Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-648-RC1, 2017

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nitrous acid formation in a snow-free wintertime polluted rural area" *by* Catalina Tsai et al.

Anonymous Referee #1

Received and published: 3 September 2017

General Comments. The manuscript by Tsai et al. reports results of field measurements of nitrous acid (HONO) during a field campaign in the Uintah Basin during the winter of 2012. A long-path DOAS system measured atmospheric composition at three different altitude intervals, while a suite of accompanying measurement techniques provided trace gas and meterological data during the month-long field campaign. The data showed HONO gradients, with clear upward fluxes during the day. In addition, the authors were able to show that daytime HONO fluxes tracked solar irradiance. This rich dataset and powerful modeling analysis [1D chemical transport model (RCAT) and WRF-Chem] of the dataset provided opportunities to test out current hypotheses regarding HONO formation mechanisms. For example, one daytime event dominated by fresh emissions from a nearby coal-burning power plant where low HNO3 levels were

measured showed that photochemical NO2 to HONO conversion on soil surfaces was the dominant formation mechanism. Other occasions provided opportunities to test mechanisms involving surface nitrate photolysis, acid displacement of soil nitrite, and biological HONO releases.

The dataset acquired by the authors is unique and the study is quite novel. There are few studies published in the literature that focus on HONO formation during the wintertime. Moreover, the study was carried out in an arid region where snow was completely absent. This means the campaign provided a unique opportunity to study HONO chemistry over cold soil surfaces with little complication from vegetation surfaces. The study has some weakness and the authors are fully aware of the knowledge gaps and discuss them. For example, the study showed that daytime HONO production rates are correlated to both J(NO2) and J(HNO3) values, so there is still the question as to whether NO2 reduction by soil surfaces or nitrate photolysis (or both) are responsible for the surface daytime HONO source. However, the location and conditions of the field site, in addition to the quality and breadth of measurements made, and the use of models to interpret results and test hypotheses, enables insights into HONO formation mechanisms that were not previously possible in other studies. Most importantly, the study suggests that (at least for this region) surface photochemistry of NO2 and nitrate can account for the missing HONO source that is often cited in HONO studies. I know of few studies that have been able to show this so clearly.

The only major comment I have is regarding the likely speciation of nitrate as one of the HONO sources considered. The authors refer to HNO3(ads) or HNO3/nitrate(ads) photochemistry on soil surfaces as being responsible for a significant portion of the observed HONO, where (ads) refers to the adsorbed phase. While HNO3(g) is certainly present (it is measured by CIMS), it is highly unlikely that HNO3 is actually present as molecular nitric acid on soil surfaces in Uintah Basin. Nitric acid will dissociate upon contact with surfaces, even in the presence of minute amounts of water. In the presence of aluminosilicate soil minerals present in the region and at the alkaline soil pH

(NOAA measured a soil pH of 8.06) it is highly likely that hydrated nitrate (not molecular HNO3) is responsible for the observed HONO. The authors make the argument that HONO from microbial sources is not likely because of the alkaline soil and the fact that HONO's pKa is $\sim$3. Nitric acid's pKa is -1, so it is even less likely to be present in molecular form on surfaces. Realizing this may have some implications for some of the data analyses. For example, perhaps nitrate photochemistry parameters (absorption cross sections and quantum yields) may be more appropriate at describing the daytime HONO production rates than those of HNO3. It is clear that an estimate of the daytime surface flux of HONO due to nitrate is not possible without knowing nitrate densities at the soil surface. However, it may be worth noting that the correlation between HONO flux and [HNO3] x UV Solar Radiation shown in Figure 11 may be strong not because HNO3 is a direct photochemical source of HONO, but rather a source of surface nitrate (via deposition of HNO3) which is rather the direct source.

Minor Comments: [page, line]

[1, 13]: spell out 'agl' at first use.

[4, 15-17]: insert comma within numbers to denote place value – makes the numbers easier to read.

[6, 23]: replace "until" with "when"

[15, 15-21]: Consider including reference to Laufs et al. (ACP 2017, 17, 6907) who also showed recently that HONO production was correlated to [NO2]xJ(NO2).

[16, 1]: As per above comment, one may also have to consider [nitrate]xUV solar radiation.

[17, 12-14]: In discussing how much HONO is stored in soil could be released via strong acid displacement the next day, the authors state "...in this case one would expect that, as the surface reservoir is depleted throughout the night, the flux would also decrease..." Don't the authors mean during the day? It is the nitrite accumulated

during the nighttime that is the source of HONO during the day via the acid displacement mechanism. Presumably, displacement during the day would be what depletes the nitrite, while it accumulates during the nighttime.

[18, 6-8]: A sentence in quotes is given here. I assume it is quoted from Yan et al (2016) which appears earlier in the paragraph and somewhat removed from the sentence in question. I feel that the reference should again be referenced at the end of the paragraph to make that connection better.

[Figure 5D]: This figure is used to demonstrate that there is an elevation gradient of HONO concentration during the day, with higher concentrations at ground level compared to aloft. The mean values show this, although the differences are small due to the scale of the figure. In addition, the grey shading denoting 1-sigma variability are very large (spanning +/-0.05 ppb). Accounting for this variability, would not one conclude that there is no statistically significant difference between HONO concentration at the various altitudes? I realize the data are averages of all the sunny day data from the entire field campaign so there is tremendous variability. So, I can imagine the gradient is much more evident and variability insignificant if one restricts oneself to viewing data for a particular day. The authors may want to comment on this since at first glance with the plotted variability bands it may not be clear how one could say there are statistically significant differences in HONO for the various heights.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-648, 2017.