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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Comparison of methods for evaluation of wood smoke and estimation of UK ambient concentrations" *by* R. M. Harrison et al.

R. M. Harrison et al.

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The revised manuscript has been attached as: acp-2012-supplement.pdf

RESPONSE TO REVIEWERS: Atmos. Chem. Phys. Discuss., 12, 6805, 2012 Comparison of methods for evaluation of wood smoke and estimation of UK ambient concentrations, by R.M. Harrison et al.

We are grateful to the reviewers for raising many interesting issues which have strengthened the paper.

Anonymous Referee #1 The paper is interesting and brings light to the field. Some

issues should be addressed and/or clarified:

SPECIFIC COMMENTS: - page 6808, line 16: a factor of approximately two in what? Levoglucosan concentrations? RESPONSE: The text has been enhanced to say ".....A divergence of a factor of approximately 2 in levoglucosan measurements between Dr Fuller and ourselves .....".

- Page 6810, 2.1 sampling procedures: include here the sampling schedule for each of the sites. It is not said clearly anywhere in the paper, just some dates are included in figure legends. Probably a table with a summary of the sampling schedule could be provided in Supp. Material RESPONSE: Dates of the sampling campaigns are now included in the main text alongside the name of the sampling site.

- Page 6810, lines 8-11: It is deduced that the Andersen high volume sampler was used for the sites other than North Kensington, please clarify. RESPONSE: This has now been clarified with additional text.

- Page 6810, line 18: "for some of the sampling periods". Say exactly when and where RESPONSE: Dates have now been included in the text.

- Page 6811, line 16: clarify how you calculate Casoil and Canss, the reader only knows that you got Ca measured, which is not in the formula. RESPONSE: The following explanatory words have been added below the equation: "..... and [K/Ca]soil is the measured elemental ratio in soil and Canss is the measured Ca in air corrected for sea salt Ca, calculated from the Na concentration."

- Page 6811, line 16: clarify what the "ws" subscript makes reference to. It is deduced it is wood smoke, but it should be said. Moreover, during the rest of the paper you use ws and wb, and the difference is not clarified until page 6817. It should be explained before and keep coherent nomenclature throughout the paper. The fact that authors say 'wood smoke' but write wb and the other way around is confusing if they are really trying to mean different things (or the same thing calculated by different methods, as

ACPD

12, C4771–C4796, 2012

deduced by text in page 6817) RESPONSE: The explanatory footnote from page 6817 is repeated here beneath the equation.

- Page 6813, lines 8-10: what are the results of this intercomparison? RESPONSE: The following sentence has been added: “Both methods were acceptable with a slight under-estimation (up to 10%) from the former and over-estimation (up to 20%) from the latter.”

- Page 6813, lines 19-20: from the current text, it seems that CMtotal=PMtraffic + PMwb, and it should be CMtotal=CMtraffic + CMwb. Clarify. RESPONSE: The reviewer is correct and the text has been modified accordingly.

- Page 6814 and 6815: add numbers to the equations RESPONSE: The equations have now been numbered as have those before and after this point.

- Page 6814 and 6815: keep nomenclature coherent: babs(950nm)traffic vs babs(950)traf. RESPONSE: The nomenclature has now been modified to be consistent.

- Page 6815, line 15: during the course of the work, which work? This one? Then say the present work RESPONSE: This has now been amended to read: “this work”.

- Page 6815, line 17: it is the first time BC appears in the text. It needs to be introduced before (probably page 6813, line 14). How was this BC measured? It is very important to define. RESPONSE: BC has been amended to read “black carbon”.

- Page 6816, lines 9-11: re-write the sentence, the calculation was done for wood smoke and for traffic. RESPONSE: This is now re-written to read “calculation of wood smoke and traffic particle concentrations .....”.

- Page 6817, line 2: how was this traffic PM estimated? RESPONSE: The traffic PM was estimated from the aethalometer data as described in the previous section. This is now stated.

ACPD

12, C4771–C4796, 2012

- Page 6817, line 3: how was this BC measured? RESPONSE: BC was directly measured by the aethalometer by absorption at 880 nm. This is now explained.

- Page 6817, line 5: which gradient do you mean? where do we have the OC:EC in the equation from line 4? We have PM/BC RESPONSE: The assumption is made that the PMtraffic comprises BC + organic matter.

