

We thank the reviewers for the comments and suggestions to improve the manuscript. We here provide point-by-point responses and necessary changes to those comments and suggestions. The responses are in blue. The original text for change is in red and the revised text in in green.

Anonymous Referee #1

General comments

The manuscript of Y. J. Li et al. presents the seasonal characteristics of fine PM in Hong Kong (chemical composition, size distribution, degrees of oxygenation, organic apportionment and air mass influences) based on high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) measurements, positive matrix factorization (PMF) and air mass back-trajectory analyses. The manuscript is well structured and presented in a clear way. The methods used (PMF, back-trajectory analysis) are not innovative but are valid and well applied. The conclusions of this manuscript (e.g. the influence of air mass origins and the season studied on the relative chemical composition of NR-PM₁ and the degree of oxygenation of organics at Hong Kong) are of scientific significance. I therefore recommend publishing this work in Atmospheric Chemistry and Physics after the authors respond to the following comments.

Specific comments

1. NR-PM₁ levels at your HKUST suburban site (15.3 µg/m³, Fig. 2) are extremely low compared to what is reported at neighbouring sites of the Pearl River Delta (PRD) region (29.4-38.2 g/m³ for rural and urban sites). This surprising result requires more justifications than what is mentioned in the manuscript (p. 20270 and 20277). If available, comparisons between fine PM mass determined by HR-ToF-AMS and independent analytical techniques – such as Tapered Element Oscillating Microbalance – Filter Dynamic Measurement System (TEOM-FDMS), filter measurements, etc. -should be reported and discussed in the supplementary material. In addition, HR-ToF-AMS measurements could be compared to i) Sunset ECOC Analyzer for the determination of organic matter, and ii) MARGA for the quantification of inorganic species (nitrate, sulphate, ammonium), if these independent instruments were operating at HKUST as mentioned in the following link: <http://envr.ust.hk/research/researchfacility/instrument.html>.

The HKUST suburban site is considered as a coastal background site with little anthropogenic influence. Most of the studies in the nearby area were either in the urban area (e.g., SZC, urban) or with strong influences of urban outflow or biomass burning (e.g., HSC, urban outflow; KPC, rural with biomass burning) and in general cities in the PRD are more polluted than HK. It is not surprising that the average NR-PM₁ mass concentration in our study is lower than those reported for the nearby sites. Even at the rural site (QYC), it had an episode (24-25 July, 2006) with a huge impact by biomass burning, which led to an NR-PM₁ mass concentration of up to 200 µg/m³ (Xiao et al., 2011). On the contrary, the highest NR-PM₁ mass concentration was around 60 µg/m³. In fact, when the rural site of QYC was influenced by a relatively clean air mass from the East, the average NR-PM₁ concentration was 15.9 µg/m³ (Table 2 in Xiao et al., 2011), similar to what we have observed at the HKUST Supersite.

Most of the other instruments measure PM_{2.5} while AMS measures NR-PM₁. Some discrepancy is expected from the difference in size cut. Figure R1 below shows the time series and correlation analysis between AMS and MARGA (for sulfate, ammonium, nitrate and chloride) or Sunset EC/OC analyzer (for organics, with an OM/OC ratio of 1.4). Around 70-80% of sulfate, ammonium and organics can be captured by AMS. Given that the size cut of AMS is less than those of PM_{2.5}, this is an acceptable percentage. Furthermore, using a MOUDI and off-line IC analysis, Bian et al. (2014) showed that at the HKUST site sulfate and ammonium had a substantial fraction (10-20%) of mass extending beyond 1

micron to coarse mode (a few microns of MMAD) (See Table R2 below and Figure 2 in Bian et al., 2014), which can be mostly captured by MARGA or EC/OC analyzer but not by the AMS. These are consistent with Figure R1.

However, nitrate and chloride can have worse agreement. Bian et al. (2014) showed that normally over 85% of the nitrate mass was in the two coarse modes (I and II) except for winter (Table R1), as a result of “chloride depletion” (Yao et al., 2003). This resulted in only 40% of PM_{2.5} nitrate was captured by AMS which measured NR-PM₁ (Figure R1). Our results are also consistent with the size distribution result in Bian et al. (2014) that in winter the AMS can capture more nitrate than in other seasons (Figure R1) because higher fraction of nitrate was in the smaller size (Bian et al., 2014). Chloride as a major component in sea salt aerosols, mostly in the form of sodium chloride, is even more dominant in the coarse modes (Bian et al., 2014). If chloride is in the form of sodium chloride, it would be difficult for the AMS vaporizer (600 °C) to vaporize it for detection (Zhang et al., 2005) even if it is in the size range the AMS can sample. All the above reasons can contribute to that the AMS measured chloride in NR-PM₁ contributed only to 13% of that in PM_{2.5} measured by MARGA.

As for the total PM_{2.5} mass concentration by TEOM, there are even more issues that hinder direct comparison other than the size range. For instance, the contribution by refractory materials such as EC, crustal materials, and sea salt cannot be captured by the AMS.

Overall, the characteristics of this site lead to typically lower PM concentrations compared to many cities in the PRD. AMS gave comparable sulfate, ammonium and organics to PM_{2.5} measurements but much lower chloride and nitrate than PM_{2.5} measurements. These discrepancies are not unusual, given the dominance of coarse mode nitrate and chloride in Hong Kong.

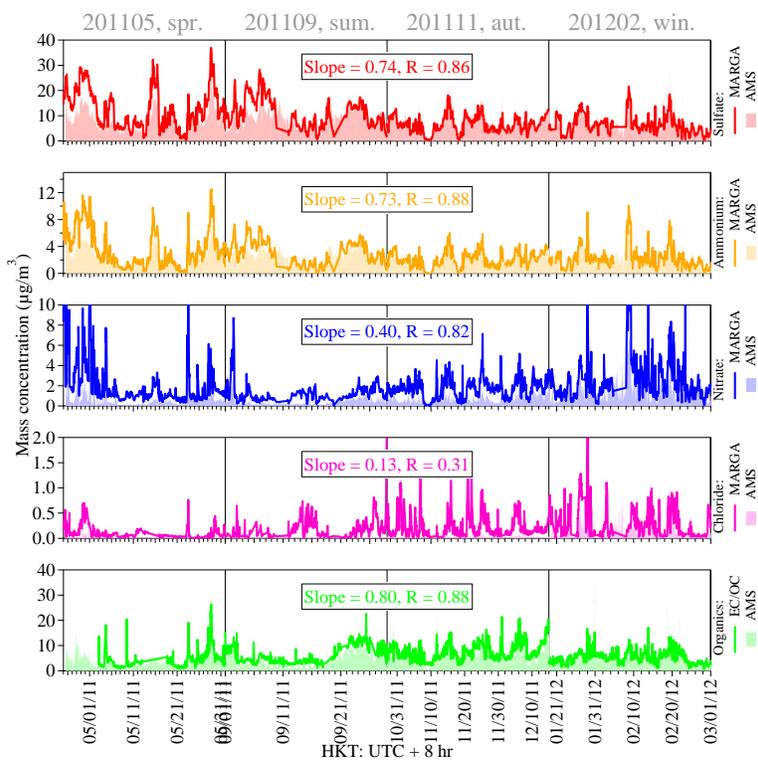


Figure R1. Time series of AMS measured species and those measured by MARGA (sulfate, ammonium, nitrate, and chloride) or EC/OC analyzer (organics). Correlation analyses were performed with hourly time resolution.

Table R1. Percentage of mass concentration for inorganic species in different seasons from Bian et al. (2014).

Species	Mode	MMAD (nm)	Mass percentage (%)			
			spr.	sum.	aut.	win.
SO4	condensation	240-280	5	5	6	3
	droplet	800-840	75	81	77	78
	coarse	4380-5130	21	14	17	19
NH4	condensation	240-260	6	6	7	3
	droplet	780-840	81	89	86	81
	coarse	4250-5060	13	4	7	16
NO3	droplet	770-1030	13	6	4	37
	coarse_I	2960-4180	41	31	47	22
	coarse_II	6830-7380	45	62	49	41
Chl	droplet	1270-1590	4	2	2	4
	coarse_I	3370-3890	13	37	11	9
	coarse_II	7490-8090	83	61	88	87

2. The cooking OA (COA) factor identified by PMF shows surprising diurnal profiles with the presence of an evening peak but the absence of lunch peaks during all seasons (Fig. S11, S13, S15, S17). How do the authors explain the absence of lunch peaks for this factor? It is mentioned that a small canteen operates near your sampling site during evenings only (p20264, 1.8). Could the COA factor be related to local emissions of this canteen? In other words, to which extent is your COA factor representative of the Hong Kong urban area? Please comment and mention the limitations related to this COA factor in the manuscript if necessary.

