Anonymous Referee #1

The manuscript "Characterization of carbonaceous aerosols in Singapore: insight from black carbon fragments and trace metal ions detected by a soot-particle aerosol mass spectrometer" investigated the sources of carbonaceous aerosol in Singapore by using Positive Matrix Factorization. Besides utilizing the mass spectra of organics, they inserted the mass fragments of rBC and metals in the data matrix in order to improve the interpretation of the aerosol sources in urban area. The authors were able to resolve five sources/types of organic aerosols; hydrocarbon-like OA, oxygenated-HOA, cooking-related OA, less-oxidized oxygenated OA and more-oxidized oxygenated OA.

This paper presents interesting results and novel data analysis methods. Paper is well-written and fluent, and in most parts also easy to understand. It utilizes nicely the whole high resolution mass spectra provided by the SP-AMS, and thoroughly validates the PMF results. However, the interpretation of the PMF factors is sometimes confusing. Additionally, there are shortcomings in the measurement methods, and the authors have drawn some conclusion based on rather weak evidences. Therefore I recommend publication of the manuscript only after the comments below are adequately addressed.

Author's response: We thank for the positive comments from the reviewer. We have provided our point-to-point responses below (in blue colour) to address the questions/comments as shown below:

General comments

The quantitativity of the SP-AMS results is not considered adequately. Since there are several sources of uncertainty in the AMS measurement, e.g. CE, IE and RIE values, the validation of the SP-AMS needs to be done more accurately. Additionally, the weakness of this paper is that only the data from the SP-AMS is utilized. I assume there were also other instruments at the site (for PM, size distribution, BC etc.), or at the air quality monitoring stations nearby, that could be used for the validation/comparison of the SP-AMS data. Without auxiliary data, there accuracy of the given concentrations remains vague.

Author's response: Thanks for the reviewer's suggestion for addressing the SP-AMS measurement uncertainties. In this field study, we conducted four calibrations and obtained an average IE_{NO3} (ionization efficiency of nitrate) value of 7.92e-8 ($\pm$ 4.08e-09). The standard deviations of RIEs (relative ionization efficiency) for NH_4^+ and rBC have been added in the main text.

The SP-AMS measurements were compared with other co-located measurements from an aethalometer (model AE33, Magee scientific), an OC/EC analyser (Sunset Laboratory) and a Monitor for AeRosols and GAses in ambient air analyzer (MARGA, Metrohm) over the sampling period. Sulfate (SO_4^{2-}) and organic mass concentrations from the SP-AMS (CDCE-corrected) were compared to SO_4^{2-} and OM measured by the MARGA and the OC/EC analyser, respectively (Figure S3a and b in the revised SI). Aside from the good correlations that underline a good temporal response from all instruments, the slopes are in the range of 0.81-0.88, suggesting that the mass concentrations of SO_4^{2-} and organic measured by the SP-AMS are ~12-19% lower than those measured by the MARGA and the OC/EC analyser, respectively. This could be partially explained by the 1 µm cut-size of the SP-AMS, while the two other instruments were measuring $PM_{2.5}$.

The rBC mass concentrations (CE = 0.6) were compared with BC and EC measured by the aethalometer and the OC-EC analyser, respectively (Figure S3c and d in the revised SI). Scatter plots of those comparisons show Pearson coefficients > 0.84, and respective slopes of 0.83 and 1.10, supporting that CE = 0.6 for rBC is a reasonable CE correction approach. Note that no standard approach has been developed for determining CDCE of rBC measured by SP-AMS. As shown in our response to the second reviewer, we determined the CDCE of rBC by comparing BC and EC measured by the aethalometer and the OC/EC analyser, respectively. The median CDCE values ranged between 0.52

and 0.69 as shown in Figure S2 of the revised SI. The following sentences and Figure S3 have been added to the revised manuscript and SI based on the above observations:

Page 2 lines 7-9: "Other co-located instruments for $PM_{2.5}$ characterizations include an aethalometer (AE33, Magee Scientific), a Monitor for Aerosols and Gases (MARGA, Metrohm) and a semi-continuous organic and elemental carbon (OC/EC) analyser (Sunset Laboratory)."

Page 4 lines 27-29: "The campaign averages of RIE_{rBC} and RIE_{NH4} were 0.15 (±0.04) and 4.24 (±0.04), respectively. The default RIE values of nitrate (1.1), sulfate (1.2) and organics (1.4) were used for respective mass concentration quantification (Jimenez, 2003)."

Page 4 lines 33-38: "The SP-AMS measurements were compared with the sulfate and OM concentrations measured by the MARGA and the OC/EC analyser, respectively, showing strong temporal (r = 0.77 and 0.93) and quantitative (slopes = 0.81 and 0.88) agreements between these measurements (Figure S3a and b). A collection efficiency (CE) of 0.6 was used for rBC quantification due to incomplete overlap between the laser vaporizer and the particle beam (Willis et al., 2014). The corrected rBC concentrations were also comparable to those measured by the aethalometer (r = 0.96, slope = 0.83) and the EC measured by the OC/EC analyser (r = 0.84, slope = 1.1) (Figure S3c and d)."
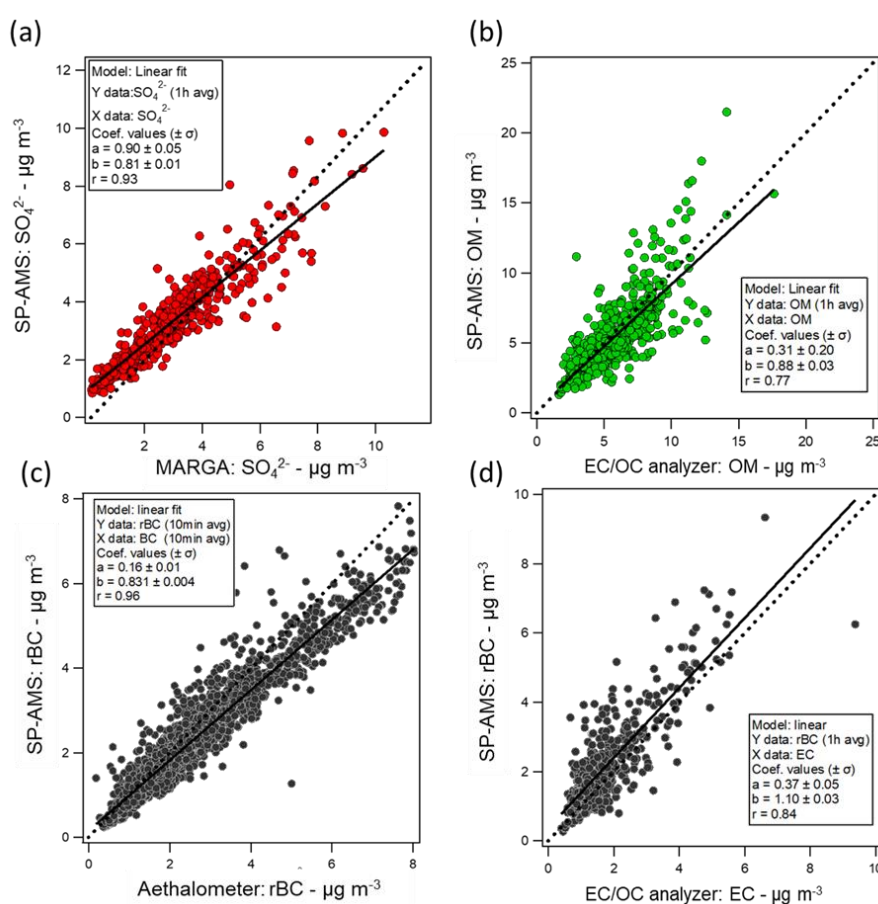

