

# Iron Mobilization in Mineral Dust: Can Anthropogenic SO<sub>2</sub> Emissions Affect Ocean Productivity?

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**Abstract:** In order for Fe contained in aeolian dust to act as a micronutrient for oceanic phytoplankton it must be first mobilized or dissolved. We propose that significant Fe-mobilization can occur in mineral dust from East Asia as a result of the incorporation of SO<sub>2</sub> from pollutant emissions into the advecting dust plumes and the subsequent acidification of the dust by heterogeneous SO<sub>2</sub> oxidation. To test this acid-mobilization hypothesis, we consider a dust plume that originated from the gobi deserts and advected over the Yellow Sea in March of 2001. Data collected during the TRACE-P field campaign confirm that this plume contained high concentrations of both dust and SO<sub>2</sub>. Measurements within the plume of significant concentrations of gaseous HNO<sub>3</sub> suggest that the dust particles were highly acidified (i.e., pH < 2). At these pH's, approximately 1–2% of the Fe contained in a deliquescent mineral dust particle would be mobilized within the nominal 3–5 day lifetime of the particle. These results suggest that there may be a link between the rate of C-fixation in so-called High-Nitrate-Low-Chlorophyll regions of the ocean and the rate of SO<sub>2</sub> emissions from East Asia.

## 1. Introduction

Iron (Fe) is one of the nutrients needed by phytoplankton to carry out photosynthesis. The transport and deposition of mineral dust from arid and semi-arid continental regions is believed to be a major, if not the dominant source of Fe to the remote ocean [Duce and Tindale, 1991; Jickells and Spokes, 2001]. One of the major uncertainties in modeling Fe input to the ocean relates to mobilization or dissolution of the Fe contained in mineral dust. While only soluble Fe is bioavailable virtually all the Fe found in sands from arid and semi-arid regions is in a highly insoluble, crystalline Fe-III form [Hseung and Jackson, 1952; Claquin et al., 1999; Spokes et al., 1994]. For phytoplankton to utilize the Fe deposited in mineral dust, some fraction of the Fe must first be mobilized into a form soluble in ocean water. The magnitude of the dissolved iron fraction (DIF) in mineral dust is uncertain. Previous estimates of DIF generally range from less than 1% to more than 10% (c.f., Duce and Tindale, 1991; Fung et al. 2000; Gao et al., 2003). Jickells and Spokes [2001] estimated a range in DIF from 0.8 to 2.1 % on the basis of estimated fluxes of dust to the ocean and data on the abundance and residence time of dissolved Fe in the ocean. We will use this range as reasonable target for assessing the viability of a hypothesized mechanism for mobilizing Fe in mineral dust.

In addition to the uncertainty in the magnitude of DIF, little is known of the processes that mobilize Fe in dust. This work examines the viability of one possible mechanism: acid mobilization. It is well-established that mineral Fe can be mobilized in highly acidic ambient aerosol solutions [Duce and Tindale, 1991; Zhu et al., 1992; Spokes et al., 1994]. However, sands from arid and semi-arid regions are typically alkaline, and before acid mobilization of Fe can occur, the dust must be acidified. We

hypothesize, that acidification is driven by the incorporation of SO<sub>2</sub> into dust plumes as they advect over urban and industrial centers and the subsequent heterogeneous oxidation of the SO<sub>2</sub> on deliquescent dust particles within the plume. To test this hypothesis, we examine the chemical composition of plumes containing wind blown dust from the gobi deserts in the springtime Asian outflow.

