissolves into the ocean and/or the fraction that is bioavailable in the ocean.

[13] Sulfate or oxalate could change the solubility of iron. Laboratory studies have shown that reaction of sulfate [Zhu *et al.*, 1992] can change the solubility of iron, so we explore the relationship between iron and these compounds here. Figure 2 and Table 1 show the relationship between observed sulfate and oxalate against iron solubility defined as either Fe(II) or labile iron. Although for some cruises there are relationships, overall, across all cruises, there is no statistically significant relationship between the iron solubility and either the sulfate or the oxalate in the observations, similar to Hand *et al.* [2004]. We will explore our expected relationship from a model in a later section, and draw conclusions from the observed and modeled results of relationships between sulfate and oxalic acid. Also shown in Figure 2 are the relationships between Fe(II) and labile iron as defined in this study. The average fine mode Fe(II)/Fe ratio is 0.035 ± 0.069 , while for labile Fe/Fe the ratio is 0.075 ± 0.100 . The average Fe(II)/Fe ratio in the coarse mode is 0.015 ± 0.030 and the average labile Fe/Fe is 0.041 ± 0.073 . There is a correlation coefficient of 0.94 and 0.83

between Fe(II)/Fe and labile Fe/Fe for the fine and coarse mode, respectively. This implies that there is almost twice as much labile Fe as Fe(II), but that the solubility defined as either Fe(II)/Fe or labile Fe/Fe seem to vary spatially and temporally together (see Figure 3).

[14] Correlations between observed Fe(II)/Fe vs Fe are -0.24 , and 0.16 for fine and coarse mode respectively, suggesting that there is no clear relationship between soluble iron fraction and total iron. Figure 4 shows the cruise tracks for the 2001–2003 cruises used in the model-data comparison, and Table 2 shows the time period for each cruise.

3. Model Description

[15] The chemical transport model used to simulate aerosols and dust is the Model of Atmospheric Transport and Chemistry (MATCH, version 4.2) [Rasch *et al.*, 1997], driven by NCEP analysis dataset [Kistler *et al.*, 2001; Mahowald *et al.*, 1997]. The horizontal resolution of the model is T62 ($\sim 1.9 \times 1.9$ degree), and 28 vertical levels from surface to 10 mb (the same as the resolution of the NCEP reanalysis made available at NCAR).

3.1. Aerosol Model Description

[16] The mineral aerosols sources are calculated using the Desert Entrainment And Deposition (DEAD) model [Zender *et al.*, 2003]. This mobilization scheme is based on the wind tunnel and in situ studies of Iversen and White [1982], Marticorena and Bergametti [1995], Gillette *et al.* [1997], and Fecan *et al.* [1999]. It is similar to those used in Tegen and Fung [1994], Mahowald *et al.* [1999], Guelle *et al.* [2000], Ginoux *et al.* [2001], and Tegen *et al.* [2002] in that it is based on a wind threshold velocity and has a wind speed cubed relationship for dust mobilization, but the details of the mobilization are slightly different in each case. The DEAD module mobilization scheme [Zender *et al.*, 2003] is based on the friction velocity (wind stress at the surface), consistent with the original derivations [e.g., Gillette and Passi, 1988]. The wind stress is a function of the wind speed, roughness length and the atmospheric stability at the surface. The surface roughness length in dust producing regions is set to the globally uniform value of 100 μm , a value typical of erodible soil beds [Gillette *et al.*, 1997] than the large-scale roughness lengths for bare ground (~ 5 cm) used in general circulation models [e.g., Bonan, 1996]. The mass flux of saltating particles depends on the excess of the wind friction speed over the threshold wind friction velocity for saltation. More details about the source parameterizations are available in Zender *et al.* [2003] and Luo *et al.* [2003]. In this study, we follow Ginoux *et al.* [2001], Zender *et al.* [2003], and Mahowald *et al.* [2002], and assume that all topographic lows with little vegetation and low soil moisture are dust sources, using the time independent source area from Ginoux *et al.* [2001], which includes only non-vegetated low-lying regions. There is some debate about the anthropogenic sources of desert dust [e.g., Prospero *et al.*, 2002; Mahowald *et al.*, 2002; Luo *et al.*, 2003; Mahowald and Luo, 2003; Mahowald and Dufresne, 2004; Tegen *et al.*, 2004], however modeling studies have indicated the low sensitivity of downwind concentrations to the exact location of sources

Figure 1. Observations of iron solubility in percentages, defined as $\text{Fe(II)}/\text{Fe(total)} * 100\%$ and Labile $\text{Fe}/\text{Fe(total)} * 100\%$, from the cruises described in the text.

Figure 2. Scatterplots showing the relationship between observed iron solubility (defined as $\text{Fe(II)}/\text{Fe(total)} \times 100\%$ and $\text{Labile Fe}/\text{Fe(total)} \times 100\%$) and observed SO_4 and oxalate for fine and coarse mode aerosols, and the relationship between Fe(II) and labile Fe. Stars represent Atlantic cruises and rectangles represent Pacific cruises.

[e.g., Mahowald *et al.*, 2002; Luo *et al.*, 2003]. We chose a globally constant particle size distribution; the fractions are 0.1 for the class $0.1\text{--}1\text{ }\mu\text{m}$, and .3 for the classes $1\text{--}2.5$, $2.5\text{--}5.0$, and $5.0\text{--}10\text{ }\mu\text{m}$, where the sizes are diameters of the particle. Within each bin we assume log normal distributions in aerosol sizes [Zender *et al.*, 2003].

[17] Both dry deposition and wet deposition are included as loss processes for all aerosols [Rasch *et al.*, 1997]. Dry depositional processes for dust aerosol are simulated following Seinfeld and Pandis [1996] and include turbulent

deposition and gravitational settling, with the latter dominating for large particles.

