

Letter of Responses

Manuscript: Trends of non-methane hydrocarbons (NMHC) emissions in Beijing during 2002–2013 (Ref. No.: acp-2014-501).

Anonymous Referee #1

This is a useful paper to refine knowledge about VOC emissions in China. Bottom-up emission inventories have had difficulty assembling data for VOC, due to lack of knowledge about the many individual source components of VOC in China (see, e.g., Klimont et al., 2002). This paper circumvents that difficulty by relying on observations of NMHC and their trends, and using PMF to connect back to sources. The priorities of some important source types are changed as a result of this work. The methodology seems sound and I recommend the paper be published after attending to some details.

Response: The encouragement is appreciated. We have carefully taken the following comments into consideration in revision. Please see the following point-by-point responses.

(1) It is clear that industry is an important source of NMHC. In fact it is the second largest source, according to Figure 1. Yet there is no mention of this source category in the analysis. Because it is so large (and potentially increasing according to Figure 1), there is the possibility of confounding the PMF analysis, if some of the same NMHC species are emitted from industry as from, say, vehicles or paints. Industrial sources of NMHC need to be discussed in the text at minimum. If no analysis can be included for them, then at least the paper should reassure the reader that industrial sources cannot compromise the analysis performed here.

Response: Accepted. This is an important point, and thus we re-thought the identification of PMF-resolved factors in previous manuscript. As shown in Fig. 8d, the fourth factor largely consisted of toluene, ethylbenzene, and xylenes. These aromatic compounds can be emitted from both paint and solvent utilization (Yuan et

al., 2010) and chemical industries (Liu et al., 2008). This factor is the largest contributor (39%) to *n*-hexane, which is one product of crude oil refining and is also commonly-used solvent in industrial processes. In addition, this factor is the second largest contributor (28%) to ethene and propene. These light alkenes can also be emitted from petrochemical industry (Jobson et al., 2004; Wei et al., 2014) besides vehicular exhaust. Based on these thoughts, the fourth factor was considered to be not only related to paint and solvent use but also influenced by industrial sources, and therefore it was referred to as *Paint and solvent use & Industry* in the revised manuscript.

The identification of PMF-resolved factors in Sect. 3.3.1 of the revised manuscript was modified accordingly.

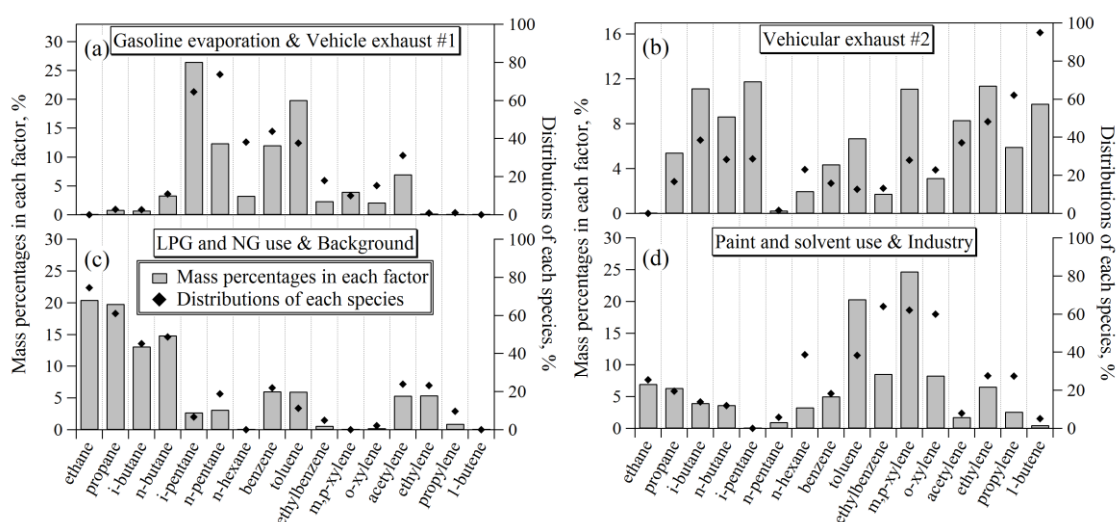


Fig. 8 Profiles of four PMF-resolved factors (gray bars) and distributions of each species among these factors (black diamonds): (a) *Gasoline evaporation & Vehicle exhaust #1*, (b) *Vehicle exhaust #2*, (c) *LPG and NG use & Background*, and (d) *Paint and solvent use & Industry*.

(2) It seems to me that the paper should discuss the implications of the fact that there is only one monitoring location. This is worrying, as it will only give a representation of NMHCs in the source configuration relative to that site. Can the authors say a little more about the site itself and its proximity to highways, factories, etc.? Is this important? Do we expect spatial differences in NMHC around the city? What

would be the implication for the results of having two or several monitoring sites around the city?

Reply: Accepted. In this study, ambient measurements of NMHCs were conducted at the same urban site in Beijing from 2002 to 2013. This site was located at a six-story building on campus of Peking University (PKU, 40.00 °N, 116.31 °E) in northwest of Beijing city, which is about 200 m north from the Fourth-Ring Road with high traffic density and is distant from industrial or agricultural sources. This site was considered to be representative of a typical urban environment in Beijing (Song et al., 2007; Zhang et al., 2014). This information was added in the Sect. 2.2 of the revised manuscript.

In order to investigate the spatial distribution characteristic of NMHC levels in Beijing, sixteen regional measurement campaigns were conducted at 27 sites across the whole city from September 2009 to January 2011. Detailed descriptions on these regional sites and sampling strategies were provided by Wang et al. (2014). Figure S5 shows the spatial distribution of annual average NMHCs levels measured at 27 sites in Beijing from September 2009 to January 2011. It can be found that the mixing ratios of NMHCs in downtown and southern areas of Beijing were significantly higher than those for suburban/rural sites in northern and western regions. The emission ratios for most NMHC species showed good agreements between the PKU site and the 27 regional sites in Beijing, with r of 0.99 and linear regression slope of 0.91 ± 0.02 (Fig. S6) (Wang et al., 2014).

