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# Uptake of $NO_3$ and $N_2O_5$ to Saharan dust, ambient urban aerosol and soot: a relative rate study

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**Abstract.** The uptake of $NO_3$ and $N_2O_5$ to Saharan dust, ambient aerosols and soot was investigated using a novel and simple relative rate method with simultaneous detection of both $NO_3$ and $N_2O_5$. The use of cavity ring down spectroscopy to detect both trace gases enabled the measurements to be carried out at low mixing ratios ($<500$ pptv or $1\times10^{10}$ molecule cm$^{-3}$). The uptake coefficient ratio, $\gamma(NO_3)/\gamma(N_2O_5)$, was determined to be $0.9\pm0.4$ for Saharan dust, independent of relative humidity, $NO_3$ or $N_2O_5$ mixing ratio and exposure time. Ambient (urban) aerosols showed a very limited capacity to take up $N_2O_5$ but were reactive towards $NO_3$ with $\gamma(NO_3)/\gamma(N_2O_5) >15$. A value of $\gamma(NO_3)/\gamma(N_2O_5) \sim1.5$–$3$ was obtained when using candle generated soot. The relative rate obtained for Saharan dust can be placed on an absolute basis using our recently determined value of $\gamma(N_2O_5)=1\times10^{-2}$ to give $\gamma(NO_3)=9\times10^{-3}$, which is significantly smaller than the single previous value. With the present uptake coefficient, reaction of $NO_3$ with mineral dust will generally not contribute significantly to its $NO_3$ loss in the boundary atmosphere or to the nitration of mineral dust.

## 1 Introduction

$NO_3$ radicals, generated mainly in the oxidation of $NO_2$ by $O_3$ (Reaction R1), are important reactive intermediates in the nocturnal atmosphere (Wayne et al., 1991). Due to reaction with $NO_2$ (Reaction R2a) and the thermal decomposition of the product (Reaction R2b), $NO_3$ and $N_2O_5$ concentrations are closely linked. The rapid daytime photolysis of $NO_3$ and reaction with NO prevent build up of significant $NO_3$ (and $N_2O_5$) concentrations during the day.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad \text{(R1)}$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \qquad \text{(R2a)}$$

$$N_2O_5 + M \rightarrow NO_3 + NO_2 + M \qquad \text{(R2b)}$$

$NO_3$ plays an important role in nocturnal oxidation of some organic trace gases including various alkenes and dimethyl sulphide (Atkinson et al., 2006). Reactions of $NO_3$ and $N_2O_5$ also impact on the partitioning of $NO_x(NO+NO_2)$ and $NO_y$ (the sum of all nitrogen oxides), the removal of $NO_x$ from the atmosphere and thus indirectly the budgets of nitrogen oxides, ozone, and OH radicals (Dentener and Crutzen, 1993; Evans and Jacob, 2005). The heterogeneous reactions of $NO_3$ and $N_2O_5$ are important for the formation of aerosol nitrate (see e.g. Zhang et al., 1994; Tang et al., 2004; Vrekoussis et al., 2006; Sullivan et al., 2007), and also the aging of ambient organic aerosols (Rudich, 2003).

Mineral dust, with a currently estimated emission of about 2000 Tg per year, constitutes a major component in atmospheric aerosols (Lunt and Valdes, 2002; Tegen et al., 2002; Luo et al., 2003), and has a significant impact on direct and indirect radiative forcing (Li et al., 1996; Sassen et al., 2003), and on heterogeneous removal of several trace gases (Dentener et al., 1996). The heterogeneous reaction of $N_2O_5$ with mineral dust and mineral dust proxies has been studied using bulk (Seisel et al., 2005; Karagulian et al., 2006; Wagner et al., 2008) and dispersed samples (Mogili et al., 2006; Wagner et al., 2008, 2009). Problems associated with extraction of accurate kinetic data from experiments using powdered or porous bulk samples are well documented (IUPAC, 2009) and arise from uncertainties in estimation of the surface area
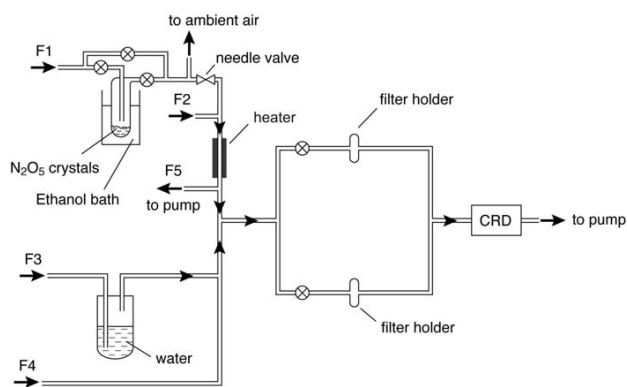
**Fig. 1.** Schematic diagram of experimental set-up. F1 (200), $F_2$ (300), F3 (5000), F4 (5000), and F5 (400) are mass flow controllers. The values in parentheses are typical flow rates in sccm. The heater was operated at 60–65 °C. The ethanol bath housing the $N_2O_5$ crystals was kept at −60 °C.

available for reaction. This can be largely overcome by using dispersed aerosol samples with appropriate techniques for particle sizing and counting, though uncertainties associated with effects of aspect ratio and particle shape remain for non-spherical particles.

In the present work we have developed a simple method to study the relative efficiency of uptake of $NO_3$ and $N_2O_5$ to Saharan dust particles at different humidities. Similar to relative-rate methods applied to the study of gas-phase reactions, kinetic data is obtained by comparing the relative rates of removal of two traces gases (in this case $NO_3$ and $N_2O_5$) with a further reactant (in this case a bulk sample). As both trace gases are exposed simultaneously to the same sample (and detected simultaneously) the available surface area is not required in the analysis to derive a relative uptake coefficient. Thus no assumptions about particle size, surface roughness or rate of diffusion in interstitial space need to be made. The only assumption is that both trace gases are well mixed and thus exposed to the same surface.