We believe that the COA is indeed mainly affected by the canteen, given its distinct diurnal pattern that matches with the operating hours of the canteen. We compare this COA factor with the COA factor from our recent campaign at an urban site in Hong Kong (Mong Kok, MK; unpublished). Figure R2 below shows the mass spectrum COA factor at MK and the average mass spectrum of COA over the four months at HKUST. Reasonable agreement between these two spectra is observed, especially the characteristic feature that m/z 55 is higher than m/z 57 (He et al., 2010) and the high intensity of m/z 41.

In short, the COA factor obtained in this study is consistent with those obtained in urban environments in HK. However, the loading of such factor is much smaller here. This highlights the importance of AMS studies in other areas in HK.

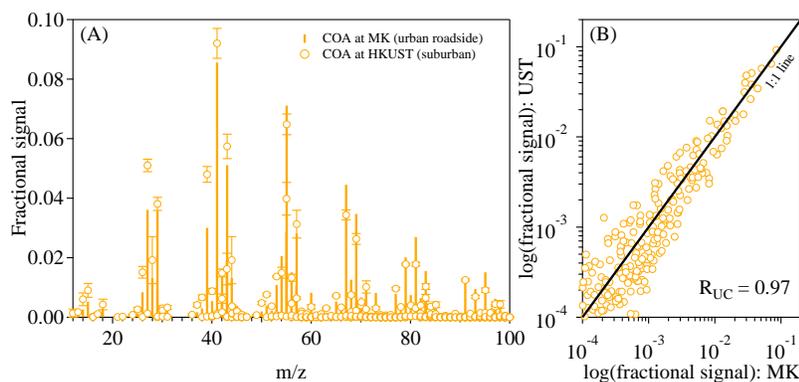


Figure R2. Comparison of COA factor from the current study (HKUST) and that from an urban site (Mong Kok, MK). The COA factor from HKUST is an average from all four months with standard deviation.

3. p.20264, 1.7: could your site be influenced by maritime transport emissions? Is there a harbour in the vicinity?

There is no harbor in the vicinity. The major harbor terminal in Hong Kong is some 15 km on the southwest of the site, and it is to the same direction as the highly populated urban area. Therefore, if there is any influence from maritime transport emissions, it would be most likely mixed with local urban emission when we had air mass from the south (Cluster 4 in Figure 7).

There are a few local ferry terminals and a few yacht clubs at ~5 km northeast of the site. It is possible that they could contribute some HOA to the NR-PM₁ when we have relatively stagnant air mass (e.g., Cluster 3 in Figure 7). Without further evidence, we do not intend to speculate to attribute the slightly higher (3%) of HOA in Cluster 3 than those (2%) in Clusters 1, 2, and 5 to those local ship emissions.

4. p.20266, 1.15: How do the authors explain that seed=0 is the most appropriate for all months? If no local minimum is found, the chosen seed should not influence your results (in general random seeds are chosen in classical PMF analyses).

The reviewer is right that random “seeds” are used to test the robustness of PMF analysis (Ulbrich et al., 2009; Zhang et al., 2011). Figure R3 below shows an example of such test by using seed value from 0 to 100 with a step of 5. No local minima were shown, which indicates the results are insensitive to the choice of the seed value. Therefore, further analysis was proceeded with a seed value of 0 (Table 1 in Zhang et al., 2011).

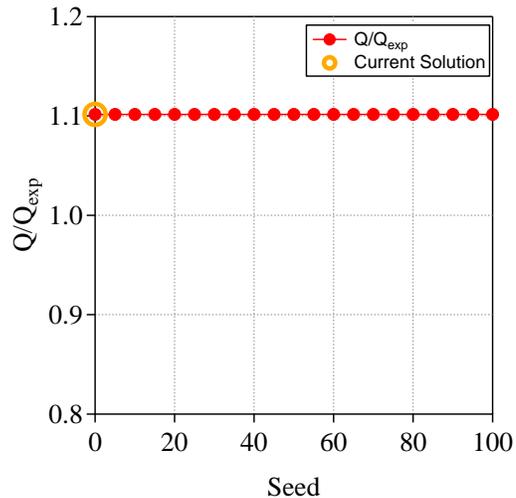


Figure R3. Example of an exploration analysis for seed values.

The sentence has been changed from:

“PMF was first run under “exploration” mode with the Seed value varying from 0 to 100 in steps of 5 and Seed=0 was found to be the most appropriate for all months.”

To:

“PMF was first run under the “exploration” mode with the Seed value varying from 0 to 100 in steps of 5 (Ulbrich et al., 2009;Zhang et al., 2011) and Seed = 0 was found to be appropriate for all months.”

5. p.20267, 1.8: please provide further explanations on how the output data of the WRF model were used to drive the HYSPLIT model.

When the WRF simulations are finished, the necessary parameters, including 14 surface and 5 upper-level variables, are extracted from hourly WRF outputs, and converted into the compatible format for HYSPLIT (Draxler et al., 2012).

6. p.20267, 1.12: please provide more explanations on how back trajectories were clustered into groups with similar patterns.

Some more details has been added to Section 6 in the Supplementary Information, as below.

“The clustering of trajectories is based on the total spatial variance (TSV) method (Draxler et al., 2012). This method minimizes the intra-cluster differences among trajectories while maximizing the inter-cluster differences.

In the clustering process, the spatial variance (SV, the squared distances between the endpoints of the cluster’s component trajectories and the mean of the trajectories in that cluster), the cluster spatial variance (CSV, the sum of the SVs of all trajectories within the cluster), and the total spatial variance (TSV, the sum of the CSVs for all clusters) are calculated.

Initially, both CSV and TSV are zero, with each trajectory being defined to be a cluster, which means that there are N trajectories and N clusters. The clustering involves combination of two clusters with the lowest increase in TSV. In the first iteration, the two clusters that result in the lowest increase in TSV are combined. Then, the number of clusters reduced to N-1, with one cluster consisting of two trajectories and

the others consisting of one. The process continues until the last two clusters are merged, resulting in N trajectories in one cluster.

In the first few iterations, the TSV increases dramatically, then gradually levels off and lifts again by the end of calculation. The final increase happens when disparate clusters start to be merged, indicating that the paired clusters are no longer similar. The ideal final number of clusters is just before the inflection point where the final rise occurs.”

7. p.20268, l.11: “NR-PM₁ concentration show little seasonal variation”, was it expected? Is it in agreement with previous studies? Please discuss.

There is no previous measurement on NR-PM₁ in different seasons in this region, especially at a background site. There is a previous study on seasonal characteristics of PM_{2.5} at different sites in Hong Kong (Louie et al., 2005). Table R2 below shows the sum of relevant components (sulfate, nitrate, ammonium, and organic matter) in different seasons and at different sites.

Table R2. Seasonal major components (sulfate, nitrate, ammonium, and organic matter) in PM_{2.5} from Louie et al. (2005) at three different sites.

Season	Time span	Sulfate + nitrate + ammonium + organic matter ($\mu\text{g}/\text{m}^3$)		
		HT: rural site	TW: urban site	MK: roadside site
Winter	Nov. 6, 2000 - Mar. 13, 2001	24	33	48
Spring	Mar. 19, 2001 - May 15, 2001	16	22	32
Summer	May 17, 2001 - Sep. 20, 2001	12	19	31
Autumn	Sep. 23, 2001 - Oct. 26, 2001	19	26	34

There are two things to note from this table. First, the sum of sulfate, nitrate, ammonium and organic matter in PM_{2.5} had an average of $\sim 18 \mu\text{g}/\text{m}^3$ for the rural site HT, while those for the urban site (TW) is $25 \mu\text{g}/\text{m}^3$ and for the urban roadside site (MK) is $36 \mu\text{g}/\text{m}^3$. The rural site has similarly low concentration as our background site at HKUST although there are some differences expected between PM_{2.5} and PM₁. Second, all three sites did show different extent of seasonal variability in the summed concentrations of the relevant species. The high concentrations in winter (e.g., the sum of the above four species is $24 \mu\text{g}/\text{m}^3$ for the rural site HT) was due to a strong regional pollution episode in Feb. 28, 2000 (Louie et al., 2005), in which the 24-h averaged PM_{2.5} concentration was as high as $68 \mu\text{g}/\text{m}^3$ at HT. Such high-PM regional episode did not occur in our winter campaign in 2011. On the other hand, the low concentration of $12 \mu\text{g}/\text{m}^3$ for the four species at HT in summer was probably due to the fact that the cut off day for summer in Louie et al. (2005) was Sep. 20, while in our study we presented the results of the whole month of Sep. in 2011 as summer. After all, September is near the end of the summer and the beginning of autumn and year-to-year variations of weather patterns and air quality are not unexpected. As can be seen in Figure 1 (panel b-1) in our manuscript, the latter part of September was a transient period when summer characteristics shifted to autumn characteristics with high an NR-PM₁ concentration. For the other two seasons (spring and autumn), the summed concentration of the four relevant species at the rural site HT were 16 and $19 \mu\text{g}/\text{m}^3$, respectively, which are close to the observed PM₁ concentration ($\sim 15 \mu\text{g}/\text{m}^3$) in the current study.

