A point-by-point response to Referee #1

We would like to thank Referee #1 for the valuable comments and thoughtful suggestions to help improve the quality of the manuscript. 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:

This paper reports on measured exchange fluxes of HONO (along with NO and NO_2) using the aerodynamic gradient method during the growth process of paddy fields in the Huaihe River Basin, China during 2021. Maximal NO and HONO emissions were observed during rotary tillage. The measurement methods and quality control schemes were published previously and are solid. The length (1.5 months) and representativeness of this dataset in terms of agricultural practices are certainly unique and worth publishing. The manuscript is well-thought-out, and the discussion of the results is very impressive and complete, thus being highly informative and relevant because nearly all previous publications on soil HONO emissions are included. I do have some points for improvement that are listed below. My main concern is the treatment of data with chemical flux divergence. This part must be improved. The manuscript should be edited by a native English speaker. Please find below my detailed comments that should be addressed before publication.

Response: Many thanks to Referee #1 for the constructive comments and thoughtful suggestions, which significantly enhanced the clarity of the manuscript. The revised manuscript has been edited by a native English speaker, as the referee suggested. The following are point-to-point responses to the referee's comments.

Detailed comments:

Lines 29-30: "… affect the chemistry of the troposphere…".

Response: Revision has been made as the referee suggested.

Lines 29-30 in the tracked changes manuscript:

“Significant amounts of nitrous acid (HONO) released from soil affect the chemistry of the troposphere, as a major precursor of hydroxyl radical.”

Line 30: “… the scarcity of in-situ data on soil-atmosphere HONO exchange fluxes has constrained…”.

Response: Revision has been made as the referee suggested.

Lines 30-32 in the tracked changes manuscript:

“However, the scarcity of in-situ data on soil–atmosphere HONO exchange flux has constrained the comprehension of emission mechanisms and reactive nitrogen budget.”

Line 39: “… HONO and NO fluxes…”.

Response: Corrected as the referee suggested.

Line 49: “… and soil emissions for HONO production.”.

Response: Corrected as the referee suggested.

Lines 110-112: This is a repetition and was written already before. Could be deleted or rephrased.

Response: Thank you for your suggestion. As suggested, we have deleted the sentence.

Line 150: “… in the ambient air were…”.

Response: Revision has been made as the referee suggested.

Lines 154-156 in the tracked changes manuscript:

“The concentrations of HONO and NO_2 in the ambient air were measured using a homemade BBCEAS instrument with a time resolution of 1 min and detection limits of 54 pptv (2σ) for HONO and 98 pptv (2σ) for NO_2.”

Line 155: Sentence is misleading. The molybdenum converter is not required for NO measurements.

Response: We appreciate the referee for pointing out the issue, and we have removed the “equipped molybdenum converter” to avoid reader misunderstanding.

Lines 158-161 in the tracked changes manuscript:

"NO was measured by custom-built chemiluminescence (Model 42iTL, Thermo Scientific, USA), and O_3 were measured with Thermo Scientific Model 49i, with detection limits of 50 pptv for NO and 500 pptv for O_3, respectively"

Lines 160-170: What was the length and the material of the inlet lines, and what was the residence time of the air within the tubing? HONO may still adsorb on surfaces. Was the intercomparison of the two instruments made with the same inlet length/type?

Response: The inlet lines have a length of 7.5 m and an external diameter of 6 mm, constructed from PFA material to minimize the HONO loss. The flow rate at sampling ports for the BBCEAS instrument and NO_x analyzer is a total of 10.2 L min^{-1} (9 L min^{-1} for BBCEAS and 1.2 L min^{-1} for NO_x analyzer), and the residence time of the air within the tubing is approximately 0.01 s. Considering the short residence time, the adsorbed HONO on the surface could be neglected. Furthermore, we have also determined HONO loss with and without a 10 m sampling tube at different RH levels. As illustrated in Fig. 1, the sampling loss for HONO was found to be below 3 %, suggesting a weak sample loss of BBCEAS instruments for HONO.

