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Trends of non-methane hydrocarbons (NMHC) emissions in Beijing during 2002–2013

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Abstract

Non-methane hydrocarbons (NMHCs) play a critical role in the photochemical production of ozone (O_3) and organic aerosols. Obtaining an accurate understanding on NMHC emission trends is essential for predicting air quality changes and evaluating the effectiveness of current control measures. In this study, we evaluated temporal trends in NMHC emissions in Beijing based on ambient measurements during the summer at an urban site in Beijing from 2002 to 2013. In contrast to the results of the most recent inventory (Multi-resolution Emission Inventory for China, MEIC), which reported that total NMHC emissions increased at a rate of $\sim 4\,\%\,yr^{-1}$, mixing ratios of NMHCs measured at this urban site displayed an obvious decrease ($\sim 30\,\%$) during the last decade. A Positive Matrix Factorization (PMF) model was applied to the NMHC measurements for source apportionment, and the results showed a decrease in the concentrations contributed by transportation-related sources to total NMHC emissions by 66 % during 2004–2012, which was comparable to the relative decline of 65 % reported by the MEIC inventory. This finding indicates that the implementation of stricter emissions standards and control measures has been effective for reducing transportation-related NMHC emissions. In addition, the PMF results suggested that there were no significant temporal changes in NMHC concentrations from paint and solvent use during 2004–2012, in contrast with the rapid rate of increase ($27.5\,\%\,yr^{-1}$) reported by the MEIC inventory. To re-evaluate the NMHC emissions trends for paint and solvent use, annual variations in NMHC / NO_x ratios were compared between ambient measurements and the MEIC inventory. In contrast to the significant rise in NMHC / NO_x ratios from the inventory, the measured ratios declined by 14 % during 2005–2012. However, the inferred NMHC / NO_x ratios based on PMF results exhibited a comparable decline of 11 % to measurements. These results indicate that the increase rate for NMHC emissions from paint and solvent use in Beijing might be overestimated in the current inventory; therefore, additional research is necessary to verify the NMHC emission trends for this source.

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1 Introduction

The temporal trends in tropospheric ozone (O_3) levels has been of great concern during recent years. Over the past three decades, significant declines in O_3 levels have been observed in urban areas of the United States (Lefohn et al., 2010; Warneke et al., 2012). However, recent studies have suggested that O_3 levels in China have been increasing (Wang et al., 2009; Zhang et al., 2014). Non-methane hydrocarbons (NMHCs) and nitrogen oxides (NO_x) are precursors of photochemically produced O_3; therefore, obtaining accurate knowledge on temporal trends in NMHC emissions is helpful for understanding O_3 trends in urban regions (von Schneidemesser et al., 2014; Zhang et al., 2014).

One approach to investigating trends in NMHC emissions is based on emissions inventories, which are established by summing the products of activity data (A) and emission factors (EFs) for various sources (Bo et al., 2008; Lei et al., 2011b). Owing to the complexity of NMHC sources and the lack of a local emission characteristic database, large inherent uncertainties are expected for NMHC emission inventories in China. Several studies that evaluated NMHC emissions inventories in Beijing based on ambient measurement data identified large uncertainties in the estimates, speciation, spatial distribution, and sources of NMHC emissions (Tang et al., 2011; Liu et al., 2012; Wang et al., 2014). However, temporal trends for NMHC emissions in Beijing have not been evaluated using ambient measurements so far.

During the past decade, there has been a rapid increase in energy consumption in Beijing. Meanwhile, various control measures have been implemented to reduce anthropogenic emissions of NMHCs, such as stricter vehicle emissions standards, the elimination of heavy-polluting vehicles, improvements in fuel quality, the installation of gasoline vapor recovery systems at gas stations, and restrictions on NMHC fractions in paint and solvents (Wei et al., 2011; Wang and Hao, 2012). The implementation of these control measures is helpful for reducing the emission factors of NMHCs for stationary sources, vehicular exhaust, gasoline vaporization, and paint and solvents

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utilization. It is being challenged to obtain accurate understanding on NMHC emission trends in Beijing due to the interaction between decreasing NMHC emission factors and increasing energy consumption.

Because large uncertainties possibly exist in current emissions inventories, trend analysis on long-term measurements of ambient NMHCs is another important method for investigating emissions trends and evaluating the accuracy of emissions inventories. Parrish (2006) used NMHC measurement data to critically evaluate emissions inventories for US on-road vehicles, and found that the temporal trends in both emissions estimates and speciation for NMHCs were not consistent with ambient measurements. In China, only a few studies have reported temporal changes in ambient NMHC levels. Wang et al. (2012) measured NMHC levels during the summer at an urban site in Beijing from 2003 to 2007, and found that NMHC levels increased from 2000 to 2003 and decreased from 2003 to 2007. Zhang et al. (2014) found that the mixing ratios of most anthropogenic NMHC species in August significantly decreased from 2005 to 2011. While these studies provide useful information about NMHC trends in Beijing, their results have not been used to evaluate the accuracy of NMHC emissions trends in current inventories and to examine the effectiveness of NMHC control measures.

In the present study, we evaluated the accuracy of NMHC emissions trends in Beijing based on ambient NMHC measurements collected during the summer at an urban site in Beijing from 2002 to 2013. We first introduced the temporal changes of anthropogenic NMHC emissions in Beijing reported by the multi-resolution emission inventory for China (MEIC). Temporal trends in ambient levels of NMHCs during 2002–2013 were then analyzed using simple linear regression and compared with NMHC emission trends reported by the MEIC inventory. A Positive Matrix Factorization (PMF) model was applied to NMHC measurement data for source apportionment and to investigate temporal changes in NMHC concentrations from major sources. Finally, we used the ratios of NMHC to NO_x to reanalyze the temporal changes in NMHC emissions from paint and solvent use.

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2 Materials and methods

2.1 Anthropogenic NMHC emissions inventory

Data on annual NMHC emissions in Beijing from 2002 to 2012 were obtained from the Multi-resolution Emission Inventory for China (MEIC, http://www.meicmodel.org/). This inventory was developed by a group at Tsinghua University in China that used a dynamic, technology-based methodology to estimate anthropogenic emissions in China from 1990 to 2012 (Zhang et al., 2009; Lei et al., 2011a; He, 2012; Li et al., 2014). Anthropogenic NMHC emissions were estimated using detailed activity data and local emission factors in China and were categorized into five sources: transportation, industry, solvent use, residential, and power (Figs. 1 and 2). Details about the methodology used to establish the NMHC emission inventory can be found in Zhang et al. (2009) and Li et al. (2014).

2.2 NMHC measurements

Long-term NMHC measurements were collected in the summer at an urban site (the PKU site) in Beijing from 2002 to 2013. Details regarding the systems used to analyze NMHCs, measurement periods, and related references are provided in Table 1. It is important to note that in August 2004, atmospheric samples were collected in canisters and were analyzed offline for NMHCs using a GC-MS system in the lab to detect target compounds (Liu et al., 2005), whereas atmospheric NMHCs were analyzed online during all the other years. In 2002, an online GC-FID system developed by Peking University was used to measure the mixing ratios of C6–C8 aromatics and C5–C8 alkanes, with a time resolution of 30 min. Ambient C4–C12 NMHCs were first initially trapped on carbon molecular sieves (i.e. the absorbent tube); then they were vaporized by thermal desorption and transferred into a deactivated quartz capillary for secondary enrichment (i.e. the enrichment trap). The enrichment trap then was rapidly heated to 200 °C, and the target compounds were carried into the GC-FID system for separation

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and detection. In 2005, mixing ratios of NMHCs were measured using an online GC-MS/FID system developed by the Earth System Research Lab (ESRL; NOAA, US). A detailed description of this system can be found in Goldan et al. (2004). In 2006, ambient levels of NMHCs were measured using an online GC-FID system built by the Research Center for Environmental Changes (RCEC; Taiwan). A detailed description of this system and QA/QC procedures can be found in Wang et al. (2004). In 2007 and 2009, NMHCs were measured using a commercial GC-FID/PID system (Syntech Spectra GC955 series 600/800 analyzer). Detailed descriptions of this system can be found in Xie et al. (2008) and Zhang et al. (2014). From 2010 to 2013, NMHCs were measured using a cryogen-free online GC-MSD/FID system developed by Peking University (Yuan et al., 2012; Wang et al., 2014).

