Response to review comments by 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.

"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 are made in the manuscript as follow,

"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,

"One field blank sample was taken during each sampling event and analyzed in the laboratory together with the samples."

"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:

"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)."

- 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 K_e' 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 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:

"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

"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 (see the figure 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.

"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…"
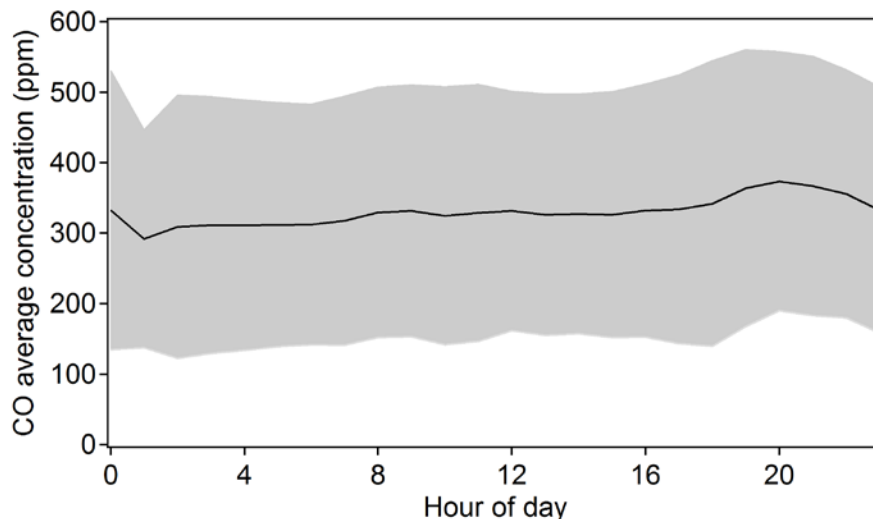
Diurnal variation of CO on the sampling days.

-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.

"… 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:

Fujitani, Y., Hasegawa, S., Fushimi, A., Kondo, Y., Tanabe, K., Kobayashi, S., and Kobayashi, T., Collection characteristics of low-pressure impactors with various impaction substrate materials, Atmos. Environ., 40(18), 3221-3229, 2006.

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.

Huang, X.H.H., Bian, Q. J., 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.

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.

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.

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.

Yao, X.H., Fang, M., and Chan, C.K.: The size dependence of chloride depletion in fine and coarse sea-salt particles, Atmos. Environ., 37, 743-751, 2003.

Yao, X.H. and Zhang, L.M.: Chemical processes in sea-salt chloride depletion observed at a Canadian rural coastal site. Atmos. Environ. 46, 189-194, 2012.

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.