Formation of Reactive Nitrogen Oxides from Urban Grime Photochemistry

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Abstract. Impervious surfaces are ubiquitous in urban environments and constitute a substrate onto which atmospheric constituents can deposit and undergo photochemical and oxidative processing, giving rise to "urban grime" films. HNO_3 and N_2O_5 are important sinks for NO_x in the lower atmosphere and may be deposited onto these films, forming nitrate through surface hydrolysis. Although such deposition has been considered as a net loss of NO_x from the atmosphere, there is increasing evidence that surface-associated nitrate undergoes further reaction. Here, we examine the gas phase products of the photochemistry of real, field-collected urban grime using incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS). Gas phase nitrogen oxides are emitted upon illumination of grime samples and their production increases with ambient relative humidity (RH) up to 35% after which the production becomes independent of RH. These results are discussed in the context of water uptake onto and evaporation from grime films.

1. Introduction

Atmospheric NO_x (=NO+NO_2) is an important reactant in the formation of urban pollutants such as ground level O_3, while $HONO_{(g)}$ is an important photochemical source of OH (Finlayson-Pitts and Pitts, 1999). Therefore, in order to quantify the local atmospheric oxidative capacity, it is important to understand the processes mediating the concentrations of these species in the urban atmosphere. A major sink for nitrogen oxides in the troposphere is the formation of gas phase HNO_3 or N_2O_5, followed by the deposition of these species to surfaces and their subsequent hydrolysis to form nitrate. This anion is considered to be a sink for the gas phase NO_x because its aqueous phase photochemistry is very slow. However, there is an increasing body of literature which suggests that surface bound nitrate and HNO_3 are not terminal sinks, but rather can undergo further recycling back to the gas phase. For example, HNO_3 has been shown to react on surfaces with gas phase NO and HONO to form NO_2 (Mochida and Finlayson-Pitts, 2000; Rivera-Figueroa et al., 2003; Saliba et al., 2001) and photochemical mechanisms for the conversion of HNO_3 and nitrate anion to gaseous nitrogen oxide species have been proposed on a variety of surfaces including glass (Zhou et al.,

2003), snow (Grannas et al., 2007; Mochida and Finlayson-Pitts, 2000; Rivera-Figueroa et al., 2003; Saliba et al., 2001), organic films (Handley et al., 2007), leaves (Zhou et al., 2011), plants (Ye et al., 2016), building materials (Ye et al., 2016) and mineral oxide surfaces such as aluminum oxide and zeolite (Gankanda and Grassian, 2013; Nanayakkara et al., 2014; Rubasinghege and Grassian, 2009; Schuttlefield et al., 2008). There is particular interest surrounding whether such processes could explain an as of yet unconfirmed source of daytime HONO in urban centers. Field studies have indicated that this missing source is photochemical in nature and acts at or near ground level (Lee et al., 2015; Wong et al., 2013; 2012; Young et al., 2012). Other processes, such as reactions of NO_y (total reactive nitrogen) on aerosols (Ma et al., 2013) and soil mediated processes (Oswald et al., 2013; Scharko et al., 2015), have also been proposed but have not been confirmed at this time.

When studying atmospheric surface reactions, an often-overlooked surface is that of human-made structures (eg. buildings, roadways). These surfaces, when exposed to the atmosphere, become coated in a complex surface film over time due to the deposition and subsequent processing of atmospheric constituents (Chabas et al., 2008; 2012; Diamond et al., 2000; Duigu et al., 2009; Favez et al., 2006; Ionescu et al., 2006; Lam et al., 2005; Law and Diamond, 1998; Liu et al., 2003; Lombardo et al., 2010; 2005; Simpson et al., 2006; Wu et al., 2008a; 2008b). Referred to as "urban grime", these films have generally been thought of as merely a surface for deposition as a terminal sink for species. However, there is increasing understanding that these films could also play a role in mediating environmental cycling. Most attention has been brought to the idea that the films can sequester gas phase compounds and enhance pollutant concentrations in rainfall runoff (Diamond et al., 2010; 2001; Priemer and Diamond, 2002), but there is evidence suggesting that they can also impact the reactivity of species contained within the film, such as PAHs (Ammar et al., 2010; Kwamena et al., 2007), and nitrate/HNO_3 (Baergen and Donaldson, 2013; Baergen et al., 2015).

Additionally, it has been predicted that there is enough water present on all environmental surfaces, even those hydrophobic in nature, to influence heterogeneous reactions (Sumner et al., 2004). Rubasinghege and Grassian have discussed the role of water on environmental surfaces outlining a wide range of mechanisms through which water can impact reactivity (Rubasinghege and Grassian, 2013). These include altering reaction pathways, promoting hydrolysis reactions, ionic dissociation and solvation of ions, inhibiting reactivity through blocking reactive sites, enhancing ion mobility on the surface and altering the stability of surface species. For example, both the extent of reaction and the distribution of products change as a function of relative humidity (RH) for nitrate photolysis on aluminum oxide and Pyrex substrates but their response is substrate dependant (Rubasinghege and Grassian, 2009; Zhou et al., 2003). Such studies have generally investigated the impact of water on atmospheric surface chemistry by varying the ambient RH. However, because different surfaces have different water affinities, they may be expected to display different responses to changes in relative humidity. For example, a study by Nguyen *et al.* shows that estimating water content in the aerosol, rather than just using RH data, is important for predicting the

formation of biogenic secondary organic aerosol (Nguyen et al., 2015). Related to grime surfaces, Sumner *et al.* have shown how different surfaces, representing building surfaces, vary in their water uptake behaviour (Sumner et al., 2004). There are only minimal studies performed looking at water interactions with grime, but they show that grime films impact water uptake on surfaces (Baergen and Donaldson, 2013; Chabas et al., 2014). Thus it is important to characterize the change in surface water content as a function of RH as well as grime photochemistry. In the following we present results of experiments, which monitor the photochemical release of gas phase nitrogen oxides from urban grime as a function of RH, in conjunction with water uptake measurements on grime.

2. Experimental

2.1 Sample collection

Grime samples were collected by placing the substrate, either 3 mm diameter glass beads (Fisher Scientific) or quartz crystal microbalance (QCM) crystals, outside in downtown Toronto, Canada for up to one year. The beads were placed on metal mesh shelves underneath a building overhang, sheltering the sampler from precipitation. Sunlight was blocked with a black cloth covering the front of the sample and a building blocking the sunlight from the other direction. The QCM crystals were placed in holders where the face of the crystal was facing the ground while the back was within the holder, preventing the collection of grime on this backside, which would impact the QCM response. In this way both types of samples were shielded from light and precipitation while still being open to the atmosphere.

