

Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution plumes

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Received: 18 October 2009 – Published in Atmos. Chem. Phys. Discuss.: 17 November 2009

Revised: 22 March 2010 – Accepted: 31 March 2010 – Published: 29 April 2010

Abstract. We use a 3-D global chemical transport model (GEOS-Chem) to interpret aircraft observations of nitrate and sulfate partitioning in transpacific dust plumes during the INTEX-B campaign of April–May 2006. The model includes explicit transport of size-resolved mineral dust and its alkalinity, nitrate, and sulfate content. The observations show that particulate nitrate is primarily associated with dust, sulfate is primarily associated with ammonium, and Asian dust remains alkaline across the Pacific. This can be reproduced in the model by using a reactive uptake coefficient for HNO_3 on dust ($\gamma(\text{HNO}_3) \sim 10^{-3}$) much lower than commonly assumed in models and possibly reflecting limitation of uptake by dust dissolution. The model overestimates gas-phase HNO_3 by a factor of 2–3, typical of previous model studies; we show that this cannot be corrected by uptake on dust. We find that the fraction of aerosol nitrate on dust in the model increases from ~30% in fresh Asian outflow to 80–90% over the Northeast Pacific, reflecting in part the volatilization of ammonium nitrate and the resulting transfer of nitrate to the dust. Consumption of dust alkalinity by uptake of acid gases in the model is slow relative to the lifetime of dust against deposition, so that dust does not acidify (at least not in the bulk). This limits the potential for dust iron released by acidification to become bio-available upon dust deposition. Observations in INTEX-B show no detectable

ozone depletion in Asian dust plumes, consistent with the model. Uptake of HNO_3 by dust, suppressing its recycling to NO_x , reduces Asian pollution influence on US surface ozone in the model by 10–15% or up to 1 ppb.

1 Introduction

Mineral dust is the largest single contributor to particulate matter in the atmosphere (Forster et al., 2008; Rind et al., 2009). Dust is mobilized to the atmosphere by strong surface winds over arid terrain (Ginoux et al., 2001; Prospero et al., 2002). Principal source regions in East Asia include the Gobi desert of Northern China and Mongolia, and the Taklimakan desert of western China (Prospero et al., 2002). Dust is an important air quality problem in the large population centers of Eastern China, Korea, and Japan, particularly in spring when dust storms are most active. Lofting to the free troposphere can result in long-range transport of Asian dust across the Pacific, impacting surface aerosol concentrations in North America (Jaffe et al., 1999; Husar et al., 2001; Szykman et al., 2003; Fairlie et al., 2007).

Dust particles can become coated with sulfate, nitrate, organic, and black carbon as they age in the atmosphere (Tabazadeh et al., 1998; Clarke et al., 2004; Jordan et al., 2003; Dibb et al., 2003; Kim et al., 2004; Ooki and Uematsu, 2005; Sullivan et al., 2007). Nitrate and sulfate form on dust through the uptake of acidic gases HNO_3 , SO_2 , and H_2SO_4



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(Usher et al., 2003). Global and regional-scale modeling studies have shown significant consequences for sulfate and nitrate partitioning, tropospheric oxidants, and aerosol size distributions (Dentener et al., 1996; Song and Carmichael, 2001a, b; Liao et al., 2003; Bauer et al., 2004; Bauer and Koch, 2005; Hodzic et al., 2006; Shindell et al., 2007). Tabazadeh et al. (1998) suggested that uptake on dust could explain why many models overestimate $\text{HNO}_3(\text{g})$ in the remote free troposphere (Chatfield et al., 1994; Thakur et al., 1999; Lawrence et al., 1999). Acidification of dust by uptake of sulfate could provide bio-available iron to the ocean surface (Meskhidze et al., 2005, and references therein). A shift of nitrate or sulfate towards larger particle sizes can change their direct radiative forcing characteristics (Liao and Seinfeld, 2005; Kim et al., 2004). In addition, coating of dust with soluble nitrate or sulfate can enhance its cloud condensation nuclei potential (Kelly et al., 2007), while reducing its ice nuclei efficiency (Koehler et al., 2007), with consequences for cloud properties and precipitation (Rosenfeld et al., 2001; Fan et al., 2004).

In this paper, we use a 3-D global chemical transport model (GEOS-Chem CTM) to investigate the effect of mineral dust on the chemical partitioning of total inorganic nitrate and sulfate over the Northeast Pacific during the spring 2006 INTEX-B airborne campaign (Singh et al., 2009). This campaign focused on intercontinental transport of pollution from Asia to North America. Dust outflow from East Asia was a pervasive feature. We consider flights of the NASA DC8 out of Honolulu, Hawaii, and Anchorage, Alaska (Regions 3 and 4 in Fig. 2a of Singh et al., 2009). We focus particularly on explaining observed particulate nitrate levels, ramifications for the lifetime of $\text{HNO}_3(\text{g})$ with respect to uptake on dust, and whether dust can account for the high bias of $\text{HNO}_3(\text{g})$ in models. Further, we use the model to describe the chemical ageing of mineral dust during transpacific transport from the Asian continent in terms of accumulation of nitrate and sulfate, titration of dust alkalinity, and impact on NO_x and O_3 .

2 GEOS-Chem model

2.1 General description

The GEOS-Chem CTM was originally described by Bey et al. (2001). We use here version v8.01.01 (<http://acmg.seas.harvard.edu/geos/index.html>). The model is driven by assimilated meteorological analyses from the Goddard Earth Observing System (GEOS-4) including 6-h average winds, temperatures, convective mass fluxes, and clouds, and 3-h average mixing depths and surface variables. These are available at $1^\circ \times 1.25^\circ$ horizontal resolution, and 48 vertical sigma-pressure hybrid levels extending from the surface to 0.01 hPa. The horizontal resolution is degraded here to $2^\circ \times 2.5^\circ$ for input to GEOS-Chem.

The aerosol simulation in GEOS-Chem represents the sulfate-nitrate-ammonium system (Park et al., 2004), organic and black carbon (Park et al., 2003; Liao et al., 2007), sea salt (Alexander et al., 2005), and mineral dust (Fairlie et al., 2007), as an external mixture. The aerosol and gas phases are coupled through (1) aqueous-phase sulfur oxidation; (2) heterogeneous uptake of NO_3 , NO_2 , N_2O_5 , and HO_2 (Jacob, 2000; Evans and Jacob, 2005); (3) aerosol effects on photolysis frequencies (Martin et al., 2003); and (4) gas-aerosol partitioning of total ammonia and inorganic nitrate, computed with the MARS-A thermodynamic model for the sulfate-ammonium-nitrate-water system (Binkowski and Roselle, 2003). MARS-A does not include mineral ion components; we treat the uptake of acidic gases by dust separately, and maintain fine dust-nitrate and dust-sulfate components distinct from the fine-mode sulfate-nitrate-ammonium system, as described below. Some thermodynamic models, e.g. ISORROPIA II (Fountoukis and Nenes, 2007) do include metal and chloride ions, but our results indicate that rapid equilibrium of HNO_3 , SO_2 , and bulk minerals is not appropriate, at least for coarse-mode dust.

