Authors' Response to Referees' Comments

Anonymous Reviewer #1

This paper presents measurements of ambient non-methane hydrocarbons (NMHCs) from an urban site in Beijing. Although the observation was conducted only for one month (from 15 December 2015 to 14 January 2016), more than 700 samples were taken and analyzed using a custom-built online gas chromatograph so that good, quasi-continuous time series of NMHCs were obtained. There were some haze periods during the observation, which makes possible to discuss the NMHCs measurements for different pollution conditions. In addition to the characterization of concentrations and diurnal variations of NMHCs, the authors show the estimation of wintertime OH and NO3 concentrations, discuss the species vs species ratios and the implication to sources, and present the results of source apportionment from the PMF analysis. It is shown that coal combustion is the most important NMHCs source during haze days in winter. The data presented in this paper are of high quality and valuable for atmospheric environmental studies. The results, in particular, the importance of coal combustion to NMHCs and the concentrations of OH and NO3 in winter in Beijing, are not previously reported. In general, the paper is well structured and written. The paper can be improved by appropriately addressing the following major and minor issues. I recommend publication of this paper in ACP after revisions

Answer: We appreciate your positive comments about our manuscript. The questions raised by you were responded point by point as followings.

(1) Given the inhomogeneous sources distributions and the combination with the winter meteorological conditions, particularly wind direction (e.g., Lin et al., 2011, Zhang et al., 2014), not only wind speed but also wind direction should be used for the interpretation of the NMHCs measurements. Source apportionment suggests that the most important source in haze conditions is coal combustion emission. And it is mentioned that coal combustion is prevailing for heating and cooking by farmers in rural areas. Then the question is: does the dependence of the concentrations of NMHCs and other pollutants on wind direction agrees with the source apportionment and directional distributions of major sources?

Answer: Yes, the concentrations of NMHCs indeed depended on wind direction. The time series of the contributions from the five factors to atmospheric NMHCs were reanalysed (Fig. 7). It is evident that the contribution from coal combustion was the maximum during the most serious pollution episode II (25-26 December 2015) when the wind direction was from southwest, implying that the air parcel transportation from southwest was an important source for NMHCs in Beijing (Wang et al., 2013). According to your valuable suggestion, the corresponding paragraph was revised as following:

In general, the variation trends of the contributions from gasoline related emissions (gasoline exhaust and evaporation), diesel exhaust, coal combustion emissions and acetylene-related emissions to atmospheric NMHCs were closely related with the variation trend of atmospheric

NMHCs measured, while the contribution from the consumer and household products had less correlation with the atmospheric NMHCs measured. The daily emissions from gasoline related sources (gasoline exhaust and evaporation), diesel exhaust, coal combustion sources and acetylene-related sources are usually stable, and hence, the similar variation trends of their contributions to atmospheric NMHCs were mainly ascribed to the variation of meteorological condition. The sources of consumer and household products were suspected to be irregular for explaining the abnormal variation trends of their contributions to atmospheric NMHCs. It should be mentioned that the contribution from coal combustion was the maximum during the most serious pollution episode II (25-26 December 2015) when the wind direction was from southwest, implying that the air parcel transportation from southern was an important source for NMHCs in Beijing (Wang et al., 2013).

