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August 31, 2018

Dear Editor,

We hereby submit a revision of our manuscript entitled "Source apportionment of fine particulate matter in Houston, Texas: Insights to secondary organic aerosols."

We appreciate the careful reviews of the two referees and additional comment on this work. We have revised the manuscript in accordance with these comments and attach here a point-by-point response to each referee and a marked-up version of the manuscript that indicates the changes that were made.

In addition, we have changed updated the terminology of the AMS factors reported herein, to better align with the community. In particular, the factor previously called low volatility oxygenated organic aerosol (LV-OOA) has been changed to more-oxidized oxygenated organic aerosol (MO-OOA). The factor previously called semi-volatile oxygenated organic aerosol (SV-OOA) has been changed to less-oxidized oxygenated organic aerosol (LO-OOA). These changes in naming reflect that PMF results do not provide insight to volatility, but do provide insight to the oxygen-to-carbon ratios. This change is not reflected in the responses to the referees, but is implemented in the revised manuscript.

Please let me know if you have questions concerning the subject manuscript.

Sincerely,

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Anonymous Referee #1

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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 $PM_{2.5}$, 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 NO_x 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 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-NO_x 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 $PM_{2.5}$ 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 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 $C_3H_3O^+$ 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).

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)

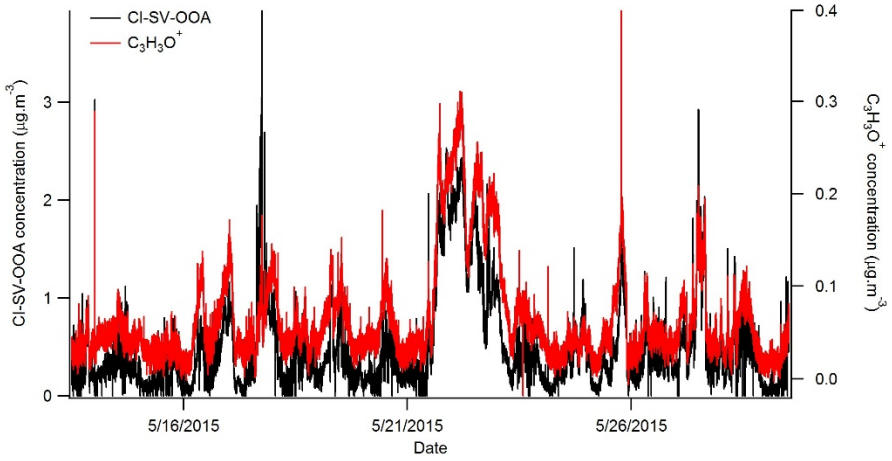

Figure R1. Time series of concentration of CI-SV-OOA and $C_3H_3O^+$ during the field campaign.

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 µgC m^{-3} (29%) in the daytime and 0.86 µgC 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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Referee #2 general comments: This manuscript reports a compositional analysis of PM2.5 by offline filter measurement on a day-night basis and NR-PM1 by an in-situ HR-TOF-AMS near the HSC in May 2015. Integrated source apportionment analysis for OC was conducted incorporating AMS-PMF, MM-PMF and CMB methods. The three source apportionment models are in agreement that ~50% of OC was formed from primary fossil fuel combustion. SOA was further apportioned to anthropogenic and biogenic sources by combing results from MM-PMF and CMB. The comprehensive nature of this work in data and source apportionment analysis bring to the literature a valuable case study report. This work nicely contributes to our improved understanding of SOA sources. I have the following specific points that need clarification/more discussion in their next revision.

Response to Referee #2 general comments: We thank the reviewer for their careful review of the manuscript and suggestions to improve it. We have responded point-by-point to the specific suggestions below.

Referee #2 major comment 1: The offline and online measurements overlapped between 13-27 May. Some comparison of the two measurements would be useful as data cross checking and verification. Such comparisons are currently lacking. For example, what's the percentage of PM1 contributed to total PM2.5 and how the two mass concentrations correlated with each other? This is important not only for data validation, but also for the latter comparison between AMS-PMF and MM-PMF and CMB.

Response to Referee #2 major comment 1: As suggested by the reviewer, we have added a comparison of AMS and filter-based measurements. We focus on three major species common to both sets of measurements. We do not compare PM mass, because PM mass was not measured on filters (instead by TEOM). The organic matter estimated from filters and organic aerosol measured by AMS is the most relevant to the comparison of source apportionment results. The following text has been added to section 3.2 on page 7 at lines 25-32:

"Filter-based $PM_{2.5}$ measurements indicate the same major PM species as AMS NR-PM_1 measurements and their ambient concentrations are compared here. The linear regression of the filter-based estimate of $PM_{2.5}$ OM and NR-PM_1 AMS OA had a slope of 0.61 and a low, but significant correlation ($r = 0.48$, $p = 0.005$), indicating that more OM was captured by the filter-based measurements than by the AMS. Sulfate measured by both techniques correlated strongly ($r = 0.90$, $p < 0.001$), with a slope of 0.89 indicating only a minor increase in filter-based sulfate relative to the AMS. Ammonium correlated moderately ($r = 0.72$, $p < 0.001$) with a slope of 0.73. The consistently lower NR-PM_1 concentrations measured by AMS relative to filters suggests the presence of OA, sulfate, and nitrate in the 1-2.5 micron size range and/or refractory matter that was not captured by the AMS."

Referee #2 major comment 2: There are inconsistencies among the source apportionment results by the different approaches. AMSPMF resolved a cooking influenced factor but no BB related OA, and the authors proposed the loss of the m/z 60 signatures during transport as possible reason. This reason is not supported by their data, as MM-PMF resolved both BB and cooking sources and BB even contributed more than cooking emission (11% vs 1%). It is odd that the authors didn't include cooking emission profiles in CMB. Previous studies have successfully apportioned PM2.5 to cooking emission (6%) in Fraser e al. [2003], as mentioned in the introduction part.

Response to Referee #2 major comment 2: We agree with the reviewer that the results from different source apportionment approaches could seem inconsistent. However, inherent differences between how the factors are resolved in each technique should be considered. In the case of AMS-PMF, 3 factors were selected as the main contributors to the observed PM_1 concentrations. This selection was supported by evaluating variations in Q/Qexp and residual levels as additional factors were added to the model (SI section). Similar to the 3-factor solution, the solution containing 4 factors did not resolve a BB factor. As

stated in the manuscript (line 25, page 13), the CI-SV-OOA factor exhibited low but statistically significant correlation with CMB BB, indicating potential inclusion of BB signatures in this factor. This is also evidenced by (i) a coefficient of correlation of 0.67 between the CI-SV-OOA and m/z 60 concentration time series and (ii) a CI-SV-OOA m/z 60 fraction (f_{60}) of 0.003, the largest among the 3 factors retained in the AMS-PMF model. Although f_{60} in CI-SV-OOA falls at the lower edge of the region defined by Gilardoni et al (2016) to consider a factor influenced by BB, its proximity to this region indicates potential association between CI-SV-OOA and BB. These observations suggest that although BB signatures are likely present in the CI-SV-OOA factor, AMS-PMF cannot effectively resolve these signatures, while MM-PMF is able to clearly separate the contributions of BB and food cooking. This reinforces the notion of complementarity between mass apportionment techniques and highlights the advantages associated to studying aerosol concentrations by employing simultaneous measurement and analyses techniques. Additional text including further reference to the potential inclusion of BB signatures in the CI-SV-OOA factor has been included in the manuscript (lines 29-34, page 13).

In regards to the CMB analysis, the reviewer is correct that a food cooking profile was not included and consequently this source was not apportioned by CMB. This choice was made in recognition that food cooking emissions vary greatly by type, style, and temperature of cooking. CMB-based source apportionment that relies upon a single, fixed source profile is ill equipped to capture this variability and the cooking signatures affecting ambient PM in HSC. Meanwhile, PMF is well suited to this task as it derives factor profiles from ambient measurements. Consequently we rely upon the MM-PMF result as a more accurate estimate of food cooking contributions to OC.

Referee #2 major comment 3: The AMS-PMF resolved a CI-SV-OOA factor that contributed to 31% of ambient OC (Table 5), but such a considerable contribution seems inconsistent with the minor cooking contribution estimated from MM-PMF (1%). This inconsistency calls into question whether naming the SV-OOA factor as "cooking-influenced" is appropriate, as it may imply this factor is largely influenced by cooking emissions.

Response to Referee #2 major comment 3: As stated in our answer to the previous comment, we agree with the reviewer that the contributions from cooking to OC derived from the different source apportionment approaches could seem inconsistent. However, it is worth noting that recognizing the influence of food cooking on the CI-SV-OOA factor is not equivalent to classifying this factor as cooking organic aerosol (COA). As included in our response to Referee #1, although the primary character of CI-SV-OOA would be mostly reflected by classifying this factor simply as atmospherically processed aerosol with a semi-volatile character, this denomination would omit relevant mass spectral signatures of the CI-SV-OOA. To increase clarity, we have added some text in the manuscript emphasizing the fact that CI-SV-OOA is not to be confused with COA (lines 28-32, page 8). Additional reasoning behind the classification of this factor as CI-SV-OOA is included in our response to Referee #1 and has been added to the manuscript (lines 32-37, page 8).

Referee #2 major comment 4: The identification of different vehicle emission factors, i.e. diesel engines, gasoline engines and nontailpipe vehicle emissions, is not very convincing, considering alkanes, PAHs are not unique source tracers to vehicle emissions. It is unusual that norhopane and hopane are separated into two different factors. The two species are usually highly correlated with each other. What's the correlation between the two species in this study? Also, a high amount of EC was present in low-NOx anthropogenic SOA factor. Does this indicate the mixing of primary sources in this factor?

Response to Referee #2 major comment 4: We agree with the Referee that the diesel emissions, gasoline emissions and non-tailpipe emissions cannot be distinguished based on alkanes and PAH's, which are key chemical species in these factors. While these chemical species are indicative of a vehicle source, these are not unique tracers for diesel, gasoline, or non-tailpipe emissions. The identification of

these three sources is thus based on EC:OC or PAH ratios, which are distinctive among these sources. For example, the EC:OC ratio of diesel engine emissions is greater than the EC:OC ratio of gasoline engine emissions and within the range of the values reported for these sources in the literature. Whereas, the absence of EC in the factor identified as non-tailpipe emissions is indicative of a non-combustion vehicle source. Furthermore, the ratio of benzo(a)pyrene to the sum of benzo(a)pyrene and chrysene in this factor is similar to the non-tailpipe emissions reported in the previous literature. In addition, the identification of the diesel and gasoline engines is supported by their correlations with the corresponding CMB source contributions. The separation of norhopane and hopane into two separate factors can be explained by their weak correlation ($r = 0.239$, $p = 0.110$). This result suggests that two or more sources of hopane were present, each having different hopane ratios.

We agree with the Referee that the presence of EC in the low-NOx anthropogenic factor is indicative of some mixing with primary fossil fuel combustion sources. To clarify this point, the following text has been added to lines 2-6 on page 13: "EC is also present in this factor, suggesting some mixing of this factor with combustion sources. Such mixing likely arises from VOC and precursors of oxidants co-emitted with EC from combustion contributing to SOA formation. However, the predominance of secondary organic markers over signatures of primary emissions suggests that this factor primarily represents SOA."

Referee #2 major comment 5: In the CMB model (section 2.5), were EC and levoglucosan included in the calculation? If not, which species was/were mainly responsible for determining the contributions from diesel engines and biomass burning? Also, it would be better if the statistical performance of the CMB results can be reported (e.g., $\chi 2$, calculated vs. modelled species concentrations, species source contributions).

Response to Referee #2 major comment 5: EC and levoglucosan were included in the CMB model calculation. While sitostanes, cholestane, and some PAH were included in the input data files, they were not used in the final model calculation, because some of these species were not available for the source profiles utilized. We have revised the methods section 2.5 to reflect the species included in the final model calculation (lines 2-5, page 6): "Species included in the CMB model included EC, levoglucosan, 17α(H)-21β(H)-hopane, 17α(H)-22,29,30-trisnorhopane, 17β(H)-21α(H)-30-norhopane, PAH (benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene, and benzo(ghi)perylene), isoprene SOA tracers (2-methylglyceric acid and 2-methyltetrols), one α-pinene SOA tracer (cis-pinonic acid), one naphthalene SOA tracer (phthalic acid), and one toluene SOA tracer (2,3-dihydroxy-4-oxopentanoic acid)."

As suggested by the reviewer, a summary of the model diagnostics have been added to the supporting information as Table S6: R^2, χ^2, calculated-to-measured ratios for fitting species (EC, levoglucosan, 17α(H)-21β(H)-hopane, 17α(H)-22,29,30-trisnorhopane, 17β(H)-21α(H)-30-norhopane, benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene, and benzo(ghi)perylene). The following text has been added to section 3.4.1 (line 26 page 9): "CMB model diagnostics, including R2, χ 2, calculated-to-measured ratios for fitting species are summarized in Table S6."