Wet deposition is represented using the scheme of Liu et al. (2001), which accounts for scavenging by convective updrafts as well as rainout and washout. Dry deposition of gases and fine aerosol uses the resistance-in-series model of Wesely et al. (1989) as described by Wang et al. (1998). Dry deposition of dust and sea salt aerosols uses size-resolved calculations (Zhang et al., 2001), and accounts for gravitational settling (Seinfeld and Pandis, 1998).

GEOS-Chem has been used previously to show that Asian emissions can lead to enhanced concentrations of CO, ozone, sulfate, and dust aerosols in North America (Heald et al., 2003; Jaegle et al., 2003; Hudman et al., 2004; Park et al., 2004; Heald et al., 2006; Park et al., 2006; Fairlie et al., 2007; Nam et al., 2009). The model has been applied previously to simulation of the INTEX-B data by Zhang et al. (2008), focusing on ozone, and by van Donkelaar et al. (2008), focusing on sulfate and organic aerosol. Here, we focus on the impact of dust on nitrate and sulfate partitioning in transpacific transport.

We use the same suite of emission inventories as Zhang et al. (2008) with the following exceptions. Global anthropogenic emissions of NO_x , SO_x and CO are taken from the EDGAR 3.2FT2000 emission inventory based on the year 2000 (Olivier et al., 2001), instead of the Global Emission Inventory Activity (GEIA). We supplant the global inventory over Asia with an inventory for 2006 compiled by Zhang et al. (2009), which shows 65% higher emissions for NO_x , and 60% higher emissions for SO_2 compared with the year 2000.

2.2 Mineral dust module

Dust in GEOS-Chem is distributed in 4 size bins (radii 0.1–1.0, 1.0–1.8, 1.8–3.0, and 3.0–6.0 μm), following Ginoux et al. (2004). The smallest size bin is further divided into 4 sub-

bins (radii 0.1–0.18, 0.18–0.3, 0.3–0.6, 0.6–1.0 μm) for optical properties and heterogeneous chemistry. We use the dust entrainment and deposition (DEAD) mobilization scheme of Zender et al. (2003), combined with the source function used in GOCART (Ginoux et al., 2001; Chin et al., 2004), as described by Fairlie et al. (2007), who used the model to study the impact of transpacific transport of dust on aerosol concentrations in the United States in 2001. Fairlie et al. (2007) found that the dust simulation captured the magnitude and seasonal cycle of dust over the Northeast Pacific, the timing and vertical structure of dust outflow in the free troposphere from Asia during the spring 2001 TRACE-P and ACE-Asia aircraft missions, and the timing and distribution of Asian dust outbreaks in the United States.

The dust simulations described by Fairlie et al. (2007) were driven by GEOS-3 meteorological analyses. Comparison of simulated dust emissions for spring 2001 using GEOS-3 and GEOS-4 fields indicates a doubling of dust emissions, both globally and from Asia, due to stronger surface winds in GEOS-4. Accordingly, we apply a factor of 2 reduction to the dust emissions computed from the GEOS-4 fields. Generoso et al. (2008) previously applied a factor of 3 reduction to the GEOS-Chem dust source computed from GEOS-4 winds in their study of Saharan dust outflow in 2006 and 2007. Our simulated global and Asian emissions for April–May 2006 are 287 and 25 Tg respectively, compared to 321 and 33 Tg for April–May 2001.

2.3 Acid gas uptake on dust

For this study we include in the model the reactive uptake of HNO_3 and SO_2 on dust, limited by dust alkalinity, and the uptake of gas-phase H_2SO_4 limited by competition with other aerosol surfaces. We exclude direct uptake of ozone on dust, because the DC8 data show no significant negative correlation of ozone and dust (see discussion below). Laboratory studies indicate that uptake of ozone on dust is slow and subject to surface passivation (Hanisch and Crowley, 2003; Mogili et al., 2006). We also neglect particle coagulation since most studies of Asian outflow indicate that urban and dust aerosols are largely externally mixed (Mori et al., 2003; Maxwell-Meier et al., 2004; Tang et al., 2004; Song et al., 2005).

Laboratory studies have shown that dust alkalinity, comprising carbonates and mineral oxides, enables reactive uptake of acidic gases HNO_3 and SO_2 (Usher et al., 2003, and references therein). Uptake of HNO_3 takes place by acid-base titration on surface sites for dry dust, or in solution with adsorbed water (Goodman et al., 2000). Uptake of SO_2 is thought to take place by aqueous-phase oxidation of SO_3^{2-} by O_3 (Ullerstam et al., 2002). We use a standard first-order reactive uptake parameterization with rate constant k_i to describe the loss of species i from the gas phase, for dust radius size bin $[r_1, r_2]$:

$$k_i = \int_{r_1}^{r_2} 4\pi r^2 N(r) \left(\frac{r}{D_g} + \frac{4}{v\gamma} \right)^{-1} dr \quad (1)$$

Here $N(r)$ is the number density of dust particles of radius $[r, r + dr]$, D_g is the molecular diffusion coefficient (taken as $0.2 \text{ cm}^2 \text{ s}^{-1}$), v is the mean molecular speed (taken as $3.0 \times 10^4 \text{ cm s}^{-1}$), and γ is the reactive uptake coefficient.

Previous model studies tend to lump dust into one or two size bins for gas-particle interactions (e.g., Song and Carmichael, 2001b; Liao et al., 2003; Solmon et al., 2009). Here, we compute the acid uptake separately for each dust size bin (plus the 4 sub-bins within the smallest size bin), and maintain dust nitrate, dust sulfate, and dust alkalinity as separate size-segregated constituents in the model. These constituents are subject to the same transport and deposition processes as the corresponding dust components.

Dust alkalinity is introduced in the model at the point of dust emission and is represented as the sum of calcium and magnesium carbonates, assuming that the Ca^{2+} and Mg^{2+} cation equivalents constitute 3.0 and 0.6% of the dust by mass, respectively. A 3% estimate for soluble calcium lies in the range of estimates from observations near East Asian source regions (Claquin et al., 1999; Shi et al., 2005; Jeong, 2008) and is consistent with the estimate by McNaughton et al. (2008) for Asian dust sampled in INTEX-B. The $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio is obtained from the INTEX-B data. Dust alkalinity is consumed by the uptake of HNO_3 , SO_2 , and H_2SO_4 ; once the alkalinity is titrated the uptake of HNO_3 and SO_2 ceases.

