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## Heterogeneous uptake of NO<sub>2</sub> on soils under variable temperature and relative humidity conditions

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### Abstract

Heterogeneous reactions of nitrogen dioxide (NO<sub>2</sub>) on soils collected from Dalian (S1) and Changsha (S2) were investigated over the relative humidity (RH) range of 5%–80% and temperature range of 278–328 K using a horizontal coated-wall flow tube. The initial uptake coefficients of NO<sub>2</sub> on S2 exhibited a decreasing trend from  $(10 \pm 1.3) \times 10^{-8}$  to  $(3.1 \pm 0.5) \times 10^{-8}$  with the relative humidity increasing from 5% to 80%. In the temperature effect studies, the initial uptake coefficients of S1 and S2 decreased from  $(10 \pm 1.2) \times 10^{-8}$  to  $(3.8 \pm 0.5) \times 10^{-8}$  and from  $(16 \pm 2.2) \times 10^{-8}$  to  $(3.8 \pm 0.4) \times 10^{-8}$  when temperature increased from 278 to 288 K for S1 and from 278 to 308 K for S2, respectively. As the temperature continued to increase, the initial uptake coefficients of S1 and S2 returned to  $(7.9 \pm 1.1) \times 10^{-8}$  and  $(20 \pm 3.1) \times 10^{-8}$  at 313 and 328 K, respectively. This study shows that relative humidity could influence the uptake kinetics of NO<sub>2</sub> on soil and temperature would impact the heterogeneous chemistry of NO<sub>2</sub>.

**Key words:** heterogeneous reactions; soil particles; uptake coefficients; temperature dependence; relative humidity effect

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### Introduction

As a major component of tropospheric aerosol, mineral dust is injected into the troposphere with an annual amount of 1000–3000 Tg (Li et al., 1996; Prospero, 1999). It can provide a large reactive surface area for heterogeneous reactions with various atmospheric trace gases. Heterogeneous surface chemistry on mineral dust is also potentially catalytic, magnifying any potential impact on chemical cycles and trace gas concentrations. Previous studies on authentic and model mineral dust suggested that these particles could play an important role in atmospheric processes (Andreae and Crutzen, 1997; Molina et al., 1996; Rudich, 2003). Modeling studies suggested that approximately 40% of nitrate formation was associated with mineral aerosols (Dentener et al., 1996). Aerosol samples collected in East Asia showed a good correlation between nitrate and calcium (Song et al., 2005; Sullivan et al., 2007; Zhuang et al., 1999). A study by Tang et al. (2004) simulated a 20% decline in near-surface ozone and a 95% decrease in nitric acid levels in this region. Besides, mineral dust particles can also scatter and absorb incoming solar radiation (Sokolik and Toon, 1996) and act as cloud condensation nuclei (CCN) (Levin et al., 1996; Yin et

al., 2002). Heterogeneous chemical reactions of mineral dust with HNO<sub>3</sub> and NO<sub>2</sub> could influence photochemical cycles in the troposphere (Dentener et al., 1996; Jacob, 2000). In addition, laboratory studies have demonstrated that humic acid films and aerosols reduce NO<sub>2</sub> to HONO, an important precursor of the OH radical, providing a potential pathway to explain a missing daytime source of HONO (Stemmler et al., 2006; Stemmler et al., 2007). This is of particular interest given the importance of humic and fulvic acids in soils and the extent of humic-like substances in the troposphere (George et al., 2005). The variability in mineral dust surface properties and the composition of particles results in a variable affinity for various trace gas components.

Roughly half of the current atmospheric dust is estimated to be anthropogenic in origin, a result of soil degradation by agriculture, overgrazing and deforestation (Tegen and Fung, 1995; Tegen and Lacis, 1996). Dust aerosols originate as soil particles lofted into the atmosphere by wind erosion. The soil is most vulnerable to erosion in dry regions, where particles are only loosely bound to the surface by the low soil moisture. Larger particles fall out near the source region, but smaller particles can be swept thousands of kilometers downwind. As a result, the main components of mineral dust consist of soil particles, including quartz, feldspar, carbonate (e.g., calcite, dolomite) and clay (Usher et al., 2003). Mineral

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dust and soils generally have similar chemical and mineralogical composition, which is a reflection of dominant crustal materials in the source region.

Nitrogen oxides play a central role in tropospheric chemistry.  $\text{NO}_2$  is directly produced in small quantities along with  $\text{NO}$  in the processes of fossil fuel combustion, biomass burning, and lightning and by microbial activity in soils. It is also formed in the atmosphere by the oxidation of  $\text{NO}$  with ozone and peroxy radicals. The latter reaction leads to ozone production, since the steady-state  $\text{O}_3$  concentration is proportional to the ratio of the concentrations of  $\text{NO}_2$  and  $\text{NO}$ . The major chemical sink for nitrogen oxides is the reaction of  $\text{NO}_2$  with  $\text{OH}$  radicals, followed by formation and precipitation of nitric acid. Another pathway to remove nitrogen oxides from the gas phase is heterogeneous processes, for example, the uptake of  $\text{NO}_2$  on mineral dust. As far as we know, there have been many laboratory investigations of the reactions of  $\text{NO}_2$  on mineral dust (Angelini et al., 2007; Börensén et al., 2000; Finlayson-Pitts et al., 2003; Goodman et al., 1999; Miller and Grassian, 1998; Ullerstam et al., 2003; Underwood et al., 2000; Underwood et al., 1999, 2001). However, research on temperature and humidity effects in these heterogeneous processes is very limited (Li et al., 2010). No literature report concerning the temperature effects of the heterogeneous reaction of  $\text{NO}_2$  with concentrations close to the actual atmospheric environment has been found.

