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PRIMARY AND SECONDARY ORGANIC AEROSOLS
AEROSOLS ORGANIQUES PRIMAIRE ET SECONDAIRE
AEROSOL ORGANICO PRIMARIO E SECONDARIO

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Abstract

In this work are presented results from recent intensive field measurements conducted in the Po Valley region in the frame of the EC-funded EUCAARI project, where state-of-the-art instruments were run in parallel in the joint effort to quantitatively apportion the primary and secondary fractions of the organic aerosols (OA) and their origins. We focused on the results obtained by applying factor analysis methodologies (i.e. positive matrix factorization, PMF) to spectroscopic data such as those produced by aerosol mass spectrometry (AMS) and nuclear magnetic resonance spectroscopy (NMR) while aiming at OA source apportionment.

Key-words: *primary organic aerosol (POA); secondary organic aerosol (SOA); aerosol mass spectrometer (AMS); Nuclear Magnetic Resonance (NMR) spectroscopy; Positive Matrix Factorization (PMF); biomass burning aerosol*

Résumé

Dans cet article on présente les résultats d'une campagne de mesure intensive dans la vallée du Pô, dans le cadre du projet EUCAARI (financé par l'UE), dans laquelle plusieurs instruments de nouvelle génération on été employés en parallèle dans le but de faire la part entre aérosols organiques primaire et secondaire. On focalise sur les résultats en appliquant des méthodes d'analyses statistiques multivariées et factorielles (positive matrix factorization, PMF) aux données de spectroscopie comme celles produites par l'AMS (spectrométrie de masse) et par la résonance magnétique nucléaire (RMN) dans le but d'identifier l'origine des aérosols organiques.

Mots-clés: *aérosol organique primaire; aérosol organique secondaire; spectrométrie de masse; Résonance Magnétique Nucléaire (RMN) spectroscopie; Positive Matrix Factorization (PMF); biomass burning aerosol*

Riassunto

In questo lavoro vengono presentati risultati ottenuti in recenti campagne di misura dell'aerosol atmosferico effettuate in Val Padana nell'ambito del progetto europeo EUCAARI. Durante le campagne intensive di misura strumenti di nuova generazione sono stati impiegati in parallelo allo scopo di determinare l'origine

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della frazione organica dell'aerosol, con particolare attenzione alla componente primaria e secondaria. In particolare vengono descritti i risultati ottenuti applicando metodi di analisi statistica multivariata, ad es. analisi dei fattori (PMF), a dati spettroscopici ottenuti sia tramite spettroscopia di risonanza magnetica nucleare (NMR) che spettrometria di massa (AMS).

Parole chiave: *aerosol organico primario; aerosol organico secondario; AMS; spettroscopia di Risonanza Magnetica Nucleare (NMR); PMF; aerosol da combustione di biomasse*

Introduction

Ambient organic aerosols (OA) comprise either primary organic aerosol (POA, particles directly emitted into the atmosphere by combustion and mechanical processes) and secondary organic aerosol (SOA, particles formed in the atmosphere due to the photochemical conversion of gaseous precursors) (Kroll and Seinfield, 2008). OA originate from a wide range of both natural and anthropogenic sources including combustion of fossil fuels, direct injection of un-burnt fuel and lubricants, industrial emissions, plant matter debris, biomass burning, and biogenic emissions (Jacobson et al., 2000).

SOA have recently gained much attention because current models estimate that they account for a dominant fraction of the total organic particulate mass (Hallquist et al., 2009) nevertheless the relative contributions of POA and SOA to the overall OA budget remain controversial due to the lack of observations capable to discern accurately between the different sources and processes.

The organic source apportionment has been approached by numerous techniques. In the last years the development of new aerosol spectroscopic techniques such as aerosol mass spectrometry (AMS), Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopies bypassed the constraints of molecular speciation looking to the integral chemical features of the organic mixture and have been used aiming to OA source apportionment (Lanz et al., 2007; Schwartz et al. 2010, Decesari et al., 2007).

