

1 **Understanding primary and secondary sources of ambient carbonyl**
2 **compounds in Beijing using the PMF model**

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Abstract

Carbonyls are important intermediates in atmospheric photochemistry. To determine the relative contributions of primary and secondary carbonyl sources in Beijing, carbonyls and other VOCs were measured at an urban site in both winter and summer. The Positive Matrix Factorization (PMF) model was used for source apportionment of VOCs. As volatile organic compounds (VOCs) undergo photochemical processes in the atmosphere, and such processes may interfere with factors identification, the relationships between the contributions of the resolved PMF factors to each non-methane hydrocarbon (NMHC) species and its k_{OH} value were used to distinguish between photochemically aged factors and fresh factors. As the result of PMF, five factors were resolved in winter, and two of them were identified as sources of photochemical aged emissions. In summer, four factors were resolved, including an aged factor. Carbonyls in the aged factors were simulated by VOCs consumption and the corresponding carbonyl production yields, and the simulated abundances agreed well with the results obtained by PMF. The source apportionment results indicated that secondary formation was the major source of carbonyls in both winter and summer, with the contribution of 51.2% and 46.0%. For the three major carbonyl species, primary anthropogenic sources contributed 28.9% and 32.3% to ambient formaldehyde, 53.7% and 41.6% to acetaldehyde, 68.1% and 56.2% to acetone in winter and summer, respectively.

1. Introduction

Carbonyls, including aldehydes and ketones, are a group of important oxygenated volatile organic compounds. As important intermediates in the photo-oxidation of hydrocarbons, carbonyls are major sources of free radicals and are important precursors of ozone, peroxyacyl nitrates and secondary organic aerosol (Singh et al., 1995; Finlayson-Pitts and Pitts, 1997; Liggio et al., 2005). As well as being produced from the photo-oxidation of hydrocarbons, carbonyls also can be emitted into the atmosphere by a variety of natural and anthropogenic sources. The major anthropogenic emission sources of carbonyls include incomplete combustion of fuels, industrial processes, and solvent usage (Zhang and Smith, 1999; Ban-Weiss et al., 2008; Kim et al., 2008). Carbonyls can be lost from atmosphere through reactions with the hydroxyl radical (OH), photolysis, and deposition (Lary and Shallcross, 2000). Due to the complexity of carbonyl sources and sinks, quantifying the relative contributions of primary emissions and secondary formation is a challenge.

Several previous studies have applied source apportionment techniques for the assessment of carbonyls. Multi-linear regression method has been widely used, which separates primary and secondary carbonyls based on their correlations with primary emission markers (i.e. CO, ethyne) and secondary production markers (i.e. O₃, glyoxal) (Friedfeld et al., 2002; Garcia et al., 2006). However, this approach depends on marker selection, and improper markers may give misleading results. For primary emissions, different markers might be suitable for different emission sources (Rappenglück et al., 2010), and the use of a single marker for all primary emissions should be cautious (Friedfeld et al., 2002). In addition, reactive VOCs that are co-emitted with a primary emission marker will form secondary carbonyls during air mass transport. Therefore, the correlation will also be found between secondary carbonyls and the primary marker. For secondary formation, the correlation coefficient and the slope between carbonyls and the marker vary significantly depending on the VOCs/NO_x ratio and the degree of processing. Furthermore,

primary carbonyls are also precursors of these secondary markers, and this may lead to a correlation between them (Parrish et al., 2012).

To improve the multi-linear regression method, de Gouw et al. (2005) developed a parameterization method based on photochemical age, with the consideration of the production of carbonyls by their precursors and the chemical removal of carbonyls during transport. This method makes some assumptions which should be carefully considered: (1) anthropogenic emissions of carbonyls and their precursors are proportional to a marker. (2) The removal of VOCs is governed by the reaction with OH radicals. (3) Biogenic sources of carbonyls are proportional to the emission of isoprene. (4) Photochemical age can be determined and reflect the scale of photochemical processes (de Gouw et al., 2005). Positive Matrix Factorization (PMF), a receptor model, has also been used to separate sources of carbonyls (Bon et al., 2011; Buzcu Guven and Olaguer, 2011; Yuan et al., 2012; Zheng et al., 2013). Compared with multi-linear regression method which employs one species for a certain source, PMF model can use a number of species for source identification. Most previous studies identified several primary emission sources and a mixed secondary source among the PMF-resolved factors. However, Yuan et al. (2012) found that the PMF-resolved factors were attributed to a common source at different stages of photochemical processing, rather than several independent sources. In addition to the various source apportionment approaches based on carbonyl measurements, Parrish et al. (2012) compared the primary emission flux of formaldehyde with fluxes of its precursors to quantify the relative contribution of primary and secondary formaldehyde sources. However, such estimations rely on the accuracy of emission inventories and reaction simulation.

Large differences in the results have been found among the several methods that have been used to calculate sources of carbonyls. For example, several studies have been undertaken in the Houston TX area of the USA to determine the contribution of primary anthropogenic sources of formaldehyde. By using multi-linear regression and using CO as a marker, Friedfeld et al. (2002) determined that 36% of atmospheric formaldehyde occurred as primary emissions. In a later study, Rappenglück et al.

(2010) determined that 38.5% and 8.9% of formaldehyde arose from primary vehicular emissions and industrial emissions, using CO and SO₂ as markers, respectively. By using PMF, Buzcu Guven and Olaguer (2011) estimated that mobile sources and industrial sources contributed 23% and 17% of formaldehyde respectively. In contrast, by comparing emissions of formaldehyde and its precursors, Parrish et al. (2012) found that only 1% and 4% of formaldehyde arose from direct vehicle exhaust and industrial emissions, and that secondary formation accounted for the overwhelming majority of atmospheric formaldehyde. Similar observations have been made in Beijing. Li et al. (2010), using multi-linear regression, attributed 76% of atmospheric formaldehyde to direct emissions from anthropogenic sources, although Yuan et al. (2012) calculated this ratio to be only 22% using the parameterization method. Compared with the number of formaldehyde studies, there are fewer source apportionment studies for other carbonyls, and hence further investigations are required.

Beijing is the capital of China and suffers from serious secondary air pollution problems, as characterized by high ozone and PM_{2.5} levels (Shao et al., 2006; Wang et al., 2012a). Ambient carbonyls have been detected at high levels in Beijing (Liu et al., 2009; Zhang et al., 2012) and formaldehyde displayed a significant positive trend from 1997 to 2010 (De Smedt et al., 2010). However, concentrations of non-methane hydrocarbon (NMHC) have decreased since 2003 (Wang et al., 2012b). It is essential to quantify different sources of carbonyls for understanding such trends and improving air quality in Beijing. Yuan et al. (2012) have used PMF for carbonyl source apportionment in 2010 summer and found that factors in PMF were extracted according to different degree of photochemical processing rather than individual sources. In this study, online measurements of carbonyls and other VOCs were conducted at Peking University (PKU) site in winter and summer. We used PMF to apportion carbonyl sources in these two seasons with different degree of photochemical processing. The degradation of NMHCs and production of carbonyls in the aged factors were analyses based on the process of photochemical aging to validate the result of PMF analysis. Differences in carbonyl sources between winter

and summer were discussed and compared with previous studies.

2. Methods

2.1. VOCs measurements

Online measurements of VOCs were conducted at an urban site in Beijing from 4 August 2011 to 9 September 2011 and from 29 December 2011 to 18 January 2012. The sampling site is on the top of a six-floor building (~20 m above ground) on Peking University campus. The PKU campus is located in the northwest of Beijing, about 500 m north of the Fourth Ring Road. This site has been described in detail elsewhere (Song et al., 2008; Liu et al., 2009).

A custom-built online gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID) was used to measure C₂–C₁₀ hydrocarbons, C₃–C₆ carbonyls, C₁–C₄ alkyl nitrates, halocarbons, and methyl tert-butyl ether (MTBE), with a time resolution of 1 h. CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) was used as an “intrinsic” internal standard as its long lifetime and minimal emissions (Liu et al., 2012). Daily calibration was taken, and the day to day response was within 20% of the calibration value. The detection limit of each species varied from 1~20 ppt, and the relative standard deviation varied from 1% to 6%. The detailed information of this system has been described by Yuan et al. (2012).

A commercial high-sensitivity proton-transfer-reaction mass spectrometry (PTR-MS) (Ionicon Analytik, Innsbruck, Austria) was used to measure 28 masses, including C₁–C₄ carbonyls and C₆–C₉ aromatics, with a time resolution of about 30 s. Background signals were measured for 15 min every 2.5 hours by diverting the sample flow through a Pt-coated quartz wool converter at 370 °C (Yuan et al., 2013). Calibration was taken every two or three days, and the response factor varied within 20%. The detection limit of each species varied from 40~200 ppt except for formaldehyde. As the proton affinity of formaldehyde is only slightly higher than water, the back reaction of proton transfer becomes significant. The kinetic of

PTR-MS formaldehyde detection was investigated to be mainly influenced by humidity (Vlasenko et al., 2010; Warneke et al., 2011). Therefore, we calibrated our formaldehyde measurement by using a permeation tube (Kin-Tek, USA) at the humidity from 0–30 mmol mol⁻¹ to obtain the response curve of formaldehyde response factor on humidity. During ambient measurement, formaldehyde signal was corrected according to the response curve. As the different ambient humidity between winter and summer, the detection limit of formaldehyde was 0.22–0.34 ppb in winter and 0.45–0.80 ppb in summer at a time resolution of 30 s. Among all our data, only less than 0.2% of samples in summer fell below the detection limit.