Table S6: CMB model performance metrics. The R^2 values indicate the fit of the profile to the ambient data, with values greater than 0.8 indicating a good model fit. The χ^2 values are the weighted sum of squares of the differences between the calculated and measured fitting species concentrations, with a value of 0 indicating a perfect model fit, <1 indicating a very good fit, 1-2 indicating an acceptable fit, and >4 indicating that one or more species concentrations are not well explained by the model. In one sample (21 May, nighttime) this value was greater than 4, with 2.85 the next-highest value. The calculated-to-measured concentration ratios of the fitting species indicate the extent to which individual tracers were fit by the model. SOA tracers, which behaved ideally coming from only one source, had calculated-to-measured concentrations of 1.

Performance Metric	Range			Mean	Median
R^2	0.833	-	0.999	0.979	0.987
χ^2	0.06	-	4.35	0.93	0.71
Calculated-to-measured concentration ratios					
elemental carbon	0.99	-	1.01	1.00	1.00
levoglucosan	0.61	-	1.32	0.98	0.99
17α(H)-21β(H)-hopane	0.00	-	0.42	0.21	0.20
17α(H)-21β(H)-30-norhopane	0.75	-	1.07	0.99	1.00
17α(H)-22,29,30-trisnorhopane	0.67	-	1.33	0.99	1.00
benzo(b)fluoranthene	0.67	-	2.00	1.05	1.00
benzo(ghi)perylene	0.00	-	1.78	0.92	1.00
indeno(1,2,3-cd)pyrene	0.00	-	2.00	1.06	1.00

The sample-by-sample CMB model results, including source contributions, the associated standard errors, measured and modeled OC, R^2, and χ^2 values will be archived in an open access data base, along with the other data products linked to this manuscript.

Referee #2 major comment 6: The sample size of MM-PMF for PM2.5 OC is 46 in the study, but in the introduction section it is suggested the sample size should be 60–200 (P.2 line 39–40). It seems, because of this reason, the MMPMF performance is not very robust as shown in Table S2 (some key species like cis-pinonic acid and phthalic acid are not well modelled) and Table S5 (only 54% of bootstrap BB factor was mapped). The uncertain BB factor contribution in MM-PMF would also weaken the reliability of BB SOA estimation in this study. Please comment on how the small sample size affect the MM-PMF results in this work.

Response to Referee #2 major comment 6: We thank the reviewer for pointing this out and clarify the introduction point with a more up-to-date reference. The revised text reads (lines 2-4, page 3): "While PMF requires a relatively large sample size, MM-PMF has generated stable solutions with as little as 35 observational data points, which is expected to arise from the high specificity of primary and secondary source tracers Hu et al., (2010)."

We agree with the reviewer that there is uncertainty associated with the BB and BB SOA source estimates. We have added the following text to section 3.4.2 in introducing this factor (line 17-18, page 12): "Notably, only 54% of the bootstrap BB factor was mapped (Table S7; the lowest of any factor) indicating a greater relative uncertainty associated with this factor." We have also added the following text to section 3.5 (lines 3-6, page 14): "The BB SOA estimate is considered to be a best-estimate with the available data set, but contains uncertainties both from the MM-PMF and CMB estimates. Strategies to

reduce the relative uncertainty associated with this source, include using a larger number of observations and more specific BB SOA tracers in MM-PMF."

Referee #2 major comment 7: Fig. 8 shows that the non-tailpipe vehicle emissions (marked largely by 17α(H),21β(H)-hopane only) made a notable contribution after 20 May (except 10 May daytime), is there any reason for it?

Response to Referee #2 major comment 7: The temporal variation of this factor is influenced by the detection of 17α(H),21β(H)-hopane. This species was detected only in 17 of the 46 $PM_{2.5}$ samples analyzed, including 10 May in the daytime and 16 samples collected from 20-27 May.

Referee #2 major comment 8: Is there any reason to select 17β(H)-21α(H)-30-norhopane over 17α(H),21β(H)-30-norhopane as the vehicle emissions tracer in CMB and MM-PMF? The former species should be less abundant in ambient and source PM, and therefore is less commonly used in receptor models (e.g., Yu et al., 2011, Analytical and Bioanalytical Chemistry, 401, 3125-3139).

Response to Referee #2 major comment 8: We thank the reviewer for pointing this out. We have indeed used 17α(H)-21β(H)-30-norhopane in this study. We have corrected this typo throughout the manuscript, figures, tables, and supporting information.

Referee #2 major comment 9: When the source apportionment results from AMS-PMF, MM-PMF and CMB were integrated to obtain insights in SOA contributions (section 3.5), it seems the conclusion that anthropogenic SOA is the dominant contributor is largely drawn from the MM-PMF results, while the CMB and AMS-PMF results do not converge to the same conclusion (e.g., P.14 line 17: CMB is unable to provide a reliable estimation of total anthropogenic SOA, … ; and line 20–21: AMS-PMF is unable to distinguish between anthropogenic and biogenic origins of SOA, …). However, the MM-PMF results may have large uncertainties, especially considering the small sample size and poor stability (e.g., only 67% of bootstrap high-NOx anthropogenic SOA factor can be mapped as shown in Table S5), making such a conclusion less convincing. Additional supportive evidence/argument for this point is recommended.

Response to Referee #2 major comment 9: The three models converge on the conclusion that anthropogenic SOA is a major source of ambient OC in HSC, with this finding led by the MM-PMF results and supported by the CMB and AMS-PMF results. In order to clarify this finding through additional evidence and argument, we have revised the last paragraph in section 3.5 (beginning on line 42, page 14):

"MM-PMF holds the advantage of identifying anthropogenic SOA for several reasons. First, these estimates are based on molecular tracers selective to this source (Al-Naiema and Stone, 2017). Second, these estimates were developed from ambient measurements within the HSC airshed and are considered to be the best representation of anthropogenic SOA in this location. Unlike CMB, MM-PMF requires neither a priori knowledge of tracer-to-OC ratios nor the assumption that these ratios are constant across chamber experiments and the study site. Third, by analyzing the co-variation of species over time, MM-PMF can capture anthropogenic SOA from other precursors that co-vary in time, even if they have a different precursor and are not defined by tracers in the source apportionment model (e.g., alkanes).

Nonetheless, CMB results support that anthropogenic SOA is an important source of OC in the HSC. Using available profiles for anthropogenic SOA in CMB, 3% of OC was attributed to monoaromatic-derived SOA (e.g., benzene, toluene) and 5% was attributed to naphthalene-derived SOA. Larger SOA contributions from PAHs compared to monoaromatic precursors agrees with controlled chamber photo-oxidation of diesel exhaust, in which PAH-derived SOA was estimated to account for up to 54% to the total SOA mass formed in the first 12 h of oxidation (Chan et al., 2009). The total PAH

contribution to SOA in HSC is expected to be larger, since other 2-3 ring PAHs with SOA-forming potential (Shakya and Griffin, 2010) are co-emitted with naphthalene; however, molecular tracers for larger PAH oxidation products are not yet defined, so the associated OC is unapportioned by the CMB model. Because the CMB-based estimate of anthropogenic SOA is limited to two classes of VOC precursors—aromatics and naphthalene derivatives—for which SOA profiles are available it is considered to be only a partial estimate of anthropogenic SOA. Anthropogenic SOA from other precursors contribute to the CMB unapportioned OC. The CMB-estimates of aromatic and naphthalene-derived SOA is valuable, however, because it provides specificity in the relative and absolute source contributions for these VOC classes.

The AMS-PMF LV-OOA factor that accounts for an average of 32% of PM_1 OC is expected to be influenced by anthropogenic SOA based on the correlation observed with high-NO_x anthropogenic SOA in MM-PMF ($r=0.515$, $p=0.004$). The MM-PMF and CMB methods that rely on specific tracers overcome the AMS limitation of being unable to distinguish between anthropogenic and biogenic origins of SOA in the absence of a strong signal that can identify a specific VOC precursor (Wallace et al., 2018; Xu et al., 2015). Relying on MM-PMF as the best estimate of anthropogenic SOA, we estimate that this source contributes an average of 28% of $PM_{2.5}$ OC, making it a major aerosol source in HSC second only to primary fossil fuel emissions. Led by MM-PMF and supported by CMB and AMS-PMF, these reveal the important contributions of anthropogenic SOA to $PM_{2.5}$ OC in the HSC area of Houston."

Finally, we have added the following sentence regarding the results of the bootstrapping analysis (line 42, page 14): "The former source contribution is considered to be stable with > 80% of bootstraps matched, while the latter has a larger relative uncertainty with 67% of bootstraps matched (Table S7)." We have addressed the reviewer's concerns about the number of observations used in the MM-PMF model in response to Referee #2 Comment 6.

Minor comment 1: Line 4-5 in p7: "organic carbon", "elemental carbon" and "Organic matter" should be removed as the abbreviations have been introduced before. Check throughout the context to avoid redundant words.

Response to minor comment 1: We prefer to maintain the definitions of these abbreviations at the start of the results and discussion section. We have checked the remaining text and can confirm that they are not repeated in the text after this occurrence.

Minor comment 2: Include the measured OC concentrations in Figure 8, which can help visualize directly how MMPMF predicts the measured concentrations.

Response to minor comment 2: As suggested by the reviewer, we have added the measured OC concentrations to Figure 8 and updated the figure caption accordingly.

Minor comment 3: Line 16 in p1: Change "fine" to "ambient".

Response to minor comment 3: We have made this change as suggested by the reviewer.

Minor comment 4: Line 25 in p1 and line 11 in p2: "VOC" should be "VOCs".

Response to minor comment 4: We define VOC as volatile organic compounds (note: in the plural form) on page 1 at line 25, such that an additional "s" is not needed in subsequent occurrences. We have checked the manuscript to ensure that "VOC" is used consistently.

Minor comment 5: Line 21 in p2: "for" should be "from".

Response to minor comment 5: We have made this change as suggested by the reviewer.

Minor comment 6: Line 13-16 in p6: the correlations are R or R2?

Response to minor comment 6: We have clarified at line 16 on page 6 that these are "correlation coefficients (r)…"

Minor comment 7: Figure S10, correct the typo mistake for the y-axis.

Response to minor comment 7: We have corrected this alignment error in the revised manuscript.

Minor comment 8: P.5 line 36: Bituminous coal source profile was said to be included in CMB, but it is not reported in the result section (3.4.1), please check.

Response to minor comment 8: The reviewer is correct that the bituminous coal source profile was tested in the CMB model; however, its source contributions were not statistically significant. We have added the following text to page 9 line 25: "The bituminous coal source contribution was not statistically significant."

Minor comment 9: P.8 line 25–26: The order of HOA, CI-SV-OOA and LV-OOA should be reversed to be consistent with the statement in the next sentence, as well as the abstract (line 20–22).

Response to minor comment 9: As suggested by the reviewer, we have revised the order of the AMS factors to be lowest to highest contribution. The revised text reads (line 1, page 8): "The time series of concentration of the AMS factors and their diurnal trends are presented in Fig. 5. The average mass concentrations observed for LV-OOA, CI-SV-OOA, and HOA during the field campaign were 0.37 ± 0.73 μg m^{-3}, 0.48 ± 0.47 μg m^{-3}, and 0.72 ±0.52 μg m^{-3}, respectively, indicating a predominant contribution from secondary factors to the PM_1 OA. The contribution to the OA mass concentration during the sampling period followed the sequence LV-OOA < CI-SV-OOA < HOA, with average abundances of approximately 22.33%, 29.44, and 48.23% respectively."

Minor comment 10: p.10 line 13: Full stop missing in "… comparing this study to Buzcu et al., (2006)."

Response to minor comment 10: We have corrected this error as suggested by the reviewer.

Minor comment 11: P.11 line 34–36: Yan et al. (2008) did not report isophthalic acid in aged BB plumes, please consider citing another reference.

Response to minor comment 11: Yan et al. (2008) reports in their table 2 (page 6390) that aromatic dicarboxylic acids are distinctively high in aged BB plumes compared to non-aged BB, including 1,3-benzenedicarboxylic acid (a.k.a. isophthalic acid).

Minor comment 12: P.13 line 8 & 9: section 3.5.2 □ section 3.4.2

Response to minor comment 12: We have corrected this text to read "section 3.4.2."

Minor comment 13: P.13 line 33–34 argued that isoprene-derived SOA contribution estimated by MM-PMF is more reliable than that by CMB, is there any further support/reference for this argument?

Uncertainties associated with ambient measurements and temporal correlation between species in PMF should not be neglected.

Response to minor comment 13: We have clarified this point by adding the following text to section 3.5 (lines 27-30, page 14): "In contrast, CMB relies upon tracer-to-OC ratios observed in the laboratory (Kleindienst et al., 2007) where reactant concentrations greatly exceeded those observed in HSC (Figure S4). In particular, chamber concentrations were approximately 10-fold higher for NO_x, 2-3 orders of magnitude higher for isoprene, and 3-4 orders of magnitude higher for toluene." Further, at line 25 on page 14, we have also added that the similar MM-PMF and CMB results "[indicate] good agreement between these two approaches."

