Response to Anonymous Referee #2

We appreciate your valuable comments and suggestion, which significantly improved the manuscript. We carefully answered them point-by-point as below and improved the corresponding parts in the manuscript.

Reviewer's comments are in plain face.

Author's responses are in blue color.

Changes in the manuscript are in red color.

General comments

The article submitted is suitable for publication in ACP as the topic is within the scope of the journal. This work presents a detailed interpretation of results obtained from a source apportionment analysis of hourly resolved $PM_{2.5}$ and PM_{10} chemical composition, followed by a health risk evaluation of some metals and the obtained sources. The concept is not novel, but high resolution chemical analysis is not performed as a general routine and the important health issues related to coal combustion emissions in an area of high pollution make this work relevant.

The conclusions are clearly drawn from the work, evidencing the importance of pollution and control and emission abatement, especially regarding industrial emissions and coal combustion in the study area.

The title is appropriate, the article is well-structured and the length of the text is adequate. The writing of the article is in general clear (I am not a native English speaker myself). The abstract is clear and concise, the references given throughout the text are appropriate and the supplementary material appropriate.

The scientific methods are clearly explained in the methodology section. However, I have a remark on the use of gaseous compounds together with particulate matter components in the source apportionment analysis. It is not clear to me if the authors use all components only to draw the chemical profiles of the different factors or if they are also used to determine the mass contribution of the sources to the total PM concentrations. This should be clearly explained in the text, and in the latter case, if gaseous compounds and particulate matter components are used together in the

analysis this should be discussed carefully when the contributions of the different sources to PM mass concentrations are discussed.

An important drawback of this study is the lack of the measurement of some major compounds, such as organic carbon (OC), nitrate or ammonium. These are related to the non-determined PM mass in the discussion but it is a pity that they are not determined experimentally. This result in important PM components missing from the database for the PMF analysis, which could affect the results obtained. Regarding this issue, there is a paragraph on mass closure with the objective of defining and calculating RM (remaining mass), which is used as an input in the PMF analysis but I would recommend the authors to add more discussion on the limitations related to this.

Taking advantage of the hourly resolution of the measurements, I think it could be interesting to show some results and add some more discussion on the diurnal evolution of hourly resolved components.

As the streaker sampler collects $PM_{2.5-10}$ and $PM_{2.5}$ fractions separately, I think it could be interesting to study these two fractions separately, instead of PM_{10} and $PM_{2.5}$. Have the authors tried to perform the apportionment analysis with these two fractions?

Response: Thank you very much for your comments.

(1) We provide more details on the PMF receptor model, such as the calculation of uncertainties of elements, and the reasons for choosing the number of factors in the section 2.3 and section 3.2. We explained in the text why we used gaseous compounds together with particulate matter components in the source apportionment analysis.

(2) It is better to have additional chemical data, such as organic carbon (OC), nitrate and ammonium to reach a more robust result. We have thought of this problem before and added some discussions in the present version of manuscript (section 3.1, lines 27-).

(3) More information on the diurnal evolution of hourly resolved components can be found in a separate paper (Zhou et al, 2016).

(4). All modelling combinations were run. In fact the fine and coarse elements are

included in this work separately. We have used $PM_{2.5}$ and PM_{10} as the mass variables, as we did not measure coarse PM ($PM_{2.5-10}$) concentrations directly. Unsurprisingly modelling the size fractions separately gives similar results since we do not alter the underlying variance of the data.

Reference:

Zhou Shengzhen, Perry K. Davy, Wang Xuemei*, Jason Blake Cohen, Liang Jiaquan, Huang Minjuan, Fan Qi, Chen Weihua, Chang Ming, Travis Ancelet, William J. Trompetter. High time-resolved elemental components in fine and coarse particles in the Pearl River Delta region of Southern China: Dynamic variations and effects of meteorology. Science of The Total Environment, 2016, 572: 634-648.

Specific comments

(1). Page 9, line 5. I suggest the authors to add some discussion on the limitations of indirect calculations. For example sea salt calculated from chlorine could be affected by the volatilization of Cl from the sample.

Response: Thank you for the comments. One paragraph was added to discuss the limitations of this indirect calculation (page 9, lines 13-15).

"though care was taken with the interpretation of this pseudo source due to the potential for Cl loss by volatilization from aerosol (or from filters) in the presence of acidic aerosol species, particularly in the fine fraction (Lee et al. 1999; Chen et al 2016)."

References:

Lee, E., C. K. Chan and P. Paatero. Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong. Atmos. Environ., 33(19), 3201-3212, 1999.

