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Interactive comment on "Surface–atmosphere fluxes of volatile organic compounds in Beijing" *by* W. Joe F. Acton et al.

Anonymous Referee #2

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This manuscript presents the VOC concentration and flux measurements using a PTR-MS at a tower in Beijing during the China-UK APHH summer and winter campaigns. Large concentrations and fluxes of small OVOCs were measured in both winter and summer. The measurements also show high concentrations of isoprene and aromatics in both summer and winter, although the surface-to-air fluxes were small. The authors compared the results to the fluxes predicted by the MEIC (anthropogenic) and MEGAN (biogenic) emission inventories and attempted to explain some of the discrepancies.

The topic of the manuscript is of interest to the community and certainly within the scope of ACP. The measurement methodology and analytical methods are standard. Most of the results appear reasonable. However, the interpretation of the isoprene and aromatic sources have some contradictions with previous studies and the known

characteristics of the urban site, warranting more in-depth analysis. Also, the writing has a fairly large number of errors in grammar and punctuation usage. The senstences were often too long and commas are often missing. I therefore recommend that the paper undergo major revision to address some of the key issues and also to improve the writing.

Major comments:

Figure 3a: Why was the timeseries of the meterological variables drawn for November 16 to December 7 for the winter campaign? This does not match the duration of the winter campaign nore that of the PTR-MS measurements stated in lines 254-255.

Lines 308-309: "In addition, isoprene, which has both biogenic and anthropogenic sources, had a median mixing ratios of 1.08 and 0.38 ppb in the winter and summer campaigns respectively.": This is an interesting result. Although several studies have indicated possible anthropogenic emissions of isoprene (potentially related to traffic), the origin of this anthropogenic isoprene have not been fully explored. Most researchers still predominantly associate isoprene with biogenic emissions. Also, I do not think I have ever seen isoprene concentrations this much higher in winter (median 1.08) than in summer (median 0.38). Could the authors elaborate a little on this anthropogenic isoprene? Were there strong correlations between isoprene concentrations or fluxes with other source-specific VOCs? Figure 5 shows that there was not a strong positive flux of isoprene in winter. This contradicts (1) the findings from previous studies suggesting that the anthropogenic isoprene is traffic-related, and (2) the fact that the IAP tower is located near major roads with heavy traffic (major ring roads within its 1-2 km flux footprint). Also, it would be helpful to cite some key reference on the anthropogenic isoprene source in lines 308-309.

Lines 346-348: "The weak VOC flux observed in the winter may, in part, be caused by low volatilisation of VOCs in winter conditions, where the average temperature was 3.6 °C compared to 25 °C in the summer.": But most of the the species shown in Fig 5 and

Table 2 should be sufficiently volatile even at 3.6oC (e.g., methanol, ethanol, acetaldehyde, etc). I think, to be more illuminating, the authors should state the known major sources of these low-molecular-weight organics and indicate whether those sources are smaller in winter.

Lines 380-384: What seasons were these measurements conducted?

Lines 386-388: If the anthropogenic contribution of isoprene is so significant at this site in winter (especially given the much larger concentration in winter than in summer), how can one catagorically label isoprene as biogenic, even in summer?

Lines 399-401: "The relationship between the fluxes of VOC species which contribute more than 0.75% to the total measured VOC flux and 400 the NOx flux in the summer measurement period is shown in Fig. 7.": This sentence is grammatically incorrect and therefore impossible to understand. Please kindly revise.

Lines 402-403: "NOx in urban areas is a combustion product so the NOx flux is used here as proxy for combustion sources of pollutants": At this site, the NOx flux is most strongly a proxy for vehicular emissions.

Lines 426-428: "The close correlation with the NOx flux and aromatics such as toluene suggests a combustion source contributes to the total methanol flux but the summer methanol flux also correlates well with small oxygenated VOCs such as acetaldehyde.": What is the evidence for the first half of this statement? Particularly since it contradicts the second half of the sentence.

Section 3.4.3: Again, I think the source of isoprene at this IAP site should be more carefully interpreted, given that a large concentation was observed in winter.

Lines 468-470: "The low winter isoprene flux suggested a small contribution of anthropogenic isoprene to the total flux.": I am not convinced. Previous studies indicate that the anthropogenic emission of isoprene was vehicular. And this IAP tower site should be strongly affected by traffic emissions.