Minor comment 14: Space missing: after Table S2 in P. 10 line 28; between "models reveals" in P.14 line 25; after NRPM1 in P.33 Table 2 title.

Response to minor comment 14: We have corrected these three errors as suggested by the reviewer.

Minor comment 15: P.14 line 32: …, from BB (5%), …

Response to minor comment 15: We have improved the readability of this sentence (line 39, page 15): "Together, these models were used to estimate primary sources of OC that included fossil sources (37-49%), BB (5%), and cooking (1%)."

Minor comment 16: P.15 line 5: … to organic aerosol by can be estimated by…

Response to minor comment 16: We have improved the readability of this sentence (line 35, page 16): "For instance, BB SOA contributions to organic aerosol can be estimated by…"

Minor comment 17: Missing close parenthesis for graph (a) and (b) in Fig. S3.

Response to minor comment 17: The parentheses have been added as suggested by the reviewer.

Minor comment 18: Misaligned unit in the y-axis title of Fig. S10.

Response to minor comment 18: We have corrected this misalignment in the revised manuscript.

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Source apportionment of fine particulate matter in Houston, Texas: Insights to secondary organic aerosols

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Abstract.

Online and offline measurements of ~~fine~~ ambient particulate matter (PM) near the urban and industrial Houston Ship Channel in Houston, Texas, USA during May 2015 were utilized to characterize its chemical composition and to evaluate the relative contributions of primary, secondary, biogenic, and anthropogenic sources. Aerosol mass spectrometry (AMS) on non-refractory PM_1 ($PM \leq 1$ µm) indicated major contributions from sulfate (averaging 50% by mass), organic aerosol (OA, 40%), and ammonium (14%). Positive matrix factorization (PMF) of AMS data categorized OA on average as 22% hydrocarbon-like organic aerosol (HOA), 29% cooking influenced ~~semi-volatile~~less oxidized oxygenated organic aerosol (CI-~~SV~~LO-OOA), and 48% ~~low-volatility~~more-oxidized oxygenated organic aerosol (~~LV~~MO-OOA), with the latter two sources indicative of secondary organic aerosol (SOA). Chemical analysis of $PM_{2.5}$ ($PM \leq 2.5$ µm) filter samples agreed that organic matter (35%) and sulfate (21%) were the most abundant components. Organic speciation of $PM_{2.5}$ organic carbon (OC) focused on molecular markers of primary sources and SOA tracers derived from biogenic and anthropogenic volatile organic compounds (VOC). The sources of $PM_{2.5}$ OC were estimated using molecular marker-based positive matric factorization (MM-PMF) and chemical mass balance (CMB) models. MM-PMF resolved 9 factors that were identified as diesel engines (11.5%), gasoline engines (24.3%), non-tailpipe vehicle emissions (11.1%), ship emissions (2.2%), cooking (1.0%), biomass burning (BB, 10.6%), isoprene SOA (11.0%), high-NO_x anthropogenic SOA (6.6%), and low-NO_x anthropogenic SOA (21.7%). Using available source profiles, CMB apportioned 41% of OC to primary fossil sources (gasoline engines, diesel engines, and ship emissions), 5% to BB, 15% to SOA (including 7.4% biogenic and 7.6% anthropogenic), and 39% to other sources that were not included in the model and are expected to be secondary.

This study presents the first application of *in situ* AMS-PMF, MM-PMF, and CMB for OC source apportionment and the integration of these methods to evaluate the relative roles of biogenic, anthopogenic, and BB-SOA. The three source apportionment models agreed that ~50% of OC is associated with primary emissions from fossil fuel use, particularly motor vehicles. Differences among the models reflect their ability to resolve sources based upon the input chemical measurements, with molecular marker-based methods providing greater source specificity and resolution for minor sources. By combining results from MM-PMF and CMB, BB was estimated to contribute 11% of OC, with 5% of primary emissions and 6% BB-SOA. SOA was dominantly anthropogenic (28%) compared to biogenic (11%) or BB-derived. The three-model approach

demonstrates significant contributions of anthropogenic SOA to fine PM. More broadly, the findings and methodologies presented herein can be used to advance local and regional understanding of anthropogenic contributions to SOA.

1 Introduction

Organic aerosol (OA) comprises a significant fraction of atmospheric particulate matter (PM) in urban environments (Aiken et al., 2009; Cao et al., 2004; Fraser et al., 2002). Secondary organic aerosol (SOA), formed in the atmosphere through the chemical transformation of volatile organic compounds (VOC~~s~~), is a major source of organic aerosol mass (Kroll and Seinfeld, 2008; Henze et al., 2008). Current knowledge of the precursors, mechanisms of formation, and properties of SOA is incomplete, leaving major gaps in understanding of exactly how, and to what extent, SOA affects air quality and climate (Foley et al., 2010). In particular, the roles of natural and anthropogenic precursors to SOA are highly uncertain and variable: results of some published studies indicate dominance (>90%) of biogenic precursors like isoprene (Hallquist et al., 2009), while others studies highlight the importance of anthropogenic VOC (>30%), such as benzene and toluene (Volkamer et al., 2006; Henze et al., 2008). In this study, a measurement-based approach is taken to evaluate the relative contributions of biogenic and anthropogenic VOC to SOA, and their role in relation to primary PM sources, in an urban location in Houston, TX.

Source estimation of SOA in the atmosphere is challenging due to the complexity of precursors to and chemical reactions that form it (Hallquist et al., 2009). Model predictions of SOA rely on knowledge of VOC abundance, product volatility, and SOA yields from chamber studies (Seinfeld and Pankow, 2003; Chan et al., 2009; Donahue et al., 2006). Predictions undergo continuous improvement as knowledge of SOA precursors and formation pathways evolves (Robinson et al., 2007; Ng et al., 2007). Measurement-based approaches can be used to provide ground-truthing for model predictions.

The SOA tracer method estimates SOA contributions to ambient organic carbon (OC) or organic aerosol (OA) through measurements of SOA tracers ~~for~~ from VOC (i.e., isoprene, α-pinene, toluene, or naphthalene) using the tracer-to-SOA mass fraction obtained from laboratory chamber experiments (Kleindienst et al., 2007; Kleindienst et al., 2012). This approach is useful in identifying and estimating SOA contributions from SOA precursors at receptor sites and can be used in combination with other organic molecular markers in the source apportionment of OC (Lewandowski et al., 2008). The SOA-tracer method, however, is limited to a handful of VOC precursors and should be further expanded to represent the broader diversity of VOC precursors to SOA.

Receptor models are widely applied for the source apportionment of ambient PM (Belis et al., 2013) and provide valuable information to support air quality management (Hopke, 2016). Among these models, molecular marker-based chemical mass balance (CMB) modeling apportions PM or OC measured at the receptor based on least-squares solution to the linear combination of source profiles and their relative contributions to fit ambient measurements (Watson et al., 1984). Accurate solutions for CMB apportionment largely depend on the representativeness of the profiles to the receptor site. CMB has been successful in apportioning the carbonaceous PM to primary sources for which profiles are available (Lough et al., 2007; Schauer et al., 2002; Simoneit et al., 1999; Rogge et al., 1998). However, the CMB model is often unable to apportion OC for which sources are unknown or not well defined (Stone et al., 2009; Sheesley et al., 2017). Even with the incorporation of SOA tracers into CMB modeling (following the previously described SOA-tracer method), a significant fraction of OC remains unapportioned, suggesting that better representation of SOA is needed in this model (Stone et al., 2009). Molecular marker-based positive matrix factorization (MM-PMF) does not require source profiles and instead decomposes ambient measurements into factors and factor contributions that need to be interpreted in order to identify the source types, based on the knowledge of source signatures (EPA-PMF, 2014). This approach has been particularly useful in

the elucidation of SOA contributions to ambient PM, by providing insight into the precursors and pathways by which they form (Hettiyadura et al., 2018; Srivastava et al., 2018a; Srivastava et al., 2018b; Wang et al., 2017). ~~MM-~~While PMF requires a relatively large sample size, MM-PMF has generated stable solutions with as little as 35 observational data points, which is expected to arise from the high specificity of primary and secondary source tracers Hu et al. (2010)~~(60-200) to provide a statistically meaningful solution (Jaeckels et al., 2007)~~. Studies that have compared CMB and MM-PMF results generally show agreement in their estimation for the primary sources, but systematically give higher MM-PMF source estimates than CMB (Shrivastava et al., 2007; Jaeckels et al., 2007).

In recent years, aerosol mass spectrometry (AMS) has been widely used to characterize the OA of non-refractory submicron PM ($NR\text{-}PM_1$) and is related to source types using AMS-PMF (Paatero and Tapper, 1994; Ulbrich et al., 2009). This approach overcomes the complexity and challenges associated with the quantification of the organic species in atmospheric matrixes (Seinfeld and Pankow, 2003; Goldstein and Galbally, 2007) and apportions OA into factors based on their mass fragmentation fingerprints (Zhang et al., 2011). The high time-resolution of AMS enables the identification of diurnal source variations. However, ambiguity can arise in apportioning sources with similar mass fragmentation fingerprints such as cooking and vehicular emissions (Mohr et al., 2009) and with specifying contributing sources.

Houston, TX, an industrial coastal city, experiences elevated traffic-related air pollution and VOC emissions from petroleum facilities (Zhang et al., 2017; Buzcu and Fraser, 2006). The urban and industrial areas near the Houston Ship Channel (HSC) have been the subject of source apportionment of VOC~~s~~ (Xie and Berkowitz, 2006; Buzcu and Fraser, 2006; Dechapanya et al., 2004) and PM. Sullivan et al. (2013) apportioned $PM_{2.5}$ using metals data from 2005 to 2012 with PMF near the HSC and reported major contributions from secondary inorganic sources (33.9% ammonium sulfate and 4.2% ammonium nitrate), followed by vehicles (17.5% light duty and 4.8% heavy duty) and crustal elements (11.9% calcium sulfate and 6.3% crustal elements), with minor contributions from fires, sea salt and oil combustion. Using molecular marker-based CMB, Fraser et al. (2003) apportioned $PM_{2.5}$ to vehicle emissions (30% from gasoline and diesel), road dust (11%), fuel oil combustion (7%), meat cooking (6%), wood combustion (2%), and vegetative detritus (2%). Also using molecular-marker based CMB, Buzcu et al. (2006) apportioned 49% of $PM_{2.5}$ OC near HSC, predominantly to vehicle emissions (36% of OC). Applications of AMS-PMF near the HSC suggested that secondary sources contribute 55-68% of OA, but did not distinguish between biogenic and anthropogenic precursors (Cleveland et al., 2012; Wallace et al., 2018)~~.~~. These source apportionment studies indicate significant influences on PM from motor vehicles and secondary reactions~~,~~ but lack understanding on the precursors to SOA. Combining these apportionment techniques would be helpful to gain better insights about the composition of organic aerosol (OA) and provide more accurate source characterization.

In this work, we report a compositional analysis and source characterization of the $PM_{2.5}$ and ~~non-refractory~~NR-PM_1 near the HSC in May 2015. An Aerodyne high-resolution time-of-flight AMS (HR-ToF-AMS) provided ~~non-refractory~~ NR-PM_1 composition and elemental ratios. AMS-PMF was applied to further categorize PM_1 OA. $PM_{2.5}$ filter samples were collected on a day-night basis and were analyzed for OC, ionic species, organic molecular markers, and SOA tracers from biogenic and anthropogenic precursors. CMB and MM-PMF modeling were applied to apportion the primary and secondary sources of $PM_{2.5}$ OC. The outcomes of these source apportionment models were compared and are discussed along with the meteorological data and real time measurements of VOC~~s~~ in order to gain a robust understanding for the sources, abundance, and variability of fine PM, particularly SOA, in HSC.

2 Experimental methods

2.1 Site description

Fine PM was studied at the Clinton Drive monitoring site in Houston, TX (29.733943° N, 95.257684° W), that is maintained by the Texas Commission on Environmental Quality (TCEQ). Clinton Drive is located 11 km west of the city

center and is adjacent to the HSC. The immediate surroundings include industrial facilities (e.g., oil refineries), heavily trafficked roadways, and several neighborhoods.

2.2 Co-located measurements

The Clinton Drive site provided access to co-located hourly measurements of VOC that were measured using an automated gas chromatograph (GC), fine PM ($PM_{2.5}$) measured by tapered element oscillating microbalance (TEOM), and meteorology. Quality-controlled data were collected~~,~~ and accessed through TCEQ (TCEQ, 2017).

2.3 High resolution time of flight aerosol mass spectrometer (HR-ToF-AMS)

2.3.1 PM_1 measurements

Real time measurements of NR-PM_1 were taken with a HR-ToF-AMS (Aerodyne Research) for the period 13-29 May, 2015 at the Clinton Drive monitoring site, with a time resolution of 1 minute. The HR-ToF-AMS has been described in detail previously (DeCarlo et al., 2006); the sampling protocol utilized in this study is identical to that described by Wallace et al. (2018).

