

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 #2 October 1, 2007

Anonymous Referee #2 Received and published: 26 July 2007 Review of "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. Submitted to ACP. Summary This paper shows the impact on the soluble iron content in dust when exposed to HNO₃ as acidifying agent and compare with the effect of acidification by SO₂. The authors use a global atmospheric transport and chemistry model (MOZART-2) to run three experiments. The impact of the individual effect of HNO₃ and SO₂ and their combined effect on iron solubility is estimated. They conclude that iron mobilization by HNO₃ is signifi-

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cantly higher than that by SO₂. They suggest that given the future pollution scenarios, HNO₃ fertilization can have a larger relative contribution to iron mobilization. This paper nicely shows an alternative pathway by which iron in dust can become soluble. However, there are some concerns that need to be addressed before recommending this paper for publication.

General comments Many of my comments refer to missing information which ostensibly is included in another submitted manuscript by the same authors. Since the manuscript is not available, this reviewer is left with many pieces of information missing as noted. I leave it to the Editor to include my suggestion of additional information. Below I make some general comments and then I show some major (points regarding paragraphs 10048:20-10049:3, 10051, 10052, 10054) and minor comments that should be addressed.

Response: We now have inserted an appendix in the revision to provide the related information regarding dust simulation and validation.

I think the authors should make an effort to provide more specifics on details of the processes explained from the viewpoint of the possible audience. This paper has implications related to marine biology, aerosol and gas transport modeling and detection (e.g. satellite monitoring) and aerosol-cloud interaction (Fe processing in cloud). Because the potential audience will include researchers with disparate background such as marine biology and aerosol remote sensing, the authors should explain more the setup and conditions of the simulations as well as provide more background on the explanations suggested. Specific points are detailed in the next section.

Response: Thanks for the constructive suggestions. We have accommodated them as far as possible in the revision to make the paper more useful to the community.

Although this paper deals exclusively the chemical aspects of this effect, it does not emphasize the importance of the right dynamics conditions that need to occur too. A major condition needed for dust transformation into a soluble form is the transport of

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the dust into an area of high humidity. Without the mixing with clouds and exposure to high levels of humidity, this phenomenon would not happen or be extremely minimized. However, I find that there is little discussion of the relevance of this fact and possible pathways through which it may occur. For example, many of the big dust sources in the NH are in large subsidence areas where dry air is common in the free troposphere. When the dust is lifted to the FT and advected away, it will have little contact with high humidity unless encounters a different weather pattern. Dry dust can travel thousands of km as demonstrated by the hygroscopicity measurements of Li-Jones et al., (1998) in Bermuda. So, for example, the explanation in 10049, 5-10, "little solubility of dust in the N tropical Atlantic is due to its proximity of the source", (also the explanation starting on 10049, 21-23 "The smaller . . ."). However, what would happen if dust near the source is processed by a cloud? Would this near source dust become more soluble? In this scenario, one conceivable could have soluble Fe near the source. Another interesting pathway is the dust that travels in the oceanic boundary layer (and exposed by sea-salt) and then processed by clouds. Dust does travel long distances in the BL (Gassó and Stein, 2007) and it can be impacted sea-salt (thus becoming more hygroscopic) as it was shown by Levin et al, (2005).

Response: We agree with you that it is important to include a discussion of the dynamic condition that is necessary for the mobilization of Fe carried on dust. We will include such a discussion in the revised manuscript.

Specific comments Major Concerns: 10048, 20-10049, 3: The description of data in Figure 1 is poor. It does not explain the origins of the data sets and some basics. Several questions and comments arise from the comparison offered in this plot: 1) Are the in-situ data collected in airborne (such on the ship's deck) or extracted from the ocean?

Response: The in-situ data were collected in the air.

2) There is no explanation or descriptions of the time resolution (yearly or monthly) and

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spatial resolution (cruises or sites?) of the in-situ data.

Response: Most of the information regarding the origins, the temporal and spatial resolutions of the in-situ data sets is included in Fan et al (2006). We put the reference in the caption of Figure 1, which however seems not sufficient and is causing confusion. In the revised manuscript, we have added a new table to provide the related information on the in situ data.

3) Why comparing data taken in a period of 1988-2002 is comparable to a simulation run over year 2001?

Response: We believe that the simulation and observation over slightly different time periods (without too much offset like in this study) are comparable in a climate sense. The comparison shown in Figure 1 is either long-term average at a specific location (monthly or annual means), or average over a large area (the cruise data) that have been used widely for comparison. We think we still can learn from such kind of rough comparisons; however, we agree that such a practice could cause some deviation between the simulation and observation.