During these two campaigns, C3–C4 carbonyls, C6–C9 aromatics, isoprene and MVK+MACR (methyl vinyl ketone + methacrolein) were measured simultaneously by online GC-MS and PTR-MS. Good agreements were found between these two systems for most species, with correlation coefficients larger than 0.90 and slopes ranging from 0.8 to 1.2. Formaldehyde and acetaldehyde were only measured by PTR-MS during these two campaigns. However, inter-comparison between PTR-MS and DNPH-HPLC method (EPA TO11A) has been done before and the results showed good agreements. After correcting the influence of humidity on formaldehyde response, a correlation coefficient of 0.93 and a slope of 1.06 were found between PTR-MS and DNPH-HPLC method. The detailed results of inter-comparison were shown in supplement.

2.2.Positive Matrix Factorization (PMF)

The U.S. Environmental Protection Agency's PMF 3.0 receptor model was used in this study. PMF assumes that concentrations at receptor sites are linear combinations of different sources, which are derived as factors in the model (Paatero and Tapper, 1994). The basic model assumptions of PMF do not allow for chemical losses or productions when fitting the species. Thus, it should be careful to apportion carbonyl sources using PMF. As mentioned in the introduction, several studies have apportioned carbonyl sources using PMF (Bon et al., 2011; Buzcu Guven and Olaguer,

2011; Zheng et al., 2013). However, the validity of the results has been seldom investigated. Yuan et al. (2012) proved the capacity of PMF approach in identifying the role of chemical aging for better understanding the PMF factors. As the result of that study, VOC emission ratios derived from PMF fresh factors agreed well with the emission ratios calculated based on photochemical ages, so PMF can identify the contribution from primary emissions reasonably. And the abundances of NMHCs in PMF aged factors can be reproduced by the photochemical aging of fresh factors. In this study, we run PMF using two sets of VOC data for different seasons, and discussed the results to see whether PMF can separate carbonyl sources reasonably.

For PMF analysis, uncertainties arising from Online GC-MS/FID and PTR-MS were calculated using the method of Yuan et al. (2012). Generally, for the species measured by GC-MS/FID, the uncertainties were calculated as the sum of 10% of measured concentrations and 1/3 of detection limits. For the species measured by PTR-MS, the uncertainties were calculated as the sum of 10% of concentrations and the errors from mass spectrometer measurements. Finally, only species with high signal-to-noise ratios and few missing data values were used for PMF analysis. In winter, 10 carbonyls, 26 NMHCs, 2-butyl nitrate (2-BuONO₂), tetrachloroethylene, and MTBE were used. In summer, most of the values of cis/trans-2-butene and cis/trans-2-pentene fall below the detection limits, so these 4 species were not used for PMF analysis.

As the PMF-resolved factors may be influenced by photochemical processes, we used the relationship between the contribution of each factor to each NMHC species and its chemical reactivity (k_{OH}) to distinguish fresh and aged factors, as performed by Yuan et al. (2012). Generally, if all PMF factors originated from fresh emissions, the distribution of each species would not be correlated with its chemical reactivity in each factor. As a source ages, NMHCs undergo photochemical reactions, and the more reactive species will be consumed to a greater extent. As a result, a negative correlation would be displayed between an aged factor contribution to each NMHC species and its k_{OH} value. Considering that such complex relationships are difficult to express in mathematical formulae, Spearman's coefficient of rank correlation (r_s) was

used to represent the relationship.

3. Results and Discussion

3.1.Characteristics of ambient carbonyls in Beijing

The average concentration of the 10 measured carbonyls in Beijing was 13.2 ± 7.9 ppb (average concentration \pm standard deviation) in winter. In summer, the concentration was slightly higher, with the value of 16.3 ± 7.4 ppb. Formaldehyde, acetone, and acetaldehyde were the three major species, contributing more than 80% of the total measured carbonyls in both of these two seasons. Several studies have measured carbonyl concentrations in Beijing since 2005 (Pang and Mu, 2006; Shao et al., 2009; Xu et al., 2010; Zhang et al., 2012). During these years, VOCs sources have changed markedly in Beijing, including sharp increment of the number of vehicles, stricter standards for vehicle emissions (Zhang et al., 2012), stricter standards for solvent compositions (Yuan et al., 2010), and dramatically changing industry. Table 1 shows the sum of formaldehyde and acetaldehyde concentrations measured in Beijing. Acetone is a widely used solvent, and its concentration might be influenced by surrounding laboratories. So the concentration of acetone is not included in Table 1. A decreasing trend was found in summer. The concentration showed a significant decrease from 2005 to 2006 and from 2010 to 2011. By comparison, the concentrations have not changed much in winter. Some of the above studies measured daily average concentrations, and some measured only in daytime. To exclude the effect of diurnal variation, we compared the daytime concentration (from 8:00 to 20:00 LT) and daily concentration of these two carbonyls in 2011. The result showed that the daytime concentration was 7% higher than the daily average values in summer and 1% higher in winter. It seems that different sampling time have little effects on our concluded carbonyl trends. The decreasing trend of carbonyls obtained from ground-based measurements contrasted with the increasing formaldehyde trend obtained from satellite (De Smedt et al., 2010). As the satellites measured

formaldehyde concentrations in midday, and the measurements covered a larger spatial scale, we considered our result can better represent the trend of 24-h carbonyl concentrations in the urban region of Beijing. Such trends illustrate that the emission control do make efforts in Beijing. However, there might be some sources which contribute mainly in winter have not been controlled effectively.

Figure 1 shows the diurnal variations of ratios of formaldehyde/ethene, acetaldehyde/propene, and acetone/ethane. Concentrations of carbonyls in the atmosphere will be influenced by many meteorological conditions and the emission strength of carbonyls and their precursors. Assuming that the direct emissions of carbonyls from anthropogenic sources were proportional to the emissions of NMHCs, the diurnal variations of carbonyl/NMHC ratios can reflect the importance of secondary formation to ambient carbonyls. These three pairs of carbonyls and NMHCs were chosen because the two species in each pair have similar reaction rates with OH radical (Atkinson et al., 2006). As a result, the two species have approximately equal removal rates by OH reaction, and photochemical degradation has little effect on their ratios. As shown in Fig. 1, the carbonyl/NMHC ratios were stable in the evening, increased after sunrise (about 08:00 LT), and reached a maximum in the early afternoon (about 13:00–15:00 LT), then decreased to low values at night. This variation indicates an important contribution from secondary production during the day time, both in winter and summer. The diurnal variations of the acetone/ethane ratios were not as great as formaldehyde/ethene and acetaldehyde/propene. Such difference is consistent with previous studies, which have found that secondary production of acetone is less than formaldehyde and acetaldehyde (de Gouw et al., 2005; Yuan et al., 2012).

Though the diurnal pattern of carbonyl/NMHC ratios were similar in winter and summer, the values of carbonyl/NMHC ratios were approximately 3–5 times higher in summer than those in winter. As mentioned above, the concentration of carbonyls have no distinct difference between winter and summer. So such differences were mainly due to much higher NMHC levels in winter. This indicated significant differences in VOC sources between these two seasons. Primary sources emitted more

NMHCs in winter than in summer and fewer carbonyls in winter.

Previous studies usually supposed that carbonyls in winter come mainly from direct anthropogenic emissions (Pang and Mu, 2006; Cerón et al., 2007). As our analyzed diurnal variations, the differences between carbonyl/NMHC ratios at noon and the ratios at night in summer were only a bit larger than the differences in winter. The noon/night ratios were 2.6 and 3.1 for formaldehyde/ethene, 2.6 and 3.5 for acetaldehyde/propene, and 1.4 and 1.5 for acetone/ethane in winter and summer, respectively. Thus, secondary formation is still an important source of carbonyls in winter. It should be noted that photolysis of carbonyls have not been considered here. As our estimation, reaction with OH was the main pathway of carbonyl removal. The photolysis contributes 33%, 1% and 12% to the losses of formaldehyde, acetaldehyde and acetone at daytime. And the contributions have no significant difference between winter and summer. The detailed information for calculating removal rates is shown in supplement. As a result, neglecting the photolysis of carbonyls has little effect on comparing the contribution of secondary formation between winter and summer, and the variation of carbonyl/NMHC ratios can reflect the importance of secondary formation for carbonyls. For further discussion, PMF was used for carbonyls source apportionment to determine relative contributions from primary and secondary sources.

3.2. Identifying PMF factors

In summer, 593 samples were used for PMF analysis, and four factors were identified. Profiles of the PMF factors and the distribution of species among the factors are shown in Fig. 2. The profiles correspond to the mass percentage of individual VOC species in each factor, and the distributions represent the contributions of individual factors to the level of each species.

