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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Formation of Reactive Nitrogen Oxides from Urban Grime Photochemistry" *by* A. M. Baergen and D. J. Donaldson

Anonymous Referee #1

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General Comments

The manuscript has scientific merit and provides information that will benefit the atmospheric chemistry and physics community. This study investigates the photolysis of urban grime coated on glass beads by measuring gas phase HONO and NO2 as a function of relative humidity using incoherent broad band cavity enhanced spectroscopy (IBBCEAS). The generation of reactive nitrogen oxides from urban grime photolysis could be, at least in part, the missing source of daytime HONO, which may help link the atmospheric models with field measurements.

In addition, the authors further investigate the urban grime by ion analysis using ion chromatography (IC) and water uptake analysis using a quartz crystal microbalance.

My most involved request would be to include additional details regarding the composition of the grime. I ask the authors to provide the results from the IC and any other characterization of the urban grime in the SI for those of us who are curious. The manuscript is well written, well organized and concise.

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

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.

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?

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.

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 $\sim$ 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.

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.

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.

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?

In the Supplement:

Sentence 8: The authors refer to an “Equation 1,” but I did not find this anywhere.

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)?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-156, 2016.