

Interactive comment on “Air-to-sea flux of soluble iron: is it driven more by HNO₃ or SO₂? – an examination in the light of dust aging” by H. Yang and Y. Gao

H. Yang and Y. Gao

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Point-by-Point Responses to Anonymous Referee #1 October 1, 2007

Anonymous Referee #1 Received and published: 1 August 2007 Review of manuscript “Air-to-Sea Flux of Soluble Iron: Is It Driven More by HNO₃ or SO₂? - An Examination in the Light of Dust Aging by Yang and Gao I have reviewed this paper about a year ago when it was submitted to Geophysical Research Letters. Although paper has been changed to some extent and some of specific comments I had at that time have been taken into account, my general comment about the paper remains the same. As most of the conclusions of the manuscript are based on iron dissolution method that in my opinion is incorrect (see below), I would not recommend publication

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without successful resolution of this issue.

Response: We appreciate the constructive comments from this reviewer this time and last time as well. We have carefully considered all comments, and have accommodated them in so far as possible in the text. We chose not to resubmit it to GRL as the modified manuscript exceeds GRL's page limit. We have to admit that the science community is only beginning to examine systematically the Fe solubility on dust. At present, we are not much more than extrapolating sparse data. In a few years, theories we believe today could be revised significantly. In this context, it is reasonable for us to study the relative contributions of HNO₃ and SO₂ to Fe mobilization, considering that future air quality control will have different impacts on NO_x (the precursor of HNO₃) and SO₂ emissions. Then we like to know what the most important parameters to measure and to include in the model for this objective.

General comments: This study aims to quantify the relative importance of HNO₃ and SO₂ on soluble iron (Fe) fluxes to the oceans through numerical model simulations. For Fe dissolution authors adopt a scheme proposed by Fan et al. (2006) where three types of dust/iron tracer are carried in the model to separate the three life stages for dust particles: fresh, coated, and dissolved (for Fe). The transformation of dust from fresh to coated is controlled by heterogeneous uptake of gases on dust, and the transformation of dust from coated to dissolved is controlled by the dissolution rate of Fe. The model was run for the year of 2001. Followed John Martin's iron hypothesis there has been increased interest in Fe solubilization and deposition to the oceans. In general, modeling studies can be divided in three broad categories: 1. Studies that try to quantify deposition of soluble Fe assuming a constant dissolved Fe fraction (i.e., between 1-10%); 2. Studies that model Fe solubilization based in the first principles (i.e., acid mobilization hypothesis); 3. Studies that try to parameterize Fe solubilization process using the experimental data. This study by Yang and Gao falls in this latest category. Authors correctly notice potential problems relevant to the soluble Fe budget (i.e., future trends in the emissions of NO_x vs SO₂) and therefore it is

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interesting to explore the relative role of nitrate and sulfate in Fe solubilization process (although the paper fails to consider heterogeneous uptake of NO₂ on dust particles).

Response: We did not include NO₂ in this work, because the heterogeneous uptake coefficient of NO₂ on dust particles is too small ($\sim 10^{-6}$, Underwood et al. 2001) for NO₂ to be an effective coating gas compared with HNO₃ and SO₂.

However, I have a major problem with this manuscript that needs to be resolved prior to its consideration for publication. In their acid mobilization hypothesis Meskhidze et al. (2003; 2005) only consider sulfate because, as they discuss in the paper, at pH required for the acid mobilization of hematite, both chloride and nitrate will be driven out from the solution phase to gas phase (i.e., HCl and HNO₃). If authors want to consider nitrate, they need to say which mechanism they envision for the hematite dissolution. Such mechanism should cause significant dissolution of hematite at pH > 3.

Response: The paper examines the relative role of HNO₃ versus SO₂ and sulfate through dust aging, the first step of dust mobilization. We did not explicitly distinguish the role of different species in the second step, which is controlled by many factors beyond HNO₃, SO₂ and sulfate. The Fe dissolution promoted by organic ligands is a possible mechanism in which HNO₃ plays an important role at pH > 3. For example, the oxalate-promoted Fe dissolution rate at pH = 5.0 could be as high as the one catalyzed by proton at pH = 2.0 (Cornell and Schwertmann, 2003; Martin 2005). Organic acids are ubiquitous in the atmosphere, however, the atmospheric sources of them are still open to question, and they have not been simulated in the atmospheric chemistry models yet.