The main focus in this work was on the heterogeneous interaction of $NO_3$ and $N_2O_5$ with Saharan dust, though limited datasets were obtained with soot and ambient aerosols to illustrate the range (and limitations) of the method.

## 2 Experimental section

### 2.1 Instrumentation

The apparatus for relative uptake measurements (Fig. 1) consists of three main parts: $NO_3$ and $N_2O_5$ production, trace-gas sample exposure and $NO_3/N_2O_5$ detection.

### 2.1.1 NO₃ and N₂O₅ generation

Gaseous $N_2O_5$ was eluted from a crystalline sample at ∼213 K in a 200 cm³ (STD) min⁻¹ (henceforth "sccm") flow of He (F1) and diluted dynamically to generate a flow (∼500 sccm) containing several hundred pptv of $N_2O_5$. This was then passed through a section of PFA tubing heated to 60–65 °C to convert some (usually ∼50%) of the $N_2O_5$ into $NO_3$ (Reaction R2b). The flow containing $NO_3$ and $N_2O_5$ was subsequently diluted further (F3+F4) by synthetic air to 10 dm³ (STD) min⁻¹ (henceforth SLM), the relative humidity of which could be adjusted by changing the ratio of flows through F3 and F4. The concentration of $NO_3$ and $N_2O_5$ could be readily changed by adjusting F5. The mixed $NO_3$ and $N_2O_5$ sample generated in this manner should contain a similar amount of $NO_2$. Previous work has showed that $NO_2$ interacts only weakly with mineral dust (the uptake coefficient is estimated to be less than 10⁻⁶, IUPAC, 2009) and should not significantly affect our measurements. $N_2O_5$ crystals were generated as described previously in this group (Wagner et al., 2008). To reduce the danger of explosion, only small (<1 g) amounts were prepared without further distillation.

### 2.1.2 Trace gas – sample interaction

The total 10 SLM flow was directed through a clean, 2-µm pore Teflon (PTFE) membrane filter (Pal Teflo R2PJ047) held in a PFA filter-holder (referred to as the "blank" path) or through an aerosol-loaded Teflon filter (referred to as the "sample" path). The gas-flow could be alternately directed through each path via PFA valves and the two paths were the same in terms of tubing material and residence time, the only difference being the state of the filter. Saharan dust aerosols (aerodynamic diameter ∼1 micron, for details see (Hanisch and Crowley, 2001; Wagner et al., 2008) were produced by a rotating brush generator and collected on Teflon filters. The mass of the aerosol deposited was recorded (∼0.4–2 mg) though this parameter is not required for the analysis. Ambient aerosols were sampled directly onto Teflon filters from outside of our lab in the second floor of the MPI Chemistry main building. A sampling flow rate of 1 m³/h over a typical sampling time of about 48 h was sufficient to collect between ∼0.4 and 0.8 mg of aerosol. The filters were sealed and stored at 4 °C before use. As the MPI is close to busy roads and several large motorways pass through Mainz, the aerosol is expected to be mainly transport generated carbonaceous aerosol. No aerosol characterisation was carried out, though visual inspection confirmed the discolouration of the filter by dark (soot) particles. Freshly generated soot particles were sampled from the flame of a burning candle onto clean glass microscope slides before transfer to the PFA filters using a clean knife edge. The soot particles did not adhere well to the PFA filters and their weight was not obtained. The composition of soot generated using a candle flame is

expected to depend on the burning mode of the candle and on chemical additives to the wax and wick (Pagels et al., 2009), hence the mass fractions of elemental carbon, inorganic and organic matter in our samples are not known.

### 2.1.3 Detection of NO$_3$ and N$_2$O$_5$

After exiting the filters the gas-mixture was directed into the two cavities of a Cavity Ring-Down spectrometer (CRD). The two-channel CRD instrument has been developed in this group chiefly as a field instrument and is described in detail elsewhere (Schuster et al., 2009; Crowley et al., 2010). Briefly, the CRD technique relies on measurement of the rate of decay of light exiting a high-finesse optical cavity to derive a ring-down constant ($k_{rd}$), which depends on scattering and absorption losses in the cavity. NO$_3$ is detected in its strong visible absorption band using a 662 nm laser-diode modulated at 100 Hz. The change in ring down times ($\Delta k_{rd}$) in the presence and absence of NO$_3$ (which was removed by titration with NO at regular intervals) is used to calculate the NO$_3$ concentration in an ambient temperature optical cavity through which 4 SLM of the total flow passed:

$$[NO_3] = \frac{\Delta k_{rd} \cdot L}{\sigma(NO_3) \cdot c \cdot d} \qquad (1)$$

where [NO$_3$] is the concentration of NO$_3$ (molecule cm$^{-3}$), $\Delta k_{rd}$ is the difference in the ring-down decay constant (s$^{-1}$) with and without NO$_3$, $L$ is the distance between the cavity mirrors (70 cm), $d$ is the length of the cavity which is filled with absorber, and $c$ is the speed of light. $\sigma(NO_3)$ is the effective NO$_3$ absorption cross section at the laser wavelength and was calculated using temperature dependent cross sections from Yokelson et al. (1994), Orphal et al. (2003) and Osthoff et al. (2007).

