We thank reviewer #1 for the helpful comments. In what follows, we respond (*in italics*) to each point raise in the review.

Specific Comments:

Introduction: Significance of research is clearly stated, and the authors are familiar with the associated literature. The authors may want to discuss or cite the following article that recently appeared in ES&T: Ye et al. "Photolysis of Nitric Acid and Nitrate on Natural and Artificial Surfaces." DOI: 10.1021/acs.est.5b05032

We have added this paper as a citation.

Experimental: Methods and procedures are comprehensible and clear. Ion Analysis: Please provide more details of the composition of the surface grime, if possible–including which ions were analyzed for and found.

A table has been added to the supplementary information of the ion content of grime samples used for the photochemistry experiments. The ion content of the grime samples used for the water uptake normalization will be presented and discussed in detail in an upcoming publication.

Results: Photochemical production of nitrogen oxides: Pg. 5, s 26: I don't find an Eq. 1; perhaps delete "via Eq. (1)" in this sentence?

This equation should have appeared in the pdf file submitted; we will ensure it does not get omitted in the final version.

Pg. 5, s 31: This sentence is unclear to me. When the products decreased in the light vs dark by 60%, are you referring to the NO2 controlled experiment? If so, it might be helpful to explicitly state it. Also, the NO2 controlled experiments were carried out with high NO2 concentrations that do not necessary reflect possible NO2/HONO levels in the photolysis experiments.

We have clarified that we are talking about the NO_2 control experiments in the manuscript. The concentrations used for these control experiments are quite close to those detected in the grime experiments. In the control light experiments approximately $6x10^{11}$ molecules/cm^3 are detected in comparison to a range of 3.5 $x10^{11}$ molecules/cm^3 to 6.5 $x10^{11}$ molecules/cm^3 for the initial illumination of grime samples at a relative humidity of 35%. Thus, we expect these control experiments to reflect what is happening in the grime experiments. We have clarified that it is this diluted concentration that we are using.

Once nitrite is formed, it needs to be protonated for it to be desorbed as HONO (g). It would be interesting to know the pH of the urban grime coated on the glass beads. Since HONO is the dominate nitrogen (III) species below pH 3 (and HONO is emitted in this study), I'm guessing that the urban grime coated on glass beads would be more on the acidic side. The reason why I mention pH is because I am wondering how much nitrite is on the surface; and I am thinking about it in regards to surface pH and to the acid

displacement process proposed by VandenBoer. If the photolyzed urban grime contains liberal amounts of nitrite, and if exposed to gas phase acids, there is potential for additional HONO production.

In a previous study (ES&T, 2015), we have suggested that the grime may actually be somewhat basic due to a complete loss of ammonium, something that we would not expect from an acidic film. If HONO is being formed directly in the photochemistry (which we cannot confirm with the present study), we anticipate that it is not via the protonation of nitrite but rather arises from secondary chemistry of NO_2 formed from nitrate photolysis, for example, photoreduction of NO_2 or NO_2 hydrolysis, or perhaps due to photochemistry of any organic nitrogen species within the film. We have expanded the discussion of possible ways in which HONO could be formed.

Pg. 6, s 8-11: Clarify the rationale for using nitrate to sulfate ratios as an indicator. If I am understanding this correctly, there was a depletion in gas phase reactive nitrogen oxides, but no change in the amount of nitrate, yet there was a decrease in the amount of sulfate? It would be helpful to have a table in the SI showing concentration of the ions before and after illumination.

Sulfate is not anticipated to be photolabile and thus we use sulfate as a means to normalize the nitrate concentration to the amount of grime. The bulk of the mass measured is due to the mass of beads, so normalizing to an ion within the film is a more precise method for seeing changes in nitrate rather than normalizing to the mass of sample. This ratio was used in our previous study, which showed a depletion of the nitrate to sulfate ratio when the grime was exposed to light. We have clarified the wording of this section.

Discussion: Pg. 7, s 25: The growth of the non-photoactive proportion of the films is dependent on the duration of the collection time and probably also dependent on it being shielded from precipitation.

We have included being shielded from precipitation as another factor that could influence the non-photoactive fraction.

Pg. 8: In the results section, the change in the nitrate to sulfate ratio is reported, but there is no mention of the ratio in the discussion. Is there a link between the nitrate to sulfate ratio and the water content of the film?

The nitrate to sulfate ratio was introduced to show that no nitrate loss was detected from samples that were illuminated. This lack of detected loss is discussed on pg 7. The link between nitrate to sulfate ratio and water content is an interesting question, but goes beyond the scope of this study. We will hopefully investigate this in the future.

In the Supplement: Sentence 8: The authors refer to an "Equation 1," but I did not find this anywhere.

See above about equation 1

Figure S1a: This figure is somewhat unclear. The figure is showing the amount of NO2 and HONO measured when 6 ppm of NO2 is flowed through the chamber and cell as a function of RH? If so, the NO2 to HONO conversion is higher than I would have thought. I am surprised to see more HONO than NO2. Is this related to the very high concentrations of NO2 used (6 ppm)?

We have added some clarification concerning the NO_2 concentration being flowed through the chamber. The conversion is indeed surprising! The concentrations we used led to similar concentrations when the NO_2 stream was illuminated as when the grime was illuminated, and thus this suggests is a reasonable expectation that a similar high conversion would be happening for sample illumination.

