Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-152-RC2, 2020

Atmospheric Chemistry and Physics Discussions
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Interactive comment on "Measurement Report: important contributions of oxygenated compounds to emissions and chemistry of VOCs in urban air" *by* Caihong Wu et al.

Anonymous Referee #3

Received and published: 15 July 2020

This manuscript presents an analysis of atmospheric VOCs in Guangzhou over roughly a two-month intensive sampling period, Sept-Nov 2016. The authors use the significant uncalibrated and/or unattributed ion response from a high-resolution PTR-MS instrument to estimate the total OH reactivity and compare this quantity to a direct measurement.

This type of analysis has been published previously, as the authors acknowledge and rely upon as a basis for their own work. The combination of the setting of their measurements in the Pearl River Delta and the use of a state-of-the-art instrument make this manuscript scientifically important. The writing is clear and presented in a logical

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Discussion paper

format.

Generally, this manuscript is missing error analysis and an adequate description of the many ions that were observed. The authors often will make a simplifying assumption for their data to ease their analysis, but either do not provide enough information to allow the reader to evaluate this assumption (e.g. OH reactivities of detected ions) or perhaps over-simplify in spite of their own data indicating a more detailed analysis is warranted (e.g. assumed sensitivities). The authors provide only cursory description of measurement uncertainties, and instead rely upon the observed dynamic range of reported mixing ratios or signal in section 3.3 (Sources analysis of OVOCs). Even these ranges are dropped in 3.4 (OH Reactivity) and the results from this section, which hinge upon numerous assumptions presented earlier, are stated with far greater precision than is merited. This can be contrasted with other manuscripts that have previously presented this type of analysis (e.g. De Gouw et al., 2009) that the authors cite.

While I do have some criticisms of this manuscript, I believe that this work should be accepted for publication with revisions to address these issues.

Specific comments

Line 39-44. The authors cite a number of percentage contributions of OVOCs, HCs, etc. to the total VOC burden. These values are overly precise and lack a statement of uncertainty. Uncertainties should be in the abstract, and significant digits should be made appropriate based upon those uncertainties.

Line 108. “Field measurements were conducted . . .” Figure S1 shows a map of the local region but is never cited in the text.

Line 114. “commercial PTR-QiTof-MS”. The authors should provide a brief description of this instrument, specifically with regards to the meaning of “QiToF”.

Line 116. “Ambient air was continuously . . .” Figure S2 shows the plumbing scheme for the instrument but is never cited in the text.

Line 117. “Teflon tubing” Which type of Teflon tubing is this (e.g. PFA, FEP, PTFE)?

Line 119-120. “the PTR-ToF-MS automatically switched between H3O+ and NO+ chemistry every 10-20 minutes” The authors should provide a description of how this was accomplished, or a reference if this was previously published.

Line 127-129. “At this condition, the fractions of water-cluster ions are small, and the fragmentation of most VOCs product ions is not significant” This assumption is fundamental to the analysis presented in the remainder of the text, and the authors provide no evidence that this is true for their work. I would strongly suggest that they show some metric of the fragmentation and clustering that their instrument produced. A simple means would be to show the mass spectrum during a zero and calibration with known mixture (e.g. Apel Riemer standard) and quantify the ion(s) from each calibrant species.

Line 130-131 “The additional species measured by NO+ chemistry are discussed in a companion paper (Wang et al., 2020).” I did not find this listed in the reference section.

Line 153-154. “A total of 56 non-methane hydrocarbons (NMHCs) were measured using a gas chromatography-mass spectrometer/flame ionization detector (GC-MS/FID) system.” This description could use a few more details: at least sample frequency, sample collection time and volume.

Line 158-160. “formaldehyde was also measured by a custom-built online instrument based on the Hantzsch reaction and absorption photometry from October 16 to November 20, 2018.” Is there any reference for this instrument? Can the authors provide LOD, sensitivity and/or accuracy for this measurement if not?

Line 164-165. “Formaldehyde measured by PTR-ToF-MS shows reasonable agreement with the Hantzsch formaldehyde instrument.” The authors do not provide slopes for any of the plots in Figure S5 to allow the reader to evaluate. In particular, the slope of the formaldehyde inter-comparison looks to be approximately 2.5, which would not be a “reasonable agreement”. The authors should discuss this discrepancy between the techniques, as the absolute mixing ratio of formaldehyde is important to understanding overall OH reactivity.

