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Interactive comment on "Primary sources of PM$_{2.5}$ organic aerosol in an industrial Mediterranean city, Marseille" *by* I. El Haddad et al.

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First we want to thank reviewer 1 for raising these relevant comments and questions. We appreciate so much his detailed review that helped us improving the readability of the manuscript. As suggested by the reviewer, the manuscript was shortened (comments #7, 17, 19, 42, 44, 45, 46, 47 and 54) and its structure was heavily reorganized (comments #6, 20, 25, 27, 30, 34 and 40). Now, the manuscript includes 4 sections: Introduction, Methods, CMB setup, Results and discussions.

Minor corrections/comments regarding spelling mistakes and phrase structures (comments # 8-14, 16, 18, 21-24, 28, 33, 39, 41, 43, 48, 50, 51, 58, 61, 66 and 70) were also taken into consideration. In the corrected manuscript, further important references proposed by the reviewer (comments #4, 15, 26, 32, 36, 53 and 65) were added and

the results found here were compared with those reported for similar environments (comments #5 and 65). Finally, contribution from shipping emissions was mentioned separately (comments # 3 and 67-69), as recommended by the reviewer.

Below are our responses on the points raised by the reviewer.

Response for comment #1, 49, 59 and 60 – Distinction between LDV and HDV:

Reviewer 1 have proposed that we provide a distinction between light-duty and heavy-duty vehicles (LDV vs. HDV) by including two corresponding profiles in the CMB, instead of one profile representative of an overall French fleet as we did. Even though, this distinction might be, theoretically, useful, in practice it is not possible in our case.

In order to apportion two different sources by CMB their profiles have to be statistically different, otherwise the model cannot converge (Watson et al., 1998;Subramanian et al., 2007). With respect to vehicular emission profiles, the main differences are observed between emissions from diesel vehicles and gasoline vehicles (Rogge et al., 1993a;Subramanian et al., 2006). In the US, the majority of the on-road fleet is attributed to light-duty vehicles, which are fuelled almost entirely by gasoline; the remainder is heavy-duty (or medium duty) diesel trucks (Gertler, 2005). This net separation renders possible the distinction between LDV (gasoline) and HDV (diesel) using CMB modeling, as the emission profiles of the two types of vehicles is statistically different (Fraser et al., 2003;Subramanian et al., 2006).

In contrast, in our case, light-duty diesel powered vehicles constitute the half of the French light-duty vehicular fleet. Owing to their higher emission rates, the emissions from this vehicle type dominate the overall PM from LDV (El Haddad et al., 2009). As a result, in our case the LDV profile, determined in the tunnel of Marseille, is thoroughly similar to emission profiles from heavy-duty diesel trucks determined by chassis dynamometer studies (Rogge et al., 1993a;Schauer et al., 1999;El Haddad et al., 2009), which can be noticed from the hopanes-to-EC ratios in our case (white square, Fig. 10) that compares with those of diesel emissions (black diamond, Fig. 10). These similarities make the distinction between LDV and HDV impossible by the CMB, in our case.

Response for comment #2 and 32 – Natural gas combustion:

Reviewer 1 wonders why emission from natural gas combustion is included as a source profile in CMB, but it is not in the results. We have included the profile representative of these emissions (Rogge et al., 1993b), but their contributions computed by CMB were not significantly different from 0. More details regarding this source have been provided in the results section of the corrected manuscript.

Response for comment #29 – 2 factors PCA:

Remark/question #29 states: *"Only 2 factors were identified in the PCA? Was it forced to 2 factors? Please explain."*

The number of principal components is not fixed. Here, we have reported only the first two factors (F1 and F2) that explain 70% of the total variance and that provide information regarding the sources of these markers. The third factor (F3) accounts for only 10.2% of the variability and does not show any relevant correlation with the marker concentrations, at least for our applications.

Response for comment 38 and 52 – Missing sources of PAH and OC:

The questions of the reviewer regarding Missing sources of PAH and OC were:

#38: *"PAH can not be secondary? The fact that there is unaccounted PAH is not enough to say there are missing primary sources"*

#52: *"with PAHs, the authors say that it is because of additional primary sources not included in the CMB, now the un-apportioned OC is due to SOA. Why?"*

In the traditional meaning of secondary organic aerosol (ie: formed in situ in the atmosphere through oxidation processes), PAH are not secondary compounds. In CMB modeling, which apportions exclusively primary sources, all included markers have to be of primary origins. In addition, all the major sources of the included markers have to be well known and considered in the model (Schauer et al., 1996;Watson et al., 1998); otherwise the model will not be able to explain correctly the observed concentrations of these markers (calculated-to-measured«1). In the case of PAH, emitted strictly from combustion sources, when industrial profiles were not included, the CMB was not able to explain the concentrations of these markers indicating that these primary emissions have to be included.

