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Light induced conversion of nitrogen dioxide into nitrous acid on submicron humic acid aerosol

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Abstract

The interactions of aerosols consisting of humic acids with gaseous nitrogen dioxide (NO_2) were investigated under different light conditions in aerosol flow tube experiments at ambient pressure and temperature. The results show that NO_2 is converted on the humic acid aerosol into nitrous acid (HONO), which is released from the aerosol and can be detected in the gas phase at the reactor exit. The formation of HONO on the humic acid aerosol is strongly activated by light: In the dark, the HONO-formation was below the detection limit, but it was increasing with the intensity of the irradiation with visible light. Under simulated atmospheric conditions with respect to the actinic flux, relative humidity and NO_2 -concentration, reactive uptake coefficients γ_{rxn} for the $\text{NO}_2 \rightarrow \text{HONO}$ conversion on the aerosol between $\gamma_{\text{rxn}} < 10^{-7}$ (in the dark) and $\gamma_{\text{rxn}} = 6 \times 10^{-6}$ were observed. The observed uptake coefficients decreased with increasing NO_2 -concentration in the range from 2.7 to 280 ppb and were dependent on the relative humidity (RH) with slightly reduced values at low humidity (<20% RH) and high humidity (>60% RH). The measured uptake coefficients for the $\text{NO}_2 \rightarrow \text{HONO}$ conversion are too low to explain the HONO-formation rates observed near the ground in rural and urban environments by the conversion of $\text{NO}_2 \rightarrow \text{HONO}$ on organic aerosol surfaces, even if one would assume that all aerosols consist of humic acid only. It is concluded that humic materials present on the Earth surface will have a much larger impact on the HONO-formation in the lowermost layer of the troposphere than humic materials potentially occurring in airborne particles.

1 Introduction

The formation of nitrous acid (HONO) in the atmosphere is of considerable interest as HONO is a major precursor of atmospheric hydroxyl radicals in the lowest layer of the troposphere (Acker et al., 2006b; Alicke et al., 2002, 2003; Aumont et al., 2003; Harrison et al., 1996; Kleffmann et al., 2005; Ren et al., 2003; Vogel et al., 2003; Zhou

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et al., 2002). Recent atmospheric measurements and model calculations (Acker et al., 2006b; Honrath et al., 2002; Kleffmann et al., 2003, 2005; Ren et al., 2003; Staffebach et al., 1997; Vogel et al., 2003; Zhou et al., 2001, 2002, 2003) show a strongly enhanced formation of HONO during daytime, which is inconsistent with known gas phase formation mechanisms, direct emissions and heterogeneous processes occurring in the dark, i.e. during night. In our previous studies (George et al., 2005; Stemmler et al., 2006) it has been shown that nitrogen dioxide (NO_2) is effectively reduced to HONO on light activated surfaces containing humic acids, soil or selected synthetic aromatic compounds. The $\text{NO}_2 \rightarrow \text{HONO}$ conversion rate on irradiated soil surfaces in contact with moderate NO_2 -concentrations was found to be sufficient to explain the high daytime concentrations of HONO observed in the ground near levels of the troposphere.

In this study the previous experiments on the photoreactivity of humic acid films and soil surfaces are extended to humic acid aerosol particles. This system has the advantage that aerosol flow tube studies allow a better characterization of the reaction conditions with regard to light intensity, to relative humidity, and especially to the surface area, than in the case of films with a potentially complex structure. This study also aims to investigate the behaviour of particulate matter of complex organic composition in aerosols and its processing by atmospheric oxidants. It will provide an estimate of the significance of this process for HONO-formation on aerosol particles.

Humic substances are the most abundant group of organic species on the Earth surface (Batjes, 1996; IPCC, 2001; Janzen, 2004; Swift, 2001). They stem from the degradation of biological materials. As humic matter is ubiquitously found on ground surfaces, it is likely that such materials also exist on airborne surfaces (due to soil abrasion or biomass burning). Also atmospheric oxidation of VOC is a source of similar polymeric particle bound materials (Jang et al., 2002; Kalberer et al., 2004). Many studies focus now on the characterization of the complex organic material (the so called humic like substances) found in natural aerosol samples from different environments and search for the origins of these materials (Graber and Rudich, 2006). Such mate-

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rials resemble in many properties the humic material found in the terrestrial or aquatic environment, but depending on the isolation methods and the type of analytical characterization significant differences between terrestrial and aquatic humic substances and aerosol borne humic-like substances were evident (Graber and Rudich, 2006). For example, airborne humic like matter appears to be of lower molecular size, may exhibit a lower aromaticity and a smaller light absorption in the visible range as compared to aquatic or terrestrial humic acids.

Despite these differences, a humic acid model compound (Aldrich Humic Acid) was chosen in this aerosol study, which shows a similar photoreactivity towards NO_2 like humic acids from soil, brown coal or peat (Stemmler et al., 2006), but has a nearly tenfold higher photoreactivity towards NO_2 during 400–700 nm irradiation compared to an aquatic fulvic acid (Suwannee River Fulvic Acid, (Stemmler et al., unpublished result), which properties might be closer to that of humic like organic matter in aerosol (Graber and Rudich, 2006). Aldrich humic acid was chosen because it is available in sufficient quantities for aerosol experiments and to allow a better comparison with a previous study on stationary humic acid films (Stemmler et al., 2006).

2 Experimental

The experiments were performed in a horizontal aerosol flow tube (190 cm × 7.1 cm i.d.) at a pressure of ~980 mbar. The glass flow tube was equipped with a movable 20 cm long Teflon plug, which bore conically widens to reach the flow tube dimensions, allowing an adjustment of the gas-aerosol contact time between 1 and 10 min (0–150 cm flow path length, 0.6–2.1 L min⁻¹ gas flow). At the reactor exit, the gas flow was recollected by an identical Teflon plug. The reactor was installed in an air cooled lamp housing holding 7 fluorescence lamps (150 cm × 2.6 cm o.d.), in a circular arrangement surrounding the reactor tube. Two types of lamps were used to examine the HONO-production under irradiation in the UV-A range (Philips Cleo Effect 70 W: 300–420 nm) and in the visible part of the tropospheric light spectrum (Osram Lumilux Deluxe 954,

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58 W: 400–750 nm). The spectral actinic flux in the reactor was measured by a calibrated spectroradiometer (Hofzumahaus et al., 1999) with an optical receiver scaled down for the measurements in the flow tube and corrected for the imperfect angular response. Actinic flux spectra for the different sets of lamps are shown in Fig. 1a.