Chen W.H., Wang X. M., Jason Blake Cohen, Zhou S.Z., Zhang Z.S., Chang M., and Chan C.Y.. Properties of aerosols and formation mechanisms over southern China during the monsoon season. Atmos. Chem. Phys., 2016, 16, 13271-13289.

(2). Page 9, line 17. I suggest the authors to explain better why they use the remaining mass of $PM_{2.5}$ but not that of PM_{10} in the PMF analysis.

Response: We have changed this part and make explanations to this method (page 9, lines 27-): "Analysis of the data showed that most of the remaining mass (RM) for PM_{10} was in fact $PM_{2.5}$, as would be expected for such aerosol species as OC (including secondary organic aerosol) and nitrate. Therefore, an extra variable was calculated, $RMPM_{2.5}$ (where $RMPM_{2.5} = PM_{2.5} - RCMPM_{2.5}$) to include in the PMF analysis as a placeholder for the unmeasured components, an approach that has been successfully applied in other studies (Belis et al., 2013). The advantage of such an approach is that all of PM mass is accounted for in the PMF model. However, the limitation is that it still does not define exactly what aerosol species that the $RMPM_{2.5}$ variable includes, although some inferences can be made depending on the source association."

(3) Page 9, line 21. I think more information should be given on the database used for the PMF analysis. The use of gaseous compounds together with particulate components in the same analysis should be explained more carefully as the source contributions are finally calculated to the total PM mass concentrations.

Response: Thank you for your comments. We provide more details on the calculation of uncertainties of elements, and the reasons for choosing the number of factors in the section 2.3 and section 3.2.

We have used gaseous compounds together with particulate matter components in the source apportionment analysis. This is not a new method, which has been applied in previous studies (e.g., Zhou et al, 2005; Liu et al, 2006). Liu et al (2006) found that inclusion of gas phase data and temperature-resolved fractional carbon data can enhance the resolving power of source apportionment studies. We explain more about this method in the text, and we interpret the results with care as you recommended.

Page 6, lines 6-9: "Another advantage of PMF is that PM mass concentrations can be included in the model as another variable and the results are directly interpretable as the covariant PM mass contributions associated with each factor (source)."

Page 10, lines 15-19: “Note that the gaseous components (SO_2, NO_2, CO) have been included to aid with source identification and to examine those PM emission sources or secondary aerosol sources they are closely associated (covariant) with. This method has been also adopted by the previous studies, and proved to enhance the resolving power of source apportionment studies (Zhou et al 2005; Liu et al 2006).”

References:

Zhou, L.P.K., Hopke, C.O., Stanier, S.N., Pandis, J.M., Ondov, K., Pancras, J.P. Investigation of the relationship between chemical composition and size distribution of airborne particles by partial least squares and positive matrix factorization. J. Geophys. Res.-Atmos., doi:10.1029/2004JD005050, 2005.

Liu, Wei, Wang, Yuhang, Russell, Armistead, Edgerton, Eric S. Enhanced source identification of southeast aerosols using temperature-resolved carbon fractions and gas phase components. Atmos. Environ, 40: S445-466, doi:10.1016/j.atmosenv.2005.11.079, 2006.

(4) Page 9, line 26. These sources explain 89% and 91% of the $PM_{2.5}$ and PM_{10} mass. . .I don’t understand if the gaseous compounds are included in these sources to calculate the total contribution.

Response: We have added some explanation to this method.

Page 6, lines 6-9: “Another advantage of PMF is that PM mass concentrations can be included in the model as another variable and the results are directly interpretable as the covariant PM mass contributions associated with each factor (source).”

Page 10, lines 15-19: “Note that the gaseous components (SO_2, NO_2, CO) have been included to aid with source identification and to examine those PM emission sources or secondary aerosol sources they are closely associated (covariant) with. This method has been also adopted by the previous studies, and proved to be enhanced the resolving power of source apportionment studies (Zhou et al 2005; Liu et al 2006).”

(5). Page 11, line 5. These percentages are not the same as in Figure 4. Please correct.

Response: Modified in the text.

(6) Page 11, lines 6-9. I suggest the authors to give mass concentration values in the text, as it is useful to follow the discussion. I suggest adding them also to Figure 4.

Response: Thank you for your suggestion. Added in the text and Figure 4.

(7). Page 11, lines 13-15. This sentence is not clear. If CO is associated with gaseous combustion products, it should be also associated with the industrial coal combustion and motor vehicle emissions sources. I suggest the authors to explain this.

