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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Fine particulate matter associated with monsoonal effect and the responses of biomass fire hotspots in the tropical environment" *by* M. F. Khan et al.

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Interactive comment on "Fine particulate matter associated with monsoonal effect and the responses of biomass fire hotspots in the tropical environment" by M. F. Khan et al. Anonymous Referee #2 Received and published: 13 September 2015

The manuscript of Khan et al. focuses on the health implications of fine particulate matter (PM2.5) and its main constituents in the western part of Malaysia. The study period covers two monsoonal regimes, one coming from the south-west and one from the north-east and levels of PM, heavy metals and main ions are determined for both

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regimes. Overall it has been found that 48% of the samples were 4 times or more than guideline values, with the north-east monsoon regime exhibiting somewhat higher values. Based on the enrichment factor of metals it occurred that the majority of heavy metals were attributed to anthropogenic sources, while arsenic was identified as a potentially significant health concern as its concentrations were nearly equal to the WHO and US EPA guideline values, posing an exposure risk for inhabitants in the specific location. Using a mass closure model a mineral component was found to comprise 35% of the PM2.5 concentration, followed by 11% by secondary inorganic aerosol, while 45% was unidentified, possibly a large part of it being the organic aerosol fraction. Using positive matrix factorization (PMF) analysis as a source apportionment tool, motor vehicle and biomass burning emissions were the dominant sources, followed by marine and sulfate aerosol, coal burning, nitrate aerosol and mineral dust. Finally, based on the health risk assessment and the PMF-identified sources, the non- carcinogenic risk posed by exposure of PM was at a safer level than the respective one in the South and East Asian region while the cancer risk posed by the exposure to toxic metals was 3 to 4 in 1 million people in the specific location. Motor vehicle emissions and trans-boundary pollution were the major identified reasons for change in the chemical composition of PM in tropical Peninsular Malaysia. The manuscript is well written and interesting, with an added value of the presented results being from an area of the globe that is not very well documented. It is a pity that analysis of the organic fraction is not available, as it is expected that a large portion of the unidentified mass from the mass closure model will be the organic component. There are several details missing and more thorough discussion should be made in specific sections. Other than that the paper can be recommended for publication after addressing the issues listed below.

1) One of the features of the manuscript that the authors draw our attention to is the comparison between the PM2.5 from the PMF and from the high volume samplers (HVS) which was found to have a slope of 0.91 and a very good correlation. It appears somewhat strange that even though 45% of the PM2.5 mass remains unidentified, the comparison of the mass concentrations from the PMF and the HVS results in a slope

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of 0.91. Please comment. Also, do the authors believe that the remaining 45% of the unidentified mass, with the organics possibly being a large part of this mass, will be part of the already identified components? Please clarify in the text that the PMF analysis results are based on the obtained filter analyses results.

Authors' response We understand the reviewer's concern and thus add the following explanation in the text as follows (Page 22232, lines 22-27; Page 22233; lines 1-2):

"Using US EPA PMF 5.0, the ïňĄve identiïňĄed sources of PM2.5 were (i) mineral and road dust, (ii) motor vehicle emissions and biomass burning, (iii) nitrate aerosol, (iv) coal burning and v) marine and sulfate aerosol. Each of the source proïňĄles is shown in Fig. 6a which demonstrates the concentration and percentage of the variables to each factor. The integrated contribution of five factors was then regressed (through origin) over the measured PM2.5 (HVS). The results showed strong and significant correlation (slope = 0.91, r2 = 0.88, $p < 0.01$) (Fig. 6b). As linear correlation between the predicted and measured mass represents the goodness-of-fit for linear regression, our value strongly suggest that the five identified sources was readily interpreted with an error of less than 10%. The reported source apportionment result is based on the analyzed chemical components of filter samples ($\sim$ 55%). As described in the mass closure, a large portion of PM2.5 mass ($\sim$ 45%) was left unidentified which is believed to be the organics as reported by Yin et al. (2010), Husain et al. (2007) and Pachauri et al. (2013)"

Comment to "slope of 0.91 regression result of PMF-HVS" We acknowledge the reviewer's concern regarding the PMF-MLR results. However, we would like to inform that we did follow all the crucial and necessary steps in running the PMF tools as per mentioned in section 2.7. The mass contribution was calculated following procedure as per mentioned in Ke et al. (2008) where first, regressing the factor scores obtained from the PMF using multi linear regression against the PM2.5 measured mass concentration of each sample; and secondly, the regression coefficients were used to convert the contributions of each factor score into a physical mass.