5 The humic acid particles were produced by nebulising a solution containing 20 g L⁻¹ Aldrich humic acid sodium salt acidified to pH 4.6 with HCl into a stream of N₂. The nebulised humic acid was initially dried in a 1.2 m long Silica Gel diffusion drier, and then the particles were passed through a bipolar ion source (⁸⁵Kr) to establish an equilibrium charge distribution. An electrostatic precipitator removed all charged particles
10 ensuring that only neutral particles were passing on through the experiment. The particles were rehumidified to the desired relative humidity and mixed with a prehumidified stream of NO₂ in an O₂/N₂-mixture before the entrance of the reactor. The final carrier gas is a 1:4 mixture of O₂ and N₂. The aerosol produced by this way has a log-normal size distribution with a mean diameter of 100 nm and a geometric mean standard deviation of 1.85 at relative humidities of 20–40%. Figure 1a shows the absorption spectrum
15 of the employed humic acid in aqueous solution.

The Reynolds numbers of the reactor under the given flow conditions were ~12–43 and indicate laminar flow conditions, but the laminar flow may be distorted by the fact that the reactor housing was heated by the lamps to about 300 K compared to
20 the temperature of the entering gas of 296 K. The heating of the gas on the warmer reactor walls is expected to induce some turbulence in the gas flow. Figure 1b shows a residence time analysis of the aerosol particles in the flow tube. The reactor was operated at a total flow of 2.18 L min⁻¹ corresponding to a calculated mean residence time of $t_m = 180$ s. In Fig. 1b the aerosol concentration measured at the reactor exit during
25 an “aerosol on-off” cycle is compared with modeled aerosol concentrations for plug flow and for laminar conditions. The particle diffusion is neglected in the models. The first aerosol signal at the reactor exit is observed after 50% of the mean retention time ($t = t_m/2$) as expected for a laminar flow profile (Fitzer and Fritz, 1989). The comparison further indicates that the real residence time distribution is less tailing towards higher

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retention times than that expected from a laminar flow, indicating some radial transport in the flow tube. The reaction times given in this study refer to the calculated mean residence time. To justify this approach, the aerosol was injected for 20 min in each experiment to reach a homogeneous aerosol concentration in the reactor. The periods for which the aerosol concentration at the reactor exit was rising or falling due to the switch on-off were not used for the analysis, as it is expected that in this situations the aerosol exposure to NO₂ was not constant.

The NO₂-concentration entering the reactor was measured with a chemiluminescence detector (Monitor Labs 9841 NO_x-analyzer with a detection limit 0.5 ppb and a precision of ±5%) and the aerosol concentration at the reactor entrance was measured by Scanning Mobility Particle Sizers (SMPS) consisting of a differential mobility analyzer (TSI Model 3071) and a condensation particle counter (TSI, Models 3022 and 3025, 13–777 nm, aerosol size range). At the exit of the reactor a LOPAP-instrument (Long Path Absorption Spectrometer) was used to determine the concentration of the reaction product HONO in the gas phase (Heland et al., 2001; Kleffmann et al., 2002, 2006). The instrument collects HONO by a fast chemical reaction in a stripping coil and converts it into a dye, which is measured in a long path absorption cell. Interferences for particles in the diameter range of the present study can be neglected, since the uptake of particles <600 nm are found to be ≤1% (Bröske et al., 2003) and thus, the arising potential interferences are corrected for by the two channel instrument. During the campaign the instrument had a detection limit of 5 ppt and a total accuracy ±10%. The instrument was collecting two data points per minute, but its actual time resolution was 3 min under the employed operation conditions. NO_x at the reactor exit was detected by means of NO/NO_x-chemiluminescence detector (CLD, Eco Physics, model CLD 77AM, with an external home made molybdenum converter at 653 K and a detection limit 0.1 ppb and a precision of ±1%). The NO_x-detector was used in combination with a sodium carbonate denuder tube (50 cm×0.8 cm) at the inlet of the analyzer to remove HONO from the gas stream and therefore eliminate the known interference of HONO in the NO₂→NO conversion. For a continuous relative measurement of the

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aerosol surface concentration at the reactor exit, the aerosol was recharged using a ^{85}Kr source and deposited in an annular flow-through capacitor loaded by a 600 V battery and the resulting current was monitored by an electrometer.

The general experimental procedure was the following: First the reactor was equilibrated under a given reaction condition (flows, length, humidity, light intensity, NO_2 -concentration). After equilibration, the conditions and the HONO-formation was monitored for 20 min in absence of the aerosol. Then the aerosol was injected for 20–25 min by pumping the humic acid solution into the nebulizer and by bypassing an aerosol filter system. After the aerosol was switched off all parameters were monitored for another 20 min under the same conditions. This procedure was necessary as a significant HONO-concentration (150–900 ppt) was observed in the reactor in the absence of the aerosol. This background depended on the experimental conditions, the cleanliness of the reactor, and on the purity of gas supplies. As the aerosol surface in the experiments is small compared to the surface of the flow tube wall, heterogeneous processes on the reactor wall, such as heterogeneous hydrolysis of NO_2 (Finlayson-Pitts et al., 2003) or reaction with deposited particles, lead to a significant background HONO-formation. It was therefore necessary to monitor this background HONO-concentration under all conditions and subtract it from the measured concentrations in presence of aerosols in order to obtain the excess HONO-formation on the particle surface. Typical experimental results for the HONO-formation during the injection of the humic acid aerosol and the procedure for the HONO-background subtraction are shown in Fig. 2.

For comparison purposes, some additional measurements in which the photochemical HONO-formation was investigated on humic acid coatings were performed with an experimental set-up described previously (Stemmler et al., 2006). This experimental set-up is briefly summarized here. The irradiations of the humic acid coatings were performed in 50 cm×0.8 cm Duran glass photo reactor cells installed in an air cooled lamp housing holding 7 fluorescence lamps (44 cm×2.6 cm o.d.), in a circular arrangement surrounding the reactor tube. The spectral distribution of the employed lamps (VIS-lamps: Osram Luminux Deluxe 954, 400–750 nm, UV-A lamps: Phillips Cleo Compact

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300–420 nm) are very similar to that of the lamps used in the aerosol study (Fig. 1a). But the integrated actinic fluxes in the coated wall flow tubes are 12% and 40% higher for the visible and UV-A irradiations, respectively. The inner surface of the tubular glass flow reactor (surface=125 cm², surface to volume ratio=5 cm⁻¹) was coated with a thin layer of humic acids. This glass reactor surface was sandblasted to prevent droplet formation during the coating procedure and therefore to reach a relatively homogeneous distribution of the organic test compound on the reactor walls. The humic acid coatings on the reactor wall were produced by gently drying 0.5 ml aliquots of aqueous solutions of the humic acids dispersed on the reactor walls in a nitrogen stream at room temperature. In general, a quantity of 1 mg of humic acid (8 μg cm⁻²) was used as coating. This amount had little effect on the spectral intensity distribution in the reactor, but was sufficient for a fast photochemical HONO-production. The carrier gas flow (synthetic air) and the NO₂-addition, from a 959 ppb mixture in synthetic air (Carbagas AG, Switzerland), was controlled by mass flow controllers. The total flow rate was 2.4 L min⁻¹ at ambient pressure leading to gas residence times of 0.6 s in the photo-reactor. The NO₂-concentrations were adjusted in the 5–100 ppb range and the relative humidity between 0–50%.