## **2. Acid dissolution of Fe containing minerals**

Analyses of mineral aerosols downwind from the gobi deserts show that acidic substances deposited/formed on the aerosol surface can change them from hydrophobic to hydrophilic (e.g., Song and Carmichael [2001]). When such aerosols are advected to the warm and moist marine boundary layer, they will likely deliquesce [Phadnis and Carmichael, 2000]. Deliquescence of mineral dust particles is a necessary but not sufficient condition for solubilization of Fe. Fe(III) oxides are highly insoluble under alkaline conditions, so the pH of a solution in contact with Fe-containing minerals must decrease before the Fe in these minerals can begin to dissolve. Since most of the Fe in surface soils of the gobi deserts is found in the form of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) [Hseung and Jackson, 1952; Claquin et al., 1999], we focus here on hematite dissolution. Figure 1 illustrates measured and calculated dissolution rates,  $R_d$ , for hematite as a function of pH. The rates are expressed in units of moles of mineral dissolved per m<sup>2</sup> of mineral surface area per hour. Values for  $R_d$  are shown for two temperatures: 298 K in order to compare calculated rates with experimental data; and 288 K for simulating conditions encountered in the marine boundary layer over the Yellow Sea.

### 3. What rate of iron dissolution is needed? How acidic does the dust need to be?

If all Fe in mineral dust is originally in insoluble form and DIF when it deposits on the ocean surface is 1–2%, then  $R_{Fe}$ , the average fractional rate of iron mobilization in mineral dust as it is transported through the atmosphere, must be given by

$$R_{Fe} = \text{DIF}/\tau = (0.01-0.02)/\tau \quad (1)$$

where  $R_{Fe}$  has units grams of dissolved Fe per grams of Fe in the mineral per unit time and  $\tau$  is the average residence time of mineral dust in the atmosphere. Assuming a nominal atmospheric lifetime of 3 to 5 days for dust particles [Ginoux et al., 2001], then

$$R_{Fe} \sim (8 \times 10^{-5} - 3 \times 10^{-4}) \text{ g Fe dissolved}/(\text{g total Fe})/\text{hr} \quad (2)$$

If soluble iron is arising from hematite dissolution and  $R_d$  is the rate of hematite dissolution, then

$$R_{Fe} = R_d A n M/w \quad (3)$$

where  $A$  is the specific surface area of hematite ( $\text{m}^2 \text{g}^{-1}$ ),  $n$  is the number of moles of Fe mobilized for each mole of hematite dissolved (i.e., 2),  $M$  is the gram-molecular weight of Fe, and  $w$  is the mass fraction of Fe in hematite (i.e., 0.7). Adopting an average value for  $A$  of  $100 \text{ m}^2 \text{g}^{-1}$  [Cornell and Schwertmann, 1996; Skopp, 2000] and combining Equations (2) and (3)

$$R_d = R_{Fe} w/(A n M) \sim (5-20) \times 10^{-9} \text{ moles m}^2 \text{ hr}^{-1} \quad (4)$$

Inspection of Figure 1 indicates that this range of hematite dissolution rates (at 288K) is attained for pH values less than 2. So, for acid mobilization to be a viable mechanism, the mineral dust over the ocean must have a  $\text{pH} \leq 2$ .

#### 4. Is there any evidence that mineral dust pH falls below 2?

To assess the acidity of mineral dust as it is advected in the Asian outflow over the western Pacific Ocean, we examine data from the TRACE-P (TRANsport and Chemical Evolution over the Pacific) field campaign [Jacob et al., 2003]; and, in particular data collected by the NASA DC-8 on March 21, 2001 (TRACE-P Flight 13). The aircraft intercepted a plume containing both mineral dust and air pollutants over the Yellow Sea (30°N) on that day at about 4:40 UTC. Back trajectory analysis indicates that the dust originated from the gobi deserts, was then transported to the Shanghai metropolitan area where air pollutants could have mixed with the dust and then moved out over the Yellow Sea and the Pacific Ocean [Fuelberg et al., 2003]. The large mixing ratios of highly reactive species along with the back trajectory analysis suggest that the plume had left the East Asian continent less than one day before it was sampled [Talbot et al., 2003].

Measured concentrations of selected trace gases and particle-phase components during Flight 13 are plotted as a function of time in Figure 2. Of particular interest are the data collected between 4:30 and 5:00 UTC; unless otherwise stated, when we discuss TRACE-P data below we will be referring to the data from this segment of Flight 13. During this period the aircraft descended into the boundary layer and elevated concentrations of  $\text{Ca}^{2+}$ ,  $\text{SO}_2$  and gas-phase  $\text{HNO}_3$  ( $\text{HNO}_3(\text{g})$ ) were observed.