2.3.2 Positive matrix factorization analysis of PM_1 OA (AMS-PMF)

Source apportionment of the organic fraction of NR-PM_1 was conducted using AMS-PMF (Paatero and Tapper, 1994). The PMF evaluation tool (PET v.2.08D, (Ulbrich et al., 2009)) employing the PMF2 algorithm (Paatero, 2013) running in robust mode with model error set to 0 was used for analysis of the HR OA mass spectra (*m/z*=12 to *m/z*= 115). The HR OA concentration matrix and associated error matrix resulting from PIKA v 1.16H were used as input for AMS-PMF application. Prior to analysis, mass fragments with signal to noise ratio (SNR) below 0.2 were removed from the dataset, while ions with SNR between 0.2 and 2 were down weighted by a factor of 3, following Paatero and Hopke (2003). Similarly, a down weighting factor of $\sqrt{5}$ was applied to CO_2^+-related ions to prevent excessive influence of the m/z 44 signal, as recommended by Ulbrich et al. (2009). AMS-PMF model solutions including from 1 to 7 factors were fit using multiple initialization points in order to ensure convergence to global rather than local minima. Each set of AMS-PMF model output was evaluated based on the ratio of the summation of the scaled residuals (Q) to the expected value of Q ($Q/Q_{expected}$) (Supplemental Information; Table S1 and Fig. S1-S3), its convergence to a global minimum, and its ability to reproduce the OA mass concentrations measured during the field campaign. These parameters were examined and used as selection criteria for the number of factors in the final AMS-PMF model. Additionally, the physical meaningfulness of the retained factors in each model and their similarity with factors reported in previous OA studies employing HR-ToF-AMS were considered when selecting the number of AMS-PMF components. Based on these criteria, a model including three factors was found to be the most appropriate for describing the dataset under analysis. Further details on AMS-PMF application and the criteria for factor selection are presented in Fig. S1-S3.

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2.4 Filter sample collection and offline chemical analysis

2.4.1 Filter sample collection

$PM_{2.5}$ samples were collected using a medium-volume URG air sampler (3000B, URG Corp.) with a cyclone (URG) operating at a flow rate of 90 L min^{-1}. Air flow rate was monitored before and after sampling using a rotameter (Gilmont Inst.). $PM_{2.5}$ samples were collected on 90-mm quartz fiber filters (Pallflex® Tissuquartz™, Pall life science) that were pre-cleaned by baking for 18 hours at 550 °C. Samples were collected for the period 5-27 May 2015 twice daily, during

daytime (7:00 - 18:00 LT) and nighttime (19:00 – 6:00 LT). After sampling, filters were transferred to Petri dishes lined with pre-baked aluminum foil, sealed with Teflon tape, transported to the laboratory, and stored frozen at -20 °C until analysis. One field blank was collected for every five samples by loading a blank filter into the filter holder, pulling no air through it, and removing it from the filter holder.

2.4.2 Measurements of organic carbon, elemental carbon, and organic species

Organic carbon (OC) and elemental carbon (EC) were measured by thermal-optical analysis (Sunset Laboratory Inc.) on a 1 cm^2 filter portion following Schauer et al (2003). Filters were extracted into acetonitrile following the method described by Al-Naiema and Stone (2017). Briefly, isotopically-labelled internal standards were added onto each filter. Then, filters were extracted sequentially with three 10 mL portions of acetonitrile (Optima-Fisher Scientific-Fisher Chemical) for 15 minutes by ultra-sonication (Branson 5510, 60 Sonics per minute). The combined extracts were reduced to 2 mL by rotary-evaporation at 30 °C, 120 rpm, and 200 mbar (Heidolph, Hei-vap G1). Extracts were filtered with 0.25 µm PTFE syringe filters (Whatman) and stored frozen at – 20 °C. Immediately prior to analysis, the extracts were evaporated to 100 µL under a gentle stream of ultra-pure nitrogen at 30 °C. All glassware used in extraction was first baked (500 °C for 5 hours) to remove organic contaminants and then silanized using 5% solution of dichlorodimethylsilane (Fluka), prepared in toluene (Sigma-Aldrich). Organic species were analyzed using an Agilent 7890A GC coupled to a 5975C MS (Agilent Technologies). Polycyclic aromatic hydrocarbons (PAH), n-alkanes, and hopanes were directly injected to the GC-MS equipped with a DB-5 column and electron impact (EI) ionization source (70 eV). The GC inlet temperature was 300 °C. An aliquot of the extract was trimethylsilylated with N,O-bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane (BSTFA+TMCS, 99:1, Fluka Analytical 99%). A 20 µL aliquot of the extract was dried under a gentle stream of nitrogen, 10 µL of the silylation agent was added, and the mixture was reacted at 100 °C for 90 min. Details about species quantification by GC-MS are provided elsewhere (Al-Naiema and Stone, 2017).

2.4.3 Ion Analysis and pH estimation

Filters were extracted into ultra-pure (UP) water (Barnstead EasyPure II) by shaking (125 rpm) for 10 minutes, sonication (60 sonics min^{-1}) for 30 minutes, followed by shaking (125 rpm) for 10 minutes. Extracts were filtered with 0.45 µm syringe filters (PTFE, Whatman). Ions were analyzed by a Dionex ICS-5000 ion chromatograph (Dionex ASDV). Details regarding ion separation and quantification are described elsewhere (Jayarathne et al., 2016).

Ion results along with other meteorological data such as relative humidity and ambient temperature were introduced to the Extended Aerosol Inorganics (E-AIM IV) model (Friese and Ebel, 2010), available interactively from http://www.aim.env.uea.ac.uk/aim/model4/model4a.php, to estimate aerosol pH. In this study, model input included the molar concentrations of sulfate, nitrate, chloride, ammonium, sodium, calcium, and magnesium; the pH was estimated by calculating the $[H^+]$ required to balance any cation deficiency.

2.5 Chemical mass balance (CMB) modeling

The contribution of different sources to the OC fraction was estimated using the EPA CMB receptor model (v8.2). CMB model employs source profiles to estimate source contributions to ambient PM by solving for the least-squares solution (Watson et al., 1984). In this study, the input source profiles included diesel engines and both smoker and non-smoker gasoline engines (Lough et al., 2007); secondary organic carbon (SOC) from isoprene, α-pinene, and toluene (Kleindienst et al., 2007); bituminous coal (Oros and Simoneit, 2000); biomass burning (Lee et al., 2005); and ship emissions (Agrawal et al., 2010). The naphthalene SOA profile was obtained from Kleindienst et al. (2012) and had a

phthalic acid-to-SOC mass fraction of 0.0389, phthalic acid-to-SOA mass fraction of 0.0199, and the average SOA:SOC of 1.95. Species included in the CMB model included EC, levoglucosan, 17α(H)-21β(H)-hopane, 17α(H)-22,29,30-trisnorhopane, 17α(H)-21β(H)-30-norhopane, ~~ABB 20(R+S) C27 cholestane, ABB 20(R+S) C29 sitostane, n-alkanes (C_{25}-C_{31}),~~ PAH (benzo(b)fluoranthene, ~~benzo(k)fluoranthene, benzo(e)pyrene,~~ indeno(1,2,3-cd)pyrene, and benzo(ghi)perylene~~, and dibenz(ah)anthracene~~), isoprene SOA tracers (2-methylglyceric acid and 2-methyltetrols), one α-pinene SOA tracer (cis-pinonic acid), one naphthalene SOA tracer (phthalic acid), and one toluene SOA tracer (2,3-dihydroxy-4-oxopentanoic acid).

2.6 Molecular marker based-positive matrix factorization (MM-PMF)

The EPA PMF (version 5) was used for source apportionment of $PM_{2.5}$ OC based on organic species and EC as input data. The MM-PMF input data statistics are summarized in Table S2. MM-PMF solutions for 3 to 11 factors were analyzed using 20 base runs. To determine a final solution, MM-PMF solutions with 5 to 9 factors were further analyzed using 100 base runs each starting with a random seed. The stability of the PMF solutions were assessed using displacement (DISP), bootstrapping (BS), and BS-DISP error estimation methods following the recommendations of Brown et al. (2015) and Norris et al. (2014). PMF settings for base runs and error estimation are summarized in Table S3.

2.7 Statistical analysis

Correlation analysis among the measured species and VOC~~s~~ were evaluated using Minitab statistical analysis software (version 17). Correlation coefficients (r)~~s~~ were interpreted as follows: very high (0.9-1.0), high (0.7-0.9), moderate (0.5-0.7), low (0.3-0.5), and negligible (0.0-0.3). The statistical significance of correlations was evaluated at the 95% confidence interval ($p < 0.05$).

3 Results and discussion

Clinton Drive is a long-term monitoring site near the HSC in Houston where $PM_{2.5}$ mass, select gases, and meteorology are measured hourly (TCEQ, 2017)~~,~~ (Fig. S4). Several extreme rain events and flooding occurred during the study period of 5-27 May 2015 (Fig. S5). Winds were predominantly southerly, transporting air from the Gulf of Mexico, suggesting minimal influence of continental transport on ambient air at Clinton Drive. Daily $PM_{2.5}$ mass concentrations averaged 14.0 ± 5.1 μg m^{-3} and ranged from 4.4 to 30.8 μg m^{-3}, well below the daily National Ambient Air Quality Standard (NAAQS) of 35 μg m^{-3} (US-EPA, accessed 2017). Hourly $PM_{2.5}$ concentrations peaked between 7-10 am, coinciding with morning traffic. The NO_x and toluene mixing ratios also peaked in the early morning and late afternoon, coinciding with high traffic periods (Fig. S4). The daytime peaks in ozone (O_3) and isoprene were consistent with expected summertime trends.

3.1 Overview of non-refractory submicron aerosol composition measured by HR-ToF-AMS

Non-refractory ~~(NR)~~ PM_1 (NR-PM_1) measurements by the HR-ToF-AMS from 13 to 29 May are summarized in Fig. 1. Due to the rainy weather, the observed NR-PM_1 levels were low in comparison to other measurements made in the HSC area earlier in 2015 (Wallace et al., 2018). Despite the rainy conditions, periods of elevated NR-PM_1 loadings occurred (Fig. 1a). Average relative contributions from major species to NR-PM_1 quantified are shown in Fig. 1b. Sulfate and organics are the two most abundant components of the NR-PM_1, contributing 44.9% and 39.7%, respectively. Sulfate and organics exhibited periods of high loadings with concentrations over 15 μg m^{-3} and maximum 1-minute averaged concentrations of 22.2 and 57.5 μg m^{-3}, respectively. Ammonium was the next most abundant species, making up 13.9% of the NR-PM_1, followed by nitrate and chloride, which only contributed trace amounts (1% or less) to the NR-PM_1 mass

concentration. Table 1 summarizes the mean, median, standard deviation, and range of 1-minute concentrations for NR-PM_1 species. The diurnal profiles for PM_1 species (Fig. 1c) indicate no diurnal trend for the measured species, except for organic aerosol, which exhibited higher concentrations during daytime. The elemental ratios of the organic portion of NR-PM_1, including the oxygen-to-carbon ratio (O:C) and hydrogen-to-carbon ratio (H:C), as well as organic mass-to-organic carbon (OM:OC) and the average carbon oxidation state ($\overline{OSc}$) are presented in Table 2.

3.2 Composition of $PM_{2.5}$ determined by filter-based measurements

Filter-based $PM_{2.5}$ measurements indicated that, on average, organic carbon (OC) and elemental carbon (EC) contributed 17% and 4% of $PM_{2.5}$, respectively (Table 3). Organic matter (OM) was estimated by the mean OM:OC ratio of 2.11 measured by HR-ToF-AMS (Table 2 and Fig. S6) to contribute 35% of $PM_{2.5}$. The AMS-determined OM:OC ratio is considered to be the best estimate of the $PM_{2.5}$ OM:OC ratio, since it was determined at HSC for the study period. However, this estimation is limited by the differences of sizes of particles analyzed by each method as well as AMS's measurement of only non-refractory OA, while $PM_{2.5}$ OC includes refractory and non-refractory species. OM concentrations were significantly higher during daytime (4.8 ± 1.2 μg m^{-3}) compared to nighttime (3.6 ± 1.4 μg m^{-3}, $p = 0.011$, Table 3). EC concentrations were also significantly higher during daytime (averaging 0.7 ± 0.4 μg m^{-3}) compared to nighttime (0.3 ± 0.2 μg m^{-3}, $p < 0.001$). Higher daytime EC at Clinton Drive is expected to be influenced by transportation emissions near the HSC (Levy et al., 2013; Zhang et al., 2017). On average, sulfate contributed 21.4% of $PM_{2.5}$ (averaging 2.87 ± 1.39 μg m^{-3}), with minor contributions from ammonium (4%, 0.52 ± 0.40 μg m^{-3}), nitrate (3%, 0.40 ± 0.37 μg m^{-3}), sodium (5.5%), chloride (3.3%), potassium (0.6%), and magnesium (0.7%). Calcium contributed 4.3% of $PM_{2.5}$ and likely originated from road dust, which has previously been estimated to contribute to 11% of $PM_{2.5}$ at Clinton Drive (Fraser et al., 2003). On average, OM, EC, and inorganic ions accounted for 80% of the $PM_{2.5}$ mass ~~$PM_{2.5}$ mass not accounted for by the measured species~~ (Fig. 2), with the remaining mass ~~is~~ expected to arise from unmeasured species such as crustal metal oxides (e.g. silica, alumina), other metals, and particle-bound water. For samples in which the measured species exceed $PM_{2.5}$ mass, contributing factors include analytical uncertainties in chemical species measurements and $PM_{2.5}$ mass measured by tapered element oscillating microbalance (TEOM) (Ayers et al., 1999).

