Illuminating Urban Grime: The Atmospheric Impact of Urban Grime Photochemistry

by

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A thesis submitted in conformity with the requirements for the degree of Ph. D. in Environmental Chemistry

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Abstract
Deposition and subsequent processing of atmospheric species on impervious surfaces leads to the formation of surface films. Most abundant in urban environments, these films, sometimes referred to as “urban grime”, are thought to mediate environmental processing of species through adding an additional compartment into which species can partition, facilitating transfer of atmospheric species into surface water and promoting heterogeneous reactions. In this thesis, real urban grime samples are collected and used to investigate composition, growth characteristics, and reactivity of the less studied inorganic fraction of the film. Some of the reactions that we propose include the photochemical formation of nitrogen oxides, the formation of ClNO₂ from grime chloride and the re-emission of ammonia from grime.

The particular focus is urban grime photochemistry as a possible daytime source of HONO to the atmosphere. While surface nitrate/HNO₃ photolysis has been previously suggested as a HONO source, it has not been previously studied using real environmental surfaces. Using a combination of laboratory and field photochemical experiments it has been found that grime nitrate undergoes photolysis to form gas phase nitrogen oxides at a rate faster than has previously been reported for aqueous nitrate, gas-phase HNO₃ and surface deposited HNO₃ on clean glass. This chemistry is dependent on relative humidity and only involves a fraction of extractable grime nitrate. Based on these studies, urban grime photochemistry was explored as a source of HONO using a box model. The magnitude and temporal variation of this HONO source depend on the photochemical properties of the precursor including rate constant and wavelength.
dependence of its absorption cross-section, the source and rate of accumulation of the precursor as well as other factors such as latitude, season.
Acknowledgments

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Chapter One

Introduction

Contributions: The manuscript was written by Alyson M. Baergen with critical comments from D.J. Donaldson
1.1 Urban Grime

Heterogeneous reactions, in particular heterogeneous photochemistry, have been established to be an important consideration in atmospheric chemistry. While aerosol surfaces are the most well studied, another important surface is that of anthropogenic impervious surfaces. Both impervious surface area and aerosol surface area vary depending on location and aerosol surface area will vary even within a specific location depending on conditions. The relative importance of these different surfaces will also vary with altitude, because while the impervious surfaces are at the ground, aerosol particles are distributed throughout the atmosphere. However, as an estimate, modeled surface areas of urban environments have been estimated at up to more than 10 times the geographical surface area of a location based on MODIS images or estimates from surface area figures as a function of urban land use by Theurer et al. Aerosol surface area is thought to be much smaller than that. For example, aerosol surface area has been estimated at 750 times smaller than impervious surface area in China, despite high particle loading.

The formation of films, sometimes referred to as urban grime, on these surfaces is ubiquitous, and yet there is only a limited number of studies focused on understanding the composition and environmental impact of urban grime. The presence of the films was first discussed by Law and Diamond in 1998. Based on elevated concentrations of organic compounds detected on water surfaces, plant surfaces and observations of an oily sheen on roadways, they suggested that an organic coating was likely present on impervious exposed surfaces. In support of this hypothesis, Diamond et al. collected samples of the film from windows in downtown Toronto, detecting n-alkanes, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).

In these initial studies it was suggested that the films affect the environment in multiple ways. First, it was suggested that the partitioning of chemicals between the film and the atmosphere could result in a build up of organic compounds emitted in urban areas due to continued partitioning rather than depositional loss. Secondly, it was proposed that films increase mobility of the chemicals in the environment through film wash off, transporting the film components into surface water. Due to the high surface area to volume ratio of the films, it was also suggested that they could be a surface on which photolytic degradation could occur. While not the focus of this thesis research, the films are also of concern due to the possible degradation of monuments and building materials and the visual nuisance of blackening surfaces.
and reduced visibility through windows. In the past, this was of particular concern due to acidity of the deposits.\textsuperscript{12,13} More recently, decreasing SO\textsubscript{2} levels yet increasing levels of other pollutants in Europe led to the MULTI-ASSESS Project (MULTI-pollutant impact and ASSESSment of threshold levels for Cultural Heritage) to examine the impact of the changing atmospheric composition on the deterioration of surfaces.\textsuperscript{14} In addition to this project showing that corrosion and soiling of building materials it still of concern,\textsuperscript{eg.15} it has also resulted in a multi-year and multi-city data set of film growth and composition over time.\textsuperscript{16} The make up of urban grime and studies into these different hypothesized roles will be discussed below.

1.1.1 Methods of measuring grime

Before discussing the composition and role of urban grime in the atmosphere, it is important to understand the methods used to collect and study it. The most common has been to wipe off a window using dry, pre-extracted kimwipes followed by dichloromethane (DCM) wetted ones\textsuperscript{9} or using DCM\textsuperscript{17} or 2-propanol\textsuperscript{18} wetted kimwipes alone. These kimwipes are then extracted and analyzed for specific analytes. Alternatively, the film has been collected by spraying with deuterated dichloromethane and then scraping the film “clumps” into a vial.\textsuperscript{19,20} For all of these methods, the edge of the windows are avoided, preventing contamination from other building materials. In some cases the windows are first cleaned and then allowed to collect an urban grime film for a known amount of time,\textsuperscript{eg.21,22} while others sample windows with an urban grime film of unknown age.\textsuperscript{eg.10,21,23} For both cases, it is rarely specified the extent to which the films are exposed to sunlight and precipitation. Despite the repeated use of some of these techniques, none of these extractions methods have been well characterized. Extraction efficiencies for different species and biases of different techniques are not known.

Another method that has been employed to collect grime is using proxy surfaces to mimic impervious surfaces.\textsuperscript{15,24-26} For window glass proxies, straight glass pieces and glass beads have been used, where both light and precipitation exposure can be carefully controlled. For this sampling method, geometry of the samples may contribute sampling artifacts in comparison to real surfaces.\textsuperscript{27}

For sample analysis, total mass has been measured gravimetrically by difference either after drying in a desiccator\textsuperscript{28} or in one case at 75\% RH.\textsuperscript{17} Subsequent sample extraction has usually been done using Soxlet extraction with dichloromethane,\textsuperscript{9} though an acetone:dichloromethane
mixture has been used for one polycyclic aromatic hydrocarbon (PAH) analysis\textsuperscript{29} and a
toluene:acetone mixture followed by an acid and base wash has been used for polybrominated
diphenyl ether (PBDE) analysis.\textsuperscript{23} In some cases, instead of the Soxlet extraction, kimwipes have
been extracted with methanol\textsuperscript{17} or DCM using sonication.\textsuperscript{21}

Total organic carbon (TOC) and elemental carbon (EC) have been measured in film extracts
using commercial carbon analyzers with organic matter (OM) calculated by multiplying TOC by
1.5\textsuperscript{17} or 1.6.\textsuperscript{16} Extractable organic matter has been determined by weighing aliquots of organic
extracts after solvent evaporation and drying.\textsuperscript{17} For these methods the solvent needs to first be
evaporated and thus there is uncertainty added to these measurements with the possibility of
adding organic matter from solvent residue, or losing organic matter due to volatilization of film
organics. Water soluble organic carbon has also been analyzed using a TOC analyzer to analyze
a water extract.\textsuperscript{30} In one series of studies, organic functionalities were examined through a series
of extractions and analysis with NMR.\textsuperscript{19,20} More commonly, gas chromatography has been used
for the detection of specific species including n-alkanes, PAHs, polychlorinated biphenyls
(PCBs), PBDEs, methyl esthers (after derivitization), organochloride pesticides and
polychlorinated napthelenes.\textsuperscript{9,17,18,23}

For the inorganic fraction, metals have been measured using neutron activation analysis\textsuperscript{31} and by
microwave digestion followed by inductively coupled plasma optical emission spectrometry.\textsuperscript{19}
For inorganic ions, the most common method has been to extract into deionized water by
sonication for 45 minutes followed by ion chromatography. Although leaching of glass ions
only resulted in blank concentrations that were 4% for Ca\textsuperscript{2+} and 0.5% for other ions of the sample
concentration,\textsuperscript{16} long sonication should be cautioned for shorter term experiments where ion
concentrations are much lower and leached glass ions could contribute a much larger background
signal. An insoluble inorganic fraction has also been reported which is calculated from the
difference in total mass and the identified species.

As is evident, the vast majority of film analyses have involved extraction and therefore lose any
information about the matrix of the film and have possible unknown extraction biases as
mentioned above. The exception is a handful of studies that have examined the film still on the
original surface using SEM equipped with an EDX detector,\textsuperscript{32} and studies which have analyzed
the glass along with its grime coating for TOC and OC.\textsuperscript{16} However, with SEM imaging, the
results must be interpreted with caution because the films were put under a vacuum, which for example, favours crystallization of inorganic species due the low water vapour pressure.

### 1.1.2 Urban Grime Composition

Only a handful of studies have attempted to examine the entirety of the film and are shown in Table 1. In a variety of European cities, including Athens, Krakow, London, Montelibretti, Prague, and Troyes, grime films were collected onto float glass samples, contained within an enclosure shielded from rain and sunlight, but exposed to natural ventilation therefore supporting film growth. These samples were exposed to the atmosphere for up to 842 days, with multiple samples taken throughout the collection time frame. The average composition over the collection time is reported. These samples were analyzed for heterogeneity between locations on a single sample with a confidence interval of 6% found for carbon content and 10% for ions, indicating a fairly uniformly distributed bulk film composition. In a similar manner, Lombardo et al examined film composition over a number of sites classified as industrial, urban and rural and reported composition after a year of collection. The Toronto sample is a composite sample scraped from multiple windows during the summer after an unknown accumulation time.

For most grime samples, the water insoluble inorganic fraction of the film dominates the composition consistent with reports of PM$_{10}$ composition. However, the films seem to be biased high in insoluble fraction and low in organic fraction in comparison to particles. With film and particle variability as well as errors associated with measuring both the insoluble fraction and organic matter, it is not possible to be confident in trends without simultaneous particle and film measurements. Comparing the different locations does not show a clear trend based on site type. Favez et al reported a trend of higher insoluble material in the urban roadside locations than in suburban locations, however the variability in the more recent samples prevents such a trend from being clear. The Toronto sample is on the upper range of insoluble material and lower range of measured organic material for the urban sites, which could be the result of exposure to light and precipitation, preferentially removing the organic material in comparison to the shielded samples.
Table 1.1: Grime composition over a variety of location in mass percentage. Where multiple cities are listed a range of compositions over these sites is given. n.a = not analyzed.

Beyond these studies, the focus has been mainly on the organic fraction of the film and in particular, compounds of specific toxicological importance that make up only a small fraction of the film. PAHs,\(^{35}\) PCBs,\(^{36}\) PDBEs,\(^{21}\) organochloride pesticides,\(^{17}\) polychlorinated napthalenes (PCNs),\(^{37}\) and perflouroalkyl contaminants\(^{22}\) have been detected. The overall composition of the organic fraction in Toronto grime has also been studies indicating that it was made up of 35% carbohydrates, 35% aliphatics, 20% aromatics and 10% carbonyls.\(^{19,23}\) Metals have also been examined, with Ca measured as the most abundant metal in both Brisbane, Australia\(^ {38}\) and Toronto,\(^ {19}\) while Fe was reported as the most abundant in Baltimore.\(^ {17}\) Other frequently reported metals include Na, Mg, Zn, Sr, Cd, Ni and Co.\(^ {17,19,38}\)

Despite the small organic fraction of the film, it has been proposed that only the organic components make up the film, while any inorganic fraction remains as distinct particles.\(^ {9}\) This has lead to the reporting of “pure” film thickness calculated from only the organic fraction of the films\(^ {9}\) which has subsequently become a common method for reporting film growth.\(^ {21}\) In agreement with this idea, distinct particles throughout the film have been observed using an optical profilometer. Features were classified into fine(<0.8µm) and coarse (>1.6 µm) categories with number fractions ranging between 2.54 and 0.53 for sheltered conditions.\(^ {39}\) The relationship to the size distribution of deposited particles is unknown. SEM images have also been taken of

<table>
<thead>
<tr>
<th>Location</th>
<th>Classification</th>
<th>Age</th>
<th>OM</th>
<th>EC</th>
<th>Total ion</th>
<th>Metals</th>
<th>Insoluble Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottrop, Katowice, Kopisty(^ {33})</td>
<td>Industrial</td>
<td>1 year</td>
<td>12-27</td>
<td>1-3</td>
<td>3-22</td>
<td>n.a</td>
<td>51-84</td>
</tr>
<tr>
<td>Athens(^ {16})</td>
<td>Urban, roadside</td>
<td>548 days</td>
<td>8</td>
<td>5</td>
<td>24</td>
<td>n.a</td>
<td>63</td>
</tr>
<tr>
<td>Krakow(^ {16})</td>
<td>Urban, roadside</td>
<td>738 days</td>
<td>12</td>
<td>4</td>
<td>17</td>
<td>n.a</td>
<td>66</td>
</tr>
<tr>
<td>London(^ {16})</td>
<td>Urban</td>
<td>840 days</td>
<td>15</td>
<td>6</td>
<td>26</td>
<td>n.a</td>
<td>52</td>
</tr>
<tr>
<td>Prague(^ {16})</td>
<td>Urban</td>
<td>842 days</td>
<td>14</td>
<td>4</td>
<td>23</td>
<td>n.a</td>
<td>58</td>
</tr>
<tr>
<td>Toronto(^ {19})</td>
<td>Urban</td>
<td>Unknown</td>
<td>5</td>
<td>1</td>
<td>13</td>
<td>(SO(_4)(^ {2-})+NO(_3)(^ {-}))</td>
<td>18</td>
</tr>
<tr>
<td>Oslo, Paris, Stockholm, Prague, Athens(^ {33})</td>
<td>Urban</td>
<td>1 year</td>
<td>8-30</td>
<td>0-5</td>
<td>7-34</td>
<td>n.a</td>
<td>47-80</td>
</tr>
<tr>
<td>Montelibretti(^ {16})</td>
<td>Suburban</td>
<td>826 days</td>
<td>23</td>
<td>6</td>
<td>20</td>
<td>n.a</td>
<td>50</td>
</tr>
<tr>
<td>Troyes(^ {16})</td>
<td>Suburban</td>
<td>364 days</td>
<td>36</td>
<td>12</td>
<td>23</td>
<td>n.a</td>
<td>28</td>
</tr>
<tr>
<td>Chaumont, Toledo, Svanik(^ {33})</td>
<td>Rural</td>
<td>1 year</td>
<td>10-41</td>
<td>~0</td>
<td>9-20</td>
<td>n.a</td>
<td>48-70</td>
</tr>
</tbody>
</table>
the films, with gypsum (CaSO$_4$) crystals consistently observed$^{30}$ though, Na$_2$SO$_4$, NaNO$_3$ and NaCl have also been observed$^{40}$ along with particles classified as metal-rich, biogenic, quartz, NaCl crystals and fine soot clusters.$^{32}$ However, in disagreement with the idea of a pure organic film, the composition of identified crystals is not consistent with the reported composition of the inorganic species present in the film, suggesting at least some of the inorganic species must be distributed in the film amongst the organic species.$^{40}$ Chabas et al.$^{41}$ have also reported observing a film which appeared to boil when samples were placed under the electron beam of the SEM leaving behind small crystals. This indicates both that the film is a mixture of organics and inorganics, with the inorganic fraction being left as inorganic crystals when the organics and water are “boiled off”, and that the film is unstable under SEM conditions. Therefore, the structure of the film is still largely unknown.

1.1.2.1 Water content in Urban Grime

Because the majority of analysis have been done through extraction or following a drying procedure, little is known about the interaction of water with the film, despite its importance in environmental surfaces.$^{42}$ While not quantitative, Lam et al.$^{19}$ found that when the film was swollen with water, the NMR spectrum only showed polar groups such as carbohydrates and aliphatic acids, indicating these species are brought to the surface of the film. In contrast, in DMSO, the aliphatic and aromatic functionalities are also detected. It is suggested that this is evidence of the film being a dynamic system with different surface polarities depending on water content.$^{19}$ Water uptake onto grime samples has also been measured to be a factor of two greater than that for a clean surface with up to an estimated 12 monolayers of water associated with the film at 100% RH.$^{41}$ The water uptake isotherm was determined to be similar to that of a non-porous or macroporous medium where there are only weak interactions between the adsorbing gas and the surface with the enhancement attributed to increased surface roughness as well as water affinity of the deposited species.

1.1.2.2 “Rural” grime

Despite the focus on urban grime, it has been established that similar films also form on surfaces in more rural/suburban environments.$^{31,35}$ These rural sites have less accumulated mass and favour more volatile species, which can be transported far enough to reach the site before depositing, as well as more oxidized species due to the longer average transport time of the film
precursors. However, rural films can also have local sources. For example, the urban:suburban ratio for both total film and total PAH mass has been reported as 20:1 in one study, while in contrast for PCBs in the same samples the ratio was only 1.8 indicating an additional local source of PCBs or longer lifetime for PCBs. The PCB congener profile was also unique from the city, further suggesting a fresh PCB source, possibly a medical waste incinerator in the area. There may also be different growth behaviour in rural locations in comparison to urban locations. In one particular example, while the total suspended particle values were a factor of 6 lower for a rural location in comparison to an urban location, there was 10-30 times lower film mass. While the reason for this is unclear it has been suggested that the closeness of urban sites to sources such as car exhausts or micro scale wind patterns favouring deposition could play a role. It could also be indicative of film formation, speeding up further growth.

1.1.2.3 “Indoor” grime

Films have also been measured indoors. These generally show higher organic matter content than outdoor films, probably due to additional indoor sources as well as less efficient reactive loss processes. However, the indoor-outdoor comparison is complicated by numerous factors. In measurements done in Brisbane, there was strong correlation between PAH loadings indoors and outdoors, which is expected due to a climate where windows are frequently open. In contrast, for fluorinated species which have indoor and outdoor sources in the greater Toronto area, where windows are less frequently open, there are distinct profiles for indoor versus outdoor films with higher concentrations and different profiles in indoor films. There is also evidence that the type of airflow in the building will impact the film composition. Buildings with high central air flow show fairly uniform compositions throughout a building while those with lower and separate circulation systems throughout a building show greater variability, with specific local sources playing a larger role.

1.1.2.4 Urban grime on catalytic glass surfaces

Although not the focus of this thesis, the doping of glass and other building materials with species such as TiO₂ with photocatalytic activity have been investigated both as a “self cleaning” agent and for the potential to impact the NOₓ budget of the atmosphere. These surfaces have been the subject of a field study in a street canyon, where maximizing surface area to volume
should promote the importance of such surface chemistry.\textsuperscript{44} However, despite success in laboratory studies, the estimated remediation was less than 2%. There has also only been modest success in their cleaning ability.\textsuperscript{41} Under sheltered conditions, the self-cleaning glass has been found to have a lower haze measurement initially due to the enhanced destruction of organic matter deposited onto the glass. However, due to its superhydrophilicity the catalytic surface also favours the formation of gypsum crystals, which develop a crust preventing UV activity of the glass. Therefore, the concentrations of all measured species were higher for the self-cleaning surface after 12 months as compared to the reference. When both self-cleaning and reference surfaces were exposed to precipitation, there was again a lower organic matter concentration in the first 12 months for the self cleaning glass but no significant difference in film induced haze at longer times suggesting the remaining organic matter (the insoluble fraction) is insensitive to photodegradation.\textsuperscript{41}

\subsection*{1.1.3 Urban Grime Growth}

Examining film growth characteristics can also be helpful in understanding film behaviour, and the important characteristics that determine its composition. Assuming linear growth, accumulation fluxes in roadside locations in Athens and London were measured at 0.81 and 0.52 $\mu g \text{ cm}^{-2} \text{ day}^{-1}$, urban background locations in Krakow and Paris were 0.38 and 0.1 $\mu g \text{ cm}^{-2} \text{ day}^{-1}$, while suburban Paris and Rome locations were 0.033 and 0.039 $\mu g \text{ cm}^{-2} \text{ day}^{-1}$.\textsuperscript{39} These are in good agreement with the downtown Toronto data with rates of 0.16-0.26 $\mu g \text{ cm}^{-2} \text{ day}^{-1}$\textsuperscript{25} and various locations around China where growth rates between 0.44 to 1.9 $\mu g \text{ cm}^{-2} \text{ day}^{-1}$ were measured.

While this linear growth seems to describe the data well in some locations such as in Toronto\textsuperscript{25} and Rome,\textsuperscript{39} other samples deviate from linearity. A study done in Baltimore, saw evidence for enhanced deposition once the film was formed with fluxes that were 1.4-94 times higher for deposition onto films than onto the initially clean window.\textsuperscript{31} This accelerated growth has also been seen for some of the roadside grime collection sites in Athens and London.\textsuperscript{30} In contrast, in China, the growth rate has been reported to slow over a 40 day growth period.\textsuperscript{21} In Paris, film growth also slowed over time, however, this was only detectable due to the extremely long, over 5 year, study period.\textsuperscript{39}
A variety of studies, focused on the European data, have tried to model the variation in growth. However, instead of fitting growth they focus on haze measurements, which describe the light scatter and absorbance due to film formation. Initially, the Hill equation was used to describe haze measurements, which assumes an eventual saturation of the surface. Alfaro et al argue that this does not physically represent the data well for their exposure studies over two years. Instead they use their data to define empirical relations based on “land type”. They found that the growth of films in suburban locations generally slowed over time, while those in urban roadside locations grew more quickly over time. They attributed this to the difference in the fine organic particulate rich suburban films versus coarse, inorganic rich particles at the urban site. There have also been attempts to parameterize the models by atmospheric measurements. It was found that SO$_2$, NO$_2$, and PM$_{10}$ were good predictors of film growth while temperature, relative humidity were less useful. This could be due to the lower variability in the meteorological parameters between the sites examined in comparison to the gas phase concentrations. These models can help describe the important parameters determining film growth, however they are also somewhat limited. They aim to reproduce haze measurements rather than compositional measurements and therefore, may bias the importance of different sources important for haze measurements but only a small fraction of the film. They are also only empirical models, which do not seek to explain the mechanism of growth under the different circumstances.

