Biogeosciences Discuss., 12, 14377–14400, 2015
www.biogeosciences-discuss.net/12/14377/2015/
doi:10.5194/bgd-12-14377-2015

Biogeosciences
Discussions
Open Access

Influence of measurement uncertainties on soluble aerosol iron over the oceans

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Received: 30 July 2015 – Accepted: 13 August 2015 – Published: 1 September 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The atmospheric supply of dust iron (Fe) plays a crucial role in the Earth's biogeochemical cycle and is of specific importance as a micronutrient in the marine environment. Observations show several orders of magnitude variability in the fractional solubility of Fe in dust aerosols, making it hard to assess the role of mineral dust for global ocean biogeochemical Fe cycle. In this study we compare the operational solubility of dust aerosol Fe associated with one of the flow-through leaching protocols to the results of the global 3-D chemical transport model GEOS-Chem. In the protocol aerosol Fe is defined soluble by first deionized water leaching of mineral dust through a 0.45 µm pore size membrane followed by acidification and storage of the leachate over a long period of time prior to the analysis. To assess the concentrations of soluble Fe inferred by this flow-through leaching protocol we are using in situ measurements of dust size distribution with the prescribed of 50 % fractional solubility of Fe in less than 0.45 µm sized dust particles collected in the leachate. In the model, the fractional solubility of Fe is either explicitly calculated using complex dust Fe dissolution module, or prescribed to be 1 and 4 %. Calculations show that the fractional solubility of Fe derived through the flow-through leaching is typically higher compared to the model results. The largest differences (> 30 %) are predicted to occur farther away from the dust source regions, over the areas where sub-0.45 µm sized mineral dust particles contribute a larger fraction of the total dust mass. This study suggests that inconsistences in the operational definition of soluble Fe could contribute to the wide range of the fractional solubility of dust aerosol Fe reported in the literature.

1 Introduction

Earth system science models pay particular interest to interactions between ocean ecosystems and the atmosphere. These interactions have implications on trace gas exchange, bidirectional flux of particulates, and the overall global carbon budget. The improved understanding of ocean–atmosphere interaction and assessment of the ocean's role in the carbon cycle necessitates coupling of physicochemical and biological processes in the ocean. Characterization of ocean biological communities, however, requires quantitative knowledge of nutrient distribution in the Earth's oceans. Iron (Fe) is one of the crucial micronutrients in surface oceans as nearly all forms of life require sufficient amounts of Fe to carry out biological processes. Fe limitations in the oceans can be seen most readily in so-called high nitrate low chlorophyll (HNLC) waters that comprise ~ 30 % of the global oceans (Martin and Fitzwater, 1988; Boyd et al., 2000).

Previous studies that examined the sources of new Fe (not acquired via nutrient recycling) to the oceans have largely focused on the delivery of Fe and physicochemical processes that mediate the conversion of Fe from the refractory to the soluble pool either in the surface ocean (Waite and Morel, 1984; Barbeau and Moffett, 2000) or the atmosphere (Duce et al., 1991; Zhuang et al., 1992; Zhu et al., 1993; Meskhidze et al., 2003). Sources of new Fe to the surface ocean include upwelling and entrainment of Fe-rich waters from below the euphotic zone (Gordon et al., 1997), glacial meltwater (Smith et al., 2007; Raiswell, 2011), seasonal sea-ice retreat (Lannuzel et al., 2008), and aerosols associated with volcanism (Langmann, 2013; Hoshyaripour et al., 2014), biomass burning (Guieu et al., 2005), anthropogenic emissions (Chuang et al., 2005), and mineral dust (Prospero, 1981; Duce et al., 1991; Jickells et al., 2005). Although different sources of aerosols seem to contribute to total Fe fluxes to the ocean and influence the fractional solubility of Fe in the bulk aerosol, here we only consider mineral dust. It is estimated that 1.7×10^{15} g of mineral dust (Jickells et al., 2005) with an average of 3.5 wt % of Fe (Duce and Tindale, 1991) gets deposited to the surface oceans every year. The fraction of this Fe that is in a bioavailable form and the details for the pathways that may be involved in aeolian Fe acquisition by ocean biological organisms remain the subject of active research. For example, the oversimplistic nature of the term "bioavailability" has been pointed out by Shaked and Lis (2012), suggesting that elements of Fe speciation and kinetics, phytoplankton physiology, light, temperature, and microbial interactions, are all intricately intertwined into the term bioavailability. In the marine environment greater than 99 % of filterable Fe is bound to organic colloidal phases and macromolecules, usually less than 0.45 µm in size (Rue and Bruland, 1995; Barbeau, 2006; Raiswell and Cainfield, 2012). So, in the ocean "filterable" or "dissolved" Fe has been operationally defined as the size fraction that passes through a 0.45 (or 0.4) µm filter membrane (Raiswell and Cainfield, 2012). Since such organically-bound Fe can be taken up by phytoplankton through several known pathways (Shaked and Lis, 2012), it is considered to be bioavailable.