Therefore, it is not easy to generalize whether seasonal variation in PM concentration is present or not in different years because of differences in meteorological conditions and other factors. Here we just state the observation that such variation is absent in our campaigns.

8. p.20269, 1.9: NO_x could also be emitted by industrial activities. Please provide reference if NO_x is emitted by traffic only in Honk Kong. It is not clear why traffic emissions would be higher in spring, please comment.

Industrial activity is indeed a source of NO_x but there is actually little industrial activity in Hong Kong, which has a dominant financial and service industry. Lau et al. (2008) suggested that traffic volume is the main factor in NO_x level in Hong Kong.

Spring had high NO_x (most likely due to traffic in the downtown area) because this season was mostly influenced by air mass from the southwest (Cluster 4 in Table 1), which brought air pollutants from the downtown area to the site.

A reference is added to the sentence, by changing the sentence from:

“NO_x had the highest concentration in spring, indicating strongest traffic-related influence in the season.”

To:

“NO_x had the highest concentration in spring, indicating strongest traffic-related influence (Lau et al., 2008) in the season.”

9. p.20269, 1.26: as mentioned in the general comments, the concentration found in your study is very low compared to other studies conducted in the vicinity; please further discuss. Your explanations p.20270, 1.8 and p.20277, 1.15-17 are not sufficiently persuasive.

See the responses to specific comments #1 and #7 above.

10. p.20271, 1.21: it is not clear why primary contributions are smaller in autumn and winter. Please explain.

Since this is in the context of discussing characteristics of organic components, we meant the primary contribution (especially HOA) was small and it will not affect the assumption that the slopes and intercepts in the Van Krevelen plots can, to some extent, reflect the chemical processes of the organic aerosols (Heald et al., 2010;Ng et al., 2011). In fact, primary contributions to organic aerosol were generally small in all seasons (<20% with both HOA and COA). Therefore, we changed the original sentence from:

“Since primary contributions are generally small in autumn and winter, these uniform elemental ratio correlations suggest similar processes (most likely during transport) and/or precursors in the oxidation of organics during autumn and winter.”

To:

“Since primary contributions to organic aerosol are generally small, these uniform elemental ratio correlations suggest similar processes (most likely during transport) and/or precursors in the oxidation of organics during autumn and winter.”

11. p.20273, 1.5: please see general comment above.

Regarding the diurnal pattern and mass spectra of COA, it is addressed in our response to the specific comment #2 by the Reviewer.

12. p.20273, 1.18: please give more information on the bootstrapping method you used (e.g. in supplementary material). Please discuss Fig. S9. Bootstrapping is usually performed in conjunction with PMF to assess the uncertainties associated with your solution (e.g. Norris et al., 2008); such assessment is not clear from your Figure S9. What does “Profile_X_Avg” and “TSeries_X_Avg” represent here? Are

they the average of your bootstrap profiles and time series, respectively? If yes, displaying medians and interquartile ranges might better represent the uncertainties associated with your results.

A section with more detailed description on PMF analysis is included in Section 5 in the Supplementary Information, as a response to comment #1 of Reviewer #2. Regarding bootstrapping, the method description is as below:

“To assess the uncertainty of the factor time series and mass spectra, bootstrapping was run for 100 with the chosen factor number, and it is shown with the average time series and mass spectral profile with one standard deviation in Figure S9.”

The explanation of legends for Figure S9 has been added to the caption of the figure. As for the uncertainties, we tend to keep using standard deviation only, instead of displaying medians and interquartile to avoid the congested data points for these both high mass spectral resolution and high time resolution data. We believe this choice of display of uncertainties does not affect any conclusion of our work.

13. p.20274, l.11: it is surprising that concentrations are not lower than 14.0 g.m⁻³ when air masses come from East China Sea; how do the authors explain this result (e.g. anthropogenic emissions from Taiwan or Japan)?

Cluster 1 represents an average trajectory with most of the individual trajectories originated from the East China Sea. However, as shown in Figure S22 in the Supplementary Information, there are some trajectories passing the inland areas and also some passing Taiwan, Japan, and the Philippines. The average concentration that was lower than those found in those average trajectories with continental origins (e.g., Clusters 2, 3, and 5) only provides a relative scale. It is also possible that the South China sea was affected by regional pollution or long range transport from inland areas and had residual PM. Marine air mass reaching HK can therefore contain these pollutants, although it is still cleaner than continental and coastal air masses generally. Without too much information about the detailed contribution from the coastal areas and the islands to this Cluster, we do not intend to speculate too much on this.

Technical corrections

p.20263, l.1: please remove “the some”.

Changed as suggested.

p.20263, l.3: “the organic fractions in PM are higher especially in autumn and winter, although high PM episodes do not occur frequently”; please provide references justifying it.

Changed from:

“Hong Kong is influenced by long-range transport to even larger extents in the some other seasons than in spring, and the organic fractions in PM are higher especially in autumn and winter, although high PM episodes do not occur frequently.”

To:

“Hong Kong is influenced by long-range transport to even larger extents in other seasons than in spring, and the organic fractions in PM are higher especially in autumn and winter (Louie et al., 2005), although high PM episodes do not occur frequently (Huang et al., 2009).”

p.20265, 1.10: Middlebrook et al. (2012) do not explicitly mention the influence of biomass burning aerosols on collection efficiencies. They report the influences of (1) high nitrate content, (2) high relative humidity, and (3) high acidity. Please modify accordingly (also discussion 1.12-14).

Changed from:

“Middlebrook et al. (2012) recently suggested that the CE should be composition-dependent with influences of (1) high nitrate content, (2) biomass burning aerosols, and (3) high acidity, implying that the CE should depend on the phase state (liquid or solid) of the particles. In all four months, sulfate dominated the NR-PM₁ mass with only small amounts of nitrate (see Section 3.1 below), and biomass burning aerosols as primary organic aerosols did contribute significantly to the organics (see Section 3.4 below).”

To:

“Middlebrook et al. (2012) recently suggested that the CE should be composition-dependent with influences of (1) high nitrate content, (2) high relative humidity, and (3) high acidity, implying that the CE should depend on the phase state (liquid or solid) of the particles. In all four months, sulfate dominated the NR-PM₁ mass with only small amounts of nitrate (see Section 3.1 below).”

p.20266, 1.2: please replace “equals to” by “can be approximated by”.

Changed as suggested.

p.20266, 1.11: please put “weak” in inverted commas.

Changed as suggested.

p.20266, 1.14-15: please define “exploration mode” and “seed value” or provide references.

References (Ulbrich et al., 2009;Zhang et al., 2011) added

p.20269, 1.15: please also mention studies reporting an overview of the chemical composition of PM in Asia (e.g. Yang et al., 2011; Zhang et al., 2012). Please mention what is the added value of your study compared to the aforementioned ones (NR-PM₁ determined with AMS measurements, OA apportioned in POA and OOA for most sites).

A few sentences to compare the summary of NR-PM₁ in Asia and those of PM_{2.5} or PM₁₀ in the two previous studies suggested by the reviewer have been added to the paragraph, as shown below:

“Apart from temporal variations in PM concentration and composition, spatial heterogeneity of PM is also an important aspect to understand the air pollution of a region. For example, Zhang et al.(2012) compared PM₁₀ compositions in 16 sites in various regions in China and their relationship with visibility reduction and identified four major haze areas that coincided with the fast economic development therein. Yang et al. (2011) summarized chemical species measured in PM_{2.5} in China and concluded that not only the PM_{2.5} concentration varied by a factor of six but also the percentages of individual species were substantially different at different sites (e.g., urban vs. rural) and even among the four representative megacities. Herein, we put our all-four-season averages of sulfate, ammonium, nitrate, and organics (SANO) concentrations in NR-PM₁ in comparison with other available AMS measurements in Asia from the literature, as shown in Figure 2. Overall, there is a paucity of AMS measurements in China, given its large geographical coverage and the variability of air pollution and their causes in different cities. This study provides a comprehensive analysis in seasonal characteristics of NR-PM₁ compared to other AMS measurements in this region.”

p.20270, l.1: “non-urban sites have much higher fractions of OOA than POA”. Please mention that this is in agreement with what is reported worldwide (Zhang et al., 2011).

