Atmos. Chem. Phys. Discuss., 13, 15749–15781, 2013
www.atmos-chem-phys-discuss.net/13/15749/2013/
doi:10.5194/acpd-13-15749-2013

Atmospheric Chemistry and Physics
Discussions
Open Access

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

W. T. Chen, M. Shao, S. H. Lu, M. Wang, and L. M. Zeng

State Joint Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China

Received: 19 April 2013 – Accepted: 16 May 2013 – Published: 13 June 2013

Correspondence to: M. Shao (mshao@pku.edu.cn)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Carbonyls are important intermediates in atmospheric photochemistry. To determine the relative contributions of primary and secondary carbonyl sources in Beijing, carbonyls and other trace gases were measured at Peking University in winter and summer. The Positive Matrix Factorization (PMF) model was used for source apportionment. As volatile organic compounds (VOCs) will 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 photochemically aged emissions. In summer, four factors were resolved, including an aged factor. Carbonyls in the aged factors were simulated by NMHCs 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 seasons, 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; Kim et al., 2008; Ban-Weiss et al., 2008). Carbonyls can be lost from atmosphere through reactions with the hydroxyl radical (OH), photolysis, and deposition (Lary and Shallcross, 2000). As 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. O_3, glyoxal) (Friedfeld et al., 2002; Garcia et al., 2006). However, this approach depends on marker selection, and improper markers may mislead 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 transportation. Therefore, the correlation will also be found between secondary carbonyls and the primary marker. For secondary formations, the correlation coefficient and the slope between carbonyls and the marker vary significantly depending on the VOCs/NOx 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 considering of the production of carbonyls by their precursors and the chemical removal of carbonyls during transportation. 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 SO_2 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 (Zhang et al., 2012; Liu et al., 2009) and formaldehyde displayed a significant positive trend from 1997–2010 (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. In this study, online measurements of carbonyls and other trace gases were conducted at Peking University (PKU) in winter and summer. PMF was used for carbonyl source apportionment. The influence of photochemical processing on PMF factors was investigated and tested by considering the relationship between the consumption of NMHCs and the production of carbonyls. 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 was on the top of a six-floor building on Peking University campus. This site has been described in detail elsewhere (Liu et al., 2009).

A custom-built online gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID) was used to measure C_2–C_{10} hydrocarbons, C_3–C_6 carbonyls,

C_1–C_4 alkyl nitrates, halocarbons, and methyl tert-butyl ether (MTBE), with a time resolution of 1 h. This system was 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 C_1–C_4 carbonyls and C_6–C_9 aromatics, with a time resolution of about 30 s (Yuan et al., 2013). As the proton affinity of formaldehyde is only slightly higher than water, the back reaction of proton transfer becomes significant. The kinetics of PTR-MS formaldehyde detection were 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 $\mathrm{mmol\,mol^{-1}}$ 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.

2.2 Positive Matrix Factorization (PMF)

The US 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). Previous studies have shown that carbonyl concentrations exhibit significant diurnal variations, with high values at noon due to secondary formation (Zhang et al., 2012). Because of the temporal variations of secondary carbonyls, we expected that the diurnal formation pattern would be recognized as a factor by PMF.

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-$BuONO_2$), 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 emission 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 13.19 ± 7.91 ppb in winter. In summer, the concentration was slightly higher, with the value of 16.26 ± 7.39 ppb. Such seasonal variation agreed with previous studies in Beijing, but the difference between winter and summer was much smaller than the one reported previously (Pang and Mu, 2006). Formaldehyde, acetone, and acetaldehyde were the three major species, contributing more than 80 % of the total measured carbonyls in both of these two seasons.

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 used as their reaction rates with OH were similar (Atkinson et al., 2006), so they have approximately equal removal rates. 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). 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. 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 winter, 341 samples were used for PMF analysis, and five 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 produced high values of C_2–C_3 NMHCs. These light hydrocarbons are generated mainly by combustion processes. Naphthalene, which arises largely from coal burning and diesel vehicle exhaust, can be used as a tracer (Liu et al., 2008). Factor 1 contributed 27.3 % of the measured level of naphthalene, and diesel vehicle exhaust contributes more long-chain alkanes than short-chain alkanes (Liu et al., 2008). Therefore, we identified this factor as coal burning. In addition, benzene and toluene made important contributions to this factor, and the ratio of benzene to toluene (2.31) falls between the ratios measured by Liu et al. (2008) for residential coal burning (1.81) and industrial coal burning (2.62). This ratio is much higher than the one measured in tunnel experiment (0.70) (Liu et al., 2008).