Because it is so difficult to quantify the bioavailability of particulate Fe in mineral dust, studies often report soluble Fe (sol-Fe) in aerosols and define this as the fraction of total Fe that contributes to the dissolved Fe inventory of surface seawater (e.g., Sholkovitz et al., 2012). However, compared to seawater, the definition of sol-Fe in mineral aerosols is less straightforward as Fe in sub-0.45 µm sized dust particles can contain crystalline Fe-(oxyhydr)oxides (e.g., hematite and goethite), Fe-substituted into aluminosilicate minerals, and Fe-rich nanoparticles (Claquin et al., 1999; Nickovic et al., 2013; Shi et al., 2009) that may not be readily bioavailable in seawater. Different research groups have been using a range of different leaching techniques ("batch" leaching, "flowthrough" leaching, and a combination of these two), types of Fe extraction solutions (seawater or high-purity deionized (DI) water), pH values of the solutions (from less than 2 to greater than 8), extraction times (from minutes to days), and (photo)reductant agents (oxalic, ascorbic, glyoxalic, and pyruvic acids) leading to large discrepancies in sol-Fe results (e.g., Sholkovitz et al., 2012). In addition to the range of different methods used for Fe extraction, different groups are using different operational definitions for fractional solubility of Fe in mineral dust. The sol-Fe is defined as the material that passes through a 0.2, 0.4, or 0.45 µm pore diameter filters and commonly detected through Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES), or High Resolution Inductively Coupled Plasma–Mass Spectrometry (HR-ICP-MS) (e.g., Lim and Jickells, 1990; Zhuang et al., 1990; Bonnet and Guieu, 2004; Baker et al., 2006; Mackie et al., 2006; Buck et al., 2006, 2010; Paris et al., 2011). As mentioned above, sub-0.45 µm sized dust particles can contain numerous different forms of Fe (both in a soluble and insoluble form), so the operational definition based on the size-sorting is bound to introduce some uncertainty in sol-Fe results. Finally, the sol-Fe portion of mineral Fe can also be defined as the sum of aqueous ferrous iron (Fe(II)) and reducible ferric (Fe(III)) iron species and measured in the solution using the hydroxylamine hydrochloride-ferrozine technique (e.g., Zhu et al., 1997; Chen and Siefert, 2004). However, such a definition is also not precise as it is known that hydroxylamine hydrochloride can reduce ferric iron in forms ranging from aqueous to amorphous and even in some crystalline forms (Chao and Zhou, 1983; Lovely and Phillips, 1987; Verschoor and Molot, 2013).

Despite the wide variety of methods that have been used to define sol-Fe, the global-scale compilation of data carried out by Sholkovitz et al. (2012) revealed a remarkably consistent trend (similar to hyperbolic cotangent function) in the fractional solubility of aerosol Fe as a function of total aerosol Fe loading. Baker and Jickells (2006) suggested that such variability in aerosol Fe solubility is physical rather than chemical in nature, caused by preferential removal of larger mineral dust particles during atmospheric transport. Increase in surface area to volume ratio of mineral aerosol particles with transport time was proposed to yield higher solubilities (Baker and Jickells, 2006). However, using a combination of laboratory measurements of sol-Fe (in dust particles with diameters from less than 0.18 to greater than 18 µm) and global aerosol model simulations, Shi et al. (2011a) showed that that physical size sorting alone can not explain observed large variability in sol-Fe values of mineral dust samples. The chemical and/or physical processing of soil dust during long-range atmospheric transport, as well as source-dependent chemical and mineralogical variations in the Fe-bearing aerosols were proposed as possible explanations for the observed variability of sol-Fe (Sholkovitz et al., 2012).

In this study using the 3-D global chemical transport model GEOS-Chem, implemented with a complex dust-Fe mobilization scheme (Johnson and Meskhidze, 2013), we examine the uncertainty in Fe solubility values associated with leaching techniques.