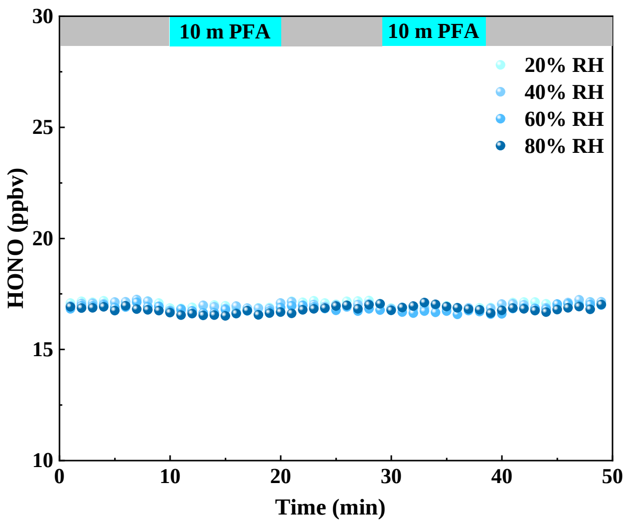

Figure 1. The sampling loss of the BBCEAS instrument for HONO at different RH levels (20%, 40%, 60% and 80%). The sampling loss of HONO was determined with and without a 10 m sampling tube, as denoted at the top of the graph.

As noted by the referee, identical types and lengths of inlet lines were used during the intercomparison of the two BBCEAS instruments.

Line 178: the correct name is “von Kármán constant”.

Response: Corrected as the referee suggested.

Line 290-311: In fact, if a chemical divergence is present, the fluxes cannot be calculated. Please refer to the Damköhler numbers (Da) here and rephrase the text accordingly. First you talk about upward NO_2 fluxes due to chemistry and then downward NO_2 fluxes due to photolysis. This must be proven with some Da numbers and a flux estimate should not exist for these conditions.

Response: Thanks for your great comments. We have revised the manuscript and supplementary material as suggested. For the NO-O_3-NO_2 triad, the chemical reactions induced a divergence of flux that was primarily attributed to the reaction of NO and O_3 and was limited by the NO mixing ratio, and a sharp increase in flux divergence occurred when DA became greater than 1 (Stella et al., 2012). As the referee suggested, the NO and NO_2 fluxes with DA exceeding 1 have been excluded from further discussion.

A significant correlation (R = 0.82) was observed between the upward NO_2 flux and NO flux, as illustrated in Fig. 2. This suggested that the upward NO_2 fluxes might be ascribed to the reaction of NO and O_3 (Fang and Yujing, 2009; Tang et al., 2020). As the referee suggested, the fluxes for these conditions were disregarded. Additionally, a greater daytime downward NO_2 flux (-0.85 ± 0.27 nmol m^{-2} s^{-1}) compared to nocturnal NO_2 flux (-0.57 ± 0.23 nmol m^{-2} s^{-1}), which could be attributed to an increase in the dry deposition velocity of NO_2 during the daytime. In conclusion, the influence of chemical reactions involving the NO-O_3-NO_2 triad on the fluxes is complex, the chemical reactions induce a flux divergence and fluxes with chemical correction still need further study.

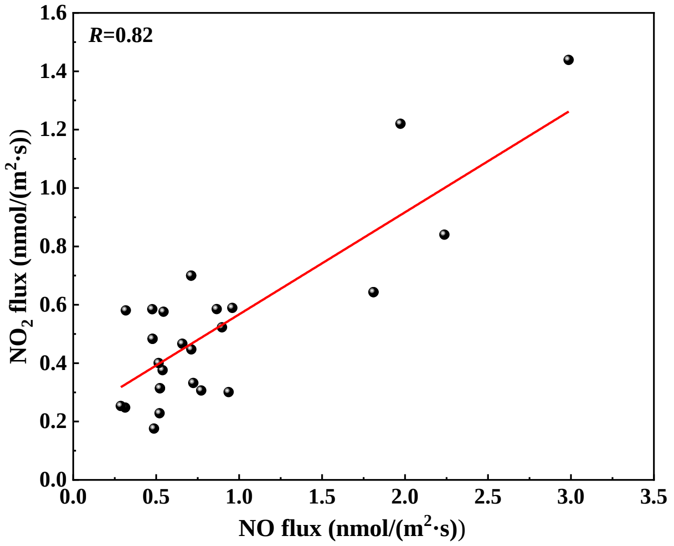

Figure 2. Correlation between the upward NO_2 flux and NO flux.