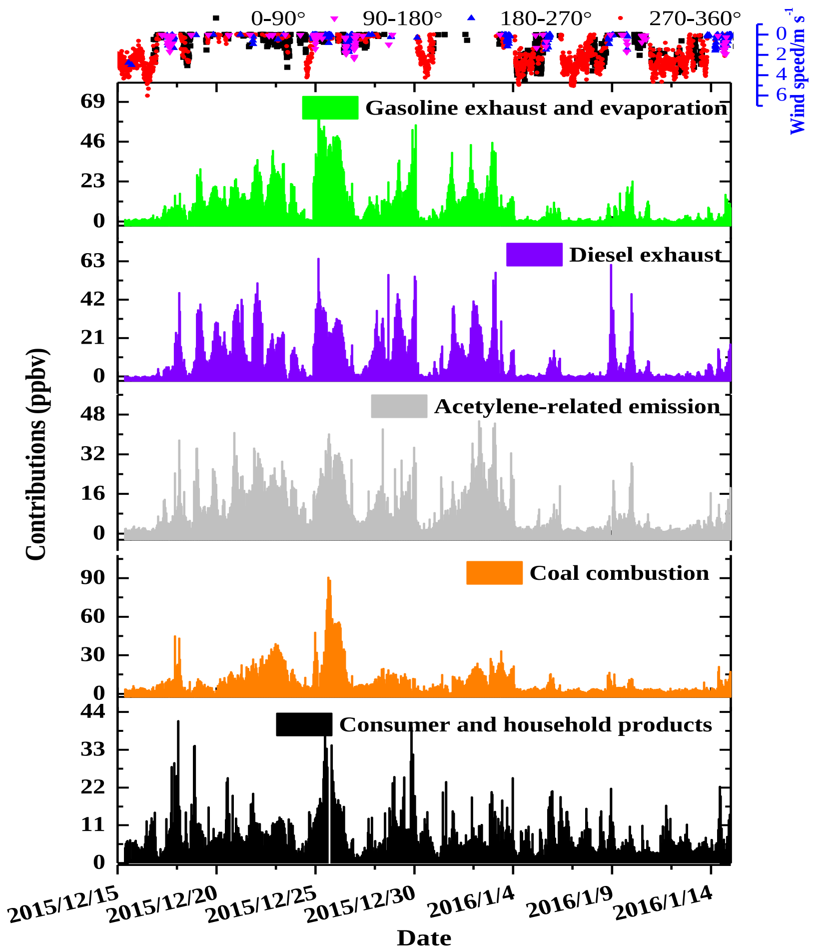

Fig.7 The time series of the contributions from gasoline related emissions, diesel exhaust, coal combustion, acetylene-related emission and consumer and household products to atmospheric NMHCs

(2) The observation period is grouped into clear, light haze and heavy haze days, which are normally closely related with wind speed and direction. Therefore, there might be significant differences in sources impacting the NMHCs at the receptor site. To be able to find the differences, it is suggested to make the PMF analysis separately for the groups of days. However, it seems to me that the PMF analysis was only performed for the entire dataset (section 3.3.2) though the portions of each source

are given for different pollution conditions (Fig. 7).

Answer: Yes, the sources' contribution to the NMHCs at the receptor site during clear, light haze and heavy haze days were separately derived from the PMF analysis. Because the source profiles for the PMF analysis during different pollution conditions were similar, only the source profiles of the PMF analysis for the entire database are presented in the manuscript. According to your valuable suggestion, the corresponding paragraph was revised as following:

The PMF model was performed based on the 740 samples collected and the NMHCs species with highly reactive or high uncertainty were excluded to reduce the possible bias of the modeling results. Eventually, 17 NMHCs species were selected for the source apportionment analysis since they are the most abundant species and/or are typical tracers of various emission sources. The sources' appointments of atmospheric NMHCs at the receptor site for the clear days, light haze days, heavy haze days and the whole days were separately analysed by the PMF model, and similar source profiles were found. As shown in Fig. 6 for the whole database, five factors were resolved from running the PMF model designated as source 1, source 2, source 3, source 4 and source 5.

(3) It is suggested to treat the data from 19-22 Dec. 2015 differently since the odd even plate number rule might have substantially changed the absolute and relative contributions of vehicle emission during this period, which may cause different source apportionment and species ratios.

Answer: According to your valuable suggestion, the PMF analysis was performed separately for the data from 19-22 December 2015 with odd even plate number rule. Compared with the similar pollution days (25-26 December 2015, 29 December 2015, 1-3 January 2016,) but without the odd even plate number rule, the relative contribution of vehicle emission to atmospheric NMHCs during the period of 19-22 December 2015 decreased from 27% to 20%.