We thank reviewer #2 for the helpful comments. In the following, we respond (*in italics*) to each point raised in the review

Specific Questions: 1. Page 6, line 180. In photolysis experiments, authors allowed the signal to return to baseline for 60 min. Highlighting that gas phase NO2 decrease as a function of RH, have authors considered any secondary reactions of HONO or NO2, i.e. acid hydrolysis of NO2, during the 60min dark periods of the experiment?

The drop off in detected HONO is quite rapid, with time taken to reach baseline thought to be due to the lifetime of the carrier gas pass through the apparatus rather than significant secondary chemistry. Since the source of HONO/NO2 is turned off in the light, even if secondary chemistry is happening, the products would quickly decrease in concentration because the primary source has been removed. Secondary chemistry is possible, but with the data we currently have, it would be difficult to say with any certainty.

2. Page 7, line 234. Since the inorganic nitrate does not show a direct link to the source of gas-phase nitrogen species and authors speculate that organo-nitrate may have a role, have authors considered investigating the change in the total nitrogen in grime samples before and after photochemical experiments.

This is an interesting suggestion for further study.

3. Page 8, line 267. The work cited here by Grassian and co-workers have reported decrease in %nitrate loss between %RH 20 and 80, due to increase in re-adsorption of gas phase NO2 at higher RHs. Did authors notice similar observation(s) in the current study? Can this be one of the dark reaction occurring during the above mentioned 60 min dark period?

We only studied nitrate loss from samples illuminated at an RH of 35%, however, the gas phase products do not suggest that this re-adsorption is as important, as it was in the Grassian study. We do not see the decrease in products at higher relative humidities, only a leveling off. However, such a process cannot be ruled out as possibly contributing to this leveling off. We have included this possibility in the manuscript in an expanded discussion of the product formation above 35%.

4. Page 7, line 215. The water uptake on grime seems to follow more like a condensation isotherm rather than a typical water adsorption isotherm with a monolayer formation. If this is the case, does the multilayers formation of water block surface sites or limit photolysis products after %RH 35?

We do not see a decrease in products, only a leveling off. This suggests that the water is not playing a significant role in hindering the photolysis products. Further study looking at relative humidities beyond 60% could help determine this aspect in the role of water for the chemistry.

We thank reviewer #3 for the helpful comments. In the following, we respond (*in italics*) to each of the points raised in the review.

Only gaseous HONO has been observed, and the authors argue that it might be due to NO2 undergoing wall losses in their reactor (acting also as a HONO source). However, HONO is lost more efficiently on surfaces than NO2. Therefore the same argument holds for HONO too i.e., this compound should also then be lost on the walls of the reactor. Also, wall losses are expected to increase with increasing humidity, and there- fore the yield of products should decrease with increasing RH, while the authors do observed opposite trends. Maybe they could/should comment describe in slightly more details potential wall losses.

This was a surprising observation, but the hypothesis of NO_2 wall hydrolysis was due to the observations from flowing NO_2 through the apparatus. In these experiments, although NO_2 was entering the system, only HONO was observed under illumination. Moreover, the HONO concentration did not change with relative humidity for this control experiment. These were the observations that led to the conclusion that NO_2 and HONO could not be distinguished under the experimental conditions. We have updated the wording to make this more clear.

It is possible that the observation made here is real i.e., only HONO is photochemical produced from urban grime as previously discussed for proxy of urban grime made of PAHs?

We have included this as one of the possible mechanisms that could explain the product formation. It is definitely possible that only HONO is being produced, we just cannot confirm this with our present set up.

Also, no nitrate loss was observed in contradiction with previous studies from the same group. It is argued that this due to the age of the film (aged vs. fresh). Do the authors mean that with ageing nitrate anions are converted into something else? Do the authors point toward the formation of organo-nitrate, and subsequent photochemistry? Otherwise, I do not follow the argument in which ageing prevents nitrate loss. . . Maybe the authors could comment on that?

When we integrated the amount of gas-phase products and convert to the corresponding nitrate mass loss expected from the film, the expected loss is below our detection limit and thus we cannot conclude that no nitrate was loss, it is just a lower percentage than what has been previously seen. We discuss ageing as a possibility for this low

percentage nitrate loss in addition to the possibility of organic nitrogen playing a role. Ageing could result in the film growing in thickness and thus photoactive sites and photoactive components may be buried becoming unreactive, with only the fresh deposits reacting. This explanation has been added to the manuscript.

Altogether, the two arguments above may suggest that HONO formation is not just due to nitrate anions photolysis, but could involve also organo nitrate or metallic complexes. Maybe the authors could strengthen their discussion on this possible pathway.

We have broadened the discussion around formation mechanisms for HONO.

Increasing humidity creates less acidic surfaces (as shown in Figure 4) but more HONO. Is this not a contradiction, as HONO would stick more to less acidic surfaces? Was NO2 measured at higher RH?

An increase in humidity results in a more dilute mixture of ions, however the above statement assumes an initially acidic film. From previous measurements (ES&T, 2015), we have concluded that the film may actually be basic due to the complete loss of ammonium from the film, which would not be expected in an acidic environment. A mention of this was added to the manuscript.

As stated by the reviewer, a less acidic surface would favour HONO to stick. Because this is not what was observed, the role of water seems to be less in controlling the pH, but rather in controlling the viscosity or mobility of reactants as discussed within the manuscript. Another possibility is that the HONO being measured is all from surface hydrolysis of an NO_2 photoproduct on the walls of the apparatus, rather than from direct formation from grime photochemistry. In that case a much smaller pH dependence would be expected. NO_2 was never detected in the grime experiments and in the control experiments less NO_2 was detected at higher RH.

