

Interactive comment on “Better constraints on sources of carbonaceous aerosols using a combined ^{14}C – macro tracer analysis in a European rural background site” by S. Gilardoni et al.

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Answer to Referee #2

R: The quality of the results depends very much on the quality of the input data. Due to the comprehensive approach, it's worthwhile to optimize these parameters as far as possible. To me, this includes:

1a. OC to levoglucosan ratio. The limitation of the range from 4 to 6 is problematic. The physical explanation is clear: a single fraction cannot be larger than total OC.

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But modifying the range of ratios towards 4-6 induces such an arbitrary cut-off that the usage of the concept of emission ratios is called into question generally. None of the data compilations I know (e.g., Puxbaum et al., 2007) would justify this constraint. However, there is one comparative dataset of levoglucosan and ^{14}C from Southern Switzerland (Sandradewi et al., Atmos. Chem. Phys. Discuss. 8, 8091-8118, 2008), which corroborates the low OC-to-levoglucosan ratios: 5.3 was measured during three episodes with dominant wood-burning contributions. Nevertheless, the range from 4 to 6 (i.e., $\pm 20\%$ from the median value) is unrealistically small.

A: In agreement with the suggestions of referee #1 and #2, the variability range of the OC to levoglucosan ratio was increased to 4-13.

R: 1b. OC to EC ratio (bb). I think that this range is too large. Only studies of fire-place burning should be considered, as open fires are excluded for this work. Probably this will reduce the upper bound substantially.

A: This study does not exclude a priori the presence of open burning, although the low concentration of levoglucosan during the drier season led the authors to conclude that wood burning for residential heating dominated biomass burning emissions. As mentioned at page 2512, episodic events of agricultural waste burning might be present during fall. As a consequence the OC to EC ratio for biomass burning should include also open burning emission ratio.

R: 1c. fM(bb). The values of Lewis et al., 2004 can not be taken without modification, as that work refers to 1999, whereas the current work was conducted in 2007. Within these 8 years, the upper bound decreased to 1.24 as shown by Mohn et al., Bioresource Technology 99, 6471-6479, 2008.

A: Lewis et al 2004 and Mohn et al. 2008 refer to wood combustion aerosol samples collected in 1999 and 2006, respectively. Although the different years, the conclusions presented in the two papers are similar. They both suggested that the average reference fraction of biomass burning aerosol fM(bb) is about 1.25. In addition, Lewis et

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al. (2004) showed that, based on the model assumptions, $fM(bb)$ can be as large as 1.31. In the present study the upper bound of the $fM(bb)$ variability range is assumed equal to the upper bound of the range reported by Lewis et al. (2004), rather than its central value. Mohn et al. (2008) is added to the reference list. Text is modified as follow : "... $fM(bb)$ depends on the age of the combusted material and the tree growth rate; literature studies calculated that $fM(bb)$ for wood harvested in 1999 and in 2005 are similar. Lewis et al. (2004) showed that, based on the model assumptions, $fM(bb)$ can vary between 1.13 and 1.31."

R: 1d. OC to OM ratios. The value of 1.4 used at 2520/11 as the overall ratio is too low. The results of equations (11) and (12) applying the data of this study should be used instead to calculate OM in Fig. 3. Moreover, the conversion factor of 1.4 for POC_{bb} and SOC_{bb} used in equations (11) and (12) is too low as well. I would recommend 1.8.

A: At page 2520 we calculated the OM concentration for the entire dataset using the OM to OC ratio of 1.4, obtaining a lower estimate of the OM concentration. The purpose of this calculation is to show the importance of organic mass relative to the fine aerosol mass. The average OM of the subset of samples is calculated using again the ratio 1.4 for consistency. A more accurate calculation of OM, based on the source apportionment results, is presented in section 3.3 and compared with the lower estimate. The following sentences are added at page 2520 and 2524.

"Organic mass (OM) was calculated assuming an OM to OC ratio equal to 1.4; this value, which is close to the lower bound observed in environmental studies, leads to a lower estimate of the OM contribution to fine aerosol mass. Nevertheless, OM represented 53% and 41% of fine mass during winter and summer, respectively, while the EC contribution was 10% and 7%."

