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Uptake of NO_3 and
 N_2O_5 to Saharan dust

M. J. Tang et al.

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

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[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Abstract

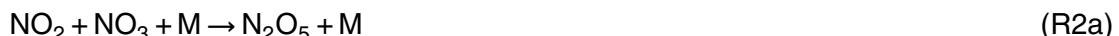
ACPD

10, 391–415, 2010

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 1×10^{10} molecule cm^{-3}). The uptake coefficient ratio, $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$, was determined to be 0.9 ± 0.4 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 $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5) > 15$. A value of $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5) \approx 1.5\text{--}3$ 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 $\gamma(\text{N}_2\text{O}_5) = 1 \times 10^{-2}$ to give $\gamma(\text{NO}_3) = 9 \times 10^{-3}$, 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 (R1), are important reactive intermediates in the nocturnal atmosphere (Wayne et al., 1991). Due to reaction with NO_2 (R2a) and the thermal decomposition of the product (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.



[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



NO₃ plays an important role in nocturnal oxidation of some organic trace gases including various alkenes and dimethyl sulphide (Atkinson et al., 2006). Reactions of NO₃ and N₂O₅ also impact on the partitioning of NO_x (NO+NO₂) 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 NO₃ and N₂O₅ are important for the formation of aerosol nitrate (Zhang et al., 1994; Vrekoussis et al., 2006), and also the aging of ambient organic aerosols (Rudich, 2003).

Mineral dust, with a currently estimated emission of about 2000 Tg per yr, 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 N₂O₅ 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 (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 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 NO₃ and N₂O₅ 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 trace gases (in this case NO₃ and N₂O₅) 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

Uptake of NO₃ and N₂O₅ to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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 5 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 $\text{NO}_3/\text{N}_2\text{O}_5$ detection.

10 2.1.1 NO_3 and N_2O_5 generation

Gaseous N_2O_5 was eluted from a crystalline sample at $\sim 213\text{ K}$ in a $200\text{ cm}^3\text{ (STD) min}^{-1}$ (henceforth “sccm”) flow of He (F1) and diluted dynamically to generate a flow ($\approx 500\text{ sccm}$) containing several hundred pptv of N_2O_5 . This was then passed through a section of PFA tubing heated to $60\text{--}65\text{ }^\circ\text{C}$ to convert 15 some (usually $\approx 50\%$) of the N_2O_5 into NO_3 (R2b). The flow containing NO_3 and N_2O_5 was subsequently diluted further (F3+F4) by synthetic air to $10\text{ dm}^3\text{ (STD) min}^{-1}$ (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 20 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.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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 5 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 \approx 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 10 was recorded (\approx 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 m^3/h over a typical sampling time of about 48 h was sufficient to collect between \sim 0.4 and 0.8 mg of aerosol. The filters were sealed and stored at 4 °C before use. As the MPI 15 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 20 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.

25 2.1.3 Detection of NO_3 and N_2O_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

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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. NO₃ is detected in its strong visible absorption band using a 662 nm laser-diode modulated at 100 Hz. The change in ring down times (Δk_{rd}) in the presence and absence of NO₃ (which was removed by titration with NO at regular intervals) is used to calculate the NO₃ concentration in an ambient temperature optical cavity through which 4 SLM of the total flow passed:

$$[NO_3] = \frac{\Delta k_{rd} \cdot L}{\sigma(NO_3) \cdot c \cdot d} \quad (E1)$$

where [NO₃] is the concentration of NO₃ (molecule cm⁻³), Δk_{rd} is the difference in the ring-down decay constant (s⁻¹) with and without NO₃, 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. The rest of the flow (\approx 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 N₂O₅ decomposed to NO₃. In this channel the sum of NO₃ and N₂O₅ concentrations was measured. The losses of NO₃ and N₂O₅ 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 NO₃ and 99% for N₂O₅. The wall loss rate constants in the NO₃ and the NO₃+N₂O₅ cavities were measured to be 0.241 ± 0.011 s⁻¹ (1 δ) and 0.168 ± 0.010 s⁻¹ (1 δ), respectively. With the total flow (and cavity pressures of \approx 600 Torr) used in these experiments, these loss coefficients correspond to transmission efficiencies of 81.6% for the NO₃ cavity and 83.8% for the NO₃+N₂O₅ cavity. The detection limits for NO₃ and N₂O₅ were a few pptv in \sim 3 s signal acquisition time, with a total measurement uncertainty of \approx 15%. As described below, in the present experiments only the change in concentration of NO₃ and N₂O₅ need be measured so that the 15% uncertainty in the absolute concentration is unimportant. The range of

