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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain" *by* M. C. Minguillón et al.

M. C. Minguillón et al.

mariacruz.minguillon@idaea.csic.es

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The authors would like to thank Anonymous Referee 2 for his/her comments.

The referee comments followed by our responses are below:

Page 23576 line 16: EC and black carbon are operationally defined and they are not the same thing.

Reply: Text has been modified in the revised manuscript as follows:

"Carbonaceous aerosols comprise a wide variety of organic compounds, collectively referred to as organic matter (OM), elemental carbon (EC), and carbonate mineral dust, [. . .]"

Page 23578 lines 25-29: it should be evidenced that this description refers to typical/ general circulation patterns, which were not often observed during DAURE (as described in section 3.5).

Reply: The different possible atmospheric scenarios are essentially the same in this section and in section 3.5, but they are explained in a different way. Nevertheless, in the revised manuscript, it has been stated that this description is general and does not correspond only to this specific campaign. It now reads as follows:

"[. . .] The WMB presents unique atmospheric dynamics regulated by complex climatic and orographic effects which control the concentration, composition and transport of PM (Millán et al., 1997). In general, in summertime, local circulation dominates the atmospheric dynamics over the WMB, enhancing the regional accumulation of pollutants and the stratification of polluted air masses (Millán et al., 1997). In winter, the inflow of clean Atlantic air masses into the WMB favors the reduction of pollution levels. However, during some periods characterized by winter anticyclonic conditions, pollution from the coast and valleys is accumulated due to thermal inversions persisting for a few days. After several days under anticyclonic conditions local upslope breezes can be driven by solar radiation pushing polluted air masses from the valley towards rural mountainous areas, thereby markedly increasing the PM levels in the rural mountainous areas (Pérez et al., 2008a; Pey et al., 2009, 2010). Specific scenarios during the campaign are described later. [. . .]"

Page 23579 line 25: how did the authors take into account sampling artefacts? Could organic carbon artefacts affect source apportionment based on radiocarbon measurements? Please add a comment in the text.

Reply: We have added the following text to the manuscript (Section 2.1. Sampling) to address this point: "We attempted to minimize artefacts after sampling by keeping the samples at -20°C after sampling and prior to analysis. With the instrumentation deployed during this study it is not possible to estimate the possible sampling artefacts, which are both positive (capture of semivolatile gases in the filter) and negative (evaporation of semivolatile particle species). For quartz filters one might rather expect positive artefacts. Those are however not expected to be very large at high OC loadings. Here we assume that the possible sampling artefacts (evaporated or condensed material) have the same fM as that of the original particle material, i.e we assume that the artefacts do not affect the fM results".

Page 23580 lines 4-5: 7samples x 2 sites in winter and 6 samples x 2 sites in summer are 26 samples in total (not 28 as reported)

Reply: The total number has been changed to 26. We apologize for the confusion, caused by the fact that we used two blank filters in addition to the 26 samples (which then adds 28). In the revised manuscript, we added the explanation of the use of two blank filters processed and analyzed following the same methodology as the collected samples (section 2.1):

"Two blank filters were processed and analyzed following the same methodology as the collected samples and concentrations were subtracted to those found for the samples in order to calculate the ambient concentrations".

Page 23580 line 14: 26 samples

Reply: Replaced.

Page 23581 lines 15-16: was the "standard" 6.6 m2/g absorption coefficient used in the MAAP data? If not, what was the value and how was it determined?

Reply: We did not use the standard absorption coefficient 6.6, which usually corresponds to a wavelength of 880nm. We used absorption coefficients of 9.2 m2 g-1 and 10.4 m2 g-1 for Barcelona and Montseny, respectively, where we used a MAAP instrument operating at 637nm. Determination of these coefficients was carried out by Reche et al. (2011) and Pandolfi et al. (2011). A brief explanation has been added in the revised manuscript (section 2.2) as follows:

"Absorption coefficients used were 10.4 m2 g-1 and 9.2 m2 g-1 for MSY and BCN, respectively (Pandolfi et al., 2011a; Reche et al., 2011)"

Page 23582 line 3: please avoid the citation of reports that are not available to the reader

Reply: We have tried to cite the peer-reviewed literature whenever possible, but in this case the report is the only source of information, so we have kept this citation.

Page 23582 line 19: Does "0.03 of fM OC" mean 3% or is 0.03 an absolute value (as it seems from line 23)? Please clarify in the text

Reply: It is an absolute value. It is now clarified in the text as follows:

"The uncertainty due to this loss of OC can be estimated as 0.03 (absolute value) of fMOC."

Page 23582 line 21: modify the sentence as follows "prior to CO2 collection"

Reply: Modified.

Page 23583 line 1: please avoid citing manuscripts in preparation if they are not at an advanced state of preparation. It is completely useless for the reader and there is no warranty that the paper will be ever published.

Reply: The reference has been removed from the main manuscript and it is only in the supplementary material, where the new EC collection method is explained.

Page 23584 line 14: please add references for the iterative procedure you are referring to.