Here we present results from recent intensive field campaign conducted in the Po Valley region employing state-of-the art instrumentation for the measurement of primary and secondary organic aerosol with a focus on AMS and NMR data.

Po Valley is a well-known polluted area, characterized by a high population density and by intensive anthropic activities (both industrial and as well agricultural) and thus represents a natural laboratory for the study of anthropogenic SOA and POA.

Materials and methods

Aerosol chemical composition have been intensively monitored at the field station of San Pietro Capofiume (SPC), located in the densely urbanized Po Valley, in spring 2008 (from March 31st to April 20th). During the intensive observation period distinct meteorological regimes could be observed: from high-stability conditions experienced at the beginning of the campaign, favourable to formation and aging of SOA, to few days characterized by decreasing temperatures and the presence of haze and fogs, and up to precipitations in the final period.

Nocturnal and diurnal aerosol filter samplings were performed using a dichotomous sampler (UAS^{TM} Model 310, MSP) equipped with a virtual impactor for separating PM_1 and PM_{10-1} and operating at 300 L/min. After collection PM_1 samples were analyzed for total carbon (TC) and extracted in water for water soluble organic carbon (WSOC) measurements. A large part of each water extract was subsequently devoted to function group characterization by proton-nuclear magnetic resonance spectroscopy (^{1}H-NMR) following the protocol detailed in Decesari et al. (2007).

The concentrations trends for major submicron aerosol species including sulphate, nitrate, ammonium ions and organics were measured on-line using two Aerodyne mass spectrometers (HR-Tof-AMS and W-Tof-AMS) running in parallel with filter samplings.

Multivariate statistical methods (i. e. positive matrix factorization, PMF) have been applied to both AMS and NMR spectra in order to isolate the principal OA components and the results have been then compared.

Results and discussion

PMF applied to the AMS spectra provided four main factors accounting for: 1) hydrocarbon-like organic compounds (HOA, a reduced OA) related to non-refractory POA, 2) two distinct types of oxygenated organic aerosols (OOA, an oxidized OA) linked to SOA and 3) biomass-burning related organic aerosols (BBOA). The percentage contribution of BBOA to total organic mass was generally much lower compared to the other components, excluding for the first part of the campaign when BBOA sporadically peaks (fig.1a).

The decreasing contribution of biomass burning products throughout the campaign was confirmed also by molecular marker analysis(levoglucosan) in the filter samples (fig.1b).

The resulted PMF-AMS factors have been averaged based on the filter sampling times and then compared to those obtained by PMF-NMR. It has to be noticed that since the water-insoluble (reduced) OA fraction was not analyzed by nuclear magnetic resonance, NMR data are thus comparable to the more oxidized AMS factors, i.e. the two OOA types and BBOA.

The analysis of the NMR spectra by PMF provided a clear split between the following components:1) a first component containing signals of levoglucosan and other polyols plus abundant aromatic signals, attributable to biomass-burning related OA, 2) a second component characterized by low-molecular weight alkyl-amines mixed with aliphatic compounds, that may be linked to landfills/animal husbandry emissions on the basis of the identified amines typical of these sources, and 3) other two components, distinct to each other but both characterized by highly oxidized aliphatic moieties plus a smaller contribution from aromatics,

