Letter of Responses

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

General comments

Validation of emission inventories is a relevant scientific issue and a prerequisite for air quality modelling and the implementation of emission control strategies. This work provides a robust evaluation of regional emission inventories by the use of VOC measurements at various sites in Beijing. The authors use different source-receptor approaches: one based on emission ratios relative to CO which are derived from three different methods and another one based on chemical mass balance modelling. Compared to past studies, the added value of this paper is to provide a through and temporally and spatially resolved evaluation of the emission inventories thanks to comprehensive field experimental efforts at various temporal and spatial scales. It is an important point that should appear in the title for which I would suggest "A temporally and spatially resolved evaluation of emission inventories by measurements of ambient VOC in Beijing, China".

Response: Thanks for your suggestions and accepted. We changed the title of our manuscript to be "*A temporally and spatially resolved evaluation of emission inventories by measurements of ambient VOC in Beijing, China.*"

The paper is of good quality. I recommend this paper for publication provided a number of revisions are provided (see below).

Response: The encouragements are appreciated. And all comments are addressed point-to-point in this reply letter and our revised manuscript.

Among requested revisions, main ones are related to a better description of the off-line sampling strategy which is not sufficient to allow a critical review of the corresponding results.

Response: Accepted. More detailed descriptions were added in supplements. Please see our answers for the specific comment on **offline VOC measurement** in Sect. 2.1.1.

Another issue is the missing discussion on the spatial variability of emission ratios.

Response: Accepted. The comparison of VOC emission ratios between the PKU site and the average values determined from regional measurements at 27 sites in Beijing was shown in Fig. 8a of the revised manuscript. More discussions please see our answers for specific comment on **comparison with other emission ratios** in Sect. 3.3.4.

Finally, several studies with similar objectives and, for some of them, similar approaches in Western Europe have been recently published and are not reported in the paper. It is recommended to include these data and conclusions of these studies in the present paper.

Gaimoz, C., et al. (2011), Volatile organic compounds sources in Paris in spring 2007. Part II: source apportionment.

VOC source appotionment using Positive Matrix Factorization and comparison to the regional emission inventory.

Borbon, A., J.B. Gilman, W. C. Kuster, N. Grand, S. Chevaillier, A.Colomb, C. Dolgorouky, V. Gros, M. Lopez, R. Sarda-Esteve, J. Holloway, J.Stutz, O. Perrussel, H. Petetin, S. McKeen, M. Beekmann, C. Warneke, D.D. Parrishand J.A. de Gouw, Emission ratios of anthropogenic VOC in northern mid-latitude megacities: observations vs. emission inventories in Los Angeles and Paris, J. Geophys. Res., 118, 2041-2057, (2013).

Many of the issues discussed in this paper are closely connected to this paper. The emission ratios were determined and reported for two northern mid-latitude megacities (Paris and Los Angeles) by the use of two independent approaches: the photochemical approach and the linear regression one on nighttime data like the ones described in this paper . The authors also discuss the consistency between ratios and other urban areas.

Boynard A., Borbon A., T.Leonardis, B. Barletta, S. Meinardi, D.R. Blake, N. Locoge, Spatial and seasonal variability of measured anthropogenic non-methane hydrocarbons in urban atmospheres: Implication on emission ratios. Atmos. Environ. 82 258-26729, 2014.

The emission ratios from French urban areas are presented and reported on a seasonal basis.

Response: Thanks for your suggestions and accepted. These publications were cited in the revised manuscript. The VOC emission ratios of Beijing obtained in this study were compared with those for Paris, Strasbourg, and Los Angeles reported by Borbon et al. (2013) and Boynard et al. (2014) in Sect. 3.3.4 and Fig. 9 in the revised manuscript.

Specific comments:

Introduction:

Page 26935, line 26: this line refers to Figure S1 which compares emission inventories for Beijing for different years. I do not agree with the interpretation of the graphs. It looks like emission inventories for the same period (90s, 2000s and mid-2000s) are consistent within the error bars. Please comment.

Response: Accepted. The interpretation of Fig. S1 in Page 26935 line 26 was not appropriate. We agreed with the reviewer that anthropogenic NMVOCs emissions during 1990s, 2000s, and mid-2000s in Beijing from different inventories were consistent within the error bars. The largest discrepancy of NMVOCs emission during mid-2000s exists between the inventories built by Bo et al. (2008) and Zhang et al. (2009), with the relative difference of 49%. It should be noted that open biomass burning was included in the emission inventory built by Bo et al. (2008), but not in INTEX-B inventory complied by Zhang et al. (2009). Therefore, the discrepancy of NMVOCs emission between these two inventories should be larger than that illustrated in Fig. S1.

Anthropogenic NMVOCs emission during 2008 reported by Su et al. (2011) was removed out Fig. S1. This is because anthropogenic NMVOCs emission during 2008 is not comparable with NMVOCs emission during other years, since Beijing Government implemented a series of long-term and short-term air quality control measures for the 2008 Olympics (Wang et al., 2010) to reduce NMVOCs emission.

Figure S1 in the supplements and its interpretation in the revised manuscript were modified accordingly.

Page 26936, lines 6-8: the authors should moderate their statement discussing Table 1; except Bo et al (2008), other studies are quite consistent.

Response: We agree with the reviewer that the statements on Table 1 should be moderated. To make the comparison of NMVOCs source structure among different emission inventories more appropriate and clear, we added result from Zhao et al. (2012) in Table 1 and modified our statements in the revised manuscript.

Actually, there is still no uniform standard to classify VOC sources in China when compiling emission inventories. The emission inventories with similar VOCs source categories can be compared with each other. For the existing emission inventories, the classification method of VOCs sources in emission inventories complied by Bo et al. (2008) and Wei et al. (2008) was similar, with transportation, solvent utilization, fossil fuel combustion, and industrial processing as the main source categories; while emission inventories built by Zhang et al. (2009) and Zhao et al. (2012) classified VOC sources mainly into transportation, industry, and residential sectors (seen in Table 1). Therefore, NMVOCs source structures reported by Zhang et al. (2009) and Wei et al. (2008) were compared with those reported by Zhao et al. (2012) and Bo et al. (2008), respectively.