Factor 1 made an important contribution to our measured alkanes and alkenes. The profile of this factor was dominated by C₂–C₅ alkanes, C₂–C₃ alkenes, ethyne, and aromatics. These species are mainly from exhaust of vehicles and evaporation of

gasoline (Liu et al., 2008). This factor explains 38.1% of the measured MTBE, which is a compound used as a gasoline additive (Chang et al., 2006). Previous studies have proved that traffic related emissions are the most important NMHCs sources in summer of Beijing (Song et al., 2008; Wang et al., 2010). We therefore attributed this factor to traffic related emissions.

In factor 2, the values of aromatics, including benzene, toluene, ethylbenzene and xylenes, were high. Aromatics are a major constituent of solvents, and are widely used in industrial processes as well as some household products (Yuan et al., 2010). Thus, we considered this factor to be related to industrial and particularly to solvent usage.

Factor 3 has contributions to almost all our analyzed VOC species, except for some very reactive species. This factor explained more than 60% of our measured carbonyls and 87.5% of our measured 2-BuONO₂. Alkyl nitrates arise mainly from secondary production and have relatively long lifetimes (Simpson et al., 2003). Thus, we identified this factor as aged emissions.

Factor 4 contributed 81.5% of measured isoprene, which is often recognized as a tracer for biogenic emissions (Stroud et al., 2001), so we attributed this factor to biogenic related emission. High values of formaldehyde, acetaldehyde, and acetone were also found in this factor. These carbonyls were important oxidation products of biogenic VOCs (Carter and Atkinson, 1996) and can be co-emitted with them (Winters et al., 2009).

Based on the profile of each factor and the distribution of species among these factors, we found that the four factors identified by PMF may represent two primary emission sources, a biogenic emission factor, and an aged emission factor. As discussed in Sect. 2.2, the relationship between the contribution of each factor to each NMHC species and its chemical reactivity can be used to distinguish factors for photochemically aged emissions from those for fresh emissions. Such relationship was shown in Fig. 3, and each NMHC species was shown as a circle. Positive correlations were identified for factors 1 and 2, so these two factors were considered to be fresh emissions. A significant negative correlation was identified for factor 3, indicating that this factor represents photochemical aging.

The distributions of carbonyls are shown by filled triangles in Fig. 3. If all factors were fresh factors, the distribution of carbonyls will be similar to the distribution of NMHCs in each factor. As aged factors existed, the distributions of carbonyls will be higher in these factors owing to secondary production via photochemical reactions, and meanwhile, the distributions of carbonyls will be lower in the fresh factors. In factors 1 and 2, the distributions of carbonyls were at the same or lower levels compared with NMHCs. And in factor 3, the distributions of carbonyls showed higher levels than the NMHCs. Such appearance agreed with our previous identification.

In this study, two fresh factors and an aged factor were identified in 2011 summer. However, Yuan et al. (2012) did a similar analysis in 2010 summer, and found one mixed fresh factor and two aged factors with different photochemical ages. It was interesting to get such different results in two consecutive years. Yuan et al. (2012) has concluded that the result of PMF depends on the importance of different degree of photochemical processing and the differences of emission compositions from various sources. We used the ratio between o-xylene to ethylbenzene as an indicator to see the difference of photochemical processing degree between 2010 and 2011. As seen in Fig. S4, the relative standard deviations of o-xylene/ethylbenzene ratios were 30% larger in 2010 than in 2011. It indicated that the difference of photochemical processing degree was much larger in 2010. As a result, PMF factors in 2010 were extracted mainly according to different degree of photochemical processing, and PMF factors in 2010 were extracted mainly based on individual sources.

In winter, 341 samples were used for PMF analysis, and five factors were identified (Fig. 4).

Factor 1 and factor 3 contributed to most of our measured alkanes and alkenes, but there were some differences between these two factors. Factor 1 has higher contributions to our measured C2-C3 NMHCs and factor 3 has higher contributions to C4-C5 NMHCs. These light hydrocarbons are generated mainly by combustion processes, such as vehicle exhaust and coal burning (Liu et al., 2008; Wang et al., 2013). Source measurements have shown that C2-C3 NMHCs contributed more than half of NMHCs emitted from coal burning (Liu et al., 2008; Wang et al., 2013).

Benzene and toluene also made important contributions to this factor. These two species are important components in the emissions from coal burning (Liu et al., 2008). The ratio of benzene to toluene (2.31) in this factor falls between the ratios measured by Liu et al. (2008) for residential coal burning (1.81) and industrial coal burning (2.62). And this ratio is much higher than the one measured in tunnel experiment (0.70) (Liu et al., 2008). Therefore, we identified factor 1 as coal burning. C4-C5 NMHCs are important species from traffic related emissions, and factor 3 shows similar characteristic with factor 1 in summer. On the other side, factor 3 explains 37.9% of the measured MTBE. We therefore attributed this factor to traffic related emissions.

Factor 2 has high contributions to aromatics, and showed similar characteristic with factor 2 in summer. Besides aromatics, this factor contributes an important part of measured long-chain alkanes (C7–C10 alkanes), with the value of about 30%. Previous studies have found high values of long-chain alkanes from printing emissions (Yuan et al., 2010). Thus, we identified this factor as industry and solvent usage.

Both factor 4 and factor 5 have important contributions to carbonyls but little contribution to reactive NMHCs, so these two factors may not represent fresh emissions. The major NMHC species in factor 4 were C2-C5 NMHCs, ethene, ethyne, benzene and toluene. These species can be emitted from all of the three primary factors we discussed above, thus we considered this factor to be aged emissions from these anthropogenic sources. NMHCs in factor 5 were dominated by very long-lifetime alkanes, such as ethane and propane, so factor 5 was at a more aged stage than factor 4. Factor 5 accounted for most of the measured 2-BuONO₂ (67.7%) and some of the measured carbonyls (19.7%). We therefore considered VOC species in this factor to represent secondary production and background levels.

As shown in Fig. 5, no significant correlation was observed for factors 1 and 2, while a positive correlation was identified for factor 3. These three factors were considered to be fresh emissions. Significant negative correlations were identified for factors 4 and 5, indicating that these two factors represent photochemical aging.

3.3.Exploring the aged and fresh emission factors

In the last section, we have distinguished photochemical aged factors from fresh factors. To better understand the relationship between these factors and the role of chemical aging in PMF analysis, we explored the relationship between VOCs consumption and carbonyls formation in aged factors.

For two factors representing different photochemical aged stages of the same source, the ratios of NMHC abundances in these two factors should follow the equation below (Yuan et al., 2012):

$$\frac{[NMHC]_{aged}}{[NMHC]_{fresh}} = D \times e^{-k_{OH,NMHC}[OH]\Delta t} \quad (1)$$

$[NMHC]_{aged}$ and $[NMHC]_{fresh}$ (ppb) refer to the abundances of NMHCs in the aged and fresh factor, respectively. D is a scaling factor, which normalizes the NMHC abundances to unity, and $k_{OH,NMHC}$ is the OH rate constant for the NMHC. $[OH]$ is the average concentration of OH radical, and Δt is the difference in the reaction time between the aged and fresh factors. In this study, the OH exposure, expressed by $[OH]\Delta t$, is calculated as a whole.

As discussed in Sect. 3.2, in winter, $[NMHC]_{aged}$ refers to the abundances of NMHCs in factor 4, and $[NMHC]_{fresh}$ refers to the sum of the abundances of NMHCs in factors 1–3. In summer, $[NMHC]_{aged}$ refers to the abundances of NMHCs in factor 3, and $[NMHC]_{fresh}$ refers to the sum of the abundances of NMHCs in factors 1 and 2. Figure 6 shows the dependence of $[NMHC]_{aged}/[NMHC]_{fresh}$ (circles in the figure) on k_{OH} , with the lines being the fitted results from Eq. (1). The values of D and $[OH]\Delta t$ were estimated to be 0.43 and 2.99×10^{10} molecule·cm⁻³·s in winter, and 1.26 and 1.05×10^{11} molecule·cm⁻³·s in summer, respectively. Referring to the calculated OH radical concentrations in Beijing summer (Liu et al., 2012) and the differences of measured OH concentrations in Tokyo between summer and winter (Kanaya et al., 2007), we assumed that the average daytime concentration of OH in Beijing is 1.5×10^6 and 6×10^6 molecule·cm⁻³ in winter and summer. Thus the photochemical age of the aged factor in winter and summer is about 5.5 and 4.9 h.

