Point by Point Response to Review Comments (acpd-14-1443-2014)

Anonymous Referee #1

This study describes a year-round observation of the size distributions of inorganic ions and oxalate in atmospheric aerosols at a coastal site in HK. A total of 43 sets of size-segregated samples were collected from March 2011 to February 2012 using a 10-stage MOUDI sampler. Although the topic on the size distributions of inorganic ions is not new, some interesting and valuable findings are presented in this study. For example, the authors provide evidence that sea salt plays an important role in modulating the amount of nitrate residing in the fine-mode particles. In addition, sulfate was successfully used to estimate the importance of local formation and regional transport to the coastal aerosols in HK through PMF analysis. In general, the methods and interpretation in the manuscript are acceptable, and the topic is certainly relevant within the scope of ACP. I recommend this paper to be published in ACP after some minor revisions listed below.

1. P1447, L21-22: The authors mentioned, "One quarter of each filter substrate was extracted with 3 mL of double de-ionized water....". The extraction of a relatively large quartz fibre filter with such a small amount of water (3 mL) may result in high uncertainties of the reported species. The authors should report the QA/QC in this section.

Response to comments 1 and 2

The filter substrate used in the MOUDI sampler is 47 mm in diameter. One-quarter of this filter can be submerged in 3 mL of water. The good agreement between MOUDI measurements (<3.2 μm) and PM2.5 measurements by SASS sampler as shown in Figure 1 demonstrates that the amount of water used for extraction of MOUDI samples was not a problem. The following text is added to provide more QA/QC information on the analytical methods.

Lines 138-139

"Full calibrations were carried out in every batch of the ionic analysis. The species concentrations were field-blank corrected"

Lines 145-148

"The analytical details of gravimetric measurements, ionic and XRF analysis of the PM2.5 samples were given in the paper by Huang et al. (2014a)."

2. P1451, Section 3.2.1: As appeared in the title of the manuscript, a little bit more information on the sources of oxalate in the atmosphere is needed in this section.

The following text is added to elaborate more about the sources of oxalate.

Lines 220-224

"Several sources are known to contribute the atmospheric presence of oxalate, including secondary formation through the oxidation of oxygenated VOCs (e.g. glyoxal) (Warneck, 2003; Carlton et al., 2007); biomass burning (Allen et al., 2004; Kundu et al., 2010), and meat charbroiling (Rogge et al., 1991)."

3. P1453, L24: I suggest the authors provide the analytical method of Si in Section 2.

Response: Suggestion taken. The following text is added to the revised manuscript:

Lines 145-148

"PM2.5 element data (i.e. Silicon) used in this study was obtained from the Teflon filters through analysis using an energy dispersive X-ray fluorescence spectrometer (ED-XRF, Epsilon 5, PANalytical, The Netherlands). The analytical details of gravimetric measurements, ionic and XRF analysis of the PM2.5 samples were given in the paper by Huang et al. (2014a)."

4. P1456, L18: (Zhuang et al., 199b)?

Corrected.

5. P1460, L20: ".... sulfate mainly exist as...." should be ".... sulfate mainly exists as...."

Corrected.

6. P1460, Section 3.3.2: The authors mentioned that the regional pollutant transport plays an important role in sulfate formation. Are there any correlations between the oxidative capacity/oxidant potential and the concentrations of sulfate in different seasons (especially in winter/spring when the impact of regional pollutant transport is significant)?

Response: As mentioned in section 3.3.1, oxidant potential ($O_x=NO_2+O_3$) was used an indicator for local formation in this study. The correlation coefficient (R) between oxidant potential and fine mode sulfate was 0.53, 0.90, 0.77 and 0.23 for spring, summer, fall and winter, respectively, suggesting the relatively strong local formation in summertime. The authors note that the sample size was relatively small in each season (~10 data points) in this study. More data are needed in order to further explore the seasonal variation in the relationship between Ox and sulfate.

7. P1461, L13: ".... characterized by abundant presence of...." should be ".... characterized by the abundant presence of...."

Corrected.

Anonymous Referee #2

Overall
This paper reports size distribution data for major inorganic ions and oxalate sampled for one year in Hong Kong. Special attention is given to nitrate and sulfate, the two most abundant inorganic ions that were observed to partition largely into coarse and fine particle modes, respectively. Factor analysis of size-resolved sulfate concentration is performed to identify the likely sources of sulfate. The major conclusion is that nitrate is inversely correlated to the sum of sodium and calcium, and sulfate at the HKUST sampling site is largely from regional transport. The paper is generally well written and well constructed. I have the following comments that need to be addressed before publication in ACP.

1. Page 1448, lines 23-26 and Page 1449 lines 1-3. These interpretations are not necessary, as the comparison for these ions are probably well within the uncertainties for each sampling technique.

Response:

We agree that measurement uncertainties alone likely have explained the comparison results. Nevertheless, other factors such as particle bouncing and the different size cut also contribute to deviation from an ideal unity slope. We now rephrase this part of the text to the following to avoid being overly speculative in our interpretation of the comparison results.

> Lines 163-166

> "Measurement uncertainties aside, additional factors, such as particle bounce, sample handling, and the different size cut point (i.e., 2.5 µm vs. 3.2 µm), could also contribute to deviation from a unity slope (Stein et al., 1994; Howell et al., 1998; Chang et al., 2000; Duan et al., 2005)."