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

72 formation of biogenic secondary organic aerosol (Nguyen et al., 2015). Related to grime surfaces, Sumner

73 *et al.* have shown how different surfaces, representing building surfaces, vary in their water uptake

74 behaviour (Sumner et al., 2004). There are only minimal studies performed looking at water interactions

75 with grime, but they show that grime films impact water uptake on surfaces (Baergen and Donaldson, 2013;

76 Chabas et al., 2014). Thus it is important to characterize the change in surface water content as a function

77 of RH as well as grime photochemistry. In the following we present results of experiments, which monitor

78 the photochemical release of gas phase nitrogen oxides from urban grime as a function of RH, in

79 conjunction with water uptake measurements on grime.

80

81 **2. Experimental**

82 **2.1 Sample collection**

83 Grime samples were collected by placing the substrate, either 3 mm diameter glass beads (Fisher Scientific)

84 or quartz crystal microbalance (QCM) crystals, outside in downtown Toronto, Canada for up to one year.

85 The beads were placed on metal mesh shelves underneath a building overhang, sheltering the sampler from

86 precipitation. Sunlight was blocked with a black cloth covering the front of the sample and a building

87 blocking the sunlight from the other direction. The QCM crystals were placed in holders where the face of

88 the crystal was facing the ground while the back was within the holder, preventing the collection of grime

89 on this backside, which would impact the QCM response. In this way both types of samples were shielded

90 from light and precipitation while still being open to the atmosphere.

91 **2.2 Incoherent Broad Band Cavity Enhanced Spectroscopy (IBBCEAS)**

92 Gas phase product formation was determined using IBBCEAS. The system is described in full elsewhere

93 (Reeser et al., 2013). Briefly, a 10 W LED with a maximum intensity at 372 nm, was focused into a 100 cm

94 cell. The cell was sealed with two highly reflective mirrors (>99.95% between 367nm and 380nm). The

95 light escaping through the back mirror was collected by a lens and focused onto a fiber optic bundle, which

96 was directed into a spectrograph with a CCD detector. The mirrors were continually purged using a flow

97 rate of 25 mL/min of N_2 directed onto the mirror surfaces. Transmission spectra were collected for 30 s

98 (averages of 30 scans with an integration time of 1 s each) over a wavelength range of 362 nm to 385 nm.

99 The concentrations of HONO and NO_2 were calculated using the method described by Fiedler and

100 Gherman (Fiedler et al., 2003; Gherman et al., 2008) and previously used by us (Reeser et al., 2013). This

101 uses measured mirror reflectivity (Washenfelder et al., 2008), Rayleigh cross sections of the carrier gas

102 (Bodhaine et al., 2010) and the absorption cross sections of NO_2 (Vandaele et al., 1998) and HONO (Stutz

103 et al., 2000) to fit the experimental spectra with DOASIS software (Lehmann, 2009). DOASIS uses a linear

104 least-squares method to fit the absorption bands to reference spectra and a polynomial to fit broad features

105 such as those from Rayleigh scattering, Mie scattering and temperature drifts. The fit is optimized by

106 including terms that allow for small shifts in absorption wavelengths and spread of peaks. A sample fit is

107   displayed as the solid line in Fig. 1. Calculated detection limits (signal/noise = 3) are 1.50×10^{11} molecules

108   cm^{-3} (~6ppb) for NO_2 and 6.5×10^{10} molecules cm^{-3} (~3ppb) for HONO.

109

110   **2.3 Photochemistry**

111   Samples of 10.0g of exposed glass beads were weighed into a glass petri dish for illumination. These were

112   placed within a stainless steel chamber (3.2" x 2.2" x 1.5") and nitrogen was flowed through the chamber

113   into the IBBCEAS cell at a rate of 0.3 L/min. RH and temperature in the chamber were monitored using a

114   Traceable® Memory Hygrometer/Thermometer. The reported accuracy is ± 2% at mid-range and ± 4%

115   elsewhere in the range of 10 to 95% RH. The calibration was checked by measuring the RH above a series

116   of saturated salt solutions in comparison to the known deliquescent RH and was the same as the reported

117   values within the stated uncertainties.

118   Nitrogen was flowed through the system for one hour prior to illumination to establish a stable background

119   in the spectrum, and equilibrate the water vapour in the chamber for the RH used in the experiment. The

120   samples, initially at a RH of 35%, were illuminated through a quartz window at the top of the sample

121   chamber with a Xe arc lamp (λ>295nm) for 60 min. The light was then blocked, the signal allowed to

122   return to baseline, and the RH adjusted for the next illumination period. After 60 min the sample was again

123   illuminated for 60 min before blocking the light and repeating the cycle for a third time. Average

124   concentrations were calculated for the second 30 min of illumination, where the signal appeared to reach

125   steady state, and then normalized to the initial steady state value at the RH of 35% to adjust for experiment

126   variability such as variations in sample, light intensity and temperature. These experiments were carried

127   out without temperature control, with the chamber operating at a temperature between 28 and 34 °C during

128   illumination.

129   Control experiments were carried out in which 10.0 g of clean beads were illuminated for one hour at a

130   relative humidity of 35%. In addition, 10.0 g of the grime coated beads were subjected to heating up to

131   36°C to study the impact of increased temperature on product formation. Both of these tests were

132   completed in triplicate with a different sample being used each time. Neither experiment showed

133   detectable levels of HONO or NO_2.