The $[carbonyl]_{aged}/[carbonyl]_{fresh}$ ratios (Fig. 6, filled triangles) are significantly higher than the ratios of $[NMHC]_{aged}/[NMHC]_{fresh}$ because secondary production enhances the abundances of carbonyls in aged factors. The abundances of carbonyls in aged factors can be separated into two parts, as shown in Eq. (2). The first part stands for aged primary emissions and the second part stands for secondary formation calculated based on the consumption of other VOCs.

$$[carbonyl]_{aged} = D \times [carbonyl]_{fresh} \times e^{-k_{OH,carbonyl} \times [OH] \Delta t} + D \times \sum([VOC]_{fresh} \times (1 - e^{-k_{OH,VOC} \times [OH] \Delta t}) \times Y_{VOC,carbonyl}) \quad (2)$$

$k_{OH,carbonyl}$ is the OH rate constant for the carbonyl. $Y_{VOC,carbonyl}$ (ppb/ppb) refers to the carbonyl production yield of the VOC, which can be estimated using the Leeds Master Chemical Mechanism (MCM v3.2 <http://mcm.leeds.ac.uk/MCM/>). The estimation of $Y_{VOC,carbonyl}$ is based on following assumptions: the removal of VOCs was governed by the reaction with OH radicals and the removal of RO₂ was governed by the reaction with NO. The $Y_{VOC,carbonyl}$ values used in this study are listed in Table 2. The VOC species not shown made no contribution to the carbonyls discussed in this study. D and $[OH] \Delta t$ were fitted result from Eq. (1).

The carbonyl abundances in aged factors calculated by Eq. (2) were shown in Fig. 7, the results agreed well with the PMF-resolved abundances. In winter, all data points were distributed near the 1:1 line. In summer, though the data points showed some variability, the agreement was also within a factor of two. The agreements between calculated carbonyl abundances and PMF-resolved abundances indicate that our understanding of the aging process of PMF factors is reasonable. Any difference between them may be due to one or more of the following reasons. (1) PMF analysis and $Y_{VOC,carbonyl}$ estimations have their own uncertainties. (2) Only reactions between VOCs and the OH radical were considered here. (3) Further reactions of secondary carbonyls were not considered here. (4) Some VOC species were not considered in our PMF analysis, and they might be precursors of carbonyls. The PMF-analyzed VOC species accounted for 90% and 87% of all VOCs measured in winter and

summer respectively, but the contribution of each VOC to the formation of carbonyls may not be equivalent to its concentrations.

3.4.Primary and secondary sources of carbonyls

Our analysis of PMF factors showed that both the NMHCs and carbonyls in the aged factors can be explained by the photochemical processing of fresh factors. This proved that PMF can be used for source apportionment of pollutants with secondary sources such as carbonyls. However, there still remains one problem unclear in PMF analysis. Photochemical aging is a continuous process, but PMF gets only two or several factors for different aged stages. We conjecture that PMF separates such continuous process into their approximate aged stages, but the influence of such approximation requires further research.

Contributions of carbonyl sources in Beijing were shown in Fig. 8. Previous studies usually attribute all carbonyls in aged factors as secondary formed. As discussed in Sect. 3.3, the abundances of carbonyls in aged factors can be explained by two parts, aged direct emissions and production from VOCs consumptions, and the former part should be treated as primary emissions. Here, the aged direct emission part was further separated into each fresh factor considering their relative contributions. For all the 10 carbonyls analyzed, secondary formation is the major source in both winter and summer, with contributions of 51.2% and 46.0%, respectively. In winter, the three primary emission sources, coal burning, industry and solvent usage, and traffic related emissions had similar contributions to ambient carbonyl levels (15.3–16.9%). In summer, 17.0% and 26.6% of carbonyls were derived from industry and solvent usage, and traffic related emissions, as well as 10.4% from biogenic related emissions.

The relative contributions of carbonyls from primary emissions and from secondary formation have not changed much between winter and summer, which agreed with the characteristic of diurnal variations of carbonyls as discussed in Sect. 3.1. However, such results contrasted with those of Possanzini et al. (2002) and

Bakeas et al. (2003) who found great differences between carbonyl sources in winter and summer. Hence, we used the carbonyl production rate (F_p) to compare carbonyl formation abilities between these two seasons. The F_p can be calculated using Eq. (3) (Lin et al., 2012).

$$F_p = \sum([VOC]_i \times k_{OH,VOC} \times [OH] \times Y_{VOC,carbonyl}) \quad (3)$$

$Y_{VOC,carbonyl}$ was the carbonyl formation yield of VOC (Table 2). $[OH]$ and $[VOC]_i$ were concentration of OH radical and each VOC species. $[OH]$ in winter and summer were assumed to be 1.5×10^6 and 6×10^6 molecule·cm⁻³, as discussed in Sect. 3.3. The calculated F_p was 2.3 and 3.6 ppb·h⁻¹ for formaldehyde, 0.9 and 1.3 ppb·h⁻¹ for acetaldehyde, 0.3 and 0.4 ppb·h⁻¹ for acetone in winter and summer, respectively. Though the OH concentration in summer was much higher than the value in winter, concentrations of NMHCs, especially alkenes, were much higher in winter. As a result, F_p in summer was only 31–53% higher than the one in winter. For primary emissions, though the levels of NMHCs were higher in winter, the emission ratios of carbonyl to ethyne derived from PMF were 2–5 times higher in summer than in winter. As a result, the contribution from primary emissions has not changed much between winter and summer.

Though primary and secondary sources have similar relative contributions to ambient carbonyls in winter and summer, there are different primary sources between these two seasons. Coal burning was an important primary source in winter. However, it was not identified in summer. In winter, coal is widely used for central heating and domestic heating as the cold weather in Beijing, and such sources are greatly reduced in summer. The emission strength of biogenic VOCs correlates with ambient temperature and light intensity (Lerdau et al., 1997; Laffineur et al., 2011), and thus the biogenic-related factor was identified only in summer.

Formaldehyde is one of the most abundant and important carbonyls in the atmosphere. Table 3 lists the source contributions of formaldehyde and compares with the results of previous studies in Beijing and other regions. Primary anthropogenic sources have similar contributions in the two seasons: 28.9% in winter and 32.3% in

summer. Biogenic sources contributed 11.8% of the measured formaldehyde in summer, but were not identified in winter. The contribution of primary anthropogenic sources in this study is a bit higher than the source apportionment result reported by Yuan et al. (2012), but the contribution of biogenic sources is much lower. In our PMF results in summer, factor 4 contributes less than 30% of the measured MVK and MACR and therefore represents relatively fresh emissions from biogenic sources. However, Yuan et al. (2012) calculated the contribution of both primary and secondary biogenic sources, and so the value presented is much higher. Li et al. (2010) calculated that 76% of formaldehyde is derived from primary anthropogenic sources; this is much higher than the values quoted in other studies. There are two possible reasons for this: (1) only 2-days data were analyzed and may not represent the actual source characteristics of formaldehyde in Beijing, and (2) the concentration of ozone, the secondary marker used in the study, might be influenced by the titration of NO. New York City and Mexico City were two mega cities with large populations and large amounts of vehicles, which were similar to the situation of Beijing. The contribution of primary anthropogenic sources in Beijing is similar to that in New York City (Lin et al., 2012) and a bit lower than Mexico City (Garcia et al., 2006).

The contributions of primary anthropogenic sources to the levels of other carbonyls are shown in Table 4. Primary anthropogenic sources have a bit higher contribution in winter, due to less secondary production and lower biogenic emissions. The contributions from anthropogenic emissions are more important for ketones than aldehydes, with the values larger than 50% in both winter and summer. Compared with previous studies in Beijing (Liu et al., 2009; Yuan et al., 2012), the contribution from anthropogenic emissions for acetaldehyde in 2011 was similar to the result of 2010, but much higher than 2005. This indicated a significant change in acetaldehyde sources from 2005 to 2011. Though the concentration of acetaldehyde have decreased from 3.6 ppb (Shao et al., 2009) to 2.3 ppb, the contribution of anthropogenic emissions increased from 0.6 ppb to 1.0 ppb. As the specific sources of primary acetaldehyde have not been distinguished in 2005, the reason for such change was unclear. For acetone, propanal, and butanal, our results calculated a bit higher

contributions from anthropogenic emissions than previous studies.

4. Summary

In this study, online VOC measurements were conducted at the PKU site in winter and summer. PMF was used as a technique for source apportionment of samples collected during these two sampling. In winter, five factors were identified: (1) coal burning, (2) industry and solvent usage, (3) traffic related emissions, (4) aged emissions, and (5) secondary formation and background levels. In summer, four factors were identified: (1) traffic related emissions, (2) industry and solvent usage, (3) aged emissions, and (4) biogenic related emissions.

Relationships between the factors contribution to each NMHC species and its k_{OH} value were used to distinguish factors for photochemically aged emissions from those for fresh emissions. Both in winter and summer, a factor accounts for aged emissions was identified. The aged factor corresponded to the aged stage of mixed fresh emissions, and the relationship between them was investigated. The results indicated that the formation of carbonyls in the aged factor can be explained by the consumption of VOCs and their carbonyl production yields. In winter, besides the factor for aged emissions, another factor attributed to secondary formation and background level was identified. This result demonstrates that PMF analysis will be influenced by photochemical processing of emissions. Secondary carbonyls may attribute to more than one factor due to different stages of photochemical processing. When using PMF for carbonyl source apportionment, the means of each factor should be carefully considered.