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). We observed that the distribution of benzene was lower than that of the other aromatics in this factor. As benzene has been proven to be toxic and carcinogenic (WHO, 2000), its usage in paints and solvents has been restricted in China. Most of the ambient benzene should therefore come from other sources (e.g. combustion process). Besides aromatics, factor 2 contributes an important part of measured long-chain alkanes (C_7–C_{10} alkanes), with the value of about 30 %. Previous studies have found high values of long-chain alkanes from printing emissions (Yuan et al., 2010). Tetrachloroethylene is an important organic solvent and chemical intermediate used in industrial processes (Blake et al., 2003), and factor 2 contributed 22.6 % of the measured tetrachloroethylene. Thus, we considered this factor to be related to industrial and particularly to solvent usage.

Factor 3 was dominated by C_2–C_5 alkanes, C_2–C_3 alkenes, ethyne, and aromatics. Vehicle exhaust contains a significant fraction of these species, and a part of alkanes may arise from gasoline evaporation (Liu et al., 2008). This factor explains 37.9 % of the measured MTBE, which is a compound used as a gasoline additive (Chang et al., 2006). We therefore attributed this factor to traffic related emissions.

Factor 4 made a significant contribution to the measured levels of MTBE (42.9 %), naphthalene (29.2 %), and tetrachloroethylene (35.4 %). We considered this factor to include contributions from all of the sources discussed above. This factor explained a significant part of our measured carbonyls (44.1 %), but reactive NMHCs (C_4–C_5 alkenes) made only a small contribution. Thus, we identified this factor as aged emissions from anthropogenic sources.

Few of the NMHCs, with the exception of some long-lifetime alkanes, were incorporated into factor 5. This factor accounted for most of the measured 2-$BuONO_2$ (67.7 %) and some of the measured carbonyls (19.7 %). Alkyl nitrates arise mainly from secondary production and have relatively long lifetimes (Simpson et al., 2003). We therefore considered VOC species in this factor to represent secondary production and background levels.

As discussed in Sect. 2.2, the relationship between the contribution of each factor to each NMHC species and its chemical reactivity was used to distinguish factors for photochemically aged emissions from those for fresh emissions. Such relationship was shown in Fig. 3. 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. The distributions of carbonyls are shown by filled triangles in Fig. 3. For the three fresh factors, the distributions of carbonyls were at the same or lower levels compared with NMHCs. For the two aged factors, the distributions of carbonyls showed higher levels than the NMHCs owing to secondary production via photochemical reactions.

In summer, 593 samples were used for PMF analysis, and four factors were identified (Fig. 4). The profiles of the first three factors were similar to the profiles of factors 2–4 in winter. So these three factors were identified as traffic related emissions, industry and solvent usage, and 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 can be co-emitted with biogenic VOCs (Winters et al., 2009), and formaldehyde was an important oxidation product of isoprene (Carter and Atkinson, 1996).

As shown in Fig. 5, only factor 3 displayed a significant negative correlation between its contribution to each NMHC species and its k_{OH} value. So factor 1 and factor 2 were considered to be fresh emissions, and factor 3 was photochemical aged factor.

3.3 Exploring the aged and fresh emission factors

In the last section, we have distinguished photochemical aged factors from fresh factors. To prove our analysis, we explored the relationship between NMHCs consumption and carbonyls formation in aged factors.

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

$$\frac{[\text{NMHC}]_{\text{aged}}}{[\text{NMHC}]_{\text{fresh}}} = D \cdot e^{k_{\text{OH,NMHC}}[\text{OH}]\Delta t} \tag{1}$$

$[\text{NMHC}]_{\text{aged}}$ and $[\text{NMHC}]_{\text{fresh}}$ (ppb) refer to the abundances of NMHCs in the aged and fresh factor, respectively. D is a scaling factor, which normalizes the NMHC abundance to unity, and $k_{\text{OH,NMHC}}$ 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 $[\text{OH}]\Delta t$, is calculated as a whole.

