A point-by-point response to all referee comments

We sincerely appreciate the editor and referees for their insightful and constructive comments, which are helpful for the improvement of the manuscript. We have revised the manuscript carefully according to the referee's comments. The following is a point-by-point response to address the referee's comments. The original comments are presented in *black* and our responses are in *blue*, respectively. The new or modified contents in the revised manuscript are marked in *red*.

Comments from Referee #1:

Thanks for addressing my comments on your manuscript, especially implementing the changes regarding chemical divergence and Damköhler numbers. However, this data quality control criterium is not properly described in the revised manuscript. Could you please include part of your response letter and explain at what times (under which conditions) chemical divergences occurred and which fraction of the data (percent) were omitted? This is an import part and should be included (not only in the supplement).

Response: Thanks for your great comments. We have incorporated pertinent statements into the revised manuscript as recommended.

Lines 184-203 in the tracked changes manuscript:

"Data from all instruments could not always be collected simultaneously for flux calculation due to various factors such as calibration, malfunction, and disturbances from agricultural activities. Consequently, the affected data were excluded when calculating fluxes. The dataset used for the determination of HONO, NO and NO_2 fluxes comprised 68 % for HONO, 81 % for NO, and 86 % for NO_2. The total uncertainty in the flux is composed of gradient error and friction velocity error (Laufs et al., 2017; Meng et al., 2022). The average uncertainty for HONO, NO, and NO_2 fluxes were 11 %, 16 %, and 20 % (median [25 percentile–75 percentile]), respectively. Furthermore, the fluxes were discarded for very stable conditions with low wind speed and friction velocity. It is important to note that HONO, NO and NO_2 are subject to chemical reactions, which could lead to a vertical divergence of flux between the surface and the measurement height. The influence of chemical reactions during turbulent transport was checked utilizing the Damköhler number (*DA*), as detailed in Text S2. The divergence by chemical reactions of HONO could be neglected when interpreting the potential sources of HONO and driving factors of HONO flux. The *DA* for the NO-O_3-NO_2 triad generally exhibited values less than 1, however, a sharp increase in flux divergence occurred when the *DA* became greater than 1 (Stella et al., 2012). Additionally, the upward NO_2 flux exhibited a significant correlation (R = 0.82) with NO flux, suggesting that the upward NO_2 fluxes could be attributed to the reaction of NO and O_3. Consequently, in light of the influence of chemical reactions on the fluxes of NO and NO_2, these fluxes (5.9 % for NO flux and 10.5 % for NO_2 flux) were excluded from subsequent analysis."

Also, at lines 455-456 instead of giving large ranges of NO and HONO fluxes, I would prefer to insert your Figure 4 on the statistical distribution from the response letter and a few statements in the text. Figure 4. The fluxes of HONO and NO experienced various agricultural management activities, including rotary tillage, flooding irrigation, fertilization, post-fertilization, paddy cultivation and growth, and top-dressing. The boxes represent 25 % to 75 % of data, and the whiskers 10 %–90 % of data, while the black line and the red circle indicate the median and mean of data.

Response: Thank you for your suggestion. Following the referee's recommendation, we have incorporated Fig. 4 and its corresponding description into the supplementary material (designated as Fig. S3) and the revised manuscript, respectively.

Lines 299-302 in the tracked changes manuscript:

"Furthermore, the notably elevated fluxes of HONO and NO were observed during rotary tillage in comparison to other phases of agricultural activities (Fig. S3). The higher emission rates of NO and HONO could account for the successive peaks in their concentrations and fluxes."

Lines 454-457 in the tracked changes manuscript:

"The successive peaks in HONO flux and NO flux were measured during rotary tillage, suggesting a potentially enhanced release of HONO and NO due to soil tillage activities."