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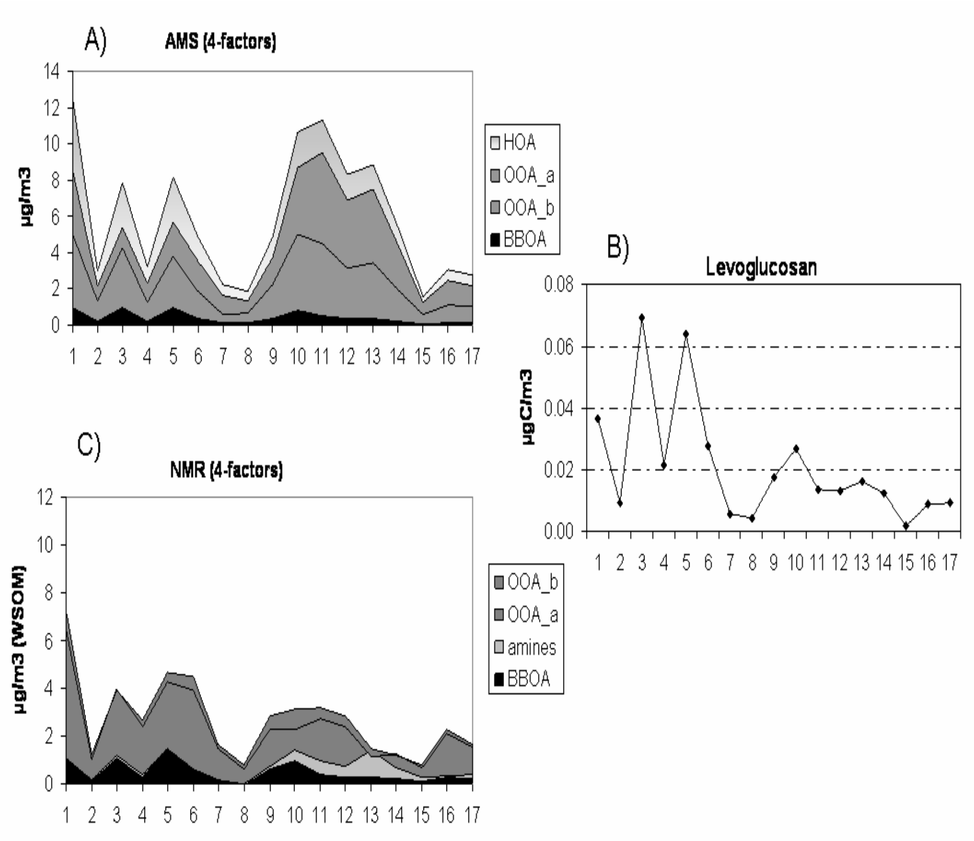
commonly observed in polluted samples collected in sites highly impacted by anthropic emissions (Finessi E., 2010).

Interestingly the PMF-NMR component linked to amines experienced an increase in the second part of the campaign when lower temperature together with higher humidity, low boundary layer (BL) stratification and high nitrate aerosol concentrations were observed.

A plot of the water-soluble organic matter accounted for by the 4-NMR factors is reported in figure 1c.

Figure 1 - *Organic matter apportionment in San Pietro Capofiume based on applying PMF (using a 4-factors solution) to AMS (a) and to NMR (c) data. Levoglucosan concentrations as measured in filter samples is reported beside (c).*



Conclusion(s)

In the frame of a EUCAARI campaign conducted in the Po Valley region in spring 2008, an OA source apportionment exercise has been performed applying PMF to AMS and NMR data. A component linked to biomass-burning products (BBOA), highly correlated with the levoglucosan concentrations, was clearly isolated by both techniques. The fact that the BBOA component contributed particularly in few nocturnal samples suggest that residential burning for domestic heating may have impacted significantly the organic composition of the collected aerosol.

The organic composition of the collected PM1 resulted mainly constituted by primary and secondary organic aerosol related to traffic emissions, as shown by the relevant HOA and OOA contributions extracted by both the techniques. One additional component linked to SOA from agricultural emissions has been isolated exclusively by PMF-NMR.

This agricultural emission component reached the highest values in days characterized by haze, low BL stratification and high nitrate aerosol concentrations and it has been likely formed by condensation mechanisms of gaseous product emitted by the ground.

The results show that the raise of organic aerosol concentrations during this campaign was triggered by the income of several sources and processes, e.g. a) the condensation of alkyl-ammonium salts during haze events and temporary descents of the temperature, b) the photochemical production of traffic-related SOA and POA, and c) the contribution from biomass-burning related organics.

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