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Nitric acid scavenging by mineral and biomass burning aerosols

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Abstract. The abundance of gas phase nitric acid in the upper troposphere is overestimated by global chemistry-transport models, especially during the spring and summer seasons. Recent aircraft data obtained over the central US show that mineral aerosols were abundant in the upper troposphere during spring. Chemical reactions on mineral dust may provide an important sink for nitric acid. In regions where the mineral dust abundance is low in the upper troposphere similar HNO_3 removal processes may occur on biomass burning aerosols. We propose that mineral and biomass burning aerosols may provide an important global sink for gas phase nitric acid, particularly during spring and summer when aerosol composition in the upper troposphere may be greatly affected by dust storms from east Asia or tropical biomass burning plumes.

Introduction

Ozone concentration in the upper troposphere is highly affected by the distribution of nitrogen between nitrogen oxides and their main reservoir species, HNO_3 [*Singh et al.*, 1996; *Jacob et al.*, 1996]. It is well-known that global chemistry-transport models overestimate the abundance of gas phase HNO_3 in the upper troposphere [*Singh et al.*, 1996; *Jacob et al.*, 1996; *Wang et al.*, 1998, *Thakur et al.*, 1998]. Several suggestions have been set-forward to resolve this issue. Some proposals suggest mechanisms to remove HNO_3 from the gas phase by scavenging of HNO_3 on cirrus ice cloud surfaces [*Abbatt*, 1997; *Zondle et al.*, 1997; *Lawrence and Crutzen*, 1997], while others discuss possibilities for conversion of HNO_3 into nitrogen oxides on sulfate and soot aerosol surfaces [*Chatfield*, 1994; *Iraci and Tolbert*, 1997; *Rogaski et al.*, 1997]. Our recent analysis of ice clouds show that cirrus is not an effective global sink for HNO_3 [*Tabazadeh et al.*, 1998]. Also recent comparisons of HNO_3 gas phase abundance against field data suggest that conversion of HNO_3 into nitrogen oxides on soot and sulfate aerosol surfaces may be less important than previously thought [*Wang et al.*, 1998, *Singh et al.*, 1998]. In this work we investigate how mineral and biomass burning aerosols may affect the HNO_3 gas phase abundance in the upper troposphere by providing a chemical sink for HNO_3.

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Data Presentation and Analysis

Figure 1 illustrates the seasonal variation in the observed HNO_3 gas phase concentration. Also shown are calculations from the Harvard/GISS model [*Wang et al.*, 1998]. Most of the HNO_3 data shown in Figure 1 was obtained during the NASA PEM-West A and B field programs over the western pacific ocean [*Thakur et al.*, 1998]. In general the majority of locations over the globe show similar seasonal patterns as that shown in Figure 1 [*Thakur et al.*, 1998]. In the upper troposphere, the observed HNO_3 values are about 2 to 10 times higher during winter, whereas the calculated values are about a factor of 2 larger during summer. The seasonal variation in the measured HNO_3 values indicates that the HNO_3 concentration may be affected by unknown chemical processes, which are highly sensitive to the seasonal and geographical variations of the background aerosol. For instance, the measured concentrations of dust and biomass burning aerosols are relatively higher during spring and summer as compared to winter over the tropics [*Penner et al.*, 1992] and south east Asia [*Carmichael et al.*, 1996]. Below we discuss several possible chemical reactions, which can remove HNO_3 from the gas phase in places where dust and/or biomass burning aerosols are abundant.

Here we analyze bulk aerosol composition data collected using the DC-8 aircraft during the recent NASA SUCCESS field program [*Toon and Miake-Lye*, 1998]. The Dual-inlet aerosol sampling system used during the flights has been described elsewhere [*Talbot et al.*, 1998]. Bulk aerosol samples were collected with 10-15 minute time resolution on Teflon filters for determination of soluble ions species [*Talbot et al.*, 1998].