[18] The model also simulates sources, simple chemistry and deposition of sulfur aerosols, carbonaceous aerosols, and sea salt aerosols [Barth *et al.*, 2000; Rasch *et al.*, 2000]. Emissions of sulfur species in the model include anthropogenic emissions of SO_2 and SO_4 and oceanic emissions of dimethyl sulfide (DMS). Anthropogenic emissions were obtained from the Global Emissions Inventory Activity (GEIA) emission inventory [Benkovitz *et al.*, 1996], which

Table 1. Correlation Between Observed Sulfate, Oxalate, and Observed Iron Solubility for Each of the Cruises^a

Cruise	nss-SO ₄ ~ Fe(sol) Fe(II)/Fe		Oxalate ~ Fe(sol) Fe(II)/Fe		nss-SO ₄ ~ Labile Fe/Fe		Oxalate ~ Labile Fe/Fe	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Atlantic	0.29	0.43	−0.16	−0.06	0.20	0.3	−0.16	−0.07
MP01	0.18	0.17	−0.09	0.26	0.10	0.045	−0.17	0.20
MP03	−0.17	−0.02	−0.11	−0.28	0.16	−0.15	−0.11	−0.17
MP08	−0.21	0.89	−0.15	0.75	−0.41	0.8	−0.42	0.6
Pacific	0.55	−0.37	−0.035	0.17	0.5	0.17	−0.06	0.14
MP02	0.62	—	−0.15	0.75	0.86	—	−0.13	0.69
MP05	−0.3	—	0.36	0.58	−0.14	—	0.34	0.35
MP06	0.79	0.21	0.49	0.56	0.65	0.20	0.39	0.55
MP09	−0.003	0.55	0.78	−0.21	−0.07	−0.52	0.54	−0.21
Overall	0.36	0.36	−0.10	−0.01	0.25	0.2	−0.12	0.012

^aDashes indicate no data; the nss-SO₄ coarse mode related correlations may not be meaningful, since there are fewer data points. Values in bold are significant at 95%.

is representative of 1995 emissions. Distributions of oxidant species (e.g. OH, H₂O₂ and O₃) come from climatologies [Rasch *et al.*, 2000].

3.2. Iron Solubility Model Description

[19] In this paper we simulate the processing of the atmospheric iron to become more soluble using several different approaches. None of these approaches are well constrained, and thus the reaction coefficients have large uncertainties, which may bias or change the results of this study. We try to show here the spatial and temporal distributions associated with different iron processing hypothesis. Insoluble iron becomes more soluble through radiation, cloud, or chemical reactions. $d[\text{Fe(II)}]/dt = k[\text{Fe(III)}]$, where k is rate constant of insoluble iron to soluble

iron, and will be discussed for different processes. The chemical reactions of iron are very complex, and not well known, which will limit our ability to conclusively decide which mechanisms appear to dominate in the real atmosphere. Here we separate out mechanisms (photolysis, clouds, sulfur processing) that may be operating at the same time in order to understand the relative importance.

3.2.1. Radiation Processing (RP)

[20] To estimate the effects of exposure to solar radiation on iron solubility, we assume that exposing insoluble iron to available solar radiation will result in some conversion to soluble iron during daylight hours as suggested by Siefert *et al.* [1997] and Zhu *et al.* [1997]. The possible reaction could be $\text{Fe(III)} + \text{H}_2\text{O} \xrightarrow{h\nu} \text{Fe(II)}$. In this case we assume there is plenty of water and acidity, but that incoming solar

Figure 3. Observed Fe(II) percentage of iron ($\text{Fe(II)/Fe} \times 100$) compared to labile iron percentage ($\text{labile Fe/Fe} \times 100$). The X-axis represents each cruise observation taken as part of the cruises shown in Figure 4.

Figure 4. Cruise tracks for the MP01–MP09 observations used for the extensive analysis in the paper.

Table 2. Time Periods of Each Cruise

Cruise	MP01 (Atlantic)	MP02 (Pacific)	MP03 (Atlantic)	MP05 (Atlantic)	MP06 (Pacific)	MP08 (Pacific)	MP09 (Pacific)	Polarstern and JCR
Time period	1/6/01 – 2/18/01	4/9/01 – 4/26/01	6/26/01 – 8/15/01	7/1/02 – 7/16/02	9/23/02 – 10/15/02	4/18/03 – 5/20/03	8/6/03 – 8/20/03	10/10 – 10/18, 2000, 9/12/01 – 10/21/01
Reference	<i>Chen and Siefert</i> [2003, 2004]	<i>Chen and Siefert</i> [2003, 2004]	<i>Chen and Siefert</i> [2003, 2004]	<i>Chen and Siefert</i> [2004]	<i>Chen and Siefert</i> [2004]	<i>Chen and Siefert</i> [2004]	<i>Chen and Siefert</i> [2004]	<i>Baker</i> [2004]

radiation is the main limiter. There were no reaction rates based just on photolysis, in the literature, so we used our observations to make estimates [Hand *et al.*, 2004]. To find an observationally based e-folding decay time scale, we assumed a transport time of 14 days for mineral aerosols to travel across the Atlantic Ocean from desert dust source in Africa to the western Atlantic cruise locations [e.g., Husar *et al.*, 1997], where there is an average iron solubility of 2–20% (which means that 98–80% of the Fe stays as Fe(III)). Assuming a linear decay rate (equation (1)):

$$A(t) = A(t=0) \cdot \exp(-t/\tau_{OBS}) \quad (1)$$

where $A(t)$ is the Fe(III) concentration of a parcel, t is the transit time, and τ_{OBS} is the estimated decay lifetime, we can deduce a decay time scale of approximately 300 days, if we assume that 95.5% of the iron stays as Fe(III) over the 2 week transit time. To make this time scale greater with stronger isolation, we make the decay rate vary with incoming solar radiation (K_{SR}), following equation (2):

$$K_{SR}(i,j) = \frac{F_{ij}}{F_{avg}} / \tau_{OBS} \quad (2)$$

where F_{ij} is the shortwave flux at the surface at every location, and F_{avg} is the global mean shortwave flux (535.25 W m^{-2}). $K_{SR}(i,j)$ is then used in the model as the first order decay constant for insoluble iron at location i,j . Any Fe(III) lost in from this decay constant is assumed to be converted to Fe(II), or soluble iron.

