Letter of Responses

Manuscript: Validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China (Ref. No.: acp-2013-752)

Overall, the manuscript is a solid evaluation of NMVOC emission inventories using measurements throughout Beijing. The authors employ a variety of measurement techniques and analysis methods to assess NMVOC emissions from spatial, temporal, and species specific aspects. More such studies are needed in other locations to improve NMVOC emission inventories.

Response: The encouragements are appreciated.

General Comments: There are a few specific items which could be addressed to improve the paper, however, generally, the paper is quite well written.

There is one exception to this, which I address in the specific comments, but also mention here for emphasis. Of the CMB assessment measures, the chi-square, is not within the target range. These results should be revisited and this fitting statistic explained or the model re-run, since this could, in theory, have a significant effect on the CMB results. I don't expect that it necessarily will, but better to assess this than to make assumptions.

Response: Yes, to meet all the statistical requirements for a reliable CMB run are indeed important. This comment will be answered in details in **Specific Comment (6)**.

Specific Comments

(1) P26943L8: This sentence mentions that the chemical composition of ambient VOCs can be affected by their emission and their photochemical removal or formation. Agree, however, the reference to 'by their emission' is not clear. The chemical composition is initially determined by the relative amounts contributed from the various VOC emission sources, is this what is meant? If yes or no, please clarify, because as written it is not really grammatically correct, but is therefore also confusing as to what is meant.

Response: Accepted. The sentence in the revised manuscript was modified to be "*The chemical composition of ambient VOCs can be affected by the relative contributions of various VOC emission sources, photochemical and mixing processes during transport.*"

(2) P26943L20-27: When discussing isoprene as an anthropogenic source, it may be of interest to also compare to earlier papers by A. Borbon et al. in Atm Env 2003 or Sci of the Total Env 2002, although they are not from measurements in China.

Response: Thanks for your suggestions and accepted. One earlier paper on isoprene emission from vehicle exhaust written by Borbon et al. (2001) was cited in the revised manuscript to compare with the findings in Beijing.

The sentence in the revised manuscript was changed to be *"Ambient levels of isoprene and 1,3-butadiene measured in Beijing during winter (November–March) showed a significant correlation (r^2 = 0.56), with the average ratio of 0.29 ppbv ppbv^{-1}. The calculated wintertime ratio of isoprene/1,3-butadiene in Beijing was close to the values of 0.30–0.34 ppbv ppbv^{-1} in vehicular exhaust reported by Borbon et al. (2001) in France and Wang et al. (2010) in Beijing, indicating that vehicular exhaust was the dominant source of isoprene during winter."*

(3) P26945L23-25: For consistency with some of the papers listed earlier in the section, it would be nice to state the correlations as r^2 values instead of just r.

Response: Thanks for your suggestions and accepted. In order to compare with previous studies, we listed the r^2 values to show the correlations between VOC species and CO. The sentences in the revised manuscript were modified accordingly.

(4) P26945L25-27: One of the explanations for the poor correlation with CO is listed as photochemical processing, which the Figure that is shown supports. However, there are also other possibilities, such as greater influence of other sources, while vehicle emissions dominate, other sources could have a significant impact and thereby influence the correlations. It might be worth mentioning this and any other possibilities, while acknowledging that the figure you show would tend to indicate photochemical processing.

Response: As the reviewer mentioned, some VOC species can be emitted from non-combustion anthropogenic sources (e.g. *i*-pentane from gasoline evaporation, toluene from paint and solvent utilization) or biogenic sources. The VOC species dominated by non-combustion sources might have bad or weak correlations with CO. For example, summertime isoprene measured in Beijing did not show a significant correlation with CO, due to the influence of biogenic emission. However, we found all anthropogenic VOC species showed significant correlations with CO in Beijing both at summer and winter, even for ethane and propane that were usually used as tracers of natural gas (NG) leakage (Katzenstein et al., 2003) and liquefied petroleum

gas (LPG) usage (Blake and Rowland, 1995), respectively. In addition, we found that the r^2 values for correlations between non-methane hydrocarbon (NMHC) species and CO at the PKU site during summer decrease with the rising of NMHC reactivity (Fig. R1), indicating the important effects of photochemical processing on measured ratios of VOC to CO.

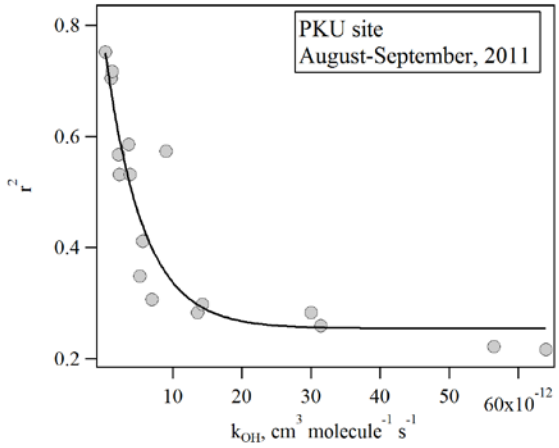

Fig. R1 Scatter plots of r^2 values for correlations between VOC species and CO at the PKU site during Aug.–Sep., 2011.

