

Point-to-point responses to anonymous referees

We appreciate the comments from two referees concerning our manuscript. Below are point-to-point responses to the comments. Changes are made in the resubmitted manuscript accordingly and are marked in blue.

Comment on egusphere-2026-2234, Anonymous Referee #1

General Comments

This manuscript presents the development of a Relaxed Eddy Accumulation (REA) system for assessing the fluxes of inorganic acidic species over cropland located in the vicinity of an industrial zone within the Chinese megacity of Wuhan. The study was conducted during late autumn and early winter 2025, with particular focus on a subset of selected 11 days period spanning November-December 2025.

The authors clearly demonstrate the development of the instrument and provide a thorough description of the uncertainty calculations used to characterise the system, including both the REA sampling setup and the offline analytical procedures. The reported measurement precision ranged from 3–30%, with LOD between 6.1×10^{-4} and $2.4 \times 10^{-1} \mu\text{g m}^{-2} \text{s}^{-1}$ across the eight monitored species.

A key finding of the study is that the observed HONO and HNO₃ fluxes were one to two orders of magnitude higher than values previously reported in the literature for similar landscapes. The authors conclude that the strong positive nitric acid fluxes were enhanced under conditions of elevated turbulence, whereas the enhancement of nitrous acid fluxes appeared to be associated with lower ambient temperatures.

Specific comments

Although the authors predominantly present the fluxes in units of $\mu\text{g m}^{-2} \text{s}^{-1}$, there are instances where inconsistent units appear to have been used, for example in Figure 3(a) (page 18) and line 326 (page 17). It is recommended that the authors review and correct all such instances to ensure consistency throughout the manuscript.

Re:

Thank you for pointing out this inconsistency in unit usage. We appreciate this valuable suggestion and have carefully addressed it as follows:

1. Textual corrections: As noted, most fluxes in the manuscript are presented in $\mu\text{g m}^{-2} \text{s}^{-1}$, but sometimes fluxes are presented in molar units to facilitate direct cross-species comparisons. We have identified the instances in the main text where $\text{nmol m}^{-2} \text{s}^{-1}$ units were used, and corrected them to $\mu\text{g m}^{-2} \text{s}^{-1}$, or added the equivalent values in $\mu\text{g m}^{-2} \text{s}^{-1}$ for each (e.g., " $-7.5 \pm 6.7 \text{ nmol m}^{-2} \text{s}^{-1}$, equivalent to $-0.47 \pm 0.42 \mu\text{g m}^{-2} \text{s}^{-1}$ ") to ensure clarity and consistency.
2. Figure 3: We have retained the original $\text{nmol m}^{-2} \text{s}^{-1}$ units in Figure 3, because this figure presents cross-species flux comparisons, which are only meaningful when using molar units to account for differences in molecular weights between the species. To clarify this choice for readers, we have added the following sentence to the Figure 3 caption: "*Fluxes are presented in molar units to facilitate direct cross-species comparisons.*"

The results are primarily presented as “diurnal” plots, despite the fact that most of the 12-hour sampling period (08:00–21:00 local time) falls largely within daytime hours (typically 06:00–17:00, even during

winter months). I would therefore advise against the use of the term “diurnal” to describe the results presented in this manuscript, as it does not accurately reflect the temporal coverage of the study.

Re:

Thank you for this thoughtful observation regarding our temporal terminology.

All measurements were conducted during winter in our study region, where sunset occurs around 17:00 local time. Our three 4-hour sampling periods therefore cover morning (08:00–12:00), afternoon (12:30–16:30), and early nighttime (17:00–21:00).

To address your concern, we have made the following revisions:

1. Updated Section 2.2 to rename the final sampling period from "evening" to "early night" for accuracy.
2. Added an explicit definition at the first use of "diurnal" (line 298-301): *"The diurnal variations of inorganic acidic gases (HNO_3 , HONO , SO_2 , HCl) and particulate ions (NO_3^- , NO_2^- , SO_4^{2-} , Cl^-) in morning, afternoon and early night during the observation campaign are shown in Figure 2a. In this study, diurnal variation is defined as changes occurring during photochemically active daytime and fully dark early nighttime."*

With clear definitions and precise hourly timings throughout, readers will have unambiguous understanding of our temporal coverage.