The rest of the flow ($\sim$6 SLM) was directed into a thermal converter in front of a second cavity, which were both held at 90 °C, so that all the N$_2$O$_5$ decomposed to NO$_3$. In this channel the sum of NO$_3$ and N$_2$O$_5$ concentrations was measured. The losses of NO$_3$ and N$_2$O$_5$ through the clean filters and through the cavities have been determined frequently and are defined by a transmission efficiency through the Teflon filter of 90% for NO$_3$ and 99% for N$_2$O$_5$. The wall loss rate constants in the NO$_3$ and the NO$_3$+N$_2$O$_5$ cavities were measured to be 0.241$\pm$0.011 s$^{-1}$ (1$\delta$) and 0.168$\pm$0.010 s$^{-1}$ (1$\delta$), respectively. With the total flow (and cavity pressures of $\sim$600 Torr) used in these experiments, these loss coefficients correspond to transmission efficiencies of 81.6% for the NO$_3$ cavity and 83.8% for the NO$_3$+N$_2$O$_5$ cavity. The detection limits for NO$_3$ and N$_2$O$_5$ were a few pptv in $\sim$3 s signal acquisition time, with a total measurement uncertainty of $\sim$15%. As described below, in the present experiments only the change in concentration of NO$_3$ and N$_2$O$_5$ need be measured so that the 15% uncertainty in the absolute concentration is unimportant. The range of measurement of the relative change in concentration is limited only by signal noise, or fluctuations in the NO$_3$ and N$_2$O$_5$ concentrations

### 2.2 Data analysis

In the experimental determination of absolute uptake coefficients for a heterogeneous process, the number of collisions of the trace gas is usually calculated (based on gas-kinetic theory) and the net rate of change in concentration of the trace gas monitored during exposure of the trace gas to the surface of interest. The experimental uptake coefficient, $\gamma$, is the fraction of collisions that lead to removal of the trace gas from the gas-phase and is related to the experimental observables by:

$$\frac{d[X]}{dt} = \frac{\gamma \cdot \bar{c}}{4} \cdot \frac{a}{V} \cdot [X] \qquad (2)$$

where $[X]$ is the gas-phase concentration of species $X$ (molecule cm$^{-3}$), $a/V$ is the surface area ($a$, cm$^2$) per volume ($V$, cm$^3$), $\bar{c}$ is the mean molecular velocity of the trace gas (cm s$^{-1}$). By measuring fractional changes in concentration this becomes:

$$\frac{d[X]}{dt[X]} = k_{exp} = \frac{\gamma \cdot \bar{c}}{4} \cdot \frac{a}{V} \qquad (3)$$

implying that measurement of the experimental uptake coefficient requires accurate knowledge of the available surface area ($a$). As described in Sect. 1, for bulk powder samples this is non-trivial and is almost always the major source of uncertainty in heterogeneous kinetics. Different treatments such as use of geometric surface area, BET surface areas or application of pore-diffusion corrections can lead to uptake coefficients that deviate by orders of magnitude for the same reaction (Goodman et al., 2000; Underwood et al., 2000; Hanisch and Crowley, 2001).

For two well mixed trace gases, in this case NO$_3$ and N$_2$O$_5$, interacting simultaneously with the same sample we have:

$$k_{exp}(NO_3) = \frac{\gamma(NO_3) \cdot \bar{c}(NO_3)}{4} \cdot \frac{a}{V} \qquad (4)$$

$$k_{exp}(N_2O_5) = \frac{\gamma(N_2O_5) \cdot \bar{c}(N_2O_5)}{4} \cdot \frac{a}{V} \qquad (5)$$

where

$$-k_{exp}(X) = \frac{(\ln[X]_0 - \ln[X]_s)}{t} \qquad (6)$$

and $[X]_0$ and $[X]_s$ are the concentrations of trace gas measured via the blank line and sample line, respectively. In the relative rate method, the parameters $a$, $V$ and $t$ are unchanged for both NO$_3$ and N$_2$O$_5$. By rearranging Eqs. (E4)–(E6) we derive:

$$\frac{\gamma(NO_3)}{\gamma(N_2O_5)} = \frac{\ln[NO_3]_0 - \ln[NO_3]_s}{\ln[N_2O_5]_0 - \ln[N_2O_5]_s} \cdot \frac{\bar{c}(N_2O_5)}{\bar{c}(NO_3)}$$
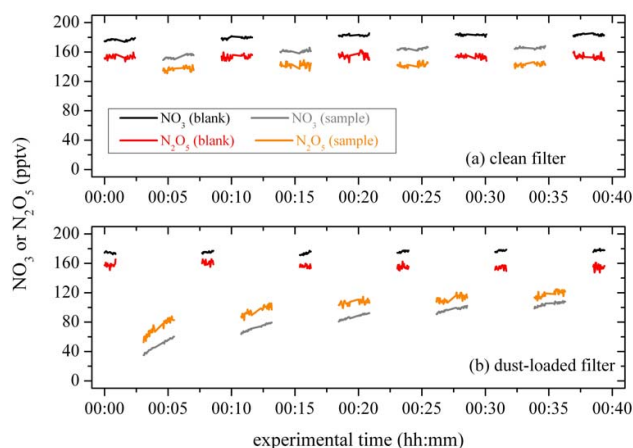
**Fig. 2.** $NO_3$ and $N_2O_5$ mixing ratios observed when the gas mixture was passed through the blank and sample filters. Upper panel: a clean (control) filter was used in the sample path; lower panel: a filter loaded with 1.15 mg of Saharan dust was used in the sample path.

The ratio of molecular velocities (last term on right-hand side of equation) is calculated from the ratio of the square roots of the molecular masses of $N_2O_5$ and $NO_3$ and is 0.758.

