

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 #3 October 1, 2007

Anonymous Referee #3 Received and published: 23 August 2007 Review of Yang and Gao. Air-to-sea flux of soluble iron: driven more by HNO₃ or SO₂?

This is a potentially interesting paper, looking at the production of soluble iron. It is weak on comparisons to observations, and more simulations/figures are required to demonstrate the main thesis of the paper, but after major revisions it should be acceptable for publications.

Major issues: Major issue #1 Comparisons to observations: There needs to be much

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more work showing that we should actually trust this model. Where is the comparison of the model dust or total iron observations? Where is the comparison of the model sulfate and nitrate to observations? How does the uptake rate change these comparisons (e.g. there is some mention in the methodology about this, but it needs real comparisons in the paper). This needs to be done first (or cited) before we can begin to trust the results of this model.

Response: The information regarding dust simulation and validation is included in another submitted manuscript. Since it is not available yet, we have included an appendix in the revision. The comparison of the model sulfate and nitrate to observations was described in Tie et al. (2005). The bulk dust simulation is changed in a subtle way when there are three categories of dust instead one in the model. The variation trend is similar to Fan et al. (2004): the dust concentration over the Pacific decreases a little bit due to the heavy air pollution in East Asia; and the dust over the Atlantic increases a little bit due to less air pollution in the Africa. The overall comparison with observations is better when there are three categories of dust.

Figure 1 needs more work. We adopt the observations in Buck et al. (2006) for the Pacific instead of using Hand et al. (2004) that has the Fe(II) solubility. I don't understand this statement. It is probably worth introducing the observations in the methodology section and what assumptions you are making about what set of observations you are comparing against, and the difficulty of measuring Fe(II), etc. It looks like you are averaging a lot of data; why? If there is spread in the original data, that is information. Does your model capture the spread? Is the spread due to uncertainty in the measurements? Or variability (spatial and temporal)? This plot is the most important in the paper, and it is not well described or apparently rigorously considered.

Response: Fe(II) and soluble Fe(III) were not distinguished in our simulation. The conversion between them is fast, and Fe(II) is less stable than Fe(III) in the atmosphere due to the existing of large amount of oxidants. For instance, Zhu et al. (1993, JGR)

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measured that only 7.5% of the soluble Fe were in the Fe(II) oxidation state. Therefore Fe(II) does not represent the whole body of soluble Fe. The reason to make an average of many data is to reduce the uncertainty in the measurements, and also to make the data more representative in a climate sense. We will add a discussion on the spread of data in the revision.

Wet deposition contributes >80% to soluble Fe flux over most of the world ocean (Gao et al., 2003; Fan et al., 2006), implying Fe mobilization generally undergoes precipitation processes besides being cycled through clouds (Junge, 1964). How does the model do compared to available observations of wet vs. dry mineral aerosol deposition?

Response: The model results are consistent with observations, e.g. Arimoto et al. (1985, JGR). In addition, Prospero et al. (1989, Chemical Oceanography) suggested that dust deposition occurred primarily with rain and that dry deposition only played a minor role. We will incorporate these references into the revision.

Major issue # 2: HNO₃ vs. SO₄ Much of what is considered in this paper is already seen in the literature, as cited by the paper. What is new is the HNO₃ vs. SO₄ part of the paper, and thus the part that makes the paper worthy of publications. This is not fully considered by the paper, and needs more work to show this clearly. The paper is pretty light on simulations and figures as it stands, so saying these are beyond the scope of the paper would be inappropriate.

Response: It is a good point to present the results regarding sulfate in a different way. Currently it is only considered as a dust transformation agent, which is not as efficient as HNO₃ and SO₂ in most cases. This suggests that the major entry path of sulfate onto dust may not be the direct coagulation of SO₄, but through SO₂ coating. Another perspective to look at dust aging is the change of its optical characteristics and radiative forcing, as discussed in Bauer et al. (2007, JGR). We will refer to Bauer et al. (2007) in the revision.

