

This document includes the authors' responses to both reviewer 1 and reviewer 2. Reviewers' comments are in bold text and the authors' responses are in plain text. Text taken from the manuscript is presented in quotation marks. The updated manuscript is presented below with changes to the text highlighted in yellow.

Response to RC1: Erik Velasco

This manuscript presents eddy covariance flux measurements of volatile organic compounds (VOCs) over a district of Beijing, China. The eddy covariance method has been widely used to measure urban fluxes of carbon dioxide (CO₂) during the last 1-2 decades, but only a handful of studies has measured fluxes of VOCs. In this context, the material presented in this manuscript gains relevance and should contribute to improve current knowledge on emission patterns of precursor species, as well as provides unique data to evaluate the accuracy of gridded emission inventories. However, before the manuscript can be considered for further revision and potential publication, the authors need to address the following issues. Details are provided in the specific comments.

Response: The authors thank the reviewer for their constructive comments and for taking time to review the manuscript, responses to specific comments are set out below.

- **The authors need to explain the advantages and disadvantages of the eddy covariance method with respect to other methods to evaluate urban emissions. The conditions in which eddy covariance flux towers can be installed need a close revision. A full understanding of the eddy covariance assumptions is also needed.**

Response: The introduction has been expanded to give a description of the advantages of eddy covariance flux measurement and to highlight previous flux measurements made in urban environments. The site description has been expanded to include discussion of the flux inlet location relative to the height of surrounding buildings.

Introduction:

“Until comparatively recently it was very difficult to validate VOC emissions inventories at the cityscape scale, but the development of the PTR-TOF technology now allows VOCs to be measured with sufficient time resolution for flux estimates to be made using the method of eddy covariance based on simultaneous micrometeorological measurements. Although the conditions under which eddy covariance can be applied in the heterogeneous city environment are somewhat limited by flow interferences from neighbouring buildings, night-time boundary layer stability and other considerations, the method has been successfully used for estimating both CO₂ fluxes (e.g. Song et al., 2013; Liu et al., 2012a; Song and Wang, 2012) and VOC fluxes (e.g. Velasco et al., 2005; 2009; Langford et al., 2009; Valach et al., 2015; Vaughan et al., 2017; Karl et al. 2018). However, VOC flux measurements have not previously been attempted in Beijing.”

Site description:

“The IAP mast was used for the flux measurements as it allowed the sampling inlet and sonic anemometer to be positioned in the constant flux layer. The flux inlet was located at 102 m, this is over twice the mean height (45 m) of the tall residential building to the southwest (Liu et al., 2012a) and below the mixing layer height (Squires et al., 2020).”

- **The facilities used in this study to deploy the eddy covariance system to measure fluxes of VOCs have been previously used to measure fluxes of CO₂ (e.g., Song et al., 2013; Liu et al., 2012; Song and Wang, 2012). A review of such studies is recommended.**

Response: A short discussion of the CO₂ fluxes made at this site has been added to section 3.4.

“Fluxes of CO₂ have been previously recorded at the IAP field site (Liu et al., 2012; Song and Wang, 2012; Song et al., 2013). Liu et al. (2012a) reported four years of CO₂ eddy covariance measurements showing a seasonal variation in emissions driven by winter heating and uptake of CO₂ by vegetation in the summer. Spatial variation in emission was shown to be determined by the surface cover and that the diurnal profile of emissions was largely dependent on traffic volumes.”

- **Previous articles describing VOC flux measurements by eddy covariance in Mexico City (Velasco et al., 2005, 2009) and Innsbruck (Karl et al., 2018) could be used as references to analyze and present the results of this study. The fluxes reported for Mexico City provide valuable information to compare the fluxes observed in Beijing considering that both are large cities of developing nations. Similarly, the way Karl et al. (2018) analysed and presented a large number of VOC species could be followed.**

Response: Discussion of the VOC fluxes has been expanded to include comparison with the measurements made in Mexico City. Reference to Karl et al. (2018) was included in the discussion (line 384 of the ACPD version). The PTR-QiTOF used by Karl et al. (2018) allows a 10-fold decrease in the flux detection limit when compared to first generation PTR-ToF-MS instruments such as the PTR-TOF-MS 2000 used in this study. Therefore, while Karl et al. detected ~300 ions which were then included in their flux analysis, in this study we identified 65 masses with a median relative random error of less than 150%. Due to this limitation, we focused this study on identifying the dominant VOC fluxes and understanding their impact on atmospheric chemistry as opposed to the detailed analysis of all masses provided by Karl et al. (2018).

- **The discussion is biased to VOC studies in cities from UK. The manuscript will be strengthened if the findings are compared to results of previous studies conducted in China and other large cities. For example, the relationship between mixing ratios of selected VOC species has been widely used as a mean to evaluate the characteristics of urban emissions (e.g., Parrish et al., 2009; von Schneidemesser et al., 2010; Velasco et al., 2007).**

Response: The discussion is limited by the manuscript’s focus on VOC flux measurements, with VOC mixing ratios described only to provide context to the fluxes. There are a limited number of studies reporting VOC fluxes in urban areas and we thank the reviewer for drawing our attention to the pioneering studies in Mexico City (see previous comment). Parrish et al. (2009) and von Schneidemesser et al. (2010) have been added to the introduction to provide additional context to this study. Reference to the influence of different VOC chemical groups on ozone production in Mexico City (Velasco et al., 2007) has been added to section 3.4.4. As suggested, we have expanded the discussion of VOC mixing ratios in section 3.3 to make reference to studies conducted in China.

- **The authors need to demonstrate that the eddy covariance set up faithfully captures the entire range of energy-carrying eddies through inspection of the (co)spectra of the measured variables, and therefore is capable of measuring meaningful and representative turbulent fluxes. Similarly, a comprehensive description of the monitored footprint is needed to explain the observed fluxes.**

Response: Many thanks for the reviewer’s suggestions, which we used as an opportunity to provide additional technical information in the manuscript. We updated section 2.5: Flux calculation to read:

“This loss of low frequency flux was investigated by Squires et al. (2020) who found that at the 102 m measurement height the flux loss was ca. 7%. Due to similarity of the transport mechanisms underlying the low frequency flux loss (e.g., Mauder et al., 2020) we assume this estimate to apply also to the simultaneously measured VOC fluxes presented here. We did not correct the fluxes presented in this paper for low frequency flux loss. We further investigated the effect of high-frequency spectral loss on the VOC fluxes using a wavelet-based methodology (Nordbo and Katul, 2013). Loss of high frequency flux due to measuring at 5 Hz was estimated to be less than 10%, which we did not correct for in the presented fluxes.”

The reviewer points out the importance of “measuring meaningful and representative turbulent fluxes”, to which we agree wholeheartedly. We would like to point out that in addition to flux spectral losses and footprint, flux data quality considerations are also important to achieve this goal. For this purpose we quality control our results using tests for covariance stationarity, atmospheric connectivity between emissions from the surface and their measurement in the boundary layer, and the flux random error. We already describe these procedures in Sect. 2.5. Flux calculation.

We believe that Sect. 3.2 Flux footprint provides a comprehensive account of the monitored footprint to explain the observed fluxes. There, we display and discuss the campaign mean flux footprint climatologies for the winter and summer field campaigns. Because we adopted the footprint results of Squires et al. (2020), we point to their publication for even more information. We feel that reciting additional details of the Squires et al. (2020) study would be at the expense of conciseness and accessibility for a substantial fraction of the readership.

- **The writing needs some improvement.**

Response: The manuscript has been proofread and the writing has been improved.

Specific comments (page, line)

2,35. The abstract can be shorter. The first paragraph provides generic information. For example, the severe air pollution problem of Beijing is well known, and there is no need to specify in which institute the measurements were conducted.

Response: As suggested the abstract has been shortened, removing the description of severe air pollution in Beijing and the institute where measurements were made.

2,51-52. In which aspects, magnitude or/and temporal distribution?

Response: Magnitude. This has been clarified in the text.

2, 68-69. Urban emissions have been widely evaluated through a number of direct and indirect methods. A brief discussion on the emissions data provided by those methods in comparison to the data obtained from eddy covariance flux towers will put in context the information presented in this study.

Response: This line has been removed and the discussion of urban VOC emission has been expanded. See response to previous comment for details.

3, 72-74. Be more specific, vehicular exhaust no. 1 and vehicular exhaust no. 2 do not provide major information.

Response: The factor names as determined by Wang et al. (2015) and quoted here are: “gasoline evaporation and vehicular exhaust no. 1” and “vehicular exhaust no. 2”. Both factors contain compounds associated with vehicular exhaust (pentanes, acetylene, benzene, and toluene in factor 1; acetylene and C2-C4 alkanes in factor 2). The compounds associated with each factor have been added to the manuscript.

“A positive matrix factorization (PMF) model applied by Wang et al. (2015) identified four major sources of VOCs in Beijing: two transportation factors denoted “gasoline evaporation and vehicular exhaust no. 1 (containing pentanes, acetylene, benzene, and toluene)” and “vehicular exhaust no. 2 (acetylene and C2-C4 alkanes)”, “natural gas and liquid petroleum gas use and background” and “paint and solvent use and industry”.

3, 78-79. One of the main goals of the quality monitoring is to evaluate the effectiveness of the control measures in place. Many cities around the world have made important investments to build air quality monitoring networks to measure and report hourly concentrations of key airborne pollutants, including particulate matter and speciated VOCs.

Response: It’s true that the evaluation of the effectiveness of control measures is one of the main objectives of air quality monitoring. We feel that it is fair to say that it can be difficult to determine the impact of specific measures. The large scale short term measures applied in Beijing are unusual and warrant discussion in the context of this paper.

3, 93. Activity data?

Response: “Activity factors” changed to “Activity data”

3, 95-97. The application of the eddy covariance method to evaluate the accuracy of gridded emission inventories of VOCs in urban areas was done by first time in Mexico City (see Velasco et al., 2005, 2009).

Response: This sentence has been removed and reference to Velasco et al., 2005 and 2009 has been added to section 3.5.

3, 99-106. A statement of the hypothesis to test including the study objectives in context of the APHH project will help to analyze the flux observations and reach strong conclusions.

Response: A statement of the objectives of this study has been added to the introduction.

“The objectives of the study were to measure the surface-to-atmosphere fluxes of VOCs using the method of eddy covariance at a site in Beijing where a very comprehensive suite of atmospheric, physical and chemical parameters were assessed by the wider APHH-Beijing project team, and to use these data to assess the validity of a widely used emissions inventory”

4, 100-119. Why was the AIP site selected to deploy an eddy covariance system? Does it meet the eddy covariance assumptions of homogeneity in terms of land cover and emissions distribution? A much more comprehensive description of the monitored site is needed. Information of the land cover distribution, urban morphology, roughness elements, trees characteristics, vehicular traffic, population density, etc. is needed. Please, consider the Local Climate Zone classification (see Stewart and Oke, 2012).

Response: This section has been updated to provide a more detailed description of the site.

“Measurements of VOC mixing ratios and fluxes were made during two intensive measurement campaigns (winter: 12/11/2016 - 10/12/2016; and summer: 15/05/2017 - 24/06/2017) from a 325 m

high meteorological mast located on the campus of the Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP) in Beijing (39°58'33"N 116°22'41"E). This site was used as the main sampling site for all APHH-Beijing programme activities (see Shi et al., 2019). The campus is situated north of central Beijing between the 3rd and 4th ring roads, with parkland to the east and west and a mix of dense residential and commercial (restaurants and shops) buildings to the north and south. Busy roads are situated 120 m north and 300 m east of the mast. For comparative purposes, the sampling location can therefore be described as being “urban background” with respect to ambient concentrations for central Beijing with the main sampling inlet being significantly elevated above ground level. Flux measurements of CO₂ have been made previously at this site (Song and Wang, 2012; Liu et al., 2012a; Song et al., 2013). The fractional land cover within 2 km of the tower was assessed by Song and Wang (2012) and found to be buildings (0.65), vegetation (0.23) and roads (0.12). Using the local climate zone (LCZ) classification system described by Stewart and Oke, (2012) this area can be classified as LCZ2 “compact mid-rise” becoming LCZ1 “compact high-rise” to the south west. The aerodynamic roughness lengths were calculated by Li et al. (2003) as cited by Liu et al. (2012) and found to be 2.5, 3.0, 5.3 and 2.8 m from the north east, south east, south west and north west respectively with the zero-plane displacement heights of 12.3, 15.0, 26.4, and 13.2 m respectively. The flux inlet was located at 102 m, this is over twice the mean height (45 m) of the tall residential building to the southwest (Liu et al., 2012a) and below the mixing layer height (Squires et al., 2020) positioning the inlet in the constant flux layer.”

4, 117-118. Urban background in terms of ambient concentrations or urban fluxes?

Response: With respect to ambient concentrations. This has been clarified in the text.

4, 126. ‘... at a height of 102 m above ground level’ was mentioned in the previous paragraph.

Response: This has been removed from the previous paragraph.

5,155. The legend should guide readers to understand the sketch of the sampling system presented in this figure without need of going back to the text.

Response: The legend has been expanded to give a description of the inlet setup.

“Figure 1: Schematic of the gradient sampling system. The PTR-ToF-MS inlet was switched between a common flux inlet line (40 min) and a gradient switching manifold (20 min) in an hourly cycle. The gradient system sampled from five heights into 10 stainless steel containers.”

5, 162-163. You may consider moving this table to the main article since it is the only material presented as Supplementary Information.

Response: In response to a comment below the supplementary information has been expanded so this has been left in the SI.

7, 200. The pioneering studies in Mexico City mentioned in a previous comment were done using the disjunct eddy covariance method and the original PTR-MS instrument.

Response: Thank you for drawing our attention to these studies, references to Velasco et al. 2005 and Velasco et al. 2009 have been added here.

7, 201. A detailed description of the flux data postprocessing? The eddy covariance method does not estimate fluxes, does measure fluxes.

Response: “estimation” has been changed to “measurement”. The flux data post-processing is described in the following paragraphs (lines 225 to 249 in the ACPD version). Storage below the measurement height was calculated and added to the flux. The flux limit of detection was calculated and fluxes failing the stationarity test described by Foken and Wichura (1996) and falling below a u^* threshold of 0.175 m s^{-1} were filtered.

7, 203-204. Turbulent fluxes are computed using instantaneous deviations or fluctuations of the vertical wind velocity and VOC mass density (e.g., mg m^{-3}).

Response: This has been corrected to show that turbulent fluxes were computed using instantaneous deviations or fluctuations of the vertical wind velocity and VOC concentration (nmol m^{-3}).

7, 211-212. What about the time taken by the instrument to analyze the sample?

Response: The PTR-ToF-MS analysed the sample at 5Hz (0.2 s) which is low compared to the time taken for the sample to travel down the inlet line.

7, 228-229. Why did Squires et al. (2020) choose this method?

Response: The method was chosen as it could be applied to all instruments measuring fluxes during these campaigns. For some species gradient data was available which could have been used to calculate a storage flux but this would have prevented direct comparison of fluxes.

7, 240-241. Do you mean stationarity?

Response: Yes, this has been corrected.

7, 242. Explain briefly the stationarity test.

Response: A description of the stationarity test has been added.

“In order to calculate a reliable flux, the averaging period must meet stationarity requirements such that this period is shorter than the time scale at which changes in atmospheric conditions occur. The stationarity of the flux across the half hour averaging period was assessed using the method described by Foken and Wichura (1996). The half hour averaged fluxes were filtered where the stationarity criterion (the difference between average flux and mean average flux of its components) exceeded 60% and were above the limit of detection.”

7, 245-247. There are methodologies available to fill gaps in time series of turbulent fluxes measured by eddy covariance. However, depending on the study purposes it may not be necessary to fill such gaps. Consider that in urban environments VOC fluxes respond mainly to anthropogenic and not natural variables like in a forest. Human actions can be random at times (e.g., traffic jams), thus very low or very high fluxes are possible.

Response: While gap filling methods exist for vegetation, gap filling urban data is harder. As the reviewer states, human actions can take place at unpredictable times and both high and low fluxes are possible. Most data falling below the u^* threshold occurred at night when fluxes were low. The decision was taken to substitute these data with campaign average values for those hours so as not to artificially raise the campaign average data.

7, 238-249. Please, indicate the number of periods excluded for further analysis due to lack of stationarity and/or enough turbulence. How many averaging periods were affected by rain/snow and instrument maintenance?

Response: In the summer field campaign, 12% of the flux averaging periods fell below the u^* filter. Of the masses contributing more than 0.75% to the total flux, the average percentage of flux files filtered for failing the stationarity test is 25%. This ranged from 52% for formaldehyde to 13% for methanol.

In the winter campaign, 25% of the flux averaging periods fell below the u^* filter. Of the masses contributing more than 0.75% to the total flux, the average percentage of flux files filtered for failing the stationarity test is 69%. This ranged from 73% for methyl vinyl ketone and methacrolein formaldehyde to 62% for acetaldehyde.

29 h (6% of the PTR-ToF-MS operational period) were lost to instrument maintenance in the winter campaign and 133h (16% of the PTR-ToF-MS operational period) were lost to instrument maintenance in the summer. Precipitation was very low in both campaigns with light rain fall on the 20th of November and snow overnight into the 21st. In the summer campaign light rain was observed on 22nd and 30th May and on 2nd, 6th, 18th and 21st – 23rd June.

This has been added to the manuscript:

“Over the course of the winter campaign 29h (6% of the PTR-ToF-MS operational period) were lost to instrument maintenance and calibration and 133h (16% of the PTR-ToF-MS operational period) were lost to instrument maintenance and calibration in the summer.”

“In the winter campaign, 25% of the flux averaging periods fell below the u^* filter. Of the masses contributing more than 0.75% to the total flux the average percentage of flux files filtered for failing the stationarity test is 69%. This ranged from 73% for methyl vinyl ketone and methacrolein formaldehyde to 62% for acetaldehyde. In the summer field campaign 12% of the flux averaging periods fell below the u^* filter. Of the masses contributing more than 0.75% to the total flux the average percentage of flux files filtered for failing the stationarity test is 25%. This ranged from 52% for formaldehyde to 13% for methanol.”

8, 254-255. This information was already provided.

Response: This sentence has been removed.