### 1.1.4 Urban Grime as a partitioning medium

Diamond et al calculated film-air partitioning coefficients ($K_{FA}$) for a variety of PAHs from measured film and air concentrations. Film concentration was calculated assuming that the PAHs only partition into the organic fraction of the film, assumed to be 20% of the film by mass, and that this organic fraction has a density equal to octanol. The calculated values were up to 3 orders of magnitude higher than literature $K_{OA}$ values. The discrepancy was attributed to PAHs deposited associated with particles that were inaccessible for partitioning but were extracted in the analysis. Later, Unger et al again looked at PAH partitioning, but this time extracting the film using toluene to estimate extractable organic matter (EOM), to better estimate the volume into which PAHs could partition. Using a previously developed linear free energy relationship (LFER) for $K_{OW}$ and octanol-lipid partitioning the gas-phase PAH concentrations could be calculated. However, this improved method still led to predicted gas-phase concentrations that were higher than measurements by factors of 4.5 to 135. This was again attributed to PAHs in
the film that were inaccessible for partitioning, this time making particular note of the black carbon onto which the PAHs could sorb. Therefore, these studies indicate that the film cannot be interpreted as a passive sampler for PAHs.

Studies have also been done looking at PCBs and PBDEs, which are less likely to strongly sorb to such particulate species. Calculated $K_{FA}$ for PCBs in the same Diamond et al\textsuperscript{9} study were closer to literature $K_{OA}$ than for PAHs with discrepancies of less than half an order of magnitude. Wu et al\textsuperscript{36} used a similar method for their samples collected in a more controlled manner on sheltered beads, comparing the concentration in air to the concentration in the film to calculate $Q_{FA}$ which was defined as the ratio of film and air PCB concentrations at a given time. In this study the $Q_{FA}$ was up to 2 orders of magnitude lower than literature $K_{OA}$ for the heavy PCBs. However, $Q_{FA}$ were also compared to air-ethylene vinyl acetate partitioning coefficients($K_{EVA-air}$) which were in much better agreement with the $Q_{FA}$ though still showing a constant offset. In this instance, the total film mass was used to calculate an approximate film thickness rather than just the organic fraction, which could explain a 1 order of magnitude offset between $Q_{FA}$ and $K_{EVA-air}$ if in reality it was only the organic fraction into which species would partition. The better agreement with the $K_{EVA-air}$ was explained by the high fraction of carboxylic acids in the organic fraction of the film,\textsuperscript{17} which the EVA ester functionality better resembles in comparison to the octanol alcohol. However, it is also discussed that the deviation between $K_{FA}$ and $K_{OA}$ may be due to the heavier PCBs not being in equilibrium with the surroundings.\textsuperscript{36}

Butt et al\textsuperscript{23} estimated gas phase concentration of PBDEs using published $K_{OA}$ values and measured film concentrations, comparing these to passive sampler data from locations close to the film locations. With the exception of BDE-17 which showed good agreement, the calculated congener concentrations were underestimated, many by over an order of magnitude. Such a discrepancy suggests either that the film is not in equilibrium or that the equilibrium is miscalculated. One such potential error for miscalculating the equilibrium was the use of a uniform film thickness of 60nm for all sites despite measurements showing the variability of film masses at different locations. Therefore, the discrepancy between measured and calculated species was high, but not necessarily indicative of lack of partitioning. PBDE partitioning was also estimated in New York following the World Trade Center (WTC) terrorist attacks, though no literature data was available for comparison. This time a film thickness of 100nm was assumed for partitioning calculations despite average film thicknesses of 209nm being
calculated, again likely leading to poor estimations of gas phase concentrations.\textsuperscript{37} However, in this same study, there was evidence for partitioning behaviour in organochloride pesticide film concentrations. Although not expected to be released from the attacks, organochloride pesticide levels were higher in the films near the WTC towers due to a greater film volume.\textsuperscript{37}

Although examined in a number of studies, the partitioning behaviour of the film is not well known. The portion of the film into which species can partition, and rate at which different species can approach equilibrium is still an open question. Furthermore, the extent to which species can be trapped on the film either through strong sorption or via some other process has yet to be established.

1.1.5 Urban Grime as a facilitator of pollutant transport to surface water

1.1.5.1 Toxicological effects of the film

Early multimedia, steady state fugacity models including urban grime used estimates for partitioning and film to water transfer coefficients to predict that urban grime facilitates the environmental mobility of contaminants both through re-emission into the air to undergo chemical transformations, and through transfer to surface waters.\textsuperscript{10,11} This is of particular concern due to toxicological impacts of film components. One method to estimate this toxicity has been to measure toxicologically significant species in the film and use this to estimate toxicity parameters such as a benzo[a]pyrene equivalent concentration for film PAHs.\textsuperscript{29} In addition, there has been a small number of studies probing more directly the toxicological impacts of the film. When exposed to grime film extracts, Zebra fish embryos had elevated mortality rates and measured teratogenic effects.\textsuperscript{9} In a follow up study, the response of the aryl hydrocarbon receptor (AhR) was studied by measuring the luciferase expression.\textsuperscript{18} Crude extract induced luciferase expression, with the extent of expression not explained by the summation of the impacts of the various extracts. Furthermore, the non-polar fraction of the film was most active, despite no known drivers expected to be present in this fraction, indicating a complex response using these experimental samples.\textsuperscript{18}

1.1.5.2 Precipitation effects

To better characterize the transfer of pollutants to the surface waters, experiments have been done examining the removal of grime film during precipitation events. It has been found that the
intensity of precipitation plays a large role in the extent of wash-off, indicating that mechanical dislodging of particles plays a role in film wash off.\textsuperscript{49} In support of this Wu et al \textsuperscript{36} examined film mass over time for samples exposed to precipitation. They found that only the most intense rainstorm restored the film mass to within error of a clean surface. However, there is also evidence suggesting that it is not just mechanical processes that removes film species. Exposure to precipitation increases the proportion of fine particles on grime-coated glass surfaces.\textsuperscript{39} This is thought to be because of coarse particles breaking up, preferential scavenging of coarse particles, or possibly reaction between rain and the glass. In addition, a comparison of surfaces exposed to and sheltered from precipitation suggest that, although all components decrease in concentration with precipitation, salts and water soluble organics are preferentially removed.\textsuperscript{41}

1.1.5.3 Multimedia Urban Grime models

Using the above data, better-constrained multimedia models could be developed, thus far focused on PCB cycling. In a steady state model, although only approximately 3\% of emitted PCBs were transferred to urban grime, the grime was calculated to contribute 260 times more PCBs to water than atmospheric deposition and 60 times more than soil runoff.\textsuperscript{50} An unsteady-state model was subsequently developed improving on this estimate, where the film grows in over time. Here wash off efficiency was modeled as 60\% except in high rain intensity where the 100\% efficiency was assumed. In agreement with the steady state model, although the film received less than 2\% of the PCB mass the grime was the dominant source to storm waters.\textsuperscript{51} It was also shown that after cold dry periods the films act as a larger PCB source back into the atmosphere, with the longer the dry period, the greater the spike into storm waters.\textsuperscript{51}

1.1.6 Urban Grime as a reactive environment

1.1.6.1 Inferred reactivity from composition

Urban grime films have a much longer lifetime than particles, and also have a large surface area to volume ratio, favouring heterogeneous reactions. Evidence of film reaction is suggested both from changes in composition over time and from comparing film composition to typical particle composition. Suggesting a reactive loss of the organic carbon, the fraction of elemental carbon/total carbon increases over time as the film ages.\textsuperscript{16,41} In support of reactive loss of organic matter, the film also has a lower fraction of organic matter, particularly water soluble organic matter, than particles collected simultaneously to film collection.\textsuperscript{30}
The pattern of PAHs detected within the film also shows an “aged” profile depleted in the more reactive species such as anthracene in comparison to the larger, less reactive species such as chrysene.\textsuperscript{9,31} This was also seen in China where Benzo(a)anthracene/chrysene values were much lower in Shanghai film samples than in dust.\textsuperscript{21} Such skew in profiles is only possible if the films are not in equilibrium with the surroundings, which is likely the case for PAHs. However, like the PAHs, the PCB profiles were also most abundant in the least reactive congeners indicative of some sort of reactivity and skew from equilibrium.\textsuperscript{9,31} Surfaces exposed to and sheltered from light and precipitation showed minimal differences in PCB profiles suggesting the PCB reactivity is not photochemical in nature.\textsuperscript{25}

For PBDEs, in China, reactive loss was indicated by a decreasing PBDE fraction in the film over the 40 days of growth period, with lighter compounds again being removed more quickly than the heavier congeners.\textsuperscript{21} There was also a skew in congener profiles between indoor and outdoor films, indicating lower brominated compounds degraded in outdoor films at a faster rate than those indoors.\textsuperscript{23}

In addition to the evidence of reactive loss of the above species, there is also evidence for the formation of polymers within the film. There is no data on concentration over time, however, polymeric material has been detected onto the film consistent with polybutadiene.\textsuperscript{20} While possibly from the deposition of polybutadiene-like substances such as suspended tire debris, Lam et al\textsuperscript{19} postulate that it could be from an in-situ reaction from oxidation followed by radical chain reaction.

There is also evidence of inorganic reactions. Compositional studies of the film indicate low to undetectable levels of ammonium in the films.\textsuperscript{16,30} Multiple pathways have been suggested for the removal of ammonium from grime including the reaction between NaCl and NH$_4$NO$_3$ to form NaNO$_3$, NH$_3$ and HCl as well as abiotic and biotic oxidation of NH$_3$ to NO$_3^-$\textsuperscript{16} Leaching of Na$^+$ from the glass has also been detected which could be responsible for slightly elevated Na$^+$ concentrations in the film.\textsuperscript{32,41}

1.1.6.2 Organic surface chemistry

Proxy film studies have also been used to study urban grime chemistry. Heterogeneous PAH ozonation has been detected on simple octanol/PAH films,\textsuperscript{52} following Langmuir-Hishelwood
More complex films have also been studied with the addition of quartz, silicone grease, vacuum grease, decanol, stearic acid or cornstarch in an attempt to better simulate the grime films. While most of these species did not impact the reactivity, squalene and oleic acid caused a significant decrease in rate,\(^{52}\) likely due to efficient reactivity of these added species with ozone\(^ {54}\) and thus the competitive reaction reducing the ability of ozone to react with the PAHs.\(^ {52}\) The rates measured in these experiments were lower than that measured in previous studies of benzo(a)pyrene on solid surfaces.\(^ {53,55}\) The explanation for the slower rate is unknown, however dimerization of the PAHs due to high surface concentration or some other substrate interaction with the PAHs was suggested.\(^ {52}\) A multimedia urban model, based on the ones used previously,\(^ {10,11}\) was used to help elucidate the atmospheric importance of heterogeneous ozonation reactions of PAHs.\(^ {5}\) It was found that for the lower volatility PAHs, the films could play an important role in determining the reactive fate of the PAHs, however for the smaller, more volatile PAHs, the main reactive sink remained as gas phase oxidation by OH.

Upon further study of film ozonation, it was found that in some instances the reaction is photoenhanced.\(^ {56}\) Photoenhanced pyrene ozonation was observed on solid pyrene films and at the air-water interface but not on octanol films.\(^ {56}\) It was suggested that in order for a reaction to be photoenhanced the substrate must be able to stabilize charged intermediates, which occurs readily at the polar aqueous interface and on the pyrene films due to delocalization of charge through extended structure of the pyrene film, but cannot be achieved on nonpolar octanol.\(^ {56}\) A similar conclusion was reached for the lack of photoenhancement of pyrene at an octanol coated air-aqueous interface.\(^ {57}\) Because of the complexity of the film, it is unknown which of these proxy surfaces best represents the film and thus further work is needed using real films. Further proxy studies of particular interest for this thesis is the work done by Ammar \textit{et al}\(^ {58}\) and Handley \textit{et al}\(^ {59}\) examining nitrate photochemistry within organic films. These will be discussed below.

### 1.2 HNO\(_3\)/nitrate photochemistry

Nitrate photolysis is well known and has been studied in a variety of media. In aqueous solution nitrate has two absorption bands one centered at 200nm from the \(\pi \rightarrow \pi^*\) transition and one at 310nm from the \(n \rightarrow \pi^*\) transition which is 440 times weaker because it is a forbidden transition.\(^ {60}\) The photolysis results in the formation of NO\(_2\) and NO\(_2^-\) with wavelength dependent yields. For 305nm light, a pH of 5.6 and temperature of 295K reported yields were 0.9 and 0.1%
for NO$_2$ and NO$_2$ respectively. In contrast, the UV absorption spectrum of gas phase HNO$_3$ has a shoulder centered around 260nm, followed by a steep, two order of magnitude drop from this shoulder to the absorption cross section at 320nm. The quantum yield of NO$_2$ formation from this photochemistry is approximately 1 between 200 and 315nm. However, these are bulk absorbance measurements and aqueous experiments have shown that a variety of factors can alter these photochemical properties. In water, nitrate at the surface has a reduced solvent cage than in the bulk, which is thought to enhance photolysis rates. The presence of halides in solution may increase surface concentration of nitrate, further enhancing nitrate photolysis. The product yields of aqueous nitrate photochemistry are also impacted by pH and organic coatings. Nitrate photochemistry has also been observed in frozen surfaces and is thought to impact NO$_x$ fluxes, in particular in pristine areas such as Antarctica and Greenland.

1.2.1 HNO$_3$/nitrate photolysis on clean glass surfaces

As is seen for the different environments at the aqueous interface, on surfaces it is expected that HNO$_3$/nitrate would have unique photochemistry. Reactions on clean glass surfaces have been used as an estimate for surface reactions in the environment. Zhou et al have examined HNO$_3$ photochemistry on glass surfaces at a range of relative humidities, detecting HONO, NO and NO$_2$, with HONO production increasing with relative humidity but total product formation decreasing with relative humidity. However, they did not take into account relative humidity dependent NO$_2$ to HONO wall conversion in their system and thus the reported values may be skewed. They measured rate constants, adjusted for noon time tropical sun, for total product formation of between $2.2 \times 10^{-5}$ and $6.0 \times 10^{-5}$ s$^{-1}$ for 0-50% RH and $0.16 \times 10^{-5}$ up to $1.4 \times 10^{-5}$ at 80% RH for HONO formation, 1-2 orders of magnitude faster than gas phase HNO$_3$ photolysis. This corresponds to HONO:NO$_x$ ratios of 0.02 at 0% to 1.2 at 50% RH. Ramazan et al followed this study, examining HNO$_3$ photolysis as a mechanism for enhanced HONO formation rates from NO$_2$ hydrolysis under illumination. They found that some surface water is required for HONO formation, but that HONO formation is RH independent between 39% and 57% RH with a rate that was approximately two orders of magnitude larger than that for gas phase HNO$_3$. They argue that the RH dependence of HONO formation, similar between the two studies, is due to the photolysis of HNO$_3$/water complexes which decrease in concentration with increasing water concentration for borosilicate glass. This is in competition with enhanced H$_2$O
displacement of HONO\(_{(ads)}\) with increasing RH and at low relative humidities the reaction of HONO with adsorbed HNO\(_3\) to form NO\(_2\) and H\(_2\)O in the reverse reaction of NO\(_2\) hydrolysis.\(^{71}\)

Laufs and Kleffmann\(^{73}\) studied HNO\(_3\) photolysis on quartz at ~50% RH and detected a much lower rate constant, again adjusted for noon time tropical sun, of 2.4x10\(^{-7}\) s\(^{-1}\) for HONO and 1.1x10\(^{-6}\) s\(^{-1}\) for NO\(_2\). In contrast to the mechanism discussed above, no direct HONO formation was observed, being formed only through the surface hydrolysis of NO\(_2\).\(^{73}\) The quartz surface used in this study takes up less water than borosilicate glass, in particular in the presence of surface adsorbed HNO\(_3\), which could impact the degree of dissociation and complexation of HNO\(_3\) with water and consequently the photochemistry observed.\(^{72}\) The photolysis of HNO\(_3\) on fused silica surfaces has also been probed using excimer laser photolysis at 308nm and 351 nm.\(^{74,75}\) A quantum yield of 1.1±0.2 at 308nm for NO\(_2\) formation was reported and no HONO was detected in the microsecond long experiments. The environmental applicability of such an experiment is unclear.

1.2.2 HNO\(_3\)/nitrate photochemistry on mineral dust

Nitrate photochemistry has also been studied on mineral oxide surfaces with NO\(_2\), NO, and N\(_2\)O detected as products, however, the set up was not sensitive to HONO.\(^{76-79}\) Surface products have also been observed, dependent on surface type. NO was observed to re-adsorb onto aluminum oxides surfaces,\(^{77}\) nitrite has been observed on zeolite surfaces\(^{78}\) and reduced nitrogen species including NO\(^{-}\) and N\(^{-}\) have been observed on hematite surfaces\(^{79}\) indicating the complexity and surface specificity of the chemistry. In addition, surface water has been shown to promote gas phase product formation.\(^{77}\) This RH dependence has been attributed to a shift in the UV absorbance peak for nitrate from 275nm under dry conditions where the nitrate is coordinated to the mineral oxides to 297nm under humid conditions where the nitrate is more solvated and in an environment more similar to aqueous nitrate.\(^{77,80}\) On more photoactive mineral dust samples and TiO\(_2\) films, nitrate photochemistry has been shown to form NO\(_x\) and HONO.\(^{81,82}\) A strong RH dependence is again observed, with increasing then decreasing NO concentrations and decreasing NO\(_2\) concentrations as a function of increasing RH, possibly due to reaction of the water vapour with the available electron holes. This consequently favours the reaction of NO\(_2\) with electrons to form nitrite and subsequently NO through photolysis. However, the water
reaction with electron holes also produces OH which could react with nitrate or nitrate on the surface which could explain the drop in NO concentration at the highest relative humidities.\textsuperscript{82}

1.2.3 HNO\textsubscript{3}/nitrate photochemistry on proxy films

The above studies were expanded on by Handley et al\textsuperscript{59} to simulate urban grime surfaces, looking at HNO\textsubscript{3}/nitrate photochemistry in the presence of an organic film composed of octanol, vacuum grease and a pH sensitive dye, acridene, which was used to track the reaction progress through pH changes. When gas phase HNO\textsubscript{3} was deposited onto the film, the pH was lowered. Upon illumination, the pH of the film increased indicating the loss of HNO\textsubscript{3}. The same experiment with HCl, with has a similar vapour pressure to HNO\textsubscript{3}, showed a much slower increase in pH upon illumination indicating that the behaviour of illuminated HNO\textsubscript{3} was due to photochemical processing rather than merely evaporation of the HNO\textsubscript{3}.\textsuperscript{59} The photochemical experiments were performed with 295 nm and 340nm filters, with no detectable change in the photochemical rate. At the time this was suggested to be due to photosensitization of the NO\textsubscript{3}⁻/HNO\textsubscript{3} photolysis as these species are not expected to absorb light above 320nm but acridine does. Investigating this claim, Laufs and Kleffman used a mixture of VOCs to simulate an organic film with species such as β-pinene, limonene, xylenes, n-butanol and methacrolein, but saw no enhancement in HNO\textsubscript{3} rate in comparison to a clean surface. However, the VOCs did not necessarily make a complete film and did not include known photosensitizers.\textsuperscript{73} Styler and Donaldson\textsuperscript{83} also investigated the photosensitization of the HNO\textsubscript{3}/nitrate photolysis using a variety of species and were unable to detect a significant impact on photolysis rates.

Since this initial study, another theory for surface enhanced HNO\textsubscript{3} and nitrate photolysis rates has been proposed. A red shift and 3-4 orders of magnitude enhancement in the surface absorption cross sections of surface deposited NO\textsubscript{3}⁻ and HNO\textsubscript{3} in comparison to gas phase HNO\textsubscript{3} has been observed, which could explain the above observations as well as those on glass surfaces.\textsuperscript{84-86} In particular, for surface nitrate the absorption cross section has been measured to be greater at 340nm than at 320nm, which could explain the lack of rate change observed in the Handley et al study.\textsuperscript{59,84} The ground state of gaseous HNO\textsubscript{3} is planar while for the electronically excited state is pyramidal making this a forbidden transition. However, it is predicted that the interaction of HNO\textsubscript{3} with a surface could skew the ground configuration towards the pyramidal geometry, enhancing the probability and slightly lowering the energy barrier of this
transition.\textsuperscript{85} For nitrate, it is believed that the reduced solvent cage on the surface enhances and red-shifts the nitrate absorption cross section in comparison to when it is in aqueous solution.\textsuperscript{84}

While giving insight to surface enhanced nitrate/HNO\textsubscript{3} photolysis rates, the difference in nitrate and HNO\textsubscript{3} absorption cross sections also indicate the importance of knowing the degree of dissociation of HNO\textsubscript{3} on the surface. No dissociation was assumed for HNO\textsubscript{3} on fused silica surfaces,\textsuperscript{86} but there was evidence for some dissociation, even under dry conditions, on a sapphire surface.\textsuperscript{84} Simulating an urban grime coating, on an alkyl self-assembled monolayer, a mixture of nitrate and HNO\textsubscript{3} was observed even under dry conditions, with the proportion of nitrate increasing up to 70-90\% RH where molecular HNO\textsubscript{3} was no longer observed.\textsuperscript{87} In comparison on a bare SiO\textsubscript{x}/Ge surface, molecular HNO\textsubscript{3} was observed up until 20\%RH, after which only nitrate was observed.\textsuperscript{88} Therefore, it is clear this nitrate/HNO\textsubscript{3} ratio is surface dependent, and could be an important dictator of photochemistry. Another consequence of a shift in the absorption cross sections for the surface adsorbed HNO\textsubscript{3} and nitrate, discussed by Laufs and Kleffman,\textsuperscript{73} is the mismatch in response window between surface HNO\textsubscript{3}/nitrate absorption and aqueous nitrate absorption. This leads to significant uncertainties in reported rate constants which use an aqueous nitrate actinometer to quantify light intensity.\textsuperscript{89,90}

\textbf{1.2.4 \textit{NO}_3^-/nitrate photochemistry on environmental samples}

In order to study more environmentally relevant surfaces, there have been a small number of studies where the source photochemistry precursors were collected by either exposing surfaces to the atmosphere or collecting particles. In one study, these atmospherically exposed samples illuminated in a chamber and gas phase products were detected with a two-channel long-path absorption photometric system (LPAP) for HONO and a chemiluminescence NO\textsubscript{x} analyzer with a molybdenum NO\textsubscript{2} to NO converter and a NaCO\textsubscript{3} coated denuder to remove HONO for NO\textsubscript{x}.\textsuperscript{26} A wide range of rate constants was measured ranging from $6 \times 10^{-6}$ s\textsuperscript{-1} up to $3.7 \times 10^{-4}$ s\textsuperscript{-1} with an average of $6.0 \times 10^{-5}$ s\textsuperscript{-1} and median of $3.4 \times 10^{-5}$ s\textsuperscript{-1} similar to that previously measured on glass, though indicating a much wider range emphasizing the uncertainty in these values. These were normalized to tropical noon time actinic flux and were measured under approximately dry conditions.\textsuperscript{26} Production rates were normalized to the nitrate loading, however, they detected a non linear response of the measured rate constant to nitrate surface loading\textsuperscript{26} indicative of film development impacting the reactive environment of the reacting species. A limitation of their
study was the exposure of their samples to light during collection. The photoactive nitrate was thus likely somewhat depleted and the samples may have shown different behaviour based on the time at which the samples were collected because of different lengths of previous light exposure.