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2) Authors mention that the K+ ion has been widely used in the literature as an excellent tracer representing wood burning, and authors examined the correlation between K+ concentrations and MODIS fire counts. To my opinion, and correlation coefficient of 0.36 does not suggest that K+ can be used as a biomass tracer. I would propose to differentiate between nss-K+ and total K+ and check if the correlation is stronger. ss-K+ can be calculated using Na as a reference and the K/Na ratio in bulk seawater.

Authors' response We agree with the reviewer's suggestions. We have revised Fig. 5, included Fig. 5b and 5c and annotated in the text as below (Page 22235; lines 19-26):

Further, a comparison of nss-K+ with the respective total K+ is shown in Fig. 5b. The correlation of nss-K+ as a function of total K+ showed a strong correlation coefficient (r2=0.95) which suggests that K+ can be used as a biomass tracer. K+ may also be emitted from local fire sources. Additionally, the molar equivalent of K+ and Na+, as shown in Fig 5c, demonstrated significant correlation (r2 = 0.70) with a slope value of 0.34 which is much higher as compared to 0.0225-0.230 and 0.0218, reported by Wilson (1975) and Hara et al. (2012), respectively. The higher molar ratio of K+ and Na+ indicates that at current location, Na+ depletion was high and that K+ might be released from other dominant sources i.e. soil dust, sea salt, vegetation or meat cooking (Zhang et al., 2010).

3) Based on the presented biomass fire hotspots, it is clear that from December 2013 to March 2014, the hotspots are a lot more compared to the respective ones from June to September 2013. Maybe authors should consider adding a comment of why this is the case. Is December-March the dry season? Is this period of intense biomass fire hotspots present every year or was the presented year uncharacteristic?

Authors' response We have revised our text as the reviewer suggested (Page 22229; lines 1-3): The back trajectory plots showed that there were high numbers of biomass fire hotspots during both seasons but from different regions (Fig. 3). June to September 2013, this is dry season each year in Malaysia and Sumatra of Indonesia. During

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this dry season, biomass fire hotspots are densely located due to the burning of agricultural waste and forest fire in Sumatra region. Several other researchers also reported the high number of biomass fire related hotspots to these regions (Khan et al., 2015a; Khan et al., 2015b; Sahani et al., 2014). On the other hand, December 2013 to March 2014 is usually wet season in Malaysia. However, the backward trajectories were transported from the Mainland China and neighboring regions. In the Mainland China and neighboring regions, this is dry season, which causes lots of fire as reported by Zhang et al. (2015) and Ho et al. (2014) and influence the polluted air mass transporting to present location. This scenario of biomass fire hotspots is commonly noticed in these two seasons. In some years Malaysia and Singapore experienced very intensified haze episode in this particular season e.g. 1997, 2005, 2013 and 2015.

4) In the enrichment factor section (2.5) in the whole paragraph EFs of two, five or even 10 are cited from the bibliography as thresholds for anthropogenic sources. Nevertheless authors choose a cut-off of EF=1. Please comment.

Authors' response We understand and accept the reviewer's concern. Therefore, we have revised the cut-off point with explanation pertaining to that as follows (Page 22223; lines 11-24): The threshold of EF > 10 to differentiate between sources from the Earth's crust and from anthropogenic sources and element might originate from natural or Earth's crust when the EF value is less than 10 (Chester et al., 2000; Cheung et al., 2012; Khan et al., 2010; Mohd Tahir et al., 2013; Torfs and Van Grieken, 1997) proposed the EF cut-off of ten to identify crustal and natural origin of heavy metals. An EF > 10 indicates that the sources of heavy metals (Zn, Cr, Rb, Be, V, Fe, Ca, Co, Sr, Pb, As and Bi) were not natural or from the Earth's crust. Thus from Fig. 5a, it can be suggested that in this study area a good number of the metals in PM2.5 originated from anthropogenic sources. Thus, we consider EF = 10 as the cut-off point. Therefore, a good number of metals in PM2.5 in this study can be assumed to originate from anthropogenic sources. No seasonal differences were observed in the EF of the heavy metals.

