

Photo-induced transformation of typical biomass burning organic species: a pathway to secondary Humic Like Substances (HuLiS) formation

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Humic-like substances (HuLiS) are major contributor of organic matter in atmospheric aerosol. These polyacidic macromolecular species have some common features with terrestrial and aquatic humic and fulvic acids (such as for example the optical properties), but they are smaller and have a smaller fraction of aromatic moieties and a larger fraction of aliphatic ones. HuLiS could be both, emitted by primary emission sources (e.g. biomass burning) and secondary formed in the atmosphere by photochemical processes involving notably OH-induced oxidation processes of aromatic hydrocarbon molecules (Graber et al., 2006).

Many investigations have been performed in order to understand the chemical composition of HuLiS extracted from atmospheric waters and aerosol particles especially concerning their fluorescence properties.

Recent studies reported the specific photochemical transformation of phenol to form some oligomers (dimer, trimer, tetramer, etc) which present some fluorescence properties which overlap the typical "C peak" of humic acids in EEM (Excitation Emission Matrix) fluorescence measurements (Barsotti et al., 2015).

The aim of this work was to study the relationship between the transformation of some typical organic species emitted by biomass burning (guaiacol, m-cresol, syringol, acetosyringone, coniferyl aldehyde, vanillin, vanillic acid and gallic acid) and the fluorescence properties detected in irradiated solutions. A particular attention has been given to fluorescence signals similar to those observed for HuLiS extracted from atmospheric waters and particles. Different photochemical processes were investigated such as direct photolysis and reaction with hydroxyls radical, originated by irradiation of hydrogen peroxide and sodium or ammonium nitrate in order to mimic a typical chemical aerosol substrate.

As example the direct photolysis degradation kinetic is reported for acetosyringone, as well as the EEM matrix of the T₀ dark (not irradiated) and the T₂₄ (24 h irradiation) solutions (Figures 1 and 2).

A tentative identification of the transformation intermediates has been performed using high resolution LC-MS/MS (QqTOF).

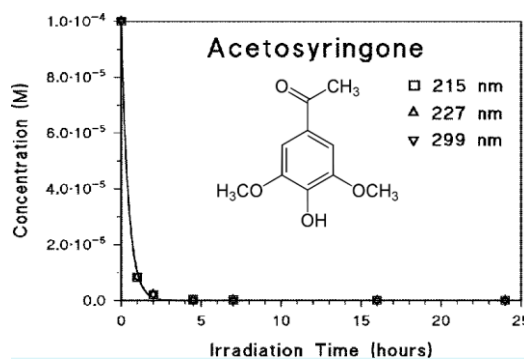


Figure 1. Acetosyringone direct photolysis degradation.

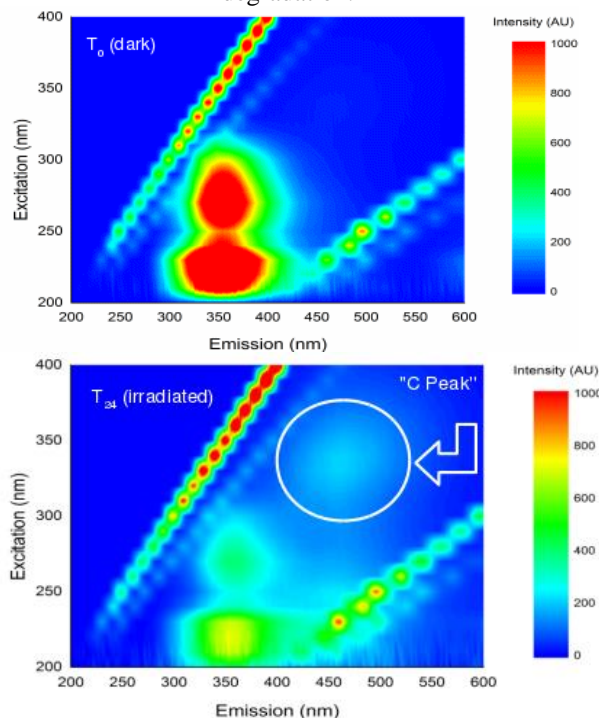


Figure 2. EEM for T₀ dark (up) and T₂₄ (down).

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