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Comment

Interactive comment on “Source apportionment of the carbonaceous aerosol in Norway – quantitative estimates based on ^{14}C , thermal-optical and organic tracer analysis” by K. E. Yttri et al.

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Response to referees _____

We thank the referees for their generally positive comments about the paper, and have improved the manuscript in a number of ways to address the specific points of each referee, as noted below. Note also that referee numbering given in the ACPD web-side is different to that given in the associated pdf files – we have used the latter.

Referee 1 _____

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1. The Monte-Carlo analysis in the way it is applied is not sensitive to the problem, whether a special fraction is significantly lower than the detection limit or not. This deficit mainly arises from the exclusion of combinations of parameters producing negative contributions (7386/9-10). This procedure produces a positive bias to those fractions, which are calculated by subtractions or complex combinations of equations.....

Reply: We have responded to this comment in the "general response" text.

2. Tab. 7-9: It is stated for many samples that the precision of OC(pbs) and OC(pbc) is too low to be shown.....

Reply: the problem with precision here arose from the use of integers in the counting scheme of the LHS. Thus, when the contributions were around 1% or so, the numbers became very uncertain. We have re-coded the LHS scheme to work with higher precision, and thus can now present the numbers directly.

3. The ranges of the emission ratios of (OC/TC)_{bb} for PM₁₀ and PM_{2.5} in Tab. 3 seems to be too narrow. I acknowledge the big advantage that the emission ratios applied in this study were thoroughly determined by the laboratory of the authors itself so that the method of OC/EC measurement can be ruled out as a source of error.....

Reply: As discussed in the "general response" text, there is no easy way to properly estimate such ranges, and all authors/experts have their own ideas on the best range. For example, if we denote our minimum, central and maximum values with the notation "central(min-max)", Table 3 in our manuscript had 0.78(0.73-0.82) for PM₁₀ and 0.71(0.66-0.86) for PM_{2.5}. These values can be compared to Szidat et al. (2006) who used the equivalent of 0.86(0.82-0.9) for PM₁₀, and the same values in Szidat et al. (2009) for both PM₂₅ and PM₁₀. Gelencser et al. used 0.86(0.71-0.91), and Genberg et al. (2011) used 0.87(0.69-0.94). The widest range was given by Gilardoni et al. (2011), who used a very wide ratio for (OC/EC)_{bb} of 1–20, giving 0.725 (0.5-0.95) in PM_{2.5}. This wider range made more use of data from North America, however, and we believe the narrower ranges (based upon European wood-types and conditions)

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are more appropriate for Norwegian conditions.

In response to the referees request though, we have re-run the LHS with a somewhat wider range for different parameters. We will retain our original estimates for the main paper, but illustrate the effects of the tests in the Supplementary.

4. Emission ratios for biomass burning in Tab. 3 are given for PM_{2.5}, whereas PM₁ filters are sampled. The difference should be considered in Tab. 3 by increasing the range between low and high values and discussed in the text.

Reply: We believe that emission factors for PM_{2.5} and PM₁ should be quite similar, since direct levoglucosan and TC emissions are mainly in the sub-micron mode. As discussed in Yttri et al.2009, we believe that extra levoglucosan in the PM₁₀ mode may be associated with re-suspension or other processes rather than direct emission, hence the higher factors used. However, calculations using a wider range will be presented in the Supplementary.

5. SOA from bb should be addressed as well, at least in the discussions. This SOA fraction adds to OC(BSOA) according to Equation (11): the (TC/LG)bb emission ratios (Equation 4) and thus the term TC(bb)*F_{14C} (Equation 11) do not allow for the SOA fraction of bb, as these value were determined in fires place experiments. Consequently, the definitions of ASOA and BSOA (Tab. 1) are misleading, as bb is an anthropogenic source but appears in the biogenic part of the calculations.