In this study, initial uptake coefficient measurements of  $\text{NO}_2$  on the surfaces of soils collected from Dalian and Changsha were investigated using a coated wall flow tube reactor equipped with a  $\text{NO}_x$  chemiluminescence analyzer, in combination with scanning electron microscopy (SEM). Soils collected from these places provide a good opportunity to study the heterogeneous reactions that occur on the surfaces of dust aerosols from such ambient environments.

## 1 Materials and methods

### 1.1 Film preparation for the coated-wall experiments

In each experiment, 0.1–0.3 g soil was dissolved in 5 mL of water and dripped uniformly into a Pyrex tube (inner diameter of 2.1 cm, length 30 cm). In our experimental conditions, a soil loading density of  $(0.97\text{--}2.9) \times 10^{-3} \text{ g/cm}^2$  and a film thickness of ca. 3–10  $\mu\text{m}$  were calculated. Because the results may be sensitive to the relative humidity (RH), the Pyrex tube was dried in an oven at 423 K for more than 3 hr, which certainly left little water on the surface. Therefore, most of the adsorbed water during an experiment was deposited from the gas phase. The resulting film covered the entire inner area of the tube and, to the eye, was fairly uniform in thickness. These film-covered tubes were used as the reaction region for the uptake coefficient measurements.

### 1.2 Coated-wall flow tube experiments

The measurements of heterogeneous uptake coefficients of  $\text{NO}_2$  onto various soil samples were carried out in a hor-

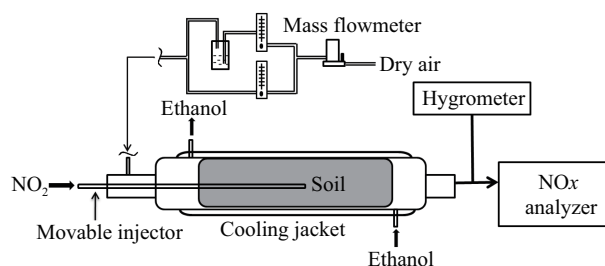


Fig. 1 Diagram of the flow tube reactor in this study.

izontal flow-tube coated with a soil sample. A schematic diagram is shown in Fig. 1. The reactor consisted of a Pyrex tube (1 m in length and 2.7 cm i.d.) with a jacket for the circulation of the thermostated liquid (ethanol). The experimental approach is based on measuring the reactant gas concentration, i.e.,  $\text{NO}_2$  gas, at the exit of a cylindrical flow reactor as a function of the contact distance (time) between  $\text{NO}_2$  gas and the soil surface.

This method provides the possibility of carrying out measurements in the presence of water, which interferes negatively in several other techniques of trace gas measurements, such as IR or mass spectrometry. The amount of water in the gas phase is very crucial for the reactivity of dust aerosols, which influences the phase state of the particles and possibly the mechanism. These features allow experiments with dust aerosol particles at humidity, temperature and concentrations of trace gas relevant to the real atmosphere.

A typical experiment proceeded as follows. At first, a constant flow of  $\text{NO}_2$  was established, with the injector placed at the end of the coated tube, such that none of the soil-coated surface was exposed to the gas flow. After the  $\text{NO}_2$  concentration was steady, the injector was withdrawn a certain distance to expose some fraction of the soil to the gas. The  $\text{NO}_2$  concentration difference between the initial region and bottom point yields the initial state loss under various conditions. After some time, the steps were reversed, pushing the injector forward to its original position. This procedure led to typical  $\text{NO}_2$  concentration profiles as shown in Fig. 2. All the experimental conditions are summarized in Table 1.

The powder samples, Dalian soil (S1) and Changsha soil

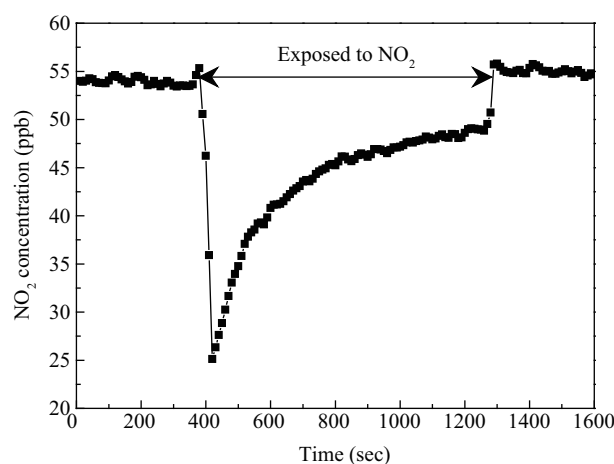


Fig. 2 Typical experimental profile for S1 at ca. 50 ppb  $\text{NO}_2$ , 298 K, 760 Torr.