3 Results and discussion

As shown previously, NO₂ is reduced on photo-activated humic acid containing surfaces to form HONO (Stemmler et al., 2006).



Here this reaction was examined on the surface of submicron humic acid aerosol. Figure 3 shows the dependence of the excess HONO-formation on the humic acid aerosol on reaction time and on the aerosol surface concentration in the reactor. For the aerosol surface concentration dependency, all experiments were performed with the same polydisperse, log normal size distributed aerosol, which concentration was

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altered by changing the partial aerosol flow directed into the flow tube. The aerosol surface concentration was measured by two SMPS systems in parallel, which results agreed within 10%. The HONO-formation depended linearly on the aerosol surface concentration $[S/V]$ and on the reaction time in the investigated interval of 0–10 min (i.e. $d\text{HONO}/dt \propto [S/V]$).

The photochemical nature of the reaction is demonstrated in Fig. 4. Humic acid aerosol at a surface concentration of $0.110 \pm 0.005 \text{ m}^2 \text{ m}^{-3}$ was introduced for periods of 20–25 min into the reactor, which was equilibrated under different visible light actinic fluxes, and the HONO-concentration was measured at the reactor exit. The experiments were performed at a NO₂-concentration of 35 ppb, a relative humidity of 30% and a reaction time of 3.75 min. In Fig. 4, the HONO-formation rate is expressed as the reactive uptake coefficient γ_{rxn} of gaseous NO₂ on the aerosol leading to the formation of HONO according to Reaction R1. The uptake coefficient γ_{rxn} is defined as the ratio between the rate of reactive collisions of NO₂-molecules on the aerosol surface to form gaseous HONO and the gas-kinetic collision rate of the NO₂-molecules with the particle surface.

The observed first order rate coefficient for the transformation of NO₂→HONO

$$k_{1.\text{order}} = -\ln \left(\frac{[\text{NO}_2](t=0) - [\text{HONO}](t)}{[\text{NO}_2](t=0)} \right) \times t^{-1} \quad (1)$$

is related to the uptake coefficient γ_{rxn} via Eq. (2), for which $[S/V]$ is the aerosol surface concentration measured during the experiment, and ω is the mean thermal velocity of NO₂, given as $\omega = (8RT/(\pi M))^{1/2}$ with R , T , and M being the gas constant, the absolute temperature, and the molar weight of NO₂, respectively.

$$k_{1.\text{order}} = \frac{\gamma_{\text{rxn}} \times [S/V] \times \omega}{4} \quad (2)$$

In the dark, the HONO-formation on the aerosol surface was below the detection limit, corresponding to an uptake coefficient $\gamma_{\text{rxn}} < 10^{-7}$. This value is in agreement with the

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upper limit given for NO₂→HONO conversion on secondary organic aerosol particles in the dark (Bröske et al., 2003). The uptake coefficient increases with increasing actinic fluxes to $\gamma_{\text{rxn}}=1.8\times 10^{-6}$ at the maximum actinic flux of 1.0×10^{17} photons cm⁻² s⁻¹ integrated over the 400–750 nm range of the lamp spectrum.

The HONO-production on the humic acid aerosol increases not linearly with the actinic flux showing less than proportional reactivity at higher light fluxes. As proposed previously (Stemmler et al., 2006), this may indicate that the photo-produced reductive species (A^{red}) formed on the humic acid (HA) surface deactivate by reaction with photo-oxidants (X^{ox}) formed simultaneously during the irradiation of humic acid surfaces in competition to their reaction with NO₂ (Reactions R2, R3, and R4). The lifetime of A^{red} is therefore decreasing with increasing actinic flux.



From the measured spectral actinic flux at full intensity (7 lamps illuminated), known absorption spectra, and quantum yields (Bongartz et al., 1994; Merienne et al., 1995; Troe, 2000), the photolysis frequencies of HONO and of NO₂ in the reactor are calculated as 5.8×10^{-5} s⁻¹ and as 5.5×10^{-4} s⁻¹, respectively. This calculated photolysis frequency of NO₂ is close to the measured value of 5.2×10^{-4} s⁻¹ (see Fig. 4) under the same light conditions. Experimentally the photolysis frequencies of NO₂ were determined from the measured NO yields at the reactor exit by modelling according to the Leighton relationship (Reactions R5–R7).


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The linear increase of the NO₂-photolysis frequencies with increasing number of lamps illuminating the reactor shows that the actinic flux in the reactor is proportional to the number of lamps used. Due to the small photolysis frequencies under the employed visible irradiation no correction for the loss of NO₂ and HONO by photolysis was applied to the uptake coefficients, which lead to an underestimation of the uptake coefficients by about 5% for the typical experimental conditions.

Figure 5 shows the dependence of the HONO-formation on the NO₂-concentration for the maximum actinic flux. The reaction is less effective at high (more than ambient) NO₂-concentrations. This manifests in decreasing uptake coefficients between 5.5×10^{-6} at 2.7 ppb and 4.3×10^{-7} at 280 ppb NO₂. Figure 5 compares the HONO-formation on humic acid aerosol and on humic acid films coated on the walls of a glass photo-reactor (Stemmler et al., 2006). It is evident that a similar saturation curve is observed on both types of surfaces with increasing NO₂-concentrations. In the inset the calculated uptake coefficients γ_{rxn} are compared for the aerosol experiments and for the experiments in the coated wall flow tube. The uptake coefficients for the coated wall flow tube are reanalyzed from data published by (Stemmler et al., 2006), where no uptake coefficients had been derived. In the coated wall flow tube the first order reactive loss rate of NO₂ according to Eq. (1) can be related to an uptake coefficient γ_{rxn} using Eq. (3):

$$k_{1,\text{order}} = \frac{\gamma_{\text{rxn}} \omega}{2r} \quad (3)$$

In Eq. (3), r is the flow tube radius (0.4 cm). However, Eq. (3) does not hold if gas phase diffusion limitations are present, i.e., when radial gas concentration profiles build up. To take into account gas phase diffusion, the Cooney-Kim-Davis (CKD) method (Cooney et al., 1974; Murphy and Fahey, 1987) was used to correct the measured uptake coefficients as described in detail by Behnke et al. (1997). Comparison of the CKD-corrected results with the uncorrected approach given by Eq. (3) was used to check to what degree uptake coefficients obtained in the coated wall flow tube were affected by gas phase diffusion limitations. At the highest observed uptake coefficients a maximum

correction of <25% was applied to account for the gas phase diffusion limitation. Contrary, the experimental results obtained from the aerosol flow tube experiments are not affected by the gas phase diffusion limitation under the given conditions.