Figure S3: Scatter plots of (a) the hourly-averaged SO_4^{2-} mass concentration measured by the SP-AMS and MARGA, (b) and the hourly-averaged OA and OM (estimated from OC concentration using a 2.2 conversion factor) mass concentrations measured by the SP-AMS and OC/EC analyser, respectively. Comparisons of 10-min averaged rBC mass concentrations measured by the SP-AMS with (c) BC and (d) EC mass concentrations measured by the aethalometer and OC/EC analyser, respectively.

Regarding PMF, I don't understand why only few five metal ions were included in the PMF model even though the SP-AMS can detect quite a few metals. For example, Al, Ca, Cd, Cr, Cu, Fe, Mn, Zn and Sn could be included. I would assume that the inclusion of more metals would improve the interpretation of PMF results. I suggest adding more metals to the PMF analysis because I think that all the interesting information in the data set is not used so far.

Author's response: We agree with the reviewer that it is important to include all the detectable metal signals in the PMF analysis if possible. However, we only reported metals with their average values higher than the limit of detection (Table S2) determined by the particle-free air to ensure the quality of our data analysis. Nickel is a marginal case but a large fraction of its signal remain above its detection limit for investigating the V^+/Ni^+ ratio. To make this point clear, we have revised the sentence in Section 2.3.1 as shown below.

Page 5 lines 24-25: "Lastly, five metal ions (K^+, Na^+, Ni^+, V^+, Rb^+) were included into the PMF model (Figure S4g-i) as the majority of their signals were higher than their respective limit of detection (Table S2)."

In terms of metals, I disagree with the authors that all of the metals presented here can be used as tracers. I agree that Na can come from fuel but it can also originate from other sources in urban areas, for example from coal and biomass burning (e.g. Hsu et al. 2011). Similarly, Rb signal in AMS can originate from coal combustion (Irei et al., 2014). I suggest that the authors consider other sources of metals in urban areas (especially close to industrial areas), and revise their conclusion regarding metals.

Author's response: We agree with the reviewer that most of the metal species that we discussed in the manuscript are not unique tracers. Therefore, our intention is not to discuss how those trace metal species can be used to specify the sources of OA. Rather, we understand that each OA factor identified by the PMF analysis in this work can be originated from different sources. To avoid confusion of our focus in Section 3.5, the sub-heading has been changed to "Characterization of metal ions associated with different OA sources".

With such information, we would like to improve our understanding on the emission characteristics of different OA factors and/or trace metals. For examples, we have pointed out in the manuscript that Na^+ was mainly associated with three OA factors (i.e., HOA, O-HOA, and LO-OOA), which reflects the fact that Na^+ could be emitted from different local combustion sources. Singapore has a biomass clean coal cogeneration plant, but it is important to highlight that natural gas is the major source of electricity (> 95%) in Singapore. Although we didn't observe BBOA factor in this study, we have mentioned that biomass burning can be a possible source of Na^+ in the revised version as suggested by the reviewer. A few sentences in Section 3.5.1 have been revised or added as shown below:

Page 12 lines 5-7: "Based on the PMF results that includes trace metal ions, sodium (Na^+) was mainly associated with HOA, O-HOA and LO-OOA (Figure 5a) that could be due to different types of fossil fuel combustion emissions (e.g., local traffic, shipping, and various industrial activities) as discussed in Section 3.4."

Page 12 lines 20-23: "Biomass burning can be a possible source of Na^+ (Hsu et al., 2011) but no major fresh biomass burning emissions were observed in this study. The MO-OOA factor is suspected to be more influenced by aged regional biomass burning emissions (see more discussion in Section 3.5.2) but Na^+ was not strongly associated with this factor."

Similar to Na^+, we understand that Rb^+ is not a unique tracer for biomass burning. Rather, Rb^+ is likely associated with multiple sources. The results of PMF analysis demonstrated that both K^+ and Rb^+ were mainly associated with MO-OOA (58-66%) followed by the two combustion-related components (HOA and O-HOA). As suggested by the reviewer, we have mentioned that Rb^+ can be a tracer of coal

combustion based on previous studies. Although local coal combustion is uncommon in Singapore, the regional transported of coal combustion plant emissions were still possible. In the revised manuscript, we have revised the discussion to highlight that both regional biomass burning and coal combustion emissions are possible sources of Rb^+. However, it won't substantially change our conclusion that trace metal can allow us to better understand the potential origins of MO-OOA. Since MO-OOA usually represents aged SOA materials in many previous field studies and is a PMF OA factor that cannot provide much mass spectral characteristic for source identification, our data interpretation can provide insight into better identification of MO-OOA sources and/or aging history for other SP-AMS measurements in the future. The majority of Section of 3.5.2 has been rewritten as following.

Page 13, line 1: The sub-heading has been changed to "Potential origins of MO-OOA" to avoid confusion of using Rb^+ as a unique tracer for biomass burning.

