# Reply to Interactive comments on "Understanding primary and secondary sources of ambient carbonyl compounds in Beijing using the PMF model" by W. T. Chen et al.

MS Number: acp-2013-309

**Anonymous Referee #2**

*Summary: This paper presents an extensive analysis of an important data set based upon VOC measurements in Beijing, both in winter and in summer. A great deal of work has been put into the analysis, but at this point a coherent picture has not emerged from the discussion, and there is a clear contradiction in the results. There are presently three major shortcomings of the paper. First, many questions remain regarding the validity of the analysis, and the robustness of the conclusions. Second, the results and conclusions of this paper are not carefully compared with the results of previous analysis of similar data sets collected in Beijing, and similar analyses in other cities. I recommend that this paper not be published until it has been extensively revised. The following comments amplify on these points, and specify required revisions.*

**Reply:** We would like to thank the referee for the valuable comments. We considered thoroughly for all the comments from the referee. In our revised manuscript, we have added more information and discussion to validate our analysis, including quality assurance and quality control of VOC measurements, the rationality of PMF results, characteristics of carbonyls in Beijing and comparison with previous studies. We smoothed the text and conclusion to prevent possible contradiction and confusion, and added several sentences in revised version as well. The response to individual comments is listed below in this file.

*Major issues:*

*(1) There is a fundamental problem underlying the entire analysis in this paper. The main goal of the paper is a source apportionment of carbonyls in Beijing. However, the authors are not clear, and I think actually confuse two questions. 1) What are the apportionment of the mass of primary emissions and mass of secondary*

*production of the carbonyls? 2) What are the apportionment of observed ambient concentrations between primary emissions and secondary formation? From an air quality policy perspective, question 1) is more important for carbonyls, since they provide precursors for photochemical ozone formation. However, the analyses in this paper are based on concentrations, and absolute mass of carbonyls is not explicitly addressed, so the authors are actually attempting to address question 2). For an analysis of data collected in summer, the importance of this question relates to the diurnal evolution of the boundary layer, when relatively low emission fluxes at night can yield high ambient concentrations under a shallow nighttime inversion layer compared to the daytime situation with a deep boundary layer. This problem is compounded in this paper when two seasons, which undoubtedly have very different meteorology, are addressed without considering this difference. For example in winter, the boundary layer evolution may be much less important than in summer. As discussed by Parrish et al. [2012], source apportionment based on concentrations gives accurate information on mass apportionment of sources only if the loss rates and the effects of transport and dilution are identical for all sources. In the case of carbonyls, this identity cannot apply, because secondary sources are at a maximum rate during the daytime when dilution through the boundary layer and photochemical loss rates are also at a maximum. The authors must carefully consider the question they wish to answer, and the impact of these effects on their analysis. One approximate approach might be to limit the PMF analysis to midday data only, but that apparently was not done in this work.*

**Reply:** The sources of carbonyls are complex in urban areas. Both the primary sources and the process of secondary production have not been well understood yet. As a result, it is difficult to calculate the mass of primary emissions and the mass of secondary production of carbonyls. In this study, we focused on the apportionment of the contribution of primary emissions and secondary formation to ambient carbonyls based on observed concentrations. We hope our study will be helpful for understanding carbonyl sources, and in future, we can apportion the mass of primary emissions and mass of secondary production of these carbonyls.

PMF assumes that concentrations at receptor sites are impacted by the linear combinations of sources, which are derived as factors in the model. If the air mass inside the boundary layer is well mixed, the variation of boundary layer has equally

effects on all VOC species, and will not affect the correlation among these species. In a word, the profile of the factors will not be affected by the diurnal evolution of boundary layer. Though the absolute contribution of each factor will decrease as the boundary layer rises, the relative contribution stays the same.

Carbonyls have both secondary production and degradation during photochemical processing, and this affects our source apportionment. Because Beijing is a large city with extensive local emissions, the air mass is in fact a mixture of fresh and aged plumes. We expect that these fresh emissions can be derived by PMF model. The reliability of our derived fresh emission was carefully checked and explained in text in section in section 3.2. Based on these result, the carbonyls in the factors representing fresh emissions have theoretically no consumption, and then the primary portion of carbonyls can be estimated. Accordingly, the aged factors from PMF run are the integral of production and degradation. By using aged profile obtained from PMF model calculation, we considered that the aged factors illustrate the contribution of combined effects of production and degradation on ambient variations of carbonyls. This is really a trial by using PMF model in exploring contribution of secondary processes to ambient carbonyls. We evaluated the PMF results by comparing them with NMHCs consumption and hence carbonyls production, as well as degradation of primary carbonyls, as shown in Fig. 7. The agreement for most carbonyl species hints that this approach was to some extent reasonable.

The variation of emissions and photochemical reaction has effects on the result of source apportionment, which reflects as the diurnal variation of different sources (Fig. R1). Fresh anthropogenic sources have higher contribution at night due to much slower photochemical reactions, and aged anthropogenic sources have higher contribution at daytime. PMF itself can distinguish such variation. And due to the limitation of data points, we haven’t run PMF using daytime data only.