(5) P26949L24-27: It is unclear if just the 2011 measurements were at the PKU site or all of them. I would assume the others, being from other studies, were measured elsewhere. It would be worth clarifying because this would be a factor that might come into play in the subsequent sentences where comparisons are made.

Response: The online VOC measurements mentioned in this sentence, including 2005, 2008, 2010, and 2011, were all conducted at the PKU site. To make this sentence more clear, we modified it to be "*Figure 7b–d compares the summertime emission ratios of individual VOC species at the PKU site during 2011with those derived from online VOC measurements during 2010 (Yuan et al., 2012), 2008 (Wang et al., 2010), and 2005 (Liu et al., 2009) at the same site*".

(6) P26954L17-20: The CMB model performance parameters listed are within acceptable intervals for the r^2, however the chi-square (χ^2) value has a target range of 0–4, not 2–6, as was mentioned. Taken directly from the EPA CMB information: 'A large CHI SQUARE (>4.0) means that one or more of the calculated species concentrations differs from the measured concentrations by several uncertainty intervals. The values for these statistics exceed their targets when: 1) contributing sources have been omitted from the CMB calculation; 2) one or more source profiles have been selected which do not represent the contributing source types; 3) uncertainty estimates of receptor or source profile data are underestimated; and/or 4) source or receptor data are inaccurate.' If these results are to remain as they are it

would be necessary to justify why the chi square value is acceptable in the 2–6 range, otherwise the CMB results may need to be re-assessed.

Response: The range of χ^2 (2.04–6.01) reported in P26954 was incorrect. The χ^2 for CMB application in this study ranged from 0.52 to 6.01 (Table S4), with the average value of 2.04. We are sorry for this mistake. The sentence was corrected in the revised manuscript.

As the reviewer mentioned, the acceptable range for χ^2 value of CMB modelling is 0–4 (EPA, 2004). In this study, three VOC datasets were applied as input data of CMB model to calculate relative contributions of each source, including the 16-month regional measurements at 27 sites in Beijing, summertime and wintertime online measurements at the PKU site. The number of measurement data for each VOC dataset (n) and CMB performance parameters (R^2, χ^2, and % Conc.) were summarized in Table S4 of the supplements.

Table S4 CMB performance parameters for three VOC datasets in Beijing.

VOC datasets for CMB model	Number of data (n)	R^2 [(c)]	χ^2 [(c)]	% Conc. [(c)]
Regional measurement at 27 sites in Beijing	844	0.65–0.98 (0.85)	0.55–6.01 (2.27)	81–118 (94)
Online measurement at PKU site during summer, 2011	1131 [(b)]	0.77–0.98 (0.89)	0.68–4.00 (2.00)	82–109 (102)
Online measurement at PKU site during winter, 2011 [(a)]	369	0.87–0.98 (0.94)	0.52–3.17 (1.64)	92–100 (101)
Total measurement data	2344	0.65–0.98 (0.88)	0.52–6.01 (2.04)	81–118 (99)
Annual emissions of NMHC derived from measurements [(a)]	1	0.93	0.78	94

[(a)] Biogenic emission was excluded when running CMB model for NMHC emissions derived from measurements.
[(b)] VOC measurement data obtained during raining period (August 14, 15, 25 and September 8, 10 during 2011) were excluded when running CMB.
[(c)] Numbers in parenthesis are the average values of CMB performance parameters (R^2, χ^2, and % Conc.).

CMB performance parameters for the online VOC measurements at the PKU site were in acceptable intervals, with R^2 in the range of 0.77–0.98, χ^2 in the range of 0.52–4.00, and % Conc. in the range of 82–109, respectively. However, the χ^2 values for four samples from regional VOC measurements were beyond its acceptable interval, with the maximum value of 6.02 (see the red filled circles in Fig. R2). These four samples were all collected at *Rural* sites (BOW1 and BOW2 in Fig. 1) and their total NMHCs concentrations ($[NMHCs]_{sum}$) were lower than 20 μg cm^{-3}. We think the possible causes for the large χ^2 values of CMB modelling at rural sites include: (1) aged background air was an important source for measured VOC at rural sites, but it

was omitted from the CMB calculation; (2) the uncertainty of VOC measurement data at rural sites is larger, especially for those species with mixing ratios at pptv levels (e.g. cycloalkane and C7–C9 alkanes).

These explanations for the higher χ^2 values of CMB modelling were added in Sect. 3.4 of the revised manuscript.

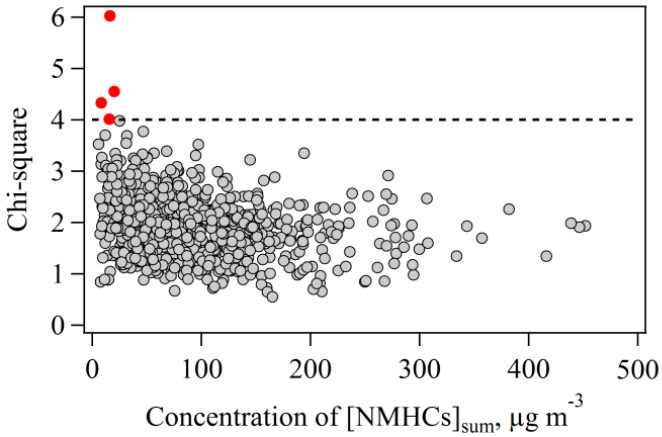

Fig. R2 Scatter plots of chi-square (χ^2) values for CMB modelling with total NMHCs concentrations ($[NMHCs]_{sum}$) from regional measurements at 27 sites in Beijing.

