



CityZen

megaCITY - Zoom for the Environment

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Identification of OM sources (primary and secondary components)

by NMR

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Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

Identification of OM sources (primary and secondary components) by NMR

Sampling

The data considered for these deliverable have been obtained from measurement campaigns carried out during various observing periods both in the city of Bologna and at the nearby station of San Pietro Capofiume (SPC). The SPC station is located in a flat rural area far about 40Km from Bologna, nevertheless due to the overall pollution level characterizing the Po Valley region it can be assumed that it had SOA concentrations comparable to those observed in the city of Bologna.

Atmospheric aerosols in the PM₁₀ and in the PM_{1,5} fractions have been collected on quartz-fiber filters during both warm season (spring/summer) and cold season (fall/winter), and analyzed off-line with the following methodology (tab. 1).

Table 1. Sampling periods

	SPC	Bologna
PM _{1,5}	Fall/winter (1998, 1999, 2003)	Fall/winter (2000)
	Spring (1998, 2008)	-
	Summer (1998)	-
PM ₁₀	-	Fall/winter (2003)
	Spring (2003, 2004, 2007)	Spring (2003, 2006)
	Summer (2007)	Summer (2005, 2006)

Methodology

After collection the filter samples were extracted in water and a large part of each water extract was subsequently devoted to functional group characterization by proton-Nuclear Magnetic Resonance (¹H-NMR) spectroscopy according to the following protocol:

a) evaporation of the water extract under vacuum, b) recovery of the dried extract with deuterium oxide (D₂O) and addition of TSP-d (*) as internal standard, c) ¹H-NMR spectrum acquired at 400 MHz using a Varian Mercury spectrometer.

Note that the water-insoluble fraction was not analyzed, therefore results refer exclusively to the water-soluble fraction of the samples. Since primary organics (POA) linked to traffic emissions are expected to be mostly insoluble in water, they should not contribute to the resulted functional groups compositions because these refer exclusively to the water-soluble aerosol organics.

(*) TSP-d: 3-(trimethylsilyl)-propionic-d₄ acid

Results and discussion

¹HNMR spectroscopy has been deployed to characterize the functional groups distributions of the aerosol water-soluble organic compounds with the aim of source attribution.

Functional groups compositions of all the collected samples have been calculated by the integration of the corresponding bands in the ¹HNMR spectra.

Source attribution of the aerosol water-soluble organic fraction has been obtained applying the method developed in the study of Decesari et al. (2007).

Basically this method allows to distinguish samples on the basis of their different functional groups patterns by means of two indexes describing their aliphatic functional groups composition: i.e. the fraction of aliphatic carbon accounted for by hydroxyl groups (H-C-O/ sum aliphatics) and the fraction of aliphatic carbon accounted for by carbonyls/carboxyls groups (H-C-C=O/ sum aliphatics). A third index is used to express the ratio of aromatic moieties to total aliphatic groups.

The functional groups distributions resulted applying this method to the analyzed set of samples are plotted in the following figure (fig.1).

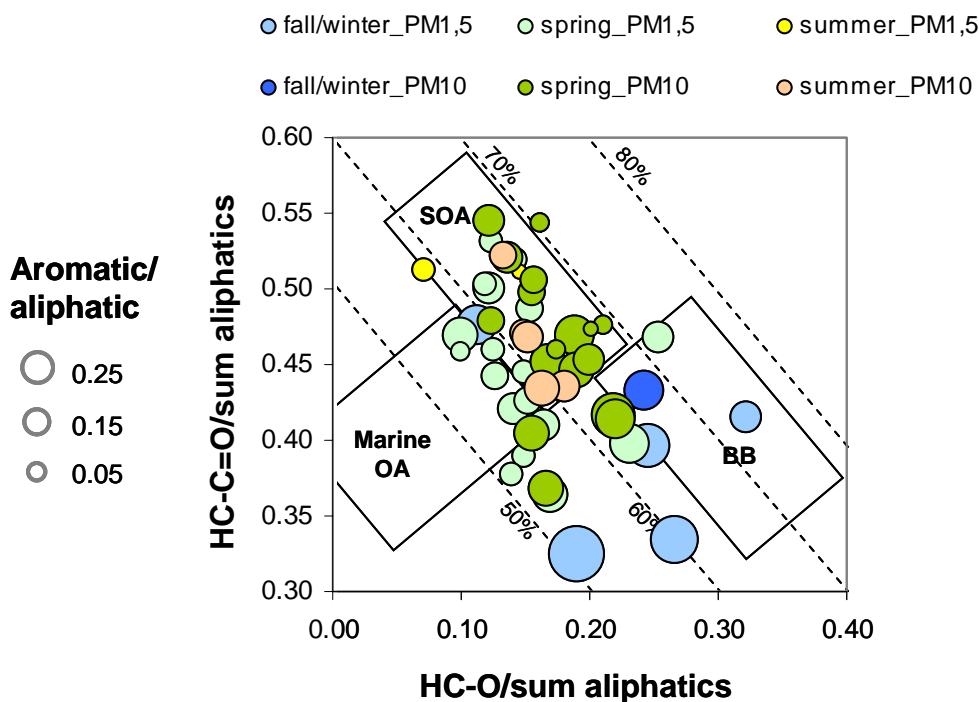


Figure 1. Functional groups distributions of WSOCs samples. Distinguishing colours are used for samples collected at different climatic conditions: summer (yellow/orange), spring (light green/green) and fall-winter (light blue/blue). Light colours identify PM_{1,5} with respect to PM₁₀.

