Letter of Responses

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

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 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.

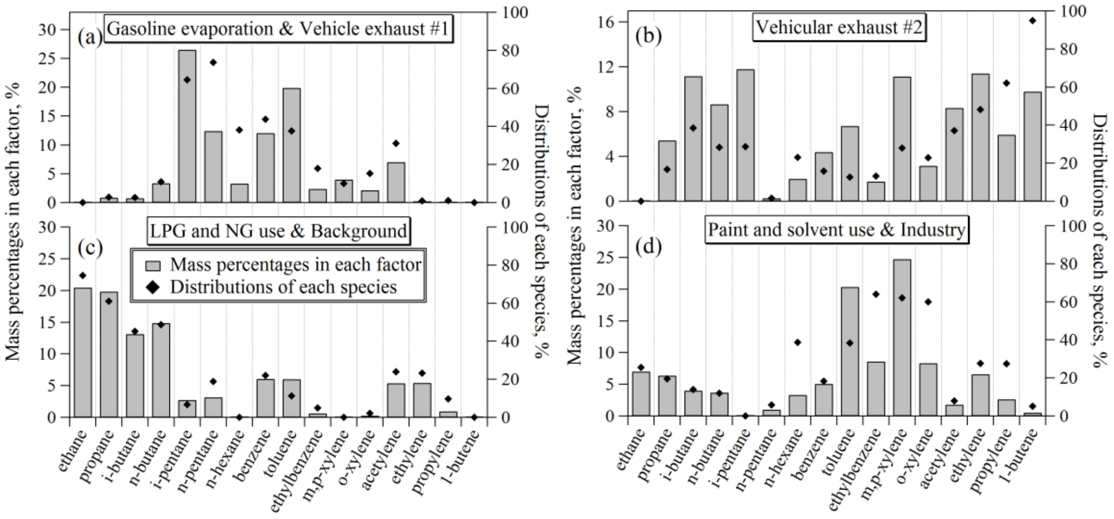

Fig. 8 Profiles of four PMF-resolved factors (gray bars) and distributions of each species among these factors (black diamonds): (a) *Gasoline evaporation & Vehicle exhaust #1*, (b) *Vehicle exhaust #2*, (c) *LPG and NG use & Background*, and (d) *Paint and solvent use & Industry*.

(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 importantâ˘A˘Tdo 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).

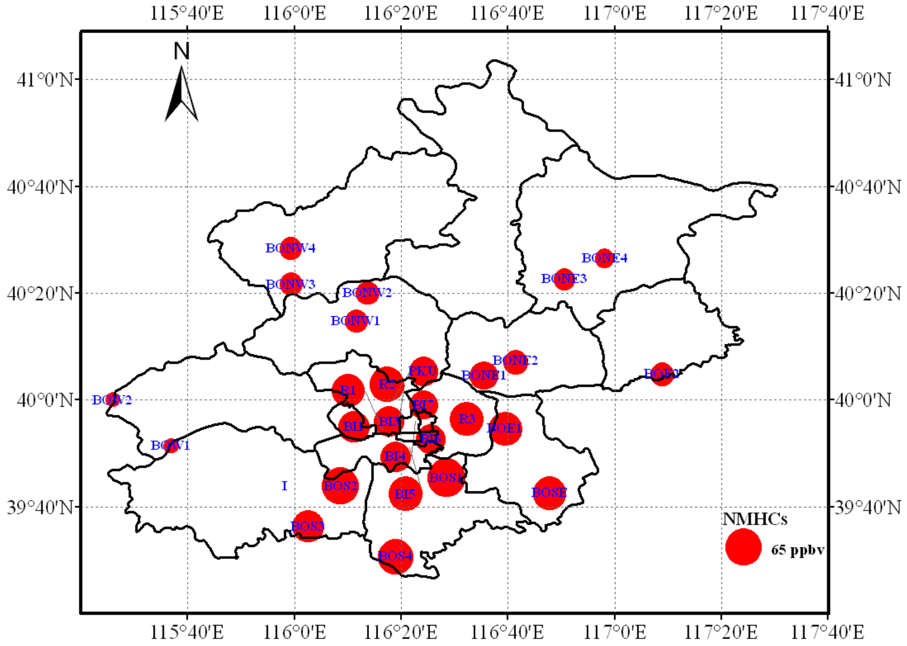

Fig. S5 Spatial distribution of annual averaged mixing ratios of NMHCs measured at 27 sites in Beijing from September 2009 to January 2011 (Wang et al., 2014).