As discussed in Sect. 3.2, in winter, $[\text{NMHC}]_{\text{aged}}$ refers to the abundances of NMHCs in factor 4, and $[\text{NMHC}]_{\text{fresh}}$ refers to the sum of the abundances of NMHCs in factors 1–3. In summer, $[\text{NMHC}]_{\text{aged}}$ refers to the abundances of NMHCs in factor 3, and $[\mathrm{NMHC}]_{\mathrm{fresh}}$ refers to the sum of the abundances of NMHCs in factors 1 and 2. Figure 6 shows the dependence of $[\mathrm{NMHC}]_{\mathrm{aged}}/[\mathrm{NMHC}]_{\mathrm{fresh}}$ (circles in the figure) on k_{OH}, with the lines being the fitted results from Eq. (1). The values of D and $[\mathrm{OH}]\Delta t$ 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 $[\mathrm{carbonyl}]_{\mathrm{aged}}/[\mathrm{carbonyl}]_{\mathrm{fresh}}$ ratios (Fig. 6, filled triangles) are significantly higher than the ratios of $[\mathrm{NMHC}]_{\mathrm{aged}}/[\mathrm{NMHC}]_{\mathrm{fresh}}$ because secondary production enhances the abundance 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 emissions and the second part stands for secondary formation calculated based on NMHCs consumption.

$$[\mathrm{carbonyl}]_{\mathrm{aged}} = D \cdot [\mathrm{carbonyl}]_{\mathrm{fresh}} \cdot e^{-k_{\mathrm{OH,carbonyl}} \cdot [\mathrm{OH}]\Delta t} + D \cdot \sum \left([\mathrm{NMHC}]_{\mathrm{fresh}} \cdot \left(1 - e^{-k_{\mathrm{OH,NMHC}} \cdot [\mathrm{OH}]\Delta t}\right) \cdot Y_{\mathrm{NMHC,\,carbonyl}} \right) \tag{2}$$

$k_{\mathrm{OH,carbonyl}}$ is the OH rate constant for the carbonyl. $Y_{\mathrm{NMHC,\,carbonyl}}$ (ppb ppb^{-1}) refers to the carbonyl production yield of the NMHC, which can be estimated using the Leeds Master Chemical Mechanism (MCM v3.2 http://mcm.leeds.ac.uk/MCM/). The $Y_{\mathrm{NMHC,\,carbonyl}}$ values used in this study are listed in Table 1. The NMHC species not shown made no contribution to the carbonyls discussed in this study. D and $[\mathrm{OH}]\Delta t$ 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 $Y_{\mathrm{NMHC,\ carbonyl}}$ 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 NMHC species were not considered in the PMF analysis, and they might be precursors of carbonyls. The PMF-analyzed NMHC species accounted for 88.2 % and 80.0 % of all NMHCs measured in winter and summer respectively, but the contribution of each NMHC to the formation of carbonyls may not be equivalent to its concentrations.

3.4 Primary and secondary sources of carbonyls

Contributions of carbonyl sources in Beijing were shown in Fig. 8. The contribution of carbonyls in the aged factors were divided into aged emission part and secondary formation part as discussed in Sect. 3.3, and the aged emission part were further separated into each fresh factor considering their relative contributions. For all 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. 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).

$$F_p = \sum \left([\mathrm{NMHC}]_i \cdot k_{\mathrm{OH,NMHC}} \cdot [\mathrm{OH}] \cdot Y_{\mathrm{NMHC,\ carbonyl}}\right) \quad (3)$$

[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 2.07 and 2.46 ppb h^{-1} for formaldehyde, 0.90 and 1.20 ppb h^{-1} for acetaldehyde, 0.31 and 0.41 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 19–33 % higher than the one in winter.

