Authors' Response to Referee #2 Comments

Thank you for the careful review and valuable comments on our manuscript. We address all the referee's comments in the revised manuscript. Here we provide our responses to each comment as follows:

Anonymous Referee #2

Received and published: 15 May 2013

General comments: Recently, awareness of the PM pollution has arisen in East Asia region due to the several reasons such as the rapid industrialization in East Asian countries, aridification of inland area, and massive forest fires in Siberia. As mentioned by the authors, long term monitoring will be required for the better understanding of the atmospheric behavior of PM ans its potential sources. The authors concluded that soil dust, biogenic emissions, and biomass burning are more important sources for Sapporo TSP than anthropogenic sources and sea-salt emissions. Unfortunately, I could not share the evidences supporting this conclusion from current manuscript. I believe that soil and biogenic factors are important contributors of PM generation. From the results of factor analysis, however, I could not confirm whether the contributions of soil and/or biogenic sources certainly exceed the anthropogenic contributions. More quantitative discussion will be strongly required. The authors tried to identify PM emission sources from the viewpoint of similarity in temporal variation of respective species. Qualitatively, this approach seems to be reasonable for primarily generated species. However, the temporal variation of secondarily generated species is generally dominated by complicated chemical reactions in the atmosphere in addition to the amount of precursors. Thus, it seems too simplistic to identify sulfate as biogenic origin from the similarity in temporal variations of SO42- concentration and BVOC emission. Moreover, the dataset is too small to discuss the correlation of the seasonal trends of respective species (Fig. 4). The factor loading matrix (Table 2) clearly indicates that several different sources are mixed together in respective factors. For example, factor 1 consists of fine mode species (i.e., SO42- and NO3-) and coarse mode species (i.e., Ca, Al, Ti, and Fe). Even though the factor loadings of coarse mode species are higher than those of fine mode species, it is not always true that the contributions of coarse mode species are more important than fine mode species. This is because the atmospheric concentrations of SO42- and NO3- are much higher than those of coarse mode species. Thus, the anthropogenic contributions may not be negligible. The poor factorization is probably due to the lack of particle size separation and coarse sampling time resolution. From this factorization, it is difficult to estimate respective source contribution quantitatively. Consequently, I conclude that the current manuscript is unsuitable for publication.

Response: *(i) We agree with the referee's opinion that our approach was qualitative and anthropogenic contributions may not be negligible for Sapporo inorganic aerosols. In order to provide quantitative discussion on possible sources and avoid the association of secondary ions together with the primary trace metals with the same factor, we conducted factor analysis-multiple linear regression (FA-MLR) for data sets of ionic species and trace metals separately. The uncertainties (≤33%, except for Na+ and Ca2+) in model estimation and correlations (≥0.70, except for V and Zn) between modeled and measured concentrations of both ionic species and trace metals as well as their comparisons with the literature (Guo et al., 2004; Rout et al., 2013) suggest that the performance of the FA-MLR model used in this study is reasonable. Based on the FA-MLR results, we found that natural (soil dust and sea-salt), anthropogenic and biomass burning emissions and secondary production are the major sources of Sapporo inorganic aerosols. We also estimated the biogenic fraction of* SO_4^{2-} *that accounted up to 22% by assuming the* $MSA^-/nss\text{-}SO_4^{2-}$ *molar ratio is a function of temperature, as reported by Bates et al. (1992) and using measured* MSA^-*. We include all these results and discussion in the revised MS. Therefore, we also reconsider our conclusion in the revised MS.*

(ii) Although the time resolution is not high, the backward air mass trajectories conducted for every 48 hours during each sample period suggest that they were originated from the same source region.

In fact, we found a clear seasonal pattern in the percent modern carbon (pMC) and the concentrations of biomarkers as well as their contributions to organic carbon (OC) and water-soluble organic carbon (WSOC) in the Sapporo aerosols (Pavuluri et al., 2013). Therefore, we believe that the implication of seasonality in the source (biogenic) strength is reasonable, although the number of the samples in each season is small.

Specific comments:

P6598, L20-21: More information is needed. Although the authors cited several papers supporting this implication in later section, but in my opinion, Zn, Cu, and Ni are not always treated as tracers of biogenic sources. They are also well known as anthropogenic origin (e.g., steel industry, waste incineration, tire wear, and brake dust) in many other papers.

Response: *We agree with the referee's comment that Ni, Cu and Zn can be originated mainly from anthropogenic sources mentioned in the above comment. However, they could also present in fungal species and pollen (Lepsova and Mejstrik, 1988; Prikhod'ko, 1985). Our results suggest that terrestrial biological sources possibly contribute to these metals in part, although anthropogenic emissions are the major sources. We discuss these points in the revised MS.*

P6601, L17-19: Do you mean acidic PM has been observed in Sapporo? How was the pH of extracts?

Response: *We do not mean that the Sapporo aerosols are acidic. The* SO_4^{2-} *might be in different forms and/or associated with metal ions. Unfortunately we did not measure the pH of extracts.*

P6606, L7-8: Pearson's correlation coefficient is applicable to the normally-distributed dataset. I wonder if mannitole is really normal distribution. Good correlation might be obtained from few high concentration data of nannitole.

Response: *We agree with the referee's opinion. The data set of either mannitol or metals is not normally distributed but the covariance and the correlation of the species show potential relationship between them. In addition, the information available in the literature on the relation between fungi and trace metals (Lepsova and Mejstrik, 1988; Prikhod'ko, 1985) supports our assumption. We provide additional discussion on possible biological origin of Cu, Ni and Zn in the revised MS.*

P6606, L28-P660, L2: This statement is very interesting. Trace elements such as V, Cr, Mn, Fe, Ni, Cu, Zn, and As have been well known as anthropogenic tracers. If these elements are originating from biological sources, can you specify their potential origins in detail? Do you have any ideas on chemical forms of these elements containing in their potential biological sources?

Response: *Yes, anthropogenic emissions are the major sources of the above trace metals however we consider the biological sources possibly contribute to Ni, Cu and Zn and even As for some extent: Fungi uptake different trace elements from the substrate and contain high amounts of Cu and Zn as well as Ni in elemental form (Lepsova and Mejstrik, 1988). In addition, Cu and Zn are abundant in pollen (Prikhod'ko, 1985). We note these points in the revised MS.*

References

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