

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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Thanks a lot to Dr. Meskhidze for his extensive comments on our paper, which highlight some important issues, and which we expect will significantly improve the clarity of the final manuscript

Comment: 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). 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-

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dust air stream”) are expected to have larger fraction of water-soluble Fe because they require lower amounts of SO₂ 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.

Response: An important finding of our paper is that consumption of dust alkalinity is generally slower than the lifetime of dust deposition, except for smallest (submicron) particle sizes, so that dust does not acidify, despite larger simulated emissions of acid precursors (SO₂ and NO_x) than combined alkaline emissions from Asia during April–May 2006 (see p. 24488). The reactive uptake of acid gases in our model is much slower than in the studies by Meskhidze et al (2005) and Solmon et al. (2009); they use a much higher uptake coefficient for SO₂ on dust, and permit SO₂ uptake to continue beyond titration of dust alkalinity, and treat HNO₃(g) in thermodynamic equilibrium with dust aerosol, even for super-micron particle sizes. We believe their approach may overestimate dust acidification and bio-available Fe, even in weak dust outbreaks.

Comment: 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 SO₂ 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.

Response: Thanks. We are aware of those papers. In trying to keep the list of references succinct, we cite the paper by Meskhidze et al. (2005), which refers to these earlier works.

Comment: 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.

Response: Indeed, the Solmon et al. (2009) study was conducted for spring 2001, not the same period as considered in this paper. Our point here is that if we applied the same acid uptake rates used by Solmon et al., specifically the uptake rate for SO₂ on dust, we would attain results inconsistent with the INTEX-B observations. The model-data comparison shown by the Solmon et al. (2009) is limited to surface platforms (no free troposphere comparisons); they also show excessive calcium sulfate in the model, and an underestimate of soluble sulfate. A possible explanation is that the uptake of SO₂ on dust in the model is simply too high.

Comment: 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

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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.

Response: The bulk soluble ion observations (Fig. 4) clearly show an anion deficit, which increases with increased dust concentrations. The clear implication, we argue, is that carbonate and bicarbonate remain unconsumed in the dust 3 – 7 days downstream of Asian source regions, despite significant (100 ppt) HNO₃. A major conclusion of our study is that to meet these bulk observations the uptake of acid gases, notably HNO₃, must be much slower than previously thought.

Comment: 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 Ca²⁺ to that of 2(NO₃)⁻)?

Response: The last option suggested by Meskhidze is the correct one. The yellow-marked model results that lie above the 1-1 line in Fig. 4(b)(f) are found below cation equivalences of 1 neq/mole, and are associated with elevated sulfate; dust alkalinity consumption is relatively small. These points show little movement from their positions in the control experiment (Fig.4(a)(f)). Our distinction of “dusty” and “low-dust” branches is based on the model results in Ca²⁺ - nitrate space for the control experiment (Fig.4(a)(a)); we thought this provided a convenient marker to show how results change with acid gas uptake. Clearly the names we have applied are leading to confusion; the “dusty” (yellow) branch also includes very low Ca²⁺ values; “nitrate deficient, without acid uptake” may be a more accurate description. High dust conditions are

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essentially those with cation equivalences greater than 3 neq / mole, none of which show alkalinity titration.

Comment: 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 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 CaCO₃ 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.

Response: The focus of our paper is to understand the nitrate and sulfate partitioning found in the bulk aerosol (SAGA) aircraft measurements in INTEX-B. We represent simple 1st-order parameterizations for the kinetic uptake of SO₂, HNO₃, and H₂SO₄, with uptake rates proportional to surface area, and uptake limited by dust alkalinity and competition from other aerosols (for H₂SO₄), as described on p. 24482-24483. Our argument with respect to bio-available Fe is a very basic one, stemming from the

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conditions described of Meskhidze et al. (2005) and others: is dust alkalinity titrated or not? The SAGA bulk aerosol data clearly indicate that the bulk dust remains alkaline even after 3-7 days downstream of Asia, and in the presence of significant (~100 ppt) HNO₃(g). This dictates that the uptake coefficients for HNO₃ and SO₂ need to be much lower than commonly assumed in models. Dust alkalinity titration comes closest for the submicron size bin. The suggestions above are well taken, changes in assumed mineral composition may alter the results. The potential model capabilities mentioned by Dr. Meskhidze were developed by Meskhidze, Solomon, and co-workers, but are not part of the standard model; we are open to collaborating with them to explore these sensitivities in future simulations.