Laboratory studies report a wide range of estimates for the reactive uptake coefficients γ of acidic gases on calcite, mineral oxides, and real dust samples. Estimates for uptake on dry calcite range from 10^{-4} to 0.1 for $\gamma(\text{HNO}_3)$ (Goodman et al., 2000; Hanisch and Crowley, 2001), and 10^{-4} to 4×10^{-2} for $\gamma(\text{SO}_2)$ (Usher et al., 2002; Ullerstam et al., 2003; Adams et al., 2005). Studies also show a marked increase in uptake rate with relative humidity for calcite, as uptake of water leads to enhanced ion mobility at the dust surface (Al-Hosney and Grassian, 2005; Vlasenko et al., 2006; Baltrusaitis et al., 2007a; Preszler-Prince et al., 2007; Liu et al., 2008). Uptake of HNO_3 and SO_2 on non-basic minerals is generally subject to surface saturation (Baltrusaitis et al., 2007b; Vlasenko et al., 2009).

Modeling studies have commonly used a constant value of 0.1 for $\gamma(\text{HNO}_3)$ and a step function of relative humidity for $\gamma(\text{SO}_2)$ (0.05–0.1 for $\text{RH} > 50\%$, 10^{-4} – 10^{-2} for $\text{RH} < 50\%$) (Dentener et al., 1996; Song and Carmichael, 2001a; Liao et al., 2003; Hodzik et al., 2006). We find here that such a high value of $\gamma(\text{HNO}_3)$ greatly overestimates particulate nitrate formation in transpacific transport during INTEX-B, as described below. A Lagrangian model study of dust aging in Asian outflow by Song et al. (2007) similarly determined much smaller uptake coefficients $\gamma(\text{HNO}_3) = 5 \times 10^{-3}$ and $\gamma(\text{SO}_2) = 1 \times 10^{-4}$. A possible explanation is that only a fraction of the dust alkalinity is available for reaction at any

time, and after initial saturation of reaction sites on the dust surface continued availability of alkalinity is limited by particle dissolution and diffusion. Fast initial uptake of HNO_3 may thus not be sustainable for multi-day atmospheric transport.

Here, we use RH-dependent functions for $\gamma(\text{HNO}_3)$ and $\gamma(\text{SO}_2)$, as shown in Fig. 1. Peak values are of similar magnitude as those determined by Song et al. (2007). The RH-dependences are based on recent laboratory results for uptake on calcite particles (Liu et al., 2008, for HNO_3 ; Preszler-Prince et al., 2007, for SO_2), and show the impact of the much lower deliquesce RH for reaction products $\text{Ca}(\text{NO}_3)_2$ (13–18%), than for CaSO_3 ($\sim 90\%$) (Preszler-Prince et al., 2007). We represent uptake of $\text{H}_2\text{SO}_4(\text{g})$ on dust in competition with uptake by other aerosol components in the model, using a weighting proportional to surface area and mass transfer limitation (Eq. 1).

We conducted fully coupled GEOS-Chem simulations of oxidant and aerosol chemistry for the April–May 2006 INTEX-B period. Each simulation was initialized on 1 March 2006 using constituent fields from the previous INTEX-B model study by Zhang et al. (2008). Initial dust components were set to zero. Separate simulations were conducted with and without acid uptake by dust.

2.4 Bulk aerosol and gas data

Bulk aerosol, HNO_3 , and fine sulfate data shown here were obtained from the University of New Hampshire (UNH) Soluble Acidic Gases and Aerosol (SAGA) instruments on board the NASA DC8. Paired filter samples of bulk aerosol were collected with the UNH dual aerosol sampling probe, and analyzed for soluble ions including NO_3^- , SO_4^{2-} , NH_4^+ , Mg^{2+} , Cl^- , Na^+ , K^+ , and Ca^{2+} (Dibb et al., 2003). Mean exposure times for the filters were ~ 5 – 6 min for altitudes below ~ 6 km and 10–14 min at higher altitudes. HNO_3 and fine sulfate were measured in a mist chamber (Scheuer et al., 2003), with an aerosol size cut diameter of ~ 1 μm ; collection intervals were typically 2 min or less. Some contamination of the HNO_3 measurement has been found in high $\text{NH}_4(\text{NO}_3)$ conditions, but no such artifact has been determined in high dust conditions. Ozone data shown here were obtained from the FASTOZ instrument at 1 Hz frequency.

3 Transpacific transport of dust during INTEX-B

Figure 2 shows model distributions of dust emission, 550 nm dust aerosol optical depth (AOD), and total AOD for the period 21 April–11 May 2006, spanning the bulk of INTEX-B flights over the Northeast Pacific. Also shown are satellite observations (MODIS) of 550 nm AOD for the same period. Model AOD at 550 nm is calculated as the sum of contributions from individual aerosol components with prescribed optical properties as a function of relative humidity (Martin

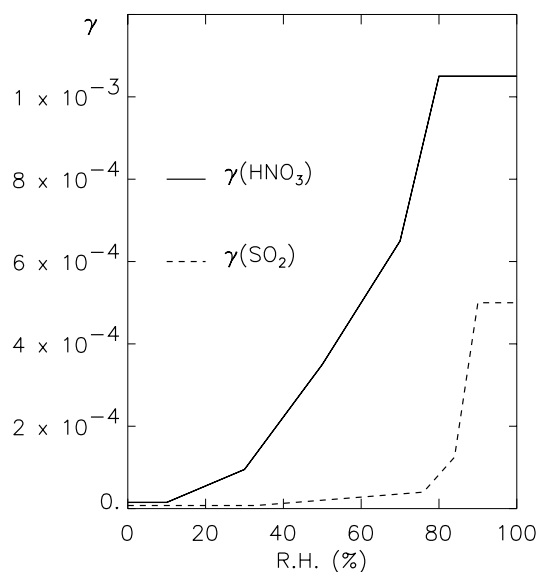


Fig. 1. Reactive uptake coefficients for $\text{HNO}_3(\text{g})$ and $\text{SO}_2(\text{g})$ on mineral dust used in this study as a function of relative humidity (RH).

et al., 2003) The Gobi and Taklimakan deserts of southern Mongolia and Western China were active dust sources during INTEX-B. The maps of simulated AOD illustrate the mean transpacific transport of dust and aerosol pollutants (principally sulfate; van Donkelaar et al., 2008) during INTEX-B. Flight tracks show that the DC-8 aircraft was well positioned to observe this transport. Van Donkelaar et al. (2008) show that GEOS-Chem captures many features of the day-to-day evolution in MODIS AOD associated with transpacific transport from Asia. We find that the model AOD is lower than MODIS, but this could reflect a MODIS high bias previously documented by comparison with island-based AOD observations from the AERONET network (Chin et al., 2004; Heald et al., 2006) and possibly reflecting the non-sphericity of dust (Chu et al., 2005). Van Donkelaar et al. (2008) show no such bias in their GEOS-Chem simulation compared to MODIS, but their dust emissions are not scaled for GEOS-4 winds and are thus twice ours (see Sect. 2.2).

