Source apportionment of Organic Aerosol in a remote Mediterranean using a combination of offline and online approaches

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Organic Aerosol (OA) phenomenology comprises multiple processes from primary emissions and secondary formation towards atmospheric removal. Southern Europe displays elevated concentrations of aerosols, mostly secondary in origin and strongly enhanced during the warm season. Due to the high oxidation state of OA in such environment sources are still largely unknown. An intensive field campaign has been carried out in summer 2013 in the regional background site of "Cap Es Pinar" (Mallorca, Spain) within the framework of SAF-MED and ChArMEx actions. Highly time-resolved online measurements of particle composition were performed using an Aerosol Mass Spectrometer (HR-ToF-AMS) combined with daily collection of PM_1 and PM_{10} samples for further analysis (OC/EC, major ions, major and trace elements), from the 3rd of July to the 12th of August (Pey et al. 2014).

Source apportionment was carried out with a ME-2 approach finder (SoFi toolkit, Canonaco et al. 2013) on both off-line and on-line measurements.

Results and Methodology

OA was the most abundant component of the PM_{10} and PM_1 fractions (3.4 μgm^{-3} and 3.0 μgm^{-3} respectively) representing 26 and 40% of the PM mass, respectively.

Source Apportionment Solutions:

PM_1 24h filter collections: a 4-factor solution emerged as the most appropriate. Among these 4 factors, one is clearly from natural origin, here named "earthbound" (EB). It is characterized by Al_2O_3, Fe, Ti and other mineral species, but also marine species Na, Mg. Another one, probably natural in origin but with a more regional nature, has been called "regional earthbound" (REG EB), as it relates mainly to Ca, consistent with the island's soil composition, and also to sea salt aerosol. Two anthropogenic factors were obtained; "Anthropogenic" (ANT), characterized by EC, SO_4^{2-}, and "Regional Anthropogenic" (REG ANT), as it contains part of Ca

OA is distributed among all the factors, with the highest abundance in the ANT factor (1.26 μgm^{-3}), closely followed by REG ANT (1.16 μgm^{-3}) and with less abundance in the EB factor (0.20 μgm^{-3}). It is negligible in REG EB (0.07 μgm^{-3}).

Regarding AMS, ME-2 was applied to the entire mass spectra (organic and inorganic ions). Again a 4 factors solution was obtained (DeWitt et al. 2014): a Semi volatile Oxygenated Organic Aerosol fraction (SVOOA) (0.54 μgm^{-3}), a Low Volatile Oxygenated Organic Aerosol (LVOOA) (1.46 μgm^{-3}) fraction, another Oxygenated Organic Aerosol fraction that was strongly associated with sulphate and MSA characteristic ion (SO4_OOA) (0.62 μgm^{-3}), and an Ammonium Sulphate fraction (AS) (0.47 μgm^{-3}).

Multiple Regression Analysis (MRA):

In order to combine online and offline source apportionment solutions for OA, different statistical approaches were employed. MRA was considered to provide the best solution in terms of how AMS-OA factors were distributed among PM_1-OA's. OA concentration for every PM_1 factor was taken as the dependent variable, and AMS-OA results were considered as independent variables. MRA was applied to each individual OA factor time series. Negative factors were considered to have zero contribution. Finally, the extracted coefficients were normalized to sum 1. Results are shown in Table 1.

%	OA EB	OA REG EB	OA ANT	OA REG ANT
SVOOA	30	23	18	12
LVOOA	19	0	56	44
SO4_OOA	51	64	26	0
AS	0	13	0	44

Table 1. AMS-OA contained in PM_1-24h OA.

In our case, the original combination of methods helps to clarify OA origins in terms of local or regional sources.

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