Response to Editor's Comments

We thank the editor for the comments and suggestions regarding the Abstract and Conclusions sections. We have carefully revised the manuscript according to the ACP guidelines for authors. Below is our point-by-point response to the specific comments raised.

Comment 1: The abstract requires "The importance and implications of the results."

Response: We thank the editor for pointing this out. We have revised the Abstract to better highlight the importance and implications of our results. Specifically, we have made the following modifications in blue fronts:
(1) We strengthened the opening of the Abstract to emphasize the research importance,
(2) We added explicit statements on the implications of our findings at the end of the Abstract.

We note that the ACP guidelines require the Abstract to be within 250 words. Given this strict word limit, the Abstract cannot be expanded substantially. We have carefully balanced the need to present the importance and implications of the results while keeping the Abstract concise and within the word count constraint. We believe the revised Abstract now adequately addresses this requirement while maintaining the necessary brevity.

"Industrial emissions in China's densely populated regions turn surrounding lands into high-deposition-load hotspots, alter physicochemical properties of soils and vegetation, and lead to complex sink-source transitions of land surface. The lack of local flux data impedes integrated air-soil pollution control. We developed a Relaxed Eddy Accumulation (REA) system capable of simultaneous flux measurements of eight inorganic species (HNO_3, HONO, SO_2, HCl, nitrate, nitrite, sulfate, chloride). System characterization showed detection limits of 6.1×10^{-4}–2.4×10^{-1} $\mu g\ m^{-2}\ s^{-1}$ and flux precisions of 5.4%–32.3%, with uncertainties dominated by mass analysis, lag time error, and sonic-temperature-derived proportionality coefficient β. Flux measurements conducted in winter at a vegetable cropland adjacent to chemical industry facilities revealed that HONO and nitrate fluxes at this site were 1–2 orders of magnitude higher than those reported in the literature. Bidirectional fluxes of the species indicate the cropland acts as both source and sink; but winter averages showed net emission fluxes only for HONO and nitrite (mean daily 2.49 and 0.53 mg m^{-2} d^{-1}). Gross upward emission fluxes of HNO_3 and HONO were 1.1 ± 0.9 μg m^{-2} s^{-1} and 0.4 ± 0.4 μg m^{-2} s^{-1}, respectively, with HNO_3 emissions enhanced by turbulence and HONO promoted at low temperatures. Such emissions are expected to enhance atmospheric nitrate aerosol formation and atmospheric oxidative capacity. These results provide critical observational constraints for acidic species exchange parameterization in industrial-influenced regions, advancing understanding of reactive nitrogen cycling and supporting air pollution control and agro-ecological protection strategies."

Comment 2: The conclusion section requires "Comparison and context: Compare the results with previous studies to put them in context. Explain consistencies, inconsistencies, and advances in knowledge."

Comment 3: The conclusion section requires "Implications: Discuss what the results mean for our understanding of the state and/or behaviour of the atmosphere and climate, which is the main requirement for publication in ACP."

Response: We thank the editor for this suggestion. We have strengthened the Conclusions section as below:

(1) We open the Conclusions section by stating that our results provide critical observational data and mechanistic insights into acidic species exchange over cropland.
(2) We compare our findings with prior studies, and highlight the key inconsistency and advance in knowledge.
(3) We provide explanations for the discrepancy with prior field observations.

(4) We discuss the atmospheric implications: upward HNO3 fluxes from cropland contribute to atmospheric nitrate aerosol formation, and HONO emissions enhance atmospheric oxidative capacity.
(5) We highlight the implications of our results in modeling and pollution control.
(6) We have also added a section on study limitations.

The revision and additions are marked in blue front:

4. Conclusions

In this study, we developed a Relaxed Eddy Accumulation system capable of simultaneous flux measurement of eight gaseous and particulate inorganic acidic species, targeting urban cropland under long-term exposure to chemical industry emissions. The system achieved a relative uncertainty of air sample volume < 0.2%, a lag time-induced analyte mass uncertainty of 2.64%, and a relative uncertainty of mass analysis ranging from 2.7% to 5.8%. Using Gaussian error propagation and the *t*-test method, we determined that the flux measurement precision of the system ranges from 5.4% to 32.3%, and the flux detection limits span from 6.1×10^{-4} to 2.4×10^{-1} μg m^{-2} s^{-1}, depending on the chemical species, ambient atmospheric concentrations and flux magnitudes during the sampling periods.

Our results provide critical observational data and mechanistic insights into acidic species exchange over cropland under the long-term influence of chemical industrial emissions in an urban environment. All inorganic acidic species exhibited bidirectional fluxes, demonstrating that cropland can act as a source of atmospheric inorganic acidic species rather than solely a deposition sink. Such bidirectional fluxes are not unique to this industrial-zone cropland, as they have been documented in nearly all prior REA measurements across sites from remote forests to urban grasslands. However, the notable difference is that the fluxes of HONO and NO_3^- at our site, both upward and downward, were 1–2 orders of magnitude higher than those values reported in the literature, while the fluxes of HNO_3, SO_2, SO_4^{2-} are comparable with prior reports. This magnitude difference reveals a previously underquantified HONO and nitrate flux hotspot in peri-industrial regions, which has been missing in regional flux inventories.

The discrepancy with prior field observations is largely attributable to the long-term cumulative effect of adjacent industrial NO_x emissions that elevate surface nitrogen loading and alter surface exchange properties. Under high NO_x conditions, upward HNO_3 fluxes may arise from heterogeneous surface reactions of NO_2, decomposition of NH_4NO_3 aerosols near warm surfaces or deposited NH_4NO_3 on the ground or leaf surfaces as water layers evaporate. These processes render cropland an HNO_3 emission source that contributes to atmospheric nitrate aerosol formation. HONO emissions from cropland stem from direct soil release, heterogeneous NO_2 reactions on wet surfaces, and nitric acid/nitrate photolysis on leaf surfaces, thus enhancing atmospheric oxidative capacity.

The diurnal pattern points to strong nocturnal production in the surface layer overnight under weak turbulent mixing, and pronounced upward fluxes in the next morning as turbulence intensifies. The apparent deposition velocities of all species were positively correlated with friction velocity for both upward and downward fluxes, highlighting the key regulatory role of turbulent mixing in acidic species exchange. Based on the mass balance equation and resistance in-series model, we estimated the gross upward fluxes of water-soluble HNO_3 and HONO. The gross flux of HNO_3 was accelerated under elevated turbulence, while HONO gross flux was enhanced at lower ambient temperatures, likely due to elevated soil and surface moisture. The quantified fluxes offer empirical constraints for improving deposition and emission parameterizations in chemical transport models, a scientific basis for formulating targeted industrial emission control and farmland ecological protection policies in densely populated industrial megacities.

Some limitations should be noted. First, measurements were conducted only in winter. Seasonal variations in flux magnitudes and driving mechanisms will be characterized in our future measurement. Second, the gross flux estimation cannot distinguish between direct surface emissions, near-surface chemical production, and storage changes, requiring further fine-scale vertical profiling to partition these contributions. Third, the results are based on a single vegetable cropland site, and generalizability to other crop types and industrial contexts requires additional multi-site observations.