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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Source apportionment of fine particulate matter in Houston, Texas: Insights to secondary organic aerosols" *by* Ibrahim M. Al-Naiema et al.

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Referee #1 general comments: This paper presents source apportionment results from a comprehensive on-line and off-line chemical datasets collected concurrently in Houston, Texas. The authors applied three different for source apportionment approaches to determine the sources and their contributions, which has not be done before to my knowledge. The source apportionment results were compared between the three approaches and their finding that the primary source contributions agreed was encouraging. Furthermore, it allowed for more in-depth characterization of the different sources of SOA by combining the results from the three methods, which will be of interest to many. My main comment would be that perhaps the authors could recommend a tracer for biogenic and anthropogenic SOA. I may have missed it but their comprehensive dataset might allow at least for a tentative proposal as applying all three source apportionment methods will not be feasible in many cases and may allow the results from this study to be applied more widely. The paper is well written and logically set out and in my opinion fits within the scope of ACP.

I have a few minor comments below that the authors may wish to consider.

Response to Referee #1 general comments: We thank the reviewer for their review of the manuscript. We agree with the reviewer's summary of this work. In regards to their main comment about providing recommendations for biogenic and anthropogenic SOA tracers for future source apportionment studies, we have significantly revised the conclusion section to provide recommendations for future studies. The revised text appears in the second-to-last paragraph in section 4 (lines 7-29, page 16):

"MM-PMF is a useful approach for estimating source contributions to OC and PM2.5, particularly when source profiles for sources are not available or are not well defined, which is often the case for SOA. In order to apportion anthropogenic SOA, it is necessary to explicitly include anthropogenic SOA tracers as fitting species in the PMF model. Initial guidance on anthropogenic SOA tracer selection was drawn from Al-Naiema and Stone (Al-Naiema and Stone, 2017). In this study, to track anthropogenic SOA formed from aromatic VOC under high NOx conditions, 4-methyl-2-nitrophenol and DHOPA served as key tracers. For PAH-derived SOA, key tracers were 4-nitrophenol, phthalic acid for naphthalene-derived SOA, and 4-methylphtalic acid for methylnaphthalene SOA. In prior MM-PMF studies in France, oxy-PAH and nitro-PAH have been useful in tracing SOA derived from larger PAH (Srivastava et al., 2018a; Srivastava et al., 2018b). The utilized tracers should be expanded as anthropogenic SOA becomes more chemically-defined. In particular, molecular tracers are needed for recognized SOA precursors that include other aromatic compounds, n-alkanes, alcohols, and PAHs (beyond naphthalene and its derivatives). While few biogenic SOA tracers

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were detected in HSC, 2-methylerythritol and 2-methylthreitol were valuable in identifying the isoprene SOA factor. Caution should be used in the use of 2-methylglyceric acid that is a high-NOx SOA product formed from MACR that can come from biogenic or anthropogenic origins; while plants are the major source of isoprene globally, motor vehicles contribute the majority of the MACR in urban Houston (Park et al., 2011). Similarly, SOA from BB was identified by way of isopthalic acid and cis-pinonic acid, consistent with aged BB emissions documented in the literature (Yan et al., 2008); however, these compounds can also have other sources, such as primary emissions and monoterpene-derived SOA, respectively. Phenolic oxidation associated with BB SOA has also been identified using methyl-nitrocatechols (Srivastava et al., 2018a, 2018b). To better define BB and anthropogenic SOA, future efforts should be placed on identifying and quantifying molecular markers to identify the specific precursors and pathways responsible for SOA formation. Better definition of the molecular profiles of anthropogenic and BB SOA will support CMB-based methods and aid in the interpretation of MM-PMF results."

Referee #1 specific comment 1: Section 3.2: did you do a PM2.5 mass balance, comparing the measured PM2.5 (gravimetric) against the reconstructed PM2.5 mass concentration from the chemical analysis?

Response to Referee #1 specific comment 1: Yes, a mass balance was performed in which the PM2.5 mass measured by the TEOM at Clinton Drive was compared to the sum of the species measured on the filters, including organic carbon converted to organic matter, elemental carbon, and inorganic ions. These data are shown in Figure 2 and we have added a statement regarding these results in section 3.2 (lines 19-21, page 7): “On average, OM, EC, and inorganic ions accounted for 80% of the PMÂň2.5 mass (Fig. 2), with the remaining mass expected to arise from unmeasured species such as crustal metal oxides (e.g. silica, alumina), other metals, and particle-bound water.”

Referee #1 specific comment 2: Page 9, line 37: Can you say there is a cooking

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influence in CI-SV-OOA if there is evening peak in the diurnal profile? Normally, a peak associated with evening meal times is a marker for cooking emissions. Without I am not sure that there is much influence from cooking, especially as your MM-PMF analysis only apportions 1% of the PM2.5 to cooking. Perhaps this is more of SV-OOA factor with some hydrocarbon/primary local emission influence.

Response to Referee #1 specific comment 2: We agree with the reviewer that classifying this factor as SV-OOA would reflect its main nature; however, we also consider that the denomination of this factor should include a reference to the observed influence of cooking activities. This influence is evidenced by (i) statistically significant association with mass fragments reported as tracers of food cooking (Table R1), (ii) co-variability between CI-SV-OOA and the C3H3O+ mass fragment, typically used to distinguish cooking organic aerosol (COA) from HOA (Figure R1) (Mohr et al., 2012; Sun et al., 2016; Wallace et al., 2018) and (iii) m/z 55 to m/z 57 ratio larger than 2, as reported previously for primary COA (Reyes-Villegas et al., 2018; Sun et al., 2011; Cao et al., 2018; Sun et al., 2016). These characteristics distinguish CI-SV-OOA from other SV-OOAs reported in the literature, and thus, we consider that the classification of this factor simply as SV-OOA would provide only a partial description of its character.