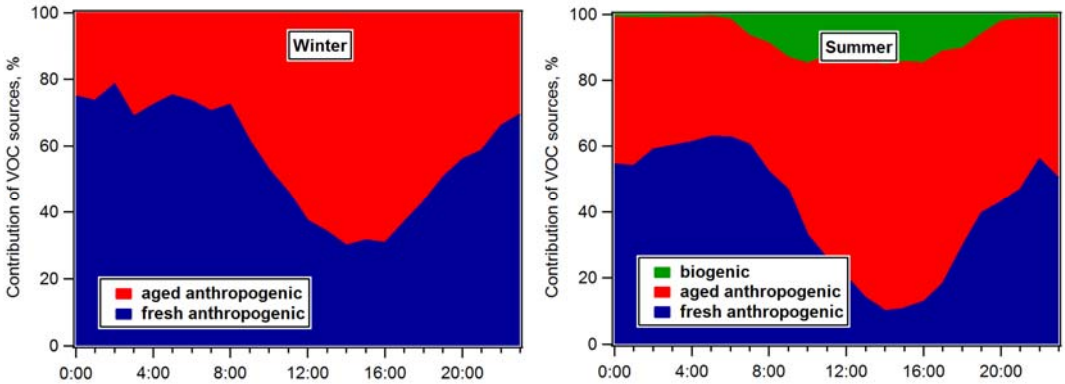


Fig. R1. Diurnal variation of VOC sources in Beijing

*(2) Examining the conclusions of this study, there seems to me to be a clear contradiction that the authors must resolve. They conclude that the contribution of secondary formation is approximately the same in the winter and in the summer. In section 3.4 the authors find that the secondary contribution (to observed ambient concentrations as indicated by Eq. 2) is nearly the same in winter and summer (51.2% and 46.0 %, respectively). They explain this rather surprising result by noting that the photochemistry is a factor of about 4 slower (i.e. lower OH in winter), but that the precursor NMHCs, especially alkenes, were much higher in winter. But these precursor NMHCs are from primary emissions, so the primary emission contribution to ambient concentrations must be much greater in winter (presumably primarily due to shallower boundary layer rather than greater emission fluxes.) Form this it follows that primary emissions of carbonyls must also be much higher in winter, but that obvious conclusion is not consistent with analysis showing that the fractional contribution of primary emissions (see Fig. 8) is approximately the same in summer and winter. I cannot really identify the source of this contradiction, but it does clearly indicate the need to completely review and modify the analysis to resolve this contradiction.*

**Reply:** It was surprising and also interesting for us that the levels of carbonyls in summer were only slightly higher than in winter and the contribution of secondary formation is approximately the same in these two seasons.

We think that the main reason for this result was that the carbonyl production rates in these two seasons were actually similar. Though the OH concentration is much higher in summer, the precursor NMHCs, especially alkenes, are much higher in

winter. As a result, our calculated carbonyl production rate in summer was only 31–53% higher than the one in winter.

The ratios of carbonyl/NMHC emitted from primary sources will not change much in one season. However, primary sources could be very different between winter and summer (e.g. Combustion sources such as coal burning has higher contribution in winter, and evaporation sources have higher contribution in summer.), and hence emission ratios of carbonyl/NMHC differ largely. Assuming that primary emissions are the major sources of VOCs at night, the values of carbonyl/NMHC ratios are approximately 3–5 times higher in summer night than those in winter night (Fig. 1). The result of PMF also showed that the emission ratios of carbonyl to ethyne were 2–5 times higher in summer than in winter. So though the levels of NMHCs are higher in winter, the primary emission contributions to ambient carbonyl concentrations are similar in these two seasons.

We have added several sentences in the section 3.4 to compare the contribution of primary emissions for carbonyls in these two seasons. "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."

*(3) Section 2.1 summarizes the measurement methods, but is very short. The reference for further details also does not give much information. It is important that the accuracy and precision of the carbonyl measurements be fully discussed in this paper, both to support the results presented and to form the basis for further discussion as suggested in many of the points below. Points to address in particular:*

*a) Evidently C3 and C4 carbonyls were measured both by GC-MS and PTR-MS; how did these measurements compare?*

**Reply:** We have added a part to discuss the inter-comparison of VOCs measurements in section 2.1 and in the supplement. C3–C4 carbonyls, C6–C9 aromatics, isoprene and MVK+MACR were measured simultaneously by online GC-MS and PTR-MS in our study. 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 (Fig.

S1 in supplement). Assuming that both of these two systems have 10% uncertainties, with the consideration of the uncertainties in VOC standard gas, in the dilution process of standard gas, and in the measurements, such agreement was reasonable and acceptable. Detailed results for inter-comparison were shown and discussed in the supplement.

*b) The measurement of formaldehyde in particular is quite difficult; have these measurements been compared with other techniques such as the DNPH technique employed by Pang and Mu (2006)? This question is particularly important given the existence of this earlier study in Beijing, which should present quite a useful comparison for and contrast with the present work.*

**Reply:** Thanks for the suggestion. DNPH measurements have not been taken during these two campaigns, but we have done an inter-comparison between PTR-MS and DNPH method at the end of 2010 (half year before our campaigns). The results showed good agreements between these two methods, with correlation coefficients larger than 0.90 and slopes ranging from 0.8 to 1.2 for formaldehyde and acetaldehyde (Fig. S2 in supplement). The results of comparison were added to section 2.1 and the supplement.