2.3 Positive Matrix Factorization (PMF) model

A PMF model, developed by the US Environmental Protection Agency (US EPA; V3.0, http://www.epa.gov/heasd/research/pmf.html), was applied to NMHC measurement data for source apportionment. PMF is a multivariate factor analytical tool that decomposes speciated measurement data matrix **x** of i by j dimensions into two matrices – factor profiles (**f**) and factor contributions (**g**) (US EPA, 2008):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{ik} + e_{ij} \quad (1)$$

where p is the number of factors and e_{ij} is the residual for each sample/species. The PMF solution minimizes the objective function Q based on the uncertainties u_{ij}:

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

where m and n are the numbers of samples and chemical species, respectively.

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The 9 year measurement data from 2004 to 2012 for 16 NMHC species, including C2–C6 straight alkanes, C6–C8 aromatics, acetylene, and C2–C4 alkenes (Table S1), were combined into one single dataset of 6062 samples to derive a consistent set of source profiles. According to the physical plausibility of PMF-resolved factors and the changes of $Q/Q_{\text{theoretical}}$ values, and the fit between predicted concentrations and measured values, we determined that the number of factors for the PMF solution was four. To investigate the free rotation of the PMF factors, the PMF model was run 33 times with F_{PEAK} ranging from −5 and 5, and the results with no rotation ($F_{\text{PEAK}} = 0$) were selected.

3 Results and discussion

3.1 Anthropogenic NMHC emissions in Beijing from the MEIC inventory

The anthropogenic NMHC emissions in Beijing from 2002 to 2012 that were estimated by the MEIC inventory are depicted in Fig. 1. Total anthropogenic NMHC emissions increased at a rate of $\sim 4\,\%\,\text{yr}^{-1}$ during the past decade. Similar to the results from previous inventories (H. Wang et al., 2010; Wu et al., 2011; Lang et al., 2012), transportation-related NMHC emissions decreased at a rate of $\sim 6.5\,\%\,\text{yr}^{-1}$, whereas NMHC emissions from solvent use, industry, and power all showed significant increasing trends, with respective rates of $27.5\,\%\,\text{yr}^{-1}$, $4.2\,\%\,\text{yr}^{-1}$, and $9.2\,\%\,\text{yr}^{-1}$.

As shown in Fig. 2, obvious changes in NMHC sources were found during the last decade in Beijing (Fig. 2). From 2002 to 2012, the relative contributions of solvent use to NMHC emissions increased from 19 % to 52 %, whereas the contributions from transportation-related sources decreased from 37 % to 9 %. Relative contributions from residential sources exhibited a slight decrease (from 14 % to 10 %), and there were no significant changes in industry contributions to NMHC emissions during this time (∼ 29 %).

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3.2 Temporal changes in ambient NMHC levels

In contrast to the MEIC inventory, which reported an increasing trend in total NMHC emissions, mixing ratios of NMHCs (i.e., the sum of ambient mixing ratios for 16 NMHC species; Table S1) measured in the summer at the PKU site and another urban site (Wang et al., 2012) both exhibited an obvious decline from the year 2003. This discrepancy suggests that there might be some uncertainty in NMHC emission trends for one or more sources from the MEIC inventory.

Vehicle exhaust, gasoline vaporization, paint and solvent utilization, natural gas (NG), and liquefied petroleum gasoline (LPG) leakage are important sources of NMHC emissions in Beijing during the summer (Song et al., 2007; Shao et al., 2011; Wang et al., 2014). To preliminary investigate temporal changes in NMHC emissions from these sources, we used a simple linear regression fit to analyze the trends in some individual NMHC species that were measured in this study. The Pearson correlation coefficient (r) and p value associated with the standard F-statistic test were used to determine the significance of these trends: trends were considered significant at the 0.05 ($p < 0.05$; *) or 0.01 level ($p < 0.01$; **). The slopes of these fits, which corresponded to the increasing (positive) or decreasing (negative) rates (ppbv yr^{-1}) of a given NMHC species, were divided by the fitted mixing ratio for the first year to calculate relative rates of their temporal changes (% yr^{-1}). It is important to note that NMHC mixing ratios in August 2008 were markedly lower than those in other years (Figs. 4–7), owing to the influence of short-term NMHC control measures implemented for the Beijing Olympic Games; therefore, the measurement data for 2008 were excluded from the trend analysis.

3.2.1 Vehicle exhaust: acetylene and alkenes

During the summer in Beijing, the main source of acetylene and alkenes emissions is vehicle exhaust (Song et al., 2007; Liu et al., 2009; B. Wang et al., 2010; Shao et al., 2011). Ambient mixing ratios of acetylene, ethene, propene, and 1-butene all exhibited

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significant declines during 2004–2013, with relative rates of decline between 6.2 % and 8.9 % yr^{-1} (Fig. 4). This finding is in agreement with the decline in transportation NMHC emissions reported by the MEIC inventory (Fig. 1b).

The significant decline in transportation-related NMHC emissions in Beijing can be mostly attributed to the implementation of more stringent standards for vehicle emissions (Tables S2 and S3 and the dark green staircase-pattern lines in Fig. 4). Regulations for new vehicle tail pipe emissions were first implemented in Beijing in 1990 with the pre-Euro I standard, followed by Euro I (1999), Euro II (2003), Euro III (2005), Euro IV (2008), and Euro V (2013). For the Euro IV and V standards, the limits for total hydrocarbon (THC) emissions from light-duty gasoline vehicles (LDGV) was reduced to 0.1 g km^{-1}, which was approximately one order of magnitude lower than the Euro I standard (Table S3). This resulted in the decline of THC emission factors from LDGV exhaust (Wu et al., 2011; Huo et al., 2012), which decreased from 0.7 (Euro I) to 0.02 (Euro IV) kg km^{-1} (Fig. S1). Although the population of vehicles in Beijing tripled from 2002 to 2012, NMHC emissions from transportation decreased during this time due to stricter emissions standards.

3.2.2 Gasoline vaporization: *i*-butane and *i*-pentane

Besides vehicle exhaust, gasoline vaporization is another important source of C4–C5 alkanes emissions, especially for *i*-butane and *i*-pentane (Harley et al., 1992; Liu et al., 2008). Different from the decline that was observed for acetylene and alkenes levels, the mixing ratios of *i*-butane and *i*-pentane increased from 2004 to 2007, and then decreased from 2007 to 2013 by 33 % and 65 %, respectively (Fig. 5).

Gasoline vapor recovery systems were installed at 1265 gas stations, and in 1026 trucks and 38 tankers during September 2007–May 2008, as part of the control measures implemented to reduce NMHC emissions from gasoline vaporization and to improve air quality in Beijing. Steep declines in C4–C5 alkanes levels were observed between 2007 and 2009 (17 % for butanes, 36 % for pentanes), which corresponded to the period of time in which gasoline recovery systems were being installed in Bei-

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jing, suggesting that these systems were effective for reducing NMHC emissions from gasoline vaporization.