2. In Figure 1, is ODR fitting used? The ODR fitting method should be used here since both x- and y-axis measurements have uncertainties. In addition, it would be better to label the slope and intercept values on the plot.

Response:

Yes, ODR fitting was used. The figure is now revised to include the slope and intercept values.

3. The interpretation of summer high MMAD of oxalate: "Oxalate had a slightly larger MMAD than sulfate…as a result of volatilization and repartitioning." This statement is speculative and not justified in the discussion (P1451). Oxalic acid has low volatility and is soluble in water. Therefore, under the summer temperature of ~30 degree C, oxalate likely remains in the particle phase. Perhaps the in-cloud formation of oxalic acid can explain the large MMAD of summer oxalate?

Response:

We disagree with the reviewer regarding the volatility of oxalic acid. Field measurements by Limbeck et al (2001) have demonstrated that oxalic acid partitions between gas and aerosol phases. This relevant finding reported in the literature is now added. We also revised the text to

include a second possible explanation for the enhanced oxalate presence in the size range of 1.0-1.8 µm in comparison with that of sulfate.

The revised text (Lines 236-245) reads:

"Oxalic acid was reported to partition between gas phase and particles under the ambient conditions (Limbeck et al., 2001). The enhanced presence of oxalate in the size range of 1.0-1.8 µm could be explained by evaporation of oxalic acid from the smaller-size particles followed by condensation onto larger particles due to their higher alkalinity. This evaporation-and-re-condensation process was proposed by Yao et al. (2002 and 2003), Mochida et al. (2003) and Sullivan and Prather (2007). Another possible explanation for the increased supermicron oxalate is more active photochemical oxidation in the gas phase in summer followed by preferential condensation onto more alkaline larger particles (Rinaldi et al., 2011; van Pinxteren et al., 2014)."

4. Section 3.2.3 (P1454-1455), the interpretation of coarse mode nitrate. One more factor that may affect the partitioning of nitrate is the amount of sulfate. In ammonia-poor system, ammonia preferentially reacts with sulfuric acid to form sulfate, which drives nitrate into the gas phase. In this study, the molar ratio of $2 \times [SO_4^{2-}]$ to $[NH_4^+]$ is 1.0, indicating that sulfate is likely in the form of $(NH_4)_2SO_4$ and there is no excess ammonium to neutralize nitrate. The influence of sulfate on the partitioning of nitrate needs to be taken into account. A plot of sulfate vs. the mass fraction of nitrate will justify this argument. In addition, as noted by the authors, nitrate is likely under-sampled by MOUDI, so Equation 1 is subject to errors and thus highly qualitative. Also the relationship of Pn_fine and $[Na^+] + [Ca^{2+}]$ only works for high P_{n_fine} values as shown in Figure 5a, which should be clearly noted in the text and abstract.

Response:

The plot of P_{n_fine} vs. sulfate (shown below, Figure R1) shows no obvious relationship between nitrate partition and sulfate concentration.
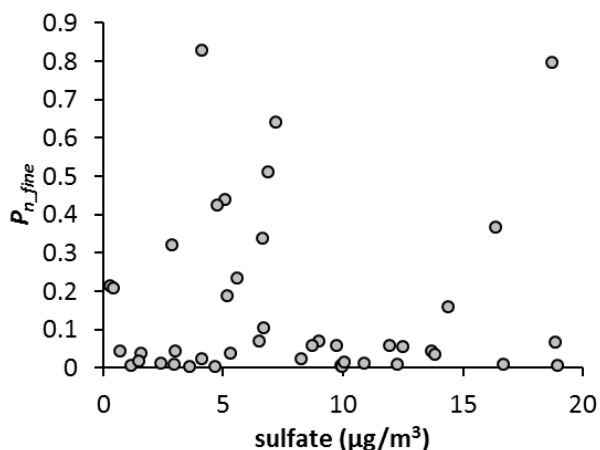

Figure R1. Plot of P_{n_fine} vs. sulfate

On the other hand, the effect from the sulfate concentration has already been considered in the calculation of K_e' (Page 1454, Lines 25–27; Page 1455, Lines 1–4 in the ACPD manuscript).

We agree that the fitting equation is driven by data when P_{n_fine} is significant (>10%) and it is unclear whether this relationship applies to lower P_{n_fine} scenarios. The abstract and Section 3.2.3 were revised as below to clarify this point:

Abstract (Lines 26-29):

"This data set reveals an inversely proportional relationship between the fraction of nitrate in the fine mode and product of the sum of sodium and calcium in equivalent concentrations and the dissociation constant of ammonium nitrate (i.e., $(1/([Na^+]+2[Ca^{2+}])\times(1/K_e'))$ when P_{n_fine} is significant (>10%). "

Section 3.2.3 (Lines 352-356):

"Due to the limited sample size and the negative sampling artifact in nitrate by MOUDI, there is a significant degree of scattering in the plot. As shown by Fig. 5b, the fitting equation is largely driven by data points when P_{n_fine} is significant (>10%). As such, whether this equation is applicable to scenarios of small P_{n_fine} can only be evaluated after more and better quality measurements are made in this regime."