Although, as noted by the reviewer, an evening peak would provide further evidence of the influence of cooking activities on CI-SVOOA, it is worth noting that this factor corresponds to atmospherically processed OA (O:C 0.61) and therefore, its diurnal behavior is not expected to resemble that of primary COA.

We have included additional text in the manuscript to provide further support for the denomination of this factor as CI-SV-OOA (lines 28-37, page 8).

Referee #1 specific comment 3: Page 10, line 19: In your CMB results you have said that the unclassified OC is likely SOA, would you expect more SOA at night (49%) compared to daytime (29%)? As you have already apportioned Biogenic and anthropogenic SOA in the model, I am guessing that this SOA is regional in nature, and so I would not expect such a difference day/night.

Response to Referee #1 specific comment 3: We thank the reviewer for making this point, as it indicates that further clarification and explanation are needed. First, we have revised this description to include the unapportioned OC on an absolute scale to account for the 33% higher concentration of OC during daytime compared to nighttime. Second, we have added possible explanations for higher SOA at nighttime. The revised text reads (line 41, page 10 to line 4 page 11): “Notably, a substantial amount of OC was unapportioned, averaging 0.68 micro-gC m-3 (29%) in the daytime and 0.86 micro-gC m-3 (49%) in the nighttime... The higher unapportioned OC levels at night may be due to nighttime SOA formation (e.g., organonitrates formed by nitrate-radical initiated reactions) and/or to a shift in gas-particle partitioning to the particle phase with lower nighttime temperatures.”

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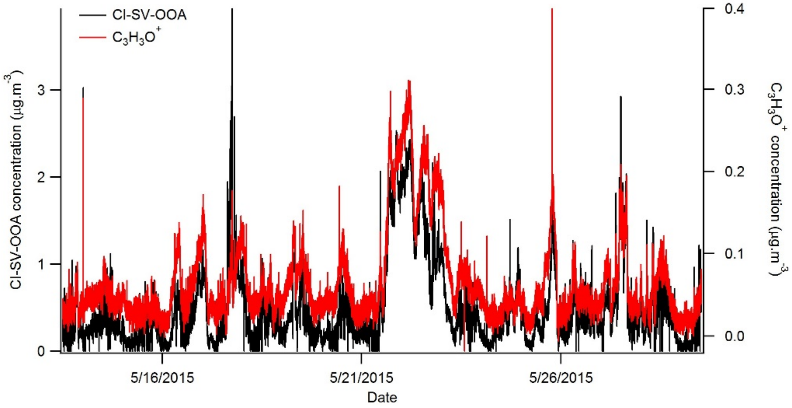

Figure R1. Time series of concentration of CI-SV-OOA and $C_3H_3O^+$ during the field campaign.

Fig. 1.

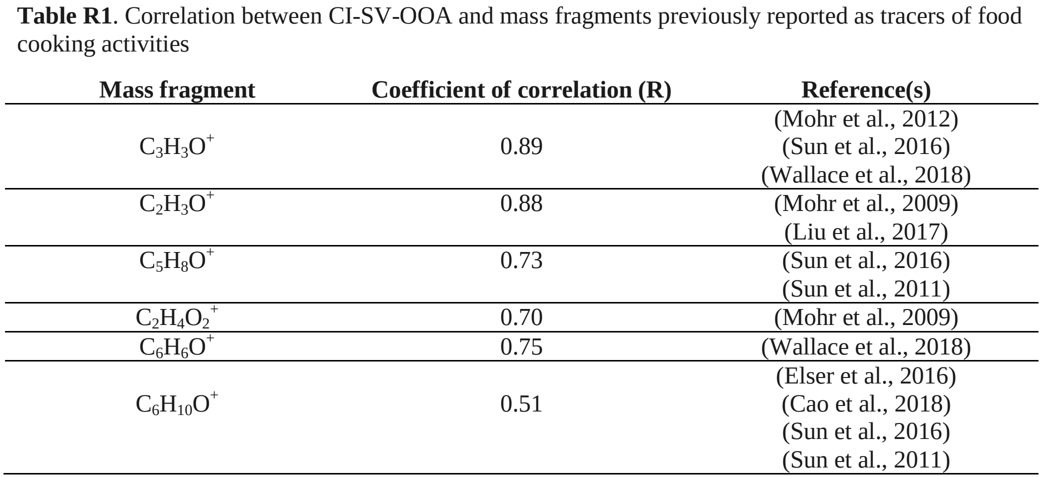

Table R1. Correlation between CI-SV-OOA and mass fragments previously reported as tracers of food cooking activities

Mass fragment	Coefficient of correlation (R)	Reference(s)
$C_3H_3O^+$	0.89	(Mohr et al., 2012) (Sun et al., 2016) (Wallace et al., 2018)
$C_2H_3O^+$	0.88	(Mohr et al., 2009) (Liu et al., 2017)
$C_5H_8O^+$	0.73	(Sun et al., 2016) (Sun et al., 2011)
$C_2H_4O_2^+$	0.70	(Mohr et al., 2009)
$C_6H_6O^+$	0.75	(Wallace et al., 2018)
$C_6H_{10}O^+$	0.51	(Elser et al., 2016) (Cao et al., 2018) (Sun et al., 2016) (Sun et al., 2011)

Fig. 2.

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