3.2.2. Cloud Processing (CP)

[21] We estimate the effects of cloud processing on soluble iron by assuming that when insoluble iron came into contact with a cloud, conversion to soluble iron occurs [Siefert *et al.*, 1997; Saydam and Senyuva, 2002]. This case assumes that the clouds are always sufficient acidic to process the iron to become more soluble, and the important process to model is whether the iron is in a cloud or not. The decay rate (K_{cld}) was computed with equation (3):

$$K_{cld}(i,j) = \frac{C(i,j)}{C_{avg}} / \tau_{OBS} \quad (3)$$

where $C(i,j)$ represents the fraction of a grid box that is cloudy in the model at each level, and C_{avg} is the average fraction in the tropics around 10°N ($C_{avg} = 0.05$). (=0.05). We picked the tropical cloud fraction because of that is the area of most of the dust transport.

3.2.3. SO₂ Heterogeneous Reaction on Dust Processing (SO₂P)

[22] Sulfur reactions with iron can be important in modifying the iron oxidation state. [e.g., Zhu *et al.*, 1992]. We use several approaches to model the sulfur-iron interactions. In this approach, we assume that the Fe(III) to Fe(II) conversion rate is proportional to the SO₂ heterogeneous reaction rate on the dust surface (equation (4))

We used the method of Dentener and Crutzen [1993] to calculated the SO₂ heterogeneous reaction rate in each grid box (K_{SO_2}):

$$K_{SO_2} = \left(\frac{r}{D_g} + \frac{4}{v\gamma} \right)^{-1} A \quad (5)$$

where r is the dust particle radius, v is the mean SO₂ molecular speed, γ is the reaction probability, and D_g is gas phase diffusion coefficient. A is dust particle surface area, which calculated by

$$A = V \frac{\int_0^\infty 3r^2 (dN/dr) dr}{\int_0^\infty r^3 (dN/dr) dr} \quad (6)$$

where N is aerosol number concentration, V is aerosol volume fraction ($\text{cm}^3 \text{ aerosol} / \text{cm}^3 \text{ air}$), assuming all sulfate to be present as ammonium bisulfate, which is calculated by

$$V = \frac{\chi \cdot D_{air} \cdot M_w}{Avog \cdot \rho_{aerosol}} \quad (7)$$

where χ is volume mixing ratio of sulfate, D_{air} is air density (molecules cm^{-3}), M_w is molecular mass of ammonium bisulfate (g mol^{-1}), $Avog$ is Avogadro's number ($6.0 \times 10^{23} \text{ molecules mol}^{-1}$), and $\rho_{aerosol}$ is the specific aerosol density (g cm^{-3}). The dust size distribution was assumed to be log-normal [Zender *et al.*, 2003]. The reaction rate between Fe(III) and SO₂ is calculated at every gridbox and time step, and then the insoluble iron, the soluble iron, and the SO₂ and SO₄ are updated.

3.2.4. SO₄ Heterogeneous Reaction on Dust Processing (SO₄P)

[23] In this approach, we assume that the rate converting Fe(III) to Fe(II) is proportional to the sulfate concentration ($Fe(III) + H_2O \xrightarrow{SO_4} Fe(II)_{aq}$). Here we are assuming that the acidity associated with existing sulfate is the limiting process, but we do not know the limit reaction rate. We applied the e-folding timescale of 300 days that fell within the range of values observed in the measurements as calculated in Hand *et al.* [2004], but allowed it to vary with different sulfate conditions. The rate was computed by equation (8):

$$K_{SO_4}(i,j) = \frac{C(i,j)}{C_{avg}} / \tau_{OBS} \quad (8)$$

where $K_{SO_4}(i,j)$ in units of s^{-1} is calculated at every grid point (i,j) in the model, $C(i,j)$ is the sulfate concentration at each grid point, and C_{avg} is the global mean sulfate concentration. Again, this allows us to estimate a reaction rate dependent on sulfate concentrations that will be roughly consistent with the observations when there are no available reaction rates in the literature.

3.2.5. Organic Acid Reaction Processing (ORGP)

[24] Organic acid species effects on the enhancement of soluble iron could be significant [e.g., Zuo and Hoigne, 1992; Zhu *et al.*, 1993; Pehkonen *et al.*, 1993; Siefert *et al.*, 1994; Zuo, 1995]. In this approach, we assume that the reaction rate converting Fe(III) to Fe(II) is proportional to the organic acid species concentrations. Since there are no organic acids in the model simulation, we used the organic carbon aerosol as the surrogate. In the model these aerosols are released from industrial activities as well as biomass burning. We again applied an e-folding timescale of 300 days from Hand *et al.* [2004]. The rate of conversion

Figure 5. Total Fe concentration comparison between model results (black line) and observations (red line). The X-axis represents each observation taken as part of the cruises shown in Figure 4, similar to Figure 3.

from insoluble to soluble iron by organic acids (K_{org}) was computed by equation (9):

$$K_{\text{org}}(i,j) = \frac{C(i,j)}{C_{\text{avg}}} / \tau_{\text{OBS}} \quad (9)$$

where $C(i, j)$ is the organic carbon concentration at each grid, and C_{avg} is the global mean organic carbon concentration.

3.2.6. Hematite Reaction Processing (HP)

[25] Meskhidze *et al.* [2003] argue using an aerosol equilibrium box model that the acidity of the aerosol is critical to the conversion of Fe(III) to Fe(II), and that anthropogenic sulfate plays an important role in modulating acidity in the Pacific. In order to test their hypothesis in a global model, we simplify the reactions considerably, looking only at hematite in dust as a source of iron, and simplify

Figure 6. Total Al comparison between model results (black line) and observations (red line), similar to Figure 5.

