Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2021-531-RC1, 2021

Comment on acp-2021-531

Anonymous Referee #1

Referee comment on "Atmospheric measurements at Mt. Tai – Part II: HONO budget and radical (RO_x□+□NO_3) chemistry in the lower boundary layer" by Chaoyang Xue et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-531-RC1, 2021

General comments:

Tropospheric chemistry often begins with a trace gas molecule reacting with one of the tropospheric oxidants: OH radicals, NO_3 radicals, or O_3 molecules. (Reactions initiated by Cl atoms, generated from $ClNO_2$ photolysis, also contribute to the atmosphere's oxidising capacity, although Cl chemistry was not considered in this paper.) Such reactions determine the lifetime of traces gases in the atmosphere; this chemistry also leads to the production of secondary pollutants such as tropospheric ozone, organic nitrates (PAN etc) and secondary aerosol particles. Under most conditions, OH radicals make the largest contribution to the atmosphere's oxidising capacity. However there are gaps in our detailed understanding of OH sources, notably concerning the importance of the photolysis of nitrous acid (HONO).

This paper reports observations of HONO made in an urban location (Tai'an city) in the central North China plain over a period of several weeks in summer. The authors find that simplest "default" HONO source from the OH + NO reaction (which is not a net source of OH) only accounts for 13% of the observed HONO, averaged over the measurement campaign. Thus a large additional "unknown" HONO source must exist, and the authors explore 6 possibilities. The dominant HONO source at the measurement site is identified as the heterogeneous conversion of NO_2 into HONO on ground surfaces, either photo-enhanced by sunlight during the day (approx. 80% of the source strength), or without light in the dark at night (approx. 70%). Small contributions (of up to around 10% each) variously come from the conversion of NO_2 into HONO on aerosol during the day or at night, the photolysis of particulate nitrate, or direct emissions of HONO (e.g. from traffic or soils). The authors have done a good job to pick apart and characterize the strengths of these different possible HONO sources. This information is valuable to atmospheric chemists and modellers.

In the second half of the paper, the authors employ a zero dimensional box model to investigate what contribution OH derived from HONO makes to the radical chemistry at their measurement site. The model is used to model OH from HONO and from other

sources (ozone photolysis, unsaturated VOCs reacting with ozone, etc), sources & sinks of HO_2 and RO_2 radicals, sources & sinks of NO_3, and the changing contributions of OH- and NO_3-initiated oxidation chemistry over the 24 hour cycle. The model's many outputs are nicely illustrated on well-constructed and informative plots. But this part of the work was less convincing due, primarily, to the simplicity of the 0-D model which cannot consider the vertical gradients in HONO concentrations that are known to exist from ground-based HONO sources. The authors are honest about the limitation of their modelling approach and say that a 1-D box model would provide better conclusions. The nighttime oxidant NO_3 and its reservoir N_2O_5 were not measured in this study, but modeled instead, and this leads to further uncertainties in assessing the relative contributions of OH and NO3 reactivity (as acknowledged by the authors).

Specific comments:

[Comment 1] The success (or otherwise) of the 0-D box model depends on making the right choice for HONO's mixing layer height (section 3.2.2.4, line 343). The authors choose 50 m for HONO's MLH because that generates the best agreement between modeled and measured HONO production rates, P(HONO), in Fig 6(b). But Figure 6(b) shows that setting MLH to 35 m instead of 50 m increases P(HONO) by roughly a factor of 1.5; alternatively, setting MLH to 100m decreases P(HONO) by a factor of 2. Thus relatively small changes in the MLH generate big changes in modeling the ground HONO source (i.e. the dominant HONO source), with implications for understanding the OH source strength and radical chemistry. This raises questions that require answers:

* How much do this paper's conclusions depend on the precise choice of the MLH? – how would the conclusions change if the actual MLH were 35 m or 100 m or 200 m?

* Is there a way to independently verify that the optimum choice of HONO's MLH is 50 m? – can this MLH value be proved by comparing HONO observations made at the foot site in Tai'an city with HONO measurements at the nearby summit of Mount Tai (using data from the companion paper)? Is the vertical gradient in HONO at this site consistent with other studies e.g. Brown et al (J GeoPhys Res, 118, 8067, 2013; doi:10.1002/jgrd.50537) who also observed vertical gradients in NO_3, N_2O_5 and $ClNO_2$?

* How does HONO's MLH change with e.g. wind speed, time of day, daytime versus night? Was a constant MLH = 50 m assumed to model the HONO time series (Fig 7a) and HONO's average diurnal profile (Fig 7b)? How would variability in MLH affect this work's conclusions?

[Comment 2] Figures 1 and 2 show detailed time series of the observations, and Table 2 provides statistics (all good). The information that is missing is average diurnal profiles of NO, NO_2, O_3, J(HONO) etc – please add these plots either in section 3.1.1 or the supporting information. Please add the diurnal profile of J(HONO) to one or all of Fig 4, Fig 6 and Fig 7(b) [and Fig S7(b) and Fig S8(b)], so that reader can easily distinguish day vs

night, sunrise and sunset, photolytic vs dark HONO sources.

Another reason why I request the diurnal plots of NO, NO_2, O_3 and J(HONO) etc is because the diurnal plot of P(HONO) is not symmetric around 12:00 noon (Fig 4 and Fig 6). The unknown HONO source is faster in the morning than the afternoon, and peaks at 11am. The authors note this asymmetry on line 259 but they don't explain it. What is the cause of this asymmetry in HONO? And is P(HONO) expected to also be asymmetric at other locations? [I'm guessing it's not due asymmetry in J(HONO) because P(OH) from ozone photolysis *is* symmetric around 12:00 noon in Fig 14c.]