Measurements have also been made of HONO production from particle samples collected onto filters with photolysis rate constants ranging from $1.3 \times 10^{-5}$ s$^{-1}$ to $3.1 \times 10^{-4}$ s$^{-1}$ at 50% RH with a median of $1.3 \times 10^{-4}$ s$^{-1}$, higher than the rates measured for most substrates discussed above.\textsuperscript{91} Formation rates were normalized to the amount of nitrate in the sample. Such a normalization assumed that all of the nitrate present has the same reactivity which is not always the case as has been indicated above and has been observed for other surface processes.\textsuperscript{eg.56}

1.2.5 HNO$_3$/nitrate photochemistry of organic species

Although it has been assumed to be nitrate and/or HNO$_3$ that undergoes photolysis in the above studies, with the film merely changing the reactive environment, organic species have also been seen to play more active roles in nitrogen oxide photochemistry. Ammar \textit{et al}\textsuperscript{58} simulated grime-coated surfaces using a pyrene/KNO$_3$ mixture. HONO was produced upon illumination in contrast to illuminated films of KNO$_3$ or pyrene, which yielded no detectable NO$_y$. Therefore, a mechanism where photo-activated pyrene reacts with nitrate forming 1-nitropyrene, which can subsequently photolyze to form HONO, was proposed. Other studies have also shown the photolysis of similar nitrogen containing organics to form gaseous nitrogen oxides both on surfaces\textsuperscript{92,93} and in the gas phase.\textsuperscript{94} In addition, NO$_2$ shows photoenhanced uptake on a variety of organic surfaces including humic acid, catechol, PAH films and soot.\textsuperscript{58,92,93,95-99} Incorporating humic acid into ice has also resulted in a photo-enhanced NO$_2$ to HONO conversion.\textsuperscript{100}

Suggested pathways from these studies are: photolysis of organic nitrogen containing species such as nitroaromatics formed as intermediates in NO$_2$ uptake, photo-oxidation through electron or hydrogen transfer of excited species and photosensitized electron or hydrogen transfer.\textsuperscript{93}

1.3 Atmospheric HONO

HONO exhibits a structured absorption spectrum in the range of 300 to 405nm with a unity quantum yield for dissociation,\textsuperscript{101} leading to the production of NO and OH. Studies have shown that HONO photolysis is an important contributor to the OH budget of the atmosphere particularly in the morning\textsuperscript{102,103} and during the winter\textsuperscript{104} when other OH sources are low,
however, the OH budget is also impacted throughout the day and in the summer.\textsuperscript{105,106} Significant impacts on ground level ozone concentrations have also been noted.\textsuperscript{7} Changes in two of the most significant atmospheric oxidants further impacts the extent of oxidation reactions\textsuperscript{107} and consequently secondary organic aerosol (SOA) levels.\textsuperscript{108} Aerosol sulphate levels have also been calculated to increase in the winter with increasing HONO concentrations.\textsuperscript{109} The impact of HONO on these other processes is seen most strongly at the surface due to vertical concentration gradients.\textsuperscript{102}

1.3.1 “Missing” HONO source

Despite its importance, the formation and removal processes for HONO are not well constrained. Many studies have identified that the balance of HONO formation from the OH and NO gas-phase reaction and removal through photolysis is insufficient to explain HONO concentrations both in the daytime and at night.\textsuperscript{eg,3,110-112} Dark heterogeneous conversion of NO\textsubscript{2} to HONO has been found to often explain night time measurements, however, daytime concentrations can still not be reproduced by such a mechanism.\textsuperscript{113}

This required daytime source has been quantified in a variety of locations with a wide range of values, summarized by Michoud \textit{et al.}\textsuperscript{112} Maximum values ranging from 0.3-1.4 ppb h\textsuperscript{-1} have been reported for suburban summer,\textsuperscript{112,114} 0.22-0.77 ppb h\textsuperscript{-1} for rural summer,\textsuperscript{115-117} 0.7-1.7 ppb h\textsuperscript{-1} for urban summer,\textsuperscript{111,118} 0.7-1.8 ppb h\textsuperscript{-1} at a forested site in Spain in winter and 0.05-1.3 ppb h\textsuperscript{-1} in a suburban Paris location in winter. An important caveat to many of the studies above is that photosteady state is often assumed, yet it has been shown that this is not necessarily a good assumption, especially for urban settings where there are fresh emissions, causing an overestimate of this unknown HONO source strength.\textsuperscript{119,120} There is also evidence that sinks of HONO are also not fully characterized which could lead to an underestimate of HONO sources, further increasing the uncertainty of the reported values above.\textsuperscript{121,122} In addition, while these values give an estimate of the strength of HONO source and possible spread of source strength depending on location and meteorological conditions, they say little about the nature and diurnal trend of the HONO sources.

The identity of the source has been suggested to be photochemical involving NO\textsubscript{2}. In summertime London, good correlation between the HONO/NO\textsubscript{x} ratio and j(NO\textsubscript{2}) has been measured, indicative of a photochemical source.\textsuperscript{123} In a forested region in Spain, the calculated
missing HONO source has been normalized to NO₂ over time to get a conversion efficiency, assuming the majority of the HONO comes from NO₂. Values up to 43% were calculated with this value depending on j(NO₂), though with only an r² of 0.32 suggesting a photochemical NO₂ source is likely but that it is not the only source.¹²¹

There is also evidence for the strong influence of a ground HONO source. Vertical gradients have been measured to characterize HONO chemistry, with a maximum concentration at the surface.¹⁰²,¹¹³,¹²²,¹²⁴ Because NOₓ can have a similar gradient and thus even gas phase HONO chemistry could result in a vertical gradient, this alone does not indicate a ground level source.¹¹¹ However, including a ground level source, and accounting for vertical transport, it is clear that for measurements in Houston during the SHARP campaign, the vertical gradient is well described by a surface HONO source.¹²⁵ For these measurements, the unknown HONO source was also found to better correlate with solar irradiance than actinic flux and the measured HONO/NO₂ diurnal profile was at a maximum at noon further pointing to a photochemical NO₂ ground HONO source.¹¹¹ A photochemical NO₂ ground source was also required to reproduce daytime HONO concentrations and vertical gradients of both HONO and HONO/NOₓ at a suburban German site.³ Similarly, in a rural field location, NO₂ and HONO vertical gradients and concentrations observed by Vandenboer et al.¹²² can be explained by surface NO₂ to HONO conversion. In contrast to the heterogeneous chemistry thought to occur on the ground, it is often predicted that heterogeneous aerosol chemistry plays a minor in HONO formation because the surface area is too small in comparison to the ground,⁶,⁷,¹²² though there are exceptions to this conclusion.¹²⁵

The dependency on NO₂ noted for the above studies is not always seen. In suburban Paris during MEGAPOLI, there was poor correlation with NO₂ concentration and calculated HONO production. Instead this source correlates with j(NO₂) and with j(NO₂)x soil moisture. When only data within a single day was used there was even better agreement, possibly suggesting a source based on a surface reservoir that would likely have day to day variability.¹¹² In a study in rural southern China, again there was poor correlation between the predicted HONO production rate, but the average noontime HONO production rate correlated well with the average HNO₃ concentration over a 24 hour period, with even better agreement when particulate nitrate was also used for the correlation.¹¹⁵ Comparison between HONO concentrations between weekend
and weekday values for two US cities, has also indicated that HONO and NO₂ concentrations are not necessarily correlated.\textsuperscript{126}

In a unique set of measurements, high HONO concentrations were measured in the residual layer where emissions, deposition and ground processes are not important.\textsuperscript{127} This showed that a non-ground photochemical source was required to maintain measured HONO concentrations and low particle surface area further suggests a gas phase source. It is unknown the importance of such an additional gas phase source when the presence of other surface sources are also active.

\subsection*{1.3.2 Proposed HONO sources}

Given the complex nature of the “missing” HONO source, many mechanisms have been proposed for HONO formation in the atmosphere.\textsuperscript{128,129} HONO has been reported to be emitted from vehicles, often referred to as a direct emission source, though it is uncertain whether this is a primary or secondary process. HONO to NOₓ ratios of 0.8\% for gasoline vehicles\textsuperscript{130} and 2.3\% for diesel vehicles have been reported.\textsuperscript{131} These are consistent with the 1.7\% value reported by Rappenglück \textit{et al.}\textsuperscript{132} for a mixed fleet.

Gas phase mechanisms have also been proposed. As stated earlier, ortho-nitrophenols photolyze in the gas phase under solar radiation\textsuperscript{94} though the photolysis parameters are also not well known.\textsuperscript{7,133} The reaction between electronically excited NO₂ and water has also been proposed,\textsuperscript{134} however, models have suggested that this is not important in the atmosphere.\textsuperscript{106,108,135} More recently a gas-phase reaction between VOCs and HNO₃ has been observed in a laboratory experiment\textsuperscript{136,137} possibly supported by a field study by Ziemba.\textsuperscript{138} However, this reaction is less efficient in the presence of light,\textsuperscript{136} thus making it less likely to explain daytime HONO concentrations. HO₂/water clusters have been proposed to react with NO₂ to form HONO, however such a reaction has yet to be characterized.\textsuperscript{127,139}

Processes deemed to be more significant are heterogeneous reactions. It is well known that NO₂ undergoes surface hydrolysis to form HONO and HNO₃.\textsuperscript{140,141} As described above, in some cases this process has been able to describe night-time HONO concentrations, but it is insufficient to explain day time concentrations.\textsuperscript{eq:111,113} There is evidence that this conversion is more efficient over water surfaces, thus the NO₂ surface hydrolysis may be more important for areas near water or for global HONO chemistry due to the prevalence of ocean surfaces.\textsuperscript{142} NO₂ conversion on
soot surfaces through a reduction reaction has also been observed in the laboratory, however, the surfaces quickly deactivates upon NO₂ exposure and thus is unlikely to be important in the atmosphere.\textsuperscript{143} However, upon light exposure, NO₂ to HONO conversion is enhanced for a wide range of surfaces described above and the surfaces remain active over longer time scales. Surface illumination also promotes HNO₃ photolysis to form HONO, also discussed above.

Other more recently proposed mechanisms include soil processes where biological activity converts ammonium into nitrite, which can be protonated and released as HONO.\textsuperscript{144,145} Soil has also been seen to be a sink of HONO.\textsuperscript{146} Vandenboer \textit{et al}\textsuperscript{147,122} also suggests that HONO uptake onto the ground could be mediated by reaction with carbonates which can subsequently be displaced by acids such as HCl and HNO₃ during the day, increasing the daytime flux of HONO. A similar mechanism has also been proposed for particulate nitrite in China.\textsuperscript{148}

1.3.3 Modeling new HONO formation pathways

Many modeling studies have been carried out to evaluate the importance of different potential sources in different regions. Two recent studies, which attempt to rank the importance of the above sources, will be focused on here. Zhang \textit{et al}\textsuperscript{7} studied a region of China over a mixed land use area with urban, oceanic and rural land area using WRF-Chem. Of the modeled HONO concentrations, 42\% was attributed to photoenhanced heterogeneous NO₂ reactions, 29\% to soil emissions, 9\% to oceanic NO₂ to HONO conversion, 6\% to gas phase chemistry, 3\% to heterogeneous aerosol reactions and 2\% to vehicle emissions accounting for a total of 85\% of daily measured HONO or 65\% of daytime measured HONO.\textsuperscript{7} There was an overestimate at night and underestimate in early morning, suggested to be due to lack of modeled HONO deposition\textsuperscript{147} and a possible dew source of HONO in the morning.\textsuperscript{149,150} They also looked at HO₂/water cluster reaction but due to lack of information, did not include this in most of the analysis. HNO₃ photolysis on the surface was not considered.

Gall \textit{et al}\textsuperscript{151} used a two layer box model and Monte Carlo simulation to estimate sources and sinks of HONO for the Dallas-Fort Worth metropolitan area. At night, there is good model and measurement agreement with NO₂ conversion on the ground (53\%), biotic emissions (25\%), re-emission from a surface nitrite reservoir (19\%), direct emissions (5.3\%) and gas phase OH+NO (1.3\%) dominating the sources. During the day, only 33\% of the measured HONO is accounted for. This is made up of re-emission from a surface nitrite reservoir (10.5\%), soil biotic emissions
(6.7%), photo-enhanced NO₂ ground conversion (5.7%), NO₂ ground conversion (4.7%), gas phase OH+NO (4.6%), HNO₃ photolysis (0.7%) and direct emissions (0.7%). The VOC+HNO₃ reaction were deemed not important and was thus not included in the simulation. Different locations and different modeling methods were used for these two studies; however, they highlight the large degree of uncertainty still remaining for HONO chemistry.

A major limitation of these and other models is the lack of good characterization of the HONO formation processes even of those to which the model is most sensitive including dark and light photoenhanced ground NO₂ conversion, soil emissions and re-emission from a surface nitrite reservoir. For example, because the impact of surface type and other environmental variables are unknown only rough parameterization of both of these processes is possible with dark NO₂ uptake coefficients used ranging from 10⁻⁶ to 10⁻⁴. Photoenhanced NO₂ uptake coefficients have ranged from 2x10⁻⁵ to 6x10⁻⁵ with the response to sunlight sometime modeled as a linear response above 400 Wm⁻² other times it is scaled as a function of the ratio of the cube of measured j(NO₂) over the cube of noontime j(NO₂). Also, the RH dependence of NO₂ surface hydrolysis and evidence of RH dependence of HONO formation from field measurements, have rarely been incorporated. Gonclaves et al included an RH dependant function, however, even at maximum RH, the rate constant used in this parameterization was 100 times less than that used for the RH-independent parameterization, and was therefore deemed unimportant. More recently, a similar parameterization was used, but with a rate constant 2 orders of magnitude larger, more similar to what has been used for RH independent values, with this value scaling with 1/30% or 1/40% RH. Model to measurement agreement was improved with this method.

One of the parameters that influences all of the heterogeneous reactions is the amount of surface area available for heterogeneous reaction. While some models have avoided defining surface area, using deposition velocities instead, many models have defined surface area to volume fractions. Values between 0.1 and 0.3m⁻¹ have been used with surface layer heights from 17-35 m corresponding to a range of 1.7 m² to 10.5 m² per geometric surface area. In other studies, only the geometric surface area is used, creating an even greater range in the surface areas used. In addition, despite it being known that species can have significant life times on a surface, only one set of modeling studies has taken into account that the surface can act a reservoir for species.
More generally, few studies take into account vertical transport processes which Wong et al\(^{125}\) have shown can have a significant impact on HONO loss and therefore on HONO concentrations. They calculated 56-59\% of the HONO loss from the lowest 20m was due to this transport and 18-24\% for the lowest 300m. Gall et al\(^{151}\) also saw a significant impact of transportation in their model. Thus, to further the study of HONO formation and loss processes in the atmosphere, it is essential to focus of these many uncertainties. Mismatches in models and measurements may be issues in parameterizations, not necessarily further missing sources.

### 1.4 Summary of thesis objectives

There is still a lot of uncertainty regarding the role that urban grime plays in the environment. In this thesis I focus on using real urban grime samples to probe urban grime photochemistry. In Chapter 2 I use infrared spectroscopy to look at film changes during illumination without having to first modify the sample. This is coupled with proxy film experiments to better understand observed photochemistry. In Chapter 3, the focus is on the gas phase products of grime photochemistry using incoherent broadband cavity enhanced absorption spectroscopy to look for NO\(_2\) and HONO. The role of surface water is also examined, looking at changes in reactivity and at water uptake as function of relative humidity.

In Chapter 4, the laboratory reactive studies are followed up with a study of urban grime nitrate photochemistry in the field, comparing the composition of samples exposed to and shielded from real sunlight. This study was also complimented by a comparison of the composition of urban grime samples and PM\(_{10}\) to help elucidate post depositional processing of particles.

In Chapter 5, the results from the previous 3 chapters are used to develop a box model of urban grime photochemistry as an atmospheric HONO source. The sensitivity of this chemistry to a variety of inputs was examined to better inform future, more complex, HONO models as to the most important parameters that are needed to adequately evaluate the role of urban grime photochemical production of HONO. Finally, Chapter 6 presents the overall conclusion and future directions of this work.

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Chapter Two

Photochemical Renoxification of Nitric Acid on Real Urban Grime

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2.1 Introduction

Growing concern about air quality and climate change stresses the importance of understanding all of the relevant chemical pathways and processes. NO\textsubscript{x} (\(=\text{NO} + \text{NO}_2\)) is a class of molecules that is especially important in the atmosphere, mediating tropospheric O\textsubscript{3} concentrations by driving O\textsubscript{3} formation until high NO\textsubscript{x} levels where it begins to hinder the process.\(^1\) NO\textsubscript{x} is also a precursor for the formation of toxic organonitrates and is an indirect precursor for NH\textsubscript{4}NO\textsubscript{3} in aerosols.\(^2,3\)

Numerous pathways remove NO\textsubscript{x} from the lower atmosphere. NO\textsubscript{2} can react with OH or be hydrolyzed on surfaces to form HNO\textsubscript{3}.\(^4\) NO\textsubscript{2} can also react with NO\textsubscript{3} to form N\textsubscript{2}O\textsubscript{5}, which again forms HNO\textsubscript{3} when hydrolyzed.\(^4\) Another removal process for NO\textsubscript{x} is the reaction of HNO\textsubscript{3} with NH\textsubscript{3} to form NH\textsubscript{4}NO\textsubscript{3} aerosols.\(^4\) The subsequent wet or dry deposition of HNO\textsubscript{3} and NH\textsubscript{4}NO\textsubscript{3} from the atmosphere is generally thought of as a final tropospheric sink of NO\textsubscript{x}.

Recently there has been interest in possible mechanisms for recycling deposited nitrate and HNO\textsubscript{3} back to gas phase NO\textsubscript{x} in a process referred to as renoxification. Most of the proposed renoxification processes have involved surface chemistry such as the production of HONO and NO\textsubscript{2} from the heterogeneous reaction of NO with HNO\textsubscript{3} on silica.\(^5\) Heterogeneous photolytic mechanisms have also been proposed such as HNO\textsubscript{3} photolysis on Pyrex,\(^6,7\) ice,\(^8\) and leaves\(^9\) to form HONO, NO\textsubscript{2} and/or NO, as well as photodissociation of nitrate on mineral dust proxies forming NO and NO\textsubscript{2}.\(^10\) Photochemical renoxification of nitrate in snow packs has also been proposed as the main source of NO\textsubscript{x} in polar regions.\(^11\)

The photolysis of HNO\textsubscript{3} is reported to occur at least 2 orders of magnitude faster on Pyrex than in aqueous solution or in the gas phase.\(^7\) The increased rate is consistent with a large increase in the absorption cross section reported for molecular HNO\textsubscript{3} deposited on a fused silica surface.\(^12\) This change in the absorption spectrum demonstrates how surfaces can influence the optical and photochemical properties of adsorbed species. Therefore it is important to examine photolytic renoxification processes in an urban environment where there is significant surface area coated in a chemically complex film\(^13\) which could mediate renoxification chemistry.

This film, often referred to as urban grime, is of interest both for its aesthetic implications and for its potential atmospheric impacts.\(^14-18\) Currently only a small number of studies of these films
have reported their chemical composition and partitioning properties.\textsuperscript{16,19} There have also been attempts to model the film’s atmospheric impact\textsuperscript{15,18} and to use various proxy substances to predict reactivity.\textsuperscript{20,21} However, these efforts have focused on the organic components of the film, which only make up 5-23\% of the total film mass.\textsuperscript{14,22}

A less examined portion of the film is the approximately 7\% nitrate fraction.\textsuperscript{22} Previously, it was held that films mediate nitrogen oxide chemistry through facilitating the runoff of the film nitrate to waterways during precipitation.\textsuperscript{15} A more recent study using an organic proxy film shows evidence that deposited HNO\textsubscript{3} may undergo photochemistry, indicating a possible renoxification role for the films.\textsuperscript{23}

In the present work we describe experimental results showing rapid nitrate photolysis on unmodified, authentic urban grime samples. Proxy film studies suggest a photolysis mechanism similar to that seen in aqueous solutions, releasing NO\textsubscript{2} and/or HONO into the atmosphere. A comparison of film and aqueous nitrate photolysis rates implies a high significance of urban grime as a mediator for renoxification through photolysis.

