Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-105-RC1, 2018

Atmospheric Chemistry and Physics
Discussions

# *Interactive comment on* "Tropospheric HONO Distribution and Chemistry in the Southeast U.S." *by* Chunxiang Ye et al.

**Anonymous Referee #1**

Received and published: 31 March 2018

The manuscript 'Tropospheric HONO distribution and chemistry in the Southeast U.S.' by Ye et al. presents HONO measurements made during the NOMADSS campaign. The two main claims presented here are: (1) there is more HONO observed than can be explained by known chemistry, and (2) photolysis of particle nitrate accounts for this so-called missing HONO source. The analysis used to make both claims are weak, therefore, unconvincing. Moreover, the analysis on nighttime chemistry and production in power plant exhaust were hastily done and written. This work can be considered for publication only after significant improvements.

As for (1), the authors claim that because HONO photo-lifetime is 8 minutes, that direct emission of HONO can be disregarded. This is a misinterpretation of the concept of lifetime. Lifetime represents an e-folding time, meaning that ∼36% of the original amount still remains after 8 minutes since time zero, or time since emission. If HONO at the emission source is 10 ppb, approximately 50 to 60 minutes is required for HONO to reach 11 ppt, the median HONO level reported. Judging by figure 2, the median HONO value of 11 ppt (what the authors claim is anthropogenic-free HONO) is observed in close proximity to urban plumes (20 to 30 ppt, identified in figure 2). This 50 to 60 minute period is an underestimate since it does not account for re-formation of HONO by OH + NO, both of which are likely to be elevated in urban plumes. Bottom line is that the authors need to demonstrate convincingly that the 11 ppt HONO is not derived from anthropogenic sources (by quantitatively accounting for mixing, emissions, and chemistry), because the case for this so-called ’extra’ HONO is the difference between 11 ppt and 2 ppt (amount of HONO expected assuming PSS without this ’extra’ source). The analysis as it currently stands in inadequate.

As for (2), the authors conclude a causal relationship between photolysis of particulate nitrate and HONO based on rather weak correlation (figure 5). That is less than convincing. Moreover, a photolysis rate of 2e-4 sec-1 means a photo-lifetime less than 1.5 hours for particulate nitrates. What are these nitrates? inorganic or organic? Has there been any reports of particle-phase nitrates exhibiting photo-lifetimes on the order of 1.5 hours? Is there a mechanism proposed? What remains in the particle-phase as the nitrate is released as HONO? Is all of the nitrate turn into HONO, or NO or NO2 or HNO3? I am concerned the photolysis conducted in the laboratory is not atmospherically relevant. More information on this lab photolysis experiment may help. How do the nitrate abundances measured with this filter method compare to what other instruments (AMS? PILS?) have measured for particle nitrates?

And as for the power plant analysis, the same concerns I have for claim (1) applies here. You cannot assume just because the plume has been transported over 1 hour that none of the HONO observed is anthropogenic in origin. You need to know what the mixing ratio was near the emission point to know whether the HONO measured downwind was or was not directly emitted because the photo-lifetime is an e-folding time, it does not just disappear after 8 minutes. Lastly, citing previous work on the subject would be useful. Recent work by Neuman et al. 2016 comes to mind (https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2016JD025197).

---

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-105, 2018.