(4) The interpretation on the different diurnal variations is vague (page 6 lines 20-25). The authors do not show any data of PBL height. The cited references (Quan et al, 2013; Liu et al., 2013) are all about September and the situation may be different in winter months. In addition, the PBL height alone cannot explain the different diurnal patterns. The author states "The boundary layer in clear day is relatively high, which favors for diffusion of pollutants (Gao et al., 2015), and hence, the distinct NMHCs peak values appeared during the two rush hours". If the high PBL in clear day favors the diffusion, emissions from vehicle as well as other sources should be better diluted. Why should the rush hours peaks so protruding? I think the key is the lowest nighttime level of pollution during clear days. It is the lowered nighttime level of pollution that makes the daytime rush hours peaks more evident. If the nighttime PBL were the highest during clear days, the lowest nighttime level of pollution would have been at least partly explained. Unfortunately, the paper presents no PBL height data. However, wind speed data are shown in Table 1 for different pollution conditions. The average wind speed during clear days was nearly twice as high as those during haze days, which could have resulted in the differences. To obtain more robust conclusion, the authors are suggested to calculate the daytime and nighttime wind speed for different pollution conditions. It would be

better if they can show data of the PBL height, too.

Answer: The references about the PBL height under different pollution conditions in winter were cited in the revised manuscript, and the PBL height were indeed the highest during clear days in both daytime and nighttime (Zheng et al., 2015;Lin et al., 2011;Zhang et al., 2014). According to your valuable suggestion, the wind speeds for different pollution days in daytime and nighttime are separately listed in Table 1. Besides the highest PBL height during clear days, the highest wind speed during both nighttime and daytime in clear days also favored diffusion of pollutants, resulting in the lowest levels of atmospheric NMHCs in clear days. Therefore, the statement was rephrased as "Both the relatively high boundary layer and wind speeds could result in the lowest levels of the pollutants during nighttime, which were suspected to make the peak levels of atmospheric NMHCs more evident during daytime rush hours."

Table 1. Classification of pollution statues and the corresponding meteorological conditions as well as the date

Pollution status	Visibility /Km	T /℃	RH /%	Wind speed /m·s^{-1}	Date
Heavy haze days	1.41±1.76	0.83±2.86 [a] -0.66±1.90 [b]	59.17±16.19 [a] 65.94±13.09 [b]	0.19±0.35 [a] 0.07±0.16 [b]	2015/12/19-23,201512/25-26, 2015/12/29, 2016/01/1-3
Light haze days	6.81±5.37	-0.72±4.04 [a] -1.19±3.28 [b]	24.39±11.28 [a] 31.92±14.58 [b]	0.37±0.68 [a] 0.07±0.23 [b]	2015/12/17-18, 2015/12/24, 2015/12/27-28, 2015/12/31, 2016/01/9, 2016/01/14
Clear days	19.96±9.7	1.63±2.18 [a] 0.20±2.11 [b]	20.35±6.01 [a] 26.26±7.56 [b]	2.02±1.29 [a] 1.78±1.51 [b]	2015/12/15-16, 2015/12/30, 2016/01/4-8, 2016/01/10-13

[a] daytime; [b] nighttime

(5) Species ratios are presented, discussed in terms of emission sources, and used for estimating the OH and NO3 concentrations. While these are good attempts, the authors did not pay attention to uncertainties in use of the ratios. Good correlations can be caused by chemical reactions of NMHCs with OH, NO3 or O3, or simply by atmospheric mixing or dilution (e.g., Parrish et al., 1992; McKeen and Liu, 1993). It seems to me that atmospheric mixing is not considered at all in this paper. The results might have been biased by such omission. I suggest that the authors discuss all the assumptions that are needed to make for the use of this ratio technique and the uncertainties associated with their results.

Answer: According to your valuable suggestion, the uncertainties in use of the Propane/propene ratios were added in Fig.5. The ratios of typical atmospheric pollutants have been widely used as indicators for revealing their sources origination and atmospheric photochemical ageing processes, which could largely counteract the influence of atmospheric dilution (Ho et al., 2004;Barletta et al., 2005;Wang et al., 2010). It should be mentioned that the OH and NO3 derived from the

Propane/propene ratios could only represent their lower limits because of the continue mixing of fresh emissions with the aged air.