Changed from:

“For the organic constituents, non-urban sites have much higher fractions of OOA than POA.”

To:

“For the organic constituents, non-urban sites have much higher fractions of OOA than POA, which is in agreement with what has been reported worldwide (Zhang et al., 2011).”

p.20271, l.8: please provide references describing the Van Krevelen diagram.

Reference (Heald et al., 2010) added

p.20272, l.18: please refer the reader to Table S3.

Changed from:

“PMF results were evaluated by time-series correlations of tracer species or ions and by mass-spectra correlations of similar factors from the literature (Zhang et al., 2011).”

To:

“PMF results were evaluated by time-series correlations of tracer species or ions and by mass-spectra correlations of similar factors (Table S3) from the literature (Zhang et al., 2011).”

p.20274, l.26: please rephrase “was strongly affected by traffic-related emissions” since one would expect higher PM concentrations and HOA contributions with such statement.

Changed from:

“In Cluster 4, the site was downwind of the highly urbanized downtown area and was strongly affected by traffic-related emissions.”

To:

“The site was downwind of the highly urbanized downtown area. It was more affected by traffic-related emissions in Cluster 4 than in other Clusters.”

p.20279, l.24: please modify the website link which is not correct.

Changed to:

“http://www.arl.noaa.gov/documents/workshop/Spring2011/HYSPLIT_Tutorial.pdf”

p.20285: Table 2, please add a row below Org reporting NR-PM1 total mass

Added as suggested.

Supplementary Material.

p.4, l. 3: please replace “201105” by spring.

Changed as suggested.

p.12: please detail the legend of the figure S9, explaining what “Profile_X_Avg” and “TSeries_X_Avg” represent.

Caption of Figure S9 changed from:

“Figure S9 Example of bootstrapping plot (201105, spring).”

To:

“Figure S9 Example of bootstrapping plot (201105, spring). “Profile_x_Avg” is the average with standard deviation (from 100 bootstrapping runs) of the mass spectra for each Factor (x represents Factor 1 to 7). “Profile_Factor_x” represents the stick mass spectra for each Factor x. “TSeries_Factor_x” is the time series of concentration for each Factor x, while “Tseries_x_Avg” is the concentration time series with standard deviation (from 100 bootstrapping runs).”

p.13: please provide more detailed information in the legend, as you did for Fig. 1 by explaining what x-c and x-d (1x7) graph represent.

Caption of Figure S10 changed from:

“Figure S10 Original 7-factor solution for 201105, spring.”

To:

“Figure S10 Original 7-factor solution for 201105, spring. x-a: concentration time series of each Factor x. The inserts of panels x-a are the diurnal patterns of each Factor. x-b: high-resolution mass spectra of each factor with elemental analysis results (OM/OC is organic matter to organic carbon ratio, O/C is oxygen-to-carbon atomic ratio, H/C is hydrogen-to-carbon atomic ratio, N/C is nitrogen-to-carbon atomic ratio, and S/C is sulfur-to-carbon atomic ratio). x-c: correlation of unit-mass-resolution mass spectra of each Factor with standard unit-mass-resolution mass spectra. x-d: correlation of high-resolution mass spectra of each Factor with standard high-resolution mass spectra. R_{Pr} is the Pearson’s R, R_{UC} is the un-centered R for whole mass spectra, and $R_{UV}^{>44}$ is the un-centered R for ions with $m/z > 44$.”

For Figures S11 to S17, “See caption of Figure S10 for detailed explanation of the legends.” is added to the captions

p.21, Table S3: please define in the legend the acronyms that are used in this table i.e. “Summary of correlation coefficients of time series (TS) with external data and mass spectra (MS) with (:::).” Please report what are the three ions used as tracers for COA in the legend too.

The title of Table S3 has been changed from:

“Table S3 Summary of correlation coefficients of time series with external data and mass spectra with those in the literature. “3ions” means the three ions used as tracers for COA. R_{Pr} is the Pearson’s R, R_{UC} is the un-centered R for whole mass spectra, and $R_{UV}^{>44}$ is the un-centered R for ions with $m/z > 44$.”

To:

“Table S3 Summary of correlation coefficients of time series (TS) with external data and mass spectra (MS) with those in the literature. UMR is for unit-mass-resolution spectra and HR is for high-resolution mass spectra. Fx (x = 1 to 8) is the Factor number. “3ions” means the three ions ($C_5H_8O^+$, $C_6H_{10}O^+$, and $C_7H_{12}O^+$) used as tracers for COA. NO_x is $NO + NO_2$. R_{Pr} is the Pearson’s R, R_{UC} is the un-centered R for whole mass spectra, and $R_{UC}^{>44}$ is the un-centered R for ions with $m/z > 44$.”

p.23, l. 11: please rephrase point (3): do you mean that anthropogenic transported species should be associated with long trajectories from the continent? As it is stated it seems that marine transported species should also be associated with continental air masses, which is not correct.

Point (3) has been changed from:

“(3) transported species (mainly anthropogenic) should be associated with long trajectories from the continent;”

To:

“(3) transported species with anthropogenic origins should be associated with long trajectories from the continent;”

The same goes to point (3) in Section 2.5 (Back-trajectory analysis) in the main text.

References

Norris, G., Vedantham, R., Wade, K., Brown, S., Prouty, J. and Foley, C.: EPA Positive Matrix Factorization (PMF) 3.0: fundamentals & user guide, US Environ. Prot. Agency, 2008.

Yang, F., Tan, J., Zhao, Q., Du, Z., He, K., Ma, Y., Duan, F., Chen, G. and Zhao, Q.: Characteristics of PM_{2.5} speciation in representative megacities and across China, *Atmospheric Chem. Phys.*, 11(11), 5207–5219, doi:10.5194/acp-11-5207-2011, 2011.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, N. L., Worsnop, D. R. and Sun, Y.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, *Anal. Bioanal. Chem.*, 401(10), 3045–3067, doi:10.1007/s00216-011-5355-y, 2011.

Zhang, X. Y., Wang, Y. Q., Niu, T., Zhang, X. C., Gong, S. L., Zhang, Y. M. and Sun, J. Y.: Atmospheric aerosol compositions in China: spatial/temporal variability, chemical signature, regional haze distribution and comparisons with global aerosols, *Atmospheric Chem. Phys.*, 12(2), 779–799, doi:10.5194/acp-12-779-2012, 2012.

Anonymous Referee #2

General comments:

The manuscript reports the seasonal characteristics of non-refractory particulate matter with vacuum aerodynamic diameter less than 1 micron (NR-PM1) in Hong Kong based on the long-term observation (i.e. chemical compositions and size distribution) from an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). The sampling site (HKUST Air Quality Research Supersite) locates at suburban and coastal region of Hong Kong. Positive matrix factorization (PMF) and air mass back-trajectory analyses are performed to study the potential sources of organic aerosol in four different seasons. To the best of my knowledge, it is the first study to report the seasonal characteristics of NR-PM1 measured by HR-ToF-AMS in Pearl River Delta (PRD) region that involves a rapid economical growth of South China in the last decade. The manuscript is well written and structured. Overall, I recommend this work to be published in Atmospheric Chemistry and Physics after addressing the specific comments below:

Specific comments:

1. Section 2.4, Page 20266, line 19-22: It is not clear how the initial factors from PMF analysis to be combined to give the final 4-factors solution. It is highly recommended to add a short description (either in the main text or Section 5 of supplement) to explain the approach used for factors combination, which can definitely help readers to follow the figures and tables in the supplementary material.

Description of the PMF diagnostics and evaluation is provided in Section 5 in the supplementary information as below.

“Figures S5 to S8 are the diagnostic plots for the PMF (with HR data) solutions with the original 7 or 8 factors for the four campaigns. Panels (a) and (b) are Q/Q_{exp} values as a function of factor number and fPeak value, respectively. Panel (c) is the mass fraction of each factor (with factor number of 7 or 8) as a function of fPeak value. Panel (d) is the correlation coefficient (R) of time series (tseries) and mass spectra (profile) for each factor pair (e.g., 1_2 represents factors 1 and 2 etc.). Panel (e) shows the measured total organic concentration and the “reconstructed” total organic concentration by all the factors (with factor number of 7 or 8). The “residual” organic concentration is the difference of the two, as shown in Panel (f). Panels (g) and (h) are the Q/Q_{exp} values for the time series and mass spectra, respectively. Panel (i) is the box-whisker plot for the scaled residual for the mass spectra. To assess the uncertainty of the factor time series and mass spectra, bootstrapping was performed for 100 runs with the chosen factor number, and it is shown with the average time series and mass spectral profile with one standard deviation in Figure S9.