Lines 485-488: "The flux predicted by MEGAN over-estimated the observed flux with the modelled mean diurnal isoprene flux peaking at 21 nmol m-2 s-1 compared to the measured isoprene flux which peaked at 14 nmol m-2 s-1 (Fig. 8b).": How does the measured flux in summer compare with the top-down estimates using satellite-based observations by Cao et al. (2018)?

Lines 512-514: "The POCPs and PPCPs of 120 organic compounds were reported by Derwent et al. (1998) for UK conditions of the 1990s, and in the absence of more Beijing-specific data these were used to scale both the mixing ratios and the fluxes emitted within the flux footprint of the individual observed VOCs." What were the NOx levels used in the Derwent et al. (1998) calculation, and how different was it with the present-day Beijing NOx levels? Also, how long were the POCPs and PPCPs calculated for in Derwent et al. (1998), i.e, were these ozone produced over a day or several days? This makes a difference because methanol and other VOCs measured in abundance in this campaign have lifetimes > 1 day. Using 1-day POCPs and PPCPs would estimate the ozone and PAN production potentials on a local scale.

Lines 547-549: "Whilst activity data is often relatively well constrained at national level, its spatial disaggregation often relying on simplified proxies such as population density, adds significant additional uncertainty for the estimate of the emission for a given location.": The emission ratios (i.e, source species profile) for different NMVOC species may present an even larger uncertainty to the final inventory.

Lines 575: "Measured emissions of aromatic compounds were 3% and 4% of those predicted by the inventory for TOL and XYL (low mass and high mass aromatics).": This is very surprising, unless the high-resolution version of MEIC placed a disproportionally large emission near the IAP site. Several previous studies have indicated at least some underestimation of Chinese aromatic emissions in MEIC or its predecessor inventory (Liu et al., 2012; Cao et al. 2018).

Lines 579-580: "Industrial emissions make the largest contribution to aromatic VOC

emission in the inventory.": Is this statement drawn from the numbers for the local grids, or from the national inventory? The authors measurements clearly show that the aromatics were traffic-related, and I think the same was true in the MEIC inventory.

Section 3.5: There has been several studies using formaldehyde and glyoxal observed by satellite instruments to constrain NMVOC emissions in a top-down fashion. While the resolutions were very different from those here, it might still be helpful to compare their results with the measurements here.

Lines 646-649: "The relatively small emissions of anthropogenic VOC species from central Beijing compared to the large mixing ratios observed suggest that the scope for policy interventions focusing on VOC emission from central Beijing is limited and that the focus must therefore be on emissions controls in regions surrounding the megacity.": Is this conclusion consistent with the observed high toluene emission and its high correlation with NOx (traffic)?

Minor comments:

Line 129-130: Is it possible that there is a negative bias of semi-volatile organics by filtering PM2.5?

Line 233: "Loss of high frequency flux was due to measuring at 5 Hz was estimated to be less than 10%.": missing 'and' between '5 Hz' and 'was'.

Line 234: "Squires et al. (2020) estimated that the average the time taken for an air parcel ...": remove 'the' before 'time'

Line 238: "quality-assessed"

Line 242-244: I do not understand why the quality control for flux was done on a 'file' basis. How long is the record in each file? Shouldn't the quality control be done on a certain timescale?

Lines 348-349: "In the winter the positive (emission) flux of VOCs from the city is likely

suppressed by deposition of VOCs transported at, high concentrations, from outside of the city.": This sentence is unclear; maybe because the first comma is misplaced?

Lines 349-351: "While most mean winter VOC fluxes remained positive this term will be a balance between emission from the city and deposition of VOCs transported into the footprint region.": I do not understand this sentence. Please kindly clarify.

Line 372: Missing comma after "In the summer campaign"

LIne 377: "can't" should be cannot

Reference: Cao, H., T.-M. Fu, L. Zhang, D. K. Henze, C. Chan Miller, C. Lerot, G. Gonzalex Abad, I. De Smedt, Q. Zhang, M. van Roosendael, K. Chance, J. Li, J. Zheng, and Y. Zhao (2018), Adjoint inversion of Chinese non-methane volatile organic compound emissions using space-based observations of formaldehyde and glyoxal, Atmospheric Chemistry and Physics, 18, 15017-15046, doi:10.5194/acp-18-15017-2018.

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