4) In any case, I see little value of inclusion of Figure 1 as it is shown and explained does not make a convincing point. Given the few points for comparison, their scatter and the diverse nature of the data set in time and space, it is not clear how much random variability is being shown in the plot and how much of the actual solubility effect is being shown.

Response: It is not a surprise to see the scatter and diverse nature of the comparison in Figure 1, just as the one shown in Fan et al. (2006), and also in the modeling studies of dust (e.g. Ginoux et al., 2001; Zender et al., 2003), due to the complexity of the processes that are involved. Our emphasis here is the overall agreement between the model and observation, which suggests that the most important processes have been captured by the model.

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In addition, this figure suggests a scaling between modeled and deposited solubility. But it is not clear from the in-situ data whether the HNO₃ is responsible of the observed solubility which is the main point of this paper. My suggestion would be to remove the comparison altogether (and limit this study to a purely model study).

Response: The purpose of Figure 1 is to illustrate the ability of the model to simulate Fe solubility, which is a prerequisite to examine the relative contribution of HNO₃ versus SO₂. This is why we conducted three experiments for each case: the first experiment with both gases is used to validate the model. We believe that our conclusion regarding HNO₃ and SO₂ in the process of Fe mobilization will not be convincing without Figure 1.

10051, 1-5. This statement refers to my previous comment regarding fig. 1.

Please see responses in the above.

10052, 24-25. I do not agree with this statement. F23 is markedly different in large area NW and SE of Australia encompass a significant portion of the South East Pacific. Please, address why since it is the only major feature observed in the SO.

Response: F23 in the NW and SE of Australia shows feature of an area in the proximity of dust source regions, as the one seen in the North Tropical Atlantic.

S10054, 20-23. The emphasis of this summary should be changed. This is a modeling study and the effect of the relevance of HNO₃ in dust solubility has not been validated by measurements. It does not show that Fe fertilization (implying a response from phytoplankton) occurs because this effect. This reference should be removed. However, it does suggest the existence of a viable alternative mechanism by which Fe can be mobilized.

Response: We have made changes in the revision to clarify that the cited references of measurements only provide indirect but not direct evidence of the dominant role of HNO₃ in Fe mobilization.

Minor comments, clarifications and suggestions Abstract 10044, 10-15: Why reporting an average as a range? not clear.

Response: This is because we did two case studies (the Base and the Ref cases). The range is produced by the two cases. Since this seems to cause confusion, the range of soluble Fe deposition per day is reported in the revision.

10044, 10-15: Last sentence is a bit confusing. This is a matter of semantics but I think it is important to stress in this sentence the following points: the emission trends of NO_x will increase according to future scenario and that this increase will be mostly anthropogenic.

Response: We will stress the anthropogenic nature of the increase of NO_x emission in the revision according to this suggestion.

Introduction 10045, 5-10: There should be an acknowledgement of the poor understanding of dust composition and mineralogy (with the consequently unknown hygroscopic affinity of the dust) in most of the deserts of the world, particularly those in the Southern hemisphere.

Response: This is a very good point, and we will include such an acknowledgement in the revision.

10045, 5-18: What is the natural or background contribution of HNO₃? Or is it exclusively of anthropogenic origin? Please make it explicit.

Response: The emission sources of NO_x in the model include industry and fossil fuel combustion, biofuel combustion, biomass burning, biogenic (soil), lightning and aircraft. The emission from Industry, fossil fuel, biofuel and aircraft is responsible for ~57% of the total emission, and there is also an anthropogenic fraction in the biomass burning (Horowitz et al., JGR 2003). We will add this additional information in the revision.

Anywhere in the introduction: this is a suggestion. Coating by sulfates and nitrates on dust is also relevant in radiative forcing and you may want to add comment on how

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it relates or complements your study a recent publication in JGR-Atmos (Bauer et al, 2007) which looks at this issue.

Response: Thanks for the suggestion. We will refer Bauer's paper in the revision.

Method 10046, 5-10: Please expand and clarify your definitions of fresh, coated and dissolve. These criteria are used several times in the next sections. Furthermore, I found the definition in Fan et al, (2006) not clear either. For example, is it a "fresh" particle a particle that has not entered to a cloud or has not been exposed to high humidities?

Response: "fresh" is used for the hydrophobic dust; "coated" is hydrophilic dust with an acid coating of 1 nm; and "dissolved" is converted from "coated" under the restriction of Fe dissolution rate. It is assumed in the model the newly entrained dust is composed of 99% "fresh" and 0.5% "coated" and 0.5% "dissolved" dust. We will incorporate these definitions into the revision.