3.2.3 Paint and solvent utilization: benzene, toluene, ethylbenzene, and xylenes

Paint and solvent utilization are also important sources of NMHC emissions in Beijing, especially for aromatics (Wei et al., 2008; Su et al., 2011; Wang et al., 2014). As shown in Fig. 6, the mixing ratios of benzene, toluene, ethylbenzene, and xylenes (BTEX) measured at the PKU site significantly decreased from 2002 to 2013. However, the relative rates of decline for BTEX species levels (2.8–5.6 % yr^{-1}) were lower than those for tracers of vehicle exhaust (i.e., acetylene and alkenes). This finding indicates that either the NMHC emissions from paint and solvent utilization did not decrease during this study period or their relative decline rates were lower than that for NMHC emitted by vehicle exhaust.

The two main uses for paint and solvent in Beijing are to paint buildings and automobiles (Su et al., 2011). During 2002–2012, the production of architectural coatings (e.g. siding materials and house/building paint) in Beijing increased from 43 000 to 110 000 t (Beijing Statistical Yearbook 2002–2012), while the production of automobiles increased from 150 000 to 1 670 000 vehicles (Chinese Automobile Industry Yearbook 2002–2012). Meanwhile, more stringent emission standards for paint and solvent utilization have been implemented and updated in recent years. Table S4 summarizes the limits on benzene and other aromatics, as well as the dates of implementation for national standards on paint for automobiles, woodenware, exterior/interior walls, floors, and toys. In addition, a series of regulations regarding the use of solvent-based coatings with high NMHC emissions was also implemented during the past decade in Beijing. The use of solvent-based coatings as water-proof material for architectural decoration was restricted in 2003 and then banned in July 2005 by the Beijing Municipal Construction Committee. For the automobile industry, the cleaner production standard–automobile manufacturing (Painting) was implemented in December 2006 (HJ/T 293-2006) that banned the use of paint and solvent containing benzene, and

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encouraged the use of water-based and powder coatings. The stringent limits on the aromatics content of paints and the increasing use of water-based coatings should reduce the emission factors of BTEX. It is challenging to investigate trends in NMHC emissions from paint and solvent use, due to the difficulty in obtaining accurate usage data and the lack of studies documenting temporal changes in NMHC emission factors for paint and solvent use.

3.2.4 NG and LPG usage: ethane and propane

NG and LPG usage were believed to be important sources of ethane and propane emissions, respectively (Blake and Rowland, 1995; Katzenstein et al., 2003). In contrast to the declines in ambient levels of other NMHC species, the mixing ratios of ethane in Beijing exhibited a significant increase of ~ 50 % (~ 1.6 ppbv) between 2004 and 2013 (Fig. 7a). Ethane has a long atmospheric lifetime of about 2 months, and thus the annual variations of ethane mixing ratios can also be related to the changes in its background levels. Simpson et al. (2012) found that the Northern Hemisphere background levels for ethane in August showed a slight increase from 0.61 to 0.66 ppbv (~ 9 %) between 2006 and 2010. This increase rate of background levels for ethane was significantly lower than that for ethane measurements in Beijing. There was no significant change in the mixing ratios of propane, with ambient levels that fluctuated between 3.4 and 4.7 ppbv (Fig. 7b).

NG and LPG are considered as cleaner sources of energy than coal and gasoline, and therefore their supply and consumption has rapidly increased in Beijing during recent years. The consumption of NG in Beijing increased from 2.5 to 8.4 billion m^3 during 2004–2012 (29 % yr^{-1}), while the supply of LPG increased from 0.16 to 0.45 million tons (23 % yr^{-1}) during the same period of time (Beijing Statistical Yearbook 2004–2012). The temporal changes in ethane and propane levels might be the result of decreasing transportation emissions and increasing NG and LPG emissions.

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3.3 Temporal changes in NMHC sources obtained by the PMF model

Based on preliminary assessments of NMHC data in Sect. 3.2, we found that the temporal changes in mixing ratios of NMHC species from vehicle exhaust were consistent with the trend in transportation NMHC emissions reported by the MEIC inventory. However, trend analysis of BTEX levels did not provide a definitive evaluation of temporal changes in NMHC emissions from paint and solvent utilization. To further investigate NMHC emission trends for major sources, a PMF model was applied to ambient NMHC measurements for source apportionment and to calculate NMHC concentrations from different sources in each year.

3.3.1 Identification of PMF factors

The profiles for the four PMF-resolved factors (i.e., the mass percentage of individual species in each factor) and the distributions of each species among these factors (i.e. the relative contributions of PMF factors to each NMHC species are shown in Fig. 8.

The first factor was characterized by high levels of pentanes, which were considered as important components of gasoline vapor (Harley et al., 1992; Zhang et al., 2013). This factor also consisted of acetylene, benzene, and toluene, which can be emitted from vehicle exhaust (Liu et al., 2008). The second factor had the most important contributions to acetylene and C2–C4 alkenes (Fig. 8b), which are typically associated with vehicle exhaust in urban areas (Parrish, 2006; Baker et al., 2008). These two transportation-related factors were referred to as *gasoline evaporation and Vehicular exhaust #1* and *vehicular exhaust #2*, respectively.

The third factor was characterized by high levels of light alkanes (Fig. 8c). Ethane and propane are commonly associated with the leakage of NG and LPG, respectively (Blake and Rowland, 1995; Katzenstein et al., 2003). It is important to point out that this factor might be influenced by background air due to the long atmospheric lifetimes of these alkanes (Atkinson et al., 2006). Therefore, this factor was referred to as *NG and LPG use and background*.

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The fourth factor largely consisted of toluene, ethylbenzene, and xylenes (Fig. 8d), which are important components of paint and solvent (Liu et al., 2008; Yuan et al., 2010). Therefore, this factor was referred to as *paint and solvent use*.

3.3.2 Temporal trends in NMHCs concentrations from different sources

The temporal changes of NMHCs concentrations (i.e., the sum of concentrations for total measured 16 NMHC species) contributed by each PMF-resolved factor during 2004–2012 are shown in Fig. 9a–d. NMHCs concentrations from *gasoline evaporation and vehicle exhaust #1* and *vehicle exhaust #2* decreased significantly by 56 % and 77 %, respectively (Fig. 9a and b). The sum of NMHCs concentrations from these two transportation-related sources decreased by 66 % between 2004 and 2012, which is very similar to the relative decline of 65 % for transportation-related emissions reported by the MEIC inventory (Fig. 1b). However, the NMHCs concentrations that contributed by *NG and LPG use and background* exhibited a significant increase of 5.3 % yr^{-1} during 2004–2012 (Fig. 9c).

The results of the PMF model indicate that there were no significant temporal changes in the contribution of *paint and solvent use* to NMHCs concentrations from 2004 to 2012 (Fig. 9d). This result is in strong contrast to the large increase in NMHC emissions from solvent use (27.5 % yr^{-1}) that was reported by the MEIC inventory. It has been challenging to estimate NMHC emissions from paint and solvent use, because paint and solvent are used in a wide variety of residential and industrial processes, making it difficult to obtain accurate usage data and representative NMHC emission factors for most of these processes. NMHC emissions from paint and solvent use are usually calculated based on either solvent consumption or production data (*solvent mass balance* approach) or per capita or employment EFs (Klimont et al., 2002; Su et al., 2011). Due to the lack of NMHC emission factors measurements and the absence of detailed information on paint and solvent use in China, surrogate indicators (e.g., population, GDP) were also used to project future NMHC emissions from paint

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and solvent use in China (Bo et al., 2008), which may result in large uncertainties in predicted NMHC emissions.

The results of the PMF model also suggest that there have been obvious changes in NMHC sources in Beijing during the past decade. As shown in Fig. 10, there has been a significant decline in the relative contribution of transportation-related sources to NMHCs concentrations, from 64 % in 2004 to 32 % in 2012. However, the relative contribution of *paint and solvent use* to NMHC concentrations increased from 18 % to 30 %, and the contribution from *NG and LPG use and background* increased from 18 % to 38 %.

