Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-783, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 16 December 2016
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Atmospheric Chemistry and Physics
Discussions

The levels, variation characteristics and sources of atmospheric non-methane hydrocarbon compounds during wintertime in Beijing, China

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Abstract. Atmospheric non-methane hydrocarbon compounds (NMHCs) were measured at a sampling site in Beijing city from 15 December 2015 to 14 January 2016 to recognize their pollution levels, variation characteristics and sources. Fifty-three NMHCs were quantified and the proportions of alkanes, alkenes, acetylene and aromatics to the total NMHCs were 49.8% ~ 55.8%, 21.5% ~ 24.7%, 13.5% ~ 15.9% and 9.3% ~ 10.7%, respectively. The variation trends of the NMHCs concentrations were basically identical and exhibited remarkable fluctuation, which were mainly ascribed to the variation of meteorological conditions, especially wind speed. The diurnal variations of NMHCs in clear days exhibited two peaks during the morning and evening rush hours, whereas the rush hours' peaks diminished or even disappeared in the haze days, implying that the relative contribution of the vehicular emission to atmospheric NMHCs depended on the pollution status. Two evident peaks of the propane/propene ratios respectively appeared in the early morning before sun rise and at noontime in clear days, whereas only one peak occurred in the afternoon during the haze days, which were attributed to the relatively fast reactions of propene with OH, NO_3 and O_3. Based on the chemical kinetic equations, the daytime OH concentrations were calculated to be in the range of 3.47×10^5 - 1.04×10^6 molecules·cm^{-3} in clear days and 6.42×10^5 - 2.35×10^6 molecules·cm^{-3} in haze days, and the nighttime NO_3 concentrations were calculated to be in the range of 2.82×10^9 - 4.86×10^9 molecules·cm^{-3} in clear days. The correlation coefficients of typical hydrocarbons pairs (benzene/toluene, o-xylene/m,p-xylene, isopentane/n-pentane, etc.) revealed that vehicular emission and coal combustion were important sources for atmospheric NMHCs in Beijing during the wintertime. Five major emission sources for atmospheric NMHCs in Beijing during the wintertime were further identified by positive matrix factorization (PMF), including vehicular emission and gasoline evaporation, coal combustion, solvent usage, acetylene-related emission and consumer and household products. Coal combustion (probably domestic coal combustion) were found to make the greatest contribution (29.4~33.4%) to atmospheric NMHCs during haze days.

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1 Introduction

As an important class of volatile organic compounds (VOCs), non-methane hydrocarbons (NMHCs) play pivotal role in atmospheric chemistry (Houweling et al., 1998; Rappengluck et al., 2014) and their degradation can cause formation of secondary products (such as ozone (O_3) and secondary organic aerosols (SOA)) which affect the oxidizing capacity, radioactive balance, and human health (Volkamer et al., 2006; Shen et al., 2013; Huang et al., 2014; Liu et al., 2015; Palm et al., 2016; La et al., 2016). NMHCs can originate either from biogenic or anthropogenic sources. Biogenic sources are mainly from emission of vegetation and anthropogenic sources are related to fossil fuel combustion (vehicle exhaust, heat generation and industrial processes), storage and distribution of fuels (gasoline, natural gas and liquefied petroleum gas) and solvent use. Because the global emission and the reaction activity of biogenic NMHCs are much greater than those of anthropogenic NMHCs (Goldstein and Galbally, 2007), atmospheric biogenic NMHCs (e.g., isoprene) are more important in global atmospheric environment. In urban areas, however, anthropogenic NMHCs greatly exceed biogenic NMHCs and have been considered as one of the most dominant drivers of air pollution (Srivastava et al., 2005; Gaimoz et al., 2011; Waked et al., 2012). In addition, some anthropogenic NMHCs (e.g., benzene and 1,3-butadiene) have been verified to be toxic, carcinogenic or mutagenic (US EPA, 2008; Møller et al., 2008). Due to the negative impact of NMHCs on atmospheric environment as well as human health, atmospheric NMHCs measurements have been world widely conducted in many urban areas (Shirai et al., 2007; Gaimoz et al., 2011; Waked et al., 2016), and the results revealed that NMHCs made remarkable contribution to atmospheric O_3 and SOA in most cities and the cancer risk of benzene evenly exceeded the value of 1.0×10^{-6} in some cities (Zhou et al., 2011; Du et al., 2014).

Beijing, as one of the world's megacities, has been encountering two prominent atmospheric environmental problems: the elevation of near-surface O_3 levels and the serious pollution of fine particles (including SOA) which result in frequent haze formation (Sun et al., 2014). Therefore, the levels and sources for atmospheric NMHCs in Beijing city have been aroused great concern (Song et al., 2007; Wu et al., 2016). More than 40 papers about NMHCs in Beijing city have been published since 1994 (Shao et al., 1994), and the results indicated that the concentrations of NMHCs in Beijing were evidently higher than those in the cities of most developed countries (Gros et al., 2007; Parrish et al., 2009). The major components of atmospheric NMHCs in Beijing city were found to be alkanes, alkenes and aromatics, and the relatively high proportions of alkenes and aromatics have been suspected to be responsible for formation of O_3 and SOA (Li et al., 2015; Sun et al., 2016). Based on the model of positive matrix factorization (PMF), several studies also investigated the major sources and their contributions to atmospheric NMHCs in Beijing city: transportation-related sources (32~46%), paint and solvent use and industry (18~30%), solvent utilization (8~14%) were found to be the major sources for atmospheric NMHCs in summer (Wang et al., 2015; Li et al., 2016), while vehicle exhaust (26~39%) and coal combustion (35~41%) were the dominant sources in winter (Wang et al., 2013). However, most studies mainly focused on summertime, the data of atmospheric NMHCs in Beijing city during wintertime were still sparse, e.g., only two reports about atmospheric NMHCs (Wang et al., 2012; Wang et al., 2013) and two reports about benzene, toluene, ethylbenzene and xylene (BTEX) (Zhang et al., 2012a;

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Zhang et al., 2012b). To comprehensively evaluate the influence of atmospheric NMHCs on the air quality and to further identify the sources of atmospheric NMCHs in Beijing city, more measurements of atmospheric NMHCs in winter are still needed.

In this study, atmospheric NMHCs were online measured using a liquid nitrogen-free gas chromatography-flame ionization detector (GC-FID) in Beijing city from 15 December 2015 to 14 January 2016. The objectives of this study are (1) to determine the concentration levels and variation characteristics of atmospheric NMHCs in Beijing during wintertime; (2) to identify the major sources for atmospheric NMHCs in Beijing during wintertime.

2 Experimental

2.1. Sampling site description

Air samples were collected on a rooftop (20 m above the ground level) in Research Center for Eco-Environmental Sciences (RCEES) which lies in the north of Beijing city (39.8°N, 116.5°E) between the 4th and 5th rings roads. The sampling site is surrounded by some residential areas, campuses and institutes. The detail information about the sampling site was described in our previous studies (Pang and Mu, 2006; Liu et al., 2009). The meteorological data, including temperature, wind speed, relative humidity (RH), visibility and Air Pollution Index of particulate matter with diameter of less than 2.5 μm ($PM_{2.5}$) at RCEES were from Beijing urban ecosystem research station, which is about 20 m away from our sampling site.