**Table 1** Properties of the soil used in the experiment

	S1	S2
Temperature (K)	278–313	288–328
Pressure (Torr)	760	760
RH (%)	—	5–80
NO <sub>2</sub> concentration (ppb)	ca. 50	25–500
<i>S</i> <sub>BET</sub> (m <sup>2</sup> /g)	33.6 ± 3.4	26.8 ± 2.7

S1 and S2 are powder samples of Dalian soil (S1) and Changsha soil (S2).

(S2), were obtained from the Institute of Environmental Reference Materials Ministry of Environmental Protection. The compositions of the soil samples are listed in Table 2. BET surface areas were determined for the samples by using an automated multipoint BET analysis (Autosorb-1, Quantachrome, USA) with N<sub>2</sub> as the adsorbate. The BET surface areas after coating and heating were measured to be (33.6 ± 3.4) m<sup>2</sup>/g for S1 and (26.8 ± 2.7) m<sup>2</sup>/g for S2, respectively. The morphology was observed using SEM (S-4300, Hitachi, Japan), as shown in Fig. 3.

The humidity of the gas flow was measured by means of a CENTER-310 hygrometer. The reactor was operated at a total flow (zero air for dilution and NO<sub>2</sub>) of 1.0 L/min. The NO<sub>2</sub>(g) (99.9%, Xian Heyu Trade Co. Ltd., China) loss in the flow tube as a function of injector position was measured using a NO<sub>x</sub> chemiluminescence analyzer (THERMO 42i, Thermo Scientific, USA) whose inlet was equipped with a carbonate denuder. The reactant gas passed the denuder coated with sodium carbonate in order to remove trace species such as HONO and HNO<sub>3</sub>. The injector position was translated to gas-solid contact times using the known total flow velocity.

**Table 2** Compositions of the soil samples in the experiments

	Composition of S1 (%)	Composition of S2 (%)
SiO <sub>2</sub>	65.64 ± 0.42	69.59 ± 0.43
Al <sub>2</sub> O <sub>3</sub>	14.95 ± 0.09	14.41 ± 0.07
Fe <sub>2</sub> O <sub>3</sub>	6.51 ± 0.16	5.85 ± 0.08
FeO	0.54 ± 0.08	0.25 ± 0.06
CaO	0.84 ± 0.04	0.08 ± 0.03
MgO	1.23 ± 0.05	0.61 ± 0.03
K <sub>2</sub> O	2.25 ± 0.06	1.7 ± 0.02
Na <sub>2</sub> O	0.81 ± 0.02	0.1 ± 0.001

S1 and S2 are powder samples of Dalian soil (S1) and Changsha soil (S2).

## 2 Results and discussion

### 2.1 Uptake coefficient measurements

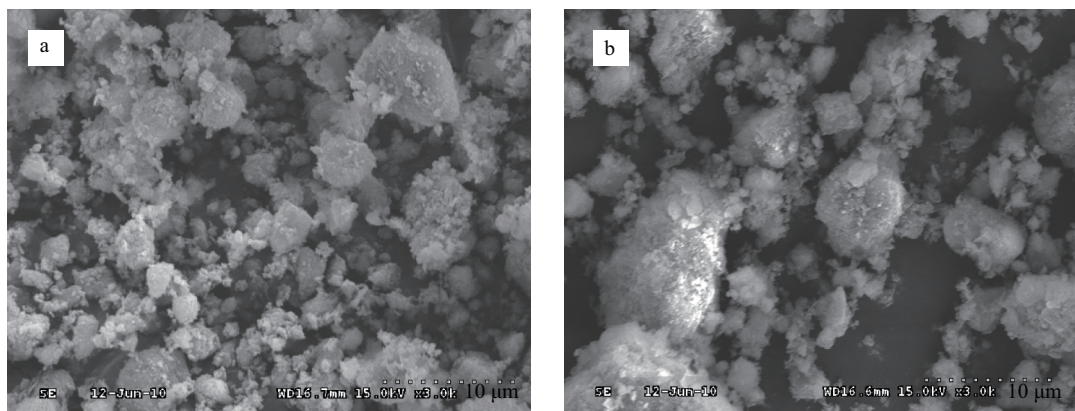
The measurements of uptake coefficients were performed by using the flow-tube reactor over the relative humidity range of 5%–80% and temperature range of 278–328 K. All the experiments were carried out in the dark.