In the present set-up, the relative change in $NO_3$ and $N_2O_5$ gas-phase concentration was measured as the trace gases passed through filters loaded with reactive particles. As described above, two filters/filter holders were used, one was used as blank and one containing the sample. As seen in Fig. 1, the gas-flows were directed through different sections of tubing on route to the CRD. Control experiments, in which both filter-holders contained fresh, un-reactive filters were conducted regularly. The result of passing a flow containing ~180 pptv $NO_3$ and 160 pptv $N_2O_5$ through the "blank" path or the "sample" path without aerosol on the filter are shown in Fig. 2. Some losses (less than 5% and quite stable) of both $NO_3$ and $N_2O_5$ are observed, showing that, despite the absence of sample on the filter, the tubing/filter holder in the "sample" path is slightly more reactive than in the "blank" path. Values of $[NO_3]_s$ and $[N_2O_5]_s$ obtained in the presence of a sample were always corrected for this effect. We note that this loss of $NO_3$ and $N_2O_5$ in the absence of a sample places a lower limit of ~10% on the change of concentration of $NO_3$ and $N_2O_5$ that can be accurately measured.

In a relative uptake experiment (i.e. with a loaded sample filter), the gas mixture was first switched through the blank filter, and $[NO_3]_0$ and $[N_2O_5]_0$ were measured by the CRD. The flow was then switched to the sample path, to monitor $[NO_3]_s$ and $[N_2O_5]_s$. During the experiment, the flow was regularly switched back to the blank path (e.g. at 8, 16, 24, 32 and 39 min in the lower panel of Fig. 2) to determine whether $[NO_3]_0$ and $[N_2O_5]_0$ were both stable over time. Only the datasets in which $[NO_3]_0$ and $[N_2O_5]_0$ fulfilled this requirement were used.

## 3 Results and discussion

### 3.1 Saharan dust

The uptake of $NO_3$ and $N_2O_5$ to Saharan dust was the main focus of this work and experiments were carried out with different dust loadings and relative humidities (RH). In order to observed a measurable change in the $NO_3/N_2O_5$ mixing ratios, dust samples in excess of ~0.5 mg were required.

The uptake of $NO_3$ and $N_2O_5$ to 1.15 mg of Saharan dust at RH=0% is displayed in Fig. 2 (lower panel). $NO_3$ and $N_2O_5$ mixing ratios decrease rapidly when the gas flow is passed through the dust-loaded filter, indicating substantial interaction. The initial change in mixing ratio is from ~180 to 40 pptv for $NO_3$ and from 160 to 60 pptv for $N_2O_5$. Both $NO_3$ and $N_2O_5$ signals did however increase again during the ~40 min of exposure, presumably due to a reduction in rate of uptake as the number of reactive surface sites depletes as reaction progresses. Using a BET surface area of $39.6\,m^2\,g^{-1}$ for our Saharan dust (Wagner et al., 2008) we calculate a total sample surface area of ~450 cm², which corresponds to about $1\times10^{17}$ surface sites (assuming each site for $NO_3$ and $N_2O_5$ is about $5\times10^{-15}\,cm^2$ in area). Over an exposure period of ~40 min, the sum of molecules of $NO_3$ and $N_2O_5$ which passed through the filter is $\sim3\times10^{15}$. Contrary to observation, the number of $NO_3$ and $N_2O_5$ molecules is thus calculated to be insufficient to deactivate a significant fraction of all adsorption/reaction sites in this Saharan dust sample. However, this simple calculation assumes that the entire BET surface area is available for $NO_3$ and $N_2O_5$ uptake. As the filters were loaded with aerosol at relatively slow flow rates (0.8 SLM) the area of the filter containing dust was larger than that through which the $NO_3/N_2O_5$ gas-flow (~5 SLM) passed during an uptake experiment. Visual inspection of aerosol deposits at high flow rates suggest that flow dynamics leads to only a small area (~1 cm²) of the total filter was used. This implies that the dust area (and thus mass) available for reaction was actually smaller than given for each sample, though the exact factor remains unknown. Indeed, we find that the rate of deactivation of the dust surface is independent of the sample mass, confirming that only a small fraction of the mass (presumably that fraction located on the filter directly under the 1/4″ inlet) is available.

