No.: egusphere-2023-2913

Title: Measurement Report: Elevated excess-NH_3 can promote the redox reaction to produce HONO: Insights from the COVID-19 pandemic

Comments:

First of all, I agree that the authors have made a great improvement in the modelling approach and the results interpretation. My concerns for the uncertainties of HONO production and NH_3 impact have been largely addressed. However, I still need to point out that the focus of this study mentioned in abstract, conclusion and even title is a very specific mechanism that, based on the output, cannot be fully confirmed. For example, based on Table S9 and Figure S7, the pH difference of PC and DC was less than half unit for most of the sites, some are very close; the effect of temperature seems to have a more significant impact on pH value compared to other factors. As the effect of temperature, the authors stated in Line 282-289 that temperature had no obvious impact on HONO soil emission. However, it is hard to judge based on the temperature – HONO relationship if soil emission was only part of the total budget. The temperature difference between PC and DC (Table S7) can be regarded as around and way above freezing point, respectively, that could lead to a certain level of difference for soil emission potential, soil water content, soil pH, etc [ref1], which could be an important factor for HONO budget difference. It will be hard to judge the contributions of different mechanisms when there are other unknown sources existing simultaneously. Therefore, I would encourage the authors to re-assess the focus of this study, and avoid overstating the importance of one specific mechanism when there are too many other uncertainties.

Thank you for your careful reading of our paper and valuable comments and suggestions. We believe that we have adequately addressed your comments. To facilitate your review, we used green highlights for your comment and red color indicating our own corrections in the manuscript.

Firstly, sorry for the misunderstanding regarding the dominant factor influencing the increase in particle pH during the DC period. We have supplemented and refined the discussion in the Discussion, Abstract, and Conclusion sections.

Results and discussion

According to the average values of input data during PC (Blue line in Fig. S8) and DC (Red line in Fig. S8) at U-ZK and R-PY sites respectively, the changes in pH (ΔpH in Fig. 5) indicate that the decrease in TNH_x concentration and the increase in T in DC led to a decrease in pH values (ΔpH: 0.09 at U-ZK and 0.08 at R-PY sites) compared to PC. However, this effect was outweighed by the decrease in TH_2SO_4 (ΔpH: 0.07 and 0.8 at U-ZK and R-PY sites, respectively) and TNO_3 (ΔpH: 0.05 and 0.4 at U-ZK and R-PY sites, respectively) concentrations as well as the increase in K^+ (ΔpH: 0.03 at U-ZK and 0.2 at R-PY site) and Mg^{2+} (ΔpH: 0.01 at U-ZK and 0.04 at R-PY site) concentrations in the DC, and resulting in an overall increase in pH values in the DC. Furthermore, the relationship between particle pH with the concentrations of Required-NH_x, and Excess-NH_x, which considers all chemical components, is investigated to examine the dominant factor on the increasing pH in DC. As shown in Fig. 6, the higher Excess-NH_x concentrations in the DC led to higher increases in pH values (ΔpH: 1 at U-ZK and 0.5 at R-PY site) than those in PC (ΔpH: 0.3 at U-ZK and 0.2 at R-PY site), thus Excess-NH_x concentrations may be the key factor in promoting the pH values.

Abstract

"Sensitivity analysis indicated that the decrease in anion concentrations (especially sulfate and nitrate) and the increase in cation concentrations during the COVID-19 pandemic led to an increase in particle pH. In other words, the excess ammonia determined the promoting pH."

Conclusions

"Furthermore, under the environmental conditions of increased anion concentrations (especially sulfate and nitrate) and increased cation concentrations, the pH values increased by 0.5 and 0.3 at U-ZK and R-PY increased during the pandemic, respectively."

Secondly, through literature review and calculations, we found that the contribution of soil emissions to HONO under low temperature conditions (below 10°C) during the observation period can be neglected. We have added this information in Section 2.3.2 on the sources of HONO.

