Response to reviewers

ACPD-14-C808-2014

Reviewer 1

This is a very good paper presenting the influence of biomass burning on regional air quality in Southeast Asia. The authors address a need for identifying suitable organic molecular tracers for peat fires in Indonesia, considered as a major source of smoke haze in the region, as well as quantifying its contribution to the atmospheric PM loading. All sections of this manuscript are scientifically sound and interesting to read. I only have a few minor issues to address.

Response: We thank the reviewer for the constructive comments on the manuscript. We have provided our point-by-point responses to the comments and suggestions of the reviewer below and will incorporate the changes into the manuscript accordingly.

Comment #1: Page2780 Lines8-9: The authors might consider using 'ends' instead of 'starts'. Of course for back trajectories the sampling point is the releasing point for calculations, but still the trajectory ends at that point.

Response: We have made appropriate changes in the manuscript text as per the reviewer's suggestion.

Comment #2: Page2782 Line24: It might be useful for the reader if the authors were to explain what 'shorter' denotes. This could be discussed more in detail by referring Hennigan's studies on levoglucosan degradation in the atmosphere.

Response: We have added the following discussion to the manuscript in accordance with the reviewer's suggestion.

"Henningan et al. (2010) reported that nearly 30-75% of levoglucosan would react within one day at typical atmospheric OH levels while Hoffmann et al. (2010) estimated the half-life of levoglucosan to be 12.7 – 83.2 h (0.5 – 3.5 days) at 90% relative humidity. From the backward trajectory analysis, it was observed that the air masses from the source regions of biomass burning reached Singapore within 2 – 3 days, which falls in the range of the half-life of levoglucosan according to Hoffmann et al. (2010). We would like to emphasize here that the ambient concentrations of anhydrosugars were up to two orders of magnitude higher during the haze period relative to the clear days, indicating a massive impact of biomass smoke emissions."

Comment #3: Page2782Line22: 'Hennigan' instead of 'Hannigan'..

Response: We have rectified the typographical error.

Comment #4: Page2785 Line6: ’Beside’ instead of ’Other than’. ’Other than’ only when the copper discussion comes earlier than that on Al, Fe and Ti.?

Response: “Other than” was a typographical error and was therefore deleted. The sentence now reads as: “Cu, Al, Fe, and Ti were the most abundant trace metals found in haze samples.”

Comment #5: Page2780Line7: remove ’very’. Page2782Line21: remove ’strong’..

Response: We have removed the words as suggested by the reviewer.

ACPD-14-C1515-2014

Reviewer 2

The paper is written by scientifically sound and concise way and brings new important data about the influence of biomass burning emissions in Indonesia influencing Singapore air quality. They provide broad range of chemical analysis data of ambient aerosol to support and prove the aerosol origin illustrating its biomass combustion origin during polluted days.

Response: We thank the reviewer for the constructive comments on the manuscript. We have provided our point-by-point responses to the comments and suggestions of the reviewer below and will incorporate the changes into the manuscript accordingly.

Comment #1: However, there is one part that might be improved. The analysis of metals provided several astonishing results that deserve more attention. Copper concentrations increased 30 times to the levels of matrix elements while common biomass tracer potassium was increased 4 times only. Although the explanation given in the paper is possible, it does not say where such high levels of copper may come from. (Are there any copper mines or any other (e.g. agriculture) possible copper sources?) There might be also copper sources emitting copper to the same air masses as those coming with biomass burning products. Zinc concentration is often elevated in biomass combustion emissions, but in this case they are even lower than in clean case. See et al. 2007 e.g. found enrichment factors for PM2.5 equal to 10ˆ7 for Zn, but only 10ˆ2-10ˆ3 for copper in peat fire episode in Indonesia. Coarse part of the aerosol may explain the difference, but this should be reflected in the text. The same results were used for CMB as peat burning source profile, how the Cu could be explained by this factor?.