Figures S10-S17 show the evaluation plots for both the original factor number (7 or 8) and the combined factors (4 factor), with concentration time series plotted with external tracer components (left column), high resolution mass spectra with elemental analysis results (second column), and correlation with “standard” mass spectra (second last column for UMR mass spectra and last column for HR mass spectra). Factor combination was done by evaluating the original factors to see whether they have similar concentration time series with the external tracer species or similar mass spectral profile with the “standard” mass spectra. If so, the factors were combined to a single factor representing the overall feature of the new factor. Concentration time series combination is a simple summation of each sub-factors. Mass spectral combination is the average mass spectrum of the sub-factors. Table S3 shows the improvements of correlations in concentration time series of the combined factors with those of the external tracer species and in mass spectra with the “standard” spectra.”

2. Section 2.4 (Figure S13 and Table S4): Hydrocarbon-like organic aerosol (HOA) mass spectrum obtained in summer has a much higher oxygenated organic signal at m/z 44 (CO_2^+) than those determined in other seasons shown in the current study and previous studies worldwide. This also results in a higher oxygen-to-carbon ratio (O:C) of HOA in summer than other seasons. Since HOA is primary organic aerosols (POA) from local sources, I would expect the HOA mass spectral features and O:C ratios are very similar in all seasons. Please clarify.

In our previous response to the Reviewer #3's quick report, we attributed this to the high oxidation level of the organics in the summer, resulting in an overwhelming dominance of the ion CO_2^+ in the mass spectra. Even after we considered the gaseous CO_2 contribution, it still remained in the HOA factor.

A few studies showed high O:C for HOA factors from PMF analysis of AMS data in remote or rural areas where organics were highly oxidized (high CO_2^+ fraction in the original mass spectra). In addition to the study we cited in our previous response to Reviewer #3 in the quick report (Hu et al., 2013), there are studies in Po Valley (Saarikoski et al., 2012; Gilardoni et al., 2014) showing that the PMF resolved HOA factors were high in CO_2^+ fraction and O:C ratio (0.2). We believe this is an intrinsic result of the PMF. Without any more information, we do not attempt to make further correction regarding this in addition to considering the gaseous CO_2 influence. The mass loading of HOA may be slightly overestimated because of these highly oxygenated components and that would further reinforce our claims that HOA is relatively unimportant at this site.

3. Section 2.5: In the back-trajectory analysis, the authors mention the evaluation criteria that local emitted species (HOA and COA) should associate with short trajectories with clam wind (page 20267, line 23-24) and there are some discussions in the Section 6 of supplementary material. However, for the arrival heights of 300m, cluster 4 in all solutions has the highest HOA but a relatively low COA concentration among the clusters (Figure S20), highlighting the fact that those POA are not associated with the air mass in a similar manner. This may affect the interpretation of the cluster results of back-trajectory analysis. Please clarify.

The two POA factors HOA and COA may behave slightly differently. As mentioned in our response to the specific comment #6 by the Reviewer below, HOA was mainly from the downtown area to the southwest of the site. Therefore HOA contribution was higher when we had air mass from that direction (i.e., spring and summer that had higher frequency of air mass origin in Cluster 4). However, COA was mostly likely from a student canteen nearby. Accumulation of COA was thus facilitated by low wind speed in spring and winter (Table 2).

In Cluster analysis, we used multiple criteria to evaluate the solutions. The inconsistency of relative contributions of SO_4 and LVOOA in the split Clusters from the 5-cluster solution to the 6-cluster solution was the main reason that we excluded the 6-cluster solution. In addition, the COA contributions in the two split Clusters (COA in Cluster 3 < COA in Cluster 5, panel c, Figure S19) were not consistent with that the relatively longer Cluster 5 has a higher average wind speed and the relatively shorter Cluster 3.

4. Section 3.3, Page 20272, line 6-8: Table S4 shows that SV-OOA and LV-OOA measured in summer are more oxygenated than those identified in other seasons. Therefore, in addition to a substantial SOA formation from BVOC, other oxidative aging mechanisms (i.e. heterogeneous oxidation of freshly formed and transported SOA) likely play a significant role to make the overall OA more oxygenated with low hydrogen-to-carbon (H:C) ratio in summer. To illustrate this concept, it is recommended adding the SV-OOA and LV-OOA data in each season to the V-K diagrams.

Agree. Figure 5 (V-K diagrams) has been updated in three aspects: 1) average O:C and H:C ratios for each month have been added to the left panels; 2) Only the slopes and intercepts from orthogonal distance regression (ODR) were shown as suggested by Reviewer #3; 3) three lines with an intercept (I) of 2.0 and slopes (S) of -0.5, -1.0, and -2.0 (Heald et al., 2010;Ng et al., 2011) were also added to each panel containing the V-K diagram for reference.

As suggested by Reviewer #3 (general comment #3), which is also related to the suggestion here, more discussion on the O:C and H:C ratios in different seasons was also included in Section 3.3, as below.

Original text:

“Summer (September 2011) had the highest O:C ratio among the four seasons, likely due to high photochemical activity. High O_x concentration was associated with high O:C ratio because of the similar secondary nature of the two parameters.”

Revised text:

“Summer (September 2011) had the highest O:C ratio among the four seasons, likely due to higher photochemical activity. This strong influence by photochemistry is also reflected by the higher average O:C ratios in the PMF-resolved SVOOA and LVOOA factors (Figure 5, left panels, large blue and red closed squares) in summer than in other seasons. In fact, the overall O:C ratio was so high in summer that it might have some effect on the PMF analysis, resulting in a high CO₂⁺ fraction (0.1) and a high O:C ratio (0.25) in the HOA factor in summer. This abnormally high O:C ratio (>0.1) was also observed in other studies in remote or rural areas where highly oxygenated organics dominated the mass spectra (Saarikoski et al., 2012;Hu et al., 2013;Gilardoni et al., 2014). High O_x concentration was associated with high O:C ratio because of the similar secondary nature of the two parameters.”

5. Section 3.4: Figure 6 b-1 shows that SV-OOA mass loading become much higher in the later period of summer, which is very different to the earlier period of summer and all other seasons. Is it a typical observation in summer? If yes, the authors should provide a more detail discussion on that period in the revised manuscript.

The reviewer has spotted an interesting phenomenon in the autumn campaign. Yes, it is quite well established that September is a transient period from summer to winter in Hong Kong (Louie et al., 2005). In this transient period, the air mass origin shifts from mainly marine to the continent, which occurs mostly in mid-September (Louie et al., 2005). It has been observed that concentrations of air pollutants tend to increase from September to October (Wu, 2014).

The special case of this campaign has been discussed in more detail in our earlier publication (Yeung et al., 2014), where September data was separated into two halves and discussed together with hygroscopicity data. In this work about the overall seasonality of NR-PM₁, we do not want to go into the specific feature of meteorological influence within one campaign, which has been reflected by the air mass origin as shown in Table 1.

6. Page 20274, line 1-4: As mentioned in this manuscript, COA and HOA are POA from local emissions. It is not clear how meteorological parameters and air mass trajectory influence the seasonal trend of those POA in different ways. Please clarify.

For the relatively higher COA in spring and winter, it was probably due to the low wind speed in these two seasons (average <1.8 m/s, Table 2). As mentioned in the manuscript and pointed out by Reviewer #1, COA was most likely from the student canteen that operates from 18:00 till midnight. Therefore, the stagnant air will facilitate the accumulation of this primary emission.

For HOA, it was mainly contributed by traffic-related emission in the downtown area. Whenever (spring and summer in this case) the site was strongly influenced by southerly wind (Cluster 4 in the back-trajectory analysis), the HOA contribution was relatively higher than other seasons (Clusters). This is discussed in Section 3.5 in the manuscript.

A sentence has been added to the end of Section 3.4 to clarify this point:

“Note that the two POA factors COA and HOA behaved slightly differently because COA was mainly contributed by a student canteen nearby and stagnant air will facilitate the accumulation of this primary emission, while HOA was mainly from the downtown area and its contribution was higher when the wind direction was from the south.”

7. Page 20275, line 12-24: What are the size distributions of Org 43, which is considered as one of the major fragment from the freshly produced OOA, in all clusters? Please discuss in the revised manuscript.