Figure 2 illustrates vertical profiles of ions measured in filter samples collected during SUCCESS. One striking feature

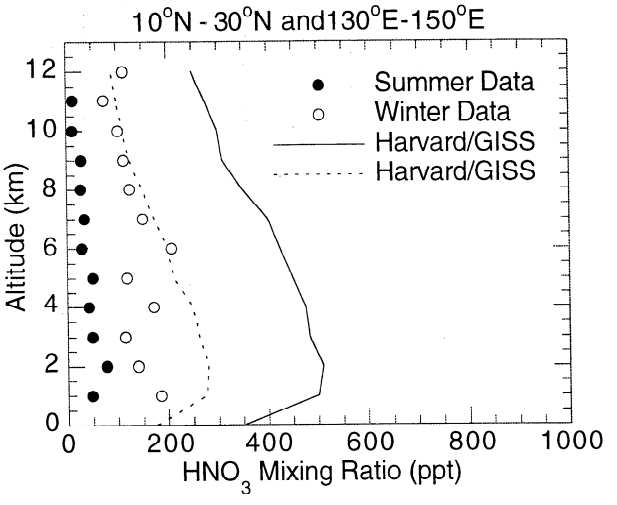

Figure 1. The variation in the observed and calculated HNO_3 gas phase concentration (adapted form *Thakur et al.* [1998]). The data points shown are mean values averaged for every kilometer. The solid (summer) and dotted (winter) lines show HARVRAD/GISS model results.

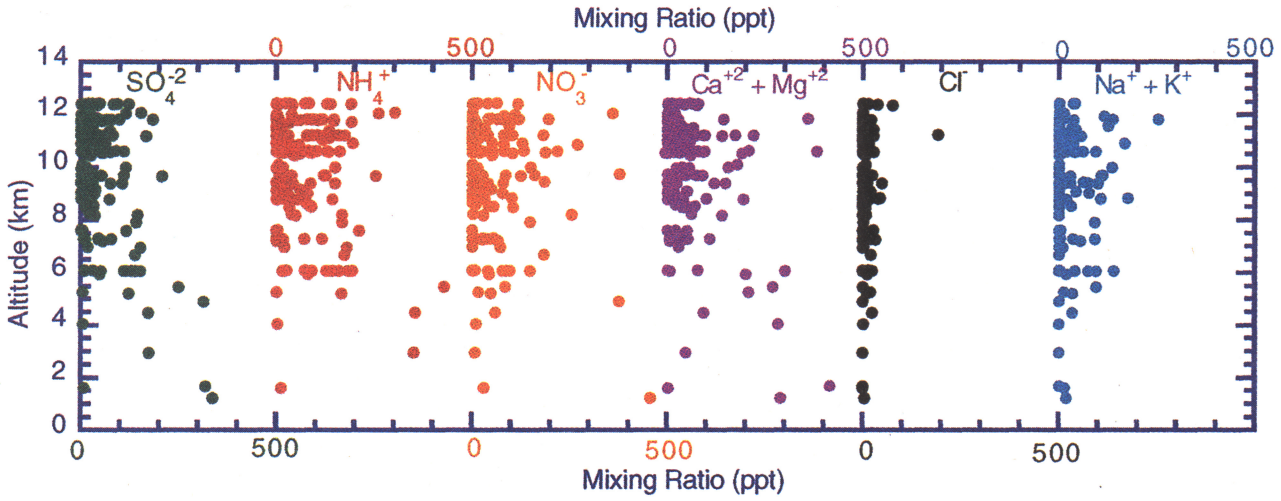

Figure 2. Altitude distribution of various ion species measured during SUCCESS.

of this profile is that in addition to the sulfate ion, upper tropospheric aerosols over the central US contained significant amounts of ammonium, nitrate, calcium and magnesium ions [*Talbot et al.*, 1998; *Dibb et al.*, 1998]. The ratio of Ca^{2+}/Mg^{2+} and Ca^{2+}/Na^{+} strongly suggest that some of the sampled particles were mineral aerosols that were transported to the upper troposphere by convection [*Talbot et al.*, 1998].

Figure 3 illustrates how the ammonium ion varied in the aerosol samples with respect to the sulfate and nitrate ions. A good correlation between ammonium and sulfate is obtained except for a few points with very low values of the ammonium ion. For the data points below the $(NH_4)_2SO_4$ line (~ 25% of the total), the ammonium ion was present in excess of the amount needed to neutralize sulfate to ammonium sulfate. This excess ammonium in the samples is perhaps neutralized by nitrate forming NH_4NO_3 particles. In fact data points containing excess ammonium when plotted (not shown) against the nitrate ion show some tendency to cluster around the NH_4NO_3 slope.