Both PMF results and diurnal variations of carbonyl/NMHC indicated that relative contributions from primary and secondary sources in Beijing have not changed much between winter and summer. Such result was proved by calculating carbonyl production rates, which showed that carbonyl production rates in summer were only 31–53% higher than the rates in winter due to higher VOCs concentrations in winter. Secondary formation is the major source of carbonyls in Beijing, with the

contribution of 51.2% and 46.0% in winter and summer, respectively. Traffic related emissions and industry and solvent usage are main sources of primary anthropogenic carbonyls in Beijing. For heating in winter, coal burning is also an important anthropogenic source of carbonyl. In summer, biogenic related sources contributed 10.4% of carbonyls. For the three major carbonyl species, formaldehyde, acetaldehyde, and acetone, the contribution of primary anthropogenic sources was 28.9% and 32.3%, 53.7% and 41.6%, and 68.1% and 56.2% in winter and summer, respectively. These results derived from source apportionment could be used to check the source inventories of carbonyls that will be updated in follow-up studies.

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References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Subcommittee, I.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, *Atmos. Chem. Phys.*, 6, 3625-4055, doi: 10.5194/acp-6-3625-2006, 2006.
- Bakeas, E. B., Argyris, D. I., and Siskos, P. A.: Carbonyl compounds in the urban environment of Athens, Greece, *Chemosphere*, 52, 805-813, Doi: 10.1016/s0045-6535(03)00257-1, 2003.
- Ban-Weiss, G. A., McLaughlin, J. P., Harley, R. A., Kean, A. J., Grosjean, E., and Grosjean, D.: Carbonyl and nitrogen dioxide emissions from gasoline- and diesel-powered motor vehicles, *Environ. Sci. Technol.*, 42, 3944-3950, doi: 10.1021/es8002487, 2008.
- Bon, D. M., Ulbrich, I. M., de Gouw, J. A., Warneke, C., Kuster, W. C., Alexander, M. L., Baker, A., Beyersdorf, A. J., Blake, D., Fall, R., Jimenez, J. L., Herndon, S. C., Huey, L. G., Knighton, W. B., Ortega, J., Springston, S., and Vargas, O.: Measurements of volatile organic compounds at a suburban ground site (T1) in Mexico City during the MILAGRO 2006 campaign: measurement comparison, emission ratios, and source attribution, *Atmos. Chem. Phys.*, 11, 2399-2421, doi: 10.5194/acp-11-2399-2011, 2011.
- Buzcu Guven, B., and Olaguer, E. P.: Ambient formaldehyde source attribution in Houston during TexAQS II and TRAMP, *Atmos. Environ.*, 45, 4272-4280, doi: 10.1016/j.atmosenv.2011.04.079, 2011.
- Carter, W. P. L., and Atkinson, R.: Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x, *Int. J. Chem. Kinet.*, 28, 497-530, doi: 10.1002/(sici)1097-4601(1996)28:7<497::aid-kin4>3.0.co;2-q, 1996.
- Cerón, R. M., Cerón, J. G., and Muriel, M.: Diurnal and seasonal trends in carbonyl levels in a semi-urban coastal site in the Gulf of Campeche, Mexico, *Atmos. Environ.*, 41, 63-71, doi: 10.1016/j.atmosenv.2006.08.008, 2007.
- Chang, C. C., Wang, J. L., Liu, S. C., and Lung, S. C. C.: Assessment of vehicular and non-vehicular contributions to hydrocarbons using exclusive vehicular indicators, *Atmos. Environ.*, 40, 6349-6361, doi: 10.1016/j.atmosenv.2006.05.043, 2006.
- de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *J. Geophys. Res.-Atmos.*, 110, D16305, doi: 10.1029/2004jd005623, 2005.
- De Smedt, I., Stavrou, T., Müller, J. F., van der A, R. J., and Van Roozendaal, M.: Trend detection in satellite observations of formaldehyde tropospheric columns, *Geophys. Res. Lett.*, 37, L18808, doi: 10.1029/2010gl044245, 2010.
- Finlayson-Pitts, B. J., and Pitts, J. N.: Tropospheric air pollution: Ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles, *Science*, 276, 1045-1052, doi: 10.1126/science.276.5315.1045, 1997.
- Friedfeld, S., Fraser, M., Ensor, K., Tribble, S., Rehle, D., Leleux, D., and Tittel, F.: Statistical analysis of primary and secondary atmospheric formaldehyde, *Atmos. Environ.*, 36, 4767-4775, doi: 10.1016/s1352-2310(02)00558-7, 2002.
- Garcia, A. R., Volkamer, R., Molina, L. T., Molina, M. J., Samuelson, J., Mellqvist, J., Galle, B.,

606 Herndon, S. C., and Kolb, C. E.: Separation of emitted and photochemical formaldehyde in
 607 Mexico City using a statistical analysis and a new pair of gas-phase tracers, *Atmos. Chem.*
 608 *Phys.*, 6, 4545-4557, doi: 10.5194/acp-6-4545-2006, 2006.
 609 Kanaya, Y., Cao, R., Akimoto, H., Fukuda, M., Komazaki, Y., Yokouchi, Y., Koike, M., Tanimoto, H.,
 610 Takegawa, N., and Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and
 611 modeled OH and HO₂ radical concentrations during the winter and summer of 2004, *J.*
 612 *Geophys. Res.-Atmos.*, 112, D21312, doi: 10.1029/2007jd008670, 2007.
 613 Kim, K.-H., Hong, Y.-J., Pal, R., Jeon, E.-C., Koo, Y.-S., and Sunwoo, Y.: Investigation of carbonyl
 614 compounds in air from various industrial emission sources, *Chemosphere*, 70, 807-820, doi:
 615 10.1016/j.chemosphere.2007.07.025, 2008.
 616 Laffineur, Q., Aubinet, M., Schoon, N., Amelynck, C., Müller, J. F., Dewulf, J., Van Langenhove, H.,
 617 Steppe, K., Simpraga, M., and Heinesch, B.: Isoprene and monoterpene emissions from a
 618 mixed temperate forest, *Atmos. Environ.*, 45, 3157-3168, doi:
 619 10.1016/j.atmosenv.2011.02.054, 2011.
 620 Lary, D. J., and Shallcross, D. E.: Central role of carbonyl compounds in atmospheric chemistry, *J.*
 621 *Geophys. Res.-Atmos.*, 105, 19771-19778, doi: 10.1029/1999jd901184, 2000.
 622 Lerdau, M., Guenther, A., and Monson, R.: Plant production and emission of volatile organic
 623 compounds, *Bioscience*, 47, 373-383, doi: 10.2307/1313152, 1997.
 624 Li, Y., Shao, M., Lu, S., Chang, C.-C., and Dasgupta, P. K.: Variations and sources of ambient
 625 formaldehyde for the 2008 Beijing Olympic games, *Atmos. Environ.*, 44, 2632-2639, doi:
 626 10.1016/j.atmosenv.2010.03.045, 2010.
 627 Liggio, J., Li, S. M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, *J. Geophys.*
 628 *Res.-Atmos.*, 110, D10304, doi: 10.1029/2004jd005113, 2005.
 629 Lin, Y. C., Schwab, J. J., Demerjian, K. L., Bae, M.-S., Chen, W.-N., Sun, Y., Zhang, Q., Hung, H.-M.,
 630 and Perry, J.: Summertime formaldehyde observations in New York City: Ambient levels,
 631 sources and its contribution to HO_x radicals, *J. Geophys. Res.-Atmos.*, 117, D08305, doi:
 632 10.1029/2011jd016504, 2012.
 633 Liu, W.-T., Hsieh, H.-C., Chen, S.-P., Chang, J. S., Lin, N.-H., Chang, C.-C., and Wang, J.-L.:
 634 Diagnosis of air quality through observation and modeling of volatile organic compounds
 635 (VOCs) as pollution tracers, *Atmos. Environ.*, 55, 56-63, doi: 10.1016/j.atmosenv.2012.03.017,
 636 2012.
 637 Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., and Tang, D.: Source profiles of volatile organic compounds
 638 (VOCs) measured in China: Part I, *Atmos. Environ.*, 42, 6247-6260, doi:
 639 10.1016/j.atmosenv.2008.01.070, 2008.
 640 Liu, Y., Shao, M., Kuster, W. C., Goldan, P. D., Li, X. H., Lu, S. H., and De Gouw, J. A.: Source
 641 identification of reactive hydrocarbons and oxygenated VOCs in the summertime in Beijing,
 642 *Environ. Sci. Technol.*, 43, 75-81, doi: 10.1021/es801716n, 2009.
 643 Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, L. G., Stickel, R., Liao, J., Shao, M., Zhu, T., Zeng, L.,
 644 Amoroso, A., Costabile, F., Chang, C. C., and Liu, S. C.: Summertime photochemistry during
 645 CAREBeijing-2007: RO_x budgets and O₃ formation, *Atmos. Chem. Phys.*, 12, 7737-7752, doi:
 646 10.5194/acp-12-7737-2012, 2012.
 647 Paatero, P., and Tapper, U.: Positive matrix factorization - a nonnegative factor model with optimal
 648 utilization of error-estimates of data values, *Environmetrics*, 5, 111-126, doi:
 649 10.1002/env.3170050203, 1994.