Filter-based $PM_{2.5}$ measurements indicate the same major PM species as AMS NR-PM_1 measurements and their ambient concentrations are compared here. The linear regression of the filter-based estimate of $PM_{2.5}$ OM and NR-PM_1 AMS OA had a slope of 0.61 and a low, but significant correlation ($r = 0.48$, $p = 0.005$), indicating that more OM was captured by the filter-based measurements than by the AMS. Sulfate measured by both techniques correlated strongly ($r = 0.90$, $p < 0.001$), with a slope of 0.89 indicating only a minor increase in filter-based sulfate relative to the AMS. Ammonium correlated moderately ($r = 0.72$, $p < 0.001$) with a slope of 0.73. The consistently lower NR-PM_1 concentrations measured by AMS relative to filters suggests the presence of OA, sulfate, and nitrate in the 1-2.5 micron size range and/or refractory matter that was not captured by the AMS. ~~and also capture refractory PM components (i.e., EC, a fraction of OM, and crustal elements).~~

Ion measurements indicate that the aerosol at Clinton Drive is acidic. The correlation between the molar concentrations of major anions (sulfate and nitrate) and ammonium measured by HR-ToF-AMS (Fig. 3) had a slope of 1.287 ± 0.002, indicating that ammonium does not fully neutralize sulfate as ammonium sulfate. Aerosol pH was estimated using E-AIM IV to range from 0.29 to 1.45 with an average of 0.44 ± 0.39. The estimated pH values might be biased because E-AIM does not account for the activity coefficient of H^+ and neglects the role of organic acid dissociation (Hennigan et al., 2015). In comparison to other locations in the summertime, the estimated pH values in HSC are less than those estimated by ISORROPIA-II for Birmingham, Alabama (1.6 – 1.9) (Rattanavaraha et al., 2016) and Centreville, Alabama (0.5 - 2) (Guo et al., 2015), but are higher than those estimated by E-AIM for four major cities in China (-0.77 to -0.52) (Pathak et al.,

2009). Acidic aerosol is expected to enhance SOA formation, as indicated in previous SOA chamber experiments (Surratt et al., 2007; Iinuma et al., 2004).

3.3 PMF of AMS data: Factor identity and contribution to OA

The mass spectra of the three-factor AMS-PMF solution are presented in Fig. 4. Each OA factor exhibited marked differences in their spectral mass signature and fragmentation patterns. Elemental ratios of O:C and H:C for the factors ranged from 0.06 to 1.24 and 1.21 to 2.03, respectively, while $\overline{OS}$c ranged from -1.91 to 1.27 (Table S4). These metrics reflect a largely different chemical character of the retained factors and indicate the likely contribution of components with primary and secondary origin to the observed OA concentrations (Zhang et al., 2011).

The hydrocarbon-like organic aerosol (HOA) factor in Fig. 4 had large signals at *m/z* 41, 43, 55 and 57 and significant contributions from mass fragments above *m/z* 60. These characteristics and O:C and H:C ratios are typical of primary organic aerosol (Zhang et al., 2011; Aiken et al., 2008). This classification was further confirmed by spectral contrast angles (θ) of ~13 to 15° between this factor and previously reported HOA factors (Aiken et al., 2009; Docherty et al., 2011; Mohr et al., 2012; Elser et al., 2016), indicating strong similarities in the mass spectra HOA (Kaltsonoudis et al., 2017).

The ~~low volatility~~ more-oxidized oxygenated organic aerosol (~~LV-OOA~~MO-OOA) and cooking-influenced ~~semi-volatile~~less-oxidized oxygenated organic aerosol (CI-~~SV-OOA~~LO-OOA) factors were characterized by large fractions of *m/z* 44 (f_{44}, associated mostly to CO_2^+ signal) and by elevated O:C ratios and $\overline{OS}$c levels (Table S4), which are indicative of atmospherically processed OA aerosol with a likely secondary origin (Zhang et al., 2011). Moreover, f_{44} and the fraction of *m/z* 43 in the mass spectrum (f_{43}, mainly related to the $C_2H_3O^+$ ion; Table S4) locate them in the ~~SV-OOA~~LO-OOA and ~~LV-OOA~~MO-OOA regions of the "triangle plot," respectively as introduced by (Ng et al., 2011).

The mass spectrum of the CI-~~SV-OOA~~LO-OOA factor (Fig. 4) closely coincides with at least one ~~SV-OOA~~LO-OOA factor included in the University of Colorado at Boulder~~UCB~~-AMS Database (θ ~13 °) (Aiken et al., 2009) and exhibits statistically significant ($p<0.01$) linear association with semi-volatile PM_1 constituents such as nitrate ($r=0.6$). Further insight on the identity of this factor was obtained by examining its correlation with markers of OA sources; this analysis showed a significant correlation of the time series of the ~~SV-OOA~~LO-OOA factor with mass fragments previously reported as tracers of cooking organic aerosol (COA) such as $C_3H_3O^+$, $C_3H_5O^+$, $C_2H_3O^+$ and $C_5H_8O^+$ ($r= 0.7$-0.9, $p<0.01$) (Mohr et al., 2012; Mohr et al., 2009; Sun et al., 2011). Specific correlations between CI-~~SV-OOA~~LO-OOA and different food cooking tracers are presented in Table S5. In addition to the observed co-variability between CI-~~SV-OOA~~LO-OOA and COA markers, the ratio between m/z 55 and m/z 57 in the CI-~~SV-OOA~~LO-OOA mass spectra provides further evidence of the likely influence of cooking activities on this factor. CI-~~SV-OOA~~LO-OOA exhibited an f_{55}/f_{57} larger than 2, consistent with typical mass signatures of urban COA (Cao et al., 2018; Reyes-Villegas et al., 2018; Sun et al., 2016). Despite the identification of ~~SV-OOA~~LO-OOA as influenced by cooking-related activities, the denomination of this factor as CI-~~SV-OOA~~LO-OOA is not to be confused with its classification as COA. The differences between CI-~~SV-OOA~~LO-OOA and COA are reflected, for instance, by the CI-~~SV-OOA~~LO-OOA diurnal profile (Figure 5), which lacks the typical meal-time increases observed in urban COA (Wallace et al., 2018). This reinforces that although CI-~~SV-OOA~~LO-OOA is associated with specific COA signatures, its contribution to PM_1 reflects only partially the impact of cooking activities.

The ~~LV-OOA~~MO-OOA factor (Fig. 4) exhibited a statistically significant moderate correlation with particulate sulfate levels ($r=0.5$, $p<0.01$), suggesting, to some extent, its formation on a regional scale (Peng et al., 2016). These observations along with the resemblance of the mass signature of this factor with ~~LV-OOA~~MO-OOA factors reported in previous studies (θ below 17°) (Docherty et al., 2011; Mohr et al., 2012), led to the classification of this factor as atmospherically processed OA resembling ~~LV-OOA~~MO-OOA.

The time series of concentration of the ~~HOA, CI-SV-OOA, and LV-OOA~~AMS factors and their diurnal trends are presented in Fig. 5. The average mass concentrations observed for ~~HOA, CI-SV-OOA, and LV-OOA~~MO-OOA, CI-~~SV-OOA~~LO-OOA, and HOA during the field campaign were ~~0.72 ±0.52 µg m^{-3}, 0.48 ± 0.47 µg m^{-3}, and~~ 0.37 ± 0.73 µg m^{-3}, 0.48 ± 0.47 µg m^{-3}, and 0.72 ±0.52 µg m^{-3}, respectively, indicating a predominant contribution from secondary factors to the PM_1 OA. The contribution to the OA mass concentration during the sampling period followed the sequence ~~LV-OOA~~MO-OOA ~~>~~ < CI-~~SV-OOA~~LO-OOA ~~>~~ < HOA, with average abundances of approximately ~~48.23, 29.44, and~~ 22.33~~%~~, 29.44, and 48.23% respectively.

As indicated by the standard deviations associated with the average mass concentrations of the PMF factors (Figure 5), large variations in their ~~OC~~ contributions to total OA occurred during the sampling interval, with particularly high variability observed for HOA. As presented in Fig. 5b, the diurnal profile of the HOA factor exhibited local maxima at ~09:00 and 17:00 LT, respectively, indicating its enhancement during periods of significant traffic activity. Thus, it is likely that the observed variability in the mass concentration of HOA is related to peak traffic times. According to Fig. 5b, ~~LV-OOA~~MO-OOA mass concentrations showed a relatively flat diurnal behavior with a slight increasing trend during daytime (7:00 to 18:00 LT), which is consistent with periods of enhanced photochemical activity and is in agreement with ~~LV-OOA~~MO-OOA diurnal patterns reported in previous studies (Sun et al., 2011, Zhang et al., 2016). The hourly behavior of the CI-~~SV-OOA~~LO-OOA factor (Fig. 5b) indicates higher concentrations during daytime, unlike the expected trends for semi-volatile species. Although a slight concentration peak at ~12:00 LT, likely related with cooking activities, was noticed in this factor, no evident late-night increases as those previously observed for COA in the Houston area (Wallace et al., 2018) were observed (Fig. 5b).

3.4 Source apportionment of $PM_{2.5}$ OC in HSC

3.4.1 Chemical mass balance (CMB) modeling

CMB modeling apportioned $PM_{2.5}$ OC to eight sources (Fig. 6, Table 4): diesel engines, gasoline engines (reported as the sum of smoking and non-smoking gasoline engines), biomass burning (BB), ship emissions, isoprene SOA, α-pinene SOA, monoaromatic SOA, and naphthalene SOA. The bituminous coal source contribution was not statistically significant. CMB model diagnostics, including R^2, χ^2, and calculated-to-measured ratios for fitting species are summarized in Table S6. Unapportioned (or other) OC was calculated as the difference between the observed OC mass and the OC apportioned to these eight sources. The average OC during daytime (2.27 ± 0.56 µgC m^{-3}) was apportioned 55% to primary sources and 16% to secondary sources, with 29% unapportioned. The average OC mass during nighttime was apportioned 37% to primary sources and 14% to secondary sources, with 49% unapportioned.

Motor vehicles were the greatest $PM_{2.5}$ OC source, with gasoline engines contributing 30% and diesel engines contributing 10% on average. OC contributions from gasoline engines were significantly higher during daytime (0.82 ± 0.37 µgC m^{-3}) compared to nighttime (0.36 ± 0.30 µgC m^{-3}, $p<0.001$, Table 4). Similarly, diesel engine contributions were significantly higher ($p=0.001$) during daytime (0.27 ± 0.15 µgC m^{-3}) compared to nighttime (0.13 ± 0.09 µgC m^{-3}). The higher daytime contributions are expected to result from greater motor vehicle activity during daytime, which captured the majority of peak traffic times in the morning and afternoon.

Biomass burning had a small impact on $PM_{2.5}$ OC, with an average contribution of 5% (0.10 µgC m^{-3}). No significant differences in daytime and nighttime concentrations were observed. The open BB profile was used in CMB because high fire activity was observed in the Yucatan Peninsula of Mexico during the time of sample collection (Fig. S7). Backward wind trajectories indicated that some air masses affecting Houston had travelled over the Yucatan Peninsula (Fig. S8). The influence of Mexico wildfires on the Houston airshed, previously noted in other studies, typically peaks during the

month of May (Duncan et al., 2003; Yokelson et al., 2009; Crounse et al., 2009). A similarly minor contribution from BB was previously reported for the same sampling site (Fraser et al., 2003).

Ship emissions contributed 1% of $PM_{2.5}$ OC, with a significantly higher (p=0.001) daytime concentration (0.02 ± 0.01 μgC m^{-3}) compared to nighttime (0.01 ± 0.01 μgC m^{-3}; Table 4). Despite the location of Clinton Drive near the HSC, ship emissions were not a major source of OC, which may be due to the prevailing southerly wind direction (Fig. S4). These results may be also biased from the use of a single source profile in CMB modeling, since ship characteristics such as vessel category, speed, and loading impact ship emissions (Williams et al., 2009).

