



Influence of measurement uncertainties on fractional solubility of iron in mineral aerosols over the oceans



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ABSTRACT

The atmospheric supply of mineral 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 mineral dust aerosols, making it hard to assess the role of mineral dust in the global ocean biogeochemical Fe cycle. In this study we compare the operational solubility of mineral dust aerosol Fe associated with the flow-through leaching protocol to the results of the global 3-D chemical transport model GEOS-Chem. According to the protocol, aerosol Fe is defined as 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 analysis. To estimate the uncertainty in soluble Fe results introduced by the flow-through leaching protocol, we prescribe an average 50% (range of 30–70%) fractional solubility to sub-0.45 μm sized mineral dust particles that may inadvertently pass the filter and end up in the acidified (at $\text{pH} \sim 1.7$) leachate for a couple of month period. In the model, the fractional solubility of Fe is either explicitly calculated using a complex mineral aerosol Fe dissolution equations, or prescribed to be 1% and 4% often used by global ocean biogeochemical Fe cycle models to reproduce the broad characteristics of the presently observed ocean dissolved iron distribution. Calculations show that the fractional solubility of Fe derived through the flow-through leaching is higher compared to the model results. The largest differences ($\sim 40\%$) 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 mineral dust mass. This study suggests that different methods used in soluble Fe measurements and inconsistencies in the operational definition of filterable Fe in marine environment and soluble Fe in atmospheric aerosols are likely to contribute to the wide range of fractional solubility of aerosol Fe reported in the literature.

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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 $\sim 30\%$ 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; 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),

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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 about 450×10^{12} g of mineral dust (Jickells et al., 2005) with an average of 3.5 weight percent 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 information for the pathways that may be involved in aeolian Fe acquisition by ocean biological organisms remains 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 $0.45 \mu\text{m}$ in size (Rue and Bruland, 1995; Barbeau, 2006; Raiswell and Canfield, 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 Canfield, 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- $0.45 \mu\text{m}$ sized 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, ‘flow-through’ 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 $0.45 \mu\text{m}$ 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; Baker et al., 1998; Bonnet and Guieu, 2004; Mackie et al., 2006; Wu, 2007; Buck et al., 2006, 2010; Aguilar-Islas et al., 2010; Paris et al., 2011). As mentioned above, sub- $0.45 \mu\text{m}$ sized 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 hydroxylamine hydrochloride can reduce ferric iron in forms ranging from aqueous to amorphous and even in some

crystalline forms (Chao and Zhou, 1983; Lovley 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 mineral dust particles with diameters from less than 0.18 to greater than $18 \mu\text{m}$) and global aerosol model simulations, Shi et al. (2011a) showed that physical size sorting alone cannot 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 mineral dust-Fe mobilization scheme (Johnson and Meskhidze, 2013), we examine the uncertainty in Fe solubility values associated with one of the leaching techniques. The technique separates soluble and particulate forms of Fe by passing mineral dust through a $0.45 \mu\text{m}$ pore size filter, followed by acidification of the leachate and storage for a long period of time prior to the analysis (e.g., Buck et al., 2010). Using the model we first estimate the concentration of mineral dust particles with diameters less than $0.45 \mu\text{m}$ over the surface of the oceans. Then, using the reported rates for dust-Fe solubility in highly acidic solutions, we estimate the contribution of sol-Fe mobilized from these dust particles to the total measured sol-Fe. The intent of this article is in no way to criticize any of the methods used in dust Fe solubility 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 is likely to be attributed to the pore diameter of the filter used for separation of soluble and particulate forms of Fe, pH of the leachate, and the time that acidified leachate is stored prior to the analysis. 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 $2 \times 2.5^\circ$ (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). Mineral 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

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