Response to comments by Anonymous referee #2

The manuscript presents a detailed study on ozone (O_3) deposition over wheat fields in the North China Plain. The authors have employed a newly developed relaxed eddy accumulation (REA) system to measure O_3 deposition flux and velocity during the 2023 wheat growing season. The study explores the variability of O_3 deposition and its influencing factors, emphasizing the importance of crop growth and environmental conditions.

Overall, the study addresses a significant gap in the measurement and understanding of O_3 deposition in agricultural settings in China, a region experiencing increasing O_3 pollution. The use of the REA system is novel and relevant for capturing detailed deposition metrics. The results are comprehensive, showing the variation in O_3 deposition flux and velocity across different times of the day and growth stages of wheat. The discussion on the predominant role of stomatal uptake and the influence of environmental factors like relative humidity, soil water content, and friction velocity is noteworthy. I would hope the following points are considered or addressed:

Response: We appreciate your time spent reviewing our manuscript and are grateful for your constructive comments and suggestions. We have revised the manuscript according to your suggestions, and made point-to-point responses, with changes in the manuscript highlighted in yellow color.

Line 52: Are there any variations?

Response: Yes, both the relative contributions of non-stomatal and stomatal O_3 deposition varied with clear diurnal cycles and changed with crop growth stage. Stomatal deposition was more pronounced during mid-day and during the most rigorous growth stage of plant. We added the variability of stomatal O_3 deposition in Lines 49-52:

"For example, the fraction of diurnal maximum stomatal O_3 deposition over boreal forests ranged from 56 to 74% (Rannik et al., 2012), while only accounting for 31.2% in a wheat field (Xu et al., 2018), with both of them peaking at mid-day during the most rigorous growth stage of vegetations (Xu et al., 2018; Rannik et al., 2012)."

Line 65: Meters?

Response: No, "2~4" refers to the number of height layers at which the FG methods needs to make simultaneous O_3 concentration measurements in order to obtain the vertical gradient of O_3 levels. This part was deleted from the revised manuscript following suggestions of Reviewer #1.

Line 91: What do you mean by polluted agricultural areas?

Response: The Gucheng site is located in a typical agricultural area of the North China Plain, that is frequently under severe regional air pollution. For example, the overall average MDA8 O_3 in the warm season (April - September) during the 2006-2019 at the site was 64 ±7.4 ppb, which was close to the Ambient Air

Quality Standards (standard code: GB3095-2012) of 75 ppb. The largest exceedance frequency of O_3 could exceed 50% in 2015, with averaged MDA8 O_3 on exceedance days reaching 102.1 ppb, indicating remarkable O_3 pollution exposure at Gucheng site (Zhang et al., 2022). We rephrased this sentence as follows:

Lines 89-91: "Observations at the site have revealed good regional representativeness of the agricultural areas in the NCP, that is heavily impacted by the severe regional air pollution (Lin et al., 2009; Xu et al., 2019; Kuang et al., 2020; Zhang et al., 2022a, b)."

Reference:

Zhang, X., Xu, W., Zhang, G., Lin, W., Zhao, H., Ren, S., Zhou, G., Chen, J., and Xu, X.: First long-term surface ozone variations at an agricultural site in the North China Plain: Evolution under changing meteorology and emissions, Sci.Total Environ., 160520, https://doi.org/10.1016/j.scitotenv.2022.160520, 2022.

For the fast response solenoid valve, can you provide the response time of them, and how does it compare with wind speed data frequency?

Response: Thank you for the suggestions. The response time of the fast-response 3-way solenoid valve was within 10 ms, and the estimated residence time from the REA system inlet to the valves was 18 ms, thus the total delay time from the inlet to the individual sampling tubes was less than 10 ms. The temporal resolution of three wind components was 100 ms, which was much larger than 10 ms. Thus, the REA system could work at a sampling frequency of 10 Hz (100 ms) according to the instantaneous vertical wind speed. The following description of the system response times was added:

Lines 129-134: "The estimated residence time from system inlet to the valves was 18 ms, while the response time of the fast-response sampling valves was less than 10 ms, leading to total time delays from inlet to individual sampling tubes of below 10 ms, thus the REA system could work at a sample frequency of 10 Hz (100 ms). Total residence time of air samples from the tip of the inlet to the point of O_3 detection was about 10 s, which was much shorter that the lifetime of O_3 reacting with NO (Supplementary methods), suggesting the chemical reaction in the two channels could be neglected."