The uptake coefficients derived from the humic acid coatings are approximately a factor of 3 higher than those obtained on the aerosol under comparable humidity and light conditions. The difference is probably related to uncertainties in the quantification of the humic acid surface areas. For the humic acid coatings the geometric surface of the inner surface of the glass reactor was used, a measure which must be viewed as an underestimation of the real surface, as it neglects any surface roughness of the sand blasted reactor surface and from the humic acid coating itself. We estimate this uncertainty in surface area to be up to a factor of 10. For the surface area of the aerosol the surface measurement with a SMPS are used. The surface is calculated from the aerodynamic diameter assuming spherical particles, which may be not true as long as the particles are not deliquesced. Furthermore, the uncertainty of SMPS surface measurements is difficult to assess. A comparison of different SMPS instruments showed a standard deviation of up to 22% for the number concentrations and 10% for the diameter (which results in an estimated standard deviation of 26% in the surface concentration measurements) (Dahmann et al., 2001). Nevertheless, the uptake coefficients obtained on the aerosol surface are favoured as (i) the overall uncertainties in the surface area determination are much lower and as (ii) the knowledge of aerosol size distribution in the real atmosphere is mainly based on SMPS measurements allowing an easier comparison of the laboratory data with atmospheric conditions.

The hypothetical elementary photochemical mechanism (Reactions R2–R4), including activation of reductive centres (A^{red}) in the humic acid aerosol by light, the corresponding deactivation process, and the reaction of A^{red} with adsorbed NO_2 , predicts such a saturation curve for the HONO-formation with increasing NO_2 -concentrations due to the competition of Reactions R3 and R4. But also alternative explanations, such as a Langmuir adsorption of NO_2 coupled to a surface reaction, which is commonly referred to in heterogeneous chemistry (Ammann et al., 2003; Arens et al., 2001; Pöschl

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et al., 2001), can explain the observed saturation curve.

As described previously (Stemmler et al., 2006) the saturation curve displayed by the concentration dependence can be analysed for the HONO-formation at low NO₂-concentrations, which is first order in NO₂ (i.e. d(HONO)/dt = k_{eff}[NO₂]), and for the limiting rate of HONO-production at highly elevated NO₂-concentration (i.e. d(HONO)/dt=k_{max}). From the data in Fig. 5 values of k_{eff}=4.3×10⁻⁴ s⁻¹ per m² m⁻³ aerosol surface concentration and k_{max}=1.1×10⁻²³ ppb s⁻¹ per m² m⁻³ aerosol surface concentration and per photon m⁻² s⁻¹ actinic flux are determined. With these parameters an empirical model description can be derived as described previously (Stemmler et al., 2006), which qualitatively describes the results for HONO-formation (ΔHONO) as a function of reaction time, aerosol surface concentration, light intensity, and NO₂-concentration.

$$\begin{aligned}\Delta\text{HONO}[\text{ppb}] &= \frac{t \times [S/V]}{k_{\text{max}}^{-1} \times [F]^{-1} + k_{\text{eff}}^{-1} \times [\text{NO}_2]^{-1}} \\ &= \frac{t \times [S/V]}{9.3 \times 10^{22} \times [F]^{-1} + 2330 \times [\text{NO}_2]^{-1}}\end{aligned}\quad (4)$$

and the uptake coefficient γ_{rxn} is described correspondingly by

$$\gamma_{\text{rxn}} = \frac{4}{\omega} \times \frac{1}{9.3 \times 10^{22} \times [\text{NO}_2] \times [F]^{-1} + 2330}\quad (5)$$

where t is the reaction time in s, $[S/V]$ is the aerosol surface concentration in m²m⁻³, F the actinic flux in the 400–750 nm range in photons m⁻² s⁻¹, ω is the mean thermal velocity of NO₂ in m s⁻¹ and $[\text{NO}_2]$ the concentration of NO₂ in ppb. In Figs. 2–5 this model description is depicted by the dashed lines.

The model is based on the spectral distribution of the visible lamps used in this study. A comparison (Stemmler et al., 2006) of two different visible light sources (400–

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700 nm and 500–700 nm range) showed little differences with respect to the HONO-formation on humic acid coatings. Therefore, it is suggested that the reaction is only weakly dependent on wavelength in the visible region. Using UV-A lamps (300–420 nm, $\lambda_{\text{max}}=355$ nm) it was observed (Stemmler et al., 2006) that the HONO-formation from humic acid coatings was enhanced by approximately a factor of 3 compared to the visible irradiations, indicating a (relatively weak) wavelength dependence towards the UV-A range. The spectral actinic fluxes used were very similar to those in the aerosol flow tube (Fig. 1a). The aerosol experiment presented here is less suitable to investigate the HONO-formation on humic acid aerosol under UV-A irradiations, as both NO_2 and HONO photolyse during the long reaction time. Nevertheless, an experiment using the UV-A light spectrum depicted in Fig. 1a was performed. The interpretation of the results is possible only if the system is modelled to account for NO_2 and HONO photolysis. This was performed in a simplified way based on the NO_2 -photolysis (Reactions R5–R7), the HONO photolysis (Reaction R8), and the secondary reaction of OH-radical with the gaseous species NO_2 , NO, O_3 , and HONO. Due to the involved modelling the results are less accurate.



A value of γ_{rxn} of 1.4×10^{-6} is modelled for an initial NO_2 -concentration of 93 ppb (which corresponds to an average NO_2 -concentration of 45 ppb in the reactor due to NO_2 -photolysis). This value is similar to the value observed at comparable NO_2 -concentrations (Fig. 5), but under visible irradiations. The absence of a clear enhancement of the HONO-formation under UV-A light, as expected from the UV-A experiments on the humic acid coatings (i.e. by a factor of ≈ 3 under comparable light intensities), is likely explainable by the formation of ozone from the NO_2 -photolysis (49 ppb in the photo-stationary state in the aerosol reactor). Ozone reacts in an analogous way and with comparable rates on the irradiated humic acid surfaces (unpublished results) as NO_2 (Reaction R1) and therefore likely competes with NO_2 for the reactive uptake on the humic acid aerosol.