Reply. Yes, this is a tricky area. Actually, some of the SOA arising from biomass-burning (let's call this BBSOA) is probably included in our assumed (TC/lev) ratios. As the latter are derived largely from ambient data, they will include both true primary TC_{bb}, plus any carbon arising from either condensation of gaseous bb emissions, or of BBSOA. We had noted this in section 3.3 (page 7388), where we regard the TC_{bb} as an 'operational' quantity.

Still, we cannot exclude that some of the calculated BSOA is indeed from biomass

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burning. We have added a comment on this in section 5.2.

The definitions of ASOA and BSOA are also difficult, and not easily defined. We have clarified this point at different parts of the text.

6. 7380/1-19: The back filters serve for two purposes; they help to correct for the positive sampling artifact and for the filter blank in one step. It seems to me that the front and back filters are treated differently, one being conditioned the other one not. This is problematic as the conditioning introduces a large blank to the front filters, which cannot be corrected for using the back filters. Consequently, the additional blank contribution must be considered independently to exclude errors of the OC/EC concentrations used for the source apportionment.

Reply: The front and the backup filters have been treated identically in all aspects, except for conditioning: i.e. the front filters were conditioned, whereas the backup filters were not. The authors agree that it would be ideal if the backup filters were conditioning as well. We do not agree though that conditioning filters “introduces a large blank to the front filters”, as stated by the referee.

It is not apparent from the referees comment what is likely to cause such a large blank during conditioning; particulate contamination or adsorption of SVOCs? We would like to argue that evaporation of SVOCs from exposed filter samples might be an equally important process. In cases when ambient aerosol filter samples collected during low (e.g. -10°C) ambient temperature is brought into the clean room for conditioning at a temperature of 20°C , the temperature difference could be sufficient to cause a substantial evaporation. The magnitude of such evaporation from exposed filters is not easily estimated and it might very well be within the 20% negative artifact that we have allowed for within our source apportionment. In addition, EC/OC analysis starts with purging the filter sample in helium at a temperature well above ambient. This will cause further SVOCs not evaporated off from the filter when conditioned in the clean room to enter the gas phase and thus not being quantified as particulate OC. Consequently,

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one cannot easily tell whether exposed front filters conditioned in the clean room will gain or lose carbon material, and far less at which levels.

Preheated non-exposed quartz fibre filters placed in our clean-room at a temperature of 20 °C and a RH of 50%, increases only to a minor degree in concentration when conditioned over a time period of 48 hours; i.e. preheated non-exposed quartz fibre filters (OC = 0.08 $\mu\text{g C cm}^2$), preheated non-exposed quartz fibre filters conditioned (OC = 0.20 $\mu\text{g C cm}^2$).

7. 7386/11: It should read “Table 2”.

Reply: corrected

8. 7387/26-28: This discussion it not clear and the numbers deviate from Tab. 3.

Reply: This paragraph has been re-phrased, and the ranges given corrected (PM10 should have been 15(7.6-17) in both table and text).

9. 7393/15-16: The results of Glasius et al. (2011) are not available yet so that numbers should be given for this comparison. Furthermore, the recent compilation by Hodzic et al. (Atmos. Chem. Phys., 10, 10997-11016, 2010) should be consulted as well.

Reply: Added. The Glasius paper has now been accepted, and we have updated the reference. Reference to Hodzic also added.

10. 7396/9: The equation for determination of OC(PBAP) should be included in Tab. 2.

Reply: Added

Anonymous Referee #2 _____

The authors use carbon-14 analysis together with a small number of specific chemical analyses to apportion carbonaceous aerosol from two sites in Norway to specific source categories. Although the sampling periods are rather brief and may be unrepresentative, the methods look broadly sound and the work merits publication subject to

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attention to a number of issues.

Specific points are as follows:

(1) Section 2.1 - details of the sampling sites are extremely limited and would benefit from more information about possible local sources including road traffic. Is the rural background site influenced by emissions from local housing? How close are the nearest source emissions?

