

This paper presents eddy-covariance measurements for fluxes of oxygenated organic molecules, OOM. The measurement site was placed in the surroundings of Wuhan and the campaign extended nearly one month during summer 2025. The experimental setup is described together with the flux obtaining. The study presents daily cycles of micrometeorological variables, OOM fluxes, concentrations and meteorological variables such as temperature and total sun radiation. In consequence, the manuscript is quite complete and some minor remarks could be introduced.

Response:

We sincerely thank for your constructive and helpful comments. Below we provide point-by-point responses. Changes in the revised manuscript are highlighted in **blue**.

Comment 1:

The measurement site is in the urban-rural interface, in the Wuhan surroundings. Since the horizontal homogeneity could not be guaranteed, the authors could indicate if the experimental response depends on the wind direction.

Response:

Thank you for raising this important point. We agree that the heterogeneous land cover surrounding the site could potentially introduce a wind-direction dependence in the measured fluxes. To examine this issue, we have added a new Figure S14 showing the horizontal wind vectors associated with positive, negative, and no/weak flux conditions for HNO_3 and each of the 16 OOM species.

As shown in Figure S14, the different flux categories substantially overlap in wind-vector space. Detectable positive and negative fluxes are not restricted to a single narrow wind sector, and we do not observe a directional dependence for the compounds, suggesting that the observed OOM fluxes were not dominated by a single localized source direction.

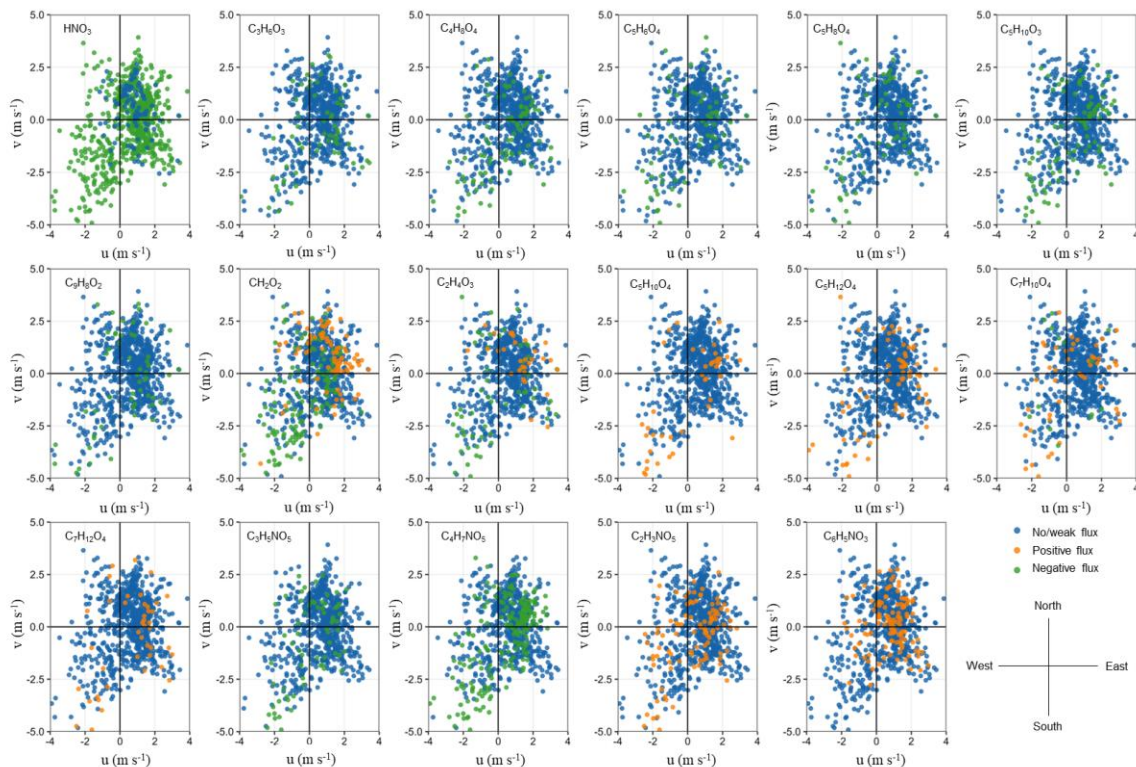


Figure S14. Horizontal wind-vector distributions associated with positive, negative, and no/weak flux conditions for HNO_3 and the 16 OOM species. Each point represents a 30-min mean horizontal wind vector corresponding to an individual flux measurement interval, with colors indicating the corresponding flux category. Positive u and v denote westerly and southerly wind components, respectively.