In particular, we will examine the effect of using 0.45 µm pore size filters for separating soluble and particulate forms of Fe. The intent of this article is in no way to criticize any of the methods used in sol-Fe measurements, but rather to make the reader aware of the fact that in addition to proposed physicochemical processing of soil dust during long-range atmospheric transport, the reported uncertainty in the fractional solubility of aerosol Fe could be attributed to the pore diameter of the filter used for separation of soluble and particulate forms of Fe. The priorities for future studies of the atmospheric deposition of sol-Fe to the oceans are also discussed.

2 Materials and methods

2.1 Model configuration

The global 3-D chemical transport model GEOS-Chem (v8-01-01) was applied in this study to quantify size-dependent emission rates, atmospheric concentrations, and deposition fluxes of mineral dust. The model was run with a $2^\circ \times 2.5^\circ$ (latitude – longitude) horizontal resolution and 47 vertical hybrid sigma-pressure levels and is driven by Goddard Earth Observing System (GEOS-5) assimilated meteorology from the NASA Global Modeling Assimilation Office (GMAO) (Bey et al., 2001). Dust mobilization is calculated through the Dust Entrainment and Deposition (DEAD) scheme (Zender et al., 2003) with the source function used in the Goddard Chemistry Aerosol Radiation and Transport (GOCART) model (Ginoux et al., 2001). The detailed mineralogy of wind-blown dust from the major desert regions is prescribed using the dust mineralogy database of Nickovic et al. (2012). Once mineral dust is mobilized from the surface, the model uses four standard dust size bins with diameter boundaries of 0.2–2.0, 2.0–3.6, 3.6–6.0 and 6.0–12.0 µm to simulate global dust transport and deposition (Fairlie et al., 2007). Dry deposition in the model is based on the resistance-in-series scheme described in Wesely (1989), with the surface resistances for aerosols following the work of Zhang et al. (2001). Dust removal by wet deposition processes includes both convec-

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tive updraft scavenging and rainout/washout from large-scale precipitation (Liu et al., 2001). Production of sol-Fe during the atmospheric transport of mineral dust is explicitly calculated based on the chemical composition of dust at the source region, aerosol solution pH, organic (oxalate)-promoted Fe dissolution processes, and photochemical redox cycling between Fe(II) and Fe(III) (Johnson and Meskhidze, 2013). Johnson and Meskhidze (2013) examined three major Fe-containing minerals within dust, however, during this study the baseline hematite-based dissolution scheme is used.

2.2 Dust size distribution

GEOS-Chem does not resolve explicitly dust size distribution within each bin. To calculate dust mass concentrations with particle diameter $D_\mathrm{p} \leq 0.45\,\mu\mathrm{m}$ [$\mathrm{Dust}_{0.45}$], we used in situ measurements of the dust particle size distributions compiled in Mahowald et al. (2014). The solid line on Fig. 1 shows the normalized volume size distribution (V_p) as a function of dust aerosols size (D_p) using Kok (2011)

$$\frac{\mathrm{d}V_\mathrm{p}}{\mathrm{d}\ln D_\mathrm{p}} = \frac{D_\mathrm{p}}{c_V}\left[1+\mathrm{erf}\left(\frac{\ln\left(D_\mathrm{p}/\overline{D_s}\right)}{\sqrt{2}\ln\sigma_s}\right)\right]\exp\left[-\left(\frac{D_\mathrm{p}}{\lambda}\right)^3\right] \tag{1}$$

with the following parameters: $c_V = 6.26$, $\overline{D_s} = 30\,\mu\mathrm{m}$, $\sigma_s = 14.5$, and $\lambda = 13$. The dashed line in Fig. 1 shows the dust size distribution at the emission source based on a brittle fragmentation theory from Kok (2011). To calculate [$\mathrm{Dust}_{0.45}$] we integrated dust volume size distributions for $0.2 < D_\mathrm{p} \leq 0.45\,\mu\mathrm{m}$ and $0.2 < D_\mathrm{p} < 2\,\mu\mathrm{m}$. The ratio of these two volume distributions multiplied by GEOS-Chem dust mass concentration within the smallest transport bin ($0.2 < D_\mathrm{p} < 2.0\,\mu\mathrm{m}$) is assumed to be equivalent to [$\mathrm{Dust}_{0.45}$]. The difference between the Kok (2011) parameterization (applicable at the source region) and the measurements of dust size distributions downwind from desert regions are thought to be attributed to differences in particle lifetime. Larger particles typically fall from the atmosphere much faster than smaller ones. Under identical atmospheric conditions, particles of size 1 and 10 µm will have deposition velocities 50 and 1000 times higher compared to 0.1 µm sized particles (Seinfeld and Pandis, 1998). Clouds also affect dust size distribution, with in-cloud and below-cloud scavenging of mostly larger (≥ 1 µm in diameter) particles (Mahowald et al., 2014 and references therein). Overall, when using the least square fit to the experimental data, mineral dust with $0.2 < D_\mathrm{p} \leq 0.45$ µm represents 1.6 % of dust within the smallest transport bin of the model ($0.2 < D_\mathrm{p} < 2$ µm).