Comment: The interesting discussion regarding the uptake of HNO₃ 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), HNO₃ 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 be due to the iron-catalyzed oxidation of SO₂ to H₂SO₄ (Brandt and Vaneldik, 1995; Qi et al., 2006; Rani et al., 1992; Yermakov and Purmal, 2003), while HNO₃ 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 (0.1–1.0 μm diameter).

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Response: As acknowledged above, changing the mineral composition for the sub-micron size bin, and including additional uptake mechanisms for fine dust to those currently represented in the model, could alter the results. On the other hand, the mass fraction of dust in the submicron size bin is a small fraction of the total, so the impact on total dust sulfate or dust nitrate mass is likely to be small. We do represent separate size-dependent uptake of acid gases (surface area, and gas-phase diffusion terms in Equ. 1), which represents an advance on models that compute acid uptake on the bulk surface area and size. We also note that the observations made by Sullivan et al. (2007) were made in ocean surface conditions, which may not be representative of the free troposphere, where we focus our attention.

Comment: Is it possible that the observed HNO₃ values could be sustained because large dust particles, that primarily contain CaCO₃, 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 HNO₃(g) uptake? Meskhidze et al. (2003) demonstrate that when pH of mineral aerosol get reduced below 4, HNO₃ 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 HNO₃ 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 HNO₃ reaction probability and lifetime, NO₃ concentrations and NO_y lifetime in general. Such treatment may also improve comparison of model predicted Ca²⁺ with the measurement data.

Response: The bulk aerosol (SAGA) measurements made during INTEX-B indicate that the dust alkalinity is not titrated. We agree that the HNO₃ uptake would cease if the dust becomes acidified. Following Dr. Meskhidze's suggestion (below), we will investigate speciated submicron aerosol measurements collected in INTEX-B to see what differences are found in the fine mode.

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Comment: Currently Asian dust mineralogical composition (Solmon et al., 2009) and four dust size bins with radii 0.1–1.0, 1.0–1.8, 1.8–3.0, and 3.0–6.0 μm (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 HNO₃ to be tested.

Response: We use the bulk (SAGA) observations from the DC8 because they provide measurements of coincident, speciated refractory and non-refractory aerosol ion composition. Distinct mineral composition for submicron aerosol would require independent verification. Day et al. (2009) show some X-ray fluorescence (XRF) measurements of trace elemental concentrations in submicron aerosol made from the NCAR C130 (their Table 1, and Fig. 4). We will take a closer look at these data. At first glance, these data indicate no obvious correlation of sulfur and calcium over the Eastern Pacific at the submicron level. The HR-ToF-AMS aboard the C130 provides measurements of submicron refractory components only (Dunlea et al., 2009). Leaitch et al. (2009) provide an examination of HR-ToF-AMS measurements both from the C-130 and at Whistler Peak during INTEX-B. They show a correlation of sulfate and calcium in coarse mode measurements, but with very low sulfate values, indicating that the uptake of sulfate on coarse dust is small. We have used the fine sulfate measurements from the SAGA gas chamber, to find that the sulfate fine mode is dominant (p. 24486). Thanks for the suggestion to examine these additional datasets.

Comment: 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. (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

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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?

Response: As explained in the paper, the reason for the scaling is to achieve a level of consistency between simulations conducted with GEOS-3 and GEOS-4 meteorological fields. An unfortunate consequence of the extreme sensitivity of simulated dust mobilization to the surface shear velocity is that in exchanging GEOS-3 wind fields for GEOS-4 wind fields, local, regional, and temporal differences in emission result. Dust mobilization in GEOS-Chem was originally constrained against observations using GEOS-3 winds (Fairlie et al., 2007). For the 2006 study, we use GEOS-4 winds. The factor of 2 is a global scaling used to approximately match global dust mobilization for the same time period with the two different meteorological sources.

Comment: 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 Ca²⁺ and Mg²⁺ cation equivalents is unclear. For example, if Ca²⁺ is associated with calcite, it can neutralize 2 equivalents of acidity, while if Ca²⁺ 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 Ca²⁺ cation equivalents constitute 3% of the dust by mass. Additional discussion is also in

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order for the Mg²⁺ containing minerals.