9, 263-264. This figure and the description of the dominant winds during the field observations are useless without a proper analysis of the land cover and distribution of the measured fluxes by wind sectors.

Response: This figure (together with figure 3) is intended to provide an overview of the meteorological conditions during the two field campaigns. Discussion of the land cover and the flux footprint is provided in section 3.2.

9, 265-266. This information was already provided.

Response: This sentence has been removed.

10, 279-281. Is this true at nighttime and daytime? Atmospheric stability evolves during the diurnal cycle, thus significant changes in the footprint can be expected.

Response: This is the campaign average including both day and night time data. Significant changes to the footprint will occur over the course of the day but this is presented to give an overview of conditions across both campaigns.

11, 292-296. This figure is incomplete. A color gradient to indicate the flux contribution is missing. No spatial scale was included neither a north indicator. The article is in English, but the map includes text in Chinese. The legend refers to a grid of cells, but no cells are included. Do these footprints correspond to nighttime or daytime?

Response: The figure has been updated. This is the campaign average including both day and night time data. Each coloured pixel represents one grid cell.

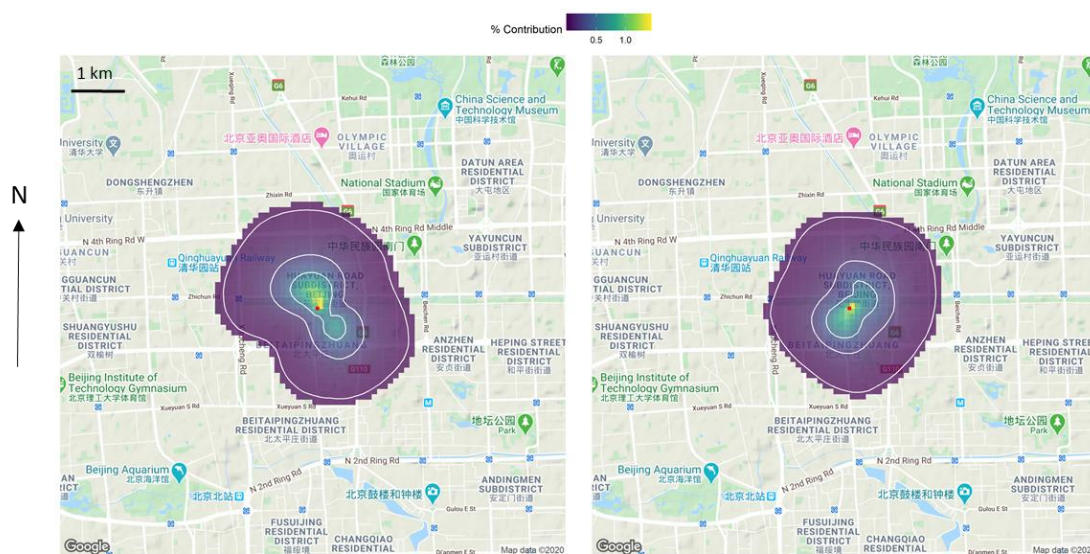


Figure 4. The campaign mean flux footprint climatologies for the winter (left) and summer (right) field campaigns. The IAP meteorological tower is represented by the red dot and surrounding 100 x 100 m cells are coloured by their mean contribution to the flux. The contour lines correspond to the distances from the tower where the surface contributions to the measured fluxes cumulate to 30, 60 and 90% respectively. Map tile sets are © Google.

11, 302-303. Define 'sawtooth cycle'. Although the paper is about fluxes, it will be good to provide a short description and a figure about their diurnal cycle.

Response: The sawtooth cycle is described in the next sentence. These sentences have been combined to make this clearer. A diurnal profile of the total measured mixing ratio is shown in Fig. 6. Diurnal mixing ratios of individual compounds have not been added as detailed discussion of the mixing ratios is beyond the scope of this work.

“Mixing ratios of these compounds tracked the pollution events in a distinctive “sawtooth cycle” described by Jia et al. (2008) where mixing ratios increased over a period of 3 - 4 days when the wind speed was low and prevailing wind direction was southerly before dropping rapidly when the wind direction moved to the North West”

12, 322-330. This paragraph should be part of the methodology. Do not repeat information.

Response: We feel that providing a brief description of fluxes when moving from discussing mixing ratios to fluxes will help those readers who have more experience working with VOCs than micro-meteorology to interpret the flux data discussed in this section.

13, 349-351. Turbulent fluxes measured by eddy covariance represent the VOC exchange within the observed footprint. Periods affected by advection were removed through the stationarity criterion, isn't it?

Response: The stationarity filter will remove averaging periods affected by a change in meteorological conditions. The transport in the winter campaign is over a longer time period with a 3-4 day period of high VOC mixing ratios (lines 302-305 of the ACPD manuscript). Deposition of these VOCs is likely to reduce the net flux measured.

13, 351-352. This is unclear. Do you mean that turbulent fluxes cannot be measured during winter in Beijing, and therefore half of the study was useless?

Response: The fluxes measured in the winter campaign are valuable as they show a low net VOC flux. However, as local emission cannot be disentangled from the deposition of VOCs transported from outside of the footprint, these data cannot be used to assess local emission.

14, 366. Table 2. A complete list of the 50 VOC species identified and evaluated in this study should be included in the Supplementary Material. You may use as reference how Karl et al. (2018) analyzed and presented an even larger list of VOC species.

Response: As suggested a list of VOC species has been added to the supplementary information.

14, 378-382. This section discusses fluxes no mixing ratios. Mixing ratios were discussed in section 3.3.

Response: This paragraph has been moved to section 3.3.

14, 380-382. London and Manchester are only two cities. There are many papers reporting mixing ratios of oxygenated VOCs for cities of China and the rest of the world.

Response: References to studies carried out in Beijing (Shao et al., 2009) and Ahmedabad (Sahu and Saxena 2015) have been added.

15, 387. Vehicular traffic is a major source of isoprene in urban areas (e.g., Borbon et al., 2001; Jaimes-Palomera et al., 2016).

Response: These papers have been added to the discussion.

“Isoprene, which has both biogenic and vehicular sources (Borbon et al., 2001; Jaimes-Palomera et al., 2016), had median mixing ratios of 1.08 and 0.38 ppb in the winter and summer campaigns respectively.”

17, 400. Do you mean less than 1%? Figure 6 has not been cited yet in the text.

Response: “VOC species which contribute more than 0.75% to the total measured VOC flux” is correct. Figure 6 is cited on line 375 of the ACPD manuscript.

17, 403. Be more specific on the type of combustion sources (e.g., vehicular traffic, industry, biomass burning).

Response: Changed to read: “NO_x in urban areas is a combustion product so the NO_x flux is used here as proxy for vehicular emissions”

17, 409. A vehicular emission control program?

Response: Changed to read “Beijing operates a motor vehicle emissions control program...”

17, 412-415. A comparison against the fluxes reported by Velasco et al. (2005, 2009) for two locations of Mexico City will help to put in context the fluxes observed in Beijing with respect to other large city of a developing nation.

Response: A comparison with the fluxes recorded in Mexico City has been added.

“The toluene flux is, however, significantly lower than the 2.5 and 9.2 nmol m⁻² s⁻¹ recorded at two sites in Mexico City (Velasco et al. 2005; 2009). Velasco et al. (2009) identified both exhaust emissions and evaporative sources contributing to the toluene flux. The addition of these evaporative sources in Mexico City as well as differences in vehicle fleets is likely to explain why these fluxes were larger than those recorded in this study and in the UK.”

17, 416-418. How do these ratios between mixing ratios and fluxes compare to those reported in the literature for other cities?

Response: The discussion of the B/T ratio has been expanded, this is discussed in more detail by Squires et al. (2020)

“Squires et al. (2020) also concluded that the benzene/toluene ratio, which for concentrations was 0.89 in the winter and 0.73 in the summer was within the range expected for primary exhaust emissions but higher than the 0.6 calculated by Barletta et al. (2005) for Beijing. For fluxes, the benzene/toluene ratio was 0.72 in winter and 0.31 in summer (Squires et al. 2020). The summer value is lower than expected for primary exhaust emissions, suggesting that fuel evaporative loss contributes to aromatic VOC emission in summer (Squires et al. 2020).”

17, 420-425. Propene is dominated by emissions from vehicular traffic in locations with heavy traffic (see Velasco et al, 2005, 2009). Averaging periods affected by large plumes are expected to be removed by the stationarity criterion. If stacks of large industries were within the monitored footprint and their impact was not filtered by the stationarity criterion, the turbulent fluxes reported in this study are suspicious.

Response: The correlation with NO_x suggests that at the IAP site emission was dominated by traffic. The reference to industrial sites was made to provide context. The sentence has been updated to make it clear we are not proposing emission from heavy industry at this site. Reference to has been made to Velasco et al (2005, 2009).

“The fluxes of other compounds shown to correlate with the flux of NO_x were propene and methanol with R² values of 0.63 and 0.71. Propene is known to be emitted by vehicular traffic (Velasco et al. 2005; 2009) and the correlation with NO_x suggests that traffic is the main source at this site. Propene has also been recorded in plumes of VOCs released from industrial activity (Karl et al., 2003), but no large industrial sites were present within the flux footprint of the IAP tower.”

17, 430-432. See Fig. 4 in Velasco et al. (2005) and Fig. 3 in Velasco et al. (2009).

Response: Comparison with these studies has been added.

“These methanol emissions are comparable to those observed in London and Mexico City with 2.5 nmol m⁻² s⁻¹ (August to December) recorded by Valach et al. (2015), 8.2 nmol m⁻² s⁻¹ (October) reported by Langford et al. (2010) in London, and 9.1 and 12.8 nmol m⁻² s⁻¹ (April and March respectively) reported in Mexico City (Velasco et al., 2005; 2009).”

19, 445. The acronyms POCP and PPCP have not been defined in the text yet.

Response: These acronyms have been explained in the caption: “Figure 6. Total observed VOC concentration (a) and flux (b) measured during the summer field campaign, scaled using photochemical ozone creation potentials (POCPs) (c, d) and photochemical PAN creation potentials (PPCPs) (e, f).”

20, 446-449. A similar figure showing the flux correlations between species during the winter period is needed.

Response: The VOC fluxes recorded in the winter campaign were low with a lot of noise. Therefore a correlation plot would not be especially meaningful. We took the decision to focus on the summer campaign where clear VOC fluxes were observed (line 351).

20, 466-467. See previous comment on the vehicular contribution to urban isoprene.

Response: The following text has been added:

“Globally, plants are the main source of VOCs into the atmosphere, with isoprene and monoterpenes the main VOC species emitted (Guenther et al., 1995; 2012). However, in urban areas, isoprene is present from both biogenic and vehicular sources (e.g. Borbon et al., 2001; Langford et al., 2010; Valach et al., 2015; Jaimes-Palomera et al., 2016).”

21, 481-482. How and who determined this emission factor for Beijing's urban vegetation?

Response: This emission factor is the default value used in MEGAN. The emission factors used by MEGAN were calculated by combining isoprene observations from numerous enclosure studies with landcover data from ground measurement inventories, satellite based inventories, and ecoregion descriptions. Calculation of emission factors is described by Guenther et al. (2006).

22, 511-514. Based on the comprehensive set of measurements conducted during the APHH study, is it possible to adjust the POCP and PPCP factors for Beijing's conditions? If it is not possible, wouldn't be better to evaluate only the OH reactivity of each compound?

Response: In response to a comment by reviewer 2, the description has been expanded to include discussion of the conditions used by Derwent et al. (1998). The conditions observed in Beijing were within the range of NO_x values tested by Derwent et al.

“Derwent et al. (1998) used NO_x levels of 0.014 mg m⁻³ as the base case when determining POCPs and tested the POCP calculation at half and double these NO_x levels. The median NO_x concentration observed in the Beijing summer campaign was 0.0213 mg m⁻³ (Squires et al., 2020), within the twice base case range.”

22, 514-516. Light alkanes can be important players if their emissions are high like in Mexico City (see Jaimes-Palomera et al., 2016).

Response: This has been acknowledged in the text.

“Due to their low POCP and PPCP relative to alkenes and many oxygenated compounds, alkanes are likely to have a limited impact on ozone and PAN formation. However, at large concentrations they can still have a significant impact (Jaimes-Palomera et al., 2016).”

24, 540. The VOC classification used here is 'strange'. Be more specific on the species included in the group 'other hydrocarbons'.

Response: Groups have been reclassified as: methanol + ethanol, oxygenated VOCs, aromatics, predominantly biogenic compounds, alkenes and other chemical groups.

24, 543. Consider a different title for this section. Why did the evaluation of the accuracy of the gridded emissions inventory was limited to the summer period?

Response: Title changed to “Emission factor analysis and validation”. The evaluation was limited to the summer period by the low net flux recorded in the winter, making it difficult to identify local emissions.

24, 544-546. This was already mentioned in the introduction (lines 90-94). Indicate the emissions inventory's year reference.

Response: We feel it aids the reader to give a brief description of the inventory at the start of this section. The emission inventory year reference (2013) is given on line 566 of the ACPD manuscript.

25, 553-554. Were any power plant or large industry within the monitored footprint? If the answer is positive, the fluxes reported here might not be valid. Review the basic assumptions for measuring turbulent fluxes by eddy covariance (Velasco and Roth, 2010).

Response: There were no power plants or heavy industry within the footprint. The footprint was made up of parkland residential and commercial buildings with large two large roads: the Jingzang Expressway and the Beitucheng West Road. This is described in section 3.2.

25, 575-576. The poor agreement between measured fluxes and estimated emissions might respond to the size of the grids in the emissions inventory. Cells of 9 km² might be too large to capture the emissions observed by the flux tower.

Response: Squires et al. (2020) tested the sensitivity to location by shifting the grid 3 km in each direction, finding the same overestimation of NO_x and CO for all directions. This suggests that there is an issue with the proxies used to scale emission to the city centre rather than the grid cells being too large to capture emissions at the IAP site.

27, 590. According to the industrial emissions reported in the inventory developed for air quality modelling and presented in this figure, the site selected to conduct flux measurements by eddy covariance in Beijing is not adequate. Review the conditions needed to perform representative eddy covariance flux measurements in urban areas (Velasco and Roth, 2010).

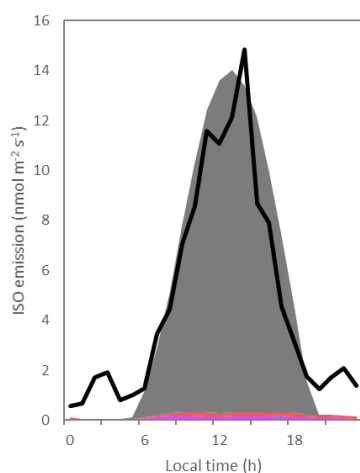
Response: While the inventory assigns large industrial emissions to this area, no large factories or industrial sites were present, making it a suitable site for eddy covariance measurements. In response to a previous comment the site description has been expanded to give a more thorough description to the fractional land cover. The large industrial emissions present in the inventory are likely to be caused by downscaling the inventory using proxies such as population. This misallocation of emissions in the inventory is discussed in lines 583-586.

28, 597-599. If it was known in advance that the inventory did not include the biogenic component, then which was the purpose of comparing the measured fluxes of isoprene? The emissions estimated by Megan should be added to those reported by the MEIC inventory.

Response: Comparison with isoprene is made for the sake of completion. As suggested the emission predicted by MEGAN has been added to this figure and the text updated.

“Isoprene emissions are significantly underrepresented in the inventory with measured fluxes 20 times higher than inventory emissions. This is expected as the inventory only considers anthropogenic emission and in the summer isoprene emissions are dominated by predominantly-biogenic isoprene. Adding the isoprene emission predicted by MEGAN to the MEIC emission (Fig. 10h) shows that the

inclusion of biogenic isoprene enables a more accurate estimate of total isoprene emission. The park at the base of the tower means that a larger biogenic source may be present at the IAP site than would on average be expected for Beijing.”



“Figure 10. Comparison of 9 VOC classes from the MEIC emissions inventory (Table 3) with measured VOC flux (black line). The diurnal profiles of the isoprene emission predicted by MEGAN using the optimised emission factor is shown in grey (h).”

28, 608-610. Indeed, the presence of methanol, aldehydes and organic acids can be explained by local atmospheric chemistry, however, it was previously proved that the time taken by an air parcel to reach the top of the tower was much less than the time needed for the oxidation of such compounds. If it was not the case, fluxes of those compounds cannot be measured by eddy covariance in Beijing.

Response: We thank the reviewer for pointing this out. The text has been amended to reflect the fact that formation in the atmosphere will not contribute significantly to the flux.

“It is possible that some underestimation of methanol, aldehydes and organic acid fluxes can be explained by their formation on surfaces following the oxidation of primary-emitted predominantly-biogenic (e.g. Lee et al. 2006; Acton et al., 2018) or anthropogenic compounds (Atkinson, 2000). However, given the ~68 s time taken for an air parcel to reach the inlet point, it is not likely that formation in the atmosphere contributes significantly to the flux of these compounds. Consumer goods are known to be a large source of oxygenated VOCs (Dinh et al., 2015; Nematollahi et al., 2019). The use of these products is likely to vary considerably between households making bottom-up emission hard to estimate.”

29, 617. Instead of presenting conclusions and final remarks, this section is a summary of results.

Response: This section has been retitled “Summary”

29, 618. Rewrite this sentence. For example: ‘Fluxes of speciated VOCs at district scale were measured by first time in Beijing’.

Response: Re-written as suggested.

“Fluxes of speciated VOCs at district scale were measured for the first time in Beijing with emissions dominated by small oxygenated compounds methanol, acetaldehyde and ethanol and formic acid which could not be separated”

29, 625. ‘Stable atmospheric conditions’ may sound better.

Response: Changed to “Stable atmospheric conditions”

29, 626-627. It may be true for VOC species emitted by evaporation of fossil fuels and solvents, but not for species emitted by other emission sources. It is not possible to talk about advection of VOCs in the case of fluxes measured at district level by eddy covariance, see previous comments.

Response: As stated in response to the previous comment this does not refer to advection within the flux averaging period but transport over a period of days leading to a high concentration of VOCs in the atmosphere dampening the net flux due to local emission.

29, 630-633. See previous comments about comparing the fluxes reported in this study with those observed in Mexico City.