2.2 Incoherent Broad Band Cavity Enhanced Spectroscopy (IBBCEAS)

Gas phase product formation was determined using IBBCEAS. The system is described in full elsewhere (Reeser et al., 2013). Briefly, a 10 W LED with a maximum intensity at 372 nm, was focused into a 100 cm cell. The cell was sealed with two highly reflective mirrors (>99.95% between 367nm and 380nm). The light escaping through the back mirror was collected by a lens and focused onto a fiber optic bundle, which was directed into a spectrograph with a CCD detector. The mirrors were continually purged using a flow rate of 25 mL/min of N_2 directed onto the mirror surfaces. Transmission spectra were collected for 30 s (averages of 30 scans with an integration time of 1 s each) over a wavelength range of 362 nm to 385 nm.

The concentrations of HONO and NO_2 were calculated using the method described by Fiedler and Gherman (Fiedler et al., 2003; Gherman et al., 2008) and previously used by us (Reeser et al., 2013). This uses measured mirror reflectivity (Washenfelder et al., 2008), Rayleigh cross sections of the carrier gas (Bodhaine et al., 2010) and the absorption cross sections of NO_2 (Vandaele et al., 1998) and HONO (Stutz et al., 2000) to fit the experimental spectra with DOASIS software (Lehmann, 2009). DOASIS uses a linear least-squares method to fit the absorption bands to reference spectra and a polynomial to fit broad features such as those from Rayleigh scattering, Mie scattering and temperature drifts. The fit is optimized by including terms that allow for small shifts in absorption wavelengths and spread of peaks. A sample fit is

displayed as the solid line in Fig. 1. Calculated detection limits (signal/noise = 3) are 1.50×10^{11} molecules cm^{-3} (~6ppb) for NO_2 and 6.5×10^{10} molecules cm^{-3} (~3ppb) for HONO.

2.3 Photochemistry

Samples of 10.0g of exposed glass beads were weighed into a glass petri dish for illumination. These were placed within a stainless steel chamber (3.2" x 2.2" x 1.5") and nitrogen was flowed through the chamber into the IBBCEAS cell at a rate of 0.3 L/min. RH and temperature in the chamber were monitored using a Traceable® Memory Hygrometer/Thermometer. The reported accuracy is ± 2% at mid-range and ± 4% elsewhere in the range of 10 to 95% RH. The calibration was checked by measuring the RH above a series of saturated salt solutions in comparison to the known deliquescent RH and was the same as the reported values within the stated uncertainties.

Nitrogen was flowed through the system for one hour prior to illumination to establish a stable background in the spectrum, and equilibrate the water vapour in the chamber for the RH used in the experiment. The samples, initially at a RH of 35%, were illuminated through a quartz window at the top of the sample chamber with a Xe arc lamp (λ>295nm) for 60 min. The light was then blocked, the signal allowed to return to baseline, and the RH adjusted for the next illumination period. After 60 min the sample was again illuminated for 60 min before blocking the light and repeating the cycle for a third time. Average concentrations were calculated for the second 30 min of illumination, where the signal appeared to reach steady state, and then normalized to the initial steady state value at the RH of 35% to adjust for experiment variability such as variations in sample, light intensity and temperature. These experiments were carried out without temperature control, with the chamber operating at a temperature between 28 and 34 °C during illumination.

Control experiments were carried out in which 10.0 g of clean beads were illuminated for one hour at a relative humidity of 35%. In addition, 10.0 g of the grime coated beads were subjected to heating up to 36°C to study the impact of increased temperature on product formation. Both of these tests were completed in triplicate with a different sample being used each time. Neither experiment showed detectable levels of HONO or NO_2.

The set up was further tested by flowing a known concentration of NO_2 through the empty chamber and IBBCEAS cell. A flow containing 6.0 ppm NO_2 in N_2 was diluted in a stream of N_2 down to $(4.76 \pm 2.4) \times 10^{12}$ molecules/cm^3 at varying RHs. NO_2 and HONO steady state concentrations measured at each RH were used to characterize the IBBCEAS response to changes in humidity and the efficiency of NO_2 hydrolysis to HONO on the walls of the reaction chamber and IBBCEAS cell.

2.4 Ion analysis

Two different ion extraction techniques were used. For ion analysis of the illuminated beads, 4.0 g of grime-coated beads were shaken for 5 minutes with 3.00 mL of deionized water with a resistivity of greater than 18 MΩcm (Baergen et al., 2015). For ion analysis to accompany water uptake measurements, samples were collected on 5 cm x 7.6 cm pieces of window glass over the same time period as the quartz crystals and extracted with 45 mL deionized water. Glass samples were first placed in 25mL of water and sonicated for 1 min. Each side of the glass was then washed twice with 5mL of water. Solutions were filtered through a 0.2 μm IC Millex®-LG syringe filter before being analyzed by ion chromatography on a Dionex ICS-2000. 1.33 mL samples were injected onto a concentrator/analytical column system: Ionpac® TAC-ULP1/AS19 with KOH eluent for anion detection and Ionpac® TCC-ULP1/CS17 with methanesulfonic acid eluent for cation detection. A second extraction resulted in concentrations of less than 10% of the first extraction for all ions. The inorganic ion content of the grime used for photochemistry experiments is given in Table S1.

2.5 Water Uptake

The mass of water taken up onto an urban grime film as a function of RH was measured using a quartz crystal microbalance (QCM), as described in Demou et al (Demou et al., 2003). Grime was collected directly onto a quartz crystal and then placed in the QCM. The QCM was housed in a plexiglass chamber whose humidity was increased by flowing air through a water bubbler at room temperature at a variable flow rate to maintain a rate of change of RH of 1%/min and decreased by flowing dry air through the chamber at variable flow rates to maintain a rate of change of -1%/min. The frequency change of the microbalance from the change in water content of the film was converted to a mass using the Sauerbrey equation ($\Delta m = C\Delta f$) where Δm is the mass change, C is a proportionality constant and Δf is the frequency change from the deposited mass. In a previous study, the Sauerbrey relationship was confirmed to hold for this apparatus only up to 1% of the fundamental frequency of the crystal (Demou et al., 2003). Due to this mass restriction, samples for QCM analysis were collected for only four weeks instead of the 1 year for the photochemistry samples. The value of the constant C is reported to be 8.147×10^7 Hz cm^2 g^{-1} for the 0.550 inch, 6 MHz crystals used in this study (Sauerbrey, 1959). The RH was measured using a Traceable® Memory Hygrometer/Thermometer.