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The reason that sulfate has been considered more than nitrate previously is because it is a much stronger acid. So using a case where the sulfate doesn't do anything and comparing to sulfate alone, does not tell us who is doing the work when they are both in the model. Or tell me how to interpret this; I am not sure what to do with these results. Some more studies are needed to do this. It's possible you could use your experiments 2 vs. 1 or 3 vs 1 to support your argument. But better would be additional studies (which should be easy to do, since you have the model working now): Can you label the soluble iron that comes out of the nitrate in the model with both compounds working? Or can you add 10% nitrate and 10% sulfate to the model (in separate simulations)? That would tell us the partial derivative. Or perhaps more usefully, do a study where you double the nitrate in the future (or use future IPCC NO_x emissions) and say what happens? This would make the paper much more useful and publishable.

Response: These are very good suggestions, and we will consider doing new experiments.

Abstract: We demonstrate that coating by HNO₃ produces over 36% of soluble Fe fluxes compared to that by SO₂ and sulfate 15 combined in every major oceanic basin; I misunderstood this statement; it needs to be rewritten to be clearer. Also, you need to say that the sulfate was completely removed from the system for this sensitivity study.

Response: The case with HNO₃ (experiment 2) does not include SO₂ and sulfate as the dust transformation agents; and the case with dust transformed by SO₂ and sulfate (experiment 3) does not include HNO₃. All this happens when dust is transformed from hydrophobic to hydrophilic. We did not distinguish the role of different species in the second step of iron mobilization, since it is not explicitly resolved in the model. We will make this point clearer in the revision.

Methodology: We therefore check the ratio of soluble Fe flux between exper-

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iment 2 and (F23), which explains the relative importance of HNO₃ compared to SO₂ and sulfate. As stated above, I'm not sure this is the right test for the relative importance.

Response: The relative importance is in terms of the direct impact on dust aging, with an assumption of the same Fe dissolution rate. Therefore, F23 is able to support our conclusion. Nevertheless, as suggested in the above, it would be better to support the conclusion with additional experiments. We will modify the statement after doing new experiments.

The global distribution of the annual mean ratio of soluble Fe flux produced by HNO₃ versus that by SO₂ and sulfate (F23) in the Base case is presented in Fig. 3. F23 is higher than 1.0 over most world oceans, suggesting that HNO₃ makes a larger contribution onto soluble Fe fluxes than SO₂ and sulfate; I'm not sure you have made this case.

Please see responses in the above.

Other details: Please discuss the relationship between Fe(II) and bio-available iron in the introduction.

Response: Photochemical reduction in more acidic cloud waters and precipitation may promote dissolution of Fe in dust, leading to the production of soluble Fe (II) which is believed to be more readily used by phytoplankton (Sunda, 2001, Biogeochemistry of Iron in Sea Water).

Figure 2: how does figure 2 compare to previous model results and data compilations? Is there anything new in Figure 2 compared to previous studies? Why is it new?

Response: The general distribution pattern of soluble Fe as shown in Figure 2 is similar to the one shown in Fan et al. (2006) that also has a variable Fe solubility, while the soluble Fe flux is about half of that study. And as discussed in Fan et al. (2006), the major difference in soluble Fe flux between this study and the one with a fixed Fe

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solubility (e.g. Fung, et al., 2000) is over the subtropical North Pacific, where much more soluble Fe flux is produced in this study and in Fan et al. (2006) due to the heavy air pollution in Asia. It is noted that the subtropical North Pacific is one of the major HNLC regions in the world ocean.

Calculations from this study show that at the surface level, HNO₃ generally has a higher conversion rate than SO₂ in major dust source regions in the NH, where over 90% dust is transformed from fresh to aged in the Base case. Is it true that you are showing the surface concentration of soluble Fe? I thought you were looking at the soluble Fe flux? Please be specific and clear. There is another example of this vagueness; in the text; make sure you are doing the comparisons that you say, and if they are not plots in the manuscript at least say (figure not shown), but you have lots of room for more plots.

Response: We apologize for the confusion. The calculation/discussion was based on the transformation rate by different species, where figures were not shown. We will include them in the revision.

The transformation takes ~33 h by HNO₃ in the North Africa and the Arabian Peninsula, and ~26 h in the Central and East 5 Asia. It takes ~887 and ~176 h by SO₂ respectively in these regions; How is this calculated?

Response: The transformation rate is calculated in MOZART in each simulation step. The average transformation time is obtained by calculating the reverse of the average rate for each region. Such a practice put a higher priority on fast transformation (e.g. during the day) than on slow transformation (at night). The average is made by using ferret.

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