3.4 Temporal trends in NMHC to NO_x ratios

Anthropogenic NO_x are mainly emitted by combustion processes, such as vehicle exhaust and coal combustion (Zhao et al., 2013), whereas NMHC species can also be emitted from non-combustion sources (e.g., paint and solvent use). Analyzing the emission ratio of NMHC to NO_x is another way to assess the accuracy of NMHC emissions and estimate the relative contribution of non-combustion sources to total NMHC emissions (Funk et al., 2001; Arriaga-Colina et al., 2004).

The MEIC inventory indicated that emission ratios of NMHC to NO_x have increased in Beijing by 45 %, from 2004 to 2012 (Fig. 11a), which is mainly attributed to decreasing NMHC/NO_x ratios for transportation (~ 45 %) and rapidly increasing NMHC emissions from solvent use (~ 300 %). However, ambient measurements at the PKU site suggested that NMHC/NO_x concentration ratios have decreased by 14 %, from 2005 to 2012 (Fig. 11b). One possible explanation for this discrepancy is that the rate of increase in NMHC emissions from solvent use was overestimated by the MEIC inventory. If we assumed constant NMHC emissions from solvent use and industry during the last decade according to the PMF results, the inferred emission ratios of NMHC to NO_x decreased by ~ 11 % from 2005 to 2012, which is similar to the 14 % decline observed in measured NMHCs/NO_x ratios.

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It is important to note the limitations and uncertainties associated with our evaluation of trends in NMHC emissions using long-term ambient measurements.

1. The NMHC measurement data in this study were obtained by seven different instruments (Table 1). To insure the accuracy of NNHC data, inter-comparisons among some of these systems have been conducted in 2005, 2008, and 2010. The good agreements for online GC-MS/FID systems from ESRL and RCEC with canister-offline GC-MS/FID system were reported by Liu et al. (2009) and Wang et al. (2010a), respectively. Additionally, the good agreements among canister-offline GC-MS/FID, online GC-FID/PID, and online GC-MS/FID (PKU) systems were also found in 2010 (Fig. S2).

2. The trends for NMHC mixing ratios might be influenced by the temporal changes in meteorological conditions. However, Zhang et al. (2014) found that the meteorological parameters (i.e. ambient temperature, wind direction speed, and precipitation) showed no significant changes during 2005–2011; therefore, the temporal changes in NMHC levels could reflect NMHC emission trends.

3. The NMHC emission trends in the MEIC inventory were estimated based on annual activities in Beijing, while the long-term NMHC measurements were only taken during the summer. Since NMHC emissions and sources in Beijing exhibited some seasonal variations (Wang et al., 2014), NMHC trends might be inconsistent during different seasons. To preliminary investigate NMHC trends during winter, mixing ratios of ethane, acetylene, 1,3-butadiene, benzene, and toluene measured during winter of 2000 (Barletta et al., 2005), 2002 (Liu et al., 2005) and 2011 (Wang et al., 2014) were compared in Fig. S3. It can be found that the wintertime levels for acetylene, benzene, and toluene also decreased obviously during the last decade, and exhibited similar decline rates with those for summertime measurements. However, ethane levels exhibited a decline of 30 % between 2000 and 2011, which is contrast with its rising trend during summer. Due to the limitation of wintertime NMHC data, it is difficult to identify the causes for this

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seasonal discrepancy of ethane trend. Therefore, more NMHC measurements in winter are needed in the future.

4. The rise of atmospheric oxidizing capacity in Beijing (Zhang et al., 2014) would increase the photochemical removal rate of NMHC species; however, this factor was not considered in this study. This means that rates of decline for some reactive NMHC species (e.g., C4–C5 alkenes and xylenes), based on ambient measurements, might be overestimated in this study.

5. The temporal changes in NMHC source profiles were not considered in the PMF source apportionments. However, the NMHC source profile possibly changed during the last decade, especially for aromatics, due to the controls on benzene fractions in paint and gasoline (Yuan et al., 2010). Additionally, Yuan et al. (2012) found that the PMF interpretations could be affected by photochemistry. However, identifying this effect would require detailed analysis of photochemical removal of NMHC species, which is beyond the scope of this work.

4 Conclusions

The ambient mixing ratios of 16 NMHC species were measured during the summer at an urban site in Beijing from 2002 to 2013. The temporal changes in NMHC levels were analyzed to evaluate temporal trends in anthropogenic NMHC emissions reported by the most recent emission inventory for China (MEIC).

The MEIC inventory indicated that total NMHC emissions have been significantly increasing by ∼ 40 % from 2002 to 2012. Transportation-related NMHC emissions have decreased by 65 %, according to the MEIC inventory, whereas NMHC emissions from solvent use and industry have increased by ∼ 300 % and 40 %, respectively. In contrast to the increase in total NMHC emissions reported by the MEIC inventory, ambient levels of NMHCs measured in the summer of Beijing exhibited an obvious decline from 2003 to 2013. Mixing ratios of those NMHC species mainly from vehicle exhaust (e.g., C2–C4

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alkenes and acetylene) decreased significantly, at rates of 6.2–8.9 % yr^{-1}, which were comparable to the temporal changes in transportation-related emissions reported by the MEIC inventory. The ambient levels for *i*-butane and *i*-pentane, which are also influenced by gasoline vaporization, started to decrease in 2007, which corresponds to the time during which gasoline vapor recovery systems were being installed in Beijing. While the decline in ambient levels for aromatics was significant, their rates of relative decline (2.8–5.6 % yr^{-1}) were lower than those for vehicle exhaust tracers (i.e., acetylene and alkenes). Ethane levels exhibited a significant increase of 5.6 % yr^{-1} during 2002–2013; however, there was no significant changes in propane levels, with concentrations fluctuated between 3.4 and 4.7 ppbv.

To further evaluate NMHC trends for major sources, a PMF model was applied to ambient NMHC measurements for source apportionment and to calculate NMHCs concentrations from different sources in each year. Four PMF-resolved factors were identified: *gasoline evaporation and vehicle exhaust #1*, *vehicle exhaust #2*, *NG and LPG use and background*, and *paint and solvent use*. The sum of NMHCs concentrations from two transportation-related sources decreased by 66 % from 2004 to 2012, which is comparable to the relative decline of 65 % reported by the MEIC inventory for transportation-related emissions. However, PMF results suggested that there was no significant temporal change in the NMHCs concentrations from *solvent and paint use* during this time. This finding is in strong contrast to the rapid increase in NMHC emissions from solvent use reported by the MEIC inventory, indicating that the largest uncertainty in NMHC trends is possibly associated with emissions from paint and solvent use. The results of the PMF model also suggested that the contribution of NG and LPG use to NMHC emissions has become more important during the last decade; however, this source is not included in the current inventory.

The comparison of temporal changes in NMHC/NO_x ratios between the MEIC inventory and ambient measurements were used to reanalyze trends in NMHC emissions from paint and solvent use. The MEIC inventory indicated that NMHC/NO_x emission ratios have increased in Beijing by 45 % from 2005 to 2012. However, measured

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NMHCs/NO_x ratios decreased by ~ 15 % during these years. The NMHCs/NO_x emission ratios that were inferred based on the PMF results exhibited a decline of 11 %, which was comparable to that for measured ratios. This finding indicates that the rate of increase for NMHC emissions from paint and solvent use might be overestimated in the MEIC inventory, and therefore, more studies are needed to verify paint and solvent NMHC emissions.

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References

Arriaga-Colina, J. L., West, J. J., Sosa, G., Escalona, S. S., Ordunez, R. M., and Cervantes, A. D. M.: Measurements of VOCs in Mexico City (1992–2001) and evaluation of VOCs and CO in the emissions inventory, Atmos. Environ., 38, 2523–2533, doi:10.1016/j.atmosenv.2004.01.033, 2004.

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 IUPAC Subcommittee: 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.

Baker, A. K., Beyersdorf, A. J., Doezema, L. A., Katzenstein, A., Meinardi, S., Simpson, I. J., Blake, D. R., and Rowland, F. S.: Measurements of non-methane hydrocarbons in 28 United States cities, Atmos. Environ., 42, 170–182, doi:10.1016/j.atmosenv.2007.09.007, 2008.