Figure 3 shows the altitude distributions of observed vs. simulated Ca^{2+} concentrations for the INTEX-B flight tracks. Here and elsewhere we exclude observations made below 1 km (where sea salt complicates interpretation) or characteristic of the stratosphere ($\text{O}_3 > 100$ ppb). We see from Fig. 3 that high dust concentrations extend through the 1–7 km column, with high variability, and drop rapidly above. Median model concentrations are about 50% higher than observed.

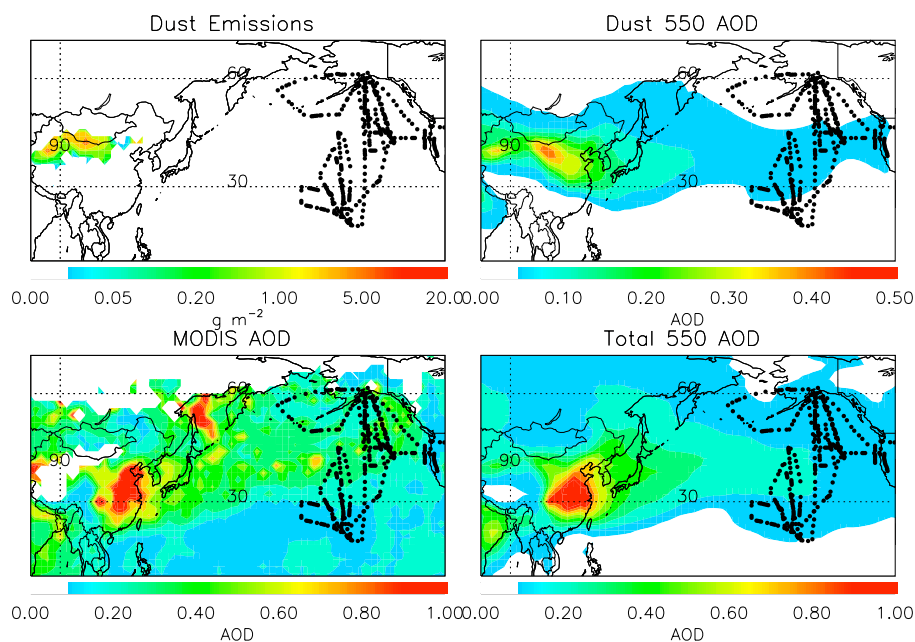


Fig. 2. Model distributions of dust emission (units: g m^{-2}), 550 nm dust aerosol optical depth (AOD), and total 550 nm AOD for the INTEX-B period of 21 April–11 May 2006. The lower left panel shows the observed MODIS 550 nm AOD (Collection 5, Terra and Aqua satellites) for the same period. INTEX-B flight tracks are shown in black, with individual symbols denoting the aerosol samples used in this work.

4 Partitioning of nitrate and sulfate

Figure 4 shows various paired relationships of observed bulk NO_3^- , SO_4^{2-} , NH_4^+ , Ca^{2+} aerosol concentrations, and $\text{HNO}_3(\text{g})$ concentrations, for the ensemble of INTEX-B data in Fig. 2. Model results without (Fig. 4a) and with (Fig. 4b) acid uptake by dust are also shown. The observations show a strong positive association of NO_3^- and a weak negative association of $\text{HNO}_3(\text{g})$ with mineral dust. The mean observed ratio of aerosol nitrate to total nitrate ($\text{NO}_3^- + \text{HNO}_3(\text{g})$) increases from 0.4 for low dust to 0.7 for high dust conditions. Sulfate shows a weak positive association with dust, but a strong association with ammonium following the 1:2 ammonium sulfate relationship. The ratio of fine sulfate (from the SAGA mist chamber) to bulk sulfate mass ($\sim 0.7\text{--}0.9$) indicates that the fine mode is dominant. The association of sulfate with Ca^{2+} may be explained by mixing of polluted and dust air streams in the Asian outflow (Clarke et al., 2001; Jordan et al., 2003; Heald et al., 2006). Panel (e) shows NO_3^- vs. NH_4^+ after accounting for ammonium sulfate; little evidence is found for ammonium nitrate in the observations. This indicates that the aerosol nitrate is present in the dust particles, rather than merely coincident with them. Data points to the right of the 1-1 line in panel (e) show ammonium in excess of ammonium sulfate and ammonium nitrate combined. The physical explanation is not clear. No such data are found in the TRACE-P dataset, for example. Concentrations of Cl^- are too small for significant formation of NH_4Cl . There may be some positive bias in the NH_4^+ observations.

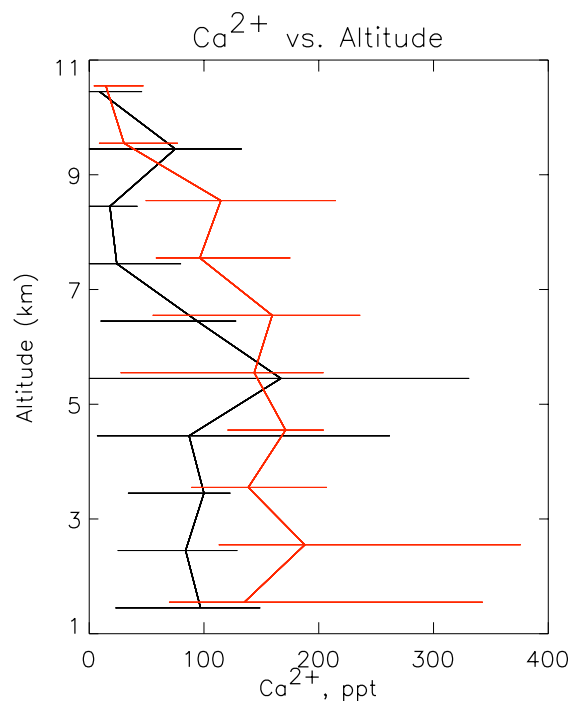


Fig. 3. Altitude distribution of observed (black) and simulated (red) Ca^{2+} concentrations during INTEX-B. The data are binned in 1 km vertical intervals. Profiles show median values in each bin. Whiskers span 50% of the data in each bin.