*c) A thorough discussion of any other work that has been done to verify that the reported measurements are indeed accurate and artifact free.*

**Reply:** Accepted. We added some description about these two systems, including the usage of internal standard for online GC-MS, background signal determination for PTR-MS, calibration for these two systems, and detection limits. For online GC-MS, 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%. For PTR-MS, 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 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.

Results of inter-comparison between different measurement methods were shown in

our revised manuscript, which we have mentioned in the reply to the last two comments.

In our paper, we cited two previous studies (Yuan et al., 2012;Yuan et al., 2013) which use the same two systems as we used here. Comparison between these two systems for some species has been reported by Yuan et al. (2012).

*(4) Section 3.1 is entitled "Characteristics of ambient carbonyls in Beijing". This discussion must be greatly expanded to take full scientific advantage of the existing data; specifically:*

*a) The authors reference Pang and Mu (2006), which reports carbonyl measurements from a site very close to the one used in the present study. If I understand correctly, emission sources in Beijing have changed markedly between the 2005 measurements of Pang and Mu (2006) and the 2011 measurements of the present study. How have the carbonyl concentrations responded to these emission changes? A quantitative discussion of the winter and summer seasons is required. Similarly Zhang et al., 2012 and Yuan et al., 2012 report carbonyl concentrations in Beijing for other summers. The results from both of these papers (and others if available) should be discussed as context for the present measurements.*

**Reply:** Accepted. We have added a part to compare our measured carbonyl levels with previous studies and discussed the change of carbonyls in Beijing in section 3.1. 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). We made a table to list the sum of formaldehyde and acetaldehyde concentrations measured in Beijing (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.

*b) The authors note that the seasonal variation found in the present study is "much smaller than the one reported previously (Pang and Mu, 2006)." This difference is large in that Pang and Mu (2006) found differences of a factor of 2 to 3, while the present work reports a difference of only about 25%. A full discussion of the following questions is required: What accounts for this large difference between the two studies? Does this point to a major change in the emissions in Beijing?*

**Reply:** Accepted. As mentioned in the reply to the last comment, we compared our measured carbonyl levels with previous studies (Table 1). A decreasing trend of carbonyl levels was found in summer, and in winter, carbonyl levels have not changed much. As a result, the difference between summer and winter reduced. It illustrated that the emission control policies in Beijing do make efforts. However, there might be some sources which contribute mainly in winter have not been controlled effectively. Further studies will be needed to quantify the emissions of both hydrocarbons and carbonyls from main sources in summer and winter, then to understand to what extent they change.

*The results illustrated in Fig. 1 are quite intriguing; however they require a much fuller discussion:*

*c) The statement "These three pairs of carbonyls and NMHCs were used as their reaction rates with OH were similar" needs to be clarified. I assume that this means that the reaction rates with OH of the species in the numerators are similar to those in the denominator, which should be clarified. How about photolysis? Is this likely to increase the rate of loss of the carbonyl significantly compared to the loss by OH for expected OH concentrations in Beijing?*

**Reply:** Accepted. We have changed the statement into "These three pairs of carbonyls and NMHCs were chosen because the two species in each pair have similar reaction rates with OH radical".

We added a part to discuss the contribution of photolysis to carbonyl degradation in section 3.1 and in the supplement. We compared the carbonyl loss rates by OH reaction and by photolysis, and found that the reaction with OH radical was indeed the major pathway for carbonyl degradation in Beijing. The photolysis contributes 33%, 1% and 12% to the losses of formaldehyde, acetaldehyde and acetone at daytime. and has no significant difference between winter and summer. The detailed estimation was given in the supplement.

To evaluate the influence of neglecting photolysis, we estimated the amount of carbonyl removal in one hour through photolysis and recalculated the carbonyl/NMHC ratios, which were shown as red dash lines in Fig R2. If there's no carbonyl photolysis, the ratios of formaldehyde/ethene will be higher at daytime, but it has little effects on the ratios of acetaldehyde/propene and acetone/ethane. The

measured noon/night ratios of formaldehyde/ethene ratios in winter and summer were 2.6 and 3.1, respectively. After correcting the effect of photolysis, such ratios increased to 2.7 and 3.4. Still, the contribution from secondary source has no great difference between these two seasons.