The comparison results of NMVOCs source structure in Beijing among existing emission inventories were modified to be "*For the NMVOC source structure in Beijing, the four emission inventories listed in Table 1 all indicate that vehicular emission is the most important NMVOC source in Beijing, with the relative contribution in the range of 40–55%. However, the relative contribution of solvent and paint utilization estimated by Wei et al. (2008) was 32%, significantly higher the value of 14% reported by Bo et al. (2008). The relative contributions of industrial and residential emissions reported by Zhang et al. (2009) and Zhao et al. (2012) also showed significant disagreements. Zhang et al. (2009) reported that industrial emissions contributed 41% of anthropogenic NMVOCs emission in Beijing, whereas Zhao et al. (2012) estimated the relative contribution of industrial emissions was only 3%. In contrast with industrial emissions, the relative contribution of residential emissions reported by Zhang et al. (2009) was 16%, significantly lower than the value of 41% reported by Zhao et al. (2012).*"

Page 26936: another criteria of using CO as a tracer is that it has a long atmospheric lifetime at the time scale of interest.

Response: Accepted. The sentence in the revised manuscript were modified to be "*In this method, carbon monoxide (CO) is usually chosen as the reference tracer due to its long atmospheric lifetime ($k_{OH} = 1.4 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}) (Atkinson et al., 2006) and significant correlations with most of anthropogenic VOC species (Baker et al., 2008; von Schneidemesser et al., 2010) in urban areas.*"

Page 26937, line 4: change the sentence by De Gouw (2005) and Warneke (2007), follwed by Borbon (2013).

Response: Thanks for your suggestions and accepted. The sentence in the revised manuscript was modified to be "*De Gouw et al. (2005) examined the oxidation of VOC species by OH radical and developed two parameterization equations to* *describe the photochemical evolution of measured ratios of NMHC/CO and Carbonyls/CO. Based on these equations, the emission ratios of anthropogenic VOC relative to CO can be derived from measured ratios (Warneke et al., 2007; Borbon et al., 2013).*"

Page 26937, line 25: add Gaimoz et al. (2011) for source receptor modelling reference.

Response: Thanks for your suggestions and accepted. The sentence in the revised manuscript was modified accordingly.

Section 2.1.2 : offline VOC measurements

The strategy for NMHC sampling is not detailed enough to allow a critical review of CMB application and result interpretation. Missing information concerns the number of samples per site, the frequency and periods of sampling (i.e. month, time of the day). This information has to be reported in the revised manuscript (i.e. supplement material).

Response: Accepted. More detailed descriptions about sampling date, frequency, and the number of samples for VOC regional measurement in Beijing were added in Sect. 2.1.2 of the revised manuscript and summarized in Table S2 of supplements.

"*Sixteen sampling days from July 2009 to January 2011 were selected carefully to conduct VOC regional measurements. Most sampling campaigns were conducted on those days characterized by low wind speed, high relative humidity, and poor visibility. Ambient air samples were collected at 09:00 and 13:00 LT on each sampling day. Details of the sampling periods and meteorological parameters are summarized in Table S2. The abnormal data that were obviously influenced by local sources were excluded from the following analyses in Sect. 3, and a total of 844 valid VOCs data were obtained from regional measurements.*"

Section 2.2. : receptor model

Page 26941, line 19: the fitting species for CMB application only include "light" hydrocarbons that are mostly tracer of gasoline emission combustion. Please comment on the CMB results that extract a diesel factor which would not a priori be expected (see also figure 11).

Response: As the reviewer mentioned, diesel vehicle exhaust usually had significant emissions of heavy hydrocarbons, such as 2,3-dimethylpentane, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, and *n*-dodecane (Liu et al., 2008). Figure R1 compared VOC source profiles for diesel and gasoline vehicle exhaust that applied in this study. It can be found that percentages of 2,3-dimethylpentane, *n*-octane, *n*-nonane in NMHCs emissions from diesel vehicle exhaust were significantly higher than those from gasoline vehicle exhaust. Therefore, 2,3-dimethylpentane, *n*-octane, and *n*-nonane were included in the fitting species for CMB application in this study (Table S3 in supplements) to estimate relative contributions of diesel vehicle exhaust. C10–C12 alkanes were not applied as fitting species in this study, because their ambient levels were too low to detect in the atmosphere of Beijing.

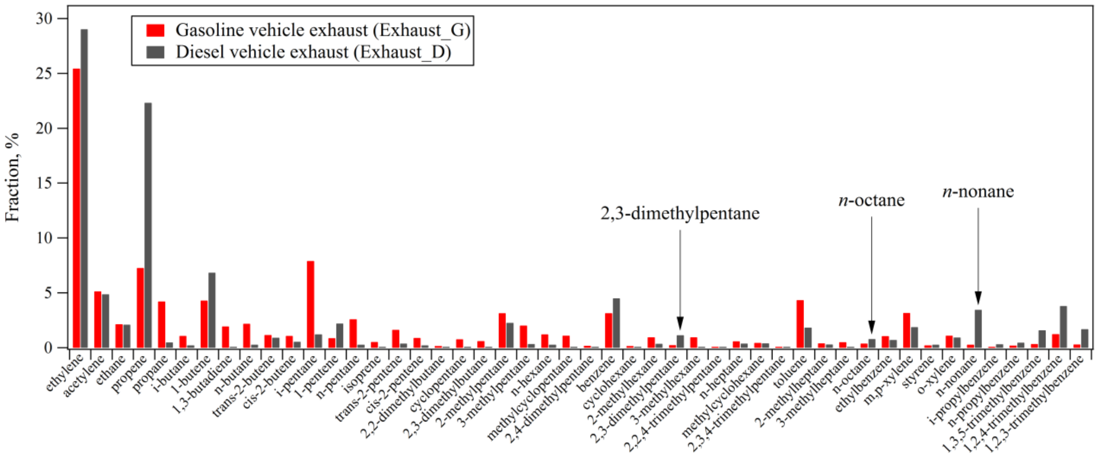

Fig. R1 VOC source profiles of gasoline and diesel vehicle exhaust in China (Liu et al., 2008).