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 (Laffineur et al., 2011; Lerdau et al., 1997), 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 2 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 are 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 use of CO as a primary anthropogenic marker incorporated part of the secondary formaldehyde into primary anthropogenic emissions due to the correlation between the precursors of formaldehyde and CO (Parrish et al., 2012). Compared with source apportionment studies in other regions, the contribution of primary anthropogenic sources in Beijing is similar to that in New York City, USA (Lin et al., 2012) and a bit lower than Houston, TX, USA (Buzcu Guven and Olaguer, 2011; Rappenglück et al., 2010; Friedfeld et al., 2002) and Mexico City (Garcia et al., 2006).

The contributions of primary anthropogenic sources to the levels of other carbonyls are shown in Table 3. Primary anthropogenic sources have a bit higher contribution in winter, due to less secondary production and lower biogenic emission. 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 (Yuan et al., 2012; Liu et al., 2009), our results calculated higher contributions from anthropogenic emissions for acetone, propanal, and butanal. The two previous studies in Beijing used ethyne as a primary anthropogenic marker to calculate its contributions. As demonstrated in our PMF result, there are several different primary anthropogenic sources in Beijing, and the emission ratio of carbonyl/ethyne varies among these sources. For measurements conducted inside the city, it is likely that the emissions from these sources had not effectively mixed, and the use of ethyne as a marker might have caused deviations in the results.

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 NMHCs 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 19–33 % higher than the rates in winter due to higher NMHCs 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.

Acknowledgements. This study was funded by the Natural Science Foundation for Outstanding Young Scholars (Grant No. 41125018).

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Table 1. Production yield of carbonyls from NMHCs (unit: $\text{ppb}\,\text{ppb}^{-1}$).

NMHC	Formaldehyde	Acetaldehyde	Acetone	Propanal	Butanal
Ethane		0.991			
Propane			0.705	0.259	
i-Butane	0.773		0.774		
n-Butane		0.581			0.024
i-Pentane		0.606	0.611		
n-Pentane		0.114		0.116	
2,2-dimethylbutane	0.282	0.289	0.282		
2,3-dimethylbutane			1.638		
2-methylpentane		0.035	0.195	0.192	
3-methylpentane		0.491			
Ethene	1.6				
Propene	0.979	0.979			
trans-2-Butene		1.918			
1-Butene	0.961			0.961	
i-Butene	0.988		0.988		
cis-2-Butene		1.918			
1,3-Butadiene	0.73				
1-Pentene	0.941				0.941
cis-2-Pentene		0.936		0.936	
trans-2-Pentene		0.936		0.936	
Isoprene	0.709				
Styrene	1				

Table 2. 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
Houston, autumn[d]	40	24	36	
Houston Texas region[e]	5	–	95	–
Houston, autumn[g]	47.4	–	24.1	28.5
Houston, summer[h]	36	–	64	–
New York City, summer[i]	30	–	70	
Mexico City, spring[j]	42	–	> 38	< 21

Values are presented as percentages (%) of formaldehyde emissions.

[a] This study

[b] Yuan et al. (2012)

[c] Li et al. (2010)

[d] Buzcu Guven and Olaguer (2011)

[e] Parrish et al. (2012)

[g] Rappenglück et al. (2010)

[h] Friedfeld et al. (2002)

[i] Lin et al. (2012)

[j] Garcia et al. (2006)

Table 3. Percentages of carbonyl emissions from primary anthropogenic sources in this 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 emissions from primary anthropogenic sources.

[a] This study

[b] Liu et al. (2009)

[c] Yuan et al. (2012)

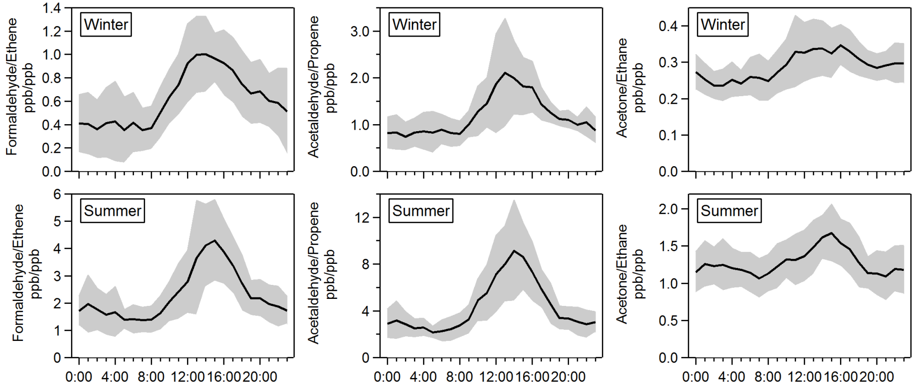

Fig. 1. Diurnal variations of ratios of formaldehyde/ethene, acetaldehyde/propene, and acetone/ethane in Beijing. Black lines are average values and grey shaded areas indicate standard deviations.