Line 332: Could it also be possible that drying of soil in the morning (occurrence of optimum WFPS) was causing the HONO emissions (related to direct emission from ammonia oxidizing bacteria)?

Response: Figure 3 illustrates the diurnal variation of WFPS during the period of rotary tillage, revealing that the daily average of WPFS fluctuated between 45.7% and 45.9%, with a minimum value occurring at night. Nevertheless, previous laboratory studies have demonstrated that the optimum WFPS for HONO emission is approximately 20% (Huang et al., 2024). This suggests that the morning emissions of HONO observed over rotary tillage could not be attributed to the optimum WFPS.

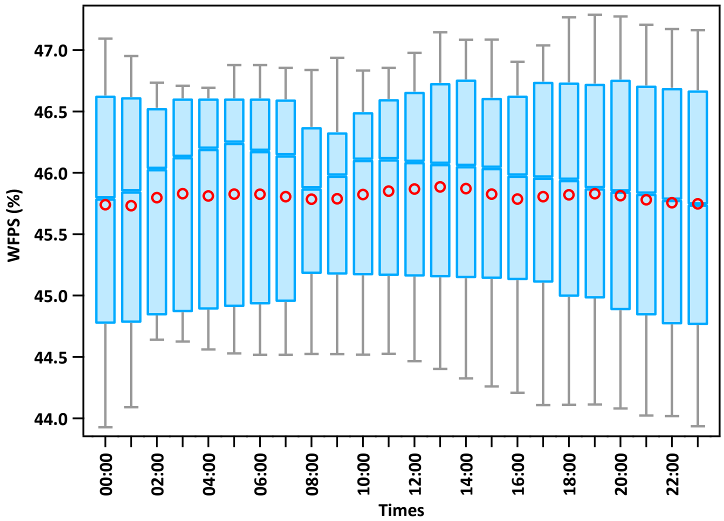

Figure 3. Diurnal variations of WFPS over the rotary tillage

Line 395: Could you please double check the units in equation S10? I am surprised that the ground HONO source is very low, especially in the afternoon.

Response: We appreciate the referee for pointing out the issue regarding the units. We have revised the units in the supplementary material, and the corrected units are g m^{-2} s^{-1}.

Line 430: … not only from agricultural soils in China….

Response: Revision has been made as the referee suggested.

Lines 450-451 in the tracked changes manuscript:

"However, the available HONO emission fluxes from agricultural soils are relatively limited."

Line 434: Can you mention here how much higher (factor) the HONO fluxes were during tillage compared to other conditions?

Response: Thanks for your suggestion. Figure 4 and Table 1 in the manuscript illustrate the variations in HONO and NO fluxes associated with various agricultural management activities. As the referee suggested, we have mentioned the change factors of HONO and NO fluxes over rotary tillage compared to other conditions in the revised manuscript.

Lines 454-457 in the tracked changes manuscript:

"The successive peaks in HONO flux and NO flux were measured during rotary tillage, in which HONO fluxes were 4.2–12 times and NO fluxes 2–529 times higher than other conditions, suggesting a potentially enhanced release of HONO and NO due to soil tillage activities."