134

135   The set up was further tested by flowing a known concentration of NO_2 through the empty chamber and

136   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 ± 2.4)

137     $\times 10^{12}$ molecules/cm^3 at varying RHs. NO_2 and HONO steady state concentrations measured at each RH

138   were used to characterize the IBBCEAS response to changes in humidity and the efficiency of NO_2

139   hydrolysis to HONO on the walls of the reaction chamber and IBBCEAS cell.

140

141   **2.4 Ion analysis**

142   Two different ion extraction techniques were used. For ion analysis of the illuminated beads, 4.0 g of

143   grime-coated beads were shaken for 5 minutes with 3.00 mL of deionized water with a resistivity of greater

144   than 18 MΩcm (Baergen et al., 2015). For ion analysis to accompany water uptake measurements, samples

145   were collected on 5 cm x 7.6 cm pieces of window glass over the same time period as the quartz crystals

146   and extracted with 45 mL deionized water. Glass samples were first placed in 25mL of water and sonicated

147   for 1 min. Each side of the glass was then washed twice with 5mL of water. Solutions were filtered

148   through a 0.2 μm IC Millex®-LG syringe filter before being analyzed by ion chromatography on a Dionex

149   ICS-2000. 1.33 mL samples were injected onto a concentrator/analytical column system: Ionpac® TAC-

150   ULP1/AS19 with KOH eluent for anion detection and Ionpac® TCC-ULP1/CS17 with methanesulfonic acid

151   eluent for cation detection. A second extraction resulted in concentrations of less than 10% of the first

152   extraction for all ions. The inorganic ion content of the grime used for photochemistry experiments is

153   given in Table S1.

154   **2.5 Water Uptake**

155   The mass of water taken up onto an urban grime film as a function of RH was measured using a quartz

156   crystal microbalance (QCM), as described in Demou et al (Demou et al., 2003). Grime was collected

157   directly onto a quartz crystal and then placed in the QCM. The QCM was housed in a plexiglass chamber

158   whose humidity was increased by flowing air through a water bubbler at room temperature at a variable

159   flow rate to maintain a rate of change of RH of 1%/min and decreased by flowing dry air through the

160   chamber at variable flow rates to maintain a rate of change of -1%/min. The frequency change of the

161   microbalance from the change in water content of the film was converted to a mass using the Sauerbrey

162   equation ($\Delta m = C\Delta f$) where Δm is the mass change, C is a proportionality constant and Δf is the frequency

163   change from the deposited mass. In a previous study, the Sauerbrey relationship was confirmed to hold for

164   this apparatus only up to 1% of the fundamental frequency of the crystal (Demou et al., 2003). Due to this

165   mass restriction, samples for QCM analysis were collected for only four weeks instead of the 1 year for the

166   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

167   inch, 6 MHz crystals used in this study (Sauerbrey, 1959). The RH was measured using a Traceable®

168   Memory Hygrometer/Thermometer.

169   **3 Results**

170   **3.1 Photochemical Production of nitrogen oxides**

171   Figure 1 shows a typical absorption spectrum collected upon illumination of a grime sample. One can see

172   two features, typical of HONO absorption, a stronger signal at 368nm, and a second peak appearing at

173   384nm, at the longer edge of our wavelength range. The IBBCEAS is also sensitive to NO_2, which absorbs

174   in this wavelength region. However, this molecule was not detected in any of the photochemical

175   experiments performed here. We argue in the Supplementary Information that NO_2 hydrolysis on the walls

176   of the chamber and/or IBBCEAs cell via Eq. (1) (Finlayson-Pitts et al., 2002) would prevent NO_2 from

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

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

178   uncertainty as to whether the HONO we observe in the illumination experiments was originally NO_2, which

179   was hydrolyzed prior to detection, or if it is HONO being produced directly from the sample. Therefore,

180   we cannot attribute the observed HONO product exclusively to direct photochemistry of the grime sample;

181   rather we use the HONO signal to indicate the combined total emission of NO_2 and HONO. We further

182   note that the total product detected decreases when NO_2 is flowed through the apparatus in the light as

183   compared to in the dark by approximately 60%, indicating gas phase photolysis of products (see Fig. S1).

184   This highlights the importance of such considerations to be made whenever HONO and NO_2 are being

185   measured. Each system needs to be classified individually over a range of RH conditions.

186

187   Figure 2 depicts the results of a typical experiment where a grime sample is placed within the chamber and

188   exposed to three separate 60 min illumination periods at different relative humidities.   The yellow

189   highlighted regions indicate illumination. It is clear that nitrogen oxides are released to the gas phase

190   during illumination and that the amount of products formed is dependent on the relative humidity. A repeat

191   illumination of a sample at an RH of 35% showed an average ratio of 0.88 ± 0.06 compared to the original

192   illumination. This provides evidence of some precursor depletion due to illumination, however, the much

193   smaller signals at 20% RH indicate that the RH dependence, apparent in Fig. 2, is related to the formation

194   of nitrogen oxides and not merely due to sample depletion. The nitrate to sulfate ratio of the grime before

195   and after illumination was used to examine nitrate behaviour.   Sulfate is not expected to have any

196   photoreactivity on the film and thus was used to account for sample variability as was done in our previous

197   work (Baergen et al., 2015). No nitrate loss was detected between water extracts of beads before and after

198   illumination at 35% for three one-hour periods. The average change in the nitrate to sulfate ratio from

199   before to after illumination was 3.6 ± 6.6 %. There was also no nitrate loss detected for the samples that

200   were heated for three hours; these show an average change in the nitrate to sulfate ratio from before to after

201   heating of 1.0 ± 3.6 %. The amount of nitrate loss expected during illumination, based on the integrated

202   amount of gas phase nitrogen oxides produced, is in agreement with the above results.