The flow rate of your inlet sample seems to be missing. Have you synchronized your sonic data and the ozone data considering the length of your inlet tubing? Please add this information.

Response: Thank you for the reminder. We added the flow rates of the system tubes in Figure 1. The temporal revolution of sonic data is 100 ms, which is 10-fold that of the estimated residence time from the inlet to the individual sampling tubes. Thus, we just synchronized the sonic data and O_3 data according to the PC time. We added the information in Section 2.2.2.

Lines 134-135: "The O_3 analyzers recorded 1-minute averaged O_3 concentrations, which were downloaded by the PC. O_3 data were synchronized with wind data as well as sample time according to the PC time."

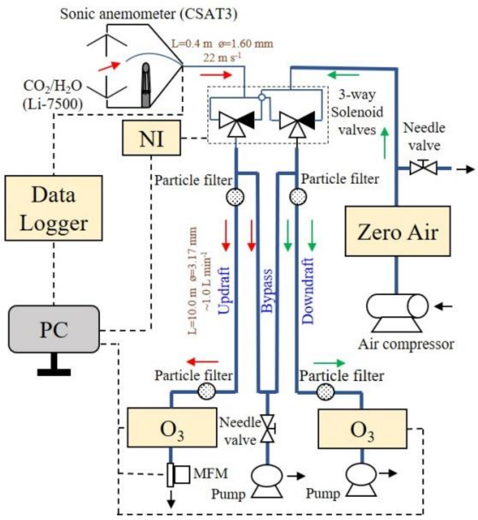

Figure 1. Schematic of the REA-O_3 flux system (w > w_0).

Lines 144-145: This sentence reads a bit unclear, please rewrite.

Response: Thanks for your suggestion. We revised this sentence as "Using raw EC data, the REA CO_2, H_2O and heat fluxes were calculated under w_0 in this study (0.05 m s^{-1} for daytime and 0.01 m s^{-1} for nighttime) and w_0 = 0, respectively, with a constant b of 0.60 (Businger and Oncley, 1990)."

Fig. S1: Is it just the data from a randomly selected day? If yes, is it from the growing season?

Response: The flux data in Figure S1 are from the whole observation period (from 12 February to 18 June 2023). To avoid the misleading, we added the time of flux data in the discussion in Section 2.2.2 and the title of Figure S1.

Lines 157-158: "As shown in Figure S2, the two flux datasets revealed excellent correlations during the whole observation period, with a correlation coefficient close to 1, confirming the reliability and stability of the REA flux measurement system."

"**Figure S1.** The influences of wind dead-bands (w_0) on (a, d) REA-H_2O, (b, e) REA-CO_2 and (c, f) REA-heat fluxes during (a-c) daytime and (d-f) nighttime from 12 February to 18 June, driven by EC raw data with a constant b = 0.60. F^* and F represent the REA fluxes with and without w_0, respectively. The linear regressions and correlation coefficients (r) between F^* and F are inset in each figure, and n is the total number of the valid fluxes.**"**

How does the agreement look during the non-growing season when plant metabolism is low? Environmental variability (e.g., changes in turbulence, vegetation state) could influence the optimal w_0 value. Different stages of crop growth and varying meteorological conditions likely require different w_0 adjustments. A static w_0 value for all conditions is overly simplistic and likely inadequate for capturing the true dynamics of ozone deposition.