An operational flow rate of 10 L min⁻¹ resulting in a 3.1 s exchange time (page 7, lines 108-109) implies an internal denuder volume of approximately 0.5 L. However, the authors state on page 8, line 159 that the volume per denuder is 0.6 m³ (i.e. 600 L), which is inconsistent with the previous inference. The authors should clarify this discrepancy.

Re:

Thanks for your comment. We clarify the two volumes here:

The 3.1 s lag time was calculated based on the internal volume of the instrument's air tubing (~0.5 L), which is the static pipeline volume for airflow transit. By contrast, 0.6 m³ is the total cumulative ambient air volume sampled by each denuder during a 4-hour measurement. They are two independent physical quantities for different calculations, so no inconsistency exists. We have added explanations in line 169 to eliminate ambiguity.

"The total cumulative ambient air volume sampled by each denuder during a 4-hour measurement was 0.6 m³"

While the reviewer agrees with the authors that the positive morning HONO fluxes are associated with lower temperatures, the same relationship also appears to apply to HNO₃ (as shown in Figure S5). However, the authors attribute the HNO₃ behaviour exclusively to enhanced morning turbulence in Figure 6. This point requires further clarification, and the conclusions and abstract may need to be revised accordingly to reflect the broader interpretation.

Re:

We have added scatter plots (as new Figure S6) to clarify the temperature dependence of HONO and HNO_3 fluxes. As shown below, an evident negative correlation exists between HONO fluxes and temperature. After excluding two high-flux outliers, HNO_3 fluxes show no or weak correlation with temperature. These findings verify our conclusion that the gross flux of HNO_3 was accelerated under elevated turbulence, while HONO gross flux was enhanced at lower ambient temperatures. To address your comment, we have revised the content at Line 454 by supplementing references to Figure S6 in the revised manuscript.

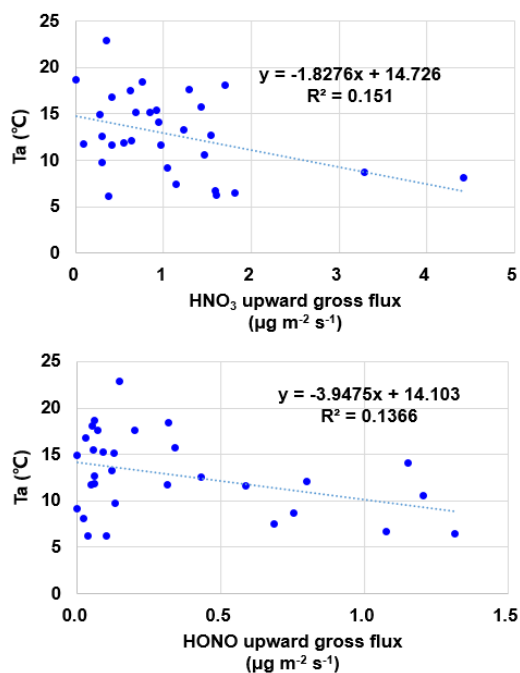


Figure S6. Scatter plots of HNO_3 and HONO upward gross fluxes against ambient air temperature (T_a). Linear regression lines and R^2 values are shown.

Technical corrections

Page 4, line 73: Typographical error: “.. an REA” should read “.. a REA”.

Re: Thank you for your comment. "An REA" is grammatically correct, as "REA" begins with a vowel sound. This is not a typo and remains unchanged.

Page 7, Figure 1: The locations and information for T_{up} and T_{down} are not shown in either the figure or the corresponding caption.