203

204   In order to further investigate the RH dependence on product formation, the initial illumination period at

205   35% RH was used to normalize the concentrations detected for the next illumination periods. This data is

206   shown for a range of RH values in Fig. 3. Up to an RH of approximately 35% the amount of products

207   formed increases, after which product formation becomes independent of RH. At a RH of 0%, no products

208   were detected.   However, from the NO_2 control experiments, there was evidence that gas phase

209   NO_2/HONO is lost to the chamber walls for these dry conditions, and thus this value was not reported.

210

211   **3.2 Water uptake by grime samples**

212   This interesting RH dependence of the amount of nitrogen oxides emitted photochemically from urban
213   grime motivates the study of water uptake onto grime. Grime-water interaction has been reported before
214   using ATR-FTIR with 1 week old grime, showing equilibrium with ambient water vapour (Baergen and
215   Donaldson, 2013). Chabas et al also reported that mass measurements on 100 month old films showed
216   enhanced water uptake on grime-coated substrates compared to clean ones (Chabas et al., 2014). Here we
217   use 4 week old samples collected throughout the year-long collection onto the glass beads, and look at both
218   water uptake and evaporation, to better probe water-grime interactions. The uptake and loss curves
219   displayed in Fig. 4 are an average of 16 curves collected at different time points through the year
220   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
221   a glass slide exposed to the atmosphere for the same length of time as the quartz crystal and scaled to the
222   same surface area as the crystal. The shaded region indicates the 95% confidence interval. The water uptake
223   onto a clean crystal was subtracted from each sample uptake before averaging, so the figure displays the
224   mass of water taken up mediated by the grime itself. The degree of uncertainty captures some of the
225   seasonality of grime water uptake, which will be discussed in an upcoming paper along with the seasonality
226   of grime ion content. The water uptake onto and evaporation from grime are both smooth curves, with no
227   indication of phase changes over the RH values spanned here. The lack of hysteresis also gives confidence
228   that the illumination experiments reflect the true state of the "real" urban grime, as the film remains
229   equilibrated with the ambient RH as this changes.

230

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

7

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

286 (Zhou et al., 2003). Humidity dependence has also been seen for nitrate photochemistry on mineral dust
287 surfaces. In this case, a minimum was seen for nitrate loss and NO_2 production at 0% and a maximum at
288 20% which subsequently decreased between 20 and 80%, while NO production continually decreased from
289 0 to 80% (Rubasinghege and Grassian, 2009). HONO production was not reported in this study.
290
291 The difference in nitrate photolysis behaviour between grime and other surfaces as a function of RH is
292 indicative of the grime providing a unique environment for the photochemistry. Many different
293 mechanisms for the role of water in surface reactions have been discussed, such as enhancing the mobility
294 of reagents, allowing them to move to more photolabile positions within in the film or enhanced hydrolysis
295 and dissociation of species such as HNO_3, NH_4NO_3 or N_2O_5 producing more of the photolabile precursors
296 (Rubasinghege and Grassian, 2013). The increased reactivity could also be the result of a viscosity change
297 within the film. It known that the viscosity of the particles changes based on relative humidity (Renbaum-
298 Wolff et al., 2013), and therefore, it is expected that the same would be true for the grime, with particles
299 being a source to the film. The film's water uptake/evaporation curve is consistent with continuous
300 viscosity change rather than phase transitions over the RH region studied. In a highly viscous film, the
301 photochemical products are more likely to be trapped and thus recombine. However, a less viscous film
302 would allow for faster diffusion and thus the release of products could become competitive and then
303 dominate in comparison to recombination. Such an impact has recently been suggested to explain a smaller
304 mass loss from illuminated SOA under low RH conditions in comparison to high (Wong et al., 2014), and
305 faster PAH ozonation within an SOA coated particles at high RH as compared to lower RH (Zhou et al.,
306 2013). This sort of behaviour would not be anticipated for a clean glass, or metal oxide surface. The
307 levelling off of product formation at relative humidities greater than 35% could indicate that a critical
308 amount of water has been reached. In the case of a viscosity effect, that would suggest that the process is
309 no longer diffusion limited. Another process that could be playing a role is the re-adsorption of the
310 products to the film, as discussed by Rubasinghege and Grassian (Rubasinghege and Grassian, 2009),
311 which would compete with further growth causing a net levelling off of product formation.
312
313 While specific atmospheric implications require a better speciation of products, the production of such
314 species can be discussed in the context of multiple recent field studies. In SHARP 2009, field
315 measurements that there was a photolytic source of HONO within 20m of the ground (Wong et al., 2012;
316 2013). Studies done in other urban centers such as London (Lee et al., 2015) and Los Angeles (Young et
317 al., 2012) also suggest there is an unknown photochemical HONO source. Many suggest that this source is
318 correlated to NO_2 however, in a study carried out in Bakersfield and Pasedena, the HONO source does not
319 correlate with NO_2 (Pusede et al., 2015). As discussed by those authors, the formation of HNO_3 and its
320 subsequent incorporation into aerosol as ammonium nitrate can extend the lifetime of airborne nitrate,
321 causing the nitrate which is deposited to not correlate temporally with $NO_{2(g)}$. Grime would likely have a
322 similar delayed response; in addition, the RH dependence of the grime photochemistry could serve as a

