Review of "The critical role of oxygenated volatile organic compounds (OVOCs) in shaping photochemical O3 chemistry and control strategy in a subtropical coastal environment" by Hui et al.

The authors provide measurements of VOCs and OVOCs by PTR-MS (and GC) at a coastal urban-influenced site near Hong Kong. They use MCM box modelling to illustrate the importance of including a large range of OVOCs in models to accurately represent O3 formation. They provide quite a detailed discussion on the mechanisms through which OVOCs influence ozone formation. The paper is well written, though the discussion of the modelling could be shortened. The authors have a clear research question and use appropriate methods, but their data are not exactly suitable to provide an answer to their research question. There are large unclarities as to how the PTR-MS data was processed and how the large range of OVOCs was identified and quantified. Furthermore, instrument-specific product-ion distributions for different VOCs complicates the analysis and reduces confidence when associating an ion formula to a compound. This makes the modelling more complicated, and the conclusions of the paper may be in jeopardy. The authors should be given a chance to justify their methodology and how this affects the modelling.

The introduction reads very well.

L 94: The continuous field campaign spanned from September 4 to December 20 in 2021, covering three seasons: summer (September 4 - October 12), autumn (October 13 - December 1), and early winter (December 2 - December 20). Seasonal divisions was based on the timing of the first synoptic event, as detailed in our previous studies (Feng et al. 2023)

The categorisation of campaign dates by season seems strange. Figure S1 makes it clear though that the meteorological conditions (temperature largely) were summer-like and autumn-like during these time intervals. Maybe the authors could elaborate on their reasoning why they chose these dates, rather than just referring to Feng et al. Or include more meteorological details in the main manuscript as a figure?

L101: The sampling line was made of PEEK and the authors fitted a PTFE filter. Additionally it was heated to 80 degC.

Typically the inlet would be made of a larger and faster diameter PTFE tube, PEEK is considered stickier than PTFE. The community is split on the use of PTFE filters as to whether they affect the measurement or not. Additionally, heating the inlet to 80 degC bears the risk of evaporating organics from the aerosol phase into the gas phase. It would be important for the authors to include a short discussion here as to how their air inlet setup may have impacted the VOCs they measured.

L110: 98 Td may be considered as a low Td by some readers. Please compare to this paper: https://amt.copernicus.org/articles/12/6193/2019/amt-12-6193-2019.pdf

L121: There is a large change of transmission for compounds between m/z approx. 75 to 0. How did the authors determine the transmission of these lower mass compounds?

L125: The description of the quantification and identification of OVOCs lacks clarity. It underpins much of the modelling and the main message of the paper and needs improvement. A decision tree may be useful here.

1. Identification; Presumably the authors determined the mass of a compound by high resolution mass peak fitting. They then used an algorithm using combinations of elements to attain a mass close to the observed peak. This analysis is highly dependent on the accuracy of the mass calibration and the elements chosen and cannot differentiate isomers (e.g. types of monoterpenes). One compound might generate multiple product ions e.g. https://amt.copernicus.org/articles/18/1013/2025/ . So the approach taken by the authors may result in miss-identification. Note that product ions are highly dependent on instrument settings/operation.

2. Fragmentation; The C5H9+, commonly associated to isoprene, is also a common fragment from larger chain aldehydes e.g. https://amt.copernicus.org/articles/17/801/2024/ The PTR-MS analysis presented here does not allow to differentiate isoprene from these fragments and thus over-estimates isoprene in air measurements. These larger chain aldehydes are common emissions from cooking https://acp.copernicus.org/articles/24/4289/2024/. The authors loosely acknowledge the uncertainty related to isoprene fragmentation in Table S2, but it is unclear how this uncertainty is propagated into the modelling. The benzenoids also suffer from fragmentation and the PTR-MS analysis presented here does not allow to distinguish primary ion from fragments or the degree of fragmentation which is crucial for quantification.

3. Quantification; The authors apply a kPTR of $2 \times 10^{-9}$ cm3 s−1 for all non-calibrated compounds. Note they only calibrate for 19 VOC/OVOCs. A more accurate quantification could be achieved by using molecule specific kPTR rates e.g. https://www.sciencedirect.com/science/article/pii/S1387380616302494 and others. The authors should make it clear how much of the carbon mass or how many of the compounds (CxHyO1-3) is quantified in different ways using direct calibrations, molecule-specific kPTR or generic kPTR of $2 \times 10^{-9}$ cm3 s−1.

The authors acknowledge some uncertainty associated with this analysis, but the way this is dealt with is not clear or sufficient. E.g. "Most molecular formulas were therefore evenly distributed among potential isomers (e.g., phenols, nitrophenols)" – Conceptually this is incorrect as the isomer composition varies largely amongst different air masses and emission sources. This issue applies also to the monoterpenes. L135 to 142 reads well.

The reviewer acknowledges that the main compounds of interest may be quantified satisfactorily here for use in MCM modelling. If so, the authors should make it clear that the compounds they identified and quantified with high confidence are the ones important for O3 formation. If it turns out that the poorly quantified compounds are important for O3 formation, the conclusions from the paper are not as convincing.

It is not clear how the authors handled primary emissions e.g. isoprene and the oxidation products (MVK etc.) in the model and measurement. If the modelled and measured MVK etc. concentrations are similar, it increases the confidence that the isoprene measurements are not overly influenced by large chain aldehyde fragments.

L143; Have the authors considered comparing the GC measurements to the continuous PTR measurements to increase the confidence in their measurement e.g. for isoprene, monoterpenes, benzenoids etc.

L161; "VOC species from daytime canister samples were linearly interpolated to hourly resolution for the model input (Yang et al., 2018)" "These approximations were used primarily to

pre-run the model and were not expected to affect daytime simulation results (Chen et al., 2020)" – Can the authors provide more details how this was done please and how this could affect the conclusions from the paper?

L243 and onwards: Give the compound names these formulas have been identified as please.

L246; Could boundary layer height be influencing the diurnal variations?

L285: Given isoprene and monoterpenes show such a high RIR, uncertainties from their quantification/identification need to be assessed. See previous comment.

L293; "with limited consideration of OVOCs" – I agree with the other reviewer; Previous studies have included key OVOC species e.g. methanol, acetone and acetaldehyde. The novelty of this work lies in the inclusion of OVOCs which were previously not included and semi-quantified here with PTR-ToF.

Sections 3.2 and 3.3 read really well.

L415; "Sensitivity analysis revealed that Pnet underestimations without OVOCs constraints ranged from 43.4% to 52.1%, depending on whether the minimum and maximum photolysis frequencies or KOH values of potential isomers were assumed (Figure 4d)" It's great to have this sensitivity analysis, but the authors could have provided it at the beginning of the model discussion maybe? More technical details on the upper and lower bound constraints used in the modelling should be provided.

Sections 3.4 and 3.5 should be substantially shortened (e.g. by 30 %) as much if this feels like repetition.

The conclusion reads well

Data availability: Emailing the authors to obtain the data is not adequate, nor compliant with publisher's guidance. Please upload on a repository.