Reference: Reference to this study has been added: “Both fluxes and mixing ratios of toluene were lower than those recorded in Mexico City (Velasco et al., 2009)”.

Response to RC2: Anonymous Referee #2

This manuscript presents the VOC concentration and flux measurements using a PTRMS 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 sentences 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.

Response: The authors thank the reviewer for taking the time to review this manuscript and for their constructive comments. The interpretation of isoprene and aromatic compounds has been expanded (see responses to specific comments below) and, as well as addressing the sentences identified by the reviewer, the manuscript has been proofread to improve the writing.

Major comments:

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

Response: The campaign dates (line 254) in the APCD manuscript are those of the broader APHH-Beijing winter campaign (Shi et al. 2019). The meteorological variables plotted in Figure 3a began when the sonic anemometer used during this campaign was set up. The start of the PTR-ToF-MS operational period was delayed by technical issues with the instrument setup. PTR-ToF-MS measurements therefore started later, as stated on line 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.

Response: The discussion of isoprene mixing ratios has been expanded with the following text added:

“High winter isoprene concentrations have been observed previously in Beijing (Li et al., 2019) where an average value of 1.01 ppb was observed as well as during haze periods (Sheng et al., 2018). High winter isoprene has also been reported in other Asian countries with isoprene mixing ratios of 1.6 and 1.1 ppb recorded in Ahmedabad (Sahu and Saxena 2015) and Kathmandu (Sarkar et al., 2016). These studies are all characterised by the use of a PTR-MS, it is possible that an isomer of isoprene contributes to the high winter time concentrations observed in Asian cities. In contrast, other studies have reported higher summer time isoprene concentrations in Beijing (e.g. Cheng et al., 2018). In the winter, isoprene mixing ratios peaked during haze events and correlated well with anthropogenic and oxygenated VOCs. R^2 values of 0.82, 0.77 and 0.74 were observed for the correlation of isoprene with propenal, benzene and toluene respectively.”

The weak isoprene flux in the winter does not necessarily contradict the high mixing ratios observed in the winter. As isoprene correlates well with the haze periods and other VOCs this suggested that high concentrations are a result of transport from outside the flux footprint and not enhanced local emission. This is discussed on lines 465-468 of the ACPD paper:

“In the winter campaign, emissions of both isoprene and monoterpenes were comparatively small with average fluxes of 0.79 and 0.06 $\text{nmol m}^{-2} \text{s}^{-1}$, respectively. Despite the weak isoprene flux, mixing ratios were larger in winter than in summer with mixing ratios consistent through the day at an average value of 1.21 ppbv. The high isoprene mixing ratio in the winter suggests transport of anthropogenic isoprene from outside of the flux footprint together with a lower rate of photochemical loss than in the summer.”

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 3.6°C (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.

Response: The winter campaign is characterised by large pollution events controlled by meteorological processes (lines 301 to 305 of the ACPD manuscript). As we are recording the net flux of VOCs it is likely that deposition of VOCs transported from outside the flux footprint will dampen the emission flux from local sources recorded (lines 348-349 of the ACPD manuscript). While small OVOCs will be sufficiently volatile even at low temperatures, the low temperatures observed in the winter campaign will reduce the rate of evaporation. As suggested, a short description of possible sources has been added. This section has been reordered to put more focus on the impact of transport from outside the footprint.

“In the winter, the high concentrations of VOCs at this site, mainly resulting from advection from outside the city, might lead to deposition of VOCs. This would have the effect of suppressing the net VOC emission rate measured at the site. The average temperature in the winter campaign was 3.6 °C compared to 25 °C in the summer, and this would result in lower volatilisation of liquid VOCs (for example in gasoline), suppressing the emission rates. Sources such as cooking and solvents in cleaning products, cosmetics and paints contribute to urban VOC emission (Karl et al., 2018) and these sources are likely to be reduced in the winter when cold weather causes ventilation of buildings to be reduced. Measured VOC emissions from indoor and outdoor sources may therefore be lower in

winter. In addition the lower atmospheric turbulence in winter and generally lower fluxes resulting in greater uncertainty in our winter fluxes compared to summer fluxes.”

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

Response: Updated to read “These compounds have been observed at high concentrations in many cities (Langford et al., 2009 (summer); Valach et al. 2015 (August-September)) with ethanol reported to be the most abundant VOC in London with a mean mixing ratio of 5 ppb in summer and winter (Dunmore et al., 2016)”

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 categorically label isoprene as biogenic, even in summer?

Response: This is correct and has been reworded as “predominantly biogenic”. It should be noted that there is a difference between the concentration, which in the winter is mostly a result of regional transport, and the flux, which is emitted locally. The large winter concentration does not imply a large local emission. Given that the summer isoprene flux shows a clear diurnal profile which fits a biogenic model (Fig. 8) and no clear rush hour peaks we feel it can be labelled as predominantly biogenic.

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 NO_x flux in the summer measurement period is shown in Fig. 7.": This sentence is grammatically incorrect and therefore impossible to understand. Please kindly revise.

Response: Re-worded to read: “The correlation between (a) the NO_x flux and (b) those VOC species that contribute more than 0.75% to the total measured VOC flux is shown in Fig. 7.”

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

Response: "NO_x in urban areas is a combustion product so the NO_x flux is used here as proxy for combustion sources of pollutants" changed to read "In urban areas NO_x is also exclusively produced by combustion sources of which motor vehicles are the main source. The NO_x flux is therefore used here as a proxy or vehicular emissions.”

Lines 426-428: "The close correlation with the NO_x 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.

Response: The correlation with NO_x is shown in Fig. 7. There is not a close correlation with toluene, we thank the review for pointing out this error. This has been rewritten:

“The close correlation with the NO_x flux 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 (Fig. 7).”

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

Response: A more detailed discussion of the large winter concentration has been added to section 3.3 (see response to second comment).

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.

Response: Anthropogenic isoprene is known to be emitted from traffic (Borbon et al., 2001). This has been added to the discussion. The correlation of VOC fluxes recorded in the summer campaign is shown in Fig. 7. Isoprene shows a very poor correlation with traffic tracers such as toluene, C₂-benzenes (R^2 0.26 and 0.25) and NO_x (R^2 0.38) which suggests that the contribution from traffic emissions to the summer isoprene flux is low compared to the biogenic source. In addition to this the isoprene flux profile could be modelled well using MEGAN (a biogenic isoprene emission model), see Fig. 8. We therefore feel that it is sensible to assume that biogenic emission is the dominant source of isoprene in the summer campaign. A discussion of the isoprene correlation with aromatics and NO_x has been added to the manuscript:

"The summer isoprene flux correlated well (R^2 0.85) with the flux of the isoprene oxidation products methyl vinyl ketone and methacrolein (MVK+MACR) and poorly with traffic tracers such as toluene, C₂-benzenes (R^2 0.26 and 0.25) and NO_x (R^2 0.38) (Fig. 7). This suggests that the contribution from traffic emissions to the summer isoprene flux is low compared to the biogenic source."

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)?

Response: Cao et al. (2018) report an annual isoprene emission for China of 9.6 Tg yr⁻¹, this equates to 0.47 nmol m⁻² s⁻¹. The median summer isoprene emission reported in this study (Table 2 ACPD) is 2 nmol m⁻² s⁻¹. Given that the Cao et al. (2018) value is an annual average across a large country with many different ecosystems, these values appear broadly sensible.

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 NO_x levels used in the Derwent et al. (1998) calculation, and how different was it with the present-day Beijing NO_x 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.

Response: Derwent et al. (1998) used NO_x concentration of 0.014 mg m⁻³ as the base case but tested POCP calculation at half and double these NO_x levels, reporting that "The methodology used to generate the POCPs therefore appeared to return self-consistent values over a factor of four variation in NO_x emissions which confirms their robustness over a wide range of European conditions." The median NO_x concentration observed in the Beijing summer campaign was 0.0213 mg m⁻³, within the twice base case range tested by Derwent et al. (1998). The model runs used by Derwent et al. (1998) were 5 days long. The following description has been added to section 3.4.4:

“Derwent et al. (1998) used NO_x concentrations of 0.014 mg m⁻³ as the base case when determining POCPs and tested the POCP calculation at half and double these NO_x levels. The median NO_x concentration observed in the Beijing summer campaign was 0.0213 mg m⁻³ (Squires et al., 2020), within Derwent et al.’s (1998) twice base case range.”

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.

Response: This has been acknowledged in the text: “The emission ratio of different VOC species present within each grouping could represent a source of error in the 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 disproportionately 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).

Response: We agree with the reviewer that the high-resolution version of MEIC is placing a disproportionately large emission of aromatics near the IAP site. A similar overestimation was reported by Squires et al. (2020) for NO_x and CO. This is in part caused by a large industrial source MEIC predicts for the IAP, which seem unrealistic given the residential and commercial building surrounding the site. This is described in lines 575 to 589 in the ACPD manuscript. Reference to the underestimation has been added to the discussion:

“Previous studies have shown that the inventory underestimates aromatic emission at a China scale (Liu et al., 2012b; Cao et al., 2018), again indicating that the overestimation observed here is a result of the downscaling of the inventory.”

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.

Response: This was drawn from the local grid cells with the contribution of each grid cell weighted by the flux footprint in that cell. As shown in figure 10 the largest inventory contribution to “TOL” and “XYL” is industrial. We agree with the reviewer that the main local source of these compounds will be traffic but this is not currently represented in the 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.

Response: Reference to satellite studies has been added when discussing aromatics (see response to previous comments). As the resolution of the satellite studies differ greatly from the flux footprint, we feel direct comparison of individual compounds will not add significantly to the interpretation of individual fluxes.

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 NO_x (traffic)?

Response: While toluene emission is significant, it is comparable to that observed in London (Valach et al., 2015) and lower than that observed in Mexico City (Velasco et al., 2009) so is therefore not large in comparison to other major urban areas. The winter concentration, while lower than Mexico City, is high compared with European cities, suggesting that a significant contribution to the total toluene concentration is coming from outside of the city. This is supported by the fact that in winter concentrations of aromatic compounds follow the "saw tooth" pattern (line 303) common to many pollutants in Beijing. These pollution events are thought to be meteorologically controlled and represent transport from outside the city instead of local emission (this is discussed in more detail by Squires et al., 2020).

Minor comments:

Line 129-130: Is it possible that there is a negative bias of semi-volatile organics by filtering PM_{2.5}?

Response: Most semi-volatile compounds likely to be lost to filtering PM_{2.5} would be too heavily oxygenated to be detected by the PTR-ToF-MS 2000 used in this study. This could be an issue if using an instrument more sensitive to higher mass compounds.

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'.

Response: First "was" deleted.

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

Response: "the" removed

Line 238: "quality-assessed"

Response: "quality assessed" changed to "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?

Response: We agree this description is unclear. The flux files each contained half an hour of data. "Flux files" has been removed and replaced by "The half hour averaged fluxes".

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?

Response: This sentence has been reworded. Together with the preceding sentence it now reads: 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. In addition 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.

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.

Response: This sentence has been removed.

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

Response: Comma added.

Line 377: "can't" should be cannot

Response: "Can't" changed to "cannot"

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Changes made to Manuscript

Changes to sentence structure throughout to improve writing

Line 30: Update to show author's new institution

Lines 36-48: Abstract has been shortened

Lines 64-69: Introduction expanded to include Parrish et al. (2009) and von Schneidmesser et al. (2010).

Lines 71-72: description of transportation factors expanded

Lines 95-109: Introduction expanded to give a description of the eddy covariance method.

Lines 129-138: Site description expanded to provide a more detailed description of the land cover.

Lines 175-177: Caption expanded to give more detail.

Lines 195-197: Time lost to instrument maintenance and calibration added

Lines 221- 223: Sentence added to clarify mixing ratio terminology

Lines 259-299: Detail added flux processing and quality control methodology

Line 340: Figure updated to show north arrow, scale and street names in Latin characters

Lines 358-373: Discussion of mixing ratios expanded

Lines 401-405: A brief discussion of CO₂ fluxes previously made at this site has been added

Lines 423-432: Description of winter VOC fluxes rewritten to clarify discussion

Line 453-457: Comparison of methanol fluxes with measurements made in Mexico City added

Line 459-462: Comparison of acetone fluxes with measurements made in Mexico City added

Lines 494-499: Comparison of toluene flux with measurements made in Mexico City added

Lines 500-504: Discussion of benzene/toluene ratio expanded

Lines 505-509: Discussion of propene sources expanded

Lines 519-521: Comparison of methanol flux with Mexico City added

Lines 533-535: Figure updated to show more appropriate names for VOC groupings. Caption updated to define POCP and PPCP

Lines 543-545: Discussion of anthropogenic isoprene sources expanded

Lines 551-552: Discussion of isoprene correlation with aromatic compounds

Lines 603-606: Discussion of conditions used by Derwent et al. (1998) added

Line 610: Reference to Jaimes-Palomera et al. (2016) added

Lines 617-620: Comparison with measurements made in Mexico City added

Line 636: Figure updated to show more appropriate names for VOC groupings

Line 640: Title updated to "Emission factor analysis and validation"

Lines 655-656: Sentence added to acknowledge that grouping of VOC species in the inventory could be a source of error

Lines 678-680: Sentence added discussing underestimation of aromatic emission at a Chinese scale

Line 688: Figure updated to show modelled biogenic isoprene emission

Lines 697-699: Isoprene emission predicted by MEGAN discussed

Lines 710-712: Sentence added to show that gas phase chemical formation of oxygenated VOCs below the inlet is likely to contribute significantly to the flux

Line 716: "Conclusions" changed to "summary"

Lines 732-733: Reference to measurements made in Mexico City added

Line 759: contact address on data availability statement changed

Surface-atmosphere fluxes of volatile organic compounds in Beijing

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Abstract. Mixing ratios of volatile organic compounds (VOCs) were recorded in two field campaigns in central Beijing as part of the Air Pollution and Human Health in a Chinese Megacity (APHH) project. These data were used to calculate, for the first time in Beijing, the surface-atmosphere fluxes of VOCs using eddy covariance, giving a top-down estimation of VOC emissions from a central area of the city. The results were then used to validate the Multi-resolution Emission Inventory for China (MEIC). The APHH winter and summer campaigns took place in November and December 2016 and May and June 2017 respectively. The largest VOC fluxes observed were of small oxygenated compounds such as methanol, ethanol + formic acid and acetaldehyde, with average emission rates of 8.02, 3.88 and 1.76 nmol m⁻² s⁻¹ respectively in the summer. A large flux of isoprene was observed in the summer with an average emission rate of 4.63 nmol m⁻² s⁻¹. While oxygenated VOCs made up 60% of the molar VOC flux measured, when fluxes were scaled by ozone formation potential and peroxyacyl nitrate (PAN) formation potential the high reactivity of isoprene and monoterpenes meant that these species represented 30 and 28% of the flux contribution to ozone and PAN formation potential respectively. Comparison of measured fluxes with the emission inventory showed that the inventory failed to capture the magnitude of VOC emissions at the local scale.

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1. Introduction

Air quality in urban areas is a pressing issue worldwide and is becoming the subject of much scientific, political and media focus. The Chinese capital Beijing is a megacity situated on the north China plain with a population of 22 million. Beijing suffers from periods of severe air pollution resulting from pollutant emissions occurring both within the city and from sources in the wider North China Plain region (Wehner et al., 2008). This pollution has a substantial impact on human health and economic output due to the large exposed population and the commercial and political importance of the city. For example, Gao et al. (2015) estimated that a single pollution event in January 2013, when the maximum hourly particulate matter (PM_{2.5}) concentration in Beijing reached 650 µg m⁻³, caused 690 premature deaths and ~250 million USD in economic losses.

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Volatile organic compounds (VOCs) play an important role in local and regional air quality as they can oxidize and condense to form secondary organic aerosol (SOA) (Hallquist et al., 2009; Ehn et al., 2014) and because they take part in chemical reactions in the presence of NO_x that can form ozone (Fehsenfeld et al., 1992). In addition, some VOCs, e.g. benzene, have direct detrimental impacts on humans and animals. Urban areas, especially major cities, are important sources of these compounds into the atmosphere (Langford et al., 2009; Valach et al., 2015; Karl et al., 2018).

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Several studies have reported VOC concentrations in Beijing, identifying alkanes, aromatics and oxygenated VOCs (Shao et al., 2009; Yuan et al., 2012; Wang et al., 2015). Comparison of air pollutant emissions between megacities (Parrish et al., 2009) showed that gasoline-fuelled vehicles were a major source of hydrocarbon emission and in countries such as China industrial sources may also have a strong influence on hydrocarbon emission (von Schneidmesser et al., 2010). A positive matrix factorization (PMF) model applied by Wang et al. (2015) identified four major sources of VOCs in Beijing: two transportation factors denoted “gasoline evaporation and vehicular exhaust no. 1 (containing pentanes, acetylene, benzene, and toluene)” and “vehicular exhaust no. 2 (acetylene and C2-C4 alkanes)”, “natural gas and liquid petroleum gas use and background” and “paint and solvent

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75 use and industry”. Biogenic VOCs (BVOCs) represent an additional source of VOCs into the urban environment, the relative importance of which varies from city to city and from season to season. Ghirardo et al. (2016) used leaf-level emission measurements to estimate BVOC emissions in Beijing, including sesquiterpenes, benzenoids and fatty acid derivatives.

80 In most cities of the world it is difficult to directly observe the effectiveness of pollution control measures on ambient concentrations in real time. However, in Beijing the strict short-term emission controls applied during the 2008 Olympic Games (Liu et al., 2015) and the 2014 Asia-Pacific Economic Cooperation (APEC) summit (Li et al., 2017) allowed the impact of pollution control measures in Beijing and the surrounding area on VOC concentrations to be investigated. Liu et al. (2015) reported that the emission controls during the 2008 Olympic Games caused a concentration reduction of 13 – 20% in a range of oxygenated VOC species but that acetone concentrations remained unaffected. Li et al. (2017) found that when emission controls were applied to Beijing alone only a small decrease in VOC concentrations was observed but when controls also covered surrounding cities a large decrease (>40%) in most anthropogenic VOC concentrations was observed. This suggests that the atmospheric transport of pollutants from surrounding areas makes a large contribution to VOC concentrations in Beijing.