5. P1458, "30% of the corresponding concentration for CO, SO$_2$ and O$_x$" is used as uncertainty. This seems arbitrary and is not justified. How is this criterion derived? Typically the uncertainty of these gases can be obtained by measuring the standard concentrations of the gases for a period of time and calculating their standard deviations.

Response:

CO, SO2, NOx and O3 measurements were not made by our team. Although calibrations of the relevant instruments were routinely made according to operating instructions recommended by manufacturers, the measurement uncertainties for the CO, SO$_2$, NOx and O$_3$ data were not reported. The EPA PMF 3.0 user guide describes the following practice in the case that uncertainties were not regularly reported (e.g., PAMS VOC data): 20% of the VOC concentration was assigned as the initial uncertainty for each species and the final uncertainties for the study were adjusted based on the source profile and result stability. In our case, uncertainties for CO, SO$_2$ and O$_x$ data was adjusted from 5% to 30%. Based on variation of Q values, the interpretability of source profiles and stability of bootstrap results, application of 30% of the concentration for these three gaseous species leads to the most reasonable results in PMF analysis.

6. Figure S7 shows that the theoretical Q value is 191. How is this value obtained? The theoretical Q value should be approximately m x n, where m and n are number of rows and columns of the input date matrix, respectively. In this case, the theoretical Q is 43 x 8 = 344, which is much larger than 191. A Q vs FPEAK plot for the coarse mode sulfate PMF should also be shown. In addition, negative FPEAK values should also be examined.

The EPA PMF3.0 user guide suggests that theoretical Q is calculated by $m \times n - p \times (m + n)$, where n is the number of species, m is the number of samples in the data set, and p is the number of factors fitted by the model. The following plots (Figure R2) were added into the supplementary materials (Figure S8).
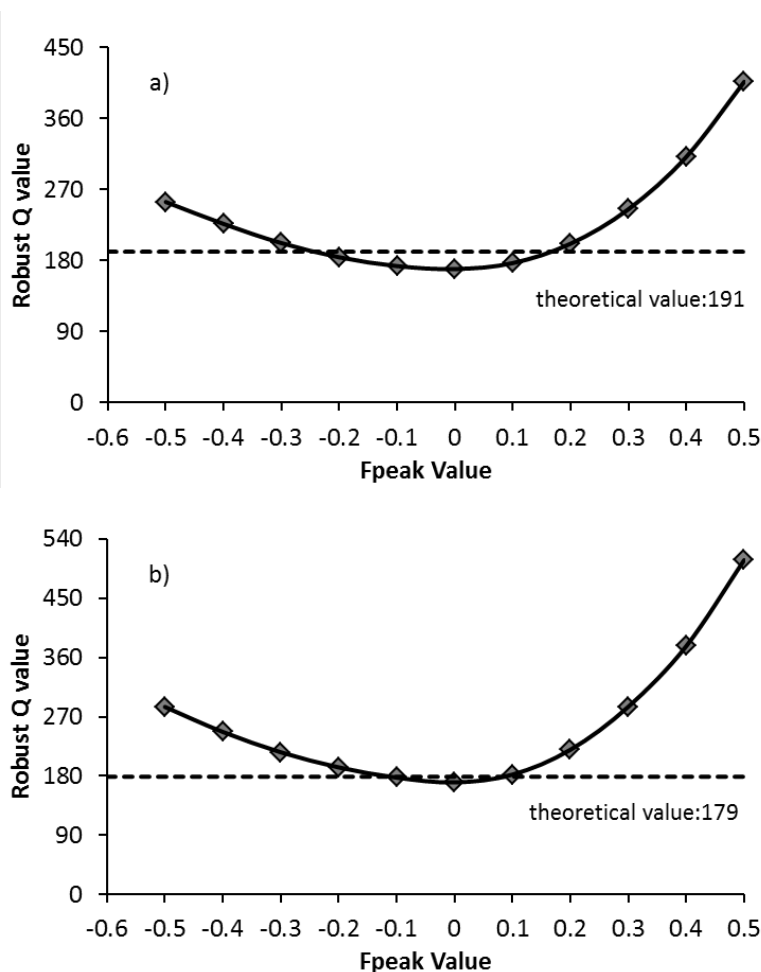
Figure R2. Robust Q as a function of Fpeak value from -0.5 to 0.5 in the PMF analysis of (a) the size-segregated sulfate data; (b) the coarse sulfate data. The dot line represents the theoretical value and is included to serve as a reference.

7. P1458, the use of CO as a tracer for transport. It says there was not obvious combustion source found in the vicinity of the sampling site. But google map shows that there are several major roads within 2-3 kilometers to the west and southwest of the HKUST site. Therefore, it is expected that vehicular exhaust contributes to CO. Since CO is the key tracer to justify factor 2 as a transport factor that is a major conclusion, more evidence is needed to exclude the local source of CO. I suggest the authors to show the diurnal cycle of CO for the sampling days. Local contribution would be minor if no CO peaks show up during rush hours.

The vehicular emissions from the roads in the vicinity of a few km of the sampling site did not contribute much to CO at the site, as seen in the diurnal variation (see Figure R3 below, also included in the supplementary material as Fig. S6), which did not show any peaks during the anticipated local rush hours. The roads near HKUST do not carry heavy traffic as the university is located in a low density residential district in Hong Kong. The following text is added to better explain the source of CO.

