

Interactive comment on “Chemical characterization of submicron regional background aerosols in the Western Mediterranean using an Aerosol Chemical Speciation Monitor” by M. C. Minguillón et al.

Anonymous Referee #1

Received and published: 5 February 2015

The manuscript of Minguillón et al. represents the results obtained by using an Aerosol Chemical Speciation Monitor over a one-year period in a regional background station of the Western Mediterranean (Montseny, Spain). The mass concentrations of submicron organics, sulphate, ammonium, nitrate and chloride obtained by the ACSM are compared to concurrent off-line PM₁ chemical (for inorganics) and thermal-optical (for organic carbon) analysis of filters. The sum of the ACSM components, using a time-dependent collection efficiency instead of the widely used constant 0.5, together with black carbon correlated well with PM₁ concentrations determined by an optical particle

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counter. Nevertheless discrepancies were observed, mainly for organics, which was attributed to an underestimation of the relative ionization efficiency of the organic aerosol (OA). The importance of these discrepancies become more important if one considers the fact that the OA was found to be the major constituent of the submicron aerosol throughout the year. The source apportionment of the OA, using the ME-2 toolkit within the Positive Matrix Factorization analysis environment, revealed three major sources both during summertime and during wintertime, as well. During summer the main OA identified were hydrocarbon-like OA (HOA), and two oxygenated OA; one semi-volatile (SV-OOA) and one of low volatility (LV-OOA). During winter again an HOA was identified, together with a biomass burning OA (BBOA) and oxygenated OA (OOA), while the two different OOA components that were identified during summer could not be resolved. Finally, focusing on an intense wildfire episode close to the measurement site, a BBOA profile was identified, which was found to be very similar to BBOA profiles formerly identified in former studies at the same site, establishing a region-specific BBOA_MSY mass spectrum.

The paper is well written and easy to follow, though there are several details missing and more thorough discussion should be made in specific sections. Other than that the paper can be recommended for publication after addressing the issues listed below.

Specific comments:

1) One of the main features of the manuscript that the authors draw our attention to is the comparison of the ACSM data with collocated off-line PM₁ measurements and with total PM₁ measured by an optical particle counter. Nevertheless it is clearly stated that the OPC is corrected with the simultaneous 24h gravimetric measurements, but there is no mentioning of why the gravimetric measurements are believed to be the reference. Quartz filters are known to absorb water and volatile organics, depending on the sampling protocol (preheated filters or not). I assume that, as no preheating of the filters is mentioned, there was none, but still, with the high RHs that can be seen in Figure S2, how is it guaranteed that the filters do not contain significant amounts of

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humidity from the sampling? Apart from the Quartz filters, are there also any Teflon filters, which are not expected to absorb neither water nor volatiles, collected in order to compare? Furthermore, I would expect a significant daily variability in the 30-min ACSM measurements that, for sure, cannot be captured in the 24h filters. Therefore, how is this correction made? Finally, in Cusack et al. (2013) it is mentioned that a Scanning Mobility Particle Sizer (SMPS) is also located in the Montseny Station; were the PM1 concentrations (ACSM+BC) compared to the mass estimated using the SMPS volume?

2) It is mentioned in the manuscript that instead of a constant, collection efficiency (CE) of 0.5, a time-dependent CE is used, following the approach of Middlebrook et al. (2012). In the cited paper, an algorithm is developed in order to calculate composition-dependent CE values, in order to account for acidic sulfate particles, aerosol containing a high mass fraction of ammonium nitrate and high organic fraction from biomass burning emissions. In the current manuscript there is no mention of the aerosol acidity, biomass burning emissions appear to be limited and also nitrate concentrations seem to have a maximum contribution (around 20%) during winter. It would be helpful if the authors provided, even in the supplementary material, a figure that shows if and how much the used time-dependent CE deviated from the constant 0.5, especially if there is a seasonal variability observed.

3) The claim that the second identified factor by the PMF analysis, during the wildfire episode, is and Aged BBOA, clearly needs a better reasoning and a more thorough discussion. The mass spectrum is very similar with common OOA found in the literature and no correlations are given with external tracers, such as black carbon, to support this assumption. Furthermore, why should that OOA factor have only one source origin and not be, partially, a pre-existing, background OOA that, clearly from the time series, may be also the end product of atmospheric transformation of BBOA, as well? What do their diurnal variability look like, is it similar? My greatest concern is the nomenclature, solely stating it as "Aged BBOA".

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4) I would have expected, even in the supplementary material, a more thorough discussion on the selected PMF solutions; stability of the solution, residuals, correlations with external tracers, possibly a more detailed comparison with external mass spectra (e.g. squared Pearson coefficients).

Technical corrections:

P967, L6: Carbonaceous aerosols are comprised of. . .

P968, L21: . . . was estimated to be (instead of "estimated in")

P970, L2: . . . the Azores, highly favors. . . (instead of "high")

P975, L5: It is not clear whether the comparisons are made before or after the ACSM components concentrations are calculated using the time-dependent collection efficiency or from the raw data. Because, how can it be that slope between the sum of the ACSM+BC is very close to unity compared to the PM1 concentrations from the OPC (which is corrected with the 24h gravimetric measurements) but ammonium from the ACSM is almost double, nitrate is 2.8 times higher and organic matter is 4.25 times higher than the OC from the filters?

P975, L12: It is stated that the slopes of sulphate and ammonium are relatively close to unity. For sulphate this may be the case (1.15) but for ammonium, I wouldn't call 1.72 close to unity, as it is closer to be the double.

P975, L20-25: Based on Aiken et al. (Environ. Sci. Technol. 42, 4478-4485, 2008) an estimate is proposed in order to calculate the OM-to-OC ratio base on the f44. Was this estimate used in order to see whether it compares to the slope obtained? Even though indeed, SOA is expected to have a high contribution at Montseny, I wouldn't expect a conversion factor for OC to OM higher than 2.2-2.4.

P977, L20: . . . due to shipping emissions (delete "the")

P981, L15-16: Apart from the MAAP, is there an aethalometer available at Montseny

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station, in order to get and estimate on BC source apportionment? I would expect correlations with BC from fossil fuel and/or BC from wood burning to be higher.

Figure S6: What is the difference between the two diagrams in the bottom? Because all axes and annotations are the same. From what I gather, the panel in the left seems to be the so-called Aged BBOA and not the BBOA.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 965, 2015.