2.2 Experimental Methods

Experiments consisted of exposing “real” or proxy urban grime films, which had been deposited on the face of a ZnSe Attenuated Total Reflection (ATR) crystal, to simulated solar output and following changes in the film’s composition using ATR-FTIR spectroscopy.

2.2.1 Authentic Films

Authentic pollutant films were collected by placing the ATR crystals outside in downtown Toronto. They were either positioned vertically or mounted onto the underside of a platform at a 45° angle and were protected from precipitation using an open enclosure. Sampling periods and meteorological conditions surrounding the crystal during grime growth for each sample are given in Table 7.1.

2.2.2 Proxy Films

Proxy films were composed of a 1:1 by mass mixture of Apiezon N vacuum grease and glycercyl trioleate. Approximately 1 mg of the mixture was applied as a thin film to an ATR crystal using a Kimwipe. In order to dope the films with HNO\textsubscript{3}, approximately 5 mL of concentrated HNO\textsubscript{3}
was put in a stoppered 50 ml Erlenmeyer flask and allowed to equilibrate for at least 15 min. A portion of the headspace was drawn up into a Pasteur pipette and expelled onto the film on the ATR crystal.

2.2.3 Photochemical Experiments

Samples were illuminated on the ATR crystal in a Suntest CPS solar simulator equipped with a xenon lamp with a 290 nm filter and a water cooled base held at 4°C. “Dark” experiments were carried out by covering the crystals with aluminum foil during the illumination period. The radiative flux in the nitrate absorption region was quantified using an aqueous nitrate actinometer in order to provide a good estimate of the intensity of light that can be absorbed by grime nitrate. The full actinometry is described by Jankowsiki but a brief overview will be provided here.

Solutions of 1 mM benzoic acid, 2.5 mM potassium nitrate and 10 mM sodium bicarbonate were prepared and transferred to quartz wells with a quartz cover to prevent water evaporation. The wells were illuminated in the solar simulator alongside film experiments. Aqueous nitrate photolyses upon illumination and forms OH, which can react with the benzoic acid (BA), forming salicylic acid (SA). Aliquots were taken throughout the illumination period and analyzed by fluorescence at 410 nm to detect the SA. An average quantum yield of $2.08 \times 10^{-3}$ at 298K for SA formation and an average nitrate absorption coefficient of $2.89 \times 10^{3}$ cm$^2$ mol$^{-1}$ in the bandwidth of interest, allowed for the calculation of a cumulative photon exposure. Plotting photon exposure as a function of time yielded a slope of radiant flux as shown in Figure 7.1. The nitrate photolysis rate was found by multiplying the SA formation rate by a factor of 4.6 as determined experimentally by Jankowski.

Authentic and proxy pollutant films were analyzed using attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR) using a 5 cm, 25 reflection trapezoidal ZnSe crystal and an incident angle of 45°. The illuminated samples were removed from the solar simulator periodically for the time required to measure the spectra. Spectra were referenced to a background spectrum collected before the film was applied. 16 scans were acquired for each spectrum with a 2 cm$^{-1}$ resolution. Following the collection of each spectrum, an ATR correction followed by a baseline correction was carried out using the Spectrum v5.0.1 software (Perkin-Elmer) with a contact correction factor of zero.
2.2.4 Materials

Glyceryl trioleate was purchased from Sigma-Aldrich with stated purity of 99+%. Benzoic acid (99.5+%), potassium nitrate (99+) and reagent grade HNO₃ were purchased from ACP. All chemicals were used without further purification.

2.3 Results

2.3.1 Real films

![IR spectrum of grime collected in downtown Toronto after approximately 1 week of atmospheric exposure (black) and the same grime sample following illumination by the solar simulator for 90 min (red). The inset shows a magnification of the spectrum below 2000 cm⁻¹. Note the loss of intensity in the ~3400 cm⁻¹ region due to decreased RH and the decrease in intensity in the 1300-1400 cm⁻¹ range due to the loss of nitrate. The features observed around 2800 cm⁻¹ are thought to be artifacts due to the weeklong time delay between background and sample measurement. They are not important to the chemistry discussed here.](image)

_Figure 2.1:_ IR spectrum of grime collected in downtown Toronto after approximately 1 week of atmospheric exposure (black) and the same grime sample following illumination by the solar simulator for 90 min (red). The inset shows a magnification of the spectrum below 2000 cm⁻¹. Note the loss of intensity in the ~3400 cm⁻¹ region due to decreased RH and the decrease in intensity in the 1300-1400 cm⁻¹ range due to the loss of nitrate. The features observed around 2800 cm⁻¹ are thought to be artifacts due to the weeklong time delay between background and sample measurement. They are not important to the chemistry discussed here.
A representative IR spectrum of grime collected for 7 days in downtown Toronto is shown in Figure 2.1 as the black trace. There is a strong, broad peak centered at 3415 cm\(^{-1}\) characteristic of the presence of OH functionality. Figure 2.2a depicts how that region of the spectrum changes as the relative humidity (RH), measured using a Traceable\textsuperscript{®} Hygrometer, is changed by exposing the crystal to different mixtures of ambient air and dry air. A plot of the intensity measured at 3415 cm\(^{-1}\) is shown in Figure 2.2b with vertical lines indicating a change in RH.

The film responds quickly to a change in humidity, with the new equilibrium being reached in less than 10 minutes. The decrease in intensity observed when the RH drops from 20% to 10%, followed by its increase when the RH is raised to 15%, indicates that the change in the OH peak intensity is reversible. These observations suggest that ambient water vapor undergoes equilibrium adsorption to the film and is an important contributor to the IR absorption at 3415 cm\(^{-1}\). Because the film spectrum is referenced to the bare crystal, it is clear that this water affinity is a property of the film rather than the underlying substrate. Although previous work on silicon ATR crystals has shown RH dependent OH features, the absolute change in intensity for a change in RH of 13% to 22% was reported to be approximately 0.0005.\textsuperscript{6} This is negligible in comparison to the more than 0.01 change in absorbance observed here from 15% to 20% RH, again indicating a unique property of the film. The film’s water affinity has not previously been observed because past studies have been limited to extracting the components of urban grime using organic solvents,\textsuperscript{16,19,22} thus preventing the detection of water. The presence of water could have a significant impact on the properties of the film, such as enhancing the uptake of soluble species and allowing ion dissociation.
Figure 2.2: (a) 4000-2500 cm\(^{-1}\) region of grime spectrum at varying relative humidities. (b) Plot of the absorbance at 3415 cm\(^{-1}\) as a function of time with vertical lines indicating a change in RH. For both plots, RH of 20% is depicted in black, 15% is in red and 10% is in blue.

Other noteworthy peaks shown in Figure 2.1 are observed at 1412 cm\(^{-1}\) and 1320 cm\(^{-1}\) and are characteristic of the nitrate moiety, probably arising from the dissociation of HNO\(_3\) on the film,\(^{26}\) consistent with previous film composition studies by Lam et al.\(^{22}\) and Chabas et al.\(^{27}\) The presence of nitrate anion is also consistent with previous work on organic films containing pH-sensitive dyes.\(^{23}\) These show spectral changes implying acid dissociation when the film is
exposed to an approximately 1:1 mixture of gas phase HNO$_3$ and H$_2$O$_{(g)}$, using the method described above. It is not clear from spectra such as that displayed in Figure 2.1 whether molecular HNO$_3$ is also present on the film, because peaks for molecular HNO$_3$ are too weak to distinguish from overlapping water and nitrate peaks. However, as we discuss below, if molecular HNO$_3$ is present in the film and contributing to the IR intensity in the nitrate region, it does not seem to photoreact as rapidly as the anion.

The red trace in Figure 2.1 shows the IR spectrum of the film after 90 minutes of illumination. A clear decrease in the intensity of the nitrate peaks is observed, suggesting a photochemical process that removes nitrate. In order to characterize the nitrate disappearance, its IR absorption was monitored over time as shown in Figure 2.3a, where the light was turned on at 0 min. The 1320 cm$^{-1}$ peak was chosen for monitoring because changes in water vapor levels interfere with the peak at 1412 cm$^{-1}$. When experiments were run for up to 4 hours, the nitrate signal decayed to a constant value. Therefore, the data was fit with equation 2.1, where $I_0$ is the initial intensity, $I$ is the intensity at time $t$, $J$ is the J-value for the photochemical process and $B$ is the background signal intensity.

$$I = I_0 e^{-Jt} + B$$  \hspace{1cm} (2.1)

The average rate of loss over 4 different grime samples, with error reported as one standard deviation, is $(5.4 \pm 2.7) \times 10^{-4}$ s$^{-1}$. Experiments were also performed in which the film was doped with additional nitrate through the addition of gas phase HNO$_3$ as described above. The average rate of loss for 4 trials is $(3.6 \pm 1.2) \times 10^{-4}$ s$^{-1}$. No loss was observed in the dark for either type of experiment.

The background signal is only observed for the grime samples and increases when HNO$_3$ is added to the sample, suggesting that this term relates to the presence of unreacted HNO$_3$. It is possible that there are sites within the urban grime which bind the HNO$_3$ either as nitrate or in its molecular form, preventing it from undergoing photolysis and thereby giving rise to the observed background.
Figure 2.3: Plots showing representative nitrate loss kinetics in the solar simulator (a) Nitrate loss from urban grime: Plot of the natural logarithm of the absorbance at 1320 cm\(^{-1}\) in a representative grime sample as a function of time where the film is exposed to the output of the solar simulator at 0 min (data points). The data is fit to a first order decay to a background level as described by equation 2.1 (solid trace). (b) Growth of salicylic acid due to aqueous nitrate photolysis: Plot of salicylic acid concentration as function of time upon illumination of the nitrate actinometer (data points) with a linear fit (solid trace).

### 2.3.2 Actinometry

To adjust the measured J-value to one that is appropriate to ambient sunlight, the radiant output of the solar simulator was quantified. Aqueous nitrate photolysis was used for this purpose in order to closely resemble the experimental system and therefore accurately measure the light intensity in an appropriate bandwidth for film nitrate photochemistry. The disappearance of
nitrate due to aqueous photolysis was too slow to obtain a photolysis rate by monitoring nitrate directly. Therefore, a previously developed nitrate actinometer was used where BA serves as an OH scavenger for the nitrate photolysis product OH forming SA. The rate of SA formation is found from the plot of SA concentration as a function of time as shown in Figure 2.3b. The average rate of aqueous nitrate photolysis from 6 trials is \((4.5\pm0.7) \times 10^{-8} \text{ s}^{-1}\), significantly slower than that measured on grime.

### 2.3.3 Proxy film

**Figure 2.4:** IR spectrum of components added to the film upon addition of gaseous HNO\(_3\) to an Apiezon N film calculated from the subtraction of the pure Apiezon N film spectrum from the film spectrum after the HNO\(_3\) addition. Note the features at \(~3400\ \text{cm}^{-1}\) and \(1700\ \text{cm}^{-1}\), corresponding to water, and at \(1300\-1400\ \text{cm}^{-1}\) corresponding to nitrate. Molecular HNO\(_3\) cannot be distinguished from the more intense water and nitrate peaks.

After establishing the J-value for the nitrate ions in real films, experimental focus shifted to organic proxy films in order to probe the nitrate loss mechanism. Initially a film of Apiezon N was spread on the crystal with HNO\(_3\) being added from the gas phase as described above. Figure 2.4 shows the difference spectrum calculated by the subtraction of the initial film from that with added gas phase HNO\(_3\). The resulting spectrum shows both added H\(_2\)O from the headspace above the nitric acid at \(~3400\ \text{cm}^{-1}\) and \(~1600\ \text{cm}^{-1}\) as well as nitrate with peaks at the same shifts.
as those assigned for the real films. The nitrate peak at 1314 cm\(^{-1}\) was monitored over time during illumination and the intensities were also fit to equation 2.1. For these films the calculated B terms were negligible. The resulting rate of nitrate photolysis is close to that seen on authentic films. The nitrate decay rates are presented in Table 1.

<table>
<thead>
<tr>
<th>Surface</th>
<th>J-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grime</td>
<td>((5.4 \pm 2.7) \times 10^{-4} \text{ s}^{-1})</td>
</tr>
<tr>
<td>HNO(_3) doped grime</td>
<td>((3.6 \pm 1.2) \times 10^{-4} \text{ s}^{-1})</td>
</tr>
<tr>
<td>HNO(_3) doped proxy grime</td>
<td>((2.7 \pm 1.0) \times 10^{-4} \text{ s}^{-1})</td>
</tr>
<tr>
<td>Aqueous nitrate</td>
<td>((4.5 \pm 0.7) \times 10^{-8} \text{ s}^{-1})</td>
</tr>
</tbody>
</table>

**Table 2.1:** J-values for nitrate decay on different surfaces. The uncertainties represent one standard deviation.

**Figure 2.5:** Initial IR spectrum of proxy grime composed of Apiezon N and glyceryl trioleate (black) and IR spectrum of the same film after 300 min of illumination by the solar simulator (red). Note the significant growth at 3387 cm\(^{-1}\) due to OH functionality following illumination.
Glyceryl trioleate was added to the proxy film to provide some mechanistic insight about the nitrate loss. It is a common biogenic molecule, which can simulate real film components and will also react quickly with OH. The mixture of grease and glyceryl trioleate was spread on the ATR crystal and an IR spectrum was collected resulting in the black trace of Figure 2.5. A baseline photochemical process was established by illuminating the proxy film in the absence of HNO$_3$ for 300 min, resulting in the red trace. An increase in the absorption in the $\sim$3500 cm$^{-1}$ region is observed following illumination (not observed in the dark). This is probably due to formation of alcoholic groups following photo-oxidation in air. Figure 2.6 shows a representative result of this absorption intensity over time fit to first order kinetics. The average rate constant given by the fits for 4 samples is $(4.2\pm0.3) \times 10^{-4}$ s$^{-1}$.

![Figure 2.6: Plot of absorbance at 3387 cm$^{-1}$ of a proxy film, similar to that whose spectrum is shown in Figure 2.5, as a function of illumination time (data points). The fit to first order growth kinetics is shown as the solid trace.](figure)

Having established the baseline photochemical process occurring on the proxy film, the impact of nitrate photochemistry on the film could be examined. Gas phase HNO$_3$ was added to the film as outlined above. The film with added nitrate showed significantly faster growth of the OH feature as shown in Table 2. Due to interference of the glyceryl trioleate signal, nitrate loss could not be measured directly in these experiments. Again, no oxidation was observed in the dark.
Table 2.2: Oxidation kinetics of proxy films with and without added HNO\textsubscript{3(g)}. The uncertainties represent one standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>$k_{OH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proxy Film</td>
<td>$(4.2 \pm 0.4) \times 10^{-4}$ s\textsuperscript{-1}</td>
</tr>
<tr>
<td>Proxy Film with HNO\textsubscript{3}</td>
<td>$(6.0 \pm 1.2) \times 10^{-4}$ s\textsuperscript{-1}</td>
</tr>
</tbody>
</table>

2.4 Discussion

The IR absorption intensity of nitrate present in real urban grime decreases upon illumination, clearly indicating a loss of nitrate. This suggests that the deposition of HNO\textsubscript{3} to urban surfaces is not the final fate of reactive nitrogen in the urban troposphere. The nitrate loss is possibly due to rapid nitrate photolysis which has also been proposed for other surfaces.\textsuperscript{6,8,9} Equations 2.2 and 2.3 describe the mechanism observed for aqueous phase nitrate photolysis; this has also been suggested as the photochemical mechanism giving rise to the loss of HNO\textsubscript{3} from an organic film during illumination.\textsuperscript{23} Due to the acidity of the nitric acid doped film, the chemistry shown in Equation 2.2 is expected to result in the formation of HONO, as seen by Zhou et al\textsuperscript{7} while equation 2.3 results in the formation of OH as well as NO\textsubscript{2}.

An alternative mechanism for nitrate loss is HNO\textsubscript{3} evaporation. However, the stable nitrate signal observed for experiments in which the sample was covered, but subject to the same temperature conditions as the uncovered samples, suggests that this is a photochemical mechanism and not merely thermal evaporation. The significant water presence on the real grime samples and the nitrate features in the IR spectrum suggest that the majority of the deposited HNO\textsubscript{3} dissociates to nitrate on the film. The nitrate would have to recombine with a proton before evaporation could occur, creating a potentially significant barrier for HNO\textsubscript{3} desorption. A previous study of nitrate loss from an organic film doped with HNO\textsubscript{3(g)} also suggests evaporation is unlikely. Upon illumination, both nitrate and protons were lost much more quickly from the film than for HCl doped films.\textsuperscript{23} This is inconsistent with evaporation because evaporation of those molecular acids is expected to occur at the same rate.\textsuperscript{23}
To further investigate the mechanism of nitrate loss, an organic proxy film containing an OH scavenger was used. Because the J-value for nitrate photolysis on the proxy film is similar to that observed on authentic films, it is possible that the nitrate is experiencing a similar environment on both types of films. As such, mechanistic information gained on the proxy film can be used to predict what is occurring on the real film.

The addition of HNO₃ to the proxy grime film causes an increase in the glyceryl trioleate oxidation rate. This indicates the formation of OH, which reacts with the glyceryl trioleate to form alcoholic groups. OH formation is consistent with the photolytic mechanism forming OH directly via Equation 2.3, or possibly through HONO photolysis subsequent to its production as written in Equation 2.2. The rate of nitrate loss on the proxy grime is the same order of magnitude as the increase in the oxidation rate of the HNO₃ doped proxy film. This suggests that nitrate photolysis forming OH is not only occurring, but it is a dominant loss process for grime nitrate.

A significant implication of nitrate being lost by photolysis is that the formation of OH is accompanied by the simultaneous production of NO₂ and/or NO that can be released into the urban atmosphere. As such, the nitrate loss from urban grime results in the recycling of NOₓ making the film a NOₓ reservoir rather than a NOₓ sink.

The measured photolysis rates can be adjusted to atmospherically relevant rates by comparing the radiant output from the solar simulator calculated from the actinometer to that of the sun. The solar radiant output in the bandwidth of the nitrate actinometer for noontime Toronto in July is approximately $3.7 \times 10^{-3}$ µeinsteins cm⁻² s⁻¹ ⁴ corresponding to an aqueous nitrate photolysis rate of $(1.0 \pm 0.1) \times 10^{-7}$ s⁻¹. ²⁴ Adjusting the film’s measured photolysis rate by scaling the solar simulator output to this actual solar output, results in a lifetime of 14 min for nitrate in the film, which is four orders of magnitude shorter than the 116 days for aqueous nitrate. The grime nitrate lifetime is also four orders of magnitude shorter for gas phase HNO₃ photolysis and more than an order of magnitude shorter for nitrate photolysis on glass in comparison to the corresponding sunlight-adjusted lifetimes. ⁷ Such an enhancement from that on glass may be due to the presence of photosensitizers in both the real and proxy urban grime samples enhancing the effective absorption of light by nitrate.
2.5 Conclusions

The short lifetime of nitrate on the grime in comparison to other media indicates the role of urban grime surfaces in changing the fate of nitrate in the atmosphere, and implies a potentially significant impact on atmospheric concentrations of NO$_x$. The grime may facilitate the renoxification of the troposphere meaning that impervious surfaces are not a long-term sink of NO$_x$. Instead these surfaces allow for grime to grow forming merely a short-term reservoir of NO$_x$ before it is released back into the atmosphere. In the future the possibility of renoxification from other grime nitrate sources will be examined.

2.6 References


(4) Finlayson-Pitts, B. J.; Pitts, J. N. *Chemistry of the upper and lower atmosphere: Theory, experiments, and applications*; Academic Press: San Diego, California, USA, 2000.


Chapter Three

Formation of Reactive Nitrogen Oxides from Urban Grime Photochemistry


**Contributions:** Experiments were designed and performed by Alyson M. Baergen. The manuscript was written by Alyson M. Baergen, with critical comments from D.J. Donaldson
3.1 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\(_{\text{g}}\) is an important photochemical source of OH.\(^1\) 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\(_2\)O\(_5\), 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\(_2\)\(^2\)\(^-\) 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,\(^5\) snow,\(^2\)\(^-\)\(^4\),\(^6\) organic films,\(^7\) leaves,\(^8\) plants,\(^9\) building materials\(^9\) and mineral oxide surfaces such as aluminum oxide and zeolite.\(^10\)\(^-\)\(^13\) 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.\(^14\)\(^-\)\(^17\) Other processes, such as reactions of NO\(_x\) (total reactive nitrogen) on aerosols\(^18\) and soil mediated processes,\(^19\),\(^20\) 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 (e.g., 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.\(^21\)\(^-\)\(^34\) 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,\(^35\)\(^-\)\(^37\) but there is evidence suggesting that they can also impact the reactivity of species contained within the film, such as PAHs,\(^38\),\(^39\) and nitrate/HNO\(_3\).\(^40\),\(^41\)
Additionally, it has been predicted that there is enough water present on all environmental surfaces, even those hydrophobic in nature, to influence heterogeneous reactions.\textsuperscript{42} Rubasinghege and Grassian have discussed the role of water on environmental surfaces outlining a wide range of mechanisms through which water can impact reactivity.\textsuperscript{43} 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.\textsuperscript{5,10} 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 \textit{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.\textsuperscript{44} Related to grime surfaces, Sumner \textit{et al.} have shown how different surfaces, representing building surfaces, vary in their water uptake behavior.\textsuperscript{42} There are only minimal studies performed looking at water interactions with grime, but they show that grime films impact water uptake on surfaces.\textsuperscript{40,45} 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.

3.2 Experimental

3.2.1 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.