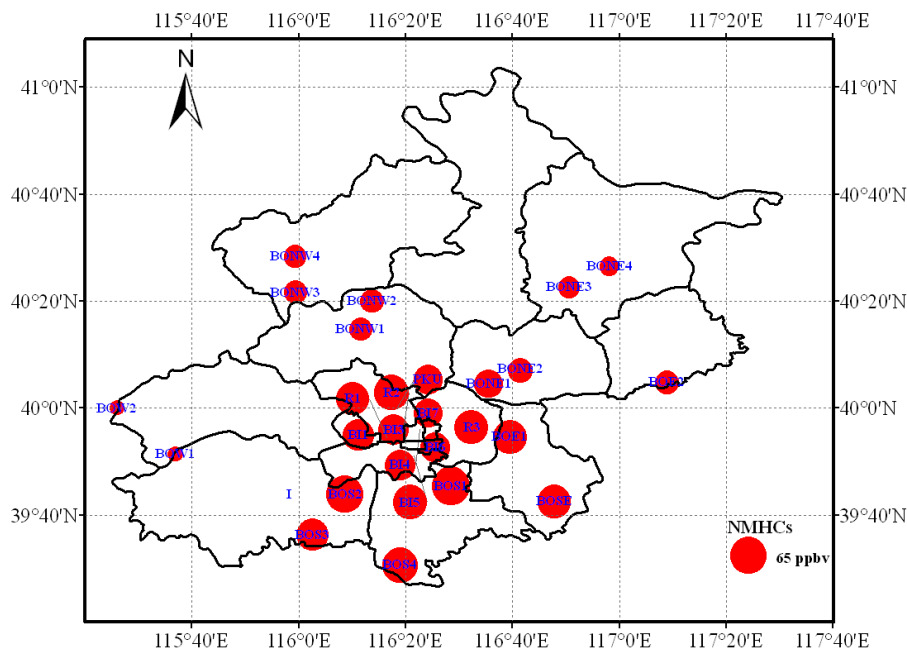


Fig. S5 Spatial distribution of annual averaged mixing ratios of NMHCs measured at 27 sites in Beijing from September 2009 to January 2011 (Wang et al., 2014).

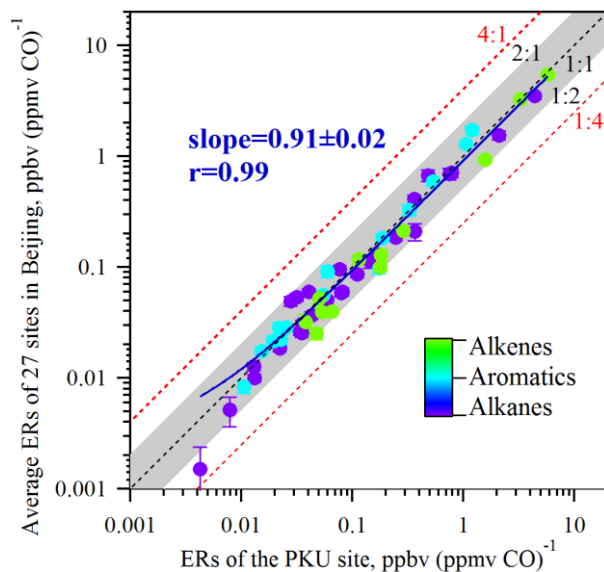


Fig. S6 Comparisons of VOC emission ratios determined at the PKU site with those determined from regional measurements at 27 sites in Beijing from September 2009 to January 2011 (Wang et al., 2014).

In fact, the spatial distribution of industry and urbanization level in Beijing has been evolving during the last two decades (Wang et al., 2014). High pollution industries have gradually moved out of the urban center of Beijing; meanwhile,

industrial clusters have been developed in southern suburban areas. Accompanied by the rapid economic development, southern suburban areas of Beijing have become more urbanized during these years. Although we can not obtain NMHC measurement data during the last decade for southern regions of Beijing, the Beijing government have selected 5 routine monitoring sites, two of them are located in southern regions, to measure the levels and speciation of NMHCs in entire Beijing since 2012. This will provide an opportunity for us to investigate the temporal trends of NMHCs at more sites of Beijing in the near future.

The above discussions were added in the supplement as ***Sect. 6 Spatial distribution of NMHC levels and chemical compositions in Beijing***. In addition, a brief version was added in Sect. 3.4 of the revised manuscript as the fourth limitation/uncertainty of this study.

“(4) The trend analyses for NMHCs levels and sources were based on measurement data obtained at one urban site, whereas the temporal changes of NMHC emissions during August in Beijing reported by the MEIC inventory were for the entire city. The regional measurements during 2009–2011 at 27 sites in Beijing suggested that NMHCs levels in downtown and southern areas of Beijing were significantly higher than those for suburban/rural sites in northern and western regions (Fig. S5). The emission ratios of individual NMHC species relative to carbon monoxide showed good agreements between the PKU site and the 27 regional sites in Beijing (Fig. S6) (Wang et al., 2014a). In fact, the spatial distribution of industry and urbanization level in Beijing has been evolving during the last two decades (Wang et al., 2014a). Most industries had been moved out of downtown area and assembled in industrial parks in southern regions of Beijing (Wang et al., 2014a). Accompanied by the rapid economic development, southern suburban areas of Beijing have become more urbanized during these years. Although we can not obtain NMHC measurement data during the last decade for southern regions of Beijing, the Beijing government have selected five routine monitoring sites, two of them are located in southern regions, to measure the levels and speciation of NMHCs in entire Beijing since 2012.

This will provide an opportunity for us to investigate the temporal trends of NMHCs at more sites of Beijing in the near future.”

(3) Point 4 on Page 19012 is interesting. I can understand that this is not an air modeling study, but it might be of value to discuss trends in summertime ozone or even summertime high temperatures. Does this explain any of the deviations from year-to-year in reactive species or the sources that emit the most reactive species? It is also implied that there might have been a systematic trend in the oxidizing capacity of the Beijing atmosphere. That would definitely skew the trend of reactive species. I think this issue is worthy of further discussion or presentation of other trends, even if no atmospheric modeling can be done.

Reply: Agree. The daytime average mixing ratios of O₃ measured at the PKU site increased rapidly at an annual rate of 2.6 ppbv yr⁻¹, around 5% yr⁻¹ between August 2005 and August 2011 (Zhang et al., 2014). The photo-dissociation of ozone is a primary pathway to form hydroxyl (OH) radical in the atmosphere, and thus the rising O₃ levels will possibly result in the increase of OH abundance. Although there are no direct measurements of OH radical over long time periods in Beijing and its surrounding regions, the average abundance of OH radical ([OH]) can be estimated based on measured ratios of two hydrocarbons that have similar sources but different reaction rates with OH radical using the following equation (McKeen et al., 1990; Ehhalt et al., 1998):

$$[\text{OH}] = \frac{1}{(k_{\text{HC}_2} - k_{\text{HC}_1})\Delta t} \times \left(\ln \left(\frac{[\text{HC}_2]_{t_0}}{[\text{HC}_1]_{t_0}} \right) - \ln \left(\frac{[\text{HC}_2]_{t_0+\Delta t}}{[\text{HC}_1]_{t_0+\Delta t}} \right) \right) \quad (\text{S1})$$

where k_{HC_2} and k_{HC_1} are rate constants for the oxidation of HC₁ and HC₂ by OH radical, respectively. $[\text{HC}_2]_{t_0}/[\text{HC}_1]_{t_0}$ and $[\text{HC}_2]_{t_0+\Delta t}/[\text{HC}_1]_{t_0+\Delta t}$ are the ratios of HC₂ with HC₁ measured at the time of t_0 and $t_0+\Delta t$, respectively. Δt is the reaction time of hydrocarbons. In this study, the ratio of propene/ethene was selected to estimate [OH] for the following reasons: (1) ethene and propene are both mainly emitted from vehicular exhaust during summer of Beijing (Song et al., 2007; Liu et al., 2009), and

therefore variations in measured ratios of propene/ethene were mainly associated with photochemical processing; (2) the rate constant of propene with OH radical ($k_{\text{OH}} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is significantly higher than that for ethene ($k_{\text{OH}} = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson et al., 2006); (3) mixing ratios of propene and ethene in Beijing were high enough to be accurately quantified by VOC analysis systems.