ACPD
14, 18997–19031, 2014

Barletta, B., Meinardi, S., Rowland, F. S., Chan, C. Y., Wang, X. M., Zou, S. C., Chan, L. Y., and Blake, D. R.: Volatile organic compounds in 43 Chinese cities, Atmos. Environ., 39, 5979–5990, doi:10.1016/j.atmosenv.2005.06.029, 2005.

Blake, D. R. and Rowland, F. S.: Urban leakage of liquefied petroleum gas and its impact on Mexico City air quality, Science, 269, 953–956, doi:10.1126/science.269.5226.953, 1995.

Bo, Y., Cai, H., and Xie, S. D.: Spatial and temporal variation of historical anthropogenic NMVOCs emission inventories in China, Atmos. Chem. Phys., 8, 7297–7316, doi:10.5194/acp-8-7297-2008, 2008.

US Environmental Protection Agency (USEPA): EPA Positive Matrix Factorization (PMF) 3.0 Fundamentals & User Guide, http://www.epa.gov/heasd/products/pmf/pmf.html (last access: 12 December 2013), 2008.

Funk, T. H., Chinkin, L. R., Roberts, P. T., Saeger, M., Mulligan, S., Figueroa, V. H. P., and Yarbrough, J.: Compilation and evaluation of a Paso del Norte emission inventory, Sci. Total Environ., 276, 135–151, doi:10.1016/s0048-9697(01)00776-8, 2001.

Goldan, P. D., Kuster, W. C., Williams, E., Murphy, P. C., Fehsenfeld, F. C., and Meagher, J.: Non-methane hydrocarbon and oxy hydrocarbon measurements during the 2002 New England Air Quality Study, J. Geophys. Res.-Atmos., 109, D21309, doi:10.1029/2003jd004455, 2004.

Harley, R. A., Hannigan, M. P., and Cass, G. R.: Respeciation of organic gas emissions and the detection of excess unburned gasoline in the atmosphere, Environ. Sci. Technol., 26, 2395–2408, doi:10.1021/es00036a010, 1992.

He, K. B.: Multi-resolution Emission Inventory for China (MEIC): model framework and 1990–2010 anthropogenic emissions, International Global Atmospheric Chemistry Conference, 17–21 September, Beijing, China, S1-I-2, 2012.

Huo, H., Yao, Z. L., Zhang, Y. Z., Shen, X. B., Zhang, Q., Ding, Y., and He, K. B.: On-board measurements of emissions from light-duty gasoline vehicles in three mega-cities of China, Atmos. Environ., 49, 371–377, doi:10.1016/j.atmosenv.2011.11.005, 2012.

Katzenstein, A. S., Doezema, L. A., Simpson, I. J., Blake, D. R., and Rowland, F. S.: Extensive regional atmospheric hydrocarbon pollution in the southwestern United States, P. Natl. Acad. Sci. USA, 100, 11975–11979, doi:10.1073/pnas.1635258100, 2003.

Klimont, Z., Streets, D. G., Gupta, S., Cofala, J., Lixin, F., and Ichikawa, Y.: Anthropogenic emissions of non-methane volatile organic compounds in China, Atmos. Environ., 36, 1309–1322, doi:10.1016/s1352-2310(01)00529-5, 2002.

ACPD
14, 18997–19031, 2014

Lang, J. L., Cheng, S. Y., Wei, W., Zhou, Y., Wei, X., and Chen, D. S.: A study on the trends of vehicular emissions in the Beijing-Tianjin-Hebei (BTH) region, China, Atmos. Environ., 62, 605–614, doi:10.1016/j.atmosenv.2012.09.006, 2012.

Lefohn, A. S., Shadwick, D., and Oltmans, S. J.: Characterizing changes in surface ozone levels in metropolitan and rural areas in the United States for 1980–2008 and 1994–2008, Atmos. Environ., 44, 5199–5210, doi:10.1016/j.atmosenv.2010.08.049, 2010.

Lei, Y., Zhang, Q., He, K. B., and Streets, D. G.: Primary anthropogenic aerosol emission trends for China, 1990–2005, Atmos. Chem. Phys., 11, 931–954, doi:10.5194/acp-11-931-2011, 2011a.

Lei, Y., Zhang, Q., Nielsen, C., and He, K.: An inventory of primary air pollutants and CO_2 emissions from cement production in China, 1990–2020, Atmos. Environ., 45, 147–154, doi:10.1016/j.atmosenv.2010.09.034, 2011b.

Li, M., Zhang, Q., Streets, D. G., He, K. B., Cheng, Y. F., Emmons, L. K., Huo, H., Kang, S. C., Lu, Z., Shao, M., Su, H., Yu, X., and Zhang, Y.: Mapping Asian anthropogenic emissions of non-methane volatile organic compounds to multiple chemical mechanisms, Atmos. Chem. Phys., 14, 5617–5638, doi:10.5194/acp-14-5617-2014, 2014.

Liu, Y., Shao, M., Zhang, J., Fu, L. L., and Lu, S. H.: Distributions and source apportionment of ambient volatile organic compounds in Beijing city, China, J. Environ. Sci. Heal. A, 40, 1843–1860, doi:10.1080/10934520500182842, 2005.

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.

Liu, Z., Wang, Y. H., Vrekoussis, M., Richter, A., Wittrock, F., Burrows, J. P., Shao, M., Chang, C. C., Liu, S. C., Wang, H. L., and Chen, C. H.: Exploring the missing source of glyoxal (CHOCHO) over China, Geophys. Res. Lett, 39, L10812, doi:10.1029/2012gl051645, 2012.

Lu, S., Liu, Y., Shao, M., and Huang, S.: Chemical speciation and anthropogenic sources of ambient volatile organic compounds (VOCs) during summer in Beijing, 2004, Front. Environ. Sci. Eng. China, 1, 147–152, doi:10.1007/s11783-007-0026-0, 2007.

ACPD
14, 18997–19031, 2014

Parrish, D. D.: Critical evaluation of US on-road vehicle emission inventories, Atmos. Environ., 40, 2288–2300, doi:10.1016/j.atmosenv.2005.11.033, 2006.
Shao, M., Wang, B., Lu, S. H., Yuan, B., and Wang, M.: Effects of Beijing Olympics control measures on reducing reactive hydrocarbon species, Environ. Sci. Technol., 45, 514–519, doi:10.1021/es102357t, 2011.
Simpson, I. J., Sulbaek Andersen, M. P., Meinardi, S., Bruhwiler, L., Blake, N. J., Helmig, D., Rowland, F. S., and Blake, D. R.: Long-term decline of global atmospheric ethane concentrations and implications for methane, Nature, 488, 490–494, doi:10.1038/nature11342, 2012.
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.
Su, J., Shao, M., Lu, S., and Xie, Y.: Non-methane volatile organic compound emission inventories in Beijing during Olympic Games 2008, Atmos. Environ., 45, 7046–7052, doi:10.1016/j.atmosenv.2011.09.067, 2011.
Tang, X., Zhu, J., Wang, Z. F., and Gbaguidi, A.: Improvement of ozone forecast over Beijing based on ensemble Kalman filter with simultaneous adjustment of initial conditions and emissions, Atmos. Chem. Phys., 11, 12901–12916, doi:10.5194/acp-11-12901-2011, 2011.
von Schneidemesser, E., Vieno, M., and Monks, P. S.: The changing oxidizing environment in London – trends in ozone precursors and their contribution to ozone production, Atmos. Chem. Phys. Discuss., 14, 1287–1316, doi:10.5194/acpd-14-1287-2014, 2014.
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, H., Fu, L., Zhou, Y., Du, X., and Ge, W.: Trends in vehicular emissions in China's mega cities from 1995 to 2005, Environ. Pollut., 158, 394–400, doi:10.1016/j.envpol.2009.09.002, 2010.
Wang, J. L., Din, G. Z., and Chan, C. C.: Validation of a laboratory-constructed automated gas chromatograph for the measurement of ozone precursors through comparison with a commercial analogy, J. Chromatogr. A, 1027, 11–18, doi:10.1016/j.chroma.2003.08.099, 2004.
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.