90 The impact of VOC emissions on local and regional air quality is examined using atmospheric chemistry and transport models, which rely on accurate estimates of the surface – atmosphere emission rates of pollutants. Much of the air quality modelling in Beijing relies on the Multi-resolution Emission Inventory for China (MEIC; available at <http://www.meicmodel.org/>, Qi et al. 2017) developed at Tsinghua University (e.g. Zhang et al., 2015; Hu et al., 2016). This relies on estimates of both source-specific emission factors and activity data and is hence a “bottom-up” estimation of emissions within a defined grid square. Validation of such an inventory is important in order to ensure they accurately represent real world emissions (Zhao et al. 2017).

100 Until comparatively recently it was very difficult to validate VOC emissions inventories at the cityscape scale, but the development of the PTR-TOF technology now allows VOCs to be measured with sufficient time resolution for flux estimates to be made using the method of eddy covariance based on simultaneous micrometeorological measurements. Although the conditions under which eddy covariance can be applied in the heterogeneous city environment are somewhat limited by flow interferences from neighbouring buildings, night-time boundary layer stability and other considerations, the method has been successfully used for estimating both CO₂ fluxes (e.g. Song and Wang, 2012; Liu et al., 2012a; Song et al., 2013) and VOC fluxes (e.g. Velasco et al., 2005; 2009; Langford et al., 2009; Valach et al., 2015; Vaughan et al., 2017; Karl et al. 2018). However, VOC flux measurements have not previously been attempted in Beijing.

105 The work presented here was carried out as part of the “Sources and Emissions of Air Pollutants in Beijing” (AIRPOLL) project, itself part of the joint UK-Chinese “Air Pollution and Human Health in a Chinese Megacity” (APHH) programme, described by Shi et al. (2019). The objectives of the study were to measure the surface-to-atmosphere fluxes of VOCs using the method of eddy covariance at a site in Beijing where a very comprehensive suite of atmospheric, physical and chemical parameters were assessed by the wider APHH-Beijing project team, and to use these data to assess the validity of a widely used emissions inventory. In this paper we therefore present the results of two intensive measurement campaigns covering both summer and winter conditions in Beijing. VOC

115 mixing ratios were recorded using a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) at a location in central Beijing. These data were then used, with three-dimensional wind velocity data, to calculate emission rates (fluxes) of VOCs, using the eddy covariance method (e.g. Müller et al., 2010) for the first time in Beijing. The calculated fluxes were then compared with the MEIC emissions inventory estimates for the measurement location.

2. Methodology

120 2.1. Site description

Measurements of VOC mixing ratios and fluxes were made during two intensive measurement campaigns (winter: 12/11/2016 - 10/12/2016; and summer: 15/05/2017 - 24/06/2017) from a 325 m high meteorological mast located on the campus of the Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP) in Beijing (39°58'33"N 116°22'41"E). This site was used as the main sampling site for all APHH-Beijing programme activities (see Shi et al., 2019). The campus is situated north of central Beijing between the 3rd and 4th ring roads, with parkland to the east and west and a mix of dense residential and commercial (restaurants and shops) buildings to the north and south. Busy roads are situated 120 m north and 300 m east of the mast. For comparative purposes, the sampling location can therefore be described as being “urban background” with respect to ambient concentrations for central Beijing with the main sampling inlet being significantly elevated above ground level. Flux measurements of CO₂ have been made previously at this site (Song and Wang, 2012; Liu et al., 2012a; Song et al., 2013). The fractional land cover within 2 km of the tower was assessed by Song and Wang (2012) and found to be buildings (0.65), vegetation (0.23) and roads (0.12). Using the local climate zone (LCZ) classification system described by Stewart and Oke, (2012) this area can be classified as LCZ2 “compact mid-rise” becoming LCZ1 “compact high-rise” to the south west. The aerodynamic roughness lengths were calculated by Li et al. (2003) as cited by Liu et al. (2012) and found to be 2.5, 3.0, 5.3 and 2.8 m from the north east, south east, south west and north west respectively with the zero-plane displacement heights of 12.3, 15.0, 26.4, and 13.2 m respectively. The flux inlet was located at 102 m; this is over twice the mean height (45 m) of the tall residential building to the southwest (Liu et al., 2012a) and is below the mixing layer height (Squires et al., 2020) positioning the inlet in the constant flux layer.

140 2.2. Instrumental setup

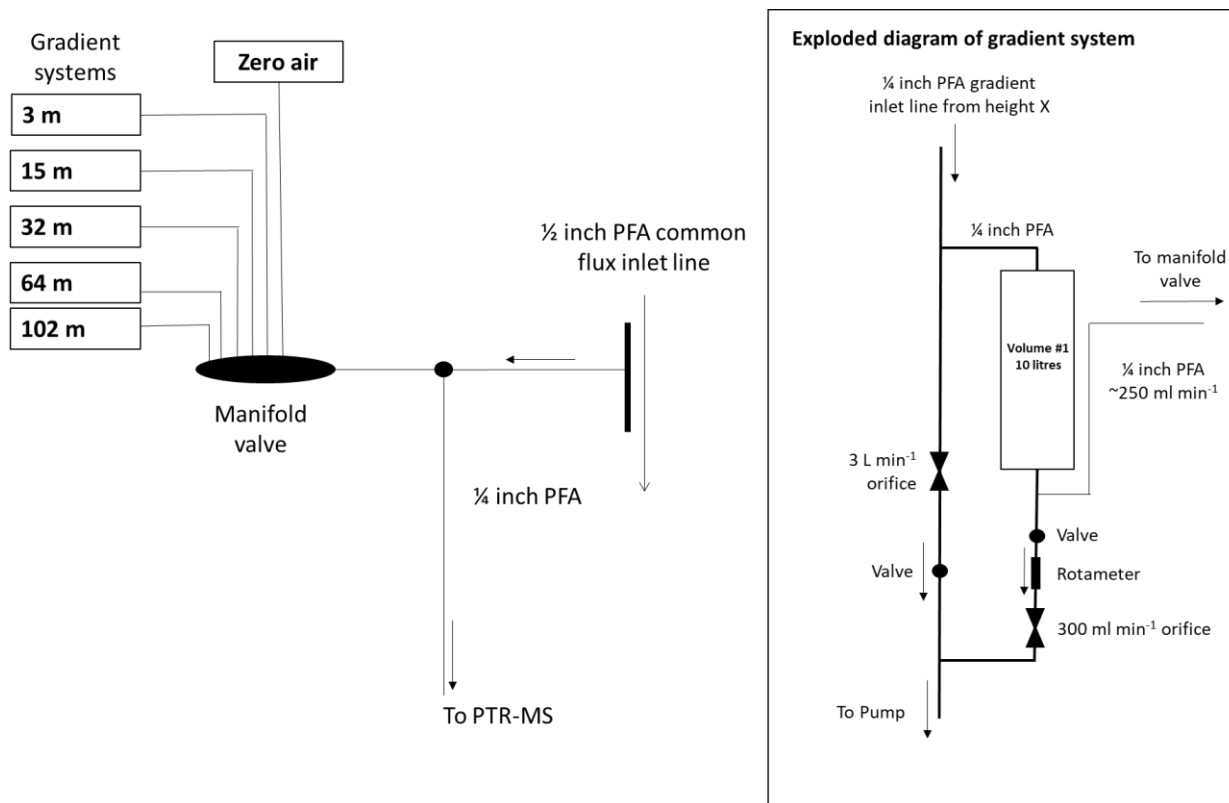
A PTR-ToF-MS 2000 (Ionicon Analytik GmbH, Innsbruck) was housed in an air-conditioned container ~10 m from the base of the mast. The core operating principle of the instrument is described in detail by Jordan et al. (2009). The PTR-ToF-MS subsampled from two inlet systems, a common flux inlet line and a gradient switching system. The common flux inlet was 0.5 inch O.D. (I.D 3/8 inch) PFA and sampled air from ~50 cm below a sonic anemometer (Gill R3, Gill Instruments, Lymington, UK) which was mounted on a 3 m horizontal boom positioned on the mast at a height of 102 m above ground level. Air was drawn through the inlet line using a rotary vane pump (Model VT4.8; Becker, Hull, UK). The flow rate in the inlet line was recorded using a mass flow meter (TSI Mass Flowmeter 4043, TSI, Shoreview, USA) and remained in the range 90 - 103 L min⁻¹ during both campaigns. At 90 L min⁻¹ the Reynolds number in the inlet line is 12900, indicating turbulent flow. Particulates

150 were removed from the air flow by a 90 mm Teflon filter installed near the inlet. This filter was replaced each day.

To minimise the impact of the tower on flux measurements, the sonic anemometer was positioned so that air from the prevailing wind directions would not be disturbed by the tower. The sonic anemometer was installed on the north west side of the tower in the winter and the south east in the summer. Analysis of the turbulence characteristics (Squires et al., 2020) did not show an impact from the structure even when the air flow passed through the tower. This is likely due to the open lattice construction of the tower and the predominance of larger eddy scales at 102 m.

160 Gradient measurements were made by switching between five sampling heights (3, 15, 32, 64 and 102 m) and zero air. Air was drawn down five separate 0.25 inch O.D. (I.D. 1/8 inch) PFA lines using a common second rotary vane pump (Model VT4.8; Becker, Hull, UK). For each height, the flow was sampled at 3.3 L min⁻¹ of which ~300 ml min⁻¹ was drawn through a 10 L stainless steel container and an additional bypass flow of 3 L min⁻¹ was used to reduce the residence time in each line (Fig. 1). The five containers were heated to 30 °C to limit adsorption/desorption effects and had a turn-over time of approximately 30 minutes. For two minutes each hour the PTR-ToF-MS sequentially subsampled from the flow exiting each container via a manifold valve, providing 165 hourly 30-minute average mixing ratio at each of the five heights. The PTR-ToF-MS was operated in an hourly cycle switching between the flux and gradient measurements. The PTR-ToF-MS sampled from the gradient system for the first twenty minutes of each hour and from the flux line for the final 40 minutes of the hour. A zero air generator was built in house and made up of a platinum catalyst heated to 260 °C, and zero air was sampled for 5 minutes each hour at the end of the gradient cycle.

170 The PTR-ToF-MS was operated with an inlet flow rate of 30 sccm and an E/N ratio (where E is the electric field strength; N is the buffer gas density) of 130 Td. To achieve this, the drift tube was maintained at 60 °C with a pressure 1.9 mbar and a voltage of 490 V applied across it. Data were acquired by the PTR-ToF-MS at a 5 Hz time resolution, allowing VOC fluxes to be calculated using the eddy covariance method. In order to facilitate mass calibration, trichlorobenzene was introduced by diffusion through a needle valve into the inlet stream.



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Figure 1: Schematic of the gradient sampling system. The PTR-ToF-MS inlet was switched between a common flux inlet line (40 min) and a gradient switching manifold (20 min) in an hourly cycle. The gradient system sampled from five heights into 10 stainless steel containers.

180 **2.3. Calibration**

The PTR-ToF-MS was calibrated twice weekly using a 15 component VOC standard (National Physical Laboratory, Teddington, UK) during both the winter and summer campaigns. This standard contained methanol, acetonitrile, ethanol, 1,3-butadiene, acetone, isoprene, butenone, butan-2-one, benzene, toluene, m-xylene and 1,2,4-trimethylbenzene at 1 ± 0.1 ppmv each. The standard was dynamically diluted in zero air to provide a six point calibration. The sensitivities to these compounds in the winter and summer campaigns are summarised in the supplementary information.

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During the winter campaign, the instrument was also calibrated three times using a second independent 15 component VOC standard (Ionicon Analytik, Innsbruck, Austria) containing methanol, acetonitrile, acetaldehyde, ethanol, acrolein, acetone, isoprene, crotonaldehyde, butan-2-one, benzene, toluene, o-xylene, chlorobenzene, α -pinene and 1,2-dichlorobenzene at 1 ± 0.05 ppmv each. At the end of the campaign the PTR-ToF-MS was also calibrated using an aldehyde standard (Ionicon Analytik, Innsbruck, Austria) made up of formaldehyde, acetaldehyde, acrolein, propanal, crotonaldehyde, butanal, pentanal, hexanal, heptanal and octanal at 1 ± 0.05 ppmv each, nonanal at 600 ± 0.07 ppbv and decanal at 500 ± 0.08 ppbv. Calibration using both Ionicon standards was performed following dynamic dilution in zero air to give a six point calibration. In the summer campaign,

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195 four point calibrations were performed using both Ionicon VOC standards once a week.

Over the course of the winter campaign 29 h (6% of the PTR-ToF-MS operational period) were lost to instrument maintenance and calibration and 133 h (16% of the PTR-ToF-MS operational period) were lost to instrument maintenance and calibration in the summer.

2.4. Volume mixing ratio calculation

200 PTR-ToF-MS mass calibration and peak fitting was performed on the 5 Hz data using PTRMS Viewer 3 (Ionicon Analytik, Innsbruck). VOC mixing ratios were then calculated using the method based on that previously applied by Acton et al. (2016), Tani et al. (2004) and Taipale et al. (2010). Counts per second (cps) of each protonated VOC species (RH^+) were normalized against the primary ions (H_3O^+ and the $H_2O.H_3O^+$ cluster ion) and background counts were subtracted to give background corrected normalised count rates $I(RH^+)_{norm}$:

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$$I(RH^+)_{norm} = I(RH^+) \left(\frac{I_{norm}}{I(H_3O^+) + I(H_3O^+H_2O)} \right) \quad (1)$$

$$- \frac{1}{n} \sum_{i=1}^n I(RH^+)_{zero,i} \left(\frac{I_{norm}}{I(H_3O^+)_{zero,i} + I(H_3O^+H_2O)_{zero,i}} \right),$$

210 where $I(H_3O^+)$ and $I(H_3O^+H_2O)$ represent the measured count rate for H_3O^+ and the $H_3O^+H_2O$ cluster, respectively. Zero air measurements were labelled using the subscript zero and the number of zero air measurements was represented by n . The total reagent ion count rate (H_3O^+ and $H_3O^+H_2O$) was normalised to a count rate of 10^6 cps (I_{norm}).

Following calculation of the background corrected normalised count rate, the volume mixing ratio (VMR) was calculated, as a wet mass fraction, as:

$$215 \quad VMR_{VOC} = \frac{I(RH^+)_{norm}}{S_{norm}}, \quad (2)$$

where S_{norm} is the normalised sensitivity (ncps/ppbv) for each mass calculated using a transmission curve as described by Taipale et al. (2008). Mixing ratios of specific compounds were then determined by summing parent ion and fragment ion mixing ratios. For direct comparison with the molar flux, the volume mixing ratio was converted to a molar concentration (χ_{VOC}) using equation 3.

$$220 \quad \chi_{VOC} = \frac{P \times VMR_{VOC}}{R \times T}, \quad (3)$$

where P is the atmospheric pressure, T is atmospheric temperature and R is the molar gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). Note that in the following presentation of results and discussion, the abundance of VOCs in air are described in terms of volume mixing ratio (parts per billion; ppbv) although strictly speaking they should be described as the wet mass fraction (with the same units).

2.5. Flux calculation

225 The continuous fast measurement of PTR-ToF-MS for all compounds allows the estimation of fluxes using direct eddy covariance rather than the virtual disjunct eddy covariance methods that had to be applied when using older PTR-quad-MS instruments (e.g. Karl et al., 2002; Langford et al., 2009; Velasco et al., 2005; 2009). Eddy covariance fluxes of VOCs using PTR-ToF-MS were first made by Müller et al. (2010). A detailed description of

230 flux measurement using eddy covariance and its limitations is provided by Aubinet et al. (2012). Here fluxes were calculated using the eddy4R routines (Metzger et al., 2017). The flux (F_x) of each compound was determined by calculating the covariance function between the vertical wind velocity (w) and the VOC concentration (χ_x ; nmol m⁻³):

$$F_x(\Delta t) = \frac{1}{N} \sum_{i=1}^N w'(i - \Delta t / \Delta t_w) \chi_x'(i), \quad (4)$$

235 where w' and χ' represent momentary deviations from the mean concentration or vertical wind speed (i.e. $w' = w - \bar{w}$). N is the number of PTR-ToF-MS measurements in our half hour averaging window (9000 for 5 Hz measurements), Δt_w is the sampling interval between wind measurements (0.2 s) and Δt is the lag time between the vertical wind measurements recorded by the sonic anemometer at 102 m and the concentrations recorded using the PTR-ToF-MS instrument at ground level.

240 The lag time between the vertical wind velocity measurement and VOC concentration measurement is primarily controlled by the inlet line length and the flow rate in the line. However, small variations in temperature, pressure, humidity and pump performance, and also horizontal displacement between anemometer and inlet coupled with changes in wind speed and direction can all cause deviation in the lag time. The lag time can be determined by assessing the covariance between w and χ as a function of time. The lag time can then be identified by selecting
245 the maximum of this covariance function (Taipale et al., 2010). For many of compounds recorded in this study only a weak flux was observed. This results in a low signal-to-noise ratio, introducing a large uncertainty into the identification of the cross-covariance maximum. Adsorption and desorption rates to the inlet line are compound specific and dependent on polarity. Therefore, the lag times for more polar compounds such as oxygenated VOCs will differ slightly from pure hydrocarbons but weak covariance peaks made the identification of the lag-times
250 difficult for many masses. Lag times were therefore determined by calculating the lag for compounds where a strong covariance peak was observed (isoprene and C2-benzene (C₈H₁₀) in the summer and winter campaigns respectively) and applying their modal lag times as a fixed value to all masses. The calculation of lag time for eddy covariance data with low signal-to-noise ratio is described in detail by Langford et al. (2015).

The effect of storage below the measurement height was calculated for flux averaging period t as:

255 $Storage F_{x,t} = h \frac{\chi_{x,t-1} - \chi_{x,t+1}}{3600}$. (5)

Where $\chi_{x,t-1}$ and $\chi_{x,t+1}$ are the concentration (nmol m⁻³) of compound X in the averaging periods before and after flux averaging period, t , and h represents the measurement height in meters (102 m). This method was chosen so as to be comparable with the other flux measurements made during this project (e.g. Squires et al. 2020). This storage term was then added to the calculated turbulent flux term.