In the above diagram, the rectangular areas mark the regions assigned to three major organic aerosol (OA) sources –marine OA, biomass burning OA (BB) and secondary organic aerosol (SOA)- as derived in the study of Decesari et al. (2007). These areas were calculated on the basis of the observed variability in the composition of samples selected as representative for the above-mentioned sources, and for which a source apportionment was already performed using: back-trajectories, chemical tracers and emissions analyses.

As can be seen in figure 1, most of the samples collected during warm season (spring and summer) scatters in the middle of the scatter plot within the area assigned to SOA, as expected for a region of strong traffic emissions and prolonged clear-sky conditions.

Among the warm season samples, PM_{1,5} and PM₁₀ show slightly different composition patterns, having the latter systematically higher hydroxyls to alkyls ratios.

This displacement in the composition may reflect the enrichment of primary biogenic organics in PM₁₀ with respect to PM_{1,5}. Primary organics (e.g. vegetation debris) are actually known to be mainly composed by sugars and polyols and thus they may be good candidates to explain the observed systematically higher hydroxyls to alkyls ratios shown by PM₁₀ samples..

Few SOA samples overlapping the marine OA area can also be observed. The NMR spectra corresponding to these samples were actually characterized by intense signals due to methane sulfonic acid, a secondary organic compound typically found in marine aerosol samples. The samples are thus thought to be impacted by air masses of marine origine.

The few samples collected in the cold season are characterized as well by a high hydroxyls to alkyls ratio but have a lowest fraction of total oxygenated groups, appearing in the lower left corner associated to BB source. Even if the number of samples is very low, it allows to clearly see the effect on the WSOCs composition due to the contribution of the source linked to wood combustion, expected actually to be mainly active in the cold season (e.g. domestic heating).

Finally, no source apportionment could be provided for few samples which fall in the lowest portion of the diagram, and characterized by the lowest fraction of total oxygenated groups, occupying a region of unexplained assignment.

A statistical resume of the number of samples distributed among the identified sources is reported in the figure below (fig.2).

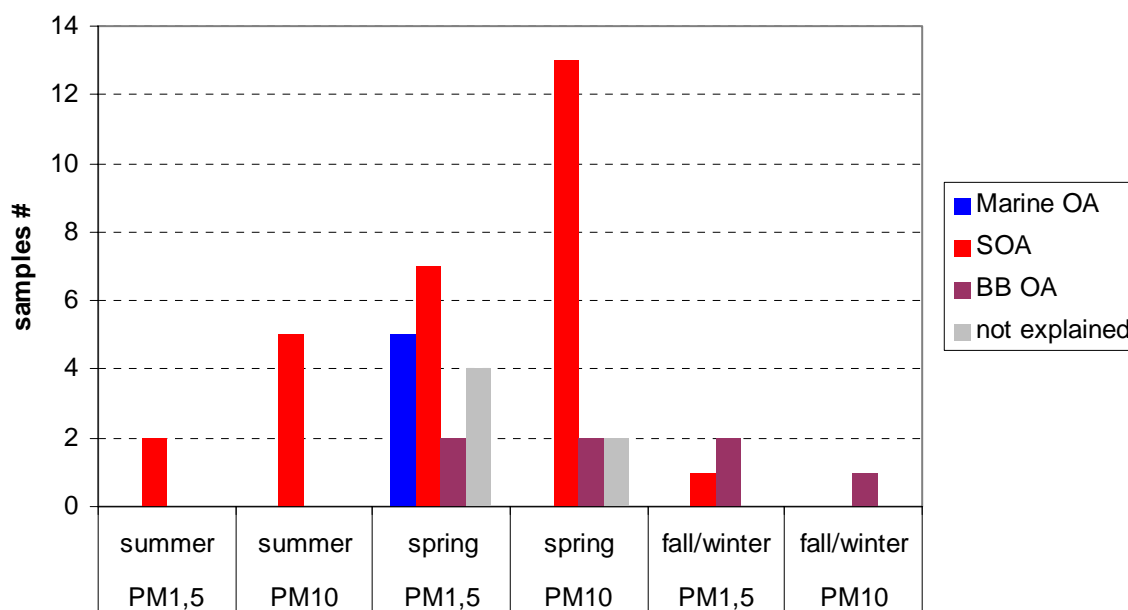


Figure 2. Distribution (in number) of samples among the identified OA sources.

Reference:

Decesari, S., Mircea, M., Cavalli, F., Fuzzi, S., Moretti, F., Tagliavini, E., Facchini, M. C. (2007): Source attribution of water-soluble organic aerosol by nuclear magnetic resonance spectroscopy. *Environmental Science & Technology*, **41** (7), pp. 2479-2484.