

Review of "Understanding primary and secondary sources of ambient carbonyl compounds in Beijing using the PMF model" by W.T. Chen et al.

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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 I recommend that this paper not be published until it has been extensively revised.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.

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.
- 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.) From 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.

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

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?

- 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.
- 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.)
 - 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?

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.

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.

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.

- 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.
- 7) Pg. 15758, lines 23-26 - the statement "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." is not clear, and its significance must be discussed.
- 8) Pg. 15759, lines 4-6 - The following statement is misleading: "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)." Any primary biogenic emission of carbonyls is minor compared to the secondary formation from oxidation of isoprene. The secondary formation should be emphasized first, and the possible primary emissions mentioned later, if at all.
- 9) Pg. 15763, lines 8-12 - The comparison to other urban areas is poorly done. It is useful to compare Beijing to New York City and Mexico City, but not to Houston, which is unique due to the very large industrial sources of alkenes. For Houston *Parrish et al.* [2012] find a very low primary contribution (5%), which does disagree with the other references, but is much more likely correct than the other references. A more balanced discussion is required.
- 10) Much of the discussion at the end of Section 3.4 is highly speculative, and not supported by strong evidence. It should be so supported or eliminated.

Minor issues:

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

- 1) P. 15751, line 5 - "As the complexity of carbonyl sources and sinks, ..." would be better worded as "Due to the complexity of carbonyl sources and sinks, ..."
- 2) P. 15751, line 13 - "may mislead results" better as "may give misleading results"
- 3) P. 15751, line 19 - "For secondary formations" better as "For secondary formation"
- 4) P. 15751, line 24 - "with considering of the pro-" better as "with the consideration of the pro-

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

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.

Reference

Roberts, J.M., et al., Application of a sequential reaction model to PANs and aldehyde measurements in two urban areas, *Geophys. Res. Lett.*, 28, 4583-4586, 2001

Stroud, C.A., et al., Isoprene and its oxidation products, methacrolein, and methyl vinyl ketone, at an urban forested site during the 1999 Southern Oxidants Study, *J. Geophys. Res.*, 106, 8035-8046, 2001.