Response: As described on p. 24483, the calcium and magnesium components are assumed to represent carbonates: e.g. calcite, dolomite. The bulk (SAGA) aerosol measurements are for soluble ions; insoluble components, e.g. gypsum, are not measured. The 3% Ca²⁺ by weight then translates to a mass fraction of 7.5% calcite. The 0.6% mass fraction for Mg²⁺ corresponds directly to a compact 1:3 equivalence ratio we find between Ca²⁺ and Mg²⁺ in the SAGA observations. The 3% mass fraction of Ca²⁺ is consistent with the 10% calcite estimate of McNaughton, based on the INTEX-B volumetric measurements, given the lower density for dust they assume in their calculations.

Comment: P. 24483, Line 15. How were Ca²⁺ and Mg²⁺ containing mineral dissolution/reaction kinetics treated in the paper? Is it reasonable to assume that Ca²⁺ and Mg²⁺ can instantly react with acidic species? If not, how will the mineral reaction/dissolution kinetics affect the HNO₃ uptake on mineral dust?

Response: As explained in the paper, the sum of Ca²⁺ and Mg²⁺ equivalences are assumed to correspond with equivalent carbonate (size-segregated dust alkalinity). The uptake of HNO₃ is the normal acid base reaction, displacing the carbonate as CO₂; the uptake of SO₂ is assumed to involve reaction with O₃ in the presence of liquid water. The relative humidity dependence of these uptake processes in the model is illustrated in Fig. 1.

Comment: P. 24484, Line 8. Depletion of calcium rich reactive surface sites by the uptake of HNO₃ 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 HNO₃ 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 CaCO₃ containing dust particles where, due to surface to bulk transport, acidic proton can be readily neutralized. I just wonder in case

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when the fast initial uptake of HNO₃ is reduced due to saturation of reactive surface sites, should such aerosols be treated as “alkalinity titrated?” This example also clearly demonstrates that HNO₃ uptake coefficient is likely be different for different size dust particles.

Response: This is an interesting point. The question is how efficient is the surface to bulk transport for calcite-containing dusts in the real atmosphere? The coexistence of residual dust alkalinity with significant HNO₃(g) 3-7 days downstream of Asia suggests that the surface-bulk transport is slower (kinetic limited) than commonly assumed in models, or determined from relatively short-duration laboratory experiments with pure calcite or idealized dusts.

Comment: P. 24485, Line 21. What is the possible reason for about 50% overestimation of Ca²⁺ 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 Ca²⁺/Mg²⁺ ratio is used in the model is Mg²⁺ also overestimated?

Response: The 50% overestimate of Ca²⁺ in the model is most likely associated with the mobilization/ transport/ deposition of dust in the model. Assuming a smaller mass fraction for calcite in dust could improve this bias. However, the assumed mineral composition is consistent with the conclusions of McNaughton et al. (2009).

Comment: P. 24485, Line 24. Separation of high and low dust conditions based on the comparison of Ca²⁺ to that of 2(NO₃)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.

Response: We apologize for the confusion. The results of the control simulation fall into 2 modes in nitrate-Ca²⁺ space (Fig.4(a)(a)); it was convenient to refer to these modes

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separately, and follow the impact of acid uptake on the “dusty” mode in particular. The names we have used “dusty” and “low-dust” may not be the best, e.g. “dusty” might better be described as “nitrate deficient, without acid uptake.” We will revisit this for the revised manuscript. In any case, the classification is not reapplied for the uptake simulation; points marked yellow in Fig.4(a), are also yellow in Fig.4(b).

Comment: P. 24487, Line 18. While the model overestimates the HNO₃ (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 HNO₃ by the dust would really be improved if the NO_y and 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 NO_x and NO_y with the observations?

Response: The argument is that HNO₃ can be reduced close to observed levels with a higher uptake coefficient, but the cost is excessive nitrate. Zhang et al. (2009) show mean profiles of observed and simulated NO_x and NO_y from GEOS-Chem for the INTEX-B mission. In our simulation the uptake of HNO₃ results in a ~10% increase in median NO_x/NO_y ratios for Ca(2+)> 200 ppt, which brings the model closer to observed median ratios of ~0.08.

Comment: P. 24488, Line 6. I find discussion about ammonium volatilization very interesting, but somewhat hard to explain. The NH₃ 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 (NH₄⁺) 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 NH₄⁺ ion?

Response: we are talking about volatilization of ammonium nitrate to HNO₃(g) and NH₃(g).

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References:

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