- Page 6817, line 7: where is this OM:OC ratio of 1.5 coming from? RESPONSE: If OC/EC is taken as 0.35 and OM/OC equals 1.5 and it is assumed that BC equals OC, simple algebra reveals that PMtraffic equals 1.52 BC which is very close to the relationship given in the equation.

- Page 6817, lines 14-15: re-write. They are scatter plots and linear regressions. RESPONSE: The words “regression plots” have been changed to “linear regression calculations”.

- Page 6817, lines 14-17: were these regressions orthogonal distance regressions? If not, they should, and the information should be specified. The scatter plots could be shown in Supp. Material. RESPONSE: The regression calculations used the Reduced Major Axis method which is almost equivalent to the orthogonal regression method.

- Page 6817, lines 16 and 17: define MR and NK, despite one can deduce easily what they are. RESPONSE: The abbreviations are now explained in the note under the equations.

- Page 6818, line 8: the correlation was much weaker?? The r2 was 0.27, and the r2 for MR was 0.32, which is not so different. RESPONSE: The word “much” has been removed.

- Page 6818, line 9: the lev/K showed a strong seasonality. Try to distinguish winter and summer in figure 2 so that this seasonality could (or should) also be seen there somehow. RESPONSE: A new figure has been produced which distinguishes the seasons for all of the sites.

ACPD

12, C4771–C4796, 2012

- Page 6818, line 9: data (as plotted in fig. 4) is not shown for the rest of the sites. It needs to be said (or the plots shown) RESPONSE: It is already stated in the text that the strong seasonality was not seen at the other sites and there seems to be little benefit in adding new graphs. Relevant data appear in Table 1.

- Page 6818, lines 20-21: should the correction be re-considered and adjusted to the reality? If too many negative values are obtained probably the correction is not good. RESPONSE: It is not clear what the reviewer is suggesting here. It is inevitable that at low concentrations of potassium from wood smoke and a variable K/Ca ratio according to the source of the soil, there may be some values of KWS which go negative. Without being able to know the source of the soil and to measure its composition, there is no rational way of correcting this problem. We have just been very honest about it.

- Page 6819, lines 2-3: why do you take the slopes as levoglucosan/K ratios instead of taking the mean or median from table 1? Comment on this, or justify why you disregard table 1 at this point RESPONSE: Gradients derived from the figures take account of all of the data and eliminate interfering sources which would appear as an intercept. Consequently, they give the best representation of the ratio from the common source (i.e. wood burning).

- Page 6822, lines 20-22: one would also say that at Budbrooke they are not correlated, given the r2=0.2. Why don't you report the data here? (you could write r2<0.1, if this is the case). Scatter plots could be provided in Supp. Material RESPONSE: We would disagree with the reviewer. R2 = 0.2 is a very weak correlation. There seems little to be gained from showing scatter plots of poorly correlated data.

- Page 6822, lines 23-24: consistent with the ratio measure at Budbrooke?? The r2 is very low. Is the ratio meaningful?? RESPONSE: We have been perfectly clear about the weakness of the correlation in our data. We leave it to the reader to draw their own conclusions. We do not state whether the ratio is meaningful or not.

- Page 6824, lines 16-20: why Marylebone is not included? RESPONSE: Marylebone

ACPD

12, C4771–C4796, 2012

Road has not been included because the dataset is relatively small, reflective of only one season, and the concentrations during that season were very close to those in North Kensington.

- Page 6825, line 9: two sets of earlier data? You say in the methods section that data from this study was used by Yin et al. (2010). Hence, they are they same data, not earlier data. Clarify. RESPONSE: They are in fact earlier data and we have now added the year to make this clear (2007/2008).

- Page 6825, lines 16-17: What is the lev/OC in the profile used for CMB? It would be helpful to include this lev/OC ratio in the profile for CMB, and compare to the lev/OC ratio used here RESPONSE: CMB uses far more than the levo/OC ratio to calculate the wood smoke contribution. We do not feel that adding this would be helpful.

- Page 6825, lines 24-27: It could be due to several things, not necessarily an artefact of the selected days. Modern carbon may come from biogenic sources, more abundant in summer, which then compensates the lower biomass burning in summer RESPONSE: Our comment refers not to modern carbon but to contemporary elemental carbon which is primarily from biomass combustion and not from other biogenic sources.

- Page 6826, lines 4-5: EC content in what? PM? or CM? RESPONSE: It is the EC content of CM and this has now been clarified in the text.

- Page 6826, lines 10-12: possible reasons for differences? Different methods? RESPONSE: The different methods were intercalibrated (as explained earlier) and did not diverge sufficiently to account for this difference.