3.2.2 Incoherent Broad Band Cavity Enhanced Spectroscopy (IBBCEAS)

Gas phase product formation was determined using IBBCEAS. The system is described in full elsewhere. 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\textsubscript{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\textsubscript{2} were calculated using the method described by Fiedler and Gherman\textsuperscript{47,48} and previously used by us.\textsuperscript{46} This uses measured mirror reflectivity,\textsuperscript{49} Rayleigh cross sections of the carrier gas\textsuperscript{50} and the absorption cross sections of NO\textsubscript{2}\textsuperscript{51} and HONO\textsuperscript{52} to fit the experimental spectra with DOASIS software.\textsuperscript{53} 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 Figure 3.1. Calculated detection limits (signal/noise = 3) are 1.50x10\textsuperscript{11} molecules cm\textsuperscript{-3} (~6ppb) for NO\textsubscript{2} and 6.5x10\textsuperscript{10} molecules cm\textsuperscript{-3} (~3ppb) for HONO.

3.2.3 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 (\(\lambda > 295\text{nm}\)) 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 NO₂.

The set up was further tested by flowing a known concentration of NO₂ through the empty chamber and IBBCEAS cell. A flow containing 6.0 ppm NO₂ in N₂ was diluted in a stream of N₂ down to \((4.76 \pm 2.4) \times 10^{12}\) molecules/cm³ at varying RHs. NO₂ and HONO steady state concentrations measured at each RH were used to characterize the IBBCEAS response to changes in humidity and the efficiency of NO₂ hydrolysis to HONO on the walls of the reaction chamber and IBBCEAS cell.

3.2.4 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. 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 7.2.

3.2.5 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. 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 \(\Delta m\) is the mass change, \(C\) is a proportionality constant and \(\Delta f\) 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. 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 \(8.147\times10^7\) Hz cm\(^2\) g\(^{-1}\) for the 0.550 inch, 6 MHz crystals used in this study. The RH was measured using a Traceable® Memory Hygrometer/Thermometer.
3.3 Results

3.3.1 Photochemical Production of nitrogen oxides

Figure 3.1: Experimental absorption spectrum fit with a reference HONO spectrum\textsuperscript{52} using DOASIS.\textsuperscript{53} This spectrum was measured at RH = 37\% and represents a concentration of $2.17 \times 10^{11}$ molecules cm$^{-3}$.

Figure 3.1 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 368 nm, and a second peak appearing at 384 nm, 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 in chapter 7 that NO$_2$ hydrolysis on the walls of the chamber and/or IBBCEAS cell via equation 3.1\textsuperscript{56} would prevent NO$_2$ from being detected even if it was originally formed in the chamber. Because of this hydrolysis there is an 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 Figure 7.2). 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.

\begin{equation}
2 \text{NO}_2 \rightarrow \text{HONO}_{(g)}^{+} + \text{HNO}_3(\text{surface})
\end{equation}
Figure 3.2: 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.

Figure 3.2 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 RHs. 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 RH. 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 Figure 3.2, 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.\(^\text{41}\) 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.

**Figure 3.3**: 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.

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 Figure 3.3. 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.

### 3.3.2 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. 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. 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 Figure 3.4 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.

**Figure 3.4:** 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.
3.4 Discussion

The illumination of urban grime results in the release of gas phase nitrogen oxides in the form of NO₂ and/or HONO. While previously predicted,⁴⁰,⁴¹ 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 films²⁵,²⁷ and that this nitrate is photolabile.⁹,⁴⁰,⁴¹ Nitrate photolysis is known to form NO₂ 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 NO₂ at varying ratios depending on the surface.⁹ If HONO is a product for this chemistry one possibility is the protonation of nitrite, another known product of aqueous nitrate photochemistry. However, the results discussed in the next chapter is consistent with a basic film due to the loss of ammonium therefore, we do not expect the film to be acidic and for this mechanism to be important.⁴¹ The organic fraction of the film could also play a role in the conversion of NO₂ to HONO such as has been seen on organic surfaces such as humic acid⁵⁷ and PAH films.⁹ NO₂ to HONO conversion could also occur through NO₂ hydrolysis within the film, which has recently been reported to constitute the only mechanism observed for HONO formation from HNO₃ photolysis on quartz.⁵⁸ 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 photochemically active organo-nitrogen compounds may be present, though they have yet to be detected within grime films. If present, these compounds may react as indicated by Han et al⁵⁹ who have reported the formation of R-NO, R-NO₂ and R-ONO₂ species on NO₂ exposed soot, which can photolyze to form NO and HONO.

In contrast to our previous studies showing the photolability of nitrate in grime,⁴⁰,⁴¹ the current study does not show nitrate depletion upon illumination. This apparent discrepancy can be explained by the difference in experimental methods between studies. In both previous studies, the films were “younger”, with between 1 and 6 weeks of collection time, in comparison to the year-long collection here. In addition, for the Leipzig samples described in Baergen et al⁴¹ the “light” sample was continually exposed to ambient sunlight, whereas in the present experiment, like the previous Toronto study,⁴⁰ the samples were shielded from the light for the entire collection and then illuminated in a controlled laboratory setting. Both of the previous studies
suggested that only a portion of the film is photolabile and the current result indicates that this non-photoactive proportion of the film forms a greater proportion of the film over time. Continued growth of the film may block photoactive sites or bury photoactive components of the film, making a smaller portion available for reaction. Ye et al found a logarithmic relationship between surface density of nitrate/HNO$_3$ and reaction rate$^9$ which could also indicate only nitrate/HNO$_3$ on the surface remains reactive in comparison to the nitrate/HNO$_3$ within the film. Whether a film grown under continual exposure to ambient light would show the same trend is an open question. Exposure to precipitation could also impact the photoactive fraction, both in potential compositional changes as different fractions are removed from the film during precipitation and in preventing such long-term film growth. This large non-photoactive fraction may also explain the disparity between the depletion of gas phase products over time and the lack of a corresponding nitrate drop; the photolabile fraction is small enough that the approximately 12% loss of reactive precursor implied by the gas phase result is too small of a proportion of the total nitrate to be detected within the extracts of the whole film.

The photochemical release of gas phase NO$_2$ and/or HONO is clearly dependent on relative humidity and therefore, as seen through the water uptake experiments, on the water content of the film. In particular, the product formation increases as the amount of water on the film increases, up to a relative humidity of 35% after which case, the chemistry is not impacted by further addition of water up to 60%. This behaviour is different from what has been seen from nitrate photolysis experiments on other surfaces. In a study performed on HNO$_3$ deposited on pyrex glass, the combined NO$_x$ and HONO formation rate was highest at 0% and decreased for 20% and 50% while the reported HONO production rate was lowest at 0% and then increased up to 80%.$^5$ However, the authors assumed a constant NO$_2$ to HONO wall conversion independent of relative humidity taken from a measurement in a different system and thus the determined ratios may not reflect the real distribution of products emitted as a result of the photochemistry.$^5$ 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%.$^{10}$ 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 the film or enhanced hydrolysis and dissociation of species such as HNO₃, NH₄NO₃ or N₂O₅ producing more of the photolabile precursors.⁴³ The increased reactivity could also be the result of a viscosity change within the film. It is known that the viscosity of the particles changes based on relative humidity,⁶⁰ 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,⁶¹ and faster PAH ozonation within SOA coated particles at high RH as compared to lower RH.⁶² This sort of behaviour would not be anticipated for a clean glass, or metal oxide surface. The leveling off of product formation at RHs 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 has been discussed by Rubasinghege et al,¹⁰ which would compete with further growth causing a net leveling 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 indicate that there was a photolytic source of HONO within 20m of the ground.¹⁴,¹⁵ Studies done in other urban centers such as London¹⁶ and Los Angeles¹⁷ also suggest there is an unknown photochemical HONO source. Many suggest that this source is correlated to NO₂ however, in a study carried out in Bakersfield and Pasadena, the HONO source does not correlate with NO₂.⁶³ As discussed by those authors, the formation of HNO₃ 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 NO₂(g). Grime would likely have a similar delayed response; in addition, the RH dependence of the grime photochemistry could serve as a further mechanism for an offset in NO₂ values and HONO
production, due to the cycling of RH conditions in the atmosphere and therefore, the cycling of this source strength. However, more quantification and speciation is required to evaluate the importance of such a grime source.

3.5 Conclusions

Urban grime was collected onto glass substrates without modification and illuminated. Grime photochemistry produced nitrogen oxides in the form of NO$_2$ and/or HONO. Such chemistry is not currently included in urban air models, but could impact NO$_x$ and/or HONO levels in these centers. The production of these species is dependent on RH, again highlighting the need to consider water content when studying environmental surfaces.

3.6 References


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Chapter Four

Chemistry of Urban Grime: Inorganic Ion Composition of Grime vs. Particles in Leipzig, Germany


Contributions: Experiments were designed by Alyson M. Baergen and Sarah A. Styler with assistance from Dominik van Pinxteren and Konrad Müller. Sample extraction and analysis was done by Alyson M. Baergen, Anett Dietze and Susanne Fuchs. Data interpretation and writing of the manuscript was done by Alyson M. Baergen, with critical comments from Sarah A. Styler, Dominik van Pinxteren, Konrad Müller, H. Herrmann and D. James Donaldson
4.1 Introduction

Heterogeneous and multiphase reactions are important in the troposphere, promoting reactions that are not favourable in the gas phase.\(^1\) \(\text{N}_2\text{O}_3\) and \(\text{NO}_2\) hydrolysis,\(^2,3\) \(\text{ClNO}_2\) formation,\(^4,5\) heterogeneous \(\text{SO}_2\) oxidation,\(^6\) interactions of trace gases with mineral dust components\(^7,8\) and surface photochemistry\(^9\) are all examples of such important atmospheric-surface interactions. The studies of these reactions are usually limited to particle and sea surfaces; however, in an urban setting, there are many impervious surfaces, such as buildings, roadways and windows providing another type of surface that is often overlooked despite having a combined surface area estimated to be similar to that of atmospheric particles.\(^10,11\) When impervious surfaces are exposed to the atmosphere, surface films form over time.\(^12-26\) Sometimes referred to as urban grime, the films are a complex mixture of species formed via the deposition and subsequent processing of atmospheric species.\(^27\)

Models have been developed that try to characterize the growth of urban grime and give insight into the growth mechanism. Many of these are empirical models, fitting observed changes in total film mass, a particular constituent’s mass or changes in optical properties to descriptive equations as a function of time.\(^17,20,28\) These models highlight the complexity of the growth mechanisms and the variability of film formation depending on location. More recently the models have been further parameterized to include atmospheric measurements, giving more insight into the growth mechanism. They show that \(\text{PM}_{10}\) is the dominant driver for film formation but also that the inclusion of \(\text{SO}_2\) and \(\text{NO}_2\) into the models allows for a better fit to the observed growth characteristics.\(^29,30\) Semi-volatile compounds have also been observed to approach an equilibrium between the film and surrounding atmosphere,\(^25\) implying dynamic partitioning behaviour, and polymers have been detected that are suggested to form through reactions within the film.\(^16\) This highlights that grime is not merely a collection of deposited particles, but rather acts as a dynamic system, which is influenced by the continued exposure to the atmosphere.

While such models are helpful in understanding film formation, they say little about the potential environmental impact of urban grime. Diamond and coworkers have begun to address this issue by developing regional models which include film dynamics, showing that the films enhance the mobility of organic constituents in the environment through partitioning and water
At this point, however, there is limited work on inorganic species and understanding the films as a reactive environment. Reactive studies have been limited to the use of organic proxy films, such as PAH films, a mixture of potassium nitrate and pyrene, or octanol spread on a film of silicon vacuum grease. The exception is our recent laboratory report on nitrate photochemistry within real grime, which demonstrated that the grime-associated nitrate is photolabile.

In the current study, we measured the composition of one of the major sources of these films, PM$_{10}$ (particles smaller than 10µm in diameter), simultaneously with that of grime samples collected at the same location. The inorganic composition will be the focus of this paper, while the organic composition will be reported separately. There has been only a single study published to date in which particle composition was measured simultaneously to that of grime, with the particles being collected over 3 months using an air filtration unit. Further investigation is clearly warranted, using a more standardized particle sampling method and with samples taken at a higher time frequency to more fully track the formation of the grime in the context of changing particle concentrations. The goal of the present study is to utilize the comparison of particle and grime compositions during initial grime formation to begin to identify grime-mediated processes that could impact environmental cycling of some key chemical species. Here we also report the first measurement of urban grime photochemistry derived from field measurements using real sunlight.

### 4.2 Experimental

Sampling of urban grime and atmospheric particles was carried out in Leipzig, Germany between September 16 and October 25, 2014 at the “Leipzig-Mitte” (51.33°N, 12.38°E) site described previously. Briefly, this is a roadside site at the corner of a major intersection opposite the main train station in the middle of Leipzig. Figure 7.3a of the Supporting Information (SI) shows a photograph of the sampling site. Local meteorological, NO$_x$ and SO$_2$ measurements were collected over the duration of the campaign from the same location by the Saxon State Agency for Environment, Agriculture and Geology and are presented in Figure 7.4.
4.3 Film Sampling

Film samples were collected by exposing 3 mm diameter soda-lime glass beads (Sigma Aldrich) to the atmosphere. These beads, similar to those used by Wu et al., were chosen to provide a high surface area surrogate for common window glass. A possible impact of using bead surrogates is that the geometry of the beads, with both horizontal and vertical surfaces, may favour the collection of larger particles in comparison to vertical window surfaces. Beads were prepared by soaking in a base bath for one hour followed by rinsing the beads ten times with tap water, soaking overnight in de-ionized water and a further eight rinses in deionized water. They were then baked in a 100°C oven overnight to remove residual water.

Beads were divided into 80.0 g samples and each sample was placed into one of the 48 compartments within the sampler, forming a single layer of beads, as illustrated in Figure 7.3b. It was built out of stainless steel with stainless steel mesh tray bottoms and open sides to allow gas flow. The sampler was covered by a Plexiglas GS, UV transmitting clear 2458 window, shielding the sampler from precipitation while allowing light through to the samples. The beads were further protected from precipitation with metal slats around the outside of each layer, which could be removed to access the beads. As shown in Figure 7.3a, there were three trays of beads. Only the top two were used for this study. Below the first level of beads there was a sheet of stainless steel shielding the bottom two levels of beads from direct sunlight. In this way, light-exposed and light-shielded samples were collected in parallel, and thus photochemistry occurring on the film could be probed.

The grid boxes of each tray were numbered from one to sixteen. Once every three days, a grid box number was selected using a random number generator. At 11:00 local time (GMT+2) all of the beads for each of the “light” and “dark” samples corresponding to the chosen number were collected into amber vials for transport. Samples were kept refrigerated until analysis. Field blanks were measured by placing three 80.0 g bead samples onto the sampler and then collecting immediately. Laboratory blanks were also analyzed in which three clean 80.0 g bead samples were analyzed without being transported to the field site.
For analysis, 4.0 g of beads were transferred to a Nalgene bottle and extracted into 3.00 mL of deionized water by shaking the bead/water mixture for 5 min, while the remaining 76.0 g of beads were used for analysis of the organic components of the film. The aqueous extract was removed and analyzed for ions as described below. The extraction efficiency was examined by performing serial extractions where a previously analyzed sample was extracted for a second time. For all ions, less than 9% remained in the second extraction. While attempts were made to allow equal airflow to all compartments in the sampler, there is some variability depending on location in the sampler. To examine this variability between samples, samples were taken from three different compartments on October 7, 2014, indicating less than 35% deviation from the mean value. This is shown in Figure 7.5.

4.3.1 Particle Sampling

PM$_{10}$ (particles below 10 µm in diameter) were sampled through an inlet with a 10 µm cut-off for 72 hours (11:00-11:00 local time) with a ‘Partisol 2000’ low volume sampler at a sampling rate of 1.0 m$^3$/hr. Particles were collected onto 45 mm diameter quartz filters which were preconditioned by heating at 105°C for 24 hours. Sections of the filter (1 cm$^2$) were removed for organic carbon/elemental carbon analysis while two 6 mm diameter circles were removed for GC-MS analysis of PAHs and alkanes. The remaining filter area (1434 mm$^2$) was extracted into 1.50 mL of deionized water through 10 minutes of sonication, 10 minutes of shaking and a further 10 minutes of sonication. Beginning on October 20, 2015, the composition of size-resolved particles was also determined by collecting samples using a five-stage (stage 1: 0.05–0.14 µm, stage 2: 0.14–0.42 µm, stage 3: 0.42–1.2 µm, stage 4: 1.2–3.5 µm, stage 5: 3.5–10 µm, aerodynamical particle diameter) stainless steel low pressure Berner impactor (Hauke, Austria) with a flow rate of 4.5 m$^3$/hr.$^{45}$ The particles were collected onto aluminum foil for 24 hours and a fraction of this foil was extracted into 2.00 mL of deionized water using the technique described above for filters. Foils had a calcium contamination contributing up to 89% of the measured calcium mass. Reported values were corrected by subtracting the average of the blank values from the sample measurements, with the exception of two samples from stage 1 which were within error of the blank values and are reported as 0 µg/m$^3$. 
Because 3-day filter collection times were used, we expect the occurrence of sampling artefacts such as volatilization of high vapour pressure compounds like ammonium nitrate and small organics. Similar processes are expected for the aging of film samples, thus biasing the measured particle compositions towards that of the grime film. Therefore, the film and particle composition may appear more similar than they are in reality. However, we note that the particle filter was within a temperature controlled environment, with the temperature maintained at 20.7 ± 0.4°C. Therefore the collected filter samples did not undergo the same temperature cycles as the film (as shown in Figure 7.4a).

4.3.2 Ion Analysis
All aqueous extracts were filtered using a 0.45µm Acrodisc syringe filter to remove insoluble materials. The resulting solutions were analyzed using ion chromatography to detect the main water-soluble ions (Cl⁻, SO₄²⁻, NO₃⁻, C₂O₄²⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺) using a Thermo ion chromatograph (ICS3000) with AS18/AG18 column/guard column with potassium hydroxide eluent for anion analysis and CS16/CG16 column/guard column with methanesulfonylic acid eluent for cation analysis. Conductivity detection was used for all ions with the exception of NO₃⁻ that was detected using UV at 208nm.

4.4 Results
Particle and grime samples were each collected at the Leipzig-Mitte site during the period between September 16 and October 25, 2014 and the major water-soluble ions in each sample type were analyzed via ion chromatography. Figure 4.1 displays the observed ion mass fractions, Figure 4.2 displays the moles of ions normalized to total sulfate, and Figures 7.5 and 7.6 present the absolute concentrations determined for the particles and light-exposed grime samples, respectively. Variability of the grime extraction is displayed in the scatter plots, which show three separate data points (hollow circles) for the three grime samples collected on October 7. Sulfate was chosen as the normalizing species because it is expected to be stable within the film, having low volatility and photoactivity. We note that there may be additional gas phase sources of sulfate to the film, such as SO₂ deposition and oxidation, akin to particulate sulfate sources, due to the grime's continued exposure to the atmosphere. Chabas and coworkers have also suggested that SO₂ can react with sodium and calcium, either in the film or within the glass substrate, to form salts such as CaSO₄ and Na₂SO₄. Extra sulfate sources to the film would
result in the sulfate-normalized values underestimating additional sources of ions to the film or overestimating the losses of ions from the film. Further study is warranted to establish the relative importance of such sulfate sources in addition to particulate deposition. However, for the subsequent discussion it is assumed that sulfate sources from such heterogeneous reactions are minor in comparison to particulate sulfate sources to the film.

In general, we note that the particle ion compositions fall within the range of mass fractions and mass loadings observed at this site in the past. A similar comparison to past film composition measurements is not possible because there are no urban grime composition measurements reported over these timescales, nor are there any reported from this area. However, comparing to the few compositional studies performed in other cities and over much longer time frames, the Leipzig mass fractions are similar to that reported in Paris but generally more sulfate rich and calcium poor than a separate study with film compositions reported from six different European cities.

**Figure 4.1:** Mass fraction of the major ions: Cl⁻ (orange), SO₄²⁻ (red), NO₃⁻ (dark blue), Na⁺ (light blue), NH₄⁺ (yellow), Ca²⁺ (brown) and the sum of the minor ions C₃O₄²⁻, Mg²⁺ and K⁺ (pink) measured in the a) light-exposed grime and b) particle samples.
4.4.1 Depletion of ammonium and nitrate in grime versus particles

From examination of Figure 4.1, it is evident that both the film and particle compositions are dominated by the presence of sulfate and nitrate anions. Notably, however, ammonium, which is the dominant cation measured within the particles, is hardly observable within the grime samples. For most samples ammonium was below the detection limit and thus the values herein are reported as the detection limit of the system and are upper limits for the ammonium present in the film. This contrast between the ammonium presence in particles versus film samples has been reported previously, also indicating that there were low or undetectable levels of ammonium in urban grime films.\textsuperscript{18,22} The authors of those previous studies suggested that the lower-than-expected concentration of ammonium is due to the loss of ammonium nitrate. In support of this hypothesis, we observe that nitrate is also significantly lower in the grime than in the particles, most clearly seen by the nitrate to sulfate ratio shown in Figure 4.2c. Ammonium nitrate is semivolatile, and there are many reports of its loss by evaporation from filter samples and particles (e.g.\textsuperscript{48,49}). Because the grime film is exposed to the atmosphere for an extended time period, it cycles through different temperature and relative humidity regimes (as displayed in Figure 7.4). High temperatures and low relative humidities have been shown to favour ammonium nitrate evaporation.\textsuperscript{49}

As a further investigation into ammonium nitrate evaporation, the size resolved particle data collected during the final 5 days of measurements can be examined; this is displayed in Figures 7.7 and 7.8 of the SI. The particles rich in ammonium and nitrate are the fine particles in the size bins below 1.3\(\mu\)m, while the coarse particles, between 1.3\(\mu\)m and 10\(\mu\)m, are ammonium-poor with nitrate likely present as salts such as \(\text{Ca(NO}_3)_2\).\textsuperscript{50} The average nitrate to sulfate ratio for the total PM\(_{10}\) over the five days is 1.4 ± 0.5 (mean ± 1 standard deviation), significantly larger than the campaign average of 0.48 ± 0.06 observed for the film. This ratio becomes lower if it is assumed that all of the nitrate associated with deposition of fine-mode particles evaporates as ammonium nitrate, leaving only the coarse mode nitrate. Under this assumption, the average nitrate to sulfate mole ratio is reduced to 0.7±0.5, which lies within the uncertainty of the ratio observed in the film. While the possibility of gas phase nitrate sources to the grime such as N\(_2\)O\(_5\) or NO\(_2\) hydrolysis or HNO\(_3\) deposition cannot be ruled out, the comparison of these nitrate to sulfate ratios suggest the importance of evaporation for much, if not all, of the nitrate that is deposited as ammonium nitrate.
However, if ammonium nitrate loss from deposited particles is the sole mechanism for ammonium depletion (i.e. if the grime ammonium and nitrate amounts are initially the same as those in particles, but are then altered via ammonium nitrate evaporation) we would expect a smaller decrease in the total amount of ammonium than that which is observed in the grime samples. Subtracting the average ammonium-to-sulfate and nitrate-to-sulfate mole ratios in the grime over the course of the campaign from the corresponding average particle ratios, the ammonium to sulfate mole ratio decreases by 2.1±0.6 while the nitrate to sulfate mole ratio only decreases by 0.8±0.6. Therefore, ammonium nitrate evaporation cannot fully explain the observed loss of ammonium. As shown in the size-resolved particle measurements displayed in Figures 7.7 and 7.8, larger particles contain minimal quantities of ammonium, while maintaining moderate amounts of nitrate. Measured dry deposition velocities are lowest for particles between 100nm and 1µm, increasing above below and above this range,\cite{Seinfeld:2016wg} suggesting that the coarse particles may be preferentially deposited. It is unknown how the geometry of the sampler and glass beads and the surface composition of the beads and grime would impact the capture of different sized particles on the surface. If large particles are preferentially deposited and retained on the grime film, or if significant amounts of particles larger than PM$_{10}$ (also expected to show minimal ammonium, see for instance VandenBoer et al$^{51}$) are deposited onto the grime, this would lower the ammonium fraction measured within the film to a greater extent than for nitrate.

