

Response to review comments by 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:

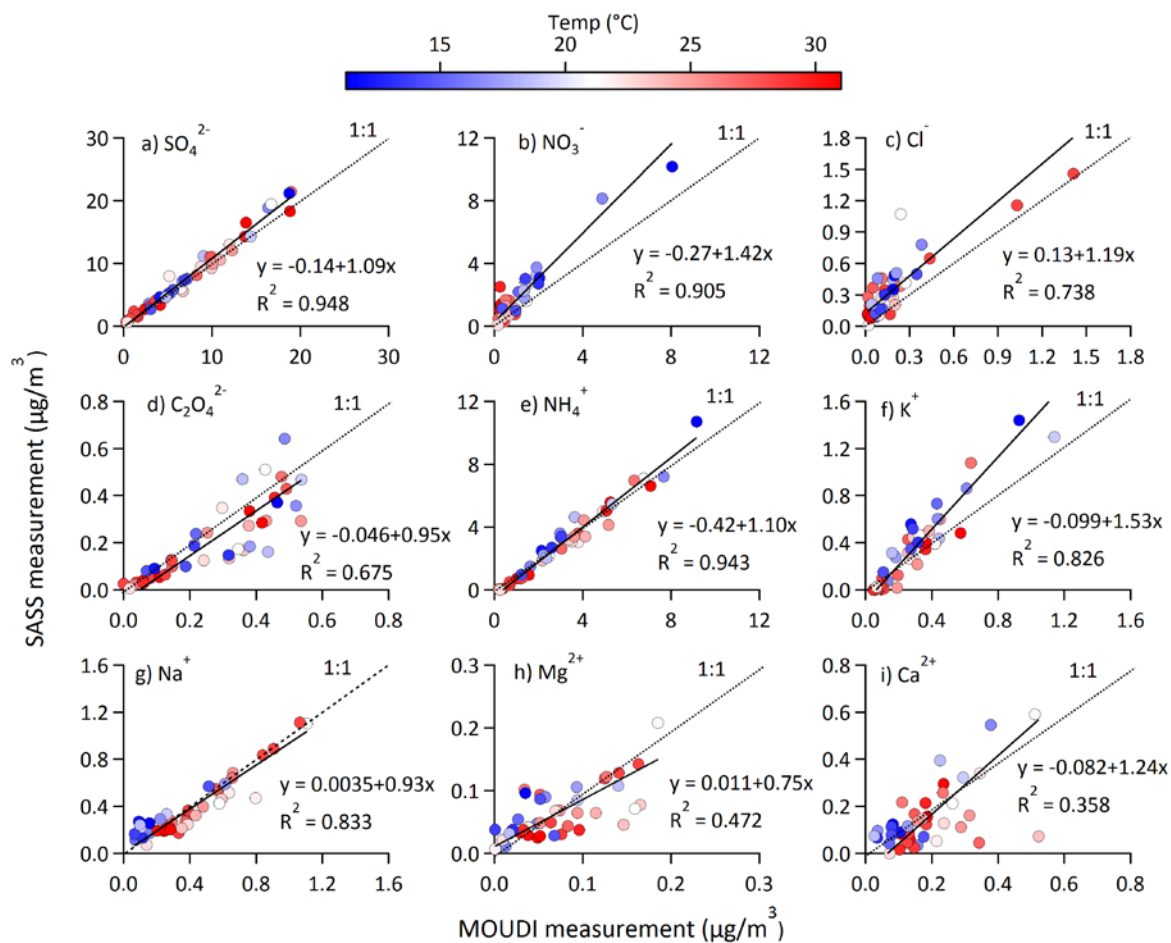
We agree that measurement uncertainties alone likely have explained the comparison results. Nevertheless, other factors such as particle bouncing and the different size cut also contribute to deviation from an ideal unity slope. We now rephrase this part of the text to the following to avoid being overly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

“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 (see below) to include the slope and intercept values.



Revised Figure 1.

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 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-recondensation 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 $2x[\text{SO}_4^{2-}]$ to $[\text{NH}_4^+]$ is 1.0, indicating that sulfate is likely in the form of $(\text{NH}_4)_2\text{SO}_4$ 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 P_{n_fine} and $[\text{Na}^+] + [\text{Ca}^{2+}]$ 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.