Figure 2 shows the raw data under the typical conditions. The curve displays a pattern with a large initial NO<sub>2</sub> uptake followed by a decrease as the reaction proceeds. In the temperature effect studies, it was found that the decreasing trend became slower with increasing temperature. The result suggests that the uptake mechanism was influenced by temperature. Details of the mechanism will be discussed below. When the movable injector was pushed back to the start position after the initial exposure to soil, the NO<sub>2</sub> was no longer in contact with the soil surface and the NO<sub>2</sub> concentration returned to initial NO<sub>2</sub> concentration rapidly. The observed time dependence of the uptake rate and the saturation of the NO<sub>2</sub> uptake of soil particles may be explained by different uptake mechanisms as follows: (1) the uptake of NO<sub>2</sub> is reversible. With increasing NO<sub>2</sub> adsorption, the desorption rate increases which leads to a reduced net uptake. (2) The uptake of NO<sub>2</sub> is irreversible. Reactive sites for NO<sub>2</sub> adsorption are blocked by NO<sub>2</sub> molecules, which leads to a decrease in the adsorption. (3) (1) and (2) both exist. In this study, hypothesis (3) is discussed first and the results of the temperature dependence prove that the hypothesis is reasonable.

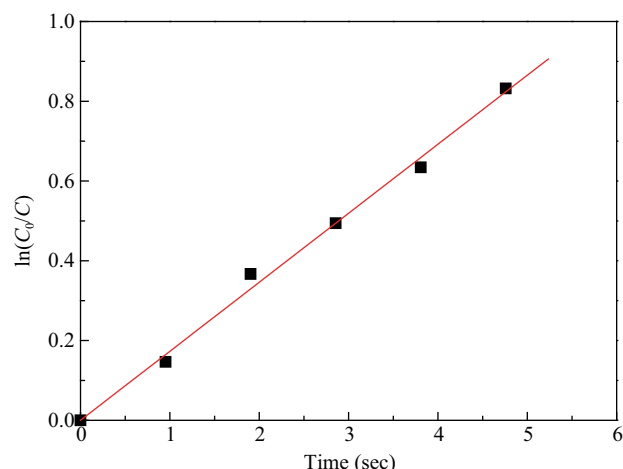
The initial uptake coefficient,  $\gamma_0$ , was calculated by Eq. (1):

$$\gamma_0 = \frac{4k_{\text{obs}}V}{\omega S} \quad (1)$$

where,  $k_{\text{obs}}$  (sec<sup>-1</sup>) is the first-order rate constant of NO<sub>2</sub> loss,  $\omega$  is the average molecular speed,  $V$  is the volume of the reaction zone, and  $S$  is the surface area of the soil sample. To calculate the uptake coefficients, two parameters should be determined experimentally: the rate constant  $k_{\text{obs}}$  and the soil surface area  $S$  involved in the interaction with NO<sub>2</sub>. The  $k_{\text{obs}}$  were observed to be linearly dependent on the mass of the sample deposited into the flow tube, strongly suggesting that the total internal surface was available for heterogeneous reactions involving NO<sub>2</sub>.



**Fig. 3** SEM pictures of S1 (a) and S2 (b). The scale is 10 μm. The size of the soil particles is in the range of 0.5–7 μm.



**Fig. 4** Uptake kinetics of NO<sub>2</sub> as a function of the reaction time on S1. The experimental conditions are as follows: RH < 5%, 760 Torr, 298 K, NO<sub>2</sub> initial mixing ratio of 50 ppb.

Therefore, the surface area used in this study was the BET surface area, which took into account the internal surface of our sample and represented an upper limit on the reactive surface area available for each powder sample.

The first-order loss approximation can be used for determining  $k_{\text{obs}}$  from NO<sub>2</sub> loss kinetics. The kinetics of NO<sub>2</sub> loss on soil at a given exposure time can be treated as the first-order kinetic formalism and the rate constant can be determined by using Eq. (2):

$$\ln\left(\frac{C_0}{C}\right) = k_{\text{obs}}t \quad (2)$$

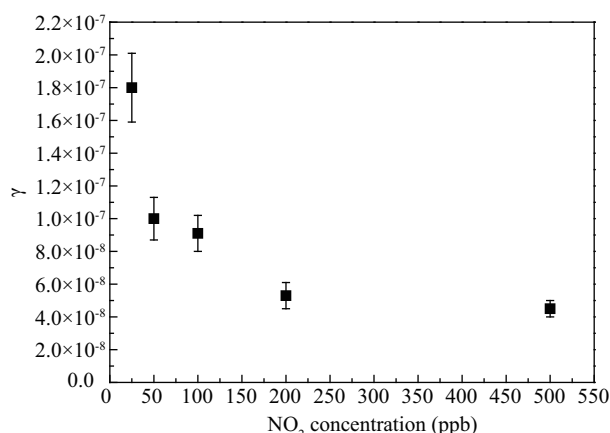
where,  $C_0$  and  $C$  give the NO<sub>2</sub> concentrations in the absence and presence of reaction, and  $k_{\text{obs}}$  and  $t$  are the first-order rate constant of NO<sub>2</sub> loss and the reaction time, respectively. As shown in Fig. 4, the variations of  $\ln(C_0/C)$  as a function of exposure time can be best fit, assuming a first-order process with respect to the gas phase concentration of NO<sub>2</sub>. In addition, the measured uptake coefficients were observed to be strongly dependent on the NO<sub>2</sub> gas phase concentrations, in the range from 25 to 500 ppb, as shown in Fig. 5. This behavior can be explained via a Langmuir-Hinshelwood mechanism.