Reply: We have added the following text to the manuscript in section 2.1:

Aerosol filter samples were collected at an urban background site in Oslo, Norway, (Veterinary Institute, 59 56'N, 10 44' E, 77 m a.s.l.) and at a rural background site (Hurdal, 60 22'N, 1104'E, 300 m a.s.l.) situated 70 km north east of Oslo, for a summer period (19 June - 15 July 2006) and winter period (1 - 8 March 2007).

The Veterinary Institute measurements site is situated in the middle of the Oslo metropolitan area. Oslo is located in the innermost part of the Oslo fjord, and is largely surrounded by forested hills . The City of Oslo has a population of 0.6 million inhabitants, while the population of the greater Oslo-region is approximately 0.9 million. The Veterinary Institute measurements site is surrounded by buildings of 2-3 storeys. The nearest major road is situated approximately 120 m from the site (25 000 cars/day).

The EMEP (European Monitoring and Evaluation Programme, www.emep.int) site Hurdal is situated in the Boreal forest with mixed conifer and deciduous trees, which together with the Hurdal Lake (32 km²) account for the majority of the surrounding land use. The nearest local emission source is the local community of Hurdal (600 inhabitants), located 7 km north of the measurements site, which is known to have minor or even negligible influence on the air quality at the site. The nearest road is situated 200 m away from the site (< 500 vehicles/day).

(2) The source apportionment is quite sensitive to the analysis of the specific chemical components and especially levoglucosan. While a reasonable level of detail is given

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over the analytical procedures, it is unclear how much quality assurance has been undertaken. In particular, the level of levoglucosan content of SRM 1649B is well known and evidence of measurement accuracy is required.

Reply: Some of the coauthors of the actual paper are currently interpreting the results from an inter comparison on various analytical methods used for quantification of levoglucosan in ambient aerosol filter samples. As part of the quality assurance of this exercise, 96 punches from 6 different filters (i.e. 16 punches pr filter) have been extracted and analyzed to address the reproducibility of the analytical method, i.e. the same analytical method as used in the current paper. The result from this exercise includes also the heterogeneity of levoglucosan deposited on the actual filters. The results show that the reproducibility is within a range of 4 – 11%.

In the intercomparison it is found that the levoglucosan, measured by the same analytical method as in the current paper, range between 86 – 97% (mean: 93%) of the mean value composed by the results of all the participants ($n = 13$). The corresponding percentages for the median were 81 – 92% (mean: 89%) of the median value composed by the results of all the participants ($n = 13$).

These results are not yet published, thus the results should be considered preliminary.

(3) Page 7386, LHS analysis - this seems a sensible way of dealing with uncertainty but two specific issues arise. Firstly, it is hard to believe that parameters are equally likely across the entire range between the low limit and the central value and the central value and the high limit..... The second issue is that combinations of parameters leading to negative contributions have been excluded which will presumably lead to a positive bias in those outcomes...

Reply: We have responded to these concerns in the "general response" text.

(4) Page 7390, last paragraph - the lack of partitioning of OC_{nf} into primary and secondary components is unfortunate. While the elemental carbon tracer technique is

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likely to prove highly misleading under these circumstances, the OC/EC ratio for road traffic emissions is rather well established and could be used to estimate a breakdown.

Reply: In the first manuscript we deliberately excluded this extra of the calculation, because of both conceptual and practical difficulties. However, as we did make some use of the information, we agree with the referee that it would be valuable to add these calculations explicitly. We have also stressed the large uncertainties of this last step of the calculation, both on the practical and conceptual side.

The comparison between the urban and rural sites would be interesting. This would be likely to enhance the discussion in Section 5.1 on page 7394.

Reply: Text added, along with the new calculations.

(5) Section 5.2 - why is OC-BSOA higher during daytime sampling and higher at the rural background site? This seems to suggest rather rapid formation. Is this consistent with the anticipated precursors?