Now, with respect to the OC that can be of primary (POA) or secondary (SOA) origins, CMB can only provide a direct estimation of the contributions of specific primary sources to the OC. However, it is also possible to infer a global SOC mass, considered as the mass of OC that is not attributed to the included primary sources (see for example (Schauer et al., 1996;Subramanian et al., 2007)).

Response for comment 55 – 14C/12C conversion factor:

We are aware that the choice of 14C/12C conversion factor to calculate the fraction of non-fossil carbon is not straightforward and may influence the results. This factor is dependent on the age of the emitting plants, as biomass photosynthesized 30, 20, 10, and 0 years before the FORMES study in 2008 would have a factor of 1.35, 1.18, 1.11, and 1.05, respectively (Levin et al., 2010). As a result, biogenic emissions have the current 14C/12C ratio of about 1.05, but the ratio for biomass burning is significantly higher (burned woods are more aged), which complicates the choice of this ratio. However, as biomass burning constitute in our case a minor source, the isotopic signal of the collected organic aerosol is expected to have a ratio close to the current ratio. Here, we have chosen the low value of 1.1 for this ratio, a value that is usually used in source apportionment studies using 14C data (Zheng et al., 2006;Ding et al., 2008). More clarifications regarding this choice and associated uncertainties are added in the corrected manuscript.

Response for comment #56 – comparison between CMB non-fossil TC and total non-fossil TC:

In this paper, we have used the comparison between total fossil TC and CMB fossil TC, to validate CMB outputs for fossil sources (vehicular + industrial) that constitute the major primary sources considered in the model. The comparison between CMB non-fossil TC and total non-fossil TC is performed implicitly in the companion paper to infer that secondary organic carbon is predominantly of biogenic non fossil origins.

Response 1 for comment #63 – Phthalates and primary biogenic organic aerosol (PBOA):

In this study, we have highlighted the contribution from plasticizers through the study of phthalate esters levels and temporal trends. However, we were not able to apportion the contribution of the total plasticizers to the organic aerosol, as there are no available profiles for this source (expressed as) in the literature. It should be noted though that the phthalates that we have quantified here represent the major plasticizers used (Staples et al., 1997). Hence, the contribution from total plasticizers is expected to be almost equal to the concentration of phthalate esters.

In the same consideration, although we have quantified sugar derivatives, characteristic markers of PBOA, we were not able to provide a quantitative estimation of the contribution of the total PBOA to organic aerosol, as there is a paucity of profiles in literature. Nevertheless, comparing concentrations of these markers observed here with those reported in other studies (Yttri et al., 2007;Kourtchev et al., 2008;Jia et al., 2010) reveals that our concentrations are by a factor of 10 lower, suggesting little contribution from the total PBOA to organic aerosol, in our case.

Response 2 for comment #63 – OM-to-OC ratios:

The reviewer have pointed out that the ratio of OM-to-OC of 1.67 used here was based on PM1 measurements, which may not reflect our PM2.5 data. Indeed, this can be another source of uncertainties. However, it should be noted that in average more than 80% of the PM2.5 OA are comprised in the PM1 fraction (see LPI data figure 1). Accordingly, as the majority of PM2.5 OA is comprised in the PM1 fraction, it can be expected that PM1 OM-to-OC ratio is roughly the same as the ratio for PM2.5. In our opinion, this is our best estimate for the OM-to-OC ratio.

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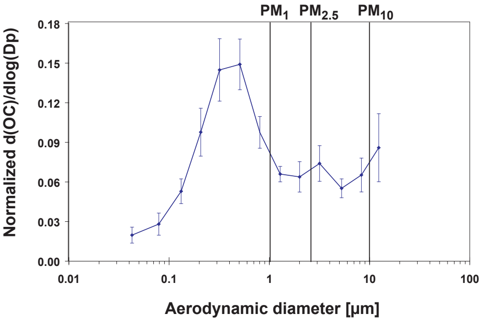

Fig. 1. Averaged OC size-distributions (obtained from the 24-h LPI measurements)