Figure S4 shows the average diurnal variations of propene/ethene during August 2005 and August 2011. As shown in this figure, the relative decline of propene/ethene between 6:00 LT and 14:00 LT was 62.1% during August 2011, significantly higher than that for August 2005 (30.6%). This indicates that the average photochemical removal degree of these two hydrocarbons at 14:00 LT during August 2011 was higher than that for August 2005.

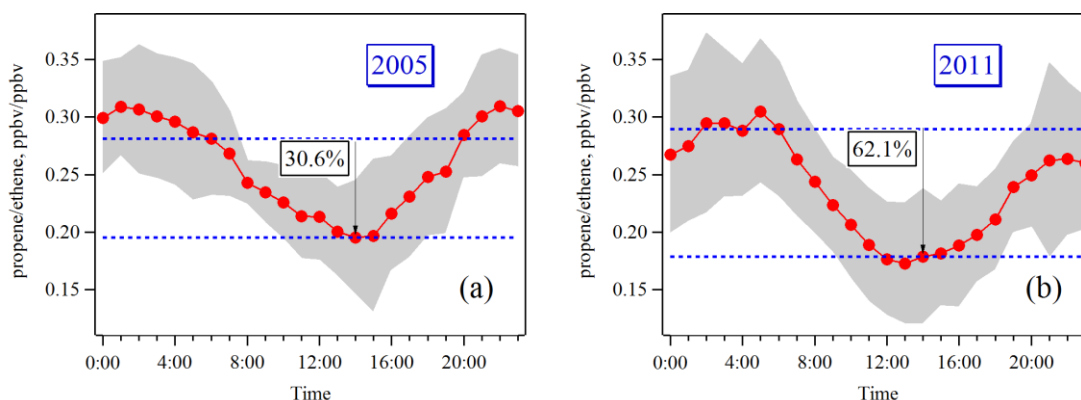


Fig. S4 Diurnal variations in hourly averaged ratios of propene to ethene (propene/ethene) during (a) August 2005 and (b) August 2011, respectively.

Assuming that the difference of average reaction time (Δt) between August 2005 and August 2011 was negligible (i.e. $\Delta t_{2005} = \Delta t_{2011}$), the relative change of average OH abundance (RC) between these two years can be described by the following equation:

$$\begin{aligned}
RC &= \frac{[\text{OH}]_{2011} - [\text{OH}]_{2005}}{[\text{OH}]_{2005}} \times 100\% \\
&= \frac{[\text{OH}]_{2011} \Delta t_{2011} - [\text{OH}]_{2005} \Delta t_{2005}}{[\text{OH}]_{2005} \Delta t_{2005}} \times 100\%
\end{aligned} \tag{S2}$$

Applying Eq. (S1) to calculate average OH abundance during 6:00-14:00 LT, then the RC was estimated to be 32.3% based on propene/ethene ratios using the following equation:

$$RC = \frac{\left(\ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{6:00,2011} - \ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{14:00,2011} \right) - \left(\ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{6:00,2005} - \ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{14:00,2005} \right)}{\left(\ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{6:00,2005} - \ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{14:00,2005} \right)} \times 100\% \tag{S3}$$

This means the average OH abundance during 6:00-14:00 LT at the PKU site increased by 32.3% between August 2005 and August 2011, with speed of 5.4% yr⁻¹, close to the rising rate of O₃ levels (5% yr⁻¹) at the same site reported by Zhang et al. (2014).

The influence of rising OH abundance on temporal trend of acetylene levels was considered to be negligible, due to the low reactivity of acetylene ($k_{\text{OH}} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The rate constants of OH oxidation for ethene ($k_{\text{OH}} = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and propene ($k_{\text{OH}} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were significantly higher than that for acetylene, but the relative declines of ethene and propene levels measured at the PKU site were close to that for acetylene (Fig. 4a-c). This indicates that the rise of atmospheric oxidizing capacity was not an important cause for the decline of hydrocarbon levels measured at the PKU site.

The above results and discussion were added in the supplement as **Sect. 5 Temporal trend of oxidizing capacity in Beijing**. In addition, main results about the temporal change in oxidizing capacity and its influence on trends of hydrocarbon levels measured at the PKU site were added in Sect. 3.4 of the revised manuscript.

“(5) The daytime average mixing ratios of O₃ measured at the PKU site increased by 30% between August 2005 and August 2011 (Zhang et al., 2014). The

photo-dissociation of O_3 is a primary pathway to form hydroxyl (OH) radical (Lu et al., 2013), and thus the rising O_3 levels could result in the increase of OH abundance. Although there are no direct measurements of OH radical over long time periods in Beijing and its surrounding regions, the average abundance of OH radical ($[OH]$) can be estimated based on measured ratios of two hydrocarbons that have similar sources but different reaction rates with OH radical (McKeen et al., 1990; Ehhalt et al., 1998). In this study, the relative increase of daily average OH abundance at the PKU site was estimated to be 32.3% between August 2005 and August 2011 based on propene/ethene ratios. The calculation details can be found in Sect. 5 of the supplement. The rate constants for OH oxidation of ethene ($k_{OH} = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and propene ($k_{OH} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were significantly higher than that for acetylene ($k_{OH} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), but the relative declines for these alkenes levels measured at the PKU site were close to that for acetylene (Fig. 4a–c). This indicates that the rise of atmospheric oxidizing capacity was not an important cause for the decline of hydrocarbon levels measured at the PKU site.”

(4) I understand the point that tightening of emission standards has driven down VOC emissions from vehicles, but this presumably only applies to newly purchased vehicles. Please say something about the persistence of older vehicles in Beijing and the (nighttime?) influx of poorly controlled vehicles from outside the city.

Reply: Accepted. As the reviewer mentioned, the Beijing government also implemented specific measures to control VOC emissions from in-use vehicles besides tightening VOC emission standards for new vehicles (Wu et al., 2011). (1) The inspection and maintenance (I/M) program was implemented by Beijing Environmental Protection Bureau (EPB) to reduce VOC emissions from in-use vehicles from 1994. (2) Beijing EPB also carried out some retrofit programs for light-duty vehicles and gasoline-powered taxis. (3) Some high-emitting vehicles were restricted to drive in specific regions of Beijing city during specific time periods. The yellow-labeled vehicles (YLVs, vehicles that fail to meet Euro I standards for tailpipe

emissions) were banned to drive inside the Second-Ring Road of Beijing from 2003 and the restriction area subsequently expanded to the Sixth-Ring Road. Motorcycles were not allowed to drive within the Fourth-Ring Road since 2001. Heavy-duty trucks were banned to drive within the Fourth-Ring Road during daytime (6:00-23:00 LT). (4) Scrapping high-emitting YLVs is another method to reduce VOCs emissions from in-use vehicles. (5) There are other control measures that were implemented in Beijing to reduce traffic-related VOCs emissions, such as improving fuel quality, developing public transport system, promoting vehicles powered by green energy (e.g. compressed natural gas and electricity), implementing temporal control measures that restricted drivers on one day a week by license plate number, and some economic policies (Wu et al., 2011). The recent study by Wu et al. (2011) evaluated the effectiveness of these control measures to reduce traffic-related VOCs emission. The implementation of stringent emission standards for new vehicles was found to contribute more than 90% of the traffic-related VOCs emission reduction benefit.