ACPD
14, 18997–19031, 2014

Wang, S. X. and Hao, J. M.: Air quality management in China: issues, challenges, and options, J. Environ. Sci.-China, 24, 2–13, doi:10.1016/s1001-0742(11)60724-9, 2012.
Wang, T., Wei, X. L., Ding, A. J., Poon, C. N., Lam, K. S., Li, Y. S., Chan, L. Y., and Anson, M.: Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994–2007, Atmos. Chem. Phys., 9, 6217–6227, doi:10.5194/acp-9-6217-2009, 2009.
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, J. Environ. Sci.-China, 24, 95–101, doi:10.1016/s1001-0742(11)60732-8, 2012.
Warneke, C., de Gouw, J. A., Holloway, J. S., Peischl, J., Ryerson, T. B., Atlas, E., Blake, D., Trainer, M., and Parrish, D. D.: Multiyear trends in volatile organic compounds in Los Angeles, California: five decades of decreasing emissions, J. Geophys. Res.-Atmos., 117, D00V17, doi:10.1029/2012jd017899, 2012.
Wei, W., Wang, S. X., Chatani, S., Klimont, Z., Cofala, J., and Hao, J. M.: Emission and speciation of non-methane volatile organic compounds from anthropogenic sources in China, Atmos. Environ., 42, 4976–4988, doi:10.1016/j.atmosenv.2008.02.044, 2008.
Wei, W., Wang, S., Hao, J., and Cheng, S.: Projection of anthropogenic volatile organic compounds (VOCs) emissions in China for the period 2010–2020, Atmos. Environ., 45, 6863–6871, doi:10.1016/j.atmosenv.2011.01.013, 2011.
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, doi:10.1021/es1014289, 2011.
Xie, X., Shao, M., Liu, Y., Lu, S. H., Chang, C. C., and Chen, Z. M.: Estimate of initial isoprene contribution to ozone formation potential in Beijing, China, Atmos. Environ., 42, 6000–6010, doi:10.1016/j.atmosenv.2008.03.035, 2008.
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.
Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: how chemistry affects the interpretation of Positive Matrix Factorization (PMF) analysis, J. Geophys. Res.-Atmos., 117, D24302, doi:10.1029/2012jd018236, 2012.
Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I. S., Reddy, S., Fu, J. S., Chen, D., Duan, L., Lei, Y., Wang, L. T., and Yao, Z. L.: Asian

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14, 18997–19031, 2014

emissions in 2006 for the NASA INTEX-B mission, Atmos. Chem. Phys., 9, 5131–5153, doi:10.5194/acp-9-5131-2009, 2009.
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 O_3 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.
Zhang, Y. L., Wang, X. M., Zhang, Z., Lu, S. J., Shao, M., Lee, F. S. C., and Yu, J. Z Species profiles and normalized reactivity of volatile organic compounds from gasoline evaporation in China, Atmos. Environ., 79, 110–118, doi:10.1016/j.atmosenv.2013.06.029, 2013.
Zhao, B., Wang, S. X., Liu, H., Xu, J. Y., Fu, K., Klimont, Z., Hao, J. M., He, K. B., Cofala, J., and Amann, M.: NO_x emissions in China: historical trends and future perspectives, Atmos. Chem. Phys., 13, 9869–9897, doi:10.5194/acp-13-9869-2013, 2013.

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Table 1. Summertime VOCs measurements datasets at the PKU site in Beijing from 2002 to 2013.

Year	Instruments	Observation period (time resolution)	Reference
2002	Online GC-FID (PKU)	8–30 Sep (30 min);	–
2004	Canister-offline GC-MS/FID*	11–20 Aug	Lu et al. (2007)
2005	Online GC-MS/FID (ESRL)	1–27 Aug (30 min)	Liu et al. (2009)
2006	Online GC-FID (RCEC)	15–24 Aug (1 h)	Xie et al. (2008)
2007	Online GC-FID/PID	7–31 Aug (30 min)	Zhang et al. (2014)
2008	Online GC-MS/FID (RCEC)	27 Jul–30 Aug (1 h)	Wang, B. et al. (2010)
2009	Online GC-FID/PID	8–31 Aug (30 min)	Zhang et al. (2014)
2010	Online GC-MS/FID (PKU)	12–31 Aug (1 h)	Yuan et al. (2012)
2011	Online GC-MS/FID (PKU)	3 Aug–13 Sep (1 h)	Wang et al. (2014)
2012	Online GC-MS/FID (PKU)	1–31 Aug (1 h)	–
2013	Online GC-MS/FID (PKU)	7–25 Aug (1 h)	–

* VOC data were offline measured using canisters for sampling and analyzed by an GC-MS/FID system.

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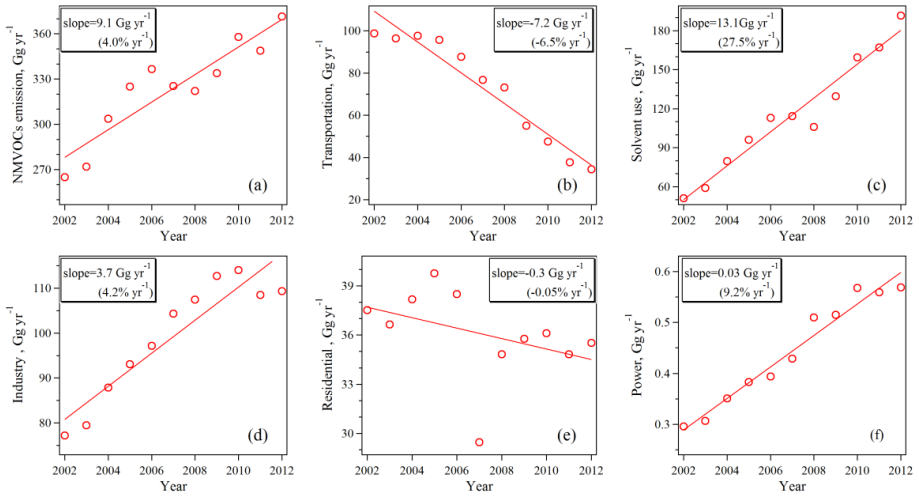

Figure 1. Anthropogenic NMVOCs emissions in Beijing during 2002–2012 from the MEIC inventory: **(a)** total emissions, **(b)** transportation, **(c)** solvent use, **(d)** industry, **(e)** residential, and **(f)** power.

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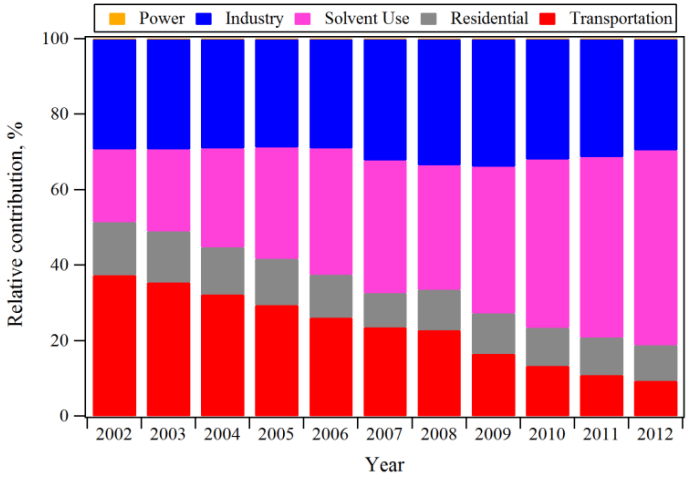

Figure 2. Relative contributions of five VOCs sources in Beijing during 2002–2012 from the MEIC inventory.