"Soil emission has been demonstrated to be a major source of HONO, which is affected by temperature to some extent (Liu et al., 2020b;Liu et al., 2020a). However, during the sampling periods, there was no significant positive correlation between HONO concentration and temperature (Fig. S4). In addition, temperatures did not exceed 10°C, under which the soil HONO emission rate is generally considered to be zero (Zhang et al., 2023). Furthermore, the equilibrium gas-phase concentration over an aqueous solution of nitrous acid, [HONO]*, a key parameter controlling the exchange of HONO between the gas and aqueous phase in soil, is calculated according to Su et al. (2011)The results indicate that the temperature difference between PC and DC periods only led to approximately a 0.01% concentration change. On the other hand, studies on the sources of HONO in the North China Plain of China during winter consistently showed that soil HONO emissions contribute around 1%(Zhang et al., 2023;Liu et al., 2020a;Liu et al., 2020b). Therefore, this study does not consider soil HONO emissions."

Lastly, we also recognize that further research is needed to support the conclusions regarding the generation of HONO from redox reactions. Therefore, we have added a discussion on the limitations of the calculation methods and conclusions in the revised manuscript, and we have modified the Abstract and Title accordingly.

Considering the conclusions of this study are based solely on observational data, there are certain limitations. For example, only the changes in the R_1 reaction of $PM_{2.5}$ were calculated, without considering variations in components, pH values, and R_1 reaction rates of coarse particles. Additionally, although this study selected scenarios with RH > 60% to calculate the R_1 reaction to ensure the presence of a liquid phase, it is evident that this approach overlooks some R_1 reactions. Furthermore, due to thermodynamic model calculations of pH values, changes in the mixed state of particle components, and the omission of organic acids, alongside the absence of gaseous HNO_3 and HCl in this study, these factors may lead to inaccuracies in pH value simulations and uncertainty in R_1 calculations(Pye et al., 2020;Haskins et al., 2018;Nah et al., 2018). Therefore, there is a certain degree of uncertainty in the conclusions regarding the growth of R_1 reactions in this paper. Nevertheless, by calculating the changes in R_1 reactions, this study provides a possible explanation for the relatively small decrease in HONO during the epidemic period.

Title

"Measurement Report: Elevated atmospheric ammonia may promote the particle pH and HONO formation: Insights from the COVID-19 pandemic"

Abstract

"The calculation of reaction rates indicates that during the epidemic, the increase in pH may promote the generation of HONO by facilitating redox reactions, which highlights the importance of coordinating the control of SO_2, NO_x, and NH_3 emissions."

Line 295-297: This is a very ideal situation that is based on the assumption of fully internal mixing of PM components. For example, with the reduced level of SNA, there could be more externally mixed dust particles that have higher pH values and also behave as better temporal sink for HONO [ref2].

Response: Thanks for your suggestion. We have added a discussion on the limitations of the calculation methods and conclusions in the revised manuscript.

Considering the conclusions of this study are based solely on observational data, there are certain limitations. For example, only the changes in the R_1 reaction of $PM_{2.5}$ were calculated, without considering variations in components, pH values, and R_1 reaction rates of coarse particles. Additionally, although this study selected scenarios with RH > 60% to calculate the R_1 reaction to ensure the presence of a liquid phase, it is evident that this approach overlooks some R_1 reactions. Furthermore, due to thermodynamic model calculations of pH values, changes in the mixed state of particle components, and the omission of organic acids, alongside the absence of gaseous HNO_3 and HCl in this study, these factors may lead to inaccuracies in pH value simulations and uncertainty in R_1 calculations(Pye et al., 2020;Haskins et al., 2018;Nah et al., 2018). Therefore, there is a certain degree of uncertainty in the conclusions regarding the growth of R_1 reactions in this paper. Nevertheless, by calculating the changes in R_1 reactions, this study provides a possible explanation for the relatively small decrease in HONO during the epidemic period.

Line 55-56, the reduction of HONO seems not significantly different than that of NO2 value. Considering that there is already wet surface production mechanism of HONO [ref3], is there any potential artifact for the surface production of HONO on wet liquid surface of MARGA sampling inlet? Has the relevant quality control been performed to verify the influence?

Response: Thanks for your comment.

To highlight the difference in HONO and NOx concentration reductions, we further supplemented the description: "Liu et al. (2020a) observed that the decrease in HONO concentration during the pandemic period was only 31% (from 1.5 ppb to 0.9 ppb), which was significantly lower than the reductions in NO (62%, from 26.3 to 4.2 ppb) and NO_2 (36%, from 15.5 to 6.2 ppb)."