Time dependent uptake coefficients (decreasing with exposure time), indicating consumption of reactive sites on bulk mineral dust samples have been reported previously for the reaction with $N_2O_5$ (Seisel et al., 2005; Karagulian et al., 2006; Wagner et al., 2008) and also with $NO_3$ (Karagulian and Rossi, 2005). The Knudsen reactor studies of Seisel et al. (2005) and Karagulian et al. (2005, 2006) used orders of magnitude larger $NO_3$ and $N_2O_5$ concentrations, but generally also much larger sample masses in the 100–1000 mg range. Those studies were also carried out using very dry samples, with relative humidities close to 0% and were not able to investigate the role of $H_2O$ in the reactivation of the
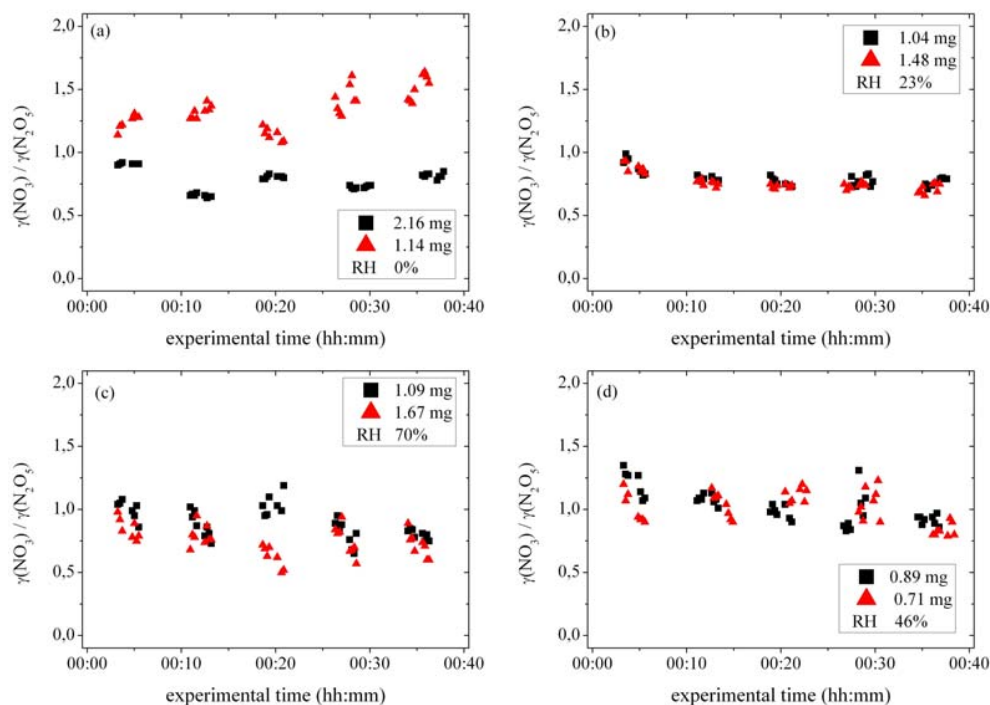
**Fig. 3.** Uptake coefficient ratios for NO$_3$ and N$_2$O$_5$ uptake to Saharan dust particles at four different relative humidities. The sample masses used in each experiment are also indicated.

dust sample due to surface reorganisation of (soluble) nitrate containing sites. The phenomenon of reactivation is anticipated to take place in the atmosphere as evidenced by measurements of a substantial nitrate mass fraction (and loss of carbonate) in chemically aged mineral dust particles implying that (on sufficiently long time scales) reaction with acidic trace gas is not confined to the initially available surface following dust mobilisation (see e.g. Carmichael et al., 1996 or Matsuki et al., 2005). This has been confirmed qualitatively in laboratory experiments on CaCO$_3$ (Krueger et al., 2003). In our study, surface saturation/deactivation also occurred at relative humidities up to 70% and at approximately the same rate as at 0% RH. A deactivation rate which is independent of RH may simply indicate that the rate limiting step in surface reorganisation (e.g. nitrate dissolution and re-crystallization) takes place over longer time scales than the 40 min duration of the experiment.

Although the rates of uptake of NO$_3$ and N$_2$O$_5$ decreased with time, the uptake coefficient ratio, $\gamma(\mathrm{NO}_3)/\gamma(\mathrm{N}_2\mathrm{O}_5)$, changed only slightly or insignificantly during the experiment as shown in Fig. 3, which summarises results for Saharan dust at different relative humidities and different masses of dust. A slight decrease in the $\gamma(\mathrm{NO}_3)/\gamma(\mathrm{N}_2\mathrm{O}_5)$ was observed for most samples (generally less than 15%) though this is close to the minimum in discernible change in $\gamma(\mathrm{NO}_3)/\gamma(\mathrm{N}_2\mathrm{O}_5)$ above the experimental noise. For this reason, average (exposure independent) values of $\gamma(\mathrm{NO}_3)/\gamma(\mathrm{N}_2\mathrm{O}_5)$ are listed in Table 1. Also apparent from Fig. 3, is the fact that the value of $\gamma(\mathrm{NO}_3)/\gamma(\mathrm{N}_2\mathrm{O}_5)$ did not

change systematically with relative humidity between 0 and 70%. Within our experimental uncertainty, we can state that the uptake coefficient does not change by more than 50% within this RH range. Initially, this result may appear unexpected, as heterogeneous reactions of N$_2$O$_5$ are generally considered to be driven by hydrolysis (Mentel et al., 1999; Thornton et al., 2003), whereas the reaction of NO$_3$ should not depend on available surface H$_2$O, but on the number of oxidisible sites.

On the other hand, our result substantiates our previous report that the uptake coefficient for N$_2$O$_5$ with the same Saharan dust sample is independent of the relative humidity (up to 58%) and close to $1 \times 10^{-2}$, which is similar to the value found on water. We also found no significant change in $\gamma(\mathrm{NO}_3)/\gamma(\mathrm{N}_2\mathrm{O}_5)$ upon varying the absolute mixing ratios of NO$_3$ and N$_2$O$_5$ within the range indicated in Table 1. The ratio of NO$_3$ to N$_2$O$_5$ concentration was also varied by a factor of $\sim$ three, with no measurable change in the relative uptake coefficient. This is related to the use of relatively low concentrations of both reactants, which (at least at low exposure times) will not modify the surface reactivity significantly.

The results were generally consistent from experiment to experiment (using slightly different aerosol masses), the exception being the data set displayed in panel (a) where ratios of 0.75 and 1.3 were obtained. Taking this as an indication of the maximum variability, for all data sets we derive an average uptake coefficient ratio of $\gamma(\mathrm{NO}_3)/\gamma(\mathrm{N}_2\mathrm{O}_5)=0.9\pm0.4$, independent of concentration of NO$_3$ or N$_2$O$_5$ and independent of the relative humidity.