Supplementary material:

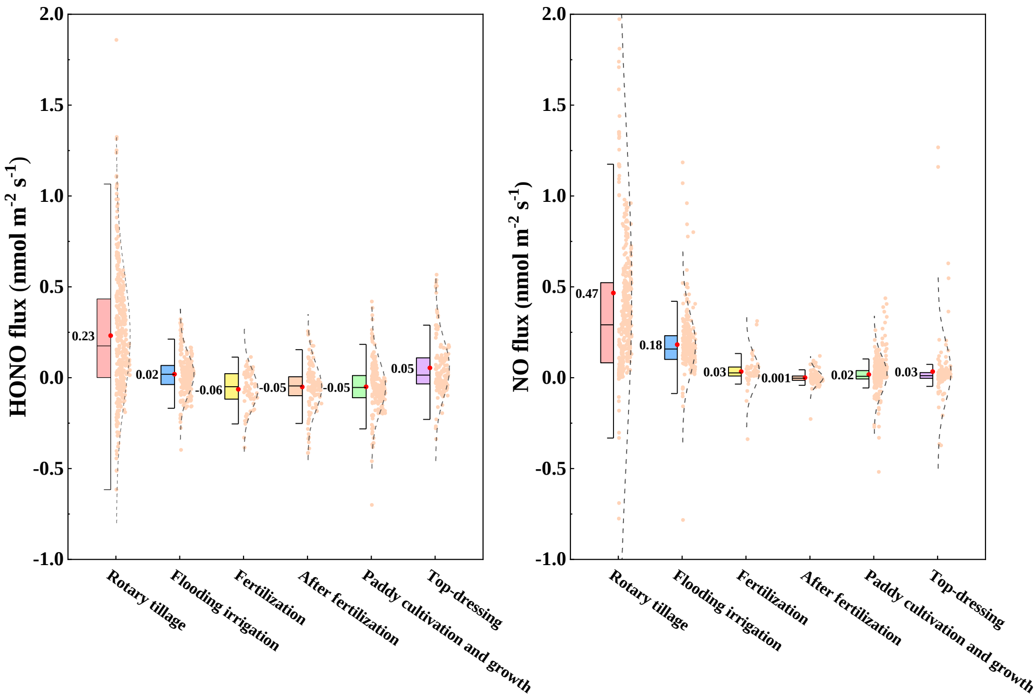

Figure S3. The fluxes of HONO and NO experienced various agricultural management activities, including rotary tillage, flooding irrigation, fertilization, post-fertilization, paddy cultivation and growth, and top-dressing. The boxes represent 25 % to 75 % of data, and the whiskers are 10 %–90 % of data, while the black line and the red circle indicate the median and mean of data.

Comments from Referee #2:

L35: The HONO flux was not consistently positive.

Response: Revision has been made as the referee suggested.

Lines 35-36 in the tracked changes manuscript:

"HONO and NO exhibited more upward fluxes, whereas NO_2 deposited to the ground, with average hourly fluxes of 0.07 ± 0.22, 0.19 ± 0.53 and -0.42 ± 0.44 nmol m^{-2} s^{-1}, respectively"

L43 and L47: The conversion of surface NO_2 is important according to the observation and analysis. However, one concern arises: when the paddy field was flooded, was the surface for NO_2 conversion still the ground surface, or did it become the water surface?

Response: Thanks for your great comments. The significance of surface NO_2 conversion was demonstrated during the rotary tillage. In flooded paddy fields, the soil surface is predominately inundated with water. Consequently, the surface for NO_2 conversion became the water surface.

Figure 3: It's evident that there is an increase in ambient HONO levels after fertilization compared to the fertilization or flooding irrigation periods, despite lower NO_2 levels. Do you have any insights regarding these observations?

Response: As the referee mentioned, there was an increase in ambient HONO levels following fertilization, while NO_2 concentrations were relatively low. This suggests that the heterogeneous conversion of NO_2 might be minimal at this moment. The process of fertilization can enhance the content of available mineral nitrogen (such as ammonium nitrogen) in the soil, providing a rich nitrogen source for soil microorganisms. This increase in mineral nitrogen availability may subsequently enhance the HONO release by promoting the activity of soil microbial communities (such as nitrifying or denitrifying bacteria). We appreciate your question as it has provided us with a new perspective. In future research, we will incorporate measurements of soil mineral nitrogen to elucidate the effects of fertilization more clearly.

