

HULIS characterisation and attribution to potential source by UV-Vis measurement

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Many studies have shown that "Humic Like Substances" (HULIS) may represent a significant fraction (between 15 and 40 % in mass) of the organic carbon (OC) of atmospheric aerosols. Research on atmospheric HULIS is characterized by the lack of knowledge of their sources. Variations of their concentration and characteristic during yearly monitoring are ascribed to variability in the sources and formation processes, with the hypotheses that HULIS may be generated through various chemical pathways and consist in a mixture of primary and secondary products (Graber & Rudich, 2006).

In this study we investigate the temporal and structural variation of the HULIS fraction collected in different environments and the possibility of using UV-Vis measurement to identify the potential sources of HULIS.

HULIS fractions are isolated with a selective extraction scheme with DEAE anionic exchange resin complemented by carbon quantification with DOC analyser. UV spectroscopy is performed on line for the chemical characterisation of HULIS. UV absorbance of these compounds in function of their carbon mass give an indication on their chemical structure (relative aromaticity). Strong difference of the optical properties and therefore of the chemical structure between HULIS formed during summer- and wintertime is found for urban background samples. This difference highlights the different seasonal processes responsible for emissions and formation of HULIS (Figure 1).

Characteristic specific absorbencies of HULIS compounds were also observed for different aerosol sources: biomass burning, fossil fuel combustion, marine, and secondary formation from anthropogenic and biogenic. Backward trajectory analysis allowed the selection of a representative sample set of marine and anthropogenic conditions for samples collected in Marseilles during the FORMES program. Other samples representative of biomass burning aerosol were collected in very close proximity to combustion-generated aerosol activity.

Functional analysis was performed by APCI/MS/MS to investigate the chemical composition of organic aerosol in terms of functional group quantification. This new approach enables to group chemical compounds by their ability to lose a known neutral molecular fragment for neutral loss

mode or to produce a characteristic ion in the collision cell for the precursor ion scanning mode. This analysis allows a quantitative determination of total carbonyls, carboxylic and nitro groups and provides an apparent molecular weight distribution of the compounds bearing the function under study. Comparisons between functional groups contents and UV absorbance of HULIS will be presented in order to investigate chemical modification of high molecular weight compounds as a function of sources and ageing processes.

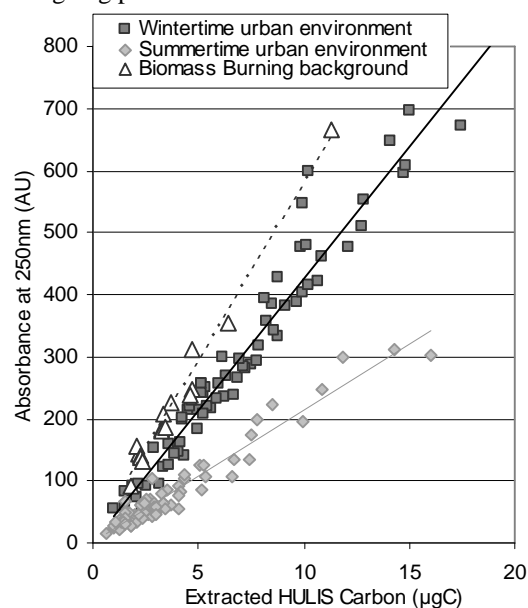


Figure 1: Variation of HULIS structure (relative aromaticity) in function of the extracted HULIS carbon mass for different backgrounds.

Graber, E. R., & Rudich, Y. (2006). *Atmos. Chem. Phys.*, 6, 729-753.

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