Chemical characterization of submicron organic aerosol sources in Po Valley by advanced spectroscopic techniques

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More than 20 million people living in the Po Valley are exposed to Particulate Matter (PM) levels well above the limit set by the World Health Organization, especially during the colder season. Organic compounds constitute a large fraction of submicrometer particles mass and their accurate quantification and source apportionment are necessary in order to determine their role in air quality issues and to define efficient abatement strategies.

In the framework of the Emilia-Romagna regional project "SUPERSITO", the submicron aerosol chemical composition was characterized by means of Aerosol Mass Spectroscopy (AMS) and proton-Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy used in parallel with aim of organic aerosol (OA) characterization and source apportionment. Eight intensive campaigns were carried out over four years (from 2011 to 2014, see Table1) at two different sites (Bologna, BO, urban background and San Pietro Capofiume, SPC, rural background), trying to characterize spatial variation and seasonality of the OA sources in the Po valley.

OA sources were identified for all the IOPs from the Aerosol Mass Spectrometer (HR-TOF-AMS) on-line measurements using either the Positive Matrix Factorization (PMF) or the multi-linear engine (ME-2) algorithm implemented with the toolkit SoFi, developed by Canonaco et al. (2013). During four of these IOPs the water soluble fraction (WSOC) of parallel sets of ≈12 hours PM_1 filter samples were analyzed by ^{1}H-NMR spectroscopy and the resulting collection of spectra was processed using a suite of Factor Analysis techniques (Non-negative Matrix Factorization or NMF, Multivariate Curve Resolution or MCR) aiming to identify WSOC specific sources or processes. The contributions of the organic-factors identified by AMS and ^{1}H-NMR were compared each other and with additional chemical tracers, in order to identify correlations and to better characterize prevalent OA sources.

During the cold seasons both AMS and NMR agree in highlighting the importance of biomass burning products as major constituents of OA in the Po valley area, even in the urban background, not only in the primary but also in the secondary fraction. In fact factor analysis identified some oxidized components of clear secondary origin still retaining characteristics of fresh smoke particles (like traces of levoglucosan, polyols and aromatic compounds) and interpretable as SOA coming from processing and ageing of combustion emissions (or SOA containing similar products). AMS data indicate contributions of this SOA influenced by wood-combustion in the order of 15-40% of the total mass of OA whereas ^{1}H-NMR data show contributions even around 50-60% of WSOC, which confirm unequivocally the dominant impact of biomass combustion on the particulate OM composition in the Po valley during cold months. Other OA factors found in the cold seasons are associated with low molecular weight amines, whose possible sources are the products of livestock activities. Contributions from alternative sources (e.g., anthropogenic SOA originating from oxidation of volatile and semi-volatile hydrocarbons) can not be excluded even if not identified selectively.

		AMS		NMR	
		BO	SPC	BO	SPC
SPRING	2013	✓	✓		
	2014	✓			
SUMMER	2012	✓		✓	
FALL	2011	✓	✓		✓
	2012	✓			
	2013	✓	✓	✓	✓
WINTER	2013	✓		✓	
	2014	✓		✓	

Table1: field campaigns and datasets object of the study

During summer the prevalent OA sources change substantially: biomass-burning disappears and the secondary fraction reaches about 90% of the total OA mass. Within this SOA the alkyl-amines are still present and very oxidized factors (with "HULIS" features) increased their contributions (about 60-70% of total WSOC). The latter factors were clearly enriched in daytime and were present in both polluted and more background conditions indicating that they are mainly associated to low-volatility organic compounds forming from photochemical activity and accumulating in regional pollution.

In general, factor analysis applied to ^{1}H-NMR atmospheric datasets complement AMS in lumping the complex oxidized organic mixtures into chemical classes characterized by specific sources or ageing states.

Canonaco, F., Crippa, M., Slowik, J., Baltensperger, U., and Prevot, A. (2013), *Atmos. Meas. Tech.*, **6**, 3649-3661.