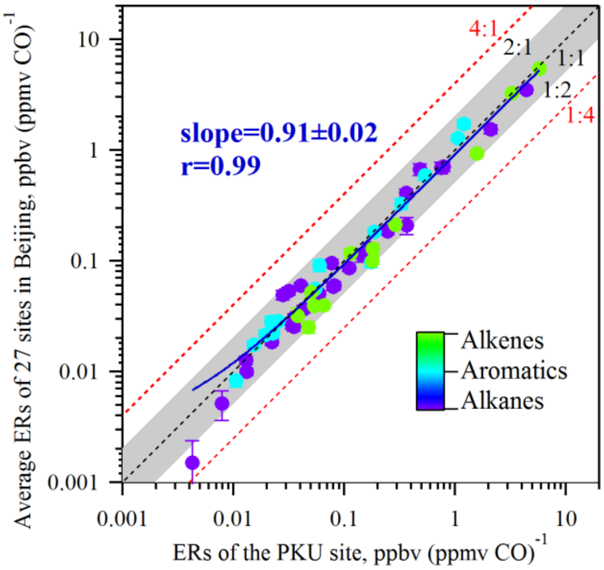

Fig. S6 Comparisons of VOC emission ratios determined at the PKU site with those determined from regional measurements at 27 sites in Beijing from September 2009 to January 2011 (Wang et al., 2014).

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 HMHCs 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., 2014). 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 HMHCs 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 O_3 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 O_3 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):

$$[\mathrm{OH}]=\frac{1}{(\mathrm{k}_{\mathrm{HC}_2}-\mathrm{k}_{\mathrm{HC}_1})\Delta t}\times\left(\ln\left(\frac{[\mathrm{HC}_2]_{t_0}}{[\mathrm{HC}_1]_{t_0}}\right)-\ln\left(\frac{[\mathrm{HC}_2]_{\mathrm{t}_0+\Delta t}}{[\mathrm{HC}_1]_{\mathrm{t}_0+\Delta t}}\right)\right) \qquad \text{(S1)}$$

where k_{HC_2} and k_{HC_1} are rate constants for the oxidation of HC_1 and HC_2 by OH radical, respectively. $[HC_2]_{t_0}/[HC_1]_{t_0}$ and $[HC_2]_{t_0+\Delta t}/[HC_1]_{t_0+\Delta t}$ 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_{OH} = 3.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1}) is significantly higher than that for ethene (k_{OH} = 9.0×10^{-12} cm^3 $molecule^{-1}$ 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.

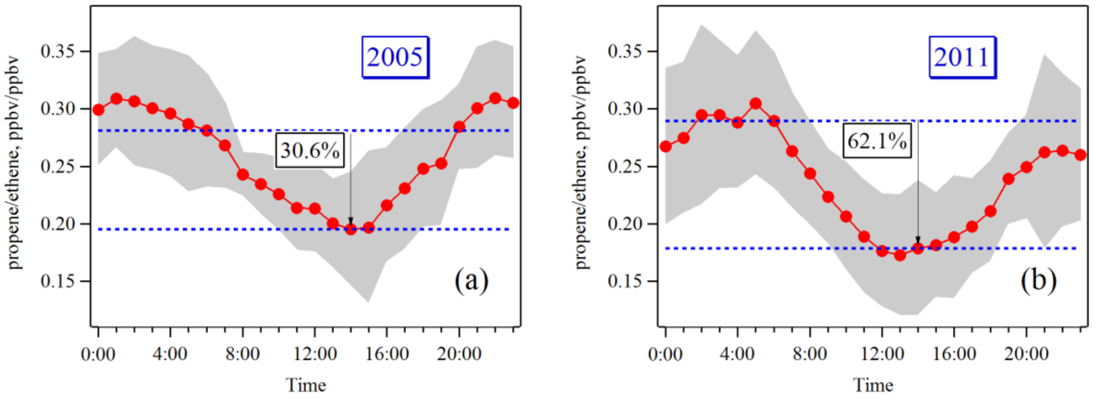

Fig. S4 Diurnal variations in hourly averaged ratios of propene to ethene (propene/ethene) during (a) August 2005 and (b) August 2011, respectively.

