

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 #1

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Review of Gilardoni et al.

This study presents a very valuable data set, and analysis in terms of source-apportionment. Such data are of great value for understanding organic aerosols in the atmosphere. The data as presented are in principal very interesting, but I think the analysis neglects some important factors. I think the authors need to re-do their QMC analysis with more realistic uncertainty bounds before this work can be published.

The most puzzling feature of the results of this paper is illustrated very clearly in Fig.5.
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The summertime results show essentially zero uncertainty for EC and SOC_{bio}. Such accuracy and precision is not possible in my opinion, especially for these components, and such results reflect the lack of appropriate uncertainty in the inputs rather than any real accuracy.

A likely reason for the precision of these values is the limited attention payed to some important sources of uncertainty. Indeed, as the authors claim to be using a very efficient solver (QMC), it is hard to see why they limited their analysis to the uncertainty of just five factors (Table 2).

Some major difficulties with interpreting this paper are:

- Artifacts in the measurements themselves. For example, Gelencser et al. (2007) and Szidat et al. (2009) used error-factors for EC, which is always a significant source of uncertainty.
- No uncertainty is allowed in the measured fM values. Although AMS instruments are renowned for their accuracy, ambient TC sampling is also renowned for its difficulty. Such filters are not always homogeneous, and the material used in the AMS does not necessarily have the same fM as the true OA at the site.
- The authors restrict the range of OC to levoglucosan ratios to just 4–6 for the whole period, on the grounds that larger ratios would have led to POC_{bb} exceeding total OC. This is likely a significant source of error in summertime, as one would actually expect larger OC/levoglucosan ratios in that period. Firstly, a likely source of levoglucosan is wildfires or other open burning sources, and these have very different emission ratios to those of wintertime residential burning. Secondly, there is increasing evidence that levoglucosan can be oxidized in atmospheric conditions (e.g. Hennigan et al., 2010), and thus the measured levoglucosan may well be just a fraction of the emitted amount.

- There is no distinction between OC from BSOA and OC from PBAP, so only one value of $fM(\text{bio})$ of 1.05 is used. Although PBAP are later demonstrated to be small, the methodology would have allowed for a different value from PBAP, and the methodology would have been cleaner.
- The data chosen are a subset, chose partly to have large TC values. This obviously biases the results, and perhaps favors one type of source (e.g. anthropogenic plumes) more than others (e.g biogenic or PBAP)? How representative were these data then? Were these the top 50% of TC samples, the top 10% or what? (I realize this is likely not possible at this stage, but it would have been useful to aggregate several low TC filters for further analysis, to get some statistics on the source of aerosol on the cleaner days.)
- There is no tabulation of the uncertainty bounds of the different contribution estimates.
- The raw data are not presented, so it is impossible for others to reproduce the results given. As there are only 48 samples the measurements could easily be tabulated, perhaps as supplementary material.

Other comments

The paper implies that the QMC method has several advantages over other methods such as LHS, but these advantages are hard to see. On p2508 it is stated that the QMC is very efficient and does not need the number of input variable combinations to be specified in advance. Does that matter? Is CPU usage for this kind of calculation worth a mention? As noted above the uncertainty analysis performed here is in fact very limited.

The terminology used for fM is confusing. For example, $fM(\text{non-fossil})$ is sometimes called the reference fraction of modern carbon in non-fossil aerosols. As is made clear

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by Table 2, this is not a constant, and so how is it a 'reference' fraction? Other papers make do with the simpler terminology fraction of modern carbon, percent modern carbon (pMC). I suggest the authors use one of the simpler terminologies, and restrict the word reference to the value used in the actual definition of fM . The comparison with model results is very thin, and wordy. Not a single figure or table is presented. Why did the authors not attempt the same type of analysis as Simpson et al. (2007), who did such an analysis with the CARBOSOL source-apportionment data? They showed that one could use the discrepancy between model and observed levoglucosan to explain the total discrepancy in a convincing way, obtaining a very good time-series.

Abstract

p2505 Line 10. The CARBOSOL project was the first long-term analysis of ^{14}C data. The current data's improvement is to use better time resolution, so it is best to make this clear.

Lines 19 onwards. Include the uncertainties in the numbers given for the different TC components.

Line 21. This line (and elsewhere) refers explicitly to burning of fossil fuels, but what about OC from e.g. evaporative emissions?

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Line 3. There is no proof in this paper that it is just intermediate volatility products that are oxidised. Both volatile and semi-volatile VOC oxidation can lead to OA.

Introduction

p2506. Line 9. Recently is a vague term.

p2506. Lines 11–13. It would be interesting to see references for such a strong statement concerning OA trend in Europe. I am not aware of any good data for this.

p2506. Lines 25–27. Make it clear that the results of Zhang et al. are global. What about European data - there are plenty of AMS results available now.

p2507. Lines 1–3. This sentence is unclear. There are many tracer methods, and many of these do not use chemical profiles (for example, ^{14}C is a common tracer). Kleindienst et al., (2007) used tracers but not really profiles - the latter word is usually associated with CMB type analysis.

Line 9. Why say “seldom verified”? This methodology is fraught with weaknesses, and so “verification” would be impossible.

