Sun et al. reported the OOMs flux measurements using the eddy covariance method and ICIMS. In this manuscript, the authors discussed the spectral analysis and flux loss correction, the influence of sampling frequency and water vapor, and the analysis of OOMs flux. The author claimed that they addressed the challenges of retrieving reliable fluxes for reported 16 OOM species, and the measured fluxes of 16 OOMs were significantly lower than those previously reported for forest environments. This manuscript presents an important contribution to OOM flux measurement methods and helps us understand surface-atmosphere exchange of OOMs. Based on this version, I think this topic is more relevant to the scope of Atmospheric Measurement Techniques rather than Atmospheric Chemistry and Physics. No matter what, I recommend that the manuscript be considered for publication after major revisions addressing the comments and concerns raised below.

Response:

We thank the reviewer for the positive assessment and constructive comments. Although the manuscript includes a methodological evaluation, its primary objective is not to develop new instrumentation or data-processing methods, but to apply eddy-covariance measurements to investigate the surface-atmosphere exchange of OOMs in an urban environment. The methodological analysis serves to ensure the reliability of the flux measurements, while the main scientific focus is on the magnitude, direction, and chemical characteristics of OOM exchange. We therefore believe that the manuscript fits well within the scope of Atmospheric Chemistry and Physics.

Major comments:

The author reported that the significant lower flux of 16 OOMs comparted to the forest region. My main concern was that these results was possible not realistic due to following details:

Overall response to the major concern:

We sincerely thank the reviewer for raising this important concern. The reviewer's comments prompted us to re-examine several key aspects of the I-CIMS quantification and flux retrieval, and to perform additional experiments during the revision. In particular, we conducted humidity-dependent sensitivity experiments, additional PFA-tube

concentration-loss tests, and compound-specific lag-time measurements. These new experiments revealed the most important issue in our original result: **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.**

After applying the experimentally determined humidity corrections, we recalculated all OOM mixing ratios and fluxes. The difference between our urban observations and previous forest-canopy measurements became substantially smaller than that reported in the original manuscript. For example, the mean daily maximum formic acid mixing ratio at our site was 1.146 ± 0.166 ppbv, compared with approximately 2.5 ppbv above forests. Our 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. The summed downward and upward fluxes of the 16 OOMs in our study were 0.60 and 0.34 nmol C nmol m^{-2} s^{-1}, respectively, compared with approximately 2.5 nmol C nmol m^{-2} s^{-1} for 85 I-CIMS-detected OOMs over a coniferous forest. We emphasize that the latter totals are not directly comparable because the two studies cover different numbers and identities of OOM species.

Accordingly, we have revised our conclusion: the urban fluxes were generally lower, but the differences were typically within one order of magnitude. The remaining differences may partly reflect the contrasting measurement environments: previous forest-canopy 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.

The detailed responses to each methodological concern, together with the corresponding additional experiments and manuscript revisions, are provided below.

Comment 1

The accurate calibration of 16 OOMs: in this study, the indirect calibrations would introduce much uncertainty.

Response:

We agree that indirect calibration introduces additional uncertainty compared with compound-specific calibration using authentic standards. However, authentic standards are

unavailable for most OOMs detected by I-CIMS, particularly for non-target OOM flux screening strategy used in our study. We therefore followed the collision-limited sensitivity calibration approach widely used in previous I-CIMS studies (Isaacman-VanWertz et al., 2018; Lopez-Hilfiker et al., 2016; Ye et al., 2021; Song et al., 2024; Wang et al., 2026). Direct calibrations of HNO_3 and formic acid using certified permeation tubes were also performed to validate this approach. The estimated overall calibration uncertainty was 33–65% (2σ, 95% confidence interval), depending on the target species (Text S5).

We acknowledge that the previous version did not sufficiently account for the humidity dependence of I-CIMS sensitivity, as both S_{max} and the direct calibrations of HNO_3 and formic acid were determined under dry carrier gas conditions.