3 Results

3.1 Photochemical Production of nitrogen oxides

Figure 1 shows a typical absorption spectrum collected upon illumination of a grime sample. One can see two features, typical of HONO absorption, a stronger signal at 368nm, and a second peak appearing at 384nm, at the longer edge of our wavelength range. The IBBCEAS is also sensitive to NO_2, which absorbs in this wavelength region. However, this molecule was not detected in any of the photochemical experiments performed here. We argue in the Supplementary Information that NO_2 hydrolysis on the walls of the chamber and/or IBBCEAs cell via Eq. (1) (Finlayson-Pitts et al., 2002) would prevent NO_2 from

being detected even if it was originally formed in the chamber. Because of this hydrolysis there is an

$$2\,NO_2 \rightarrow HONO_{(g)} + HNO_{3(surface)} \quad (1)$$

uncertainty as to whether the HONO we observe in the illumination experiments was originally NO_2, which was hydrolyzed prior to detection, or if it is HONO being produced directly from the sample. Therefore, we cannot attribute the observed HONO product exclusively to direct photochemistry of the grime sample; rather we use the HONO signal to indicate the combined total emission of NO_2 and HONO. We further note that the total product detected decreases when NO_2 is flowed through the apparatus in the light as compared to in the dark by approximately 60%, indicating gas phase photolysis of products (see Fig. S1). This highlights the importance of such considerations to be made whenever HONO and NO_2 are being measured. Each system needs to be classified individually over a range of RH conditions.

Figure 2 depicts the results of a typical experiment where a grime sample is placed within the chamber and exposed to three separate 60 min illumination periods at different relative humidities. The yellow highlighted regions indicate illumination. It is clear that nitrogen oxides are released to the gas phase during illumination and that the amount of products formed is dependent on the relative humidity. A repeat illumination of a sample at an RH of 35% showed an average ratio of 0.88 ± 0.06 compared to the original illumination. This provides evidence of some precursor depletion due to illumination, however, the much smaller signals at 20% RH indicate that the RH dependence, apparent in Fig. 2, is related to the formation of nitrogen oxides and not merely due to sample depletion. The nitrate to sulfate ratio of the grime before and after illumination was used to examine nitrate behaviour. Sulfate is not expected to have any photoreactivity on the film and thus was used to account for sample variability as was done in our previous work (Baergen et al., 2015). No nitrate loss was detected between water extracts of beads before and after illumination at 35% for three one-hour periods. The average change in the nitrate to sulfate ratio from before to after illumination was 3.6 ± 6.6 %. There was also no nitrate loss detected for the samples that were heated for three hours; these show an average change in the nitrate to sulfate ratio from before to after heating of 1.0 ± 3.6 %. The amount of nitrate loss expected during illumination, based on the integrated amount of gas phase nitrogen oxides produced, is in agreement with the above results.

In order to further investigate the RH dependence on product formation, the initial illumination period at 35% RH was used to normalize the concentrations detected for the next illumination periods. This data is shown for a range of RH values in Fig. 3. Up to an RH of approximately 35% the amount of products formed increases, after which product formation becomes independent of RH. At a RH of 0%, no products were detected. However, from the NO_2 control experiments, there was evidence that gas phase NO_2/HONO is lost to the chamber walls for these dry conditions, and thus this value was not reported.

3.2 Water uptake by grime samples

This interesting RH dependence of the amount of nitrogen oxides emitted photochemically from urban grime motivates the study of water uptake onto grime. Grime-water interaction has been reported before using ATR-FTIR with 1 week old grime, showing equilibrium with ambient water vapour (Baergen and Donaldson, 2013). Chabas et al also reported that mass measurements on 100 month old films showed enhanced water uptake on grime-coated substrates compared to clean ones (Chabas et al., 2014). Here we use 4 week old samples collected throughout the year-long collection onto the glass beads, and look at both water uptake and evaporation, to better probe water-grime interactions. The uptake and loss curves displayed in Fig. 4 are an average of 16 curves collected at different time points through the year normalized to the mass of major ions in the film (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}), extracted from a glass slide exposed to the atmosphere for the same length of time as the quartz crystal and scaled to the same surface area as the crystal. The shaded region indicates the 95% confidence interval. The water uptake onto a clean crystal was subtracted from each sample uptake before averaging, so the figure displays the mass of water taken up mediated by the grime itself. The degree of uncertainty captures some of the seasonality of grime water uptake, which will be discussed in an upcoming paper along with the seasonality of grime ion content. The water uptake onto and evaporation from grime are both smooth curves, with no indication of phase changes over the RH values spanned here. The lack of hysteresis also gives confidence that the illumination experiments reflect the true state of the "real" urban grime, as the film remains equilibrated with the ambient RH as this changes.

4. Discussion

The illumination of urban grime results in the release of gas phase nitrogen oxides in the form of NO_2 and/or HONO. While previously predicted (Baergen and Donaldson, 2013; Baergen et al., 2015), this is one of the first observation of such gas phase products. Field-collected grime samples were illuminated, without any alteration, clearly showing that urban grime is a source of nitrogen oxides back into the atmosphere. Our previous work, as well as that of others, has shown that nitrate is present within urban grime films (Favez et al., 2006; Lam et al., 2005) and that this nitrate is photolabile (Baergen and Donaldson, 2013; Baergen et al., 2015; Ye et al., 2016). Nitrate photolysis is known to form NO_2 within other media. Recent work by Ye *et al* also looked at surfaces exposed to the atmosphere for much shorter exposure times detecting HONO and NO_2 at varying ratios depending on the surface(Ye et al., 2016). If HONO is a product of this chemistry one possible source is via the protonation of nitrite, another known product of aqueous nitrate photochemistry. However, our previous study was consistent with an alkaline film due to the loss of ammonium, therefore we do not expect the film to be acidic enough for this mechanism to be important (Baergen et al., 2015).The organic fraction of the film could also play a role in the conversion of NO_2 to HONO, such as has been seen on organic surfaces such as humic acid (Stemmler et al., 2006) and PAH films (Ammar et al., 2010). NO_2 to HONO conversion could also occur through NO_2 hydrolysis within the film. Although it seems likely that nitrate is responsible for the observed chemistry due to its high concentration and known photoactivity on other surfaces, it is also possible that