260 At the 102 m measurement height, large eddies mean that some of the flux may not be captured in the 30 min flux averaging period used here. This loss of low frequency flux was investigated by Squires et al. (2020) who found that at the 102 m measurement height the flux loss was ca. 7%. Due to similarity of the transport mechanisms underlying the low frequency flux loss (e.g., Mauder et al., 2020) we assume this estimate to apply also to the simultaneously measured VOC fluxes presented here. We did not correct the fluxes presented in this paper for
265 low frequency flux loss. We further investigated the effect of high-frequency spectral loss on the VOC fluxes

using a wavelet-based methodology (Nordbo and Katul, 2013). Loss of high frequency flux due to measuring at 5 Hz was estimated to be less than 10%, which we did not correct for in the presented fluxes. Fluctuations in air density caused by changes in temperature and humidity can impact fluxes (Webb et al., 1980). As a closed path system was used in this study, the impact of air density variations caused by changes in sensible heat flux are negligible but variations in air density caused by changes in the latent heat flux may impact the VOC flux calculation. The impact of changes in latent heat flux on the NO_x flux at this site was assessed by Squires et al. (2020) and found to be significantly less than 1% throughout both campaigns. As the sensitivity of a trace gas flux to density fluctuations is controlled by the ratio of its constituent density over its flux (Pattey et al., 1992) this ratio was assessed for the measured VOC species. This ratio was found to be comparable to that observed for NO_x by Squires et al. (2020), suggesting that the uncertainty in VOC flux as a result of changes in latent heat flux was less than 1%. Therefore the Webb-Pearman-Leuning correction (WPL: Webb et al., 1980) for changes in the density of air to the calculation of fluxes was not applied. Squires et al. (2020) estimated that the average time taken for an air parcel to reach the inlet point at 102 m was ~68 s. Assuming a OH concentration of 1×10^6 molecules cm⁻³ and an ozone concentration of 1.2×10^{12} molecules cm⁻³ only ~1% of monoterpenes (the most reactive species recorded) would have reacted before the measurement height.

Half hour averages were quality-assessed using three tests after a 2-dimensional coordinate rotation to correct for tilting of the sonic anemometer. The limit of detection was calculated for each mass by determining the cross-covariance between 150-180 s, a region outside the expected time lag range (Spirig et al., 2005). In order to calculate a reliable flux, the averaging period must meet stationarity requirements such that this period is shorter than the time scale at which changes in atmospheric conditions occur. The stationarity of the flux across the half hour averaging period was assessed using the method described by Foken and Wichura (1996). The half hour averaged fluxes were filtered where the stationarity criterion (the difference between average flux and mean average flux of its components) exceeded 60% and were above the limit of detection as for fluxes below the limit of detection a robust statement on their stationarity could not be made. Lastly, files were also flagged if the mean frictional velocity (u_*) fell below 0.175 m s⁻¹, this threshold was derived from assessment of the u_* dependence of the sensible heat flux. Data falling below this threshold were substituted by the campaign average value for that hour so as not to introduce a positive bias to the VOC flux. The random error of each half hour flux average was assessed using the method described by Lenschow et al. (1994) and fluxes with a relative random error greater than 150%, averaged across the campaign, were discarded.

In the winter campaign, 25% of the flux averaging periods fell below the u_* filter. Of the masses contributing more than 0.75% to the total flux, the average percentage of flux files filtered for failing the stationarity test is 69%. This ranged from 73% for methyl vinyl ketone and methacrolein formaldehyde to 62% for acetaldehyde. In the summer field campaign 12% of the flux averaging periods fell below the u_* filter. Of the masses contributing more than 0.75% to the total flux, the average percentage of flux files filtered for failing the stationarity test is 25%. This ranged from 52% for formaldehyde to 13% for methanol.

3. Results and Discussion

305 3.1 Meteorology

During the winter measurement campaign (7th November to 10th December), wind speeds were low, ranging between 0.3 and 9.7 m s⁻¹, with a mean value of 2.4 m s⁻¹, and with the highest wind speeds observed from the North West (Fig. 2). The predominant wind directions were southerly and north westerly. Temperatures, measured at 102 m on the IAP tower, ranged from -7 to 15 °C with a mean value of 3.6 °C. Relative humidity ranged from 15 to 92% with a mean value of 45% (Fig. 3). Precipitation was small during the campaign period with light rain on 20th November and snow on 21st November.

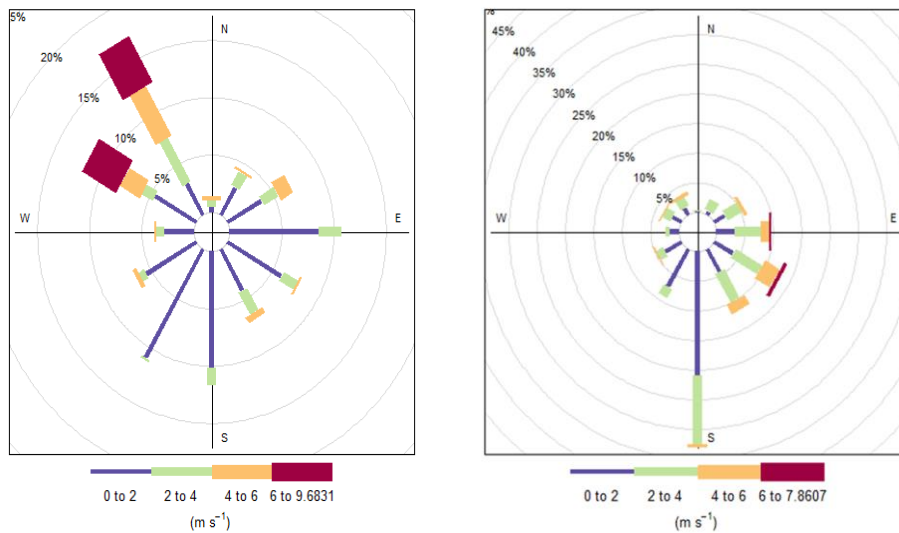


Figure 2: Wind conditions during the winter campaign (left) and summer campaign (right). The plots show the percentage of time the wind was from each direction and are coloured by wind speed.

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During the summer measurement campaign (20th May - 22nd June 2017) wind speed ranged between 0.5 and 7.9 m s⁻¹, with a mean value of 2.3 m s⁻¹. The predominant wind direction was south-easterly (Fig. 2). Temperatures at 102 m ranged from 15 to 37 °C with a mean value of 25 °C and the relative humidity ranged from 13 to 93% with a mean value of 44% (Fig. 3). Precipitation was low during the campaign period with light rain observed on 22nd and 30th May and on 2nd, 6th, 18th and 21st – 23rd June.

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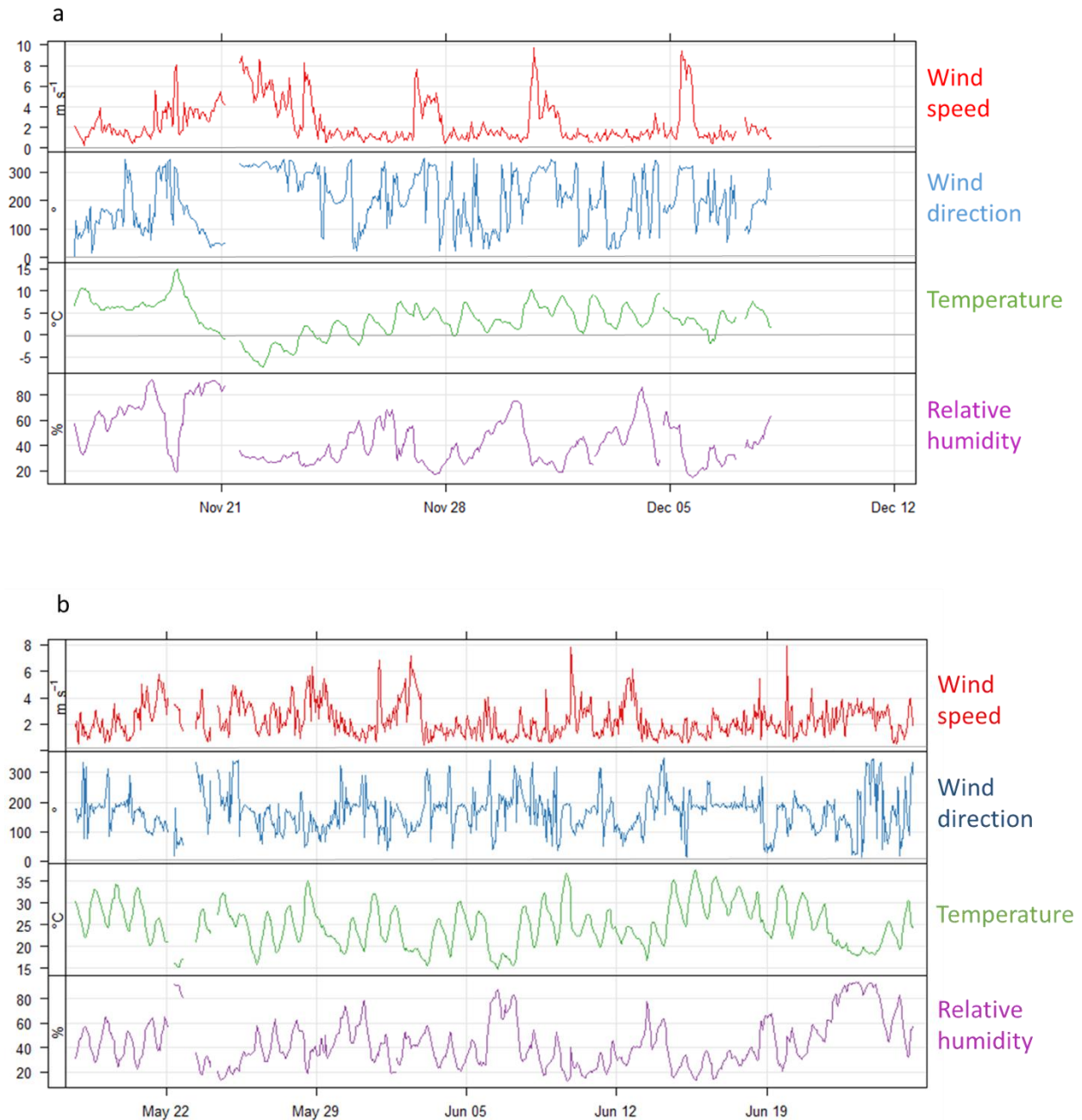


Figure 3: Summary of meteorological data in winter measurement campaign (a) and summer measurement campaign (b).

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3.2 Flux footprint

The flux footprint was calculated for each half hour flux averaging period of both field campaigns using the method described by Kljun et al. (2004) and Metzger et al. (2012). The calculation of the flux footprint for this campaign is described in detail by Squires et al. (2020). During both the summer and winter field campaigns 90% of the measured flux originated from an area within 7 km of the IAP tower; however, 90% of the contribution to the campaign average flux footprint extended just 2 km from the tower. Mean flux footprint climatologies for the

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summer and winter campaigns are displayed in Fig. 4, with contour lines showing the distances from the tower where the surface contributions to the measured fluxes cumulate to 30, 60 and 90%, respectively. In the winter campaign the main contribution to the average flux was predominantly from the northwest and southeast, encompassing two large roads: the Jingzang Expressway and the Beitucheng West Road and a mix of commercial and residential buildings, and urban park land. In the summer campaign, the largest contribution to the flux came from regions approximately 1 km south west of the tower and approximately 1 km north east of the tower now encompassing different sections of the Jingzang Expressway, Beitucheng West Road, residential buildings, commercial buildings (shops and restaurants) and a larger contribution from urban park land compared to the winter campaign.

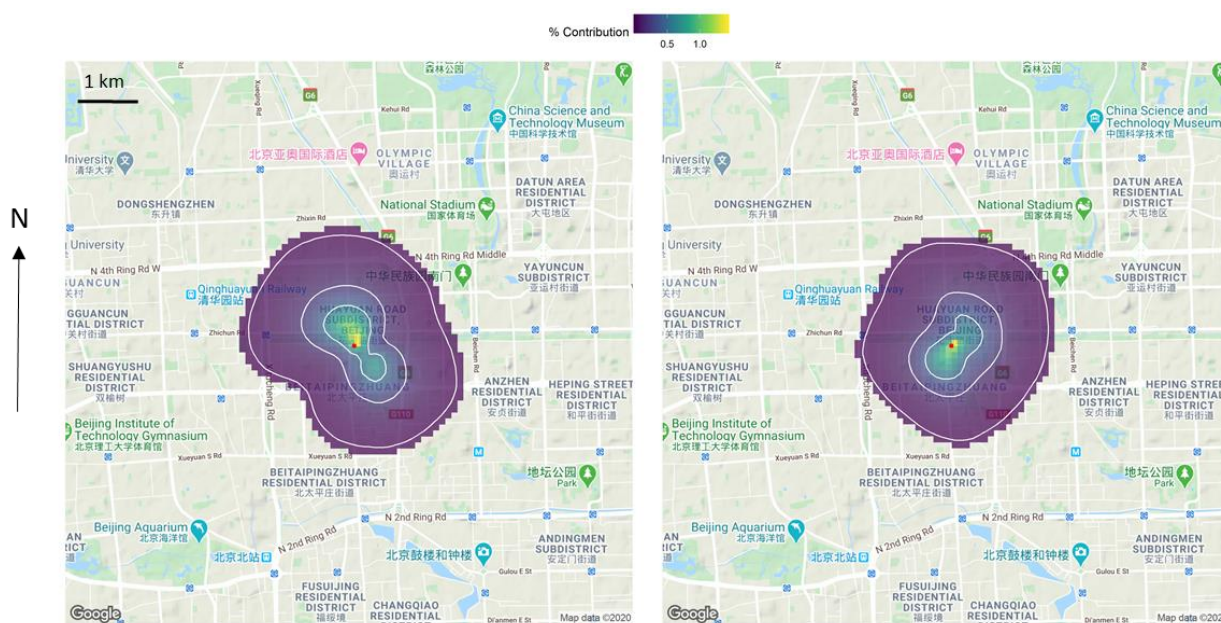


Figure 4. The campaign mean flux footprint climatologies for the winter (left) and summer (right) field campaigns. The IAP meteorological tower is represented by the red dot and surrounding 100 × 100 m cells are coloured by their mean contribution to the flux. The contour lines correspond to the distances from the tower where the surface contributions to the measured fluxes cumulate to 30, 60 and 90% respectively. Map tile sets are © Google.

3.3. VOC mixing ratios

In the winter campaign the detected VOC species with the largest mixing ratios were the small oxygenated VOCs (OVOCs) methanol, acetaldehyde and acetone, with median mixing ratios of 19.29, 4.59 and 2.57 ppbv, respectively. Large mixing ratios of aromatic compounds were also observed, with median mixing ratios between 1.5 and 2.0 ppbv for each of benzene, toluene and C₂-benzenes. Mixing ratios of these compounds tracked the pollution events in a distinctive “sawtooth cycle” described by Jia et al. (2008) where mixing ratios increased over a period of 3 - 4 days when the wind speed was low and prevailing wind direction was southerly before dropping rapidly when the wind direction moved to the North West. In the summer campaign, the dominant VOC species

observed were again methanol, acetaldehyde and acetone (26.39, 3.50 and 3.67 ppbv respectively), but the mixing ratios of aromatic compounds were lower, with median values of 0.30, 0.37 and 0.47 ppbv observed for benzene, toluene and C₂-benzenes respectively. Methanol and ethanol + formic acid together account for approximately one third of the total oxygenated VOC mixing ratio. These compounds have been observed at high concentrations in many cities (Langford et al., 2009 (Manchester; summer); Shao et al., 2009 (Beijing; summer); Valach et al. 2015 (London; August-September); Sahu and Saxena 2015 (Ahmedabad; winter)) with ethanol reported to be the most abundant VOC in London with a mean mixing ratio of 5 ppbv in summer and winter (Dunmore et al., 2016).

Isoprene, which has both biogenic and vehicular sources (Borbon et al., 2001; Jaimes-Palomera et al., 2016), had median mixing ratios of 1.08 and 0.38 ppbv in the winter and summer campaigns respectively. High winter isoprene concentrations have been observed previously in Beijing (Li et al., 2019) where an average value of 1.01 ppbv was observed as well as during haze periods (Sheng et al., 2018). High winter isoprene has also been reported in other Asian countries with isoprene mixing ratios of 1.6 and 1.1 ppbv recorded in Ahmedabad (Sahu and Saxena 2015) and Kathmandu (Sarkar et al., 2016). These studies are all characterised by the use of a PTR-MS, it is possible that an isomer of isoprene contributes to the high winter time concentrations observed in Asian cities. In contrast, other studies have reported higher summer time isoprene concentrations in Beijing (e.g. Cheng et al., 2018). In the winter, isoprene mixing ratios peaked during haze events and correlated well with anthropogenic and oxygenated VOCs. R² values of 0.82, 0.77 and 0.74 were observed for the correlation of isoprene with propenal, benzene and toluene respectively.

In contrast to the winter campaign, VOC mixing ratios during the summer campaign showed a clear diurnal cycle with mixing ratios peaking at night and dropping during the day as the planetary boundary layer expanded during the day-time and contracted at night-time. A summary of VOC mixing ratios for the principal VOC species observed during the two campaigns are displayed in Table 1. For a more detailed discussion of VOC mixing ratios recorded during this campaign see Zhang et al. (2020).

390 Table 1. Summary of VOC mixing ratio for the dominant VOCs observed in Beijing during APHH-Beijing winter and summer campaigns (in ppbv).