Response:

CO, NO_x and SO_2 emissions are certainly associated with the **light-duty motor vehicle** source (i.e., petrol vehicles), which emit very few particles directly. The petrol vehicles as well as coal combustion emitted NO_x and SO_2 would transform to nitrate and sulfate particles through chemical reactions (secondary inorganic aerosol). Therefore, CO is associated with secondary inorganic aerosol and coal combustion.

Diesel-powered vehicles produce very little CO in the first place (Rhys-Tyler, Legassick et al. 2011). It is assumed that diesel vehicle tailpipe emissions are primarily responsible for motor vehicle related $PM_{2.5}$ concentrations, consistent with international research (Kirchstetter, Aguiar et al. 2008, Kim Oanh, Thiansathit et al. 2009, Wang, Tao et al. 2012, Targino, Gibson et al. 2016).

Therefore, CO was primarily associated with the industrial coal combustion and secondary inorganic aerosol sources. Meanwhile, CO is not associated with motor vehicle directly emitted particulate matters (primary aerosol).

We explained more in the text (page 12, lines 13-23):

"CO, NO_x and SO_2 emissions are associated with the light-duty motor vehicles (i.e., petrol vehicles), which emit few particles directly. The light-duty vehicles as well as coal combustion emitted NO_x and SO_2 would transform to nitrate and sulfate particles through chemical reactions. The association of CO with secondary inorganic aerosol is explained by co-emission of CO with the gaseous combustion product precursors (e.g. SO_2, NO_x) of secondary inorganic aerosol and they are therefore present (covariant) in the same air mass. Diesel-powered vehicles produce very little

CO in the first place (Rhys-Tyler et al. 2011). It is assumed that diesel vehicle tailpipe emissions are primarily responsible for motor vehicle related $PM_{2.5}$ concentrations in the Foshan urban airshed, consistent with international research (Kirchstetter et al. 2008, Kim et al. 2009, Wang et al. 2012, Targino et al. 2016). Therefore, CO is not associated with motor vehicle emitted particulate matters (primary aerosol)".

References:

Kim Oanh, N. T., W. Thiansathit, T. C. Bond, R. Subramanian, E. Winijkul and I. Paw-armart. Compositional characterization of $PM_{2.5}$ emitted from in-use diesel vehicles. Atmos. Environ. 44(1): 15-22, doi:10.1016/j.atmosenv.2009.10.005, 2009.

Kirchstetter, T. W., J. Aguiar, S. Tonse, D. Fairley and T. Novakov. Black carbon concentrations and diesel vehicle emission factors derived from coefficient of haze measurements in California: 1967-2003. Atmos. Environ., 42(3): 480-491, doi:10.1016/j.atmosenv.2007.09.063, 2008.

Rhys-Tyler, G. A., W. Legassick and M. C. Bell. The significance of vehicle emissions standards for levels of exhaust pollution from light vehicles in an urban area. Atmos. Environ. 45(19): 3286-3293, doi:10.1016/j.atmosenv.2011.03.035, 2011.

Targino, A. C., M. D. Gibson, P. Krecl, M. V. C. Rodrigues, M. M. dos Santos and M. de Paula Corrêa. Hotspots of black carbon and $PM_{2.5}$ in an urban area and relationships to traffic characteristics. Environ. Pollut. 218: 475-486, https://doi.org/10.1016/j.envpol.2016.07.027, 2016.

Wang, R., Tao S., Wang W., Liu J., Shen H., Shen G., Wang B., Liu X., Li W., Huang Y., Zhang Y., Lu Y., Chen H., Chen Y., Wang C., Zhu D., Wang X., Li B., Liu W. and Ma J. Black carbon emissions in China from 1949 to 2050. Environ. Sci. Technol., 46(14): 7595-7603, doi: 10.1021/es3003684, 2012.

(8). Page 11, lines 24-16. It is not possible that biomass combustion is also related to domestic heating or industry?

Response: Satellite fire map showed that lots of fire spots were distributed around the Pearl River Delta region (suburban and rural areas) from November 1 to 31, 2014 over southern China (in supplementary materials).

From our results we can also detect high concentrations of potassium during the fire burning episodes (Zhou et al, 2016).

And also, we can see the obvious burning of crop straw residues alongside the

highway during the autumn season. Therefore, I think it is most likely that the biomass combustion source is associated with agricultural burn-off outside Foshan and would think that very little biomass is used for domestic heating or industry.

