

We would like to thank the referees for all the comments. The authors' responses are listed as follows with corresponding changes made in the manuscript.

Anonymous Referee #1

This paper describes extensive measurements of water soluble elements in PM_{2.5} aerosol in the southeastern US. This work is a tour-de-force in terms of the numbers of measurements (500), which permit analysis of spatial homogeneity and seasonal dependencies. For the most part, the measurements were made by a commercial x-ray fluorescence system, along with some measurements of WSOC using a TOC analyzer. In particular, samples were collected on filters and then solubilized and atomized, before being directed to the analyzers. The authors do an extensive characterization of the efficiency of detection of elements from solutions of known concentrations from which they extract a correction factor applied to their data. They also compare sulfur analyzed by ion chromatography to that measured by XRF. All-in-all, the analytical measurements are first-class, made by a group known for its experimental rigor. The data are analyzed largely by PMF (along with some COD work) and a good justification of a four-factor solution is given in the Supplementary Information, including illustration of the size of the residuals for each element. I think this is an excellent study and I highly recommend publication.

My comments are all relatively minor:

1. Are there any analytical matrix effects associated with the XRF detection, i.e. presence of one element affecting the signal from another? With this being XRF, I would not expect so but just wondering if the authors examined this?

Authors' response: The XRF run through a peak deconvolution process to separate near spectra. Under extreme circumstances when a particular element has extremely high concentration, its signal may overwhelm all the other nearby elements, but the authors believe this was not the case in our study as the concentration were not too high.

Changes in manuscript: No changes.

2. I am puzzled why some elements were given a value of 0.5 of LOD when they were not detected, for the PMF analysis. Why not give them a value of zero? Does this affect the PMF solutions?

Authors' response: PMF does not allow a zero value in the input files.

Changes in manuscript: No changes.

3. Can the WSOC data also be presented, for example in Figures 5 and 6?

Authors' response: This work is focused on water-soluble elements and since WSOC has been discussed in our previous work [Verma *et al.*, 2014], the authors believe it is more suitable to put the WSOC data in the supplement.

Changes in manuscript:

Page 17201 line 15: changed “Monthly average concentrations of water-soluble elements at various sampling sites are given in Fig. 5.” to “Monthly average concentrations of water-soluble elements and WSOC at various sampling sites are given in Fig. 5 and Fig. S9, respectively.”

Page 17203 line 3. Add “The COD and correlation coefficient (r) for WSOC were also included in Table S2 in the supplement.” after the sentence “and r values are shown in Fig. 6.”.

4. Lastly, is there a way to substantiate the suggestion that some elements (e.g. those in dust) are higher in summer periods because the weather is drier? In particular, is there a way to summarize or incorporate the meteorological conditions into the analyses? e.g. lower dust or break/tire wear after precipitation? Higher sulfur after high pressure times, etc?

Authors' response: This is a good suggestion, but since this is a minor issue, we have decided not to discuss further to keep the paper focused.

Changes in manuscript: No changes.

Anonymous Referee #2

This manuscript presents a comprehensive study on PM_{2.5} water-soluble metals regarding their temporal and spatial variations, as long as the source apportionments of these metals. A new method of quantifying water-soluble metals in filter extractions was introduced based on a commercially available metal monitor. Source apportionment of important water-soluble metals and WSOC are performed by using PMF method. Overall, this manuscript is very well written, fits perfectly for the scope of ACP journal, and more importantly provides significant insight on important redox-active water-soluble metals in PM_{2.5}. Findings described in this manuscript are very informative in both ambient aerosol studies as well as aerosol related health studies. In my view, this manuscript is acceptable for publication after the authors address my minor comments as below.

Specific comments:

1. Line 90: The author's statement regarding total and water-soluble metals is too strong and needs to be rephrased. The exact role of metal solubility on introducing health effects is not clear yet and apparently still being studied. There have been at least quite a few studies showing significant evidences on the role of insoluble/total metals leading to different health outcomes. Although it is widely accepted that water-soluble metals are more likely bioavailable and therefore having a more obvious effect in generating oxidative stress, making such as statement is likely to be too subjective at this stage.

Authors' response: The authors agree with the reviewer and changed the statement as follows.

Changes in manuscript: Page 17192 line 10: changed “Since most metals in PM have low solubilities (e.g., Zn~50%; Cu and Mn 10–40%; Fe<10 %) (Birmili et al., 2006; Espinosa et al., 2002), total element concentrations cannot be used to assess the roles of redox-active metals’ potential effects on human health.” to “Since most metals in PM have low solubilities (e.g., Zn~50%; Cu and Mn 10–40%; Fe<10 %) (Birmili et al., 2006; Espinosa et al., 2002), total element concentrations may not represent the biological roles of redox-active metals’ potential effects on human health.”

2. Line 188: The description about the system purging is not clear and more clarifications are needed. Is the DI (with 2% nitric acid) also coming from the same sampling streamline out of the auto sampler? Based on the description I assume that the DI with acid is also aerosolized and collected by filter on Xact? If so, was this collection spot skipped?