Section 3.2: Temporal variations in VOC species

Page 26943, line 9: "the chemical composition of ambient VOCs can be affected by their emission, their photochemical removal or formation and dilution". Please add the third term dilution to the sentence.

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, and photochemical or mixing processes during transport*".

Page 26943, line 24: add Borbon et al. (2001) who first clearly showed the anthropogenic origin of isoprene in urban areas.

Response: Thanks for your suggestions and accepted. The paper by Borbon et al. (2001) was cited in the revised manuscript. The sentence was modified to be "*The calculated wintertime ratio for isoprene/1,3-butadiene in Beijing was close to the* *value 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.*"

Page 26944, line 25: please add Warneke, 2007 and Borbon, 2013 that showed the effect of chemistry has to be taken into account when determining emission ratios.

Response: Thanks for your suggestions and accepted. The papers by Warneke et al. (2007) and Borbon et al. (2013) were cited in the revised manuscript. The sentence in the revised manuscript was modified to be "*Therefore, the photochemical removal or production of VOCs must be considered and excluded when determining VOCs emission characteristics from measurement data (Warneke et al., 2007; Borbon et al., 2013).*"

Page 26945, line 3: the authors state that to estimate the emission ratios of target species have to be affect by photochemical processing. It is surprising after showing the necessity to exclude chemistry effect. Please comment or provide more details.

Response: Accepted. The emission ratio for VOC species was defined as the ratio of VOC to a reference compound in fresh emissions without undergoing photochemical processing. However, as shown in the discussions on seasonal and diurnal variations of VOC ratios (Sect. 3.2), photochemical processing is an important influence factor of VOC chemical compositions in ambient air. Therefore, the determination of VOC emission ratios from measurement data include two important steps: (1) the selection of a suitable reference compound and (2) the derivation of VOC emission ratios from measured ratios, excluding or correcting the effect of photochemical processing on measured VOC ratios.

The sentences in the revised manuscript were modified accordingly.

Page 26945, line 18: please provide value of the uncertainty on CO emissions.

Response: Accepted. The uncertainty of CO emission from inverse modelling is ± 46% (Tang et al., 2013), and this information was added in the revised manuscript.

Page 26945, line 23: it is surprising to see a good correlation between ethane and propane, two tracers of natural gas and LPG emissions, and CO. Please comment.

Response: As the reviewer mentioned, ethane and propane were commonly used as tracers for natural gas (Katzenstein et al., 2003) and LPG usage (Blake and Rowland, 1995), respectively; while, CO is mainly emitted from combustion sources, such as vehicular exhaust, and coal combustion. We think the strong correlations of ethane and propane with CO in Beijing atmosphere were possibly caused by the effects of mixing among different air masses. Even though C2–C3 alkanes and CO could be emitted into different air parcels from different sources, these air parcels still can mix well before they reached our sampling sites.

Lines 19 to line 4 (page 26946): this part is not very useful.

Response: We guess the reviewer want to suggest us the lines 1 to line 4 in Page 26946 is not very useful. We agree with the reviewer that this part not very useful for checking the rationality of selecting CO as the reference compound in Sect. 3.3.1. Considering the purpose of this part in page 26946 is to illustrate the effect of photochemical processing on measured ratios of VOC to CO, this part was moved to Sect. 3.3.2 in the revised manuscript.

Section 3.3.2

Page 29946: To strengthen the choice of time-of-the-day filters to determine emission ratios, I would suggest to add two figures (fig 4c and 4d) to figure 4 (same as fig 4a and 4b) color-coded by the time of the day on order to show that low ozone values correspond to early morning period 03:00-07:00 AM.

Response: Thanks four suggestions and accepted. We added scatter plots of 1-butene and formaldehyde vs. CO color-coded by time intervals between measurement time (t_M) and 14:00 LT in Fig. 4c and Fig. 4d of the revised manuscript, respectively.

In her paper (2013) for Los Angeles, Borbon et al. used a larger nighttime filter (10:00 PM to 05:00 AM). I am wondering why time-of-the-day filter here is smaller.

Response: Similarly with results for Los Angeles by Borbon et al. (2013), the measured ratios of reactive NMHC (e.g. 1-butene) to CO at the PKU site remained at maximum levels during nighttime (Fig. R2), indicating photochemical processing of most VOC species can be neglected during nighttime. In this study, the temporal filter for the calculation of VOC emission ratios using linear regression method was selected based on the diurnal variation of not only photochemical processing extents but also measured VOC mixing ratios. Most NMHC species exhibited maximum mixing ratios during 03:00–07:00 LT (Fig. R3). Selecting VOC data with maximum mixing ratios to calculate emission ratios is especially important for those reactive NMHC species at pptv levels (e.g. *trans*-2-pentene), because the uncertainty of its measurement data will increase with the decline of measured levels.

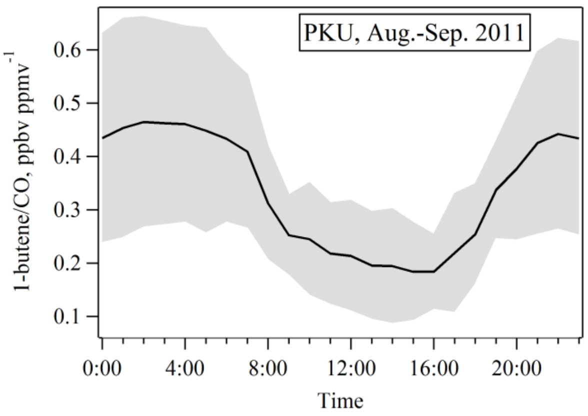

Fig. R2 Diurnal profile of measured ratios of 1-butene to CO at the PKU site during Aug.–Sep., 2011.