The uptake coefficient is a phenomenological quantity, defined as the fraction of collisions a gas-phase reagent makes with the surface, resulting in the net loss of that reagent from the gas phase. Eqs. (1) and (2) do not account for the possible diffusion limitations caused by a radial gradient in the gas concentrations, which could occur if the loss at the surface is faster than gas-phase diffusion replenishes the near-surface regime. Therefore, the rate constant for removal of NO<sub>2</sub>,  $k$  (sec<sup>-1</sup>), can be determined by correcting  $k_{\text{obs}}$  for diffusion (Gershenson et al., 1995) by Eqs. (3) and (4):

$$\frac{1}{k} = \frac{1}{k_{\text{obs}}} - \frac{1}{k_{\text{diff}}} \quad (3)$$

$$k = \frac{3.66D_i}{r^2} \quad (4)$$

where,  $r$  (cm) is the inner radius of the coated tube and  $D_i$  is the diffusion coefficient which can be calculated



**Fig. 5** Dependence of the uptake coefficients ( $\gamma$ ) of NO<sub>2</sub> on S2 as a function of the NO<sub>2</sub> gas phase concentration. All experimental were conducted at 298 K, RH < 5%. Each point was obtained from measurements on fresh samples.

using the formula proposed by Fuller et al. (1966). The quoted uncertainties represent  $2\sigma + 10\%$ , which represents a combination of statistical, estimated systematic errors.

## 2.2 Relative humidity effects

The uptake coefficients measured under different experimental conditions are all summarized in Table 3.

The uptake coefficients of NO<sub>2</sub> on S2 particles were investigated as a function of RH (Fig. 6). As shown in Fig. 6, the uptake coefficient decreased from  $(10 \pm 1.3) \times 10^{-8}$  to  $(3.1 \pm 0.5) \times 10^{-8}$  with RH increasing from 5% to 80%. This result indicates water vapor could influence the uptake kinetics of NO<sub>2</sub> on soil particles. Under dry conditions (RH < 5%), there was still some water vapor remaining and the surface adsorbed water on the soils equilibrated with water vapor. With increasing RH, water

**Table 3** Values of initial uptake coefficients ( $\gamma_0$ ) of NO<sub>2</sub> on two soil samples under different conditions for this work

RH (%)	Temp. (K)	$\gamma_0$ (S1) ( $\times 10^{-8}$ )	$\gamma_0$ (S2) ( $\times 10^{-8}$ )
< 5	278	$10 \pm 1.2$	$16 \pm 2.2$
< 5	283	$7.0 \pm 1$	–
< 5	288	$3.8 \pm 0.5$	$11 \pm 1.3$
< 5	298	$5.3 \pm 0.7$	$10 \pm 1.3$
< 5	303	$6.5 \pm 0.8$	–
< 5	308	–	$3.8 \pm 0.4$
< 5	313	$7.9 \pm 1.1$	–
< 5	318	–	$9.7 \pm 1.2$
< 5	328	–	$20 \pm 3.1$
Temp. (K)	RH (%)	$\gamma_0$ (S1) ( $\times 10^{-8}$ )	$\gamma_0$ (S2) ( $\times 10^{-8}$ )
298	< 5	$5.3 \pm 0.7$	$10 \pm 1.3$
298	20	–	$4.9 \pm 0.7$
298	40	–	$4.4 \pm 0.5$
298	60	–	$4.3 \pm 0.6$
298	80	–	$3.1 \pm 0.5$
Temp. (K); RH (%)	NO <sub>2</sub> concentration (ppb)	$\gamma_0$ (S1) ( $\times 10^{-8}$ )	$\gamma_0$ (S2) ( $\times 10^{-8}$ )
298; RH < 5	25	–	$18 \pm 2.1$
298; RH < 5	50	$5.3 \pm 0.7$	$10 \pm 1.3$
298; RH < 5	100	–	$9.1 \pm 1.1$
298; RH < 5	200	–	$5.3 \pm 0.8$
298; RH < 5	500	–	$4.5 \pm 0.5$

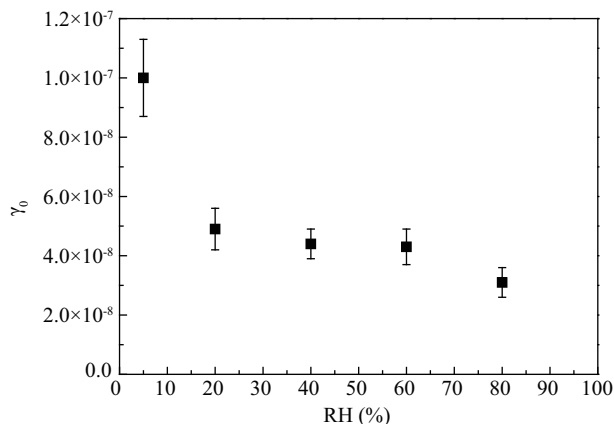
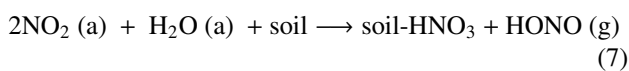


