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Atmospheric
Chemistry
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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.

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The authors would like to thank Anonymous Referee 1 for his/her comments.

The referee comments followed by our responses are below:

**General comments:**

**Comment:** Perhaps the biggest shortcoming of this paper is that it relies very heavily on work that is yet to be submitted, specifically in the works by Zhang, Mohr and Pandolfi that are extensively cited as 'in preparation'. The authors do report the details of the EC collection method in the supplementary material, however it is a little disconcerting that the technique is described as ‘still under development’. I think it would have been preferable to have covered this as a technical section within the main manuscript. However, I won’t go as far as to say its inclusion in this paper is vital for publication because I do not see that the conclusions of this paper rely too heavily on this part of the analysis. Assuming that it is left with the current level of detail in the supplementary material, I should stress that this paper should not, in the future, be used as a technical reference for the technique, as the technical details cannot be said to have passed proper peer-review. By that token, the authors should endeavour to get the Zhang et al. paper published soon.

**Reply:** The paper by Mohr et al. is now published in ACPD and the reference has been updated in the revised manuscript. The paper by Pandolfi et al. is in a very advanced form, and hopefully it will be in ACPD soon. The paper by Zhang et al. is still in preparation, but the information from this paper that is needed for the present manuscript has been included in the supporting material so that the reviewers and editor can evaluate this part of the manuscript. The authors prefer to keep this information in the supporting material and do not move it to the main manuscript in order to keep the main manuscript focused on the results obtained and not the methods used, and since the EC method will be described more extensively in a forthcoming manuscript.

**Comment:** In contrast, the lack of detail regarding the factor analyses does present a more significant issue because unlike the 14C analysis, these results could be subject to change between now and the publication of the Mohr et al. and Pandolfi et al. papers. For this reason, I would consider it important that the key technical details of the factorisations are documented here, specifically the software used, what error estimation and data pretreatment methods were employed and whether any special variables (e.g. FPEAK) were used. It would also be useful (perhaps in the supplementary ma-

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terial) if the authors could report on what basis the solution sets used was selected (in terms of the number of factors and FPEAK, etc.) and whether they were subjected to any tests such as seed variation or bootstrapping. I should note that I am not requesting that this paper becomes the primary reference for these analyses, nor should it preclude the factorisation being modified before the submission of another paper if it is deemed necessary for whatever reason; this is more so that the consistency (or otherwise) with future publications can be verified by the reader.

**Reply:** The paper by Mohr et al. is now published in ACPD. It includes the High Resolution (HR) PMF for BCN, which was not available at the moment of submitting this ACPD manuscript, and which differs slightly from the solution used in this manuscript which was based on PMF of the unit mass resolution (UMR) data. Since the HR PMF version is generally thought to be preferable to the UMR one, in the revised version of this manuscript we use the HR PMF results, and we have updated figures and text when necessary. The details on the HR PMF results can now be found in the Mohr et al. paper, so the reader is referred to this paper and the details are not included in the manuscript.

For MSY, the PMF details are not published yet, so we have added the following text to explain briefly the application of PMF to the MSY dataset:

“For MSY, PMF was performed on the organic m/z vs. time matrix using the PMF2.exe program and analyzed with the PMF Evaluation Tool (PET, http://tinyurl.com/PMF-guide) according to the procedures described on Ulbrich et al. (2009). 771 resolvable ions were fitted in the high-resolution analysis software, PIKA, for m/z 10-206, and were used in the PMF analysis. An 8-factor solution (FPEAK=0) was used since this was the lowest number of factors at which the HOA and BBOA factors showed a clear separation from each other and from OOA. Six factors were recombined to make up the OOA factor. The BBOA and HOA factors used here are those from the 8-factor solution. More details can be found in the Supp. Material (Sect. S6).”

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A more detailed description has been added in the supplementary material (Sect. S6):