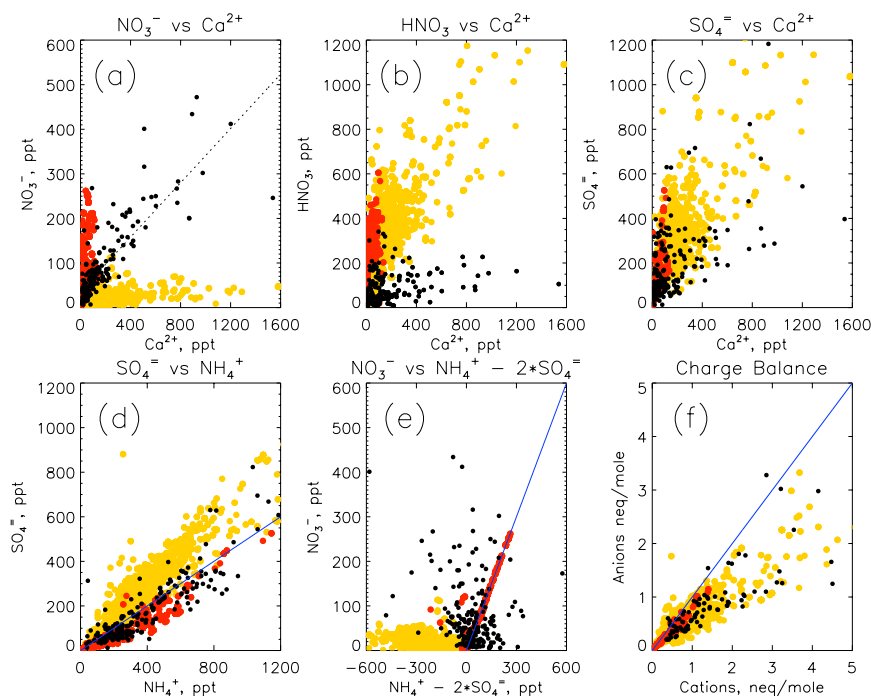


Fig. 4a. Relationships between bulk aerosol components and $\text{HNO}_3(\text{g})$ concentrations along the INTEX-B flight tracks, excluding data below 1 km or in the stratosphere. Observations are shown in black, with each data point corresponding to an aerosol sample along the tracks shown in Fig. 2. Model values not including acid uptake by dust are shown in color, separately for dusty ($[\text{Ca}^{2+}] > 2[\text{NO}_3^-]$; yellow) and non-dusty ($[\text{Ca}^{2+}] < 2[\text{NO}_3^-]$; red) conditions. The bottom right panel shows the equivalent balance between the sum of measured cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+) and the sum of measured anions (SO_4^{2-} , NO_3^- , Cl^-). The black line in panel (a) shows the linear best fit to the observations; blue lines in panels (d), (e), and (f), show the 1:2, 1:1, and 1:1 relationships, respectively.

Panel (f) of Fig. 4a shows measured negative vs. positive equivalent charges in the bulk aerosol observations. The data show an anion deficit, which is positively correlated with Ca^{2+} (not shown), implying the presence of residual dust alkalinity at least in the bulk. In addition, the observations indicate that ~ 100 ppt $\text{HNO}_3(\text{g})$ coexists with the dust alkalinity (panel b). The dust plumes intercepted by the INTEX-B aircraft were 3–7 days downstream of Asian source regions (H. Fuelberg, personal communication, 2008). The coexistence of significant HNO_3 and dust alkalinity implies that the time scale for HNO_3 uptake on dust must be on the order of days, consistent with the low $\gamma(\text{HNO}_3)$ values used in this work, rather than hours as would result from $\gamma(\text{HNO}_3) \sim 0.1$. The observed HNO_3 values cannot be sustained by replenishment from NO_x because observed NO_x concentrations (~ 10 – 40 ppt) are too small. We note that the CIMS instrument on board the NSF C130 aircraft (Crouse et al., 2006) measures lower, yet significant, values of $\text{HNO}_3(\text{g})$ (20–80 ppt) for dustiest conditions in the eastern Pacific during INTEX-B (J. Crouse, personal communication, 2010).

The model results without acid uptake by dust (Fig. 4a) show a striking difference with observations in the NO_3^- vs. Ca^{2+} relationship. Simulated NO_3^- vs. Ca^{2+} shows 2 distinct

populations: one characterized by low NO_3^- ($< \sim 100$ ppt) (yellow points), the other characterized by low Ca^{2+} ($< \sim 200$ ppt) (red points). We refer to the former as the “dusty air stream,” and the latter as the “low-dust air stream.” In contrast with the observations, the model dusty air shows no correlation of dust with nitrate (panel a) and shows much higher HNO_3 increasing with Ca^{2+} (panel b). It shows a weak positive relationship of SO_4^{2-} with Ca^{2+} , similar to observations, further evidence that sulfate and dust are largely externally mixed. The charge balance plot (panel f) shows an anion deficit (residual alkalinity) in the model dusty air, comparable with observations. The low-dust population is much closer to charge balance (panel f).

Figure 4b shows the model results with acid uptake by dust, using $\gamma(\text{HNO}_3)$ and $\gamma(\text{SO}_2)$ from Fig. 1. The dusty air stream in the model (yellow) shows an average six-fold increase of nitrate, bringing the model results closer to observations (panels a and e). The slope of the NO_3^- vs. Ca^{2+} regression line for the dusty air stream (0.35) is comparable to the observations (0.31). Dust nitrate now accounts for 80–90% of aerosol nitrate in the dusty air, and $\text{HNO}_3(\text{g})$ is reduced by 20–30%. There is negligible change in total sulfate but the partitioning has changed; for the dusty air we now find 8–12% of the sulfate on dust. The sulfate fraction

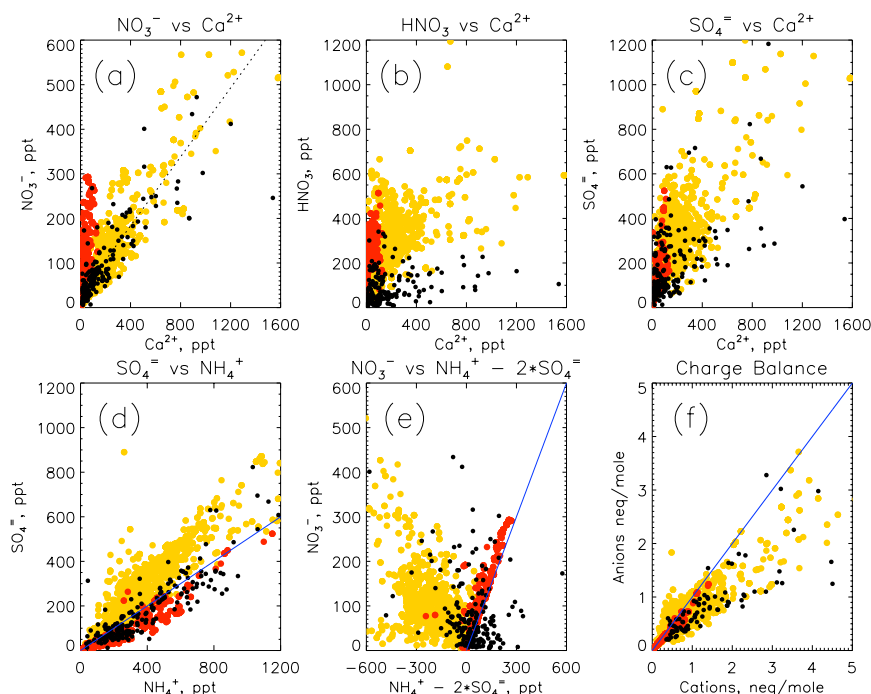


Fig. 4b. Same as Fig. 4a, but for the simulation including acid uptake on dust. The same colors mark the same points in both simulations. Black line in panel (a) is linear best fit to the model (yellow) results.

