

Response to Reviewer's Comments

We thank the reviewer for his helpful comments. We have incorporated as many of the reviewer's suggestions as possible into the revised manuscript.

Replies to specific comments follow.

Reviewer #1

#1. Reaching an accurate estimate of aerosol iron fractional solubility, as well as the factors affecting the solubility, is an ongoing challenge for the research community and the modeling community will play a role in furthering our understanding. An important point that I feel is missing from this paper's discussion is the ultimate fate of aerosol particles within the ocean. While understanding dissolution immediately upon deposition is vitally important subsequent dissolution and/or scavenging in the upper ocean will also play an equally important role in the marine iron cycle.

We agree with the reviewer. There is a great need for improved quantification of the fate of aerosol-delivered iron within the ocean. This is a topic of our next paper (to be submitted soon). It was our conscious decision to publish two papers separately to avoid reader confusion. The main objective of the current study is to i) highlight the ambiguity in the operational definition of the fractional solubility of Fe in dust aerosols and ii) examine the resulted uncertainty in model-measurement comparison of iron solubility in dust particles of different size. The discussion on ultimate fate of aerosol particles within the ocean is outside the scope of the current paper.

#2. The terms in Equation 1 need to be defined.

Terms in the equation have been defined in the updated manuscript.

#3. The authors argue that particles between 0.2-0.45 μm make up 1.6% of dust particles between 0.2-2.0 μm . Is this value true regardless of aerosol source region? Transport time? Are there any caveats that need to be included?

The following discussion has been added to the updated manuscript "There are caveats associated with this dust mass ratio as most of the data used in Fig. 1 were collected close to North Africa sources; therefore, this ratio is expected to represent North African dust. The value of this ratio could vary over different source regions and is likely to increase as a function of transport time."

#4. Why was the DI Method fractional solubility set at 50% for one of the model simulations? This value is not representative of most bulk aerosol fractional solubilities from the literature (e.g. Sholkovitz et al., 2012). If derived from size-fractionated aerosol data (<0.45 μm) then the sources should be cited. R would be considerably lower and closer to 1 if a more realistic fractional solubility was set for Fed_1 .

This is an important part of the paper that we believe may have not been clearly described. The following discussion has been added to the updated manuscript: “The possible disadvantage of the DI method is the long-term acidification during storage (often months) of samples prior to the analysis with potential mobilization of sol-Fe from sub-0.45 μm dust particles. 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 the 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 with $\text{pH} < 2$ over different time periods (from several days to one month) (Kim et al., 1999; Mackie et al., 2006; Cwiertny et al., 2008). Here we prescribe 50% sol-Fe in sub-0.45 μm dust particles to represent the fraction of acid-leachable Fe through the DI-Method.”

Also the following statement was added in the conclusions section “The variability in prescribed fraction of acid-leachable Fe in the DI-Method (potentially caused by the dust aerosol mineralogical composition and size) will affect the uncertainty in derived sol-Fe estimates, but will not alter the conclusions of the paper.”

#5. In two other simulations, the fractional solubility of aerosol iron is set at 1% and 4% because “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...” Are these values relevant for <0.45 μm particles?

Typically, global ocean biogeochemical Fe cycle models assume constant Fe solubility between 1% and 4% irrespective of dust particle size. However, the reviewer is correct noticing that technically, the requirement for <0.45 μm dust particles to have this range is not essential to reproduce the broad features of the Fe distribution in the modern ocean. The sentence now reads: “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 often prescribed by global ocean biogeochemical Fe cycle models to calculate the amount of Fe that enters the ocean as bioavailable Fe.”

#6. Page 14386: The authors mischaracterize observational efforts. “A large number of studies have attempted to measure sol-Fe concentrations in mineral dust particles present over the ocean.” Oceanographers are interested in the fractional solubility of all aerosols that deposit to the oceans because they are all potential sources of iron. Why have the authors chosen to only focus on mineral dust when combustion emissions are significant sources of soluble iron in many regions?

We agree with the reviewer that atmospheric aerosols other than mineral dust can be significant sources of soluble iron in certain regions. However, in the current study we focus on mineral dust aerosols due to the availability of data. Future studies should look into contribution of measurement uncertainties to biomass burning and fossil fuel (coal burning, ship plumes, automobile exhaust, etc.) emissions. We have changed the title to highlight this point. New title now reads “Influence of Measurement Uncertainties on Fractional Solubility of Iron in Dust Aerosols Over the Oceans.”