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Technical corrections:âĂĺ P22217, L15-18: Not clear, especially the part ". . .with respect to inhalation follows the order. . .". Also in PMF 5.0 delete the ">".âĂĺ

Authors' response We agree with the suggestion. We have revised the sentences as below (Page 22217; lines 14-17): The non-carcinogenic risk level for four selected metals (Pb, As, Cd and Ni) in PM2.5 and in the identified major sources by PMF5.0 follows the order of PM2.5 > coal burning > motor vehicle emissions/biomass burning > mineral/road dust.

P22219, L17: . . ..a period from July to SeptemberâĂĺ

Authors' response We have revised the sentence as below (Page 22219; lines 17-18): Sampling was carried out on a 24 h basis for a period from July to September 2013 and January to February 2014 for a total of 27 samples.

P22220, L27: . . .ionic composition was determined

Authors' response We have corrected the error (Page 22220, line 27): the water-soluble ionic composition (Na+, NH4+, K+, Ca2+, Mg2+, Cl-, NO3- and SO42-) was determined

P22221, L18: Replace "fresh" for the calibration curves. Maybe use "updated" instead.

Authors' response We have revised the sentence as below (Page 22221, line 18): During the trace element analysis by ICP-MS, two modes of analysis were applied with updated calibration curves each time.

P22223, L14: . . .metals in PM2.5 originated from. . . (delete "had")âĂĺ

Authors' response We have updated the sentence as below (Page 22223, line 14): Thus from Fig. 5a, it can be suggested that in this study area a good number of the metals in PM2.5 originated from anthropogenic sources.

P22227, L18: . . .classified by the International Agency. . .âĂĺ

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Authors' response We have corrected the sentence as below (Page 22227, line 18): Further, we examined the non-carcinogenic risk by the hazard quotient (HQ) and carcinogenic risk (CR) of selected heavy metals as classified by the International Agency for Research on Cancer (IARC).

P22230, L28: Boreddy et al. (2014) also notice a chlorine depletion due to atmospheric processing in the western north Pacific.

Authors' response We have added the new reference suggested by the reviewer as below (Page 22230, line 28): However, the average molar ratio of Cl- to Na+ did not reflect the seawater ratio. "Cl loss" may be the cause of the drop in Cl- to Na+ ratio. Boreddy et al. (2014) also notice a chlorine depletion due to atmospheric processing in the western north Pacific.

P22233, L1: Based on Figure 6a the slope is 0.91 and R2=0.88 and not the other way round.

Authors' response We have corrected the typo errors as below (Page 22233, Line 1): The correlation of this pair of PM2.5 (PMF) and PM2.5 (HVS) showed a strong and significant correlation (slope = 0.91, r2 = 0.88, $p < 0.01$) (Fig. 6b).

P22235, L8: Zhang et al. (2015) demonstrate that during the dry season there is an important biomass burning activity in the Pearl River Delta (China), which can result in trans-border transport and a regional scale character of biomass burning. Therefore under the north-east monsoonal regime it is possible that outflow from that area can maybe influence the specific area.

Authors' response We are thankful to the reviewer suggesting the reference as below (Page 22235, line 8): In this period of time, a high density of fire locations were found on the Indochina and China mainland. Zhang et al. (2015) demonstrate that during the dry season there is an important biomass burning activity in the Pearl River Delta (China), which can result in trans-border transport and a regional scale character of

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biomass burning. Therefore under the north-east monsoonal regime it is possible that outflow from that area might influence the specific area.

P22235, L22: An r=0.36 does not suggest that K+ can be used as a biomass tracer.

Authors' response We have revised the text as the reviewer suggested. Please find the revised text as shown below (Page 22235, line 22): Further, a comparison of nss-K+ with the respective total K+ is shown in Fig. 5b. The correlation of nss-K+ as a function of total K+ showed a strong correlation coefficient (r2=0.95) which suggests that K+ can be used as a biomass tracer. K+ may also be emitted from local fire sources. Additionally, the molar equivalent of K+ and Na+, as shown in Fig 5c, demonstrated significant correlation (r2 = 0.70) with a slope value of 0.34 which is much higher as compared to 0.0225-0.230 and 0.0218, reported by Wilson (1975) and Hara et al. (2012), respectively. The higher molar ratio of K+ and Na+ indicates that at current location, Na+ depletion was high and that K+ might be released from other dominant sources i.e. soil dust, sea salt, vegetation or meat cooking (Zhang et al., 2010).