Fig. 6 Initial uptake coefficients ( $\gamma_0$ ) of NO<sub>2</sub> on S2 as a function of RH.

starts to compete with NO<sub>2</sub> for active sites and the uptake coefficient decreases with the increasing of RH. Therefore, the reasonable explanation of the water dependence is probably the Langmuir-Hinshelwood mechanism with co-adsorption of water and NO<sub>2</sub> on the active sites of soil particles. The following reactions likely occur on the soil surface during adsorption:



This system has been studied extensively (Angelini et al., 2007; Börensén et al., 2000; Finlayson-Pitts et al., 2003; Goodman et al., 1999; Miller and Grassian, 1998; Ndour et al., 2008; Ullerstam et al., 2003; Underwood et al., 1999, 2000, 2001) and many studies observed the formation of HONO, when water was present (Finlayson-Pitts et al., 2003; Goodman et al., 1999). But Underwood et al. (1999, 2001) did not observe gaseous HONO or HNO<sub>3</sub>, only NO and N<sub>2</sub>O. It was found that chelating nitrite surface species were formed at the lowest pressure (5 mTorr) and monodentate, bidentate and bridging nitrate species were formed at higher pressure (30 mTorr). Thus, the adsorption of water would be especially important in

the chemistry of atmospheric gases on mineral dust that can easily ionize, e.g., the heterogeneous chemistry of NO<sub>2</sub> and HNO<sub>3</sub> (Börensén et al., 2000; Miller and Grassian, 1998). The humidity dependence in our experiments is different from that proposed by Finlayson-Pitts et al. (2003). This may be related with the low concentration of NO<sub>2</sub> and the composition and properties of the soil particles, which will be discussed below.

Using DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy), Li et al. (2010) investigated NO<sub>2</sub> uptake on CaCO<sub>3</sub> under dry and wet conditions. The uptake coefficients decreased initially with RH and then increased slightly with increasing RH. The result observed in this study is consistent with that of NO<sub>2</sub> on CaCO<sub>3</sub> at low RH conditions (RH < 52%). But over the RH range studied, the result of uptake coefficient increasing with increasing RH was not observed. The reason is that the composition of soil is more complicated and its properties are different from CaCO<sub>3</sub>. Compared with CaCO<sub>3</sub>, the soil is more hydrophilic and porous because of the clay in the soil. Therefore, water could occupy the active site more easily, which would inhibit the adsorption of NO<sub>2</sub>. The results support the hypothesis of the reactions above. In the experiments, water could not form a liquid film on the surfaces of soil particles and the surface reactions would not transform from gas-solid to gas-liquid. Besides, the concentration of NO<sub>2</sub> in our experiment (ca. 50 ppb) is different from that (ca. 200 ppm) used by Li et al. (2010). Thus, over the RH range studied, water always plays a negative role in the heterogeneous reactions of NO<sub>2</sub> on soils, which leads to the uptake coefficient decreasing with increasing RH.

### 2.3 Temperature effects

Besides relative humidity, temperature is also an important factor for both homogeneous and heterogeneous reactions in the atmosphere. Therefore, it is of interest to study the temperature effect of the reaction of NO<sub>2</sub> on the soil particles.

As shown in Fig. 7 for S1, over the temperature range of 278–313 K, at 760 Torr and under dry conditions (RH < 5%),  $\gamma_0$  first decreased from  $(10 \pm 1.2) \times 10^{-8}$  to  $(3.8 \pm 0.5) \times 10^{-8}$  with the temperature increasing from 278