"Positive Matrix Factorization (PMF) was performed on the organic m/z vs. time matrix using the PMF2.exe program and analyzed with the PMF Evaluation Tool (PET, http://tinyurl.com/PMF-guide) according to the procedures described on Ulbrich et al. (2009). 771 resolvable ions were fitted in the high-resolution analysis software, PIKA, for m/z 10-206, and were used in the PMF analysis. Solutions with p = 1 to 12 factors were computed. Rotational parameters (FPEAK) values between -1 and 1 were explored. An 8-factor solution (FPEAK=0) was used since this was the lowest number of factors at which the HOA and BBOA factors showed a clear separation from each other and from OOA. FPEAK=0 was used because this solution yielded the lowest Q value and the factor spectra were very similar for other FPEAK values. Six factors were recombined to make up the OOA factor since separately some of the factor spectra were not meaningful, the time series of some factor pairs had very high correlation, and other factor pairs showed signs of intermittent splitting, with one nearly disappearing when the other one appeared. No clear interpretation of the OOA subfactors was possible, as is sometimes the case in rural / remote datasets (Jimenez et al., 2009). The BBOA and HOA factors used here are those from the 8-factor solution. On average, OOA comprised 86% of the organic mass with BBOA and HOA comprising 10% and 4%, respectively. Oxygen-to-carbon (hydrogen-to-carbon) ratios for BBOA, HOA, and OOA were 0.29 (1.49), 0.09 (1.83), and 0.67 (1.37), respectively, which are consistent with other studies (e.g. Aiken et al., 2008). BBOA showed moderate to strong correlation with levoglucosan, black carbon, and total particle concentrations. HOA showed strong correlation with black carbon and total particle concentrations and moderate correlation with NOx. The OOA factor showed correlations with black carbon and the secondary inorganic species (sulfate, nitrate, ammonium). These correlations are mostly consistent with factor identifications in other studies (Zhang et al., 2011, and references therein)."

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**Specific comments:**

**Page 23581, line 20:** More details should be provided on the discrepancy between the AMS and OC measurements, as the lack of agreement could undermine the comparisons presented later in the paper. Looking at the graph in the supplementary material, the difference appears to be systematic, so this is not simply a signal-to-noise issue. The magnitude of the discrepancy and the modifications to the AMS should be stated explicitly. Could a collection efficiency issue be responsible?

**Reply:** The discrepancy is now smaller in the revised version, when applying the OM/OC ratios determined experimentally for BCN using the high-resolution mass spectra (Mohr et al., 2011), instead of using the estimated ones (that we used before because the experimental ones were not available yet). The difference between OC concentrations measured by AMS and OC concentrations measured by thermal-optical techniques are mostly within the uncertainties of the measurements, which are typically +/-35% for the AMS and often a similar level (when potential positive and negative artefacts are accounted for) for the thermal-optical instruments. The details of the settings for the AMS deployed in BCN can be found in Mohr et al. (2011). Regarding the collection efficiency (CE), it was dependent on the nitrate fraction fNO3 (e.g. Middlebrook et al., 2011), with CE=0.5 for fNO3 $\leq$0.25, CE=1 for fNO3 $\geq$0.78 and a linear increase of CE between these values for 0.25$\leq$fNO3 $\leq$0.78 (Mohr et al., 2011).

**Page 23581:** How did the assumed OM/OC values for BCN compare with the measured values for MSY?

**Reply:** The measured OM/OC values are now available for BCN, so in the revised version of this manuscript we use this measured OM/OC values instead of the values estimated from the previous literature. On average, OM/OC ratio at BCN was 1.6 and OM/OC ratio at MSY was 2.0. Regarding the specific OM/OC ratios for different OA

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components, they are very similar: 1.29 at MSY and 1.21 at BCN for HOA; 1.52 at MSY and 1.53 at BCN for BBOA; 2.04 at MSY for OOA and 1.61 (SV-OOA) and 2.14 (LV-OOA) at BCN. This information is included in the revised version as follows:

“[. . .] The calculations were done using OM/OC ratios determined by high-resolution analysis of the AMS mass spectra. On average, OM/OC ratio was 1.6 at BCN and 2.0 at MSY. The specific OM/OC ratios for different OA components were very similar: 1.29 at MSY and 1.21 at BCN for HOA; 1.52 at MSY and 1.53 at BCN for BBOA; 2.04 at MSY for OOA and 1.61 (SV-OOA) and 2.14 (LV-OOA) at BCN”.

**Technical comments:**

**Page 23576, line 16:** EC and BC aren’t technically the same thing, as they are both operationally-defined metrics

**Reply:** Text has been modified in the revised manuscript. It now reads 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 23577, first paragraph:** The statement on the most important sources of carbonaceous aerosols should be backed up by a reference.

**Reply:** Text has been modified and references included as follows:

“Known sources of carbonaceous aerosols are biomass, biofuel, and waste burning, residential heating, cooking, fossil-fuel combustion (including road traffic emissions), and biogenic emissions (Hildemann et al., 1994; Schauer et al., 1996)”.

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**Page 23578, line 10:** Recommend rephrasing as, “the difference between summer and winter”.

**Reply:** Text has been modified accordingly.

**Page 23579:** How far apart were the two sites?

**Reply:** The two sites are 50 km apart. Information has been added in the revised manuscript as follows:

“[. . .] and Montseny (MSY), a forested regional background site 50 km away from Barcelona [. . .]”

**Section S1:** “Theoretical T” seems an odd choice of words. Referring to it as the “setpoint” would be more conventional.

**Reply:** ”Theoretical T” has been replaced by “set T” in the revised manuscript.

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

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