- Page 6826, lines 20-22: before you say that info about fire places in UK is not available, but you say there was an increase in the use of wood for heating and you assume the new devices are more efficient and emit less organics (including lev) and more K. Why do you say now that there are no fireplaces in modern houses? RESPONSE: The new devices which use wood for heating are much larger than domestic wood stoves

ACPD

12, C4771–C4796, 2012

and are used for heating larger buildings such as schools. The text in Section 4.3 refers to “larger, more efficient installations”.

- Page 6826, lines 10-11: it is the first time HULIS are mentioned. Shouldn’t it be discussed before (in the discussion section)? RESPONSE: We agree with the reviewer and have added the following sentence to the end of Section 4.2: “Such an interference could be due to UV absorbing organic compounds, including species known has humic-like substances (HULIS) and would affect the multi-wavelength aethalometer data analysis, as well as the simpler Delta-C method.”.

- Page 6826, lines 13-19: this should be discussed in the discussion section? RESPONSE: The new text concerning HULIS in the discussion section addresses this point.

- Page 6826, lines 13-15: the r2 in the present study is very low, so not sure if the slope is meaningful. Conclusions need to be softened. RESPONSE: The slope remains a good guide to the typical relationship between the magnitudes of the variables and we feel that the conclusion is warranted.

GENERAL/TABLES/FIGURES COMMENTS: - A review of lev/OC and lev/PM ratios and lev/K ratios with more recent additional data could be done (for instance to add in Page 6824, line 8) RESPONSE: Some new data has been added at the point suggested.

- Table 1: add number of samples RESPONSE: The table has been revised to include the number of samples.

- Table 1: in Budbrooke, summer only includes April. Sampling periods and number of samples need to be included here or elsewhere, otherwise the data is meaningless RESPONSE: We agree with the reviewer and inclusion of the number of samples makes this reservation clear.

- Figure 1: add number of samples for each month? RESPONSE: This information has

ACPD

12, C4771–C4796, 2012

been added to the experimental section: “Samples were collected daily on around 8 days of each month.”.

- Figure 1 legend: levoglucosan concentrations measured RESPONSE: Amended as suggested.

- Figure 2: use coherent nomenclature for the sites RESPONSE: We feel that the main point is to identify the sites and this has been done quite clearly.

- Figure 2: distinguish winter and summer for all sites RESPONSE: This has been done in a revised figure.

- Figure 2: slope 0.18 for MR, very different from the mean and median in Table 1. Comment on this somewhere in the text. RESPONSE: There is quite a large intercept in Figure 2 from Marylebone Road. A comment about this has been added to Section 4.1: “Gradients were preferred to simple ratios of means as they are less subject to the effects of unaccounted sources which appear as intercepts in the regression.

- Figures 3 and 6: including the sites and weekday/weekend info on the plots themselves (instead of the legend) would help RESPONSE: This could not easily be accommodated.

EDITING COMMENTS: - page 6807, line 12: Chow et al., 2007 - page 6809, line 2 : an urban - Page 6817, line 2: North - Page 6817, line 22 : than for potassium - Page 6818, line 21 : North - Page 6819, line 3: remove respectively - Page 6819, line 4: North Kensington, respectively, and. . . - Page 6820, line 2: three sites? Aren’t they 4? - Page 6825, line 24: fraction of modern carbon RESPONSE: All have been accepted.

Anonymous Referee #2 The paper is an interesting contribution to the field. Wood burning has been shown at many places to be important. The comparison of different methods is important as well.

I recommend publication after taking the following comments (mostly minor but some major) into account:

ACPD

12, C4771–C4796, 2012

- page 6808, lines 9-16: Are the two studies using the same levoglucosan/PM2.5 ratios? RESPONSE: This section refers to a single study sampling two separate sites. The wood smoke contributions were estimated from a CMB model and are independent of levoglucosan/PM2.5 ratios.

- Page 6810, line 13: QMA instead of QM-A RESPONSE: This has been amended.

- Page 6810, line 16: instead of fine particle fractions: be specific about the diameter RESPONSE: This has been amended to read: “PM2.5-10 and PM2.5 particle fractions”.

- Page 6811, line 13: please list the [K/Ca]soil values at the different locations RESPONSE: We do not feel that such information is helpful to the reader and have therefore not included it. In no way does it influence the discussion of the paper.

