

## Responses to Referee #2

### **General comments:**

This manuscript presents measurement results of aerosol particles from a mountain site in east China as part of the MTX2006 campaign. A large number (~130) of individual organic compounds was quantified in the ambient particulate matter which was collected with rather high time resolution (compared to typical filter-based sampling). The detailed chemical speciation included numerous molecular source tracers, which allowed for a qualitative assessment of different types of source contributions. Specifically, the strong influence from biomass burning was demonstrated with the chemical aerosol characteristics along with fire counts and air mass history analysis. Diagnostic tracer ratios confirmed that the biomass burning activities occurred in form of agricultural residue (i.e., wheat straw) combustion, which resulted in a substantial increase in the aerosol loadings and was characterized by different diurnal patterns. Stable isotopic composition of total carbon in the aerosol samples revealed additional insights into the sources and transformations of aerosol particles during atmospheric transport, highlighting the importance of secondary organic aerosol formation.

As measurements of individual organic compounds and stable isotopic carbon ratios at high-elevation sites are rare, the findings from this study are very valuable in the context of regional-scale pollution sources, transport and effects. The results presented in this manuscript are obtained from experiments that had a sound scientific approach and were carried out with sufficient QA/QC measures. The interpretation of the data is reasonable and the discussion of the implications is logical, except for the attempt to quantify the relative source contributions, as discussed in more detail under the specific comments. In conclusion, I highly recommend publication of this manuscript in ACP upon consideration of the comments and suggestions given below.

**Response:** The authors are grateful to the reviewer's comments and suggestions on this manuscript.

### **Specific comments:**

Page 9088, lines 10-11: The measurement period during this study was rather short, while this limitation is, to some extent, compensated by the relatively large number of samples (due to the high sampling frequency of 3 hours), yet caution should be used with the interpretation of the resulting data due to the limited number of sampling days.

Page 9088, lines 10-11: The statement that "the concentrations of WSOC are well correlated with those of OC, suggesting a similar source" is obvious, as WSOC is, by definition, a portion of OC, and thus the implication is self-explanatory. On the other hand, it would be more meaningful to state that WSOC constituted an important fraction of OC based on both the good correlation and high percentage.

**Response:** The statement that "Clearly, the concentrations of WSOC are well correlated with those of OC, suggesting a similar source. Although only minor differences in the WSOC/OC ratios were observed between early June (0.49-0.77) and late June (0.37-0.76), the average WSOC/OC ratio was higher in early June (0.65) than in late June (0.55) (Table 1)." has been modified to: "Clearly, the concentrations of WSOC are well correlated with those of OC. Although only minor differences in the WSOC/OC ratios were observed between early June (0.49-0.77) and late June (0.37-0.76), the average WSOC/OC ratio was higher in early June (0.65) than in late June (0.55) (Table 1). These results suggest that WSOC constituted an important fraction of OC." (see Page 7, Line 211-215)

Page 9088, lines 14-15: It seems as if the authors mistakenly wrote "black carbon" instead of "WSOC", or else this statement is out of place here. Coincidentally, this raises the question regarding the BC or EC content in the TSP samples in early and late June – while the ambient EC concentrations are listed in Table 1, it would be helpful for the readers to have a short statement regarding the EC patterns in this paragraph. In addition, the authors should discuss the OC/EC ratios here, which can be a useful indicator of biomass burning (and/or biogenic) source influence.

**Response:** According to the reviewer's comments, the statement that "It is well documented that biomass burning emits a large amount of black carbon. In the present study, the enhancement of WSOC in OC in early June may be caused by intensified biomass burning, which is also a significant source of water-soluble organics." has been revised as follows:

"In addition, the enhancement of WSOC in OC in early June may be caused by intensified biomass burning, which should be a significant source of water-soluble organics. It is well documented that biomass burning emits a large amount of black carbon. In the present study, EC concentrations in early June ( $0.95\text{--}5.9\text{ }\mu\text{g m}^{-3}$ ,  $3.3\text{ }\mu\text{g m}^{-3}$ ) were double those ( $\text{nd}\text{--}2.4\text{ }\mu\text{g m}^{-3}$ ,  $1.4\text{ }\mu\text{g m}^{-3}$ ) in late June. However, similar EC/OC ratios were found between early (0.09-0.26) and late June (0-0.29). Such low values indicate that SOA is an important fraction of organic aerosols over Mt. Tai in summer." (see Page 8, Line 216-222)