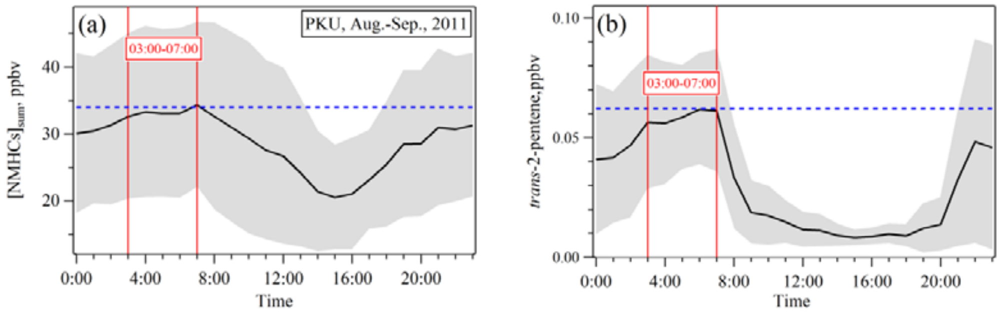

Fig. R3 Diurnal profile of ambient mixing ratios of (a) total NMHCs ($[NMHCs]_{sum}$) and (b) *trans*-2-pentene at the PKU site during Aug.–Sep., 2011.

Line 13: please add Borbon et al. (2013) reference that used the same approach and showed that emission composition between day and night is not different.

Response: Accepted. The paper by Borbon et al. (2013) was added in the revised manuscript. As mentioned in Borbon et al. (2013), the linear regression method based on nighttime data relies on the assumption that VOC emission ratios relative to CO do not change between day and night. In order to check whether VOC emission ratios between day and night are different in Beijing, we analyzed correlations between several species with long atmospheric lifetime and CO at the PKU site during summer (Fig. S2). The calculated ratios for ethane, propane, *n*-butane, benzene, and acetone to CO using measurement data of 03:00–07:00 LT and all data agrees very well, suggesting that VOC emission ratios during daytime and nighttime do not change. These discussions were added in Sect. 3.3.1 of the revised manuscript.

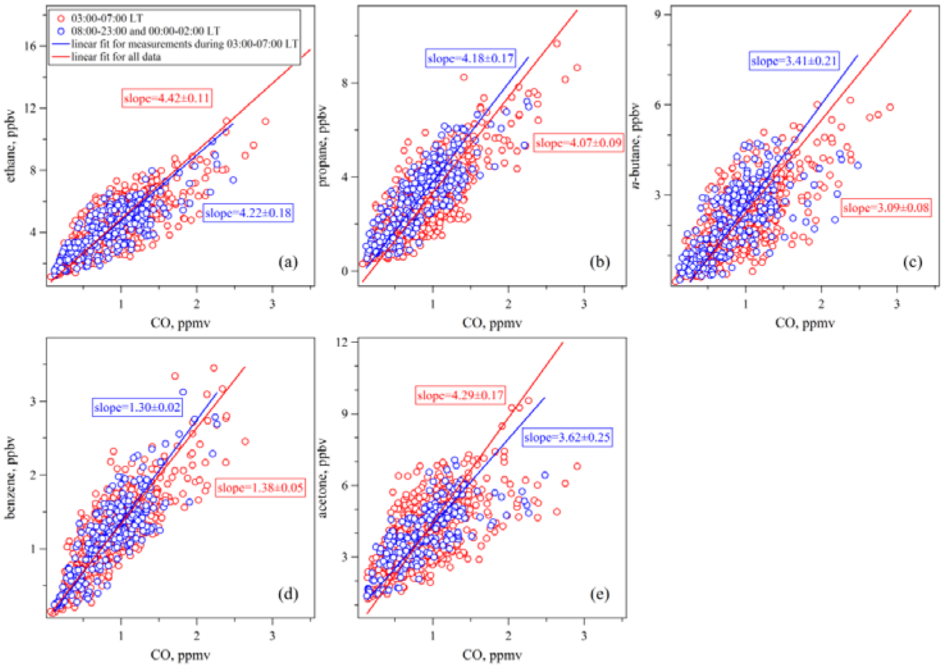

Fig. S2 Scatter plots of ethane, propane, *n*-butane, benzene, and acetone with CO at the PKU site during Aug.–Sep., 2011. The two-sided linear fit (ODR) is applied on measurement data of 03:00–07:00 LT and all data.

Page 26948: explain the reason of choosing o-xylene to ethylbenzene ratios to estimate OH time exposure.

Response: In this study, we chose *o*-xylene to ethylbenzene ratios to investigate the age of urban air masses for the following reasons: (1) xylenes and ethylbenzene have similar sources and their emission ratios from different sources remain persistent (Monod et al., 2001), and therefore the measured X/E ratios were mainly influenced by photochemical processing; (2) the atmospheric lifetime of *o*-xylene (k_{OH} = 13.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) is significantly shorter than that of ethylbenzene (k_{OH} = 7.1×10^{-12} cm^3 $molecule^{-1}$ s^{-1}); (3) the ambient levels of ethylbenzene and *o*-xylene in Beijing were significantly higher than the detection limits of VOC analysis systems in this study. This information was added in the revised manuscript.

Section 3.3.3: Temporal variations in VOC emission ratios

The results presented here should be also discussed by comparing to Boynard et al. (2014) emission ratios determined on a seasonal basis in French urban areas. The seasonal differences in emission ratios should be also addressed regarding CO emission variations which are not discussed here.