2.2. Analytical methods

Air samples were analyzed continuously and automatically using a custom-built/liquid nitrogen-free GC-FID online instrument, with a time resolution of 1 h. The online instrument is mainly consisted of a cooling unit, a sampling unit, a separation unit and a detection unit, and the detailed description of the analytical instrument is described in Liu et al. (2016a). Briefly, a sample amount of 400 mL (50 mL·min^{-1} × 8 min) of the air was pre-concentrated in a stainless steel tube filled with Carbopack™ B adsorbent (60/80 mesh). Once the pre-concentration was finished, the adsorption tube was quickly heated to about 100℃ and the NMHCs desorbed were injected into a single column (OV-1, 30 m × 0.32 mm I.D.) for separation. The temperature program of the capillary column used was as follows: 3 min at -60℃, ramp at 12℃ min^{-1} to -20℃, ramp at 6℃ min^{-1} to 30℃, ramp at 10℃ min^{-1} to 170℃, then hold for 2 min. The detection unit is a FID, and the temperature of the FID is operated at 250℃.

We used an external standard method for the quantification of C2-C12 hydrocarbons by diluting 1.0 ppmv standard gas mixtures of 57 NMHCs (provided by Spectra Gases Inc., USA) with high pure nitrogen gas. Five concentrations (1.0-30.0 ppbv) were used to perform calibrations. R^2 values for calibration curves were all above 0.99 for NMHCs, indicating that integral areas of peaks were proportional to concentrations of target compounds. We performed weekly calibrations, and the variations in target species responses were within 6 % of the calibration curve. The method detection limit for each species

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quantified in this system ranged from 0.02 to 0.10 ppbv.

2.3 PMF model analysis

The US PMF 5.0 was applied to identify major emission sources of NMHCs sources. PMF is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices-factor contributions and factor profiles which can be interpreted by an analyst as to what sources are represented based on observations at the receptor site (Guo et al., 2010; Ling et al., 2011; Ou et al., 2015; Shao et al., 2016). The object function Q, based on the uncertainties inherent in each observation, can allow the analyst to review the distribution for each species to evaluate the stability of the solution:

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad (1)$$

where u_{ij} is the uncertainty estimate of source *j* measured in sample *i*, x_{ij} is the *j*th species concentration measured in the *i*th sample, g_{ik} is the species contribution of the *k*th source to the *i*th sample, f_{kj} is the *j*th species fraction from the *k*th source, and p is the total number of independent sources.

For the PMF input, it is not necessary to use all of the measured NMHCs for the PMF model due to the fundamental assumption of non-reactivity and/or mass conservation of the PMF model (Guo et al., 2011a;Ling and Guo, 2014). The selection of the NMHCs species for the input of the PMF model was based on the adopted principles in previous studies (Ling and Guo, 2014). In total, 17 major NMHCs, which accounted for about 90% (ppbv/ppbv) of the total concentrations of the measured NMHCs species, were input into the PMF model to explore the sources of observed NMHCs. The uncertainty of input data is another input required by PMF. According to the method recommended by EPA PMF Fundamentals, the uncertainties for each sample/species with values high the detection limit (DL) were calculated using the following equation:

$$\text{uncertainty} = \sqrt{Precision^2 + DL^2} \quad (2)$$

where the precision accounts for the relative measurement error determined by calibration of the instruments. Values below the detection limit were replaced by 1/2 of the DL and their overall uncertainties were set at 5/6 of the DL values. In this analysis, different numbers of factors were tested, and an optimum solution was determined based on both a good fit to the data and the most reasonable results. In addition, many different starting seeds were tested and no multiple solutions were found. More than 95% of the residuals were between -3 and 3 for all compounds. The Q values in the robust mode were approximately equal to the degrees of freedoms. These features demonstrated that the model simulation results were acceptable.

3 Results and discussion

3.1 The levels and variation characteristics of NMHCs during the sampling period

Fifty-three NMHCs were quantified and classified into alkanes, alkenes, aromatics and acetylene. The variations of total NMHCs (TNMHCs), alkanes, alkenes, aromatics and acetylene together with meteorological parameters during the

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measurement period are shown in Fig. 1. It is evident that the variation trends of the NMHCs concentrations were basically identical and exhibited significantly fluctuation, which were mainly ascribed to the variation of surface wind speed, e.g., the TNMHCs concentrations were lower than 30 ppbv when wind speeds were greater than 7.2 $km \cdot h^{-1}$, whereas sharply increased as the wind speed decreased. Although the surface wind speeds were relatively higher on 25-26 December 2015 than other days with pollution episodes, the concentrations of NMHCs were the highest. The relatively stable and low air temperature during 25-26 December 2015 (Fig. 1D) indicated that the surface wind with the cold air might result in advection inversion which favored accumulation of the pollutants. The daily average concentration of TNMHCs increased from about 30 ppbv to about 100 ppbv within 3-6 days during the three pollution episodes on 17-22 December, 27-29 December and 31 December-3 January, whereas increased from about 30 ppbv to 165 ppbv within one day during the pollution episode on 25-26 December. The strong wind only lasted 5 h before the sever pollution episode on 25-26 December, whereas the strong wind events lasted at least one day before the other pollution episodes. High concentrations of the pollutants after the strong wind event with duration of short period on 24 December were suspected to distribute in the neighbor of Beijing, which could accelerate the accumulation of the pollutants in Beijing after the strong wind event.

It should be noted that the variation trend of TNMHCs was almost same as that of $PM_{2.5}$, and significant linear correlation with coefficient (R^2) of 0.9 was found. Because NMHCs are solely from direct emissions and $PM_{2.5}$ is from both direct emissions and secondary formation, the almost same variation trends of them further indicated that meteorological conditions, especially the surface wind speed played pivotal role for their accumulation and dispersion. On the other hand, some of the NMHCs (e.g., aromatics) measured are the precursors for SOA, the remarkable elevation of the NMHCs during pollution episodes would also make more contribution to $PM_{2.5}$ through SOA formation because of relatively high OH radical concentration during the pollution episodes (see Sect. 3.2.2). It should be also mentioned that odd-even license plate number rule was adopted in Beijing on 19-22 December 2015. Compared with the two pollution events on 27-29 December and 31 December-3 January, although the wind speeds were slightly faster, the peak values and the daily average concentrations of TNMHCs and $PM_{2.5}$ during the period of 17-22 December 2015 were almost same as the two pollution events without adopting the rule, implying that the sources other than vehicle emission might be dominant for atmospheric NMHCs and $PM_{2.5}$ during the haze days.