CMB was used to apportion OC to four SOA precursors, following the SOA-tracer approach (Kleindienst et al., 2007). SOA from monoaromatic VOC~~s~~ was estimated by 2,3-dihydroxy-4-oxopentanoic acid (DHOPA, detected in 80% of samples) at 3% of OC (Table 4). Toluene is a known precursor to DHOPA (Kleindienst et al., 2004) and monoaromatic SOA correlated significantly with toluene during daytime (r=0.52, p=0.039) and nighttime (r=0.725, p<0.001). The diurnal trend in toluene concentrations coincides with peak traffic times (Fig. S4) suggesting that vehicles are the major source of monoaromatic SOA precursors.

Naphthalene SOA contributed an average of 4.6% to $PM_{2.5}$ OC (Table 4). To our knowledge, this is the first study to use ambient concentrations of phthalic acid in CMB modeling to estimate naphthalene SOA, following our previous recommendations (Al-Naiema and Stone, 2017). Phthalic acid concentrations were converted to SOA yields using the mass fraction of phthalic acid-to-OC in SOA generated in naphthalene photooxidation chamber experiments (Kleindienst et al., 2012). The estimated naphthalene SOA correlated significantly with gasoline engines (r = 0.409, p = 0.012), suggesting gasoline engines are an important sources of naphthalene, which is consistent with a previous report of naphthalene accounting for 56% of PAH emitted from gasoline engines (Khalili et al., 1995).

Isoprene SOA was estimated to contribute 7% of the $PM_{2.5}$ OC by way of three tracers: 2-methylthreitol, 2-methylerythritol, and 2-methylglyceric acid (Fig. 6, Table 4). On average, isoprene SOA was higher during daytime (0.18 ± 0.11 μgC m^{-3}) compared to nighttime (0.11 ± 0.13 μgC m^{-3}), consistent with the hourly diurnal profile of isoprene that follows ambient temperature and UV radiation (Fig. S4) and prior studies of isoprene SOA (Budisulistiorini et al., 2015; Xu et al., 2015). Industrial emissions can be sources of isoprene in the HSC, with two point sources identified near the sampling location (Fig. S9). Isoprene SOA contributions were seven times lower than those reported in June-July 2013 in Look, Rock TN, which has a much higher isoprene concentration (2 ppbv) (Budisulistiorini et al., 2015) than the HSC area average during this study (0.1 ppbv, Fig. S4).

α-Pinene SOA contributed 0.5% of $PM_{2.5}$ OC, based on the ambient concentrations of cis-pinonic acid that forms by ozonolysis of α-pinene (Christoffersen et al., 1998). Only one α-pinene SOA tracer was detected, consistent with the low mass contributions of this source to OC and the low monoterpene emission potential near the HSC (Brown et al., 2013).

The CMB-source apportionment of primary sources (contributing an average of 46% of OC) agrees well with previous studies in the HSC. For a non-wood smoke event of summer 2000, Buzcu et al. (2006) reported that primary sources contributed 49% to OC, with contributions from diesel (21%) and gasoline (15%) vehicles, BB (8%) and meat cooking (3%). Absolute contributions of these primary sources to OC have decreased by 33-83% over that last decade, when comparing this study to Buzcu et al.~~,~~ (2006). ~~I~~In February 2015, Wallace et al. (2018) identified three primary PM_1 OA factors: hydrocarbon-like (14%), BB (22%), and cooking (8%). Altogether, this and prior studies indicate that motor vehicles contribute significantly to OC year-round, that summertime contributions from BB are smaller than winter, and that cooking contributions are relatively small. The SOA-tracer method was applied to the HSC for the first time, and yielded the estimates that anthropogenic SOA from monoaromatic VOC and naphthalene contributed an average of 7.5% to $PM_{2.5}$ OC, with biogenic SOA from isoprene and α-pinene contributing 7.4% of OC. Notably, a ~~major fraction~~substantial amount of OC was unapportioned, averaging 0.68 μgC m^{-3} (29%) in the daytime ~~samples~~ and 0.86 μgC m^{-3} (49%) in the nighttime ~~samples~~. Considering the strong agreement of primary source contributions with the other two approaches in this work (section 3.6) and in prior studies, it is expected that the unapportioned OC is due to SOA. The SOA not accounted for in the CMB model

includes SOA precursors for which the SOA tracer method has not been developed and also arises from differences in the SOA tracer-to-OC ratios across chamber experiments and the Houston airshed. 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.

3.4.2 Molecular marker-based positive matrix factorization model (MM-PMF)

The 9 factor solution was identified as the optimal solution by analyzing Q, error estimation diagnostics and factor interpretability (Table S7). The difference between Q_{robust} and Q_{true} is smallest for the 9-factor solution, indicating a minimum impact from outliers. The difference between Q_{robust} to $Q_{expected}$ ratio is smallest when moving from 8 to 9 factors in the solution. The base model diagnostics and error estimation for the 9-factor solution are summarized in Table S2 and Fig. S10, respectively. The sources associated with each factor were identified by the key chemical species apportioned to each factor (Fig. 7), factor contributions (Fig. 8), and factor correlations with co-located measurements and CMB source contribution estimates.

The diesel engines factor contributed 12% of average OC (equivalent to 0.22 µgC m^{-3}). The key chemical species apportioned to this factor include cyclopenta(cd)pyrene (76%), benz(a)anthracene (88%), chrysene (64%), EC (41%), and 17α(H)-21β(H)-30-norhopane (39%) that are components of fossil fuel combustion emissions (Lough et al., 2007; Rogge et al., 1993a). This factor contributes significantly more OC during daytime (0.369 µgC m^{-3}) compared to nighttime (0.066 µgC m^{-3}, $p<0.001$). The factor EC:OC ratio of 0.92 suggests contributions from light-duty (<33,000 lb) diesel-powered motor vehicles (1.9±0.53) (Lough et al., 2007). The factor identification is further supported by its positive correlation with the CMB-diesel engine source ($r=0.727$, $p<0.001$) and slope of 1.5±0.2.

The gasoline engines factor contributed an average of 24% of OC (0.46 µgC m^{-3}). The major chemical species apportioned to this factor include *n*-alkanes such as tetracosane (37%), pentacosane (39%), hexacosane (38%), heptacosane (33%), octacosane (50%), and nonacosane (37%), and 17α(H)-21β(H)-30-norhopane (38%) that have been detected among fossil fuel combustion emissions (Lough et al., 2007; Rogge et al., 1993a). The EC:OC ratio of this factor (0.29) is within the range of EC:OC ratios for non-smoking (0.20 to 0.52) and smoking (0.0 to 2.5) gasoline vehicles (Lough et al., 2007). The moderate and significant correlation of this factor with CMB-gasoline engines ($r=0.479$, $p=0.001$) and slope of 0.6±0.2 further support the identification of this factor as gasoline engines.

The non-tailpipe vehicle emissions factor contributed an average of 11% of $PM_{2.5}$ OC (0.21 µgC m^{-3}). The key chemical species apportioned to this factor includes 17α(H)-21β(H)-hopane (82%), pristane (32%), and nonadecane (20%), while the absence of EC indicates a non-combustion source. 17α(H)-21β(H)-Hopane is a tracer for fossil fuel combustion and has been detected in both tailpipe and non-tailpipe vehicle emissions and is present in the higher boiling point fractions of crude oil that are used to manufacture lubricating oils, waxes, tires, and asphalt (Rogge et al., 1993a, b). Hopanes in the atmosphere come from engine oil evaporation, tire wear, and paved road dust and to a lesser extent from brake wear particles (Rogge et al., 1993a, b). Pristane and nonadecane have also been detected in tire dust, brake lining wear particles, and paved road dust particles (Rogge et al., 1993b). This factor contributes significantly more OC during daytime (0.249 µgC m^{-3}) compared to nighttime (0.171 µgC m^{-3}, $p=0.050$) (Fig. 8). This factor identification is further supported by the ratio of benzo(a)pyrene to the sum of benzo(a)pyrene and chrysene of this factor (0.29), which is within the range of non-tailpipe vehicle emissions (0.23-0.32) (Rogge et al., 1993b). The factor contribution averaged 29% of OC for samples in which 17α(H)-21β(H)-hopane was detected, suggesting that the detectability of this tracer influenced this factor's contributions to OC.

The ship emissions factor contributed an average of 2% of $PM_{2.5}$ OC (0.04 µgC m^{-3}). The key species attributed to this factor were benzo(b)fluoranthene (42%), benzo(k)fluoranthene (79%), benzo(e)pyrene (40%), benzo(a)pyrene (77%), indeno(1,2,3-cd)pyrene (42%), and benzo(ghi)perylene (51%), nonadecane (34%), 5-nitro-salicylic acid (36%), and 2-

methyl-4-nitrophenol (59%). The PAH and *n*-alkanes indicate a primary fossil fuel combustion source, while the nitromonoaromatic compounds can be either emitted by fossil fuel combustion or formed by the photooxidation of aromatic VOC in the presence of NO_x (Al-Naiema and Stone, 2017; Harrison et al., 2005; Lin et al., 2015). Since these nitromonoaromatic compounds are primarily attributed to this factor, fossil fuel combustion is expected to have been their major source. The absence of EC in this factor is consistent with the very small EC:OC ratio of ship emissions (0.03±0.002) and the ratio of indeno(1,2,3-cd)pyrene to the sum of indeno(1,2,3-cd)pyrene and benzo(ghi)perylene of 0.28 that is similar to that of ship emissions (0.36) (Agrawal et al., 2010).

The cooking factor contributed an average of 1% of $PM_{2.5}$ OC (0.02 µgC m^{-3}). The key chemical species apportioned to this factor include cholesterol (90%), a tracer for meat cooking (Rogge et al., 1991), 4-methyl-3-nitrophenol (86%) and *n*-alkanes such as docosane (51%), tricosane (40%), and heptacosane (34%) that have been also been detected during commercial food cooking (Roe et al., 2004; Rogge et al., 1991). Factor contributions were observed only in samples with detectable levels of cholesterol, for which the average contribution to OC was 2.4%. Overall, these results suggest cooking was a minor source of $PM_{2.5}$ OC in this study.

The BB factor contributed 11% of OC on average (0.20 µgC m^{-3}). This factor is the major source of levoglucosan (60%), a tracer for BB emissions (Simoneit et al., 1999). Other key species apportioned to this factor include SOA products such as isophthalic acid (38%) and cis-pinonic acid (63%) that have been observed among aged BB emissions (Yan et al., 2008). The factors' EC:OC ratio (0.044) is also closer to the EC:OC ratio of aged BB emissions (0.039) that contain both primary and secondary BB aerosols (Yan et al., 2008) compared to fresh, primary BB emissions (0.065) (Lee et al., 2005). These results suggest that the BB emissions observed in the sampling site represent aged BB emissions that were likely transported from Yucatan Peninsula in Mexico (Fig. S7, S8). These results are consistent with prior studies that reported BB emissions in southern Texas were transported from Mexico during the months of April to May during major fire events (Kaulfus et al., 2017; Rogers and Bowman, 2001; Wang et al., 2006). Notably, only 54% of the bootstrap BB factor was mapped (Table S7; the lowest of any factor) indicating a greater relative uncertainty associated with this factor.

The factor identified as isoprene SOA contributed an average of 11% of OC (0.20 µgC m^{-3}). The key species apportioned to this factor include 2-methylthreitol (56%) and 2-methylerythritol (62%) which are isoprene SOA tracers from the photooxidation of isoprene under low-NO_x conditions (Lin et al., 2013). This factor is significantly higher during daytime (0.275 µgC m^{-3}) than nighttime (0.134 µgC m^{-3}; $p=0.036$) which is consistent with the high photochemical activity and high isoprene emissions that is triggered by high daytime temperatures and sunlight (Sharkey et al., 1996). This factor identification is further supported by its very high and positive correlation with CMB-isoprene SOA ($r=0.934$, $p<0.001$), although the slope of 1.8 ± 0.1 suggests the SOA tracer method in CMB underestimated its contribution to OC.

The high-NO_x anthropogenic SOA factor contributed 7% of OC on average (0.12 µgC m^{-3}). The key chemical species apportioned to this factor include 4-methyl-2-nitrophenol (74%), DHOPA (48%) and 2-methylglyceric acid (54%). 4-Methyl-2-nitrophenol forms by the photooxidation of monoaromatic compounds such as toluene, *p*-xylene and *p*-ethyltoluene in the presence of NO_x (Forstner et al., 1997). Similarly, DHOPA is formed by photooxidation of toluene under high-NO_x conditions (Kleindienst et al., 2007). 2-Methylglyceric acid forms from methacrolein (MACR) in the presence of NO_x; MACR can form by the oxidation of isoprene (Nguyen et al., 2015) or can be directly emitted from vehicles (Park et al., 2011), making it either biogenic or anthropogenic, respectively. Vehicle emissions are expected to be the major source of MACR in an urban site located close to the HSC (Park et al., 2011), suggesting that 2-methylglyceric acid in HSC is likely to originate from anthropogenic sources. This factor identification is further supported by its high positive correlation with CMB-monoaromatic SOA ($r=0.754$, $p<0.001$).