The above descriptions about control measures focusing on in-use vehicles were added in Sect. 3.2.1 of the revised manuscript.

Minor points:

(5) Too much use of the word “obvious” in describing trends. The reader can judge for him/herself how clear the trends are.

Reply: Accepted. These “*obvious*” words were deleted accordingly in the revised manuscript.

(6) Page 19000, first line: “It is a challenge to obtain: : :”

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

(7) Page 19000, line 12, I think it should be “2000 to 2007.”

Reply: We are sorry for the mistake. This sentence was corrected accordingly in the revised manuscript.

(8) In a couple of places, not “to preliminary investigate.” Preliminary is an adjective. Either say “to first investigate” or “to preliminarily investigate” (the first option is best).

Reply: Thanks for your suggestion and accepted. The sentences were modified accordingly in the revised manuscript.

Anonymous Referee #2

Using NMHC data taken during selected time frames in summertimes of the years 2002-2013 the authors infer decreasing trends of NMHC emissions in Beijing which contrasts the assumptions made in the emission inventory. Overall, this paper is well written and shows some valuable material and associated discussion. It also mentions various limitations of this study. After addressing the issues lined out below I would recommend the publication of this manuscript in ACP.

Response: The encouragements are appreciated. We have carefully taken the following comments into consideration in revision. Please see the following point-by-point responses.

Major issues:

(1) Figure 3 suggests that at least in 2003, 2004, 2005, 2006 and 2007 NMHC concentrations were different at two different sites in Beijing. How representative is PKU for entire Beijing for the entire timeframe 2002-2013?

Response: Besides the spatial variations of VOC levels, there are another two possible explanations for the difference of VOCs mixing ratios at these two urban sites in Beijing: (1) The VOC species measured at these two sites are different. Ambient levels of NMHCs measured at the PKU site refer to the sum of mixing ratios for 16 hydrocarbons with carbon atoms of 2–8 (Table S1), while the VOCs levels measured at the Beijing Meteorological Tower (BMT) site correspond to the sum of 55 VOCs with carbon atoms of 4–10, including alkenes, alkanes, cycloalkanes, halocarbons, and aromatics (Wang et al., 2012; Mao et al., 2008). (2) The sampling methodologies

of ambient air samples at these two sites are different. Ambient air samples at the BMT site were collected using canisters at 14:00 LT of every Thursday since the year of 2000, whereas ambient air at the PKU site were online measured with time resolutions of 30 min or 1 hr.

Based on the above discussions, we think it is inappropriate to directly compare mixing ratios of NMHCs measured at the PKU site with total VOCs levels at the BMT site. Therefore, in the revised manuscript, we used two terms *NMHCs* and *TVOCs* to express the mixing ratios of 16 C₂–C₈ hydrocarbons measured at the PKU site and 55 C₄–C₁₀ VOC species measured at BMT site, respectively. The *NMHCs* and *TVOCs* values were plotted at the left and right axes of Fig. 3, respectively.

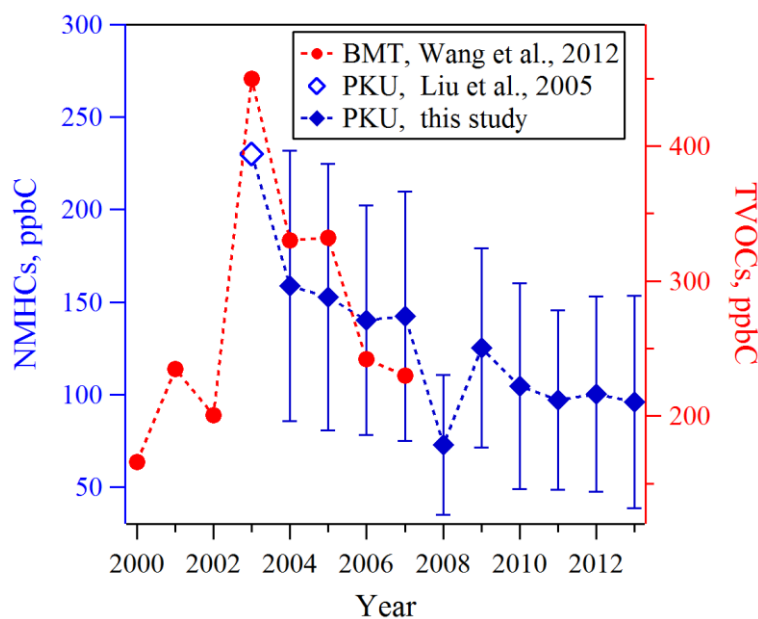


Fig. 3 Temporal changes of NMHCs mixing ratios (i.e. the sum of mixing ratios for 16 C₂–C₈ hydrocarbons) measured at the PKU site (blue diamonds) during August from 2003 to 2012 and summertime levels of TVOCs (i.e. the sum of measured 55 C₄–C₁₀ hydrocarbons and halocarbons) measured at Beijing Meteorological Tower (BMT) site (red dots) reported by Wang et al. (2012) from 2000 to 2007. The error bars correspond to standard deviations of NMHCs levels for each year.

Figure S5 shows the spatial distribution of annual average NMHCs levels at 27 sites in Beijing from September 2009 to January 2011. It can be found that the mixing

ratios of NMHCs in downtown and southern areas of Beijing were significantly higher than those for suburban/rural sites in northern and western regions. However, as shown in Fig. S6, the emission ratios for most NMHC species showed good agreements between the PKU site and the 27 regional sites in Beijing, with r of 0.99 and linear regression slope of 0.91 ± 0.02 (Wang et al., 2014).