Authors' response: Yes, the DI is also loaded into the sampling flow from the auto sampler, then aerosolized and sampled by the XRF, the same way as sample. The time interval set for the XRF between samples is 30 min. DI with 2 % nitric acid is added to the system after 14 min (as stated in line 14 page 17196) following the sample, thus both are loaded to the same XRF collection spot. Changes were made to clarify the procedure as follows.

Changes in manuscript: Page 17196 line 21: changed “At the same time, the system repeated the process for measuring the next sample.” to “At the same time, the system repeated the process for measuring the next sample (i.e., load sample-inject sample-load 2% HNO₃-inject 2% HNO₃, 2.5min-14min-2.5min-11min cycle).”

3. Line 380–397: In Figure 7(b), it seems that the brake/tire wear factor is also showing higher contributions in winter time comparing to summer, although the authors mentioned in previous sections (line 320) that higher loadings of Cu, Fe and etc. were observed in summer and were attributed to drier conditions, which enhance the re-suspension of road dust. These two observations seem to be inconsistent and more explanations are needed on this point.

Authors' response: Besides brake/tire wear source, secondary formation is also an important contributor to these metals (39 % to Cu and 47 % to Fe) and this source is much higher in summer than in winter. The combined contribution from these two sources (brake/tire wear and secondary formation) results in higher loadings of Cu and Fe in summer. More explanations are added as follows.

Changes in manuscript:

Page 17190 line 20: deleted “These two factors were higher in warm (drier) periods that favored particle re-suspension.”.

Page 17202 line 1: changed “Elevated concentration of some elements (Ca, Fe, Cu, Mn, and Sr) may be attributed to drier conditions in summer favoring the re-suspension of dust (e.g.,

tire/brake wear or mineral dust, discussed in the source apportionment in Sect. 3.2.3), while Se is likely due to its coal combustion origins (Bell et al., 2007), thus following a similar trend as S.” to “Elevated concentration of some elements (Ca, Mn, and Sr) may be attributed to drier conditions in summer favoring the re-suspension of mineral dust; Cu and Fe may be related to secondary formation (discussed in the source apportionment in Sect. 3.2.3); and Se is likely due to its coal combustion origins (Bell et al., 2007), thus following a similar trend as S.”

Page 17204 line 13: Added “It can be seen from Fig. 7(b) that this factor has a higher contribution in winter than in summer, however, there is not enough evidence to explain the seasonal trend.” before the sentence “A biomass burning factor is identified by high concentrations...”.

Page 17208 line 21: changed “Elements associated with vehicle emissions (brake/tire wear) and mineral dust (water-soluble Ca, Fe, Cu, Mn, and Sr) were higher during warm/dry seasons when aerosol re-suspension is favored.” to “Elements associated with secondary formation and mineral dust were higher during warm/dry seasons when aerosol re-suspension is favored (water-soluble Ca, Mn, and Sr) and secondary formation is high (water-soluble Fe and Cu).”

4. Line 410, 435-446: The authors discussed the possible reasons why a large fraction of Fe is associated with Secondary sources, but not for Cu, which is also a major species shown in secondary sources. Additional discussions on this point are needed as well. It is not intuitively obvious to me why Cu is found in the “Secondary source” factor given the known origins of this metal.

Authors’ response: For Cu, the secondary processing may play the same role as that for Fe, i.e. metal mobilization by formation of an aqueous particle with secondary acids.

Changes in manuscript:

Page 17206 line 21: Added “Metal mobilization by formation of an aqueous particle with secondary acids may also explain the important contribution of secondary formation (39%) to Cu in the Southeastern US, although the correlations between Cu and S were weaker compared to those between Fe and S (Cu - S $r=0.51$, 0.09 , and 0.66 at JST, YRK, and GT in summer, respectively, Table S3).” before the sentence “The correlation between Fe and S might explain past associations...”.

Page 17206 line 22: changed “The correlation between Fe and S might explain past associations found in other studies between...” to “The correlation between S and water-soluble Fe and Cu might explain past associations found in other studies between...”

Page 17190 line 23: changed “Roughly 50 % of Fe and 40 % of Cu was apportioned to the secondary formation factor, likely through increased solubility by sulfur-driven aerosol acidity.” to “Roughly 50 % of Fe and 40 % of Cu was apportioned to the secondary

formation factor, possibly through increases in the soluble fraction of these elements by sulfur-driven aerosol water and acidity.

Reference:

Verma, V., T. Fang, H. Guo, L. E. King, J. T. Bates, R. E. Peltier, E. S. Edgerton, A. G. Russell, and R. J. Weber (2014), Reactive oxygen species associated with water-soluble PM_{2.5} in the southeastern United States: spatiotemporal trends and source apportionment, *Atmos. Chem. Phys.*, *14*(23), 12915-12930.