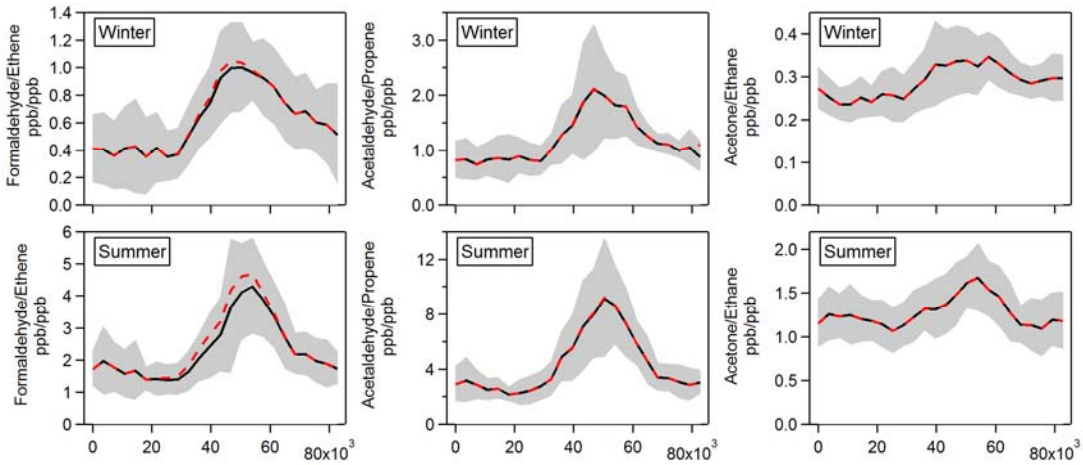


Fig. R2. Diurnal variations of ratios of formaldehyde/ethene, acetaldehyde/propene, and acetone/ethane in Beijing. Black lines are average values and grey shaded areas indicate standard deviations. Red dash lines are the ratios with the correction of the effect of photolysis.

Neglecting the carbonyl photolysis will underestimate the contribution of secondary production at daytime. However, our aim is to compare the diurnal variation of carbonyl/NMHC ratios between winter and summer. As the contribution of photolysis to the removal of carbonyls has no difference between these two seasons (see Fig. S3 in supplement), neglecting photolysis has little effect on comparing the contribution of secondary formation between winter and summer.

*d) The authors report relatively small seasonal difference in the absolute carbonyl concentrations (see point 2b above), yet the ratios in Fig. 1 are much higher in summer than in winter. Evidently this means that the concentrations of the hydrocarbons are much smaller in summer than in winter. Is this true? If so this should be discussed in this section.*

**Reply:** Accepted. The concentrations of NMHCs were about two times higher in winter. Especially for some alkenes, the concentrations can be 2-5 times higher in winter. We added some sentences in section 3.1 to discuss the different carbonyl/NMHC ratios between winter and summer. “Though the diurnal patterns 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."

*e) The diurnal variation shown in Fig. 1 is qualitatively taken to indicate "an important contribution from secondary production during the day time, both in winter and summer." This qualitative indication must be put on a much more quantitative basis. Specifically:*

*i) Can the magnitudes of the diurnal cycles for the three pairs species be rationalized on the basis of the differences in OH rate constants with the same assumed diurnal profile of OH concentrations for each pair? (Calculations similar to those presented by Stroud et al., 2001 and Roberts et al., 2001 would be appropriate.)*

**Reply:** Thanks for the suggestion. Stroud et al. (2001) have calculated the ratios of MVK/isoprene and MACR/isoprene, and Roberts et al. (2001) have calculated the ratios of PAN/acetaldehyde and PPN/propanal. They compared the relationship between two pairs of VOC species with the predicted line to study the photochemical process. Such estimation based on two important assumptions: (1) the measured sample is an isolated air plume, and will not mix with other air plumes; (2) the species in the denominator is the only precursor of the species in the numerator, and the species in the numerator has no other primary sources. With such assumptions, the degradation of the species in the denominator and the production of the species in the numerator can be estimated based on the process of photochemical reactions.

However, the relationship between the carbonyl/NMHC pairs is much more complex in this study. The NMHC in the denominator is not the precursor, or not the only precursor of the carbonyl in the numerator. And for carbonyls, they have primary emissions other than secondary production.

As a try, we calculated the predicted relationship between two pairs of carbonyl/NMHC ratios, and showed as a blue line in Fig. R3. The process of

calculation was described briefly as follow.

(1) The OH exposure of each sample was calculated based on the ratio of 2-BuONO$_2$/n-Butane (Shao et al., 2011).

(2) The emission ratio of each NMHC was calculated based on Eq. (R1) (Yuan et al., 2012).

$$[\mathrm{NMHC}] = ER_{\mathrm{NMHC}} \times [C_2H_2] \times exp\left(-\left(k_{\mathrm{NMHC}} - k_{C_2H_2}\right)[OH]\Delta t\right) \quad \text{(R1)}$$

(3) The predicted NMHC concentration at given OH exposure value was calculated using Eq. (R1).

(4) The predicted carbonyl concentration at given OH exposure value was calculated as the sum of the residual primary emissions (Eq. (R2)) and secondary production from all VOC species (Eq. (R3)).

$$[\mathrm{Carbonyl}] = ER_{\mathrm{Carbonyl}} \times [C_2H_2] \times exp\left(-\left(k_{\mathrm{Carbonyl}} - k_{C_2H_2}\right)[OH]\Delta t\right) \quad \text{(R2)}$$

$$[\mathrm{Carbonyl}]_{formation} = Y_{VOC,carbonyl} \times ER_{VOC} \times [C_2H_2] \times \frac{k_{VOC}}{k_{carbonyl} - k_{VOC}} \times \frac{exp(-k_{VOC}[OH]\Delta t) - exp(-k_{carbonyl}[OH]\Delta t)}{exp(-k_{C_2H_2}[OH]\Delta t)} \quad \text{(R3)}$$

In this work, we cannot calculate the exact photochemical ages, so we used OH exposure to weigh the extent photochemical aging. In winter, we calculated the carbonyl/NMHC ratio with OH exposure ranging from 0 to 3 × $10^{10}$ molecule cm$^{-3}$ s (from 0 to 5.6 hour at an average OH concentration of 1.5 × $10^6$ molecule cm$^{-3}$). In summer, we calculated the carbonyl/NMHC ratio with OH exposure ranging from 0 to 1.5 × $10^{11}$ molecule cm$^{-3}$ s (from 0 to 6.9 hour at an average OH concentration of 6.0 × $10^6$ molecule cm$^{-3}$). We compared the predicted acetaldehyde/propene ratios with formaldehyde/ethene ratios and acetone/ethane ratios with formaldehyde/ethene ratios at different OH exposure, and showed as blue lines in Fig. R3. The measured ratios in diurnal cycles were shown as red circles. Generally, the two sets of data agreed with each other. The carbonyl/NMHC ratios were higher at noon, which corresponded to higher OH exposure.