Response: Thank you for the comment. We regarded the CO_2 flux in the agricultural ecosystem as an indicator for plant metabolism, and further investigated the influence of crop growth on O_3 deposition. We added the variation of cropland CO_2 flux in Figure 6, and adjusted the discussion as follows:

Lines 273-282: "To investigate the influences of wheat growth on O_3 deposition, the characteristics of O_3 deposition were further examined in connection to the different growth stages. During the O-W stage, wheat was in dormancy and leaves had not begun to turn green (LAI < 0.5, Figure 6b), with CO_2 flux in the agricultural ecosystem closed to zero (Figure 6c). V_d in the O-W stage barely changed, exhibiting a low average value of 0.20 ± 0.28 cm s^{-1} and a median of 0.12 cm s^{-1} (Table 1). Wheat grew vigorously in the G-F stage, with LAI and CO_2 assimilation flux exhibiting rapid increases until the early and late flowering stage, respectively, after which both of them gradually decreased (Figure 6b-c). O_3 deposition varied nearly in synchronization with LAI and wheat growth, with V_d reaching a peak when cropland CO_2 assimilation was the highest during the G-F stage (Figure 6a), reaching highest daytime and nighttime averages of 0.46 ± 0.41 cm s^{-1} and 0.24 ± 0.28 cm s^{-1}, respectively (Table 1). Afterwards, with the maturing of wheat and the aging of leaves in the R-H stage, V_d quickly dropped back to a low average level of 0.20 ± 0.25 cm s^{-1}, similar to that observed in the O-W stage."

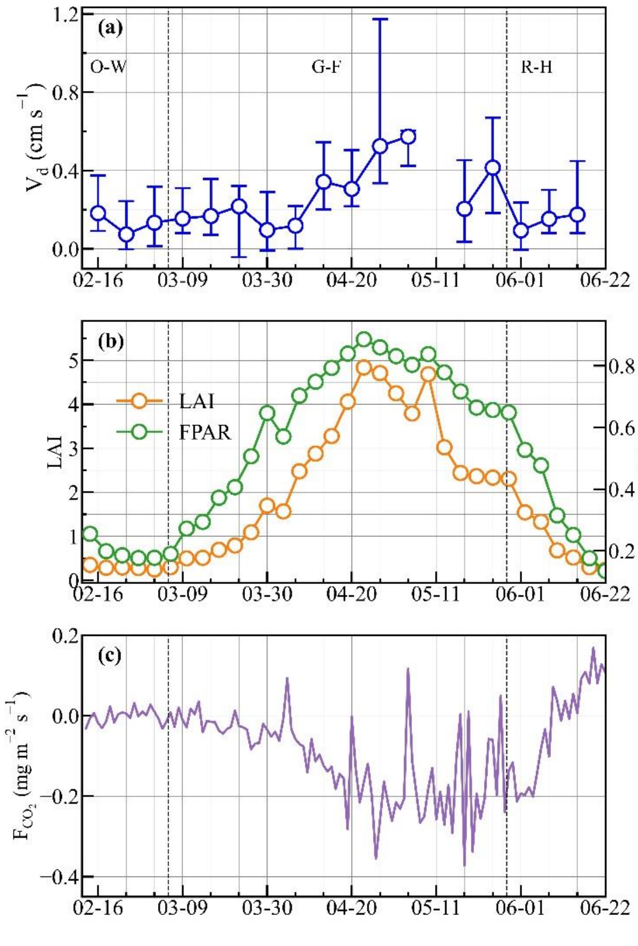

Figure 6. (a) O_3 V_d, (b) LAI and FPAR, (c) CO_2 flux (F_{CO_2}) in different wheat growing stages. The circles and error bars in (a) denote the weekly medians and quantiles of V_d, respectively. O-W, G-F and R-H represent Over-Wintering, Green-Flowering and Ripening-Harvest stages.

We agree on the notion that environmental variability could affect the choice of the optimal w_0 values, and that adopting a dynamic w_0 could reduce the impact of atmospheric environment variabilities on observed flux to certain extents (Grönholm et al., 2008; Nelson et al., 2017). In previously reported field experiments, the dynamic w_0 was mainly dependent on the deviation of vertical velocity (Grönholm et al., 2008), for example, $w_0 = \frac{\sigma_w}{0.35}$ in the REA system of Grelle and Keck (2021) for H_2O, CO_2, CH_4, N_2O flux measurements. During our observation period, u_* fluctuated in the range of 0.05-0.30 m s^{-1}, and exhibited no obvious seasonal changes with crop growth (Figure 2b), implying that the variabilities of vegetation state and other meteorological conditions at our site played minor roles in the determination of the optimal w_0 value.