Reply: This is an interesting question, and we have addressed it with more text in the revised manuscript:

The reason for mean BSOA levels being higher at Hurdal than at Oslo may well be geographical. Hurdal is surrounded in all directions by forested areas, whereas Oslo lies on the edge of a Fjord. Air masses arriving from southern wind directions may have passed over extensive oceanic areas. The increased daytime BSOA compared to nighttime BSOA at both sites is at first site puzzling. One simple possibility would be that the aerosol is being generated by fairly local sources, and since BVOC emissions are higher in daytime the BSOA contribution should also be higher. Modelling or observation-derived studies (e.g. Simpson et al., 2007, Tunved et al., 2006) suggest that BSOA formation should be a long-range process however, except for extreme situations such as Mexico city (Jimenez et al., 2009). Another possibility is related to loss processes. Many OA species are expected to be lost to deposition (Bessagnet et

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al., 2010, Hallquist et al., 2009), and near-surface loss rates will be greater at night, below any nocturnal boundary layer.

(6) Page 7400, first paragraph - it is now revealed to the reader that the LHS processing gives a split between secondary and primary OC from fossil fuel sources. What is the mathematical basis by which LHS calculates this? How does it vary between the urban and rural sites?

Reply: As noted under point (4) above, we will add these details to the revised manuscript, along with the necessary caveats.

(7) Why was PM1 studied rather than PM2.5? There is an argument that PM1 gives a cleaner split between the coarse and fine fraction but hard evidence of this is lacking. Since PM2.5 is far more important in a regulatory context, would it not have been better to study this fraction?

Reply: There are many measurements in Nordic and indeed European areas showing that accumulation-mode particles fall below the 1 μ m threshold, indeed usually below 500nm (e.g. Tunved et al., 2003, Spindler et al., 2004). This PM1 level captures both the peak contributions from combustion emissions and SOA formation. Further, fine aerosol (<1 μ m) is important for radiative forcing issues, and is usually a very significant fraction of PM2.5 anyway (e.g. Spindler et al., 2004). PM2.5 is indeed important for regulatory purposes, but this size fraction is more difficult to interpret, since it captures the low-end of the coarse-mode emissions which include difficult source categories (dust, re-suspension, tyre-wear, etc.).

There are several minor corrections required.

Reply: we made the corrections

Referee #3 —————

The paper is aimed at source apportionment of carbonaceous aerosol in Norway, however, it has a broader appeal in terms of method development to correctly apportion

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multitude of carbonaceous aerosol sources. The paper should certainly be published in ACP subject to addressing the comments listed below.

My major comment and concern is about LHS method used for source apportionment.

Reply: We have responded to this comment in the "general response" text.

I am not convinced that equal assignment of parameters between low and high limits is realistic. If you relax parameters too much, the solution will easily be found, but will it be valuable?

Reply: We have responded to the first part of this comment in the "general response" text. The point that if parameters are relaxed too much solutions are easily found is valid, but that is why we need to restrict the ranges to those we think are realistic. Once this is one the solution space is greatly reduced, and many combinations of parameters result in negative (and hence impossible, see again the general response) solutions.

There seems to be no validation presented in the paper which would help assessing usefulness of LHS or superiority over e.g. Monte Carlo or any other method.

Reply: The difference between LHS and Monte-Carlo is not too significant, except in CPU time requirements. As noted in the general response, other factors are much more uncertain.

It is not clear at which stage negative contributions are excluded. If at the end for representations purposes only, then it is fine, but if in the process, then LHS must be positively biased.....

Reply: We have responded to this comment in the "general response" text.

At the moment there seems to be no validation of the method, just the output. For example, if LHS output is 16% OC_{bb} it should be compared against (OC/LG)_{bb} relationship (especially Norwegian data) and so for other parameters. Or EC_{bb} and EC_{ff} should be

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summed up and compared with the measured EC. At the moment Table 4 and Table S4 suggest to me that EC is systematically overestimated by LHS when compared to measurements, especially during summer....

Reply: It is not easy to validate any source-apportionment method, including that used here, but as noted in the general response the results are constrained by the observations. Differences between Table 4 and Table S4 partly reflect that the LHS does indeed allow for uncertainty in EC, and partly that the 50th percentile value of EC_{bb} cannot simply be added to the 50th percentile of EC_{ff} - they are points on different probability curves. In general though, the source-apportionment method will return “central” values of EC that differ from the observed values - this is a feature of the method rather than a weakness. In principal it might be possible to extract more information from the LHS results, but in practice conditions vary so much from period to period, and site to site, that we have insufficient data with which to attempt such an analysis.