Lines 409-416:

"Diurnal variation of CO at our measurement site was almost flat and no rush hour peak was observed (Fig. S6). This was clearly different from the diurnal patterns of elemental carbon and NOx as observed at a roadside location in Hong Kong showing concentration peaks during local rush hours in the morning and in the early evening (Huang et al., 2014b). Hence, the diurnal pattern of CO rules out vehicular emissions from nearby roads in the vicinity of a few kilometers as a major contributor to at HKUST. This is reasonable in view of that the roads near HKUST do not carry heavy traffic as the university is located in a low density residential district in Hong Kong…"
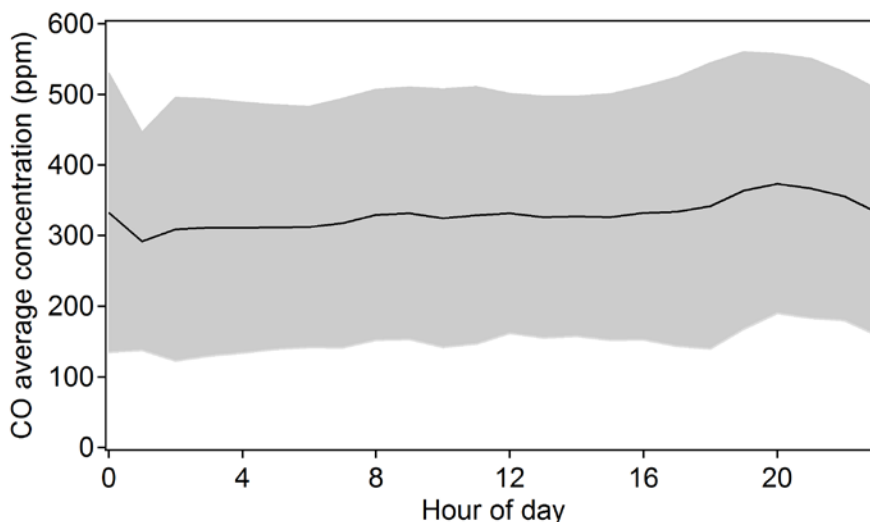

Figure R3. Diurnal variation of CO on the sampling days.

8. Figure 6, the profile of the transport factor. Why does transported sulfate have the largest contribution of sulfate in 1.0-3.2 um? I would expect the transported sulfate is dominated by submicron sulfate since submicron sulfate has longer lifetime.

The 1.0-3.2 µm size range consists of two size bins, 1.0-1.8 µm and 1.8-3.2 µm. A close examination of the size distribution of sulfate (top row in Fig. 2a) indicates that the droplet mode of sulfate was broad and dominant, encompassing most of sulfate in the 1.0-3.2 µm range. As part of the droplet mode (which tend to be more aged), it is not surprise to see these particles contributed significantly to the transported sulfate. The study by Guo et al (2010) provides field measurements-based evidence for super-micron sized droplet mode sulfate as a result of regional transport. They made simultaneous measurements of ionic species in Yufa (upwind) and PKU (downwind) in Beijing. A bigger size droplet mode with the modal peak exceeding 1 µm was observed at the downwind PKU site and this droplet mode had a moderate correlation with the droplet mode at Yufa, consistent with the possible growth of the droplet aerosols from Yufa to PKU during the transport.

The following text is added to provide a more detailed explanation for the abundant presence of 1.0-3.2 µm size sulfate particles in the transported sulfate factor:

Lines 451-456:

"It is noted that nearly all the sulfate in the size range of 1.0-3.2 µm is associated with this factor. A close examination of the size distribution of sulfate (top row in Fig. 2a)

indicates that the droplet mode of sulfate was broad and dominant, encompassing most of sulfate in the 1.0-3.2 µm range. The abundant presence of the super-micron droplet mode sulfate particles suggests a major contribution from aged air masses which makes possible significant growth in particle size (Guo et al., 2010)."

9. Section 3.3.3, time series of the four factors of coarse sulfate need to be shown and discussed to confirm the identity of the four factors. For example, the fresh sea salt factor concentration is expected to be lower in summer and winter due to low salinity.

Response:

The time-series plot for the four factors of coarse mode sulfate is shown below (Figure R4 and also Figure S9). We note that the combined fresh and aged sea salt concentration (not fresh sea salt alone) is higher in spring and fall than in summer and winter.
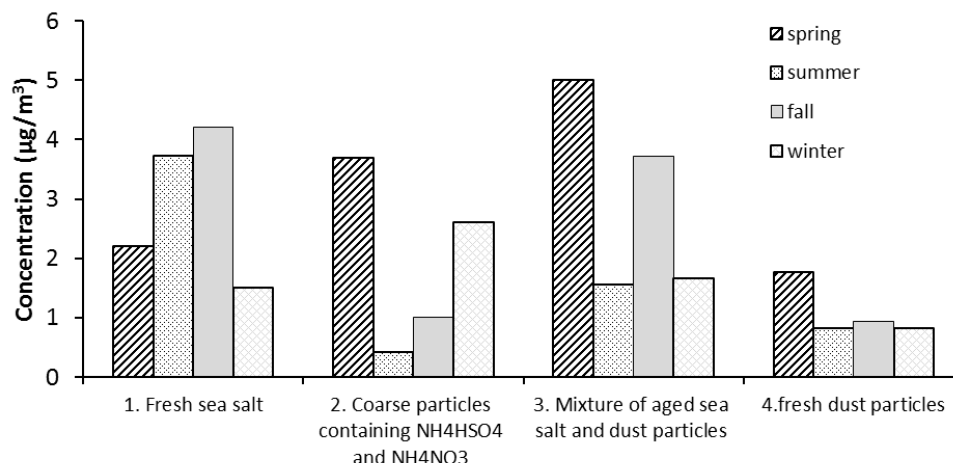