Figure 7. SO₄ and oxalate comparisons between model results (black line) and observations (red line), similar to Figure 5.

our alkalinity calculation considerably. Following their hypothesis, we implement a mass balance equation for dissolved Fe (equation (10)):

$$\frac{d[Fe(II)]}{dt} = W(Fe_{hem}) \cdot R_{hem} \cdot [dust] \quad (10)$$

where $[Fe(II)]$ is the soluble concentration, $[Dust]$ is the mass of the mineral aerosol (g/g), WFe_{hem} is the number of moles of Fe in a mole of hematite (2); and R_{hem} is the hematite dissolution rate (moles of dissolved hematite (g of dust)⁻¹ s⁻¹). For, R_{hem} , we adopt the formulation of *Lasaga et al.* [1994], similar to *[Meskhidze et al., 2003]* (equation (11)):

$$R_{hem} = K_r(T) \cdot a(H^+)^m \cdot f(\Delta G_r) A_{hem} W_{hem} \quad (11)$$

where K_r is the temperature (T) dependent reaction coefficient (moles dissolved m⁻² of mineral s⁻¹), $a(H^+)$ is the H⁺ activity, m is an empirical parameter, f is a function of Gibbs free energy (ΔG_r), and accounts for the variation of the rate with deviation from equilibrium *[Cama et al., 1999]*, A_i is the specific surface area of mineral aerosols in units of m² g⁻¹, and W_i is the weight fraction of the mineral in dust in units of g of mineral (g of dust)⁻¹. $f(\Delta G_r) = 1$ was used in our simulation. Values for hematite are $m = 0.5$; $A_i = 100$ (m²/g); and $W_i = 5\%$; while reaction coefficient K_r depend on the total amount of the hematite already dissolved, following *[Meskhidze et al., 2003; Azuma and Kametani, 1964; Blesa et al., 1994; Cornell and Schwertmann, 1996; Zinder et al., 1986; Skopp, 2000]*:

Stage I (0 to 0.8% of total oxide dissolved)

$$K_r = 4.4 \times 10^{-12} \exp[9.2 \times 10^3(1/298 - 1/T)]$$

Stage II (0.8 to 40% of total oxide dissolved)

$$K_r = 1.8 \times 10^{-11} \exp[9.2 \times 10^3(1/298 - 1/T)]$$

Stage III (40 to 100% of total oxide dissolved)

$$K_r = 3.5 \times 10^{-12} \exp[9.2 \times 10^3(1/298 - 1/T)]$$

(12)

[26] For the pH value calculation, we simply set pH = 7.5 when concentration of Ca is larger than the concentration of SO₄ concentration, and pH = 2 when concentration of SO₄ is larger than the concentration of Ca, and assume that 6% of dust is soluble Ca. K_r was calculated depending on the amount of hematite dissolved and temperature.

4. Results and Comparisons

4.1. Aerosol Model-Data Comparisons

[27] The dust model used for the simulations here has been extensively compared to available observations for mean *[Luo et al., 2003]*, interannual variability, and event behavior *[Hand et al., 2004]*. We use a slightly different wet deposition scheme than in previous simulations *[Rasch et al., 2000]*, which impacts slightly our simulations, especially the seasonality over the Pacific Ocean. The model/data comparison shown in Figure 5 (and following figures) shows the observations and models as time series in time order. The cruise tracks shown in Figure 4 indicate where each cruise takes place, while Table 2 shows the time period for each cruise. Overall, the model does a good job in simulating the spatial and temporal variability of desert dust. Iron in mineral aerosols from the model and observations for the cruises is shown in Figure 5. Over 4 orders of magnitude the model does a good job of simulating the spatial and temporal variability, except for MP09. It is unclear why the model is unable to capture the MP09 cruise, perhaps due to errors in the sources of iron (either different dust sources, or and anthropogenic source of iron) or transport. The mean Fe concentration in the fine mode is 137 and 410 ng m⁻³, for the observations and model results, respectively; and in the coarse mode 112 and 130 ng m⁻³, for the observations and model results, respectively. As previously shown, the model over predicts the fine mode dust *[Hand et al., 2004]*. The correlation coefficient between the model and observations is 0.67 and 0.44 in the fine and coarse mode, respectively, suggesting that there are discrepancies in the simulation, but that the model on

Figure 8. Soluble iron (Fe(II)) comparisons between model results (black line) and observations (red line), for each of the different processes described in the text. The number on X-axis represents cruise number.

Table 3. Correlation of Soluble Fe (Fe(II)) Between Model Simulation and Observation for All Cruises^a

	Mean (f)	Std. Dev. (f)	R	Mean (c)	Std. Dev. (c)	R
Obs	1.95	3.52		0.74	1.48	
CP	6.69	10.13	0.49	1.85	2.96	0.23
RP	7.47	11.35	0.46	2.06	3.46	0.13
SO ₂ P	4.99	9.53	0.60	0.16	0.27	0.25
SO ₄ P	19.16	33.89	0.19	5.88	12.04	0.0089
HP	0.71	0.88	−0.094	0.23	0.34	−0.035
ORGP	25.24	63.84	0.58	5.18	12.56	0.48

^aUnits are in ng m^{-3} . Values in bold are significant at 95%.

the whole is capturing the spatial and temporal variability accurately.

[28] Figure 6 illustrates the comparison between observed Al and model calculated Al. Model Al was calculated by assuming 7.5% of dust mass. It can be seen that the model reproduces the Al for MP01, MP02, MP03, and over-predicts the observation for MP05, and under-predicts for MP08 and MP09. The fine mode Al concentrations are 273 and 776 ng m^{-3} for the observations and model simulation, respectively. The correlation coefficient between the model and observations for fine mode is 0.59. The coarse mode mean Al concentrations are 227 and 246 ng m^{-3} , for the observations and model simulation, respectively. The correlation coefficient for coarse mode between model and observations is 0.28. It is unclear why the model tends to do a worse job simulating Al concentrations than total Fe. Overall the ratio of Fe/Al is thought to be constant within a factor of 2 [Mahowald *et al.*, 2005].

[29] Figure 7 shows nss-SO₄ and oxalate comparisons between model simulations and observations of each cruise. Notice that we used organic carbon aerosol as substitute for oxalate in the model calculation. The overall correlation of nss-SO₄ between model and observation are 0.22, and are 0.11, 0.33, 0.42, −0.082, −0.029, 0.55, −0.34 for MP01, MP01, MP02, MP03, MP05, MP06, MP08, MP09 each cruise, respectively. These comparisons suggest less ability to simulate sulfate than desert dust for these cruises. The overall correlation of oxalate between observation and model is −0.047. The model over-predicts oxalate for MP01, MP02, MP03, and MP09 and the over-prediction in the Atlantic during MP01 and Pacific during MP09 are very large. This suggests that our assumption that organic carbon aerosols can be a proxy for oxalate is not good; we include the case for completeness, but this implies our simulation will be biased.