There may also be chemical mechanisms at play that remove the ammonium from the grime film. Favez et al. suggested that ammonium could be lost from grime via either or both of the exchange of ammonium nitrate with NaCl to form NaNO$_3$ and gas phase HCl and NH$_3$, or the biological conversion of ammonium to nitrate.$^{18}$ Another possibility is suggested by the long integration time for collection of the film sample, which could lead to the mixing of the components of the externally mixed coarse and fine particles. This mixing of the particles' components has previously been discussed as a potential artefact for samples collected on filters under high relative humidities,$^{52}$ where the presence of water can facilitate ionic mixing. In the present study, the particles were collected in a climate-controlled environment, lowering the possibility of this occurring on the particle filters. However, in the case of grime collected onto glass substrates, we note that glass surfaces themselves are hygroscopic; lab studies also show significant water uptake mediated by the grime film itself.$^{26,27,42}$ At the high relative humidities,
mostly above 60%, which existed during the campaign (shown in figure 7.4), there will be water associated with the grime.

Although the ion balance of the particles is quite variable, half of the PM$_{10}$ samples collected measured excess cations; this suggests that the mixture of these ions could be alkaline. Because the larger particle classes contain fewer sulfate and ammonium ions and more of the crustal cations such as sodium and calcium (see Figures 7.7 and 7.8), they are more alkaline than the smaller ones. Upon mixing of the components of these more basic particles with those from the smaller acidic ammonium rich particles, there would be an increase in the pH, favouring the formation of ammonia from ammonium. The ammonia could then partition to the gas phase, depending on the local ammonia levels, depleting the film ammonium and giving rise to a smaller proportion of ammonium in the grime than measured in the PM$_{10}$ particles.

Figure 4.2: Sulfate normalized mole ratios of a) Chloride b) Sodium c) Nitrate d) Calcium e) Ammonium extracted from film and particle samples. Light-exposed grime values are shown in black circles while particle values are red bowties. The spread in data from collection and analysis is displayed
for the three separate samples collected on October 7, 2015 shown in hollow circles. When ammonium was not detected, values were calculated from the detection limits, and are thus upper limits for ammonium in grime.

4.4.2 Temporal changes in grime and particle compositions

Figure 4.2 illustrates that for all of the ions measured here, there is much more variability in particle composition over time than there is for the film. Because the film is continually collecting mass over the course of the campaign, its measured composition results from an integration of particle and gas phase species deposition, evaporative losses and chemical processing. This long-time averaging has the result that fluctuations in atmospheric composition are smoothed in comparison to the particle samples, which are averaged over a shorter period. Another consequence of this averaging is that the film may maintain a “memory” of periods of time where there is high deposition of a specific chemical species. At the beginning of this campaign, between September 19 and 28, 2015, there was an episode where particles showed high levels of chloride and sodium (see Figure 7.6). Hysplit back trajectories run for the previous 24 hours period suggest that the air mass sampled during that time was mostly transported over the North Sea prior to arriving in Leipzig leading to marine influenced particles, high in sodium and chloride. In these particles, the sodium to chloride mole ratio is above one (2.6±1.1), typical of marine particles undergoing chloride displacement by HNO$_3$ during transport over continental air. Following September 28, the masses of chloride and sodium in the particles drop due to a shift in the geographic origin of the particles to continental areas. This change in particle composition also results in a drop of both chloride and sodium in the film, as the composition is diluted with particles lower in chloride and sodium, but to a much lesser extent than is evident in the particles.

The change in chloride amount in the grime can be represented by assuming that there is a period, between September 19 and 28, 2015, of fast chloride growth on the film ($6.7 \times 10^{-4}$ µmol/day). The growth rate is calculated from a linear fit of the moles of chloride in the film over time displayed in Figure 4.3a, where the amount on September 19 is fixed. After September 28, the growth rate is assumed to be 25% of the fast growth rate ($1.7 \times 10^{-4}$ µmol/day) for the remainder of the campaign. This corresponds to the ratio of the average amount of chloride in the particles between September 28 and October 25 to the average chloride content in the particles between September 19 and 28 (Figure 7.6). By normalizing the resulting growth
curves of chloride to experimental sulfate values, these results can be compared to experimental values as shown in Figure 4.3b. Although there is significant scatter, the calculated chloride values demonstrate that a one-week period of elevated chloride mass in the particles can result in a high chloride concentration in the film maintained for over a month. However, this does not exclude the possibility of an additional source from HCl or a chloride source from the deposition of particles greater than 10 µm in diameter. The scatter in the sodium data limits the certainty of carrying out a similar analysis for this ion.

![Graph showing mole per area vs. date and Cl:/SO₄ mole ratio vs. date](image)

**Figure 4.3:** Comparison of experimental (black) and calculated (orange) values for a) moles of chloride per area and b) sulfate normalized moles of chloride in grime over time.

The calcium to sulfate mole ratios in the grime also show a gradual increase over time (Figure 4.2d). In this case, the calcium to sulfate ratio for the final two particle samples are also higher than the first 3 samples, and thus the film may be responding to these changes. Chabas et al. suggested the possibility of the leaching of calcium from the glass into the film both through the reactions with gas phase species as mentioned above, or through cation exchange with film protons. One would also expect an enhancement of these ions if there were a large input of...
particles larger than PM$_{10}$. However, because there does not seem to be a large difference between the calcium to sulfate ratios between the film and particle these processes do not seem to be playing a large role under the present conditions. The times of greatest discrepancy can be attributed to the film’s slow response to decreasing particle concentrations, as discussed for chloride.

4.4.3 Photochemical processing of nitrate

Previous work from our lab$^{41,42}$ and others$^{57}$ has shown that nitrate deposited onto environmental surfaces as HNO$_3$ shows rapid photochemical loss, orders of magnitude faster than aqueous nitrate, and that this process is a potential renoxification mechanism in the environment. As part of the present campaign, we explored such a loss process from ambient film samples. This was probed by collecting samples both exposed to and shielded from sunlight. Figure 4.4 displays the ratio of the light to dark mole fractions of the ions investigated here over the course of the campaign. One expects that the ions that are neither photolabile nor photoproducts will show no preference for light versus dark, therefore showing a ratio of unity for the duration of the experiment. This is indeed seen for the majority of the ions within the film, with the ratios
scattered around a value of 1.0.

**Figure 4.4:** Light to dark ratio for the mole fractions of ions extracted from the film with the dotted line showing unit ratio. a) Chloride 1.00±0.06 b) Sodium 0.99±0.2 c) Nitrate 0.90±0.05 d) Calcium 1.03±0.09 e) Sulfate 1.03±0.06. Values are displayed as the campaign average ± 1 standard deviation.

The notable exception is nitrate, whose average light to dark ratio is 0.90 ± 0.05, which is statistically lower than unity with greater than 99% confidence. The 10% difference between the light-exposed and non-exposed samples, maintained over the entire campaign, is consistent with a photochemical loss pathway for film-associated nitrate observed in the laboratory studies.\(^{41,42,57}\)

We note that a slight temperature gradient between the dark and light samples cannot be ruled out, raising the possibility of enhanced nitrate loss by ammonium nitrate evaporation from the light-exposed sample.\(^{48,49}\) However, we do not observe any greater amounts of ammonium ion in the dark film sample than in the light-exposed one, suggesting that this pathway is probably not important here.
4.5 Discussion

Diamond and coworkers have demonstrated that urban grime films can increase the mobility of species in the environment, both by being a temporary reservoir for organic species to partition into, and through film wash-off during precipitation events.\textsuperscript{10,11,31,32} In the present study we see not only this increased mobility in the volatilization of ammonium nitrate, but also evidence for potential chemical transformations of inorganic ions. As shown in Figure 4.2, the grime film’s composition changes over time in a way distinct from that seen in the surrounding particles, despite the particles being a major source of ions to the film. Following deposition onto a hygroscopic urban surface, particles of different composition and size are subject to mixing when water is taken up onto the grime film. In this medium, further processing is possible through reaction or through the exchange of gas phase species, which can be released from or deposited onto the surface.

One such species is ammonia, a basic gas that plays an important role in particle nucleation and neutralizing aerosols, reacting with acidic species to form ammonium.\textsuperscript{46} While ammonium is clearly present in the particles we monitored here, we do not measure quantifiable amounts of ammonium in grime, suggesting a loss of ammonium during the grime film formation and growth. There are different hypotheses to explain this loss, but it is clear that deposition to the film is altering the cycling of ammonium in the environment, in contrast to a simple deposition framework. It has been shown that it is important to use a scheme including bidirectional ammonia flux when describing atmosphere-biosphere interactions.\textsuperscript{58} Our results demonstrate that bidirectional exchange between urban grime films and the surrounding atmosphere may also need to be considered to understand urban atmospheric chemistry. A study of the pH of the grime would be required in order to investigate ammonia-ammonium equilibrium on the film, and the corresponding equilibrium ammonia vapour pressure and thereby obtain the potential for the release of ammonia. However during this campaign, the observed low level of grime ammonium suggests that the film was releasing ammonia back into the atmosphere. A study completed in Toronto observed a significant ammonia source within a street canyon, attributing this to the green space contained within the cavity;\textsuperscript{59} however, if ammonium is being lost from grime the urban films formed along the building could also be playing a role in the ammonia gradient measured.
A further impact of the film environment on the nitrogen cycling is nitrate photolysis in the grime. Over the campaign, nitrate samples exposed to solar illumination showed statistically significant lower nitrate concentrations than the corresponding dark samples, providing the first direct field evidence for nitrate photochemistry in urban grime. Studies are still ongoing to classify the gas phase products of the nitrate chemistry in grime; however earlier studies of nitrate photolysis in water and on ice, metal oxides and glass, suggest that this photochemistry would lead to the formation of the reactive nitrogen species NO, NO2 and HONO (e.g. Ref. 42,57,60,61). Thus the observed photolability of film nitrate could provide a renoxification process in the urban environment. We note that such processes could contribute to unknown reactive nitrogen sources such as a fixed photochemical source of HONO within 20m of the ground found in Houston, TX. 62,63

Another aspect of the grime-associated atmospheric processing is “capture events”, in which particular ions are elevated due to an influx of these species associated with a particular population of particles. As seen here, particulate chloride can be episodic in nature such as when marine-influenced particles are transported inland or in regions where chloride salts are used for snow management. When particulate chloride levels are high, large amounts of chloride can be captured on the film extending the period in which elevated chloride levels are exposed to the atmosphere. Chloride levels are of interest due to known heterogeneous reaction between N2O5 and chloride to form ClNO2. 5 This reaction, which also produces nitrate anion, releases active chlorine and nitrogen in the morning when ClNO2 photolyzes thereby increasing the oxidative capacity of the atmosphere. 4,64 Although previously thought of as only important in marine regions, there have now been multiple observations of ClNO2 in mid-continental environments through reaction of N2O5 with chloride attributed to transported sea spray, biomass burning and coal fired power plants. 65,66 ClNO2 production is limited by the availability of chloride which is currently defined in terms of the sum of particulate chloride and HCl. 66,67 However, the chloride captured on the film may also be available for reaction with N2O5, which in turn could impact the ClNO2 production in these urban continental regions.

By comparing the composition of particles and films collected simultaneously, possible processes were elucidated that could both help to understand film formation and continue to suggest that these films could have an important environmental impact. These possibilities
include the potential for grime to act as a source of ClNO₂ as well as to recycle ammonia and reactive nitrogen back into the atmosphere. Further study into these processes is warranted.

4.6 References


(15) Liu, Q.-T.; Chen, R.; McCurry, B. E.; Diamond, M. L.; Bahavar, B. Characterization of


Chapter Five

Modeling a Photochemical Urban Grime Surface Source of HONO

Contributions: Model runs were designed and analyzed by Alyson M. Baergen with technical assistance from A. Tilgner. The manuscript was written by Alyson M. Baergen with critical comments from A. Tilgner, H. Herrmann and D. James Donaldson
5.1 Introduction

Over the last decade, there has been significant interest in understanding HONO chemistry, motivated by the influence that HONO can have on the oxidative capacity of the atmosphere. However, measured concentrations of HONO are not well described by gas-phase chemistry models; rather such models require additional sources which are thought to involve heterogeneous photochemistry on or near ground surfaces. Sources that have been suggested include soil chemistry, ocean emissions, photoenhanced conversion of NO₂ on polycyclic aromatic hydrocarbon (PAH) or humic acid films, direct emissions, reduction of HNO₃ to HONO by VOCs, nitrite chemistry on the ground, and HNO₃ photolysis on surfaces or particles.

Zhou et al. reported the first experimental study of HNO₃ photolysis on a surface in which gas-phase HNO₃ was deposited onto a glass surface and then illuminated. Gas-phase products NO, NO₂ and HONO were detected, with a HONO to NOₓ ratio ranging from 0.03 at a relative humidity (RH) of 0% to 1.2 at 50% RH. The total photolysis rate constant or j-value, ranged from $6.0 \times 10^{-5}$ at 0% RH to $2.2 \times 10^{-5}$ s⁻¹ at 50% RH, adjusted for a solar zenith angle of 0°. These rate constants were measured once product signals had stabilized and do not capture what appears to be a faster initial rate of product formation that was not quantified. Even without including this initial fast rate, the j-value calculated for surface HNO₃ photolysis is enhanced by about two orders of magnitude in comparison to those of both gas-phase HNO₃ and aqueous nitrate. Subsequently, the photolysis of HNO₃ deposited onto quartz was studied and the production of HONO, NO₂ and NO was again detected. In contrast with the previous study, j-values of $1.1 \times 10^{-6}$ for NO₂ formation and $2.4 \times 10^{-7}$ s⁻¹ for HONO formation at a solar zenith angle of 0° and 50% RH were reported. It was concluded that HONO was not formed directly from photochemistry, but was due to photochemically produced NO₂, which hydrolyzed on the surface, in agreement with a mechanism proposed by Zhou et al.

While the reason behind the discrepancy in rate constants between these two studies is not clear, an enhancement and red shifting of the absorption cross section of surface adsorbed HNO₃ and nitrate have been detected, which could explain the surface enhanced rate constant measured by Zhou et al. Although Laufs and Kleffmann did not see an enhancement in the rate constant over gas phase HNO₃ or aqueous nitrate, they did provide evidence for a red shifted absorption
cross-section by examining the rate of nitrate photolysis on a glass surface with two different lamps whose wavelength ranges differed by 20nm. Theoretical values for the ratio of j-values using the shorter vs. the longer wavelength lamps for gas-phase and aqueous HNO₃ are 10.9 and 14.1 respectively, but a ratio of 3.6 was observed for the surface adsorbed HNO₃ showing a greater importance in the absorption at longer wavelengths assuming a wavelength independent quantum yield. Though these absorption cross-section studies point to an explanation of an enhanced surface rate constant, they also reveal a limitation of their reported rate constants. Zhou et al. monitored the intensity of their light source using a nitrate actinometer in order to scale the measured rate constant to a relevant sunlight intensity. However, as discussed by Laufs and Kleffmann the same red shift in the surface absorption predicted to explain the faster rate constant measured for the above samples, means that the surface HNO₃ will not have the same response window as aqueous nitrate, and thus the accuracy of the scaled value to a SZA of 0° is uncertain. The shifted absorbance cross section also indicate that the j-values for surface HNO₃ and nitrate will each have a unique dependence on SZA.

The importance of this photochemistry has been evaluated in a number of models with wide ranging values. For example, in Dallas-Fort Worth, surface HNO₃ photolysis was predicted to contribute 0.7% of daytime HONO production, while it was predicted to contribute 8.24% in Beijing, 32% in northeast United States, and the majority of the HONO flux in a forested area in Michigan. However, there are many assumptions being made in these models for surface HNO₃ photochemistry, limiting the reliability of these values. The most common method for this prediction is by calculating a surface HNO₃ concentration from gas phase HNO₃ concentration and deposition velocity. This value is multiplied by the rate constant j(HNO₃)ₙ, scaled up by a factor of 24 to 100, with an added factor to adjust for only a fraction of the surface HNO₃ being exposed to full sunlight. Accumulation time is assumed to be either the time since rainfall or 24 hours. Such calculations assume that all surface-deposited HNO₃ is reactive and that its photolysis is slow enough that pseudo zero-order kinetics can be assumed so the depletion of surface HNO₃ can be ignored. It also assumes that deposition of HNO₃ is the only source of surface HNO₃, that only this surface HNO₃ is photoactive, photolysis of surface HNO₃ will have the same dependence on SZA as that of gaseous HNO₃ and that the strength of the HONO source is linearly dependent on j-value.
In a small number of studies, other approaches have been taken. For example, in Zhou *et al.*\(^{28}\) instead of using calculated HNO\(_3\) deposited values, measured surface HNO\(_3\)/nitrate concentrations were used, assuming all of the extractable nitrate was photo-reactive. In another study, the measured wavelength dependent absorption cross section for surface HNO\(_3\) was used, however this was accompanied by the addition of secondary chemistry of photochemically produced NO\(_2\) masking the effects of updated absorption cross section.\(^{30}\) A more sophisticated method was used by Karamchandani and co-authors,\(^{31}\) in which HONO sources were modeled accounting for deposition, sorption, penetration into soils and vegetation and volatilization. This model accounts for depletion of a surface source of HNO\(_3\) and allows for alternative loss processes for surface HNO\(_3\), meaning that not all deposited HNO\(_3\) will react to form HONO. However, the j-value is still assumed to be that of gaseous HNO\(_3\), scaled by some factor, and no other sources of surface HNO\(_3\)/nitrate are taken into account.

In addition to limitations discussed above for models incorporating HNO\(_3\) surface photolysis, these models are based on experiments using clean glass or quartz substrates and do not take into account that real outdoor urban surfaces are subject to the formation of films, called urban grime, from the deposition of atmospheric constituents.\(^{32,33}\) Studies of HNO\(_3\) reactivity on clean glass may not adequately describe the chemistry of HNO\(_3\)/nitrate deposited onto real urban surfaces, and so it is important to characterize this chemistry on atmospherically exposed, realistic substrates and then use these values in models. Previously, we have reported photochemical nitrate loss from urban grime samples collected in Toronto, Canada for 1 week on ZnSe crystals. A rate constant of 1.2x10\(^{-3}\) s\(^{-1}\) was measured for a solar zenith angle of 20° at an unknown RH.\(^{34}\)

We have also recently shown that this photochemistry produces gas-phase reactive nitrogen oxides,\(^{35}\) with the total gas-phase product concentration increasing with RH up to 35% RH, after which product formation is RH-independent to at least 60% RH. This finding is in contrast to the anti-correlation between product formation and relative humidity measured on glass,\(^{18}\) highlighting the difference in environment between the clean glass and urban grime-coated glass. A similar study was performed by Ye *et al.*\(^{36}\) for urban grime samples collected on a variety of natural and artificial surfaces in downtown Albany, New York. Gas-phase HONO, NO and NO\(_2\) were detected with HONO:NO\(_x\) ratios of 0.1 to 6.7 and j-values ranging from 6x10\(^{-6}\) up to 3.7x10\(^{-4}\) s\(^{-1}\) for a solar zenith angle of 0° under approximately dry conditions. Ye and coauthors\(^{19}\) also illuminated atmospheric particles collected on filters and measured j-values of 1.3 x 10\(^{-5}\) to
3.1 x 10^4 s^{-1} for a solar zenith angle of 0° and 50% RH. These studies also indicate a possible enhancement of photolysis rate in comparison to glass photochemistry and furthermore suggest a higher HONO:NO_x ratio for photochemistry on grime-coated surfaces in comparison to clean glass.