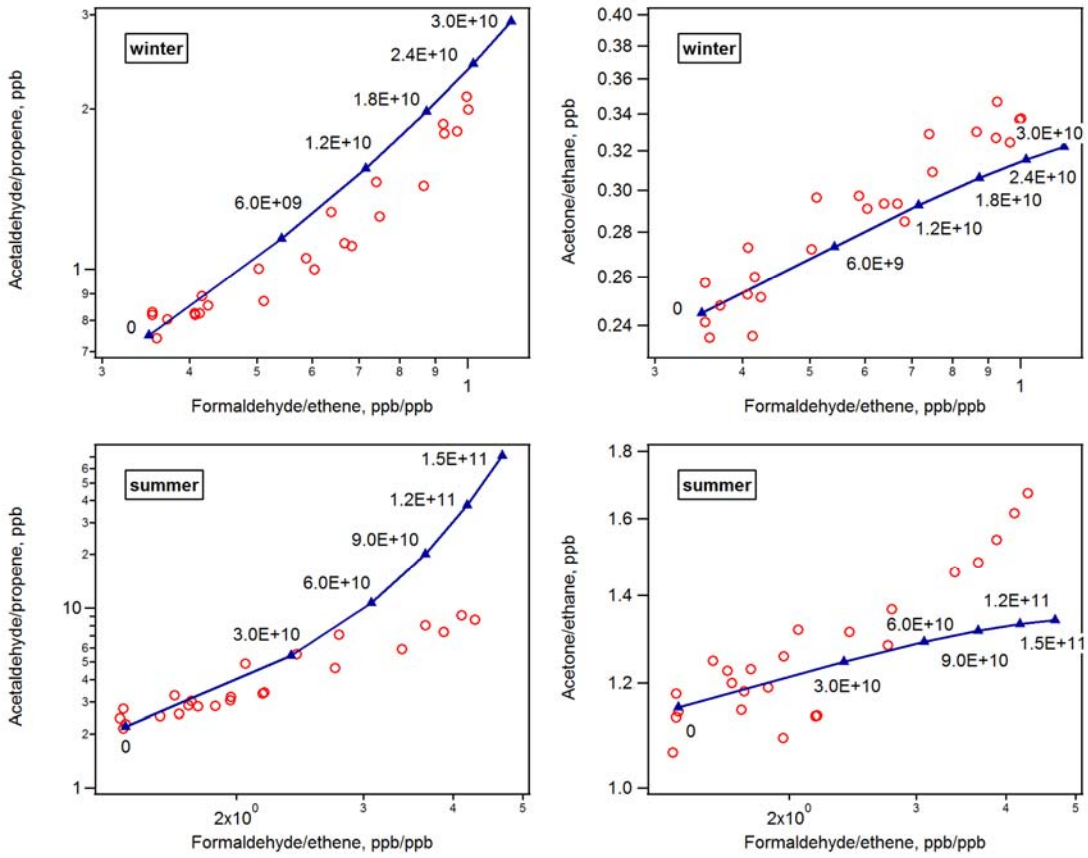


Fig. R3. Correlation of two pairs of carbonyl/NMHC ratios. The blue lines indicate aging of an isolated air plume beginning at the estimated emission ratios. The numbers on the lines are OH exposure, in units of molecule $cm^{-3}$ s. Red circles indicate our measured carbonyl/NMHC ratios.

The measured ratios of acetaldehyde/propene to formaldehyde/ethene were a bit lower than the predicted lines, and the measured ratios of acetone/ethane to formaldehyde/ethene were a bit higher than the predicted lines. As mentioned above, the predicted lines are calculated based on the assumption that the measured sample is an isolated air parcel. However, Beijing is a large city with extensive local emissions, and our measured sample is in fact a mixture of fresh and aged plumes. Parrish et al. (2007) have studied the effect of mixing on hydrocarbon ratios in the troposphere. While studying an air plume with species emitted at different times, an average photochemical age can be used. However, the average photochemical ages are different for each species. The photochemical ages for longer-lived VOCs are older than shorter-lived VOCs. Acetaldehyde is more reactive than formaldehyde. As a result, the photochemical age of acetaldehyde is shorter than the age of formaldehyde in our measured air plumes. This explains the reason that our

measured ratios of acetaldehyde/propene to formaldehyde/ethene were lower than the predicted lines. Similarly, acetone is less reactive than formaldehyde, and the measured ratios of acetone/ethane to formaldehyde/ethene were higher than the predicted lines.