- Page 6811, lines 22-23: Are losses for the internal standard the same as for levoglucosan RESPONSE: The internal standard used has a similar structure to levoglucosan and it is anticipated that their losses will be similar.

- Page 6812, line 8: change derivatied RESPONSE: Corrected.

- Page 6812, line 11: Is the recovery the same for 1-phenyl dodecane as for levoglucosan RESPONSE: Since the use of the 1-phenyl dodecane was to compensate for injection volume variations and variations in the GC/MS detector response, its recovery is immaterial.

- Page 6813, line 3: trifluoroacetamide RESPONSE: Corrected.

- Page 6813, lines 8-10: How good was the comparison? What is the uncertainty, precision? RESPONSE: The question of the comparability of the methods was dealt with in the response to Reviewer 1 and this information has now been given in the text. The precision for the measurement of levoglucosan is better than 10%, and for potassium better than 3.5% relative standard deviation.

ACPD

12, C4771–C4796, 2012

- Page 6815, line 12: Where is the CM(PM2.5) coming from? How was it calculated? RESPONSE: CM (PM2.5) was calculated from EC + 1.8 OC.

- Page 6815, line 12: This formula is only valid for a location where other carbonaceous sources (OM and BC) than traffic and wood burning are negligible. I assume that secondary organic aerosol is not negligible at these locations here. The formula cannot be used here this way. An option is to show only babs instead of mass. Otherwise one needs to discuss how C1 and C2 were obtained here properly. RESPONSE: This point is discussed in detail in the response to the comments from Grisa Mocnik. The text has also been modified substantially to reflect the fact that we did account for a third component.

- Figure 2: Were orthogonal regressions used? As both x and y have errors, this should be done. RESPONSE: Regressions were calculated using the Reduced Major Axis method which also takes account of the fact that both x and y variables have errors and gives rather similar results to orthogonal regression.

- Page 6816, lines 11-14: The choice of alpha(traffic) is probably crucial here. One should discuss if and at which values of alpha the dips disappear. RESPONSE: Some sensitivity analysis to the values of alphas has now been conducted and is described in detail in the response to the comments of Grisa Mocnik. New text has been added accordingly.

- Page 6817, line 3: How mass determined? What light absorption efficiency was used? RESPONSE: The mass of traffic particles was estimated from equation (9).

- Page 6817, line 4: How was PM2.5 traffic determined? RESPONSE: It was calculated as for page 6817, line 3 above.

- Page 6817, line 6: Please compare also to real measurements (e.g. Chirico et al.,: Aerosol and trace gas vehicle emission factors measured in a tunnel using an aerosol mass spectrometer and other on-line instrumentation, Atmos. Environ., 45, 2182-2192,

ACPD

12, C4771–C4796, 2012

2011). - Page 6817, lines 16,17: Did you use orthogonal regressions? It should be used. RESPONSE: Reference is now made to the Chirico et al. study. The following sentence has been added: “An organic aerosol: BC ratio measured at low concentrations in a road tunnel (Chirico et al., 2011) is also consistent with the Pio et al. (2011) estimate of OC:EC in traffic emissions.”. All of the regressions were determined by the Reduced Major Axis method referred to above.

- Page 6817, lines 21-26: Is the uncertainty and/or precision of the levoglucosan measurements higher than for potassium? RESPONSE: The precision of the levoglucosan measurements is lower than that for potassium but at 10% RSD is unlikely to explain the weaker relationship.

- Page 6826, line 5: How are the 14% calculated? RESPONSE: The calculation simply uses the fact that EC/EC = 0.3 and OM/OC = 1.8. Consequently, EC/OM = 0.16 and EC/OM + EC = 0.14. The term “below 14%” was used to allow for the non-carbonaceous content.

- Page 6826, lines 12-14: The missing seasonality could be due to compensation by other effects like more secondary aerosol in summer. Try to make the argument stronger. RESPONSE: The argument has been elaborated somewhat since there is actually less secondary aerosol in summer. New text has been introduced as follows:

“An analysis of data from North Kensington for 2001-2008 by Bigi and Harrison (2010) shows no seasonal influence upon PM10 concentrations, despite a fall in traffic-generated gases in the summer months (CO and NOx). The main components of PM10 in London are nitrates, sulphates, elemental carbon and organic compounds, sodium chloride, calcium-rich dust and iron-rich (traffic associated) dust (Harrison et al., 2004). The elemental and primary organic compounds are largely traffic-related and hence are expected to exhibit a higher concentration in winter, due to poorer dispersion, as for CO and NOx. Sodium chloride is also elevated in winter. Sulphate shows no seasonal trend in the UK, and nitrate is lower in summer due to ammonium