4.2. Soluble Iron and Iron Solubility Comparison

[30] Modeled Fe(II) compared with observations is shown in Figure 8. Much of the 3 order of magnitude differences in Fe(II) is captured, similar to that of total Fe. Correlation coefficient for each process is shown in Table 3, suggesting that most of the different atmospheric processing mechanisms result in simulations that have statistically significant correlations with the observations, with the exception of SO₄P and HP. The model simulations tend to do better in the fine than the coarse mode.

[31] Figure 9 compares the modeled and observed iron solubility at specific points along the cruise track. The overall mean and correlation coefficients for the cruise

tracks are shown in Table 4. In terms of the overall average iron solubility (Fe(II)/Fe * 100), the organic acid processing (ORGP) or radiative processing (RP) cases seem to do the best. But the correlation coefficients are only statistically significant for the cloud processing (CP) and the sulfur dioxide processing (SO₂P) cases, and these correlations are low (0.20–0.24). Again, the model seems to capture the processing of fine particles better than coarse particles, which may be due to differences in conversion rate between fine and coarse particles, due either to differences in the surface area/volume ratios, or due to differences in chemical or mineralogical composition of different sized particles. Note that the statistically significant negative correlations, and the not statistically significant correlations between the model and observations suggest that the model is not able to capture the soluble iron processes well in these regions. Tables 5 and 6 show the mean solubility and correlations in solubility for each of the cruises and processes. It can be seen that no one processing can reproduce iron solubility well for all cruises. For the Atlantic, the CP or ORGP cases do the best capturing the overall average, but note that in the Atlantic, the model is over-predicting organic acids by a large margin (Figure 7), implying that this correspondence between model and observations is not for the right reasons. In the Pacific, the RP or HP cases do the best in predicting the overall average solubility iron. Table 6 shows that the CP and SO₂P processing tend to do better than other cases if we look at correlation coefficients. The overall correlations for cloud processing and SO₂ processing are around 0.19–0.24 for fine mode and 0.13–0.22 for the coarse mode. Table 6 shows that overall correlations are better in Atlantic than in Pacific especially for cloud process and SO₂ process. There is no single process that works best in both basins for all metrics.

[32] Above we study the single processing of iron conversion, but the conversion of iron could be due to multiple processes. Here we explore some combinations of processes for MP01–MP08. We simply allow both processes to occur at the same time using the equations described in section 3, but do not link the processes. We tested SO₂P + RP, RP + HP, SO₂P + HP, SO₂P + CP and CP + HP, because analyses show SO₂P, RP, HP, and CP each single process has a relative higher correlation between model and observation comparing with other processes. Figure 10 and Table 7 show the daily iron solubility and correlations between model simulation and observations for the mixed processes. It can be seen that the correlations of coupled SO₂P + CP, and CP + HP are higher than other processes. This is consistent with cloud processing and acidity playing a role

Figure 9. Percent iron solubility ($\text{Fe(II)/Fe} \times 100$) comparisons between model results (black line) and observations (red line), for each of the different processes described in the text. The number on X-axis represents cruise number.

Table 4. Correlation of Iron Solubility (%) Between Model Results and Observed Concentrations for All Cruises^a

Case	Mean (Fine)	Std. Dev. (Fine)	R (Fine)	Mean (Coarse)	Std. Dev (Coarse)	R (Coarse)
OBS	5.08	8.44		4.20	11.31	
RP	3.42	1.68	0.07	2.95	1.42	0.15
CP	6.34	4.79	0.24	5.67	4.38	0.22
SO ₂ P	1.67	1.04	0.20	0.23	0.18	0.13
SO ₄ P	9.88	6.88	0.03	8.48	6.29	0.11
HP	2.78	3.15	0.09	2.37	2.84	0.10
ORGP	4.57	3.79	−0.01	3.86	3.82	0.09

^aValues in bold are significant at 95%.

in the processing of atmospheric iron. It can be seen that mean solubility and correlations are better for mixed processes than single process, even though we have not tuned our coefficients in any way. Table 8 shows the iron solubility for mixed processes for each cruise and compared with observations. It can be seen that for the overall mean, the SO₂P + RP and RP + HP cases are better than other mixed processes. The SO₂P + HP case under-predicts iron solubility and SO₂P + CP and CP + HP cases over-predict iron solubility.

[33] In order to compare the importance of different processes in different regions and different seasons, the normalized iron solubility were calculated. The normalized iron solubility was defined as the regionally and seasonally averaged ocean iron solubility divided by global annually averaged ocean iron solubility (Figure 11). Nine ocean regions, North Pacific (10°N–40°N, 155°E–180°E, 140°W–180°W), South Pacific (40°S–10°S, 155°E–180°E, 140°W–180°W), Equatorial East Pacific (10°S–10°N, 80°W–155°W), North Atlantic (10°N–40°N, 10°W–60°W), South Pacific (40°S–10°S, 10°W–60°W), Caribbean Sea (10°N–20°N, 60°W–90°W), Arabian Sea (0°–20°N, 50°E–70°E), Indian Ocean (30°S–20°N, 60°E–100°E), and South Ocean (70°S–55°S, 0°–180°E, 0°–180°W), were calculated. Because the reaction rates given in section 3.2 are very uncertain, but perhaps the processes are correct, we can use these normalized solubilities to examine when and where each process is most effective. It can be seen from Figure 11 that the normalized iron solubility is higher in Pacific (North Pacific, South Pacific, and Equatorial East Pacific) than in other ocean regions for all processes. Cloud processing is the most able to process iron in the Southern Ocean. There are seasonal differences in the different processes, such as a higher HP or SO₄P

conversion rate during the summer time in the North Pacific than other seasons. The highest season for conversion of iron solubility in the Arabian Sea is the fall for the SO₂P, SO₄P and HP processes. The differences obviously have to do with higher relative reaction rates for the processes. For example, there are more clouds in the North Pacific than North Atlantic downwind of the dust sources, since for the North Pacific, the dust is being transported in the storm track, but farther south in the subtropics for the North Atlantic deposited dust.