Although the analysis shown in Figure 3 indicate that sulfate aerosols in the upper troposphere contain significant amounts of ammonium ion, no obvious correlation is seen between the ammonium and nitrate ions. In fact Figure 3 shows that nitrate ion was often present in the samples in excess of the ammonium ion. Indeed in many samples the excess nitrate considerably exceeded the amount that might be present as ammonium nitrate. Our recent thermodynamic calculations show that nitrate can only be present in neutral or basic aerosol solutions in the upper troposphere [*Tabazadeh and Toon*, 1998]. Therefore, the excess nitrate in the samples cannot be accounted for by the H^+ ion, which is not measured in filters, and is often added to the samples for charge balance calculations. Thus we suggest that the excess remaining nitrate was on dust particles and was associated with one of the metallic ions shown in Figure 2.

In Figure 3 a correlation plot is shown for mineral ions with respect to the nitrate ion (note that the amount of nitrate needed to neutralize excess ammonium to NH_4NO_3, as described above, has been subtracted from the total nitrate mixing ratios shown in Figure 2). The data points show some tendency to cluster around the calcium (or magnesium) nitrate slope. However, the agreement is not as good as that shown for the $(NH_4)_2SO_4$. This is probably related to the fact that some of the nitrate associated with dust was perhaps present on the particles before transport to the upper troposphere. In fact many observations show that dust particles are a major sink for nitrate ions in the boundary layer air [*Carmichael et al.*, 1996; *Prospero and Savoie*, 1989; *Carmichael et al.*, 1997], and it is very likey that some of the nitrate in the particles, measured during SUCCESS, originated from the surface.

Figure 4 illustrates a histogram where we have used ion abundances shown in Figure 2 to calculate the net charge for each aerosol sample collected. The samples where the calculated net charge is negative can be balanced out by adding to the system H^+ ions . However, over 60 % of the time the net change for a given aerosol sample is positive. The most likely explanation for balancing the excess positive charge, which is commonly used for composition analysis of boundary layer aerosols, is to add carbonate ions to the system [*Hayami and Carmichael*, 1997; *Russell and Gass*, 1984]. In fact in Figure 3 there are many data points in which the measured mineral ion mixing ratios greatly exceeded the amount that could have been neutralized by the nitrate ion. For such cases, the mineral ion in the aerosol is perhaps associated with the carbonate ion and can be replaced by gas phase HNO_3, as described in the next section.

Discussion

We inferred above that a significant amount of carbonate is present in aerosol samples collected during SUCCESS in the upper troposphere. Following the suggestion of Dentener *et al.* [1996], we propose that the carbonate in mineral aerosols can be replaced by gas phase HNO_3 according to the following neutralization reaction:

$$CaCO_3(s) + 2HNO_3(g) \rightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(aq)$$

In order to estimate the time required for carbonate displacement by nitrate to occur within aerosols, a box-model simulation of nonequilibrium transfer between the gas and aerosol phase coupled with equilibrium chemical reactions within the aerosol phase was performed. The model used for this simulation (APD/EQUISOLV) is described in *Jacobson* [1998]. For this case, gas phase HNO_3 transfer to and reaction within a monodisperse distribution of 2 micron diameter aerosols containing $CaCO_3$ was simulated for different relative humidities and species concentrations.