249 photochemically active organo-nitrogen compounds may be present, though they have yet to be detected
250 within grime films. If present, these compounds may react as indicated by Han et al (Han et al., 2013) who
251 have reported the formation of R-NO, R-NO_2 and R-ONO_2 species on NO_2 exposed soot, which can
252 photolyze to form NO and HONO.
253
254 In contrast to our previous studies showing the photolability of nitrate in grime (Baergen and Donaldson,
255 2013; Baergen et al., 2015), the current study does not show nitrate depletion upon illumination. This
256 apparent discrepancy can be explained by the difference in experimental methods between studies. In both
257 previous studies, the films were "younger", with between 1 and 6 weeks of collection time, in comparison
258 to the year-long collection here. In addition, for the Leipzig samples described in Baergen et al (Baergen et
259 al., 2015) the "light" sample was continually exposed to ambient sunlight, whereas in the present
260 experiment, like the previous Toronto study (Baergen and Donaldson, 2013), the samples were shielded
261 from the light for the entire collection and then illuminated in a controlled laboratory setting. Both of the
262 previous studies suggested that only a portion of the film is photolabile and the current result indicates that
263 this non-photoactive proportion of the film forms a greater proportion of the film over time. Continued
264 growth of the film may block photoactive sites or burry photoactive components of the film, making a
265 smaller portion available for reaction. Ye *et al* found a logarithmic relationship between surface density of
266 nitrate/HNO_3 and reaction rate (Ye et al., 2016) which could also indicate only nitrate/HNO_3 on the surface
267 remains reactive in comparison to the nitrate/HNO_3 within the film. Whether a film grown under continual
268 exposure to ambient light would show the same trend is an open question. Exposure to precipitation could
269 also impact the photoactive fraction, both in potential compositional changes as different fractions are
270 removed from the film during precipitation and in preventing such long-term film growth. This large non-
271 photoactive fraction may also explain the disparity between the depletion of gas phase products over time
272 and the lack of a corresponding nitrate drop; the photolabile fraction is small enough that the approximately
273 12% loss of reactive precursor implied by the gas phase result is too small of a proportion of the total
274 nitrate to be detected within the extracts of the whole film.
275
276 The photochemical release of gas phase NO_2 and/or HONO is clearly dependant on relative humidity and
277 therefore, as seen through the water uptake experiments, on the water content of the film. In particular, the
278 product formation increases as the amount of water on the film increases, up to a relative humidity of 35%
279 after which case, the chemistry is not impacted by further addition of water up to 60%. This behaviour is
280 different from what has been seen from nitrate photolysis experiments on other surfaces. In a study
281 performed on HNO_3 deposited on pyrex glass, the combined NO_x and HONO formation rate was highest at
282 0% and decreased for 20% and 50% while the reported HONO production rate was lowest at 0% and then
283 increased up to 80% (Zhou et al., 2003). However, the authors assumed a constant NO_2 to HONO wall
284 conversion independent of relative humidity taken from a measurement in a different system and thus the
285 determined ratios may not reflect the real distribution of products emitted as a result of the photochemistry

(Zhou et al., 2003). Humidity dependence has also been seen for nitrate photochemistry on mineral dust surfaces. In this case, a minimum was seen for nitrate loss and NO_2 production at 0% and a maximum at 20% which subsequently decreased between 20 and 80%, while NO production continually decreased from 0 to 80% (Rubasinghege and Grassian, 2009). HONO production was not reported in this study.

The difference in nitrate photolysis behaviour between grime and other surfaces as a function of RH is indicative of the grime providing a unique environment for the photochemistry. Many different mechanisms for the role of water in surface reactions have been discussed, such as enhancing the mobility of reagents, allowing them to move to more photolabile positions within in the film or enhanced hydrolysis and dissociation of species such as HNO_3, NH_4NO_3 or N_2O_5 producing more of the photolabile precursors (Rubasinghege and Grassian, 2013). The increased reactivity could also be the result of a viscosity change within the film. It known that the viscosity of the particles changes based on relative humidity (Renbaum-Wolff et al., 2013), and therefore, it is expected that the same would be true for the grime, with particles being a source to the film. The film's water uptake/evaporation curve is consistent with continuous viscosity change rather than phase transitions over the RH region studied. In a highly viscous film, the photochemical products are more likely to be trapped and thus recombine. However, a less viscous film would allow for faster diffusion and thus the release of products could become competitive and then dominate in comparison to recombination. Such an impact has recently been suggested to explain a smaller mass loss from illuminated SOA under low RH conditions in comparison to high (Wong et al., 2014), and faster PAH ozonation within an SOA coated particles at high RH as compared to lower RH (Zhou et al., 2013). This sort of behaviour would not be anticipated for a clean glass, or metal oxide surface. The levelling off of product formation at relative humidities greater than 35% could indicate that a critical amount of water has been reached. In the case of a viscosity effect, that would suggest that the process is no longer diffusion limited. Another process that could be playing a role is the re-adsorption of the products to the film, as discussed by Rubasinghege and Grassian (Rubasinghege and Grassian, 2009), which would compete with further growth causing a net levelling off of product formation.

While specific atmospheric implications require a better speciation of products, the production of such species can be discussed in the context of multiple recent field studies. In SHARP 2009, field measurements that there was a photolytic source of HONO within 20m of the ground (Wong et al., 2012; 2013). Studies done in other urban centers such as London (Lee et al., 2015) and Los Angeles (Young et al., 2012) also suggest there is an unknown photochemical HONO source. Many suggest that this source is correlated to NO_2 however, in a study carried out in Bakersfield and Pasedena, the HONO source does not correlate with NO_2 (Pusede et al., 2015). As discussed by those authors, the formation of HNO_3 and its subsequent incorporation into aerosol as ammonium nitrate can extend the lifetime of airborne nitrate, causing the nitrate which is deposited to not correlate temporally with $NO_{2(g)}$. Grime would likely have a similar delayed response; in addition, the RH dependence of the grime photochemistry could serve as a

323 further mechanism for an offset in NO_2 values and HONO production, due to the cycling of RH conditions
324 in the atmosphere and therefore, the cycling of this source strength. However, more quantification and
325 speciation is required to evaluate the importance of such a grime source.
326
327 **5 Conclusions**
328 Urban grime was collected onto glass substrates without modification and illuminated. Grime
329 photochemistry produced nitrogen oxides in the form of NO_2 and/or HONO. Such chemistry is not
330 currently included in urban air models, but could impact NO_x and/or HONO levels in these centers. The
331 production of these species is dependant on RH, again highlighting the need to consider water content when
332 studying environmental surfaces.
333
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337
338 **References**
339 Ammar, R., Monge, M. E., George, C. and D'Anna, B.: Photoenhanced NO_2 Loss on Simulated Urban
340 Grime, Chem Phys Chem, 11(18), 3956–3961, doi:10.1002/cphc.201000540, 2010.

341 Baergen, A. M. and Donaldson, D. J.: Photochemical renoxification of nitric acid on real urban grime,
342 Environ Sci Technol, 47(2), 815–820, doi:10.1021/es3037862, 2013.

343 Baergen, A. M., Styler, S. A., van Pinxteren, D., Muller, K., Herrmann, H. and Donaldson, D. J.: Chemistry
344 of Urban Grime: Inorganic Ion Composition of Grime vs Particles in Leipzig, Germany, Environ Sci
345 Technol, 49(49), 12688–12696, doi:10.1021/acs.est.5b03054, 2015.

346 Bodhaine, B. A., Wood, N. B., Dutton, E. G. and Slusser, J. R.: On Rayleigh Optical Depth Calculations, J
347 Atmos Ocean Tech, 16(11), 1854–1861, doi:10.1175/1520-0426(1999)016<1854:ORODC>2.0.CO;2,
348 2010.