650 Pang, X., and Mu, Y.: Seasonal and diurnal variations of carbonyl compounds in Beijing ambient air,
 651 *Atmos. Environ.*, 40, 6313-6320, doi: 10.1016/j.atmosenv.2006.05.044, 2006.
 652 Parrish, D. D., Ryerson, T. B., Mellqvist, J., Johansson, J., Fried, A., Richter, D., Walega, J. G.,
 653 Washenfelder, R. A., de Gouw, J. A., Peischl, J., Aikin, K. C., McKeen, S. A., Frost, G. J.,
 654 Fehsenfeld, F. C., and Herndon, S. C.: Primary and secondary sources of formaldehyde in
 655 urban atmospheres: Houston Texas region, *Atmos. Chem. Phys.*, 12, 3273-3288, doi:
 656 10.5194/acp-12-3273-2012, 2012.
 657 Possanzini, M., Palo, V. D., and Cecinato, A.: Sources and photodecomposition of formaldehyde and
 658 acetaldehyde in Rome ambient air, *Atmos. Environ.*, 36, 3195-3201, doi:
 659 10.1016/s1352-2310(02)00192-9, 2002.
 660 Rappenglück, B., Dasgupta, P. K., Leuchner, M., Li, Q., and Luke, W.: Formaldehyde and its relation to
 661 CO, PAN, and SO₂ in the Houston-Galveston airshed, *Atmos. Chem. Phys.*, 10, 2413-2424,
 662 doi: 10.5194/acp-10-2413-2010, 2010.
 663 Shao, M., Tang, X., Zhang, Y., and Li, W.: City clusters in China: air and surface water pollution, *Front.*
 664 *Ecol. Environ.*, 4, 353-361, doi:10.1890/1540-9295(2006)004[0353:CCICAA]2.0.CO;2, 2006.
 665 Shao, M., Lu, S., Liu, Y., Xie, X., Chang, C., Huang, S., and Chen, Z.: Volatile organic compounds
 666 measured in summer in Beijing and their role in groundlevel ozone formation, *J. Geophys.*
 667 *Res.-Atmos.*, 114, D00G06, doi: 10.1029/2008jd010863, 2009.
 668 Simpson, I. J., Blake, N. J., Blake, D. R., Atlas, E., Flocke, F., Crawford, J. H., Fuelberg, H. E., Kiley,
 669 C. M., Meinardi, S., and Rowland, F. S.: Photochemical production and evolution of selected
 670 C₂–C₅ alkyl nitrates in tropospheric air influenced by Asian outflow, *J. Geophys. Res.-Atmos.*,
 671 108, 8808, doi: 10.1029/2002jd002830, 2003.
 672 Singh, H. B., Kanakidou, M., Crutzen, P. J., and Jacob, D. J.: High concentrations and photochemical
 673 fate of oxygenated hydrocarbons in the global troposphere, *Nature*, 378, 50-54, 1995.
 674 Song, Y., Dai, W., Shao, M., Liu, Y., Lu, S. H., Kuster, W., and Goldan, P.: Comparison of receptor
 675 models for source apportionment of volatile organic compounds in Beijing, China, *Environ.*
 676 *Pollut.*, 156, 174-183, doi: 10.1016/j.envpol.2007.12.014, 2008.
 677 Stroud, C. A., Roberts, J. M., Goldan, P. D., Kuster, W. C., Murphy, P. C., Williams, E. J., Hereid, D.,
 678 Parrish, D., Sueper, D., Trainer, M., Fehsenfeld, F. C., Apel, E. C., Riemer, D., Wert, B., Henry,
 679 B., Fried, A., Martinez-Harder, M., Harder, H., Brune, W. H., Li, G., Xie, H., and Young, V. L.:
 680 Isoprene and its oxidation products, methacrolein and methylvinyl ketone, at an urban forested
 681 site during the 1999 Southern Oxidants Study, *J. Geophys. Res.-Atmos.*, 106, 8035-8046, doi:
 682 10.1029/2000jd900628, 2001.
 683 Vlasenko, A., Macdonald, A. M., Sjøstedt, S. J., and Abbatt, J. P. D.: Formaldehyde measurements by
 684 Proton transfer reaction – Mass Spectrometry (PTR-MS): correction for humidity effects,
 685 *Atmos. Meas. Tech.*, 3, 1055-1062, doi: 10.5194/amt-3-1055-2010, 2010.
 686 Wang, B., Shao, M., Lu, S.H., Yuan, B., Zhao, Y., Wang, M., Zhang, S.Q., Wu, D.: Variation of ambient
 687 non-methane hydrocarbons in Beijing city in summer 2008, *Atmos. Chem. Phys.*, 10,
 688 5911-5923, doi: 10.5194/acp-10-5911-2010, 2010.
 689 Wang, Q., Geng, C., Lu, S., Chen, W., and Shao, M.: Emission factors of gaseous carbonaceous species
 690 from residential combustion of coal and crop residue briquettes, *Front. Environ. Sci. Eng.*, 7,
 691 66-76, 10.1007/s11783-012-0428-5, 2013.
 692 Wang, Y., Konopka, P., Liu, Y., Chen, H., Müller, R., Plöger, F., Riese, M., Cai, Z., and Lü, D.:
 693 Tropospheric ozone trend over Beijing from 2002–2010: ozonesonde measurements and

modeling analysis, *Atmos. Chem. Phys.*, 12, 8389-8399, doi: 10.5194/acp-12-8389-2012, 2012a.

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, 2012b.

Warneke, C., Veres, P., Holloway, J. S., Stutz, J., Tsai, C., Alvarez, S., Rappenglueck, B., Fehsenfeld, F. C., Graus, M., Gilman, J. B., and de Gouw, J. A.: Airborne formaldehyde measurements using PTR-MS: calibration, humidity dependence, inter-comparison and initial results, *Atmos. Meas. Tech.*, 4, 2345-2358, doi: 10.5194/amt-4-2345-2011, 2011.

Winters, A. J., Adams, M. A., Bleby, T. M., Rennenberg, H., Steigner, D., Steinbrecher, R., and Kreuzwieser, J.: Emissions of isoprene, monoterpene and short-chained carbonyl compounds from *Eucalyptus* spp. in southern Australia, *Atmos. Environ.*, 43, 3035-3043, doi: 10.1016/j.atmosenv.2009.03.026, 2009.

Xu, Z., Liu, J., Zhang, Y., Liang, P., and Mu, Y.: Ambient levels of atmospheric carbonyls in Beijing during the 2008 Olympic Games, *J. Environ. Sci. -China*, 22, 1348-1356, doi: 10.1016/s1001-0742(09)60261-8, 2010.

Yuan, B., Shao, M., Lu, S., 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.

Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., Zeng, L. M., and Hu, M.: VOC emissions, evolutions and contributions to SOA formation at a receptor site in Eastern China, *Atmos. Chem. Phys. Discuss.*, 13, 6631-6679, doi: 10.5194/acpd-13-6631-2013, 2013.

Zhang, J., and Smith, K. R.: Emissions of carbonyl compounds from various cookstoves in China, *Environ. Sci. Technol.*, 33, 2311-2320, doi: 10.1021/es9812406, 1999.

Zhang, Y. J., Mu, Y. J., Liu, J. F., and Mellouki, A.: Levels, sources and health risks of carbonyls and BTEX in the ambient air of Beijing, China, *J. Environ. Sci. -China*, 24, 124-130, doi: 10.1016/s1001-0742(11)60735-3, 2012.

Zheng, J., Garzón, J. P., Huertas, M. E., Zhang, R., Levy, M., Ma, Y., Huertas, J. I., Jardón, R. T., Ruíz, L. G., Tan, H., and Molina, L. T.: Volatile organic compounds in Tijuana during the Cal-Mex 2010 campaign: Measurements and source apportionment, *Atmos. Environ.*, 70, 521-531, doi: 10.1016/j.atmosenv.2012.11.030, 2013.

Tables

Table 1. The sum of formaldehyde and acetaldehyde concentrations in Beijing (Unit: ppb)

Year	Summer	Winter
2005	21.7 ^a	7.0 ^a
2006	13.12 ^b	
2008	13.3 ^{c, d}	6.6 ^e
2009	11.4 ^e	5.9 ^e
2010	12.6 ^e	
2011	8.0 ^f	8.1 ^f

^a (Pang and Mu, 2006)

^b (Shao et al., 2009)

^c (Xu et al., 2010)

^d data before traffic restriction in 2008

^e (Zhang et al., 2012)

^f This study

740 Table 2. Production yields of carbonyls from VOCs (Unit: ppb/ppb)

741 (<http://mcm.leeds.ac.uk/MCM/>)