ACPD
12, C4771–C4796, 2012

nitrate vaporisation (Harrison and Charron, unpublished data). It therefore appears that in summer a lower primary carbonaceous emission component from traffic and lower sea salt component is compensated by a higher coarse particle component from the calcium and iron-rich dusts. However, a preliminary analysis of one year of PM2.5 data for the UK (Harrison et al., 2012) does show a marked seasonality in PM2.5 with higher winter concentrations. The extent to which this can be accounted for by a higher traffic contribution in winter and reduced nitrate in summer is yet unclear, and calls for more chemically speciated measurements.

Perhaps the most persuasive data are from Birmingham (where EROS is located), collected by Harrison and Yin (2008) who found that the OC/EC ratio for the urban increment (i.e. ïĄĎOC (urban minus rural)/ïĄĎEC (urban minus rural)) was very close to that for the roadside traffic increment (i.e. ïĄĎOC (roadside minus urban)/ïĄĎEC (roadside minus urban)), where the urban site was at a central urban background location. This demonstrates that carbonaceous aerosol emitted within the urban area had a composition close to that of traffic emissions and was not appreciably influenced by wood smoke, which has a much higher OC/EC ratio (close to 5, as opposed to 0.35 for traffic emissions).".

- Page 6826 conclusions: It would be good to make in the conclusions or somewhere else the link to studies in Paris. E.g. Favez et al.: Evidence for a significant contribution of wood burning aerosols to PM(2.5) during the winter season in Paris, Atmos. Environ., 43, 3640-3644. RESPONSE: Additional comparisons have been included as follows:

"Data from France provide an interesting comparator. Favez et al. (2009) sampling with an aethalometer in Paris concluded that carbonaceous aerosols originating from wood burning represented about 20% of PM2.5 over the winter period that was sampled. Absolute masses were not reported. Sciare et al. (2011) sampled at a suburban site 20 km southwest of the city of Paris over a 10-day winter period. Results from an aethalometer indicated mean concentrations of organic aerosol of 2.26 μg m-3 from

ACPD

12, C4771–C4796, 2012

wood burning, 0.23 μg m-3 from fossil fuel and 2.65 μg m-3 residual component from the aethalometer model, attributed to secondary organic aerosol. In a study conducted in the Alpine city of Grenoble (France), Favez et al. (2010) compared CMB, aethalometer and AMS-PMF model results for wood burning organic aerosol, finding rather divergent estimate of 68%, 61% and 37% of total organic aerosol from the three methods, respectively.

Herich et al. (2011), sampling in Switzerland used the aethalometer to apportion black carbon to fossil fuel and wood-burning sources, but declined to apportion the organic matter (and hence wood smoke mass) because of the high standard errors shown in the data analysis, and the sensitivity of CÂň1Âň and C2 to the chosen alpha values. In our work, the value of R2 for the estimation of C2 and C3 in the aethalometer method was 0.43, also indicative of appreciable scatter. We therefore believe that the multi-wavelength aethalometer method is subject to substantial random errors due to treating C3 as a constant (which manifestly it is not) and possibly also to systematic errors due to the likelihood of the presence of other UV-absorbing components. Coal smoke was considered as a contributor (Bond et al., 2002) but, like wood smoke, is unlikely to have major sources in London.".

- Page 6827, lines 8-19 The discussion of the aethalometer method should be toned down as the C1 and C2 values used here are likely not appropriate. RESPONSE: The interpretation of the aethalometer data has been heavily revised in response to the comments from Grisa Mocnik but the main conclusions stand.

- Table 1: some numbers contain too many numbers after the comma. RESPONSE: The number of figures presented has been reduced.

- Figure 5: The inverse relationship is not so obvious in this graph. Maybe add a Figure on potassium or on the ratio versus temperature? RESPONSE: Figure 5 has been replaced by a graph showing potassium concentrations which we feel makes the point more clearly. The graph for the levo/KWS ratio shows no obvious sensitivity to

ACPD

12, C4771–C4796, 2012

temperature as would be expected.

