Chemical characterization of polar organic markers in PM 2.5 during an intensive campaign of Supersito Project in Po Valley (Italy)

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The composition and seasonal variations of a wide range of water-soluble organic compounds (WSOCs) were determined in the atmospheric aerosol in Emilia-Romagna region (Northern Italy), as a part of the "Supersito" Project (http://www.arpa.emr.it/supersito/). The present study is focused on dicarboxylic acids, sugars and methoxyphenols, as chemical tracers giving valuable information for elucidating sources, processes and pathways of organics in the atmosphere.

$PM_{2.5}$ filters were collected in two intensive field campaigns in winter 2011 (November 14th to December 6th) and summer 2012 (June 13rd to July 10th). The investigated sites were two locations representing an urban background station of Bologna city, a great urban centre in Northern Italy, and a rural site (about 30 Km north-east of Bologna in the Po Valley) representing an agricultural and remote region.

An analytical protocol, including solvent extraction and derivatization reaction, has been properly optimized to permit the simultaneous analysis of 48 target WSOCs, including 18 dicarboxylic acids, 17 sugars and 13 methoxyphenols (Pietrogrande *et al*, 2011; Pietrogrande *et al*, 2013). The developed method provided rapid and accurate quantification of WSOCs with low detection limits ($\leq 1 ngm^{-3}$) and good reproducibility (RSD%$\leq$11%) useful for aerosol monitoring.

The developed method was applied for chemical characterization of different classes of WSOCs in the $PM_{2.5}$ filters collected in both the seasons in urban and rural sites (mean values of total concentrations of acids, sugars and phenols are reported in Table 1).

Table 1. Mean concentration values of total acids, sugars and phenols and levoglucosan in $PM_{2.5}$ filters collected in winter and summer in urban and rural sites.

Analytes	Winter		Summer	
	Urban ngm^{-3}	Rural ngm^{-3}	Urban ngm^{-3}	Rural ngm^{-3}
Total acids	272	301	n.d.	0.5
Total sugars	1263	1135	6.7	43
Levoglucosan	1028	918	2.2	5.4
Total phenols	13.3	9.7	0.0	0.5

In general, data similarities indicate the regional nature of the primary sources and atmospheric processes affecting the $PM_{2.5}$ composition that seems weakly influenced by local emission sources.

In all seasons the most abundant compound is levoglucosan, as the major by-product from biomass burning, suggesting that this is the major source of aerosol, accordingly with values measured in other Italian cities (Piazzalunga, 2011). In addition to levoglucosan, less abundant degradation products from biopolymers (e.g. galactosan and mannosan from cellulose, methoxyphenols from lignin) were quantified as useful tools for identifying combustion sources: the data obtained in both the seasons are diagnostic for wood combustion with a predominant contribution of hardwood fuel.

As expected, a pronounced season pattern of dicarboxylic acids was observed, with higher winter concentrations compared with summer: this is a consequence of the higher anthropogenic emissions in the cold season combined with winter atmospheric conditions in the investigated area that are characterized by low mixing heights and possible formation of inversion layers (Balducci, 2010).

Some biogenic sugars were quantified, as indicators of primary emissions from the terrestrial biomass (plant detritus, airborne microbes, spores of lichens and fungi). The relative contribution of such sugars is higher in summer compared with winter closely reflecting the higher sugar production and utilization by the ecosystem as well as the enhanced agricultural activity in the hot season.

The distribution profiles and the diagnostic ratios of the target WSOCs provided relevant information for estimating the contribution of primary emission sources (power plants, vehicular circulation, biomass burning) associated with secondary constituents from both biogenic and anthropogenic precursors.

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