9

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

337

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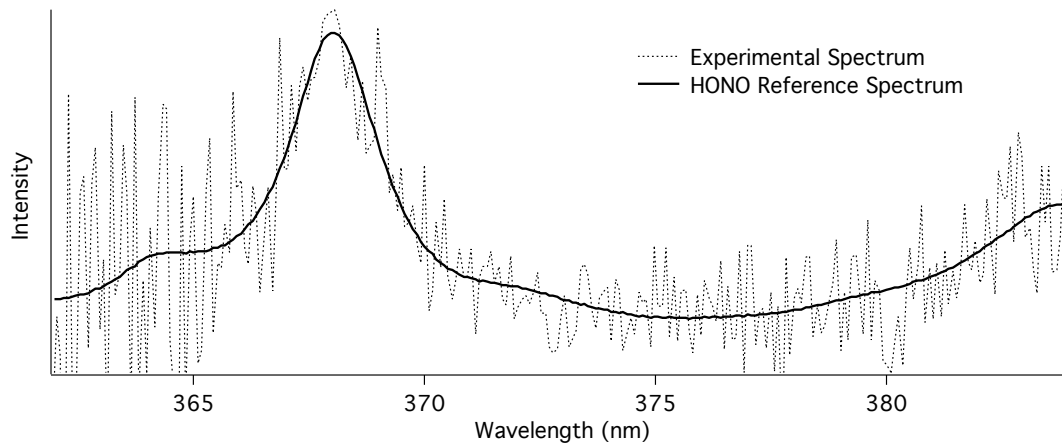
**Figure 1: Experimental absorption spectrum fit with a reference HONO spectrum (Stutz et al., 2000) using DOASIS (Lehmann, 2009). This spectrum was measured at RH = 37% and represents a concentration of 2.17×10^{11} molecules cm^{-3}**
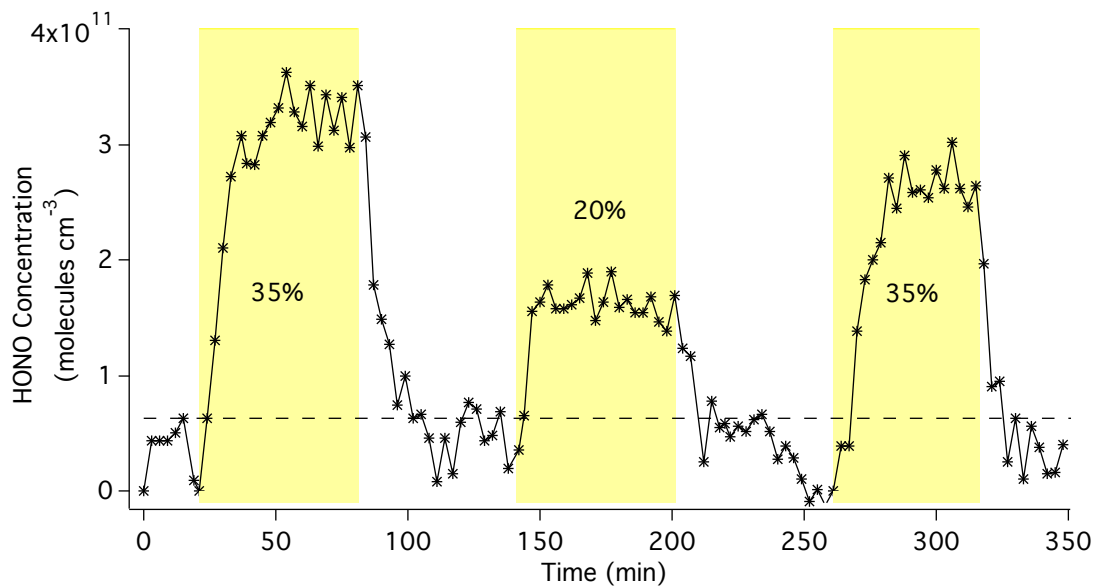

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Figure 2: Time trace of an experiment where the sections highlighted in yellow indicate when the sample is exposed to light. The relative humidity in the chamber during each illumination period is indicated. The HONO detection limit is indicated by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