NMHC	Formaldehyde	Acetaldehyde	Acetone	Propanal	Butanal
Ethane	0	0.991	0	0	0
Propane	0	0	0.705	0.259	0
i-Butane	0.773	0	0.774	0	0
n-Butane	0	0.581	0	0	0.024
i-Pentane	0	0.606	0.611	0	0
n-Pentane	0	0.114	0	0.116	0
2,2-dimethylbutane	0.282	0.289	0.282	0	0
2,3-dimethylbutane	0	0	1.638	0	0
2-methylpentane	0	0.035	0.195	0.192	0
3-methylpentane	0	0.491	0	0	0
Ethene	1.6	0	0	0	0
Propene	0.979	0.979	0	0	0
trans-2-Butene	0	1.918	0	0	0
1-Butene	0.961	0	0	0.961	0
i-Butene	0.988	0	0.988	0	0
cis-2-Butene	0	1.918	0	0	0
1,3-Butadiene	0.73	0	0	0	0
1-Pentene	0.941	0	0	0	0.941
cis-2-Pentene	0	0.936	0	0.936	0
trans-2-Pentene	0	0.936	0	0.936	0
Isoprene	0.709	0	0	0	0
Styrene	1	0	0	0	0
Acetaldehyde	0.999	0	0	0	0
Acetone	1.998	0	0	0	0
Propanal	0	0.991	0	0	0
MEK	1.390	0.540	0	0	0
n-Butanal	0.013	0.013	0	0.832	0
MACR	0.978	0	0	0	0
MVK	0.994	0	0	0	0
n-Pentanal	0	0	0	0	0.154

742

743 Table 3. Sources of ambient formaldehyde and compared with previous studies

City, season	Primary anthropogenic	Biogenic	Secondary	Background
Beijing, winter ^a	28.9	-		71.1
Beijing, summer ^a	32.3	11.8		55.9
Beijing, summer ^b	22	36	28	15
Beijing, summer ^c	76	-	18	5
New York City, summer ^d	30	-		70
Mexico City, spring ^e	42	-	>38	<21

744 Values are presented as percentages (%) of formaldehyde concentration.

745 ^a This study.

746 ^b (Yuan et al., 2012)

747 ^c (Li et al., 2010)

748 ^d (Lin et al., 2012)

749 ^e (Garcia et al., 2006)

750

Table 4. Percentages of carbonyl concentration from primary anthropogenic sources in present and previous studies in Beijing

Carbonyl	2011-2012 Winter ^a	2011 Summer ^a	2005 Summer ^b	2010 Summer ^c
Acetaldehyde	53.7	41.6	16	46
Acetone	68.1	56.2	40	38
Propanal	33.9	15.8	14	3
MEK	71.0	62.2	47	80
Butanal	49.0	15.5	8	1

Values are presented as percentages (%) of carbonyl concentration from primary anthropogenic sources.

^a This study.

^b (Liu et al., 2009)

^c (Yuan et al., 2012)

Figures

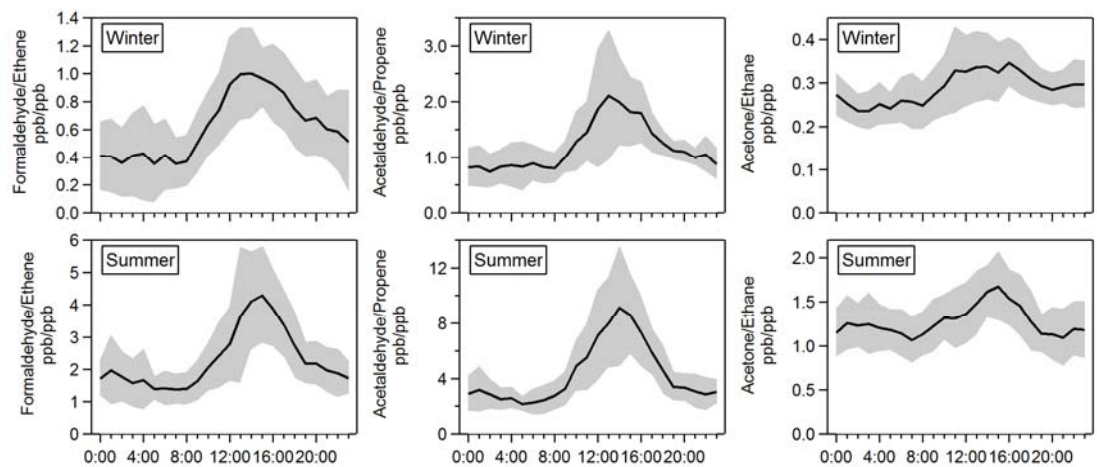


Fig. 1. Diurnal variations of ratios of formaldehyde/ethene, acetaldehyde/propene, and acetone/ethane in Beijing. Black lines are average values and grey shaded areas indicate standard deviations.

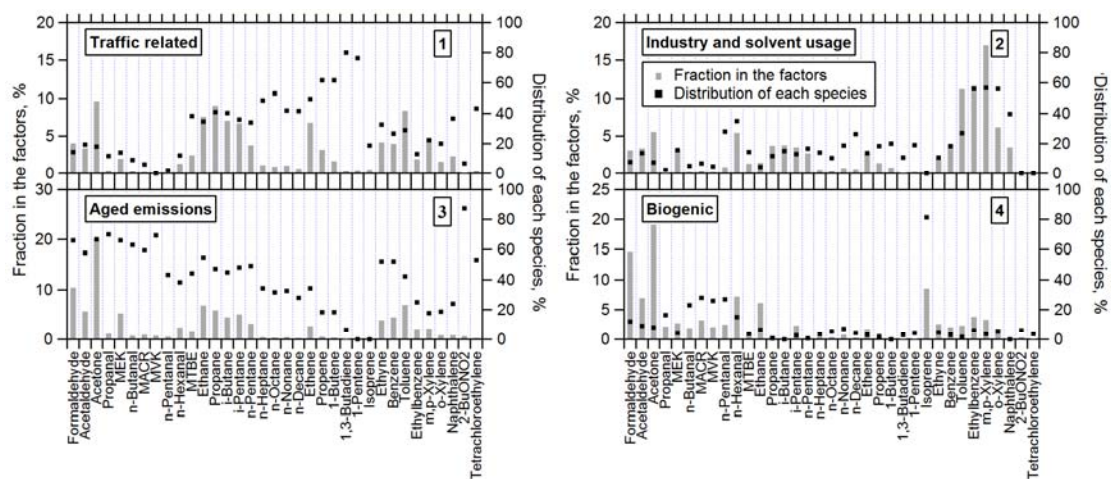


Fig. 2. Profile of the four factors resolved by PMF and the distribution of species among these factors in summer.

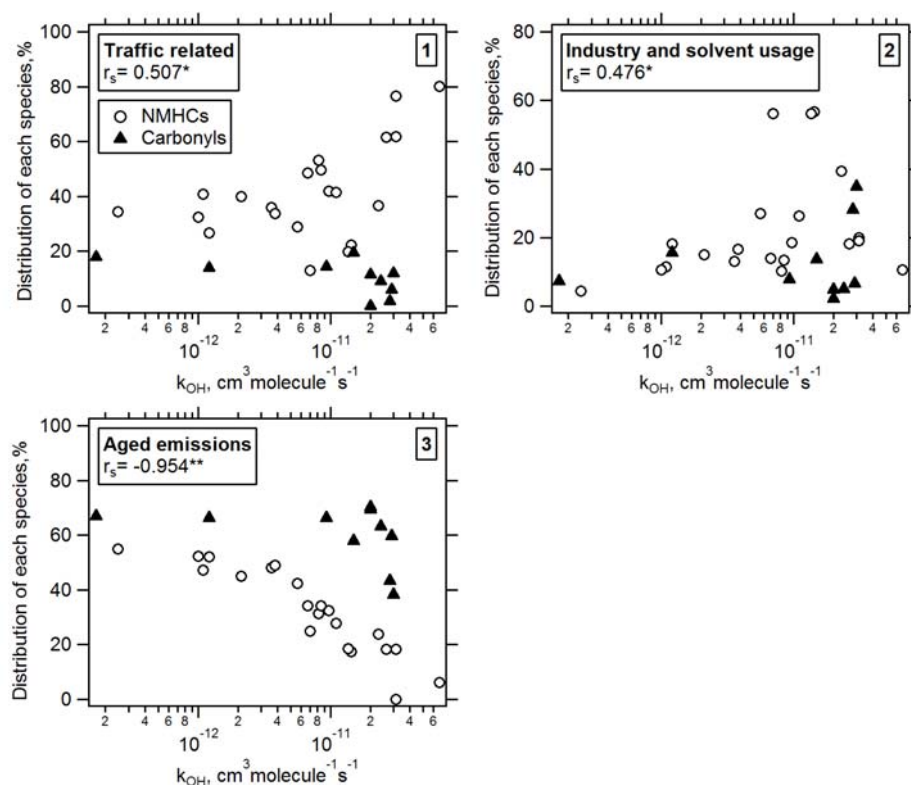


Fig. 3. Relationship between the factors contributing to each NMHC species and its k_{OH} value in summer, where each circle represents one compound. Carbonyls are shown as filled triangles in the graph, but were not used for correlation analysis due to their secondary production.

*indicates a significant correlation at a confidence level of 0.05.