The experiments by Lindsay et al. (2026)， Lee et al. (2014)， Ye et al. (2021), and Song et al. (2024) showed that water vapor can either decrease iodide-adduct sensitivity by competing with analytes for I^-, or increase sensitivity by stabilizing iodide–analyte clusters through third-body collisions, and the magnitude and direction of this effect are dependent on molecular structure, including the type and number of functional groups.

When revising the manuscript, we therefore conducted additional humidity-dependent experiments for seven surrogate compounds: nitric acid, formic acid, acetic acid, lactic acid ($C_3H_6O_3$), 4-nitrophenol ($C_6H_5NO_3$), pimelic acid ($C_7H_{12}O_4$), and erythritol ($C_4H_{10}O_4$).

The humidity-dependence experiment details are added as Text S6.

The experimental results are added in “3.2.2 Assessment of Water Vapor Effects”. All affected concentrations, fluxes, figures, tables, and related discussions have been updated throughout the revised manuscript.

“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."

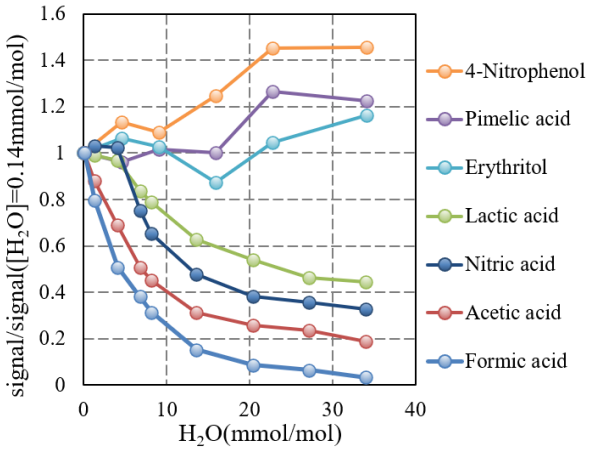

Figure S7. Humidity dependence of I-CIMS sensitivity for seven representative compounds. Signals are normalized to those measured under unhumidified dry-air conditions ([H_2O] = 0.14 mmol mol^{-1}).

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

Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T., Worsnop, D. R., & Thornton, J. A. (2014). An iodide-adduct high-resolution time-of-flight chemical-ionization mass spectrometer: Application to atmospheric inorganic and organic compounds. *Environmental Science & Technology*, *48(11)*, 6309-6317.

https://doi.org/10.1021/es500362a

Lindsay, A. J., et al. (2026). CIMS Detection of Hydroxymethyl Hydroperoxide: Insights into Alkene Ozonolysis in a Variety of Environments. *ACS Environmental Science & Technology Air*, *3*, 1832-1842. https://doi.org/10.1021/acsestair.6c00053

Lopez-Hilfiker, F. D., Iyer, S., Mohr, C., Lee, B. H., D'Ambro, E. L., Kurtén, T., & Thornton, J. A. (2016). Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts. *Atmospheric Measurement Techniques*, *9(4)*, 1505-1512. https://doi.org/10.5194/amt-9-1505-2016

Song, M., He, S., Li, X., Liu, Y., Lou, S., Lu, S., Zeng, L., & Zhang, Y. (2024). Optimizing the iodide-adduct chemical ionization mass spectrometry (CIMS) quantitative method for toluene oxidation intermediates: experimental insights into functional-group differences. *Atmospheric Measurement Techniques*, *17(17)*, 5113-5127. https://doi.org/10.5194/amt-17-5113-2024

Wang, Y., et al. (2026). Voltage scanning to calibrate Multi-Reagent Chemical Ionization Mass Spectrometers (MR-CIMS): from signal to sensitivity. *Atmospheric Measurement Techniques*, *19(13)*, 4583-4599. https://doi.org10.5194/amt-19-4583-2026

Ye, C., Yuan, B., Lin, Y., Wang, Z., Hu, W., Li, T., Chen, W., Wu, C., Wang, C., & Huang, S. (2021). Chemical characterization of oxygenated organic compounds in the gas phase and particle phase using iodide CIMS with FIGAERO in urban air. Atmospheric Chemistry and Physics, 21(11), 8455-8478. https://doi.org/10.5194/acp-21-8455-2021

Major comment 2

The interference of relative humidity: the author claimed a minor volume fraction (0.5-2 %) of water was hypothesized to have a significant influence on flux measurement. And the results showed that water vapor-induced bias is within 2%. This seems contradictory? How the author gets this result? Is it similar for CH_2O_2 and HNO_3, which were very sensitive to water?