10046, 5-10: Model was run for year 2001. Is there a particular reason why? Was it just the modeled data was just available for that year? Because actual measurements are shown later, there should be a bit of discussion of worldwide dust activity and pollution in 2001. For example, was this year particularly dusty? Did pollution traveled more or less than past or following years? I think the point is that there should be more context added on the election of this year for the simulation.

Response: Initially we planned to do the simulation from the year 2001 to 2003, and ended up with 2001, since our simulation of dust over 2001 to 2003 does not show significant annual variation (Yang et al., submitted 2007), and the primary gas emission data used for this study does not change annually. The other reason to choose the simulation at 2001 is our intention to compare with the MODIS satellite retrieved aerosol data that began from 2000, although this was not carried in the study finally. Nevertheless, it is a good idea to discuss the worldwide dust activity and pollution in

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2001 to provide more background information. We will include such a discussion in the revision.

10047, 1-5: Equation 2), there must be a typo since there is a reference to N2 in the text but there is no N2 in the equation.

Response: Thanks for pointing out the typo. There should not be N2 in the text. Correction has been made.

10048, 5-10: This paragraph is the only one that discusses or mentions the fate of Fe in a cloud. I think more context should be added here and refrain to leave the explanations to the referenced study (Fan et al, 2006). For example, these questions should help as a guide: does the model deal only with water phase clouds? What happens with dust in the presence of ice? How good is the MOZART-2 model in representing realistic wet removal processes and microphysics (if it has any)? Information on the strengths and weaknesses of the model on these points would be very useful.

Response: Clouds are not explicitly included in the mechanism. Instead, a relative humidity threshold (RHsh) is used as a switch to control the Fe dissolution process. It is mentioned later in section 3.4 (on page 10053) that the use of a threshold RHsh as of 76% for Fe dissolution in the Base case is close to being able to include cloud processing. Nevertheless, it is still helpful to include a discussion of the cloud and wet removal processes in MOZART, which will be made in the revision.

10048, 10-20. It is not clear the definition of the experiments E2 and E3. Can you clarify more the nature of tests ran? For example, if E2 only deals with the effects of HNO₃, does it mean that $k_s[\text{SO}_2]$ is set to zero in eq 1?

Response: Experiment 2 has HNO₃ as the coating gas, and experiment 3 has SO₂ and sulfate as the dust transformation agents. This is reflected in the calculation of K_c ($K_c = K_g + K(\text{SO}_4)$, see equation (1) and (2)). For experiment 2, $K_c = K_g(\text{HNO}_3)$; for experiment 3, $K_c = K_g(\text{SO}_2) + K(\text{SO}_4)$.

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Results and discussion 10049, 3-4. Figure 2 depicts global distribution corresponding to E1, E2 or E3?. Please, clarify.

Response: It is the global distribution corresponding to experiment 1.

10049, 15-16. Please provide range of values for this estimation and average solubility. These absolute values do not have much meaning without a sense how much variable they can be.

Response: We will include the monthly and seasonal variation range in the revision.

10050, 20-21. Same comment as before. Please provide range of values for this estimation and average solubility. These absolute values do not have much meaning without a sense how much variable they can be.

Please see responses in the above.

References Li-Jones, X., H.B. Maring, and J.M. Prospero, Effect of relative humidity on light scattering by mineral dust aerosol as measured in the marine boundary layer over the tropical Atlantic Ocean, *J. Geophys. Res.*, 103(D23), 31,113-31,122, 1998. Gassó, S., and A. F. Stein, 2007: Does dust from Patagonia reach the sub-Antarctic Atlantic Ocean?. *Geophys. Res. Lett.*, 34, L01801, doi:10.1029/2006GL027693. Bauer, S.E., M.I. Mishchenko, A.A. Lacis, S. Zhang, Ja. Perlwitz, and S.M. Metzger, 2007: Do sulfate and nitrate coatings on mineral dust have important effects on radiative properties and climate modeling? *J. Geophys. Res.*, 112, D06307, doi:10.1029/2005JD006977. Levin, Z., A. Teller, E. Ganor, and Y. Yin (2005), On the interactions of mineral dust, sea-salt particles, and clouds: A measurement and modeling study from the Mediterranean Israeli Dust Experiment campaign, *J. Geophys. Res.*, 110, D20202, doi:10.1029/2005JD005810 Interactive comment on *Atmos. Chem. Phys. Discuss.*, 7, 10043, 2007.

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