Page 13, lines 16-37: "Figures 6c and S14b show that high Rb^+ and K^+ signals were associated with more oxygenated ($f_{44} > 0.7$) fraction of OA, and moderate correlations between MO-OOA and the two metal were observed (Rb^+, r = 0.58 and K^+, r = 0.71, Figure S13b). Furthermore, the results of PMF analysis demonstrated that both K^+ and Rb^+ were mainly associated with MO-OOA (58-66%, Figure 5a) followed by the two combustion-related components (HOA and O-HOA). Although potassium and rubidium are not unique tracers for a specific combustion source, previous studies have shown that these two metals can be largely associated with biomass burning emissions (Artaxo et al., 1993; Lee et al., 2016; Achad et al., 2018). Note that rubidium has also been used as a coal combustion tracer in previous studies (Fine et al., 2004; Irei et al., 2014). Unlike ambient OA component, the chemical identities of K^+ and Rb^+ are unlikely modified by the oxidative aging of aerosol particles. Therefore, a strong temporal correlation between Rb^+ and K^+ (r = 0.85, Figure 6b) further suggests that they were likely of similar origins in this study.

The regional origin of K^+, Rb^+, $C_2H_4O_2^+$ and MO-OOA were investigated through their PSCF. Their PSCF graphs (Figures 6d and S15a- c) show several common origins with high probability that the highest concentrations could be influenced by biomass burning events from Indonesia (Figure S12a). Nevertheless, coal-fired power plants are located nearby the identified hotspots of Rb^+ and K^+ (Figure S12b) so that a regional transport of coal-fired power plant emissions alongside biomass burning plumes were possible. Note that MO-OOA contributes to the highest fraction of nitrogen-containing organic fragments ($C_xH_yNO_z^+$ ~ 32% and $C_xH_yN^+$ ~ 46%) that can be generated by biomass burning emissions (Mace et al., 2003; Laskin et al., 2009; Desyaterik et al., 2013; Mohr et al., 2013). It is important to point out that most of the previous studies usually describe MO-OOA (or LV-OOA in some earlier studies) as aged SOA component without providing further detail on their potential origin and emission characteristics. Our observations underline the possibility of better understanding the origin of the MO-OOA component through measurements of refractory metals even when atmospheric oxidative processing has made the mass spectral features of aged OA materials less distinguishable."

Specific comments
1. Page 1, Abstract; lines 19-20; "local combustion sources" and "industrial emissions" need to be described in more detailed. What kind of combustion sources, just traffic? What industry there are in that area?

Authors' response: The major industrial activities occurring on Jurong Island (i.e., the large industrial zone in Singapore) have been added in Table S1. Additional locations for some of the industries referred in the table have been added on Figure S1a following the second reviewer's suggestion. The abstract has been modified as follow:

Page 1, lines 21-24: "This work provides evidence that over 90% of rBC was originated from local combustion sources with a major part related to traffic and ~30% of them associated with fresh

secondary organic aerosol (SOA) produced under the influences of shipping and industrial emissions activities (e.g., refineries and petrochemical plants) during daytime."

2. Page 4, line 27; "composition –dependent approach" CE values need to be shown in the paper and the uncertainty of the CE has to be evaluated carefully. Since the RIE for sulfate was not determined, the uncertainty analysis is very important.

Authors' response: The CDCE time series has been added in Figure S2 as shown below. Note that CDCE approach is a well-developed data analysis algorithm for correcting the mass concentrations of NR-PM measured by AMS. To further validate this approach for our dataset, the hourly averaged CDCE-corrected SO_4^{2-} and OM mass concentrations are compared with other co-located measurements of SO_4^{2-} (MARGA) and OM (OC/EC analyser) as shown in Figure S3a and b. The strong agreements between the different measurements were observed as discussed in our responses for the general comments above, suggesting that the CDCE derived for our dataset are reasonably good. The manuscript and SI have been revised accordingly as presented in the responses to the general comments.
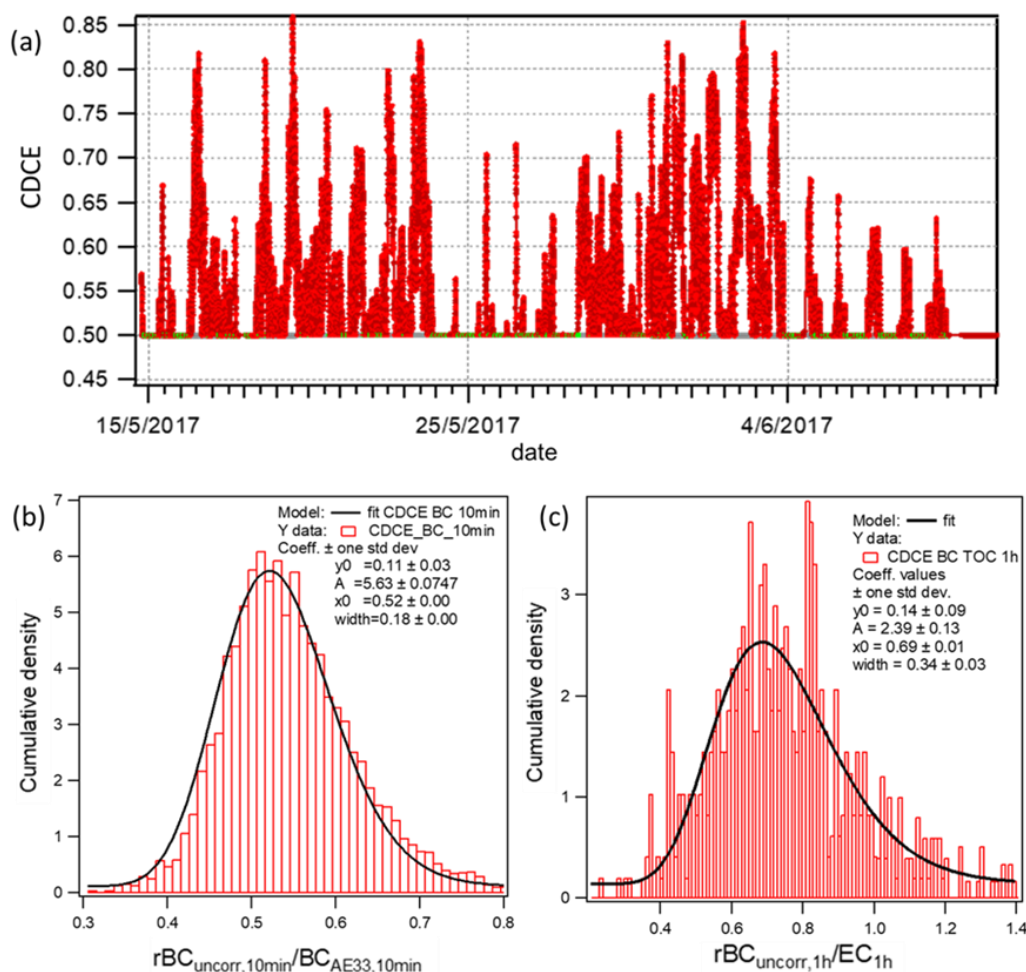

