Sun et al. reported measurements of the fluxes of trace oxygenated organic molecules (OOMs) in an urban environment. According to their statement, this is the first OOM flux measurements in urban environments, in which the OOM fluxes are found to be significantly lower than those previously reported for forest environments. They hence discussed the methods to retrieve the OOM fluxes with low signal-to-noise ratios, and then reported the fluxes of 16 OOMs and their characteristics. This study has a major contribution to the methods of flux measurements and also provides observational constraints for understanding surface-atmosphere exchange. The topic fits the scope of Atmospheric Chemistry and Physics, and I recommend acceptance after major revisions.

Response:

We sincerely thank the reviewer for the positive assessment and for providing constructive comments that have helped us improve the scientific clarity and robustness of this manuscript.

Comment 1 (General):

My main concern is whether the significantly lower flux compared to previously reported values for clean environments represents certain urban environments or only this specific observational site? Such a difference was attributed to the fact that the measurement in this study was conducted away from emission sources. Could there be data, e.g., a comparison of OOM concentrations between different environments, supporting this argument? Are the OOM concentrations reported in Figure 3 comparable to previous studies? Could the low flux be associated with measurement biases (e.g., insufficient correction for sampling losses)? I encourage the authors to expand the discussion of potential limitations on this topic.

Response:

We thank the reviewer for this important comment. We agree that the originally reported difference between our urban fluxes and previous forest-canopy measurements

required a more careful evaluation of both measurement uncertainty and site representativeness.

1. In the original analysis, **the I-CIMS response factors from collision-limited sensitivity calibration were actually derived under DRY nitrogen calibration conditions, whereas the effect of water vapor in ambient sample air flow on the sensitivity had not been considered.** When revising the manuscript, we therefore performed additional humidity-dependent sensitivity experiments using seven surrogate compounds under field-relevant water-vapor conditions. The resulting compound-specific or structurally assigned humidity correction factors (RH_{corr}) were incorporated into the response factors, and all OOM mixing ratios and corresponding EC fluxes were recalculated.

   Section 2.2.2 was revised and Text S6 was added to describe the humidity correction experiment of I-CIMS sensitivity:

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.

Section 3.2.2 was expanded to present the humidity-dependence results.

We conducted humidity-dependent experiments using surrogate compounds (Text S6). Nitric acid, formic acid, and lactic acid are themselves species for which fluxes were observed in this study. Based on structural similarity, acetic acid was used as a surrogate for monocarboxylic acid other than formic acid, lactic acid for hydroxyl carboxylic acids, pimelic acid for dicarboxylic acids, erythritol for multifunctional alcohols, and 4-nitrophenol for nitrophenol and organonitrate. The experiments showed pronounced compound-dependent humidity effects (Figure S7): sensitivities of nitric acid, formic acid, lactic acid, and acetic acid decreased with increasing water vapor, whereas those of 4-nitrophenol, pimelic acid, and erythritol increased. For all tested compounds, however, the sensitivities became relatively stable above ~20

mmol mol^{-1} [H_2O]. During our field campaign, ambient water vapor ranged from approximately 18 to 36 mmol mol^{-1}, with ~98% of the observations above 20 mmol mol^{-1}. For each surrogate compound, we therefore defined a humidity correction factor (RH_{corr}) as the ratio of the mean signal response measured at H_2O concentrations above 20 mmol mol^{-1} to that measured under unhumidified dry-air conditions ([H_2O] = 0.14 mmol mol^{-1}). RH_{corr} ranges from 0.06 (formic acid) to 0.48 (lactic acid) for water competing compounds and from 1.10 to 1.145 for water stabilizing compounds. The compound-specific RH_{corr}, or that of the structurally most similar surrogate, was then applied to each target OOM. The surrogate assignments and RH_{corr} values for all target species are shown in Table S1.

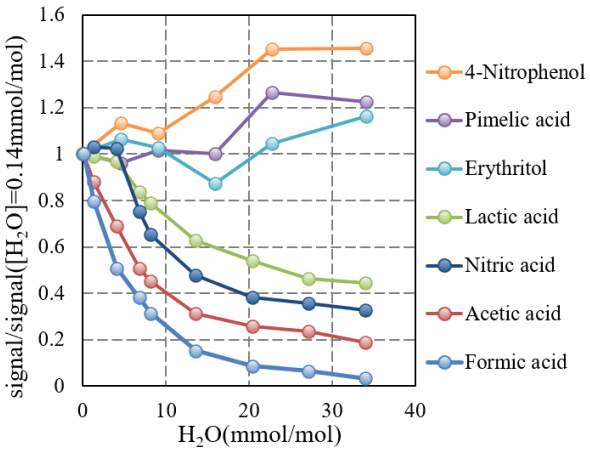

Figure S7. Humidity dependence of I-CIMS sensitivity for seven representative compounds. Signals are normalized to those measured under unhumidified dry-air conditions ([H_2O] = 0.14 mmol mol^{-1}).

