

Interactive comment on “A technique for rapid source apportionment applied to ambient organic aerosol measurements from the Thermal desorption Aerosol Gas chromatograph (TAG)” by Yaping Zhang et al.

Yaping Zhang et al.

zhangyaping@wustl.edu

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*A revised document (with Track Changes enabled) has been provided to the editor.

Anonymous Referee #2

General Comments This paper has introduced a very interesting approach of using GC/MS data for source apportionment. I agree with the authors that this approach should be of interest for other measurement techniques. However, I suggest more discussions about the following issues to help readers better understand this new approach, the PMF analysis of the TAG (GC/MS) data and sampling methods. Author

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Response: The authors thank the reviewer for the comments and address further questions below.

1) Correction for positive sampling artifacts. In this paper, the gas-phase inference on OA sampling was corrected for by subtracting organics collected downstream of a Teflon filter (vapors) from organics collected through a bypass line (vapors+particles). Does the consistency in the PMF analysis of different data inputs suggest that this approach of correction for positive sampling artifacts is sufficient for source apportionment or to correct for gas-phase interference on OA sampling?

Author Response: Yes, this approach of correction is sufficient for both source apportionment and correcting gas-phase interference on OA sampling as has been applied in previous reports (Zhang et al., 2014; Williams et al., 2010), although subsequent field studies have deployed a diffusion denuder upstream of the collection cell as opposed to subtraction through this filter method. Table 2 shows the factor correlations of source apportionment between TAG-Bin and AMS. TAG instrument deployed here is good at measuring MV-OOA and HOA. Correlations for MV-OOA and HOA are 0.87 and 0.80, respectively. These correlations are higher than for the same PMF factors found from the TAG-Integrated method that targeted tracer species with minimal gas-phase interference, further suggesting this approach of correction is reasonable for source apportionment.

2) Organics measured by AMS and GC/MS. The thermal desorption temperature is 310°C for GC/MS and 600°C for AMS. Worton et al. (2014) has reported that GC/MS with the desorption temperature of 300°C only recover about 60% of organics collected in a traffic tunnel. Does this suggest that organics desorbed at 310°C can represent the variation of low-volatility organics? D. R. Worton et al., Lubricating Oil Dominates Primary Organic Aerosol Emissions from Motor Vehicles. Environ. Sci. Technol. 48, 3698-3706 (2014).

Author Response: It is agreed that traditional GC/MS utilizing a traditional 30-m GC

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column without derivatization only detects a portion of OA specifically missing highly oxygenated and low-volatility organics. The correlation (0.55) of low-volatility organics (cLV-OOA) between TAG-Bin and AMS in Table 2 supports the argument here. To solve this problem, the TAG research community has begun to apply online-derivatization in some cases (Isaacman et al., 2014), shorter GC column lengths to enhance recovery of oxygenated material (Martinez et al., 2016), and has now started to detect the thermal decomposition products that come from the heating of low-volatility and highly functionalized OA (Williams et al., 2016).

A statement has been added to the manuscript (Page 12, Line 6-10): "To address low detection of this analytically challenging OA fraction, subsequent TAG field deployments have applied a range of methods to increase detection through online-derivatization in some cases (Isaacman et al., 2014), shorter GC column lengths to enhance recovery of oxygenated material (Martinez et al., 2016), or in other cases the thermal decomposition products from heating of low-volatility and highly functionalized OA have been detected and analyzed (Williams et al., 2016)."

3) Response factors of binned organics. The response factors of organic compounds are influenced by their functional groups, volatility and organic loadings. For quantification of individual species, the response factors of different compounds can be corrected for by internal standards. Have the variations in response factors of binned mass spectra been accounted for during the PMF analysis? Or these variations won't influence the results of the PMF analysis significantly?

