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 #1

This paper investigates the contributions of primary anthropogenic sources and secondary formation to atmospheric carbonyls in Beijing during summer and winter, based on PMF model for source appointment of VOCs measured by the authors. The techniques used for measurements of VOCs and carbonyls are reliable, and the data analysis is logical and comprehensives. This reviewer recommend the paper be published in the Journal after considering the following specifics.

Reply: We thank the referee for his valuable comments. We considered thoroughly for the comments from the referee, the point-to-point responses are listed below.

It is better to consider the loss of photolysis of carbonyls, especially for formaldehyde and acetone, besides the loss of their reactions with OH. The estimation of photochemical reactions to atmospheric carbonyls might be largely underestimated without considering their loss from photolysis. Page 8 line 175-177, this statement is not correct, because the dominant loss paths for atmospheric formaldehyde and acetone in Beijing are through photolysis, not by the reactions with OH radicals. The three pairs of ratios of the carbonyls to the NMHCs also largely masked the contribution of photochemical reactions to atmospheric formaldehyde and acetone.

Reply: Accepted. This is an important point. We add a few lines 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.

We have changed the statement of that sentence into "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.” At the end of section 3.1, we pointed out that photolysis of carbonyls have not been considered while using the carbonyl/NMHC ratio method. Then we listed the relative contribution from photolysis to carbonyl removal to improve that OH reaction was the major pathway for carbonyl degradation.

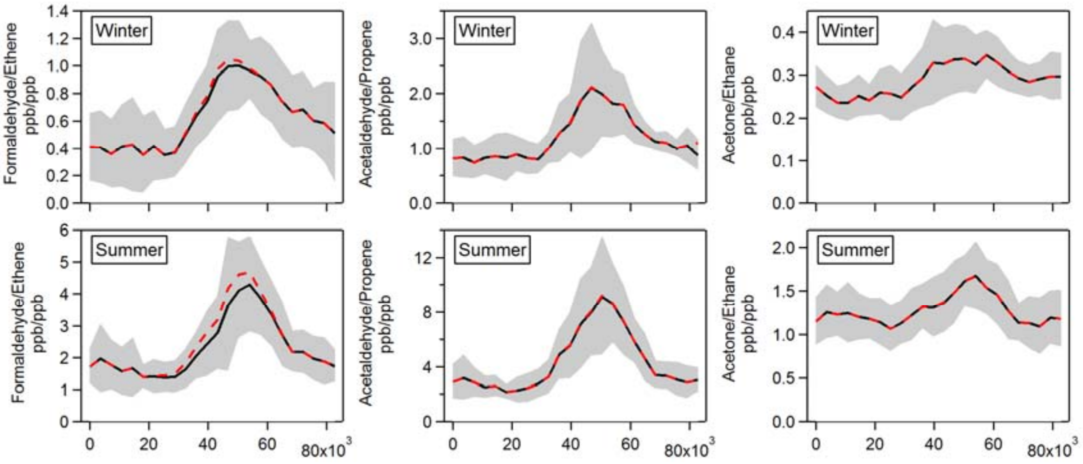

Fig. R1. Diurnal variations of ratios of formaldehyde/ethene, acetaldehyde/propene, and acetone/ethane in Beijing. Black lines are average values and grey shaded areas indicate standard deviations. Red dash lines are the ratios with the correction of the effect of photolysis.

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 R1. 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.

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.

Page 9 line 201, it is better replaced "produced" by "accompanied".

Reply: Accepted and changed.

In addition to the NMHC, the contribution of acetaldehyde degradation is better to be considered, as its fast reaction with OH and it is abundant in the atmosphere of Beijing.

Reply: Accepted. Now we have considered the contribution from carbonyl degradation while calculating secondary formation for carbonyls. We found that acetaldehyde degradation do have important contribution to formaldehyde production. Specifically, in section 3.3, we considered the contribution from carbonyl degradation while calculating carbonyl abundances in the aged factor. The results agreed with the PMF-resolved abundances as well. In section 3.4, we considered the contribution from carbonyl degradation while calculating carbonyl production rates (F_p). The calculated F_p turned higher than previous results, but F_p in summer was only 31–53% higher than the one in winter. It indicated that carbonyl formation abilities had no great difference between winter and summer.

The contribution of extremely high reactive NMHCs to atmospheric carbonyls may be underestimated based on the kOH and their concentrations measured, because large faction of these NMHCs has been lost from their sources to the sampling sites.

Reply: High reactive NMHCs will be consumed in the process of transport, and their measured concentration will be lower than the initial concentration from sources. The aim of PMF analysis was to separate fresh emissions from aged emissions. 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 according to the correlations among our analyzed species. We derived VOC emission ratios from fresh factors in summer and compared with the emission ratios calculated by the photochemical age-based parameterization method in 2010 summer (Figure R2) (Yuan et al., 2012). The emission ratios of reactive NMHCs agreed well between these two methods, indicating that our extracted fresh factors can reflect the characteristic of fresh emission, so the contribution of reactive NMHCs will not be underestimated using Eq. (2).

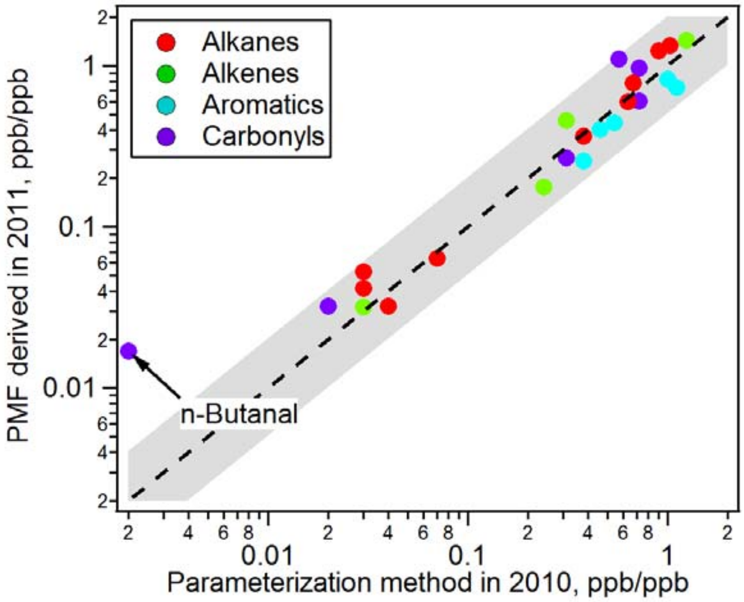

Fig. R2. Comparison of emission ratios of VOCs to ethyne from PMF in 2011 with the photochemical age-based parameterization method in 2010. The dashed line indicates the 1:1 relationship, and the grey shaded area shows an agreement within a factor of two. The emission ratios calculated by parameterization method were reported by Yuan et al. (2012).

References

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.