on dust is still small, comparable to observations. Uptake of H_2SO_4 accounts for 70–80% of the dust sulfate in the model, the rest is due to direct uptake of SO_2 . Acid uptake reduces model dust alkalinity by 20–25% (panel f) but does not titrate it, again consistent with observations.

The uptake of $\text{HNO}_3(\text{g})$ on dust in the model still leaves $\text{HNO}_3(\text{g})$ about 2–3 times too high, and the aerosol to total nitrate ratio (~ 0.5) is too low. We show in Fig. 5 that $\text{HNO}_3(\text{g})$ in dusty air can be reduced to observed levels by increasing $\gamma(\text{HNO}_3)$ by a factor of 10, but this causes excessive aerosol nitrate. $\text{HNO}_3(\text{g})$ can also be reduced by increasing dust surface area by scaling emissions (Sect. 2.2), but this causes excess nitrate and calcium. (Particulate nitrate and sulfate, and dust alkalinity consumption, respond quasi-linearly to scaling of dust emissions because uptake rates depend linearly on dust surface area, Eq. 1). Furthermore, we find that the model high bias of $\text{HNO}_3(\text{g})$ is present in both dusty and non-dusty conditions, and represents a general overestimate of total inorganic nitrate. Such an overestimate is a well-known problem of global tropospheric chemistry models (Chatfield et al., 1994; Thakur et al., 1999; Lawrence et al., 1999; Bey et al., 2001) and we see that it cannot be resolved by uptake of $\text{HNO}_3(\text{g})$ on dust.

5 Transpacific dust effects on nitrate, sulfate, and ozone

Figure 6 shows maps of simulated dust and non-dust (ammonium) nitrate columns over the northern Pacific for the INTEX-B period. Dust nitrate accounts for $\sim 30\%$ of aerosol nitrate over East Asia but 80–90% over the Northeast Pacific. Dispersion and scavenging during Asian outflow and transpacific transport affect both dust and non-dust nitrate in a similar way, but ammonium nitrate drops far more sharply downwind of Asia due to volatilization as NH_3 partial pressures fall. By contrast, production of dust nitrate is sustained across the Pacific from $\text{HNO}_3(\text{g})$ produced both from oxidation of NO_x and from ammonium nitrate volatilization. Previous model studies for Asian outflow using $\gamma(\text{HNO}_3) = 0.1$ report a larger fractionation of nitrate as dust (Dentener et al., 1996; Song and Carmichael, 2001b; Liao et al., 2003), but this appears inconsistent with the INTEX-B data as discussed above.

Figure 7 shows corresponding maps of dust and non-dust sulfate. In contrast to nitrate, the ratio of dust sulfate to total sulfate is small (8–10%) over East Asia, falling to 5–8% over the Northeast Pacific. Unlike ammonium nitrate, ammonium sulfate does not volatilize, and $\text{SO}_2(\text{g})$ declines much more steeply than $\text{HNO}_3(\text{g})$ off the coast, precluding significant sulfate production in transpacific transport. The decline in the dust to total sulfate ratio downstream can be explained by enhanced settling of the super-micron dust compared with fine sulfate. Previous model studies using a higher value for

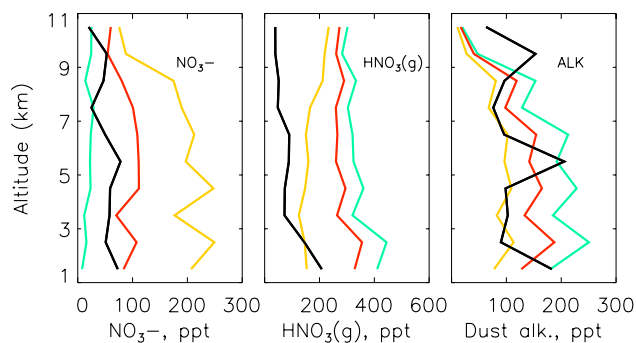


Fig. 5. Altitude profiles of observed (black) and simulated aerosol nitrate, $\text{HNO}_3(\text{g})$, and dust alkalinity for the INTEX-B flights. Values are medians in 1-km vertical bins. Profiles are shown for the standard simulation with no acid uptake (green), the standard simulation with acid uptake (red), and a simulation with $\gamma(\text{HNO}_3)$ increased by a factor of 10 from the values in Fig. 1 (yellow). Observed alkalinity is inferred from the anion deficit shown in Fig. 4.

$\gamma(\text{SO}_2)$ show a much larger fractionation of sulfate as dust in Asian outflow and globally (Dentener et al., 1996; Song and Carmichael, 2001a; Liao et al., 2003), but this seems inconsistent with the low fraction of sulfate on dust apparent the INTEX-B data.

Dust alkalinity is regulated by the balance in supply between acids and bases, and by the time scales for alkalinity consumption vs. dust deposition. Simulated emissions of acid precursors from East Asia for April–May 2006 amount to 258 G eq. (83 G moles SO_2 plus 92 G moles NO_x), more than the combined alkaline emissions of 192 G eq. (142 G moles NH_3 plus 25 G moles dust alkalinity). Yet, model results show only 20–25% consumption of dust alkalinity across the Pacific. Only dust in the smallest size bin (radius $< 1.0 \mu\text{m}$) comes close to complete alkalinity titration (up to $\sim 90\%$ locally, accounting for 60–70% of alkalinity consumption over the Pacific) due to its greater surface to volume ratio. The time scale for consumption of bulk dust alkalinity in transpacific transport in the model is 15–20 days, twice that for dust deposition. Thus the titration of dust is kinetically limited. Some studies indicate that the calcite content of the clay fraction of Asian dust is much smaller than for the bulk (Claquin et al., 1999; Shi et al., 2005). If we eliminate dust alkalinity from the smallest size bin, removing it as a sink for HNO_3 , we match the bulk consumption rate by increasing $\gamma(\text{HNO}_3)$ by a factor of 2–3.