2.3 Model simulations for sol-Fe

To determine the possible uncertainty in sol-Fe concentrations introduced by size-sorting of sol-Fe, we have selected a method (hereinafter called DI-Method) in which dust is leached though a 0.45 µm pore size filter using high-purity DI water (pH 5.6) and subsequently acidified (typically at pH ∼ 1.7) and stored (often more than several months) for the offline analysis (Buck et al., 2006). The advantages of such a method are: (i) the similar operational definition of sol-Fe in atmospheric aerosols as does for dissolved Fe in the ocean, (ii) the use of a rapid, flow-through leaching protocol alleviates the potential for precipitation of iron hydroxides prior to collection of the leachate solution, and (iii) the Fe extraction from the solution happens through the use of an Fe chelating resin, allowing high efficiency and recovery (Buck et al., 2006; Milne et al., 2010).

We have carried out three model simulations. In the first model simulation we explicitly calculate sol-Fe production during the atmospheric transport of mineral dust, while in the last two simulations 1 and 4 % fractional solubility of Fe is prescribed to GEOS-Chem dust. Note, that the last two simulations are independent from the GEOS-Chem Fe dissolution scheme and the range in fractional solubility of Fe is the value required by global ocean biogeochemical Fe cycle models to enter the ocean as bioavailable Fe to reproduce the broad features of the Fe distribution observed in the modern ocean (Aumont et al., 2003; Parekh et al., 2004; Tagliabue et al., 2014). All model results are then compared to the value expected from the DI-Method. The following ratio, R, can be viewed as the difference between the DI-Method determined and model-predicted fractional solubility of Fe:

$$R = \frac{\left([\mathrm{Dust_{tot}}] - [\mathrm{Dust_{0.45}}]\right) \times \mathrm{Fe_w} \times \mathrm{Fe_{d2}} + [\mathrm{Dust_{0.45}}] \times \mathrm{Fe_w} \times \mathrm{Fe_{d1}}}{[\mathrm{Dust_{tot}}] \times \mathrm{Fe_w} \times \mathrm{Fe_{d2}}} \tag{2}$$

where [$\mathrm{Dust_{tot}}$] is the surface level (from surface to ~ 100 m) concentration of dust predicted by GEOS-Chem (in µg m^{-3}), $\mathrm{Fe_w}$ is the weight percentage of Fe in dust (assumed to be 3.5 %), $\mathrm{Fe_{d1}}$ is the fractional solubility of Fe predicted by the DI-Method, and $\mathrm{Fe_{d2}}$ is explicitly calculated through GEOS-Chem Fe dissolution scheme or prescribed to be 1 and 4 %. Past studies designed to mimic acidification of mineral dust aerosols during atmospheric transport showed that the rate of release of Fe from acid-leachable pool is directly related to pH of the solution (e.g., Mackie et al., 2006; Cwiertny et al., 2008). The fractional solubility of Fe was shown to vary from 30 to 70 % when treated extensively with different acids of pH ~ 1.7 over different time periods (e.g., Kim et al., 1999; Mackie et al., 2006; Cwiertny et al., 2008). These studies also revealed that the release of acid-leachable Fe continued even after 25 days (e.g., Mackie et al., 2006). Here we prescribe the fraction of acid-leachable Fe (i.e., $\mathrm{Fe_{d1}}$) in the DI-Method to be 50 % of total mineral Fe in the dust.