L249-250: HONO and NO fluxes were not always upward, so please be precise in your statements.

Response: We appreciate the referee for pointing out the issue, and we have revised the statements to make it more precise.

Lines 257-258 in the tracked changes manuscript:

"Upward fluxes were commonly observed for HONO and NO, while NO_2 was deposited to the ground."

Figure 4: Was JNO$_2$ measured or modeled? Please clarify, as this detail is important for the subsequent budget analysis and OH production calculations. If it wasn't measured, the associated uncertainties need to be acknowledged.

Response: Thanks for your great comments. The J(HONO) and $J(NO_2)$ were calculated from global radiation (G) according to Trebs et al. (2009). The $J(O^1D)$ was simulated using the Tropospheric Ultraviolet and Visible (TUV) radiation model and subsequently corrected based on the observed UV intensity. The details have been presented in supplementary material Text S1. In situations where direct measurements of $J(NO_2)$ are unavailable, the calculation from global radiation demonstrated reliability in comparison to the TUV model with poorly known input parameters, especially in the presence of clouds. The uncertainty of $J(NO_2)$ is > 40 % for G < 100 W m^{-2}, 10 %–40 % for G = 100–500 W m^{-2} and ≤ 10 % for G > 500 W m^{-2} (Trebs et al., 2009). The global radiation predominately exceeds 500 W m^{-2} throughout the campaign, with a subset falling within the range of 100–500 W m^{-2}. Consequently, the associated uncertainties are estimated to be between less than 10 % and 40 %.

One additional point for consideration in future work: The chemiluminescence NO_x monitor may experience interference from relative humidity (RH), potentially leading to uncertainties in NO flux. I conducted lab tests (with zero air and zero air + RH) and found an interference of <0.1 ppb in my case. You can refer to several studies where a dryer/condenser, such as a Nafion dryer, was used during sampling. However, a recent study (https://pubs.acs.org/doi/full/10.1021/acs.est.2c05944) discovered that Nafion dryers could convert HONO to NO, which may result in NO overestimation.

Response: We sincerely appreciate the referee for the valuable and constructive suggestion. In future works, we will pay more attention to the influence of relative humidity on NO measurements, with the aim of enhancing the precision of flux measurements.

Figure 9: It might be helpful to increase transparency so that POH-O_3 is not fully concealed.

Response: Thank you for your suggestion. Figure 9 has been modified as suggested.

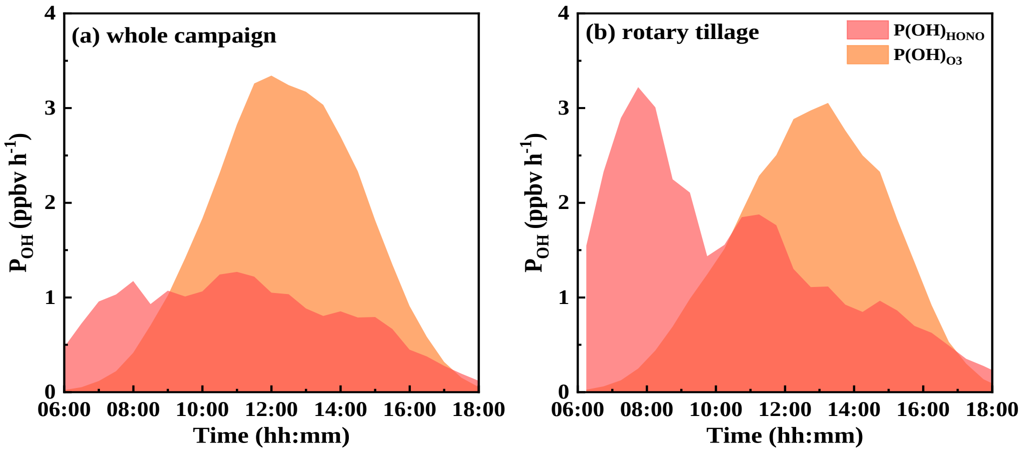

Figure 9. Diurnal variation of net OH production rate of the photolysis of HONO ($P(\mathrm{OH})_{\mathrm{HONO}}$) and O_3 ($P(\mathrm{OH})_{O_3}$) during (a) the whole campaign and (b) the rotary tillage.