*Evidence of the presence of mineral dust:* The measured Ca ranged from 10–15 ppbv; this is significantly larger than 30-45 pptv typically observed in the marine boundary layer [Dibb et al., 1999]. There are two likely Ca sources: sea salt and mineral dust. However, given the ~ 6 ppbv Na concentration measured during the same period we can exclude

sea salt as a significant contributor to the measured Ca. Na over the ocean, like Ca, can have sea salt and mineral dust origin. An upper limit estimate of the sea salt contribution to the observed Ca concentrations can be obtained by assuming that all of the observed Na came from sea salt. With this assumption and a Ca:Na ratio in seawater of 0.038 g/g [Stumm and Morgan, 1981], we find that less than 1% of the Ca was from sea salt.

Assuming that all of the Ca arose from mineral dust and an average Ca-to-total mineral dust ratio of 7:100 [Song and Carmichael, 2001], we obtain a mineral dust concentration of  $\sim 300 \mu\text{g}/\text{m}^3$ , suggesting the presence of a large dust plume.

*Evidence of the presence of urban/industrial air pollutants:* Under typical springtime conditions in the marine boundary layer of the Yellow Sea,  $\text{SO}_2$  generally ranges from  $\sim 0.03\text{--}1$  ppbv [Thornton et al., 1997]. Thus, the measured  $\text{SO}_2$  of 20–30 ppbv is a clear indication of the presence of air pollution. Consistent with this inference are the high concentrations measured for  $\text{SO}_4^{2-} \sim 11$  ppbv,  $\text{NO}_3^- \sim 13$  ppbv,  $\text{NH}_4^+ \sim 14$  ppbv,  $\text{C}_2\text{H}_2 \sim 10$  ppbv [Talbot et al., 2003].

*Evidence of acidification:*  $\text{HNO}_3(\text{g})$  over the Yellow Sea typically ranges from 0.2–0.6 ppbv [Kondo et al., 1997]. However, the measured  $\text{HNO}_3(\text{g})$  exceeded 2 ppbv and, at approximately the same time that  $\text{SO}_2$  reached its peak,  $\text{HNO}_3(\text{g})$  approached 10 ppbv. The enhanced  $\text{HNO}_3(\text{g})$  could perhaps be viewed, like the enhanced  $\text{SO}_2$ , as simply reflecting the fact that the plume being sampled had been impacted by air pollutants. However, the presence of air pollutants is not sufficient to explain the extremely large  $\text{HNO}_3(\text{g})$ .

$\text{HNO}_3$  is a strong acid with a high solubility [Clegg et al., 1998]. According to several laboratory studies [Underwood et al., 1999; Goodman et al., 2000; Hanisch and

Crowley, 2000] and model simulations [Dentener et al., 1996; Metzger et al., 2002], HNO<sub>3</sub>(g) rapidly partitions to the particulate phase when non-acidic aerosols are present. Moreover, modeling studies of the Asian outflow predict that under normal conditions, with dust concentrations of 150 μg m<sup>-3</sup> or less, NO<sub>3</sub><sup>-</sup> will almost exclusively reside in the particulate phase [Dentener et al., 1996; Phadnis and Carmichael, 2000]. In our case, we have HNO<sub>3</sub>(g) concentrations orders of magnitude higher than normal despite the presence of 100's μg m<sup>-3</sup> of mineral dust.