Yes, I agree with your opinion, the use of the wet-flow diffusion tube method by MARGA can result in the generation of HONO from NO_2, which is a limitation of the instrument. However, a significant decrease in NO_2 during DC should also lead to a corresponding decrease in surface production of HONO, at least it will not promote HONO generation during the DC period.

Figure 7&8, the results of the uncertainties analysis done in Text S4 have not been incorporated into these two figures and the relevant discussions.

Response: Thanks for your suggestion. We added two figures (Figures S9 and S10, two extreme scenarios) to illustrate the impact of the uncertainty in HONO calculations on HONO sources.

"Moreover, all the known HONO production sources rates including P_{emi}, P_{OH+NO}, P_{ground}, $P_{ground+hv}$, $P_{aerosol}$, $P_{aerosol+hv}$, and $P_{nitrate}$ (Fig. 7, Fig S9 and S10) show a decreasing trend from PC to DC, with the total reductions of 38% (from 30% to 45% in the scenario with the minimum and maximum uncertainty, respectively) and 79% (from 77% to 82% in the scenario with the minimum and maximum uncertainty, respectively) for U-ZK and R-PY sites, respectively."

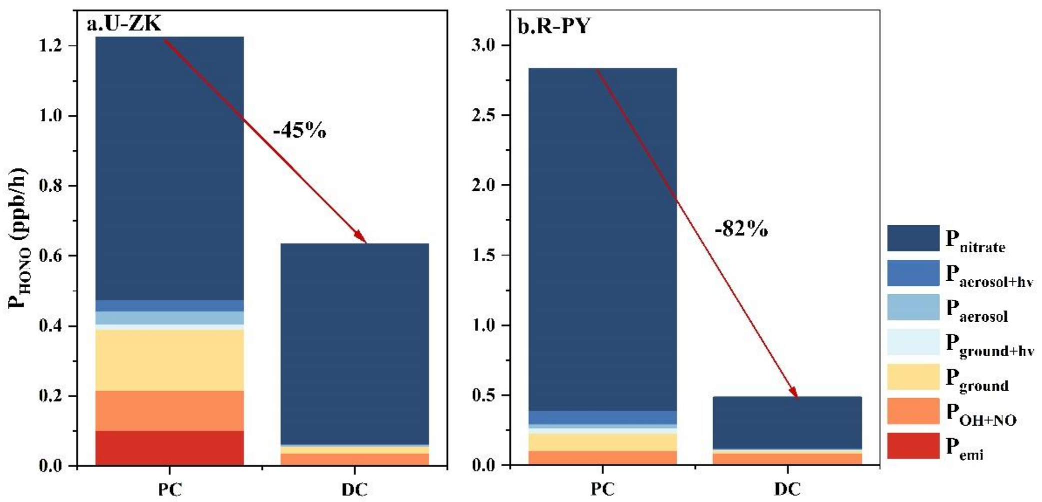

Figure S9. Maximum uncertainty values for HONO sources at U-ZK and R-PY sites were compared between the pre-COVID-19 outbreak (PC) and during the COVID-19 (DC). Refer to Text S4 for details on the calculation methods.