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 results showed that the water-vapor-induced flux bias was within ±2% for all examined species. Specifically, fluxes calculated using the wet formulation were ~1.1% higher for HNO_3 (slope = 1.0108), ~1.2% higher for $C_4H_7NO_5$ (slope = 1.0122), and ~1.3% lower for CH_2O_2 (slope = 0.9871). All fluxes reported in the manuscript were therefore 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.

Major comment 3

The error of the peak fitting of ICIMS using high time resolution of 1 HZ or 10 HZ: in fact, ICIMS could provide 1 HZ or 10 HZ data, but during high time resolution, the mass spectrum fluctuate more serious, it would cause the fitting errors of target species.

Response:

We agree that, at high time resolution, fewer ions are accumulated in each 0.1-s mass spectrum, resulting in larger ion-counting fluctuations and increased uncertainty in high-resolution peak fitting. This peak-fitting uncertainty is an important contributor to the enhanced point-to-point fluctuations in the retrieved 10 Hz concentration time series, which is essentially the same high-frequency instrumental noise issue that we have explicitly investigated in the manuscript. In our study, we used SNR screening, spectral/cospectral diagnostics, and an independent 1-Hz peak-fitting analysis to evaluate its influence:

1. stringent criteria were applied during peak fitting and target-ion selection. Mass assignments were constrained to a mass error of <10 ppm. Only iodide-adduct ions with sufficient SNR at 0.1-s integration time were initially retained, species suffering from severe interference by adjacent peaks were discarded, and the selected target ions were subjected to a second round of refined peak fitting.
2. power spectral analysis was used to evaluate the remaining instrumental noise (Figure 1a). For example, $C_3H_4O_4$ with an SNR of 2.2 showed an almost completely noise-dominated power spectrum and was therefore excluded; accordingly, only OOMs with SNR >2.2 were used for subsequent flux analysis.
3. random peak-fitting/instrumental noise is expected primarily to increase flux uncertainty rather than systematically bias the EC covariance. If the measured concentration fluctuation is expressed as $c'_{\mathrm{meas}} = c'_{\mathrm{true}} + \epsilon'$, where ϵ' represents random instrumental/peak-fitting noise, then $w'c'_{\mathrm{meas}} = w'\bar{c}'_{\mathrm{true}} + \overline{w'\epsilon'}$. Because ϵ' is not expected to systematically co-vary with vertical wind velocity, mean contribution of $\overline{w'\epsilon'}$ to the EC flux should approach zero. Consistent with this expectation, Figure 1b shows that the noise-dominated high-frequency portions of our OOM ogives fluctuate around zero and contribute negligibly to the integrated covariance.
4. The comparison between the fluxes derived from the independently fitted 1-Hz and 10-Hz dataset demonstrates the trade-off inherent in reducing the mass spectral integration time: co-adding spectra improves the SNR and reduces peak-fitting fluctuations, but it also sacrifices high-frequency turbulent information and may affect spectral correction. We therefore retained the 10-Hz measurements for the final EC analysis.

High-time-resolution mass-spectrometric measurements are well established in previous EC studies. PTR-MS has been extensively used for VOC flux measurements at ~10 Hz, and previous studies have successfully applied field-deployable negative-ion CIMS at 5-10 Hz to measure fluxes of organic acids and other oxidized compounds (e.g., Fulgham et al., 2019; Nguyen et al., 2015; Schobesberger et al., 2016; Vermeuel et al., 2023). Thus, high-frequency CIMS measurement itself is feasible for EC applications, provided that SNR screening, peak interference, and spectral behavior are carefully evaluated, as done here.