As discussed above, we can rationalize the diurnal variation of carbonyl/NMHC ratios reasonable and explain the difference between measurement and prediction qualitatively. However, the process of calculation is complex and beyond the scope of this work. In our study, we calculated the diurnal variations of these three pairs of carbonyl/NMHC mainly aim to compare the diurnal pattern of secondary formation between winter and summer.

*ii) Can the seasonal differences in the magnitude of the ratios and in their diurnal cycle magnitudes really be rationalized by a reasonable seasonal difference in OH concentration and diurnal cycle?*

**Reply:** As mentioned in the reply to last comment, we have tried to rationalize the diurnal cycles of carbonyl/NMHC ratios in winter and summer (Fig. R3). The maximum carbonyl/NMHC ratios appear at noon, and refer to OH exposure of $2.4 \times 10^{10}$ molecule $cm^{-3}$ s in winter and $1.2 \times 10^{11}$ molecule $cm^{-3}$ s in summer. Assuming that average OH concentration is $1.5 \times 10^{6}$ molecule $cm^{-3}$ in winter and $6.0 \times 10^{6}$ molecule $cm^{-3}$ in summer, the photochemical ages at noon are 4.4 and 5.6 hour in winter and summer, respectively. We think such result is reasonable.

*As the authors note, previous work (in Beijing and elsewhere) has generally concluded that primary emissions dominate urban carbonyl concentrations in wintertime. Thus, the authors must strongly support their contention that photochemical production is an important source in winter in Beijing.*

*5) Section 3.2 is devoted to "Identifying PMF factors". I do not believe that the identification of the factors is completely objective and rigorous, and doubt the validity of the results. Indeed, I strongly question the value of using PMF analysis in any attempt to apportion the sources of pollutants with strong secondary sources such as these carbonyls. The work of Parrish et al. [2012] and Yuan et al. [2012] (this latter paper is from the same laboratory as the authors of the present paper) provide strong support for these doubts and questions.*

**Reply:** Parrish et al. (2012) have pointed out that separating carbonyl sources based

on correlation with tracers of primary emission and secondary production may mislead, as we mentioned in the 2nd paragraph of introduction. Yuan et al. (2012) proved the capacity of PMF approach in identifying the role of chemical aging for better understanding the PMF factors. Specifically, VOC emission ratios derived from PMF fresh factors agreed well with the ERs calculated based on photochemical ages (Fig. 11 in that paper), so PMF can identify the contribution from primary emissions reasonably. And the amounts of NMHCs in PMF aged factors can be reproduced by the photochemical aging of fresh factors (Fig. 12 in that paper) (Yuan et al., 2012).

In our study, we attempt to perform a quantitative analysis of carbonyls sources based on the progress given by Yuan et al. (2012). Here we also compared our derived VOC emission ratios in 2011 summer to the emission ratios calculated by the photochemical age-based parameterization method in 2010 summer (Fig. R4). The emission ratios derived from PMF were calculated by adding the traffic related factor and the industry and solvent usage factor together. The results showed good agreement between these two independent method for both NMHCs and carbonyls (slope = 1.06, R = 0.91). This indicated that our PMF analysis derived fresh emissions reasonably and primary carbonyl emissions can be distinguished. The emission ratio of n-butanal was quite low, and this may lead to larger errors.

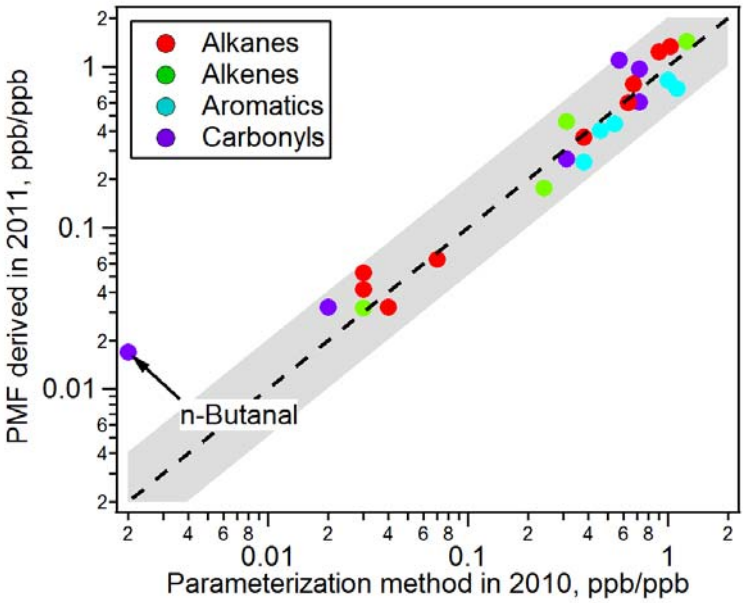


Fig. R4. Comparison of emission ratios of VOCs to ethyne from PMF in 2011 with the photochemical age-based parameterization method in 2010. The dashed line indicates the 1:1 relationship, and the grey shaded area shows an agreement within

a factor of two. The emission ratios calculated by parameterization method were reported by Yuan et al. (2012).

For understanding the carbonyls in the aged factors, we reproduced the abundances of carbonyls in the aged factors using eq. (2). We found that the abundances of carbonyls can be explained by two parts, aged direct emissions and production from VOCs consumptions. Such results indicated that the sources of carbonyls apportioned by PMF can be explained by the process of photochemical aging, and PMF can be used for source apportionment of VOCs with secondary production.

