

## ***Interactive comment on “Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution plumes” by T. D. Fairlie et al.***

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The paper presents GEOS-Chem simulations to interpret gas and particle-phase chemical measurements in transpacific dust plumes during the INTEX-B campaign. While a number of previous studies have already addressed nitrate and sulfate partitioning in Asian dust, paper provides some interesting insight into the uptake of sulfur dioxide and gas phase nitric acid on mineral dust. As a broader impact of the study authors attempt to generalize their results for bioavailability of mineral dust-iron upon deposition to the ocean. I present a number of questions and suggestions that may help improving the revised manuscript.

I will start with acid-mobilization of iron (Fe). The results of the current paper are in a good agreement with findings of Meskhidze et al. (2005) and Solmon et al. (2009).

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Paper shows nicely that large dust advection episodes (“dusty air stream”), that can export vast amounts of mineral dust to the open ocean, may not acidify and therefore contain insignificant amounts of water-soluble (or bioavailable) iron. The amount of acidic trace gases required to acidify such dust plumes is much higher than what can typically be entrained in the plume during its advection. Smaller dust plumes (“low-dust air stream”) are expected to have larger fraction of water-soluble Fe because they require lower amounts of SO<sub>2</sub> and, even if such small plumes may not cause large visible algae blooms, they could still be important sources of bioavailable Fe to the North Pacific Ocean. This point should be better explained in the paper as it is somewhat lost in the discussion.

P. 24479, Line 16. Several closely related papers proposing the acidification of mineral dust aerosols during atmospheric transport as the primary mechanism for the production of water-soluble form of Fe in mineral dust are missing here including (Duce and Tindale, 1991; Zhu et al., 1992; Zhuang et al., 1992a; b; Zhu et al., 1993; 1997). Meskhidze et al. (2003; 2005) suggested that SO<sub>2</sub> emissions from the urban and industrial centers of China (i.e., *anthropogenic pollution*) can lead to the mobilization of Fe in mineral dust and developed first prognostic, physically based dust-Fe dissolution module.

p. 24489, line 8: I found discussion of Solmon et al. (2009) misleading. Not only “a different scheme for acid uptake on dust” was used in that paper, but all the parameters were different. Dust and acidic trace gas concentrations, dust mineralogy (e.g., Ca content of mineral dust), advection pathways, mineral dissolution kinetics, etc. . . It should also be noticed that the GEOS-Chem model has been extensively evaluated over the domain and the model simulations of Solmon et al. (2009) were shown to be consistent with the observations conducted during the TRACE-P and ACE-Asia field campaigns. The inconsistency between TRACE-P/ACE-Asia and INTEX-B observations suggested in the current paper is interesting and needs to be further explored. The potential reasons for the inconsistencies should be addressed.

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P. 24486, Line 15. The charge balance or the “titration of dust alkalinity” is not always a good parameter for assessing the acidity of ambient aerosols. For high ionic strength aerosol solutions ion concentrations can be significantly different from their corresponding activities. It gets increasingly complicated when activities of multicomponent electrolyte solutions are considered (e.g., Bromley, 1973; Pitzer and Mayorga, 1973; Kusik and Meissner., 1978; Nenes et al., 1998). By definition, charge balance suggests that when anions are in the excess of cations, activity of  $H^+$  will tend to neutralize the solution. For pH 5 to 7 that means that activity of  $H^+$  is on the order of  $10^{-5}$  to  $10^{-7}$  M. Or the measured/modeled anion and cation activities (in M) should be accurate for up to seven digits after zero. Thus for the assessment of aerosol acidity, accurate estimation of the aerosol water content is crucial. If the evaluation of aerosol acidity/alkalinity is important in the current paper, I recommend using a version of GEOS-Chem that can explicitly calculate aerosol water uptake for different RH and temperature conditions.

Pg. 24505 Fig. 4(b) (f) shows that even for the dusty conditions the alkalinity of mineral dust was frequently titrated. This is against the hypothesis that large dust storms generally do not get acidified and therefore I think it would be interesting to address those episodes separately. Was the titration of alkalinity caused by the unusually high amounts of acidic trace gases? Was it somehow associated with different outflow trajectories (northern vs. southern branches)? Or could it be that points above 1:1 line on Fig. 4(b) (f) are simply misclassified as dusty air streams (see below discussion about the separation of high and low dust conditions based on the comparison of  $Ca^{2+}$  to that of  $2(NO_3)_3^-$ )?