Reply: It is a simple iterative procedure. An explanation is now included in the manuscript to clarify what the authors meant with it. The text is now as follows:

"An iterative procedure could be used to refine the initial estimates. It would consist of calculating fMnf based on the fractions of biogenic and biomass burning contributions derived from the analysis, and using fMnf to the initial calculations, recalculating the fractions of biogenic and biomass burning contributions, and with those recalculate fMnf, and keep doing so until the recalculated fMnf shows a very small change with respect to the previous iteration one. However the subsequent differences in the results are small, especially compared to the measurement and method uncertainties, and

such a procedure is not used here".

Page 23585 lines 8-9: check the chronological order of the references

Reply: Modified.

Page 23585 line 16: Table S1 can be removed and replaced by giving the range of the values used in this work and adding references. Indeed, the authors use an average value calculated considering only a couple of references. Moreover, even when all values are reported it is not clear which ones were averaged according to the authors' criteria.

Reply: Although we agree that Table S1 is very long and gives information that is not directly used in this paper, the authors prefer to keep Table S1 to illustrate the wide range of values found in literature, which is stated in the text, and to serve as a reference for future studies. In the main text, we specify which references we use (three) and by which criteria they were chosen.

Page 23586 line 5: as in the case of EC-OC measurements, the existence of 4 different datasets produced by different labs and laboratories is quite confounding. In the end, the authors use the average value obtained by lev-HAS and lev-ISAC concentrations. Therefore, the referee suggests simplifying the text reporting only data/information related to these 2 datasets.

Reply: The text has been modified. In the main manuscript, only lev-HAS and lev-ISAC data sets are explained and used. The reader is referred to the Supp. Material

for information on additional levoglucosan data sets. The authors think they should still be included in the Supp. Material since we can not ignore those two additional datasets that exist. The text reads now as follows:

“Levoglucosan was determined using the same filters used for 14C analyses (PM1 48h samples) by two methods: gas chromatography-mass spectrometry (Agilent 6890N gas chromatograph coupled to a mass spectrometer Agilent 5973N) by the Hungarian Academy of Sciences (lev-HAS), and by proton nuclear magnetic resonance (HNMR, Tagliavini et al., 2006) by the Institute of Atmospheric Sciences and Climate of the Italian National Research Council (lev-ISAC). There are two additional data sets of levoglucosan concentrations (Supp. Material Sect. 5 and Fig. S5) measured by different laboratories, but in this work we used the average of the concentrations of lev-HAS and lev-ISAC as they are consistent with each other, and for maximum overlap with the 14C dataset”.

Page 23587 line 2: as suggested before, Table S1 should be removed and replaced by the range of values and appropriate references

Reply: As discussed above, we prefer to keep this table in the Supp. Info.

Page 23590 line 12: in MSY a contribution by wild fires up to 1 μg/m3 corresponds to about one half of the average concentration (about 2 μg/m3 as reported in Figure 1). Should it be considered to have a “low” impact?

Reply: We were estimating a range of contributions in that sentence. During some short events the impacts may not be ’low’, but we expect them to have low impact when integrated over the campaign, based on the output of FLEXPART in Fig. S6 (Fig. S7 in the revised version). We have rephrased this sentence for improve clarity as:

"The higher contributions of ECnf in winter with respect to summer are likely due to higher emissions from residential heating and open burning of agricultural biomass (banned by law from 15 March to 15 October, Spanish Decreto 64/1995), as wildfires are expected to make a low contribution, with the exception of infrequent short impact periods (Fig. S7)."

Page 23592 line 13: the 20% assumption is valid everywhere? Can BCN and MSY be considered “equally” urban?

Reply: The authors decided to assume the same 20% for both sites for two reasons: a) there is no more information/differentiation between urban and rural sites on the references checked; and b) if the urban fossil contribution at MSY is assumed to be transported from BCN or similar source regions in NE Spain, the ‘urban non-fossil’ contribution can be assumed to be transported from BCN as well, and it is reasonable to assume that it will have a proportion fossil/non fossil that is present in BCN, and therefore one can estimate the same % at MSY as for the urban environment. Further data to constrain this paper would indeed be very useful.

Reference section: please check carefully because some references are missing, some are not cited in the text, and others are in the wrong order.

Reply: The reference list has been checked thoroughly and any errors have been corrected.

REFERENCES:

Genberg, J., Hyder, M., Stenström, K., Bergström, R., Simpson, D., Fors, E., Jönsson, J. Å., and Swietlicki, E.: Source apportionment of carbonaceous aerosol in southern Sweden, Atmos. Chem. Phys. Discuss., 11, 13575-13616, doi:10.5194/acpd-11-13575-2011, 2011.

Pandolfi, M., Cusack, M., Alastuey, A., and Querol, X.: Variability of aerosol optical properties in the Western Mediterranean Basin, Atmos. Chem. Phys., 11, 8189-8203, doi:10.5194/acp-11-8189-2011, 2011.

Reche, C., Querol, X., Alastuey, A., Viana, M., Pey, J., Moreno, T., Rodríguez, S., González, Y., Fernández-Camacho, R., de la Rosa, J., Dall'Osto, M., Prévôt, A. S. H., Hueglin, C., Harrison, R. M., and Quincey, P.: New considerations for PM, Black Carbon and particle number concentration for air quality monitoring across different European cities, Atmos. Chem. Phys., 11, 6207-6227, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 23573, 2011.