

Secondary particulate matter formation during foggy days

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In Milan, one of the largest cities in Italy, strong atmospheric stability conditions cause prolonged periods with high pollution levels exceeding the EU threshold limits. In many winter episodes secondary aerosol prevails on primary aerosol (Vecchi et al., 2004) but the mechanisms which cause secondary aerosol formation are not completely clear yet.

In this work, we present the results obtained in two different winter campaigns (2006 – 2007). PM10 was sampled in parallel on quartz fibre and PTFE filters with 4 hour and 8 hour time-resolution.. A detailed chemical characterisation (with quantification of elements, inorganic ions, OC/EC fractions, WSOC, and levoglucosan) was carried out on the samples.

The data analysis presented here is mainly focused on the secondary aerosol formation occurring during foggy days.

In the first campaign (November/December 2006 – 4 hour resolution) we used the Hydroxymethanesulfonate (HMS) as a tracer for heterogeneous chemical reactions (Dall'Osto et al., 2009) as it is a product of the aqueous reaction between dissolved SO₂ and HCHO. HMS was detected in more than 90% of our samples. HMS concentration ranged between 12 ng m⁻³ and 3500 ng m⁻³ and increased during the fog events as shown in figure 1. HMS concentrations resulted well correlated with sulphate values. This shows that sulphate is probably formed in cloud droplets (Choulaton and Bower, 2001).

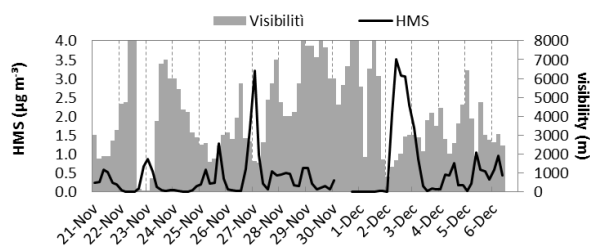


Figure 1. comparison between trend of HMS and visibility.

During the second field campaign (February 2007 – 4 and 8 hour resolution) we investigated the secondary nitrate formation. As shown in figure 2, the nitrate concentration increased from 20 to 110 µg m⁻³ in about 36 hours during the fog event. In the same period, an increase in WSOC (water soluble organic compounds), concentration and relative humidity levels was also detected. During the fog event, we also observed an increase of HMS concentration (concentration up to 700

ng m⁻³), which was fostered by the low solar radiation. This day was also characterised by a high OC/EC ratio.

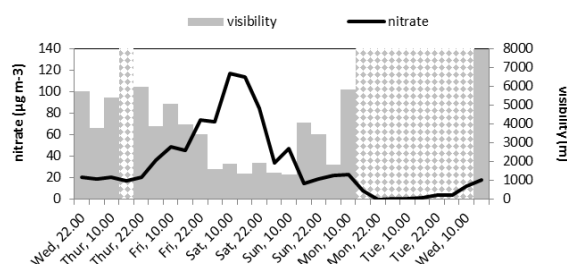


Figure 2. comparison between trend of nitrate and visibility.

In order to evaluate the acidity of the WSOC, we also quantified the organic carbon extracted at two different pH values (2.5 and 5.5). The concentration trend of the compounds extracted at lower pH is well correlated to the K⁺ concentrations. K⁺ is known to be related to wood burning. Therefore, this source is probably an important source of organic acid compounds too. On the other hand, the concentration of compounds extracted in less acidic solution increased during the night. The insoluble organic compounds are well correlated to the primary components of particulate matter.

Choulaton, T., Bower, K. (2001) *Water, Air, & Soil Pollution*: 1 365-372.

Dall'Osto, M., Harrison, R. M., Coe, H., Williams P., (2009) *Atmos. Chem. Phys.* 9 2459-2469

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