Response to Comments by Grisa Mocnik The contribution of wood/biomass combustion to the particulate air pollution is a very important topic in air quality research, especially so for large urban areas. The contribution of Harrison et al. is therefore highly relevant and shows great promise. Comparing the different methodologies is an additional strong point of the manuscript. The authors have used levoglucosan and water-soluble potassium as tracers of wood combustion, and compared these estimates of wood burning contribution to the aerosolized particulate matter to the ones resulting from the "Aethalometer model". The authors report a difference between the levoglucosan-based determination of wood smoke and the Aethalometer model, and comment on the applicability of the Aethalometer model. I believe the application of the Aethalometer model could be enhanced with the more detailed application and further description of the details, which are now omitted from the manuscript. The authors could also compare their results with those reported for Paris (Favez 2009, Sciare 2011) and, perhaps, Grenoble (Favez 2010), all of which include systematic and detailed source apportionment efforts, where the Aethalometer model is described and compared to other source apportionment methods and measurements. RESPONSE: Additional text has been included to address this point as reported in the response to Reviewer 2.

The comments below are described in the order corresponding to the data processing within the Aethalometer method, starting with the determination of source specific absorption, then proceeding to the determination of Black Carbon (BC) concentrations, apportioned to fossil fuel and wood combustion, and, finally, to the determination of the carbonaceous matter from all sources.

The authors applied the Weingartner loading compensation (Weingartner 2004) to the Aethalometer data. Several details on the methodology, which are omitted from the manuscript, would elucidate the application of the Aethalometer model. Did they use C=2,14? How did they determine the loading compensation parameter f? Was a single

ACPD

12, C4771–C4796, 2012

f used for the whole measurement period? The determination of the loading compensation parameter f is crucial. Loading compensation factors have been shown to exhibit seasonality (Virkkula 2007). If a single fixed parameter f was determined for the data whole campaign at each site (how?), this would most certainly affect the determination of the source specific contributions to BC and PM_wb. This would be most notably apparent for the measurements on the EROS site, where the campaign lasted almost one year and could, possibly explain why this site shows the unusual diurnal patterns. A short explanation on the "despiking" algorithm would also be welcome. RESPONSE: Yes, we used C = 2.14. The loading compensation parameter f was used for the whole measurement period and was determined according to the method described in Sandradewi (2008). The despiking algorithm was as follows: "For each sequence of measurements between spot changes bATN(ïĄň)i ... bATN(ïĄň)i+1, the 'despiking' algorithm replaced extraordinarily high values with values linearly interpolated from the sequence. The spikes were identified as those points with a value greater than trimmed-mean(bATN(ïĄň)i ... bATN(ïĄň)i+1) +2 ïĆť StDev(bATN(ïĄň)i ... bATN(ïĄň)i+1).

The authors do not report which mass absorption cross section was used to determine the BC from the absorption coefficients. Plotting the b_abs(950 nm) vs. EC would show whether the MAC is identical for all sites. The thermo-optical method for the determination of the OC and EC should also be reported, as this is highly relevant for the understanding of possible artefacts, leading to the systematic bias in the determination of EC (especially for wood-smoke rich samples), which consequently influences the determination of the MAC. RESPONSE: We have plotted the babs (950 nm) versus EC and it shows different gradients for Budbrooke and North Kensington. We have now included details of the OC/EC method in the experimental section.

The source specific Angstrom exponents, used in the study, were 1,0 and 2,0 for traffic and wood combustion, respectively. Values close to these ones are used in the similar studies (all references below), however the wavelengths used in the Aethalometer

ACPD
12, C4771–C4796, 2012

model in these studies were 470 nm and 950 nm! Our experience in Nova Gorica (Slovenia) tells us that using either of the two: 370 nm or 470 nm, paired with 950 nm in the Aethalometer model gives identical results, with a notable difference: higher values of the Angstrom exponents need to be applied if using 370 nm (Mocnik 2012). The explanation for this dependence of the Angstrom exponent on the wavelength is given in Moosmueller 2011. The value of the exponent used for traffic emissions is especially important and the results should be carefully examined when varying this, and other parameters. Plotting diurnal variations of source specific BC would be instructive, as well as comparing the diurnal profiles to traffic counts at major near-by roads. A sensitivity analysis would constrain the accuracy of the model. Do the rush-hour artefacts disappear at a specific value of a_ff (but see also below for additional comments on the apportionment of carbonaceous matter)? RESPONSE: The data have been reworked using the absorption values at 470 nm and 950 nm. This showed a strong sensitivity to the exponent used for the traffic emissions which has been tuned to give the best diurnal patterns for both traffic and wood burning aerosol. We do not feel that it would be helpful to compare diurnal profiles to traffic counts at major nearby roads partly because traffic counts were not available (other than at the Marylebone Road site where the Delta-C method gives negative values) and because source strength alone does not determine the diurnal profile of traffic-generated pollutants. A sensitivity analysis was run as far as varying the alpha values for traffic and wood smoke. If the value of alpha for traffic is increased from 0.9 to 1.1, any traffic trend is removed from the diurnal trend of PMWB but the diurnal trend in PMtraffic remains.