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Figure 6 shows the $\text{NO}_2 \rightarrow \text{HONO}$ conversion on humic acid aerosols at different relative humidities. At low humidities ($<10\%$) the aerosol shows a somewhat reduced reactivity, indicating that the presence of water promotes the reaction. A similar deactivation was observed on humic acid coatings at low humidity. In these experiments, which were characterized by a much higher NO_2 -conversion, it was evident that both, the loss of NO_2 from the gas phase and the formation of gaseous HONO are affected identically. Therefore, it is not the partitioning of HONO causing the effect. In the humidity range between 20 and 60% a constant reactivity of NO_2 with humic acid aerosol was observed, which appears to drop somewhat at humidities above 60%. The observed kinetic data can be compared with humidograms of Aldrich humic acid aerosol (Badger et al., 2006; Gysel et al., 2004). Gysel et al. report a steadily growing aerosol diameter upon hydration from 0–60% relative humidity, which is believed to be due to water adsorption and solubilisation of the most soluble humic acid molecules, followed by an apparent size decrease between 60–75%, which they attribute to the full deliquescence of the particle. The particles then homogeneously grow further up to 90% RH (total growth factor 1.18). According to this explanation the observed decrease in the humic acid aerosol reactivity towards NO_2 above 60% RH would correspond to the deliquescence of the particles. Two different explanations of the apparent decreasing reactivity above the deliquescence point could be equally valid. Either the reactivity of the surface may be lowered due to the dilution by water or the aerosol transformed from an irregularly shaped particle to a spherical particle due to the deliquescence. The latter would signify that below the deliquescence point the reactive surface of the particles has been underestimated by the SMPS measurement. Some indication for the latter explanation is given by Gysel et al. (2004), who observed a decreasing aerodynamic diameter in the range between 60–75% relative humidity in their humidograms of monodisperse humic acid aerosol, a sign for such an aerosol restructuring process. In contrast, Badger et al. (2006) did not observe a deliquescence point of humic acid aerosol and suggested that the particles are deliquesced over the entire 0–90% humidity range and that the aerosol may efflorescence only under extended residence times

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at zero humidity. From the present experiments one cannot decide at which humidity the aerosol gets deliquesced. However, we observed that a thin film of humic acid on a reactor glass surface visibly appeared deliquesced at 88% relative humidity. It is interesting to note that the overall humidity dependence as shown in Fig. 6 resembles that observed in the dark reaction of NO_2 with soot by (Kalberer et al., 1999).

Figure 7 shows the effects of the aerosol acidity on the formation of gaseous HONO. As nitrous acid is a weak acid ($pK_a=3.0\text{--}3.3$) (da Silva et al., 2006; Park and Lee, 1988) it forms involatile nitrite salts in basic environments, which could be retained in the aerosol phase and would not be detected as gaseous HONO. Solutions of 20 g L^{-1} humic acid sodium salts were acidified with HCl to pH 3–7 to produce humic acids with different degree of protonation. As humic acid contains large quantities of acidic organic functional groups they act as pH-buffers over a wide pH-range and stabilize the acidity of the aerosol depending on the degree of protonation. Figure 7a demonstrates no significant change in the yields of gaseous HONO for moderate acidic to neutral aerosols. This indicates that nitrite salts are sufficiently rapidly desorbing as HONO to not affect the HONO-yields of the experiments with acid to neutral aerosols. As a comparison, also for water droplets, which may be viewed as a model for the humid humic acid aerosols, one would expect that less than 5% of the HONO is partitioning into the droplets at pH-values lower than 7.4, based on its Henry's law solubility ($43\pm 3\text{ M atm}^{-1}$ at 28°C (Park and Lee, 1988), its pK_a of 3.3 (Park and Lee, 1988) and the total aerosol volume concentration in the experiment ($3.5\times 10^{-3}\text{ cm}^3\text{ m}^{-3}$), leading to an effective solubility of $<5.7\times 10^5\text{ M atm}^{-1}$. Figures 7b–d show the acidity dependence for the $\text{NO}_2\rightarrow\text{HONO}$ conversion on humic acid coatings, which gives more insights, as here also the NO_2 -removal can be observed due to the larger conversion. The NO_2 -removal and the HONO-production is compared for humic acid coatings produced from stock solutions acidified with phosphoric acid to pH 4.4, 7.5, and 10.3, respectively. At pH 4.4 and with some constraint also at pH 7.5, the formation of gaseous HONO is hardly retarded compared to the observed loss of gaseous NO_2 , whereas at pH 10.3 only a delayed evolution of gaseous HONO occurs. The reason for this

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behavior is that HONO partitions stronger to more alkaline reactor surfaces resulting in higher retention of HONO by chromatography through the reactor tube. The loss of NO₂ occurs instantaneously upon irradiation at all pH-levels and the magnitude of the NO₂-consumption by the photoreaction is similar in all cases ($7\text{--}8 \times 10^{10}$ molecules s⁻¹ cm⁻²). This indicates, that the rate of the photo-reduction of NO₂ on the humic acid surfaces is not dependent on pH, but the accumulation of the reaction product ($pK_a(\text{HONO}/\text{NO}_2^-) \approx 3.0\text{--}3.3$, da Silva et al., 2006; Park and Lee, 1988) on the humic acid surface, which is much larger in the coated wall flow tube than in the aerosol flow tube and its travel time through the reactor increases with pH.

It appears that the dark reaction of NO₂ with the humic acid coating increases with pH, leading also to an enhanced formation of HONO. This effect is pronounced between pH 4.4 and 7.5, but a further increase between pH 7.5 and 10.3 has not been detected. This might be related to the dark reaction between NO₂ and the abundant phenolic groups or aromatic amines, within the humic acid and the reactivity of such compounds increases drastically with deprotonation (Ammann et al., 2005). But as deprotonation will additionally affect the conformation and the surface structure of humic acid, the observed changes cannot be related unequivocally to the direct effects of the deprotonation.

4 Conclusions and atmospheric implications

In the presented kinetic experiments the photochemical formation of HONO by heterogeneous conversion of NO₂ on aerosol surfaces was simulated under realistic atmospheric conditions with respect to humidity, NO₂-concentration, and actinic flux. However, the employed aerosol concentrations of $5\text{--}30 \times 10^5$ particles cm⁻³ are approximately a factor of 50 higher than the aerosol concentrations found in the urban or rural atmosphere ($10^4\text{--}10^5$ particles cm⁻³) due to experimental constraints. In the real atmosphere, where significant amounts of aerosol have a diameter below 100 nm, typical aerosol surface concentrations in the rural and urban atmosphere are 10^2--

$10^3 \mu\text{m}^2 \text{cm}^{-3}$, respectively (Seinfeld and Pandis, 1997; Wehner and Wiedensohler, 2003). In the present experiments the aerosol surface concentrations are roughly 200 times higher and amounted between $2\text{--}14 \times 10^4 \mu\text{m}^2 \text{cm}^{-3}$.