Indeed Org43 was probably mainly contributed by fresh SOA (if the OOA is a suitable surrogate), specifically by the ion $C_2H_3O^+$ (see Figure R4 below in the response to Reviewer #3). But the HOA-related ion ($C_3H_7^+$) also contributed by 20-30% to this ion signal (Figure R4). For discussion in Section 3.2 and Figure 4 that shows the size distributions of Org44, Org43 and Org57, we considered that Org43 is somewhere between the most oxygenated Org44 and the least oxygenated Org57. For discussion here and Figure 8, we merely wanted to show the two extremes of the most oxygenated Org44 and the least oxygenated Org57, without including the intermediate case of Org43.

8. Page 20275, line 23-24: Similar to comment 4 above, in addition to the conversion of HOA to SOA (i.e. heterogeneous chemistry), SOA formation from gas-phase chemistry is also possible but it is difficult to differentiate the two pathways based on the AMS measurements.

The reviewer is correct that one cannot easily distinguish these two pathways by AMS measurements. In our discussion, we simply stated that conversion from HOA to SOA could result in increase of degree of oxygenation of OA (e.g., O:C ratio) but did not attempt to specify the major pathway leading to such an increase.

Technical comments:

Page 20263, line 1-4: Please provide references to support these arguments.

Changed from:

“Hong Kong is influenced by long-range transport to even larger extents in the some other seasons than in spring, and the organic fractions in PM are higher especially in autumn and winter, although high PM episodes do not occur frequently.”

To:

“Hong Kong is influenced by long-range transport to even larger extents in other seasons than in spring, and the organic fractions in PM are higher especially in autumn and winter (Louie et al., 2005), although high PM episodes do not occur frequently (Huang et al., 2009).”

Page 20265, line 13: Please correct the text to “:::primary organic aerosols did not contribute significantly:::”.

The reviewer is correct that this is due to a typo. In accordance to response to reviewer #1 above, the whole sentence has been changed from:

“Middlebrook et al. (2012) recently suggested that the CE should be composition-dependent with influences of (1) high nitrate content, (2) biomass burning aerosols, and (3) high acidity, implying that the CE should depend on the phase state (liquid or solid) of the particles. In all four months, sulfate dominated the NR-PM₁ mass with only small amounts of nitrate (see Section 3.1 below), and biomass burning aerosols as primary organic aerosols did contribute significantly to the organics (see Section 3.4 below).”

To:

“Middlebrook et al. (2012) recently suggested that the CE should be composition-dependent with influences of (1) high nitrate content, (2) high relative humidity, and (3) high acidity, implying that the CE should depend on the phase state (liquid or solid) of the particles. In all four months, sulfate dominated the NR-PM₁ mass with only small amounts of nitrate (see Section 3.1 below).”

Page 20266, line 2: Please change “equal to” to “can be estimated by”.

Changed from:

“equals to”

To:

“can be approximated by”

Page 20269, line 6-8: Please provide references to support the argument about the air mass origin in different seasons.

A reference (Yuan et al., 2006) has been added to the sentence.

Table 1: Please add a short description (e.g. marine, long range transported form North China, etc.) for each air mass cluster.

Added as suggested

Figure 2: It is suggested to add the site information (i.e. urban, sub-urban, remote, etc.) in this figure. It makes readers easier to follow the discussions in Section 3.1.

Added as suggested

Page 20272, line 11-13: Please provide references to support the argument about BVOC emission as a function of temperature.

A reference (Guenther et al., 1993) has been added to the sentence.

Anonymous referee #3

This manuscript reports results obtained during intensive field campaigns undertaken at Hong Kong during four different seasons. The authors deployed an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) to measure the concentration, chemical composition and size distribution of non-refractory submicron particles (NR-PM1). The authors performed a source apportionment by positive matrix factorization (PMF) and discussed the properties of NR-PM1 as a function of the air mass origin. This manuscript is well written and fits the scope of Atmospheric Chemistry and Physics. I recommend publication of the paper, after the authors have addressed the following comments.

General comments:

1. Size distributions: what is the relative contribution of ions from the CH, CHO1, and CHOgt1 families to the total signals of Org43, Org44, and Org57? Do these contributions change with season? This information can help a lot when the authors discuss the size distributions of these m/z.

Figure R4 below shows the relative contribution of ions from different families to the total signals of Org43, Org44, and Org57. Generally, Org43 can be mainly attributed to $C_2H_3O^+$ (70% or above), Org44 to CO_2^+ (94% or above), and Org57 to $C_4H_9^+$ (62% or above). Therefore, it is reasonable in our size distribution discussion that Org57 mainly reflects the distribution of hydrocarbon-like organics, Org44 represents the highly oxidized organics, and Org43 is somewhere in between (probably fresh SOA).

There is slight seasonal dependence of the contribution of ions from different families in these four campaign. But there is also an issue of absolute abundance (e.g., although $C_2H_3O^+$ had similar fraction in summer and autumn, but the absolute intensity in autumn is much higher than in other season due to higher organic concentrations in autumn). Therefore, we do not want to go too far to emphasize this seasonal dependence with ion contributions. This dependence is probably more properly reflected in the difference in overall O:C ratio in different seasons, which has been discussed in the manuscript.

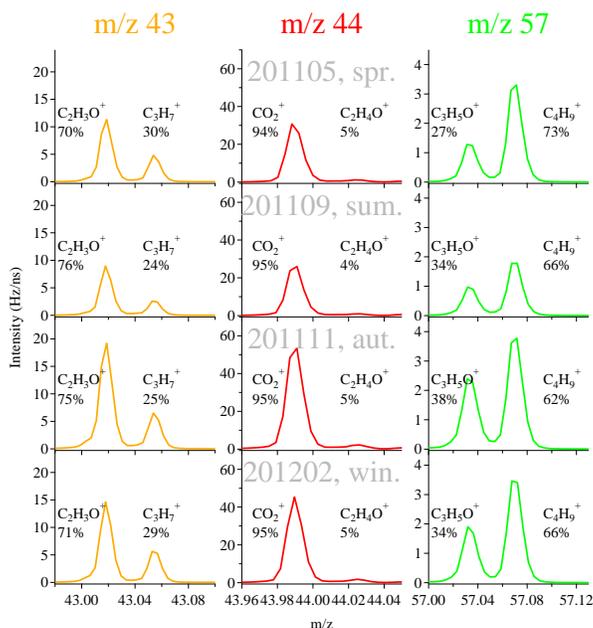


Figure R4. Contributions of ions from different families (CH, CHO1, and CHOgt1) to the signals of m/z 43, 44, and 57 in different seasons.

A sentence has been added to Section 3.2 to reflect this point:

“Signals with m/z 43 can be mainly attributed to $C_2H_3O^+$ (>70%), m/z 44 to CO_2^+ (>94%), and m/z 57 to $C_4H_9^+$ (>62%), and they only showed marginal seasonal dependence (1 – 11% in their contributions).”

2. PMF analysis, figure S13: in my initial quick report, I had mentioned that there was obviously an issue in the PMF analysis of the summer dataset. Indeed, the HOA factor has a very high signal of CO_2^+ (and thus of CO^+ , which is scaled to CO_2^+), increasing the O/C ratio up to 0.25. In their responses to the reviewers, the authors said that this could be a result from highly oxidized organics in summer. I’m not convinced by this explanation, because if it was the case, we would also see other oxygenated fragments in the HOA profile. It is unlikely that photooxidation of organics induces an increase of CO_2^+ (which is related to carboxylic acids) without inducing an increase of other oxygenated fragments related to intermediate oxidation (i.e., aldehydes, ketones). Therefore, I still believe that the CO_2^+ signal has not been correctly apportioned into the different factors, and that a large portion of its signal in the HOA factor should not be there.

We agree with the reviewer that this large portion of CO_2^+ signal should not be in the HOA factor. In our previous response to the reviewer’s quick report, we stated that because the organics in summer were highly oxidized, such that the ion CO_2^+ may be overwhelmingly dominant in the mass spectra. In that case, even after we considered the gaseous CO_2 contribution, it cannot be well resolved from the HOA factor and leaves some “residual” signal in it. As for other oxygenated compounds like aldehydes and ketones, they will result in oxygenated fragments such as CHO^+ and $C_2H_3O^+$ etc. But these ions did not dominate the overall mass spectra. Therefore, they will not be carried in the HOA factor in a high fraction during the PMF analysis.