349 Chabas, A., Alfaro, S., Lombardo, T., Verney-Carron, A., Da Silva, E., Triquet, S., Cachier, H. and Leroy,
350 E.: Long term exposure of self-cleaning and reference glass in an urban environment: A comparative
351 assessment, Build Environ, 79, 57–65, doi:10.1016/j.buildenv.2014.05.002, 2014.

352 Chabas, A., Lombardo, T., Cachier, H., Pertuisot, M. H., Oikonomou, K., Falcone, R., Verità, M. and
353 Geotti-Bianchini, F.: Behaviour of self-cleaning glass in urban atmosphere, Build Environ, 43(12), 2124–
354 2131, doi:10.1016/j.buildenv.2007.12.008, 2008.

355 Chabas, A., Lombardo, T., Verney-Carron, A. and Ausset, P.: Predicting the soiling of modern glass in
356 urban environments: A new physically-based model, Atmos Environ, 60(C), 348–357,
357 doi:10.1016/j.atmosenv.2012.06.050, 2012.

358 Demou, E., Visram, H., Donaldson, D. J. and Makar, P. A.: Uptake of water by organic films: the
359 dependence on the film oxidation state, Atmos Environ, 37(25), 3529–3537, doi:10.1016/S1352-
360 2310(03)00430-8, 2003.

361 Diamond, M. L., Gingrich, S. E., Fertuck, K., McCarry, B. E., Stern, G. A., Billeck, B., Grift, B., Brooker,

D. and Yager, T. D.: Evidence for Organic Film on an Impervious Urban Surface: Characterization and Potential Teratogenic Effects, Environ Sci Technol, 34(14), 2900–2908, doi:10.1021/es9906406, 2000.

Diamond, M. L., Melymuk, L., Csiszar, S. A. and Robson, M.: Estimation of PCB Stocks, Emissions, and Urban Fate: Will our Policies Reduce Concentrations and Exposure? Environ Sci Technol, 44(8), 2777–2783, doi:10.1021/es9012036, 2010.

Diamond, M. L., Priemer, D. A. and Law, N. L.: Developing a multimedia model of chemical dynamics in an urban area, Chemosphere, 44(7), 1655–1667, doi:10.1016/S0045-6535(00)00509-9, 2001.

Duigu, J. R., Ayoko, G. A. and Kokot, S.: The relationship between building characteristics and the chemical composition of surface films found on glass windows in Brisbane, Australia, Build Environ, 44(11), doi:10.1016/j.buildenv.2009.02.019, 2009.

Favez, O., Cachier, H., Chabas, A., Ausset, P. and Lefevre, R.: Crossed optical and chemical evaluations of modern glass soiling in various European urban environments, Atmos Environ, 40(37), 7192–7204, doi:10.1016/j.atmosenv.2006.06.022, 2006.

Fiedler, S. E., Hese, A. and Ruth, A. A.: Incoherent broad-band cavity-enhanced absorption spectroscopy, Chem Phys Lett, 371(3-4), 284–294, doi:10.1016/S0009-2614(03)00263-X, 2003.

Finlayson-Pitts, B. J. and Pitts, J. N., Jr: Chemistry of the upper and lower atmosphere: theory, experiments, and applications, Academic Press, San Diego, California. 1999.

Finlayson-Pitts, B. J., Wingen, L. M., Sumner, A. L., Syomin, D. and Ramazan, K. A.: The heterogeneous hydrolysis of NO_2 in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism, Phys Chem Chem Phys, 5(2), 223–242, doi:10.1039/b208564j, 2002.

Gankanda, A. and Grassian, V. H.: Nitrate Photochemistry in NaY Zeolite: Product Formation and Product Stability under Different Environmental Conditions, J Phys Chem A, 117(10), 2205–2212, doi:10.1021/jp312247m, 2013.

Gherman, T., Venables, D. S., Vaughan, S., Orphal, J. and Ruth, A. A.: Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy in the near-Ultraviolet: Application to HONO and NO_2, Environ Sci Technol, 42(3), 890–895, doi:10.1021/es0716913, 2008.

Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Dominé, F., Frey, M. M., Guzmán, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H. W., Klán, P., Lefer, B., McConnell, J., Plane, J., Sander, R., Savarino, J., Shepson, P. B., Simpson, W. R., Sodeau, J. R., Glasow, von, R., Weller, R., Wolff, E. W., Zhu, T.Zhu: An overview of snow photochemistry: evidence, mechanisms and impacts, Atmos Chem Phys, 7, 4329–4373, doi:10.5194/acpd-7-4165-2007, 2007.

Han, C., Liu, Y. and He, H.: Heterogeneous photochemical aging of soot by NO_2 under simulated sunlight, Atmos Environ, 64(C), 270–276, doi:10.1016/j.atmosenv.2012.10.008, 2013.

Handley, S. R., Clifford, D. and Donaldson, D. J.: Photochemical Loss of Nitric Acid on Organic Films: a Possible Recycling Mechanism for NO_x, Environ Sci Technol, 41(11), 3898–3903, doi:10.1021/es062044z, 2007.

Ionescu, A., Lefèvre, R. A., Chabas, A., Lombardo, T., Ausset, P., Candau, Y. and Rosseman, L.: Modeling of soiling based on silica-soda-lime glass exposure at six European sites, Sci Total Environ, 369(1-3), 246–255, doi:10.1016/j.scitotenv.2006.04.009, 2006.

Kwamena, N.-O. A., Clarke, J. P., Kahan, T. F., Diamond, M. L. and Donaldson, D. J.: Assessing the

importance of heterogeneous reactions of polycyclic aromatic hydrocarbons in the urban atmosphere using the Multimedia Urban Model, Atmos Environ, 41(1), 37–50, doi:10.1016/j.atmosenv.2006.08.016, 2007.

Lam, B., Diamond, M. L., Simpson, A. J., Makar, P. A., Truong, J. and Hernandez-Martinez, N. A.: Chemical composition of surface films on glass windows and implications for atmospheric chemistry, Atmos Environ, 39(35), 6578–6586, doi:10.1016/j.atmosenv.2005.07.057, 2005.

Law, N. L. and Diamond, M. L.: The role of organic films and the effect on hydrophobic organic compounds in urban areas: an hypothesis, Chemosphere, 36(12), 2607–2620, doi:10.1016/S0045-6535(97)10222-3, 1998.

Lee, J. D., Whalley, L. K., Heard, D. E., Stone, D., Dunmore, R. E., Hamilton, J. F., Young, D. E., Allan, J. D., Laufs, S. and Kleffmann, J.: Detailed budget analysis of HONO in central London reveals a missing daytime source, Atmos Chem Phys Discuss, 15, 22097–22139, doi:10.5194/acpd-15-22097-2015, 2015.