The entire sampling period was divided into three categories based on the daily average visibility values: clear days (≥ 10 km, RH < 90%), light haze days (5-10 km, RH < 90%) and heavy haze days (≤ 5 km, RH < 90%) (Yang et al., 2012; Lin et al., 2014). As shown in Table 1, there were 11 heavy haze days, 8 light haze days and 12 clear days during the 31 sampling days (non-precipitation days). The mean concentrations and standard deviations of TNMHCs, alkanes, alkenes, aromatics and acetylene during the three categories are presented in Table 2. It is evident that the average concentrations of alkanes, alkenes, aromatics, acetylene and TNMHCs remarkably increased from clear days to heavy haze days, and their average concentrations during heavy haze days were at least a factor of 5 higher than those during clear days, which were in good agreement with the previous studies (Zhang et al., 2014). Alkanes accounted for the largest proportions (49.8% ~ 55.8%), followed by alkenes (21.5% ~ 24.7%), acetylene (13.5% ~ 15.9%) and aromatics (9.3% ~ 10.7%). The proportion order of

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alkenes, acetylene and aromatics obtained by this study in winter were different from that reported by previous studies in summer (Wang et al., 2010; Li et al., 2016) which was probably due to the different sources (e.g., additional domestic coal combustion in winter) for atmospheric NMHCs in Beijing between the two seasons. The top ten NMHCs measured in this study are presented in Table 3 for comparison with those from the cities in China. The average concentrations of the top ten NMHCs observed in this study were basically within the values reported in various Chinese cities (Barletta et al., 2005; Song et al., 2012; An et al., 2014; Li et al., 2015; Zou et al., 2015; Jia et al., 2016). During haze days, the average concentrations of the NMHCs in winter of Beijing were less than those reported in Foshan (Guo et al., 2011b), whereas remarkably greater than those reported in summer of Beijing (Guo et al., 2012). With only exception of isobutane and isopentane, the average concentrations of other eight NMHCs during both the whole measurement period and haze days in this study were evidently greater than those reported in summer of Beijing. The relatively higher of the NMHCs measured in this study during the wintertime than those measured in summer were suspected to be due to the different meteorological conditions and different sources between the two seasons.

3.2 Diurnal variations of NMHCs and the propane/propene ratios

3.2.1 Diurnal variations of NMHCs

Diurnal variations of alkanes, alkenes, aromatics and acetylene under different visibility levels are presented in Fig. 2. The two obvious peaks for the NMHCs in the morning and evening rush hours under clear days (Fig. 2a) indicated that exhaust of vehicles was an important source for atmospheric NMHCs in Beijing. For light haze days (Fig. 2b), only small peak of NMHCs could be observed during morning rush hours, and the concentration of NMHCs steady increased from 18:00 to 01:00 of the next day. For heavy haze days (Fig. 2c), the peak levels of NMHCs during the two rush hours disappeared, and the concentration of NMHCs steady increased from 17:00 to 20:00 and began to level off until 07:00 of the next day. The three distinct diurnal variations of NMHCs under the three typical days were suspected to relate with the diurnal variations of boundary layer. 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. In contrast to the clear day, the height of boundary layer in haze day is relatively low (Quan et al., 2013; Liu et al., 2013), which favors for accumulation of pollutants and resulted in the disappearance of the peak values during the rush hours.

3.2.2 Diurnal variations of propane/propene ratios

Diurnal variations of propane/propene ratios under clear days, light haze days and heavy haze days were shown in Fig. 3. Two evident peaks of the propane/propene ratios respectively appeared in the early morning (about 5:00) before sun rise and at noontime (about 12:00) in clear days, whereas only one peak occurred around 15:00 during the haze days. Distinct peaks of the propane/propene ratios were mainly ascribed to the different reactivity of propane and propene, because of their possible common sources indicated by the significant correlation (R^2=0.8) between propane and propene during the measurement period. The atmospheric reactions of propane and propene include:

Propane + OH $\xrightarrow{k_1}$ Products k_1=1.09 × 10^{-12} $cm^3\cdot molecule^{-1}\cdot s^{-1}$ (Atkinson, 2003) (3)

Propene + OH $\xrightarrow{k_2}$ Products k_2=2.57 × 10^{-11} $cm^3\cdot molecule^{-1}\cdot s^{-1}$ (Daranlot et al., 2010) (4)

Propene + O_3 $\xrightarrow{k_3}$ Products k_3=1.06 × 10^{-17} $cm^3\cdot molecule^{-1}\cdot s^{-1}$ (Wegener et al., 2007) (5)

Propane + NO_3 $\xrightarrow{k_4}$ Products k_4=7.00 × 10^{-17} $cm^3\cdot molecule^{-1}\cdot s^{-1}$ (Atkinson et al., 2001) (6)

Propene + NO_3 $\xrightarrow{k_5}$ Products k_5=9.54 × 10^{-15} $cm^3\cdot molecule^{-1}\cdot s^{-1}$ (Atkinson et al., 2001) (7)

O_3+ NO_2 $\xrightarrow{k_6}$ NO_3 k_6=3.52 × 10^{-17} $cm^3\cdot molecule^{-1}\cdot s^{-1}$ (Atkinson et al., 2004) (8)

The rate constants for the reactions of OH and NO_3 with propene are a factor of 2.4 and 136.3 greater than with propane, respectively. In addition, O_3 can react with propene but not with propane. The evident O_3 concentrations (about 25 ppbv) during nighttime in clear days could react with NO_2 to form NO_3 radicals via reaction (8), whereas the formation of NO_3 radicals was completely blocked during haze days because O_3 concentrations were extremely low (nearly zero). Therefore, the peak of the propane/propene ratios appeared in nighttime during clear days was rationally ascribed to the additional consumption of propene by O_3 and NO_3. Based on the data measured, the OH and NO_3 concentrations were roughly estimated according to following chemical kinetic equations:

$$[\mathrm{Propane}]_0 = [\mathrm{Propane}]_t \times e^{k_1[\mathrm{OH}]\Delta t} \tag{9}$$

$$[\mathrm{Propene}]_0 = [\mathrm{Propene}]_t \times e^{(k_2[\mathrm{OH}]+k_3[\mathrm{O_3}])\Delta t} \tag{10}$$

$$\ln\frac{[\mathrm{Propane}]_t}{[\mathrm{Propene}]_t} = \{(k_2-k_1)[\mathrm{OH}] + k_3[\mathrm{O_3}]\}\Delta t + \ln\frac{[\mathrm{Propane}]_0}{[\mathrm{Propene}]_0} \tag{11}$$

$$[\mathrm{OH}] = \frac{1}{k_2-k_1} \times \left\{\left(\ln\frac{[\mathrm{Propane}]_t}{[\mathrm{Propene}]_t} - \ln\frac{[\mathrm{Propane}]_0}{[\mathrm{Propene}]_0}\right)/\Delta t - k_3[\mathrm{O_3}]\right\} \tag{12}$$

$$[\mathrm{Propane}]_0 = [\mathrm{Propane}]_t \times e^{(k_4[\mathrm{NO_3}])\Delta t} \tag{13}$$

$$[\mathrm{Propene}]_0 = [\mathrm{Propene}]_t \times e^{(k_5[\mathrm{NO_3}]+k_3[\mathrm{O_3}])\Delta t} \tag{14}$$

$$\ln\frac{[\mathrm{Propane}]_t}{[\mathrm{Propene}]_t} = \{(k_5-k_4)[\mathrm{NO_3}] + k_3[\mathrm{O_3}]\}\Delta t + \ln\frac{[\mathrm{Propane}]_0}{[\mathrm{Propene}]_0} \tag{15}$$

$$[\mathrm{NO_3}] = \frac{1}{k_5-k_4} \times \left\{\left(\ln\frac{[\mathrm{Propane}]_t}{[\mathrm{Propene}]_t} - \ln\frac{[\mathrm{Propane}]_0}{[\mathrm{Propene}]_0}\right)/\Delta t - k_3[\mathrm{O_3}]\right\} \tag{16}$$

