Point-to-point responses to anonymous Referee #1

Thank you for your comments 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 2.4×10^{-1} μg m^{-2} 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 μg m^{-2} 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 μg m^{-2} 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 nmol m^{-2} s^{-1} units were used, and corrected them to μg m^{-2} s^{-1}, or added the equivalent values in μg m^{-2} s^{-1} for each (e.g., "-7.5±6.7 nmol m^{-2} s^{-1}, equivalent to -0.47±0.42 μg m^{-2} s^{-1}") to ensure clarity and consistency.
2. Figure 3: We have retained the original nmol m^{-2} 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 m^3 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 m^3*"

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.

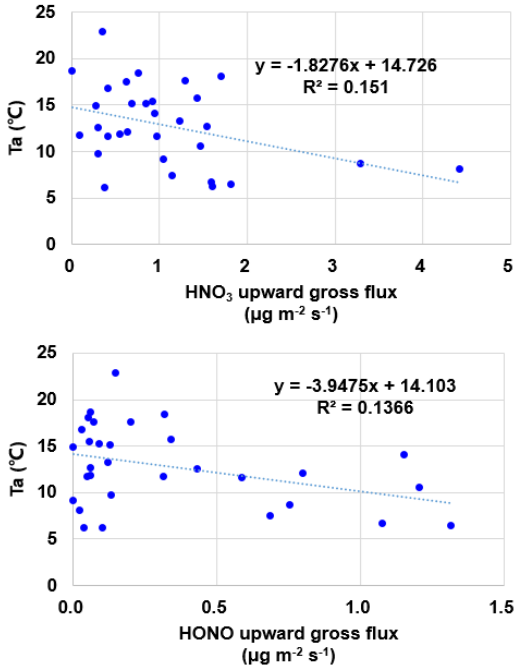


Figure S6. Scatter plots of HNO_3 and HONO upward gross fluxes against ambient air temperature (T_a). Linear regression lines and R^2 values are shown.

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 Tup and Tdown 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 0.6σ_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 ± 8.0 μg m^{-3} (mean ± 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 ± 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±0.27 μg m^{-2} s^{-1}) and NO_3^- (0.26±0.17 μg m^{-2} 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 ± 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:

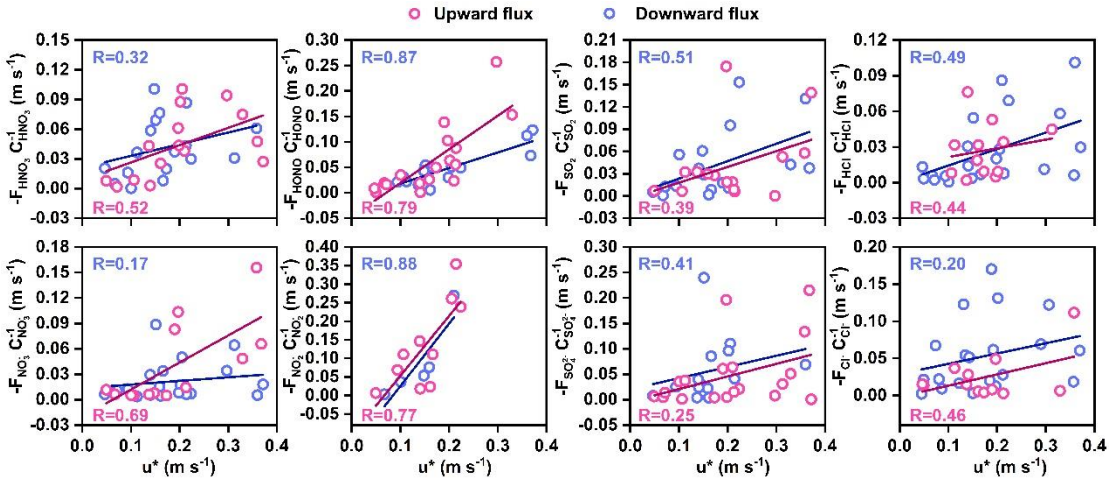
We add the sentence in Figure 4 caption:

"*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:

"HNO_3 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:

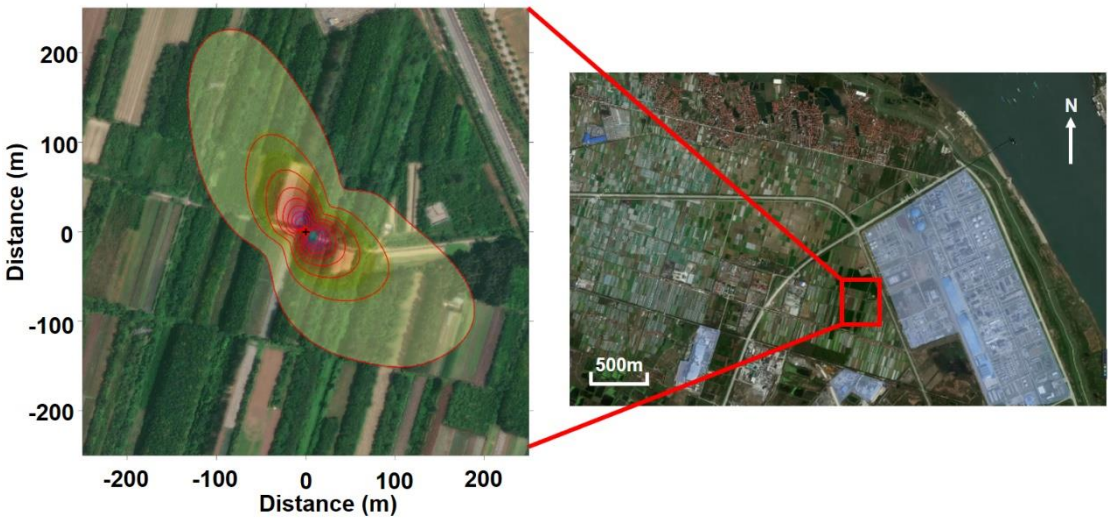


Figure. S1. The cumulative flux footprint during the sampling periods from 29 October to 30 December 2025 at a vegetable cropland adjacent to the Wuhan Chemical Industrial Park. The light-blue shaded areas represent the nearest emission facilities in the Chemical Industrial Park. The satellite base map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