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:

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

Appling 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:

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

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% yr^{-1}, close to the rising rate of O_3 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_{OH} = 1.0×10^{-12} cm^3 $\mathrm{molecule}^{-1}$ s^{-1}). The rate constants of OH oxidation for ethene (k_{OH} =9.0×10^{-12} cm^3 $\mathrm{molecule}^{-1}$ s^{-1}) and propene (k_{OH} = 3.0×10^{-11} cm^3 $\mathrm{molecule}^{-1}$ 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 O_3 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 (*$k_{OH} = 9.0\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}*) and propene (*$k_{OH} = 3.0\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}*) were significantly higher than that for acetylene (*$k_{OH} = 1.0\times10^{-12}$ cm^3 $molecule^{-1}$ 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.

References:

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Subcommittee, I.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, doi: 10.5194/acp-6-3625-2006, 2006.

Ehhalt, D. H., Rohrer, F., Wahner, A., Prather, M. J., and Blake, D. R.: On the use of hydrocarbons for the determination of tropospheric OH concentrations, J. Geophys. Res., 103, 18981-18997, doi: 10.1029/98jd01106, 1998.

Jobson, B. T., Berkowitz, C. M., Kuster, W. C., Goldan, P. D., Williams, E. J., Fesenfeld, F. C., Apel, E. C., Karl, T., Lonneman, W. A., and Riemer, D.: Hydrocarbon source signatures in Houston, Texas: Influence of the petrochemical industry, J. Geophys. Res.-Atmos., 109, D24305, doi: 10.1029/2004jd004887, 2004.

Liu, Y., Shao, M., Fu, L. L., Lu, S. H., Zeng, L. M., and Tang, D. G.: Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmos. Environ., 42, 6247-6260, doi: 10.1016/j.atmosenv.2008.01.070, 2008.

Liu, Y., Shao, M., Kuster, W. C., Goldan, P. D., Li, X. H., Lu, S. H., and De Gouw, J. A.: Source Identification of Reactive Hydrocarbons and Oxygenated VOCs in the Summertime in Beijing, Environ. Sci. Technol., 43, 75-81, doi: 10.1021/es801716n, 2009.

McKeen, S. A., Trainer, M., Hsie, E. Y., Tallamraju, R. K., and Liu, S. C.: On the Indirect Determination of Atmospheric OH Radical Concentrations From Reactive Hydrocarbon Measurements, J. Geophys. Res., 95, 7493-7500, doi: 10.1029/JD095iD06p07493, 1990.

Song, Y., Shao, M., Liu, Y., Lu, S. H., Kuster, W., Goldan, P., and Xie, S. D.: Source apportionment of ambient volatile organic compounds in Beijing, Environ. Sci. Technol., 41, 4348-4353, doi: 10.1021/es0625982, 2007.

Wang, B., Shao, M., Lu, S. H., Yuan, B., Zhao, Y., Wang, M., Zhang, S. Q., and Wu, D.: Variation of ambient non-methane hydrocarbons in Beijing city in summer 2008, Atmos. Chem. Phys., 10, 5911-5923, doi: 10.5194/acp-10-5911-2010, 2010.

Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., and Wang, Q.: A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China, Atmos. Chem. Phys., 14, 5871-5891, doi: 10.5194/acp-14-5871-2014, 2014.

Wang, Y. S., Ren, X. Y., Ji, D. S., Zhang, J. Q., Sun, J., and Wu, F. K.: Characterization of volatile organic compounds in the urban area of Beijing from 2000 to 2007, Journal of Environmental Sciences-China, 24, 95-101, doi: 10.1016/s1001-0742(11)60732-8, 2012.

Wei, W., Cheng, S., Li, G., Wang, G., and Wang, H.: Characteristics of volatile organic compounds (VOCs) emitted from a petroleum refinery in Beijing, China, Atmos. Environ., 89, 358-366, doi: 10.1016/j.atmosenv.2014.01.038, 2014.

Wu, Y., Wang, R. J., Zhou, Y., Lin, B. H., Fu, L. X., He, K. B., and Hao, J. M.: On-Road Vehicle Emission Control in Beijing: Past, Present, and Future, Environ. Sci. Technol., 45, 147-153, 2011.

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, 2010.

Zhang, Q., Yuan, B., Shao, M., Wang, X., Lu, S., Lu, K., Wang, M., Chen, L., Chang, C. C., and Liu, S. C.: Variations of ground-level O3 and its precursors in Beijing in summertime between 2005 and 2011, Atmos. Chem. Phys., 14, 6089-6101, doi: 10.5194/acp-14-6089-2014, 2014.