Overall, it is a good idea to use the results from multiple different measurement campaigns for improved quantification of water-soluble Fe in ambient aerosols; however, more detailed simulations need to be conducted. The absence of such simulations may lead to erroneous conclusions about the formation of bioavailable Fe in mineral dust. Below I show the list of parameters that I hope authors will consider in their

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model simulations for the revised manuscript. All the options are currently available in GEOS-Chem and therefore can be easily incorporated in the current study:

1. Mineralogical composition of dust at the source regions;
2. Thermodynamic module capable of explicit calculation of aerosol pH;
3. Mineral dissolution kinetics of calcite and dolomite (see more discussion below);
4. Different outflow conditions (marine boundary layer vs. free troposphere) should be addressed separately;
5. Since the mineralogy of desert dust (and in particular  $\text{CaCO}_3$  and Fe content, e.g., Sullivan et al., 2007) can vary with the grain size, simulations should be conducted with explicit treatment of dust composition in different size bins (or at least separating sub-micron and super-micron fractions of mineral dust);
6. Sensitivity studies should be conducted to examine the effect of water-soluble fraction of Fe at the source regions (e.g., Shi et al., 2009), composition of dust at the source regions (e.g., carbonate content at the source region can change from 0.3 to 10.5 % of dust, e.g., Li et al., 2007) and different amounts of acidic pollutants available to be entrained in the dust plumes during advection.

The interesting discussion regarding the uptake of  $\text{HNO}_3$  on mineral dust particles would really be improved if the size range of aerosol chemistry and dust mineralogy is considered in the model. The size dependent dust mineralogy plays crucial role for the formation of secondary acidic species (e.g., nitrate, chloride and sulfate) on mineral dust. Therefore, considering dust mineralogy and the size range of the aerosol chemistry is very important as different acidity/alkalinity values can be obtained for fine and coarse dust particles. For example, the results of Sullivan et al. (2007) show that the submicron dust particles can be very acidic, while the bulk dust can remain alkaline. Since the sulfate rich dust particles are commonly associated with aluminum (Al) and Fe containing particles (indicating association with aluminosilicate-dust particles) while the nitrate-dust particles are mostly associated with calcium (e.g., Sullivan et al., 2007),  $\text{HNO}_3$  uptake kinetics on acidic submicron dust particles could be very different from the supermicron ones. The association of sulfate with Al-and Fe-rich dust could

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be due to the iron-catalyzed oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  (Brandt and Vaneldik, 1995; Qi et al., 2006; Rani et al., 1992; Yermakov and Purmal, 2003), while  $\text{HNO}_3$  can be readily neutralized upon reaction with alkaline species such as carbonate. In addition, accumulation of sulfate on mineral dust particles occurs preferentially in the particle size mode with the greatest surface area (reaction is diffusion limited), which is typically the accumulation mode ( $0.1\text{--}1.0\mu\text{m}$  diameter).

Is it possible that the observed  $\text{HNO}_3$  values could be sustained because large dust particles, that primarily contain  $\text{CaCO}_3$ , were preferentially removed from the plume due to their shorter lifetime and small dust particles that contain larger quantities of sulfate are acidic enough not to allow  $\text{HNO}_3(\text{g})$  uptake? Meskhidze et al. (2003) demonstrate that when pH of mineral aerosol get reduced below 4,  $\text{HNO}_3$  uptake will cease and nitrate volatilization will start. This way the uptake mechanism as well as uptake coefficient will be consistent with the published literature, demonstrating very fast uptake (with uptake coefficient  $> 0.1$ ) of  $\text{HNO}_3$  on alkaline dust, while the uptake coefficient decreases to near zero values (as low as  $10^{-6}$ ) when the dust gets acidified. The segregation of nitrate and sulfate in mineral dust particles has been previously reported and may have important implications for  $\text{HNO}_3$  reaction probability and lifetime,  $\text{NO}_3^-$  concentrations and  $\text{NO}_y$  lifetime in general. Such treatment may also improve comparison of model predicted  $\text{Ca}^{2+}$  with the measurement data. Currently Asian dust mineralogical composition (Solmon et al., 2009) and four dust size bins with radii  $0.1\text{--}1.0$ ,  $1.0\text{--}1.8$ ,  $1.8\text{--}3.0$ , and  $3.0\text{--}6.0\mu\text{m}$  (Fairlie et al., 2007) are available in GEOS-Chem. Also both total aerosol chemical composition on filters and sub-micrometer aerosol chemistry using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) are available for INTEX-B campaign. This gives unique opportunity for the mineral dust-size (and mineralogy) dependent uptake of  $\text{HNO}_3$  to be tested.

P. 24482, Line 7. Application of different factors for scaling dust emissions computed from the GEOS-4 fields needs to be better explained. According to Generoso et al.