Line 191. “3.1 Characteristics of selected VOCs” Throughout this section, I found it difficult to understand which instrument was used to produce the data discussed. For example, line 194 (“Diurnal variations of hydrocarbons”) is this NO+ PTR data or GC; line 203 (“The diurnal variation of aromatics”) is this PTR or GC data?

Line 215-217. “The estimated OH concentration is in good agreement with simulated average OH concentration during the same period using an observation-constrained box model” The authors should provide further description and/or reference to this model.

Line 260. “A peak list with more than 1700 ions was used to perform high-resolution peak fittings” Please cite the software used for peak fitting.

Line 268-269. “We also tried the method proposed in Sekimoto et al. (2017), but no clear relationship between calibration factors and their capture kinetic rate constants was derived.” This is a surprising result. Do the authors understand why no relationship was found?

Line 270-271. “Therefore, we used the average calibration factor of 4170 cps/ppb to quantify those species without external calibration measured by PTR-ToF-MS.” The authors should estimate the uncertainty of the cal factor and propagate that uncertainty throughout the ensuing discussion. Also, Table S1 shows that organic acids and N-containing species typically had sensitivities significantly lower than 4000 cps/ppb. Does this imply that a single calibration factor is appropriate across all of the binned formulas discussed later?

Line 273-274 “We divided the VOCs measured by PTR-ToF-MS into groups according to the oxygen atoms in the formula” This analysis assumes that fragmentation and clustering are insignificant contributors to the mass spectra of ambient air. As noted above, the authors should defend this assumption and/or provide some measure of the uncertainty of their assumption.

Line 284 “The low contributions from OVOCs with three or more oxygen atoms are different from the concurrent observations of iodide ToF-CIMS during the campaign” This is the only mention of the IâĂŤCIMS instrument that I can find in the manuscript. The authors should provide some description of this instrument in Section 2, especially the inlet used by the I-CIMS as that would be relevant to the discussion here. The language in this comparison of relative abundance of more-highly oxidized OVOCs implies that the PTR method is less sensitive to these species due to losses. The authors should also consider that the I-CIMS technique is relatively insensitive to less oxidized OVOCs.

Line 308-309. “If only considering the six common OVOCs measured by PTR-MS, i.e. formaldehyde, acetaldehyde, methanol, acetone, MEK and MVK+MACR”. Where do the authors get this list of OVOCs? They should cite the reference, or the survey of references used for this.

Line 313. Source analysis of OVOCs. This section describes an analysis method that attributes OVOC sources to primary anthropogenic, secondary formation, biogenic and background. An implicit assumption here is that a single anthropogenic tracer (acetylene or CO) can characterize all primary anthropogenic emissions. That is, primary anthro emissions are homogeneous for the sampling site. The authors should state this in the text.

Line 377-378. “An effective OH rate constant of 2×10-11 cm3 molecule-1 s-1 was applied for different ion groups.” It is not clear how this value was determined to be appropriate. Please provide some rationale for using this value.

Line 394. “VOCs reactivity can visually and effectively characterize” It’s not clear what the authors mean by “visually” here.

Line 809. Figure 2. This appears to be GC data, based upon the species shown (e.g. isomers). The authors should state explicitly if this is the case. Also, In Figure 2b, the labeling of some dots in the figure seems arbitrary. Consider limiting labels to those species discussed in the main text or significant outliers, e.g. the point in the top right corner, which seems a significant, and perhaps interesting, outlier to the overall good fit of the data.

Line 820. Figure 3. I found this figure difficult to interpret as the colors are similar and the figure is highly detailed. My suggestion: could the authors reformat as a stacked-axis plot, with the five categories of ions on their own y-axis?

Line 823. Figure 4. The pie charts in (a) and (c) don’t seem to match the diurnal trends in (b) and (d), respectively. The mixing ratios shown in (b) and (d) would imply different sizes of the wedges that make up each pie chart than are shown. Perhaps I am mis-interpreting what is presented? Supplement, Table S4. I found this table to be especially problematic, as the authors provide an enormous list of ions with associated OH reactivities. Since the authors never attribute a parent molecule to these ions, this makes these attributions impossible to evaluate. For comparison, Koss et al. (2018) provides a similar table in their supplemental materials, but also provides a master table that links each ion with a suspected or confirmed parent. The authors should revise this table to give a suspected / confirmed parent in each case.

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