

How did chemical composition of the Po Valley radiation fog change in the last twenty years?

L. Giulianelli¹, M.C. Facchini¹, S. Gilardoni¹, S. Decesari¹, M. Rinaldi¹, C. Carbone¹, M. Paglione¹, and S. Fuzzi¹

¹ Institute for Atmospheric Science and Climate (ISAC), CNR, Bologna, Italy

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Presenting author email: l.giulianelli@isac.cnr.it

Radiation fog is formed by the steady cooling of air close to the ground where main emissions take place, and is characterized by strong atmospheric stability and low wind speed. Fog is an atmospheric multiphase system where water droplets, aerosol particles and gases interact. Gas to particle partitioning, chemical reactions in liquid phase or at the gas-liquid interface and scavenging of aerosol particles take place. The presence of fog has a relevant impact on atmospheric chemistry and air quality and by deposition it can affect the natural ecosystem and historical artifacts.

For these reasons it is important to have a detailed knowledge of the chemical composition of fog samples, especially in areas like the Po Valley (northern Italy) where fog episodes are very frequent during the fall-winter season. The Po Valley is a densely inhabited region characterized by numerous agricultural and industrial activities and intense vehicular traffic, making it one of the most polluted region in Europe. The interest in having a deeper knowledge about fog chemical composition goes back to the early eighties when the first fog samples were collected at the field station of San Pietro Capofiume, Fuzzi *et al.* (1983). The station is located in the south eastern part of the Po Valley between the cities of Bologna and Ferrara. Initially fog droplets were sampled occasionally. Starting from November 1989 up to now fog samples have been collected throughout the fall-winter season during each dense fog episode, Fuzzi *et al.* (1992, 1996, 1997).

This allowed us to build a more than twenty years long database of chemical composition (NH_4^+ , SO_4^- , NO_3^- , soluble organic compounds, etc.), pH, conductivity and liquid water content (LWC). The observation of this unique database showed a decreasing trend of conductivity and ionic strength, that is a lower content of ionic species in the fog droplets. Mean conductivity values range from 460 $\mu\text{S}/\text{cm}$ in 1989/90 to 114 $\mu\text{S}/\text{cm}$ in 2010/11. Analyzing the trend of the single ionic species, also the three major ions (NH_4^+ , SO_4^- , NO_3^-) that alone represent up to 90% of the total ionic strength, decrease. Sulphate shows the highest relative decrease, as demonstrated by the negative trend of $\text{SO}_4^-/\text{NO}_3^-$ ratio. Ionic concentrations within each season are very variable: 0.03-27.87, 0.02-16.90, 0.04-25.04 $\mu\text{eq}/\text{l}$ for NO_3^- , SO_4^- , NH_4^+ respectively. Trends are built using the seasonal volume weighted means for each species, in order to take into account the contribution of LWC and lifetime of each fog event. Also pH values are very variable, ranging from 2.44 to 8.83, but the annual

trend calculated by the weighted means of each season shows an increase: fog droplets are less acidic now than 20 years ago. During the 90s mean pH values ranged from 3.7 to 4.7, while values ranged from 4.1 to 6.9 from 2000 to 2011. We suppose this is correlated with the decrease of sulphate. Not much is known about the role of organic compounds in fog droplets pH. Water soluble organic carbon (WSOC) analysis are available only from 1997 and the results do not show any correlation to pH. More detailed analysis of the organic fraction should be carried out to address this topic.

Having available such a long database allows to observe differences in fog chemical composition through the years and eventually relate them with emission changes. This could be useful to determine the effectiveness of past policies and could be helpful for future choices.

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