Response: Thanks for your suggestions and accepted. The seasonal variations of VOC emission ratios in Beijing (Fig. 7a) were compared with results in French urban areas reported by Boynard et al. (2014) in the revised manuscript. "*Figure 7a compares the emission ratios of VOC species relative to CO at the PKU site during summer and winter. The wintertime emission ratios for most VOC species were lower than summertime values in Beijing by a factor ≥ 2, with the exception of acetylene, alkenes (e. g. ethylene, propene, 1,3-butadiene), benzene, ethane, and formaldehyde. A recent study in French urban areas by Boynard et al. (2014) also found that emission ratios of benzene and alkenes relative to acetylene were similar during summer and winter, whereas other NMHC species exhibited higher emission ratios in summer.*"

As the reviewer mentioned, seasonal variation of CO emission is another important cause for the seasonal difference in VOC emission ratios. Figure R6 shows the seasonal profile of CO emission in China reported by Zhang et al. (2009). The CO emission strengths during November–March were higher than those for April–October due to heating activities during winter. This information was added in Sect. 3.3.3 of the revised manuscript.

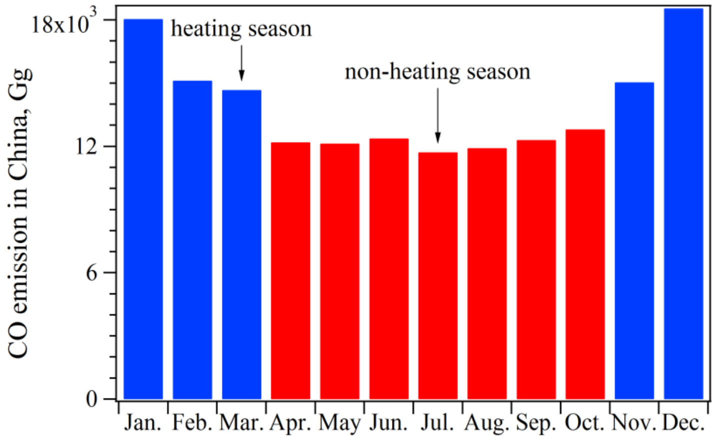

Fig. R4 Seasonal variation of CO emission in China reported by Zhang et al. (2009).

Page 26950, line 1: please change the sentence by "these results suggest a similarity between VOC emission composition."

Response: Thanks for your suggestion and accepted. This sentence in the revised manuscript was modified accordingly.

Section 3.3.4: Comparison with other VOC emission ratios

The comparison here should include the most recent results by Borbon et al (2013).

Response: Thanks for your suggestion and accepted. The VOC emission ratios for Beijing were compared with those determined in Los Angles, Paris, and Strasbourg reported by Borbon et al. (2013) and Boynard et al. (2014). Please see the Fig. 9g–k and Sect. 3.3.4 in the revised manuscript.