Figure S2: (a) Time series of composition-dependent collection efficiency ($CDCE_{Mid}$) determined over the entire campaign. Cumulative frequency of (b) aethalometer-based CDCE and (c) OC/EC-based CDCE, and their respective lognormal fitting determined over the entire campaign (with the fitting parameters corresponding to the following equation: $Y = y_0 + A \exp\left\{-\left[\frac{\ln(x/x_0)}{width}\right]^2\right\}$).

3. Page 5, line 13; I don't understand why only few five metal ions were included in the PMF model. I suggest adding more metal ions.

Authors' response: The presence of other metal ions have been investigated in our data analysis but we have decided to exclude those metal ions with signal below the limit of detection. Please refer detail to our response to general comments above.

4. Page 5, line 13-14; metals ions were included in Hz's into the PMF. How does that affect the results of the PMF?

Authors' response: We thank the reviewer for pointing out this. Metal signals in Hz were used for time series comparisons and NWR plots. While for PMF, metal signals were converted to nitrate equivalent mass concentrations assuming their RIE equal to 1. This approach keeps all the signals of organic, C_n^+ and metal fragments within similar order of magnitude. Note that we attempted PMF analysis after applying RIEs on metals – Na^+, Rb^+, V^+, Ni^+ from Carbone et al., (2015) and K^+ from Drewnick et al., (2006) – on the PMF inputs. However, metal signals would drive PMF solutions because of their strong intensities after such RIE correction. Therefore, the RIE of 1 were applied to all metals and the K^+ signals were downweight by a factor 2 for the final PMF solution. To make sure such information clearly delivered in the manuscript, the following sentences have been revised or added in the revised version.

Page 5 lines 2-3: "The signals of these trace metal ions were not calibrated and thus their raw signals were used for investigating their temporal variations."

Page 5 lines 24-27: "Lastly, five metal ions (K^+, Na^+, Ni^+, V^+, Rb^+) were included into the PMF model (Figure S4g-i) as the majority of their signals were higher than their respective limit of detection (Table S2). The metal ion signals were corrected to nitrate equivalent mass concentrations by assuming their RIE values equal to 1 and the K^+ signals were downweight by a factor 2"

5. Page 5, line 30; sulfate increase starting from 10:00 can be explained by the active photochemistry. Could you add a diurnal plot showing solar radiation and sulfate in the same figure?

Authors' response: We have added the diurnal variation of solar radiation to Figure 1c to emphasize the hours of day with intense photochemistry as suggested by the reviewer.
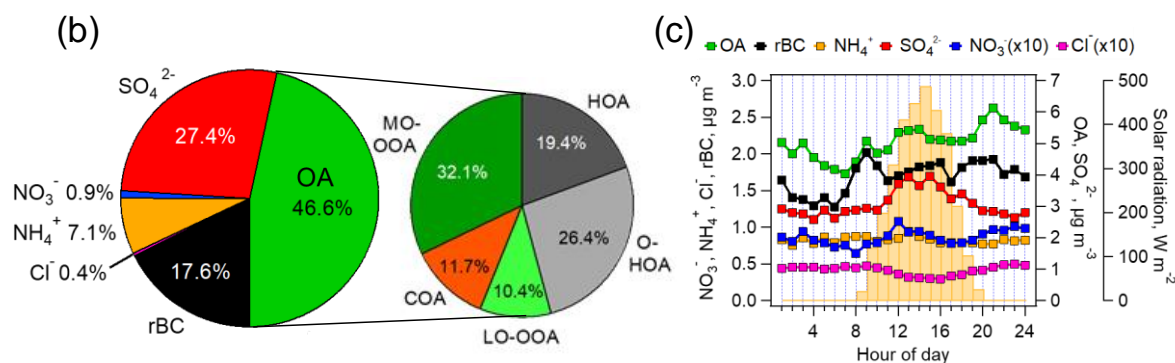

Figure 1: […] (b) Average chemical compositions of NR-PM and rBC with the contribution of the PMF factors to total OA. (c) Diurnal patterns of rBC, total OA, inorganic species and solar radiations (represented by the yellow bars).

6. Page 5, line 30; NH4 ratio and acidity; the discussion on acidity is somewhat unreliable because the RIE for sulfate was not measured. For example in Fig. S4a, it's hard to understand why all the points are below 1:1 line. To me, this seems to be due to the incorrect RIE for sulfate. Could you comment on that?

Authors' response: Regarding the accuracy of SO_4^{2-} mass concentration, we have discussed in our response to the general comments above and we could conclude that the RIE applied for sulfate are reasonable. Note that the main purpose of showing the ratios between measured and predicted NH_4^+ (Figure S6a-c) is to highlight the relative changes in aerosols acidity especially when the high SO_4^{2-} loadings were observed. This relative observation should not be affected by the absolute SO_4^{2-} mass concentrations. Furthermore, previous studies have reported that fine particles encountered in Singapore and Southeast Asia are usually acidic (Budisulistiorini et al., 2018; Pye et al., 2019). Budisulistiorini et al., (2018) recently reported an average $NH_{4,meas}/NH_{4,pred}$ ratio of 0.7 (±0.3) underlining the acidic nature of aerosols outside of hazy periods. Indeed, ammonia emissions caused by biomass burning results in a neutralization of inorganic particles (Budisulistiorini et al., 2018), while usual ammonia level in Singapore remain relatively low compare to other region of the world (Behera et al., 2013).

7. Page 7, line 5; industrial emission; be more specific what kind of emissions

Authors' response: It is rather difficult for us to pin point the exact types of industrial emissions. However, we know that refineries, petrochemical industries and shipping emissions are some of the key emission sources from the industrial zone as reported in Table S1. The sentence has been revised as following.