These recent studies used environmental samples without further sample preparation, and neither the reactive environment nor the chemical identity of the NO_x/HONO precursor was well characterized. IR studies of the photochemistry of the Toronto-collected grime suggested that nitrate anion was responsible for the photochemistry. However, investigations of deposited HNO_3 onto self-assembled alkyl monolayers, simulating long-chain organics known to be an important constituent of urban grime, suggest that molecular HNO_3 is present in such an organic matrix even at RHs up to 90%, indicating that the nitrate/HNO_3 equilibrium is not well understood on the surface. Furthermore, nitrogen-containing organics have not been ruled out as the precursor. The mechanism for HONO production from grime is also not known at this time; however, secondary reactions of a NO_2 photoproduct has been predicted. NO_2 hydrolysis could play a role, such as suggested for the glass samples, as well as photo-enhanced NO_2 reduction to HONO, mediated by organic compounds. In aqueous solution it has been suggested that HONO is formed from protonation of NO_2^-, however, urban grime films may be basic, limiting the likelihood of such a mechanism. It should also be noted that in all of our previous photochemical studies, only a fraction of the extractable nitrate has been photoactive, the reason for which is not known.

Using a similar modeling methodology as others described above, Ye and coworkers attempted to update the previous HONO flux estimates taking into account the presence of grime. They used their measured faster rate constants and higher HONO:NO_x ratios, experimentally measured concentrations and accounted for a decreasing trend in j-value with increasing surface nitrate density they observed. However, this study assumes that the j-value is that of gas-phase HNO_3, with a scaling factor applied, that only HNO_3 is responsible for the photochemistry, and that HNO_3 depletion from the grime is not important, limiting the accuracy of such a prediction.

In the following chapter, we use a box model to explore urban grime nitrate photolysis, with particular focus on constraining the model using grime-specific measurements and investigating the impact of the assumptions discussed above. Specifically, we explore the impact of varying
the nitrate deposition rate, the available surface area within the (fixed) box size, the photolysis characteristics (the total $j$-value, the wavelength dependence of the product of absorption cross section and quantum yield and the solar illumination intensity) and the source of surface nitrate (deposition of particles, HNO$_3$ or N$_2$O$_5$) on HONO fluxes from urban surfaces. Because the speciation of the urban grime HONO precursor is unknown, it will be referred to as surface nitrate because it is measurements of nitrate concentration in a water extract of urban grime (which could have many sources) that have been used to constrain the model.

5.2 Methods

![Reaction scheme for HONO chemistry](image)

**Figure 5.1:** Reaction scheme for HONO chemistry

We explored the sensitivity of predicted HONO fluxes from urban grime chemistry by including surface nitrate photolysis into the box model SPACCIM (SPectral Aerosol Cloud Chemistry Interaction Model). In the model, a precursor species (either particulate nitrate, HNO$_3$ or N$_2$O$_5$) is deposited onto a surface by a reaction producing “surface nitrate” (modeled as a gas-phase species) where the deposition rate is constrained by measurements of surface accumulation and scaled to a total surface area. In this treatment, the model is similar to a multimedia environmental model, with the surface as a separate environmental compartment. A defined fraction of 0.1 of the surface nitrate is available for photolysis which constitutes the “reactive surface nitrate”. This reactive surface nitrate is photolyzed, causing its depletion and the production of HONO, which is assumed to be instantaneously mixed throughout the box. When required, gas phase chemistry was included in the form of the master chemical mechanism (MCM v3.2). Models runs cover 4 days with data output at time steps of 10 minutes except where stated otherwise. Temperature and pressure were set at 288K and 1 atm respectively with a relative humidity of 90%. A reaction scheme for HONO chemistry is given in Figure 5.1 and base conditions are given in Table 5.1.
Deposition Rate 4.6x10^9 molec cm\(^{-2}\) s\(^{-1}\)

Boundary height 1000 m

Surface Area Index 2

Reactive fraction 0.1

Starting Date June 19

Parameterization of surface nitrate/HNO\(_3\) photolysis*

<table>
<thead>
<tr>
<th>SZA function</th>
<th>j(HNO(_3)(g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>j-value at SZA=0°</td>
<td>1.47x10(^{-4}) s(^{-1})</td>
</tr>
<tr>
<td>i factor</td>
<td>2.00x10(^{-4}) s(^{-1})</td>
</tr>
<tr>
<td>m factor</td>
<td>1.23</td>
</tr>
<tr>
<td>n factor</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Cloud conditions clear sky

Latitude 45°

HONO yield 100%

Table 5.1 Base case model conditions. *The j-value dependence on SZA is described by the equation

\[ j = i \times \cos(SZA)^m \times e^{-n \times \sec(SZA)} \] (MCM v3.2: http://mcm.leeds.ac.uk/ MCM)

5.2.1 Dry Deposition

In the base case, we assume nitrate deposition is via particulate deposition to the exposed surface area. Dry deposition of particles depends on many criteria such as particle size, the nature of the deposition surface, wind speed, temperature, turbulence etc.\(^{44}\) and there is evidence to suggest there is significant nitrate evaporation after deposition.\(^{33}\) Deposition velocities were constrained here by the measured growth of nitrate on urban surfaces, thus only taking into account the nitrate that reaches and remains on the surface. Data collected in Leipzig over 6 weeks showed a linear nitrate growth rate of 4.6x10^9 molecule cm\(^{-2}\)s\(^{-1}\)\(^{33}\) corresponding to an effective deposition velocity of 0.29 cm s\(^{-1}\) for particles, assuming all of the film nitrate comes from particle deposition. For other European cities, values range from 3x10^8 to 4x10^9 molecules cm\(^{-2}\)s\(^{-1}\) from a linear fit of surface nitrate concentration over a multiyear collection period\(^{45}\) while Dolske et al.\(^{46}\) calculated particle deposition velocities onto monuments of between 0.06 and 0.18 cm s\(^{-1}\).

These studies are all in reasonable agreement, taking into account the wide range of conditions in
the measurement sites. To estimate nitrate surface deposition in a more heavily polluted region, an average nitrate loading of 13.76 mg/m$^3$, reported for PM$_{10}$ in China,$^{47}$ was multiplied by the above deposition velocities, resulting in a calculated deposition rate between 2.29x10$^9$ to 3.81x10$^{10}$ molecules cm$^{-2}$ s$^{-1}$ for nitrate on surfaces. With these empirical constraints in hand, 3 deposition rates were investigated, 4.6x10$^8$, 4.6x10$^9$ and 4.6x10$^{10}$ molecules cm$^{-2}$ s$^{-1}$. For the base case, constant deposition rates were used, assuming constant particle loading throughout the day.

5.2.2 Surface Area

Previous modeling has included surface area using a term analogous to leaf area index, referred to as Impervious Surface Index (ISI), where the impervious surface area is calculated by multiplying the geometric area by the ISI. The early modeling efforts of Diamond and coworkers used an ISI factor of 2,$^{48,49}$ Clarke et al.$^{50}$ used a factor of 2.3 and Kwamena et al.$^{51}$ used a factor of 4 for an urban center and 10 for a super urban center, each of these based on surface area estimates scaled to urban land use determined by Theurer.$^{52}$ In urban HONO modeling studies, rather than this surface area index term, a surface area to volume ratio (S/V) is generally used, analogous to what is used for aerosol surface area. However, different models use different surface level heights, and thus the same S/V term represents a different surface area for the same sized grid. For example Sarwar et al.,$^{27}$ Goncalves et al.$^{53}$ and Zhang et al.$^{4}$ used a maximum S/V of 0.3 m$^{-1}$, based on information from MODIS images, for a surface layer of 35 m corresponding to an ISI of 10.5 but Vogel et al.$^{54}$ and Zhang et al.$^{29}$ used 0.3 m$^{-1}$ with a surface layer of 17m corresponding to an ISI of 5.1. Li et al.$^8$ used a value of 1.7 m$^2$ per geometric surface area, a value that is equivalent to the ISI. From the range of these previous studies, in this study we examined ISI values between 1 and 10.

5.2.3 Photolysis characteristics

5.2.3.1 Wavelength Dependence

As discussed earlier, when incorporating HNO$_3$ photochemistry into the model, previous models chose to scale the j-value to that of gas-phase HNO$_3$. However, measurements of adsorbed HNO$_3$ and nitrate indicate a significant red shifted absorbance and greater overall absorption compared to that of HNO$_3$(g). Sangwan et al.$^{23}$ have reported j-values as a function of SZA for surface
HNO$_3$ and nitrate assuming a wavelength independent quantum yield of 1; these were used to investigate the impact of different dependencies of j-value on SZA.

5.2.3.2 Total J-value

A range of rate constants was modeled, using data from Baergen and Donaldson,$^{34}$ Zhou et al.$^{18}$ and Ye et al.$^{19,36}$ Rate constants at a SZA of 0° of 1.69x10$^{-5}$, 1.47x10$^{-4}$, 1.25x10$^{-3}$ s$^{-1}$ were studied. In order to simulate a hazy or cloudy day, modeled sunlight intensity was adjusted by adding a scaling factor to the sunlight intensity of 0.25. For these studies, 14 days were modeled with time steps of 40 minutes and the rate constants were scaled to gas-phase HNO$_3$.

5.2.3.3 Daily variability of Solar Zenith Angle

In order to study the impact of variability of SZA over the day, the impact of season and latitude was examined. Latitudes of 23°N (corresponding to the minimum SZA at the summer equinox), 45°N and 65°N were used. A comparison was also done between summer and winter, with a winter start date of December 19. For these runs, the rate constants were scaled to those for gas-phase HNO$_3$.

5.2.3.4 Source of surface HNO$_3$ or nitrate

The deposition of HNO$_3$ and N$_2$O$_5$ was investigated and compared to the base case of constant particle deposition. Reactions were added in which each of these gas-phase species were converted to surface nitrate with rate constants optimized so that the average surface nitrate formation rate is equal to the rate of surface nitrate formation in the particulate scenario once the model is in steady state. HNO$_3$ and N$_2$O$_5$ gas-phase concentrations we modeled with gas phase chemistry was taken from MCM v3.2,$^{43}$ via website: http://mcm.leeds.ac.uk/MCM with initial conditions set for the urban scenario in Ervens et al.$^{55,56}$

5.3 Results

The modeled surface nitrate concentration for the base case is shown in Figure 5.2a with and without sunlight, where the photochemistry is evident by the lower concentrations in the “with sunlight” case. The solar zenith angle is shown in orange, which indicates both a change in sunlight intensity and wavelength distribution over the day. Because only a fraction of the film was defined as reactive, even with the modeled photochemistry there is an increase in nitrate
concentration over time due to the constant deposition. This shows that the continued growth of nitrate that has been observed on surfaces is not necessarily indicative of a slow reaction rate or no chemistry occurring. This also highlights that taking into account that only a fraction of the surface nitrate is reactive, will lead to a smaller HONO source strength estimate than for models assuming the entirety of the deposited surface nitrate is reactive.

![Figure 5.2: Model output for the first four days of the simulation of the base case showing a) the deposited surface nitrate without (solid line) and with (dotted line) photolysis, b) the concentration of reactive surface nitrate and c) the HONO flux. Solar zenith angle is shown in orange.](image)

Looking at only the photoactive fraction of surface nitrate, illustrated in Figure 5.2b, the nature of the photochemical source is clearer. During the night, the reactive surface nitrate concentration increases, growing the photoactive pool of nitrate. Due to the fast rate constant predicted for this chemistry, the surface nitrate quickly decreases upon exposure to sunlight. This is followed by an increased concentration as the sunlight intensity decreases because the source of surface nitrate becomes larger than the photolytic sink. The impact of this behaviour is seen in a plot of HONO flux over time for one day, shown in Figure 5.2c. There is a morning maximum of HONO flux because surface nitrate has built up overnight. By the time peak
sunlight has been reached, nitrate accumulated overnight has been depleted to the extent that the HONO flux has already dropped off, causing the HONO flux not to track with the solar zenith angle. Note that a different choice of scaling for reactive surface nitrate will yield different results; if all of the nitrate is allowed to react then the surface nitrate concentration will remain very low over the sunlit hours and only increase overnight. If the depletion of reactive surface nitrate over the day is not accounted for, not only will the HONO source be overestimated, the model will also lose the temporal variation of the HONO source caused by the changing reactive surface nitrate concentration over a day. In addition, the significant temporal variation of the HONO flux emphasizes that reporting and comparing a single value for the magnitude of HONO sources is not sufficient to characterize the importance of different sources.

To further demonstrate the importance of knowing and accounting for grime film history, the impact of a series of cloudy days was modeled, where during the cloudy days the sunlight intensity is only 25 percent of the clear-sky value. The reactive surface nitrate concentration increases above that of the base case due to the slower photochemistry rate constant. When full sun returns, this leads to a spike of HONO, due to the greater pool of nitrate in the film, despite there being no change in the deposition rate.

![Figure 5.3: Surface nitrate for the first 5 days of the simulation for cloud case (dotted line) and base case (black line) a) reactive surface nitrate concentration b) HONO flux. Solar zenith angle is shown in orange and period of 75% light attenuation is indicated by the grey box labeled “cloud”.

Film history also impacts the response of the film to seasonal and latitudinal changes. Figure 5.4a displays three different HONO flux curves calculated for three different latitudes (65°N, 45°N and 23°N), each with a different daily cycle of SZA, while Figure 5.4b compares summer and winter at a latitude of 45°N. There is no change in total integrated daily HONO flux at
steady state for any of these cases, but there are differences in the temporal variation of the HONO flux. For the change in latitude, there is a balance between how quickly the SZA and therefore rate constant changes in the morning versus the time in the morning at which the SZA becomes less than 90°, initiating photolysis. When the SZA for the different latitudes are the same, the higher latitude has a smaller HONO flux because at the higher latitude there has been more time since the SZA reached 90° and therefore more time for reactive surface nitrate to deplete. For a change in season, the SZA is significantly higher throughout the day in the winter than in the summer and therefore, it takes more days for the winter case to reach steady state. However, once steady state is achieved, there is a larger maximum HONO flux in the winter than in the summer because of the short time over which the same amount of deposited nitrate is converted to HONO.

**Figure 5.4:** Impact of a) latitude where 23°N is showing in blue, 45°N in black and 65°N in red (thin), and b) season, where summer is shown in black and winter in blue, on HONO flux at steady state (solid lines). The corresponding SZA are shown in dotted lines.

### 5.3.1 Photolysis Rate Constant

Previous calculations of the surface HNO₃ photolytic HONO source have assumed a source that is proportional to the gas phase HNO₃ j-value. However, as discussed earlier, due to accumulation of reactive surface nitrate over night and its depletion during the day, the HONO source strength does not necessarily track the gas-phase HNO₃ j-value over the course of the day. As shown in Figure 5.5a, this skew towards an early morning HONO peak is more drastic with higher j-values, while the significant build-up of reactive surface nitrate over time for lower j-values, shown in Figure 5.5b means that only a small fraction of the reactive surface nitrate is depleted before maximum j-value and thus the HONO flux is more closely correlated with j-value over the day. In addition to changing the temporal behaviour, the rate constant determines
the time it takes for the film to reach steady state, as shown in Figure 5.5c as a plot of the daily-integrated HONO source over time. Before steady state, the rate constant dictates the amount of HONO being released from the film, but not in a linear manner. In contrast, at steady state, the build up of reactive surface nitrate concentration discussed previously causes the daily HONO flux to no longer be impacted by rate constant.

**Figure 5.5:** Impact of rate constant on a) HONO flux at steady state and b) reactive surface nitrate concentrations for maximum j values of $1.69 \times 10^{-5}$ s$^{-1}$ (dashed line), $1.47 \times 10^{-4}$ s$^{-1}$ (solid line) and $1.25 \times 10^{-3}$ s$^{-1}$ (dotted line) and c) daily integrated HONO flux over time for maximum j-values of $1.69 \times 10^{-5}$ s$^{-1}$ (diamond), $1.47 \times 10^{-4}$ s$^{-1}$ (circle) and $1.25 \times 10^{-3}$ s$^{-1}$ (star). SZA is shown in orange.

### 5.3.2 Deposition Rate

The deposition rate of particulate nitrate to the surface is not well known and thus the sensitivity of the HONO source to this value was investigated. The result is shown in Figure 5.6. It is clearly evident that HONO flux is linearly dependent on deposition rate when the film is at steady state and thus deposition rate is one of the key variables determining the daily HONO flux. While this is taken into account in multiple models, which determine nitrate loading by calculating the product of deposition rate and time since precipitation, eg. the simple calculation does not account for the complexities of the system as discussed above.
**Figure 5.6:** Impact of deposition rate on a) HONO flux for deposition rates of $4.6 \times 10^8$ (dotted line), $4.6 \times 10^9$ (solid line), and $4.6 \times 10^{10}$ (dashed line) and b) daily integrated HONO flux plotted as a function of deposition rate. SZA is shown in orange

### 5.3.3 Source of Nitrate

An assumption made in all previous simulations is that there is a constant deposition rate of surface nitrate. The impact of such an assumption was examined by comparing this constant deposition rate scenario to ones in which gaseous HNO$_3$ or N$_2$O$_5$ deposition is the source of surface nitrate, where each is adjusted to have the same average deposition rate as in the particle scenario. The resulting surface nitrate concentrations are shown in Figure 5.7a. Using HNO$_3$ as the surface nitrate source results in no large changes in the deposition rate over the day because there is less than a 40% change in HNO$_3$ concentration over the day. Therefore, the temporal variation of the HONO source does not differ significantly between HNO$_3$ deposition and constant deposition. Particle loading variations are expected to be smaller than even this HNO$_3$ variation and thus it appears that the assumption of constant loading does not significantly skew the HONO flux values as compared to taking into account diurnal variation of particle loading. In contrast, for N$_2$O$_5$ deposition we see only a morning peak in HONO flux because there is negligible N$_2$O$_5$ deposition during the day; when the nitrate accumulated overnight has been depleted, there is no further reactive surface nitrate source. To achieve equivalent average deposition rates, an N$_2$O$_5$ deposition rate that was an order of magnitude larger than that of HNO$_3$ was required, suggesting that N$_2$O$_5$ deposition plays only a minor role as a reactive surface nitrate source and a constant rate of precursor deposition can be assumed without large errors being incorporated into the model output.
Figure 5.7: Impact of the source of nitrate on a) surface nitrate concentration without illumination starting after 36 hours of model time, b) HONO flux at steady state and c) HNO$_3$ and N$_2$O$_5$ gas-phase concentrations. The constant rate scenario is indicated by a solid line, HNO$_3$ deposition as a dashed line and N$_2$O$_5$ deposition as a dotted line. SZA is shown in orange.

5.3.4 Surface Area

Another factor that will impact the HONO source strength is the available surface area, which was modeled by multiplying the deposition rate by a scaling factor due to the increased surface area onto which nitrate deposits. Figure 5.8 shows the response of HONO flux to different ISIs. Under the model conditions, the HONO source scales linearly with the surface area chosen and thus this is again important to properly characterize for a particular location. However, it should also be noted that the impact of exposed surface area on the growth in surface nitrate is not known. In the scenario modeled here, it is assumed that with more surface area a greater fraction of gaseous precursors are captured on surfaces to form surface nitrate. However, the assumption could also be made that the same fraction of atmospheric nitrate is going to be captured independent of surface area. In this scenario, surface nitrate concentrations would decrease with increasing surface area causing the HONO flux to be independent of surface area. Another complicating factor for surface area is that the more surface area in an urban setting, the more
likely that some of the surface area will be shielded from the light for part or all of the day. This will again impact the HONO flux but is not examined further in this study.

**Figure 5.8:** Impact of surface area on HONO flux. An ISI of 10 is shown in a dashed line, ISI of 2 in a solid line and an ISI of 1 in a dotted line.

### 5.3.5 Scaling Factor for j-value

One of the assumptions made in previous models is that the j-value for surface HNO$_3$ photolysis can be modeled by multiplying the gas phase HNO$_3$ j-value by a constant factor between 24 and 100. It has also been assumed that experimentally measured rate constants can be scaled to an environmentally relevant solar intensity using an aqueous nitrate actinometer. This assumes that absorbance of surface HNO$_3$ has the same wavelength dependence as both aqueous nitrate and gas-phase HNO$_3$, and that the light sources used in experiments have the same wavelength distribution as the SZA being scaled to. Measurements of surface HNO$_3$ absorption cross section $^{21,22}$, and more recently that of surface nitrate, $^{23}$ have been made and are shown in Figure 5.9a along with the absorption cross section of gas-phase HNO$_3$ $^{59}$ with each curve normalized to its maximum value in the range of 290 to 350 nm. Sangwan et al. $^{23}$ used these values to calculate j-values as a function of SZA; we normalized these curves to yield a j-value of $1.47 \times 10^{-4}$ s$^{-1}$ at a SZA of 0°. The corresponding j-values plotted as function of time for a model day are shown in Figure 5.9b, and compared to that of gaseous HNO$_3$ as implemented by the MCM v.3.2. $^{43}$ It is evident that the rate constant increases more quickly in the morning when the j-values are scaled to the measured surface cross sections than when gas-phase HNO$_3$ data is used due the sizable red shift of the surface nitrate and HNO$_3$ absorption cross sections. $^{21-23}$ The modeled HONO fluxes shown in Figure 5.9c indicate that compared to the base case, the peak HONO flux is
shifted earlier by 40 min using the surface HNO$_3$ j-values and 60 min earlier assuming the surface nitrate j-values hold.

**Figure 5.9**: Impact of function of j-value on SZA a) absorption cross section normalized to its maximum value between 290 and 350 nm and b) j-value over the day, adjusted to a value of $1.47 \times 10^{-4}$ s$^{-1}$ at a SZA of 0° c) HONO flux at steady state. Gaseous HNO$_3$ is shown in a solid line, surface HNO$_3$ as a dashed line and surface nitrate as a dotted line.

### 5.4 Discussion

Photolysis of nitrate on urban grime surfaces has been investigated using a box model, identifying the need for better-constrained and more complex modeling methods for identifying the importance of surface photolysis as a HONO source. The values here are upper limits for the conditions described because transport of species to and away from the surface is not considered, rather assuming instantaneous deposition and mixing. The model used here assumes 100% HONO yield and does not take into account any dependence on relative humidity. Nevertheless, the results we report indicate significant limitations to previous models of HONO production from surface HNO$_3$ photolysis. In particular, previous models have generally failed to account
for nitrate precursor depletion during photolysis, they use inappropriate absorption cross sections (scaled to gas-phase HNO$_3$), they do not account for any reactive surface nitrate sources other than gas-phase HNO$_3$ and they fail to account for faster photolysis rates measured for grime photochemistry compared to HNO$_3$ on clean glass.