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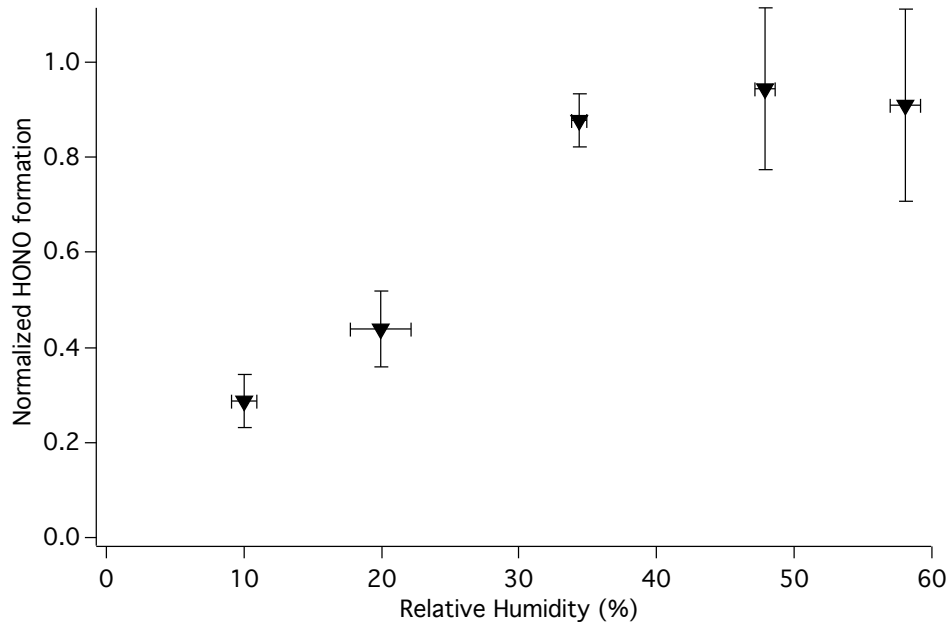
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534 **Figure 3: HONO production as a function of relative humidity. Values are normalized to the steady state**
535 **concentration of HONO formed during an initial illumination period at a relative humidity of 35%. The average**
536 **of at least 3 measurements on different samples is shown; error bars represent 1 standard deviation.**
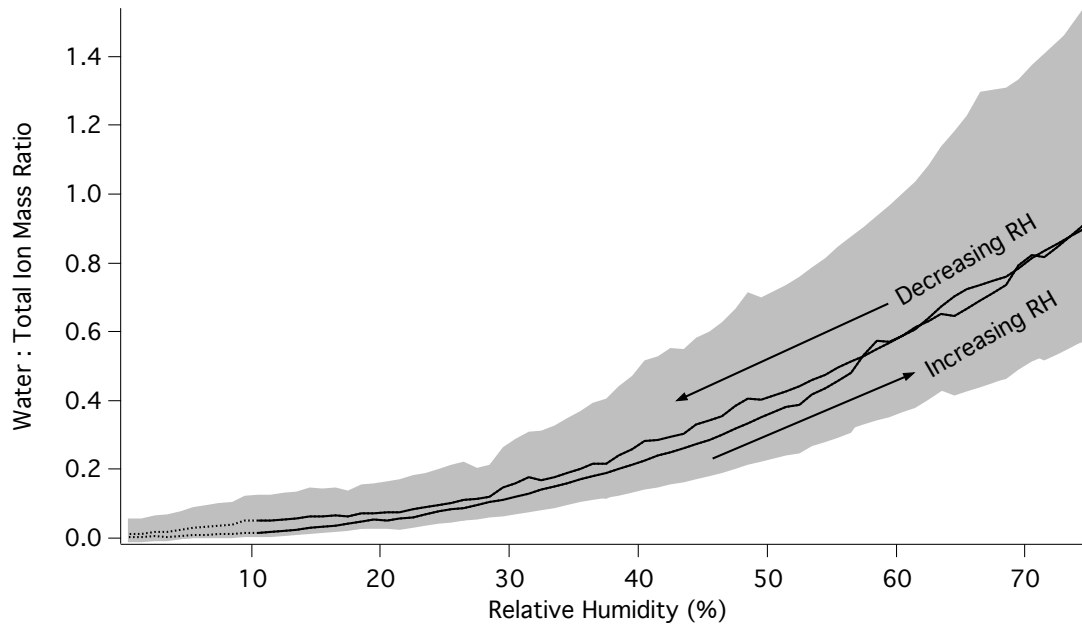
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538 **Figure 4: Average ratio of water mass to total ion mass within grime as a function of relative humidity. Water**
539 **uptake onto clean crystals was subtracted from the grime uptake curves and thus only grime-mediated uptake is**
540 **shown here. The shaded region indicates a 95% confidence interval base on 16 measurements of different**
541 **samples.**

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S1. Characterization of Experimental Chamber

Known amounts of NO_2 in N_2 were flowed through the sample illumination chamber and IBBCEAS cell in order to characterize the observed HONO for different experimental variables. The current set up facilitates an efficient NO_2 surface hydrolysis, forming HONO. Results are shown in Fig. S1 for both dark and light experiments as a function of RH. An input NO_2 concentration of 6.0 ppm, based on the reported value from the supplier (Linde), was further diluted with N_2 using needle valves and mass flow meters with uncertainties of $\pm$ 0.5 mL/min to a concentration of (4.76 ± 2.4) x10^{12} molecules/cm^3. The figure displays the measured NO_2 and HONO concentrations detected by the IBBCEAS as a function of RH. The calculated total concentration measured from the sum of NO_2 and twice the HONO, following the mass balance implied by Equation 1, was (3.6 ± 0.3) x10^{12} molecules/cm^3 which is within error of that calculated from the NO_2 concentration coming from the cylinder reported above. This suggests that this technique can quantify the total concentration of NO_2 + HONO here, though cannot accurately speciate NO_2 and HONO. Fig. S1b shows that the total concentration decreases upon illumination, due to the photolysis of NO_2 and HONO. The HONO concentration measured is independent of relative humidity within the 30% coefficient of variability measured between samples. No NO_2 was detected. This shows that the NO_2 to HONO conversion is complete within error, and that there is no significant impact on the IBBCEAS NO_2 + HONO response as a function of relative humidity. We note that if the photochemical product distribution between NO_2 and HONO changes with relative humidity, this will impact the total amount measured, because it takes two NO_2 molecules to make one HONO molecule. Thus a change from only NO_2 production to only HONO production would appear as a 50% change in the total amount detected as HONO. However, the changes measured as a function of RH are larger than can be explained by this mechanism.