Page 7 lines 27-29: "It is important to note that the period with elevated concentrations of sulfate and sulfur-containing fragments were synchronized with the sea breeze from the southwest, from which refineries, petrochemical industries and shipping emissions could be carried to our sampling site (Figure 2 and S6e)."

8. Page 7, line 28; define POA, is it only HOA? Isn't COA also primary?

Authors' response: Both HOA and COA are primary in nature. The focus of Section 3.3.1 is combustion emissions, COA are discussed in Section 3.3.2. To avoid such confusion, a sentence has been added at the beginning of Section 3.3.2 to highlight that COA are also one of the major POA component.

Page 9 line 11: "COA is another major POA component identified in this study."

9. Page 7, line 38; "large combustion sources during nighttime" needs to be elaborated since it has such a large effect on diurnal cycle of HOA

Authors' response: We agree with the reviewer that the unknown combustion sources can have substantial impact to the diurnal cycle of HOA. However, their influences were occasionally observed within our sampling period as highlighted in our original discussion. It is difficult to identify the exact emission sources but the elevated concentrations were observed at low wind speed condition, suggesting that they were likely due to local emissions from the city. We do believe it can be related to the local industrial emission, such as the flaring emissions from petrochemical industries. The related text have been revised as following to give the reader some ideas about the potential night time combustion sources.

Page 8 lines 24-35: "High concentrations of rBC, NO_x and HOA were observed during the mid-night between May 25th and 28th, indicating the presence of large combustion sources during nighttime that might impact the air quality at our sampling site occasionally (Figure 1a). This observation also reflected from the diurnal plots (Figures 3 and S8) that the mean mass concentrations of HOA, rBC, NO_X and CO during the mid-night were much higher than their corresponding median values. Figure S8a shows that the highest N:C ratio was observed during the morning traffic peak hours but remained relatively low for the rest of the period. Such observation suggests that the emission characteristics of these unknown combustion sources at nighttime could be different to those associated with traffic emissions during the daytime. Although it is difficult to confirm the origin of those nighttime combustion emissions without further evidence, the observed events were coupled to low wind speed condition, suggesting that they were likely due to local emissions from the city. For example, significant emissions due to flaring from petrochemical industries, which largely depends on plant operation, during the relatively stagnant atmospheric condition could lead to elevated concentrations of the combustion-related species."

10. Page 9, lines 11-15; "organo-nitrate and nitrogen-containing fragments increased during the daytime in this field study." Why there is not more discussion on these species if they were detected? What is their contribution to OA or LO-OOA? Add the ratio of N to C (and S:C) to Figure 3.

Authors' response: N:C ratios have been added to Figure 3 for each factor in the revised version. As shown in the figure below (submitted for Kasthuriarachchi et al., (2020)), nitrogen fragments can be originated from different sources. Since we don't have strong evidence to develop conclusive arguments regarding the nitrogen compounds chemistry from primary emissions and secondary aerosol formation, we have decided to added/revised a few sentences throughout the manuscript to briefly highlight how nitrogen fragments may be associated with different emissions. Given that the contribution of nitrogen-containing fragments were only ranged from 0.6 to 1.4 % for each PMF OA factor, adding detail discussion for nitrogen-containing fragments may dilute the focus of this manuscript.

Page 8 lines 28-31: Discussion for HOA - "Figure S8a shows that the highest N:C ratio was observed during the morning traffic peak hours but remained relatively low for the rest of the period. Such observation suggests that the emission characteristics of these unknown combustion sources at nighttime could be different to those associated with traffic emissions during the daytime."

Page 10 line 10-15: Discussion for LO-OOA - "Furthermore, Kasthuriarachchi et al. (2020) reported that the concentrations of organo-nitrate and nitrogen-containing fragments (i.e., $C_xH_yN^+$ and $C_xH_yNO_z^+$) slightly increased during daytime (e.g., Figure S8a) with LO-OOA, contributing to 30% of observed $C_xH_yNO_z^+$ fragments (Figure S10). This suggests that photo-oxidation of VOCs under high-NO_X condition could be a potential pathway toward LO-OOA formation given that the NO_X concentrations reached up to 160 ppb (Figure 1a, mean = 16.5 ppb) during the campaign."

Page 13, lines 30-32: Discussion for MO-OOA - "Note that MO-OOA contributes to the highest fraction of nitrogen-containing organic fragments ($C_xH_yNO_z^+$ ~ 32% and $C_xH_yN^+$ ~ 46%) that can be generated by biomass burning emissions (Mace et al., 2003; Laskin et al., 2009; Desyaterik et al., 2013; Mohr et al., 2013)."
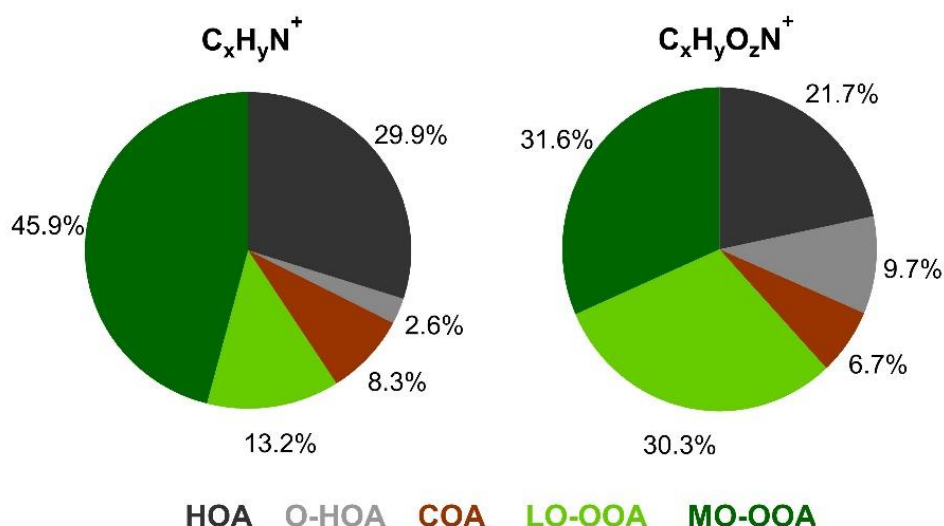
Figure S10: Contributions of each OA factor to the N-containing fragment groups (Kasthuriarachchi et al., (2020)).