3 Results

3.1 Dissolved Fe fraction in mineral dust particles

Figure 2 shows the yearly averaged (from March 2009 to February 2010) distribution of R values when GEOS-Chem model-predicted fractional solubility of Fe is used in Eq. (2). According to this figure the higher R values ~ 1.2 to 1.25 (i.e., 20 to 25 % higher sol-Fe by the DI-Method) are expected to occur farther away from the source regions, over the areas where mineral dust particles with $D_p \leq 0.45$ µm contribute a larger fraction of the surface level dust mass concentration. The R values close to 1 are predicted in the vicinity of large desert regions, e.g., North African and Middle East regions, where the majority of dust mass is in particles with $D_p > 1\,\mu m$ and therefore the amount of Fe mobilized in sub-0.45 µm particles (due to extended treatment of the leachate with acidic solution) will add minor amounts to total sol-Fe.

Figure 3 shows model-predicted normalized frequencies of daily averaged R values from March 2009 to February 2010 over the Southern Ocean (defined here as oceanic regions south of 40° S), Equatorial Pacific (15° S–15° N, 75–150° W), the North Pacific Ocean (40–80° N, 130° E–120° W), and globally. The data show that for the prescribed range of Fe solubility (1 % in Fig. 3a and 4 % in Fig. 3b), the globally averaged R values are ~ 1.02 and 1.2, i.e., sol-Fe overestimation over the oceans ranges from ~ 2 to 20 %. According to Fig. 3, the calculated R values are predicted to be highest over the Equatorial Pacific, while the North Pacific Ocean and the Southern Ocean show lower (and comparable) values.

4 Discussion

A large number of studies have attempted to measure sol-Fe concentrations in mineral dust particles present over the oceans. However, differences in the dust source regions (i.e., mineralogy and size distribution), environmental conditions (contamination of in situ measurements by species other than dust, interaction of mineral dust particles with different acidic and organic species at variable relative humidity and temperature encountered during the atmospheric transport), sol-Fe definitions (i.e., aqueous Fe(II) and reducible Fe(III), or 0.2, 0.4, and 0.45 µm pore size filtered), and measurement methodologies (leaching procedures, chemical composition and pH values of the solutions), lead to large uncertainty in fractional solubility of Fe reported in the literature (Shi et al., 2012; Sholkovitz et al., 2012).

The DI-Method, although using a similar operational definition of sol-Fe as the dissolved Fe used in marine environments, is not consistent with the definition of bioavailable Fe in the oceans. The differences stem from the fact the sub-0.45 µm sized organically-bound Fe (the vast majority of all dissolved Fe in the oceans) can be acquired by most phytoplankton, while particulate dust-Fe in the form of crystalline Fe-(oxyhydr)oxides such as hematite and goethite, and as Fe(III) substituted into aluminosilicate minerals that could be present in sub-0.45 µm sized mineral dust is not bioavailable. To date, major ligand-complexed Fe uptake pathways have been described for phytoplankton (e.g., Shaked and Liss, 2012), while only a few organisms, e.g., the dinitrogen-fixing cyanobacterium, *Trichodesmium* spp., were shown to be capable of dissolving mineral Fe on the cell surface, and acquiring bioavailable Fe directly from dust particles (Rueter et al., 1992; Rubin et al., 2011). All studies agree that long-term exposure of dust samples to low pH conditions can cause sol-Fe release from the crystalline Fe pool that is not expected to be easily soluble under typical atmospheric conditions (e.g., Mackie et al., 2006; Cwiertny et al., 2008). Therefore, passing mineral dust through 0.45 µm sized filters followed by extensive acid digestion of samples is likely leading to overestimations of sol-Fe values in dust aerosols.

To assess the possible uncertainty in sol-Fe concentration measured using the DI-Method, we carried out GEOS-Chem model simulations in which model-predicted fractional solubility of Fe were compared to the expected Fe_{d1} from the DI-Method. If one assumes that particle morphology and Fe content does not change with size (we will come back to this point below), model simulations for annually-averaged R values for surface-level mineral dust reveal that overestimations in sol-Fe are trivial (i.e., $R \sim 1$) near the source regions and increase with the distance downwind as large particles get removed from the atmosphere through dry and wet deposition. In the regions where dust concentration is high (i.e., above 100 µg m^{-3}), sub-0.45 µm sized mineral particles contribute less than 0.3 % of total dust. Therefore when dust in this small size fraction is assumed to be 50 % soluble, its contribution to total fractional solubility of Fe in dust samples is small. It should be noted here that no model is precise and our past studies show that GEOS-Chem derived daily averaged sol-Fe values often have more than 50 % biases compared to the measurements (Johnson and Meskhidze, 2013).