Re:

In line 187-190, we add “the β coefficient was explicitly determined using temperature measurements from the sonic anemometer (No. 14 in Figure 1), calculated as $\frac{w'T'}{\sigma_w(T_{up}-T_{down})}$, where T_{up} and T_{down} were derived from sonic temperatures sampled under the same switching frequency and $0.6\sigma_w$ dead-band conditions.”

Page 15, line 303: The concentrations presented here are mean values, the authors should explicitly state this in the text.

Re:

In line 299, we add “*At the sampling site, the mean concentration of total nitrogen-containing acidic species (gaseous + particulate) was $8.4 \pm 8.0 \mu\text{g m}^{-3}$ (mean $\pm$ standard deviation; the same applies hereinafter).*”

Page 16, Figure 2: Panels (a) and (b) are not labelled in the figure.

Re:

We rephrased Figure 2 caption as below:

Figure 2. Box-and-whisker plots with overlaid data points for eight inorganic species, grouped by diurnal time intervals. Top two rows: diurnal concentration variations of gaseous (HNO_3 , HONO , SO_2 , HCl) and particulate (NO_3^- , NO_2^- , SO_4^{2-} , Cl^-) species. Bottom two rows: REA-measured fluxes of the same species, with flux points color-coded by horizontal wind speed. Horizontal lines mark means, and boxes denote interquartile ranges.

Page 16, line 314: In Figure 3(a), “proportion” of flux should be replaced with “percentage” of flux. The authors should correct all similar instances throughout the manuscript (see also page 17, line 337).

Re:

Corrected

Page 16, line 315: The authors should also refer to Figure 3(b) in the text as part of the description of the mean $\pm$ SD values.

Re:

We added “(b) Campaign-averaged net flux per day for the eight target species.” in Figure 3 caption.

Page 17, lines 337-338: Figure 2(b) does not present information on flux percentage, but rather the flux magnitude. Please clarify this in the text.

Re:

We report counts of upward flux events in Figure 2(b), not flux percentages. Each data point in the plot represents one flux event.

Page 18, lines 344-346: This statement is not clearly described and should be rewritten for clarity.

Re:

In line 362-364 we rewrote the sentence as below:

“Like downward flux, upward fluxes of HONO ($0.30 \pm 0.27 \mu\text{g m}^{-2} \text{s}^{-1}$) and NO_3^- ($0.26 \pm 0.17 \mu\text{g m}^{-2} \text{s}^{-1}$) are again one or two orders of magnitude higher at our site than all prior measurements, while those of HNO_3 , SO_2 , SO_4^{2-} are comparable with prior reports (**Figure 4**).”

Page 19, Figure 3: The caption does not include descriptions for panels (a) and (b).

Re:

Figure 3 caption is revised:

“Figure 3. (a) Flux detection rates (percentages of measurement above the detection limit) and mean $\pm$ standard deviation of flux values for the eight target species. (b) Campaign-averaged net flux per day for the eight target species. Fluxes are presented in molar units to facilitate direct cross-species comparisons.”

Page 19, Figure 4: The downward fluxes are shown as negative values in the figure. This should be clarified either in the main text or in the figure caption.

Re:

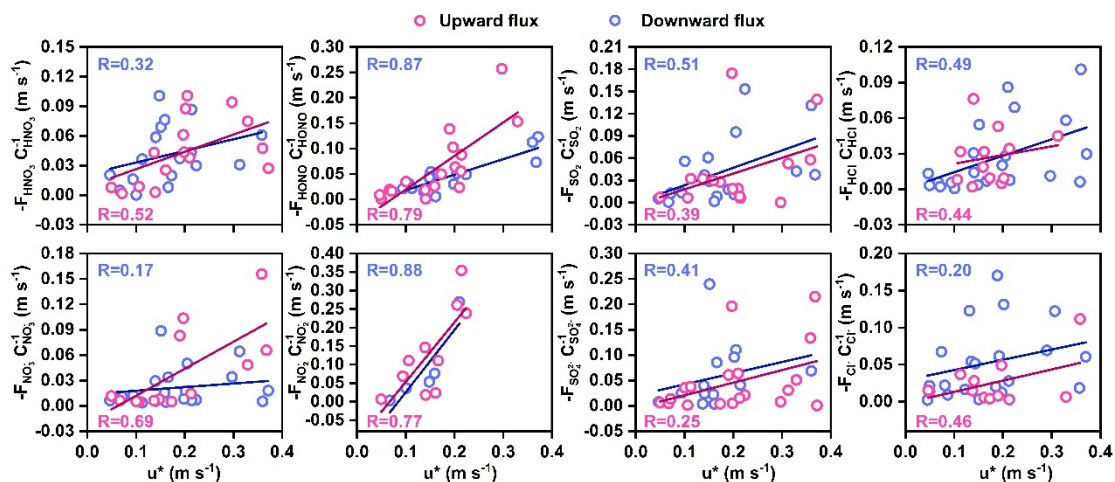
We add the sentence in Figure 4 caption:

“Downward fluxes are represented as positive values in blue to simplify plotting, while upward fluxes are shown in red.”

Page 20, Figure 5: A legend distinguishing upward and downward fluxes, similar to that used in Figure 4, should be added. I would also suggest changing the colours of R+ and R- to match the corresponding flux directions.

Re:

Figure 5 is revised as below



Page 20, lines 387-388: The word “reaction” is duplicated.

Re:

Thank you for pointing out the mistake, which is revised as below:

“HNO₃ is thought to deposit with a zero resistance even over slightly wet surfaces, where it can also be formed via $NO_2 + H_2O_{(surface)} \rightarrow HONO + HNO_3$ and $N_2O_5 + H_2O_{(surface)} \rightarrow 2 HNO_3$.”

Figure S1 could be improved by adding annotations indicating the industrial area, as well as a distance scale on the map shown on the right-hand side.

Re:

We revise Figure S1 as below:

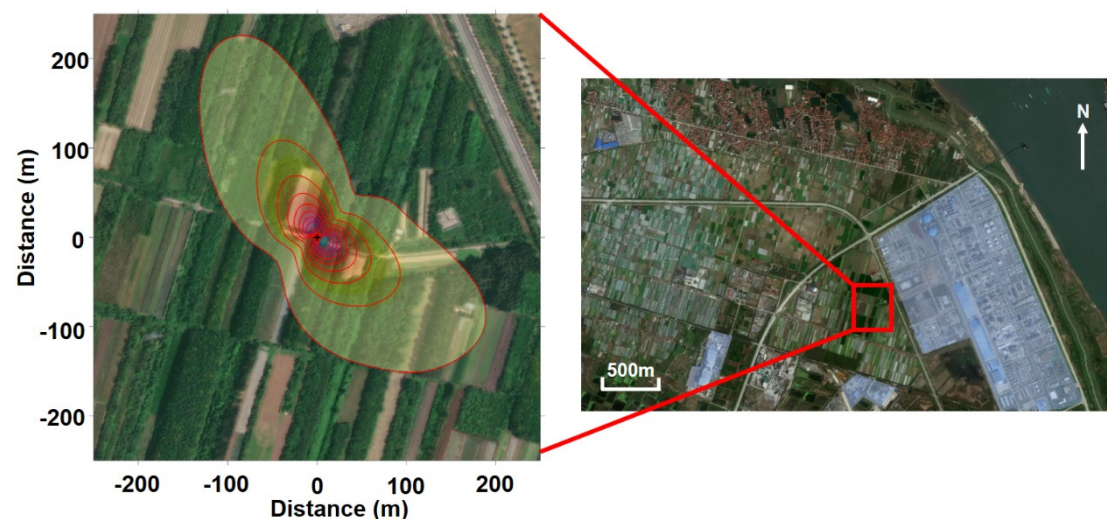


Figure. S1. The cumulative flux footprint during the sampling periods from 29 October to 30 December 2025 at a vegetable cropland adjacent to the Wuhan Chemical Industrial Park. The light-blue shaded areas represent the nearest emission facilities in the Chemical Industrial Park. The satellite base map in this figure is sourced from Ovital Map (Omap) and is used for non-commercial academic purpose only.