Figure R4. The seasonal variation in source contributions by the four PMF-derived sources

10. The coagulation factor of coarse mode sulfate. Heterogeneous reaction of ammonia, sulfuric acid, and nitric acid on sea salt or dust particles is also a likely formation mechanism for this factor.

Response:

We do not think this is the case. The following text is added to the paper to support our point.

Lines 494-497:

"… The possibility of heterogeneous reaction of ammonia, sulfuric acid, and nitric acid on sea salt or dust particles could be ruled out since when exposed to abundant acids, since the alkaline sea salt or dust particles tend to react with them to form more stable salts (e.g. $CaSO_4$ and $NaNO_3$)."

11. P1461, Lines 13-15, I don't understand why the presence of nitrate, Ca^{2+}, and chloride depleted sea salt species indicates aged sea salt aerosols? This factor should be compared with CO to check if there is a correlation, since CO is used as a tracer for transport in this study.

Response:

We note this factor was identified as the mixture of aged sea salt and dust particles, not just aged sea salt. Fresh sea salt particles would react with HNO_3 to produce $NaNO_3$ and HCl. The longer the sea salt particles stayed in polluted air masses, which typically contain elevated levels of HNO_3, the more Cl^- would be replaced by NO_3^-, leading to chloride depletion. Therefore, the presence of nitrate and chloride depleted sea salt species indicates the aged sea salt aerosols. The PMF-derived source profile for aged sea salt (Figure S10) shows that the amount of Na^+, Mg^{2+} and K^+ was similar to those in the fresh sea salt, except that Cl^- was replaced by abundant NO_3^-.

Ca^{2+} and Si are tracers for dusts. The concurrent appearance of Ca^{2+}, Si and sea salt species in Factor 3 (Fig. 8) suggests that the dust was mixed with local aged sea salt in this source. It was not expected that the regional indicator CO would correlate well with this factor (shown in the plot below, Fig. R5).
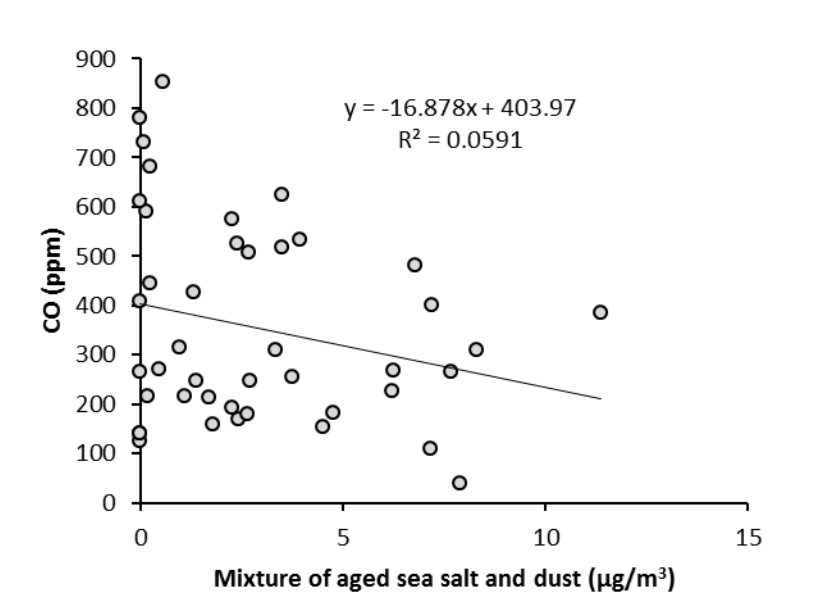

Figure R5. Correlation of CO with the mas concentration attributable to the mixed aged sea salt and dust factor.

Technical corrections:

- P1446 L14: Opening bracket missing in front of URL

- P1450 L10: "droplet mode" instead of "condensation mode"?

- P1447 L25: Please include manufacturer and model of IC

Response: Corrected.

- P1451 L27-28: as K+ is chemically inert in a cloud, "in-cloud processing" is not an appropriate term here, in my opinion.

Response: "in-cloud processing" is revised to "in-cloud processes".

- P1454 L24: Change the arrow in R1 to appropriate equilibrium reaction arrows (two arrows above each other, pointing into opposite directions). The symbol shown is reserved for mesomeric structures in chemistry.

- P1454 L24 and L26: Change liquid to aqueous, as it is not synonym for aerosol particles

Corrected.

- Figure 2: Hardly readable in the present form. Please make sure it will be printed much larger in the final manuscript.

We believe this is a problem with how figures are shown in ACPD. The figure supplied in our word document will allow a readable view in the final publication.