We add line 238-245 to Section 3.1 to clarify the origin of instrumental noise:

For species with SNR > 2.2, the spectra flatten above ~0.1 Hz as instrumental white noise becomes dominant. At 10-Hz acquisition, fewer ions are accumulated within each 0.1-s mass spectrum, leading to larger ion-counting fluctuations and increased uncertainty in high-resolution peak fitting, particularly for low-intensity ions. This contributes to enhanced point-to-point fluctuations in the retrieved concentration time series and constitutes an important source of the observed high-frequency instrumental noise. Other instrumental fluctuations, such as detector and ion-source variability, may also contribute.

We revised line 292-297 in Section 3.2.1 to clarify the comparison between 10 Hz and 1 Hz fluxes was made using the 1-Hz dataset generated by co-adding raw mass spectra before independent peak fitting, rather than by averaging the fitted 10-Hz concentration data:

Because 10 Hz CIMS sampling introduces significant high-frequency noise, we tested whether increasing the spectral integration time could reduce this noise and thus improve flux retrieval. Specifically, every ten consecutive 0.1-s raw mass spectra were co-added to generate 1-s spectra, which were then independently peak-fitted to produce a 1-Hz concentration dataset. Fluxes derived from this independently processed 1-Hz dataset were compared with those obtained from the native 10-Hz peak-fitted dataset.

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

Schobesberger, S., Lopez-Hilfiker, F. D., Taipale, D., Millet, D. B., D'Ambro, E. L., Rantala, P., Mammarella, I., Zhou, P., Wolfe, G. M., & Lee, B. H. (2016). High upward fluxes of formic acid from a boreal forest canopy. *Geophysical Research Letters*, *43(17)*, 9342-9351. https://doi.org/10.1002/2016GL069599

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

Major comment 4

The interference of 20.8 m inlet tube: the Teflon tube could adsorb particles, and the residual time was evaluated to about 5 s based on the sampling flowrate, thus it would cause uptake and heterogenous reaction of OOMs in summer (with relative high temperature and relative humidity), resulting in concentration changes in OOMs rather than flux variation. Meanwhile, wall loss of the OOMs itself in long sampling tube induced the changes of fluxes.

Response:

We would first clarify that the nominal residence time in the 20.8-m PFA inlet was approximately 1.1 s rather than ~5 s, because ambient air was drawn through the 3/8-inch ID main sampling line at 80 SLPM. As already noted in the manuscript, previous studies (Liu et al., 2019; Nguyen et al., 2015) have shown that reversible adsorption/desorption of OOMs on PFA tubing primarily attenuates high-frequency concentration fluctuations rather than substantially changing the bulk concentration. Long PFA tubes have also been used in previous tower-based OOM flux measurements (Fulgham et al., 2019; Vermeuel et al., 2023).

To further evaluate potential OOM losses in the 20.8-m inlet, when revising the manuscript, we performed additional tube loss experiments with six representative compounds: formic acid (CH_2O_2), acetic acid ($C_2H_4O_2$), lactic acid ($C_3H_6O_3$), pimelic acid ($C_7H_{12}O_4$), erythritol ($C_4H_{10}O_4$), and 4-nitrophenol ($C_6H_5NO_3$). These compounds were selected, because they are themselves target OOMs with measurable fluxes or structurally similar surrogates of target OOMs. Their signals were measured by direct introduction into the I-CIMS and then after passage through the 20.8-m PFA tube. The relative signal changes were −1.49%, −3.36%, +0.30%, −3.39%, −1.42%, and −0.57%, respectively, i.e., within ±3.4% for all tested compounds. These results indicate negligible bulk concentration

loss through the inlet for the representative OOMs tested.

Although this experiment does not separately quantify particle-mediated heterogeneous chemistry, the short ~1.1 s residence time together with the small measured signal changes suggests that substantial inlet-induced changes in OOM concentrations are unlikely. The new inlet-loss test has been added to line 107-116:

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.