Response: There is a copper mine (Beutong mine, one of the largest copper mines in Indonesia) in the Sumatra region where peat fires occurred during the haze episode. In addition, agricultural activities are also very prevalent in the region. These are the major possible sources of copper. As for zinc, previous measurements in Mexico City and in Beijing showed that Zn particles were mainly derived from industrial activities and waste incineration (Moffet et al., 2008; Li and Shao, 2009). There is also some Zn emission from biomass burning (Gaudichet et al., 1995). See et al. (2007) carried out the field study in the vicinity of small-scale peat fires. However, the current study was conducted at an urban location in Singapore at a different time period, so there might be differences in the abundance and distribution of metals because of differences in the type and age of biomass burning plumes.

Moffet, R. C., de Foy, B., Molina, L. T., Molina, M. J., and Prather, K. A.: Measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry, Atmos. Chem. Phys., 8, 4499–4516, doi:10.5194/acp-8-4499-2008, 2008.

Li, W. and Shao, L.: Transmission electron microscopy study of aerosol particles from the brown hazes in northern China, J. Geophys. Res., 114, D09302, doi:10.1029/2008JD011285, 2009.

Gaudichet, A., Echalar, F., Charenet, B., Quisefit, J. P., and Malingre, G.: Trace elements in tropical African savanna biomass burning aerosols, J. Atmos. Chem., 22, 19–39, doi:10.1007/BF00708179, 1995.

During CMB runs some of the chemical species which do not lead to convergence of the source estimates are typically excluded from the model runs. Therefore we did not use Cu as one of the source species in the model for the samples with extreme Cu concentrations. We added the following text in the revised manuscript.

"There is a copper mine (Beutong mine, one of the largest copper mine in Indonesia) in the Sumatra region where peat fires occurred during the haze episode which could be one of the additional sources of copper apart from peat emissions. However, whether or not the soil in this local area contains high concentration of copper needs to be further investigated."

Comment #2: p. 2775, line14: reference Muraleedharan et. al., 2000 is missing in reference list

Response: The following reference is now added in the manuscript.

Muraleedharan, T.R., Radojevic, M., Waugh, A., and Caruana, A.: Emissions from the combustion of peat: An experimental study, Atmos. Environ., 34, 2733 – 2738, 2000.

Comment #3: p. 2776, line18: reference Sundarambal et. al., 2010 is missing in reference list

Response: The following reference is now added in the manuscript.

Sundarambal, P., Balasubramanian. R., Tkalich, P., He, J.: Impact of biomass burning on ocean water quality in Southeast Asia through atmospheric deposition: Field observations, Atmos. Chem. Phy., 10, 11323–11336, 2010.

Comment #4: p. 2776, line 21: SI units are preferred nowadays

Response: We now presented the value in SI units.

Comment #5: p. 2776, line 24 -25. It is not clear from the text when the filters were folded – before or after the analysis as I would expect.

Response: We rewrote the sentence as follows.

"The TSP filters were folded in half lengthwise after sampling, so that only surfaces with collected particulate matter were in contact, when placed in the filter holder (glassine envelope)."

Comment #6: p. 2777, line20: reference Birch and Carry, 1996 is missing in reference list

Response: This reference was added in the revised manuscript: Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, Aerosol Sci. Tech., 25, 221–241, 1996.

Comment #7: p. 2778, line4: references Engling et al., 2006 and Iinuma et al. 2009 are missing in reference list

Response: The following references are now added in the manuscript.

"Engling, G., Carrico, C. M., Kreidenweis, S. M., Collett, J. L., Day, D. E., Malm, W. C., Lincoln, E., Hao, W. M., Iinuma, Y., Hermann, H.: Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection, 40, S299 – S311, 2006.

Iinuma, Y., Engling, G., Puxbaum, H., Hermann, H.: A highly resolved anion-exchange chromatographic method for determination of saccharidic tracers for biomass combustion and primary bio-particles in atmospheric aerosol, 43, 1367 – 1371, 2009."

Comment #8: p. 2779, line 19, a short explanation to representativeness of US EPA data for Singapore emission profile should be given

Response: We provide the following discussion in the manuscript as per reviewer's suggestions.