Uptake of NO₃ and N₂O₅ to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



measurement of the relative change in concentration is limited only by signal noise, or fluctuations in the NO_3 and N_2O_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, γ , 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:

$$\frac{d[X]}{dt} = \frac{\gamma \cdot \bar{c}}{4} \cdot \frac{a}{V} \cdot [X] \quad (\text{E2})$$

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:

$$\frac{d[X]}{dt[X]} = k_{\text{exp}} = \frac{\gamma \cdot \bar{c}}{4} \cdot \frac{a}{V} \quad (\text{E3})$$

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_2O_5 , interacting simultaneously with the same sample we have:

$$k_{\text{exp}}(\text{NO}_3) = \frac{\gamma(\text{NO}_3) \cdot \bar{c}(\text{NO}_3)}{4} \cdot \frac{a}{V} \quad (\text{E4})$$

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



$$k_{\text{exp}}(\text{N}_2\text{O}_5) = \frac{\gamma(\text{N}_2\text{O}_5) \cdot \bar{c}(\text{N}_2\text{O}_5)}{4} \cdot \frac{a}{V} \quad (\text{E5})$$

$$\text{where } -k_{\text{exp}}(X) = \frac{(\ln[X]_0 - \ln[X]_s)}{t} \quad (\text{E6})$$

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_2O_5 . By rearranging Eqs. (E4)–(E6) we derive:

$$\frac{\gamma(\text{NO}_3)}{\gamma(\text{N}_2\text{O}_5)} = \frac{\ln[\text{NO}_3]_0 - \ln[\text{NO}_3]_s}{\ln[\text{N}_2\text{O}_5]_0 - \ln[\text{N}_2\text{O}_5]_s} \cdot \frac{\bar{c}(\text{N}_2\text{O}_5)}{\bar{c}(\text{NO}_3)}$$

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 with out 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 $[\text{NO}_3]_s$ and $[\text{N}_2\text{O}_5]_s$ 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 $\approx 10\%$ 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 $[\text{NO}_3]_0$ and $[\text{N}_2\text{O}_5]_0$ were measured by the

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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).

10 In order to observe 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 decreased rapidly when the gas flow was passed through the dust-loaded filter, indicating substantial interaction. The initial 15 change in mixing ratio was 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 the rate of uptake as the number of reactive surface sites depletes as reaction progresses. Using a BET surface area of $39.6\text{ m}^2\text{ g}^{-1}$ for our Saharan dust (Wagner et al., 2008) we calculate a total sample surface area of 20 $\approx 450\text{ cm}^2$, which corresponds to about 1×10^{17} surface sites (assuming each site for NO_3 and N_2O_5 is about $5 \times 10^{-15}\text{ cm}^2$ 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 $\approx 3 \times 10^{15}$. Contrary to observation, the number of NO_3 and N_2O_5 molecules is thus calculated 25 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

Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



with aerosol at relatively slow flow rates (0.8 SLM) the area of the filter containing dust was larger than that through which the $\text{NO}_3/\text{N}_2\text{O}_5$ 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 ($\approx 1 \text{ cm}^2$) of the total filter being 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 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). 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.

Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Although the rates of uptake of NO_3 and N_2O_5 decreased with time, the uptake coefficient ratio, $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$, 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 $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$ ratio was observed for most samples (generally less than 15%) though this is close to the minimum discernable change in $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$ above the experimental noise. For this reason, average (exposure independent) values of $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$ are listed in Table 1. Also apparent from Fig. 3, is the fact that the value of $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$ did not change systematically with relative humidity between 0 and 70%. Initially, this result may appear unexpected, as heterogeneous reactions of N_2O_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_2O , but on the number of oxidisable sites. On the other hand, this result substantiates our previous report that the uptake coefficient for N_2O_5 with the same Saharan dust sample is independent of the relative humidity (up to 58%) and close to 1×10^{-2} , which is similar to the value found on water. We also found no significant change in $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$ upon varying the absolute mixing ratios of NO_3 and N_2O_5 within the range indicated in Table 1. 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 $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5) = 0.9 \pm 0.4$, independent of concentration of NO_3 or N_2O_5 and independent of the relative humidity. This result is the first measurement of a relative uptake coefficient for NO_3 and N_2O_5 to any surface but can be compared to absolute values for $\gamma(\text{NO}_3)$ and $\gamma(\text{N}_2\text{O}_5)$ obtained using similar samples. Uptake coefficients for NO_3 (Karagulian and Rossi, 2005) and N_2O_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. ($[\text{NO}_3] = 4 \times 10^{12}$ and $[\text{N}_2\text{O}_5] = 3.8 \times 10^{12}$ molecules cm^{-3})

Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



we calculate $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5) \approx 1.8$ for the initial uptake and a steady state value of ≈ 1.1 . Experiments with $[\text{NO}_3] = 7 \times 10^{11}$ and $[\text{N}_2\text{O}_5] = 4 \times 10^{11}$ molecules cm^{-3} , resulted in values of $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5) \approx 0.8$ (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 $\gamma(\text{N}_2\text{O}_5) = 1 \times 10^{-2}$ of (Wagner et al., 2008) for RH up to $\approx 60\%$ (this is the value presently preferred; IUPAC, 2009) we derive a value of $\gamma(\text{NO}_3) = 9 \times 10^{-3}$ with an uncertainty that stems mainly from uncertainty in the absolute value of Wagner et al. (2008), which is suggested to be up to a factor of two. This value is \approx a factor of 10 lower than the uptake coefficient of 0.1–0.2 reported by (Karagulian and Rossi, 2005) using bulk samples of Saharan dust.

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 far from unity was sought. The uptake of N_2O_5 to ambient surfaces can be important for the night-time NO_x budget, whereas NO_3 is generally thought 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 $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$ expected for aqueous, inorganic particles and a larger value if the particles were coated with organics or nitrates, which tend to reduce the uptake coefficient for N_2O_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_2O_5 with ambient aerosols was investigated at RH=0% only. Raw data from the uptake of NO_3 and N_2O_5 to three ambient aerosol samples are displayed in Fig. 4. The behaviour is quite different to that of Saharan dust, with

Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



a relatively small uptake of N_2O_5 compared to NO_3 . In the top panel of Fig. 4, the N_2O_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_2O_5 is close to that detectable with our instrument (noise levels in the N_2O_5 detection channel are ≈ 20 ppt) so that we report only a lower limit of $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5) > 15$. 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 formation 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

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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 5 deactivation for N_2O_5 than NO_3 , with the ratio $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$ 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 10 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 15 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 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).

20 4 Conclusions 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, $\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$, was determined 25 to be 0.9 ± 0.4 , indicating similar reactivity for NO_3 and N_2O_5 and resulting in an uptake coefficient of $\gamma(\text{NO}_3) = 9 \times 10^{-3}$ with an associated uncertainty of at least factor of two. The limited set of experiments with poorly characterised soot and ambient aerosols

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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 5 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_2O_5 can be examined. The maximum (or minimum) measurable change in concentration could be improved by increasing the stability of the $\text{NO}_3/\text{N}_2\text{O}_5$ source and reducing the noise in the N_2O_5 channel.

10 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 15 $1\text{ }\mu\text{m}$ and a density of 2.7 g cm^{-3} , and neglecting diffusive limitations to mass transport, the lifetime (τ , in s) of a trace gas with respect to the reaction with dust can be estimated using the following expression (Wagner et al., 2008):

$$\tau(\text{NO}_3 + \text{dust}) = \frac{4}{\gamma(\text{NO}_3) \cdot \bar{c} \cdot M} \cdot 4.5 \times 10^7 \quad (\text{E7})$$

where $\gamma(\text{NO}_3)$ is the uptake coefficient, \bar{c} is the average molecular speed in cm s^{-1} , and M is the atmospheric dust loading in $\mu\text{g m}^{-3}$. Using the value of $\gamma(\text{NO}_3)$ from 20 this work and incorporating $\bar{c}=31\,800\text{ cm s}^{-1}$ at 296 K a mineral dust concentration of about $20\text{ }\mu\text{g m}^{-3}$ (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 $100\text{ }\mu\text{g}$ and above (dust plume) 25 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

