Soluble and insoluble carbon content in fog: a 16 year long study in the Po Valley (Italy)

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Fog chemical composition has been studied for decades, but most of the studies were addressed to the characterization of inorganic water soluble species, while in the last years the research mostly focused on the organic matter in fog water. Only a few works focused on the insoluble fraction, characterizing the inorganic species and usually not accounting for carbonaceous compounds, despite they play a role in cloud absorption properties (Jacobson, 2012) and can affect the activation of a droplet or its tendency to evaporate.

At the field station of San Pietro Capofiume (Bologna, Italy), fog samples have been collected throughout the fall-winter season during each dense fog episode since 1989. The sampling site is located in a rural area in the south-eastern part of the Po Valley, 30 km north-east of Bologna. Initially chemical analysis have been carried out to characterize the inorganic soluble fraction. Since the fall-winter season 1997/98 both soluble and insoluble carbon content was also measured and now a sixteen years long dataset is available.

The insoluble fraction of fog samples was isolated filtering fog water through quartz fibre filters a few hours after sampling. Quartz filters were then subjected to thermal analysis to determine the total insoluble carbon content, while the liquid fractions were analysed to quantify the amount of water soluble organic carbon (WSOC). The temporal trends of both soluble and insoluble carbon content in fog samples will be presented in this work.

Filters collected from 2001/02 and 2010/11 were analysed to determine the total carbon content. Filters collected in 1997/98, 1998/99, 1999/2000, 2000/2001, 2012/2013 and 2013/2014 were analysed by a Sunset EC-OC analyser. This technique allows to discriminate between elemental carbon (EC) and organic carbon (OC). Preliminary results show that carbonaceous matter accounts for a significant fraction of the insoluble material suspended in fog water. The sum of EC and water insoluble organic mass accounts on average for 46%-56% of the mass of total suspended material. Insoluble carbonaceous material is composed mainly by organic matter, EC accounting on average only for 17% of the total insoluble carbon. Absolute concentrations of OC and EC are highly variable. OC ranges between 1.6 and 109 mgC L^{-1} with a median value of 5.3 mgC L^{-1}, and EC ranges from 0.1 to 22.5 mgC L^{-1}, with 1.1 mgC L^{-1} as median value. A correlation was observed between EC and OC through the different years, with an average EC to OC ratio of 21%. This suggests that anthropogenic combustion processes, which represent the main source of EC, are also the most important source of OC in fog droplets.

The water soluble organic carbon (WSOC) represents on average 25% of the total solute mass and its contribution to the total organic carbon (TOC) ranges from 52 to 95% with an average of 86%.
The amount of WSOC is highly variable within the samples. WSOC concentrations range from 3 mgC L^{-1} to 350 mgC L^{-1} and seasonal median concentrations range from 15 mgC L^{-1} to 49 mgC L^{-1}.

The carbonaceous fraction in the Po Valley fog water shows concentrations up to one order of magnitude higher than values reported in previous works for rural sites (Herckes *et al.*, 2013), but comparable to urban fog as reported by Capel *et al.* (1990).

The high amount of carbonaceous compounds in the Po Valley fog, and a simultaneous decrease of the main inorganic species concentration (Giulianelli *et al.*, 2014) highlight the increasing relevance of these species in the fog system. Further efforts are needed to better understand the role of carbonaceous matter in the fog chemistry.

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