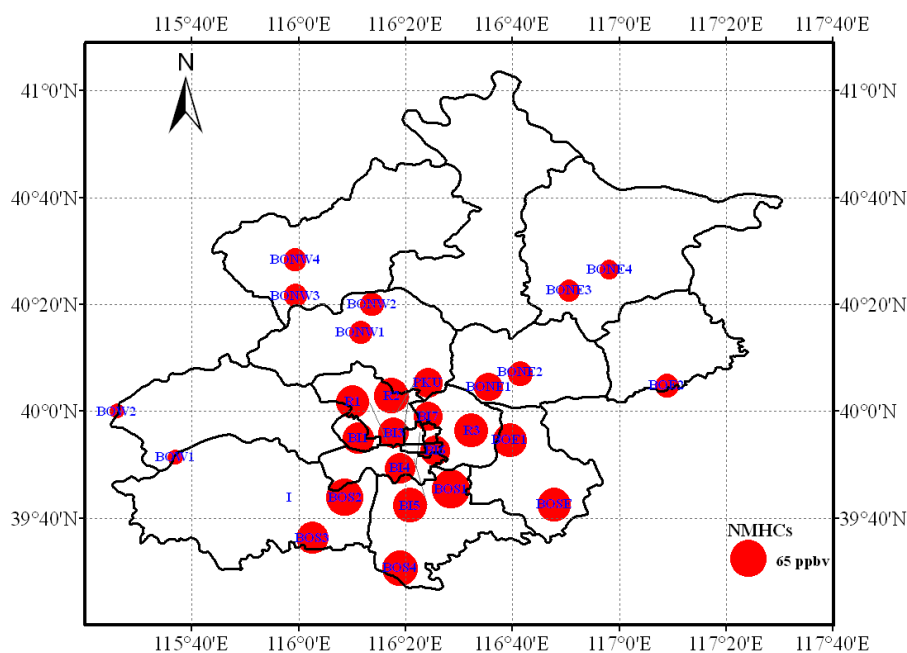


Fig. S5 Spatial distribution of annual averaged mixing ratios of NMHCs measured at 27 sites in Beijing from September 2009 to January 2010 (Wang et al., 2014).

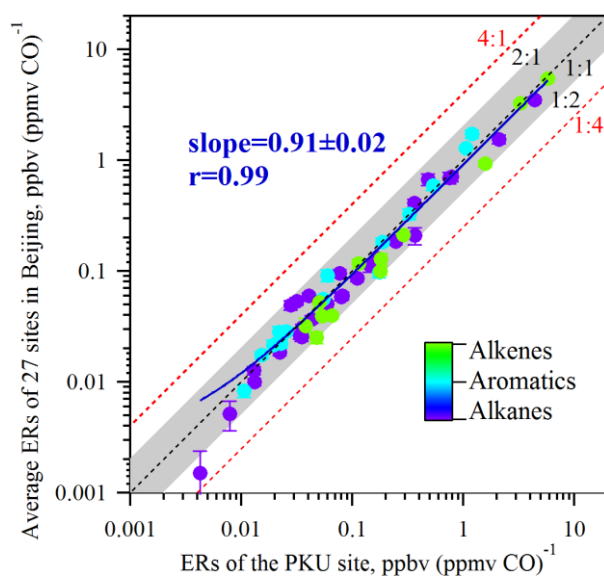


Fig. S6 Comparisons of VOC emission ratios determined at the PKU site with those

determined from regional measurements at 27 sites in Beijing from September 2009 to January 2011 (Wang et al., 2014).

In fact, the spatial distribution of industry and urbanization level in Beijing has been evolving during the last two decades. High pollution industries have gradually moved out of the urban center of Beijing; meanwhile, industrial clusters have been developed in southern suburban areas. Accompanied by the rapid economic development, southern suburban areas of Beijing have become more urbanized during these years. Although we can not obtain NMHC measurement data during the last decade for southern regions of Beijing, the Beijing government have selected five routine monitoring sites, two of them are located in southern regions, to measure the levels and speciation of NMHCs in entire Beijing since 2012. This will provide an opportunity for us to investigate the temporal trends of NMHCs at more sites of Beijing in the near future.

The above discussions were added in the supplement as ***Sect. 6 Spatial distribution of NMHC levels and chemical compositions in Beijing***. In addition, a brief version was added in Sect. 3.4 of the revised manuscript as the fourth limitation/uncertainty of this study.

“(4) The trend analyses for NMHCs levels and sources were based on measurement data obtained at one urban site, whereas the temporal changes of NMHC emissions during August in Beijing reported by the MEIC inventory were for the entire city. The regional measurements during 2009–2011 at 27 sites in Beijing suggested that NMHCs levels in downtown and southern areas of Beijing were significantly higher than those for suburban/rural sites in northern and western regions (Fig. S5). The emission ratios of individual NMHC species relative to carbon monoxide showed good agreements between the PKU site and the 27 regional sites in Beijing (Fig. S6) (Wang et al., 2014a). In fact, the spatial distribution of industry and urbanization level in Beijing has been evolving during the last two decades (Wang et al., 2014a). Most industries had been moved out of downtown area and assembled in industrial parks in southern regions of Beijing (Wang et al., 2014a). Accompanied by

the rapid economic development, southern suburban areas of Beijing have become more urbanized during these years. Although we can not obtain NMHC measurement data during the last decade for southern regions of Beijing, the Beijing government have selected five routine monitoring sites, two of them are located in southern regions, to measure the levels and speciation of NMHCs in entire Beijing since 2012. This will provide an opportunity for us to investigate the temporal trends of NMHCs at more sites of Beijing in the near future.”

- (2) For some years the MEIC database has monthly emissions available. I think for those years the authors should compare their specific summertime data with the corresponding months in the inventory.

Response: Accepted. In the revised manuscript, temporal changes of NMHC levels measured at the PKU site were compared with those for anthropogenic NMHC emissions in Beijing during August reported by the MEIC inventory (Fig. 1 and Fig. 2). Owing to the influence of short-term control measures for Beijing Olympic Games (Wang et al., 2010; Su et al., 2011), the anthropogenic NMHC emission for August 2008 was excluded from linear regression fits for NMHC emissions from 2002 to 2012. Total anthropogenic NMHC emissions during August increased at a rate of 3.5% yr⁻¹ from 2002 to 2012 (Fig. 1a). Transportation-related NMHC emissions during August decreased at a rate of 6.7% yr⁻¹ (Fig. 1b), similar to previous inventory results for on-road vehicles (Wang et al., 2010b; Wu et al., 2011; Lang et al., 2012); whereas, anthropogenic NMHC emissions from solvent use, industry, and power plant during August all showed significant increasing trends, with respective rates of 23.7% yr⁻¹, 4.0% yr⁻¹, and 8.8% yr⁻¹ (Fig. 1c–f).

Figure 2 shows relative contributions of different sources to anthropogenic NMHC emissions in Beijing during August from 2002 to 2012. It should be noted that the source structure of NMHCs emissions for August 2008 was different from those for August 2007 and 2009 because a series of short-term control measures for Beijing Olympic Games were conducted in Beijing during that time (Wang et al., 2010a; Su et al., 2011). For other years, the relative contributions of solvent use to NMHC

emissions during August increased gradually from 21% to 54%, whereas the contributions from transportation-related sources decreased from 39% to 10%. Relative contributions from residential sources exhibited a slight decrease (from 7% to 5%), while industry contributions to NMHC emissions (31–32%) did not show significant changes during 2002–2012.

The Sect. 3.1 and Figs. 1–2 in the revised manuscript were modified accordingly.