**Table 1.** Uptake coefficient ratios and experimental conditions.

| Particle type | RH (%) | NO$_3$ (pptv) | N$_2$O$_5$ (pptv) | Particle mass (mg) | $\gamma$(NO$_3$)/$\gamma$(N$_2$O$_5$)[a] |
|---|---|---|---|---|---|
| | 0 | 200 | 160 | 0.43 | [c] |
| | 0 | 630 | 340 | 0.53 | [c] |
| | 0 | 175 | 155 | 1.15 | 1.33±0.15 |
| | 0 | 560 | 320 | 2.15 | 0.78±0.09 |
| | 23 | 335 | 440 | 1.04 | 0.80±0.07 |
| Saharan dust | 23 | 360 | 430 | 1.48 | 0.77±0.07 |
| | 46 | 220 | 320 | 0.71 | 1.01±0.13 |
| | 46 | 320 | 410 | 0.89 | 1.04±0.14 |
| | 70 | 365 | 200 | 1.09 | 0.91±0.14 |
| | 70 | 360 | 165 | 1.67 | 0.73±0.13 |
| Soot | 0 | 295 | 190 | [b] | 1.2–1.8[d] |
| | 0 | 510 | 370 | [b] | 2.31±0.26 |
| Ambient aerosols | 0 | 450 | 310 | 0.36 | > 15 |
| | 0 | 450 | 360 | 0.55 | > 15 |
| | 0 | 450 | 390 | 0.80 | > 15 |

[a]The errors (1$\sigma$) are statistical only. [b]Not measured. [c]Uptake coefficient ratios were not reported due to the relative small change in [NO$_3$] and [N$_2$O$_5$]. [d]time dependent, see text for details.

This result is the first measurement of a relative uptake coefficient for NO$_3$ and N$_2$O$_5$ to any surface but can be compared to absolute values for $\gamma$(NO$_3$) and $\gamma$(N$_2$O$_5$) obtained using similar samples. Uptake coefficients for NO$_3$ (Karagulian and Rossi, 2005) and N$_2$O$_5$ (Karagulian et al., 2006) with Saharan dust are presented in different publications but were obtained by the same group using the same Knudsen reactor method. From the uptake coefficients (both initial and steady state) reported by Karagulian et al. ([NO$_3$]=4×10$^{12}$ and [N$_2$O$_5$]=3.8×10$^{12}$ molecules cm$^{-3}$) we calculate $\gamma$(NO$_3$)/$\gamma$(N$_2$O$_5$) ∼1.8 for the initial uptake and a steady state value of ∼1.1. Experiments with [NO$_3$]=7×10$^{11}$ and [N$_2$O$_5$]=4×10$^{11}$ molecules cm$^{-3}$, resulted in values of $\gamma$(NO$_3$)/$\gamma$(N$_2$O$_5$) ∼0.8 (initial uptake) and ∼0.6 (steady state uptake). Considering the large uncertainties in uptake coefficients of heterogeneous reactions, the ratios directly measured in present work agree well with the values calculated from the previous absolute studies (Karagulian and Rossi, 2005; Karagulian et al., 2006).

Combining our relative measurement with the absolute value of $\gamma$(N$_2$O$_5$)=1×10$^{-2}$ that we determined using the same Saharan dust sample (Wagner et al., 2008) for RH up to ∼60% we derive a value of $\gamma$(NO$_3$)=9×10$^{-3}$ with an uncertainty that stems mainly from uncertainty in our absolute value which is up to a factor of two. This value is a factor of ∼10–20 lower than the uptake coefficient of 0.1–0.2 reported by (Karagulian and Rossi, 2005) using bulk samples of Saharan dust. The large difference in these results is most likely related to the use of Karagulian and Rossi (2005) of the geometric surface area of the sample to calculate the uptake coefficient, which must result in an upper limit.

## 3.2 Ambient aerosols

The underlying intention behind conducting experiments using ambient aerosol was to establish the operational range of the relative method, so that a sample with a relative reactivity not close to unity was sought. The uptake of N$_2$O$_5$ to ambient surfaces can be important for the night-time NO$_x$ budget, whereas NO$_3$ is generally though to be lost less rapidly to aerosol, its lifetime usually dominated by gas-phase reactions. Carrying out relative uptake experiments on real samples could thus provide a means to characterise the aerosol "reactivity", with a low value of $\gamma$(NO$_3$)/$\gamma$(N$_2$O$_5$) expected for aqueous, acidic inorganic particles and a larger value if the particles were coated with organics or nitrates, which tend to reduce the uptake coefficient for N$_2$O$_5$ (Mentel et al., 1999; Hallquist et al., 2000; Folkers et al., 2003; Thornton and Abbatt, 2005; Cosman et al., 2008; Griffiths et al., 2009).

The interaction of NO$_3$ and N$_2$O$_5$ with ambient aerosols was investigated at RH=0% only. Raw data from the uptake of NO$_3$ and N$_2$O$_5$ to three ambient aerosol samples are displayed in Fig. 4. The behaviour is quite different to that of Saharan dust, with a relatively small uptake of N$_2$O$_5$ compared to NO$_3$. In the top panel of Fig. 4, the N$_2$O$_5$ mixing ratio initially decreased slightly from ∼380 to 360 pptv upon exposure, whereas the NO$_3$ mixing ratio plummeted from 450 to about 50 ppt. The small change in the mixing ratio of N$_2$O$_5$ is close to that detectable with our instrument (noise levels in the N$_2$O$_5$ detection channel are ∼20 ppt) so that we report only a lower limit of $\gamma$(NO$_3$)/$\gamma$(N$_2$O$_5$) >15. Laboratory experiments have shown orders of magnitude larger

efficiency of uptake of $NO_3$ to large, unsaturated organic species (e.g. such as oleic acid) compared to $N_2O_5$ (Gross et al., 2009) and we expect that a significant organic fraction is responsible for the large $NO_3$ uptake observed here. During a recent field campaign (Crowley et al., 2010) using similar filters (but exposed to ambient air for only 1 h) we also noticed an occasional loss of $NO_3$ on the filter, (but never loss of $N_2O_5$) and concluded that the aerosol at the rural measurement site was largely organic or coated with organic compounds. As mentioned above, the dark colour of the urban aerosol sampled at the institute indicates a significant mass fraction of elemental carbon, though it is possible that during generation and through aging this has become coated with organics.