Comment on egusphere-2026-2234, Anonymous Referee #2

The manuscript by Hua et al. addresses an important flux research gap through the self-designed Relaxed Eddy Accumulation (REA) system: the air-surface exchange of multiple inorganic acidic species over cropland chronically influenced by industrial emissions. The authors comprehensively evaluated the precision and detection limit of the REA system. They analyzed the bidirectional flux characteristics of target species, and further estimated the gross upward emission fluxes of HNO₃ and HONO. The topic is original and practically valuable, and key findings are meaningful for regional air-soil-water pollution mitigation. The manuscript aligns with the scope of Atmospheric Chemistry and Physics. I recommend publication after the authors address the following questions.

- (1) This manuscript employs the REA method to calculate fluxes and presents a relatively comprehensive uncertainty analysis. The β coefficient serves as a key parameter in flux estimation, but the current error estimation does not fully account for the β variability. I encourage the authors to include a complete the calculation process and uncertainty analysis for the β coefficient.

Re:

Thank you for your suggestion. Now we provide an uncertainty analysis of β and incorporate it into the overall uncertainty estimate of flux. In line 191-195, we add:

“The β coefficients for 33 4-hour sampling periods fell within the typical range of 0.47 to 0.62. While a single β coefficient was used for each 4-hour sampling period, β exhibited intra-period variability. We therefore calculated β at 30-minute intervals, and used σ_{β}/β within each 4-hour period as the relative uncertainty of the corresponding period-averaged β . The relative uncertainties of β for the 33 sampling periods ranged from 2.80% to 26.14% (Table S1)”

Table S1 and Table 2 are updated accordingly.

Table 2. Concentration and flux detection limits, mass analysis precision and flux measurement precision of the acidic species.

	Concentration detection limit ($\mu\text{g m}^{-3}$)	Mass analysis precision (RSD, %)	Flux measurement precision (RSD, %)	Flux detection limit ($\mu\text{g m}^{-2} \text{s}^{-1}$)
HNO ₃	0.027	4.4	8.5–37.7	1.5×10^{-2} – 2.1×10^{-1}
HONO	0.034	4.6	8.8–28.0	1.5×10^{-2} – 1.2×10^{-1}
SO ₂	0.121	5.8	9.1–30.3	9.5×10^{-3} – 1.3×10^{-1}
HCl	0.047	4.7	11.6–32.3	8.2×10^{-3} – 1.1×10^{-1}
NO ₃ [−]	0.027	2.7	7.3–31.6	2.2×10^{-2} – 2.4×10^{-1}
NO ₂ [−]	0.034	3.0	5.4–26.3	6.1×10^{-4} – 2.8×10^{-2}
SO ₄ ^{2−}	0.121	4.6	6.7–28.6	1.2×10^{-2} – 1.3×10^{-1}
Cl [−]	0.047	3.2	7.1–21.6	6.6×10^{-3} – 1.0×10^{-1}

Table S1. Relative uncertainties of β coefficient and sampled M induced by lag time inaccuracy in different samples.

Sample run No.	Relative deviation of β (% $\pm$)	Relative deviation of M (% $\pm$)					
		0.1s		0.3s		1s	
		Up	Down	Up	Down	Up	Down