Page 9090, lines 1-6: Indeed, the L/M ratio can be a useful indicator of specific types of biomass that were burned. Therefore, the authors should compare their findings with those from other studies, such as those reported in Fabbri et al. (2009) or Sheesley et al. (2003). In fact, the L/M ratio calculated from the data by Sheesley et al. for rice straw smoke aerosol is very similar to that reported in this study. Moreover, Engling et al., (2009) discuss the use of these diagnostic ratios with a specific focus on emissions from agricultural residue combustion. The high ratios observed in this study in early June (with enhanced biomass burning activity) agree very well with those for other types of straw (especially rice straw), confirming the utility of these characteristic ratios as indicators of straw burning.

**Response:** As suggested by the reviewer, the following sentence has been added in the revised manuscript: "The higher *L/M* ratios observed in early June than in late June agree

well with those for other types of straw burning smokes (especially rice straw) (Sheesley et al., 2003; Engling et al., 2009), confirming the usefulness of these characteristic ratios as indicators of straw burning.” (see Page 9, Line 265-268)

Page 9091, lines 5-12: The discussion on the ambient temperature dependence of phthalates is not logical to me. First, how is the presence of these species in particulate matter explained if they are released due to evaporation (i.e., going into the gas phase) from polymers? Second, if the concentrations show a noontime peak, wouldn't that indicate local emission sources rather than regional-scale transport? Presumably, there are no (or insignificant) local sources at this mountain site, and therefore the origin is expected to be from upwind source regions, which are not expected to show a clear diurnal pattern.

**Response:** As suggested by the reviewer, the following sentences have been added in the revised manuscript.

“Although such a temperature-dependence is in accordance with higher phthalate concentrations reported in urban aerosols in summer, which was associated with volatilization from substrates (Wang et al., 2006), attentions should be paid that there are other factors causing to such a trend. For example, evaporation of phthalates from substrates, concentrations in both gas and particle phases in upwind regions and their transport from the ground surface to the mountaintop, gas/particle partitioning (Teil et al., 2006), photodegradation, as well as wet/dry scavenging (Staples et al., 1997) may influence the atmospheric level of phthalates over Mt. Tai.” (see Page 10, Line 299-306)

Page 9092, lines 13-14: Even higher contributions were found in the study by Zhang et al., (2010) at a remote site in South China, which can be mentioned here, especially as their findings are from the same country and a remote site (even though at lower altitude and latitude) as well.

**Response:** The following sentence has been added in the revised manuscript. “Zhang et al. (2010) reported even higher contributions of these sugar alcohols to OC (4.6-26%, mean 12%) in PM10 collected in a tropical rainforest in South China.” (see Page 11, Line 333-335)

Page 9092, lines 16-19: Another very recent study also showed a good correlation between biomass burning and fungal spore tracers (Yang et al., 2012), and can therefore be cited here.

**Response:** The reference has been cited as “Recently, Yang et al. (2012) also observed elevated fungal tracers in atmospheric aerosols due to biomass burning in Chengdu City, China.” (see Page 11, Line 340-341)

Page 9098, lines 10-17: It is not clear how the authors derived these numbers – please specify! Merely adding up the individual tracer compound concentrations and calculating the relative

abundance does not indicate source contributions in a quantitative manner, in my opinion. If this is what the authors did with the percentages listed here, then there is little meaning to those numbers. On the other hand, estimating source contributions based on emission factors and ambient tracer concentrations is a valid method that has been used in a number of studies, although there are, without doubt, uncertainties associated with this approach, as indicated by the authors. Thus, the contributions from biomass burning, fungal spores and SOA presented here are warranted, whereas the other percentages should be omitted. One more comment/question (related to page 9098, line 22): while there have been at least a few source profiles published for agricultural residue burning, why do the authors use factors from a study in the Amazon basin (which may have been strongly influenced by biomass burning activities, yet it doesn't provide true source emission factors)?

