

## Deliquescence and crystallization of aerosol in the Po Valley: measurements, comparison with model outputs and applications

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Aerosol chemical composition determines the relative humidity at which the aerosol deliquescence or crystallization occurs (Martin, 2000). The level of aerosol hydration impacts a wide range of aerosol properties (both physical-chemical and optical) and processes; it is of fundamental importance in several areas of aerosol research such as climate forcing, visibility, atmospheric aerosol chemistry, energy saving in data centers, etc. (Ferrero et al., 2013; Martin, 2000; Martin et al., 2003).

Thus, in this work, the aerosol mutual deliquescence and crystallization relative humidity (MDRH and MCRH) were determined on PM<sub>2.5</sub> samples (FAI-Hydra sampler; 2.3 m<sup>3</sup> h<sup>-1</sup>, PTFE filters, Ø=47 mm) collected in the Po Valley during the last decade (2003-2013). MDRH and MCRH were determined in a new developed aerosol exposure chamber (AEC) measuring both aerosol conductivity (Agilent 34411A 6½ digital multimeter) and aerosol mass (Sartorius microbalance, 0.1 µg sensitivity) changes while varying the RH at constant temperature. Temperature and RH in the AEC are constantly monitored by means of a DMA 572.1 thermo-hygrometric sensor (LSI Lastem). In the AEC it is possible to achieve up to 0.5% sensitivity in terms of RH variation. Up to six conductivity cells can be housed in the AEC, in order to perform simultaneously conductivity measurements. The method was validated through the analysis of pure aerosol types (i.e. pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) generated for this purpose (Topas Aerosol Generator).

Ambient PM<sub>2.5</sub> samples were also chemically analysed by ion chromatography (IC, Dionex ICS-90 and ICS-2000) and the aerosol chemistry was used as an input parameter to calculate: 1) the aerosol MDRH, using both the Extended-Aerosol Inorganic Model (E-AIM) and ISORROPIA and 2) the aerosol MCRH obtained by the parametric model reported in Martin et al. (2003).

Results first evidenced that MDRH in winter (60±4%) in the Po Valley was lower than in summer (73±1%); the same happened for MCRH: 39±6% in winter and at 52±5% in summer. IC analysis showed that NH<sub>4</sub>NO<sub>3</sub> dominate in winter while (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> dominate in summer allowing to explain the seasonal behaviour of MDRH and MCRH. Comparison with models gave the following results: for the MDRH the predicted mean MDRH values substantially corresponded to the mean experimental values while, for what concern the MCRH, substantial differences were found between modelling results and experimental values (up to 30% of RH); this difference was due to the presence of insoluble inclusions and carboxylic acids in the ambient aerosol that can act as crystallization nuclei driving a crystallization at higher RH values than that predicted. Experimental MDRH and MCRH values were then used in two applications.

The first one concern data centers; they are responsible for a large electricity usage (~27% in Europe) mainly due to their air conditioning cooling systems (35-50% of energy used). Direct Free Cooling (DFC) systems could be used to reduce energy consumption; they use outside air to directly cool the information technology. However this approach involves the risk to introduce outdoor aerosol which can become electrically conductive and corrosive if the surrounding air promotes aerosol hydration. The investigated data centre was constructed in Italy at Sannazzaro de' Burgondi (Po Valley) for the Italian Oil and Gas Company (ENI) (5200 m<sup>2</sup> of computer installed, 30 MW) (Ferrero et al., 2013 and 2014). The basic concept was to optimize the DFC (RH limits) avoiding the reaching of the aerosol hydration from the knowledge of measured MDRH and MCRH: this increase the DC energy efficiency, whilst preventing the aerosol corrosion at the same time. On annual basis, considering the Po Valley MDRH and MCRH values, the DFC application originated an energy saving of 79% (compared to the energy consumption of a traditional air-conditioning system): 215 GWh of energy and 78 fewer kt of equivalent CO<sub>2</sub> were saved per year.

A second application allowed to study different hazards for cultural heritage induced by deposited aerosol. The knowledge of MDRH and MCRH and ambient T and RH conditions allowed to determine in the Po Valley the time of wetness (TOW: percentage of time in which aerosol was "wet") and number of dissolution and crystallization cycles (N<sub>cy</sub>: when RH decrease under MCRH starting from a condition in which aerosol was "wet"). TOW is related to presence of liquid water on stone surfaces able to trigger "chemical" decay-mechanisms. N<sub>cy</sub> is instead related to mechanical stress occurring during crystallization.

Results pointed out that, depending on the season, different hazards can be present: high TOW (89±11%) and low N<sub>cy</sub> (3±3 cycles/month) were found in winter; in summer, low TOW (20±13%) and high N<sub>cy</sub> (11±5 cycles/month) were present. Fall and spring resulted the most damaging seasons for stones since they had both TOW and N<sub>cy</sub>. The proposed method takes into account both climatic data and PM hydration characteristic and it proves to be an efficient tool to make hazard assessment with an heritage climatology approach (Casati et al., 2015).

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