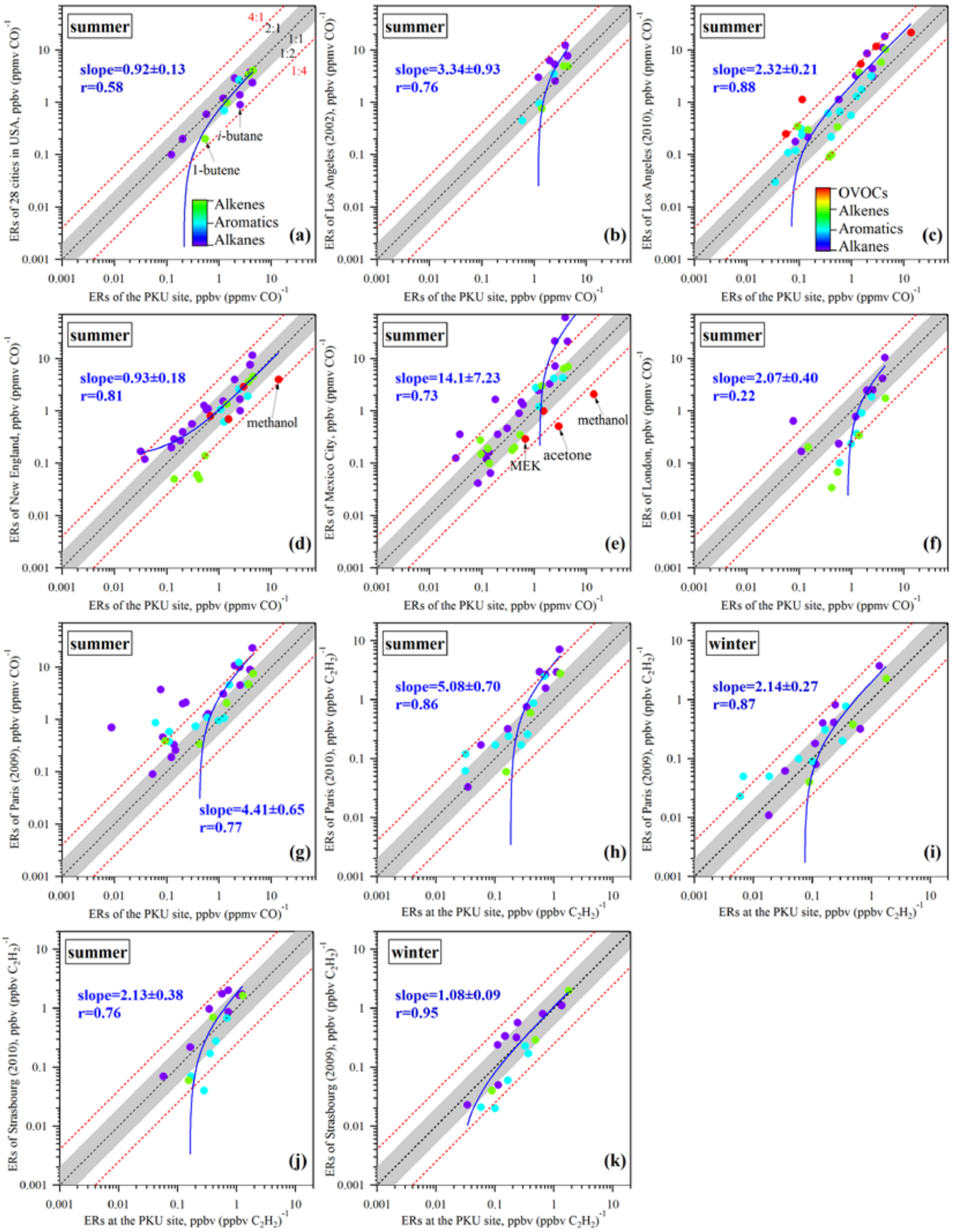

Fig. 9 Comparisons of VOC emission ratios determined at the PKU site with those for (a) 28 cities in US (Baker et al., 2008), (b) Los Angeles, USA (Warneke et al., 2007; Borbon et al., 2013), (d) New England area, US (Warneke et al., 2007), (e) Mexico City, Mexico (Bon et al., 2011), (f) London, UK (McMeeking et al., 2012), (g–i) Paris, France (Borbon et al., 2013; Boynard et al., 2014), and (j–k) Strasbourg, France (Boynard et al., 2014).

While it is not always clear in the text, the emission ratios were determined in Beijing not only from the PKU dataset but also from the regional measurements. Therefore it would be more appropriate to calculate an average emission ratio from all measurement sites and associate a standard deviation to this averaged emission ratios. Indeed the spatial variability of emission ratios is not discussed in the paper and one can wonder how much the PKU ratios are representative of the urban mixture of VOC anthropogenic emissions. It might be the case but this has to be addressed. Calculating a standard deviation will also be useful when comparing to emission ratios from emission inventories in order to test whether a factor of 2 is significant or not.

Response: As the reviewer mentioned, VOC emission ratios in Beijing were estimated both based on online measurements at the PKU site and regional measurements at 27 sites in Beijing. In this study, VOC emission ratios at the PKU site was calculated using the [OH]Δt method based on all measurement data, while the average VOC emission ratios for 27 sites in Beijing were calculated as the slopes of ODR linear regression fit for regional measurement data at 09:00 LT from all sites ("linear regression" method). The standard deviations of linear regression slopes correspond to the standard deviations of average VOC emission ratios for regional sites. The relative standard deviations (RSD) of emission ratios for most VOC species were lower than 20%.

Another method to calculate average value and standard deviation of VOC emission ratios in Beijing is based on the calculated VOC emission ratios at each regional site. For the VOC regional measurements in Beijing, there are two samples (09:00 and 13:00 LT) that were collected at each site during each month. VOC emission ratios at each site were calculated only based on 09:00 data due to the influence of photochemical processing on 13:00 data. Considering the limited data at each site (i.e. 6 data for winter, and 10 data for summer), the VOC emission ratio at each site was estimated as the average value of VOC/CO ratios in each sample ("average" method). Average VOC emission ratios of Beijing calculated using "average" and "linear regression" methods showed a good agreement, with slope of 1.01 and r of 0.98 (Fig. R5). However, the relative standard deviations of VOC emission ratios calculated using "average" method were larger than those determined by "linear regression" method, with values in the range of 23–71%.

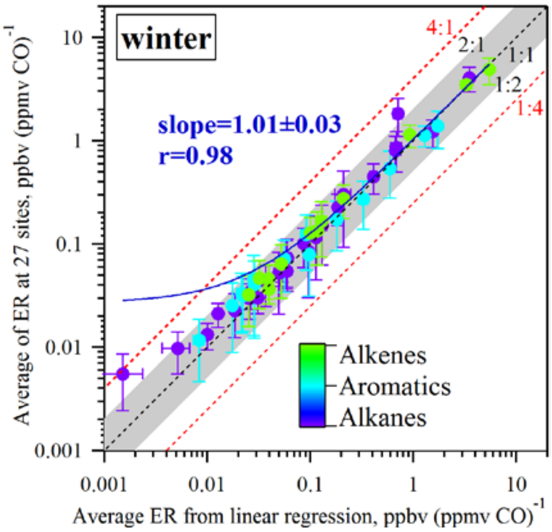

Fig. R5 Comparison of average VOC emission ratios at 27 sites calculated using "average" and "linear regression" method. The error bars correspond to the standard deviations of average VOC emission ratios.

Emission ratios for most VOC species determined at the PKU site agreed with average emission ratios of Beijing calculated using both methods within a factor 2 (Fig.R6 and Fig. 8a), with *r* of 0.98–0.99 and linear regression slope of 0.91, indicating that VOC emission ratios determined at the PKU site can represent the urban mixture of VOC anthropogenic emissions in Beijing.

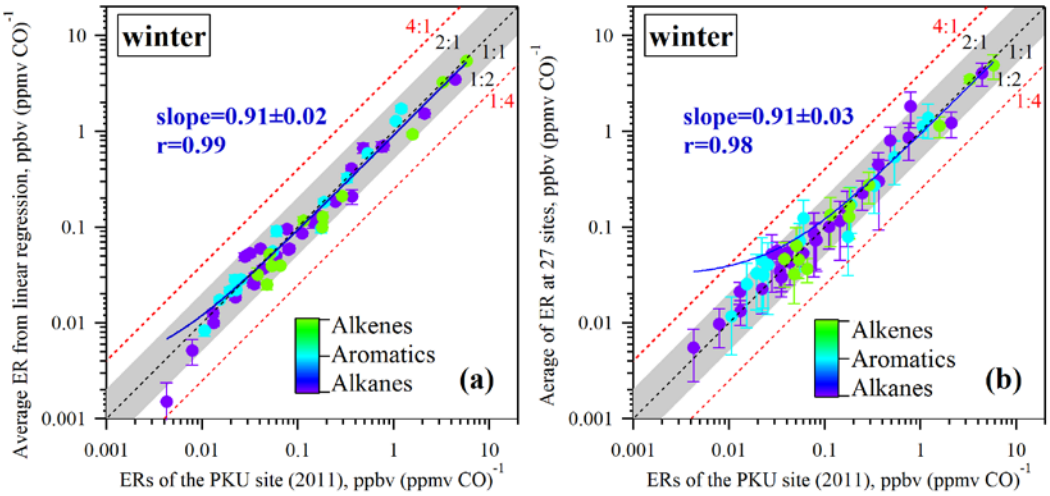

Fig. R6 Comparison of VOC emission ratios determined at the PKU site with average emission ratios in Beijing calculated using (a) "average" and (b) "linear regression" method. The error bars correspond to the standard deviations of average VOC emission ratios.