There is one problem still remains 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. The influence of such approximation requires further research, and a photochemical model may validate such approximation.

*I am most skeptical about the first factor discussed: coal burning. As far as I am aware, coal burning is not a significant source of light hydrocarbons. If I am mistaken in this regard the authors must provide definitive references showing such emissions from coal combustion. In particular, the light alkenes are important markers for traffic related emissions, so should appear primarily in the "traffic related" pattern. My suspicion is that the first, second and third wintertime factors somehow mix multiple sources, and the correlations on which they based are really caused by completely different factors than simply the sources. These confounding factors could be nighttime vs. daytime data. As far as I am aware (and as is implicitly implied by later discussion in this paper, as well as the discussion in Yuan et al., 2012) there is no guarantee that any particular PMF factor actually corresponds to any particular source, or indeed any source at all. The authors must remember that PMF is just a fancy technique for dealing with correlations between data, and does not necessarily indicate cause. Correlations between ambient concentrations can arise from a wide variety of transport, dilution and loss processes, in addition to source processes.*

**Reply:** Source profile of coal burning has been measured by Liu et al. (2008) and Wang et al. (2013), and light hydrocarbons are major NMHC species emitted from coal burning. As the result of these two studies, C2–C3 NMHCs contributed 53–63% of all measured NMHCs. Vehicles do emitted light hydrocarbons, but also with large

amount of C4–C5 NMHCs. C2–C3 NMHCs only contributed 20–24% of all measured NMHCs in vehicle exhaust (Liu et al., 2008). On the other side, 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). However, in tunnel experiment, the measured benzene to toluene ratio is 0.70 for traffic related sources (Liu et al., 2008), much lower than our calculated ratio. So we considered the first factor in winter could better be coal burning rather than traffic related emissions. On the other side, this factor was identified only in winter, because coal is widely used for central heating and domestic heating as the cold weather in winter of Beijing, and such sources are greatly reduced in summer. The work of Wang et al. (2013) has proved the importance of coal burning in winter of Beijing.

The contribution of each factor has its own diurnal cycle. For example, fresh factors have larger contribution at night, and aged factors have larger contribution in the daytime (Fig. R1). We think the diurnal variation of factors are reasonable and reflect the characteristic of sources. Because photochemical reactions are quite slow at night, most of measured VOCs are from fresh emissions, and contributions from these fresh factors are high. In the daytime, intensive light speeds up photochemical reactions and fresh emissions aged quickly. So contributions from fresh factors are low, and most of measured VOCs are identified as aged emissions.

*However, some of the other factors, particularly the summertime factors, do seem to be physically reasonable. If the authors do wish to present the PMF analysis, I suggest they begin by discussing the summer factors, since those factors seem to be simpler. Then follow with the discussion of the winter factors, pointing out similarities and differences. Finally discuss the three primary emission factors (currently identified as wintertime "coal burning", "industry and solvent use" and "traffic related"), and emphasizing the large uncertainties involved. A better approach may be to not attempt to identify a factor with a particular source category, and simply point out that (based on Fig. 5) in summer factors 1 and 2 correspond to fresh emissions, and factor 3 to aged emissions; this approach is close to that of Yuan et al. [2012]. Regardless, the authors must clearly discuss the uncertainty inherent in assigning PMF factors to particular sources.*

**Reply:** Thanks for the suggestion. Now we begin our PMF factors analysis with the

summer factors, and then follow with winter factors. The first factor in winter has very similar characteristic with coal burning, which has been discussed in the reply to the last comment. The other two fresh factors ("industry and solvent" and "traffic related") were similar to the corresponding factors in summer. For these three primary emission factors, we have compared their profiles with previous reported source characteristics to identify their actual meaning. As a result, we think our identification of primary factors is reasonable.

6) *If this PMF analysis is included in this paper, it must be fully discussed in the context of other PMF analysis performed on Beijing data. Yuan et al. [2012] report such an analysis for a data set collected at this same site in summer one year earlier than the present data set. However, the PMF analysis seems to be completely different. A clear discussion comparing these two analyses (and any others available) must be included.*

**Reply:** Accepted. We think there is no essential difference between our result and the work of Yuan et al. (2012). Both of these two works found that photochemistry plays an important role while using PMF to analysis reactive VOC species. Yuan et al. (2012) identified a mixed fresh emission factor and two aged factors with different photochemical ages. In our study, we identified two separated fresh factors and an aged factor. We added a paragraph in section 3.2 to discuss the reasons of such difference. Yuan et al. (2012) has concluded that the result of PMF dependes 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. The detailed information about calculating o-xylene/ethylbenzene ratios was introduced in supplement. Figure S4 in the supplement showed the diurnal variations of o-xylene/ethylbenzene ratios in 2010 and in 2011. As the chemical reactivity of o-xylene is higher than ethylbenzene, the ratios of o-xylene to ethylbenzene will be higher in fresh air mass and lower in aged air mass. The o-xylene/ethylbenzene ratios have similar diurnal variations in these two years. However, the relative standard deviations of o-xylene/ethylbenzene ratios were 30% higher in 2010 than in 2011. This means the variation of degrees of photochemical processing is larger in 2010. As a result, PMF factors in 2010 were extracted mainly according to different degrees of photochemical processing, and PMF factors in 2011 were extracted mainly based on individual sources.