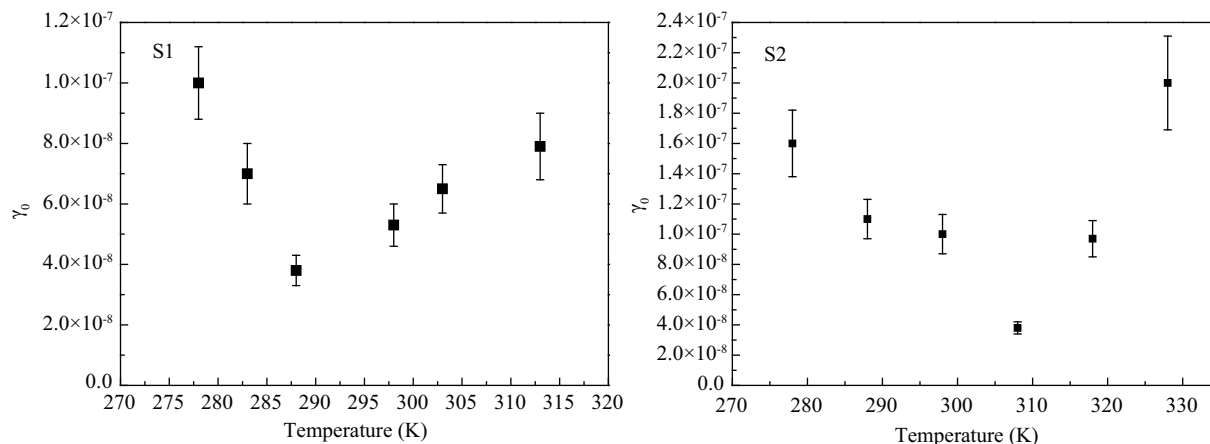


Fig. 7 Initial uptake coefficients ( $\gamma_0$ ) of NO<sub>2</sub> as a function of the temperature. Conditions: RH < 5%, 760 Torr, NO<sub>2</sub> initial mixing ratio of ca. 50 ppb.



to 288 K. However, with the temperature increasing from 288 to 313 K,  $\gamma_0$  increased from  $(3.8 \pm 0.5) \times 10^{-8}$  to  $(7.9 \pm 1.1) \times 10^{-8}$ . Similar results were also observed for S2 with a different inflection point. For S2,  $\gamma_0$  decreased from  $(16 \pm 2.2) \times 10^{-8}$  to  $(3.8 \pm 0.4) \times 10^{-8}$ , when temperature increased from 278 to 308 K, and with the increasing of temperature from 308 to 328 K,  $\gamma_0$  increased from  $(3.8 \pm 0.4) \times 10^{-8}$  to  $(20 \pm 3.1) \times 10^{-8}$ . The different values of the inflection points may be related to the compositions and properties of the soil particles.

From Eq. (1), the parameters related to temperature are  $k_{\text{obs}}$  and  $\omega$ . In the temperature range of 278–328 K,  $\omega$  would change from 357.7 to 388.5 m/sec. The influence of this change on the uptake coefficients is slight. Thus,  $k_{\text{obs}}$  plays the most important role in the temperature effect of uptake coefficients. According to the hypothesis of the uptake mechanisms above, the uptake mechanisms of  $\text{NO}_2$  on the soil particles consist of (1) and (2) stages. That means the initial uptake of  $\text{NO}_2$  on soil particles includes two parts: (1) adsorption process and (2) chemical reaction. Compared with Fig. 8a and b, the returning trend is slower accompanied with a smaller rate of desorption. That means the ratio of chemical reaction/adsorption increased with increasing temperature. The result suggests that the initial uptake process is controlled by chemical reaction at high temperature, while at low temperature, it is controlled by adsorption. It has been reported that the reversible adsorptions of gas phase  $\text{NO}_2$  and water are exothermic (Bartels-Rausch et al., 2002; Majzlan et al., 2007). Therefore, it is reasonable to assume that  $\Delta H_{\text{ads}} < 0$ . The fact that the chemical Reaction (7) with a positive

temperature dependence has been reported (England and Corcoran, 1974). In addition, the condensation point of  $\text{NO}_2$  is 294 K, as the temperature decreases, which could facilitate the adsorption of gaseous  $\text{NO}_2$  on the soil particles. Thus, in Fig. 7, the uptake coefficients decrease with increasing temperature initially and then display a negative temperature dependence.

### 3 Atmospheric implications

The rate of removal of  $\text{NO}_2$  by uptake onto soil can be approximated in a simple model. We assume that the lifetime  $\tau$  for removal of  $\text{NO}_2$  by soil is given by Eq. (8),

$$\tau = \frac{4}{\gamma \bar{c} A} \quad (8)$$

where,  $A$  ( $\text{cm}^2/\text{cm}^3$ ) is the soil surface area density,  $\bar{c}$  is the mean molecular speed, and  $\gamma$  is the uptake coefficient.

An estimation of the gas-lifetime of  $\text{NO}_2$  may be also obtained from the reaction rates at room temperature with tropospheric agents such as OH,  $\text{O}_3$  and  $\text{NO}_3$ , taking into account their average concentrations and the measured room temperature rate constants, by using the expression below:

$$\tau = \frac{1}{k[X]} \quad (9)$$

where,  $[X]$  is the typical atmospheric concentration of the oxidant (OH,  $\text{O}_3$  and  $\text{NO}_3$ ) and  $k$  is the rate coefficient of the reaction of between  $\text{NO}_2$  and X. The values determined above are presented in Table 4.