For NO_2 -concentrations of 10 ppb and 20 ppb (typical for rural and urban regions in Europe), an actinic flux of $1.7 \times 10^{17} \text{photons cm}^{-2} \text{s}^{-1}$ (typical clear sky flux in the 300–750 nm range, 40° Zenith angle), relative humidities between 20–60% uptake coefficients in the order of $\gamma_{\text{rxn}} = 3.7 \times 10^{-6}$ and 2.6×10^{-6} for the $\text{NO}_2 \rightarrow \text{HONO}$ -conversion on humic acid aerosol are expected according to Eq. (5). Under the assumption that all aerosol is composed from humic acids and for typical aerosol surface concentrations of $100 \mu\text{m}^2 \text{cm}^{-3}$ for rural and $1000 \mu\text{m}^2 \text{cm}^{-3}$ for urban conditions, this leads to an estimated HONO-formation of 1.2ppt h^{-1} and 17ppt h^{-1} on aerosol surfaces in rural and urban environments, respectively. These values are upper limits as in reality rural and urban continental aerosol is composed only by 20–30 mass% of organic matter (Hueglin et al., 2005; Putaud et al., 2004) and the photo-reactivity of these real existing airborne organic materials towards NO_2 has never been shown. These low upper limits for the HONO-production on humic acid aerosol can be compared with reports of daytime HONO-formation in ground near air over a forested or rural sites of $170\text{--}500 \text{ppt h}^{-1}$ (Acker et al., 2006b; Kleffmann et al., 2005; Zhou et al., 2002) or in urban environments of up to 2ppb h^{-1} (Acker et al., 2006a; Ren et al., 2003, 2006). Therefore, we suggest, that it is likely that photochemical HONO-formation on organic aerosol may be only a minor (or even no) contributor to the HONO-formation observed in the ground near atmosphere. Only at places with exceptional high pollution by organic aerosol and nitrogen oxides, as in biomass burning plumes or in mega-cities, a comparable HONO-photo-formation on organic aerosol may occur.

In a previous study (Stemmler et al., 2006) the total photochemical HONO-production on a soil sample was estimated as $5 \times 10^{10} \text{molecules cm}^{-2} \text{s}^{-1}$ for a urban pollution situation ($\sim 20 \text{ppb NO}_2$) and solar irradiances (300–700 nm) of $\sim 400 \text{Wm}^{-2}$. Such a HONO-formation at the ground surface is sufficient to establish a HONO source strength integrated over the lowest 100 m height of the atmosphere of $\sim 700 \text{ppt h}^{-1}$

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and appears to have a much larger impact on the HONO-formation in the lowermost part of the atmosphere than the reaction on aerosol investigated in this study.

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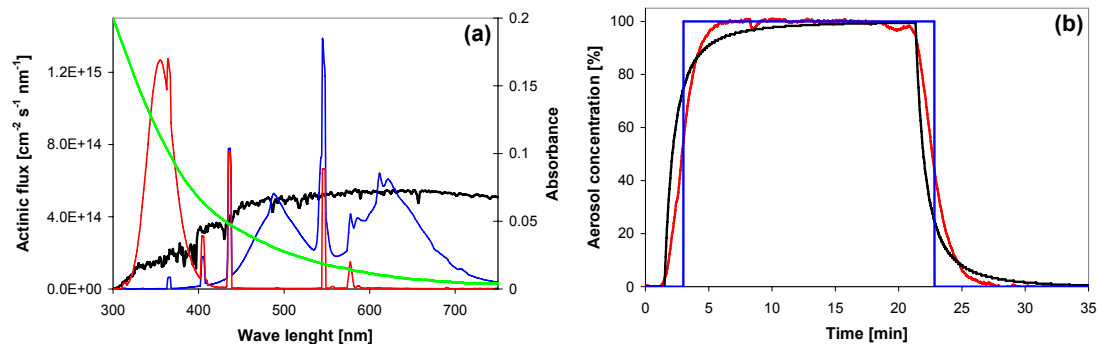


Fig. 1. Panel (a): Spectral actinic flux measured in the aerosol flow tube under visible and UV-A irradiation in comparison with the spectral actinic flux on the Earth surface and the absorption spectra of the humic acid. The red line depicts the spectrum of the UV-lamps; the blue line is for the visible lamps. The black line is the modelled clear sky actinic flux at the Earth surface for a Zenith angle of 40° , a ozone column of 300 DU, a surface albedo of 0 and a standard aerosol of the Tropospheric Ultraviolet and Visible Radiation Model (TUV version 4.3; NCAR, 2006). The absorption spectrum (base 10) of the employed humic acid in solution (pH 4.3, 10.5 mg L^{-1} , pathlength 1 cm) is shown as green line (right scale). Panel (b): Aerosol concentration measured at the reactor exit by an electrometer during a 20 min aerosol injection starting at $t=0$ min (red line, maximum concentration scaled to 100%) in comparison with the aerosol concentrations modelled assuming plug flow (blue line) or laminar flow conditions (black line).

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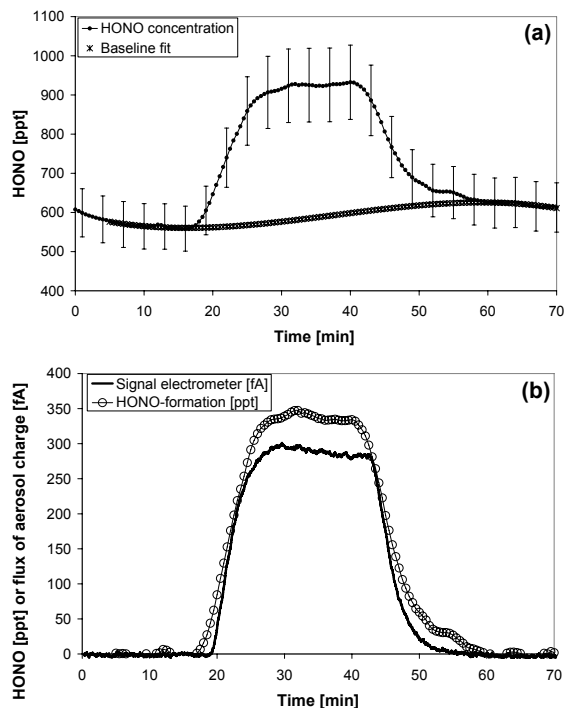


Fig. 2. Typical experimental result for the formation of HONO from gaseous NO_2 on photoactivated humic acid aerosol. Panel (a): Measured HONO-concentration during the injection of the aerosol under visible light irradiation (400–750 nm). A significant HONO-formation (500–600 ppt in this case) occurs on the reactor walls in the absence of aerosol. This background, which depends on the experimental conditions, the cleanness of the reactor, and the purity of gas and aerosol supplies was fitted before and after the aerosol injection (baseline fit) and was subtracted to obtain the excess HONO-formation on the comparatively small aerosol surface. Panel (b): Excess HONO-formation on the particle surface compared to the aerosol concentration measured at the reactor exit by the electrometer [fA].

