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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #2

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The manuscript "Better constraints on sources of carbonaceous aerosols using a combined 14C - macro tracer analysis in a European rural background site" by Gilardoni et al. describes the apportionment of carbonaceous aerosols to eight sources using different molecular tracers and 14C analysis of TC. Applying several individual emission ratios, all results are combined by a Quasi-Monte-Carlo approach, which provides realistic uncertainties of the final source contributions. This technique was adapted to 49 daily samples from the rural site Ispra in Northern Italy producing an integrative picture of all seasons for the year 2007. Results indicate that primary emissions from wood burning and biogenic SOA are the dominant sources during winter and summer, respectively. I asses this work as comprehensive and very important for the investigation of sources of carbonaceous particulate matter and I recommend it for publication. In order to improve the final outcome of the manuscript, however, some revisions are necessary.

Main comments:

1. 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 then total OC. 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 14C 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.

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.

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.

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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 POCbb and SOCbb used in equations (11) and (12) is too low as well. I would recommend 1.8.

2. There are several indications that the data treatment should be improved as well: first, the skewed frequency distributions of POCbb, SOCbio and other sources shown in Fig. 1; second, the jumps in the box-whisker plots (Fig. 5) of POCff and SOCbio 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. SOCbio 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, POCbb concentrations are much larger than SOCbio so that the determination SOCbio = OC- POCbb - other OC will imply large uncertainties. b) As reference fM values of POCbb and SOCbio 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 SOCbio during winter. By deleting these solutions, a positive bias is produced resulting in the statement that SOCbio 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.

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.

3. I cannot comprehend the evidence of biogenic SOA formation on the surface of pri-

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mary 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, 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).

Further comments:

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

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

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 (k4) can be included in Table 2.

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?

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

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

10. Figure 1: As the frequency distributions provide important information on the quality of the appraoch, four subfigures should be shown: winter OC, winter EC, summer OC, summer EC. Furthermore, SOCbb and SOCff can hardly be distinguished; dashed lines should be used.

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

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