In general, because of its constantly evolving composition, when modeling grime chemistry it is important to consider the history of the film. On a daily scale, this means that under most scenarios the maximum HONO flux from a surface nitrate photochemical source is in the morning before the peak j-value of the parent species has been achieved, due to the nightly buildup of reactive surface nitrate. The degree of this skew of peak HONO flux from peak j-value is more significant with larger maximum j-values. On a longer time scale, it is the build-up of reactive surface nitrate over time that causes the daily-integrated HONO flux to be non-linearly dependent on rate constant as a steady state concentration of reactive surface nitrate is approached, and independent of j-value at steady state. It is therefore important to know the time since there was a clean surface in order to determine the dependence of the HONO flux on j-value. It is also important to consider past fluctuations in solar intensity, caused by overcast conditions, for example. In the case depicted here, a series of cloudy days were followed by a sunny day resulting in a spike of HONO that cannot be explained without knowledge of the conditions over the previous days.

It is also the dependence on history that causes significantly different temporal variations in HONO flux with different patterns of daily SZA. As compared to summer, in winter, the peak HONO flux is larger despite higher SZA, due to the slow depletion of reactive surface nitrate and therefore a much larger steady state reactive surface nitrate concentration in the winter. In contrast, the peak HONO flux scales with decreasing SZA for different latitudes because higher peak SZAs correspond to instances of the sun rising earlier in the day.

In addition to this dependence on grime history, it is important to characterize specific variables of the urban grime photochemistry. We have seen that the key factors determining the daily magnitude of this photochemical HONO source are the deposition rate of the surface nitrate precursors and the surface area of the impervious surfaces onto which grime can form. While previous models have used literature dry deposition rates for estimating the surface deposition of HNO$_3$, the current model was constrained by measurements of nitrate concentration over time on
an exposed surface. Constraining surface nitrate concentration by surface measurements over time, takes into account, in an empirical manner, the possibility of multiple surface nitrate sources and accounts for any resistances for nitrate deposition onto surfaces, non-photochemical loss processes such as evaporation and, from light exposed versus light shielded measurements, that only a fraction of measured surface nitrate is reactive. The impact of accounting for non-HNO₃ surface nitrate precursors has been shown to mainly be a consideration for the magnitude of deposition rather than changing the temporal variation because when each source is normalized to the same average surface nitrate growth rate, there is minimal difference between assuming a constant particle deposition and modeling HNO₃ deposition. There are more significant differences for N₂O₅ as a precursor, however under the model conditions, the order of magnitude larger N₂O₅ deposition rate required to match the same surface concentrations modeled for HNO₃ deposition suggests that N₂O₅ is not an important precursor.

We also found that the use of an appropriate cross section is important in order to accurately model how the j-value changes as a function of SZA and therefore the temporal variation of the HONO source. Reported values for the absorption cross section and the values calculated from these as a function of SZA indicate that surface HNO₃ and nitrate have a red shifted absorption cross section in comparison to that of gaseous HNO₃ and therefore these surface values result in higher j-values than for gas-phase HNO₃ when all are normalized to the same rate at a SZA of 0°. This leads to the peak HONO flux to occur an hour earlier if it is surface nitrate photolyzing or 40 min earlier if it is molecular HNO₃ photolyzing as compared to the assumption of scaling with gaseous HNO₃. This could have significant implications because it is at this time of morning when other OH sources are small, and HONO is responsible for a larger fraction of the OH budget. This red-shifted wavelength dependence also calls into question the conclusion of Elshorbany et al. that HNO₃ photolysis is not important because of its absorbance wavelength range, assumed to be the same as gas phase HNO₃. Therefore, it is important to take into account the correct j-value dependence on SZA when trying to quantify the “missing HONO source”.

It is difficult to assess the importance of urban grime photochemistry for HONO formation in a quantitative manner in comparison to other HONO sources that have been proposed. While the current model runs were constrained by measurements, there is a wide range of measured values and thus the source strength is not well constrained. Moreover, the common method of reporting noon-time maximum or daily average HONO flux values, either of a specific source or to
quantify the required additional source to match model and measurements, is not appropriate for sources which vary so significantly over the day and are not at a maximum when j-values are at a maximum. To more accurately quantify this source, films could be collected in the light and in the dark along side gas-phase and particulate measurements expanding on our study in Leipzig. In this way, a site-specific reactive fraction and deposition rate could be identified allowing for a site-specific estimate of HONO flux from urban grime photolysis and compared to other sources throughout the day constrained by the other measurements. As identified by Laufs and Kleffmann, there is also a need to measure j-values with a light source that has a well-characterized wavelength distribution and intensity to better constrain a j-value. This also requires the measurement of a wavelength dependent quantum yield. While Laufs and Kleffmann have evidence to suggest it is wavelength dependent, it is important to look into this in more detail. The nature of the HONO source within grime must also be better characterized. Although, assumed to be a HNO$_3$ or nitrate source, an organic nitrogen source has not been ruled out.

Despite these limitations on quantifying the grime photochemical HONO source, based on the variables discussed here the urban grime photochemistry is likely to be most important in urban centers where other sources such as soil and ocean are minimal and impervious surface area is high. In particular, areas such as street canyons where the surface area is extremely high, would favour this reaction, assuming light can reach all of the surfaces within the canyon. In addition, it is early morning where this source likely plays the largest role when other HONO and OH sources are less significant. For example, this could explain some of the model morning underestimates by both Gall *et al.*, who use an incorrect surface HNO$_3$ parameterization, and Zhang *et al.*, who don’t include HNO$_3$ photochemistry.

### 5.5 Conclusions

In order to properly determine the importance of surface HNO$_3$ photochemistry for HONO cycles, it is necessary to accurately predict both the diurnal variation of the source as well as the magnitude. We have shown through a series of case studies, that at steady state the magnitude of the HONO flux is determined by deposition rate of reactive surface nitrate and surface area onto which the nitrate can collect, not the rate constant as is often assumed. This source also does not necessarily have a typical photochemical diurnal profile, with source strength scaling with solar
zenith angle, because of night-time accumulation of reactive surface nitrate. Instead, under most conditions a morning maximum in HONO flux is observed, with the time and magnitude depending on the season, latitude, rate constant as well as the wavelength dependent absorption cross section of the photolytic precursor. Furthermore, we have seen that the history of the film both of earlier in the day and of previous days is important in dictating both the magnitude and temporal variation of HONO flux. Therefore, it is important to use a surface reservoir model such as that of Karamchandani et al.\textsuperscript{31} to model this chemistry. Further study is required to better understand the grime characteristics such the wavelength dependent photochemical parameters in addition to further studies to characterize site-specific characteristics in the context of measurements constraining other HONO sources in order to evaluate the importance of urban grime photochemistry in the formation of HONO.

5.6 References


(50) Clarke, J. P. Applying the Multimedia Urban Model to Measured PCBs, PAHs and PBDEs in Urban Areas, 2006, pp. 1–124.


Chapter Six

Conclusions and Future Directions

Contributions: The manuscript was written by Alyson M. Baergen with critical comments from D. James Donaldson
6.1 Urban Grime Photochemistry

The presence of urban grime was first proposed almost two decades ago yet the environmental impacts of these films are not well understood. The composition, reactivity, growth characteristics, partitioning characteristics and role of the surface onto which deposition is occurring, are all ongoing uncertainties. This thesis focused on the atmospheric significance of the grime, in particular, of photochemical nitrogen oxide production. The use of real samples was prioritized; these were examined via photochemical lab experiments and a field study. A model was run to evaluate the chemistry identified and characterized in this work in order to better understand its significance in the environment.

Chapter 2 reports the first reactive study using a real urban grime sample, detecting fast nitrate photolysis 3-4 orders of magnitude faster than gas and aqueous rate constants and approximately an order of magnitude faster than what had been reported from glass. Urban grime was collected on an ATR-FTIR crystal so that nitrate could be tracked without modification of the sample. Using an organic film proxy, we were able to probe for the production of OH radicals showing that the nitrate/HNO₃ was undergoing photolysis and not just evaporating, as well as suggesting the formation of OH radical either through the production of NO₂ and OH or the production of HONO and subsequent photolysis to NO and OH. Following the conclusion of this study, the experimentally derived rate constant has been compared to ones derived from more recently measured absorption cross sections of surface HNO₃ and nitrate. Assuming a quantum yield of one and a solar zenith angle of 20°, the solar zenith angle for noon time sun in Toronto, (not 70° as was reported in the study) values of ~9x10⁻⁴ and 3x10⁻³ s⁻¹ were calculated for surface NO₃⁻ and HNO₃ respectively in good agreement with the experimental value of 1.2x10⁻³ s⁻¹.

Following up on this study, gas phase products of the photochemistry were detected using incoherent broadband cavity enhanced spectroscopy discussed in Chapter 3. While limitations of this set up prevented the speciation of products, the prediction of nitrogen oxide formation from Chapter 2 was supported. A relative humidity dependence was measured, different from that seen on glass or mineral oxide surfaces, showing the distinct environment for nitrate/HNO₃ within urban grime. These studies were in agreement with two other photochemistry experiments: one on grime collected on a variety of substrates and one on particles. They show nitrate/HNO₃ photochemistry forming HONO, NO and NO₂ with a wide range of measured
rates, from similar to the glass measurements up to values similar to the rate we measured, as well as a wide range of HONO:NO$_3$ ratios from 0.1 to greater than 6.$^2$

These studies highlight the need for more study to better understand the variability observed. Ye et al.$^2$ report a dependence on nitrate loading; however this is a weak dependence where surface type, film age, previous light exposure among other variables could also be playing a role. Each of these variables should be investigated to distinguish what dictates the photochemical behaviour. Surface and gas phase measurements should also be done simultaneously to distinguish between properties impacting the nitrate photolysis rate and those impacting product formation including possible secondary chemistry. The wavelength dependence should also be measured to better understand the extent to which absorption cross sections on glass reflect those of the species on grime, or if the grime matrix further impacts these cross sections and therefore, how this chemistry is going to change with solar zenith angle.

Furthermore, the nature of the urban grime precursors to nitrogen oxides should be investigated. It has been seen that nitrate and HNO$_3$ have different absorption cross sections and thus, the equilibrium between these species over a range of relative humidities could be important to understand chemistry changes. In addition, although HNO$_3$ and nitrate are assumed to be dominating the photochemistry, the role of organo-nitrates and similar species is unknown. If these species are contributing to the observed chemistry, yet a different response to changes in environmental variables such as solar zenith angle and relative humidity would be expected. All of these will be detected as aqueous nitrate, and thus other techniques are required to measure these species, such as ATR-FTIR as used in Chapter 2, or gas chromatography on an organic extract.

Chapter 4 reports our work that compared nitrate content of grime samples that were grown exposed to and shielded from sunlight. This showed the impact of real sunlight on grime composition and examined the impact of samples continually exposed to sunlight as opposed to samples grown in the dark and then exposed to light. In the latter, the film does not undergo photochemical ageing and thus the nature of the film may be different than the light-exposed sample. The continued exposure also allows for photochemistry of transient species, such as photochemical NO$_2$ uptake, to play a role that would not be captured by collecting in the dark. In this study we found only approximately 10% of the film nitrate was removed from the light
exposed film in comparison to the light-shielded film, showing that not all of the film nitrate is photochemically removed. It would be interesting to further illuminate the samples exposed to sunlight to distinguish more clearly between the nitrate that is not photoactive and the photoactive nitrate on the surface that is in photo-steady state. Our previous studies also saw non-photochemically active nitrate fractions. For the week-long collected films described in Chapter 2, we could detect the decay of nitrate to a background level, whereas films collected for a year showed no detectable nitrate depletion after 3 hours of illumination. Between these samples there was likely relative humidity differences, difference in detection methods and different atmospheric conditions during collection in addition to the different ages that could be playing a role. These different variables should be investigated to better understand the unreactive fraction, its composition and factors influencing its magnitude.

Based on the information collected in Chapters 2-4, Chapter 5 presents our work on modeling grime photochemistry as a HONO source, investigating its role in the HONO budget and determining the sensitivity of the HONO production to many of the variables previously discussed. In particular, we showed the importance of modeling the HNO$_3$ as a surface reservoir which depletes over time, such as done by Karamchandani et al. as opposed to a source that is linearly dependent on deposition rate and photochemical rate constant. Without taking into account the build up of a surface reservoir of HNO$_3$/nitrate, the magnitude and diurnal variation of the sources are not adequately captured. This modeling study also highlights the possibility of grime history influencing the source. This would be challenging to capture in models; however, the impact could be minimized if modeling a period of time with stable conditions.

In order to better inform future models and identify the importance of urban grime photochemistry as a HONO source, we need measurements that include surface concentrations. There are only a few such surface nitrate measurements in existence and none in the presence of extensive other atmospheric measurements. The proportion of species that are deposited from the atmosphere that will be captured onto grime films is not well constrained, or how this may change in areas with different magnitudes of impervious surface area. It is also not clear the extent to which transport will limit the effectiveness of the surface source.
6.2 Other urban grime chemistry

Beyond the grime photochemistry described, based on comparisons of PM$_{10}$ and grime measurements in chapter 4 other grime-mediated processes have been predicted. Low to undetectable levels of ammonium were measured in urban grime despite ammonium being measured in particles. The comparison of particle and grime composition suggests that ammonium nitrate evaporation is not sufficient to explain the extent of ammonium evaporation. A pH driven effect based on the mixing of acidic fine particles with basic coarse particles is proposed, however this process has not been further studied. Laboratory generated particles could be impacted onto a surface and examined for their behaviour to determine if the environmental phenomenon can be reproduced under controlled laboratory conditions. A skew in capture efficiency of particles could also play a role. More insights into this phenomenon may be gleaned from the organic composition data also collected from the Leipzig field study. Examining other surface types may also help to evaluate this process, to determine if grime on all surface types show the same lack of ammonium.

The detection of chloride within urban grime samples has also led to our prediction of grime as a possible ClNO$_2$ source. Such a source would not only increase the available chloride concentrations for this chemistry, but could also impact the temporal variability of this species, as urban grime chloride content is less variable than that of the particulate chloride or gas phase HCl. N$_2$O$_5$ uptake experiments should be undertaken on grime samples to determine uptake coefficients and ClNO$_2$ yield under a variety of conditions. This experiment would also help determine the yield of HNO$_3$ on the grime film and therefore would help to better predict the role of N$_2$O$_5$ hydrolysis as a HNO$_3$ source to the grime. As was seen in chapter 5, the relative importance of N$_2$O$_5$ as an HNO$_3$ source could impact the diurnal pattern of HONO flux from the film.

6.3 Urban grime and water

We have found water content of the film to be important for grime photochemistry, indicating the importance of understanding the interaction of urban grime with water. The water content of the film has not previously been focused on, likely due to the difficulty of studying water content in film extracts, however, because the grime was collected directly onto the ATR-FTIR crystals, the water associated with the unaltered film could be detected. Liquid water remained the
dominant IR peak down to 10% RH, with the water content of the film in rapid equilibrium with the surroundings in the 10-20% range examined. A more quantitative approach was taken in Chapter 3, using a quartz crystal microbalance to measure the change in water content in of grime between ~0% and 75% RH. No deliquescence or efflorescence was detected in this range, indicating likely viscosity changes but no phase transitions. More study is needed on the water uptake at higher relative humidities, which would help identify the role of organics and inorganics as it is at these high humidities where behaviour is more differentiated. In general, more research should be done on the components and processes that dictate grime water content. For example, does film ageing make the film more hygroscopic as would be suggested by particle studies, or less so as has been indicated by the drop in the water-soluble organic fraction over time in the film?

6.4 More urban grime questions

Beyond the specific questions raised by this dissertation, there is still much to understand more generally about urban grime. For example, as discussed in Chapter 1, the nature of the film is not well known. Is it a uniformly mixed film, a collection of separate deposited particles or somewhere between? What determines where on this continuum the grime lies? This could have important implications for growth characteristics, which again are not well understood, as well as partitioning characteristics and grime reactivity. The surface onto which atmospheric constituents are depositing may also play a yet unknown role in determining this.

Furthermore, a variety of techniques have been used to collect grime. An inter-comparison study should be undertaken to compare these methods to the best of our abilities to determine what type of artefacts are being introduced. For example, it has been assumed that glass beads and flat glass surfaces can both represent real surfaces, but it is unknown how the films deposited onto these different surfaces differ. Different window sampling and subsequent extraction methods have also been used without reports of comparison of techniques. These studies are needed to ensure the measurements being reported reflect real grime chemistry rather than just sample biases.

6.5 References


Chapter Seven

Appendices

Reprinted from Baergen, A. M. and Donaldson D. J. Photochemical Renoxification of Nitric Acid on Real Urban Grime *Env Sci Technol* 2013,11,815-820

**Contributions:** Experiments were designed and performed by Alyson M. Baergen. The manuscript was written by Alyson M. Baergen, with critical comments from D.J. Donaldson
7.1 Supporting Information for Chapter 3

7.1.1 Characterization of Experimental Chamber

Known amounts of NO\textsubscript{2} in N\textsubscript{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\textsubscript{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\textsubscript{2} concentration of 6.0 ppm, based on the reported value from the supplier (Linde), was further diluted with N\textsubscript{2} using needle valves and mass flow meters with uncertainties of ± 0.5 mL/min to a concentration of (4.76 ± 2.4) x10\textsuperscript{12} molecules/cm\textsuperscript{3}. The figure displays the measured NO\textsubscript{2} and HONO concentrations detected by the IBBCEAS as a function of RH. The total concentration measured from the sum of NO\textsubscript{2} and twice the HONO calculation following the mass balance implied by Equation 3.1 was (3.6 ± 0.3) x10\textsuperscript{12} molecules/cm\textsuperscript{3} which is within error of that calculated from the NO\textsubscript{2} concentration coming from the cylinder reported above. This suggests that this technique can quantify the total concentration of NO\textsubscript{2} + HONO here, though cannot accurately speciate NO\textsubscript{2} and HONO. Fig. S1b shows that the total concentration decreases upon illumination, due to the photolysis of NO\textsubscript{2} and HONO. The HONO concentration measured is independent of relative humidity within the 30% coefficient of variability measured between samples. No NO\textsubscript{2} was detected. This shows that the NO\textsubscript{2} to HONO conversion is complete within error, and that there is no significant impact on the IBBCEAS NO\textsubscript{2} + HONO response as a function of relative humidity. We note that, if the photochemical product distribution between NO\textsubscript{2} and HONO changes with relative humidity, this will impact the total amount measured because it takes two NO\textsubscript{2} molecules to make one HONO molecule. Thus a change from only NO\textsubscript{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.
Figure 7.2: Concentrations of HONO and NO$_2$ for NO$_2$ 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 Figure 7.2b because no NO$_2$ was detected. The error bars represent one standard deviation of the average of three experiments.

Thus the total product concentrations from grime photochemistry may be safely compared as a function of RH. No values are shown below 13% in Figure 3.3 and Figure 7.2 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.
Table 7.2: Inorganic ion content of grime used for photochemistry experiments (n=3)

<table>
<thead>
<tr>
<th></th>
<th>Chloride</th>
<th>Nitrate</th>
<th>Sulfate</th>
<th>Sodium</th>
<th>Potassium</th>
<th>Magnesium</th>
<th>Calcium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (µg/cm²)</td>
<td>4.8</td>
<td>0.73</td>
<td>4.27</td>
<td>4.9</td>
<td>0.34</td>
<td>1.27</td>
<td>2.11</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.1</td>
<td>0.01</td>
<td>0.04</td>
<td>0.2</td>
<td>0.01</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

7.1.2 References

7.2 Supporting Information for Chapter 4

Figure 7.3 a) shows a photograph of the sampling container positioned in downtown Leipzig, with the film sampler on the roof at the left, next to the inlet for particle samples. b) shows a close up of the upper two layers of the sampler, without the side flaps mounted on one side. The UV-transparent cover over the top layer of beads is shown at the top above the first tray of beads. Beneath this is a sheet of stainless steel that shields the second layer of glass beads from sunlight. The separate bead compartments in the second layer can also be seen. c) shows a schematic of the film sampler, indicating the location of the UV-transparent cover; the stainless steel sheet as well as both the light-exposed and light-shielded trays. The location of the particle inlet in relation to the sampler is also indicated.
Figure 7.4 shows gas phase concentration and meteorological data that were collected over the course of the campaign from the same sampling location as the grime and particles were sampled.
Figure 7.5 shows the blank-subtracted mass of ions contained within the film over time, normalized to the geometric surface area of the glass beads. All of the ions show a monotonic increase in concentration over the 6-week period, with the exception of ammonium, which is below detection limits for most of the campaign. The upper limit ammonium is displayed as the detection limit of ammonium. This uniform growth in ion concentration is consistent with previous studies which showed steady growth in total ion content, even after more than two years of collection. To examine the degree of variability in the data, three samples were collected on October 7; the analysis shows at most a 35 percent difference from the mean value.
Figure 7.6 shows the mass concentrations of ions within the sampled PM$_{10}$. An event showing elevated sodium and chloride is seen at the beginning of the campaign, as discussed in the text. As well, elevated levels of nitrate, sulfate and ammonium were observed for the samples collected from October 1 until October 4; this is also reflected in the PM$_{10}$ mass loadings displayed in Figure S2. The lack of elevated levels of calcium, sodium and chloride during this period suggests the presence of an additional source of fine particulate matter.
Figure 7.7 shows size-resolved particle ion mass concentrations collected daily from October 20 until October 25. Measured values were blank corrected to calculate the values reported herein. As discussed in the methods section, the foils contained a calcium contamination that contributed up to 89% of the measured values.
Figure 7.8 size resolved particle mass normalized to total inorganic ion mass collected daily from October 20 until October 25. For comparison PM10 composition, calculated from the sum of the mass collected from all stages, and final grime composition from October 25 are also displayed.

7.2.1 References