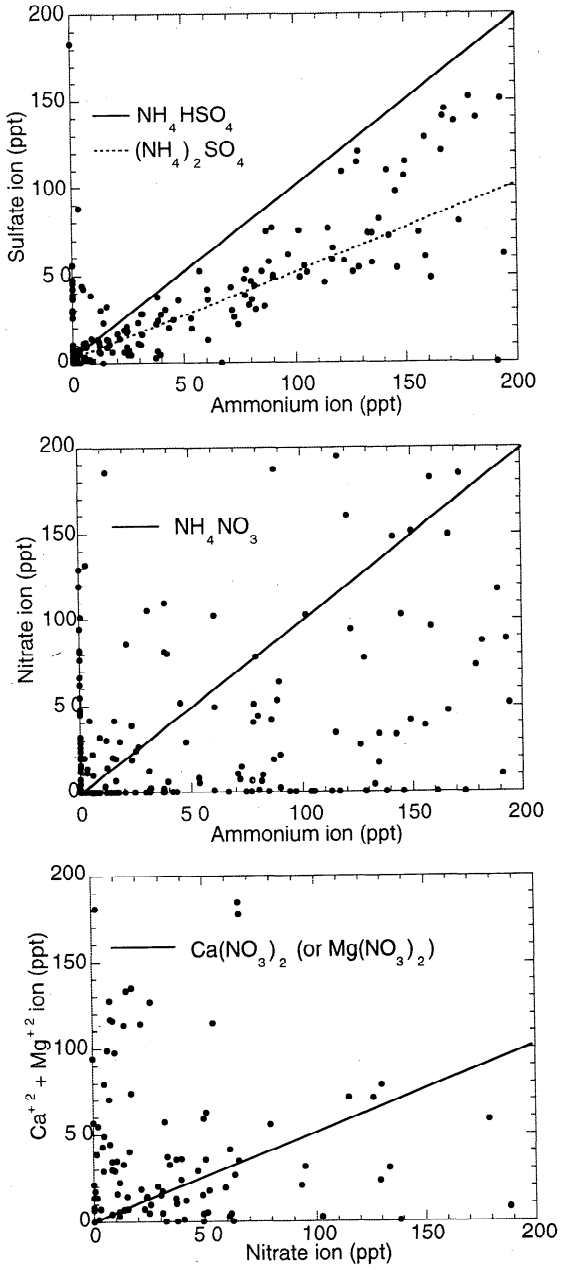

Figure 3. Ion-ion correlation plots.

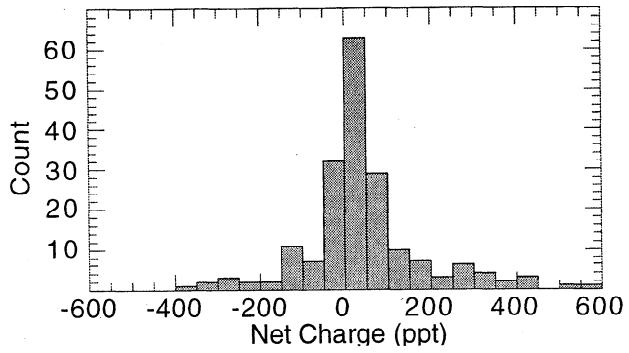

Figure 4. A histogram of the net charge for each filter sample using the ion concentrations given in Figure 1. In addition to the ions shown in Figure 1, we also used the measured oxalate ion mixing ratio to obtain the histogram.

Figure 5 shows a diagram of the time required for the displacement of carbonate by the nitrate ion. Even at 15% relative humidity and 220 K, particles are predicted to contain sufficient (although small) liquid water contents for transfer and reaction to occur. At high calcium contents, the conversion time is slightly slower than at low calcium contents simply because more conversion is required at high calcium contents. Temperature variations form 210 to 260 K seem to change the conversion times shown in Figure 5 by only about 1 to 5 hours.

Assuming that carbonate ion concentration can vary between 30 to 100 ppt (based on mineral ion mixing ratios shown in Figure 2) and including carbonate reactions to the HARVARD/GISS model (assuming that the reactions proceed to completion), the modeled HNO_3 values shown in Figure 1 can be reduced by as much as 60 to 200 ppt, which is in better agreement with the observations. The modeled winter values shown in Figure 1 will remain roughly the same since the average concentration of mineral dust acrosols in winter are much lower than 30 ppt [*Thakur et al.*, 1998].

Dust is not the only type of aerosol that may remove nitric acid vapor from the atmosphere in the upper troposphere. Roughly 14 % of the filter samples collected during spring over the US contained oxalate ion, which is often present in biomass burning plumes [*Talbot et al.*, 1988; *Andreae et al.*, 1988]. Such biomass burning was often observed during the field mission, and occurs as part of springtime agricultural processes in the US. Below we discuss how biomass-type aerosols may affect the HNO_3 budget in the upper troposphere.