Lehmann, T.: DOASIS - DOAS Intelligent System, edited by Institute of Environmental Physics, https doasis.iup.uni-heidelberg.de, 2009.

Liu, Q.-T., Chen, R., McCarry, B. E., Diamond, M. L. and Bahavar, B.: Characterization of Polar Organic Compounds in the Organic Film on Indoor and Outdoor Glass Windows, Environ Sci Technol, 37(11), 2340–2349, doi:10.1021/es020848i, 2003.

Lombardo, T., Ionescu, A., Chabas, A., Lefèvre, R. A., Ausset, P. and Candau, Y.: Dose–response function for the soiling of silica–soda–lime glass due to dry deposition, Sci Total Environ, 408(4), 976–984, doi:10.1016/j.scitotenv.2009.10.040, 2010.

Lombardo, T., Ionescu, A., Lefèvre, R. A., Chabas, A., Ausset, P. and Cachier, H.: Soiling of silica-soda-lime float glass in urban environment: measurements and modelling, Atmos Environ, 39(6), 989–997, doi:10.1016/j.atmosenv.2004.10.030, 2005.

Ma, J., Liu, Y., Han, C., Ma, Q., Liu, C. and He, H.: Review of heterogeneous photochemical reactions of NOy on aerosol — A possible daytime source of nitrous acid (HONO) in the atmosphere, J Environ Sci, 25(2), 326–334, doi:10.1016/S1001-0742(12)60093-X, 2013.

Mochida, M. and Finlayson-Pitts, B. J.: FTIR Studies of the Reaction of Gaseous NO with HNO_3 on Porous Glass: Implications for Conversion of HNO_3 to Photochemically Active NO_x in the Atmosphere, J Phys Chem A, 104(43), 9705–9711, doi:10.1021/jp001471a, 2000.

Nanayakkara, C. E., Jayaweera, P. M., Rubasinghege, G., Baltrusaitis, J. and Grassian, V. H.: Surface Photochemistry of Adsorbed Nitrate: The Role of Adsorbed Water in the Formation of Reduced Nitrogen Species on α-Fe_2O_3 Particle Surfaces, J Phys Chem A, 118(1), 158–166, doi:10.1021/jp409017m, 2014.

Nguyen, T. K. V., Capps, S. L. and Carlton, A. G.: Decreasing Aerosol Water Is Consistent with OC Trends in the Southeast US, Environ Sci Technol, 49(13), 7843–7850, doi:10.1021/acs.est.5b00828, 2015.

Oswald, R., Behrendt, T., Ermel, M., Wu, D., Su, H., Cheng, Y., Breuninger, C., Moravek, A., Mougin, E., Delon, C., Loubet, B., Pommerening-Roeser, A., Soergel, M., Poeschl, U., Hoffmann, T., Andreae, M. O., Meixner, F. X. and Trebs, I.: HONO Emissions from Soil Bacteria as a Major Source of Atmospheric Reactive Nitrogen, Science, 341(6151), 1233–1235, doi:10.1126/science.1242266, 2013.

Priemer, D. A. and Diamond, M. L.: Application of the Multimedia Urban Model To Compare the Fate of SOCs in an Urban and Forested Watershed, Environ Sci Technol, 36(5), 1004–1013, doi:10.1021/es001397, 2002.

Pusede, S. E., VandenBoer, T. C., Murphy, J. G., Markovic, M. Z., Young, C. J., Veres, P. R., Roberts, J.

M., Washenfelder, R. A., Brown, S. S., Ren, X., Tsai, C., Stutz, J., Brune, W. H., Browne, E. C., Wooldridge, P. J., Graham, A. R., Weber, R., Goldstein, A. H., Dusanter, S., Griffith, S. M., Stevens, P. S., Lefer, B. L. and Cohen, R. C.: An Atmospheric Constraint on the NO_2 Dependence of Daytime Near-Surface Nitrous Acid (HONO), Environ Sci Technol, 49(21), 12774–12781, doi:10.1021/acs.est.5b02511, 2015.

Reeser, D. I., Kwamena, N.-O. A. and Donaldson, D. J.: Effect of Organic Coatings on Gas-Phase Nitrogen Dioxide Production from Aqueous Nitrate Photolysis, J Phys Chem C, 117, 22260–22267, doi:10.1021/jp401545k, 2013.

Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T. and Bertram, A. K.: Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity, Proc Natl Acad Sci, 110(20), 8014–8019, doi:10.1073/pnas.1219548110, 2013.

Rivera-Figueroa, A. M., Sumner, A. L. and Finlayson-Pitts, B. J.: Laboratory Studies of Potential Mechanisms of Renoxification of Tropospheric Nitric Acid, Environ Sci Technol, 37(3), 548–554, doi:10.1021/es020828g, 2003.

Rubasinghege, G. and Grassian, V. H.: Photochemistry of Adsorbed Nitrate on Aluminum Oxide Particle Surfaces, J Phys Chem A, 113(27), 7818–7825, doi:10.1021/jp902252s, 2009.

Rubasinghege, G. and Grassian, V. H.: Role(s) of adsorbed water in the surface chemistry of environmental interfaces, Chem Commun, 49(30), 3071–3094, doi:10.1039/c3cc38872g, 2013.

Saliba, N. A., Yang, H. and Finlayson-Pitts, B. J.: Reaction of Gaseous Nitric Oxide with Nitric Acid on Silica Surfaces in the Presence of Water at Room Temperature, J Phys Chem A, 105(45), 10339–10346, doi:10.1021/jp012330r, 2001.

Sauerbrey, G. Z.: Use of quartz vibration for weighing thin films on a microbalance, J. Physik. 1959.

Scharko, N. K., Schuette, U. M. E., Berke, A. E., Banina, L., Peel, H. R., Donaldson, M. A., Hemmerich, C., White, J. R. and Raff, J. D.: Combined Flux Chamber and Genomics Approach Links Nitrous Acid Emissions to Ammonia Oxidizing Bacteria and Archaea in Urban and Agricultural Soil, Environ Sci Technol, 49(23), 13825–13834, doi:10.1021/acs.est.5b00838, 2015.

Schuttlefield, J., Rubasinghege, G., El-Maazawi, M., Bone, J. and Grassian, V. H.: Photochemistry of Adsorbed Nitrate, J. Am. Chem. Soc., 130(37), 12210–12211, doi:10.1021/ja802342m, 2008.

Simpson, A. J., Lam, B., Diamond, M. L., Donaldson, D. J., Lefebvre, B. A., Moser, A. Q., Williams, A. J., Larin, N. I. and Kvasha, M. P.: Assessing the organic composition of urban surface films using nuclear magnetic resonance spectroscopy, Chemosphere, 63(1), 142–152, doi:10.1016/j.chemosphere.2005.07.013, 2006.