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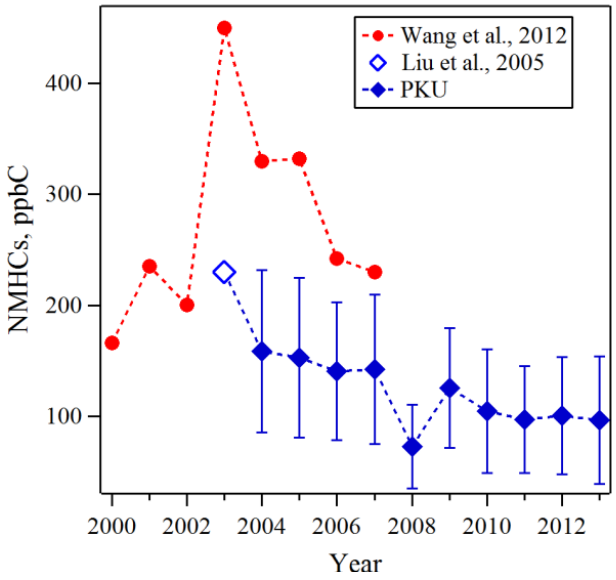

Figure 3. Mixing ratios of NMHCs (i.e. the sum of measured 16 NMHC species) measured at the PKU site (blue diamonds) from 2003 to 2012 and at another urban site (red dots) reported by Wang et al. (2012) during 2000–2007. The error bars correspond to standard deviations of NMHCs levels during each year.

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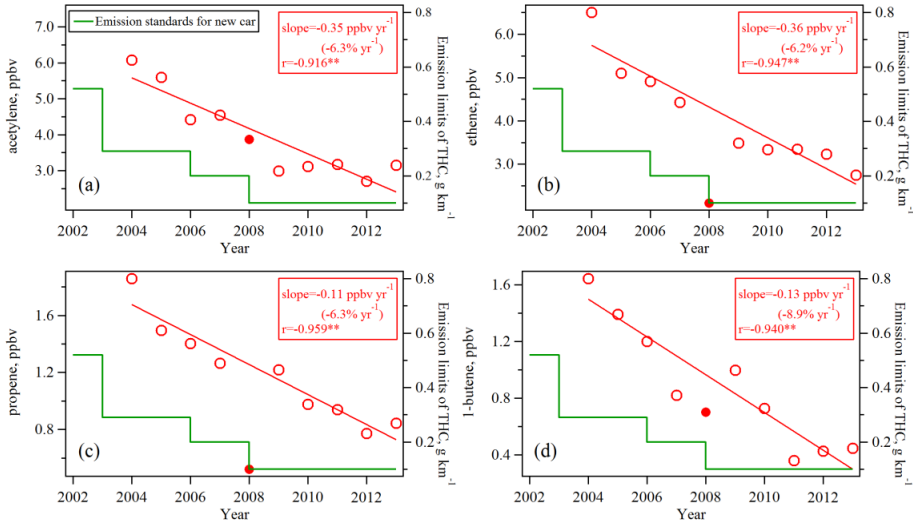

Figure 4. Temporal changes of ambient levels for **(a)** acetylene, **(b)** ethene, **(c)** propene, and **(d)** 1-butene measured at the PKU site during August of 2004–2013. The dark green staircase-pattern lines correspond to the emission limits of total hydrocarbons (THC) from light-duty vehicles. Owing to the influence from the short-term control measures for Beijing Olympic Games, the measurement data for 2008 (the red filled circle) was excluded from the linear fits. The trends that are significant at 0.05 and 0.01 levels were marked by single asterisk (*) and double asterisk (**), respectively.

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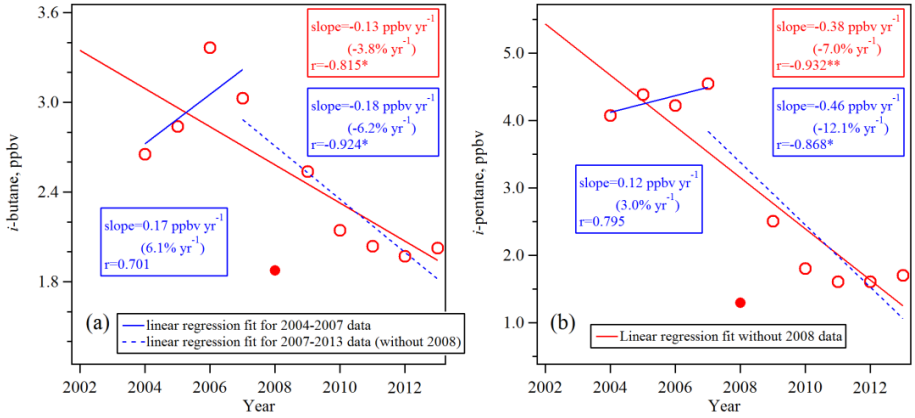

Figure 5. Temporal changes of ambient levels for **(a)** *i*-butane and **(b)** *i*-pentane measured at the PKU site during 2004–2013. The solid red lines represent linear regression fit for measured mixing ratios of *i*-butane and *i*-pentane during 2002–2013 excluding 2008 data. The dashed and solid blue lines represent linear regression fits for ambient measurements during 2004–2007 and during 2007–2013, respectively.

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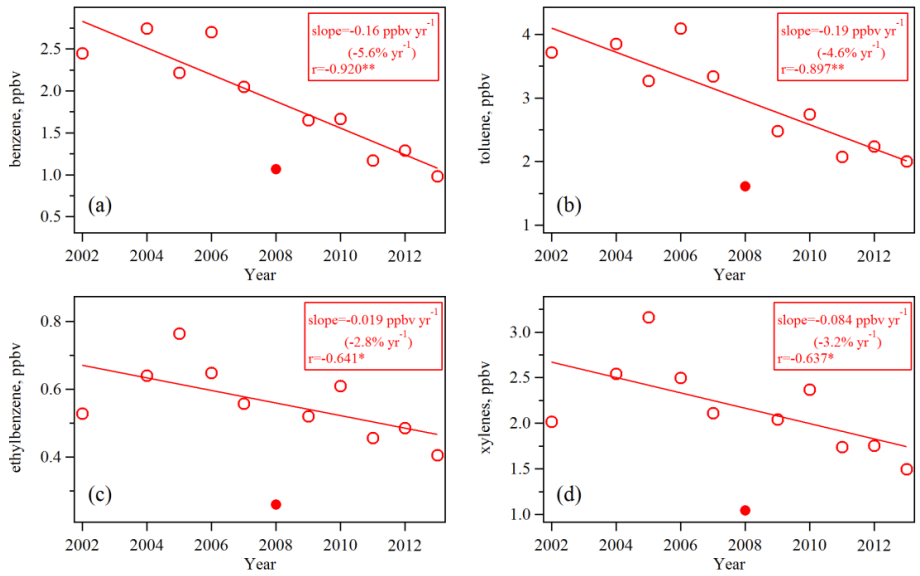

Figure 6. Temporal changes of ambient levels for **(a)** benznene, **(b)** toluene, **(c)** ethylbenzene, and **(d)** xylenes measured at the PKU site during 2002–2013. The solid red lines represent linear regression fits for aromatics levels during 2002–2013 excluding 2008 data.