Here, [OH] is the average OH radical concentration ($molecules\cdot cm^{-3}$), $[NO_3]$ is the average NO_3 radical concentration ($molecules\cdot cm^{-3}$), $[O_3]$ is the average ozone concentration ($molecules\cdot cm^{-3}$), Δt is the exposure time (s) of OH or NO_3, $[\mathrm{Propane}]_0$ and $[\mathrm{Propene}]_0$ are their initial concentrations when the propane/propene ratio began increase, $[\mathrm{Propane}]_t$ and $[\mathrm{Propene}]_t$ are their concentrations at *t* (s) during the period of increasing propane/propene ratios.

The Eq. (9) - (12) were used to estimate the concentrations of OH during daytime and Eq. (13) - (16) were used to estimate the concentrations of NO_3 during nighttime. Good linear correlations ($R^2 \geq 0.9$) between $\ln\frac{[\mathrm{Propane}]_t}{[\mathrm{Propene}]_t}$ and *t* were found during the period from 9:00 to 14:00 for most days and during the period of about 0:00-5:00 for most clear days, indicating that the

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Manuscript under review for journal Atmos. Chem. Phys.
Published: 16 December 2016
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concentration variations of propane and propene basically abided by the above chemical kinetic rules. The OH concentrations were calculated to be in the range 3.47×10^5 - 1.04×10^6 molecules·cm^{-3} in clear days and 6.42×10^5 - 2.35×10^6 molecules·cm^{-3} in haze days, which closed to the global average OH level of 8.70×10^5 molecules·cm^{-3} (Prinn et al., 1992). The relatively high OH concentrations during haze days in winter of Beijing could accelerate oxidation of gas species and further promoted formation of secondary particles. The NO_3 concentrations were calculated to be in the range from 2.82×10^9 molecules·cm^{-3} to 4.86×10^9 molecules·cm^{-3} in clear days, which were in good agreement with the maximal value (4.92×10^9 molecules·cm^{-3}) reported in the Houston city during winter (Asaf et al., 2010).

3.3 Sources of NMHCs

3.3.1 The indicator of typical ratios

The ratios of o-xylene/m,p-xylene and cis-2-butene/trans-2-butene have been widely used as the indicators for gasoline vehicle emissions (Velasco et al., 2007; Li et al., 2015). As shown in Fig. 4 A-B, the slopes (0.36, 0.94) of the linear regressions between the two hydrocarbons pairs of o-xylene/m,p-xylene and trans-2-butene/cis-2-butene were in good agreement with the ratios (0.35, 1.14) from vehicle emissions (Liu et al., 2008; Wang et al., 2010), implying that vehicle emissions were their dominant source in winter of Beijing. The ratios of propane/n-butane and propane/isobutane have been frequently used for distinguishing the contributions of gasoline vehicles and the vehicles fueled with (LPG) (Liu et al., 2008; Lai et al., 2009). The slopes of propane/n-butane (3.12) and propane/isobutane (5.98) both fell between the emission ratios of gasoline vehicles (0.49 and 0.74, respectively) and vehicles using LPG (6.12 and 9.12, respectively), suggesting that emissions from both gasoline and LPG vehicles might be their important sources in Beijing. However, the ratios of propane/n-butane (1.65 - 1.94) and propane/isobutane (1.52 - 1.97) reported in summer of Beijing (Wang et al., 2010) were much less than the values obtained in this study during wintertime in Beijing. Considering the relatively stable proportion of LPG vehicles to gasoline vehicles during the whole year, additional sources were suspected to make evident contribution to the relatively high ratios of propane/n-butane and propane/isobutane in winter of Beijing. It should be mentioned that the ratios of propane/n-butane and propane/isobutane in winter of Beijing closed to those from domestic coal combustion (4.34 and 8.68, respectively) (Liu et al., 2016b), and the ratio (1.92) of isobutane/n-butane was coincident with that from domestic coal combustion (2.0). Therefore, domestic coal combustion around Beijing in winter might make remarkable contribution to the C3-C4 alkanes. The contribution of domestic coal combustion to atmospheric NMHCs in winter of Beijing could also been confirmed by other ratios of hydrocarbon pairs. As shown in Fig. 5, the ratios of isopenatne/n-pentane, propane/isopentane, benzene/toluene and benzene/ethylbenzene were all fell between the emission ratios of vehicles and coal combustion.

Besides the above hydrocarbon pairs, the slopes of another hydrocarbon pairs were also analyzed and listed in Table 4. With exception for the hydrocarbon pairs of propane/toluene, propane/isopentane, propane/n-butane and propane/isobutane, the slopes of other pairs were within the values reported in different cities (Liu et al., 2008; Louie et al., 2013). The slopes for

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the hydrocarbon pairs of propane/toluene, propane/isopentane, propane/n-butane and propane/isobutane were remarkably greater than those reported in various cities including Beijing, which were suspected to be from the contribution of domestic coal combustion in winter around Beijing (see above discussion). Barletta et al. (2005) found that the slopes of benzene/acetylene, ethylene/acetylene and benzene/ethylbenzene in 15 Chinese cities with B/T >1 were remarkably greater than those in 10 Chinese cities (traffic related cities) with B/T of about 0.6, and attributed the relatively high slopes in the 15 Chinese cities to the emissions from biofuel and charcoal combustion. The slopes of benzene/acetylene, ethylene/acetylene and benzene/ethylbenzene obtained by this study were coincident with those in the 15 cities reported by Barletta et al. (2005), indicating that domestic coal combustion in winter around Beijing might make contribution to the species. It is interesting to be noted that the slopes or the ratios of o-xylene/m,p-xylene and trans-2-butene/cis-2-butene which have high OH radical reactivity in various cities were in good agreement with those of vehicle emissions, whereas the slopes or ratios of the hydrocarbon pairs with low OH reactivity showed obvious difference among the cities, implying that the atmospheric NMHCs with high OH reactivity are dominated by local emissions and the atmospheric NMHCs with low OH reactivity are strongly influenced by regional transportation.

3.3.2 The source profiles and apportionments of NMHCs

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. Five factors (Fig. 6) were resolved from running the PMF model for the air samples in winter of Beijing, identified as vehicular emission and gasoline evaporation, coal combustion, solvent usage, acetylene-related emission and consumer and household products.

Source 1 was characterized by high percentages of iso/n-pentanes, aromatics and other C2-C7 alkanes. NMHCs from vehicular emission have been found to be dominated by iso/n-pentanes and aromatics with the benzene/toluene mass ratio of about 0.6 (Barletta et al., 2005), which was in consistent with PMF results for source 1. Additionally, C3-C5 alkanes are also emitted from gasoline evaporations, e.g., isopentane is a typical tracer for gasoline evaporation (Liu et al., 2008). Therefore, source 1 is rationally ascribed to vehicular emission and gasoline evaporation.