The factor identified as low-NO_x anthropogenic SOA contributed 22% of OC on average (0.41 µgC m^{-3}). The key species apportioned to this factor include phthalic acid (38%), 4-methylphthalic acid (43%), terephthalic acid (42%), and 4-nitrophenol (36%). Phthalic acid and 4-methylphthalic acid are recommended as SOA tracers for naphthalene and methylnaphthalene, respectively (Al-Naiema and Stone, 2017). Nitrophenols have also been detected during the

photooxidation of PAH (Kautzman et al., 2010). In addition, this factor moderately and positively correlates with CMB-naphthalene SOA (r=0.510, p<0.001). EC is also present in this factor, suggesting some mixing of this factor with combustion sources. Such mixing likely arises from VOC and precursors of oxidants co-emitted with EC from combustion contributing to SOA formation. However, the predominance of secondary organic markers over signatures of primary emissions suggests that this factor primarily represents SOA. The SOA tracer method estimate of naphthalene SOA in CMB ~~is~~ accounts for only 22% of this factor, suggesting that the SOA tracer method underestimates the extent of low-NO_x anthropogenic SOA based on phthalic acid concentrations alone and/or that this factor contains SOA from other VOC precursors. In addition to naphthalene, several laboratory studies have shown that *n*-alkanes, lighter aromatics and other PAH, which are mainly emitted from fossil fuel combustion and industries, also contribute to SOA (Chan et al., 2009; Gentner et al., 2012; Zhang and Ying, 2012). Further identification and quantification of anthropogenic SOA tracers from other VOC precursors would improve the ability of the MM-PMF to more broadly capture the magnitude of anthropogenic SOA.

3.5 Source apportionment of fine organic aerosol in HSC: a three-method approach

Herein, source apportionment results obtained from AMS-PMF for PM_1 OC (converted from OA using OM:OC ratios in Fig. 4), and $PM_{2.5}$ OC by MM-PMF and CMB models are integrated (Table 5 and Fig. 9) with consideration of the strengths and weaknesses of each approach. The contribution from primary fossil sources are defined as the sum of contributions of diesel engines, gasoline engines, and ship emissions from CMB (41%), the sum of the three aforementioned sources with non-tailpipe vehicle emissions from MM-PMF (49%), and HOA factor from AMS-PMF (37%). A similar contribution from primary fossil sources to $PM_{2.5}$ OC (36%) was reported by Buzcu et al. (2006) in Houston near the HSC area during a non-wood smoke event. HOA resolved in AMS-PMF highly correlated with OC from diesel engines in MM-PMF (r=0.824, p<0.001) and CMB (r=0.890, p<0.001), and moderately correlated with OC from gasoline engines (r=0.645, p<0.001) and ship emissions (r=0.696, p<0.001) in CMB. These correlations indicate temporal consistency among the fossil sources of OC and the percent contributions to OC indicate that the three models resolved a consistent fossil contribution to organic aerosol. Further, the models agree that motor vehicle emissions are the major contributor to fossil-fuel derived organic aerosol, making them the dominant primary PM source in HSC. The agreement of the three models discussed here along with the results obtained from previous studies indicate a good understanding for primary fossil sources in Houston. Because motor vehicles also emit precursors to SOA such as alkanes, light aromatics, and PAHs (Gentner et al., 2012), they likely contribute to anthropogenic SOA.

Biomass burning contributions to OC were small in comparison to fossil sources. AMS-PMF did not resolve a BB factor, likely due to the inclusion of BB in the CI-~~SV-OOA~~LO-OOA factor. The presence of BB in the CI-~~SV-OOA~~LO-OOA factor is supported by the significant although low correlation with CMB BB (r=0.380, p=0.038), the moderate correlation between the time series of this factor and m/z 60 (r=0.67), and the fraction of m/z 60 (f_{60}) in CI-~~SV-OOA~~LO-OOA. This fraction (f_{60}=0.003) is the largest among the retained AMS-PMF factors ~~and~~but falls at the lower edge of the BB influence value defined by Gilardoni et al. (2016), indicating likely association between CI-~~SV-OOA~~LO-OOA and BB. CMB apportioned 5% of OC to BB. Because the CMB model utilized a BB profile collected near the source emissions, this value represents primary BB emissions. The selected source profile of open burning of pine forests (Lee et al., 2005) was considered to be the most representative of the available profiles because BB influences on Houston were traced back to open burning in the Yucatan Peninsula of Mexico (Fig. S7, S8). Importantly, the open burning profile has a relatively low levoglucosan-to-OC ratio compared to other BB profiles (Stone et al., 2009), making it an upper-estimate of BB contributions to OC. MM-PMF apportioned 11% of OC to BB; this value is expected to include both primary and secondary aerosol associated with BB ~~(section 3.5.2.)~~. Evidence of SOA from BB is indicated by the similarities in the MM-PMF BB factor profile BB and aged BB plumes (section 3.~~5~~4.2). The difference between the estimates of primary and secondary BB

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organic aerosol (by MM-PMF) and primary BB organic aerosol (CMB) is used to estimate the magnitude of BB-derived SOA at an average of 6% of OC. The combination of CMB and MM-PMF provides separate estimates of primary and secondary BB contributions to OC, which cannot be resolved using either model alone. The BB SOA estimate is considered to be a best-estimate with the available data set, but contains uncertainties both from the MM-PMF and CMB estimates. Strategies to reduce the relative uncertainty associated with this source include using a larger number of observations and/or more specific BB SOA tracers in MM-PMF.

Cooking was determined to have a minor, but uncertain contribution to $PM_{2.5}$. By MM-PMF, cooking was found to contribute to 1% of $PM_{2.5}$ OC, but with a large relative uncertainty (Fig. S10). The large relative error reflects the high degree of uncertainty in the estimation of this source contribution. Although AMS-PMF did not resolve a cooking factor, AMS-signatures of cooking and CI-~~SV-OOA~~LO-OOA correlated significantly, suggesting a cooking influence on this factor. The cooking contribution to CI-~~SV-OOA~~LO-OOA and OA, however, could not be resolved. Some degree of cooking influence on OA in Houston is expected due to the ubiquity of this source and a study near the HSC area, particularly for northerly winds (Wallace et al., 2018). The predominately southerly winds during this study (Fig S4) were associated with relatively small source contributions from cooking. Large variabilities across different studies are expected based on the sampling proximity to cooking sources and the prevailing wind direction. Cooking remains a difficult source to evaluate with receptor-based source apportionment models that require either fixed source profiles (in the case of CMB) or that resolve factors with consistent chemical composition (in the case of PMF). Cooking contributions are estimated by receptor-based models by way of a few molecular markers or AMS-signatures that may not represent the diversity of cooking activities that occur within an airshed. Consequently, these models cannot capture the inherent diurnal and spatial variability of cooking emissions. A better understanding of the variability of cooking emissions and model constraints are needed to lower uncertainties associated with contributions of cooking to ambient $PM_{2.5}$ organic aerosol.

Biogenic SOA was estimated to contribute up to 11% of organic aerosol. Among biogenic precursors to SOA, isoprene was determined to have the largest contribution. By MM-PMF isoprene SOA contributed 11% of $PM_{2.5}$ OC. This value is similar in magnitude to the 7% of $PM_{2.5}$ OC attributed to isoprene SOA by CMB that relied upon the isoprene tracer-to-OC ratios observed in chamber experiments (Kleindienst et al., 2007), indicating good agreement between these two approaches. The OC contribution estimated by PMF is expected to be more reliable for the Houston airshed, as it was derived from ambient measurements within the HSC~~s~~. In contrast, CMB relies upon tracer-to-OC ratios observed in the laboratory (Kleindienst et al., 2007) where ~~rather than chamber experiments~~ reactant concentrations greatly exceeded those observed in the HSC (Figure S4). In particular, chamber concentrations were approximately 10-fold higher for NO_x, 2-3 orders of magnitude higher for isoprene, and 3-4 orders of magnitude higher for toluene. ~~,~~ Monoterpene SOA was found to be significantly lower, with a 0.5% contribution of α-pinene to OC resolved by CMB. Monoterpene SOA was resolved by neither MM-PMF nor AMS-PMF, likely due to an overall small contribution to OC or a lack of tracers to accurately define this source. Although AMS-PMF did not resolve an isoprene OA factor, moderate correlations between CI-~~SV-OOA~~LO-OOA and CMB estimates of isoprene SOA ($r=0.637$, $p<0.001$) and MM-PMF estimates of isoprene SOA ($r=0.626$, $p<0.001$) suggest that biogenic SOA was grouped with this factor. At small contributions to OC, CMB can better distinguish monoterpene contributions to OC than multivariate models. Overall, the SOA contribution from biogenic precursors are estimated in the range of 11% of OC but would be less if isoprene also has significant anthropogenic sources in this study domain (Fig. S9).

Anthropogenic SOA was identified as a major contributor to organic aerosol. By MM-PMF, two anthropogenic SOA factors were resolved: low-NO_x anthropogenic SOA (21.7%) and high-NO_x anthropogenic SOA (6.6%) ~~and low-NO_x anthropogenic SOA (21.7%)~~. The former source contribution is considered to be stable with > 80% of bootstraps matched, while the latter has a larger relative uncertainty with 67% of bootstraps matched (Table S7). MM-PMF holds the advantage of identifying anthropogenic SOA for several reasons. First, these estimates are ~~sources~~ based on ~~unique~~ molecular tracers selective to this source (Al-Naiema and Stone, 2017). Second, these estimates were developed from ambient measurements

within the HSC airshed and are considered to be the best representation of anthropogenic SOA in this location. Unlike CMB, MM-PMF requires neither a priori knowledge of tracer-to-OC ratios nor the assumption that these ratios are constant across chamber experiments and the study site. Third, by~~it analyzes~~ analyzing the co-variation of species over time, MM-PMF can capture anthropogenic SOA from other precursors that co-vary in time, even if they have a different precursor and are not defined by tracers in the source apportionment model (e.g., alkanes). ~~but does not assume that tracer-to-OC ratios observed in chamber experiments are equivalent to the studied urban environment. Because As with biogenic SOA, the multivariate estimate of anthropogenic SOA is considered to be more reliable because it was developed from ambient measurements within the airshed and is expected to include SOA from a wide range of anthropogenic VOC.~~

Nonetheless, CMB results support that anthropogenic SOA is an important source of OC in the HSC. Using available profiles for anthropogenic SOA in CMB, 3% of OC was attributed to monoaromatic-derived SOA (e.g., benzene, toluene) and 5% was attributed to naphthalene-derived SOA. Larger SOA contributions from PAHs compared to monoaromatic precursors agrees with controlled chamber photo-oxidation of diesel exhaust, in which PAH-derived SOA was estimated to account for up to 54% to the total SOA mass formed in the first 12 h of oxidation (Chan et al., 2009). The total PAH contribution to SOA in HSC is expected to be larger, since other 2-3 ring PAHs with SOA-forming potential (Shakya and Griffin, 2010) are co-emitted with naphthalene; however, molecular tracers for larger PAH oxidation products are not yet defined, so the associated OC is unapportioned by the CMB model. Because ~~T~~the CMB-based estimate of anthropogenic SOA is limited to two classes of VOC precursors~~—~~aromatics and naphthalene derivatives~~—~~for which SOA profiles are available~~, to tracers that have been identified and are known to be specific to this source, and by the representativeness of the SOA profiles to the study domain~~ it is considered to be only a partial estimate of anthropogenic SOA. ~~Thus, a~~Anthropogenic SOA from other precursors ~~other than monoaromatics and naphthalene~~ contribute to the CMB unapportioned OC. ~~are not apportioned by CMB. For these reasons, CMB is unable to provide a reliable estimation of *total* anthropogenic SOA, but~~ The CMB-estimates of aromatic and naphthalene-derived SOA is valuable, however, because it provides ~~results yields~~ specificity in the relative and absolute source contributions for these VOC classes~~that have been characterized in chamber experiments~~.

The AMS-PMF ~~LV-OOA~~MO-OOA factor ~~-~~that accounts for an average of 32% of PM_1 OC is expected to be influenced by anthropogenic SOA based on the correlation observed with high-NO_x anthropogenic SOA in MM-PMF (r=0.515, p=0.004). The MM-PMF and CMB methods that rely on specific tracers overcome the AMS limitation of being ~~AMS-PMF is~~ unable to distinguish between anthropogenic and biogenic origins of SOA~~,~~ in the absence of a strong signal that can identify a specific VOC precursor (Wallace et al., 2018; Xu et al., 2015). Relying on MM-PMF as the best estimate of anthropogenic SOA, we estimate that this source contributes an average of 28% of $PM_{2.5}$ OC, making it a major aerosol source in HSC second only to primary fossil fuel emissions. Led by MM-PMF and supported by CMB and AMS-PMF, these ~~This novel combination and integration of *in situ* AMS-PMF, MM-PMF, and CMB models~~ reveal~~s~~ the important contributions of anthropogenic SOA to $PM_{2.5}$ OC in the HSC area of Houston.