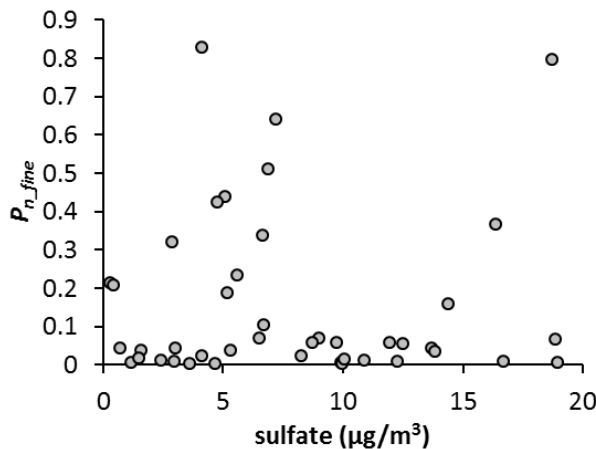


Figure R1. Plot of P_{n_fine} vs. sulfate

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 paper).

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 are revised as below to clarify this point:

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.”

5. P1458, “30% of the corresponding concentration for CO, SO₂ 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, NO_x 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, SO₂, NO_x and O₃ 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, SO₂ 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 $m \times n$, where m and n are number of rows and columns of the input data matrix, respectively. In this case, the theoretical Q is $43 \times 8 = 344$, 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.

Response:

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).

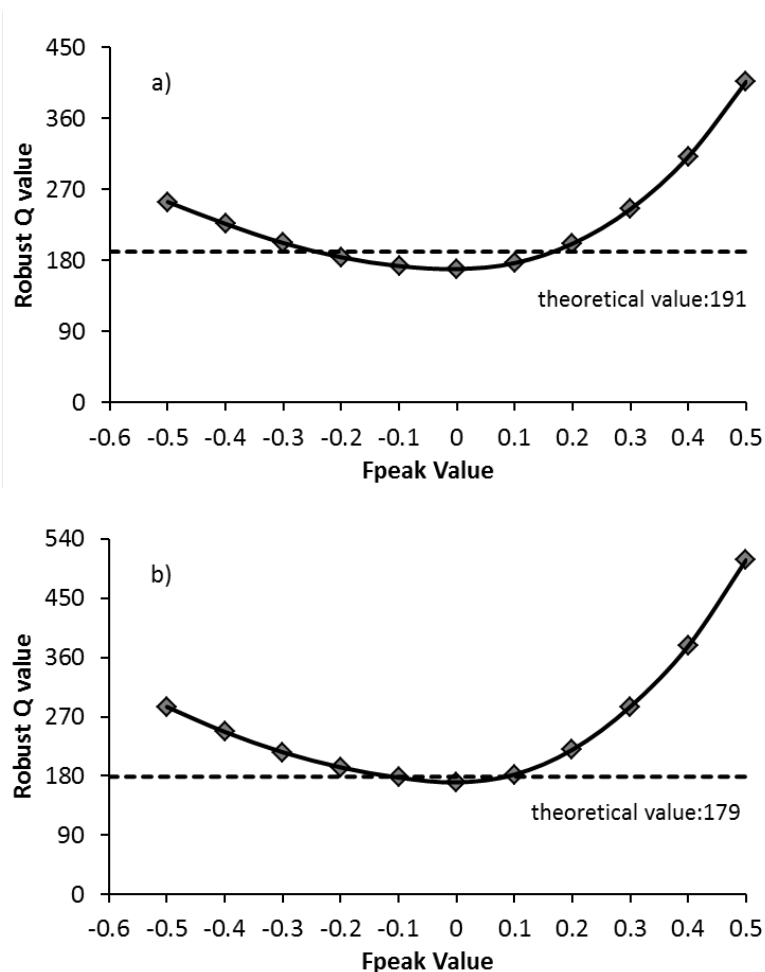


Figure R2. Robust Q as a function of Fpeak value from -0.5 to 0.5 in the PMF analysis of (a) the size-segregated sulfate data; (b) the coarse sulfate data. The dot line represents the theoretical value and is included to serve as a reference.

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.

Response:

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.

“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 NO_x 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...”