- Figure 4: Include dot in PM2.5 in x-axis label

- Figure 5b: Opening bracket missing in x-axis label

Corrected.

Anonymous Referee #3

-The introduction could be improved. Parts of it present too much general information (e.g. P1445 L21 to P1446 L10) not focused enough on the data presented later-on in the paper. The phase partitioning of nitrate for example is not motivated at all.

Response:

The part from P1445 L21 to P1446 L10 in the ACPD manuscript is now condensed. A paragraph (see below) is inserted in this section to elaborate the background information on nitrate and the significance of examining nitrate partitioning for our study region.

> Lines 80-90:
> "Nitrate is a significant, although less abundant than sulfate, component of $PM_{2.5}$. It also often has abundant presence in the coarse particles. A source analysis study by Yuan et al. (2013) using receptor modeling of near 10-year speciated PM_{10} data found secondary nitrate in PM_{10} increased by 30% from 1998 to 2007 in HK while a decreasing contribution from vehicle emissions was observed. It is observed that the improvement due to reductions of PM in local emissions has been offset by an increase in non-local contributions with nitrate being a major species. Yang et al. (2011) reported higher $[NO_3^-]/[SO_4^{2-}]$ ratio in $PM_{2.5}$ in Guangzhou than in other cities in China and implied that on-road automobiles could be the major contributor. Hence, investigation of the partitioning behaviors of nitrate between coarse and fine modes through size distribution measurements will help to quantify factors and processes affecting $PM_{2.5}$ nitrate."

-The authors used quartz filters as impaction substrates, but present their size distribution data using the nominal cut-offs of the MOUDI. These, however, are valid for flat impaction substrates (aluminum foils, cf. Marple et al., 1991). Quartz filters can be expected to modify the size cuts of an impactor due to their different surface roughness (see e.g. Fujitani et al., 2006; Marjamäki and Keskinen, 2004). This should be discussed somewhere in the manuscript.

- Related to this, on P1450 L4 the authors state that they have used the known response function of the impactor for inversion. Has the response function been experimentally determined for quartz filter substrates? In case the manufacturer-supplied response functions were used: What would be the effect of modified size cut characteristics (i.e. response function) due to the quartz filters on the inversion results?

Response:

Two factors with using quartz filter as impaction substrate might impact the cut point size. They are (1) the thickness of quartz filter larger than Al foil and (2) excess collection of particles due to occurrence of filtration collection. Regarding the first influencing factor, we used special spacers from MSP corp (0.05 inch in thickness) to compensate the shorter jet-to-plate distance due to the thicker quartz filter substrate. The details were described in previous papers from our group (Huang et al., 2006a, 2006b). We did not evaluate the degree of filtration for our MOUDI sampling set-up. According to the work by Fujitani et al (2006), they reported that mass size distribution of roadside atmospheric particles measured with a low pressure impactor using quartz fiber filters was similar to that measured with NanoMOUDI using aluminum foils. They concluded that the artifact of filtration was not important because of lower particle concentrations in the roadside atmosphere. The PM concentrations encountered in our ambient

concentrations were lower than or similar to those recorded in the roadside samples by Fujitani et al (28-42 µg/m^3). Considering the findings by Fujitani et al, we feel the modification of cut-point size was likely insignificant in our MOUDI set-up. We therefore did not apply any corrections to the response function.

Revisions were made in the manuscript as follow,

> Lines 115-118:
>
> Special spacers of 0.05 inch in thickness (MSP Corp., Shoreview, MN) were used between adjacent stages to compensate the shorter jet-to-plate distance due to the thicker quartz filter substrate than aluminum foil, on which characterization of the cut-off size and response factor of each impact stage is based."

Quartz filters are susceptible to blank values which might be significant when sampling relatively low amounts of PM with an impactor. Have the authors checked for blanks, maybe even field blanks? Has concentration data been corrected for blank values? This information should be given in the manuscript.

Response:

The blank samples were collected during each sampling event, chemically analyzed, and used in the correction of concentration data. Revisions are made in the manuscript as follow,

> Lines 123-125:
>
> "One field blank sample was taken during each sampling event and analyzed in the laboratory together with the samples."
>
> Lines 138-139:
>
> "Full calibrations were carried out in every batch of the ionic analysis. The species concentrations were field-blank corrected."

- P1451 L20-24: Experimental evidence on the semi-volatile behavior of dicarboxylic acids is available in the literature, thus a repartitioning of oxalic acid could indeed be a plausible explanation (which has, however, not only been suggested in the cited paper, see e.g. Yao et al., 2002; Mochida et al., 2003). However, it is not the only possible reason. Gas-phase formation of oxalic acid and subsequent preferential condensation onto more alkaline larger particles as well as a sea-salt source or a soil source of oxalic acid could both lead to a similar shift in the MMAD of oxalate. These sources can be expected to be high in summer (due to high photochemical activity and dry conditions), which would be consistent with Fig. 3. See e.g. van Pinxteren et al., 2014 and Rinaldi et al., 2011 for discussions on these sources.