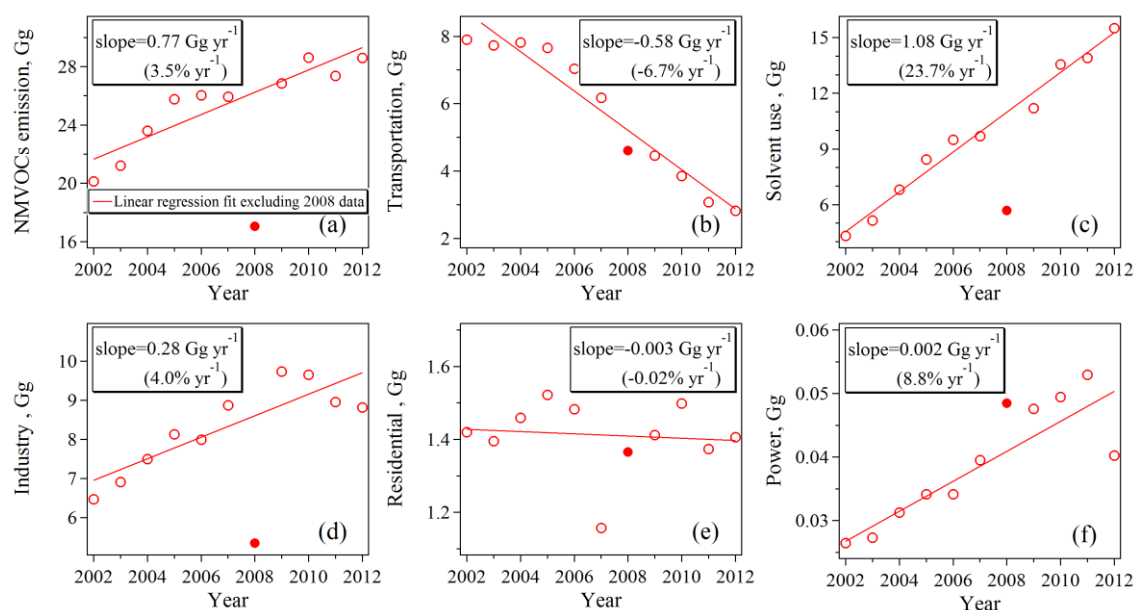


Fig. 1 Anthropogenic NMVOCs emissions in Beijing during August from 2002 to 2012 reported by the MEIC inventory (<http://www.meicmodel.org>): (a) total emissions, (b) transportation, (c) solvent use, (d) industry, (e) residential activities, and (f) power plant. Owing to the influence from the short-term control measures for Beijing Olympic Games, the measurement data for August 2008 (the red filled circle) was excluded from the linear regression fits (the red solid lines).

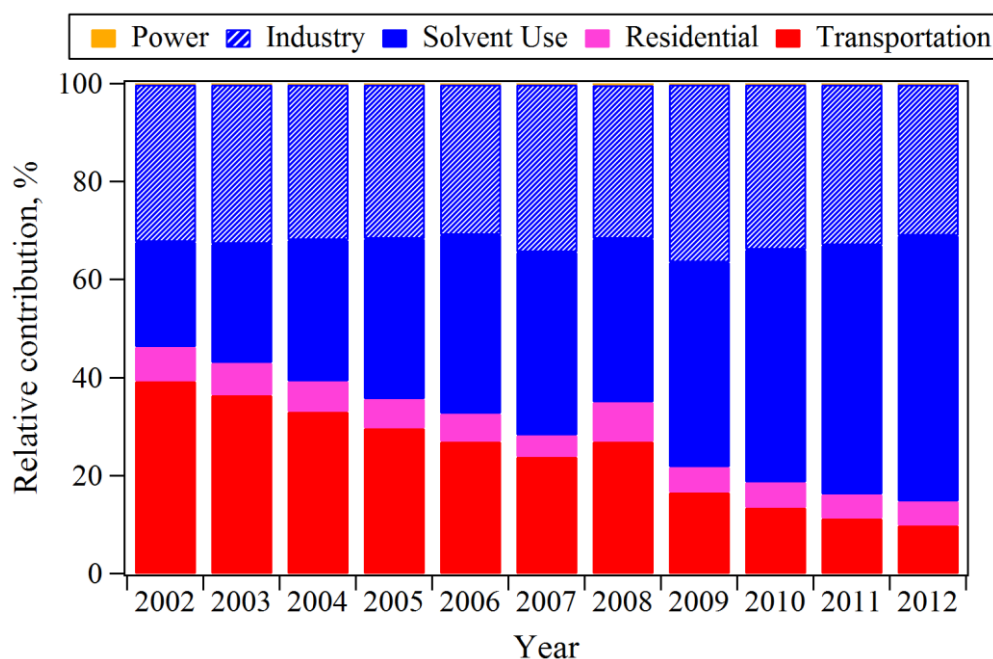


Fig. 2 Relative contributions of transportation, residential activities, solvent use, industry, and power plant to anthropogenic NMVOCs emissions in Beijing during August from 2002 to 2012 reported by the MEIC inventory (<http://www.meicmodel.org>).

(3) On page 19004, line 25, the authors mention that "During the summer main source of acetylene and alkenes emissions is vehicle exhaust". The authors should point out what other seasons changes in emissions pattern might occur in Beijing, like the use of different fuel. What would be the seasonal variation of NMHC evaporation processes?

Response: Accepted. As the reviewer mentioned, VOC sources in Beijing exhibited significant seasonal variations (Wang et al., 2014). The relative contributions of gasoline evaporation and paint & solvent use were higher during summer because the high ambient temperatures in summer could increase the evaporation rates of VOCs from gasoline and paint. Coal combustion showed larger contributions to NMHC emissions during winter because more coal was burned for heating during winter in Beijing, and its contributions in summer were considered to be negligible (Wang et al., 2014). These discussions were added in the revised manuscript.

(4) Page 19012, section 4, lines 3-8: The authors could provide upper and lower

ranges for their estimates in their paper. In particular the authors could differentiate among day- and nighttime data.

Response: Accepted. As the reviewer mentioned, the diurnal variation in ambient level and chemical composition of NMHCs can be helpful to investigate the temporal changes of atmospheric oxidizing capacity and its influence on NMHC trends. Figure S4 shows the average diurnal variations of propene/ethene during August 2005 and August 2011. As shown in this figure, the relative decline of propene/ethene between 6:00 LT and 14:00 LT was 62.1% during August 2011, significantly higher than that for August 2005 (30.6%). This indicates that the average photochemical removal degree of these two hydrocarbons at 14:00 LT during August 2011 was higher than that for August 2005.