We note, however, that the campaign included only 28 valid measurement days during summer, and the sampling of wind directions was uneven because northeasterly winds prevailed during the campaign. The present dataset therefore does not support a robust direction-resolved statistical attribution of the OOM fluxes. Moreover, OOM surface–atmosphere exchange is expected to reflect the combined effects of surface characteristics, precursor emissions, near-surface chemistry, turbulence, and meteorological conditions, with wind direction representing only one of these factors.

The primary objective of the present study is to evaluate and establish an eddy-covariance approach for measuring pptv-level OOM fluxes, particularly addressing the methodological challenges associated with their low signal-to-noise ratios, rather than to quantitatively resolve the environmental drivers of individual OOM fluxes. Longer-term

measurements are ongoing and will allow the dependence of OOM fluxes on wind direction and other environmental variables to be assessed more systematically.

Lines 386-392 in the end of results and discussion section are added to clarify the possible influence of wind direction and the limitation of the present short-term dataset:

The possible dependence of the observed fluxes on wind direction was examined by comparing horizontal wind-vector distributions among positive, negative, and no/weak flux conditions (Figure S14). The three flux categories showed substantial overlap in wind-vector space, and no directional preference was observed for HNO_3 or the 16 OOM species. Moreover, because the campaign covered only 28 valid days, the directional sampling was uneven and does not allow robust wind-direction-resolved attribution.

Comment 2:

The paper indicates that the measurements were obtained above the zero-plane displacement. Since the surface roughness depends on the wind direction, the authors could explain the determination of the zero-plane displacement.

Response:

Thank you for pointing this out. We agree that the zero-plane displacement height d may vary with wind direction because of the heterogeneous surroundings of the site. The site is bordered by wooded areas to the southwest and northeast and by a mixed building–tree campus landscape in the other directions. However, detailed sector-resolved information on the heights and spatial densities of both buildings and vegetation was not available, making a reliable direction-dependent determination of d difficult.

We therefore adopted a single representative displacement height using the commonly used first-order approximation $d = 0.67h$ (Arya, 1998; Stull, 1988; Oke, 1987), where $h = 15\text{m}$ is the mean height of the surrounding buildings and was used as a representative roughness-element height. This gives $d = 10\text{ m}$ and an effective measurement height of $z - d = 20\text{ m}$.

To assess the sensitivity of the calculated fluxes to this assumption, we repeated the EddyPro processing using representative roughness-element heights of 10 and 20 m ($d =$

6.7 and 13.4 m, respectively). For the representative OOM $\text{C}_4\text{H}_7\text{NO}_5$, the resulting fluxes differed by less than 2% from those obtained using $h = 15\text{m}$. We therefore conclude that the calculated flux magnitude is only weakly sensitive to the adopted representative displacement height within this plausible range. The determination of d has now been clarified in the revised manuscript.

We have added this clarification to line 85-89 in Section 2.1:

Because detailed wind-sector-resolved building and vegetation morphology was unavailable, wind-direction-dependent displacement heights were not prescribed. A single representative zero-plane displacement height of $d=10\text{ m}$ ($0.67\times 15\text{ m}$) was used (Arya, 1998; Stull, 1988; Oke, 1987), where the mean height of the surrounding buildings 15 m was adopted as a representative roughness-element height.

Arya, S. P. (1998). *Introduction to micrometeorology*. Academic Press, San Diego.

Oke, T. R. (1987). *Boundary layer climates* (2nd ed.). Routledge, London.

Stull, R. B. (1988). *An introduction to boundary-layer meteorology*. Kluwer Academic Publishers, Dordrecht.

Comment 3:

Since the measurement extended during one month, a comment about the measurement representativeness should be included. Moreover, the possible annual evolution of these measurements could be introduced.

Response:

We agree that the present one-month campaign cannot be considered representative of annual conditions. The measurements were conducted during midsummer in Wuhan, characterized by high temperature and solar radiation, and active photochemical production of OOMs. Therefore, the present results should be interpreted as representative of summertime OOM surface–atmosphere exchange rather than annual mean behavior.

Seasonal changes in temperature, radiation, vegetation activity, atmospheric oxidation chemistry, and boundary-layer dynamics are expected to modify both OOM abundance and surface exchange. We have added this limitation and perspective to the revised manuscript.