However, there is no need to specify dissolution mechanism in Fan et al. (2006) approach. Fan et al. (2006) simplify Meskhidze et al. (2005) formulation for Fe dissolution and adjust the rate constant to obtain a good global agreement between modeled and measured Fe solubilities. When approach like this is used there is no need to specify the type of acid (i.e., it could be HCl or organic acids), and although this approach is

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limited in its application due to sparse observations, it can lead to reasonable global budgets for soluble Fe deposition to global oceans. However, in my opinion, the approach taken by Yang and Gao is incorrect. They take dissolution rate constant (from Fan et al. (2006)) that was derived considering the effects of all acids relative to tropospheric conditions, and then use this rate constant to evaluate the relative contribution of HNO₃.

Response: The paper by Fan et al. (GRL, 2006) focused on the justification of dissolved Fe input by SO₂ specifically, not all acids; therefore the rate constant in Fan et al (2006) is acid-type-specified, although this rate is used for all acids, assuming it is applicable to all. Our work was built up on the results of Fan et al (2006) with the same assumption that this rate constant is applicable to HNO₃ as well. We acknowledge that there are substantial uncertainties involved with our approach, similar to many other modeling approaches in which the uncertainties can not be avoided and the assumptions have been made. But this approach allows us to explore the issue of dissolved Fe from a different perspective. Our intention is to examine the relative contribution of HNO₃ and SO₂ through dust aging, the first step of the two-step mechanisms of Fe dissolution. As pointed out, the Fe dissolution rate in the second step is prescribed or tuned based on the observations rather than solved explicitly in the model, since it is controlled by many factors beyond HNO₃ and SO₂, such as organic ligands and pH.

In other words, we know that HNO₃ condenses much faster on mineral aerosols compared to SO₂ and therefore in parts of the globe where HNO₃ concentration is comparable (or higher) to that of SO₂ it is known a priori that 1nm thickness acid coating (used for the separation of fresh and coated particles) will be reached much easier with HNO₃ (see also comment #2). However, what is not known is if the dissolution rate constant derived from experimental measurement is equally applicable when only the effects of HNO₃ are considered.

Response: Both HNO₃ and SO₂ are considered in our work, and the aim of this study is to distinguish the relative role of HNO₃ and SO₂ in Fe dissolution. We do not intend

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to justify that only HNO₃ is responsible for Fe dissolution when only HNO₃ is present in dust aging, just as when both HNO₃ and SO₂ are present, the Fe dissolution is still under the influence of "light and ligands". We set up different scenarios for the purpose of comparison as discussed in the text.

Specific comments: 1. Acid coating thickness is a model specific “tunable” parameter. In case of Fan et al. (2006) acid coating thickness of 1 nm (˜ 4 monolayer) provided good agreement between their model results and observations of dust concentration. There is no guarantee that 1 nm thickness will work well if only HNO₃ and with variable relative humidity is considered.

Response: The coating thickness of 1 nm is an assumption, which is put forth to increase the water-absorbing capacity of dust particles since fresh dust absorbs too little water vapor to form a solution on dust surface (Goodman et al. 2000; Vlasenko et al. 2006). The critical point here is whether we can assume the same coating mass for both HNO₃ and SO₂. The water absorbing capacity of a particle with a fixed size is determined by the moles of solute n_s it has: $n_s = n_i m_s / M_s$, where n_i is the number of ions resulting from the dissociation of one solute molecule, m_s is the coating mass, and M_s is the solute molecular weight. The physical or chemical reactions occurring on dust surface after the condensation of HNO₃ and SO₂ is still open to question, and it is not explicitly resolved in our model (or in many other models). Therefore, we can only probe several potential scenarios to see whether it is appropriate to assume the same coating mass for the two gases. In the presence of water vapor, we can assume ammonia condenses on dust together with HNO₃ and forms NH₄NO₃, or we can assume HNO₃ reacts with calcite and forms Ca(NO₃)₂. We can also assume SO₂ is oxidized to SO₄ and forms (NH₄)₂SO₄. The resulting moles of solute n_s per unit mass of NO₃ or SO₂ is similar for all three scenarios. However, the oxidation of SO₂ on dust surface is under large uncertainties since it involves other oxidants such as O₃, and it is uncertain how much of it is oxidized in the initial stage of coating accumulation. In the case that SO₂ just physically adsorbs on dust surface, it makes very little contribution

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to the moles of solute ns due to its rather small Henry's Law coefficient ($\sim 1 \text{ M atm}^{-1}$). Therefore given the hygroscopic property of HNO_3 , our assumption of 1 nm coating thickness for both gases possibly works better for HNO_3 than for SO_2 .