4 Conclusions

Comprehensive chemical analysis of fine PM in the HSC indicated a large contribution from sulfate and carbonaceous aerosol, as evidenced by offline filter-based measurements of $PM_{2.5}$ and *in situ* analysis of NR-PM_1. The novel combination of three source apportionment models (CMB, MM-PMF, and AMS-PMF) with statistical analyses provides a robust prediction of sources of OC, as well as the relative abundances of biogenic and anthropogenic SOA and the pathways by which they form. Together, these models were used to estimate primary sources of OC that included fossil sources (37-49%), ~~from~~ BB (5%), and cooking (1%).

Prior studies ~~have~~ recognized the large contribution from primary fossil sources to $PM_{2.5}$ in the HSC ~~area~~, but did not define sources of SOA. Here we show that secondary aerosols from anthropogenic origins contribute 28% of OC and ~~are~~ largely originate~~d~~ from precursors emitted from primary fossil sources. Anthropogenic SOA is among the largest sources of $PM_{2.5}$ OC near the HSC, while other SOA precursors—biogenic VOC (11%) and BB (6%)—have smaller contributions in comparison. Constraining the amount of SOA from BB and anthropogenic SOA is particularly significant because these two source categories have previously been difficult to estimate using one source apportionment method.

~~In addition, the use of aromatic SOA tracers constrains~~ MM-PMF is a useful approach for estimating source contributions to OC and $PM_{2.5}$, particularly when source profiles for sources are not available or are not well defined, which is often the case for SOA. ~~estimations of anthropogenic SOA and overcomes limitations in source profiles for use in CMB modeling.~~ In order to apportion anthropogenic SOA, it is necessary to explicitly include anthropogenic SOA tracers as fitting species in the ~~MM-~~PMF model. ~~. While i~~Initial guidance on anthropogenic SOA tracer selection wa~~i~~s ~~provided elsewhere~~drawn from Al-Naiema and Stone (2017). In this study, to track anthropogenic SOA formed from aromatic VOC under high NO_x 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~~ The utilized tracers should be expanded as anthr~~h~~opogenic 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 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-NO_x 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). ~~As more anthropogenic SOA tracers are identified and incorporated in to MM-PMF modeling, greater specificity as to the major precursor gases may be gained.~~ 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 ~~In this way, air quality management can target specific precursors and oxidants to reduce $PM_{2.5}$ levels. In the case of anthropogenic SOA, molecular tracers are needed for recognized SOA precursors like n-alkanes, alcohols, and PAHs (beyond naphthalene). Well-defined SOA profiles for these precursors~~ will support CMB-based methods and aid in the interpretation of MM-PMF results.

The analytical approaches and source apportionment methods presented herein can be applied elsewhere to develop a better understanding of BB and anthropogenic VOC to SOA. Combining multiple source apportionment techniques overcomes limitations of using these receptor models in isolation. For instance, BB SOA contributions to organic aerosol ~~by~~ can be estimated by subtracting primary BB estimated by CMB from the sum of primary and secondary BB from MM-PMF. This method is expected to be accurate when the chemical nature of the primary biomass emissions is known and a representative chemical profile is used. This approach can overcome previous limitations on constraining BB-derived SOA, which was challenged by the large number and variability of its precursors and the lack of knowledge of its major SOA products. The methodological approach presented here can be used to gain insight to sources of $PM_{2.5}$, particularly SOA derived from BB and anthropogenic VOC, in diverse urban environments. Knowedge of primary and secondary PM sources ~~that~~ can inform strategies to manage urban air quality, particularly in areas that exceed air quality standards or guidelines.

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Figure Captions

Figure 1: A summary of NR-PM_1 measurements at Clinton Drive for the period May 13th – 29th, 2015; a) Time series including organics, sulfate, ammonium, nitrate and chloride, b) average percent contributions, and c) the hourly diurnal profile (daytime hours are highlighted in yellow). The bottom whisker, bottom box line, top box line and top whisker indicate the 5th, 25th, 75th and 95th percentiles, respectively. Lines inside the boxes represent the hourly median of the data. One high data point of organic (57.42 µg m^{-3}) on 23/5/2015 at 14:05 LT is not shown.

Figure 2: Day and night $PM_{2.5}$ mass composition at Clinton Drive for the period 5-27 May 2015. Carbonaceous and ionic species account for 82% of $PM_{2.5}$, on average, and the remaining 18% was attributed to other species that were not measured, such as silica, alumina and metals. $PM_{2.5}$ mass (average ± analytical uncertainty) was obtained using TEOM from TCEQ.

Figure 3: Scatter plot of the molar ~~concentration~~ equivalents (eq) of negative charges from~~of~~ sulfate ~~plus~~ and nitrate versus the molar equivalents of positive charge from ammonium, measured by HR-ToF-AMS during May 2015. The higher anions relative to ammonium ~~suggest~~ indicates that the acids only partially neutralized and aerosols are acidic.~~that ammonium molar concentrations are insufficient to fully neutralize sulfate, indicating acidic aerosols.~~

Figure 4: Mass spectra of PMF factors in PM_1 OA at Clinton Drive during May 2015.

Figure 5: AMS-PMF factors identified in PM1 OA; a) time series of OA factors (HOA, CI-~~SV-OOA~~LO-OOA, and ~~LV-OOA~~MO-OOA) and b) diurnal profiles of OA factor mass concentrations. Bottom whisker, bottom box line, top box line and top whisker indicate the 5th, 25th, 75th and 95th percentiles, respectively. Lines inside the boxes represent the hourly median and circles represent the hourly mean.

Figure 6: Source contributions to $PM_{2.5}$ OC at Clinton Drive during May 2015 estimated by CMB modeling.

Figure 7: MM-PMF factor profiles. The y-axis represents the percentage of species attributed to each factor.

Figure 8: MM-PMF factor contributions to $PM_{2.5}$ OC at Clinton Drive in May 2015 juxtaposed with measured OC. Samples labeled D were collected during daytime (7:00 - 18:00 LT) and those labeled N samples were collected during nighttime (19:00 - 6:00 LT).

Figure 9: Summary of the average source contributions to PM OC at Clinton Drive determined for (a) NR-PM_1 by AMS-PMF, and (b) $PM_{2.5}$ by MM-PMF and CMB, including primary fossil sources (green), biomass burning (BB; yellow), cooking (orange), biogenic secondary organic carbon (BSOA; purple) and anthropogenic secondary organic carbon (ASOA; dark grey). Numerical values presented in this figure are summarized in Table 5.

Table 1. Summary of ToF-AMS high-resolution (1 min) results of NR-PM_1 composition (μg m^{-3}), measured in HSC for the period 13-29 May, 2015.

	Mean	Median	St. dev.	Max	Min
Organic	1.14	0.95	0.8	57.42	0.06
Nitrate	0.03	0.02	0.03	0.49	BDL
Ammonium	0.4	0.36	0.35	4.54	BDL
Sulfate	1.29	1.12	1.23	22.16	BDL
Chloride	0.01	0.01	0	0.05	BDL

Table 2. Summary of the elemental analysis of NR-PM_1 organic aerosol. $\overline{OSc}$ is defined as the average carbon oxidation state (Kroll et al., 2011) and is calculated by 2*O:C - H:C.

Elemental Ratio	Mean	Median	St. dev.
OM:OC	2.11	2.12	0.29
O:C	0.72	0.73	0.22
H:C	1.5	1.52	0.17
$\overline{OSc}$	-0.09	-0.07	0.6

Table 3: $PM_{2.5}$, its major components (μg m^{-3}) and estimated pH for daytime, nighttime, and overall periods (± standard deviation) at Clinton Drive during May 2015. Organic matter (OM) was estimated based on the mean OM:OC ratio of 2.11 obtained from HR-ToF-AMS (Table 2). P-values ≤ 0.05 indicate that the difference between daytime and nighttime concentrations are statistically significant at the 95% confidence interval.

	Daytime	Nighttime	Overall	P-value
$PM_{2.5}$	14.73 ± 5.08	13.35 ± 6.93	14.04 ± 6.05	0.447
Elemental carbon (EC)	0.71 ± 0.38	0.34 ± 0.24	0.52 ± 0.37	< 0.001
Organic matter	4.78 ± 1.19	3.57 ± 1.40	4.17 ± 1.42	0.011
Sodium	0.73 ± 0.37	0.79 ± 0.50	0.76 ± 0.43	0.566
Ammonium	0.47 ± 0.28	0.56 ± 0.49	0.52 ± 0.40	0.489
Potassium	0.08 ± 0.04	0.08 ± 0.06	0.08 ± 0.05	0.703
Magnesium	0.10 ± 0.04	0.10 ± 0.06	0.10 ± 0.05	0.838
Calcium	0.68 ± 0.39	0.40 ± 0.52	0.54 ± 0.47	0.044
Chloride	0.40 ± 0.31	0.48 ± 0.49	0.44 ± 0.40	0.512
Nitrate	0.45 ± 0.22	0.34 ± 0.47	0.40 ± 0.37	0.353
Sulfate	2.74 ± 0.98	3.00 ± 1.71	2.87 ± 1.39	0.529
Aerosol pH	0.54 ± 1.45	0.32 ± 0.81	0.44 ± 0.39	0.075

Table 4: Chemical mass balance (CMB) estimates of the absolute relative source contributions to $PM_{2.5}$ OC at Clinton Drive in May 2015 averaged over daytime, nighttime, and all periods. P-values ≤ 0.05 indicate that the difference between daytime and nighttime source contributions are statistically significant at the 95% confidence interval.

Source category	Daytime		Nighttime		Overall		p-value
	(μgC m^{-3})	(% OC)	(μgC m^{-3})	(% OC)	(μgC m^{-3})	(% OC)	
Diesel engines	0.27 ± 0.15	11.82 ± 6.32	0.13 ± 0.09	7.80 ± 5.14	0.20 ± 0.14	9.81 ± 6.05	0.001
Gasoline engine [1]	0.82 ± 0.37	37.14 ± 16.29	0.36 ± 0.30	22.56 ± 17.77	0.59 ± 0.41	29.80 ± 18.38	< 0.001
Ship emission	0.02 ± 0.01	1.11 ± 0.68	0.01 ± 0.01	0.73 ± 0.57	0.02 ± 0.01	0.92 ± 0.65	0.001
Biomass burning	0.10 ± 0.08	4.49 ± 3.60	0.10 ± 0.07	5.70 ± 3.52	0.10 ± 0.07	5.09 ± 3.57	0.627
Isoprene SOA	0.18 ± 0.11	7.99 ± 4.86	0.11 ± 0.13	5.90 ± 5.48	0.15 ± 0.12	6.95 ± 5.23	0.063
α-Pinene SOA	0.01 ± 0.03	0.59 ± 0.92	0.01 ± 0.01	0.38 ± 0.33	0.01 ± 0.02	0.49 ± 0.69	0.172
Monoaromatic SOA	0.06 ± 0.05	2.37 ± 1.95	0.06 ± 0.05	3.46 ± 2.63	0.06 ± 0.05	2.91 ± 2.35	0.966
Naphthalene SOA	0.12 ± 0.13	5.36 ± 5.50	0.06 ± 0.04	3.91 ± 2.36	0.09 ± 0.10	4.63 ± 4.25	0.044
Other OC	0.68 ± 0.37	29.24 ± 15.13	0.36 ± 0.30	49.56± 18.58	0.59 ± 0.41	39.40 ± 19.65	0.235

[1] Gasoline engines factor represent the sum of the contribution from smoking and non-smoking gasoline engines

Table 5: Summary of the average source contributions to OC (%) for each of the three source apportionment models. Missing values correspond to sources that were either not included in the model (i.e. CMB) or not resolved by the model (i.e. PMF). Contributions of PM_1 factors to OC were estimated from the OA contributions and OM:OC ratios for each factor (Fig. 4).

Source category / factor	CMB ($PM_{2.5}$)	MM-PMF ($PM_{2.5}$)	AMS-PMF (PM_1)
Primary fossil	41[a]	49[b]	
Cooking		1	
Biomass burning (BB)	5	11	
Biogenic SOA (BSOA)	7	11	
Anthropogenic SOA (ASOA)	8	28	
Other OC	39[c]		
HOA			37
CI-~~SV-OOA~~LO-OOA			31
~~LV-OOA~~MO-OOA			32

[a] Primary fossil sources from the CMB model were calculated as the sum of diesel engines, gasoline engines, and ship emissions; [b] Primary fossil sources of MM-PMF were calculated as the sum of diesel engines, gasoline engines, non-tailpipe emissions, and ship emissions; [c] Other OC sources in CMB represent the fraction of OC that was not apportioned by CMB model. In the absence of unidentified primary sources in CMB, other OC represents SOA.