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

Liu, X., Deming, B., Pagonis, D., Day, D. A., Palm, B. B., Talukdar, R., Roberts, J. M., Veres, P. R., Krechmer, J. E., & Thornton, J. A. (2019). Effects of gas–wall interactions on measurements of semivolatile compounds and small polar molecules. *Atmospheric Measurement Techniques*, *12(6)*, 3137-3149. https://doi.org/10.5194/amt-12-3137-2019

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

Major comment 5

The influence of lag time: the author evaluated it based on HNO_3. My concern was that the reactivity of HNO_3 in the Telflon tube was different with OOMs, which would introduce inconsistence of concentration fluctuation.

Response:

We agree that compound-dependent interactions with the PFA tubing could, in principle, introduce species-specific transport delays. To directly evaluate this effect, 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. Therefore, using HNO_3 as the reference tracer for lag-time correction is supported by these direct measurements. We have added this validation experiment to 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).

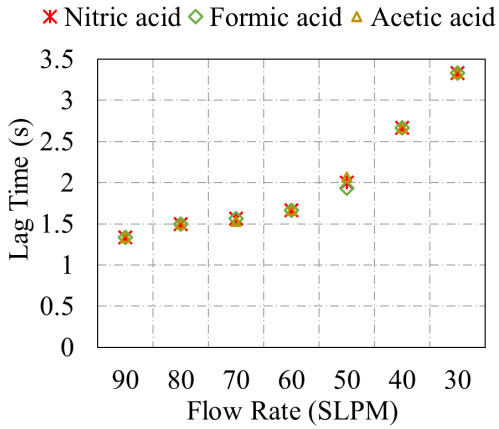

Figure S5. Lag-time measurements for gaseous nitric acid, formic acid, and acetic acid gas standards introduced at the inlet of the 20.8-m PFA sampling tube. Lag times were determined from the temporal delay between brief standard addition and the corresponding I-CIMS signal response. The three compounds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

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 comment 1:

The title using OOMs may be not accuracy. In the whole manuscript, it just discussed 16 OOMs.

Response:

We thank the reviewer for this comment. We agree that the original title could be interpreted as referring broadly to the entire atmospheric OOM pool, whereas only 16 selected OOM species with sufficiently reliable flux measurements are reported in this study.

We have therefore revised the title to "Urban surface-atmosphere fluxes of selected pptv-level oxygenated organic molecules from eddy covariance observations" to more accurately reflect the scope of the study.

Minor comment2:

Line 125, the author mentioned 21 OOMs, but 16 OOMs was discussed, please check.

Response:

The 21 OOMs refer to the target ions initially retained after peak fitting and preliminary SNR screening. Subsequent spectral analysis showed that species with SNR $\leq$ 2.2 were dominated by instrumental noise and were therefore excluded from flux analysis. This additional screening left 16 OOM species with detectable and reliable fluxes for further discussion. We have revised the text to clarify this selection procedure.

We have revised Sections 2.2.1, 3.1, and 3.3 to explicitly clarify.

In total, 21 target OOMs, in the form of iodide-adduct ions shown in Table S1, were selected for a second run of peak fitting to produce refined 10 Hz time series, which were used for subsequent spectral evaluation and flux analysis.

This spectral screening reduced the number of OOM species retained for flux analysis from 21 to 16.

After the above SNR and spectral screening, we observed 16 OOM species (including 12 CHO-OOMs and 4 CHON-OOMs) with detectable fluxes during the summer campaign.

Minor comment 3:

Section 2.2.2, it should provide the detailed calibration results of CH_2O_2 and HNO_3, and consider the effects of RH on calibration coefficient.

Response:

The calibration results of HNO_3 and formic acid was already provided in Supplement Text S5 and is now added in main text line 163-167：

To validate the approach, direct calibrations of HNO_3 and formic acid using certified Kintek permeation tubes yielded dry-condition sensitivities of 25 and 36 cps $pptv^{-1}$, respectively, which fall within the ±33% of the HNO_3 and formic acid response factors derived from our collision-limited sensitivity method (detailed calibration procedure in Text S5).

