

Size-resolved aerosol composition at an urban and a rural site in the Po Valley in summertime: implications for secondary aerosol formation

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The knowledge of aerosol size segregated chemical composition encloses a wealth of information about formation mechanisms of particles and atmospheric processing, which cannot be inferred from the bulk chemical composition alone.

The present study focuses on the size-resolved chemical composition of aerosol simultaneously collected at an urban (Bologna) and a rural site (San Pietro Capofiume, 30 km northeast of the city) in the Po Valley, Italy, during the PEGASOS (Pan-European Gas-AeroSols-climate interaction Study) 2012 summer campaign.

12 hours samples were collected during day and night by two 5-stages Berner Impactors (cut-offs at 10, 3.5, 1.2, 0.42, 0.14 and 0.05 μm) for one month during June and July 2012. Measured species included inorganic and organic ions, water-soluble organic carbon (WSOC) and total carbon (TC). The aim was to explore sources of particulate matter and formation pathways of secondary compounds in the Po Valley, a region known as strongly impacted by anthropogenic pollution.

The attribution of sources was addressed through the analysis of the time series of the main aerosol species together with meteorological parameters, and by a statistical approach. Principal component analysis (PCA) was performed on a dataset composed by size resolved chemical compositions, also including modelled and measured meteorological parameters and residence times obtained combining back-trajectories analysis with a detailed land cover analysis (van Pinxteren et al. 2011).

The analysis of back-trajectories revealed the occurrence, during the campaign, of two periods of stagnation, respectively from June 15 to 20, and again on July 5 and 6, which favoured secondary aerosol formation. Despite their proximity, significant differences emerged between the two sites, especially during the first episode, when high night-time concentrations of ammonium nitrate were observed at the rural site only, together with the simultaneous build-up of WSOC, a proxy of secondary organic aerosol. Such nitrate peaks were particularly intense in the droplet mode (0.42-1.2 μm) (Fig. 1), suggesting the existence of nocturnal aqueous phase chemistry. This local formation of ammonium nitrate, prompted by the lower temperatures and higher relative humidity at the rural site in the early morning, and by the simultaneous availability of gaseous ammonia required for nitric acid neutralization, resulted in submicron nitrate nocturnal concentrations 4 times higher in SPC than in BO.

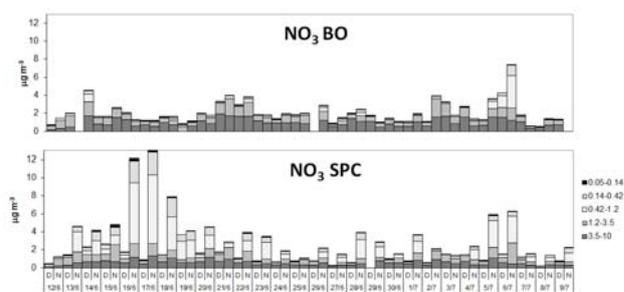


Fig. 1 – Size-resolved nitrate concentration in Bo and SPC during the campaign.

The presence of high nocturnal ammonium nitrate concentrations had important implications for aerosol processing, since its strong hygroscopicity drew significant amounts of aerosol liquid water (ALW) on particles, providing a medium for aqueous SOA formation (Hodas et al., 2014). To confirm this, the factors extracted from PCA highlighted the presence of an important source, especially in SPC, represented by secondary formation via aqueous phase processes during the night, and another important source represented by photochemical formation in the gas phase, mostly affecting small particles concentrations. Other sources, attributed to crustal materials and sea-salt, mostly interested coarse particles, while a more uncertain source was tentatively attributed to local combustion.

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