"Source profiles of inorganic ions and trace elements used in the model were obtained from SPECIATE 4.3 (SPECIATE, 2011). The source profiles for petroleum refinery (Cooper et al., 1987) and diesel emissions (Vega et al., 2004; Chow et al., 2002; Vega et al., 2000) obtained from the USEPA database are applicable to Singapore, since the process of refining crude oil, the engineering practices adopted in oil refineries, and the type of diesel used are similar to those in the studies included in the database. In Singapore most of the powerplants continue to use oil as a fuel of choice or as a fuel in tandem with natural gas. Therefore, the source profiles of oil fired powerplants (Henry and Knapp, 1980; Howes et al., 1983) included in the USEPA database were used in the model. Source profiles for Indonesian peat fires were obtained from our previous study (See et al., 2007) while for ship emissions it was obtained from Moldanova et al. (2009) and Popovicheva et al. (2009). The chemical species used in the CMB model were potassium, aluminum, cobalt, chromium, iron, manganese, lead, nickel, cadmium, titanium, vanadium, arsenic, chloride, nitrate, sulfate, ammonium, nitrite, calcium, and sodium."

Comment #9: p. 2781, lines 23-24: OM/OC conversion factor should be mentioned instead of OC/OM factor if its value is 2.

Response: We replaced "OC/OM" with "OM/OC" in the manuscript.

Comment #10: p. 2781, line25: reference Turpin and Lim, 2001 is missing in reference list.

Response: The following references is now added in the manuscript:

"Turpin, B. J. and Lim, H.-J.: Species contributions to $PM_{2.5}$ mass concentrations: Revisiting common assumptions for estimating organic mass, Aerosol Sci. Tech., 35, 602–610, 2001."

Comment #11: p. 2781, line25: using value 2 as OM/OC conversion factor apparently leads to analysed mass concentration higher than gravimetric mass concentration (see Fig. 3), therefore, based on these data, probably lower OM/OC conversion factor would be more appropriate for this type and age of biomass burning plume.

Response: We thank the reviewer for sharing the concern regarding the OM/OC conversion. There was a typographical error in the TSP mass concentrations used for the haze period in Table 1. It should be 94.1 $\mu g/m^3$ instead of 84.1 $\mu g/m^3$. As per the reviewer's suggestion, we think that a conversion factor of 1.4 would make sense numerically for OM/OC, although considering the type and age of biomass burning plume the factor should be higher. We have revised our results and the text in the manuscript accordingly.

"In the case of aerosols measured downwind of biomass burning activities, OM/OC factors of more than 1.4 have been suggested in literature for organic aerosols in urban areas (e.g., White and Roberts, 1977; Turpin and Lim, 2001). When applying a factor of 1.4 to the OC levels detected during the haze period, the content of organics in TSP was found to be extremely high (50% on average), while it was only around 25% during clear days."

Comment #12: p. 2782, line 3: a reference should be given after the world Literature.

Response: We have added the reference as per reviewer's suggestion in the revised manuscript.

Comment #13: p. 2782, line 22: reference Hanningan et al. should be Hennigan et al.

Response: We have rectified the typographical error in the revised manuscript.

Comment #14: p. 2783, line 20: reference Zhang et al. 2010 should include" a "or "b".

Response: We have rectified the typographical error in the revised manuscript.

Comment #15: p. 2784, Line 2: diagnostic ratios tend to be dependent on an aerosol age, it should be mentioned.

Response: We have mentioned the following statement in the revised manuscript:

"While PAHs are common combustion products of all carbonaceous materials, including fossil fuels and biomass, diagnostic ratios (DRs) of specific PAH species, although dependent on

aerosol age, can be used to constrain the predominant influence of emissions from certain types of combustion.“

Comment #16: p. 2785, line 6: The sentence “Other than . . . “ should be corrected.