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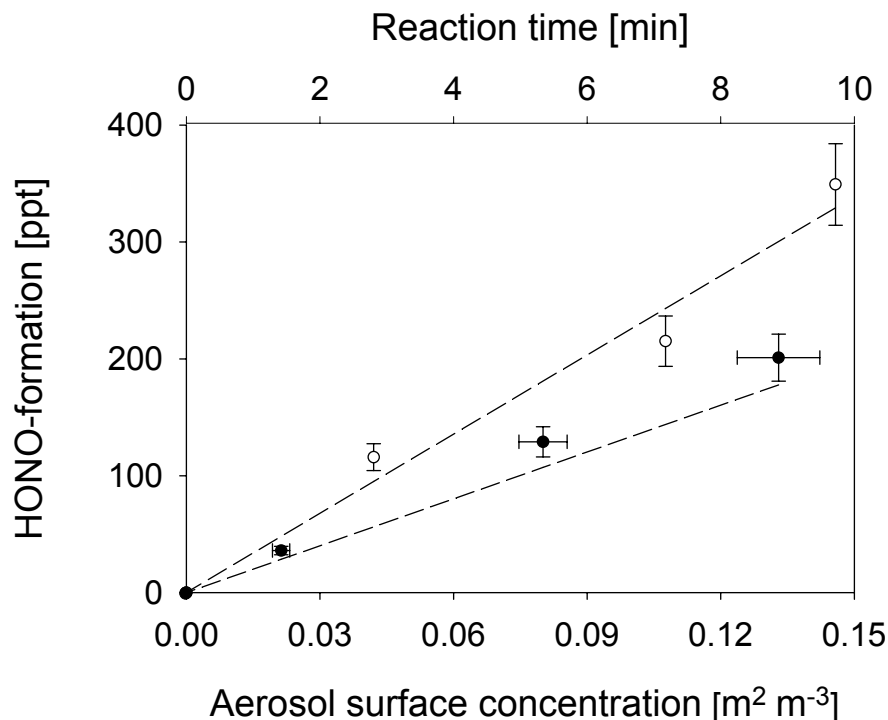


Fig. 3. HONO-formation on humic acid particles (see Fig. 2 for the raw data treatment) as a function of the aerosol surface concentration (\bullet) and as a function of the reaction time (\circ). The aerosol surface concentration experiment is performed in presence of 79 ppb NO_2 , at 26% relative humidity, and for a reaction time of 2.7 min. The reaction time experiment was performed in presence of 44 ppb NO_2 and at 24% relative humidity and for an aerosol surface concentration of $0.082 \text{ m}^2 \text{ m}^{-3}$. Both experiments were performed under visible light irradiation (Fig. 1). The black dashed lines represent a model description of the results (Eq. 4).

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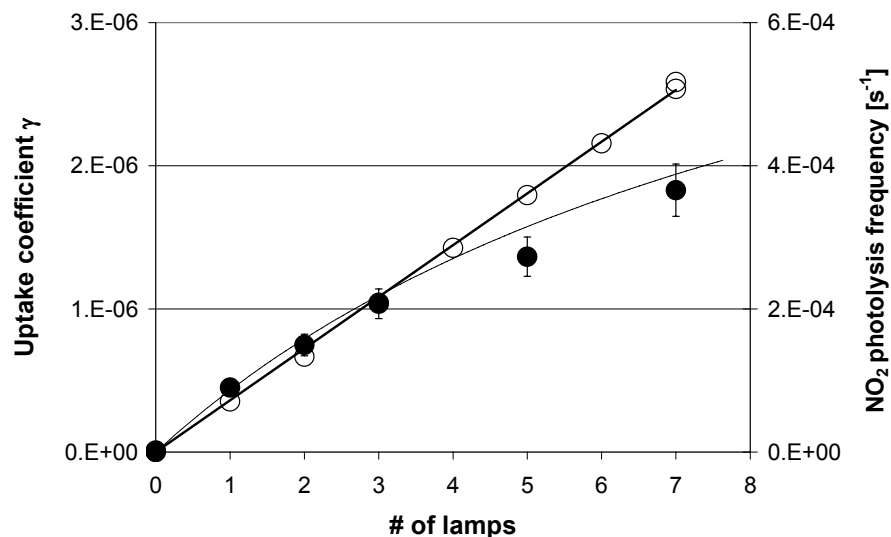


Fig. 4. Dependence of the HONO-formation on the visible light intensity expressed by the reactive uptake coefficient of NO_2 on the aerosol surface (see Fig. 2 for the raw data treatment). The filled circles (●) are the derived uptake coefficients for HONO-formation. The dashed black line represents a model description of the results (Eq. 5). The empty cycles (○) are experimentally determined $\text{NO}_2 \rightarrow \text{NO}$ photolysis frequencies from experiments without aerosol. The black line is a linear fit of the data, indicating that the actinic flux in the reactor is proportional to the number of illuminated lamps.