	<i>Methanol</i>	<i>Acetonitrile</i>	<i>Acetaldehyde</i>	<i>Acetone</i>	<i>Isoprene</i>	<i>Benzene</i>	<i>Toluene</i>	<i>C₂-Benzenes</i>
<i>Winter campaign</i>								
<i>Max</i>	93.98	2.13	17.42	9.66	4.50	9.11	9.43	13.07
<i>Min</i>	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.00
<i>Median</i>	19.29	0.38	4.59	2.57	1.08	1.59	1.65	1.65
<i>Mean</i>	24.32	0.51	4.92	2.80	1.21	2.00	1.94	2.08
<i>Standard deviation</i>	20.83	0.51	3.66	2.00	1.03	1.74	1.87	2.07
<i>Summer campaign</i>								
<i>Max</i>	73.75	24.44	26.92	11.76	3.24	1.89	2.74	3.41
<i>Min</i>	7.10	0.00	0.00	0.70	0.00	0.00	0.00	0.00
<i>Median</i>	26.39	0.29	3.50	3.67	0.38	0.30	0.37	0.47
<i>Mean</i>	28.39	0.97	4.64	3.86	0.56	0.37	0.46	0.60
<i>Standard deviation</i>	11.02	1.86	3.57	0.44	0.55	0.31	0.37	0.52

3.4 VOC fluxes

395 The mixing ratio values represent the ambient concentrations observed at the sample inlet averaged over the sampling period. However, by combining these mixing ratios with the three dimensional wind vector, the eddy covariance flux calculation method allowed for quantification of the net exchange (flux) of the observed compounds from a surface “footprint” to the point of sampling. The size of this footprint depends on the height of measurement and surface roughness as well as a number of meteorological factors including wind speed and atmospheric stability. Under the conditions in Beijing, 90% of the campaign average measured flux originated from an area within 1-2 km of the tower (see Fig. 4). The fluxes observed at 102 m are therefore predominantly controlled by local emissions, unlike the mixing ratios observed at the same point which are influenced by both local and more distant emissions, chemical processing and meteorology. Fluxes of CO₂ have been previously recorded at the IAP field site (Liu et al., 2012a; Song and Wang, 2012; Song et al., 2013). Liu et al. (2012a) reported four years of CO₂ eddy covariance measurements showing a seasonal variation in emissions driven by winter heating and uptake of CO₂ by vegetation in the summer. Spatial variation in emission was shown to be determined by the surface cover and the diurnal profile of emissions was largely dependent on traffic volumes.

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Greater surface solar heating in the summer led to stronger turbulence than was observed in the winter, with median u^* values of 0.41 and 0.26 m s⁻¹ respectively. This meant turbulent transport was more easily measured,

410 allowing the fluxes of a larger number of compounds to be quantified in summer than in the winter. Of the 179 masses observed in the summer campaign, 65 masses gave a flux with a median relative random error of less than 150%. These masses all showed a net positive flux with no masses showing net deposition. Molecular formulae were assigned to 50 of these masses using their exact mass, while 15 masses with a small negative mass defect could not be allocated a formula, based on the combination of C, H, N, O, S and Cl within 0.1 mDa of the recorded mass. Mass spectral peaks observed at m/z 47.019 and 47.053, assigned to formic acid and ethanol, respectively, 415 could not be sufficiently resolved so these compounds were considered together.

Diurnal cycles of the six compounds with the largest fluxes are shown in Fig. 5 (solid lines), showing the large VOC flux observed in the summer campaign, in comparison to the much smaller fluxes observed in the winter campaign. This figure also displays fluxes without the storage term applied (dashed lines) and the gap-filled u^* filtered flux (dotted lines). As shown, these corrections have only a small impact on the fluxes calculated. The 420 fluxes of these six compounds are summarised in Table 2. As shown in Table 2, fluxes of all compounds were larger in the summer than in the winter. This was not the case for NO_x and CO which were larger in the winter than in the summer (Squires et al., 2020). There may be several reasons why the measured VOC fluxes were lower in winter than summer. In the winter, the high concentrations of VOCs at this site, mainly resulting from advection 425 from outside the city, might lead to deposition of VOCs. This would have the effect of suppressing the net VOC emission rate measured at the site. The average temperature in the winter campaign was 3.6 °C compared to 25 °C in the summer, and this would result in lower volatilisation of liquid VOCs (for example in gasoline), suppressing the emission rates. Sources such as cooking and solvents in cleaning products, cosmetics and paints contribute to urban VOC emission (Karl et al., 2018) and these sources are likely to be reduced in the winter when 430 cold weather causes ventilation of buildings to be reduced. Measured VOC emissions from indoor and outdoor sources may therefore be lower in winter. In addition the lower atmospheric turbulence in winter and generally lower fluxes resulting in greater uncertainty in our winter fluxes compared to summer fluxes. Our detailed analysis, therefore, focuses on the fluxes recorded during the summer campaign.

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Table 2: Summary of (storage corrected) fluxes of VOCs displayed in Table 1 including the six dominant VOC fluxes recorded in Beijing during APHH-Beijing winter and summer campaigns (in $\text{nmol m}^{-2} \text{s}^{-1}$).

	<i>Methanol</i>	<i>Acetonitrile</i>	<i>Acetaldehyde</i>	<i>Formic acid + Ethanol</i>	<i>Butene</i>	<i>Acetone</i>	<i>Acetic acid</i>	<i>Isoprene</i>	<i>Benzene</i>	<i>Toluene</i>	<i>C₂-Benzene</i>
	Winter campaign										
<i>Max</i>	56.37	1.22	11.45	8.45	2.58	3.87	11.24	24.42	4.49	3.70	4.60
<i>Min</i>	-48.63	-0.71	-7.21	-8.35	-1.77	-2.24	-8.71	-8.17	-2.93	-2.64	-2.81
<i>Median</i>	1.58	0.08	0.40	0.37	0.09	0.02	0.43	0.51	0.11	0.19	0.19
<i>Mean</i>	2.15	0.11	0.54	0.57	0.12	0.12	0.44	0.79	0.17	0.23	0.26
<i>Standard deviation</i>	9.92	0.24	1.89	1.92	0.49	0.68	2.37	2.34	0.72	0.64	0.80
	Summer campaign										
<i>Max</i>	55.36	10.64	11.89	53.67	16.42	7.65	14.24	45.83	2.78	18.16	12.76
<i>Min</i>	-21.33	-17.63	-3.57	-4.19	-1.23	-1.81	-3.20	-1.92	-1.05	-0.76	-0.80
<i>Median</i>	6.21	0.15	1.41	2.98	1.07	0.74	1.22	2.00	0.25	0.54	0.55
<i>Mean</i>	8.02	0.17	1.76	3.88	1.57	0.94	1.56	4.63	0.31	0.85	0.83
<i>Standard deviation</i>	7.79	1.08	1.79	4.57	1.86	0.96	1.85	6.60	0.29	1.37	1.20

3.4.1 Total measured VOC flux

In the summer campaign, the total measured VOC flux was strongly positive with the city centre acting as a net source of VOCs into the atmosphere. In the winter campaign there was a small net positive flux of most identified VOC species but at times deposition of VOCs was also observed (Fig. 5). The total measured VOC fluxes and concentrations during the summer field campaign, coloured by compound class, are displayed in Figs. 6a and 6b respectively, with the total measured VOC flux peaking at $90 \text{ nmol m}^{-2} \text{ s}^{-1}$ at mid-day. As alkanes have a proton affinity less than that of water these compounds cannot be measured using PTR-MS so are not included here.

Methanol and ethanol + formic acid together also make up one third of the total molar flux. The mean methanol flux recorded in the summer campaign was comparable to that observed in two spring time (April and March) campaigns in Mexico City where 9.1 and $12.8 \text{ nmol m}^{-2} \text{ s}^{-1}$ of methanol were observed respectively (Velasco et al. 2005; 2009). The winter methanol flux was closer to the $2.5 \text{ nmol m}^{-2} \text{ s}^{-1}$ reported by Valach et al. (2015) in London (August-December). Other oxygenated compounds (grouped as oxygenated VOCs in Fig. 6) together make up another 31% of the summer flux. This is consistent with the large flux of oxygenated VOCs observed by

460 Karl et al. (2018) from the urban canopy in Innsbruck, Austria. Fluxes of acetone were also recorded in London
(1.5 nmol m⁻² s⁻¹; Valach et al. 2015) and Mexico City (1.9 nmol m⁻² s⁻¹; Velasco et al. 2005) both of which were
higher than the 0.12 and 0.94 nmol m⁻² s⁻¹ measured in the summer and winter campaigns in this study.
Unclassified compounds, labelled “other chemical groups” in Fig. 6 were made up primarily of masses
corresponding to compounds containing nitrogen, sulphur and halogens and make up 15% of the total
465 concentration but contribute only 9% to the total flux. The largest fluxes in this group were an unidentified mass
at m/z 40.96 and m/z 87.03 ([C₄H₆S]H⁺). The (non-oxygenated) hydrocarbons have been divided into three
categories: predominantly-biogenic compounds (isoprene and monoterpenes), aromatic compounds and alkenes.
Together these compounds make up 15% of the total VOC mixing ratio observed but make up 31% of the total
measured VOC flux, with predominantly-biogenic compounds the largest contributors.

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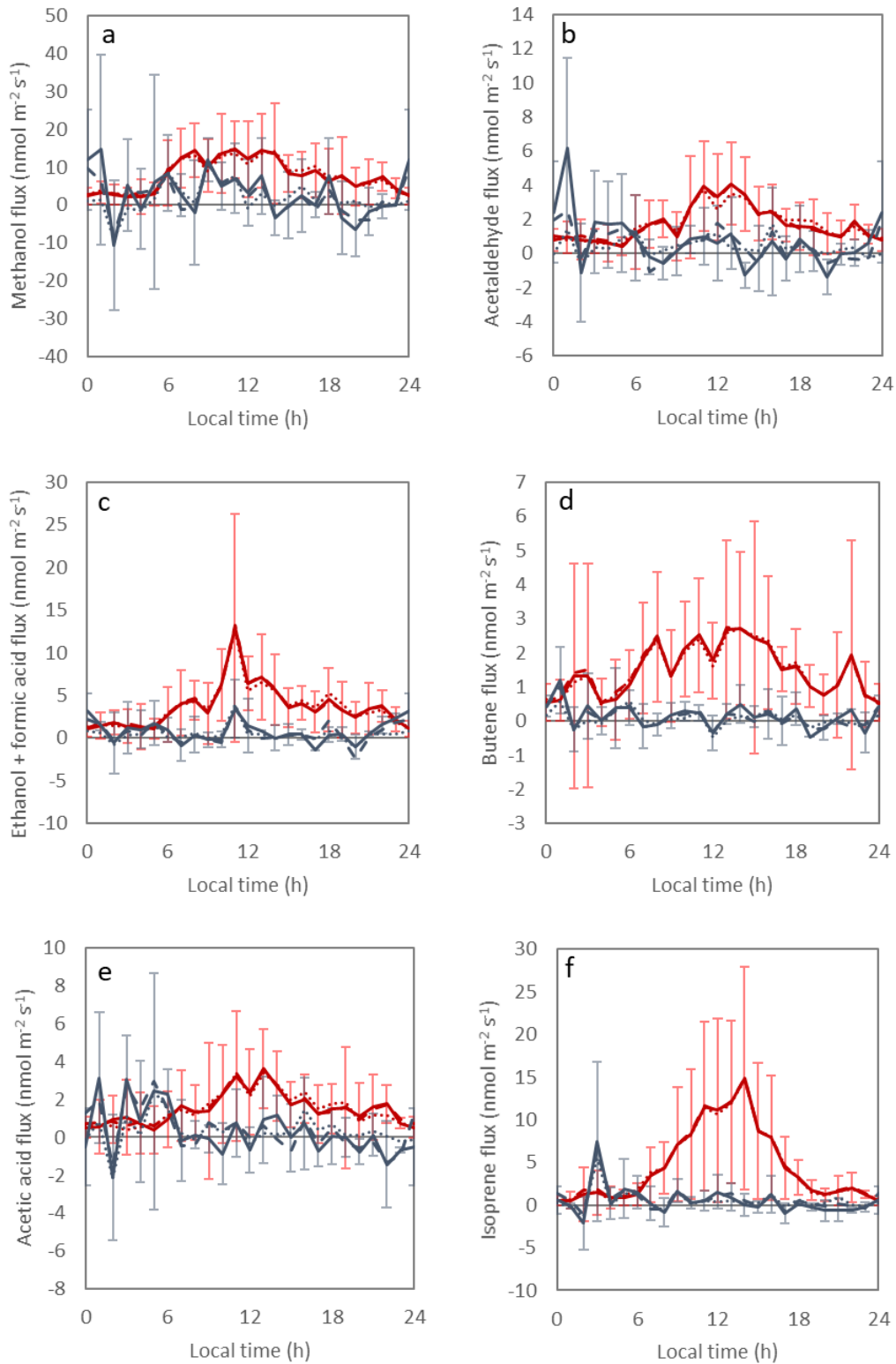


Figure 5: Diurnal cycles of the fluxes of six compounds with the largest observed fluxes for the summer (red) and winter (blue) campaigns, with error bars showing standard deviation of the stationarity filtered and fluxes including the storage term (solid lines). Dashed lines represent the flux without the storage term and dotted lines are u^* filtered fluxes including the storage term and gap filled with the average flux above the u^* threshold for that hour.

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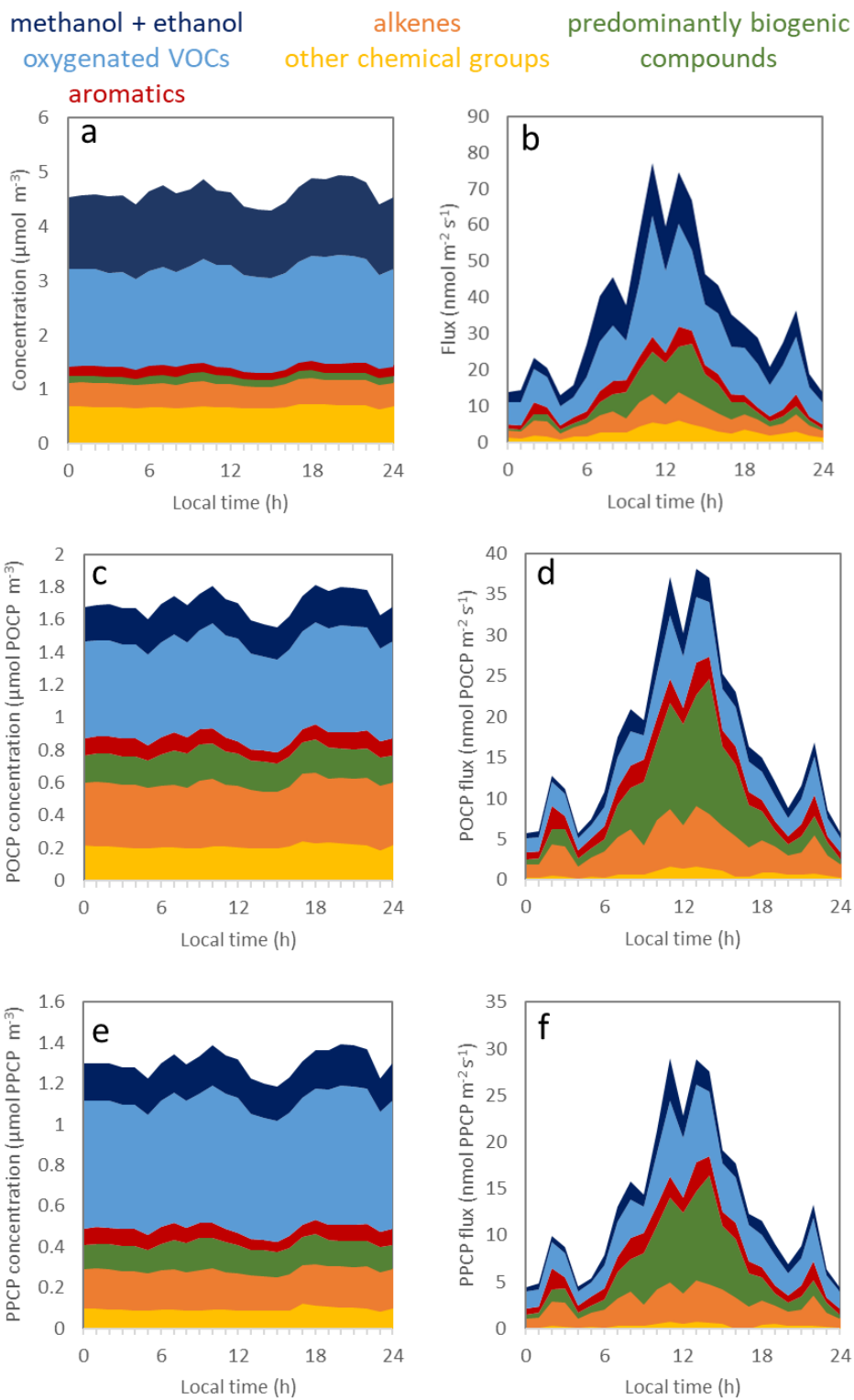
3.4.2 Anthropogenic VOC fluxes

Combustion products are a major source of anthropogenic VOCs in urban areas. The correlation between (a) the NO_x flux and (b) those VOC species contributing more than 0.75% to the total measured VOC flux is shown in Fig. 7. NO_x fluxes during the campaigns have previously been reported by Squires et al. (2020). In urban areas NO_x is almost exclusively produced by combustion sources of which motor vehicles are the main source. The NO_x flux is therefore used here as proxy for vehicular emissions. The fluxes of the aromatic VOCs toluene, C_2 -benzenes (the sum of xylenes and ethyl benzene which cannot be separated using PTR-MS) and C_3 -benzenes (the sum of all compounds featuring a benzene ring and three methyl groups) show a good correlation with the fluxes of NO_x , with R^2 values of 0.75, 0.64 and 0.61, respectively. Fluxes of toluene, C_2 and C_3 benzenes all follow a similar diurnal profile; after a small peak in the early morning emissions increase from 06:00 and peak between 10:00 and 15:00 and then decrease in the evening with another small peak at 22:00. As shown in Fig. 7 the fluxes of aromatic compounds were closely correlated, suggesting that they are emitted from the same source. Beijing operates a motor vehicle emissions control program which only allows non-local heavy duty vehicles to enter the city between 00:00 and 6:00 (Yang et al., 2015) and this may explain the peak in aromatic emission observed at 02:00 (Fig. 6). These compounds are known to be combustion products and are also emitted by evaporation. These fluxes are discussed in detail by Squires et al. (2020) who found that while the winter benzene and toluene fluxes (0.01 and $0.03 \text{ nmol m}^{-2} \text{ s}^{-1}$, respectively) were smaller than those observed in London and Manchester, the Beijing summer fluxes (0.18 and $0.61 \text{ nmol m}^{-2} \text{ s}^{-1}$ for benzene and toluene, respectively) were comparable to those reported in Europe (Langford et al., 2009; Langford et al., 2010; Valach et al., 2015; Vaughan et al., 2017). The toluene flux is, however, significantly lower than the 2.5 and $9.2 \text{ nmol m}^{-2} \text{ s}^{-1}$ recorded at two sites in Mexico City (Velasco et al. 2005; 2009). Velasco et al. (2009) identified both exhaust emissions and evaporative sources contributing to the toluene flux. The addition of these evaporative sources in Mexico City as well as differences in vehicle fleets may explain why these fluxes were larger than those recorded in this study and in the UK. Squires et al. (2020) also concluded that the benzene/toluene ratio was within the range expected for primary exhaust emissions with values for concentrations of 0.89 and 0.73 in the winter and summer respectively. These values are, however, higher than the 0.6 calculated by Barletta et al. (2005) for Beijing. For fluxes, the benzene/toluene ratio was 0.72 in winter and 0.31 in summer (Squires et al. 2020). The summer value is lower than expected for primary exhaust emissions, suggesting that fuel evaporative loss contributes to aromatic VOC emission in summer (Squires et al. 2020).

