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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.

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The authors would like to thank Anonymous Referee #3 for his/her comments.

The referee comments followed by our responses are below:

1. The authors introduced highly uncertain parameters (particularly, (1a) and (1b)) for the source apportionment of EC and OC from literatures (e.g., Hildermann and Hodzic) without discussing uncertainties. (1a) OC_urb/(OC_f+OC_urb) ratio (0.2, p.23592): This ratio affects OC_bio, and thus, assumption of this value is critical in the conclusion

about the OC_bio ratio between summer and winter. (1b) HOC_f/HOC ratio (0.8, p. 23594): This ratio affects OC_f/OC_nf ratio, and assumption of this value is critical in the conclusion about the ratio of primary-to-secondary fossil OC. As accuracy of these parameters are critical in deriving conclusions of this study, the reviewer recommends the authors to assess uncertainties in these parameters (or at least mention that the conclusions may change when these parameters change).

Reply (1a): It is true that OC_urb/(OC_f+OC_urb) ratio affects OCbio. An estimation of how much it affects OCbio has been carried out. Taking as a reference the OCbio contributions calculated with OC_urb/(OC_f+OC_urb) ratio of 0.2, varying the OC_urb/(OC_f+OC_urb) to 0.1 implies an increase in the OCbio contributions of 6-28% (relative to the values with the default assumption), whereas using OC_urb/(OC_f+OC_urb)=0.3 implies a decrease in the OCbio relative contributions of 8-37%. Regarding the summer/winter ratios, a OC_urb/(OC_f+OC_urb) ratio of 0.2 implies OCbio summer/winter ratios of 0.47 and 1.43 at BCN and MSY, respectively. A ratio of 0.1 implies OCbio summer/winter ratios of 0.51 and 1.37 at BCN and MSY, respectively. A ratio of 0.3 implies OCbio summer/winter ratios of 0.39 and 1.52 at BCN and MSY, respectively. Therefore, the conclusions regarding OCbio do not change significantly even if the assumed OC_urb/(OC_f+OC_urb) ratio varies from 0.1 to 0.3.

Information about this sensitivity test is now included in section 3.4 of the manuscript as follows:

"[. . .] A sensitivity test was carried out to check the changes that would imply an assumption of OCurb-nf/(OCf + OCurb-nf) of 10% or 30%, instead of the aforementioned 20%. The OCurb-nf contribution changes by 56-71%, although in absolute concentration the change is very low. [. . .] The same sensitivity test showed that OCbio contribution changes by 6-37%, when changing the OCurb-nf/(OCf + OCurb-nf ratio from 20% to 10-30%, with the main conclusions remaining the same. [. . .]"

Reply (1b): This HOC_f/HOC ratio is only used for MSY. An estimation of how much

it affects the primary-to-secondary fossil OC has been carried out. With the current 0.8 ratio, we conclude that 85% of fossil OC at MSY is secondary. This percentage varies from 87% to 83% if the HOC_f/HOC ratio varies from 0.7 to 0.9. Concerning the percentage of non-fossil secondary OC, now we conclude that 70% of the OOC at MSY is non-fossil. This percentage varies from 69% to 71% if the HOC_f/HOC ratio varies from 0.7 to 0.9. Therefore, the conclusions about the percentage of secondary fossil OC and the non-fossil OC at MSY do not change even if this 0.8 ratio changes.

Information about this sensitivity test is now included in section 3.6 of the manuscript as follows:

"[. . .] These conclusions remain the same if the aforementioned assumed 80% fossil origin of HOC changes from 70% to 90%".

2. The authors concluded that PMF-OF is less accurate than the other techniques for the source apportionment of biomass burning OC (p. 23596), while the authors did not show the basic information of the PMF-OF. Results of PMF-OF are expected to change depending on species selection, interpretation of factor profiles, number of factors, and other conditions. As Pandolfi et al. is not available at the moment, the authors should briefly explain these points, so that readers can judge the validity of the conclusion of this analysis. In particular, it is highly required to show a factor profile of biomass burning, so that the readers can obtain information of the key species of this source estimate.