Based on the RSD values of VOC emission ratios at regional sites in Beijing, we think a factor of 2 is significant for the comparison of VOC emission ratios between measurements and emission inventories in Beijing. However, this conclusion might not be applicable to those cities with various VOC sources in different areas.

The comparison of VOC emission ratios between the PKU site and regional measurements in Beijing was shown in Sect. 3.3.4 of the revised manuscript. The two methods of calculating average VOC emission ratios in Beijing and the comparison of these two methods were added in supplements.

Finally, no discussion is provided to explain the observed differences in Figure 9.

Response: Figure 9 in the previous manuscript compared VOC emissions determined based on measurement data with those from TRACE-P and INTEX-B emission inventories. The explanations for their discrepancies were discussed in Sect. 3.3.5 of the revised manuscript.

We guess the reviewer might want us to provide more explanations for the observed differences of VOC emission ratios between Beijing and other cities. VOC emission ratios between Beijing and other cities were compared in Fig. 9 of the revised manuscript. Emission ratios of propane in Mexico City, Mexico reported by Bon et al., (2011) were 16 times higher than that determined at the PKU site. One possible explanation for this discrepancy is that propane emission in Mexico City is likely dominated by leakage of LPG rather than combustion processes, and thus the emission ratio of propane relative to CO in Mexico City is much higher than Beijing and urban areas in US (Bon et al., 2011). Summertime emission ratios of toluene and *i*-pentane in Paris were 4–5 times higher than those determined at the PKU site. The possible causes for higher emission ratios of C7–C9 aromatics and C4–C5 alkanes in Paris have been discussed by Borbon et al. (2013), which could be due to the greater abundance of aromatics in gasoline or the higher hydrocarbon emissions from powered two wheelers (PTW) in Paris. OVOC emission ratios also exhibited large differences among Beijing, Los Angles, and Mexico City. The primary sources of OVOC species in urban areas are not well understood yet (Warneke et al., 2007). Besides vehicle exhaust, OVOC species can be emitted from biomass burning (Yuan et al., 2010b), industrial processes (Kim et al., 2008), and residential coal combustion (Zhang and Smith, 1999). Much research has to be done on OVOC sources to explain the differences of OVOC emission ratios in these cities.

Our statements on Fig. 9 were modified in the revised manuscript accordingly.

Section 3.3.5: Estimation of VOC emissions in Beijing

The comparison to emission inventories is not always straightforward because emission database usually lump VOCs according to their atmospheric reactivity (see also Borbon et al. 2013). One can wonder if this is the case here. Please comment.

Response: As the reviewer mentioned, emission database usually lump VOCs according to their reactivity or molecule structure, while measurements provide speciated VOC data. To resolve this problem, we communicated with Prof. David Streets in Argonne National Laboratory, USA and Prof. Qiang Zhang in Tsinghua University, China, and they kindly provided us speciated VOCs emission database of TRACE-P (Streets et al., 2003) and INTEX-B (Zhang et al., 2009). In this study, the comparison of VOC emissions derived from ambient measurements with those from emission inventories is straightforward for VOC species.

Section 3.4: VOC source apportionment

The way CMB model is applied to data is missing (which observed data ? which sites? Which periods?).

Response: Accepted. Three VOC datasets were inputted into CMB model for calculation relative contributions of each source category, including the 16-month regional measurements at 27 sites in Beijing and online measurements at the PKU site during summer and winter of 2011. The number of measurement data for CMB application in this study was listed in Table S4 of supplements. This information was added in Sect. 2.2 of the revised manuscript.

Also explain the statistical indicators used to test the quality of CMB modeling (lines 15-20 page 26954).

Response: Accepted. CMB performance parameters (R^2, χ^2, and %Conc.) were briefly explained in Sect. 3.4 of the revised manuscript. The R^2, χ^2, and % Conc. values of CMB modelling for regional and online VOC measurements were summarized in Table S4.

"The performance of the CMB model was checked using several parameters: including R^2, χ^2, and % Conc. (the percentage of the sum of the calculated mass concentration to the total measured concentration) (EPA, 2004). (1) The R^2 is the fraction of variance in the measured concentrations that is explained by variance in the calculated concentrations. The R^2 value can vary from 0 to 1 and CMB modelling is satisfactory when R^2 is superior to 0.8. (2) The χ^2 is the weighted sum of squares of the differences between the calculated and measured fitting species concentrations. The χ^2 value equals zero means that there would be no difference between calculated

and measured species concentrations. The χ^2 *values in the range of 0–4 are acceptable. (3) The % Conc. is the percent ratio of the sum of the model-calculated source contribution estimates to the measured mass concentration. This ratio should equal 100%, although values ranging from 80 to 120% are acceptable.”*

Comparing CMB results to calculated emission ratios would be an added value and a good way to test the consistency of both methods and the potential effect of chemistry which is assumed to be negligible by the choice of non-reactive fitting species in CMB modelling. From CMB modelling results one can derive the total concentration explained by the model for different VOC, divide it by CO and compare to the emission ratios determined in previous sections.