Stemmler, K., Ammann, M., Donders, C., Kleffmann, J. and George, C.: Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid, Nature, 440(7081), 195–198, doi:10.1038/nature04603, 2006.

Stutz, J., Kim, E. S., Platt, U., Bruno, P., Perrino, C. and Febo, A.: UV-visible absorption cross sections of nitrous acid, J Geophys Res Atmos, 105(D11), 14585–14592, doi:10.1029/2000JD900003, 2000.

Sumner, A. L., Menke, E. J., Dubowski, Y., Newberg, J. T., Penner, R. M., Hemminger, J. C., Wingen, L. M., Brauers, T. and Finlayson-Pitts, B. J.: The nature of water on surfaces of laboratory systems and implications for heterogeneous chemistry in the troposphere, Phys Chem Chem Phys, 6(3), 604–613, doi:10.1039/b308125g, 2004.

Vandaele, A. C., Hermans, C., Simon, P. C., Carleer, M., Colin, R., Fally, S., Mérienne, M. F., Jenouvrier, A. and Coquart, B.: Measurements of the NO_2 absorption cross-section from 42 000 cm^{-1} to 10 000 cm^{-1} (238–1000 nm) at 220 K and 294 K, J Quant Spectrosc Ra, 59(3-5), 171–184, doi:10.1016/S0022-4073(97)00168-4, 1998.

Washenfelder, R. A., Langford, A. O., Fuchs, H. and Brown, S. S.: Measurement of glyoxal using an incoherent broadband cavity enhanced absorption spectrometer, Atmos Chem Phys, 8(24), 7779–7793, doi:10.5194/acp-8-7779-2008, 2008.

Wong, J. P. S., Zhou, S. and Abbatt, J. P. D.: Changes in Secondary Organic Aerosol Composition and Mass due to Photolysis: Relative Humidity Dependence, J Phys Chem A, doi:10.1021/jp506898c, 2014.

Wong, K. W., Tsai, C., Lefer, B., Grossberg, N. and Stutz, J.: Modeling of daytime HONO vertical gradients during SHARP 2009, Atmos Chem Phys, 13(7), 3587–3601, doi:10.5194/acp-13-3587-2013, 2013.

Wong, K. W., Tsai, C., Lefer, B., Haman, C., Grossberg, N., Brune, W. H., Ren, X., Luke, W. and Stutz, J.: Daytime HONO vertical gradients during SHARP 2009 in Houston, TX, Atmos Chem Phys, 12(2), 635–652, doi:10.5194/acp-12-635-2012, 2012.

Wu, R. W., Harner, T. and Diamond, M. L.: Evolution rates and PCB content of surface films that develop on impervious urban surfaces, Atmos Environ, 42(24), 6131–6143, doi:10.1016/j.atmosenv.2008.01.066, 2008a.

Wu, R. W., Harner, T., Diamond, M. L. and Wilford, B.: Partitioning characteristics of PCBs in urban surface films, Atmos Environ, 42(22), 5696–5705, doi:10.1016/j.atmosenv.2008.03.009, 2008b.

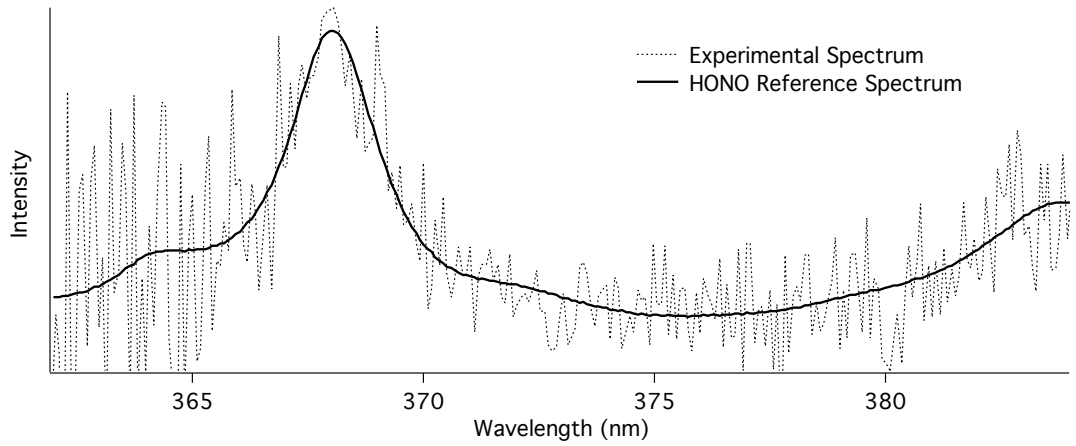
Ye, C., Gao, H., Zhang, N. and Zhou, X.: Photolysis of Nitric Acid and Nitrate on Natural and Artificial Surfaces, Environ Sci Technol, doi:10.1021/acs.est.5b05032, 2016.

Young, C. J., Washenfelder, R. A., Roberts, J. M., Mielke, L. H., Osthoff, H. D., Tsai, C., Pikelnaya, O., Stutz, J., Veres, P. R., Cochran, A. K., VandenBoer, T. C., Flynn, J., Grossberg, N., Haman, C. L., Lefer, B., Stark, H., Graus, M., de Gouw, J., Gilman, J. B., Kuster, W. C. and Brown, S. S.: Vertically Resolved Measurements of Nighttime Radical Reservoirs in Los Angeles and Their Contribution to the Urban Radical Budget, Environ Sci Technol, 46(20), 10965–10973, doi:10.1021/es302206a, 2012.

Zhou, S., Shiraiwa, M., McWhinney, R. D., Poeschl, U. and Abbatt, J. P. D.: Kinetic limitations in gas-particle reactions arising from slow diffusion in secondary organic aerosol, Faraday Disc, 165(0), 391–406, doi:10.1039/c3fd00030c, 2013.