We added some explanation in page 13, lines 5-6: "High concentrations of potassium were also detected during the biomass burning episodes (Zhou et al, 2016). It is most likely that the biomass combustion source is associated with agricultural burn-off around Foshan."

(9). Page 12, lines 4-6. The higher evening peak is also possibly related to a more stable boundary layer. I suggest the authors to explain this.

Response: Boundary layer is also an important factor to influence the air pollutant concentrations. We modified this sentence in page 13, lines 10-12: "The motor vehicles and road dust sources (Fig. 7c) showed a bimodal pattern with peaks in the morning and evening rush hours, which ascribed to the morning and evening commuter traffics and lower boundary layer."

(10). Page 12, lines 7-8. The concentration of the secondary aerosol source seems to be higher at night.

Response: Boundary layer is also an important factor to influence the air pollutant concentrations. We modified this sentence in page 13, lines 14-15: "The secondary inorganic aerosol source (Fig. 7d) demonstrated slightly higher concentrations at night than those at daytime."

(11). Page 13, lines 8-9. It is not possible that biomass combustion is also related to domestic heating or industry?

Response: **As explained in the previous question.** Satellite fire map showed that lots of fire spots were distributed around the Pearl River Delta region (suburban and rural areas) from November 1 to 31, 2014 over southern China (in supplementary materials).

From our results we can also detect high concentrations of potassium during the

fire burning episodes (Zhou et al, 2016).

And also, we can see the obvious burning of crop straw residues alongside the highway during the autumn season. Therefore, I think it is most likely that the biomass combustion source is associated with agricultural burn-off outside Foshan and would think that very little biomass is used for domestic heating or industry.

(12). Page 14, lines 4 and 6. It seems that there is some confusion between secondary inorganic and biomass burning source, because they are almost the same color in the graph. Please check and correct.

Response: Thank you for your suggestion. We have corrected in the text.

(13). Figure 2. To my understanding the Beta Attenuation monitor is not a gravimetric method and does not provide gravimetric mass. Please correct.

Response: Thank you and corrected.

(14). Figure 3. I suggest the authors to add the %species to the profiles.

Response: Added in the Figure 3.

(15). Figure 4. I suggest the authors to add mass concentrations values in the figure.

Response: Added in the Figure 4.

(16). Figure 9. This figure could be in the supplementary section.

Response: We have moved this figure in the supplementary section (Figure SM5).

(17). Figure 12. The colors in the figure are very similar for the biomass burning and secondary inorganic aerosol sources. I think this has produced confusion in the discussion. Please check and correct.

Response: Thank you and corrected.

Technical corrections

(1). I have not corrected language issues as I am not a native English speaker myself. However I list here the sentences where I find something that should be checked.

Response: Thank you very much for you suggestion. The language has been polished by a native English speaking expert.

(2). Page 2, lines 6-9. Please check verb tense.

Response: Checked and amended.

(3). Page 2, line 18. PM mass concentration IS considered as the standard metric for protecting human health.

Response: Checked and amended

(4). Page 2, line 22. PM1-2.5 is normally used instead of $PM_{2.5-1}$

Response: Checked and amended

(5). Page 2, lines 27-28. Please check verb tense.

Response: Checked and amended.

(6). Page 3, line 2. Pease check this sentence: “is increasingly DEPENDED. . .”

Response: Checked and amended.

(7). Page 3, line 28. Check word order: “PMF receptor model. . .”

Response: Checked and amended.

(8). Page 5, line 5. Check sentence: “. . .. . .was only consisted”

Response: Checked and amended.

(9). Page 6, line 8. References are repeated, please correct.

Response: Checked and amended

(10). Page 6, lines 9-13. I don't understand this sentence. Please check.

Response: Checked and amended in page 6, lines 12-15: "Due to the effect that random analytical noise can have on the receptor modeling process, variables with low signal-to-noise ratios were examined by alternate inclusion and exclusion in a modelling run and only those variables that could be explained in association with source emissions were included in the final results (Paatero and Hopke, 2003)."

(11). Page 8, lines 9-10. This sentence seems unclear, please check.

Response: Checked and amended.

(12). Page 11, line 16. Please replace , with .

Response: Checked and amended.

(13). Page 12, line 20. Figure 8 does not show the letters a, b, c, d. Please correct.

Response: Checked and amended.

(14). Page 13, lines 1-9. Figure 8 does not show the letters a, b, c, d. Please correct.

Response: Checked and amended.

(15). Page 13, line 17. "Arsenic was observed of the highest risk". This sentence does not seem correct to me, please check.

Response: Checked and amended to "Arsenic was observed to have the highest risk……"