1	3.13	/	/	/	/	/	/
2	4.91	1.69	-1.68	4.19	-4.26	7.14	-8.22
3	5.91	-3.94	3.95	-10.01	10.07	-18.26	19.41
4	6.81	-1.64	1.65	-4.20	4.23	-7.55	8.15
5	6.63	3.29	-3.28	8.15	-8.32	13.02	-16.04
6	6.55	2.82	-2.81	7.01	-7.14	11.48	-13.77
7	26.14	-0.75	0.76	-1.95	1.96	-3.47	3.77
8	5.26	0.79	-0.78	1.93	-1.96	3.34	-3.78
9	5.10	-1.09	1.10	-2.80	2.81	-5.00	5.42
10	8.16	-1.09	1.10	-2.80	2.81	-5.00	5.42
11	3.91	-0.65	0.66	-1.69	1.70	-3.01	3.27
12	6.83	0.07	-0.06	0.12	-0.13	0.20	-0.25
13	8.55	0.85	-0.84	2.07	-2.10	3.59	-4.06
14	4.90	0.85	-0.84	2.07	-2.10	3.59	-4.06
15	2.80	1.59	-1.58	3.95	-4.01	6.75	-7.74
16	3.26	-0.76	0.77	-1.98	1.99	-3.52	3.83
17	8.65	1.13	-1.12	2.79	-2.83	4.82	-5.47
18	6.43	2.44	-2.43	6.07	-6.17	10.10	-11.91
19	4.51	2.50	-2.49	6.20	-6.30	10.29	-12.16
20	9.47	1.07	-1.06	2.63	-2.67	4.54	-5.15
21	13.40	0.52	-0.51	1.26	-1.28	2.19	-2.47
22	9.32	-1.61	1.62	-4.10	4.13	-7.37	7.96
23	5.90	0.96	-0.95	2.37	-2.41	4.10	-4.65
24	7.70	-2.01	2.02	-5.13	5.16	-9.23	9.94
25	3.11	-0.73	0.74	-1.90	1.91	-3.38	3.67
26	2.92	0.48	-0.47	1.16	-1.18	2.02	-2.28
27	9.33	-0.20	0.21	-0.55	0.55	-0.97	1.04
28	8.55	-9.80	9.81	-24.88	24.98	-46.30	48.15
29	6.21	-0.85	0.86	-2.19	2.20	-3.90	4.24
30	12.97	1.27	-1.26	3.14	-3.18	5.39	-6.14
31	7.44	-0.01	0.02	-0.09	0.08	-0.17	0.16
32	5.67	1.09	-1.08	2.69	-2.73	4.64	-5.27
33	10.52	-6.89	6.90	-17.50	17.58	-32.31	33.89

(2) Why was the threshold for distinguishing updrafts and downdrafts set to $\pm 0.6\sigma_w$ instead of $\pm 0.5\sigma_w$ or $\pm 0.7\sigma_w$?

Re:

According to the conditional sampling theory of REA, a higher triggering threshold of wind speed enhances the concentration difference between the updraft and downdraft reservoirs ($C_{up} - C_{down}$), thereby improving the precision of its measurement. However, if the threshold is set too high, an excessive

fraction of low-vertical-velocity samples will be excluded, reducing the representativeness of the conditional samples relative to actual turbulent exchange. This may increase the uncertainty in fluxes derived from the REA method.

We have adapted the recommendations of Businger and Oncley (1990) and used a threshold of $\bar{w} \pm 0.6\sigma_w$. The threshold of $\bar{w} \pm 0.6\sigma_w$ has been widely adopted in relaxed eddy accumulation (REA) studies (Bai et al. 2015, Sarkar et al. 2020) and has been demonstrated in previous experiments to provide reliable flux estimates (Bowling et al. 1998, Desjardins 1977, Ge et al. 2022, Velentini et al. 1997).

In lines 116–120 of the revised manuscript, we revised:

“Three-minute running mean ($\bar{w}$) and standard deviation (σ_w) of w was calculated in real time to trigger solenoid valve (Numatics LS02M6F00B, Emerson Electric Co., St. Louis, Missouri, USA) switching: updraft sampling at $w > \bar{w} + 0.6\sigma_w$, downdraft sampling at $w < \bar{w} - 0.6\sigma_w$, and dead-band airflow within the $w \pm 0.6\sigma_w$ range. Wind speed triggering threshold selection involves a trade-off between the precision of $C_{up} - C_{down}$ measurements and sample representativeness. As an empirical threshold commonly used in REA studies, $0.6\sigma_w$ has been demonstrated to provide reliable flux estimates (Bowling et al. 1998, Businger and Oncley 1990, Bai et al. 2015, Sarkar et al. 2020).”