Source 2 was associated with high percentages of acetylene, C2-C3 alkenes, C2-C5 alkanes and benzene. It is known that acetylene is a typical species from combustion process (Barletta et al., 2005; Wu et al., 2016), and high concentrations of C2-C3 alkenes, C2-C5 alkanes and benzene have been found from resident coal combustion (dos Santos et al., 2004; Liu et al., 2008; Liu et al., 2016b). In addition, the ratios of benzene/toluene and propane/isopentane obtained from coal combustion were 1.54-2.22 (Liu et al., 2008), 8.68 (Liu et al., 2016b), respectively, which were close to the ratios in the second source profile. Source 2 has, therefore, been assigned to coal combustion.

Source 3 was associated with over 60% of the total measured acetylene, and this source is designated as acetylene-related emissions. Source 4 was dominated by high content of toluene, ethylbenzene and xylenes. It is known that these species can

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be emitted from vehicular exhaust or associated with the solvent emissions of paints, inks, sealant, varnish and thinner for architecture and decoration (Borbon et al., 2002; Guo et al., 2011a). However, aromatics emissions from vehicular exhaust or coal combustion are usually accompanied by high emissions of various species with carbon numbers less than six, suggesting that combustion or vehicular emissions were not the main contributors to source 4. Therefore, this source can be identified as solvent usage.

Source 5 was characterized by high levels of n-hexane. n-Hexane is a common constituent of glues used for shoes, leather products and roofing. Additionally, it is used in solvents to extract oils for cooking and as a cleansing agent for shoe, furniture and textile (Kwon et al., 2007; Guo et al., 2011a). Therefore, this source is identified as consumer and household products.

Fig. 7 shows the individual contributions of the five major NMHCs sources to the NMHCs concentrations measured in clear days, light haze days and heavy haze days. It is clearly that the share rates of the five major sources to atmospheric NMHCs under the three typical days varied significantly. Vehicular emission and gasoline evaporation was the largest contributor in clear days, followed by solvent usage, coal combustion, acetylene-related emission and consumer and household products, whereas coal combustion made the largest contribution in haze days, followed by vehicular emission and gasoline evaporation, solvent usage, acetylene-related emission and consumer and household products. Considering the daily emissions of NMHCs from the five major sources were relatively stable during the short period of the winter, the distinct variation of the share rates from the five major sources under the three typical days was suspected to be related to the reactivity of the dominant species from each source because of the evidently different OH concentrations between clear days and haze days (see Sect. 3.2.2). Compared with the species from the other four major sources, the dominant species of toluene, ethylbenzene and xylenes emitted from the solvent usage are highly reactive, and hence, remarkable decrease of the share rate from this source was observed from clear days to haze days. The dominant species of alkanes from coal combustion were relatively stable in comparison with those (alkenes and aromatics) from vehicular emission and gasoline evaporation, resulting in the fast increase of the share rate from coal combustion from clear days to haze days. Although the central heating stoves that used coal as energy in Beijing have been replaced by the relatively clean energies, coal combustion was still an important source for ambient NMHCs during wintertime in Beijing. It should be mentioned that domestic coal combustion is prevailing for heating and cooking by farmers in rural areas around Beijing city, e.g., the domestic coal consumption account for about 11% of the total in the region of Beijing-Tianjin-Hebei (http://www.qstheory.cn/st/dfst/201306/t20130607_238302.htm). Additionally, the emission factors of NMHCs from domestic coal combustion have been found to be a factor of 20 greater than those from coal power plants (Liu et al., 2016b). Therefore, the high share rate of coal combustion in Beijing city was mainly attributed to the regional transportation.

4. Conclusions

The variation trends of NMHCs concentrations in Beijing during the wintertime were basically identical and exhibited

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significantly fluctuation, which were attributed to the variation of the meteorological conditions. The top ten NMHCs species during the wintertime in Beijing were mainly C2-C5 alkanes, C2-C3 alkenes, acetylene, benzene and toluene. The remarkable difference of the diurnal variations of alkanes, alkenes, aromatics and acetylene between clear days and haze days indicated that the relative contribution of the vehicular emission to atmospheric NMHCs depended on the pollution status. The distinct diurnal variations of the propane/propene ratio indicated that relatively fast consumption of propene by OH radical and O_3 in the daytime and by NO_3 and O_3 in the nighttime. The relatively high concentrations of OH radicals in haze days could accelerate oxidation of gas species and further promoted formation of secondary particles. Both the correlation coefficients of typical hydrocarbons pairs and PMF analysis revealed that coal combustion (probably domestic coal combustion) was an important source for atmospheric NMHCs during wintertime in Beijing, especially in haze days. Therefore, the application of effective control measures for mitigating the serious emissions from prevailingly domestic coal combustion around Beijing in winter are urgent to improve the air quality in Beijing city.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 91544211, 21477142, 41575121, 41203070); the Special Fund for Environmental Research in the Public Interest (No. 201509002), and the Strategic Priority Research Program projects (B) of the Chinese Academy of Sciences (No. XDB05010100).

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Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-783, 2016
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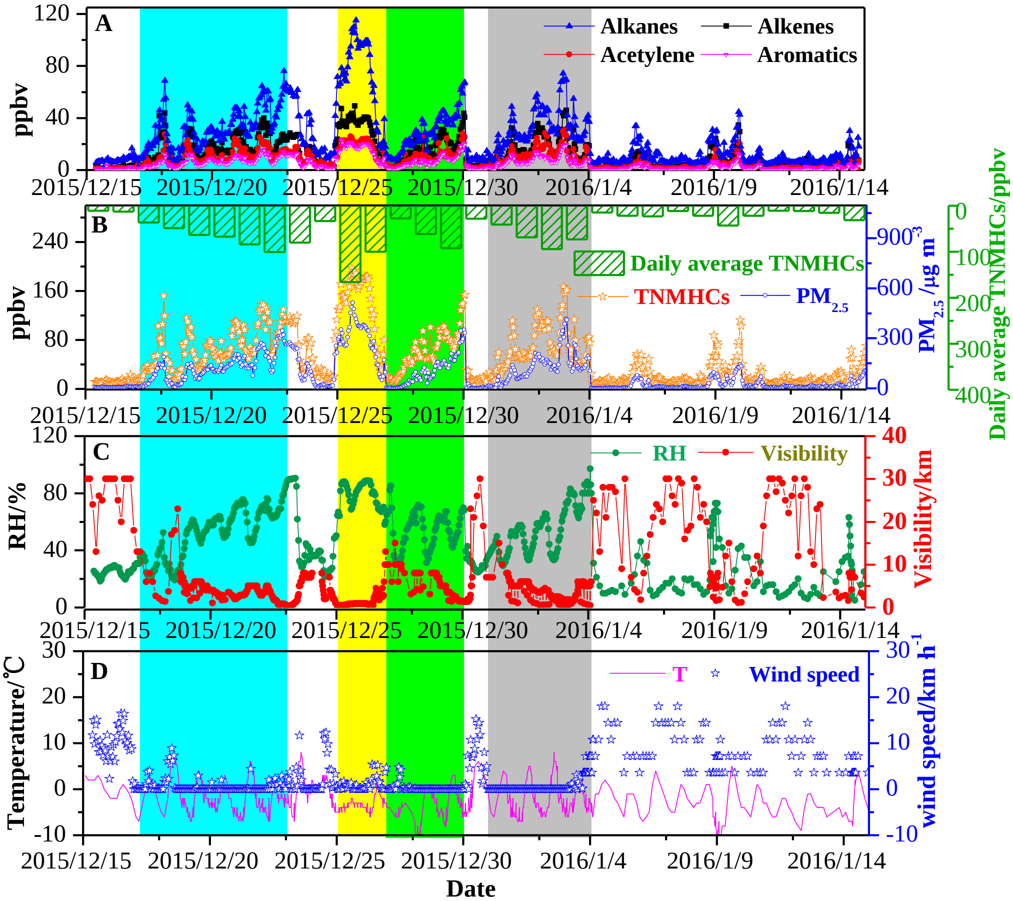