4.3. Global Implications

[34] Annual averaged global surface maps of iron solubility for 6 processes are shown in Figure 12. Figure 12 illustrates that the lowest values of iron solubility occur close to source regions, consistent with low solubility of crustal sources. The fine mode percent solubility is higher than the coarse mode globally except near source regions where it is roughly the same, due to the shorter lifetimes of larger particles (since we have no size segregated differences in processes). This means that the observation of higher solubility in fine mode aerosols than coarse mode aerosols could be simply explained by the longer lifetime [Hand *et al.*, 2004]. There is higher solubility in the Northern Hemisphere than the Southern Hemisphere in cases SO₂P, SO₄P and ORGP, consistent with the large gradients in emissions of anthropogenic compounds these processes rely on. Solubilities in the cases of RP, and HP tend to be highest in the tropical Pacific Ocean, and smaller close to source regions and increase slightly as you move to the high latitudes. For the CP case, the solubilities are smallest close to the source regions, and increase as one moves to higher latitudes. We have only two cruises which extends from the high to low latitudes in both the Northern

Table 5. Iron Solubility (%) Comparison for Each Cruise and Each Process

Cruise	Obs		CP		RP		SO ₂ P		SO ₄ P		HP		ORG	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine		Fine	Coarse	Fine	Coarse	Fine	Coarse
<i>Atlantic</i>	5.84	4.44	5.28	4.59	2.81	2.38	1.43	0.18	7.51	6.46	1.81	1.50	5.57	4.57
MP01	6.62	5.08	3.11	3.37	1.84	1.69	1.50	0.14	2.78	2.49	0.44	0.52	8.90	7.02
MP03	2.38	0.17	4.79	3.46	3.40	2.72	1.51	0.19	10.56	8.78	1.91	1.31	3.87	3.08
MP08	4.19	2.73	5.64	4.94	3.26	2.76	1.82	0.24	9.16	7.58	2.19	1.70	6.18	5.24
<i>Pacific</i>	4.32	3.94	10.35	9.56	4.94	4.26	2.44	0.41	16.15	14.56	5.53	4.93	2.48	2.01
MP02	1.66	0.50	10.56	9.11	3.67	3.06	2.09	0.37	9.68	8.11	1.13	0.98	3.69	2.85
MP05	6.60	4.63	9.52	8.87	5.49	4.88	2.02	0.34	16.21	15.04	6.19	5.29	1.97	1.69
MP06	8.49	7.57	10.22	9.88	4.30	4.06	4.17	0.66	18.21	16.72	6.19	5.67	1.79	1.59
MP09	0.53	3.08	11.10	10.39	6.30	5.03	1.49	0.27	20.49	18.37	8.64	7.80	2.47	1.91
<i>Avg</i>	5.08	4.20	7.80	7.08	3.84	3.32	1.94	0.29	11.87	10.51	3.67	3.22	4.03	3.29

Table 6. Correlation of Iron Solubility for Each Cruise Between Observations and Model Simulations^a

Cruise	CP		RP		SO ₂ P		SO ₄ P		HP		ORGP	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Atlantic	0.33	0.19	0.16	0.12	0.28	0.17	0.11	0.09	0.19	0.09	0.03	0.21
MP01	0.41	0.037	0.42	0.22	0.29	0.11	0.63	0.31	0.28	0.03	−0.04	0.20
MP03	0.31	0.66	0.24	0.48	0.16	0.59	0.09	0.22	0.31	0.50	0.13	0.25
MP08	0.25	0.11	0.15	0.09	0.26	0.12	0.11	0.052	0.21	0.10	0.26	0.15
Pacific	0.03	0.32	−0.08	0.19	−0.04	0.05	−0.12	0.14	−0.12	0.04	− 0.29	0.17
MP02	− 0.23	−0.019	−0.10	0.049	0.24	−0.063	0.21	0.22	−0.06	0.095	0.17	−0.068
MP05	− 0.44	0.26	− 0.25	− 0.22	0.22	0.11	− 0.39	− 0.77	− 0.22	− 0.47	0.08	0.1
MP06	0.17	0.25	−0.07	0.048	0.11	−0.06	− 0.26	−0.13	− 0.31	−0.18	− 0.46	− 0.26
MP09	0.44	0.18	− 0.59	0.18	−0.02	−0.04	− 0.58	0.13	− 0.65	0.09	0.59	−0.09
Overall	0.24	0.22	0.072	0.15	0.19	0.13	0.033	0.11	0.089	0.098	−0.01	0.093

^aValues in bold are significant at 95%.

and Southern Hemisphere and measured labile iron (the JCR and Polarstern cruises shown in Figures 1c and 1d), and these cruises show roughly symmetric solubilities about the equator, more consistent with CP. Note that we are assuming here that all the iron comes from dust particles—soluble iron may come from industrial processes as well. However, one would assume that anthropogenic soluble iron would be proportional to anthropogenic emissions of other compounds (sulfur dioxide, fossil fuel carbon dioxide) and thus would be larger in the Northern Hemisphere than the Southern Hemisphere. This is not seen in the limited observational data.

[35] Spatial distributions of mixed processes are shown in the Figure 13. Whether the north-south gradient typical of SO₂P, SO₄P or ORGP cases dominates or the symmetric solubilities of RP, CP or HP dominates depends on the relative reaction rates used, which are not well known. If both SO₂P and CP are operating, for example, we can have a simulation of solubilities that is symmetric about the equator, consistent with the limited observations we have.