11. Page 11, line 5-; Na as a tracer for fossil fuel combustion. Revise this section by taking into account other sources of Na in urban areas (see general comments).

Authors' response: As shown in our responses in the general comments, our intention is not to use Na^+ as a fossil fuel combustion tracer. Rather, we understand that Na^+ can be originated from various sources in urban. In particular, we pointed out that Na^+ was mainly associated with three OA factors (i.e., HOA, O-HOA, and LO-OOA), which reflects the fact that Na^+ could be emitted from different local combustion sources. In addition, although we didn't observe BBOA factor in this study, we have mentioned that biomass burning can be a possible urban source of Na^+ in general in the revised version as suggested by the reviewer. A few sentences in Section 3.5.1 have been revised or added as shown below:

Page 12 lines 5-7: "Based on the PMF results that includes trace metal ions, sodium (Na^+) was mainly associated with HOA, O-HOA and LO-OOA (Figure 5a) that could be due to different types of fossil fuel combustion emissions (e.g., local traffic, shipping, and various industrial activities) as discussed in Section 3.4."

Page 12 lines 20-23: "Biomass burning can be a possible source of Na^+ (Hsu et al., 2011) but no major fresh biomass burning emissions were observed in this study. The MO-OOA factor is suspected to be more influenced by aged regional biomass burning emissions (see more discussion in Section 3.5.2) but Na^+ was not strongly associated with this factor."

12. Page 11, Biomass burning tracers, I don't understand why the contribution of biomass burning has been investigated so extensively even though it does not show up in PMF and the metals are not very good tracers for it. Consider making Section 3.5.2. more compact.

Authors' response: The m/z 60 (or $C_2H_4O_2^+$ organic fragments) has been widely used as a tracer organic fragment for identifying BBOA in the PMF analysis. Cubison et al. (2011) have generalized observations from worldwide field data that m/z 60 signature become less and less significant in aged BBOA materials. The implication of such observation is that atmospheric aging of BBOA can lead to formation of MO-OOA (or LV-OOA in earlier studies) but their origins cannot be easily identified in

the conventional PMF analysis. Note that MO-OOA usually represents aged SOA materials in many previous field studies and is a common OA factor that cannot provide much mass spectral characteristic for source identification. How we can better understand the origin of MO-OOA is certainly an important research topic for the atmospheric science/chemistry community.

Since biomass burning emissions are commonly observed in the Southeast Asian in general (not within Singapore), we would like to examine if the regional pollutions, such as aged biomass burning and other anthropogenic emissions, may contribute to the observed MO-OOA in this study. This type of investigation is further motivated by our observation that the $f_{C2H4O2+}$ value of MO-OOA is slightly higher than the background value reported in Cubison et al. (2011) and its moderate correlation with K^+ and Rb^+. Although the metal ions that we used in this study are not unique for any specific sources, they are more persistent to atmospheric aging compared to their co-emitted OA materials, and thus can provide insight into the potential sources and/or aging history of MO-OOA. As pointed out by the reviewer in the general comment, we have revised the discussion to highlight the fact that K^+ and Rb^+ can be emitted by both coal combustion and biomass burning. However, it won't substantially change our conclusion that trace metal may allow us to better understand the potential origins of MO-OOA. We do believe the similar approach can also be applied for other SP-AMS measurements in the future.

Since our interested is not limited to the potential influences of aged regional BBOA, we have changed the sub-heading of Section of 3.5.2 to "Potential origins of MO-OOA" in order avoid confusion. Furthermore, the majority of Section 3.5.2 and Section 4 have been rewritten as following,

Section 3.5.2: Page 13, lines 16-37: "Figures 6c and S14b show that high Rb^+ and K^+ signals were associated with more oxygenated ($f_{44} > 0.7$) fraction of OA, and moderate correlations between MO-OOA and the two metal were observed (Rb^+, r = 0.58 and K^+, r = 0.71, Figure S13b). Furthermore, the results of PMF analysis demonstrated that both K^+ and Rb^+ were mainly associated with MO-OOA (58-66%, Figure 5a) followed by the two combustion-related components (HOA and O-HOA). Although potassium and rubidium are not unique tracers for a specific combustion source, previous studies have shown that these two metals can be largely associated with biomass burning emissions (Artaxo et al., 1993; Lee et al., 2016; Achad et al., 2018). Note that rubidium has been used as a coal combustion tracer in previous studies (Fine et al., 2004; Irei et al., 2014). Unlike ambient OA component, the chemical identities of K^+ and Rb^+ are unlikely modified by the oxidative aging of aerosol particles. Therefore, a strong temporal correlation between Rb^+ and K^+ (r = 0.85, Figure 6b) further suggests that they were likely of similar origins in this study.

The regional origin of K^+, Rb^+, $C_2H_4O_2^+$ and MO-OOA were investigated through their PSCF. Their PSCF graphs (Figures 6d and S15a- c) show several common origins with high probability that the highest concentrations could be influenced by biomass burning events from Indonesia (Figure S12a). Nevertheless, coal-fired power plants are located nearby the identified hotspots of Rb^+ and K^+ (Figure S12b) so that a regional transport of coal-fired power plant emissions alongside biomass burning plumes were possible. Note that MO-OOA contributes to the highest fraction of nitrogen-containing organic fragments ($C_xH_yNO_z^+$ ~ 32% and $C_xH_yN^+$ ~ 46%) that can be generated by biomass burning emissions (Mace et al., 2003; Laskin et al., 2009; Desyaterik et al., 2013; Mohr et al., 2013). It is important to point out that most of the previous studies usually describe MO-OOA (or LV-OOA in some earlier studies) as aged SOA component without providing further detail on their potential origin and emission characteristics. Our observations underline the possibility of better understanding the origin of the MO-OOA component through measurements of refractory metals even when atmospheric oxidative processing has made the mass spectral features of aged OA materials less distinguishable."