References:

- Bai, J., Guenther, A., Turnipseed, A. and Duhl, T. (2015) Seasonal and interannual variations in whole-ecosystem isoprene and monoterpene emissions from a temperate mixed forest in Northern China. *Atmospheric Pollution Research* 6(4), 696-707.
- Bowling, D.R., Turnipseed, A.A., Delany, A.C., Baldocchi, D.D., Greenberg, J.P. and Monson, R.K. (1998) The use of relaxed eddy accumulation to measure biosphere-atmosphere exchange of isoprene and other biological trace gases. *Oecologia* 116(3), 306-315.
- Businger, J.A. and Oncley, S.P. (1990) Flux Measurement with Conditional Sampling. *Journal of Atmospheric and Oceanic Technology* 7(2), 349-352.
- Desjardins, R.L. (1977) Description and evaluation of a sensible heat flux detector. *Boundary-Layer Meteorology* 11(2), 147-154.
- Ge, H., Wei, Z., Zhang, H. and Kang, L. (2022) Experimental Research of Methane Flux Measurement by the Relaxed Eddy Accumulation Method. *Acta Scientiarum Naturalium Universitatis Pekinensis* 58(3), 434-442.
- Sarkar, C., Turnipseed, A., Shertz, S., Karl, T., Potosnak, M., Bai, J., Serça, D., Bonal, D., Burban, B., Lopes, P.R.C., Vega, O. and Guenther, A.B. (2020) A portable, low-cost relaxed eddy accumulation (REA) system for quantifying ecosystem-level fluxes of volatile organics. *Atmospheric Environment* 242, 117764.
- Velentini, R., Greco, S., Seufert, G., Bertin, N., Ciccioli, P., Cecinato, A., Brancaleoni, E. and Frattoni, M. (1997) Fluxes of biogenic VOC from Mediterranean vegetation by trap enrichment relaxed eddy accumulation. *Atmospheric Environment* 31, 229-238.

(3) This manuscript should incorporate more detailed background information on the sampling site and farmland conditions. For example, the manuscript should provide the exact latitude and longitude of the flux tower site, as well as the duration over which the cropland has been continuously affected by

chemical industrial emissions. In addition, field conditions during the sampling campaign should be described in greater detail, including the crop growth stage and records of fertilization and irrigation practices. The absence of these critical details limits the comparability with previous agricultural flux studies.

Re:

We revise the paragraph in 142-155 to include more descriptions:

*“The Wuhan Chemical Industrial Park (WCIP) is located northeast to the urban area of Wuhan. The WCIP covers 71.64 km² and hosts petrochemical, fine chemical, and building material industries. Since its full operation in 2013, the WCIP has been identified as a major industrial emission source influencing atmospheric composition in the surrounding region. The flux tower (114.53° E, 30.65° N) was installed at the center of a vegetable cropland within the 7.3 km² Beihu Farm, which is immediately adjacent to the WCIP. The nearest petrochemical emission source lies approximately 1.0 km north of the tower (Figure S1). The cropland was cultivated with *Raphanus sativus* L. var. *longipinnatus* (white radish), a typical cold-season vegetable in this region. The tower is situated on flat terrain with no obstructing buildings or trees within a 500 m radius of the tower, ensuring undisturbed airflow measurements.*

*Field sampling was performed from 29 October to 30 December 2025, with 11 valid sampling days in cloudy or sunny rain-free weather. Each sampling day included three 4-hour sampling periods (morning: 8:00–12:00; afternoon: 12:30–16:30; early night: 17:00–21:00). The sampling was conducted during the vegetative growth and harvest periods of *R. sativus*, and no fertilization activities were conducted throughout the sampling period.”*

(4) Figure captions should be checked for consistency. For example, the main text states that horizontal lines in Figure 2 mark means, whereas the supplementary figures use medians.

Re:

We corrected the supplementary figures by using mean values. Figure captions were double-checked throughout the manuscript to remove any inconsistency.