# Analytical methods for quantification and characterization of HULIS (HUmic Like Substances) in atmospheric aerosol

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Keywords: HULIS, atmospheric aerosol, UV-VIS, TOT, ATR-FTIR

Atmospheric HULIS (HUmic Like Substances) represent one of the most important classes of water soluble organic compounds (Salma et al., 2008). HULIS are ubiquitous pollutants and are regarded as a polymeric material with poly-acidic properties (Graber et al., 2006). They are optically active (yellow-brown coloured), are involved in the CCN forming processes and influence the optical properties of the aerosol particles. HULIS have been so termed because they resemble to terrestrial and aquatic fulvic and humic acids. They can originate from oxidation reactions of organic precursors (both biogenic and anthropogenic) even if a debate on their origin is still open. Data set on atmospheric HULIS are quite scarce and time series are not available (Feczko et al., 2007). In the literature they have been characterized by means of different analytical methods (Graber et al., 2006). Here we propose the use of UV-VIS spectroscopy and TOT (Thermal Optical Transmittance) (Birch et al., 1996) for their quantification. Samples were prepared by means of SPE extraction of PM10 samples collected in urban and rural sites in Lombardy region.

The UV-VIS spectrophotometer has been calibrated using a standard of humic acid (Fluka, 53680) or of fulvic acid (SRFA, International Humic Substances Society - IHSS). TOT measurements have been performed spiking known quantities of the solutions containing the samples on punches of quartz fibre filters. A very good accordance has been obtained between the two methods. In the examined sites HULIS on average represents up to the 50% of OC.

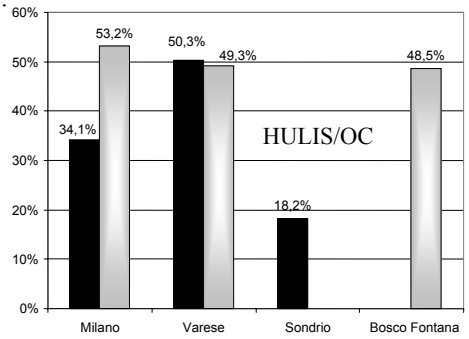


Figure 1- HULIS/OC concentrations for some sites in Lombardy region during winter (black) and summer (grey).

TOT measurements have also allowed to estimate OM/OC ratio which resulted to be in the range 1.5 – 3. For Milan, during winter time, OM/OC is lower than in summer confirming that the chemical nature of HULIS changes with the season probably because changing in the sources and in the processes of formation. These differences in the chemical nature have been also observed by ATR (attenuated total reflection)-FTIR spectroscopy. For Milan the FTIR spectra acquired on winter samples show the signals characteristic of fulvic acid (in particular the absorption at 1720 $cm^{-1}$ due to C=O stretching of the carboxylic group) while summer samples resemble more to humic acid (absorption at 2850 e 2950 $cm^{-1}$ due to methyl and methylene groups of aliphatic chains). Winter times samples are also characterized by higher values of the ratio $E_{250}/E_{365}$ (which is inversely correlated with aromaticity and molecular weight, Graber et al., 2006), in accordance with a predominance a fulvic like molecules. For the rural sites the FTIR spectra have shown a contribution due to polysacchariders.

The chemical speciation of HULIS by FTIR together with the quantification of their contribution to OC and the estimation of OM/OC ratio, allows to deep the knowledge of these ubiquitous pollutants.

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