Meskhidze et al. (2005) indicated that dust alkalinity must be titrated for the iron content to be soluble and bio-available upon deposition. They showed that calcite strongly buffers dust acidification in Asian outflow, limiting significant iron mobilization to dust plumes with high initial acid-to-dust ratios. Solomon et al. (2009) implemented the dust iron dissolution scheme of Meskhidze et al. (2005) in GEOS-Chem and predicted deposition of significant soluble iron during Asian

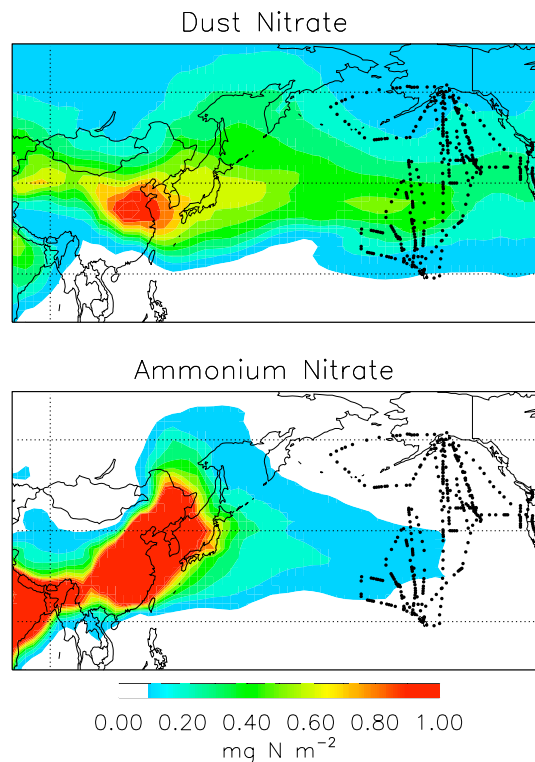


Fig. 6. Mean simulated column concentrations of dust nitrate and ammonium nitrate for the INTEX-B period (21 April–11 May 2006). Results are from the simulation including acid uptake. Black symbols show the aircraft flight tracks.

outflow in Spring 2001. They used a different scheme for acid uptake on dust than is used here. Notably, their assumed uptake rate for SO_2 was 1–2 orders of magnitude larger than is obtained with $\gamma(\text{SO}_2)$ in Eq. 1, leading to titration of dust alkalinity, which seems inconsistent with the INTEX-B observations. Our results indicate that iron mobilization may be limited to the smallest dust particles (radius $< 1 \mu\text{m}$) and to those with much lower initial alkalinity.

Figure 8 shows the observed and simulated relationship of ozone vs. Ca^{2+} at 4–6 km altitude. The observations show no apparent depletion of ozone in dust layers. In contrast, ozone reductions of up to 40% have been observed in Saharan dust outflow (DeReus et al., 2000; Umann et al., 2003; Bonasoni et al., 2004). DeReus et al. (2000) argued that direct uptake of ozone can explain about half of the depletion, while Umann et al. (2003) argued that it is due primarily to HNO_3 uptake suppressing its recycling to NO_x . In our model, dust chemistry affects ozone only indirectly, via uptake of HNO_3 , as well as of NO_3 , NO_2 , N_2O_5 , and HO_2 . The effect is too small to cause any significant ozone depletion in dust plumes, and the simulated ozone vs. Ca^{2+} relationship in Fig. 8 is consistent with observations. It has, however, a non-negligible impact for Asian pollution influence on ozone air quality in North America, as ozone production

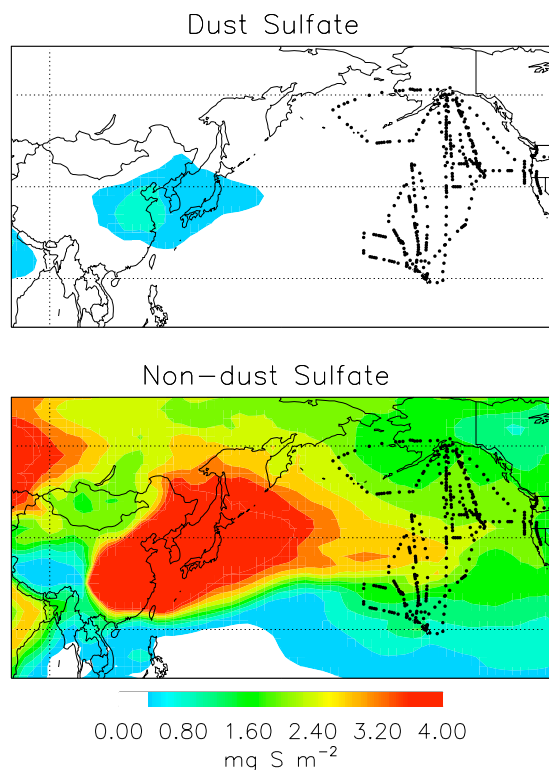


Fig. 7. As for Fig. 6, but for simulated dust and non-dust sulfate.

over the eastern Pacific from chemically recycled NO_x is an important driver for this influence (Kotchenruther et al., 2001; Heald et al., 2003; Hudman et al., 2004; Zhang et al., 2008). Figure 9 shows the mean simulated changes in the northern Pacific tropospheric ozone column and the surface ozone concentrations over North America for the INTEX-B period due to HNO_3 uptake by dust. Column ozone is reduced by up to 1 DU ($\sim 2\%$) over the Northeast Pacific, and surface ozone over North America shows mean reductions of up to 1 ppb. Zhang et al. (2008) previously found that Asian anthropogenic sources increased surface ozone over the western United States by 5–7 ppb during the INTEX-B period. We find here that HNO_3 uptake by dust decreases this Asian influence by 10–15%.

Use of a higher uptake coefficient for $\gamma(\text{HNO}_3)$ increases the impact on ozone in the model. We find $\sim 5\%$ reductions in column ozone over the Northern Pacific and up to 4 ppb reductions in surface ozone over North America when we multiply $\gamma(\text{HNO}_3)$ by a factor of 10. However, this results in a low bias compared with the ozone observations shown in Fig. 8 and nitrate levels inconsistent with the INTEX-B data (Fig. 5). Models that use higher uptake rates for HNO_3 on dust may overestimate the impact of dust on ozone.