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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_2O_5 and HNO_3 . We have shown here that the uptake coefficients for NO_3 and N_2O_5 reacting with dust are similar. N_2O_5 concentrations are however generally larger than NO_3 concentrations (especially at lower temperatures of the free troposphere) so that nitration by N_2O_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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[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Table 1. Uptake coefficient ratios and experimental conditions.

Particle type	RH (%)	NO ₃ (pptv)	N ₂ O ₅ (pptv)	Aerosol mass (mg)	$\gamma(\text{NO}_3)/\gamma(\text{N}_2\text{O}_5)$ ^a
Saharan dust	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
	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 (1σ) are statistical only.

^b Not measured.

^c Uptake coefficient ratios are not reported due to the relative small change in [NO₃] and [N₂O₅].

^d Time dependent, see text for details.

Uptake of NO₃ and N₂O₅ to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



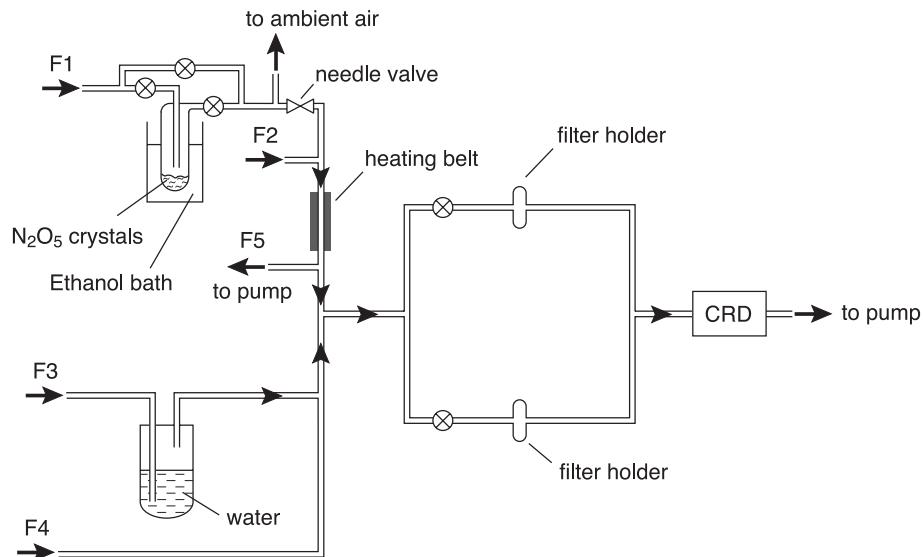


Fig. 1. Schematic diagram of experimental set-up. F1 (200), F2 (300), F3 (5000), F4 (5000), and F5 (400) are mass flow controllers. The values in parentheses are typical flow rates in sccm. The heater was operated at 60–65 °C. The ethanol bath housing the N_2O_5 crystals was kept at -60 °C.

Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



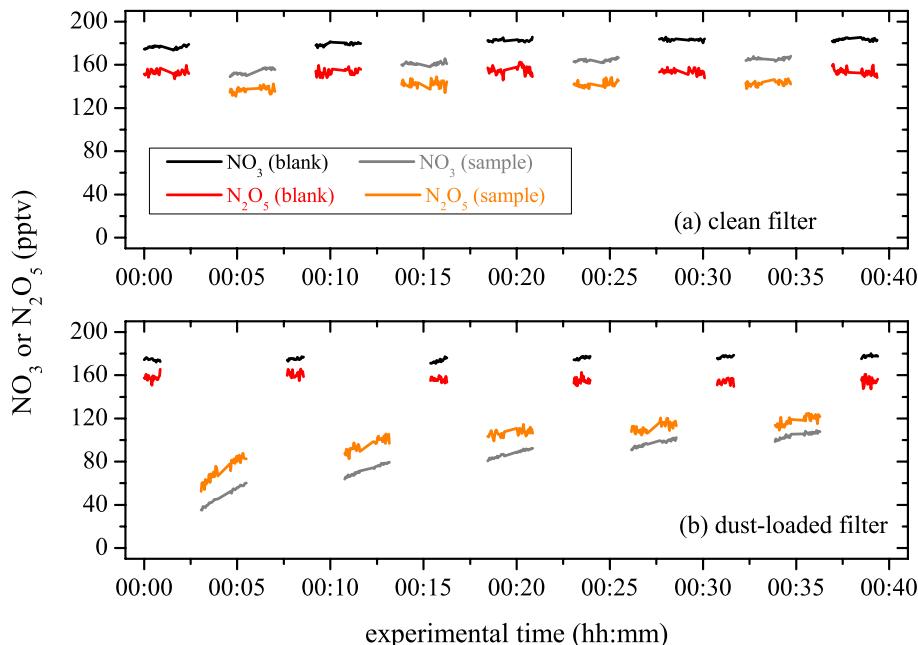


Fig. 2. NO_3 and N_2O_5 mixing ratios observed when the gas mixture was passed through the blank and sample filters. Upper panel: a clean (control) filter was used in the sample path; lower panel: a filter loaded with 1.15 mg of Saharan dust was used in the sample path.

Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



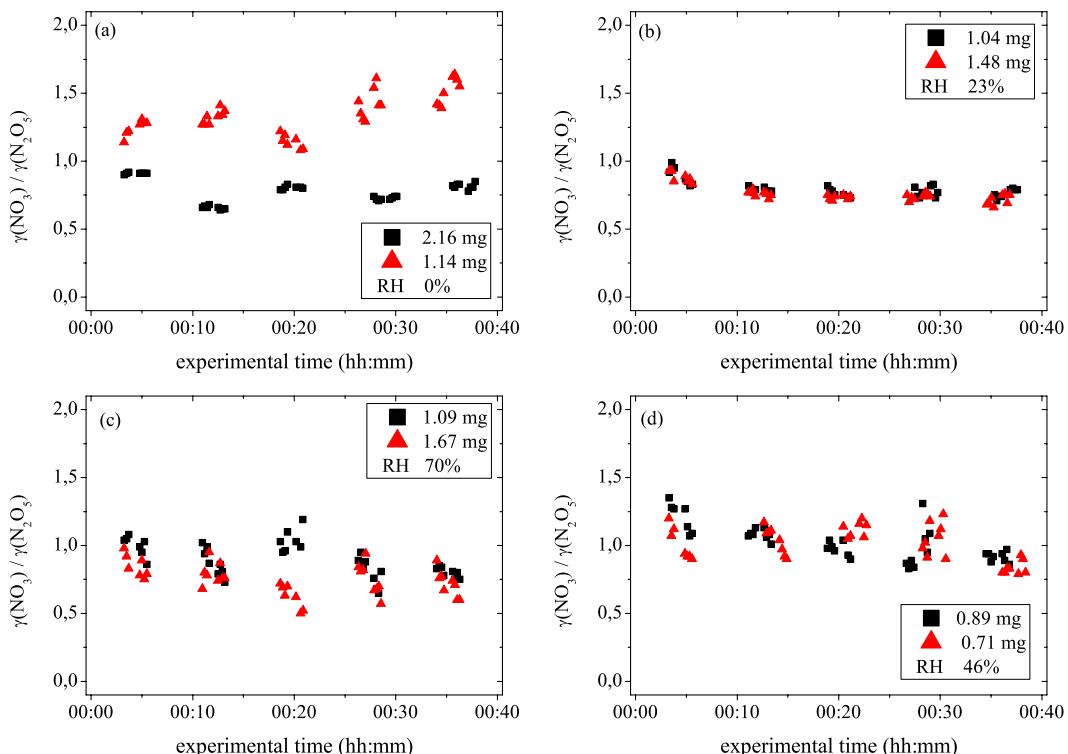


Fig. 3. Uptake coefficient ratios for NO_3 and N_2O_5 uptake to Saharan dust particles at four different relative humidities. The sample masses used in each experiment are also indicated.

Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



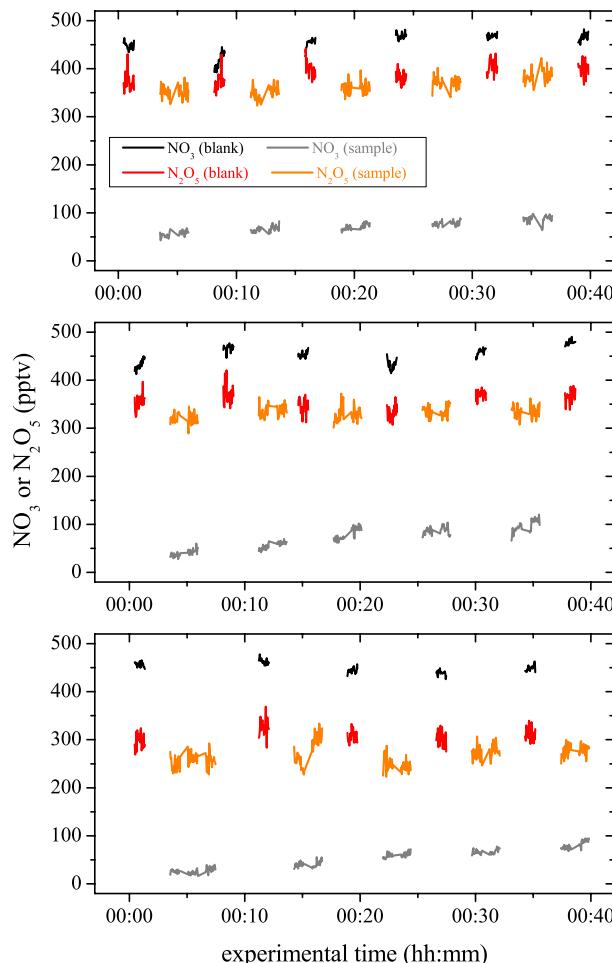


Fig. 4. Uptake of NO_3 and N_2O_5 to three different masses of filter-sampled ambient aerosol at RH=0%.

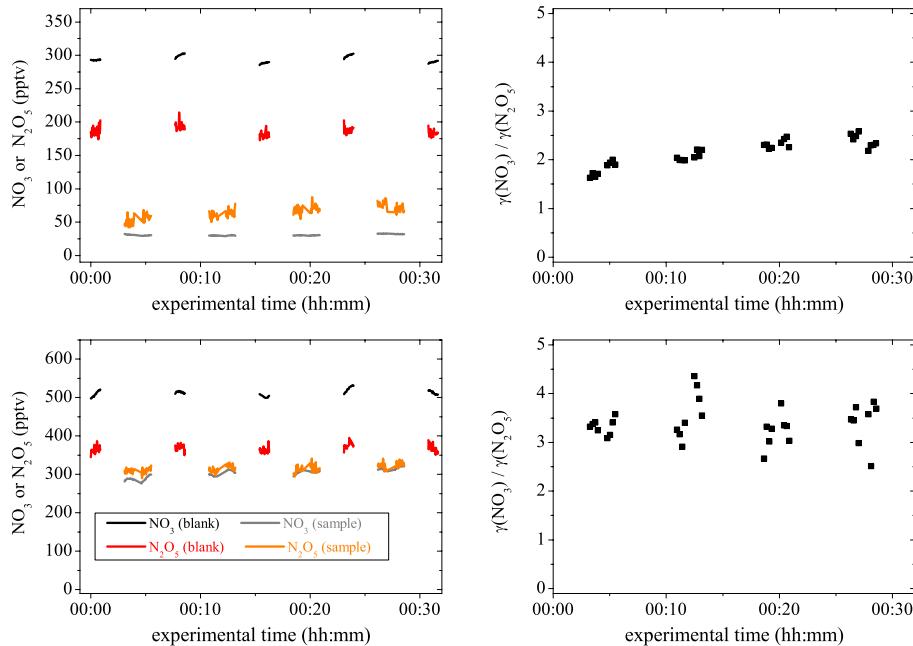


Fig. 5. Raw data (left-side panels) and uptake coefficient ratios (right-side panels) for NO_3 and N_2O_5 uptake to candle-generated soot.

Uptake of NO_3 and N_2O_5 to Saharan dust

M. J. Tang et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