However, those uncertainties are irregularly distributer over the oceans and likely associated with uncertainties in emissions, transport and deposition schemes as well as inconsistent chemical treatment of aerosols between different models. The difference between the DI-Method derived and model-predicted sol-Fe values, on the other hand, increases consistently with the distance from the dust source regions, as particles with $D_p \leq 0.45\,\mu\text{m}$ contribute a growing fraction of the surface level dust mass concentration.

Although in this study we focus on the uncertainty in sol-Fe introduced solely by the DI-Method, the derived increases in fractional solubility of Fe in dust aerosols are comparable with the results of Shi et al. (2011a) study using different measurement methodology and operational definition of sol-Fe. Using a combination of laboratory measurements of Fe solubility in size-fractionated dust samples and a global aerosol microphysical model, Shi et al. (2011a) conclude that physical size-sorting leads to a systematic increase in sol-Fe in mineral dust, but the magnitude of the increase is not high enough to explain high values in dust aerosol Fe solubility over the open-oceans. For example, both our calculated (for the DI-Method) and Shi et al. (2011a) measured (for size-fractionated dust samples) fractional solubility of Fe in mineral dust are considerably lower than 12 to 15 % average value reported for high atmospheric Fe loading ($> 2\,\mu\text{g Fe m}^{-3}$ air) of Saharan dust aerosols over the North Atlantic Ocean (Buck et al., 2010). Moreover, results of both studies are inconsistent with reported ~ 50 % and ~ 20 % Fe solubility for $1.8 < D_p < 3.2\,\mu\text{m}$ and $0.32 < D_p < 1.8\,\mu\text{m}$ sized dust particles, respectively (Buck et al., 2010). To explain these findings, we propose possible changes in dust size distribution caused by wetting of the mineral dust grains and long-term acidification involved in the DI-Method. Discrepancies between wet and dry sieved size distributions are well known in aeolian research (e.g., Marticorena and Bergametti, 1995; Chatenet et al., 1996). The wetting of dust can cause physical breakage of grains, dissolution of salts and release of finest particles (often defined as nanoparticles, i.e., particles with < 100 nm diameter) loosely bonded to each other or to the surface of larger particles. For example, high-resolution microscopy did not show Fe rich nanoparticle aggregates in dry Saharan dust samples, but revealed their presence in wet-deposited dust (Shi and Krom, 2009). Such nanoparticles, including aluminosilicates with Fe incorporated in crystal lattice, nanogoethite, hematite, and ferrihydrite (Shi and Krom, 2009; Journet et al., 2008; She et al., 2011b; Scheuvens et al., 2011) could be mobilized in the solution and pass through 0.45 µm sized filter. When highly acidified and stored over long period of time, most of the Fe in these nanoparticles will show up as sol-Fe, enhancing fractional solubility of dust Fe. Available size-fractionated dust-aerosol Fe solubility measurements (Buck et al., 2010; Shi et al., 2011a) did not specifically examine presence of nanoparticle Fe in the leaching solution, so it is hard to ascertain fractional solubility of Fe contributed by nanoparticles in different sized dust. However, as the abundance of nanoparticles bonded to the grains or the number of nanoparticles in dry dust that remain aggregated due to cohesive forces change with the aerosol size distribution (Ogata et al., 2011; Baddock et al., 2013), the measurement techniques involving separation of soluble and particulate forms of Fe by passing the Fe-laden dust solutions through different pore-size filters may not even be viable methodologies for characterization of size-fractionated dust Fe solubility.

5 Conclusion

In this study, we examined uncertainty in fractional solubility of Fe in mineral dust associated with usage of one of the flow-through leaching protocol. We argue that usage of the same operational definition of “soluble” Fe in atmospheric aerosols as “dissolved” Fe in seawater (i.e., passage of Fe-laden solutions through 0.45 µm pore-size filter) does not facilitate the companion of the results between different fields, as sub-0.45 µm sized mineral dust could include crystalline Fe-(oxyhydr)oxides such as hematite and goethite, Fe(III) substituted into aluminosilicate minerals, and nanoparticles that are not considered to be readily bioavailable in seawater. The long-term exposure of Fe-laden leachate solution to low pH conditions can then cause release of Fe from the pool that is not expected to be soluble under typical atmospheric conditions, leading to overestimation of sol-Fe values of mineral dust. Our model results show that for the three simulations carried out here (explicit calculation of sol-Fe production and prescribed 1 and 4 % fractional solubility of Fe) the DI-Method derived sol-Fe can be rioughly 30 % higher compared to the model results. The differences are particularly higher over the HNLC waters, where mineral dust particles with $D_p \leq 0.45\,\mu m$ can contribute highest fraction of the surface level dust mass concentration.