Fig. 1 Time series of measured NMHCs, $PM_{2.5}$, visibility, relative humidity, temperature and wind speed. The shaded areas indicate pollution episodes: 17-22 December (Cyan), 25-26 December (Yellow), 27-29 December (Green) and 31 December-3 January (LT Gray).

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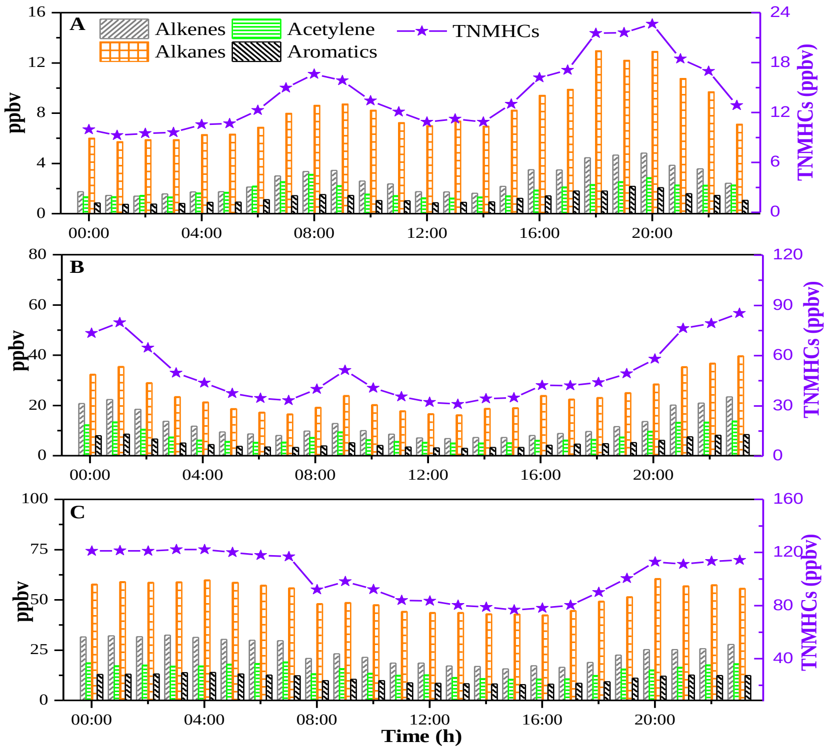

Fig. 2 Diurnal variations of alkanes, acetylene, alkenes, aromatics and TNMHC during (A) clear days, (B) light haze days and (C) heavy haze days

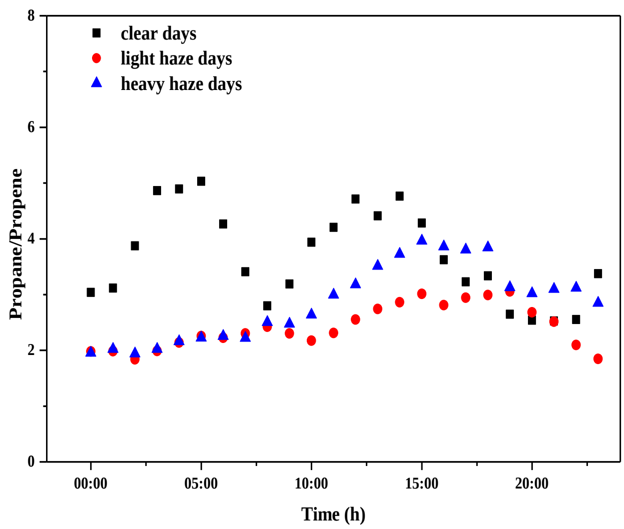

Fig. 3 Diurnal variations of propane/propene ratios during clear days, light haze days and heavy haze days

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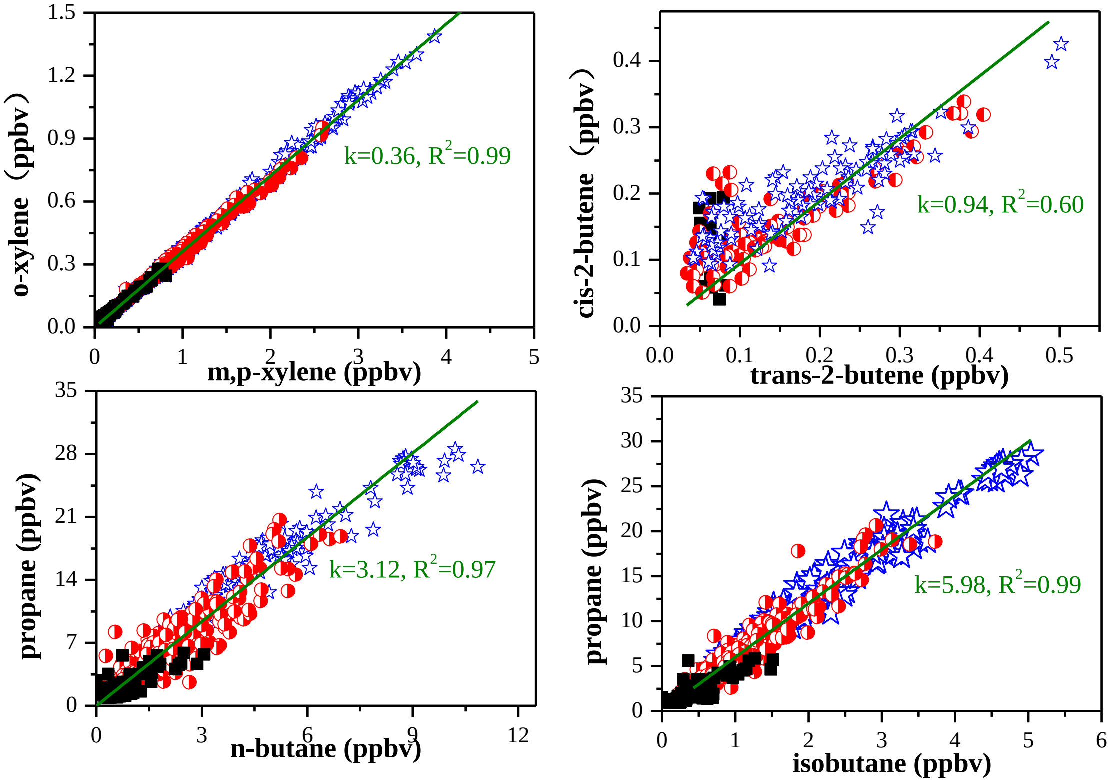