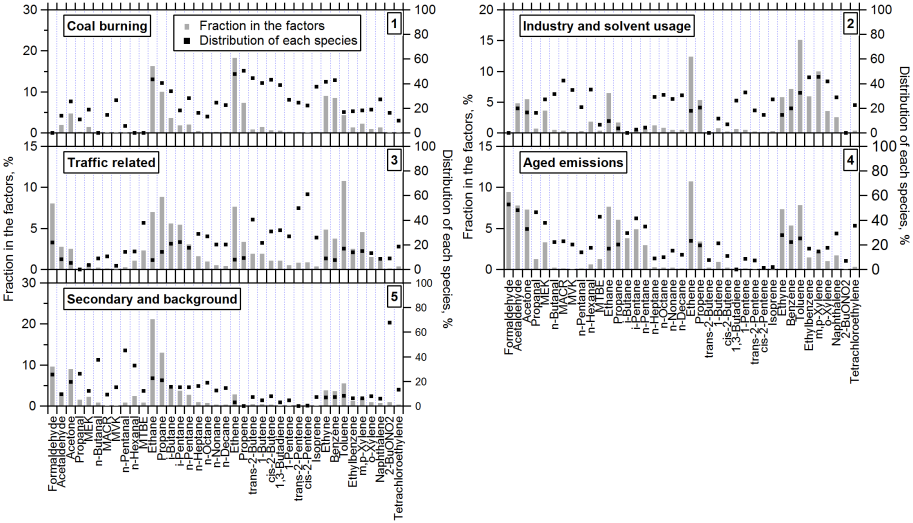

Fig. 2. Profile of the five factors resolved by PMF and the distribution of species among these factors in winter.

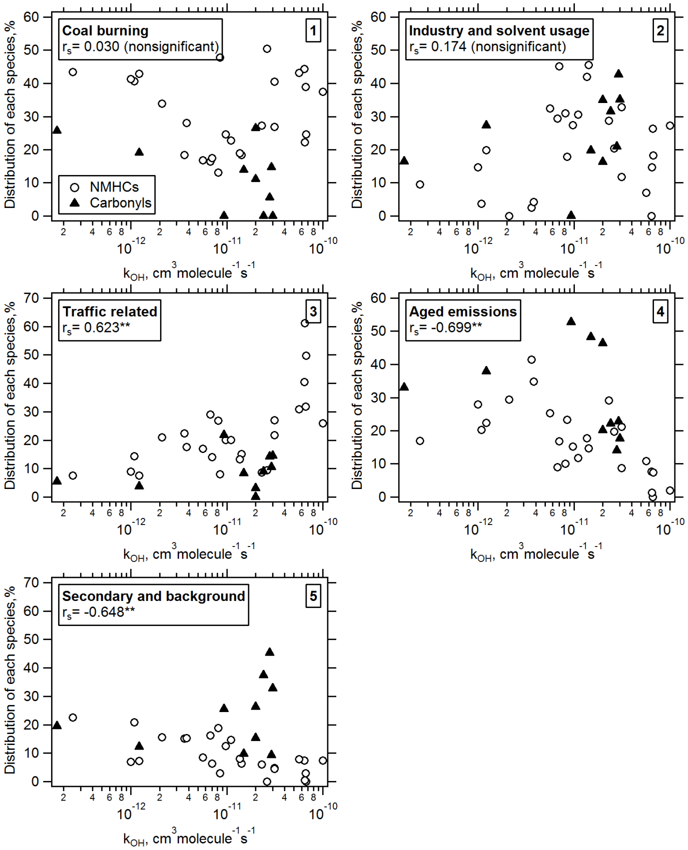

Fig. 3. Relationship between the factor contributing to each NMHC species and its k_{OH} value in winter, where each data point represents one compound. Carbonyls are shown as filled triangles in the graph, but were not used for correlation analysis due to their secondary production. **indicates a significant correlation at a confidence level of 0.01.