The application of w_0 is used to promote the sampling of larger eddies that contribute more to gas fluxes, and filter out samples with small vertical displacements that have relatively small impacts on the overall flux (Grelle and Keck, 2021). A constant w_0 would set a uniform threshold of sampled eddies, which tend to have relatively greater effects on the flux regardless of the environmental condition. Therefore, using a constant w_0 value for all conditions is beneficial to the comparison of observed fluxes under different environmental condition. In our REA system, using two static w_0 leads to ~10% overestimation to the measured fluxes, which was comparable with the influence of the dynamic w_0 in Grelle and Keck (2021)'s REA system, indicating a minor difference in their effect on flux derivations. In addition, adopting a static w_0 can avoid sampling mistakes induced by miscalculations of the dynamic w_0 or by large disturbances of environmental factors during the measurement, reducing the flux measurement errors. Therefore, we adopted a constant w_0 in our REA system.

Reference:

Grelle, A. and Keck, H.: Affordable relaxed eddy accumulation system to measure fluxes of H2O, CO2, CH4 and N2O from ecosystems, Agricultural and Forest Meteorology, 307, 108514, https://doi.org/10.1016/j.agrformet.2021.108514, 2021.

Grönholm, T., Haapanala, S., Launiainen, S., Rinne, J., Vesala, T., and Rannik, Ü.: The dependence of the β coefficient of REA system with dynamic deadband on atmospheric conditions, Environ. Pollut., 152, 597-603, https://doi.org/10.1016/j.envpol.2007.06.071, 2008.

Nelson, A. J., Koloutsou-Vakakis, S., Rood, M. J., Myles, L., Lehmann, C., Bernacchi, C., Balasubramanian, S., Joo, E., Heuer, M., Vieira-Filho, M., and Lin, J.: Season-long ammonia flux measurements above fertilized corn in central Illinois, USA, using relaxed eddy accumulation, Agricultural and Forest Meteorology, 239, 202-212, https://doi.org/10.1016/j.agrformet.2017.03.010, 2017.

Have you checked if the fetch and footprint of your REA tower exclusively covered the crop field?

Response: Yes, the height of the flux tower was designed according to the result of the fetch and footprint analysis. The range of flux source region was about 400 m, which is covered by the crop field within the Gucheng observation station. We added this information in Section 2.2.2:

Lines 111-115: "A 3-D sonic anemometer (CSAT3, Campbell Scientific Inc., USA) was used for measuring the three wind components (*u*, *v*, *w*) at 10 Hz, which was amounted at the height of 4.5 m on an eddy covariance tower, located in the middle of cropland. The height of the flux tower was designed according to the result of the fetch and footprint analysis. The range of flux source region was about 400 m, which is covered by the crop field within the GC station."

Line 166: Specify the ancillary data you have obtained.

Response: Thanks for your suggestion, the ancillary data includes meteorology, plant growth indicators and trace gas measurement data. We revised this sentenced as "Ancillary data were obtained for further analysis, including meteorology data, soil parameters, plant growth indicators and O_3 related trace gas measurement data."

Section 2.4: Provide more details on how you have normalized your environmental parameters.

Response: Thank you for the suggestion, we added the normalization method in Section 2.4.

Lines 213-217: "The Z-Score normalization method was adopted according to the following equation:

$$x = (x_{observed} - x_{mean}) \div x_{standard\ deviation}\ , \qquad \text{Eq. (9)}$$

where $x_{observed}$, x_{mean} and $x_{standard\ deviation}$ are the observed parameters, its overall average and standard deviation, respectively."

Include the life stage information of the crops in the method section.

Response: Thanks for the suggestion. We moved the life stage of wheat in Section 3.3 to Section 2.3, and added the plant height in Section 2.3.

Lines 182-185: "According to the winter wheat phenology at GC (Table S1), its entire growth season could be divided into three stages: Over-Wintering (O-W, 13 February-5 March), Green-Flowering (G-F, 6 March-28 May) and Ripening-Harvest (R-H, 29 May-18 June). The wheat height increased from 6.0 cm during the O-W stage to 61.2 cm at the R-H stage."