Lines 14–15. Better to reference here the more pioneering studies of Szidat et al., 2004, Gelencser et al., 2007. Last line. The $^{14}\text{C}/^{12}\text{C}$ ratio also depends on the age of the modern carbon sources. This is explained later, but should be mentioned when this ratio is first introduced.

p2508. QMC is introduced here, but no references are given, which makes it hard for the reader to understand what is being used (I doubt many are familiar with the term QMC).

p2508, lines 20 on - it is stated that the paper introduces uncertainty of two values, the reference fraction of aerosol modern carbon and biomass burning aerosol. This sentence makes no sense at this stage of the manuscript, and is not very clear even after reading the rest.

Methods

p2510, line 8, what do the authors mean with “large enough” to perform tracer analysis. This was not a very scientific criteria.

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p2510, line 17 — ‘the atmospheric stability of levoglucosan was verified’. This is a strong statement, especially given the mounting evidence that levoglucosan can degrade in the atmosphere. A reasonable correlation with K (and just $r^2=0.73$) might imply no more than that the sources are close by. Indeed, a correlation of 0.73 between compounds can be easily found between reactive and non-reactive gases, if subject to similar meteorology and source-areas.

p2511, line 17. CO_2 did not double ‘momentarily’.

p2511, last two lines. As the concept of standards for modern carbon and fM are often confusing, it would be good to make clear here that fM values can exceed one, and explain why.

p2512. The methodology used here follows quite closely that suggested by several other workers, e.g. Szidat et al or Gelencser et al. It would be fair to mention this at the beginning of section 2.4.

p2512, line 21. Why not consider modern carbon emissions in summertime from other sources, e.g. grilling? What about other biofuels?

p2513, line 16. When stating that something is negligible, give a reference.

p2513, lines 18–19. The authors claim that only fungal spores can contribute significantly to non-forested areas. First, what do the authors mean by significant? Puxbaum and Tenze-Kunit found significant contributions from plant-debris in downtown Vienna, and Gelencser et al found between 1–8% contributions across the CARBOSOL sites.

p2513. Why choose the lower bound of 5.2 pg C/spore from Bauer et al.? As the QMC method can look at a range of possibilities, why not specify the range and let QMC work with that?

p2513. It isn’t clear if both mannitol and arabitol are used, and how.

p2514. Why does biomass burning get reduced to bb in fM(bb), whereas non-fossil is

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fully spelled out. Be consistent (and I suggest using the shorter versions in subscripts).

Why do IVOCs get a mention, but not SVOCs? Doesn't POCff as derived from ambient studies also include some oxidized IVOC?

fM(bio) is only known if one assumes zero PBAP.

p2515. I think the authors are basically applying a top-hat distribution to their inputs, between the min and max values. Is that correct?

p2517, line 2 - what is the question mark before Schmid?

Results

p2520. The ratio of OM:OC is too low for the type of ambient sample discussed here. Indeed, later in the manuscript the authors themselves use 1.8, although for some reason using data from Amazonia. Turpin+Lim (2001) is still probably the classic paper on this issue.

p2523. Although the discussion of Fig. 4 is very interesting, it is a stretch to explain the good correlation between SOCbio and POCff only in terms of condensation effects. Meteorology is very good at generating good correlations between parameters. This could be checked by comparing correlation with other (non-carbonaceous) pollutants.

Tables and Figures

Table 2 - add the k1..k4 nomenclature here

Table 3. It isn't clear what is meant by non-null values. If concentrations are measured to be zero (or below the detection limit) then this is a valid observation and methods exist to include these in the averages. As it is, the values given for e.g. OC cannot now be compared with those for levoglucosan or mannitol. Of course, if the authors list all

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their data as suggested above this difficulty is partly removed.

Table 4 should include the uncertainty estimates.

Fig. 1: the lines are hard to see. Maybe thinner lines with different styles would help.

Fig. 4 could be merged with Fig. 6 or even omitted.

References

Hennigan, C. J.; Sullivan, A. P.; Collett, Jr., J. L. & Robinson, A. L. Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals *Geophys. Res. Lett.*, 2010, 37

Kleindienst, T. E.; Jaoui, M.; Lewandowski, M.; Offenberg, J. H.; Lewis, C. W.; Bhave, P. V. & Edney, E. O. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location *Atmos. Environ.*, 2007, 41, 8288–8300

Puxbaum, H. & Tenze-Kunit, M. Size distribution and seasonal variation of atmospheric cellulose *Atmos. Environ.*, 2003, 37, 3693–3699

Simpson, D.; Yttri, K.; Klimont, Z.; Kupiainen, K.; Caseiro, A.; Gelencsér, A.; Pio, C. & Legrand, M. Modeling Carbonaceous Aerosol over Europe. Analysis of the CARBOSOL and EMEP EC/OC campaigns *J. Geophys. Res.*, 2007, 112, D23S14

Turpin, B. J. & Lim, H. J. Species contributions to PM_{2.5} mass concentrations: Revisiting common assumptions for estimating organic mass *Aerosol Sci. Technol.*, 2001, 35, 602–610

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 2503, 2011.