498 *7) Pg. 15758, lines 23-26 - the statement "For the three fresh factors, the*
499 *distributions of carbonyls were at the same or lower levels compared with*
500 *NMHCs. For the two aged factors, the distributions of carbonyls showed higher*
501 *levels than the NMHCs owing to secondary production via photochemical*
502 *reactions." is not clear, and its significance must be discussed.*

503 **Reply:** Accepted. We have changed the statement into "If all factors were fresh
504 factors, the distribution of carbonyls will be similar to the distribution of NMHCs in
505 each factor. As aged factors existed, the distributions of carbonyls will be higher in
506 these factors owing to secondary production via photochemical reactions, and
507 meanwhile, the distributions of carbonyls will be lower in the fresh factors. In factors
508 1 and 2, the distributions of carbonyls were at the same or lower levels compared
509 with NMHCs. And in factor 3, the distributions of carbonyls showed higher levels
510 than the NMHCs." Such appearance can help us to distinguish between fresh
511 emissions and aged emissions.

512 *8) Pg. 15759, lines 4-6 - The following statement is misleading: "These carbonyls*
513 *can be co-emitted with biogenic VOCs (Winters et al., 2009), and formaldehyde*
514 *was an important oxidation product of isoprene (Carter and Atkinson, 1996)."*
515 *Any primary biogenic emission of carbonyls is minor compared to the secondary*
516 *formation from oxidation of isoprene. The secondary formation should be*
517 *emphasized first, and the possible primary emissions mentioned later, if at all.*

518 **Reply:** Accepted. We have changed the statement into "These carbonyls were
519 important oxidation products of biogenic VOCs (Carter and Atkinson, 1996) and can
520 be co-emitted with them (Winters et al., 2009)."

521 *9) Pg. 15763, lines 8-12 - The comparison to other urban areas is poorly done. It is*
522 *useful to compare Beijing to New York City and Mexico City, but not to Houston,*
523 *which is unique due to the very large industrial sources of alkenes. For Houston*
524 *Parrish et al. [2012] find a very low primary contribution (5%), which does*
525 *disagree with the other references, but is much more likely correct than the other*
526 *references. A more balanced discussion is required.*

527 **Reply:** Accepted. We have deleted the comparison with Houston. Now the
528 comparison was described as "New York City and Mexico City were two mega cities
529 with large populations and large amounts of vehicles, which were similar to the

530 situation of Beijing. The contribution of primary anthropogenic sources in Beijing is
531 similar to that in New York City (Lin et al., 2012) and a bit lower than Mexico City
532 (Garcia et al., 2006)."

533 *10) Much of the discussion at the end of Section 3.4 is highly speculative, and not*
534 *supported by strong evidence. It should be so supported or eliminated.*

535 **Reply:** Accepted. We have deleted the speculative discussion and focused on the
536 change of carbonyl sources. Compared with previous studies in Beijing (Liu et al.,
537 2009; Yuan et al., 2012), the contribution from anthropogenic emissions for
538 acetaldehyde in 2011 was similar to the result of 2010, but much higher than 2005.
539 This indicated a significant change in acetaldehyde sources from 2005 to 2011.
540 Though the concentration of acetaldehyde have decreased from 3.6 ppb (Shao et al.,
541 2009) to 2.3 ppb, the contribution of anthropogenic emissions increased from 0.58
542 ppb to 0.97 ppb. As the specific sources of primary acetaldehyde have not been
543 distinguished in 2005, the reason for such change was unclear. For acetone, propanal,
544 and butanal, our results calculated a bit higher contributions from anthropogenic
545 emissions than previous studies.

546 *Minor issues:*

547 *There are minor misusages of English. These do not really detract from the*
548 *understanding of the paper, but should be corrected if possible. The following 5 points*
549 *are examples on Pg. 15751*

550 *1) P. 15751, line 5 - "As the complexity of carbonyl sources and sinks, ..." would be*
551 *better worded as "Due to the complexity of carbonyl sources and sinks, ..."*

552 **Reply:** corrected.

553 *2) P. 15751, line 13 - "may mislead results" better as "may give misleading results"*

554 **Reply:** corrected.

555 *3) P. 15751, line 19 - "For secondary formations" better as "For secondary*
556 *formation"*

557 **Reply:** corrected.

558 *4) P. 15751, line 24 - "with considering of the pro-" better as "with the consideration*
559 *of the pro- "*

**Reply:** corrected.

*5) P. 15751, line 26 - " transportation." better as "transport."*

**Reply:** corrected.

*Other minor issues:*

*6) Attention should be paid to the proper number of significant figures. For example on pg. 15755, 13.19±7.91 ppb should be 13.2±7.9 ppb. Also, I assume that the indicated uncertainty is actually the standard deviation of the measurements. This should be explicitly stated.*

**Reply:** Accepted. The uncertainty of measured concentration is the standard deviation of the measurements. We have added such statement at the beginning of section 3.1. Considering that the accuracy of standard gas is ± 5%, there should be one significant figure after decimal point. We have corrected this problem.

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