(7) Section 3.4.3: while the differences in the previous works and this study are pointed out and certain discrepancies explain, there are no further explanations or possible explanations included as to, for example, why the solvent contribution was so much lower than some of the other inventories. Some information here might be warranted, or an acknowledgement that at this point, these differences cannot be explained.

Response: Thanks for your suggestions and accepted. As the reviewer mentioned, the relative contributions of paint and solvent utilization estimated by CMB modelling based on measurement data in this study is significantly lower than the values reported by Bo et al. (2008) and Wei et al. (2008). Besides the inherent uncertainty of VOC emission inventories, another cause for this discrepancy is the uncertainty of CMB results. Considering the effect of chemistry on VOC composition, the reactive species with atmospheric lifetime lower than toluene were usually not selected as fitting species for CMB modelling. Reactive aromatics (e.g. ethylbenzene and xylenes) are abundant species in VOC emissions from paint and solvent utilization (Liu et al., 2008; Yuan et al. 2010a), but they were not chosen as fitting species for CMB modelling based on measurement data. This would possibly bias CMB results.

To further check this explanation, the annual emissions of individual NMHC species estimated based on measurements were used as input data for CMB modelling

to re-calculate the relative contributions of each anthropogenic source. The fitting species for CMB modelling based on emissions also involved some reactive NMHC species, such as ethene, propene, ethylbenzene, and xylenes (seen in Table S3 of the supplements). The CMB result based on NMHC emissions was also listed in Table 1. The relative contribution of paint and solvent utilization from CMB modelling based on emissions increased to 14%, close to the value reported by Bo et al. (2008), but lower than the result from Wei et al. (2008).

The results and discussions in Sect. 3.4.3 of the revised manuscript were modified accordingly.

Table S3 Fitting species for CMB application in this study.

Alkanes		unsaturated NMHCs	
ethane	2,2-dimethylbutane	acetylene	styrene*
propane	methylcyclopentane	ethene*[(a)]	o-xylene*
i-butane	2-methylhexane	propene*	*i*-propylbenzene*
n-butane	3-methylhexane	*trans*-2-butene*	*n*-propylbenzene*
i-pentane	*n*-heptane	*cis*-2-butene*	1,3,5-trimethylbenzene*
n-pentane	2-methylheptane	benzene	1,2,4-trimethylbenzene*
2-methylpentane	3-methylheptane	toluene	1,2,3-trimethylbenzene*
3-methylpentane	*n*-nonane	ethylbenzene*	isoprene
n-hexane		*m*,*p*-xylene*	

[(a)] The species marked by asterisk (*) were used as fitting species for CMB modelling based on emissions, but not for CMB modelling based on measurement data.

Technical Corrections

(1) P26934L6: distributions should be singular, ‘distribution’

Response: Accepted and corrected accordingly.

(2) P26935L5: remove ‘complex’

Response: Accepted and corrected accordingly.

(3) P26939L24-25: ‘… were given priority.’ Were given priority for what? This sentence is not clear.

Response: Accepted. This sentence has been modified to be *“When choosing sampling locations for VOC regional measurements in Beijing, the environmental automatic air quality monitoring stations were given priority, in order to obtain concurrent NO_X and O_3 data.”*

(4) P26942L7-9: please specify how many NMHCs or carbonyl compounds were included in each sum.

Response: Accepted. The total NMHCs ($[NMHCs]_{sum}$) and total carbonyl compounds ($[Carbonyls]_{sum}$) included 53 hydrocarbons with carbon atoms of 2–10 and eight carbonyl compounds with carbon atoms of 1–6, respectively (see in Table S5). The sentence in the revised manuscript was modified accordingly.

(5) P26952L21: 'constrains' should be 'constraints'

Response: Accepted and corrected accordingly.

(6) P26953L4: 'influence' should be 'influenced'.

Response: Accepted and corrected accordingly.

(7) P26955L9: '… into atmosphere; and ...' Should be '… into the atmosphere; and...'

Response: Accepted and corrected accordingly.

Refernces

Blake, D. R., and Rowland, F. S.: Urban leakage of liquefied petroleum gas and its impact on Mexico City air quality, Science, 269, 953-956, doi: 10.1126/science.269.5226.953, 1995.

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Yuan, B., Shao, M., Lu, S. H., and Wang, B.: Source profiles of volatile organic compounds associated with solvent use in Beijing, China, Atmos. Environ., 44, 1919-1926, doi: 10.1016/j.atmosenv.2010.02.014, 2010a.

Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, J. Geophys. Res.-Atmos., 117, D24302, doi: 10.1029/2012JD018236, 2012.