Response: We have rectified the sentence as follows:

“Cu, Al, Fe, and Ti were the most abundant trace metals found in haze samples“

Comment #17: p. 2788, line 11: the reference “Chandra. . .” is not mentioned in the text; p. 2788, line 18: the reference “Critical. . .” is not mentioned in the text; p. 2788, line 24: the reference “Duncan. . .” is not mentioned in the text

Response: We have removed these references from the list in the revised manuscript

Reviewer 3
General comments

This manuscript provided detailed measurement of TSP and its source characterization in Singapore during both haze and non-haze periods. The results are interesting in indentifying a major PM source of biomass burning from peat fires in Indonesia over polluted days, which will be significant for the local authorities to implement air quality strategies in the region. I would suggest for acceptance and publication after completing the following corrections.

Response: We thank the reviewer for the constructive comments on the manuscript. We have provided our point-by-point responses to the comments and suggestions of the reviewer below and will incorporate the changes into the manuscript accordingly.

Comment #1: In Section 2.3, it is useful to state the original references for each source profile and the fitting species used in the CMB model.

Response: We have now included the original references for each source profile and the fitting species used in the CMB model in the revised manuscript (see below). The chemical species used in the CMB model were potassium, aluminum, cobalt, chromium, iron, manganese, lead, zinc, nickel, cadmium, titanium, vanadium, arsenic, chloride, nitrate, sulfate, ammonium, nitrite, calcium, and sodium.

POWER PLANT

Howes, J.E., Cooper, J.A., Houck, J.E., 1983. Sampling and Analysis to Determine Source Signatures in the Philadelphia Area. Draft Final Report to U. S. Environmental Protection Agency, ESRL, Research Triangle Park, NC. NEA, Inc. 1983.

Henry, W.M., Knapp, K.T., 1980. Compound Forms of Fossil Fuel Fly Ash Emissions. Environmental Science and Technology, 14, 450-456.

PETROLEUM REFINERY

Cooper, J.A., Redline, D.C., Sherman, J.R., Valdovinos, L.M., Pollard, W.L., Scavone, L.C., and Badgett-West, C., 1987. PM10 Source composition Library for the South Coast Air Basin. Volume I and II. Prepared for the South Coast Air Quality Management District, El Monte, CA. July 15, 1987.

DIESEL EXHAUST

Vega, E., Reyes, E., Ruiz, H., Garcia, J., Sanchez, G., Martinez-Villa, G., Gonzalez, U., Chow, J.C., and Watson, J.G.: Analysis of PM2.5 and PM10 in the atmosphere of Mexico City during 2000-2002. Journal of the Air & Waste Management Association, 54, 786 – 798, 2004.

Chow, J.C.; Watson, J.G.; Edgerton, S.A.; Vega, E. (2002). Chemical composition of PM10 and PM2.5 in Mexico City during winter 1997. Science of the Total Environment 287 (3), 177-201.

Vega, E.; Mugica, V.; Carmona, R.; Valencia, E., 2000. Hydrocarbon source apportionment in Mexico City using the chemical mass balance receptor model. Atmospheric Environment 34 (24), 4121-4129.

Comment #2: In Section 3.4 on source apportionment with CMB, it would be better to add a table showing the actual figures of the modeled results for the individual source contribution estimates, as the relative contribution in Figure 4 may mislead the results sometimes. As biomass smoke markers, levoglucosan in this study showed the highest elevation during haze days among all species measured, but in comparison potassium did not show much increase, why?

Response: We have included the table below in the revised manuscript in addition to Figure 4.

($\mu g.m^{-3}$)	Haze	Clear days
Ship Emissions	4.46 ± 1.77	6.48 ± 1.4
Petroleum Refinery	0.42 ± 0.17	0.59 ± 0.3
Power Plant	-	0.55 ± 0.27
Diesel Exhaust	15.64 ± 6.21	14.88 ± 3.22
Peat Fires	63.58 ± 25.25	-

Levoglucosan is a source-specific tracer for biomass burning, as it is generated during thermal breakdown of cellulose and hemicellulose molecules. Potassium, on the other hand, can be derived from various emission sources, including biomass burning, but also from cooking, vegetation, sea salt and soil, especially in the coarse particle fraction. Since in this study we collected TSP, there is a likely substantial contribution of potassium from other sources than biomass burning, i.e., sea salt and soil, for which we did not apply a correction. Thus, the increase in potassium concentrations during the haze episode is not expected to be as large as that for levoglucosan.