Reply: A factor profile is now shown in the supplementary material (new Fig. S6), and the reader is referred to it when explaining the PMF-OF methods and results. Moreover, the text has been modified in section 2.5, including some additional information. It now reads as follows:

"The third method used to estimate the biomass burning contribution is based on receptor modeling of offline filter PM1 data. The offline dataset is discussed in detail elsewhere (Pandolfi et al., 2011b). Briefly, 12h PM1 samples were collected on quartz

fiber filters (Munktell) using DIGITEL DHA-80 high volume (30 m3/h) samplers. Major and trace elements, some ions, and nitrate, sulfate, ammonium and chloride concentrations were determined following the procedure described in Querol et al. (2001). OC and EC concentrations were measured by a Sunset laboratory instrument (results intercompared in section 2.2, reported as Sunset2). Positive Matrix Factorization (PMF by means of the ME-2 scripting; Paatero, 1999; Amato et al., 2009) was applied to this dataset. Species included in the PMF can be found in Fig. S6. Results are referred to in this study as PMF-OF (OF standing for offline filter dataset). Details on the receptor model and individual uncertainties are available in Amato et al., (2009). This method provides, among other data products, an estimate of the biomass burning contribution to bulk submicron OC. Nevertheless, the model was not able to identify the biomass burning source in BCN, as explained in Section 3.7. At MSY, the solution chosen had 6 factors (mineral, anthropogenic, sea salt, biomass burning, secondary sulfate, and secondary nitrate). Source profile of the biomass burning source can be found in Fig. S6."

3. As 14C measurement uncertainty is important in this analysis, the reviewer requires the authors to clearly show overall uncertainty of 14C measurement and brief description about its derivation. Recently, it was shown that blank 14C may largely affect accuracy of 14C measurement (e.g., Fushimi et al., EST, 45, 6784-6792, 2011). Description about the treatment of blank 14C is also recommended.

Reply: We used two blank filters, processed and analyzed in the same way as the rest of the samples. The following text was added in section 2.1 (Methodology, Sampling) of the revised manuscript:

"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".

The blank concentrations were quite low compared to the samples concentrations. This

information is now included in the manuscript in section 2.2 as follows:

"[. . .] Blank OC concentrations were 4-23% (11% on average) of the samples concentrations and blank EC concentrations were below 0.1% of the samples concentrations. [. . .]"

Moreover, in the end of the section 2.3, when explaining the 14C measurements, we added an explanation of how fM uncertainties were calculated and report average values. The text is as follows:

"After the separation and collection of OC and EC as CO2 samples, 14C analyses were performed at ETH Zurich with the Accelerator Mass Spectrometer MICADAS using a gas ion source (Ruff et al., 2007, 2010). The fM for each sample was then blank subtracted using an average of the fM of the two blank filters analyzed, and taking into account the amount of C analyzed in each sample and in the blank filters. fM measurement uncertainty was calculated based on the Accelerator Mass Spectrometer sample and blank uncertainties and the amounts of C analyzed. On average, fMOC measurement uncertainty was 2.4% and 4% of the corresponding fMOC for winter and summer, respectively; and fMEC measurement uncertainty was 6% and 28% of the corresponding fMEC for winter and summer, respectively".

4. p. 23590, l. 20: Temperature is not the only key factor of biogenic VOC emissions. How about the differences in vegetation between Spain and Goteborg/Zurich? Are biogenic VOC emissions surely higher in the northeastern Spain than in the southwestern Sweden or Switzerland in winter? Figure 5 in Guenther et al. (ACP, 6, 3181–3210, 2006) shows that isoprene emissions are not necessarily higher in the northeastern Spain than in the southwestern Sweden or Switzerland in winter. What about monoterpene?

Reply: The reviewer's point is well taken. Fig. 5 in Guenther et al. (ACP, 6, 3181-3210, 2006), in March, shows similar emissions in Spain and Switzerland or southern Sweden. But this figure is supposed to be showing the variations of isoprene emissions

depending on Leaf Area Index (LAI) and leaf age with all other model drivers held constant (which includes temperature and light). So, the emissions would be similar if the rest of the parameters are the same for all the territory, but since temperature and light levels are higher in Spain than in Northern Europe in March and emissions have an exponential dependence on temperature and also an increase with light levels, then the isoprene emissions would be expected to be substantially higher in Spain. In Fig. 10 of the Guenther et al. paper, the estimated isoprene emissions (now without holding any parameter constant) are <2 mg/m2/day both in Spain and North Europe, which would be supporting the reviewers' point, but even if being <2 mg/m2/day, they would still be expected to be higher in southern European areas.

Keenan et al. (ACP, 9, 4053-4076, 2009) show also similar annual isoprene emissions (Fig. 6) in the mentioned areas (Northeast Spain, Switzerland, South Sweden); but the monoterpene emissions (Fig. 7) seem to be higher in the Spanish area. Although these are annual means, and therefore they do not differentiate for a specific time of the year, the warmer temperatures and higher light levels in winter in north-eastern Spain make highly likely to find higher emissions there than in south-western Sweden or Switzerland also in winter (see temperature response algorithm in Guenther et al., 2006).

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