

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

Only gaseous HONO has been observed, and the authors argue that it might be due to NO₂ undergoing wall losses in their reactor (acting also as a HONO source). However, HONO is lost more efficiently on surfaces than NO₂. Therefore the same argument holds for HONO too i.e., this compound should also then be lost on the walls of the reactor. Also, wall losses are expected to increase with increasing humidity, and 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.

This was a surprising observation, but the hypothesis of NO₂ wall hydrolysis was due to the observations from flowing NO₂ through the apparatus. In these experiments, although NO₂ was entering the system, only HONO was observed under illumination. Moreover, the HONO concentration did not change with relative humidity for this control experiment. These were the observations that led to the conclusion that NO₂ and HONO could not be distinguished under the experimental conditions. We have updated the wording to make this more clear.

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

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

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

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

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

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

We have broadened the discussion around formation mechanisms for HONO.

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

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

As stated by the reviewer, a less acidic surface would favour HONO to stick. Because this is not what was observed, the role of water seems to be less in controlling the pH, but rather in controlling the viscosity or mobility of reactants as discussed within the manuscript. Another possibility is that the HONO being measured is all from surface hydrolysis of an NO₂ photoproduct on the walls of the apparatus, rather than from direct formation from grime photochemistry. In that case a much smaller pH dependence would be expected. NO₂ was never detected in the grime experiments and in the control experiments less NO₂ was detected at higher RH.