"The average OM, calculated as sum of SOA and POA, was $30.2 \mu\text{g m}^{-3}$ and $10.6 \mu\text{g m}^{-3}$ in winter and summer, respectively. These values are 10 to 17% higher than the OM estimates presented in section 3.1, indicating that an accurate choice of the OM to

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OC ratio has to take into account the aerosol sources and their seasonality.”

R: 2. There are several indications that the data treatment should be improved as well: first, the skewed frequency distributions of POC_{bb}, SOC_{bio} and other sources shown in Fig. 1; second, the jumps in the box-whisker plots (Fig. 5) of POC_{ff} and SOC_{bio} in April and September, when levoglucosan measurements turn from significant values to below the detection limits. This applies to:

2a. Discarding negative solutions (2516/12-14) may appear physically sound. However, this procedure produces a positive bias to those fractions, which are calculated by subtractions or complex combinations of equations. SOC_{bio} is an example of such a fraction, especially when estimated for winter conditions. It is determined from equations (8) and (9). Unfortunately, these equations have severe drawbacks: a) Under winter conditions, POC_{bb} concentrations are much larger than SOC_{bio} so that the determination $\text{SOC}_{\text{bio}} = \text{OC} - \text{POC}_{\text{bb}} - \text{other OC}$ will imply large uncertainties. b) As reference fM values of POC_{bb} and SOC_{bio} are too little different from each other, a better constraint cannot be expected from equation (9). Therefore, I assume that QMC produced negative values for SOC_{bio} during winter. By deleting these solutions, a positive bias is produced resulting in the statement that SOC_{bio} was significant during winter (2529/9). However, by omitting to discard the negative solutions and statistically investigating the detection limit of this fraction for each individual sample, the outcome will be more reliable.

A: We agree with the referee that a negative value of carbon concentration might be physically meaningful if the value is within the blank noise. In this case, discarding this concentration would bias the best estimate solution. To investigate the blank noise, we studied the distribution of QMC solutions for a model blank sample. OC, EC, levoglucosan, arabitol, mannitol were set equal to zero, while fM was set equal to 105. The uncertainties of these variables were assumed equal to one third of their detection limits. The resulting solution frequency distributions were symmetrical around zero. For each carbon source, the minimum concentration with physical meaning was assumed

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equal to the 25th percentile of the blank solutions. Concentrations larger than the 25th percentile and smaller than the 75th percentile were considered equal to zero, while concentrations larger than the 75th percentile were considered real.

Text is modified as: “Some combinations of parameters led to negative concentrations. Negative solutions were considered meaningful if they were within or higher than the blank noise level. To investigate the blank noise, we studied the distribution of QMC solutions for a model blank sample; the resulting solution frequency distributions were symmetrical around zero. For each carbon source, the minimum concentration with physical meaning was assumed equal to the 25th percentile of the blank solutions. Concentrations larger than the 25th percentile and smaller than the 75th percentile were considered equal to zero, while concentrations larger than the 75th percentile were considered real. Combinations of input parameters that led to solutions smaller than the 25th percentile were discarded”. Figures 1, 3, and 5 are modified accordingly. The best estimate solutions differ by less than 3%, while the uncertainties differ on average by 10%.

R: 2b. The choice of the average value of the frequency distribution as the best estimate (2521/23) does not regard the skewed shape of the distributions. 50th percentiles should be used instead.

A: Average values are replaced with 50th percentiles and text is modified accordingly.

R: 3. I cannot comprehend the evidence of biogenic SOA formation on the surface of primary anthropogenic carbonaceous particles (2523/1-13). To me, the correlation of Fig.4 suggests that SOCbio has a similar history (i.e., source regions and atmospheric residence times) as the remaining carbonaceous particle fractions and a distinctly different history from the inorganic PM components (ammonium sulfate, ammonium nitrate, dust. . .). But Fig. 4 does not reveal any chemical information thus not supporting the hypothesis “that larger fractions of anthropogenic primary aerosol offer a larger surface area with chemical affinity for condensation of biogenic gas phase precursors,

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enhancing secondary biogenic aerosol formation”. I think that the whole section should be removed together with the corresponding section in the conclusions (2529/15-20).

