

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

Anonymous Referee #1

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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 without successful resolution of this issue.

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 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). 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. 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 limited in

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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. 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 1 nm 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.

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.
2. It is not clear how RH_{sh}=76% for the Base case and RH_{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 RH=76% by “trial and error”?
3. In the old manuscript there was a discussion regarding a coating rate by HNO₃ and SO₂. “The coating rate by HNO₃ is higher than SO₂ almost everywhere in the free troposphere since the concentration of SO₂ decreases faster with height than HNO₃. Similar arguments can be applied to the Southern Hemisphere (SH), but the coating

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rate by HNO₃ is higher than SO₂ 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 (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.

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?

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