**Response:** The numbers represent the relative abundances of organic species detected in the Mt. Tai aerosols, which are roughly grouped according to their potential sources. Such information has been mentioned in Figure 10 caption. Because of the shortcoming of the source apportionment approach used in this study, the authors added the following sentences in the revised manuscript. "It should be noted that this source apportionment approach is useful to roughly estimate the relative contribution from different emission sources to organic aerosols. Many organic species in atmospheric aerosols may have multiple sources, and thus a potential overlapping cannot be excluded by using such an approach (Simoneit et al., 2004)." (see Page 17, Line 504-507)

Although there have been some source profiles published for agricultural residue burning such as rice straw burning, to the best of our knowledge, there is still a lack of emission factor that is associated with the open burning of wheat straw. As a result, the authors try to use a biomass-burning factor from the study in the Amazon basin because both the Amazonian aerosols and Mt. Tai aerosols are heavily influenced by open biomass-burning activities, although such estimation may also suffer from large uncertainties.

#### Technical corrections:

1. The definite article "the" is not used properly throughout the manuscript, i.e., it is missing in many cases, such as on p. 9081, line 5 (before "Mount"); p. 9081, line 6 (before "North"); p. 9082, lines 22 (before "Asian"); p. 9083, line 1 (before "North"); etc.
2. Please, check the correct use of singular and plural forms throughout the manuscript and make corrections, such as for "plays" on p. 9082, line 9, or "compositions" on p. 9083, line 23.
3. Page 9082, line 14: Change "comprise" to "are comprised".
4. Page 9083, line 1: Delete ", which".

**Response:** These items have been corrected accordingly in the revised manuscript.

5. Page 9083, lines 11-13: It would be helpful to see references providing a general overview of the Mt. Tai Experiment 2006 (MTX2006) and some related measurements during

MTX2006, such as those by Yamaji et al. (2010).

**Response:** The reference of Yamaji et al. (2010) has been cited in the section of Introduction as “Yamaji et al. (2012) have evaluated the influence of open crop residual burning on ozone, CO, black carbon (BC) and organic carbon (OC) concentrations in NCP using a regional chemical transport model during the same campaign.” (see Page 3, Line 87-89)

6. Page 9089, line 6: Change "in" to "on".

**Response:** Corrected.

7. Page 9089, lines 19-20: While levoglucosan is released during the thermal decomposition of both cellulose and hemicelluloses, these isomeric anhydrosugars (mannosan and galactosan) are actually only emitted from hemicelluloses (i.e., from their parent sugars, mannose and galactose, which are not present in cellulose).

**Response:** Thanks. In fact, the “anhydrosugars” in the sentence of “These anhydrosugars are produced by the pyrolysis of cellulose/hemicelluloses during biomass burning” include levoglucosan and its two isomers. So we think this statement is all right.

8. Page 9092, line 6: Change "innumeros" to "numerous".

**Response:** Corrected.

9. Page 9093, lines 9-11: Additional references which are relevant to this statement are the recent papers by Despres et al. (2012) and Froehlich-Nowoisky et al., (2012).

**Response:** These two references (Després et al., 2012; Fröhlich-Nowoisky et al., 2012) have been added in the revised manuscript. (see Page 12, Line 360-361)

10. Page 9094, line 17: Change the sentence to "... an indicator of primary pollutants in motor exhausts ...".

11. Page 9096, lines 17 and 20: Add "to" before "each".

**Response:** These items have been corrected accordingly.

12. Page 9096, lines 21-22: The meaning/point of this sentence is not clear.

**Response:** The sentence of “Their temporal patterns are different from those of biomass burning tracers, which showed peaks in early morning (Figure 5)” has been changed to “These temporal patterns are different from those of biomass burning tracers, which showed peaks in early morning (Figure 5)”. (see Page 15, Line 453-455)

13. Page 9097, line 17: Change "occurred" to "occurring".

**Response:** Corrected.

14. Page 9097, lines 22-25: This sentence sounds awkward and should therefore be reworded.

**Response:** The sentence of “In addition, the correlation between levoglucosan and WSOC that was discussed in Section 3.3.1, WSOC is generally considered as components of secondary origin, suggests that biomass burning can significantly contribute to the SOA formation during the sampling period.” has been reworded as “In addition, WSOC is generally considered as components of secondary origin. The positive correlation between levoglucosan and WSOC that was discussed in Section 3.3.1 suggests that biomass burning can significantly contribute to the SOA formation during the sampling period.” (see Page 16, Line 482-485)

15. Page 9100, line 13: Change "of" to "the".

**Response:** Corrected.

16. Fig. 6: Is the number of significant figures used for the correlation coefficients really warranted by the measurement certainty? Probably not, and thus they should be reduced, e.g. similar to Fig. 13.