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(2008) comparison of MODIS and GEOS-Chem AOT over the Atlantic Ocean for the summer episode (30 June to 6 July 2006) shows that the model overestimates AOT over the eastern tropical Atlantic (east of 30W) by 30% but underestimates AOT in the remote regions (west of 30W) by 20%. During a winter episode (13 to 17 February 2007) the simulated AOT were much larger than the satellite data (by a factor of 3). Overall, Generoso et al. (2008) suggest that observed AOT are overestimated by the model close to the source regions and underestimated in the remote regions. So, can a factor of 2 reduction of dust emissions be applied everywhere on the globe, for every season and every dust outbreak (large vs. small, Northern Hemisphere vs. Southern Hemisphere)? What is the reason for such scaling?

P. 24483, Line 11. Further discussion for the assumption of Ca and Mg weight content of mineral dust should be given. Which minerals are associated with these elements? Unless the minerals are specified, the discussion about  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cation equivalents is unclear. For example, if  $\text{Ca}^{2+}$  is associated with calcite, it can neutralize 2 equivalents of acidity, while if  $\text{Ca}^{2+}$  is associated with gypsum, it will neutralize none. Calcite content in the desert soils of East Asia was shown to vary between 0 to 10% (Jeong, 2008) with average 5-20% of silt fraction (Claquin et al., 1999), 10% of dust (McNaughton et al., 2008), 8% of bulk dust samples with 6% contained in coarse calcite fraction (Jeong, 2008), 7.5 to 9.1% in PM10 and 14% in the bulk phase (Shi et al., 2005). Gypsum content in East Asian desert soils was shown to vary between 2-12% of silt fraction (Claquin et al., 1999; Jeong, 2008). So more details need to be provided to explain how was it inferred in a current paper that  $\text{Ca}^{2+}$  cation equivalents constitute 3% of the dust by mass. Additional discussion is also in order for the  $\text{Mg}^{2+}$  containing minerals.

P. 24483, Line 15. How were  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  containing mineral dissolution/reaction kinetics treated in the paper? Is it reasonable to assume that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can instantly react with acidic species? If not, how will the mineral reaction/dissolution kinetics affect the  $\text{HNO}_3$  uptake on mineral dust?

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P. 24484, Line 8. Depletion of calcium rich reactive surface sites by the uptake of  $\text{HNO}_3$  is proposed as a possible explanation for very low uptake coefficient used in the paper. Some of the recent publications (e.g., Vlasenko et al., 2009) show that the  $\text{HNO}_3$  uptake coefficient can be reduced from the measured values of 0.25-0.1 to as low as  $10^{-6}$  when reactive surface sites get depleted. However, such approach may not be applicable to  $\text{CaCO}_3$  containing dust particles where, due to surface to bulk transport, acidic proton can be readily neutralized. I just wonder in case when the fast initial uptake of  $\text{HNO}_3$  is reduced due to saturation of reactive surface sites, should such aerosols be treated as “alkalinity titrated?” This example also clearly demonstrates that  $\text{HNO}_3$  uptake coefficient is likely be different for different size dust particles.

P. 24485, Line 21. What is the possible reason for about 50% overestimation of  $\text{Ca}^{2+}$  in the model? Is that due to the overestimation of dust content or the uncertainty in mineralogical composition of dust at the source region? Also, because a fixed  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio is used in the model is  $\text{Mg}^{2+}$  also overestimated?

P. 24485, Line 24. Separation of high and low dust conditions based on the comparison of  $\text{Ca}^{2+}$  to that of  $2(\text{NO}_3^-)$  is very confusing and leads to inconsistencies between Figures 4a and 4b. Since the model results shown on Fig. 4a are without acidic uptake, the episodes with the same dust concentration may qualify for high dust conditions on Fig. 4a while for low dust conditions on Fig. 4b. I recommend using some type of threshold dust concentration as a cutoff for high and low dust conditions.

P. 24487, Line 18. While the model overestimates the  $\text{HNO}_3$  (g) by a factor of 2 to 8, the argument against using higher uptake coefficient is the production of the excessive aerosol nitrate in the model that is not supported by the observations. This interesting discussion regarding the uptake of  $\text{HNO}_3$  by the dust would really be improved if the  $\text{NO}_y$  and  $\text{NO}_x$  concentrations with and without acidic uptake were also included in Figures 4a and 4b. Does the acidic uptake also lead to better comparison of model predicted  $\text{NO}_x$  and  $\text{NO}_y$  with the observations?

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P. 24488, Line 2. Figure 6 should be Figure 5, and thereafter all the figure numbers in text should be reduced by one.

P. 24488, Line 6. I find discussion about ammonium volatilization very interesting, but somewhat hard to explain. The  $\text{NH}_3$  in the aerosol is in the unionized form and therefore cannot be controlled by the mere variation in the partial pressures. From thermodynamic point of view, for ammonium ion ( $\text{NH}_4^+$ ) to volatilize and leave the particle, some other cation should substitute to conserve charge neutrality. Since the particle coagulation is not allowed in the model, what is the other basic trace gas that can substitute for  $\text{NH}_4^+$  ion?

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