P22238, L17: . . ..follows the following order: As > Ni . . ..Also "follows" and "following" is a repetition, maybe replace one of the two

Authors' response We have corrected the sentences as shown below (Page 22238, line 17): The estimated lifetime cancer risk of the metals follows the order: As > Ni > Pb > Cd for mineral/road dust, coal burning and overall of PM2.5 concentration and As > Pb > Ni > Cd for motor vehicle/biomass burning.

L18: . . .PM2.5 concentration and As > Pb. . . (delete ";")

Authors' response We have deleted the semi-colon as below (Page 22238, line 18): PM2.5 concentration and As > Pb > Ni > Cd for motor vehicle/biomass burning

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Please also note the supplement to this comment:

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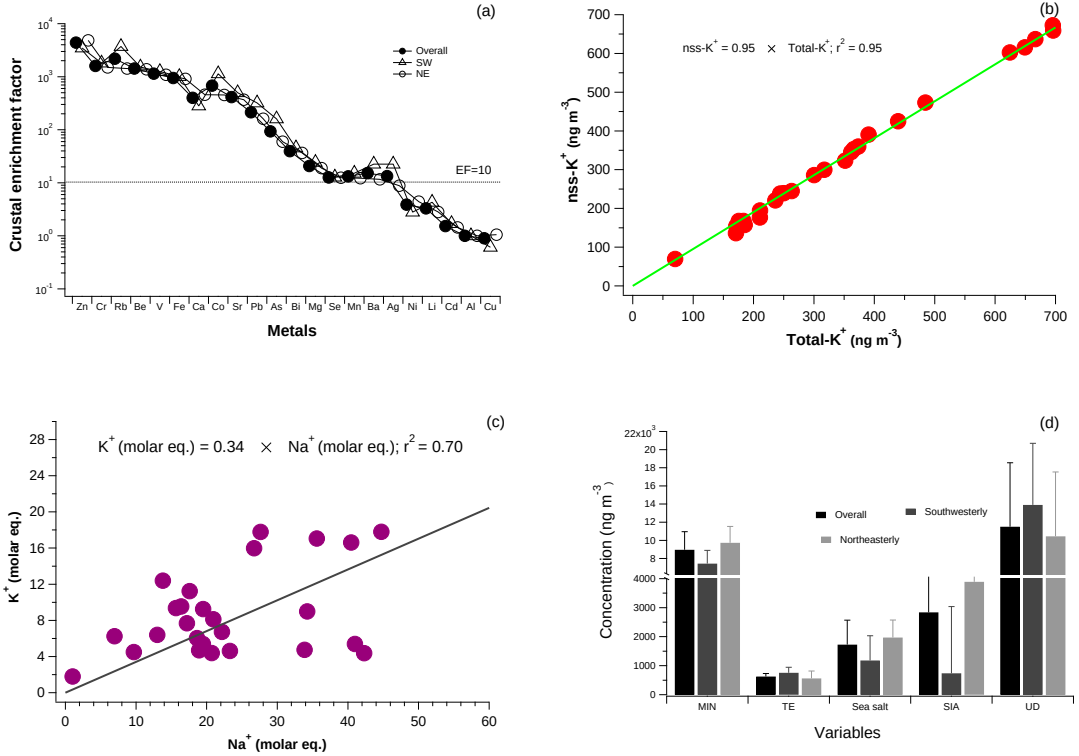

Figure 5 (a) Enrichment factor (EF) of heavy metals in $PM_{2.5}$, (b) correlation plot of nss-K^+ and total-K^+ (r^2 = 0.95), (c) correlation plot of K^+ and Na^+ and (d) reconstructed mass concentration of $PM_{2.5}$ by mass closure model

Fig. 1. Figure 5 (a) Enrichment factor (EF) of heavy metals in PM2.5, (b) correlation plot of nss-K+ and total-K+ (r2 = 0.95), (c) correlation plot of K+ and Na+ and (d) reconstructed mass concentration of PM

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