On occasion, the aerosols contained refractory water soluble chloride (Figure 1). The observed chloride cannot be seasalt in origin, due to a lack of positive correlation with the measured sodium ion. We speculate that the chloride originated from burning agricultural land. The measured chloride ion was perhaps associated with either the ammonium or potassium in particles that were produced during the burning process [*Talbot et al.*, 1988; *Andreae et al.*, 1988]. If our assumption with regard to the chloride is correct, then HNO_3 can replace the chloride in the aerosol according to the following reaction:

$$NH_4Cl(aq) + HNO_3(g) \rightarrow NH_4NO_3(aq) + HCl(g)$$

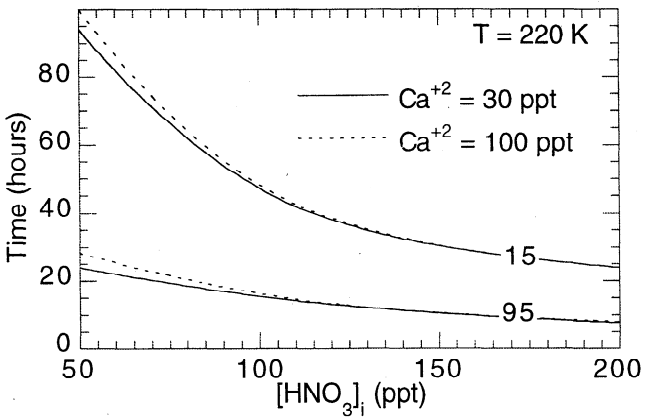

Figure 5. Time constant for the complete displacement of carbonate into nitrate ion as a function of HNO_3 gas phase concentration. The numbers on the lines indicate the relative humidity. The calcium ion concentration varied from 30 to 100 ppt. For the calculations we assumed that all the calcium ion in the particle was initially associated with the carbonate ion. The atmospheric pressure for the simulations was fixed at 200 mb.

It is well-known that nitrate replaces chloride in atmospheric particles, particularly on seasalt aerosols (see *Gard et al.* [1998] and references therein). This conversion mainly occurs because HCl ionic activities in solution are much higher than that of HNO_3 [*Tabazadeh et al.*, 1994].

As shown in Figure 2, during SUCCESS the concentration of dust particles (inferred from the $Ca^{+2} + Mg^{+2}$) is much higher than the chlorine-containing particles (inferred from the Cl^- ion), so the HNO_3 gas concentration is more affected by dust than biomass-type particles during this field experiment. However, mineral dust concentration in the atmosphere is highly variable and in some locations biomass burning aerosols may be present in much higher concentrations than dust particles. Over such locations reactions to replace chloride in the ammoniated aerosols by HNO_3 may be a more significant sink for HNO_3 removal. In addition biomass burning aerosols contain significant mass fractions of water soluble formate, acetate and oxalate ions [*Talbot et al.*, 1988; *Andreae et al.*, 1988]. As discussed above, about 14 % of the samples during SUCCESS contained oxalate ion and in a few samples the oxalate ion concentration exceeded 50 ppt. Reactions to replace these organic anions with HNO_3 may also become a major sink for HNO_3. Thus if biomass-type aerosols are present, then the most significant reactions to deplete HNO_3 would be to replace the water soluble organic anions with HNO_3, as follows:

$$NH_4HCOO(aq) + HNO_3(g) \rightarrow NH_4NO_3(aq) + HCOOH(g)$$
$$NH_4CH_3COO(aq) + HNO_3(g) \rightarrow NH_4NO_3(aq) + CH_3COOH(g)$$
$$(NH_4)_2C_2O_4(aq) + 2HNO_3(g) \rightarrow 2NH_4NO_3(aq) + C_2H_2O_4(g)$$

These reactions will occur in the atmosphere since the pK_a of HNO_3 (~ -1) is much lower than the pK_a of the organic acids involved (the pK_a range for the above acids is between 1 to 5). Hence thermodynamics will favor the displacement of a weak organic acid in solution by HNO_3. However, solubility data at low temperatures are required to investigate at what solution p*H*s these organic acids will leave the aerosol. Thus, the above reactions may not only remove the HNO_3 from the gas phase but they may also provide a source for the release of organic acids into the atmosphere far away from the source or even in the upper troposphere.

Summary

We suggested several displacement reactions on dust and biomass burning aerosls, which can irreversibly remove HNO_3 from the vapor phase. Including such aerosol reactions in global chemistry-transport models may help to reverse the current seasonal trend in models toward better agreement with the observations. Since land use changes have greatly increased the emissions of both mineral and biomass burning aerosols into the atmosphere [*Penner et al.*, 1992; *Tegen et al.*, 1996] uncovering the mysteries about their chemical and climatic affects are of great importance. Thus future field programs to investigate the composition of aerosols in the upper troposphere over locations other than central US are highly desirable for assessing the possible global impacts of soil and biomass aerosols on the composition of the upper troposphere.

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