The following text was added in the manuscript

“In comparison to levoglucosan, inorganic biomass tracer, potassium did not show much increase during the haze period. Levoglucosan is a source-specific tracer for biomass burning, as it is generated during thermal breakdown of cellulose and hemicellulose molecules. Potassium, on the other hand, can be derived from various emission sources, including biomass burning, but also from cooking, vegetation, sea salt and soil, especially in the coarse particle fraction. Since in this study we collected TSP, there is a likely substantial contribution of potassium from other sources than biomass burning, i.e., sea salt and soil, for which we did not apply a correction. Thus, the increase in potassium concentrations during the haze episode is not expected to be as large as that for levoglucosan.“

Comment #3: The total Cu concentration during haze period is about 30 times the value on clear days, but water soluble Cu only showed a factor of just over 4 for days of haze/clear. The authors argue that this may be due to that Cu oxides formed under high temperature combustion are less soluble. On the contrary, metal Al showed a factor around 30 for days of haze/clear for water soluble fraction, whereas similar values were observed for total Al. Explain.

Response: Water solubility of a metal depends on the chemical form in which it is present. The higher fraction of water solubility of Al during the haze might be due to the presence of more soluble Al in haze aerosols. However, additional investigation is necessary to examine the chemical fractionation of particulate-bound metals using a sequential extraction procedure. This investigation will account for (1) soluble and exchangeable metals; (2) carbonates, oxides, and reducible metals; (3) metals bound to organic matter, oxidizable and sulfidic metals; and (4) residual metals, while the current study quantified only the soluble and exchangeable metals. The outcome of the additional investigation will be published elsewhere. The following text was added in the manuscript

“Some of the metals such as Al have shown a significantly higher proportion of the water soluble fraction (~30 times) during the haze compared to clear days. In general, water solubility of a metal depends on the chemical form in which it is present. The higher fraction of water solubility of Al during the haze might be due to the presence of more soluble Al in haze aerosols. However, additional investigation is necessary to examine the chemical fractionation of particulate-bound metals using a sequential extraction procedure. This investigation will account for (1) soluble and exchangeable metals; (2) carbonates, oxides, and reducible metals; (3) metals bound to organic matter, oxidizable and sulfidic metals; and (4) residual metals, while the current study quantified only the soluble and exchangeable metals. The outcome of the investigation will be published elsewhere.“

Comment #4: The author needs to check the references in both the text and the reference list as there are quite a few number of references in the text are not shown in the reference list, and vice versa.

Response: We have updated the reference list in the revised manuscript.

Comment #5: P. 2775, line11: Check the year in the reference ‘’Heil and Goldammer, 2002/2001‘’??

Response: We have corrected the year of the reference in the revised manuscript.

Comment #6: P. 2779, line 2: change ‘’quipped” to ‘’equipped”

Response: We have corrected it in the revised manuscript.

Comment #7: P. 2780, line 20-21: Rewrite ‘’some of the air masses arriving at Singapore arrived from” as ‘’some of the air masses arrived at Singapore from”

Response: We have rewritten the sentence as per the reviewer’s suggestion.

Comment #8: p. P. 2782, line 22: Change ‘’Hannigan et al., 2010” to ‘’Hennigan et al., 2010”

Response: We have changed “Hannigan et al.,” to “Hennigan et al.,” in the revised manuscript.

Comment #9: P. 2783, line 20: Specify in the reference ‘’Zhang et al., 2010” as a or b

Response: We have rectified it in the revised manuscript.

Comment #10: P. 2785, line 16-17: Rewrite “The low solubility of this metal could be due to the chemical form in which it exists. For example, as metal oxides are produced during high-temperature combustion, a metal oxide is in general less soluble as compared to metal nitrates/sulfates.” as “The low solubility of this metal could be due to the chemical form in which it exists, such as metal oxides produced during high-temperature combustion is in general less soluble as compared to metal nitrates/sulfates.”

Response: We have rewritten the sentence as per the reviewer’s suggestion.