In terms of the wider significance, our study shows that operational definition of fractional solubility of Fe in dust aerosols, as the material that passes through a 0.2, 0.4, or 0.45 µm pore diameter filter, could introduce large uncertainty in the results. This is particularly true for different sized dust-aerosol Fe solubility. Wetting of dry mineral dust grains during the leaching procedures could cause physical breakage of grains, dissolution of salts and release of nanoparticles loosely bonded to each other or to the surface of larger particles. Since nanoparticles can be highly abundant in Fe and have greater dissolution rate compared to more crystalline (larger) Fe oxide minerals, operational solubility leaching procedure through 0.45 µm pore diameter filter can yield large uncertainties in aerosol Fe solubility as a function of particle size. Future studies should develop improved measurement techniques capable to chemically measure the speciation of Fe (in different size fractions) that are truly bioavailable in seawater. Results from such measurement techniques should be scalable for different environmental conditions and interpretable for the wider biogeochemical context.

Acknowledgements. This research was supported by NCSU Faculty Research and Professional Development Fund and the grant from the Office of Undergraduate Research at North Carolina State University. The authors would like to thank Daniel Jacob and the Harvard University Atmospheric Chemistry Modeling Group for providing the base GEOS-Chem model used during our research. Resources supporting this work were provided by the NASA High-End Computing (HEC) Program through the NASA Advanced Supercomputing (NAS) Division at NASA Ames Research Center.

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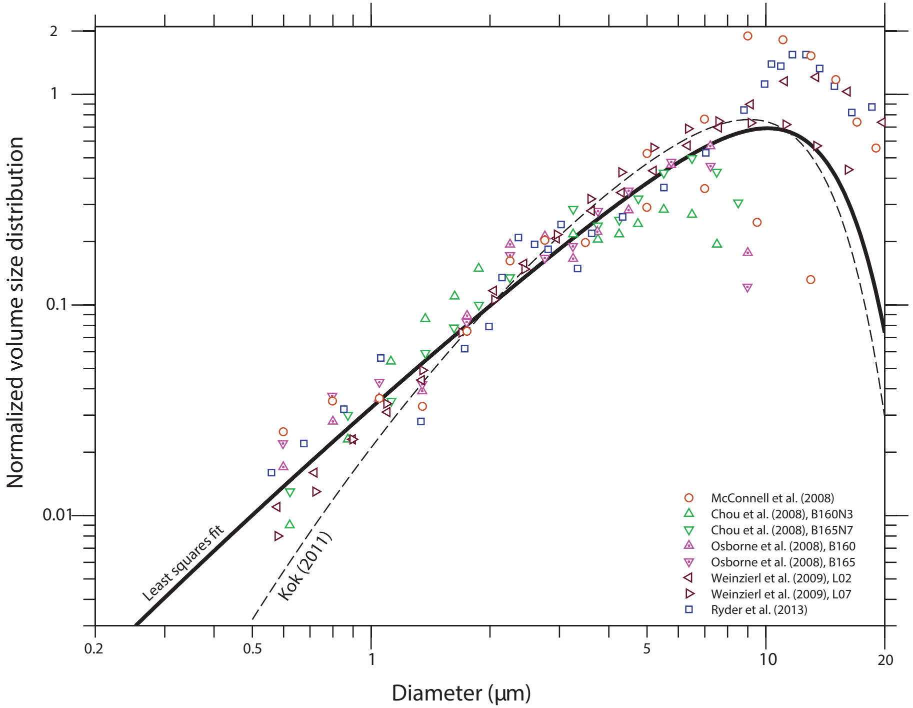

Figure 1. In situ measurements of the dust particle size distribution close to North African source regions adapted from Mahowald et al. (2014). Solid curve shows the least square fit used in this study. The measurements are from the DODO (Fig. 7 in McConnell et al., 2008), DABEX (Fig. 6 in Chou et al., 2008) and Fig. 10 in Osborne et al., 2008, SAMUM-1 (Fig. 8 in Weinzierl et al., 2009), and Fennec (Fig. 5 in Ryder et al., 2013) field campaigns. See text for more details.