Response: Thanks for your suggestions. We agreed with the reviewer that NMHC source apportionment results might be influenced by the choice of fitting species in CMB modelling, especially for those reactive NMHC species (e.g. C4–C5 alkenes). The total concentrations explained by the CMB model for C4–C5 alkenes at the PKU site were higher than measured concentrations by factors of 1.4–5.6 during summer. The high uncertainty of CMB results for reactive alkenes was possibly due to the effect of photochemical loss (Shao et al., 2011).

To test the possible effect of chemistry on CMB result, the emissions of each individual NMHC species derived from measurement data (Table S5) were applied as input data for CMB modelling and compared with the results based on measurement data. 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). The relative contributions of each anthropogenic source to NMHC emission calculated by CMB modelling based on emissions were listed in Table 1 of the revised manuscript.

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.

The relative contributions of gasoline vehicle exhaust, coal combustion, and gasoline evaporization calculated by the CMB modelling based on emissions were similar with the CMB results based on measurement data. However, the relative contributions of LPG usage and industrial processing from the CMB modelling based on emissions were lower than CMB results based on measurement data, whereas paint & solvent utilization contributions was higher for the CMB modelling based on emissions. The discrepancy between CMB results based on emissions and measurement data suggests that the choice of non-reactive fitting species would possibly bias CMB results. Therefore, the CMB results based on individual NMHC emissions were used to compare with VOC source structures reported in emission inventories. The comparison of CMB results based on measurement data and emissions were added in the revised manuscript.

Both the CMB result and the emission inventories show that transportation is the most important NMVOC source in Beijing, with relative contributions of 40–55%. The relative contribution of industrial processing estimated using the CMB model was 8%, slightly lower than the value of 10–14% from emission inventories (Bo et al., 2008; Wei et al., 2008). The relative contribution of paint & solvent utilization obtained from the CMB model based on individual NMHC emissions (14%) was close to the value reported by Bo et al. (2008), but significantly lower than value of 32% reported by Wei et al. (2008). Fossil fuel combustion contributions between emission inventories built by Wei et al. (2008) and Bo et al. (2008) showed large discrepancies. The coal combustion contribution obtained using the CMB model was 9%, within the range of 3–15% from these two emission inventories. The sentecnes in Sect. 3.4.3 of the revised manuscript were also modified accordingly.

Table 1 Comparison of the relative contributions (%) of anthropogenic sources to NMVOC emission in Beijing calculated by CMB model in this study and results from bottom-up emission inventories.

Source categories	CMB_M[a]	CMB_E[b]	Wei et al. (2008)	Bo et al. (2008)	Source categories	Zhao et al. (2012)	Zhang et al. (2009)
	This study, 2009–2011		2005	2005		2003	2006
Transportation	46	49	40	51	Transportation	55	41
Industrial processing	17	8	14	10	Industry[d]	3[e]	41[e]
Paint & Solvent utilization	5	14	32	14	Residential	41	16
Fossil fuel combustion	10[c]	9[c]	3	15	others	1	2
Petroleum storage and transport	6[d]	4[d]	--	6			
LPG usage	15	6	--	--			
others	--	--	11	4			

[a] The relative contribution of each source category calculated by CMB model based on measurement data (CMB_M) corresponds to the average value of CMB results for 824 samples collected at 27 sites in Beijing during July 2009 to January 2011;

[b] The relative contribution of each source category was calculated by CMB model based on individual NMHC emissions (CMB_E);

[c] The relative contributions of fossil fuel combustion reported by Bo et al. (2008) and Wei et al. (2008) were compared with that of coal combustion from CMB model;

[d] The relative contribution of petroleum storage and transport reported by Bo et al. (2008) was compared with that of gasoline evaporization from CMB model;

[e] The relative contribution of industry reported by Zhang et al. (2009) and Zhao et al. (2012) also included NMVOCs emissions from industrial solvent use besides industrial processing.

Finally if CMB modelling is applied to each measuring station dataset it would be interested to discuss the influence of the site typology on the results.

Response: Yes, the CMB modelling for VOC regional measurements was applied to each measuring station dataset. Figure 14 in the revised manuscript shows the relative contributions of gasoline vehicle exhaust, diesel exhaust, industrial emissions, and biogenic emission at 27 sites in Beijing. It can be found that the relative contributions of gasoline vehicle exhaust exhibited higher values at *Roadside* (R1–R3) and *Urban* (BI1–BI7) sites, while biogenic emissions showed higher contributions at suburban (*Suburban_North* and *Suburban_South*) and *Rural* sites. The highest relative contributions of industrial emissions were recorded at two *Suburban_South* sites (BOS1 and BOS2). These discussions were added in Sect. 3.4.2 of the revised manuscript.

Figures:

Figure 6: the linear regression slope does not appear on Figure 6b.

Response: Accepted. We have added the linear regression fit line (slope=1.27, r=0.955) on the Figure 6b of the revised manuscript.

Figures 1, 8 and 13 are hard to read (axis and color-coded labels especially).

Response: Accepted. The font size of axis and color-coded labels were enlarged to make them easier to read. In addition, figure 8 was separated into two figures in the revised manuscript (Fig. 8 and Fig. 9), to make the comparison of VOC emission ratios between the PKU site and other regions more clear.

Figure 2: [: : :] Error bars represent standard deviation from the mean calculated at the 27 measuring sites”. Please add “calculated at the 27 measuring sites”.

Response: Accepted. The sentence was modified accordingly.

Figure 4: ozone is used as an indicator of photochemistry. Usually it is more appropriate to use the sum of oxidants ozone+NO_2 in order to take into account the titration of ozone by NO in urban areas (Veres et al., 2011, GRL).

Response: Thanks for your suggestions and accepted. We used O_X (O_3+NO_2) levels to color data points in Fig. 4 a and b of the revised manuscript.

Figure 10: for figure 10a, precise it is Beijing measurements.

Response: Accepted. Figure 10 and its caption in the revised manuscript were modified accordingly.

Figure 13: “Spatial distribution of the relative contribution (in %) [: : :]”. Please add “in %” to the caption of the figure.

Response: Accepted and corrected accordingly.

Refernces

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