#7. Page 14388: “To explain these findings, we propose possible changes in dust size distribution caused by wetting grains of the mineral dust and long term acidification involved in the DI Method.” It appears that the authors misunderstand the flow through extraction technique. During collection using cascade impactor or slotted impactor, the bulk aerosol is divided into prescribed size classes which are collected on a filter substrate. Therefore, a filter would only collect particles within a certain diameter range e.g. 0.2-0.4 μm . The subsequent soluble fraction extraction would only include those particles so no change in size distribution outside of that range is possible. If in the short time that the particles were wetted (10-20 seconds in most cases) particles did break apart then it is reasonable to expect that these particles would also break apart upon deposition to the sea surface. The dissolution of salts and release of “finest” particles is desired as these processes are part of environmentally relevant aerosol dissolution. The comparisons to wet and dry sieving are not apt.

We thank the reviewer for bringing up this important point. We have added the following text to clarify this issue. “To explain these findings, we examine the DI-Method and discuss possible measurement artifacts that can be introduced by this method. The flow through extraction technique of dust collected on the impactor at the prescribed size range (e.g., $1.8 < D_p < 3.2 \mu\text{m}$) is expected to mobilize the soluble fraction of Fe (operationally defined as Fe in sub- $0.45 \mu\text{m}$ sized dust particles), while the low pH conditions at the leachate are designed to prevent precipitation and loss of this sol-Fe to the walls of the container during storage. In addition to collecting sol-Fe in the leachate, wetting of dust can cause physical breakage of dust grains, dissolution of salts and release of sub- $0.45 \mu\text{m}$ sized particles, finest of which are often called nanoparticles (i.e., particles with $< 0.1 \mu\text{m}$ in diameter). The high-resolution microscopy revealed the presence of Fe rich sub- $0.45 \mu\text{m}$ particle aggregates in wet-deposited dust, but did not show it in dry Saharan dust samples (Shi and Krom, 2009). While wetting of dust particles, with the subsequent breakage of dust grains, is environmentally relevant and likely happens to all particles deposited (through wet or dry removal) to the surface ocean, the long-term acidification (at $\text{pH} < 2$) of these sub- $0.45 \mu\text{m}$ sized particles involved in the DI-Method can mobilize Fe from the crystal lattice of aluminosilicates, goethite, hematite, and ferrihydrite (Shi and Krom, 2009; Journet et al., 2008; She et al., 2011b; Scheuven et al., 2011). The total sol-Fe measured in the leachate is the sum of the sol-Fe extracted by the flow through technique and the additional sol-Fe that occurred due to the breakup of the dust grains and subsequent dissolution of the sub- $0.45 \mu\text{m}$ sized particles. Presently, little evidence exists to suggest that sub- $0.45 \mu\text{m}$ sized particulate dust-Fe in the form of highly crystalline Fe-(oxyhydr)oxides such as hematite and goethite, and as Fe(III) substituted into aluminosilicate minerals is freely available for all phytoplankton species. Therefore, size-sorting of the aerosols in the DI-Method could lead to considerable overestimation of sol-Fe. Moreover, as the abundance of sub- $0.45 \mu\text{m}$ sized particles bonded to larger dust grains or the number of sub- $0.45 \mu\text{m}$ sized particles in dry dust that remain aggregated due to cohesive forces change with the aerosol size distribution (Ogata et al., 2011; Baddock et al., 2013), future studies should achieve improved characterization of size-fractionated dust Fe solubility. Potential contribution from the breakup of different sized dust grains to fractional solubility of Fe could be examined by measuring sol-Fe prior to and after the acidification of the leachate.”

#8. Page 14389: The role of nanoparticles in iron cycling is an area of current study. Might these very small particles that could be introducing variability in fractional solubility observations ultimately be dissolved iron sources in the photic zone? Baker and Croot (2010) offer extensive discussion of this topic. They are likely a source of dissolved iron in the surface ocean dependent on a number of factors reviewed by Baker and Croot (2010) among others. Analytical methodology will dictate whether nanoparticle bound iron is included in the soluble pool. It is unlikely that bound iron would be misattributed to the soluble pool by any methodology using a pre-concentration column or which relies on reaction chemistry such as DPD catalysis. “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...” Chemical oceanographer are not particularly interested the fraction of iron soluble under atmospheric conditions. The purpose of flow through extraction, or any extraction method, is to mimic dissolution under marine conditions. The low pH conditions are a necessary preservation method to prevent loss of iron to the walls of the container and to prevent precipitation during storage.

Please see our response to comment #7.

#9. Page 14390: Wet deposition is the dominant pathway in many areas. Why then is the wetting of aerosols during leaching not representative?

Please, see our response to comment #7

#10. Page 14398: None of the citations appear in the References.

Citations have been included in the updated manuscript.