Author Response: The response of organic compounds are influenced by their functional group, volatility and organic loadings. Williams et al. (2010) injected standards of 13 compounds with different polarities and volatilities when samples were collected. The results show that the response shift among these 13 compounds from the start to the finish of the sampling period ranges from -61% to 13% with a mean -18%. Some of this drift is due to a uniform detector drift that affects all compounds equally (which can be easily corrected and therefore would not significantly impact PMF results since

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there is equal impacts on compound time series variability), but the remaining drift can be due to impacts such as changes in column conditions over the course of a long study. Column conditions change more dramatically over longer study periods and impacts various compound classes differently. However, this standard injection method with the limited individual compounds, which was applied during this older study, is not sufficient for correcting the individual bins' signal drift in the binning method. Online internal standard injection is now possible (Isaacman et al., 2011) and a complex mixture of various polarity and volatility molecules would need to be analyzed as surrogate species to represent bin-response, allowing for a scale to interpolate and track bin-response drift.

While the bin signals haven't been corrected for signal drift here, the relatively high correlations of factors between TAG-Bin and AMS in Table 2 are consistent with the fact that GC/MS (TAG) deployed here is particularly performing well at measuring MV-OOA and HOA type aerosol. The source apportionment using uncorrected signal is still reliable in the qualitative perspective analyzed here. Correction of signal drift for future studies is expected to further improve correlations between TAG-Bin and AMS OA components.

We've added the following statement to Page 7, Line 10-16: "In addition to retention time shifts, detector response and GC column conditions can drift over the course of a study. Individual bin response factors have not been developed for this data set due to limited calibration standards applied during the SOAR study. Online internal standard injections are now possible (Isaacman et al., 2011) and a complex mixture of various polarity and volatility molecules would need to be analyzed as surrogate species to represent bin response, allowing for a scale to interpolate and track bin response drift corrections. Given the shorter study focus period analyzed here and the relatively high correlations observed below between several TAG-Bin components and AMS components, the bin response correction does not appear critical here, but should be included in future applications of this method."

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And again in the conclusions: "Future applications of this method should continue to apply retention time shifts when necessary and should incorporate new relationships using regularly injected calibration standards to develop bin-specific response factors, especially when longer study periods susceptible to larger drifts are to be analyzed."

4) On-line derivatization. This paper has shown that the PMF analysis of binned mass spectra in the retention time basis can resolve the SV-OOA and MV-OOA factors well. Do the authors think that the missing factor of cLV-OOA in the results from the PMF analysis of binned mass spectra can be identified by applying derivatization?

Author Response: Yes, that is the case. This point has been previously addressed in our response to Comment #2 above.

5) Comparison between the TAG-Binning method and the TAG-integration method. The strong correlations were not found for all PMF factors in results from PMF analysis of these two data formats. The binning method also provides limited chemical information compared to the TAG-integration method (Organic-tracer method). Do the authors think which one is a better method to identify major OA components for further emission controls?

Author Response: Firstly, we don't expect strong correlations for all the PMF factors between TAG-Binning and TAG-integration methods. These two methods incorporate different inputs in the PMF analysis - the whole chromatogram signal, and 123 integrated individual compounds, respectively. However, there should be significant overlap where the same type of variability was captured. In addition to the binning method requiring much less pre-processing compared to the traditional peak integration method, it also includes all of the GC/MS signal and does not risk missing an important compound or series of compounds as could easily occur for the traditional single-compound method. In terms of chemical resolution, the binning method can get down to the molecular level with appropriate retention time shifting. In this case, the operator could then go back and identify important compounds within each of the factors, after PMF analysis

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has decided they are important species for a resulting component. We feel that this method will evolve and has the potential to replace the traditional method in the future. It is worth noting that higher bin resolution will also require more computer processing power, which should also become more manageable in the future.

The following statement has been added to Page 12, Line 26-30: "By incorporating all of the GC/MS signal, the binning method does not risk missing an important compound or series of compounds as could easily occur for the traditional single-compound method since the input compounds are chosen by the operator. In terms of chemical resolution, the binning method can get down to the molecular level with appropriate retention time shifting. In this case, the operator can then go back and identify important compounds within each of the factors, after PMF analysis has decided they are defining species for a resulting component."

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