The fluxes of propene and methanol were shown to correlate with the flux of NO_x with R^2 values of 0.63 and 0.71 . Propene is known to be emitted by vehicular traffic (Velasco et al. 2005; 2009) and the correlation with NO_x suggests that traffic is the main source at this site. Propene has also been recorded in plumes of VOCs released from industrial activity (Karl et al., 2003), but no large industrial sites were present within the flux footprint of the IAP tower. Large fluxes of propene were recorded, with average emissions of 0.64 and $0.93 \text{ nmol m}^{-2} \text{ s}^{-1}$ in the winter and summer, respectively. In the winter the strongest emission occurred early in the morning with little emission later in the day. In the summer measurement period, emissions increased from 06:00 before peaking at mid-day and decreasing in the late afternoon. Methanol is emitted from plants and industry and is formed by oxidation reactions in the atmosphere (Jacob et al., 2005). It is also present in many consumer goods products (Steinemann, 2015). The close correlation with the NO_x flux 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 (Fig. 7). Methanol had the largest molar flux of any VOC species recorded in the summer (Fig. 5), with average emissions of 2.15 and 8.02 $\text{nmol m}^{-2} \text{s}^{-1}$ in the winter and summer, respectively. These methanol emissions are comparable to those observed in London and Mexico City with 2.5 $\text{nmol m}^{-2} \text{s}^{-1}$ (August to December) recorded by Valach et al. (2015), 8.2 $\text{nmol m}^{-2} \text{s}^{-1}$ (October) reported by Langford et al. (2010) in London, and 9.1 and 12.8 $\text{nmol m}^{-2} \text{s}^{-1}$ (April and March respectively) reported in Mexico City (Velasco et al., 2005; 2009). Methanol mixing ratios were, however, significantly higher in Beijing than in London with average mixing ratios in Beijing 28.2 and 24.3 ppbv in the winter and summer compared with 7.5 and 19.4 ppbv reported by Valach et al. (2015) and Langford et al. (2010) at 61 and 200 m, respectively.

525 Acetonitrile is considered a tracer for biomass burning (de Gouw et al., 2003), but can also be produced by the burning of fossil fuels (Holzinger et al., 2001). Acetonitrile fluxes in the summer field campaign were low, with a median value of 0.15 $\text{nmol m}^{-2} \text{s}^{-1}$, but regularly peaked between 16:00 and 18:00 in the evening with a maximum value of 10.6 $\text{nmol m}^{-2} \text{s}^{-1}$, potentially indicating a cooking source. In the winter the median acetonitrile flux was small (0.11 $\text{nmol m}^{-2} \text{s}^{-1}$) with peaks of up to 1.21 $\text{nmol m}^{-2} \text{s}^{-1}$ observed in the early hours of the morning. As
530 cooking rates are likely to be comparable in the summer and winter, the reduced winter acetonitrile flux could be explained by reduced ventilation of homes in the winter.



535 Figure 6. Total observed VOC concentration (a) and flux (b) measured during the summer field campaign, scaled using photochemical ozone creation potentials (POCPs) (c, d) and photochemical PAN creation potentials (PPCPs) (e, f).

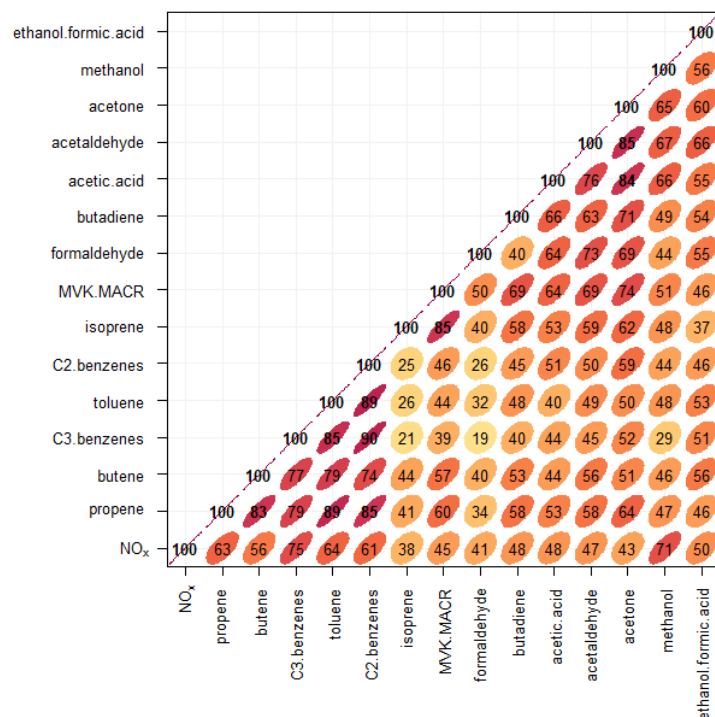


Figure 7. Correlation plot showing the relationship between the fluxes of all identified compounds that contribute more than 0.75% to the total measured VOC flux in the summer measurement campaign as well as the NO_x flux. Numbers and colour represent the % R² value of each correlation.

3.4.3 Biogenic fluxes

Globally, plants are the main source of VOCs into the atmosphere, with isoprene and monoterpenes the main VOC species emitted (Guenther et al., 1995; 2012). However, in urban areas, isoprene is present from both biogenic and vehicular sources (e.g. Borbon et al., 2001; Langford et al., 2010; Valach et al., 2015; Jaimes-Palomera et al., 2016). In the current study, significant BVOC emissions were observed in the summer campaign, with average emissions of 4.63 nmol m⁻² s⁻¹ for isoprene and 0.15 nmol m⁻² s⁻¹ for monoterpenes. At night-time, emissions of both monoterpenes and isoprene were close to zero with mixing ratios dropping to 0.3 ppbv from a mid-day peak of 0.7 ppbv. Emissions began to increase at 06:00 before peaking at mid-day and returning to zero at around 20:00 (isoprene emissions are displayed in Fig. 5). The summer isoprene flux correlated well (R² 0.85) with the flux of the isoprene oxidation products methyl vinyl ketone and methacrolein (MVK+MACR) and poorly with traffic tracers such as toluene, C₂-benzenes (R² 0.26 and 0.25) and NO_x (R² 0.38) (Fig. 7). This suggests that the contribution from traffic emissions to the summer isoprene flux is low compared to the biogenic source. In the winter campaign, emissions of both isoprene and monoterpenes were comparatively small with average fluxes of 0.79 and 0.06 nmol m⁻² s⁻¹, respectively. Despite the weak isoprene flux, mixing ratios were larger in winter than in summer with mixing ratios consistent through the day at an average value of 1.21 ppbv. The high isoprene mixing ratio in the winter suggests transport of anthropogenic isoprene from outside of the flux footprint together with a lower rate of photochemical loss than in the summer. The low winter isoprene flux suggested a small contribution of anthropogenic isoprene to the total flux. Sesquiterpenes were also recorded in the summer with a

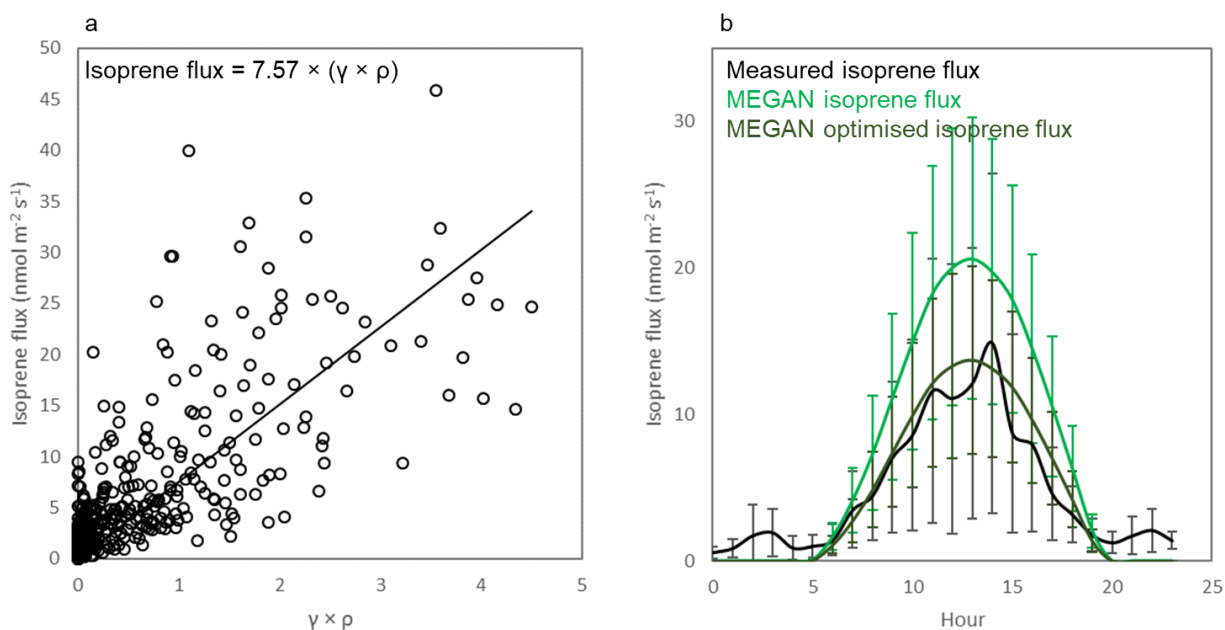
560 mean mixing ratio of 0.04 ppbv but a flux was not detected. The summer isoprene flux is larger than that recorded
in London (Valach et al., 2015) where an average emission of $0.53 \text{ nmol m}^{-2} \text{ s}^{-1}$ was observed between August
and December. This is likely to be due to the London emissions being reduced by the generally lower temperatures
and radiation levels, both due to the difference in latitude and also the inclusion of autumn and winter flux data.
In the summer campaign predominantly-biogenic compounds accounted for 13% of the total molar VOC flux and
565 42% of non-oxygenated hydrocarbon emission.

Isoprene emission from biogenic sources is commonly modelled using the Model of Emissions of Gases and
Aerosols from Nature (MEGAN, Guenther et al., 2006). Emission of isoprene in MEGAN is calculated as:

$$\text{Emission} = \varepsilon \times \gamma \times \rho, \quad (6)$$

where ε is an emission factor ($\text{nmol m}^{-2} \text{ s}^{-1}$) representative of the isoprene emission from a plant canopy under
570 standard conditions, γ is a dimensionless emission activity factor representing deviation from standard conditions
and ρ is a factor (normalised ratio) accounting for loss within the canopy. By default, the emission factor used by
MEGAN for Beijing is $11.04 \text{ nmol m}^{-2} \text{ s}^{-1}$. The expected isoprene flux from Beijing was modelled using MEGAN
together with photosynthetic photon flux density (PPFD) and atmospheric temperature recorded at the IAP
metrological tower. The leaf area index (LAI) for Beijing was 1.0 for May and 1.7 in June with these values taken
575 from the MERRA-2 reanalysis data set for 2017. The flux predicted by MEGAN over-estimated the observed flux
with the modelled mean diurnal isoprene flux peaking at $21 \text{ nmol m}^{-2} \text{ s}^{-1}$ compared to the measured isoprene flux
which peaked at $14 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Fig. 8b).

The measured isoprene flux together with the product of the emission activity factor and loss factor ($\gamma \times \rho$) can be
used to optimise the emission factor (ε) for the flux footprint. Langford et al. (2017) used a weighted mean to
580 determine the isoprene emission factor which ensures that the modelled isoprene emission has the same average
as the measured flux. This approach gives an emission factor of $10.16 \text{ nmol m}^{-2} \text{ s}^{-1}$ for the summer campaign.
Using this emission factor MEGAN estimates a diurnal flux peaking at $18 \text{ nmol m}^{-2} \text{ s}^{-1}$. This value is elevated by
the low, anthropogenic, night-time flux observed in Beijing. Alternatively, an optimised isoprene emission factor
can be calculated using the least-square regression between the measured isoprene flux and ($\gamma \times \rho$) (Fig. 8a). This
585 gave an isoprene emission factor of $7.57 \text{ nmol m}^{-2} \text{ s}^{-1}$, representing an optimised emission factor for central
Beijing. When using this emission factor, the mean diurnal isoprene flux predicted by MEGAN peaked at 14 nmol
 $\text{m}^{-2} \text{ s}^{-1}$ (Fig. 8b). This compares well with the measured isoprene flux and represents a more appropriate emission
factor than that calculated using the weighted mean approach. This optimised emission factor is 69% of the default
MEGAN emission factor value for Beijing.



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Figure 8. (a) Measured isoprene flux plotted against the product of the emission activity factor (γ), and the canopy loss and production factor (ρ). (b) Diurnal profiles of the isoprene flux predicted by MEGAN using the default and optimised emission factors together with the measured isoprene flux. Error bars represent standard deviation across the measurement period.

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3.4.4 Impact on atmospheric chemistry

The relative impact of individual VOCs on ozone and peroxyacyl nitrates (PAN) formation can be determined by considering the photochemical ozone creation potentials (POCPs) and the photochemical PAN creation potentials (PPCPs) of the observed compounds. The POCP represents the increment in ground-level ozone production due to the photochemistry of that compound relative to the ozone increment due to ethane. PPCP represents the PAN increment due to the photochemistry of that compound relative to that of propene. 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. Derwent et al. (1998) used NO_x concentrations of 0.014 mg m⁻³ as the base case when determining POCPs and tested the POCP calculation at half and double these concentrations. The median NO_x concentration observed in the Beijing summer campaign was 0.0213 mg m⁻³ (Squires et al., 2020), within Derwent's twice base case range. Where a measured mass was not reported by Derwent et al. (1998) the average POCP and PPCP for the appropriate chemical class were applied. It should be noted that as alkanes cannot be detected using PTR-ToF-MS these compounds are not included here. Due to their low POCP and PPCP relative to alkenes and many oxygenated compounds, alkanes are likely to have a limited impact on ozone and PAN formation. However, at large concentrations they can still have a significant impact (Jaimes-Palomera et al., 2016).

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Figures 6c and 6d show the concentrations and fluxes scaled by POCP, respectively. Of those compounds resolved by PTR-ToF-MS, predominantly-biogenic compounds were the largest source of POCP making up 34% of the total POCP-scaled flux. Oxygenated compounds were also a significant source of POCP due to the large molar

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615 flux of these compounds, with methanol and ethanol + formic acid making up 13% of the POCP-scaled flux and
other oxygenated VOCs 18%. The PPCP-scaled fluxes and concentrations are shown in Figs. 6e and 6f
respectively and show that, as with the POCP, oxygenated and **predominantly-biogenic** VOCs are likely to make
the largest contribution to photochemical PAN formation. **The large contribution of alkenes, grouped here as**
alkenes and predominantly biogenic compounds, to ozone formation was also observed in Mexico City where
620 **Velasco et al. (2007) found that despite making up 5% of the measured VOC mixing ratio alkenes made the largest**
contribution to ozone formation.

The influence of VOCs on OH and **o**zone reactivity was determined by the VOC reaction rate with the OH radical
and ozone, relative to that of ethane. VOC reaction rates with the OH radical and ozone were taken from Atkinson
and Arey (2003) and references therein. **Predominantly-biogenic** compounds dominate the OH reactivity scaled
625 VOC flux making up 51% of the potential OH reactivity emitted (Fig. 9b). Oxygenated VOCs and non-aromatic
hydrocarbons (predominantly butene and propene) represent 22% and 17% of the VOC flux scaled by OH
reactivity respectively. The VOC concentrations scaled by OH reactivity (Fig. 9a) shows that of the VOCs
measured using PTR-ToF-MS oxygenated compounds have the largest impact on OH reactivity. This is caused
by the very high mixing ratios of these compounds relative to other chemical groups in the atmosphere. However
630 once scaled by OH reactivity **predominantly-biogenic** compounds, which only make up 4% of the total measured
VOC concentration (Fig. 9a), are shown to contribute 21% to the total measured VOCs scaled by OH. Ozone
reactivity is dominated by alkenes with **predominantly-biogenic** compounds and non-aromatic hydrocarbons
(predominantly butane, C₆H₁₀ and C₇H₁₂) making up 31 and 61% of the potential ozone reactivity emitted
respectively (Fig. 9d).