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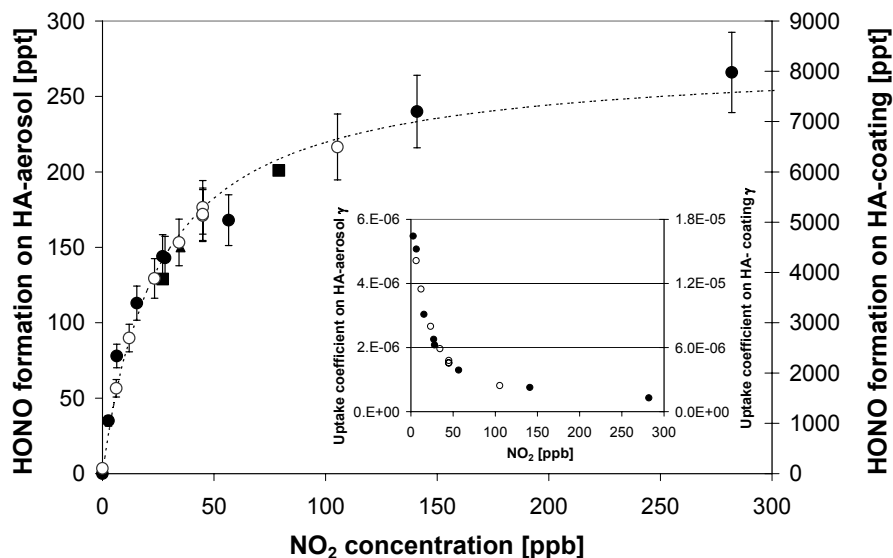


Fig. 5. Dependence of the HONO-formation on humic acid (HA) aerosols on the NO₂-concentration (filled symbols). The experimental conditions are as follows: reaction time 2.8 min, aerosol surface concentration $0.151 \pm 0.006 \text{ m}^2 \text{ m}^{-3}$, relative humidity 26%, actinic flux $1.0 \times 10^{17} \text{ photons cm}^{-2} \text{ s}^{-1}$ in the 400–750 nm range. The filled squares and the filled triangle are from the experiments in Fig. 3 (■) and in Fig. 4 (▲) under most similar, but not completely identical conditions. The thin dashed line represents a model description of the results (Eq. 4). The empty circles (○, right scale) show the dependence of the HONO-formation on the NO₂-concentration as observed on humic acid (HA) coatings at 21% relative humidity. The inset shows the dependence of the reactive uptake coefficient of NO₂ on humic acid (HA) aerosol (●, left scale) and humic acid (HA) coatings (○, right scale) as a function of the NO₂-concentration.

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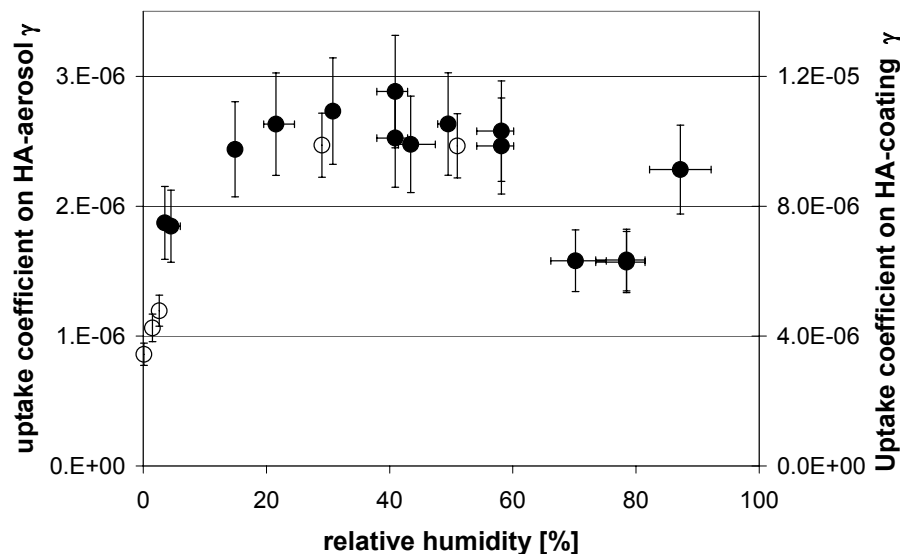


Fig. 6. Dependence of the HONO-formation on the relative humidity expressed as the uptake coefficients γ_{rxn} on humic acid (HA) surfaces. The filled symbols depict the uptake coefficient measured on humic acid (HA) aerosols at 25 ppb NO₂ and visible irradiation (left scale). The empty symbols depict the uptake coefficients measured on humic acid (HA) coatings at 20 ppb NO₂ and visible irradiation (right scale). At high humidities (i.e. 88%) it was visually observed that the humic acid coatings became deliquesced, preventing uptake measurements at such high humidities.

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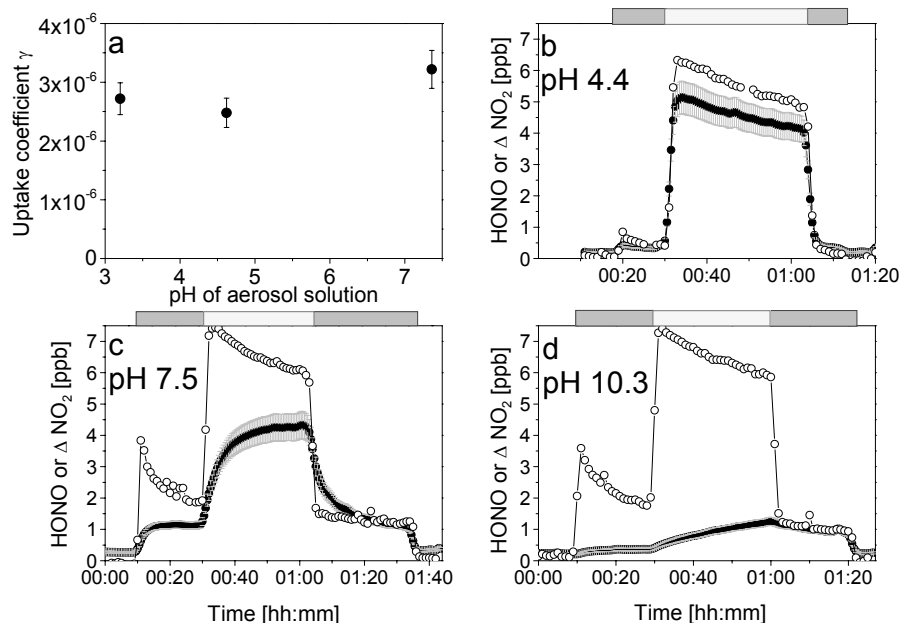


Fig. 7. Formation of HONO as a function of acidity of the humic acid aerosol and HONO-formation and NO_2 -loss on humic acid coatings of different acidity. Panel (a): HONO-formation on humic acid aerosol generated by nebulising humic acid solutions of pH 3.2, 4.6, and 7.4 in presence of 25 ppb NO_2 . Panel (b)–(d): Formation of HONO (filled circles) and removal of NO_2 (empty circles) on humic acid coatings with different acidity. The coatings are produced from 1 mg ml^{-1} stock solutions with pH 4.4, pH 7.5, and pH 10.3. The dark grey shaded area at the top of the panels indicate the periods where the humic acid surface was exposed to NO_2 in the dark, the light grey area indicates the time when the surface was irradiated (400–750 nm).

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