2. It is not clear how $\text{RH}_{\text{sh}}=76\%$ for the Base case and $\text{RH}_{\text{sh}}=45\%$ for the Ref case were determined. Eq. 1 taken from Fan et al. (2006) has already been tuned; Why was there additional need for the trial and error? What kind of trial and error was used? Were the same data sets used on Fig. 1 for the model comparison and for deriving $\text{RH}=76\%$ by trial and error?

Response: We explained this in the text: "The value of R_d as $4 \times 10^{-11} \text{ mol/ m}^2/\text{s}$ was used to match the lower limit of γ in the Ref case as by Fan et al. (2006), which has a much slower dust transformation than the Base case. For faster dust transformation produced by larger γ as in the Base case, R_d as $4 \times 10^{-11} \text{ mol/ m}^2/\text{s}$ produces a far large Fe solubility compared to observations." Now we must reduce R_d for the Base case that has a much faster dust transformation than Fan et al. (2006). Noticing that Fe dissolution always occurs in a solution, so instead of tuning a smaller R_d , we choose to put a RH threshold on Fe dissolution. A high RH_{sh} reduces Fe solubility more heavily than a low RH_{sh} , and the specific value of RH_{sh} is tuned to achieve a good agreement with observations. We have tried $\text{RH}_{\text{sh}} = 50\%, 80\%, 70\%$, and finally ended up with 76% . A similar procedure was carried for the Ref case, and the same observational data sets on Fig. 1 are used for all the experiments.

3. In the old manuscript there was a discussion regarding a coating rate by HNO_3 and SO_2 . The coating rate by HNO_3 is higher than SO_2 almost everywhere in the free troposphere since the concentration of SO_2 decreases faster with height than HNO_3 . Similar arguments can be applied to the Southern Hemisphere (SH), but the coating rate by HNO_3 is higher than SO_2 only over continents and the peripherals in lower layers: it gradually gains over ocean with height, and is higher almost everywhere above 4 km ; And my comment was: Hematite dissolution is very strong

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(exponential) function of temperature (Azuma and Kametani, 1964; Blesa et al., 1994; Cornell and Schwertmann, 1996; Skopp, 2000). I am not sure there would be any significant dissolution above 4km anyway. Also was model predicted relative humidity at 4km generally higher than 76%? In the new manuscript there is no discussion regarding height dependence of either gas deposition rate or hematite dissolution. I would like to know how this problem was resolved.

Response: We agree with you that there might not be any significant Fe dissolution due to the low temperature above 4km (below freezing point), and there is much less water at such high altitude ($RH < \sim 50\%$). Our previous description of the concentration of HNO₃ versus SO₂ is to help to explain their relative roles in dust aging, not directly on Fe dissolution. The sentence in the previous manuscript was removed since it seems causing confusion.

4. Since authors use data from NE Mediterranean, NW Mediterranean, France, Rhode Island, and North Carolina for the model comparison, I would recommend not limiting their discussion to hematite but considering a general term "iron oxides". According to the recent findings contribution of anthropogenic Fe to total dissolved Fe in these regions could be more important than that of the dust Fe. Since model only considers dust-Fe will inclusion of anthropogenic Fe have any significant effect on the conclusions reached in the paper?

Response: Thanks for the suggestion, and we have revised the text to use iron oxides as a general term and hematite in a specific situation. Our model simulation does not show a consistent evidence of anthropogenic Fe that is believed to have a higher solubility than aeolian Fe and a strong regional impact. The overall model comparison in these sites is fine except for NE Mediterranean (site 1), and we will check into it in our next step work.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 10043, 2007.