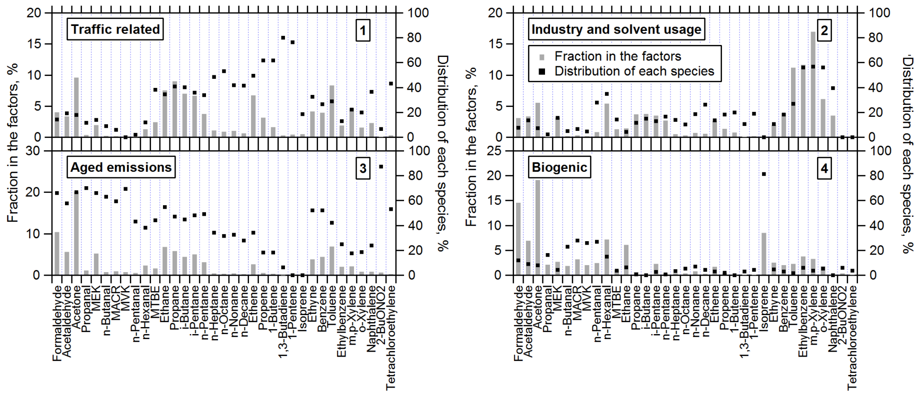

Fig. 4. Profile of the four factors resolved by PMF and the distribution of species among these factors in summer.

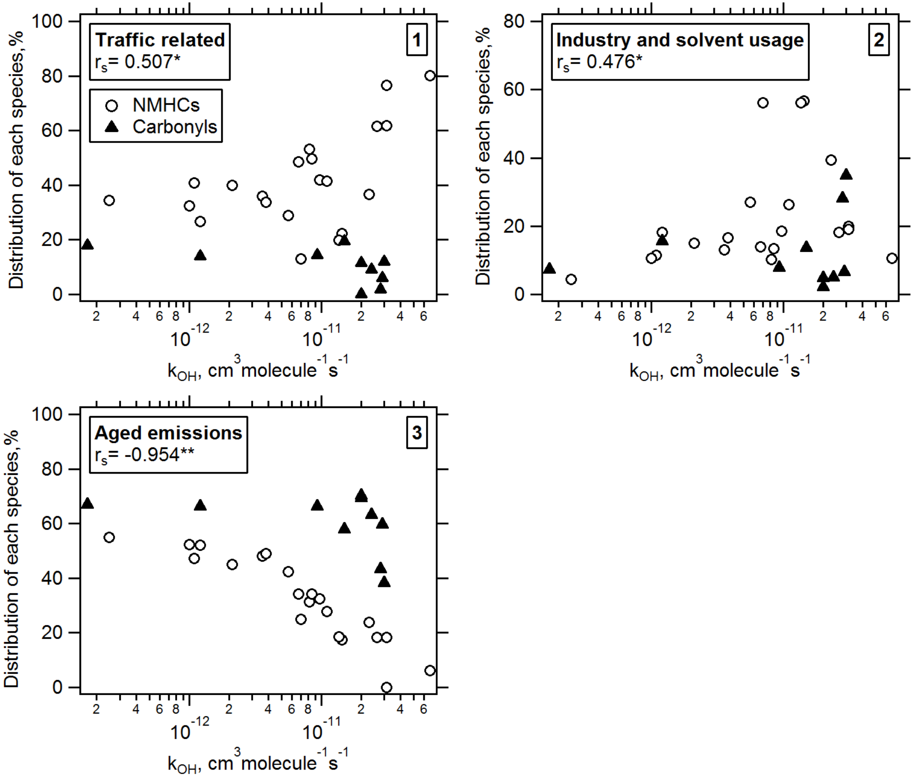

Fig. 5. Relationship between the factors contributing to each NMHC species and its kOH value in summer, where each data point represents one compound. Carbonyls are shown as filled triangles in the graph, but were not used for correlation analysis due to their secondary production.