Further evidence of the anomalous nature of the HNO<sub>3</sub>(g) observations can be obtained by considering the nitrate volatilization ratio, [NO<sub>3</sub><sup>-</sup>]<sub>vol</sub>, defined as

$$[\text{NO}_3^-]_{\text{vol}} = 1 - \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + [\text{HNO}_3(\text{g})]} \quad (5)$$

where [NO<sub>3</sub><sup>-</sup>] and [HNO<sub>3</sub>(g)] are the measured mixing ratios of NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub>(g), respectively. In Figure 3 [NO<sub>3</sub><sup>-</sup>]<sub>vol</sub>-values calculated from the observations of HNO<sub>3</sub>(g) and the particulate NO<sub>3</sub><sup>-</sup> reported by Talbot et al. [2003] are illustrated. [NO<sub>3</sub><sup>-</sup>]<sub>vol</sub>-within the plume ranged from 25–45%. For this much of the nitrate to have resided in the gas-phase as HNO<sub>3</sub>(g) in the presence of large amounts of mineral dust requires that the mineral dust, along with the rest of the particulate phase, was strongly acidified.

The aerosol acidity can be estimated by considering the conditions needed to have supported the observed values of [NO<sub>3</sub><sup>-</sup>]<sub>vol</sub>. Assuming thermodynamic equilibrium between HNO<sub>3</sub>(g) and particulate nitrate and neglecting (for the moment) solution non-idealities, it is easily shown that:

$$[\text{NO}_3^-]_{\text{vol}} = \frac{[\text{H}^+]}{[\text{H}^+] + K} \quad (6)$$

where  $K = (H_{\text{HNO}_3}^* \cdot R \cdot T \cdot \text{LWC}) / (1000 \cdot P_0)$  in units of mole/kg;  $H_{\text{HNO}_3}^*$  is the Henry's law equilibrium constant ( $\text{mole}^2/\text{kg}^2/\text{atm}$ ) for the dissolution and dissociation of  $\text{HNO}_3(\text{g})$ ,  $R$  is the universal gas constant ( $\text{J}/\text{mole}/\text{K}$ ),  $T$  is ambient temperature ( $\text{K}$ ),  $\text{LWC}$  is liquid water content of mineral dust particles ( $\text{g}/\text{m}^3 \text{air}$ ) and  $P_0$  is the standard pressure (in Pa). The  $\text{LWC}$  was  $\sim 9 \times 10^{-4} \text{ g}/\text{m}^3 \text{air}$  [Talbot et al., 2003] and  $T$  averaged 288 K. Adopting these values, along with the appropriate temperature dependence for  $H_{\text{HNO}_3}^*$  [Clegg et al. 1998], we get  $K \sim 0.15 \text{ mole}/\text{kg}$ .

In Figure 4  $[\text{NO}_3^-]_{\text{vol}}$  calculated from Equation (6) is plotted as a function of pH. Also shown are the results of a more complete calculation using the thermodynamic model ISORROPIA [Nenes et al., 1998] which accounts for solution non-idealities. While the two calculations differ somewhat, both calculations indicate that a pH of  $\sim 1$  is needed to support the observed  $[\text{NO}_3^-]_{\text{vol}}$ -values. This value is within the previously estimated pH-range to make acid mobilization a viable mechanism for producing dissolved Fe in mineral dust.

Finally, we note that we found several other TRACE-P flight segments (DC-8 flights 9 and 16) that appear to have high dust and  $\text{SO}_2$  content. During each of these segments, high values of  $[\text{NO}_3^-]_{\text{vol}}$  were also inferred, suggesting that the dust was highly acidified in these cases as well.

## 5. Conclusion

Analysis of data collected on board the NASA DC-8 aircraft during TRACE-P suggests that anthropogenic  $\text{SO}_2$  emissions from China can promote the acid-mobilization



of Fe in mineral dust plumes from East Asia. If this limited analysis is generally applicable to dust plumes from East Asia, it would imply that SO<sub>2</sub> emissions from urban and industrial centers of China can lead to the mobilization of Fe in mineral dust. To the extent that this mobilized Fe is then acting as a limiting micronutrient in oceanic ecosystems, air pollution from China would be responsible for enhancing the productivity of these waters. By extension, air pollution controls in China which lowered SO<sub>2</sub> emissions might actually depress C-uptake in these same waters. Further investigations, involving more detailed observations and modeling studies of the interactions between airborne dust and air pollutants, are needed to test this hypothesis.

