

Seasonal variation of the chemistry of submicron aerosols in Po Valley, Italy

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The chemistry of submicron particles was investigated with aerosol mass spectrometers at San Pietro Capofiume (SPC) measurement station in the eastern part of the Po Valley, Italy. The aim of the study was to investigate the chemical composition and sources of submicron particles in different seasons in order to understand the reactions and transformations of pollutants coming from different sources or processes, and to improve the assessment of potential health effects of particles.

A total of four campaigns were conducted at the SPC site, which is located at a background area approximately 30 km north-east from Bologna. In spring 2008 High Resolution – Time of Flight – Aerosol Mass Spectrometer (HR-ToF-AMS) measurements were performed, while Soot Particle Aerosol Mass Spectrometer (SP-AMS) was used in the autumn 2011 and summer 2012 campaigns and Aerosol Chemical Speciation Monitor (ACSM) in the winter 2014 campaign. The aerosol mass spectrometers measured the concentrations of sulphate, ammonium, nitrate, chloride, and organic aerosol (OA). Black carbon (BC) was measured either using the SP-AMS (refractory BC, autumn 2011), the Multi-Angle Absorption Photometer (MAAP, summer 2012 and winter 2014), or from filters by using a thermal-optical carbon analyser. Other co-located measurements included e.g. NO_x, O₃, and inorganic ions. OA sources were identified 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).

There were large variations in the concentrations inside and between the individual campaigns that were mostly caused by the fog events and/or the change in the planetary boundary layer. On average, organics had the highest contribution to submicron particulate matter (PM₁, the sum of organics, nitrate, sulphate, ammonium chloride and black carbon) in three of the campaigns followed by nitrate that composed higher fraction of PM₁ than organics in the spring campaign (Figure 1). The lowest average contribution of secondary inorganic aerosol was measured during the summer campaign, when also nitrate and ammonium concentrations were the smallest. This was probably due to more effective partitioning of semi-volatile nitrate species in the gas phase. The large emissions of nitrogen oxides, mainly from traffic, and of ammonia, from agricultural activities, are responsible for the elevated concentrations of ammonium nitrate across the basin.

In terms of diurnal trends they were different between the autumn and other seasons. In autumn the

concentrations peaked in the afternoon, whereas in summer, spring and winter the concentrations were lowest in the afternoon. Sulfate did not show any diurnal variation except in the autumn campaign. The autumn campaign was very foggy and more hygroscopic particles were scavenged leaving an aerosol enriched in organics (Gilardoni et al., 2014).

The source apportionment study showed mostly three factors for OA: oxygenated organic aerosol (OOA), hydrocarbon-like organic aerosol (HOA) and biomass burning organic aerosols (BBOA). OOA had the largest contribution to OA; however, in some of the campaigns it was divided into different oxidation levels.

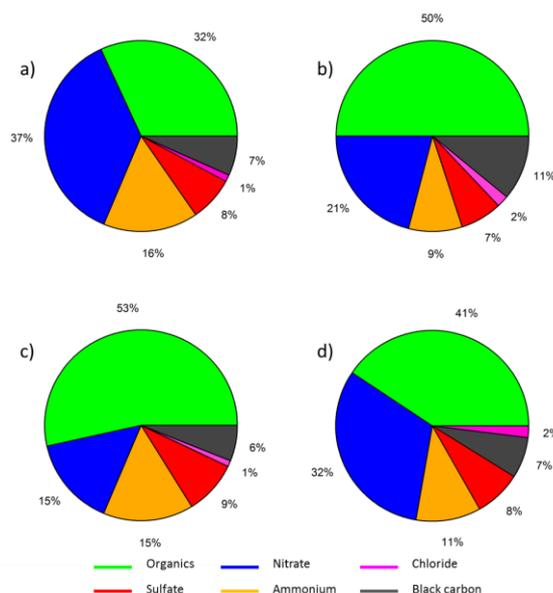


Figure 1. Campaign average chemical composition of PM₁ at SPC in a) spring 2008, b) autumn 2011, c) summer 2012 and d) winter 2014.

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