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

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

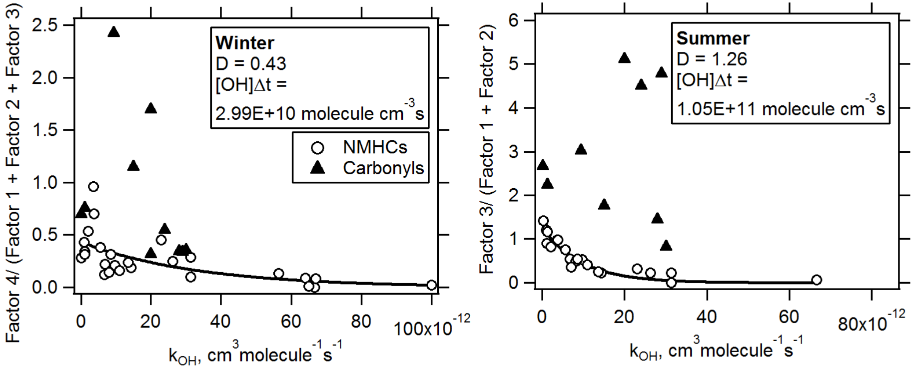

Fig. 6. Abundance ratios of NMHCs and carbonyls between the aged emissions factors and fresh emission factors, where each data point represents one compound. The lines are the fitted results from Eq. (1).

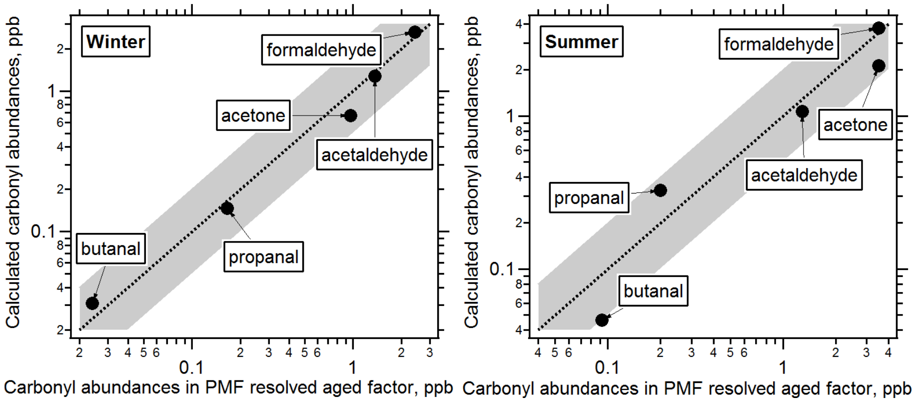

Fig. 7. Comparison of carbonyl abundances calculated by NMHC consumptions with PMF-resolved results in aged factor. The grey shaded area shows an agreement within a factor of two.

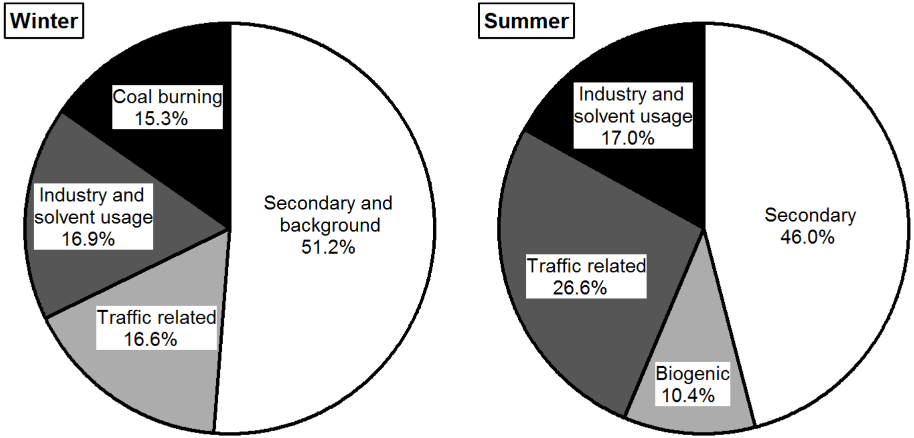

Fig. 8. Contributions of carbonyl sources in Beijing.