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Formation and partitioning of iron-organic aggregates in fog droplets

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In a recent study we have shown that organic carbon (OC) is the main identified contributor to the suspended matter of fog samples collected in the Po Valley (Italy), while the contribution of metals (Al, Fe, K, Na, Mg, Zn, Pb and Cu) is lower. Among metals studied, Fe was preferentially partitioned in the suspended insoluble matter and the partitioning ratio (defined as the ratio of metal concentration in the aqueous phase and total metal concentration) of this metal is higher than typical values found in aerosol samples. In this work we study the formation of iron-organic aggregates (iron-soluble humic-like substances) in fog samples and the partitioning of iron and humic-like substances (HULIS) in fog droplets. In analogy to natural waters, metal/organic interactions may be responsible, in fact, for the formation of suspended particulate matter in fog droplets. Samples of suspended particulate material isolated from fog water were submitted to sequential extractions with aqueous solutions at different pH, in parallel with synthesized aggregates of iron-fulvate (Fe-FA) and iron-humate (Fe-HA). Water solubility properties of fog suspended material were more similar to those of Fe-HA than Fe-FA. Moreover, on the contrary of synthesised Fe-HA and Fe-FA, the OC in fog suspended material contains substances that can be mainly extracted by dilute alkali solutions. The chemical characterisation of alkali extractable fraction, performed by HPLC and HNMR, evidenced that iron-organic aggregates are mainly formed by soluble HULIS. Thus, soluble HULIS are able to interact with iron to form particulate in fog, but the chemical composition of a large fraction of water insoluble organic carbon is still unknown. In analogy to natural waters, such aggregates can change the partitioning of C and metal species between aqueous phase and suspended insoluble material, thus influencing the chemistry and photochemistry of the droplets. Moreover, since HULIS constitute an important fraction in regulating surface tension properties of cloud droplets, these complex equilibriums can in general affect cloud formation

processes by acting on both the concentration of insoluble fraction and on surface tension.