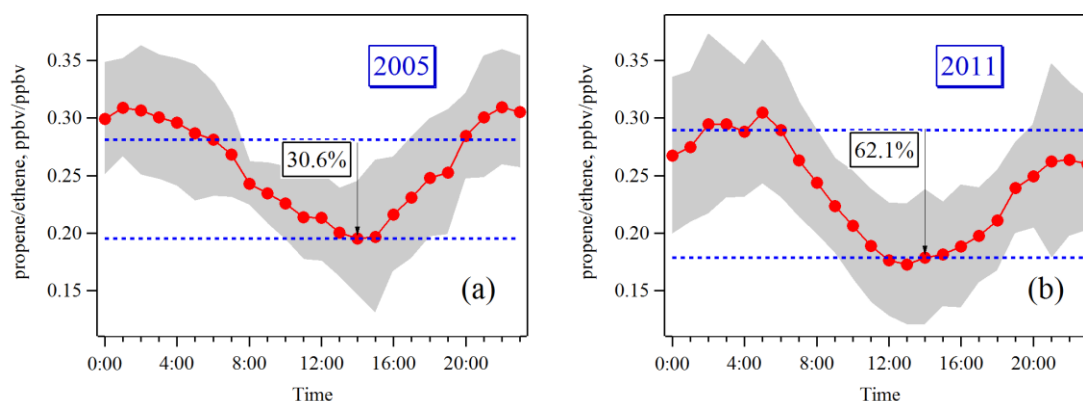


Fig. S4 Diurnal variations in hourly averaged ratios of propene to ethene (propene/ethene) during (a) August 2005 and (b) August 2011, respectively.

The most important oxidizing species for tropospheric VOCs is the hydroxyl (OH) radical. Although there are no direct measurements of OH radical over long time periods in Beijing and its surrounding regions, the average abundance of ambient OH radical ($[OH]$) can be estimated based on measured ratios of two hydrocarbons that have similar sources but different reaction rates with OH radical using the following equation (McKeen et al., 1990; Ehhalt et al., 1998):

$$[OH] = \frac{1}{(k_{HC_2} - k_{HC_1})\Delta t} \times \left(\ln \left(\frac{[HC_2]_{t_0}}{[HC_1]_{t_0}} \right) - \ln \left(\frac{[HC_2]_{t_0+\Delta t}}{[HC_1]_{t_0+\Delta t}} \right) \right) \quad (S1)$$

where k_{HC_2} and k_{HC_1} are rate constants for OH oxidation of HC_1 and HC_2 , respectively. $[\text{HC}_2]_{t_0}/[\text{HC}_1]_{t_0}$ and $[\text{HC}_2]_{t_0+\Delta t}/[\text{HC}_1]_{t_0+\Delta t}$ are the ratios of HC_2 with HC_1 measured at the time of t_0 and $t_0+\Delta t$, respectively. Δt is the reaction time of hydrocarbons. In this study, the ratio of propene/ethene was selected to estimate [OH] for the following reasons: (1) ethene and propene are both mainly emitted from vehicular exhaust during summer of Beijing (Song et al., 2007; Liu et al., 2009), and therefore variations in measured ratios of propene/ethene were mainly associated with photochemical processing; (2) the rate constant of propene with OH radical ($k_{\text{OH}} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is significantly higher than that for ethene ($k_{\text{OH}} = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson et al., 2006); (3) mixing ratios of propene and ethene in Beijing were high enough to be accurately quantified by VOC analysis systems.

Assuming that the difference of average reaction time (Δt) between August 2005 and August 2011 was negligible (i.e. $\Delta t_{2005} = \Delta t_{2011}$), the relative change of average OH abundance (RC) between these two years can be described by the following equation:

$$\begin{aligned} \text{RC} &= \frac{[\text{OH}]_{2011} - [\text{OH}]_{2005}}{[\text{OH}]_{2005}} \times 100\% \\ &= \frac{[\text{OH}]_{2011} \Delta t_{2011} - [\text{OH}]_{2005} \Delta t_{2005}}{[\text{OH}]_{2005} \Delta t_{2005}} \times 100\% \end{aligned} \quad (\text{S2})$$

Applying Eq. (S1) to calculate average OH abundance during 6:00–14:00 LT, then the RC was estimated to be 32.3% based on propene/ethene ratios using the following equation:

$$\text{RC} = \frac{\left(\ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{6:00,2011} - \ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{14:00,2011} \right) - \left(\ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{6:00,2005} - \ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{14:00,2005} \right)}{\left(\ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{6:00,2005} - \ln\left(\frac{\text{propene}}{\text{ethene}}\right)_{14:00,2005} \right)} \times 100\% \quad (\text{S3})$$

This means the average OH abundance during 6:00–14:00 LT at the PKU site increased by 32.3% between August 2005 and August 2011, with speed of $5.4\% \text{ yr}^{-1}$,

close to the rising rate of O₃ levels (5% yr⁻¹) at the same site reported by Zhang et al. (2014).

The influence of rising OH abundance on temporal trend of acetylene levels was considered to be negligible, due to the low reactivity of acetylene ($k_{\text{OH}} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The rate constants of OH oxidation for ethene ($k_{\text{OH}} = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and propene ($k_{\text{OH}} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were significantly higher than that for acetylene, but the relative declines of ethene and propene levels measured at the PKU site were close to that for acetylene (Fig. 4a-c). This indicates that the rise of atmospheric oxidizing capacity was not an important cause for the decline of hydrocarbon levels measured at the PKU site.

The above results and discussion were added in the supplement as **Sect. 5 Temporal trend of oxidizing capacity in Beijing**. In addition, main results about the temporal change in oxidizing capacity and its influence on trends of hydrocarbon levels measured at the PKU site were added in Sect. 3.4 of the revised manuscript.

“(5) The daytime average mixing ratios of O₃ measured at the PKU site increased by 30% between August 2005 and August 2011 (Zhang et al., 2014). The photo-dissociation of O₃ is a primary pathway to form hydroxyl (OH) radical (Lu et al., 2013), and thus the rising O₃ levels could result in the increase of OH abundance. Although there are no direct measurements of OH radical over long time periods in Beijing and its surrounding regions, the average abundance of OH radical ([OH]) can be estimated based on measured ratios of two hydrocarbons that have similar sources but different reaction rates with OH radical (McKeen et al., 1990; Ehhalt et al., 1998). In this study, the relative increase of daily average OH abundance at the PKU site was estimated to be 32.3% between August 2005 and August 2011 based on propene/ethene ratios. The calculation details can be found in Sect. 5 of the supplement. The rate constants for OH oxidation of ethene ($k_{\text{OH}} = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and propene ($k_{\text{OH}} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were significantly higher than that for acetylene ($k_{\text{OH}} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), but the relative declines for these alkenes levels measured at the PKU site were close to that for

acetylene (Fig. 4a–c). This indicates that the rise of atmospheric oxidizing capacity was not an important cause for the decline of hydrocarbon levels measured at the PKU site.”

(5) The findings shown in Figure 10 are not easy to compare with inventory data shown in Figure 2.