Fig. 4 Ratios and linear correlation coefficients (R^2) between (A) o-xylene and m,p-xylene, (B) cis-2-butene and trans-2-butene, (C) propane and n-butane, and (D) propane and isobutane during clear days (in black), light haze days (in red) and heavy haze days (in blue)

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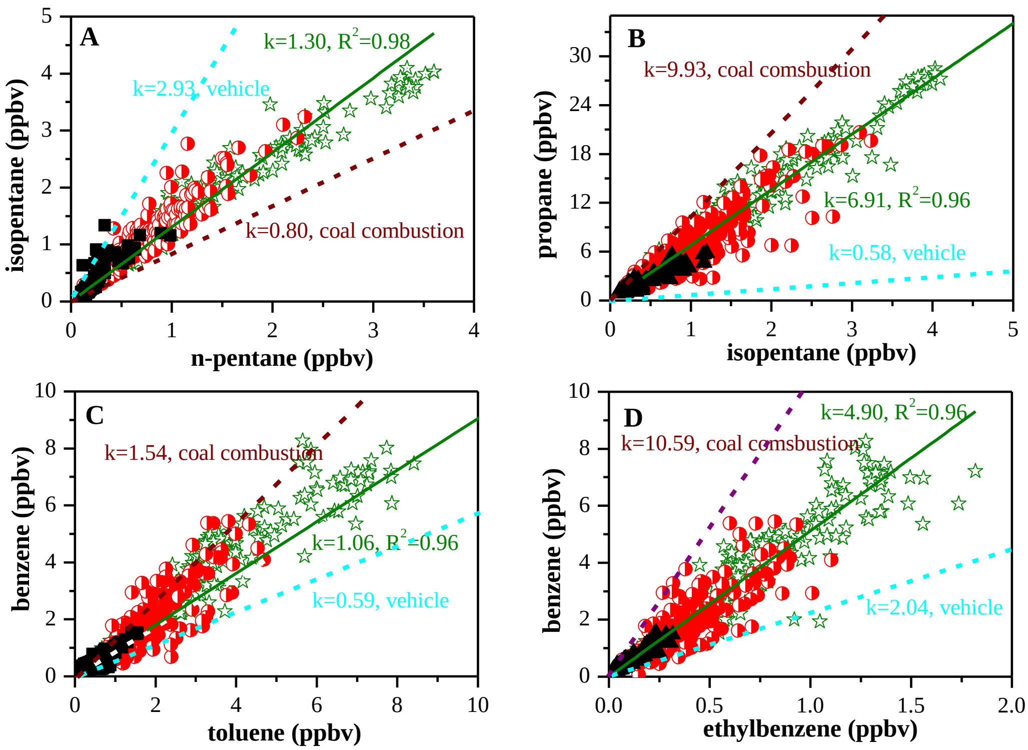

Fig. 5 Ratios and linear correlation coefficients (R^2) between (A) isopentane and n-pentane, (B) propane and isopentane, (C) benzene and toluene, and (D) benzene and ethylbezene during clear days (in black), light haze days (in red) and heavy haze days (in olive)

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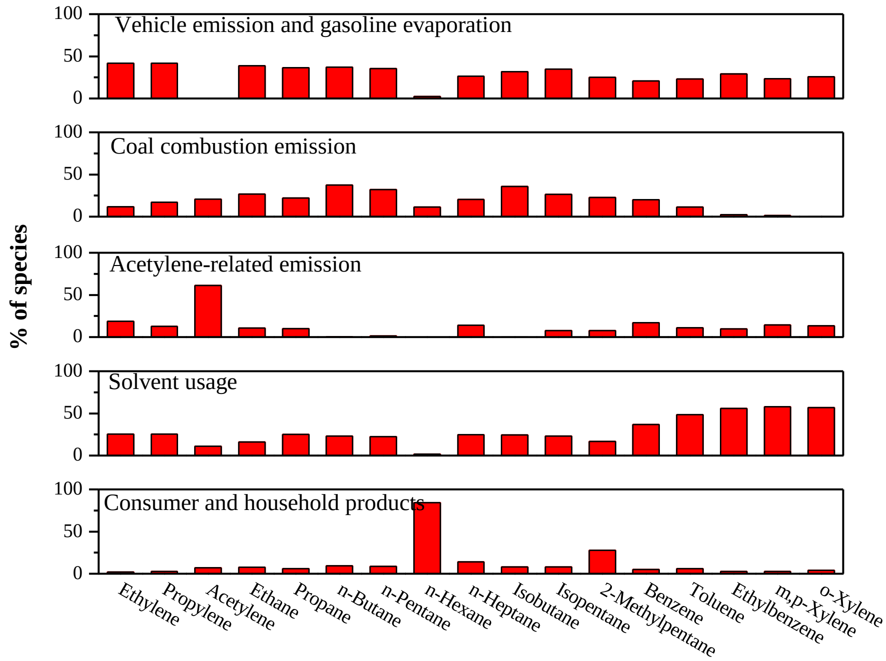

Fig. 6 Source profiles (percentage of factor total) resolved from PMF in Beijing

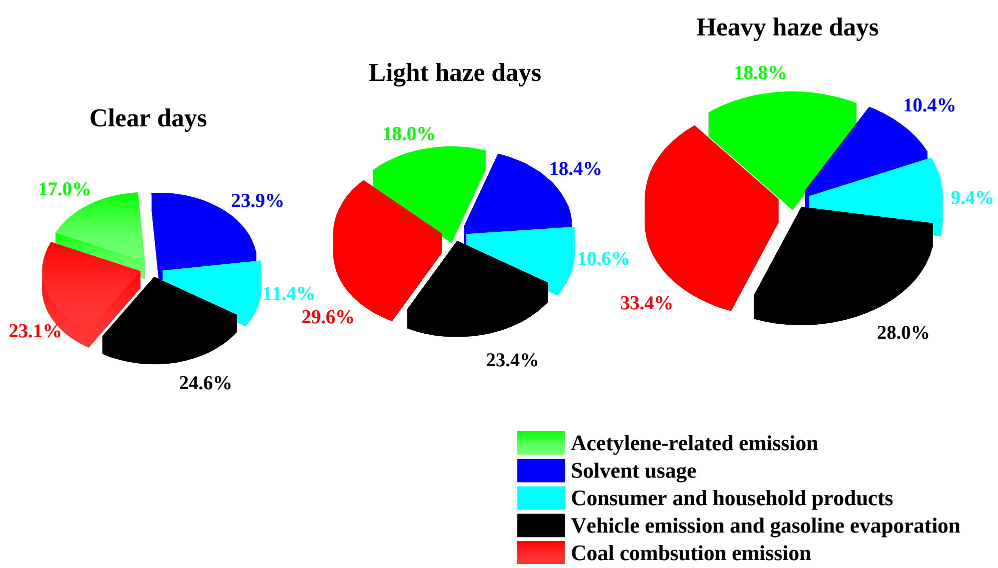

Fig. 7 Source apportionment of NMHCs in Beijing during clear days, light haze days and heavy haze days