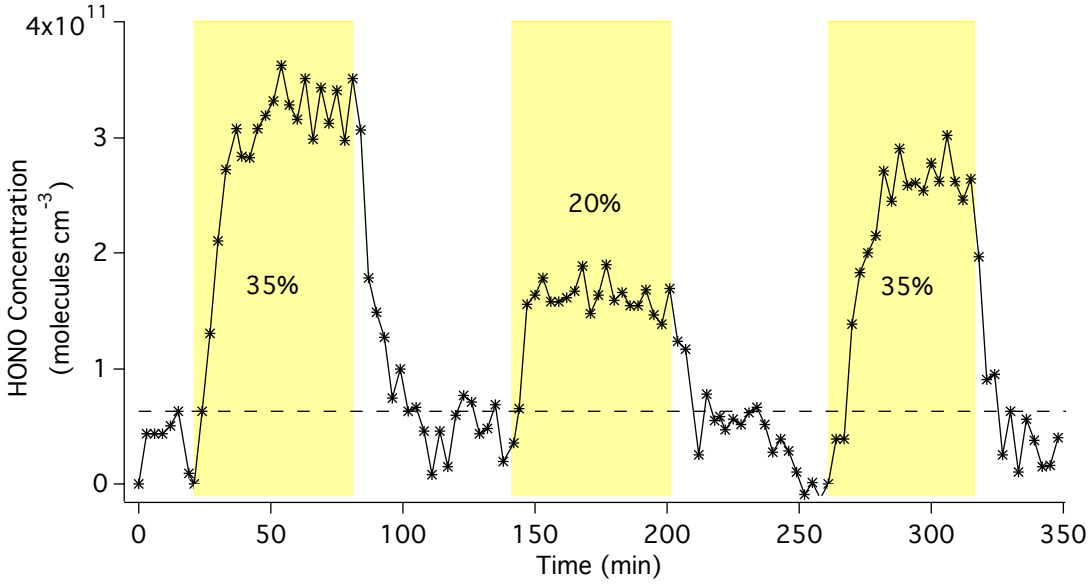
Zhou, X., Gao, H., He, Y., Huang, G., Bertman, S. B., Civerolo, K. and Schwab, J.: Nitric acid photolysis on surfaces in low-NO_x environments: Significant atmospheric implications, Geophys Res Lett, 30(23), 2217, doi:10.1029/2003GL018620, 2003.

Zhou, X., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P. B., Carroll, M. A., Griffith, S., Dusanter, S. and Stevens, P. S.: Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, Nature Geoscience, 4(7), 440–443, doi:10.1038/NGEO1164, 2011.



524

525 **Figure 1: Experimental absorption spectrum fit with a reference HONO spectrum (Stutz et al., 2000) using**
526 **DOASIS (Lehmann, 2009). This spectrum was measured at RH = 37% and represents a concentration of**
527 **2.17×10^{11} molecules cm^{-3}**
528



529

530 **Figure 2: Time trace of an experiment where the sections highlighted in yellow indicate when the sample is**
531 **exposed to light. The relative humidity in the chamber during each illumination period is indicated. The HONO**
532 **detection limit is indicated by the dashed line.**

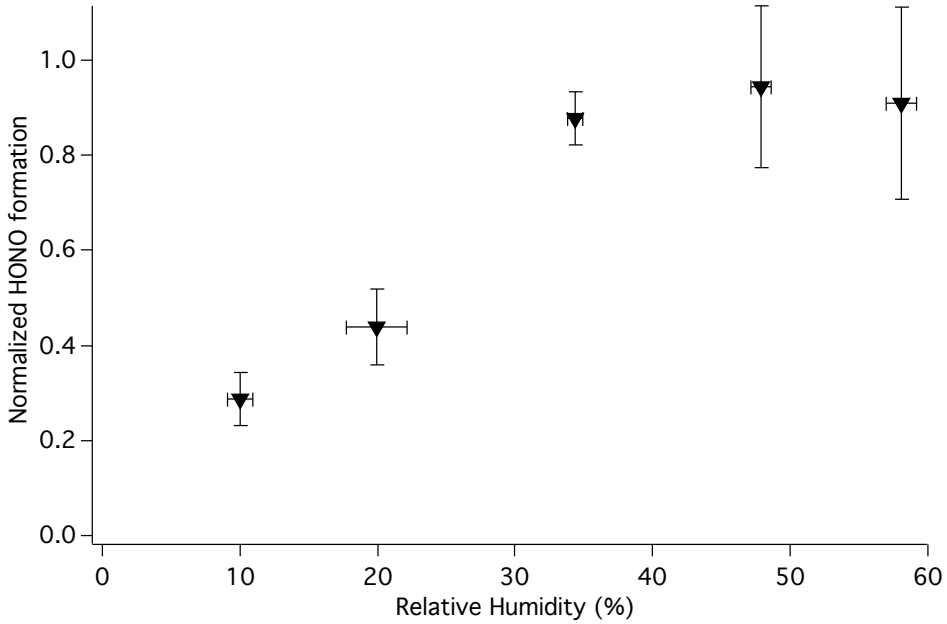


Figure 3: HONO production as a function of relative humidity. Values are normalized to the steady state concentration of HONO formed during an initial illumination period at a relative humidity of 35%. The average of at least 3 measurements on different samples is shown; error bars represent 1 standard deviation.

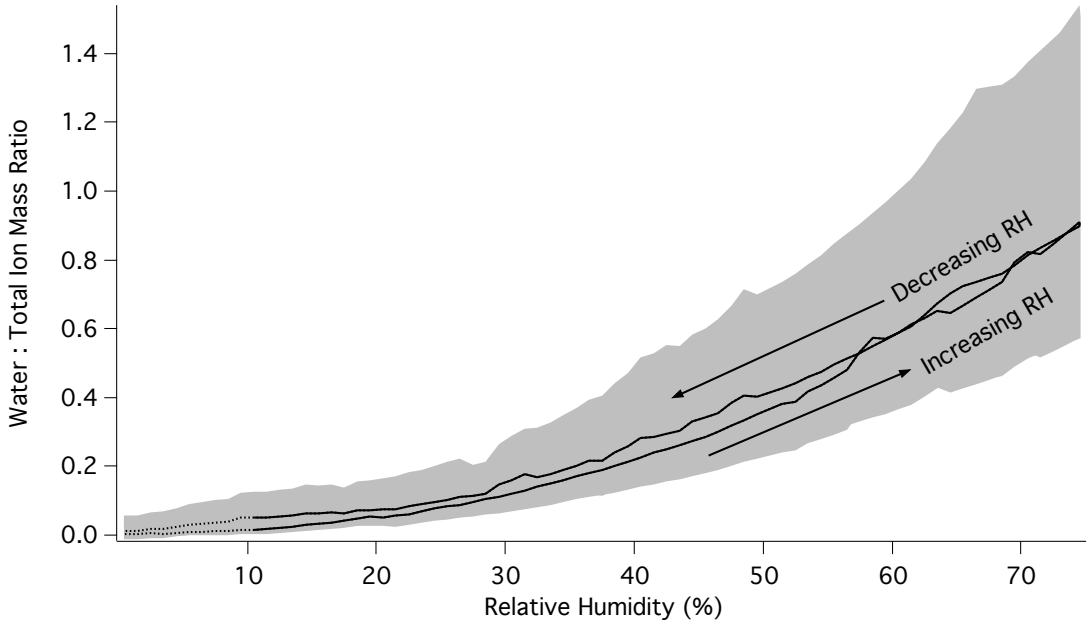


Figure 4: Average ratio of water mass to total ion mass within grime as a function of relative humidity. Water uptake onto clean crystals was subtracted from the grime uptake curves and thus only grime-mediated uptake is shown here. The shaded region indicates a 95% confidence interval base on 16 measurements of different samples.

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