The Aethalometer model, used to apportion the carbonaceous matter (CM), is applied in a wrong manner. The authors assume that all carbonaceous matter arises from just two sources. This is most certainly not true for urban sites. A third, non-absorbing term, should be added, using an additional parameter C_3 (see, for example, Favez 2010). This term describes the non-absorbing carbonaceous matter from sources other than fossil fuel combustion or wood burning. Because this term is omitted, all sources aside from traffic are most probably mis-apportioned to wood combustion, resulting in sys-

ACPD
12, C4771–C4796, 2012

tematic biases. The authors conclude that the Aethalometer model reports an erroneously high contribution of wood burning, but this is not the model's fault but rather a direct consequence of the mis-application of the model. This, together with the values of the Angstrom exponent for traffic should be re-examined in great detail and results reported. RESPONSE: In fact our method did take account of the additional parameter C3. Unfortunately it was omitted from the equation and was not reported in the results. It was certainly not apportioned to wood burning and hence we reject the suggestion that the erroneously high concentrations attributed to wood burning were because of a misapplication of the model. One weakness of the model is that it treats C3 as a constant whereas, or course, it varies from day to day hence leading to an imprecision in the results.

The authors should report how the coefficients C_i were determined. Compared to other campaign publications, the reported values seem low. Are coefficients C_i same for all sites? Are they same for all seasons? The determination of the three parameters C_i should be described in more detail. If multi-linear regression was used to determine them, reconstruction of CM could be reported. Seasonality should be examined at the EROS site as well. The authors report a regression between the PM_traffic and C for North Kensington. The relationship is very close, but more details should be given, and the consequences for the determination of C_i should be discussed. RESPONSE: The coefficents Ci were determined according to the method of Favez et al. (2010). Values of the coefficient Ci are not the same for all sites and a winter/summer division was made, with in general the summer C2 values lower which in turn means lower results for North Kensington and EROS, more in line with the levoglucosan and potassium data. The new results are reported in the revised paper. Reconstruction of CM was carried out but we do not feel it relevant to discuss this in the paper. Since we are continuing to study the aethalometer method, some of the more detailed findings may be reported later.

It is a common misconception that the Aethalometer model apportions the primary

ACPD

12, C4771–C4796, 2012

aerosols, while in effect it does not discriminate between primary and secondary aerosols. The most absorbing portion of secondary organic aerosol (SOA) from wood emissions are humic-like substances (HULIS) and they are one of the wood-smoke components and should be reported as such. The authors' conclusion that HULIS is interference is not necessarily true, unless other sources of HULIS exist in the UK. If they do, they should be described and the Aethalometer model correspondingly modified. If there are arguments for the variable contribution of HULIS to SOA, these should be explained, and should be visible in the differences in the parameter C_2 between the sites or/and seasons. A thorough analysis of the C_i parameters is necessary and details should be reported. RESPONSE: The method is potentially subject to interference from any UV absorbing organic compounds. In practice, this will be compounds with a high degree of conjugation, and humic-like substances are probably only one contributor. While HULIS may be one of the secondary products of wood smoke oxidation, it is also formed from other precursors for which there are many UK sources. In the absence of compound-specific measurements (which would be very difficult for these high molecular weight species), this remains a major unknown. Further analysis of Ci parameters is unlikely to throw light on this issue as it may point to seasonal variations, but these cannot be unequivocally linked to any specific form or precursor of HULIS.

A single levoglucosan to wood-smoke factor is used for all sites. This might be an oversimplification.The great range of the emission factors for levoglucosan and potassium make the use of these markers difficult with no knowledge of the type of combustion and the fuel, this is evident from the ratios between these two tracers, reported in the manuscript. The levoglucosan to wood-smoke factor also depends on both: the type of combustion and on the fuel used (not that these two can be treated completely separately) – the wide range is reported by the authors and an average is used in the calculation of wood-smoke concentrations. The value is chosen arbitrarily – the distribution of the values is not necessarily normal, and the uncertainty of the analysis, depending on this value, should be discussed. An inventory of the combustion ap-

ACPD
12, C4771–C4796, 2012

pliances, if it exists, could aid the choice of the value, but the inventories notoriously underestimate the recreational wood burning. RESPONSE: We very much agree that use of a single levoglucosan to wood smoke factor is an over-simplification. However, we have no information which would allow us to make a more sophisticated choice of factors. This is make clear in the paper. The value used is not chosen arbitrarily; it is justified in the text. This of course does not guarantee that it is correct but the reviewer makes no case for a different value.