[Comment 3] How do the conclusions of this paper translate to other locations in China and other countries? In terms of air quality, this is a polluted site, so are conditions here somehow special? For example, because high [NO_2] produces an especially large ground-based HONO source at this site? And/or because high ozone, [O_3] > 100 ppbv, is reacting rapidly with unsaturated VOCs to produce an especially active HO_2 and RO_2 chemistry at this site? For example, NO_3 is traditionally seen as the dominant nighttime oxidant, yet the modeling here in this study shows the sink for isoprene (C_5H_8) at night is approximately 50% to OH and 50% to NO_3 – it is unusual to see such active OH reactions at night. [BTW: I agree with the authors that it is better to measure NO_3 than to model it.]

Technical corrections:

Generally, the paper is written well. However, some of the sentence structure is long and complex, especially those sentences that list multiple measurements, ideas or findings. Consider rewording and/or breaking into separate sentences [e.g. lines 40-43; line 132 (see below)]. Some figure captions also have long and complex sentence structure; they likewise could be improved by breaking them into several shorter sentences, e.g. Fig 9 "Simulated concentrations of (A) OH… and (D) NO3. [New sentence] The different coloured lines show…". Fig 13: the 3 notes in the figure caption would work better as 3 separate sentences. Fig 4: caption needs separate sentences to explain the main panel and the pie charts.

Abstract line 32: "Our model's default HONO source from the OH + NO reaction could only reproduce 13% of the observed HONO…"

Abstract line 37: "A HONO/NOx ratio of 0.7% from direct emissions [plural] was inferred…". Also please state what are the direct sources of HONO at this measurement site?

Abstract line 43: State clearly that NO_3 concentrations come from the 0-D model. Otherwise, without reading the main body of the paper, readers might assume NO_3 was measured.

Abstract lines 46-48: the sentence repeats itself.

Line 79: NO3 radicals [plural]

Line 99: However, very few observations have been reported of OH and NO3 concentrations…

Line 115: Mt Tai is located in…

Line 117 / end of section 2.1.1: Add a sentence to explain the scientific motivation for making HONO observations at this ground site and at the summit of Mt Tai, and briefly explain what the authors found. Readers should be able to know this without having to find and read the companion paper.

Line 120-121: Here it states the LOPAP measurements took place in 2017. But line 109 and the time axis labels in Fig 1 and 2 show 2018. Which is correct?

Line 132: Reword: 10 minute data were used in X. [New sentence] Hourly data were used in Y.

Line 133: PM2.5 measurements were obtained… [plural]

Line 136: SZA functions [plural]

Line 144: interferences in [not "of"] the NO2 measurements [plural]

Line 169-171: Air masses [plural] observed at this site [delete "was"] originated from… which are shown in the wind rose plot in Figure S2.

Line 256: HONO mixing ratio differences… were calculated… and they are compared with P_unknown in Figure S5. [plurals]

Line 257: What do the authors mean by the word "typical"? – the average diurnal profile of P_unknown inferred from their HONO observations? I doubt P_unknown shown in Fig 4 can typically be applied to all other measurement sites.

Line 278: Add a reference to the recent study of HONO emissions from traffic in a road tunnel by Kramer et al, who found a similar HONO/NOx ratio of 0.85%. https://doi.org/10.5194/acp-20-5231-2020.

Line 291 / Table 4: Why are there two values listed for HONO (and two values for NO and two values for NOx)? Are they the HONO concentrations at the start and end of each plume of fresh emissions? Also units = ppbv?

Line 302: What is meant by "overestimated one" and "popularly used one"?

Line 340: "reflected by" is not the right verb. [I'm not sure what the correct verb should be because I didn't understand this sentence.]

Line 355: Therefore, the MLH for HONO was set at 50 m, with sensitivity tests performed with the MLH set at 35 and 100 m.

Line 371: the model with the present HONO source parameterizations performed well in predicting… [the original adjective "magnificent" is too strong].

Line 378: reinforcing our conclusion that aerosol-derived sources played only a minor role in daytime HONO formation.

Line 400: rather than "The former one..,", it is clearer simply to begin the sentence with "HONO emissions from soils may occur…"

Line 447 / Fig 10: I found it difficult (& sometime impossible) to distinguish the different OH sources and sinks, where two shades of the same colour are plotted next to each other. The rainbow of colours is visually pretty, but the plot is impossible to interpret. Likewise P(NO3) and L(NO3).

Line 447 / Fig 10: Why is NO_3 photolysis (during the day) not plotted in the NO_3 reactivity plot, panel (D)? Or is photolysis included in the "inorganic" reactions (orange colour)?

Line 476: hemiterpene emitted by very many species of vegetation…

Line 483 / section 3.3.3.1: In addition to forming particulate nitrate, it should also be noted that HNO3 formation from OH+NO2 and from N2O5 hydrolysis on aqueous aerosol are also the major daytime and nighttime sinks for removing NOx from the atmosphere. Without these NOx sinks, NOx photochemistry would produce tropospheric ozone even more rapidly.

Line 487: the dominant one

Line 556: The default HONO source, NO + OH, significantly underestimated the observed HONO concentrations. [New sentence] This reaction could only account for 13% of the observed HONO, revealing a strong…”