Year-round measurements are currently ongoing and will allow the seasonal and annual evolution of OOM fluxes to be assessed more systematically.

A paragraph about summer season measurement representativeness is included in line 91-96 in Methodology section:

The campaign covered the annual peak of temperature, humidity, solar radiation and atmospheric oxidation capacity in Wuhan; short rainfall events were excluded from flux analysis. Therefore, the observed OOM fluxes should be regarded as representative of summertime surface-atmosphere exchange rather than annual behavior.

We added line 503-516 in Conclusion Section:

First, the relatively short campaign limits the representation of seasonal variability, atmospheric circulation regimes, and specific synoptic events.

Year-round measurements are ongoing and will enable systematic assessment of the seasonal evolution of OOM fluxes and their dependence on meteorological, chemical, and circulation conditions.

Comment 4:

Potential readers could wonder if varied atmospheric circulations are represented. In addition, the response against specific events, such as front passages or precipitation events would be acknowledged.

Response:

The present campaign sampled a limited range of summertime atmospheric circulation and weather conditions and is therefore insufficient for a robust event-based analysis of different circulation regimes. Short rainfall periods were excluded from the flux analysis because of their influence on eddy-covariance data quality. In addition, the limited duration of the campaign did not provide enough independent cases of specific synoptic events, such as frontal passages, for statistically meaningful comparison.

The ongoing year-round measurements will cover a broader range of atmospheric circulation and weather conditions, including seasonal transitions and synoptic events, and will allow the responses of OOM fluxes to meteorological and chemical drivers to be evaluated more systematically.

We added line 503-516 in Conclusion Section:

First, the relatively short campaign limits the representation of seasonal variability, atmospheric circulation regimes, and specific synoptic events.

Year-round measurements are ongoing and will enable systematic assessment of the seasonal evolution of OOM fluxes and their dependence on meteorological, chemical, and circulation conditions.

Comment 5:

The authors indicate that daily calibrations were made. They should explain if measurements are steady and if the calibration frequency is necessary. In addition, the measurement corrections after the calibrations should be introduced.

Response:

We thank the reviewer for this comment. Now we summarize calibration, quality-control, and instrument-characterization procedures during the campaign in a table below:

Procedure	Frequency/timing	Purpose
Nitrogen blank correction	5 min in every 36-min measurement cycle	Automatic CIMS Background correction
I-CIMS mass calibration	Daily	Maintain accurate mass assignment
Main sample flow check	Daily	Verify stable flow conditions
Levoglucosan sensitivity check using FIGAERO	Every 2 days	Monitor temporal stability of I-CIMS sensitivity
Indirect sensitivity calibration ($S_{\max}$, $1/S_0$, T_M)	Before the campaign	Determine response factors for OOMs lacking authentic standards
Direct sensitivity calibration (HNO ₃ and formic acid)	Before the campaign	Verify the derived response factors
Humidity-dependence experiment	After the campaign	Quantify water-vapor effects on I-CIMS sensitivity
HNO ₃ /formic acid/acetic acid lag-time experiment	After the campaign	Evaluate possible species-dependent transport delays
Six-compound PFA-tube loss experiment	After the campaign	Evaluate possible concentration loss in the 20.8-m inlet

In line 157-160, we add:

The levoglucosan $S_{\max}$ checks performed every two days showed only small variations throughout the campaign (<2.6%), indicating that the I-CIMS sensitivity remained stable during the campaign.

Regarding post-calibration corrections, we performed additional humidity-dependent sensitivity experiments after the campaign. The resulting humidity correction factors (RH_{corr}) were incorporated into the response factors, and all target OOM mixing ratios and consequently their EC fluxes were recalculated. In line 168-172, we add:

The effect of humidity on I-CIMS sensitivity was determined using seven surrogate compounds (nitric acid, formic acid, lactic acid, acetic acid, 4-nitrophenol, pimelic acid, and erythritol (Text S6). The result of ambient humidity correction factors (RH_{corr}) relative to the sensitivity under dry-air conditions is further discussed in Section 3.2.2. Humidity corrected response factors of All target OOM are listed in Table S1.

In contrast, the post-campaign PFA-tube loss experiment showed signal changes of <3.4% for the six surrogate compounds; therefore, no additional tube-loss correction was applied to the sensitivity. In line 110-116, we add:

To assess potential concentration losses in our inlet, six compounds formic acid, acetic acid, lactic acid, pimelic acid, erythritol, and 4-nitrophenol, which are themselves target OOMs with measurable fluxes at this site or structurally similar surrogates of target OOMs, were measured under two sampling configurations: direct introduction into the I-CIMS and introduction through the 20.8-m PFA tube. The resulting signal changes range from -3.39% to +0.30%, indicating negligible concentration loss. Therefore, no concentration correction was made.