Section 4: Page 14, Lines 24-36: "One of the major challenges in interpreting the PMF results from AMS measurements is to identify the origin and aging history of ambient particles associated with highly oxidized OA components (e.g., MO-OOA in this work), as the mass spectral characteristics of OA converge along with their degree of oxidative aging. In general, the relative intensities of some highly oxygenated fragments (e.g. CO^+ and CO_2^+) increase continuously while other mass spectral

features (e.g. alkane/alkene patterns from combustion sources) being diminished during the aging processes. Ng et al., (2010) have visualized such phenomena for SOA components on the f_{43}-f_{44} space. Furthermore, the *m/z* 60 (or $C_2H_4O_2^+$ organic fragments) has been widely used as a tracer ions for BBOA. Cubison et al. (2011) have generalized observations from worldwide field data that *m/z* 60 signature become less and less significant in aged BBOA materials. In this study, we proposed that the MO-OOA component represented aged OA materials impacted by the regional biomass burning and perhaps coal combustion emissions as MO-OOA was associated with refractory K^+ and Rb^+. Given the fact that MO-OOA was the major OA components of the total OA (~32%), this result highlights the fact that the regional pollution can affect the air quality in Singapore even though fresh regional biomass burning episodes were not observed during the sampling period."

13. Page 12, line 24-26; "Kasthuriarachchi et al., (2019) also found that MO-OOA was the major contributor to the observed nitrogen-containing organic fragments that could be largely generated by biomass burning emissions" is contradictory to page 9: "Kasthuriarachchi et al. (2019) reported that the concentrations of organo-nitrate and nitrogen-containing fragments (i.e., CxHyN+ and CxHyNOz+) increased during the daytime in this field study, suggesting that photo oxidation of VOCs under high-NO_X condition could be another potential pathway toward LO-OOA formation". Please revise the sentence/sentences.

Authors' response: The elevated concentrations/signals of LO-OOA factor, $C_xH_yN^+$ and, $C_xH_yNO_z^+$ were observed during the daytime, suggesting that the formation of LO-OOA could result from VOCs photo-oxidation under-high NO_x condition. As shown in the response of comment #10, approximately 13-30% of nitrogen-containing fragments were associated with the LO-OOA factor, whereas MO-OOA accounts for ~50% of nitrogen-containing fragments. The first statement is focusing on the diurnal dynamic and the second statement is about the major contributors of those fragments so that they are not contradict to each other. Note that there were no distinct diurnal pattern for MO-OOA factor. The related sentences were slightly modified as following:

Page 10 line 10-15: Discussion for LO-OOA - "Furthermore, Kasthuriarachchi et al. (2020) reported that the concentrations of organo-nitrate and nitrogen-containing fragments (i.e., $C_xH_yN^+$ and $C_xH_yNO_z^+$) slightly increased during daytime (e.g., Figure S8a) with LO-OOA, contributing to 30% of observed $C_xH_yNO_z^+$ fragments (Figure S10). This suggests that photo-oxidation of VOCs under high-NO_X condition could be a potential pathway toward LO-OOA formation given that the NO_X concentrations reached up to 160 ppb (Figure 1a, mean = 16.5 ppb) during the campaign."

Page 13, lines 30-32: Discussion for MO-OOA - "Note that MO-OOA contributes to the highest fraction of nitrogen-containing organic fragments ($C_xH_yNO_z^+$ ~ 32% and $C_xH_yN^+$ ~ 46%) that can be generated by biomass burning emissions (Mace et al., 2003; Laskin et al., 2009; Desyaterik et al., 2013; Mohr et al., 2013)."

14. Page 12, line 31-33 and Fig. S11, Fig. S11 is confusing. It is very difficult to see which trajectories really pass the two fires shown by the MODIS. Could you just select the trajectory for the peak concentrations of m/z 60? Where are the large urban areas in the map? Do the trajectories pass large cities as well? Is it possible that biomass burning emissions were mixed with urban emissions (that increased Rb and maybe also K)? Please add cities to the map. Why Fig. S11(b) and Fig S11(c) are not on the same scale? Now it is difficult to compare (b) and (c). Add lines between markers to m/z 60 and Rb in Fig. S11a.

Author's response: We agree with the reviewer's comment and have decided to remove this figure in the revised version. Instead, we have added a map of all active fires that occurred over the region during the entire campaign (Figure S12a) with the name of large urban areas. As discussed in our above responses for general comments, we are trying to investigate the potential origins of MO-OOA due to the regional emissions based on its moderate correlation with K^+, Rb^+ and $C_2H_4O_2^+$. Since we

understand that there should be multiple sources of MO-OOA that could be produced from aging of different types of primary and secondary emissions. In the revised manuscript, we would like to highlight the possibilities that regional biomass burning and coal combustion emissions could be linked to the MO-OOA formation. The following text has been added in the manuscript.

Page 13, lines 26-30: "The regional origin of K^+, Rb^+, $C_2H_4O_2^+$ and MO-OOA were investigated through their PSCF. Their PSCF graphs (Figures 6d and S15a- c) show several common origins with high probability that the highest concentrations could be influenced by biomass burning events from Indonesia (Figure S12a). Nevertheless, coal-fired power plants are located nearby the identified hotspots of Rb^+ and K^+ (Figure S12b) so that a regional transport of coal-fired power plant emissions alongside biomass burning plumes were possible."

15. Page 13, lines 21-23; "Furthermore, Na^+ measured by the SP-AMS can potentially be useful for separating rBC from traffic and biomass burning combustion emissions, which required further investigation." I suggest revising this sentence as the evidences provided by this study are not convincing enough. I think that there are multiple sources for Na in urban areas that should be taken into account.

Author's response: As discussed above, we have revised our discussion regarding Na^+. This sentence has been removed in the revised version.

16. Page 13, lines 36-37; "This observation suggest that, in the region, both K+ and Rb+ might be more appropriate tracers for the identification of aged biomass burning than m/z 60." I suggest revising this sentence as Rb may also come from other sources.

Author's response: As discussed above, we have revised our discussion regarding K^+ and Rb^+. This sentence has been removed from the revised conclusion.

Technical corrections:

1. Page 7, line 13; less-oxidized oxygenated OA (LO-OOA)

Author's response: The sentence has been revised accordingly.

2. Supplemental material, could you add a figure showing the contribution of metals to each PMF factor? It would be interesting to see how metals divide between the factors.

Author's response: The figure showing the contribution of metals to each PMF factor is presented in Figure 5a. (Figure 5d in the original version of manuscript).

References

Hsu, L. J., Alwahabi, Z. T., Nathan, G. J., Li, Y., Z. LI, S., Aldén, M.(2011). Sodium and Potassium Released from Burning Particles of Brown Coal and PineWood in a Laminar Premixed Methane Flame Using Quantitative Laser-Induced Breakdown Spectroscopy. Applied spectroscopy, 65, 684-91.