Do authors have a support for splitting particulate mass at PM₁ which certainly does make sense but only when justified?

Reply. Please see the comments made to Ref 2 above.

Reference to Gilardoni ACPD paper in many places of the current paper would be very helpful. It is a very similar study, but by no means undermines the novelty of this paper, primarily due to the fact that Monte Carlo simulations were used in Gilardoni paper. I would also have suggested vice versa if I were a reviewer of the other paper.

Reply: We have added reference to Gilardoni and indeed some other relevant papers that became available recently.

Page 4. Experimental methods. Site description should be more informative, especially when aimed at generalizations of typical Norwegian conditions.

Reply: As noted in the response to Ref. 2, we have added site descriptions.

Page 9. Estimation of TC_{bb}. It is not clear how TC/LG relationships in PM_{2.5} or

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PM10 are adapted for PM1. Why TC is used and not OC when LG is certainly a part of OC. This would unnecessarily increase the range and uncertainty in bb source contribution.

Reply: We used (TC/LG)bb instead of (OC/LG)bb as the first step in the bb calculations for robustness. Measurements of TC are known to be more robust than measurements of OC, so the (TC/LG)bb ratio should be better than the (OC/LG)bb one. (Note that the measurements of LG are not derived from the OC measurement, but are analysed independently). For similar reasons it is better to use (OC/TC)bb as the 2nd step rather than (OC/EC)bb, and this procedure also excludes the unlikely possibility that the high end of the (OC/LG)bb distribution was used together with the high end of the (OC/EC)bb distribution.

Also, how those ranges are compatible with other studies, but that is, however, a lesser problem as study is aiming at describing Norwegian conditions and citing previous Yttri et al. paper.

Reply: We have discussed some of the other ranges as noted above, and will prepare comparison calculations for the Supplementary.

Page 18. Line 576. Consideration of natural sources in Norway without accounting for sea salt, seasalt-sulphate, biogenic sulphate and crustal material in the form of dust can not be complete and even miss-leading. It should clearly be stated that major ions have not been measured in this study and, therefore, estimation of natural sources is limited. The whole chapter is somewhat misleading as it should be named "mass closure of PCM" and not PM where other inorganic species should be measured as well to aim for mass closure.

Reply: We have re-phrased the text to focus on PCM.

Extra Refs

Bessagnet, B.; Seigneur, C. & Menut, L. Impact of dry deposition of semi-volatile or-

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ganic compounds on secondary organic aerosols *Atmos. Environ.*, 2010, 44, 1781 - 1787

Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; et al., Evolution of Organic Aerosols in the Atmosphere *Science*, 2009, 326, 1525-1529

Genberg, J.; Hyder, M.; Stenström, K.; et al., Source apportionment of carbonaceous aerosol in southern Sweden *Atmospheric Chemistry and Physics Discussions*, 2011, 11, 13575-13616

Gilardoni, S.; Vignati, E.; Cavalli, F.; et al., Better constraints on sources of carbonaceous aerosols using a combined ^{14}C -macro tracer analysis in a European rural background site *Atmospheric Chemistry and Physics Discussions*, 2011, 11, 2503-2547

Spindler, G.; Müller, K.; Brüggemann, E.; Gnauk, T. & Herrmann, H., Long-term size-segregated characterization of PM₁₀, PM_{2.5}, and PM₁ at the IfT research station Melpitz downwind of Leipzig (Germany) using high and low-volume filter samplers *Atmospheric Environment*, 2004, 38, 5333 - 5347

Tunved, P.; Hansson, H.; Kulmala, M.; et al., One year boundary layer aerosol size distribution data from five nordic background stations, *Atmos. Chem. Physics*, 2003, 3, 2183-2205

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