There are a few studies showed high O:C for HOA factors from PMF analysis of AMS data in remote or rural areas where organics were highly oxidized (high CO_2^+ fraction in the original mass spectra). In addition to the study we cited in our previous response to Reviewer #3 in the quick report (Hu et al., 2013), there are studies in Po Valley (Saarikoski et al., 2012; Gilardoni et al., 2014) showing that the PMF resolved HOA factors were high in CO_2^+ fraction and O:C ratio (0.2). Without any more information, we do not attempt to make further correction regarding this in addition to considering the gaseous CO_2 influence.

We attributed this high CO_2^+ signal a characteristic of the results of PMF when there is overwhelming dominance of CO_2^+ in the spectra. Together with the revision according to the comment #3 below, we have added the note in Section 3.3 to alert the readers.

“Summer (September 2011) had the highest O:C ratio among the four seasons, likely due to high photochemical activity. This strong influence by photochemistry is also reflected by the higher average O:C ratios in the PMF-resolved SVOOA and LVOOA factors (Figure 5, left panels, large blue and red closed squares) in summer than in other seasons. In fact, the overall O:C ratio was so high in summer that it might have some effects on the PMF analysis, resulting in a high CO_2^+ fraction (0.1) and a high O:C ratio (0.25) in the HOA factor in summer. This abnormally high O:C ratio (>0.1) was also observed in other studies in remote or rural areas where highly oxygenated organics dominated the mass spectra (Saarikoski et al., 2012; Hu et al., 2013; Gilardoni et al., 2014). High O_x concentration was associated with high O:C ratio because of the similar secondary nature of the two parameters.”

3. PMF analysis, factor profiles: it would be interesting if the authors include a discussion on the different factor profiles, especially on how these profiles change with season. For instance, we clearly see that the two OOA factors have a higher fCO_2^+ and O/C ratio in summer, stressing the influence of

photochemistry during that season. On the other hand, it seems that the profiles of HOA and COA are very similar during the four seasons (except HOA in summer, see above).

We thank the reviewer for this insightful suggestion. We now include a few sentences to discuss this point in Section 3.3, as below.

Original text:

“Summer (September 2011) had the highest O:C ratio among the four seasons, likely due to high photochemical activity. High O_x concentration was associated with high O:C ratio because of the similar secondary nature of the two parameters.”

Revised text:

“Summer (September 2011) had the highest O:C ratio among the four seasons, likely due to high photochemical activity. This strong influence by photochemistry is also reflected by the higher average O:C ratios in the PMF-resolved SVOOA and LVOOA factors (Figure 5, left panels, large blue and red closed squares) in summer than in other seasons. In fact, the overall O:C ratio was so high in summer that it might have some effects on the PMF analysis, resulting in a high CO₂⁺ fraction (0.1) and a high O:C ratio (0.25) in the HOA factor in summer. This abnormally high O:C ratio (>0.1) was also observed in other studies in remote or rural areas where highly oxygenated organics dominated the mass spectra (Saarikoski et al., 2012;Hu et al., 2013;Gilardoni et al., 2014). High O_x concentration was associated with high O:C ratio because of the similar secondary nature of the two parameters.”

4. Back trajectory analysis: the main problem of this section is that the authors decided to perform a combined cluster analysis with data from the four field campaigns. This method introduces a bias when they compare the different air masses, because the frequencies of the clusters vary a lot with season, as shown in Table 1. For example, cluster 1 shows a very strong diurnal pattern for O/C ratio (Figure 8), because this cluster is mainly observed in summer and is highly influenced by photochemistry. On the other hand, cluster 5 shows a flat diurnal pattern for O/C ratio, because this cluster is observed only in autumn, when photochemistry is less intense. Therefore, it is a bit difficult to compare the different air masses, so I would suggest to perform a cluster analysis separately for each season.

We agree with the reviewer that doing the trajectory cluster analysis in different seasons, like what we did for the PMF analysis, is an alternative way. For the cluster analysis, however, we intend to keep the four-month combined approach because of the following reasons. First, the “criterion” for grouping the trajectories in different clusters (“spatial variance”) is not expected to be dependent on season as mass spectra are in the PMF analysis. Second, seasonally separated cluster analysis might result in different numbers of clusters in each season and this could make the discussions difficult and confusing. Third, the dominating clusters in different seasons and their influence on NR-PM₁ composition have already been discussed in our seasonality analysis.

The main purpose of this work is to investigate the seasonality and influence of air mass origin on NR-PM₁ concentration and composition. The seasonality of diurnal patterns of O:C ratio, as shown in Figure 5 (right panels), is clearly affected by the dominating air mass origins, as shown in Figure 8. That is why we showed the frequencies of the clusters for each month in Table 1. We believe that air mass, instead of seasons of the year, can give a better description to the causes of the observed PM characteristics and hence we focus on an overall discussion based on air mass origin. Doing cluster analysis for individual seasons would not yield much new information towards this overall goal.

Specific comments:

Page 20264, line 12: V- and W-modes correspond to the mode of operation of the mass spectrometer, while MS and PToF modes are related to the chopper cycle. This is not clear in the text, where V-, PToF- and W-modes are mentioned together (and without MS).

The sentence from line 11-12 has been changed from:

“NR-PM₁ constituents including sulfate, nitrate, ammonium, chloride, and organics were measured with an Aerodyne HR-ToF-AMS operated under V, pToF, and W modes.”

To:

“NR-PM₁ constituents including sulfate, nitrate, ammonium, chloride, and organics were measured with an Aerodyne HR-ToF-AMS operated under V-MS, pToF, and W-MS modes.”

Page 20265, lines 12-14: I think the authors wanted to say “biomass burning aerosols as primary organic aerosols did not contribute significantly to the organics”.

The reviewer is correct that this is due to a typo. In accordance to a response to reviewer #1 above, the whole sentence has been changed from:

“Middlebrook et al. (2012) recently suggested that the CE should be composition-dependent with influences of (1) high nitrate content, (2) biomass burning aerosols, and (3) high acidity, implying that the CE should depend on the phase state (liquid or solid) of the particles. In all four months, sulfate dominated the NR-PM₁ mass with only small amounts of nitrate (see Section 3.1 below), and biomass burning aerosols as primary organic aerosols did contribute significantly to the organics (see Section 3.4 below).”

To:

“Middlebrook et al. (2012) recently suggested that the CE should be composition-dependent with influences of (1) high nitrate content, (2) high relative humidity, and (3) high acidity, implying that the CE should depend on the phase state (liquid or solid) of the particles. In all four months, sulfate dominated the NR-PM₁ mass with only small amounts of nitrate (see Section 3.1 below).”

Page 20268, line 26: the authors should be careful when they talk about ammonium nitrate and ammonium chloride, because they mention earlier that anions were not fully neutralized (section 2.3), so it is not sure that nitrate and chloride are under these forms. For nitrate, how does the scatterplot of NO⁺ vs NO₂⁺ look like (slope, correlation coefficient)? Is the slope close to that of ammonium nitrate during IE calibrations?

In certain cases, the detected nitrate, chloride and ammonium might not be in the forms of ammonium nitrate and ammonium chloride (Yoshizumi and Hoshi, 1985). We thank the reviewer for the two comments. First, the reviewer suggested that the slightly acidic nature of the aerosols may not lead to a fully neutralized form of ammonium nitrate or ammonium chloride. Second, the measured “nitrate” might be complicated by possible organic nitrogen compounds present (Farmer et al., 2010). We now provide our responses to these two concerns as below.

For the first concern, we first look at whether the lower predicted ammonium than the measured one is due to acidity or due to the presence of other alkaline ions such as sodium and potassium, for they would lead to the formation of sodium nitrate (Yoshizumi and Hoshi, 1985) or sodium chloride as in sea salt aerosols. However, it is not very likely that significant portions of nitrate and chloride were detected by the AMS in the forms of these sodium salts. This is because these salts are mainly in a size range (Yoshizumi and Hoshi, 1985) larger than that measured by the AMS (1 μm), and these salts are not very easily vaporized under the 600 °C heater in the AMS (Zhang et al., 2005). So the lower predicted ammonium than the measured one is most likely due to the presence of “excess” proton. Then can the nitrate and chloride be in the forms of HNO₃ and HCl, respectively? It is not very likely. That is because

we have a large amount of sulfate (>40% by mass) in the aerosols. The pKa value of HSO_4^- (1.99) is much higher than those of HNO_3 (-1.4) and HCl (-7). Therefore, the “excess” proton will associate with SO_4^{2-} to form HSO_4^- (e.g., ammonium bisulfate) rather than forming HNO_3 and HCl . Therefore, we argue that the less predicted ammonium than the measured one does not contradict with the presence of ammonium nitrate and ammonium chloride. In reality, these nitrate and chloride may be internally mixed with sulfate, ammonium and protons in aqueous particles. We use the term ammonium nitrate and ammonium chloride to denote the overall chemical composition of the particles but not their chemical identity in terms of molecular speciation.