Figure S3: Are you sure the fitting is correct? Why does the fitted curve consistently appear at the upper border?

Response: Thanks for your great comments. We confirm that the gaussian fitting is correct. Following the method introduced by Li et al. (2012) and Stutz et al. (2004), we analyzed the top-5 HONO and NO fluxes in each 1 ℃ interval (original 2 ℃ interval). The dependence of fluxes on temperatures was assessed through gaussian fitting. The fitted curve commonly appears at the upper boundary, which could be attributed to the selection of the top-5 fluxes for analysis. However, this does not influence the dependence of HONO and NO fluxes on temperatures.

Supplementary material:

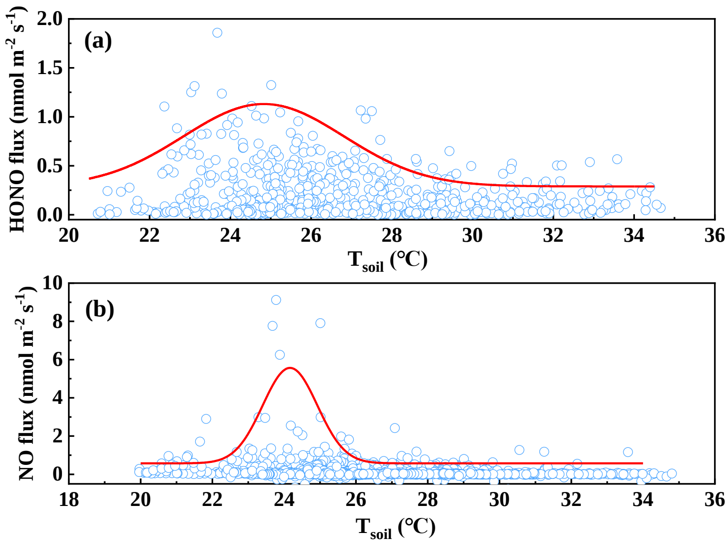

Figure S4. Emissions of (a) HONO and (b) NO as a function of soil temperature over the rotary tillage. The curves are gaussian fitting the fluxes of HONO and NO with soil temperature.

References:

Li, X., Brauers, T., Häseler, R., Bohn, B., Fuchs, H., Hofzumahaus, A., Holland, F., Lou, S., Lu, K. D., Rohrer, F., Hu, M., Zeng, L. M., Zhang, Y. H., Garland, R. M., Su, H., Nowak, A., Wiedensohler, A., Takegawa, N., Shao, M., and Wahner, A.: Exploring the atmospheric chemistry of nitrous acid (HONO) at a rural site in Southern China, Atmos. Chem. Phys., 12, 1497-1513, https://doi.org/10.5194/acp-12-1497-2012, 2012.

Stutz, J., Alicke, B., Ackerman, R., Geyer, A., Wang, S., White, A. B., Williams, E. J., Spicer, C. W., and Fast, J. D.: Relative humidity dependence of HONO chemistry in urban areas, J. Geophys. Res.-Atmos., 109, D033071-033012, https://doi.org/10.1029/2003jd004135, 2004.

Trebs, I., Bohn, B., Ammann, C., Rummel, U., Blumthaler, M., Koenigstedt, R., Meixner, F. X., Fan, S., and Andreae, M. O.: Relationship between the NO_2 photolysis frequency and the solar global irradiance, Atmos. Meas. Tech., 2, 725-739, https://doi.org/10.5194/amt-2-725-2009, 2009.