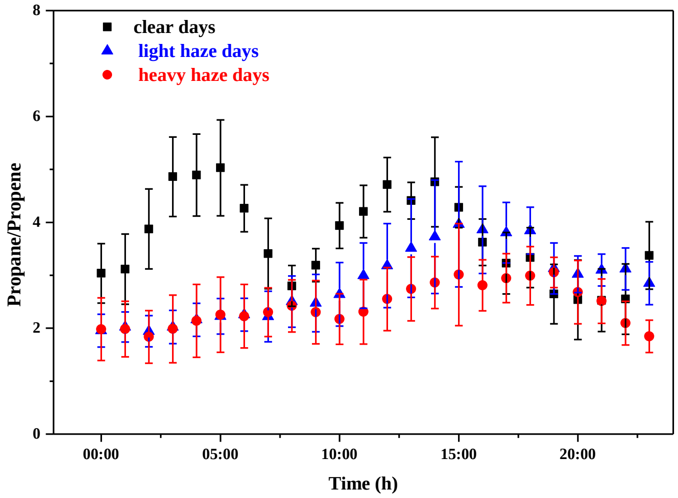

Fig. 3 Diurnal variations of propane/propene ratios during clear days, light haze days and heavy haze days

Minor points:

Page 3 line 11: I think the coordinate is that of RCEES not Beijing city so it should be placed directly after RCEES.

Answer: Yes! We have corrected the mistake in the revised manuscript.

Page 3 lines 24-25: change "ramp" to "ramped"

Answer: Sorry! We have corrected the mistake in the revised manuscript.

Page 3 line 30-page 4 line 1: how was the detection limit determined? Either give the determination method here or cite the reference, which in it is described.

Answer: The method detection limits (MDLs) of 0.02-0.10 ppbv for the NMHCs were estimated based on the signal to noise ratio of 3 and enrichment volume of 400 ml. The detail information about the MDLs could be referenced in our previous publication (Liu et al., 2016). The sentence in Page 4, line 1 was revised as following:

The method detection limits (MDLs) of 0.02-0.10 ppbv for the NMHCs were estimated based on the signal to noise ratio of 3 and enrichment volume of 400 ml (Liu et al., 2016a).

Page 4 line 3: a citation for US PMF 5.0 is necessary.

Answer: Yes! References were added in the revised manuscript.

Page 4 lines 23-24: "based on both a good fit to the data and the most reasonable results". Please be more detail about this.

Answer: Sorry! We have revised the sentence in the revised manuscript:

In this analysis, different numbers of factors were tested to find the optimal fit with the most physically reasonable results. The robust mode was used to reduce the influence of extreme values on the PMF solution.

Page 5 line 3 and page 21 Table 1: It is better to change the unit of wind speed to m/s.

Answer: Yes! the unit of wind speed were changed to m/s in the revised manuscript.

Page 6 line 10: delete "of the".

Answer: Sorry! We have corrected the mistake in the revised manuscript.

Page 7 line 11: did you measure O3? If yes, the data should be shown in Figure 1.

Answer: Yes! ozone concentrations were added in Fig. 1, and the analysis of the pollutants was revised as following:

In contrast to NMHCs and $PM_{2.5}$, ozone concentrations approached to zero during each haze events and reached to the maximum of about 35 ppbv in daytime just after the haze events followed by strong winds from northwest directions (Lin et al., 2011). Although strong winds from northwest directions occurred during the period of 12-14 January 2016, ozone concentrations didn't evidently increase during daytime, implying that ozone formation depended on the pollution levels of its precursors (e.g., NMHCs and NOx).

Page 8 line 2: are the results from daily estimation?

Answer: Yes! the daily concentrations of NO_3 and OH radicals were estimated.

Page 8 line 3: it is meaningless to compare the short-term values for ground level with the global average.

Answer: Sorry! We have corrected the mistake in the revised manuscript.

References

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