



Particulate matter (PM) formation during summertime in the Po valley: mechanisms and source apportionment

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In order to study the influence of photochemistry on PM levels in the Po Valley, diurnal trends in the mass concentration, size distribution and chemical composition of $PM_{2.5}$ were measured during a field campaign in a suburban area near Milan (Limite di Pioltello). Samples were collected in summer on a 4-hour time resolution. The inorganic fraction of $PM_{2.5}$ was dominated by NH_4^+ followed by NO_3^- and SO_4^{2-} . NH_4^+ was the compound to be better correlated with $PM_{2.5}$ suggesting that the reaction of NH_3 with H_2SO_4 , and HNO_3 was responsible for the formation of SO_4^{2-} , and NO_3^- . A photochemical episode characterized by high nighttime $PM_{2.5}$ concentrations was followed by high NO_x and high relative humidity. This could be responsible of the overall formation of sulfate. The photochemical episode was also characterized by nighttime formation of VOCs followed by daytime formation of carbonylic compounds. $PM_{2.5}$ was correlated with the lower end of the measured particle size range (0.25-0.58 μm) suggesting a clear accumulation of secondary ammonium nitrate and sulfate on the boundary layer of the site.

Positive matrix factorization (EPA PMF 3.0) was used to retrieve the main factors responsible for $PM_{2.5}$ formation. Additional retrievals were carried out by using an implemented version of the EPA PMF 3.0 program known as Multilinear-Engine (ME-2). Results showed that primary emissions were associated with elemental carbon (EC) and to the less volatile fraction of organic carbon, whereas secondary emissions were associated with secondary inorganic aerosols (SIA) mainly formed by SO_4^{2-} , NO_3^- , and NH_4^+ . EPA PMF 3.0 and ME-2 identified the same major sources responsible for the $PM_{2.5}$ in Limite di Pioltello. The three main sources were: traffic, secondary nitrate and secondary sulfate with re-suspended soil. Comparison between the two methods showed slightly differences. However, from ME-2 results we can see the three factors were more distinguishable than from EPA PMF 3.0 results. The traffic factor was better retrieved by ME-2 run, whereas the secondary nitrate and sulfate factors showed less contamination from re-suspended soil and traffic factor, respectively.