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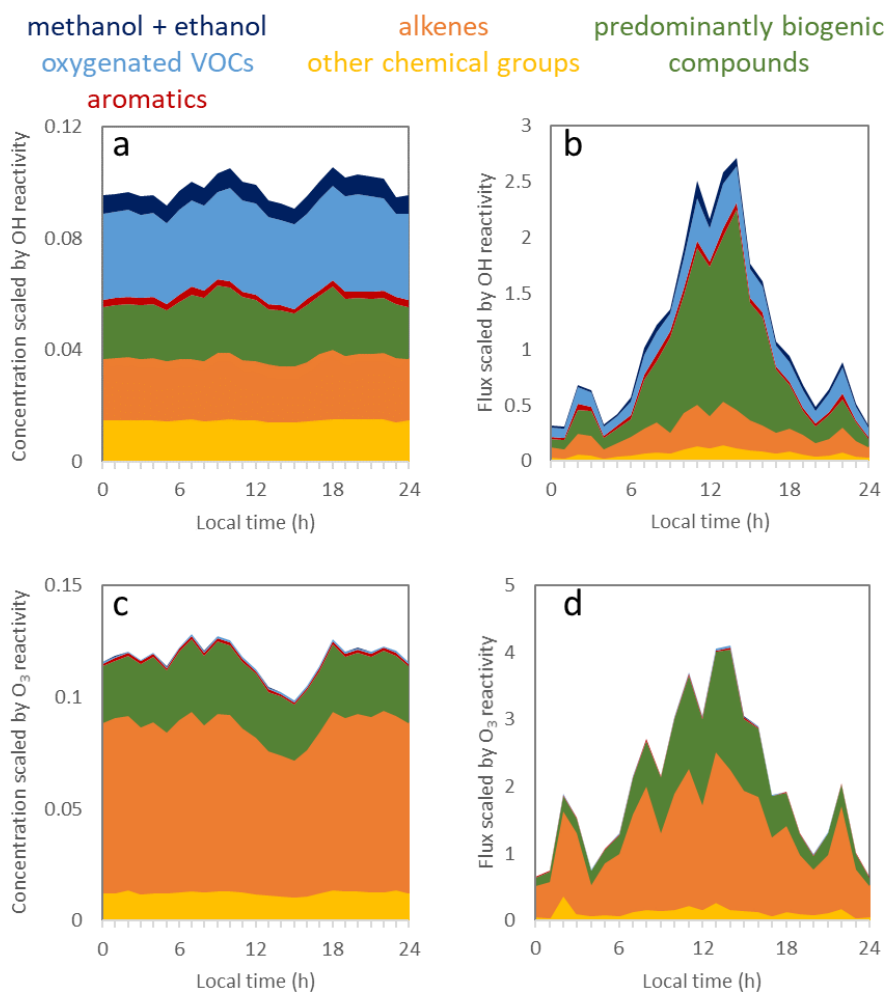


Figure 9. Total observed VOC concentration and flux measured during the summer field campaign scaled using by OH (a, b) and O₃ (c, d) reactivity relative to ethane.

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3.5 Emission factor analysis and validation

The Multi-resolution Emissions Inventory for China (MEIC, Qi et al. 2017; <http://www.meicmodel.org/>) is a comprehensive inventory of the emission of atmospheric pollutants across China and provides the emissions input to many modelling studies (e.g. Hu et al. 2016). Inventories such as MEIC use emissions estimates from individual sources scaled by activity to provide a “bottom-up” emissions estimate. 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 VOC flux measurements presented here provide a “top-down” measurement at the cityscape-scale which can be used to validate the emissions inventory encompassed by the flux footprint. Zhao et al. (2017) assessed the uncertainties in emissions inventories for China and recommended that field studies were used to improve emission estimates.

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The MEIC includes emissions from five sectors: power plants, transportation, industrial, agricultural and residential sources with VOC emissions collated by functional group. As no agricultural land was present within the flux footprint, agricultural emissions are not considered here. Within the MEIC inventory VOCs are grouped

655 into classes. Nine of these groupings were considered but those containing alkanes were not considered as alkanes
 660 have a proton affinity less than that of water and could not be detected using PTR-MS. The groupings, based on
 the speciation used by the RADM2 chemical mechanism, are summarised in Table 3. The emission ratio of
 different VOC species present within each grouping could represent a source of error in the inventory.

VOC emissions estimates for the summer campaign period were calculated through combination of the flux
 footprint (100 m × 100 m) and high resolution (3 km × 3 km) MEIC v1.3 inventory for 2013. First, the footprint
 660 for each flux aggregation period and the inventory grid for the corresponding hour of day were aligned by
 transforming the flux footprint into the coordinate reference system of the inventory. Subsequently the inventory
 values were extracted at the centre of each footprint grid cell, creating a pseudo 100 m × 100 m inventory. This
 was multiplied by the footprint grid, weighting each cell by their contribution to the measured flux. There was
 little variation between VOC emission factors from the main four emissions inventory cells contributing to the
 665 flux observed at the IAP tower site.

Table 3. The measured compounds used to validate the MEIC VOC groupings.

<i>MEIC VOC grouping</i>	<i>Definition</i>	<i>Measured compounds</i>
<i>HCHO</i>	formaldehyde	formaldehyde
<i>ALD</i>	acetaldehyde and higher saturated aldehydes	acetaldehyde; butanal
<i>CH3OH</i>	methanol	methanol
<i>C2H5OH</i>	ethanol	ethanol + formic acid
<i>TOL</i>	toluene and less reactive aromatics	toluene; benzene
<i>XYL</i>	xylene and more reactive aromatics	C2 benzenes; C3 benzenes; C4 benzenes; naphthalene; C11H14
<i>KET</i>	ketones	acetone; pentanone
<i>ISO</i>	isoprene	isoprene
<i>ORA2</i>	acetic acid and higher acids	acetic acid; propionic acid

670 Fig. 10 shows the comparison between measured VOC emission (summer campaign) and the VOC emission
 predicted by the MEIC inventory for this period with the percentage contribution of each group to the total flux
 displayed in Fig. 11. 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). Squires et al. (2020) compared NO_x and CO
 fluxes recorded during the APHH-Beijing campaigns with the MEIC inventory and also observed a similar
 overestimation of emissions by the inventory for the fluxes of NO_x by a factor of 4.2 to 25 and of CO by a factor
 675 of 1.6 to 9.7 in summer. Industrial emissions make the largest contribution to aromatic VOC emission in the
 inventory. However, inspection of the flux footprint reveals few potential industrial sources with the footprint
 encompassing roads and residential building as well as shops and restaurants. At a coarser resolution of 9 × 9 km
 the TOL emission peaked at 25 nmol m⁻² s⁻¹, 9 times higher than the measured flux indicating that the overestimate
 was in part caused by the proxies used to downscale the inventory to 3 km. Previous studies have shown that the

680 inventory underestimates aromatic emission at the Chinese scale (Liu et al., 2012b; Cao et al., 2018), again
indicating that the overestimation observed here is a result of the downscaling of the inventory. The allocation of
industrial emissions to this residential area is likely a result of downscaling the emissions using proxies such as
population (Zheng et al., 2017). Even discounting the industrial emissions, the predicted emissions of TOL and
685 XYL are still 8 times larger than the measured flux at the 3 by 3 km resolution. The inventory does capture the
diurnal cycle in emissions with a rapid increase in aromatic VOC emissions at 07:00, emissions remaining high
throughout the day before decreasing after 17:00.

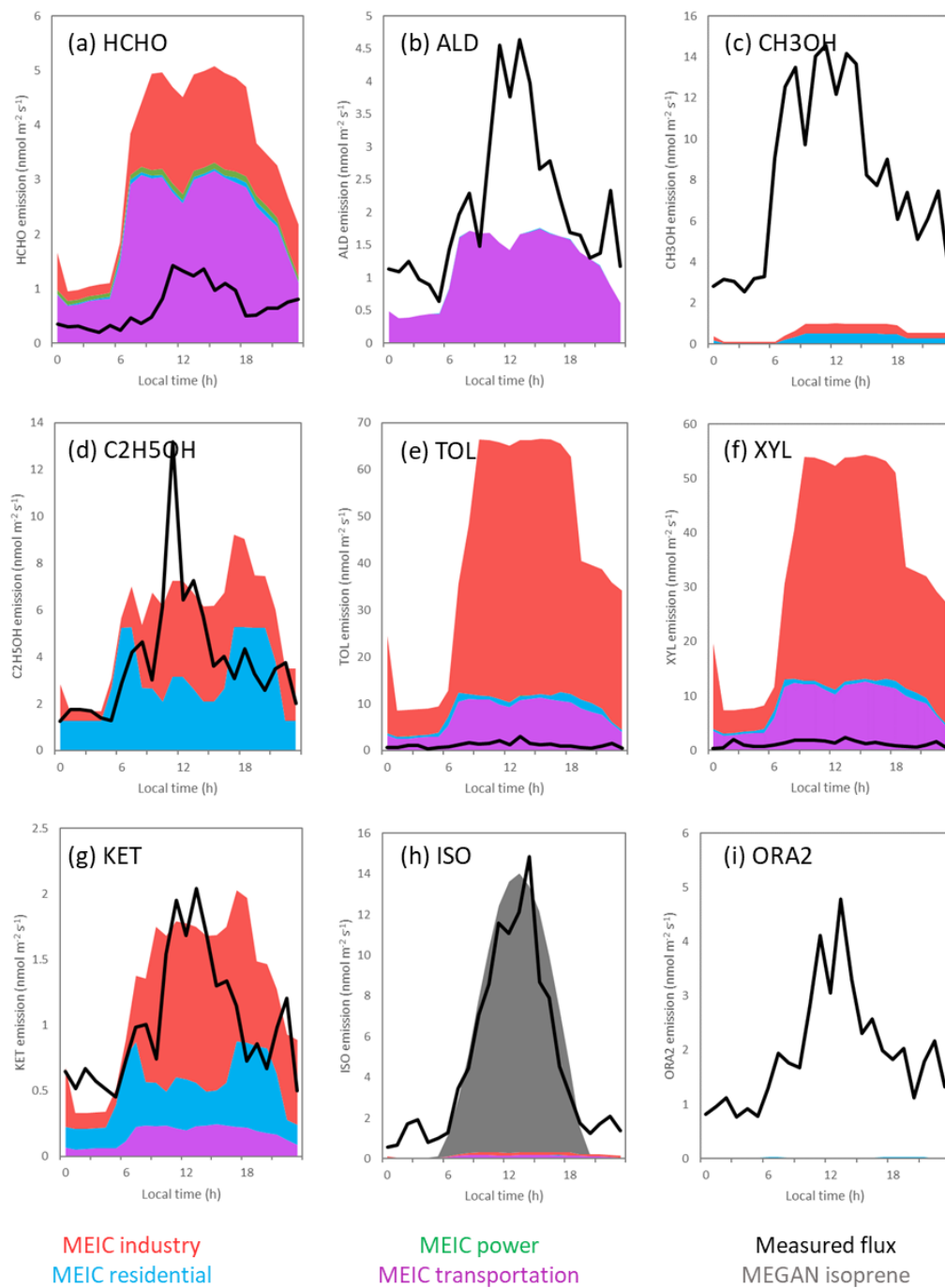
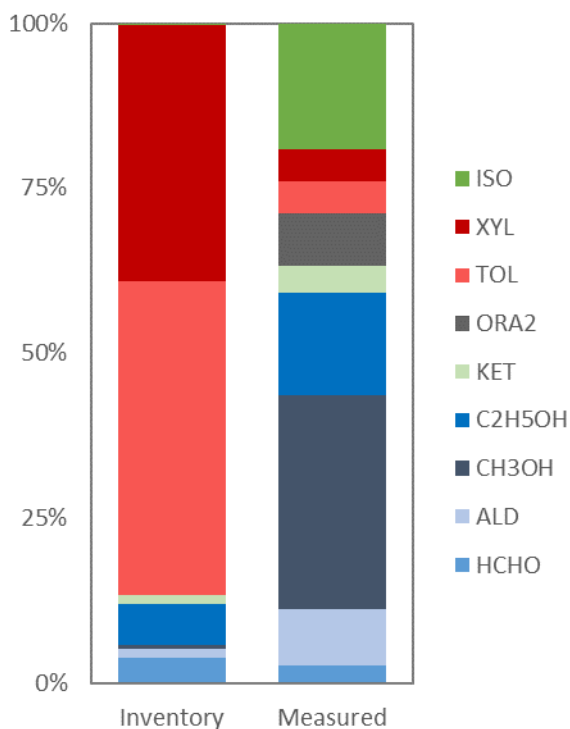


Figure 10. Comparison of 9 VOC classes from the MEIC emissions inventory (Table 3) with measured VOC flux (black line). The diurnal profiles of the isoprene emission predicted by MEGAN using the optimised emission factor is shown in grey (h).



695 Figure 11. The percentage contribution of the MEIC VOC groupings to the total emission.

Isoprene emissions are significantly underrepresented in the inventory with measured fluxes 20 times higher than inventory emissions. This is expected as the inventory only considers anthropogenic emission and in the summer isoprene emissions are dominated by **predominantly-biogenic** isoprene. **Adding the isoprene emission predicted by MEGAN to the MEIC emission (Fig. 10h) shows that the inclusion of biogenic isoprene enables a more accurate estimate of total isoprene emission.** The park at the base of the tower means that a larger biogenic source may be present at the IAP site than would be expected for Beijing **on average.**

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The performance of the inventory in relation to oxygenated VOCs varied considerably between chemical classes. The inventory was more accurate when estimating emissions of ethanol, formaldehyde and ketones with measured emissions 71, 20 and 81% of inventory emissions. When industrial emissions are removed **these** increase to 132, 30 and 194% of **the inventory** emissions suggesting that, **despite the PTR-ToF-MS only capturing two ketones,** ketone emissions are significantly underestimated from residential and transport sources. Measured methanol, aldehydes and organic acid fluxes were also underestimated by the inventory with the measured flux 13, 1.8 and 107 times higher than the inventory, respectively.

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It is **possible** that some underestimation of methanol, aldehydes and organic acid fluxes can be explained by their formation **on surfaces** following the oxidation of primary-emitted **predominantly-biogenic** (e.g. Lee et al. 2006; Acton et al., 2018) or anthropogenic compounds (Atkinson, 2000). **However, given the ~68 s time taken for an air parcel to reach the inlet point it is not likely that formation in the atmosphere contributes significantly to the flux of these compounds.** **Consumer** goods are **known to be** a large source of oxygenated VOCs (Dinh et al., 2015; Nematollahi et al., 2019). The use of these products is likely to vary considerably between households, making bottom-up emission hard to estimate.

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4 Summary

720 Fluxes of speciated VOCs at district scale were measured for the first time in central Beijing with emissions dominated by small oxygenated compounds methanol, acetaldehyde, and ethanol and formic acid which could not be separated. Mixing ratios of most species were significantly higher in the winter than in the summer with VOCs following the “saw tooth pattern” driven by meteorology that has been reported for other pollutants (e.g. Jia et al. 2008). Mixing ratios of aromatic compounds were lower in the summer than in the winter but mixing ratios of small oxygenated VOCs such as methanol were higher, possibly as a result of increased photochemistry but also consistent with their larger emission fluxes.

725 Stable atmospheric conditions in the winter led to weak turbulent transport making it more difficult to determine their surface emission rate using the micrometeorological eddy covariance method. The observed VOC fluxes in the winter were weaker than those recorded in the summer, probably due to low volatilisation of VOCs and deposition of VOCs transported from outside the city. The flux in both seasons was dominated by small oxygenated compounds: methanol, acetaldehyde and ethanol + formic acid. These compounds are known to be
730 oxidation products but are also present in many consumer goods products. Fluxes of aromatic compounds in the summer campaign were comparable to those observed over London and Manchester (Langford et al., 2009; Valach et al., 2016; Vaughan et al., 2017) despite the mixing ratios being larger than those observed in those cities. This suggests that the elevated mixing ratios are driven by transport from outside the city. Both fluxes and mixing ratios of toluene were lower than those recorded in Mexico City (Velasco et al., 2009). Comparison of measured
735 VOC fluxes with those predicted by the emissions inventory showed that the inventory failed to capture VOC emission at this local scale.

Isoprene and monoterpenes, compounds predominantly emitted from biogenic sources, contributed 13% to the measured molar flux of VOCs but just 3% of the total recorded VOC mixing ratio. Comparatively, oxygenated compounds made up 60% of the molar flux of the compounds resolved by PTR-MS, aromatic compounds made up 7% and other alkenes contributed a further 11%. However, the high reactivity of isoprene and monoterpenes means that their contribution to ozone and PAN formation was greater, with predominantly-biogenic VOCs representing 30 and 28% of the flux contribution to ozone and PAN formation potential, respectively. This effect is even larger in respect to the OH reactivity, where predominantly-biogenic VOCs represent 50% of the total potential OH reactivity of the VOCs emitted and 21% of the mixing ratio when scaled by OH reactivity.
740 Establishing local scale activity data and improved proxies for the scaling of emissions should therefore be a priority when further developing emission inventories for Beijing.

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 on all VOC sources, but particularly on vehicles,
750 in regions surrounding the megacity. Predominantly-biogenic compounds make significant contribution to the photochemical ozone creation potential (POCP), photochemical peroxyacyl nitrates (PAN) creation potential (PPCP) and potential OH reactivity emitted from the city but currently contribute only a small proportion of total reactivity in the atmosphere. However, as transport of VOCs from outside the city is reduced in the future by

755 policy interventions, biogenic sources within the city are likely to become increasingly important to atmospheric
chemistry. It is therefore important that emission inventories of VOCs in Beijing should also include an estimate
of biogenic VOC emissions, using a tool such as MEGAN with appropriate leaf area index and emission factor
values.

Data availability. Data are available at <https://catalogue.ceda.ac.uk/uuid/7ed9d8a288814b8b85433b0d3fec0300>
760 (last access: 08/04/2020). Specific data are available from the authors on request (wangxm@gig.ac.cn).

Author contributions. WJFA made VOC concentration measurements, calculated VOC fluxes and performed
VOC data analysis. WJFA prepared the manuscript with contributions from co-authors. ZH, ZW and BD assisted
with VOC concentration measurements. FAS made NO_x concentration measurements, calculated their flux and
765 reviewed the manuscript. EN, BL and NM set up instrumentation on the IAP tower, measured wind vector data,
provided advice on flux calculations and reviewed the manuscript. WSD, ARV and SM provided support
calculating fluxes using eddy4R software and reviewed manuscript. YL performed MEGAN analysis. QZ
provided high resolution emissions data. MH processed the raw emissions data into gridded format for comparison
with the measured fluxes. OW assisted with interpretation of the inventory emissions data and provided a detailed
770 review of the manuscript. XW and YZ prepared the PTR-MS instrument and calibration system. PF maintained
the tower and site necessary for this work. CER and JL reviewed the manuscript. CNH obtained funding,
interpreted data, helped prepare the manuscript and reviewed the manuscript.

Competing interests. The authors declare that they have no conflict of interest.
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