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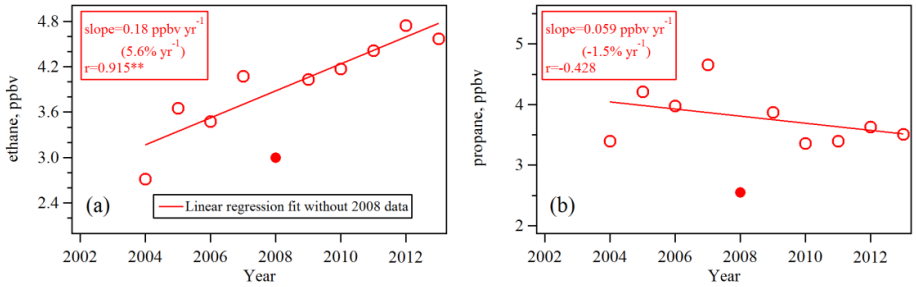

Figure 7. Temporal changes of ambient levels for **(a)** ethane and **(b)** propane measured at the PKU site during 2004–2013. The solid red lines represent linear regression fits for ethane and propane mixing ratios during 2004–2013 excluding 2008 data.

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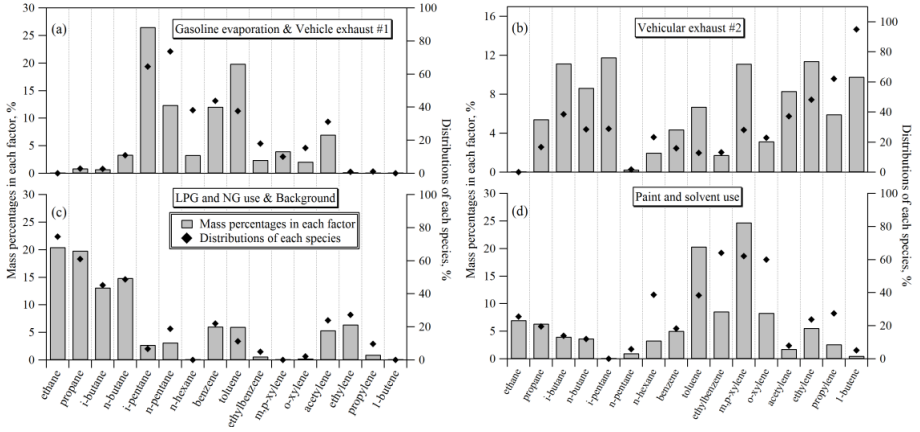

Figure 8. Profiles of four PMF-resolved factors (gray bars) and distributions of each species among these factors (black diamonds): **(a)** gasoline evaporation and vehicle exhaust #1, **(b)** vehicle exhaust #2, **(c)** LPG and NG use and background, and **(d)** paint and solvent use.

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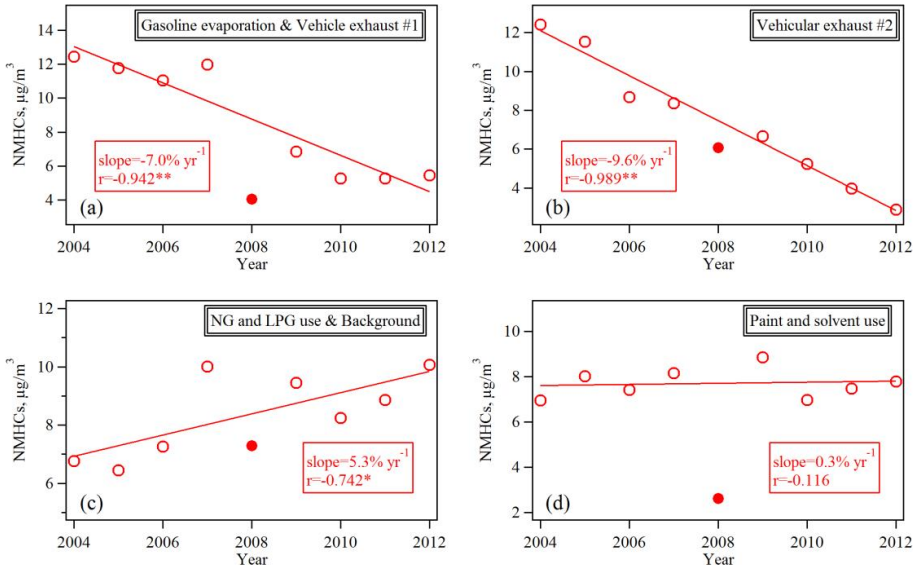

Figure 9. Temporal changes of NMHCs concentrations contributed by four PMF-resolved factors: **(a)** *gasoline and vehicle exhaust #1*, **(b)** *vehicle exhaust #2*, **(c)** *NG and LPG use and background*, and **(d)** *paint and solvent use*. The red solid lines represent linear regression fits of NMHCs concentrations from each source during 2004–2012 excluding 2008 data.

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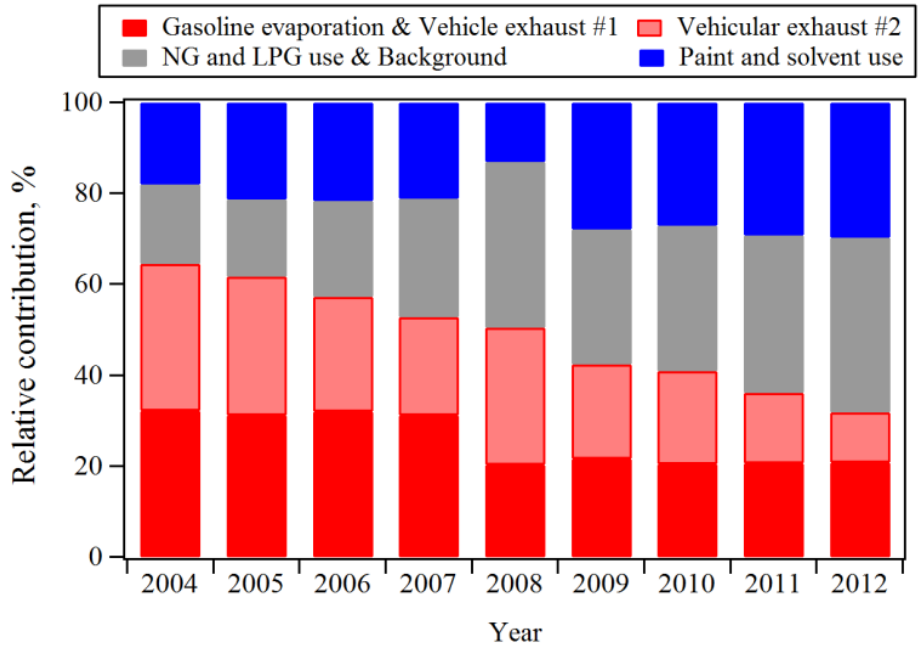

Figure 10. Relative contributions of four PMF-resolved factors to ambient NMHCs concentrations measured at the PKU site during 2004–2012.

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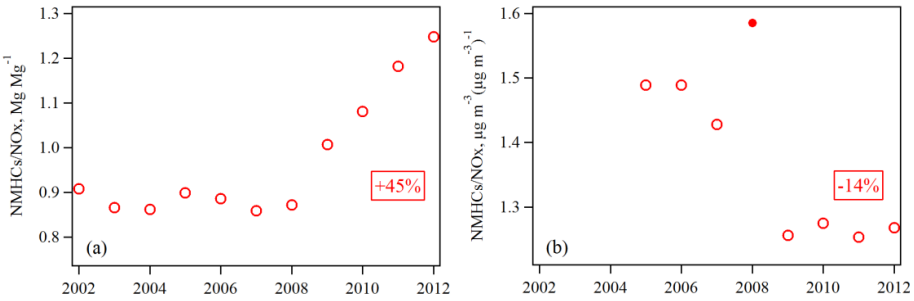

Figure 11. (a) Emission ratios of NMVOCs to NO_x ($Mg\,Mg^{-1}$) in Beijing from the MEIC inventory and **(b)** concentration ratios of NMHCs to NO_x ($\mu g\,m^{-3}\,(\mu g\,m^{-3})^{-1}$) obtained by ambient measurements at the PKU site during 2002–2012.

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