Please see our response to your earlier comment about RH effect. The addition of our RH experiment and result is now summarized in line 168-172:

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, see Text S6) and the result is further discussed in Section 3.2.2. Humidity corrected response factors of All target OOM are listed in Table S1.

Minor comment 4:

Section 3.1, the author conducted flux loss correction using 1 or 10 Hz. The time resolution of ICIMS could be 10 Hz? In Figure S6, what is the time resolution of OOMs and how to differentiate the noise of flux for $C_4H_7NO_5$, CH_2O_2, $C_3H_4O_4$?

Response:

The I-CIMS measured OOM concentrations at 10 Hz. Flux loss correction in Section 3.1 was made using 10 Hz data. We have clarified these in line 231-233:

Power spectra (w, T_s, HNO_3/OOMs) and cospectra (w-T_s, w-HNO_3/OOM) were computed via Fast Fourier Transform from 30-min 10-Hz fluctuation time series and averaged into logarithmically spaced frequency bins.

Each EC flux estimate was calculated using a continuous 30-min window within the 31-min ambient-sampling period of each 36-min measurement cycle. Therefore, the OOM flux time series has a temporal resolution of 36 min, with each flux estimate calculated from a continuous 30-min window of 10 Hz measurements. Regarding flux noise of each selected OOMs, the random uncertainty σ_F was calculated separately for each 30-min flux estimate, and its corresponding detection limit was defined as $2\sigma_F$. Thus, a flux was considered detectable only when its absolute magnitude exceeded the interval-specific $2\sigma_F$. Figure S6 shows $F \pm \sigma_F$, while Table 1 summarizes the mean detection limits and detection rate (the fractions of flux estimates exceeding their respective detection limits).

We have clarified these definitions in the revised text (line 121-125) and Figure S8 caption.

For each measurement cycle, one flux estimate was calculated using the 10 Hz data from a continuous 30-min window within the 31-min ambient sampling period. Thus, the flux averaging period was 30 min, whereas the measurement cycle was 36 min, yielding up to 40 flux estimates per day under continuous operation.

Minor comment 5:

Section 3.3, the author just mentioned the trends of OOM flux. No more detailed discussion was explored to clarify the variation reason, the influence of surface–atmosphere exchange for OOMs on their source or sinks, NPF, SOA formation, and etc.

Based on this version, I think this topic is more relevant to the scope of Atmospheric Measurement Techniques rather than Atmospheric Chemistry and Physics.

Response:

1. The causes of OOM flux variability: the heterogeneous land cover surrounding the site, together with the relatively short campaign duration, limits our ability to comprehensively disentangle the influences of different emission sources, meteorological conditions, and atmospheric circulation patterns. We therefore avoid over-interpreting the observed short-term variability. Year-round measurements are currently ongoing and will enable a more systematic assessment of the seasonal evolution of OOM fluxes and their dependence on meteorological, chemical, and circulation conditions.
2. Atmospheric-chemical implications: the causal chain is that surface–atmosphere exchange contributes directly to the source/sink term of the atmospheric OOM budget, thereby influencing OOM concentrations, which may subsequently affect processes such as NPF and SOA formation. The present study directly quantifies the surface exchange fluxes and thus provides quantitative constraints on this source/sink term. However, the subsequent effects of OOM concentrations on NPF and SOA formation are not the primary focus of this study. Moreover, we did not simultaneously quantify NPF or particles. We therefore avoid making quantitative claims about their effects on NPF or SOA formation. Instead, as stated in the Conclusion section, this work establishes the foundation for future studies. The measurements provide observational constraints for chemical transport models, which currently lack well-constrained parameterizations of OOM dry deposition because of the scarcity of field flux measurements.
3. Although the manuscript includes a substantial methodological evaluation, its primary objective is not to develop new instrumentation or data-processing methods, but to apply eddy-covariance measurements to investigate the magnitude, direction, and chemical characteristics of OOM surface–atmosphere exchange in an urban environment. The methodological analysis is necessary to establish the reliability of the flux measurements. We therefore believe that the main scientific focus of the

manuscript remains atmospheric chemistry and that the study is appropriate for *Atmospheric Chemistry and Physics*.