2. We also performed an additional inlet-loss experiment using six surrogate compounds. Their signal changes between direct I-CIMS introduction and sampling through the 20.8-m PFA inlet ranged from −3.39% to +0.30%, indicating that bulk concentration losses were within 3.4%. Therefore, no additional concentration correction for tube loss was applied.

   Section 2.1 was expanded to include the PFA-tube concentration-loss experiment.

Reversible adsorption/desorption of OOMs on PFA tubing surfaces has been documented (Liu et al., 2019; Nguyen et al., 2015), primarily causing high-frequency flux attenuation while largely preserving bulk concentrations. 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.

3. After these corrections, the difference from previous forest-canopy measurements is substantially smaller than that reported in the original manuscript. The mean daily maximum formic acid mixing ratio at our urban site was 1.146 ± 0.166ppbv, compared with approximately 2.5 ppbv reported above forests. The corresponding mean daily maximum downward formic acid flux was 0.374 nmol m^{-2} s^{-1}, compared with approximately 1-2 nmol m^{-2} s^{-1} above forests. For the multi-species comparison, the summed downward and upward carbon fluxes of the 16 OOMs in our study were 0.60 and 0.34 nmol C m^{-2} s^{-1}, respectively, whereas the mean daily maximum flux of 85 I-CIMS-detected OOMs over a coniferous forest was approximately 2.5 nmol C m^{-2} s^{-1} for both directions (Vermeuel et al., 2023). We emphasize that these summed fluxes are not directly comparable because the two studies include different numbers and identities of OOM species.

   The above comparison was updated to line 371-379.

4. We therefore revised our interpretation. The OOM fluxes at this urban site were generally lower than those reported above forest canopies, but the differences were typically within one order of magnitude rather than one to two orders of magnitude. These differences may partly reflect contrasting source environments: forest-canopy flux measurements were conducted only a few meters above strong biogenic emission sources, whereas our measurements were made at a suburban university

campus distant from downtown areas, industrial zones, and major traffic emission sources.

Conclusion section was revised to discuss the comparison between the urban and forest-canopy observations.

5. Finally, we agree that the present measurements should not be generalized to urban environments as a whole. The site has heterogeneous surrounding land cover, and the 28-day summertime campaign cannot fully represent other urban surface types, seasons, or circulation regimes. We have therefore restricted our conclusions to this specific suburban urban environment and expanded the limitations discussion in Conclusion section. Year-round measurements are ongoing to assess the seasonal evolution of OOM fluxes and their dependence on meteorological, chemical, and circulation conditions.

   In line 503-516, we add:

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.

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 2

I do not understand section 3.2.2. Since water vapor has only a minor volume fraction (0.5-2 %), why is it hypothesized to have a significant influence on flux measurement? The authors conclude that the water vapor-induced bias is within 2%, consistent with my understanding. If I did not miss something important, please consider moving this section to the SI.

Response:

We apologize for the confusion caused by our previous wording.

The I-CIMS directly reports wet mole fractions (ppbv) for OOMs and HNO_3, whereas dry mole fraction is conventionally used in eddy-covariance flux calculations. We therefore calculated the fluxes in EddyPro using dry mole fraction and dry air density (dry formulation) and compared them with those calculated using wet mole fraction and wet air density (wet formulation). This comparison was designed to quantify the potential bias arising from the use of wet rather than dry quantities.

Atmospheric water vapor accounted for only approximately 0.5–2% of the air volume during the campaign. Consistent with this, our flux calculations showed that the water-vapor-induced flux bias was within ±2% for all examined species. All fluxes reported in the manuscript were therefore simply calculated using the measured wet mole fraction and wet air density.

In the revised section, we have revised the title of Section 3.2.2 from "Assessment of Water Vapor Dilution Effects" to "Assessment of Water Vapor Effects." to discuss both effects of atmospheric water vapor: (1) its influence on the quantitative determination of OOM mixing ratios through humidity-dependent I-CIMS sensitivity,

and (2) its influence on flux calculation through the use of wet versus dry mole fraction and air density.

Minor comment 1:

Line 62. "Full spectrum OOM flux measurements". It is better to avoid this discussion, as this challenge is not addressed in this study. Iodide CIMS detects only a subset of OOMs, and only 16 OOM fluxes are reported herein.

Response:

We agree with the reviewer. Full spectrum is now avoid throughout the manuscript.

In line 63-64,

"Full spectrum OOM flux measurements remain limited" is now revised to "Multi-species OOM flux measurements remain limited"

In line 372-374

"Mean peak total fluxes of full-spectrum OOMs detected by I-CIMS were around 2.5 nmol carbon m^{-2} s^{-1}" is revised to "Mean daily maximum fluxes of total 85 OOMs detected by I-CIMS were around 2.5 nmol carbon m^{-2} s^{-1}"

Minor comment 2:

Line 160. The same tube transport delay was applied to all analyzed species. This approximation is understandable, yet it would be interesting to see the delay for other species.