For the second concern, we had a similar comment by a reviewer in our previous publication (Li et al., 2013), who also asked for the NO^+ vs NO_2^+ plot from our data. Figure R5 below shows such a plot from the spring data. With the possible contribution of other ions to m/z 30 and m/z 46 taken into account, we estimated that inorganic nitrate contributed to > 60% of the measured signals of m/z 30 and m/z 46 and concluded that inorganic nitrate was the major fraction of the nitrate concentration measured by the AMS. As for organic chlorine compounds (mainly from chlorinated pesticides), their concentrations are normally in the order of pg/m^3 (Landlova et al., 2014) level and will not contribute significantly to the chloride detected, even though their presence has high health impacts.

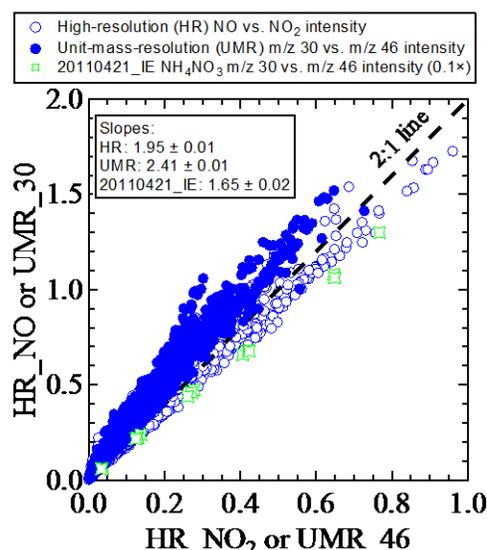


Figure R5. NO^+ to NO_2^+ ratios during the spring campaign (open blue circles for HR data and closed blue circles for UMR data) and in the pure ammonium nitrate experiment (open green symbol).

Figure 5: Concerning the slopes and y-intercepts of the Van Krevelen diagrams, I suggest to keep only those obtained with the orthogonal distance regression (ODR), and to remove the others.

Changed as suggested. There lines with an intercept (I) of 2.0 and slopes (S) of -0.5, -1.0, and -2.0 (Heald et al., 2010;Ng et al., 2011) were also added for reference.

Figures 5 and 8: please replace OSC by \overline{OS}_C in the figure captions.

Changed as suggested.

Figure 8: some information are hard to see in this figure. For each species (Org, SO_4 , Org44, and Org57), is it possible to include one panel with the size distributions of the four seasons, eventually with four different y-axes? It will be easier to see the variation of the modal diameters with the seasons.

Figure 8 is to show the size distribution of the four “species” and the diurnal patterns of \overline{OS}_C in each cluster. That was why we wanted to show them in a context of average cluster trajectories as it is now. The seasonal differences of the size distributions of those species can be found in Figures 3 and 4.

Figure S1: it would be nice if the authors include a second map with a zoom on Hong Kong and the sampling site. We would have a better view on the location of local sources.

Figure S1 has been updated, as Figure R6 below.

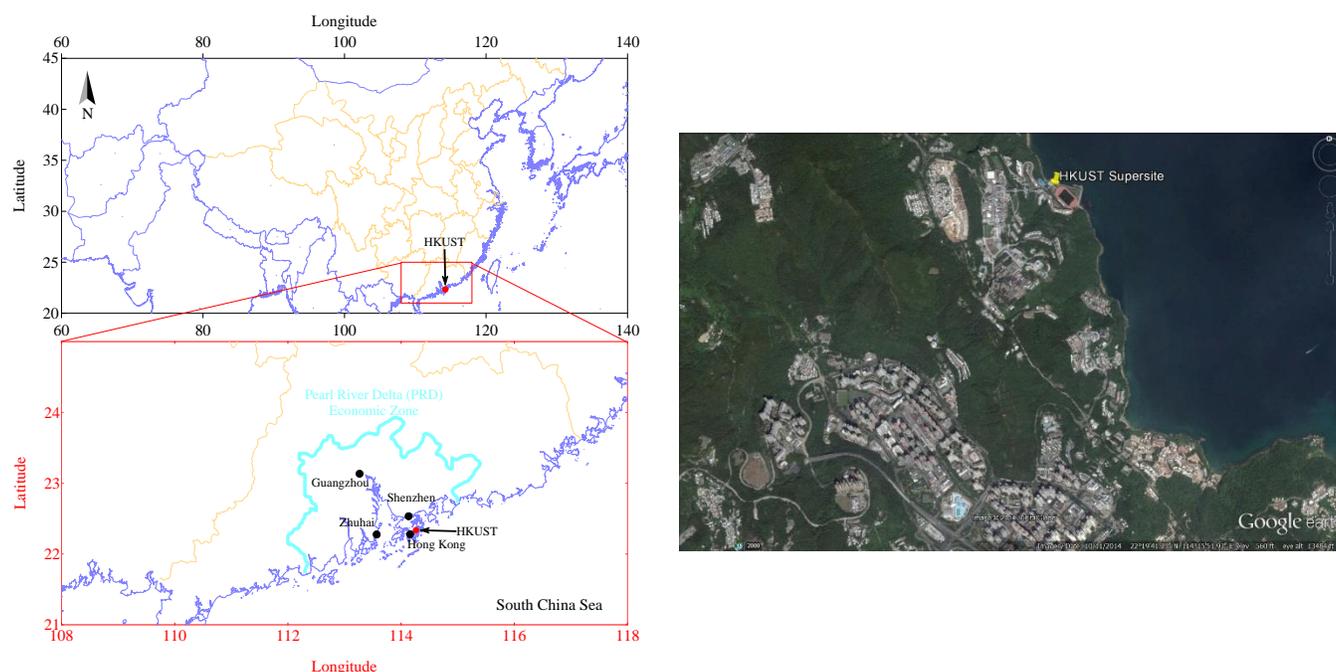


Figure R6. Location of the sampling site and its surrounding area.

Supplementary material, page 2, line 8: I think that the reference DeCarlo et al. (2006) is more appropriate here than DeCarlo et al. (2004).

DeCarlo et al. (2006) is a general paper about high-resolution time-of-flight aerosol mass spectrometry, while DeCarlo et al. (2004) includes some insightful discussions about particle diameter definitions (material diameter, volume/mass equivalent diameter, aerodynamic diameter, and vacuum aerodynamic diameter etc.). Given the relevance of these two papers discussed here, two papers are both cited.

Figure S4: please color these scatterplots by time. It seems that in spring and winter, some periods are more acidic than others. I think it would be worth including a discussion on this in section 3.1.

Figure S4 has been updated as suggested. Indeed there is some difference in acidity in some of the periods. This was discussed in our previous publication on spring data (Lee et al., 2013). For this overview section (Section 3.1), we do not intend to include particle acidity as a specific point for discussion. And it is also out of the scope of the current manuscript to include it as another section in addition to what we have currently (PMF factors, degree of oxygenation, seasonal and air mass origin dependence etc.).

Table S1: the authors mentioned earlier that they introduced a time dependent correction of the gas-phase CO₂+ signal. I suggest that they include this information in the table.

The correction factor is the “CO₂_factor” in the last column of the table. To reflect this point, the title of Table S1 has been changed from:

“Table S1 Coefficients used to correct the ion contribution to organic signals in addition to those used in the default fragmentation table.”

To:

“Table S1 Additional coefficients used to correct the ion contributions to organic signals beyond the default fragmentation table. CO₂_factor is the correction factor of gaseous CO₂ contribution to m/z 44, which was computed by the individual CO₂ concentrations (matching with AMS time steps) divided by the average CO₂ concentration in a monthly campaign.”

Table S2: I would suggest to sort the data by sampling site characteristics (i.e., urban, suburban, rural/remote) instead of sampling date.

Changed as suggested.

Figures S10 to S17: the signals in all the mass spectra are too broad, please reduce the line thickness.

The stick thickness representing signals in all the mass spectra in Figures S10 and S17 was reduced by 1/3.

Figure S22: please mention in the figure caption that the individual trajectories correspond to the 5-cluster solution with arrival height of 300 m.

The caption of Figure S22 has been changed from:

“Figure S22 Individual trajectories in each measurement month colored coded by clusters. The”

To:

“Figure S22 Individual trajectories in each measurement month colored coded by clusters. The individual trajectories are from the 5-cluster solution with an arrival height of 300 m.”

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