Thus the total product concentrations from grime photochemistry may be safely compared as a function of RH. No values are shown below 13% in Fig. 3 and Fig. S1 because the RH meter is not sensitive below 10% and thus we cannot accurately report RH values. As well, when N_2 is flowed through the chamber without humidification, the total signal for NO_2 and HONO does not reach a plateau even after one hour. This indicates that the NO_2 is being irreversibly lost to the walls, likely forming complexes with the metal (Nishino and Finlayson-Pitts, 2012).
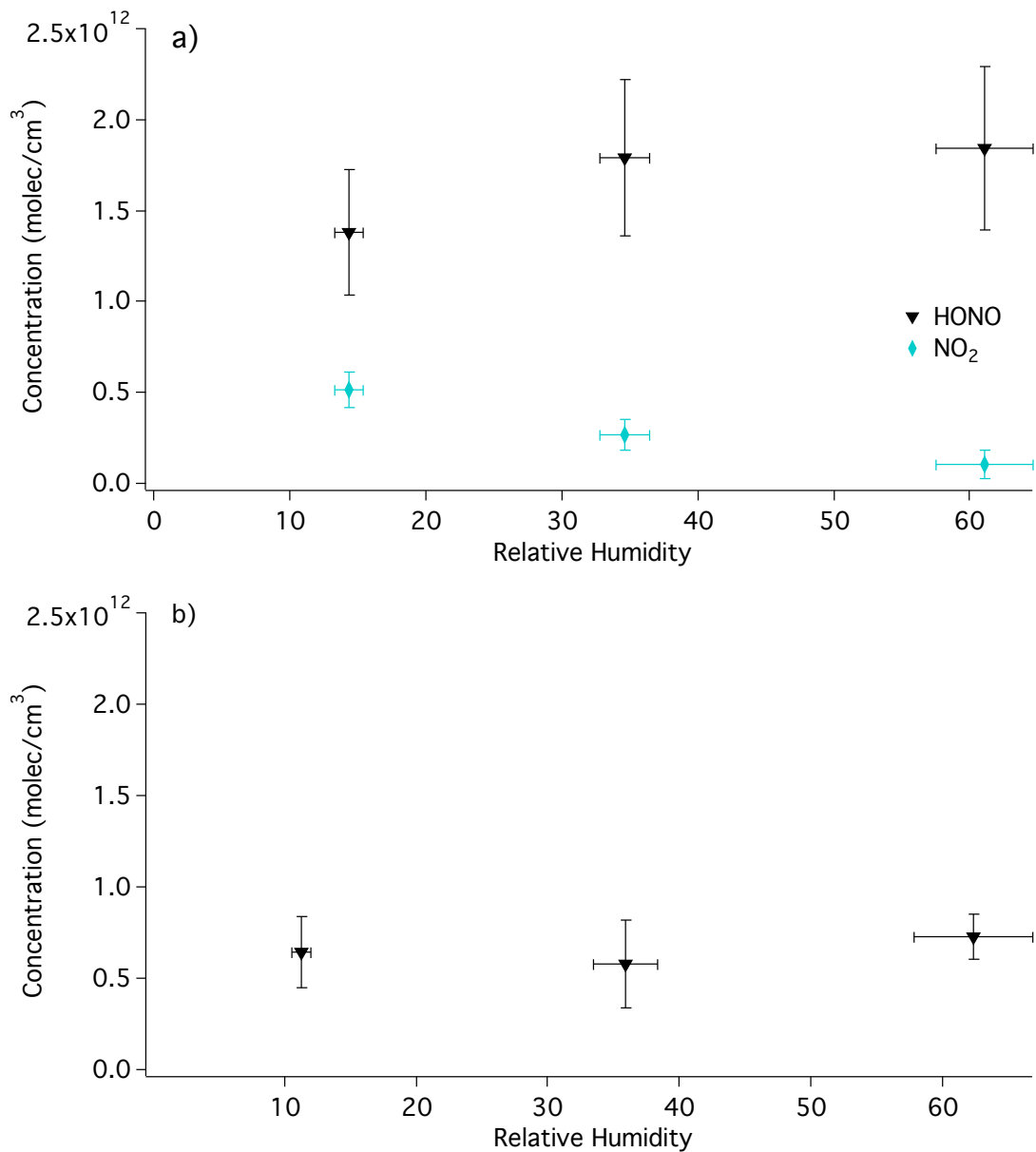
Figure S1: Concentrations of HONO and NO₂ for NO₂ flowed through the chamber and IBBCEAS cell as a function of RH a) in the dark and b) in the light. Only HONO concentrations are shown in Fig. S1b because no NO₂ was detected. The error bars represent one standard deviation of the average of three experiments.

Table S1: Inorganic ion content of grime used for photochemistry experiments (n=3)

	Chloride	Nitrate	Sulfate	Sodium	Potassium	Magnesium	Calcium
Concentration (μ g/cm^2)	4.8	0.73	4.27	4.9	0.34	1.27	2.11
Standard Deviation	0.1	0.01	0.04	0.2	0.01	0.05	0.05

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