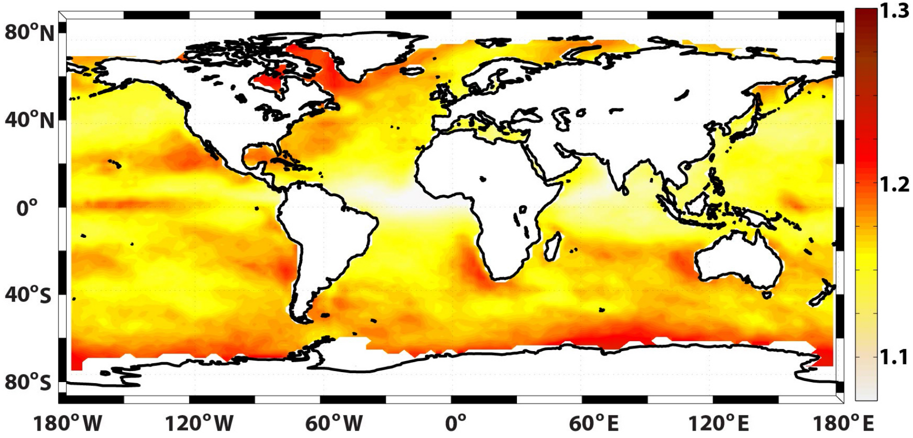

Figure 2. GEOS-Chem-predicted annually-averaged *R* values for surface-level mineral dust. Sol-Fe concentrations in mineral dust are explicitly calculated and particles with $D_p \leq 0.45\,\mu m$ are assumed to contain 50 % sol-Fe.

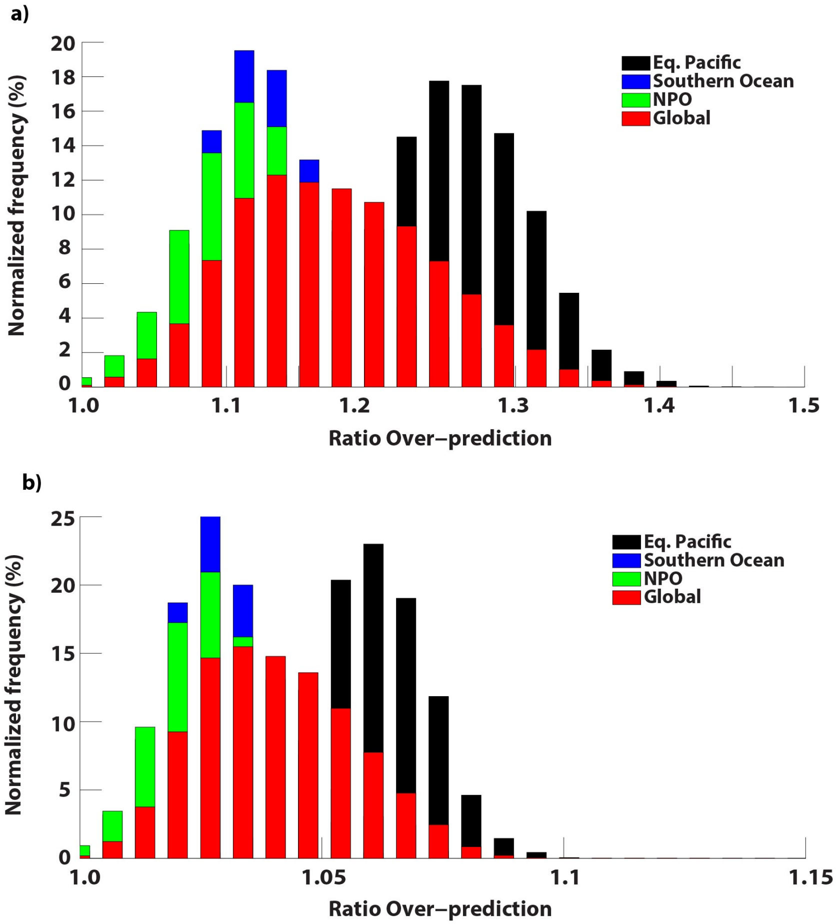

Figure 3. GEOS-Chem-predicted normalized frequencies (%) of daily-averaged R values in surface-level mineral dust when **(a)** 1 % and **(b)** 4 % all Fe is assumed to be soluble and particles with $D_p \leq 0.45\,\mu m$ contain 50 % sol-Fe.