The most important modification to the reported use of the Aethalometer model is the third term in the sum of the source specific contributions to CM. The choice of the traffic Angstrom exponent should be examined in great detail, as it influences the Aethalometer model significantly, and the compensation explained in more detail. The levoglucosan to wood-smoke factors might be site specific and should be determined with a more thorough argumentation, and the range of possible wood-smoke concentrations using this method should be reported. A factor of about 10 has been reported for conversion of Delta C to wood-smoke (Allen, 2012) and in the presented work this agrees well with the results of the Aethalometer model, however, both of these methods could overestimate wood-smoke concentrations, as they are not independent. The Aethalometer method has been shown to give consistent results in large cities and I believe a careful examination of the raw data used in the manuscript could produce a more consistent report for the UK. RESPONSE: The data analysis already included the third term in the sum of source-specific contributions to CM. New data are reported but still appear to over-estimate the wood smoke contribution relative to the other methods. Nonetheless, we are very grateful to Dr Mocnik for his illuminating commentary and for stimulating our re-evaluation of the data.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C4771/2012/acpd-12-C4771-2012-supplement.pdf

ACPD
12, C4771–C4796, 2012

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6805, 2012.

ACPD

12, C4771–C4796, 2012

Interactive Comment

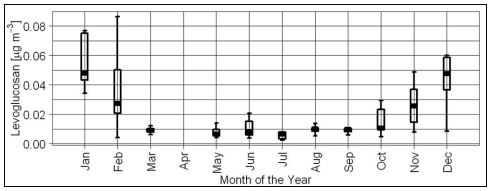

Fig. 1.

ACPD
12, C4771–C4796, 2012

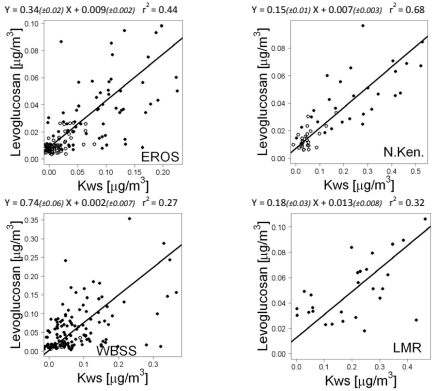

Fig. 2.

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12, C4771–C4796, 2012

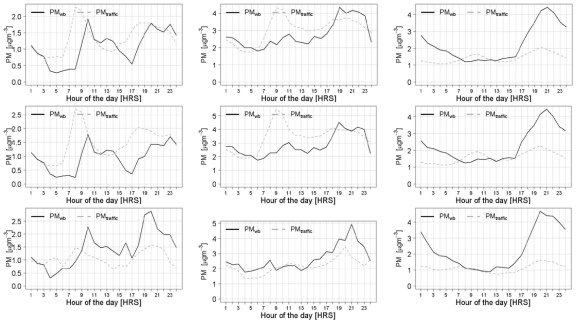

Fig. 3.

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12, C4771–C4796, 2012

Interactive Comment

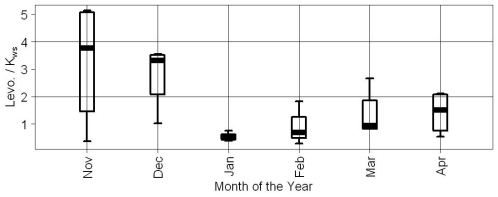

Fig. 4.

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12, C4771–C4796, 2012

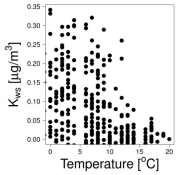

Fig. 5.

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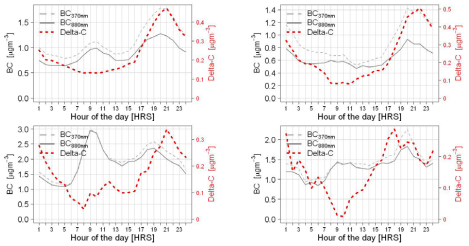

Fig. 6.

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