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## Figure Captions

**Figure 1.** Experimental and model calculated rates,  $R_d$ , of hematite dissolution. The calculated rates are based on the hematite dissolution experiments of Azuma and Kametani [1964]. Lines (1) and (2) correspond to different regimes in the dissolution kinetics; i.e. when the mass of dissolved hematite is  $< 0.8\%$  and is between  $0.8\text{--}40\%$ , respectively [Azuma and Kametani, 1964; Cornell and Schwertmann, 1996]. The shaded area shows the pH-range needed to mobilize  $1\text{--}2\%$  of the Fe in 3–5 days.

**Figure 2.** Flight altitude and observed concentrations of  $\text{SO}_2(\text{g})$ ,  $\text{HNO}_3(\text{g})$ , and particulate Ca as a function of time for TRACE-P DC-8 Flight 13. The shaded area along the x-axis highlights a period when the aircraft intercepted a plume of dust and air pollutants.

**Figure 3.** Flight altitude and observed concentrations of  $\text{SO}_2(\text{g})$ ,  $\text{HNO}_3(\text{g})$ , and particulate Ca, as well as  $[\text{NO}_3^-]_{\text{vol}}$  for highlighted portion of Flight 13.

**Figure 4.**  $[\text{NO}_3^-]_{\text{vol}}$  calculated as a function of pH.

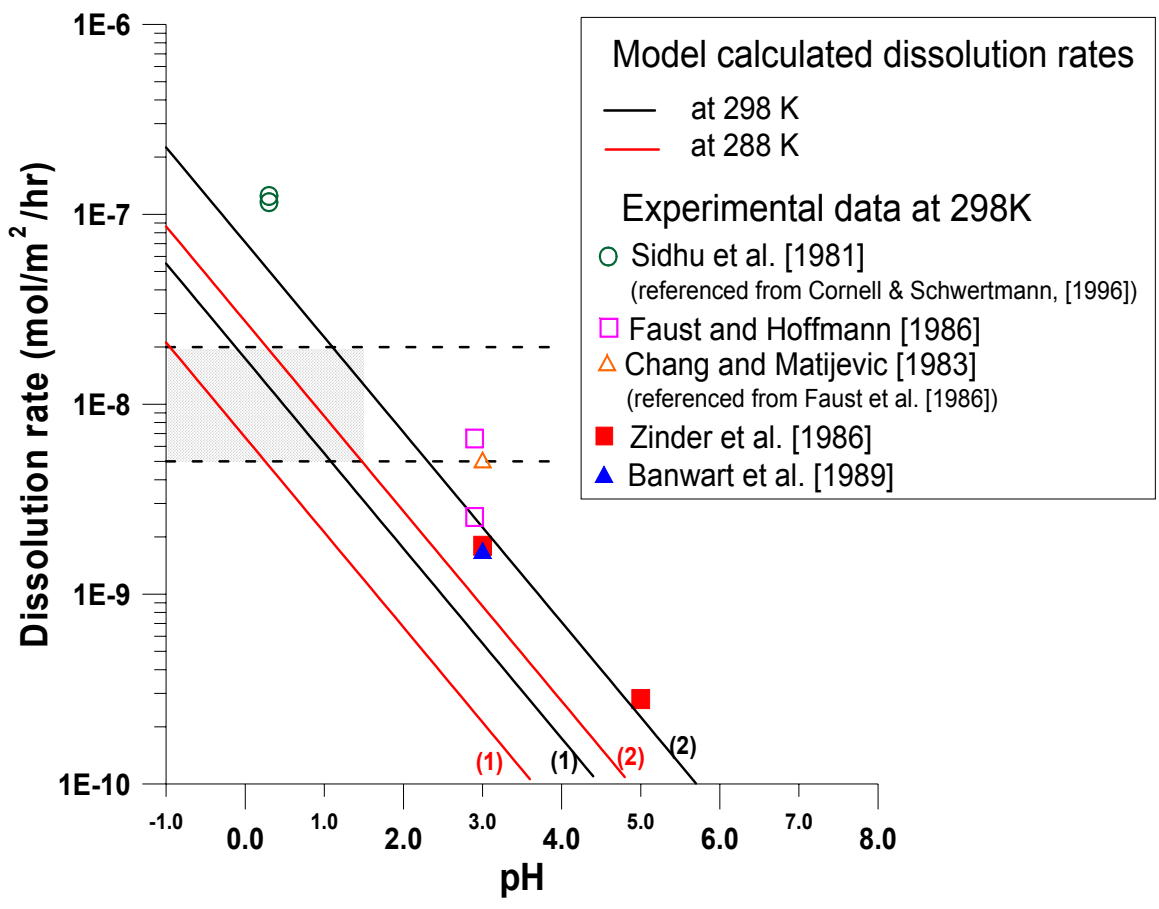


Figure 1

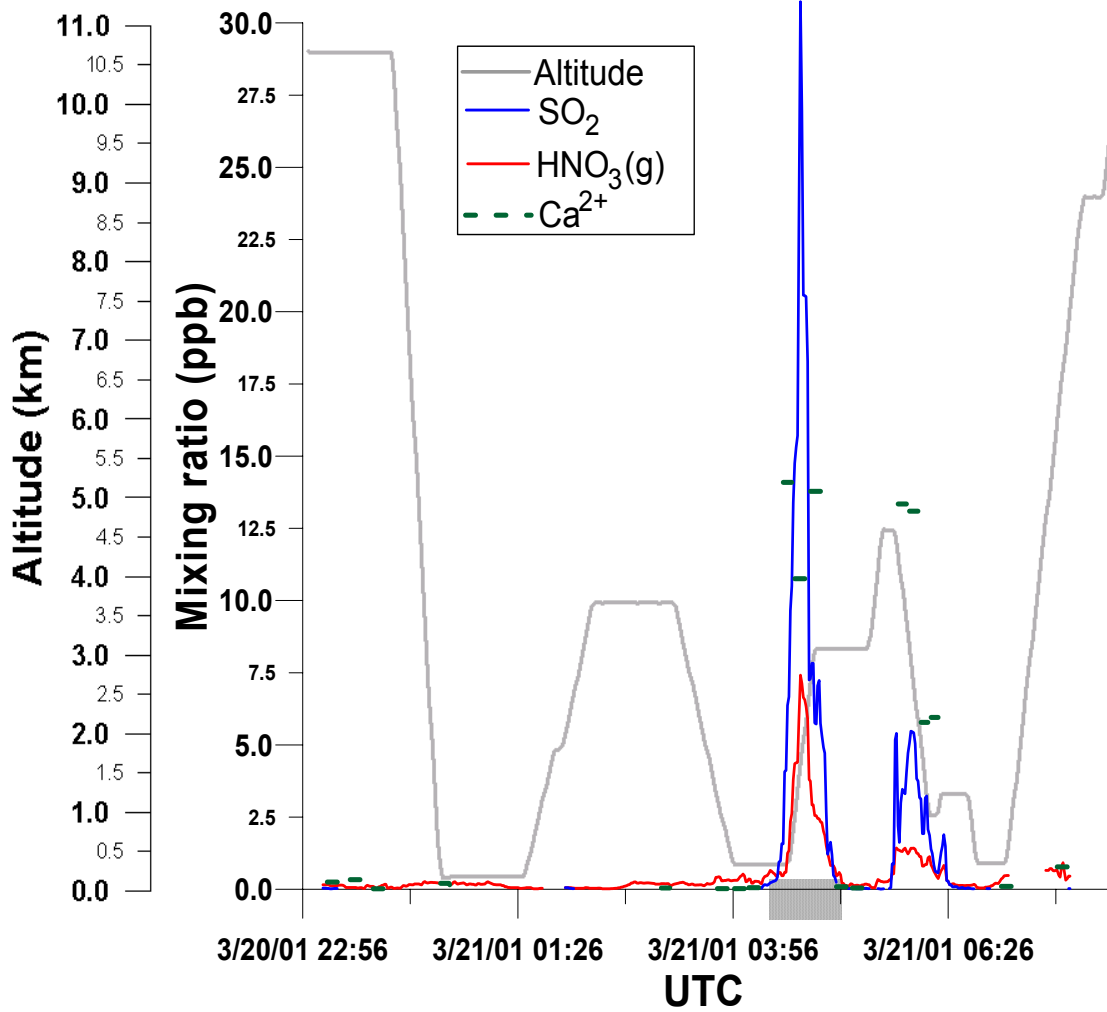


Figure 2

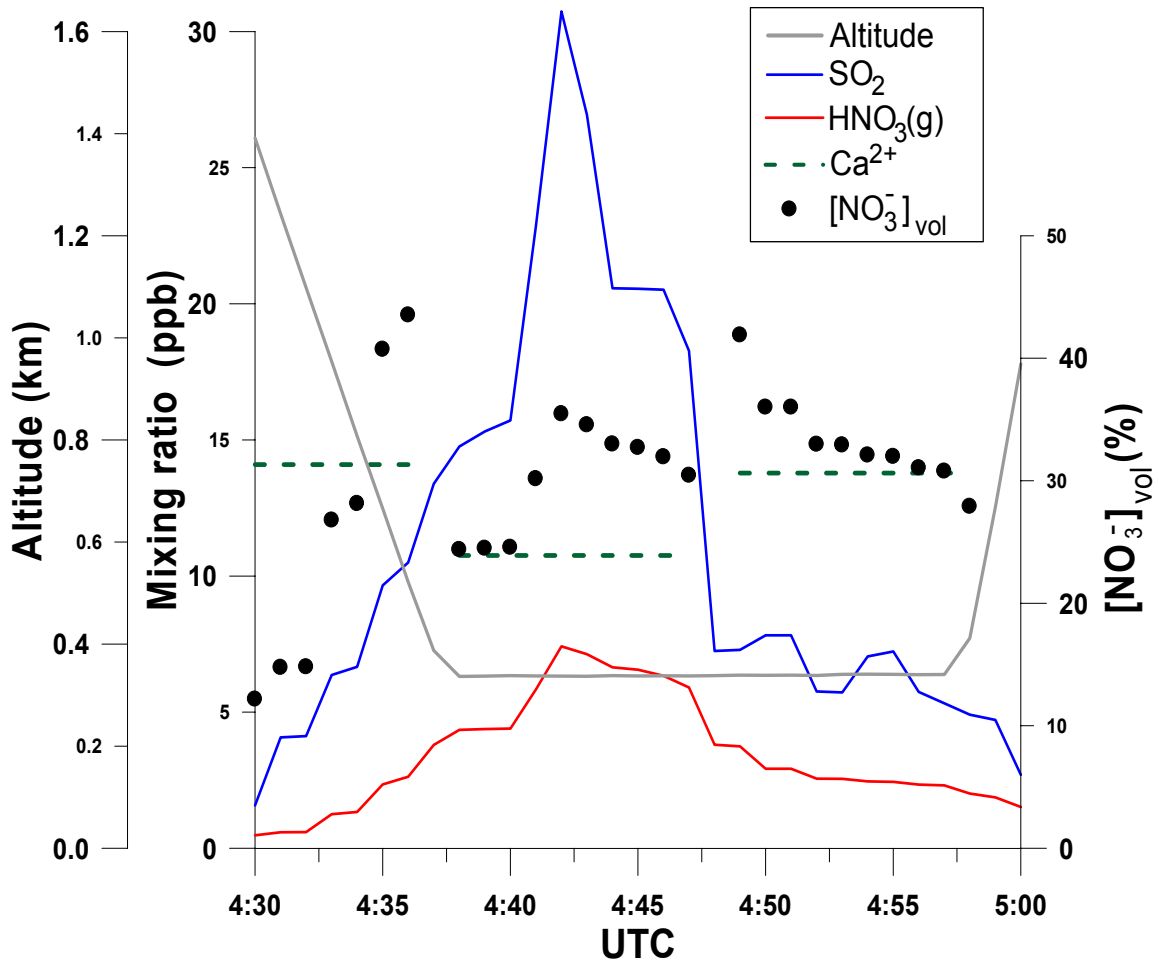


Figure 3

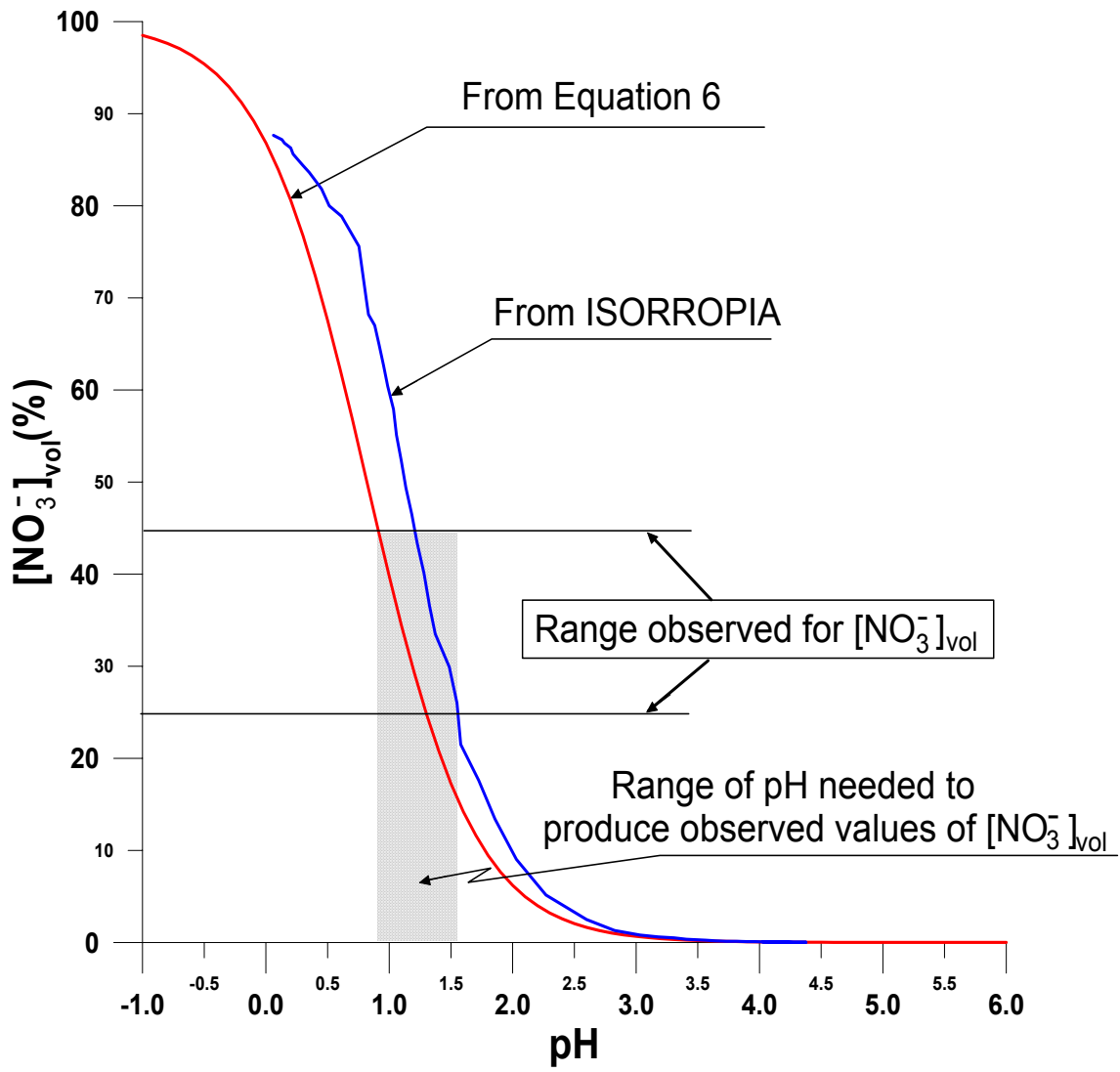


Figure 4