[36] Finally we look at the relationships between sulfate and organic aerosols and iron solubility in the model in these different cases. In section 2 we examined these relationships in the observations, and obtain no statistically significant result. Here we can test the case where if indeed the sulfur or organic aerosols are important for processes in the model, how will that show up in the observations. This is shown in Table 9. Significant positive correlation for SO₂P and SO₄P processes in MP02 and MP09 could show that these two processes play the role in iron soluble conversion in these cruises. But there are significant negative correlations for some processes in different basins at different circumstances. Although the correlation can be high for individual cruises, overall there is a lack of statistically significant correlation between sulfate and solubility, even in the cases where sulfur is the important in the process converting the iron (SO₂P or SO₄P or HP). Similarly there is no correlation between the organic acid and the solubility in the case where organic acids are in the model doing the processing of iron solubility. This is because the sulfur or organic acids are highest close to the source areas, while the iron processed by the compounds is highest downwind, which can result in negative or no correlations between solubility and sulfur concentrations. Thus this non-intuitive result appears consistent with the observations

discussed in section 2, and correlations in observations are not likely to provide us with information about what constituents are doing the processing, unfortunately.

4.4. Soluble Iron Deposition Estimation

[37] The bioavailability of iron is very important to the biogeochemistry cycle in the ocean. Here we estimate the amount of soluble iron deposited in the global open ocean by using the averaged model calculated global iron solubility from this study, and a long term average of dust deposition from a 22-year model simulation [Luo *et al.*, 2003; Mahowald *et al.*, 2003]. Figure 14 illustrates open ocean soluble iron distribution for 6 processes. The largest amounts of iron are deposited into the tropical Atlantic, Indian Ocean and North Pacific for all processes. We calculated total soluble iron to the open ocean for 6 processes. The deposited soluble iron in North Atlantic (10°W–60°W, 0°–55°N), South Atlantic (10°W–60°W, 0–55°S), Indian Ocean (60°E–100°E, 30°S–25°N), North Pacific (125°E–130°W, 0°–55°N) and South Pacific (125°E–130°W, 0°–55°S), Antarctic (0°–180°E, 0°–180°W, 60°S–90°S) and Arctic (0°–180°E, 0–180°W, 60°N–90°N) are shown in Table 10. The magnitudes range from 3.59×10^8 to 1.63×10^9 kg soluble iron per year (see Table 10). An average estimate of soluble iron in the global open ocean from all the cases considered here is $\sim 8.760 \times 10^8$ kg yr^{−1}.

5. Summary and Conclusion

[38] Analysis of available soluble iron data suggest that iron solubilities vary greatly spatially and temporally, with no consistent trends between the Pacific and the Atlantic. Limited iron measurements in the Pacific and Atlantic oceans suggest that Pacific Ocean iron solubilities should be larger [e.g., Boyle *et al.*, 2005], leaving a discrepancy between iron observed in the oceans and iron being deposited to the surface oceans. Fine mode desert dust particles are observed to have twice the solubilities of coarse mode desert dust particles (1.95% vs. 0.74%). This appears to be largely due to the difference in the lifetime of fine and coarse particles, based on the modeling conducted here. Observations show larger solubilities farther from the source areas, in general, and a solubility distribution that is symmetric around the equator. If iron solubility is defined

Figure 10. Percent iron solubility ($\text{Fe(II)/Fe} \times 100$) comparisons between model results (black line) and observations (red line), for each of the different ‘combined’ processes described in the text. The number on X-axis represents cruise number.

Table 7. Correlation of Iron Solubility of Mix-Processes Between Observation and Model Simulation From MP01–MP08^a

	Mean (f)	Std Dev (f)	R	Mean (c)	Std Dev (c)	R
Obs	5.04	8.72		3.80	11.41	
SO2P+HP	3.95	3.28	0.24	2.05	2.27	0.15
SO2P+CP	7.61	5.36	0.30	5.43	4.38	0.24
SO2P+RP	4.87	2.24	0.20	2.93	1.35	0.18
CP+HP	8.18	6.47	0.31	7.02	5.77	0.23
RP+HP	5.45	3.76	0.22	4.53	3.16	0.17
CP	6.45	4.59	0.25	5.97	4.26	0.21
RP	3.24	1.47	0.15	2.83	1.31	0.16
SO2P	1.84	1.07	0.13	0.26	0.18	0.10
HP	2.38	2.52	0.18	2.12	2.25	0.11

^aStatistics for single process cruises over MP01–MP08 are shown for comparison. Values in bold are significant at 95%.

as the labile iron fraction, it is roughly twice as large as the iron(II) fraction. Here we consider the iron(II) fraction as soluble, and thus bioavailable, but more information from oceanographers on the bioavailable fraction is required for a more definitive answer on the availability of iron being deposited in desert dust.

[39] Several different processes for conversion of Fe(III) to Fe(II) are simulated in a model, including 3 different sulfur based approaches, and one approach based on conversion by organic acids. This last case will suffer from a poor simulation of the organic acids thought to be important for conversion of Fe(III) to Fe(II). We include very simple assumptions about the conversion rates for iron, which will result in large uncertainties in our model results. We include detailed statistical analysis of the match between these different cases and the cruises considered here, which tend to show different processes do better in different basins. Overall the model calculated correlations SO₂P and cloud process tend to do a better job than other cases, and combination processes, such as SO₂P and CP (cloud processing) are even better. This is consistent with our understanding that sulfur processing of dust probably occurs in clouds. The large scale picture of iron solubility shown in Figure 1 from the observations provides important information about the relevant processes. Cases in which only sulfur or anthropogenic organic acids are allowed to convert the iron tended to result in distributions of iron solubility with

much larger solubilities in the North Hemisphere than the Southern Hemisphere, which is inconsistent with the two cruises with data in the Southern Hemisphere we consider here [Baker, 2004]. The data from Baker [2004] suggest solubilities are symmetric around the equator, more similar to cases in which cloud processing is important, either alone or with other processes. This suggests that in much of the atmosphere, cloud droplets may be acidic enough to process the iron, and that prediction of cloud processing is more important than prediction of acidity distributions. This is in contrast to the hypotheses of increased pollution driving higher solubilities of other studies [Meskhidze *et al.*, 2003, 2005]. We note that this apparent symmetry is probably governed by the fact that these cruises sampled low-solubility, near-source Saharan dust near the equator, and thus low solubility may not be a characteristic of equatorial regions *per se*. Comparisons show that the areas with the largest differences in the simulations are in the Southern Atlantic or Southern Pacific oceans. More observations in these areas will help us identify the most likely scenarios. All processes simulated in this study show higher solubilities in the Pacific than Atlantic Ocean, without including the effects of pollution, suggesting that pollution may not play an important role in the observed higher concentrations of iron in the Pacific than the Atlantic [e.g., Boyle *et al.*, 2005].