Response:

Suggestion taken and the following text is added to the paper:

> Lines 236-245：
>
> "Oxalic acid was reported to partition between gas phase and particles under the ambient conditions (Limbeck et al., 2001). The enhanced presence of oxalate in the size range of

1.0-1.8 µm could be explained by evaporation of oxalic acid from the smaller-size particles followed by condensation onto larger particles due to their higher alkalinity. This evaporation-and-re-condensation process was proposed by Yao et al. (2003, 2012), Mochida et al. (2003) and Sullivan and Prather (2007). Another possible explanation for the increased supermicron oxalate is more active photochemical oxidation in the gas phase in summer followed by preferential condensation onto more alkaline larger particles (Rinaldi et al., 2011; van Pinxteren et al., 2014)."

- P1452 L22-23: What about other possible reasons for the bi-modality in supermicron particles e.g. separate dust/soil and sea-salt modes? Can these be ruled out?

Response:

We would like to clarify that here we are discussing species-specific size distributions, not PM mass (sum of all species mass) distribution. As we have measurements of individual PM species, we can separately examine the size distributions of sea salt particles and soil particles. As shown in Table 1b, sea salt particles and soil particles are both bimodally distributed, but the MMADs of their modes were different, although the difference is not large (less than 0.6 µm). If one examines the PM mass distribution, it will be difficult to separate the dust and sea salt particle modes as the two sources have very similar MMADs.

- P1455 L21-23 and Figure 5b: The fit of this relationship to the experimental data is rather poor. Below an x-axis value of about 20 (where actually the majority of data points lie), equation 1 does not fit the data at all and even at larger values the scatter is very large and the good R squared is only obtained due to few data points with relatively large values. I am not convinced this relationship is robust enough to be in any models which question the benefit of presenting it even in the abstract.

Response:

The inverse relationships between P_{n_fine} and Ke' and between P_{n_fine} and the sum of coarse Na^+ and Ca^{2+} are clearly demonstrated in Figure 5a. It may be arguable whether the inverse relationships could be best described by the linear fitting equation between P_{n_fine} and $(1/([Na^+]+2[Ca^{2+}])\times(1/K_e')$ or another form. We agree that the linear fitting equation is driven by data points when P_{n_fine} is significant (>10%) and it may not be applicable to scenarios when when P_{n_fine} is small. Nevertheless, this is the first attempt to establish an approximate semi-quantitative relationship between P_{n_fine} and the various influencing factors. More and better measurements are definitely needed to derive a more robust relationship for the eventual use in air quality modeling studies.

The following text is revised to clearly state the limit of the equation.

Abstract (Lines 26-29):

"This data set reveals an inversely proportional relationship between the fraction of nitrate in the fine mode and product of the sum of sodium and calcium in equivalent concentrations and the dissociation constant of ammonium nitrate (i.e., $(1/([Na^+]+2[Ca^{2+}])\times(1/K_e'))$ when P_{n_fine} is significant (>10%). "

"Due to the limited sample size and the negative sampling artifact in nitrate by MOUDI, there is a significant degree of scattering in the plot. As shown by Fig. 5b, the fitting equation is largely driven by data points when P_{n_fine} is significant (>10%). As such, whether this equation is applicable to scenarios of small P_{n_fine} can only be evaluated after more and better quality measurements are made in this regime."

- Section 3.3.1: Why is only sulfate included in the PMF analysis? According to the equation given on P1458 L9 on the minimum sample size for statistically reliable results, the authors could easily include more of their measured species, especially if grouped into appropriate size ranges as done for sulfate. It would be interesting to see, how other measured species load onto the factors and more species might even help to resolve or identify more sources (see e.g. van Pinxteren et al., 2014).

Response:

Including more tracer species would surely lead to more resolved sources. However, the intention of this work was not to resolve more sources, but to quantify the relative local and regional contributions to sulfate. The species which could help identify sulfate sources (e.g. SO_2, O_x and CO) were therefore selected for the PMF analysis. In addition, inclusion of more species would lead to unstable PMF results (i.e, failing the bootstrap test). That's also one of the reasons to apportion coarse sulfate by separate PMF modeling.

P1458 L7: Can traffic as a source of CO really be excluded at the HKUST site?

Response：

Referee #2 also raised this question. The same response is copied below.

The vehicular emissions from the roads in the vicinity of a few km of the sampling site did not contribute much to CO at the site, as seen in the diurnal variation (Fig. R3, also included in the supplementary material as Fig. S6), which did not show any peaks during the anticipated local rush hours. The roads near HKUST do not carry heavy traffic as the university is located in a low density residential district in Hong Kong. The following text is added to better explain the source of CO.

Lines 409-415:

"Diurnal variation of CO at our measurement site was almost flat and no rush hour peak was observed (Fig. S6). This was clearly different from the diurnal patterns of elemental carbon and NOx as observed at a roadside location in Hong Kong showing concentration peaks during local rush hours in the morning and in the early evening (Huang et al., 2014b). Hence, the diurnal pattern of CO rules out vehicular emissions from nearby roads in the vicinity of a few kilometers as a major contributor to at HKUST. This is reasonable in view of that the roads near HKUST do not carry heavy traffic as the university is located in a low density residential district in Hong Kong…"

-P1460 L21-22: While coagulation is one possibility, heterogeneous chemistry and/or preferential condensation to more alkaline coarse mode particles could be further options.

Response:

We do not think this is the case. The following text is added to the paper to support our point.