Irei, S., Shimono, A., Hikida, T., Kuramoto, K., Suzuki, Y., Takami, A. (2014). Qualitative Evaluation of m/z 85, 87, and 133 Signals in Organic Aerosol Mass Spectra of Fly Ash Produced by Coal Combustion. Aerosol and Air Quality Research, 14: 406–412.

Author's references:

Achad, M., Caumo, S., de Castro Vasconcellos, P., Bajano, H., Gómez, D. and Smichowski, P.: Chemical markers of biomass burning: Determination of levoglucosan, and potassium in size-classified atmospheric aerosols collected in Buenos Aires, Argentina by different analytical techniques, Microchem. J., 139, 181–187, doi:10.1016/j.microc.2018.02.016, 2018.

Artaxo, P., Gerab, F. and Rabello, M. L.: Elemental composition of aerosol particles from two atmospheric monitoring stations in the Amazon Basin, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At., 75(1–4), 277–281, 1993.

Behera, S. N., Betha, R. and Balasubramanian, R.: Insights into Chemical Coupling among Acidic Gases, Ammonia and Secondary Inorganic Aerosols, Aerosol Air Qual. Res., 13(4), 1282–1296, doi:10.4209/aaqr.2012.11.0328, 2013.

Budisulistiorini, S. H., Riva, M., Williams, M., Miyakawa, T., Chen, J., Itoh, M., Surratt, J. D. and Kuwata, M.: Dominant contribution of oxygenated organic aerosol to haze particles from real-time observation in Singapore during an Indonesian wildfire event in 2015, Atmospheric Chem. Phys., 18(22), 16481–16498, doi:https://doi.org/10.5194/acp-18-16481-2018, 2018.

Carbone, S., Onasch, T., Saarikoski, S., Timonen, H., Saarnio, K., Sueper, D., Rönkkö, T., Pirjola, L., Häyrinen, A., Worsnop, D. and Hillamo, R.: Characterization of trace metals on soot aerosol particles with the SP-AMS: detection and quantification, Atmos Meas Tech, 8(11), 4803–4815, doi:10.5194/amt-8-4803-2015, 2015.

Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A. and Jimenez, J. L.: Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, Atmos Chem Phys, 11(23), 12049–12064, doi:10.5194/acp-11-12049-2011, 2011.

Desyaterik, Y., Sun, Y., Shen, X., Lee, T., Wang, X., Wang, T. and Collett, J. L.: Speciation of "brown" carbon in cloud water impacted by agricultural biomass burning in eastern China, J. Geophys. Res. Atmospheres, 118(13), 7389–7399, doi:10.1002/jgrd.50561, 2013.

Drewnick, F., Hings, S. S., Curtius, J., Eerdekens, G. and Williams, J.: Measurement of fine particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany, Atmos. Environ., 40(23), 4316–4327, doi:10.1016/j.atmosenv.2006.03.040, 2006.

Fine, P. M., Cass, G. R. and Simoneit, B. R. T.: Chemical Characterization of Fine Particle Emissions from the Wood Stove Combustion of Prevalent United States Tree Species, Environ. Eng. Sci., 21(6), 705–721, doi:10.1089/ees.2004.21.705, 2004.

Hsu, L.-J., Alwahabi, Z. T., Nathan, G. J., Li, Y., Li, Z. S. and Aldén, M.: Sodium and Potassium Released from Burning Particles of Brown Coal and Pine Wood in a Laminar Premixed Methane Flame Using Quantitative Laser-Induced Breakdown Spectroscopy:, Appl. Spectrosc., doi:10.1366/10-06108, 2011.

Irei, S., Shimono, A., Hikida, T., Kuramoto, K., Suzuki, Y. and Takami, A.: Qualitative Evaluation of m/z 85, 87, and 133 Signals in Organic Aerosol Mass Spectra of Fly Ash Produced by Coal Combustion, Aerosol Air Qual. Res., 14(1), 406–412, doi:10.4209/aaqr.2013.04.0126, 2014.

Jimenez, J. L.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, J. Geophys. Res., 108(D7), doi:10.1029/2001JD001213, 2003.

Kasthuriarachchi, N. Y., Rivellini, L.-H., Adam, M. G. and Lee, A. K. Y.: Strongly absorptive primary and secondary brown carbon in an urban, under review, Environ Sci Technol, 2020.

Laskin, A., Smith, J. S. and Laskin, J.: Molecular Characterization of Nitrogen-Containing Organic Compounds in Biomass Burning Aerosols Using High-Resolution Mass Spectrometry, Environ. Sci. Technol., 43(10), 3764–3771, doi:10.1021/es803456n, 2009.

Lee, A. K. Y., Willis, M. D., Healy, R. M., Wang, J. M., Jeong, C.-H., Wenger, J. C., Evans, G. J. and Abbatt, J. P. D.: Single-particle characterization of biomass burning organic aerosol (BBOA): evidence for non-uniform mixing of high molecular weight organics and potassium, Atmos Chem Phys, 16(9), 5561–5572, doi:10.5194/acp-16-5561-2016, 2016.

Mace, K. A., Artaxo, P. and Duce, R. A.: Water-soluble organic nitrogen in Amazon Basin aerosols during the dry (biomass burning) and wet seasons, J. Geophys. Res. Atmospheres, 108(D16), doi:10.1029/2003JD003557, 2003.

Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prévôt, A. S. H., Xu, L., Ng, N. L., Herndon, S. C., Williams, L. R., Franklin, J. P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C., Gorkowski, K. J., Dubey, M. K., Allan, J. D. and Thornton, J. A.: Contribution of Nitrated Phenols to Wood Burning Brown Carbon Light Absorption in Detling, United Kingdom during Winter Time, Environ. Sci. Technol., 47(12), 6316–6324, doi:10.1021/es400683v, 2013.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y. and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos Chem Phys, 10(10), 4625–4641, doi:10.5194/acp-10-4625-2010, 2010.

Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett Jr., J. L., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I.-T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A. and Zuend, A.: The Acidity of Atmospheric Particles and Clouds, Atmospheric Chem. Phys. Discuss., 1–143, doi:https://doi.org/10.5194/acp-2019-889, 2019.