[40] Correlations between observed sulfate or organic acids and iron solubility suggest no significant correlation.

Table 8. Iron Solubility (%) Comparison for the Mixed Processes for MP01–MP08 Cruises

		SO2P+HP	SO2P+CP	SO2P+RP	CP+HP	RP+HP	OBS
Atlantic	Fine	4.22	7.66	5.14	7.93	5.42	4.40
	Coarse	2.26	5.66	3.03	7.40	4.78	2.66
MP01	Fine	2.15	5.76	3.62	4.70	2.56	6.62
	Coarse	0.72	4.49	1.94	4.90	2.35	5.08
MP03	Fine	3.12	5.65	4.74	5.88	4.97	2.38
	Coarse	1.55	3.75	2.94	4.92	4.11	0.17
MP08	Fine	9.46	13.76	8.17	16.16	10.56	4.19
	Coarse	5.95	10.41	4.83	15.28	9.69	2.73
Pacific	Fine	4.29	10.08	5.02	11.30	6.24	5.58
	Coarse	2.71	7.86	3.30	10.05	5.49	4.23
MP02	Fine	3.35	12.22	5.84	11.31	4.93	1.66
	Coarse	1.42	9.10	3.48	9.78	4.16	0.50
MP05	Fine	4.78	7.24	4.15	9.74	6.64	6.60
	Coarse	3.53	5.80	2.86	8.96	6.0	4.63
MP06	Fine	4.78	10.31	4.94	12.54	7.17	8.49
	Coarse	3.26	8.32	3.49	11.17	6.35	7.57
Overall	Fine	3.98	7.81	4.94	8.31	5.43	4.99
	Coarse	2.23	5.86	3.04	7.61	4.97	4.20

Figure 11. Bar graph showing the normalized iron solubility for different processes in different regions and seasons. The values represent the average Fe(II) deposited in the regions defined in the text, normalized by the globally and annually average amount of Fe(II) deposited. Thus these values show the relative importance of different mechanisms, if they had the same globally and annually averaged conversion rate to soluble iron.

Figure 12. Global distribution of the modeled annually average percents of iron solubility ($\text{Fe(II)/Fe} \times 100$) for each process.

Figure 13. Similar to Figure 12, but for combined processes.

Table 9. Correlation of Model SO₄ and OC With Fe(II)/Fe for Each Cruise^a

Cruise	CP		RP		SO2P		SO4P		HP		ORGP	
	SO4 ~ Fesol	oc ~ Fesol	SO4 ~ Fesol	oc ~ Fesol	SO4 ~ Fesol	oc ~ Fesol	SO4 ~ Fesol	oc ~ Fesol	SO4 ~ Fesol	oc ~ Fesol	SO4 ~ Fesol	oc ~ Fesol
MP01	0.54	-0.60	0.10	-0.54	0.21	-0.38	0.54	-0.49	0.17	-0.55	-0.32	-0.10
MP02	-0.30	-0.46	-0.30	-0.26	0.77	0.79	0.81	0.75	-0.17	-0.13	0.75	0.75
MP03	-0.30	-0.32	-0.10	-0.30	0.05	0.02	0.08	-0.24	0.26	-0.17	0.02	-0.30
MP05	0.06	0.22	-0.06	0.02	0.09	0.13	-0.07	-0.07	-0.37	-0.23	0.10	-0.10
MP06	-0.23	-0.13	0.02	-0.15	-0.003	-0.18	0.11	-0.08	0.20	0.03	-0.38	-0.17
MP08	-0.01	0.31	0.33	0.32	-0.08	-0.11	0.05	0.004	-0.007	0.21	0.30	0.13
MP09	0.37	0.27	0.26	0.30	0.25	0.05	0.39	0.21	0.28	0.23	0.14	0.05
overall	0.02	-0.09	0.04	-0.12	0.07	0.18	0.09	-0.06	-0.21	0.027	-0.12	0.26

^aValues in bold are significant at 95%.

Figure 14. Soluble iron deposition (Fe(II)) over the global open oceans for the different processing cases, in units of $\text{mg m}^{-2} \text{yr}^{-1}$.

Table 10. Model Estimated Soluble Fe (Fe(II)) Deposited in Global Open Ocean^a

Process Basins	RP	CP	SO2P	SO4P	HP	ORGP
N. Pacific	6.42×10^7	1.82×10^8	4.67×10^7	2.31×10^8	4.48×10^7	1.52×10^8
S. Pacific	2.57×10^7	6.95×10^8	7.88×10^6	4.16×10^7	2.12×10^7	3.36×10^7
N. Atlantic	2.09×10^8	2.29×10^8	1.26×10^8	4.98×10^8	5.56×10^7	8.00×10^8
S. Atlantic	2.68×10^7	4.58×10^7	1.24×10^7	5.40×10^7	2.14×10^7	4.01×10^7
Indian Ocean	9.14×10^7	6.21×10^7	9.43×10^7	4.04×10^8	1.08×10^8	1.73×10^8
Antarctic	2.58×10^6	1.70×10^7	5.76×10^5	3.26×10^6	6.94×10^5	8.08×10^5
Arctic	6.49×10^6	3.37×10^7	3.70×10^6	1.72×10^7	1.09×10^6	1.66×10^7
Global	5.61×10^8	8.45×10^8	3.81×10^8	1.63×10^9	3.59×10^8	1.48×10^9

^aUnits are in kg yr⁻¹.

Previously this was interpreted as evidence that these processes may not play an important role, perhaps because the atmosphere is largely acidic already [Hand *et al.*, 2004]. However, in this study we show that even if sulfate is acting to convert Fe(III) to Fe(II) in the model, there is no significant correlation between sulfate and solubility. This is because the sulfur compounds are highest close to the source region, while the processed iron is higher downwind (after more processing has occurred). This makes concluding what processes dominate in the atmosphere difficult to deduce from observations of both species. More laboratory studies of the processes which convert iron to soluble iron are necessary to better constrain the solubilities deposited in different basins.

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