Response:

We assumed identical turbulent transport for all species passing through the same sampling tube and used HNO_3, with the highest SNR, as the reference tracer to calculate lag times. To validate this, we performed additional lag-time experiments by introducing HNO_3, formic acid, and acetic acid standards at the inlet of the 20.8-m PFA tube and measuring their responses with the I-CIMS. The three compounds exhibited essentially identical lag times (Figure S5), despite their different chemical properties and expected tubing interactions. This result suggests that, under our sampling

conditions, the transport delay is dominated by the common tubing/flow system rather than by strong species-specific retention.

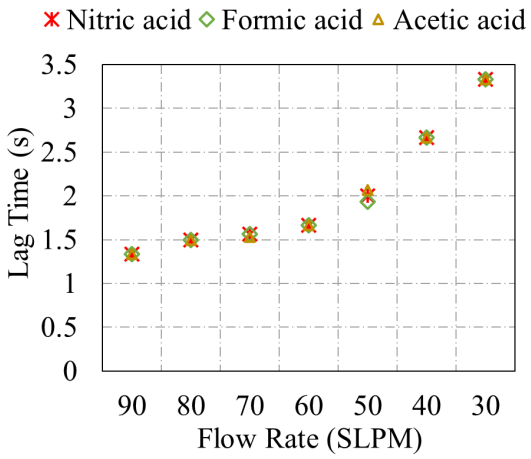

Figure S5. Lag-time measurements for gaseous nitric acid, formic acid, and acetic acid gas standards introduced at the inlet of the 20.8-m PFA sampling tube. Lag times were determined from the temporal delay between brief standard addition and the corresponding I-CIMS signal response. The three compounds exhibited essentially identical transport delays, indicating negligible species-dependent differences in lag time under the present sampling conditions.

We have added this validation experiment in line 188-194:

Following Fares et al. (2012), we assumed identical turbulent transport for all species passing through the same sampling tube. This assumption is partly supported by our direct lag-time measurements using brief pulses of gaseous nitric acid, formic acid, and acetic acid standards introduced at the inlet of the 20.8-m PFA tube; despite their different chemical properties, the three compounds showed essentially identical transport delays (Figure S5).

Fares, S., Park, J. H., Gentner, D. R., Weber, R., Ormeño, E., Karlik, J., & Goldstein, A. H. (2012). Seasonal cycles of biogenic volatile organic compound fluxes and concentrations in a California citrus orchard. *Atmospheric Chemistry and Physics*, *12(20)*, 9865-9880. https://doi.org/10.5194/acp-12-9865-2012

Minor comment3:

Figure S4. Although the results are not used, the transmission of species determined using the LSM spans 3-4 orders of magnitude. This seems to be different from previous studies (e.g., Heinritzi et al. 2016). What could be the reason, e.g., dataset or methods? Also, applying LSM to Eq. S2 may not be a good choice, as the matrix can sometimes be ill-conditioned. It may be better to use other inversion methods with constraints on smoothness. Nevertheless, this does not seem to affect the results and findings.

Response:

We would like to clarify that Figure S4 shows results from two different approaches: the unconstrained linear least-squares (LSM) solution, and the constrained-function solution. The latter was actually used for the transmission correction.

In the unconstrained LSM, the transmission coefficient at each mass is treated as an independent parameter. Because many mass channels have strongly correlated temporal variability, the inverse problem becomes poorly conditioned and the individual coefficients are not robustly constrained, resulting in the apparent 3-4-order-of-magnitude scatter. Similar instable unconstrained solution was also reported by Isaacman-VanWertz et al. (2018).

For this reason, we did not use the LSM-derived coefficients in our analysis. Instead, following Heinritzi et al. (2016) and Isaacman-VanWertz et al. (2018), we constrained T_M to a smooth Gaussian-like function of m/q. The resulting transmission coefficients for the target OOMs range 1.10 to 1.42 for the target OOMs, roughly consistent with the order of magnitude of Heinritzi et al. (2016) and Isaacman-VanWertz et al. (2018).

Heinritzi, M., Simon, M., Steiner, G., Wagner, A. C., Kürten, A., Hansel, A., & Curtius, J. (2016). Characterization of the mass-dependent transmission efficiency of a CIMS. *Atmospheric Measurement Techniques*, *9(4)*, 1449-1460. https://doi.org/10.5194/amt-9-1449-2016

Isaacman-VanWertz, G., Massoli, P., O'Brien, R., Lim, C., Franklin, J. P., Moss, J. A., Hunter, J. F., Nowak, J. B., Canagaratna, M. R., & Misztal, P. K. (2018). Chemical

evolution of atmospheric organic carbon over multiple generations of oxidation. *Nature Chemistry*, *10(4)*, 462-468. https://doi.org/10.1038/s41557-018-0002-2

Technical comment1:

Line 103: Remove "s" after the period.

Response:

Corrected.

Technical comment2:

Line 360: "Line 3.2.2" → "Line 3.3.2"

Response:

Corrected.