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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 #3

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It is believed that the deposition of NOy (mainly HNO3, even if N2O5 is also discussed here) is a sink process for NOx, however this study challenges this point of view and demonstrates, for the time, that photochemistry of photochemistry of urban grime is as a potential source of gaseous nitrous acid (HONO). This has been suggested before but never demonstrated. This study therefore a nice piece of work, which illustrates/suggests how this may feedback into air quality issues in urban environments.

The experiments presented here were performed on real "urban grime" as collected during one year at Toronto using a combined approach of Incoherent Broad Band Cavity Enhanced Spectroscopy (IBBCES) and Quartz Crystal Microbalance (QCM), and were focused on NOx emission and water uptake.

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Discussion paper

This paper reads well, and I have therefore only minor comments.

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

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

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

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

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

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