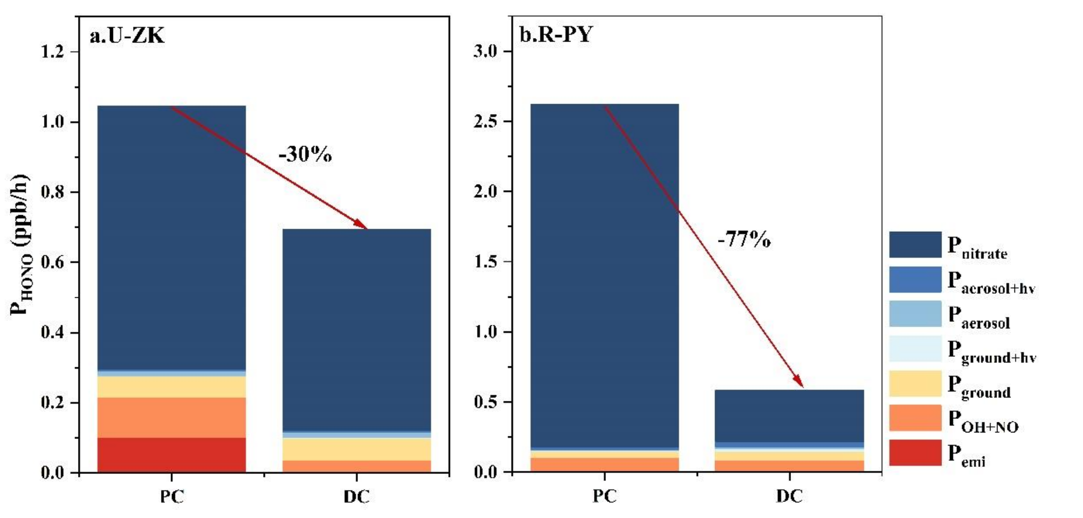

Figure S10. Minimum uncertainty values for HONO sources at U-ZK and R-PY sites were compared between the pre-COVID-19 outbreak (PC) and during the COVID-19 (DC). Refer to Text S4 for details on the calculation methods.

We incorporated the instrument's measurement uncertainties for NO_2 and HONO as well as calculation uncertainties for R_1 into Fig.8. The shadows in the figure represent the uncertainties of NO_2 measurement (±10%), HONO measurement (±20%), and the HONO formation rate of R_1 reaction (–78–123%), respectively.

"Even considering the above uncertainty in Fig. 8, it can still be observed that during the DC period, the decrease in HONO was less than that of NO_2, and the rate of the R_1 reaction increased."

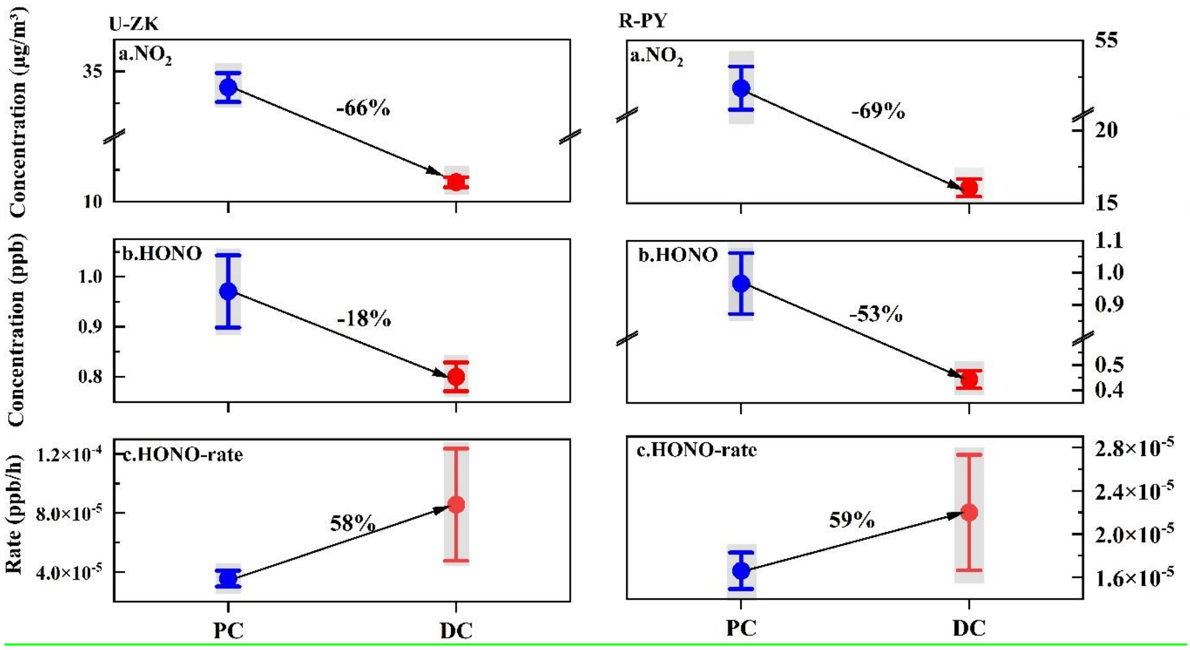

Figure 8. Decline ratios of a. NO_2, b. HONO concentration, and c. HONO production rate at U-ZK and R-PY sites before (PC) and during (DC) the COVID-19 outbreak. The center point represents the mean value, and the upper and lower whiskers represent the 95% confidence interval of the mean. The shadows in the figure represent the uncertainties of NO_2 measurement (±10%), HONO measurement (±20%), and the HONO formation rate of R_1 reaction (–78–123%), respectively.