Lines 494-497:

"… The possibility of heterogeneous reaction of ammonia, sulfuric acid, and nitric acid on sea salt or dust particles could be ruled out since when exposed to abundant acids, the alkaline sea salt or dust particles tend to react with them to form more stable salts (e.g. $CaSO_4$ and $NaNO_3$)."

Technological corrections

1. Page 1445, change "To understand" to "understanding".

This sentence has been removed in the revised manuscript.

2. P1450, Line 17-18, change "mass distribution" to "fraction".

3. Figure 1e, change legend "NH4-" to "NH4+"

Corrected.

4. Figure 4, what is the red label "(0.2)"?

(0.2) means -0.2. Now it is simply revised to -0.2.

5. Figure 5b, the x-axis label is missing a "(" before "[Na+].

6. Similar problem to 5 in the abstract.

Corrected

References:

Allen, A. G., Cardoso, A. A., and da Rocha, G. O.: Influence of sugar cane burning on aerosol soluble ion composition in Southeastern Brazil, Atmos. Environ., 38, 5025–5038, 2004

Carlton, A. G., Turpin, B. J. Turpin, Altieri, K. E., Seitzinger, S.,Reff, A., Lim, H.-J., and Ervens, B. : Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmos. Environ., 41, 7588–7602, 2007.

Guo, S., Hu, M., Wang, Z.B., Slanina, J., and Zhao, Y.L.: Size-resolved aerosol water-soluble ionic compositions in the summer of Beijing: implication of regional secondary formation, Atmos. Chem., Phys., 10, 947-959, 2010

Huang, X.H.H., Bian, Q., Ng, W. M., Louie, P.K.K., and Yu, J.Z.: Characterization of $PM_{2.5}$ major components and source investigation in suburban Hong Kong: a one year monitoring study, Aerosol Air Qual. Res., 14,237-250, 2014a.

Huang, H.X.X., Bian, Q., Louie, P.K.K. and Yu, J.Z.: Contributions of vehicular carbonaceous aerosols to PM2.5 in a roadside environment in Hong Kong, Atmos. Chem. Phys. Discuss., 14, 57-93, 2014b.

Huang, X.-F., Yu, J. Z., He, L.-Y, and Hu, M.: Size distribution characteristics of elemental carbon emitted from Chinese vehicles: Results of a tunnel study and atmospheric implications, Environ. Sci. Technol., 40, 5355-5360, 2006a

Huang, X.-F., Yu, J. Z., He, L.-Y, and Yuan, Z.: Water-soluble organic carbon and oxalate in aerosols at a coastal urban site in China: Size distribution characteristics, sources, and formation mechanisms, J. Geophys. Res., 111, D22212, doi: 10.1029/2006JD007408, 2006b.

Kundu, S., Kawamura, K., Andreae, T.W., Hoffer, A., and Andreae, M.O.: Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers, Atmos. Chem. Phys., 10, 2209-2225, 2010.

Lo, J.C.F., Lau, A.K.H., Yuan, Z.B., Fung, J.C.H., Chen, F.: A physical modeling approach for identification of source regions of primary and secondary air pollutants, Atmos. Chem. Phys. Discuss., 14, 57-93, 2014.

Limbeck, A., Puxbaum., H., Otter, L., Scholes, M.C.: Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA), Atmos. Environ., 35, 1853-1862, 2001.

Mochida, M., Umemoto, N., Kawamura, K., Uematsu, M.: Bimodal size distribution of C2-C4 dicarboxylic acids in the marine aerosols, Geophy. Res. Lett., 30, 1672, doi:10.1029/2003GL017451, 2003.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simonelt, B. R. T.: Sources of fine organic aerosol, 1. Charbroilers and meat cooking operations, Environ. Sci. Technol., 25, 1112–1125, 1991.

Rindaldi, M., Decesari, S., Carbone, C., and Tsigaridis, K.: Evidence of a natural marine source of oxalic acid and a possible link to glyoxal, J. Geophys. Res., 116, D16204, doi:10.1029/2011JD015659, 2011.

Stavrakou, T., Müller, J.-F., De Smedt, I., Van Roozendael, M., Kanakidou, M., Vrekoussis, M., Wittrock, F., Richter, A., and Burrows, J.P.: The continental source of glyoxal estimated by the synergistic use of spaceborne measurements and inverse modeling, Atmos. Chem. Phys., 9, 8431-8446, 2009.

Sullivan, R.C., and Prather, K. A.: Investigations of the diurnal cycle and mixing state of oxalic acid in individual particles in Asian Aerosol outflow, Environ. Sci. Technol., 8062-8069, 2007.

van Pinxteren, D., Neusüβ, C., and Herrmann, H.: On the abundance and source contributions of dicarboxylic acids in size-resolved aerosol particles at continental sites in Central Europe, Atmos. Chem. Phys. Discuss., 13, 32093-32131, 2013.

Warneck, P.: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, Atmos. Environ., 37, 2423–2427, 2003.

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, Atmos. Chem. Phys., 11, 5207-5219, 2011.

Yuan, Z., Yadav, V., Turner, J. R., Louie, P.K.K., and Lau, A.K.H.: Long-term trends of ambient particulate matter emission source contributions and the accountability of control strategies in Hong Kong over 1998-2008, Atmos. Environ., 76, 21-31, 2013.