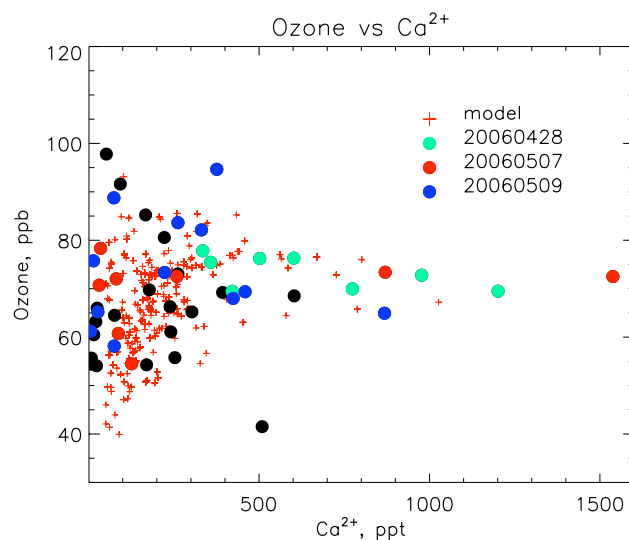


Fig. 8. Relationship between observed ozone and Ca^{2+} concentrations at 4–6 km altitude for the INTEX-B flights (filled circles). Observations on days with a large range of Ca^{2+} are colored. Corresponding model results are also shown (red crosses); low Ca^{2+} (< 50 ppt) points are excluded for clarity.

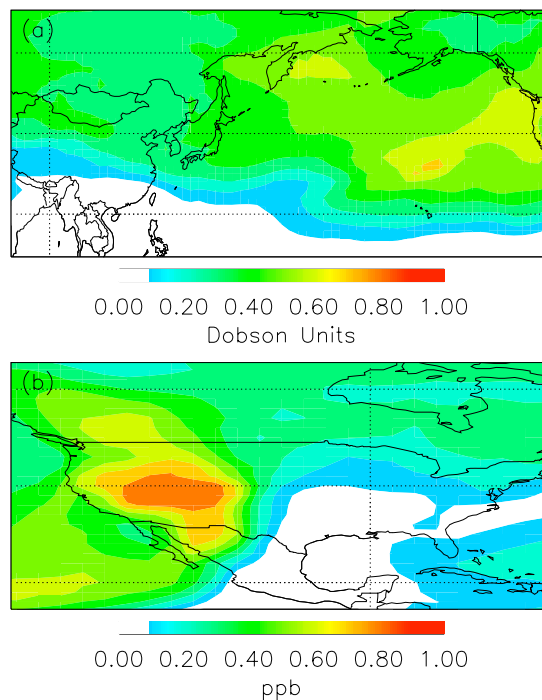


Fig. 9. Effect of HNO_3 uptake by dust on (a) tropospheric ozone columns over the Pacific, and (b) surface ozone over North America. Values are mean differences for the INTEX-B period (21 April–11 May 2006) between simulations conducted with vs. without uptake of acids on dust.

6 Conclusions

We have used a 3-D global chemical transport model (GEOS-Chem) to interpret aircraft aerosol observations over the Northeast Pacific (INTEX-B campaign) in terms of nitrate and sulfate uptake on dust during transpacific transport, and implications for ozone. The model includes explicit transport of dust alkalinity as a limiting factor for HNO_3 and SO_2 uptake, and dust uptake of H_2SO_4 in competition with other aerosol surfaces.

Active dust sources in the Gobi and Taklimakan regions of China and Mongolia were a major source of transpacific dust during INTEX-B. The aircraft observations and the model show a strong positive association of particulate nitrate with dust, a weaker positive association of sulfate, and a weak negative association of $\text{HNO}_3(\text{g})$. We show that nitrate is mainly present in the dust while sulfate is principally present as ammonium sulfate, its association with dust mostly reflecting common transport. The observations also indicate that dust remains alkaline over the Northeast Pacific, at least in the bulk, even after 3–7 days of transpacific transport.

We show that uptake of HNO_3 on dust in the model can reproduce the observed relationship between particulate nitrate and calcium as well as the observed residual alkalinity. However, this requires that the rate of uptake of HNO_3 by dust be relatively slow, represented in the model by a reactive uptake coefficient $\gamma(\text{HNO}_3) \sim 1 \times 10^{-3}$. Previous models have generally assumed $\gamma(\text{HNO}_3) \sim 0.1$, but we find that this results in excess nitrate on dust and insufficient dust alkalinity relative to the INTEX-B observations. A much lower value for $\gamma(\text{HNO}_3)$ is needed to explain the coexistence of significant HNO_3 (~ 100 ppt) with dust alkalinity in the aircraft observations, which may reflect limitation of HNO_3 uptake by dust dissolution.

Simulated $\text{HNO}_3(\text{g})$ concentrations are 2–3 times higher than observed. Such an overestimate of HNO_3 in the remote atmosphere has been a long-standing problem for global models. Uptake by dust has previously been proposed as a solution but we do not find this solution satisfactory. The model overestimate is similar for dusty and non-dusty conditions, and increased uptake of HNO_3 by the dust results in a large overestimate of observed dust nitrate.

We find that the fraction of nitrate on dust in the model increases from 25–30% in fresh Asian outflow to 80–90% across the Pacific, partly reflecting the transfer from ammonium nitrate to dust nitrate through the volatilization of ammonia. By contrast, the fraction of sulfate on dust (mostly from uptake of H_2SO_4 , with a small contribution from direct uptake of SO_2) decreases from 8–12% in fresh Asian outflow to 5–8% across the Pacific. This reflects the lack of sustained sulfate production over the Pacific.

The model shows 20–25% consumption of bulk dust alkalinity due to acid uptake by the time that Asian dust has reached the Northeast Pacific, consistent with the INTEX-B observations. Dust alkalinity is in general never titrated

in the model. This reflects a longer atmospheric time scale for dust alkalinity consumption (15–20 days) than for dust deposition (7–9 days), and argues against the possibility of bulk dust acidification releasing bio-available iron upon deposition to the oceans. Individual dust particles could still be titrated, either because of small size or low initial alkalinity.

Observations in INTEX-B show no detectable depletion of ozone in dust plumes, arguing against direct uptake of ozone by dust. We find in the model that uptake of HNO_3 , suppressing gas-phase recycling to NO_x , is too slow to deplete ozone significantly in dust plumes, consistent with observations. However, it still decreases the impact of Asian pollution on surface ozone in the United States by 10–15%, or up to 1 ppb in the West.

Acknowledgements. This work was funded by the NASA Global Tropospheric Chemistry Program, the NASA Langley Research Center Science Directorate, and the Advanced Study Program. Thanks to the following colleagues for discussions in the course of this work: M. Ammann, B. Anderson, J. Baltrusaitis, G. Chen, J. Crawford, J. Crouse, B. Doddridge, V. Grassian, C. Jordan, C. Kittaka, A. Laskin, H. Liu, C. McNaughton, R. Martin, S. Martin, N. Meskhidze, J. Olson, R. Park, E. Scheuer, Z. Shi, F. Solmon, C. Song, P. Wennberg. Thanks to the two anonymous reviewers for their comments.

Edited by: H. Singh

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