A: We agree with the referee that the information available could not be used to withdraw conclusions about the chemical composition of biogenic and anthropogenic OC. Nevertheless, SOCbio has different sources (oxidation/aging of biogenic volatile precursors) relative to primary particles (combustion processes, transportation). PSCF study (section 3.6) indicates that the source region of the carbon fractions are different: primary fossil carbon derived from emission in urban and industrial areas in the nearby Po valley, while biogenic SOA is produced by oxidation of biogenic volatile compounds, likely originated in the rural area around the sampling site. In addition, the lack of correlation among the other carbonaceous particle fractions indicates that residence time or similar history of carbonaceous particles is not enough to explain the relationship observed between biogenic secondary and primary OA. Text is modified as follow: “Daily samples collected during the same months showed that the mass fraction of biogenic secondary carbon (i.e. SOCbio normalized to the fine aerosol mass) correlated very well with the mass fraction of primary carbon (i.e. the sum of primary OC and EC normalized to fine mass), that in summer is emitted almost exclusively by anthropogenic fossil sources. The normalization to fine mass is used to remove dilution effect due to meteorology. SOCbio has different sources (oxidation/aging of biogenic volatile precursors) compared to primary organic particles (combustion processes, transportation). PSCF (section 3.6) indicates that the source region of the two carbon fractions are different: primary fossil carbon is produced by local sources and emissions of urban and industrial areas in the nearby Po valley, while biogenic SOA is produced by oxidation of biogenic volatile compounds, likely originated in the rural area around the sampling site. In addition, the lack of correlation among other carbonaceous particle fractions indicates that residence time or similar history of carbonaceous particles is not enough to explain the relationship between biogenic secondary and primary OA. In conclusion, the good correlation between SOCbio and primary carbon fractions ($r^2 = 0.79$) could be explained by the promotion of biogenic secondary aerosol formation

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by primary carbonaceous material. As suggested by Bowman et al. (2004), a larger fractions of anthropogenic aerosol can offer a larger surface area with chemical affinity for condensation of biogenic gas phase precursors.”

R: 4. 2507/25: The exact half-life of 5730 years should be given.

A: Text is corrected as” half-life of about 5730 ± 40 years”.

R: 5. 2511/12: A closing bracket is missing.

A: Bracket inserted

R: 6. 2514/2: As done for the other emission ratios, a range should be given for the value 5.2 pg OC spore⁻¹ instead of a fixed number, even if this is negligible for the final result. Maybe, another constant (k_4) can be included in Table 2.

A: The content of OC from a single spore was assumed equal to 5.2 pg C spore⁻¹, which corresponds to the lower bound reported for PM₁₀ aerosol (Bauer et al. 2002), because this study focus on PM_{2.5} fraction and the use of a larger OC content would be unrealistic.

R: 7. 2516/20-23: In principle, this should include NIOSH-to-EUSAAR1 and IMPROVE-to-EUSAAR1 correction factors. Would this improve the quality of the dataset?

A: The variability range of EC to OC emission factors are not corrected based the thermal-optical protocol used, since the correction factor would depend on aerosol thermal and optical properties, and thus it would be source dependent. Although we know that, for example, NIOSH protocol underestimates EC compared to EUSAAR protocol (Cavalli et al. 2010), no correction factors are available for specific aerosol sources.

R: 8. 2521/11-12: The correct unit is ng m⁻³ (applies twice).

A: Unit of arabitol and mannitol concentration is ng m⁻³

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R: 9. Table 5: Ispra should be denoted as rural station.

A: Rural is inserted in the table.

R: 10. Figure 1: As the frequency distributions provide important information on the quality of the approach, four subfigures should be shown: winter OC, winter EC, summer OC, summer EC. Furthermore, SOC_{bb} and SOC_{ff} can hardly be distinguished; dashed lines should be used.

A: Figure 1 is an example of frequency distribution corresponding to one sample; the figure is used to explain the output of QMC approach. Showing the same plot for all the samples would be impossible and redundant, since the same information is reported in figure 5. Graphics of Figure 1 is modified to make the figure clearer.

R: 11. Figure 3c: The ordering of the 8 sources in the legend should follow the ordering within the bars.

A: Legend of Figure 3c is modified accordingly.

References

Mohn, J., Szidat, S., Fellner, J., Rechberger, H., Quartier, R., Buchmann, B., and Emmenegger, L.: Determination of biogenic and fossil CO₂ emitted by waste incineration based on ¹⁴CO₂ and mass balances, *Bioresource Technology*, 99, 6471-6479, 2008.

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