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

Pollution statues	Visibility /Km	T /℃	RH /%	Wind speed /Km·h^{-1}	Date
Heavy haze days	1.41±1.76	-1.15±3.03	67.69±25.05	5.23±2.01	2015/12/19-23,201512/25-26, 2015/12/29, 2016/01/1-3
Light haze days	6.81±5.37	-2.17±4.17	38.54±16.5	5.81±3.67	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	-1.90±3.15	18.78±12.97	10.38±4.79	2015/12/15-16, 2015/12/30, 2016/01/4-8, 2016/01/10-13

Table 2. The mean concentrations and standard deviations of TNMHCs, alkanes, alkenes, aromatics and acetylene during clear days, light haze days and heavy haze days (ppbv)

Categories	Clear days	Light haze days	Heavy haze days
alkenes	3.67±1.78	10.01±3.21	21.84±6.12
acetylene	2.30±1.04	6.44±2.07	13.69±3.18
alkanes	9.52±2.61	20.17±4.90	44.83±16.33
aromatics	1.58±0.67	3.84±1.08	9.63±3.28
TNMHCs	17.05±5.87	40.46±10.92	89.98±28.40

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-783, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 16 December 2016
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Table 3. Comparisons of the top ten NMHCs in Beijing with other cities in China (ppbv)

	This study			43Cities	NJ	GZ	SH	FS[a]	LZ	BJ	BJ[a]
	The range	AVG	Haze								
ethane	1.89-44.34	9.68	13.46	3.7-17.0	6.90	3.66	-	18.52	-	4.37	2.26
ethylene	0.12-31.65	7.91	11.37	2.1-34.8	5.70	2.99	-	20.58	-	2.33	6.63
acetylene	0.40-30.86	7.50	10.60	2.9-58.3	3.12	-	-	23.38	-	2.17	5.47
propane	0.86-28.51	6.57	9.43	1.5-20.8	3.30	4.34	5.16	12.98	3.40	2.44	5.45
propene	0.14-24.10	2.55	3.54	0.2-8.2	2.50	1.32	1.70	6.84	2.43	-	3.32
n-butane	0.09-14.27	2.10	2.86	0.6-18.8	1.70	3.07	1.69	3.76	1.75	1.43	3.49
benzene	0.07-8.27	1.81	2.59	0.7-10.4	3.10	0.62	2.00	4.05	1.94	0.82	2.54
toluene	0.12-8.41	1.67	2.38	0.4-11.2	2.10	4.59	4.86	10.98	1.01	1.33	2.97
isobutane	0.10-5.03	1.13	1.55	0.4-4.6	1.51	2.67	1.20	3.02	2.43	1.03	2.50
isopentane	0.08-6.03	1.00	1.36	0.3-18.8	1.12	1.72	1.63	13.07	2.43	0.99	4.06

43 Cities, China, 2001/01-2001/02 (Barletta et al., 2005); NJ, Nanjing, 2011/03-2012/02 (An et al., 2014); GZ, Guangzhou, 2011/06-2012/05 (Zou et al., 2015); SH, Shanghai, 2006/12-2007/02 (Song et al., 2012); FS, Foshan, 2008/12 (Guo et al., 2011b); LZ, Lanzhou, 2013/06-2013/08 (Jia et al., 2016); BJ, Beijing, 2014/05 (Li et al., 2015); BJ, Beijing, 2006/08 (Guo et al., 2012).

[a] haze days.

- data were not available in the relative reference.

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Table 4 Emission ratios of NMHCs pairs in Beijing and other regions and comparisons with vehicle emissions

	This study	43 Chinese cities		Vehicle emissions	Beijing		Pearl River Delta		Houston	Mexico City	Northeast US	Tokyo
	Slope (R^2)	Slope [a]		ratio	Slope [b]	Ratio [b]	Slope [c]	Ratio [d]	Ratio [e]	ratio	ratio	ratio
benzene/toluene	1.06 (0.96)	> 1.18	~ 0.70			0.43/1.52 [f], 0.38/0.88		0.36				
benzene/acetylene	0.22 (0.81)	0.26	0.13	0.62 [b]	0.25/ 0.27	0.27/0.34	0.48	0.48		0.3 [g]	0.17/ 0.30 [g]	0.29 [g]
ethylene/acetylene	1.08 (0.91)	1.01	0.76			0.66/1.00		0.80				
benzene/ethylbenzene	4.90 (0.91)	4.91	2.04			0.93/2.4		1.90				
toluene/ethylene	0.20 (0.88)		0.31	0.76 [b]	0.63/ 0.68	0.61/1.26	0.46	1.67		0.67 [g]	0.48/ 0.83 [g]	1.11 [g]
benzene/ethylene	0.23 (0.96)		0.17			0.29/0.47		0.61				
toluene/acetylene	0.22 (0.81)		0.24			0.43/0.83		0.26				
ethylbenzene/toluene	0.21 (0.97)			0.24 [h]		0.31/0.37	0.20	0.19	0.14	0.12 [i]		
o-xylene/m,p-xylene	0.36 (0.99)			0.35 [h]		0.28/0.60	0.41	0.58	0.37	0.4 [i]		
propane/toluene	3.91 (0.92)			0.08/0.98 [h]		1.13/3.18	0.32	0.69				
propane/acetylene	0.93 (0.82)			0.06/1.80 [h]		0.65/1.51	0.42	0.92			2.19 [j]	2.90 [k]
propane/isobutane	5.98 (0.95)			0.74/3.85 [h]		1.65/1.94	1.91	2.00				
propane/n-butane	3.12 (0.94)			0.49/1.91 [h]		1.52/1.97	1.08	1.63				
propane/isopentane	6.91 (0.85)			0.09/0.58 [h]		1.29/1.61	1.49	2.25				
trans-2-butene/cis-2-butene	1.06 (0.60)			1.14 [b]	1.13/ 1.23	1/1.6	1.11		0.88	1.28 [i]		

[a] Results from 43 Chinese cities in 2001 (Barletta et al., 2005); [b] Results from Beijing in summer of 2008 (Wang et al., 2010); [c] Results from Guangzhou in 2006 and 2008 (Yuan et al., 2012); [d] Results from Pearl river delta in 2008-2009 (Louie et al., 2013); [e] Results from Houston in 2000 (Jobson et al., 2004); [f] Results from Beijing in 2008-2010 (Liu et al., 2009;Zhang et al., 2012a); [g] Emission ratios in Beijing, northeast US, Mexico City, and Tokyo (Parrish et al., 2009); [h] From a tunnel conducted in Guangzhou (Liu et al., 2008); [i] Geometric mean of the ratios in Mexico City in 2003 (Velasco et al., 2007); [j] Results from the Northeast United States in 2004 (Warneke et al., 2007); [k] Ratios in the winter of 2004 in Tokyo (Shirai et al., 2007).