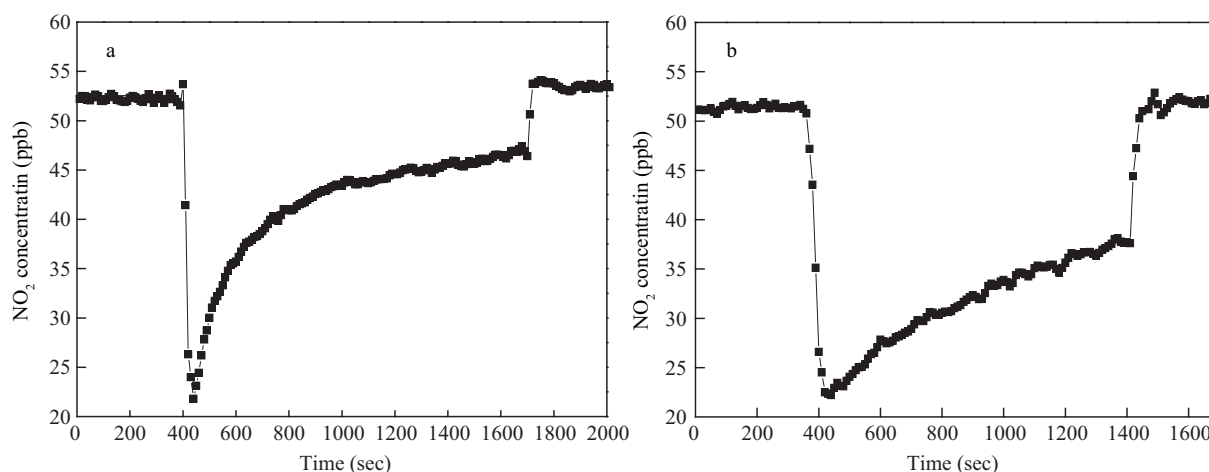


Fig. 8 Experimental profiles for S2 at 278 K (a) and 328 K (b).

Table 4 Atmospheric lifetimes of  $\text{NO}_2$  ( $\tau$ ), for studied soils and typical atmospheric oxidants

	Concentrations ( $\text{mol}/\text{cm}^3$ )	Reference	$K$ ( $\text{cm}^3/(\text{mol}\cdot\text{sec})$ )	Reference	$\tau$ (hr)
OH	$1.0 \times 10^6$	Bloss et al., 2005	$1.13 \times 10^{-11}$	D'Ottone et al., 2001	25
$\text{O}_3$	$7 \times 10^{11}$	Logan, 1985	$4.52 \times 10^{-17}$	Verhees and Adema, 1985	8.8
$\text{NO}_3$	$5 \times 10^8$	Shu and Atkinson, 1995	$1.67 \times 10^{-12}$	Orlando et al., 1991	0.33
	Surface area density ( $\text{cm}^2/\text{cm}^3$ )		$\gamma_0$ (hr)		$\tau$ (day)
S1	$1.7 \times 10^{-6} - 51 \times 10^{-6}$ *		$5.3 \times 10^{-8}$	This work	> 462
S2	$1.3 \times 10^{-6} - 39 \times 10^{-6}$ *		$1.0 \times 10^{-7}$	This work	> 320

\* We assume a conservatively low (i.e., background) dust loading of  $5 \mu\text{g}/\text{m}^3$  to a high loading of  $150 \mu\text{g}/\text{m}^3$  (Aymoz et al., 2004).

From Table 4, it is found that, using the uptake coefficient deduced from the BET surface area, the corresponding lifetimes compared with the homogeneous loss of NO<sub>2</sub> are so long as to be negligible. These simple calculations show that heterogeneous reaction of NO<sub>2</sub> on soils would be not be of any importance for the NO<sub>x</sub> balance of the atmosphere, but that the products of the reaction, e.g., nitrous acid, may be important. The reaction and products may explain the formation of HONO in the atmosphere (Harrison and Kitto, 1994). In addition, when the soil particles deposited on the ground, they would also take part in the cycles of HONO and OH (Su et al., 2011).

## 4 Conclusions

In this study, heterogeneous reactions of NO<sub>2</sub> on soil particles collected from Dalian (S1) and Changsha (S2) were investigated under dark conditions over the relative humidity (RH) range of 5%–80% and temperature range of 278–328 K using a flow-tube equipped with an NO<sub>x</sub> chemiluminescence analyzer. The magnitude of  $\gamma_0$  in this study is in good coincidence with the magnitude range of most uptake coefficients of NO<sub>2</sub> on heterogeneous interfaces (Ndour et al., 2009). In our relative humidity effect research,  $\gamma_0$  decreased from  $(10 \pm 1.3) \times 10^{-8}$  to  $(3.1 \pm 0.5) \times 10^{-8}$  with increasing RH because water competes with NO<sub>2</sub> on the surfaces of soil particles and restrains the co-adsorption of NO<sub>2</sub> on the surfaces. These results suggest that water and the properties of soil particles are important, and determine the reaction kinetics and mechanism. With the temperature increased, the dominant process of  $\gamma_0$  changes from an adsorption process (exothermic) to chemical reaction (endothermic). So, with increasing temperature, the initial uptake coefficients first decreased and then displayed a negative dependence of temperature. It is suggested that temperature could alter the kinetics and mechanisms for the heterogeneous reaction of NO<sub>2</sub> on soil particles. According to the results above, a reasonable Langmuir-Hinshelwood mechanism is proposed. Thus, the heterogeneous reactions of NO<sub>2</sub> on soil or dust should not be neglected in the whole troposphere, especially for the formation of HONO. Furthermore, our results also suggest that the temperature and RH could affect the uptake coefficients so that the temperature and RH factors should be considered when uptake coefficients are used in modeling studies.

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