

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

Specific Comments:

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

We have added this paper as a citation.

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

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

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

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

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

We have clarified that we are talking about the NO₂ control experiments in the manuscript. The concentrations used for these control experiments are quite close to those detected in the grime experiments. In the control light experiments approximately 6×10^{11} molecules/cm³ are detected in comparison to a range of 3.5×10^{11} molecules/cm³ to 6.5×10^{11} molecules/cm³ for the initial illumination of grime samples at a relative humidity of 35%. Thus, we expect these control experiments to reflect what is happening in the grime experiments. We have clarified that it is this diluted concentration that we are using.

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

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

In a previous study (ES&T, 2015), we have suggested that the grime may actually be somewhat basic due to a complete loss of ammonium, something that we would not expect from an acidic film. If HONO is being formed directly in the photochemistry (which we cannot confirm with the present study), we anticipate that it is not via the protonation of nitrite but rather arises from secondary chemistry of NO₂ formed from nitrate photolysis, for example, photoreduction of NO₂ or NO₂ hydrolysis, or perhaps due to photochemistry of any organic nitrogen species within the film. We have expanded the discussion of possible ways in which HONO could be formed.

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

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

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

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

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

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

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

See above about equation 1

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

We have added some clarification concerning the NO₂ concentration being flowed through the chamber. The conversion is indeed surprising! The concentrations we used led to similar concentrations when the NO₂ stream was illuminated as when the grime was illuminated, and thus this suggests is a reasonable expectation that a similar high conversion would be happening for sample illumination.