Response: The difficulty and uncertainty for comparing Fig. 10 with Fig. 2 were mainly due to the differences of classification methods for NMHC sources between the PMF results and the MEIC emission inventory: (1) There is no source category in the MEIC inventory that can correspond to the *NG and LPG use & Background* factor resolved by the PMF model. (2) There are no PMF-resolved factors that can correspond the source categories of *Power* and *Residential* in the MEIC inventory.

This fourth PMF-resolved factor largely consisted of toluene, ethylbenzene, and xylenes (Fig. 8d). These aromatic compounds can be emitted from both paint and solvent utilization (Yuan et al., 2010) and chemical industries (Liu et al., 2008). Another point should be noted is that this factor was also the largest contributor (39%) to *n*-hexane, which is one product of crude oil refining and is commonly used as solvent in industrial processes. In addition, this factor is the second largest contributor (28%) to ethene and propene, which can also be emitted from petrochemical industry (Wei et al., 2014) besides vehicular exhaust. Based on the above discussions, we think the fourth factor was not only related to paint and solvent use but also influenced by industrial sources, and therefore this factor should be referred to *Paint and solvent use & Industry* and corresponded with the source categories of *Industry* and *Solvent use* in the MEIC inventory. The results and discussion in Sect.3.3.1 of the revised manuscript were modified accordingly.

The sum of relative contributions from two traffic-related factors *Gasoline evaporation & Vehicle exhaust #1* and *Vehicular exhaust #2* can be compared with *Transportation* contributions reported by the MEIC inventory.

Other comments:

(6) Page 18998, line 6: Would suggest to replace "...during summers..." by "...during selected summer periods".

Response: Accepted. This sentence in the revised manuscript was modified accordingly.

(7) Page 18998, lines 9-10: Would suggest to use the same time periods concerning the NMHC growth rates.

Response: Accepted. In the revised manuscript, temporal changes of anthropogenic NMHC emissions during August from 2002 to 2012 reported by the MEIC inventory were used to compare with temporal trends of NMHC levels measured at the PKU site. The sentence in the revised manuscript was modified to be *"In the contrast to the results of the most recent inventory (Multi-resolution Emission Inventory for China, MEIC), which reported that anthropogenic NMHC emissions during August increased by 28% from 2004 to 2012, whereas mixing ratios of NMHCs measured at this urban site decreased by 37% during the same time period."*

(8) Page 19001, lines 21-22: The first sentence refers to C5-C8 NMHCs, while the second sentence refers to C4-12 NMHCs. This looks inconsistent.

Response: We are sorry for this mistake. As described in the second sentence, this online GC-FID system was developed to online measure C4–C12 hydrocarbons. In the revised manuscript, the first sentence was corrected accordingly.

"In 2002, an online GC-FID system developed by Peking University was used to measure the mixing ratios of C4–C12 hydrocarbons, including C4–C12 alkanes, C4–C6 alkenes, and C6–C8 aromatics, with a time resolution of 30 min."

(9) Page 19003, line 1: Would suggest to replace "The 9 year measurement data..." by "The data obtained in selected summer periods over 9 years....".

Response: Accepted. This sentence was modified accordingly in the revised manuscript.

(10)Page 19004, line 19-23: I would suggest to remove the July/August 2008 data

from Figure 10 as it may be biased.

Response: Accepted. The PMF results for August 2008 data was removed from Fig. 10 in the revised manuscript.

(11)Page 19006, section 3.2.3: Benzene, toluene, ethylbenzene and xylenes are also known to be emitted by traffic. How do the authors account for that?

Response: As the reviewer mentioned, traffic-related emission and solvent and paint utilization were the two most important sources for aromatics in Beijing (Wang et al., 2012; Liu et al., 2009a; Wang et al., 2014; Wei et al., 2008). The PMF results in this study also suggested that paint and solvent utilization and traffic-related emission (i.e. the sum of *Gasoline evaporation & Vehicle exhaust #1* and *Vehicle exhaust #2*) were the largest two contributors to aromatics. The relative contributions of traffic-related emission to benzene, toluene, ethylbenzene, and xylenes were 60%, 50%, 31%, and 38%, respectively.

In the revised manuscript, the first sentence in Sect. 3.2.3 was modified to be “*Traffic-related emission and solvent and paint utilization were considered to be the two most important sources for aromatics in Beijing (Wang et al., 2012; Liu et al., 2009a; Wang et al., 2014; Wei et al., 2008)*”.

(12)Page 19007, lines 12-19: I think this discussion is not very helpful as I doubt that an increase of northern hemispheric NMHC levels of would be relevant to the Beijing case. The increase of background ethane of about 50 pptv from 2006-2010 will hardly be detected in Beijing.

Response: Accepted. These sentences in the revised manuscript were modified to be “*The 50-pptv rise of background ethane reported by Simpson et al. (2012) can not explain the rapid increase of ethane levels measured at the PKU site.*”

(13)Page 19007, lines 25-26: This is a very vague statement. I assume this could be supported by inventory data. Is transportation an important emission source for ethane and propane in Beijing?

Response: In the MEIC inventory, transportation was considered to be the second largest contributor to ethane and propane in Beijing, only after industrial emission (Li et al., 2014). The relative contributions of natural gas and liquefied petroleum gas (LPG) use in Beijing were not given in current emission inventories. However, the PMF source apportionment study by Song et al. (2007) also suggested vehicular exhaust was an important source to ethane and propane in Beijing, with relative contributions of 43% and 46%, respectively. This information was added in Sect. 3.2.4 of the revised manuscript.

(14)Page 19011, line 2: "long-term" needs to be removed, as these measurements only covered a few weeks during summertime of each year.

Response: Accepted. The “long-term” in this sentence was removed accordingly in the revised manuscript.

(15)Page 19011, lines 23-27: I am not sure, if a any statement about a potential decrease of NMHCs can be made as this interpretation is only determined by one measurement period taken at the end of this decade and any supporting data in between 2002 and2012 are not available. The only statement which can be made is that the 2012 NMHC data shows lower values than in 2001 and 2002.

Response: Agree. The limited wintertime measurement data were not enough to investigate temporal trends of NMHC levels during winter in Beijing, and therefore these sentences in the revised manuscript was modified to be “*It can be found that the average levels for ethane, acetylene, benzene, and toluene during December 2011–January 2012 (Wang et al., 2014) were lower than those for January–February 2011 and December 2002 (Barletta et al., 2005; Liu et al., 2005). However, these wintertime measurement data are not enough to investigate temporal trends of NMHC levels during winter in Beijing. More NMHC observations for other seasons except summer are needed to investigate possible seasonal differences of NMHC trends.*”

(16)Figures 1, 4, 5, 6, 7, 8, 9: Scales and legends are hard to read. Would suggest to use larger fonts.

Response: Accepted. The fonts of scales and legends for these figures were increased accordingly in the revised manuscript.

(17) Figures 3, 4, 5, 6, 7, 9, 10, 11 : The way these figures are presented they suggest that data was obtained throughout the entire year. All these figures and the figure captions should indicate that a selected time frame in the summer is shown.

Response: Accepted. These figures and figure captions were modified accordingly in the revised manuscript.

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