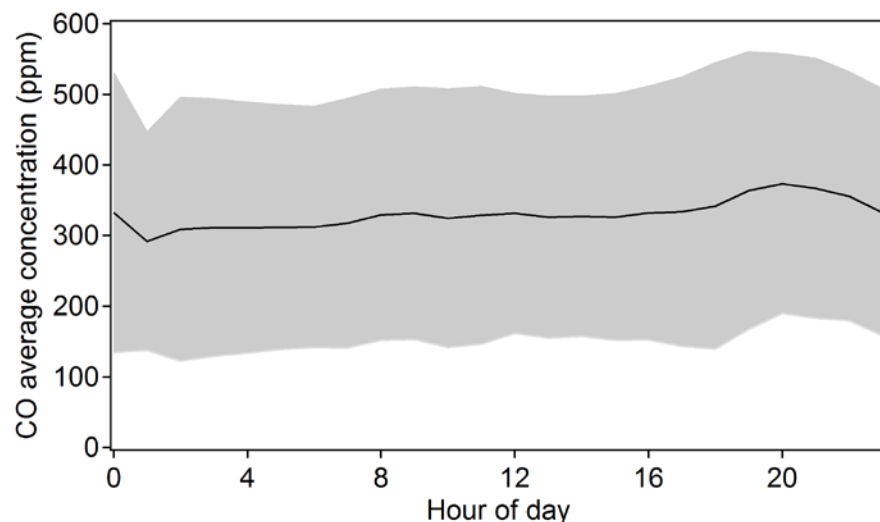


Figure R3. Diurnal variation of CO on the sampling days.

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

Response:

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:

“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.

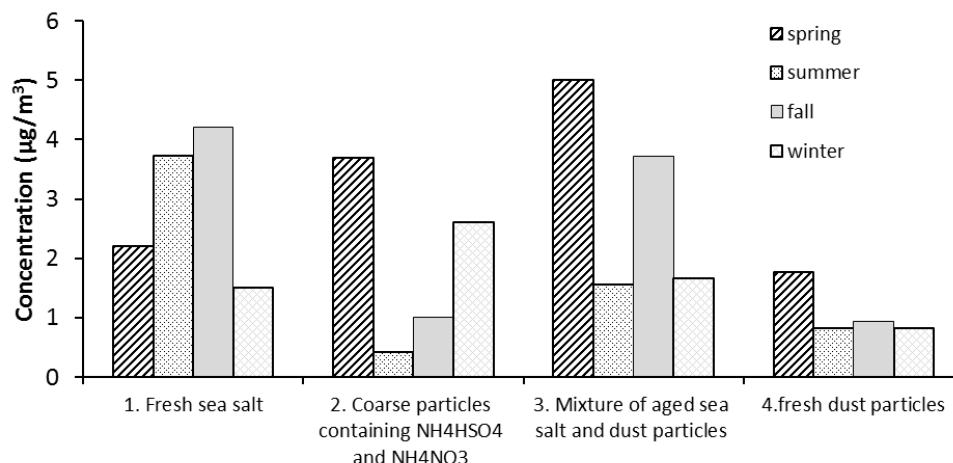


Figure R4. The seasonal variation in source contributions by the four PMF-derived sources

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.

“... 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).

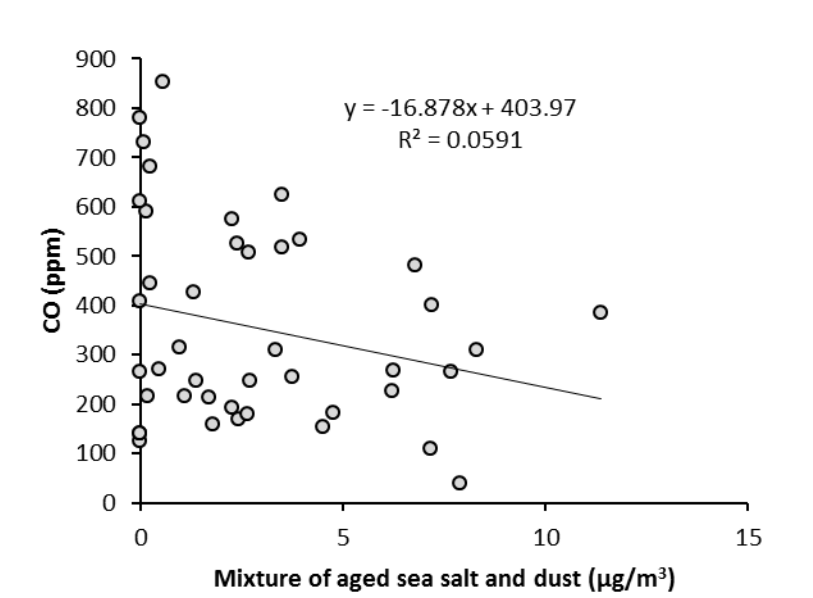


Figure R5. Correlation of CO with the mass concentration attributable to the mixed aged sea salt and dust factor.

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.

Response:

We think 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.