Comment 6:

The authors could comment if a comparison with measurements from similar or other devices was made in similar or different environments.

Response:

Because virtually no OOM flux measurements have been reported in urban environment, we compared our results with previous EC flux measurements using CIMS above forest canopy environments.

The comparison is in line 371-379 (3.3 Flux analysis):

The OOM fluxes observed at this urban site were generally lower than those reported above forest canopies, although the differences were typically within one order of magnitude (Fulgham et al., 2019; Nguyen et al., 2015; Vermeuel et al., 2023). For example, formic acid maximum fluxes above forests were around 1-2 nmol m⁻² s⁻¹, either emission or deposition, with mean maximum mixing ratio around 2.5 ppbv. Mean daily maximum fluxes of total 85 OOMs detected by I-CIMS were around 2.5 nmol carbon m⁻² s⁻¹ for both emission and deposition over a coniferous forest (Vermeuel et al., 2023), compared with summed downward and upward fluxes of 0.60 and 0.34 nmol carbon m⁻² s⁻¹, respectively, for the 16 OOM species measured in our study.

and in the Conclusion section (line 483-495):

While urban environments are generally recognized as having more severe anthropogenic organic pollution, the OOM fluxes measured at this urban site were generally lower than those reported above forest canopies, although the differences were typically within one order of magnitude. For example, the maximum formic acid flux in our study was approximately 3-5 times lower than values reported above forests. The summed downward or upward fluxes of the 16 OOMs measured here were also lower than the total flux of 85 OOMs detected by I-CIMS over a coniferous forest (Vermeuel et al., 2023), although these totals are not directly comparable because of the different numbers and identities of OOM species included. These differences may partly reflect the contrasting source environments: forest-canopy flux measurements were conducted only a few meters above strong biogenic emission sources, whereas our study was conducted at a suburban university campus distant from downtown areas, industrial zones, and major traffic emission sources.

Fulgham, S. R., Brophy, P., Link, M., Ortega, J., Pollack, I., & Farmer, D. K. (2019).

Seasonal flux measurements over a Colorado pine forest demonstrate a persistent source

of organic acids. *ACS Earth and Space Chemistry*, 3(9), 2017-2032.
<https://doi.org/10.1021/acsearthspacechem.9b00182>

Nguyen, T. B., Crounse, J. D., Teng, A. P., St. Clair, J. M., Paulot, F., Wolfe, G. M., & Wennberg, P. O. (2015). Rapid deposition of oxidized biogenic compounds to a temperate forest. *Proceedings of the National Academy of Sciences of the United States of America*, 112(5), E392-E401. <https://doi.org/10.1073/pnas.1418702112>

Vermeuel, M. P., Millet, D. B., Farmer, D. K., Pothier, M. A., Link, M. F., Riches, M., Williams, S., & Garofalo, L. A. (2023). Closing the reactive carbon flux budget: Observations from dual mass spectrometers over a coniferous forest. *Journal of Geophysical Research: Atmospheres*, 128(14), e2023JD038753.
<https://doi.org/10.1029/2023JD038753>

Comment 7:

Limitations of this study should be noted.

Response:

We thank the reviewer for this valuable suggestion. A paragraph is added at the end of Conclusion section (line 503-516):

Several limitations of the present study should be noted. First, the relatively short campaign limits the representation of seasonal variability, atmospheric circulation regimes, and specific synoptic events. Second, observations from a single urban site cannot represent the diversity of urban surface characteristics and atmospheric environments. Third, the indirect sensitivity calibration for compounds lacking authentic standards introduces larger concentration and flux uncertainties than compound-specific calibration. Finally, iodide-adduct I-CIMS selectively detects OOMs with favorable iodide-clustering efficiencies, and therefore does not capture the entire atmospheric OOM pool. Year-round measurements are ongoing and will enable systematic assessment of the seasonal evolution of OOM fluxes and their dependence on meteorological, chemical, and circulation conditions. Multi-site measurements, together with complementary chemical-ionization techniques, will be needed to better characterize the seasonal, chemical, and spatial variability of OOM surface–atmosphere exchange.

Comment 8 (Minor):

Figure S10: "temparature" should be "temperature".

Response:

Corrected.