**indicates a significant correlation at a confidence level of 0.01.

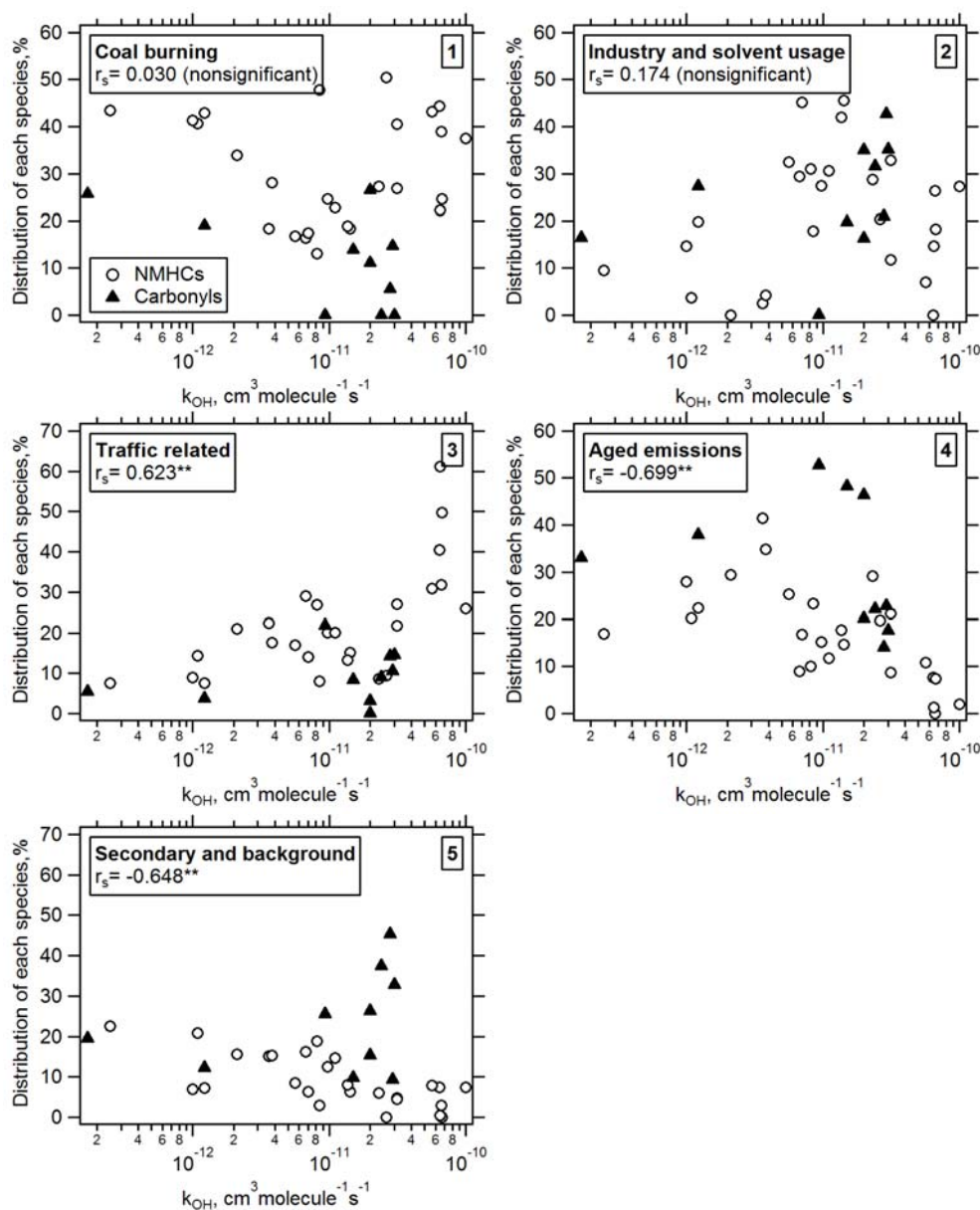


Fig. 5. Relationship between the factor contributing to each NMHC species and its k_{OH} value in winter, where each circle represents one compound. Carbonyls are shown as filled triangles in the graph, but were not used for correlation analysis due to their secondary production.

**indicates a significant correlation at a confidence level of 0.01.

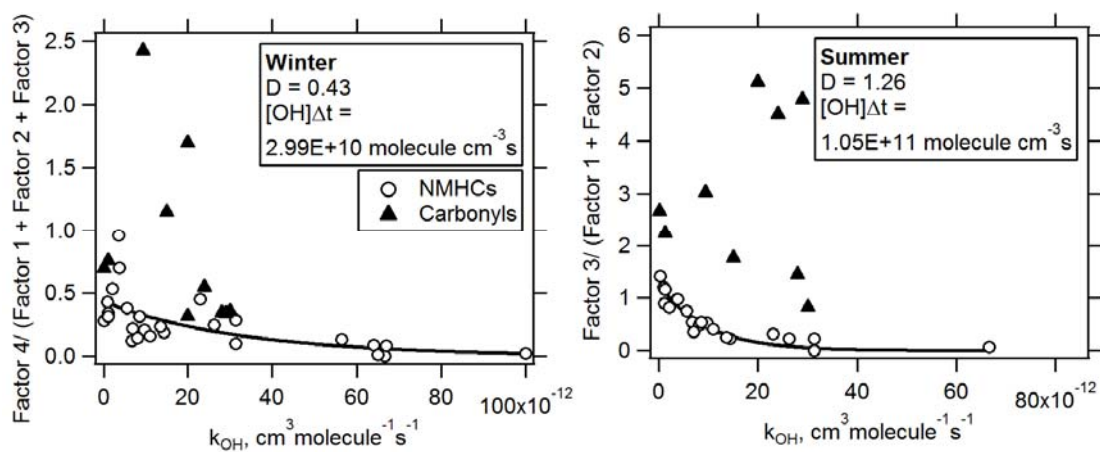
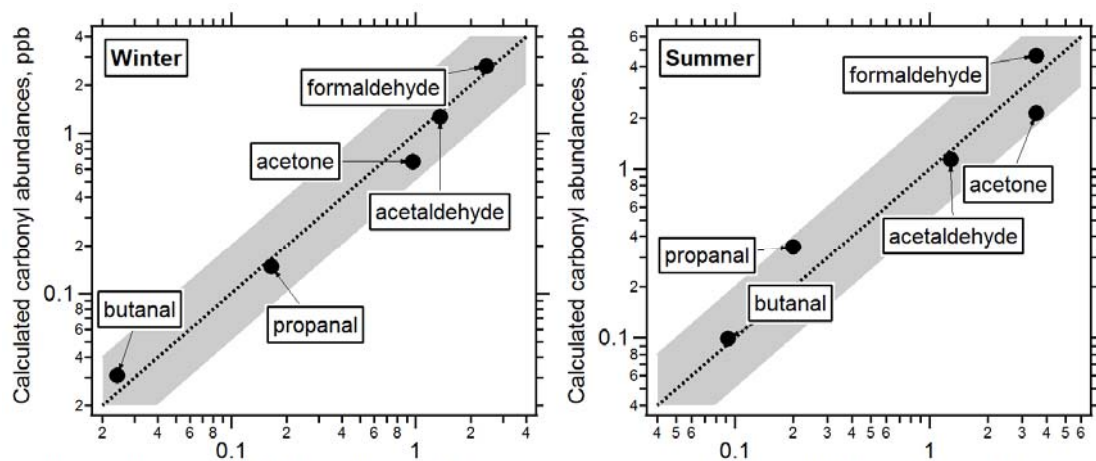


Fig. 6. Abundance ratios of NMHCs and carbonyls between the aged emissions factors and fresh emission factors, where each data point represents one compound. The lines are the fitted results from Eq. (1).



Carbonyl abundances in PMF resolved aged factor, ppb Carbonyl abundances in PMF resolved aged factor, ppb

Fig. 7. Comparison of carbonyl abundances calculated by VOCs consumptions with PMF-resolved results in aged factor. The grey shaded area shows an agreement within a factor of two.

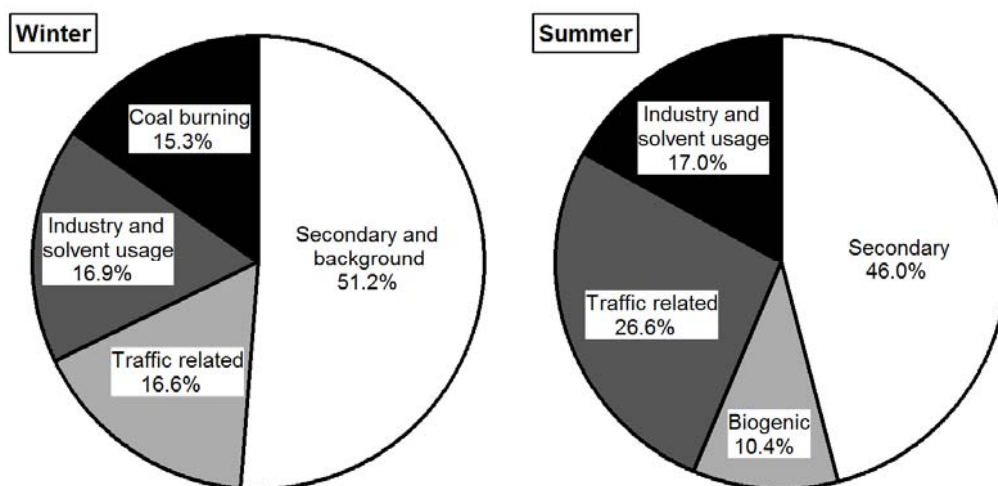


Fig. 8. Contributions of carbonyl sources in Beijing.