A further difference between the uptake of $NO_3$ and $N_2O_5$ to the ambient aerosol compared to the Saharan dust was the relatively slow deactivation of the $NO_3$ uptake despite the use of higher $NO_3$ mixing ratios. The high reactivity and large capacity is further evidence for an important role for unsaturated organic components, which are very reactive to $NO_3$ (Moise et al., 2002; Gross and Bertram, 2009). More insight into the relative reactivity of $NO_3$ and $N_2O_5$ on ambient aerosols would be gained by sampling from widely different environments (urban, rural, marine etc). This is beyond the scope of the present publication, which focuses on mineral dust, but will be explored in future studies.

## 3.3 Soot particles

As indicated above, the ambient aerosols sampled at the institute contained an elemental carbon fraction. A limited set of experiments (two) was therefore carried out to examine the interaction of $NO_3$ and $N_2O_5$ with carbonaceous aerosol, at RH=0%. The results displayed in Fig. 5 (top left) indicate that the soot particles were reactive to both $NO_3$ (initially at ∼300 pptv decreasing to 30 pptv upon exposure) and $N_2O_5$ (decreasing from ∼180 to 50 ppt). In this sample there is evidence for a more rapid rate of surface deactivation for $N_2O_5$ than $NO_3$, with the ratio $\gamma(NO_3)/\gamma(N_2O_5)$ increasing from ∼1.5 to 2.5 over the 30 min of exposure (top right panel). This contrasts the behaviour seen for Saharan dust. A change in the relative uptake coefficient with exposure indicates different modes of reactivity for $NO_3$ and $N_2O_5$ as might be expected if $NO_3$ is reacting with unsaturated hydrocarbons and $N_2O_5$ is undergoing hydrolysis The second soot sample (bottom, left panel) showed somewhat different behaviour, with no apparent saturation of either $NO_3$ or $N_2O_5$ losses during the 30 min of exposure. Also, the ratio of uptake coefficient was larger, favouring $NO_3$ uptake more strongly. The sampling of soot from a candle flame is a haphazard process and we attribute the different reactivity of the two soot samples to chaotic sampling from steady burning and flickering flames, which lead to very different chemical characteristics of the soot and different organic/inorganic contents (Pagels et al., 2009). A lack of characterisation of our soot samples
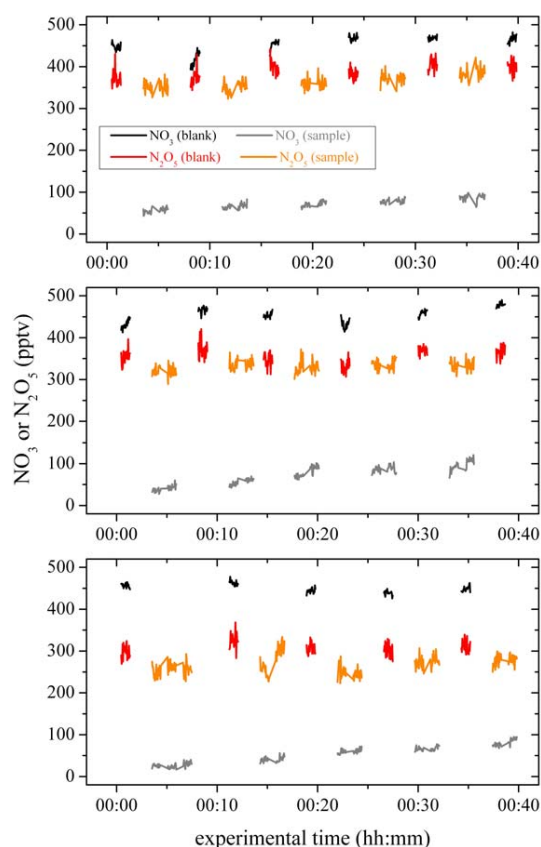


**Fig. 4.** Uptake of $NO_3$ and $N_2O_5$ to three different masses of filter-sampled ambient aerosol at RH=0%.

means that no real quantitative comparison can be made with results from other studies. We simply note that previous experiments support a larger uptake coefficient for $NO_3$ than $N_2O_5$ (Saathoff et al., 2001; Karagulian and Rossi, 2007).