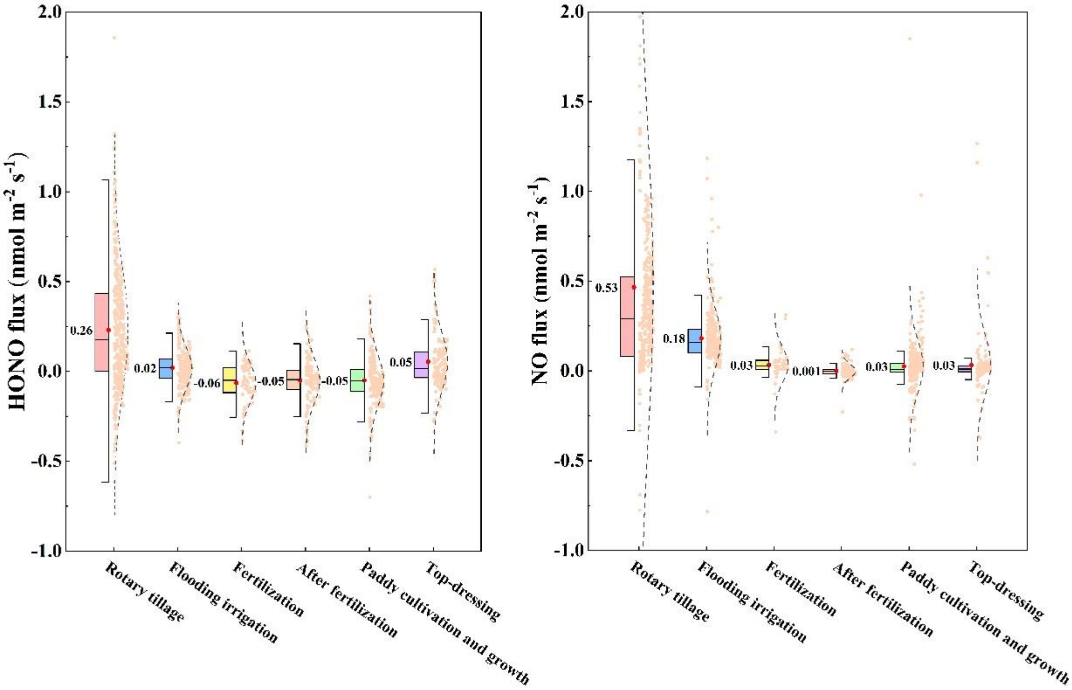

Figure 4. The fluxes of HONO and NO experienced various agricultural management activities, including rotary tillage, flooding irrigation, fertilization, post-fertilization, paddy cultivation and growth, and top-dressing. The boxes represent 25 % to 75 % of data, and the whiskers 10 %–90 % of data, while the black line and the red circle indicate the median and mean of data.

Figure 4: size should be increased.

Response: We have enlarged the size of Figure 4.

References:

Fang, S. and Yujing, M.: NO_x fluxes from several typical agricultural fields during summer-autumn in the Yangtze Delta, China, Atmospheric Environment, 43, 2665-2671, 10.1016/j.atmosenv.2009.02.027, 2009.

Huang, L., Han, B., Cheng, P., Tian, Z., Yang, W., Ling, J., Ma, W., Yu, Y., Gong, Y., Tian, Y., and Deng, H.: Nitrous Acid and Nitric Oxide Emissions from Agricultural Soils in Guangdong Province: Laboratory Measurement and Emission Estimation, ACS Earth and Space Chem., 8, 1406-1415, https://doi.org/10.1021/acsearthspacechem.4c00048, 2024.

Stella, P., Loubet, B., Laville, P., Lamaud, E., Cazaunau, M., Laufs, S., Bernard, F., Grosselin, B., Mascher, N., Kurtenbach, R., Mellouki, A., Kleffmann, J., and Cellier, P.: Comparison of methods for the determination of NO-O_3-NO_2 fluxes and chemical interactions over a bare soil, Atmos. Meas. Tech., 5, 1241-1257, 10.5194/amt-5-1241-2012, 2012.

Tang, K., Qin, M., Fang, W., Duan, J., Meng, F., Ye, K., Zhang, H., Xie, P., Liu, J., Liu, W., Feng, Y., Huang, Y., and Ni, T.: An automated dynamic chamber system for exchange flux measurement of reactive nitrogen oxides (HONO and NO_x) in farmland ecosystems of the Huaihe River Basin, China, Sci. Total Environ., 745, 140867, https://doi.org/10.1016/j.scitotenv.2020.140867, 2020.