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 (Limito 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$_2$SO$_4$, 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 Multilienar-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 Limito 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 EPF 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.