## 4 Summary and atmospheric implications

We have investigated the relative rates of uptake of $NO_3$ and $N_2O_5$ to Saharan dust at various relative humidities and made some exploratory experiments on the relative uptake to ambient aerosols sampled from outside of our laboratory and candle generated soot. The uptake coefficients ratio for Saharan dust, $\gamma(NO_3)/\gamma(N_2O_5)$, was determined to be 0.9±0.4, indicating similar reactivity for $NO_3$ and $N_2O_5$ and resulting in an uptake coefficient of $\gamma(NO_3)=9\times10^{-3}$ with an associated uncertainty of at least factor of two. The limited set of experiments with poorly characterised soot and ambient aerosols allows no comparison to be made with previous work or quantitative conclusions to be made regarding their role in the atmosphere. Of interest however is the relatively large uptake of $NO_3$ compared to $N_2O_5$ to the urban aerosol sampled at our institute and this will be explored in future applications. The experiments on soot and ambient aerosol
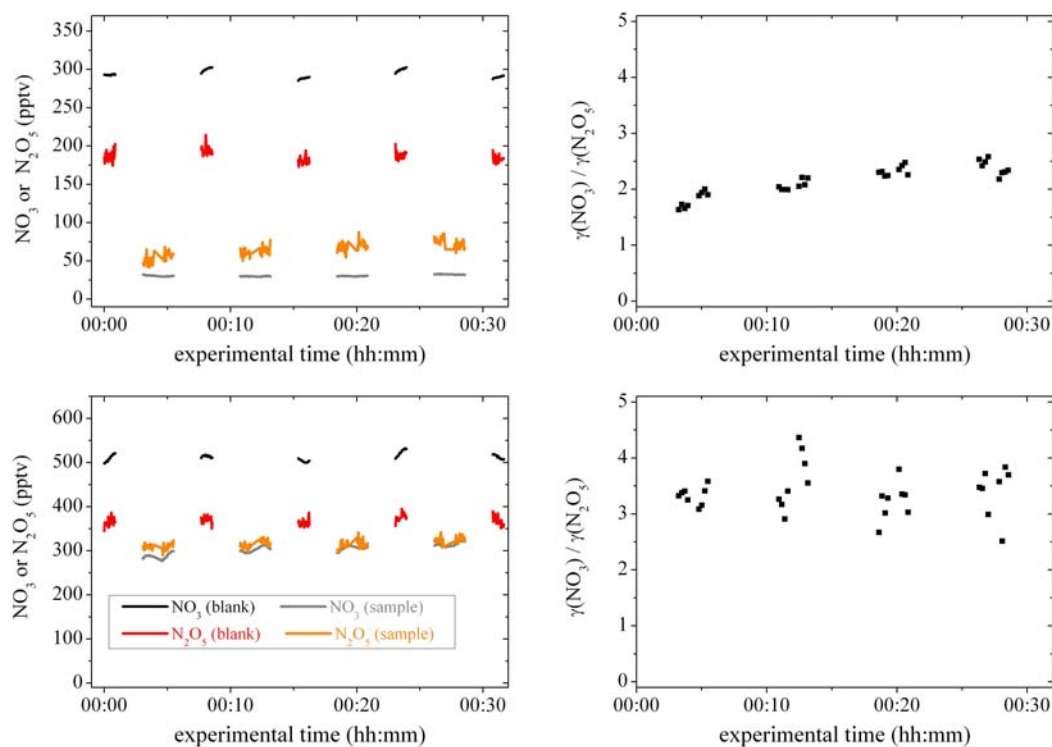
**Fig. 5.** Raw data (left-side panels) and uptake coefficient ratios (right-side panels) for NO$_3$ and N$_2$O$_5$ uptake to candle-generated soot.

also illustrate that a range of relative uptake coefficients can be made using the method and that samples with a maximum factors of ∼10 differences in reactivity for uptake of NO$_3$ and N$_2$O$_5$ can be examined. The maximum (or minimum) measurable change in concentration could be improved by increasing the stability of the NO$_3$/N$_2$O$_5$ source and reducing the noise in the N$_2$O$_5$ channel.

For Saharan dust, our measurements are only the second data set for the uptake of NO$_3$. An important role for this reaction has been proposed based on an uptake coefficient of close to 0.1 (Karagulian and Rossi, 2005) which is more than a factor of 10 larger than we derive here. Assuming an average mineral dust particle diameter of 1 μm and a density of 2.7 g cm$^{-3}$, and neglecting diffusive limitations to mass transport, the lifetime ($\tau$, in s) of a trace gas with respect to the reaction with dust can be estimated using the following expression (Wagner et al., 2008):

$$\tau(NO_3 + dust) = \frac{4}{\gamma(NO_3) \cdot \bar{c} \cdot M} \cdot 4.5 \times 10^7 \quad (7)$$

where $\gamma(NO_3)$ is the uptake coefficient, $\bar{c}$ is the average molecular speed in cm s$^{-1}$, and $M$ is the atmospheric dust loading in μg m$^{-3}$. Using the value of $\gamma(NO_3)$ from this work and incorporating $\bar{c}$=31800 cm s$^{-1}$ at 296 K a mineral dust concentration of about 20 μg m$^{-3}$ (dust-impacted background atmosphere) would result in a NO$_3$ lifetime with respect to dust uptake of about 9 h. The lifetime of NO$_3$

with respect to other direct losses in the nocturnal boundary (e.g. reaction with organics) is very variable but usually less than 1 h. Only at dust loadings of a few 100 μg and above (dust plume) would loss of NO$_3$ to mineral dust contribute significantly to its lifetime. On the other hand, NO$_3$ lifetimes in the free troposphere are significantly larger (Aliwell and Jones, 1998; Allan et al., 2002; Brown et al., 2007) due to the reduction in mixing ratio of surface emitted reactants. As a significant fraction of dust is transported above the boundary layer (typically 2–6 km), the lifetime of NO$_3$ entrained in dust plumes at such altitudes could be significantly impacted. From the point of view of dust composition, the rate of nitration of a dust surface (leading e.g. to higher solubility) by NO$_3$ can be contrasted to that by N$_2$O$_5$ and HNO$_3$. We have shown here that the uptake coefficients for NO$_3$ and N$_2$O$_5$ reacting with dust are similar. N$_2$O$_5$ concentrations are however generally larger than NO$_3$ concentrations (especially at the lower temperatures of the free troposphere) so that nitration by N$_2$O$_5$ would be expected to dominate. Similarly, HNO$_3$ is usually present at significantly higher mixing ratios than NO$_3$ (both day and night) and also has a larger uptake coefficient for uptake to mineral dust (IUPAC, 2009). Modelling studies would be useful in constraining the role of NO$_3$ interaction with mineral dust in different parts of the atmosphere.

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