**Response:** The number of significant figures has been reduced from 4 to 2. (see Page 34, Figure 6).

Here is a list of references used in this review, which should be added in the manuscript:

- Despres et al., Tellus B, 64, 2012
- Engling et al., Aerosol Science & Technology, 43, 662-672, 2009
- Froehlich-Nowoisky et al., Biogeosciences, 9, 1125-1136, 2012
- Yamaji et al., Atmospheric Chemistry & Physics, 10, 7353-7368, 2010
- Yang et al., Science of the Total Environment, 431, 68-77, 2012

**Response:** These references have been cited in the revised manuscript (see Page 21-26, References).

## References

Després, V. R., Huffman, J. A., Burrows, S. M., Hoose, C., Safatov, A. S., Buryak, G., Fröhlich-Nowoisky, J., Elbert, W., Andreae, M. O., Pöschl, U. and Jaenicke, R.: Primary biological aerosol particles in the atmosphere: a review, Tellus B, 64,

- doi:10.3402/tellusb.v3464i3400.15598, 2012.
- Engling, G., Lee, J. J., Tsai, Y.-W., Lung, S.-C. C., Chou, C. C.-K. and Chan, C.-Y.: Size-resolved anhydrosugar composition in smoke aerosol from controlled field burning of rice straw, *Aerosol Sci. Technol.*, 43, 662-672, 2009.
- Fröhlich-Nowoisky, J., Burrows, S. M., Xie, Z., Engling, G., Solomon, P. A., Fraser, M. P., Mayol-Bracero, O. L., Artaxo, P., Begerow, D., Conrad, R., Andreae, M. O., Després, V. R. and Pöschl, U.: Biogeography in the air: fungal diversity over land and oceans, *Biogeosciences*, 9, 1125-1136, 2012.
- Sheesley, R. J., Schauer, J. J., Chowdhury, Z., Cass, G. R. and Simoneit, B. R. T.: Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia, *J. Geophys. Res.*, [Atmos], 108, 4285, doi:10.1029/2002JD002981, 2003.
- Simoneit, B. R. T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H. J., Turpin, B. J. and Komazaki, Y.: Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign, *J. Geophys. Res.*, [Atmos], 109, D19S10, doi:10.1029/2004JD004598, 2004.
- Staples, C. A., Peterson, D. R., Parkerton, T. F. and Adams, W. J.: The environmental fate of phthalate esters: A literature review, *Chemosphere*, 35, 667-749, 1997.
- Teil, M. J., Blanchard, M. and Chevreuil, M.: Atmospheric fate of phthalate esters in an urban area (Paris-France), *Sci. Tot. Environ.*, 354, 212-223, 2006.
- Wang, G. H., Kawamura, K., Lee, S., Ho, K. F. and Cao, J. J.: Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities, *Environ. Sci. Technol.*, 40, 4619-4625, 2006.
- Yamaji, K., Li, J., Uno, I., Kanaya, Y., Irie, H., Takigawa, M., Komazaki, Y., Pochanart, P., Liu, Y., Tanimoto, H., Ohara, T., Yan, X., Wang, Z. F. and Akimoto, H.: Impact of open crop residual burning on air quality over Central Eastern China during the Mount Tai Experiment 2006 (MTX2006), *Atmos. Chem. Phys.*, 10, 7353-7368, 2012.
- Yang, Y., Chan, C.-Y., Tao, J., Lin, M., Engling, G., Zhang, Z., Zhang, T. and Su, L.: Observation of elevated fungal tracers due to biomass burning in the Sichuan Basin at Chengdu City, China, *Sci. Tot. Environ.*, 431, 68-77, 2012.
- Zhang, T., Engling, G., Chan, C.-Y., Zhang, Y.-N., Zhang, Z.-S., Lin, M., Sang, X.-F., Li, Y. D. and Li, Y.-S.: Contribution of fungal spores to particulate matter in a tropical rainforest, *Environ. Res. Lett.*, 5, doi:10.1088/1748-9326/1085/1082/024010, 2010.