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## Could triplet-sensitized transformation of phenolic compounds represent a source of fulvic-like substances in natural waters?

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### *Abstract*

Here we show that fluorescent compounds that could be classified as “M-like” (marine-like) fulvic acids are formed upon phototransformation of phenol by a triplet sensitiser (anthraquinone-2-sulphonate, AQ2S). The relevant process most likely involves phenol oxidation to phenoxyl radical by triplet AQ2S, followed by dimerisation of phenoxyl radicals into phenoxyphenols and dihydroxybiphenyls. It might be the first step of an oligomerization process that bears resemblance with the expected formation pathways of humic-like substances (HULIS) in the atmosphere. Such a process could account for the formation in surface waters of compounds having similar fluorescence properties as “M-like” fulvic acids. Presently it is thought that such species are formed upon photo-fragmentation of larger humic and fulvic acids (“top-down” pathway), and we propose that an opposite, “bottom-up” pathway could also be operational.

*Keywords:* Surface water; phototransformation; HULIS; oligomerization; chromophoric compounds.

## 1. Introduction

The family of humic substances, intended in its most general meaning, gathers a wide class of very important compounds that can be found in soil, surface waters and the atmosphere (Coble, 1996 ; Havers et al., 1998 ; Richard et al. 2011). Despite many similarities, there are also important differences between humic substances that are present in different environmental compartments. For instance, the diversity between surface-water humic and fulvic acids and atmospheric HULIS (HUmic-LIke Substances) is at least as important as their similarity (Piccolo, 2001; Graber and Rudich, 2006).

Humic and fulvic acids as well as HULIS can be formed by a variety of processes, which include microbial processing of biological materials (*e.g.* plant-derived lignin) as well as photochemical transformation of dissolved organic compounds (Mostofa et al., 2007; Rezende et al., 2010). In particular, several papers advance the hypothesis that atmospheric HULIS might be formed upon photoinduced oligomerization of smaller molecules (see *e.g.* Net et al., 2010, and Liu et al., 2012).

Fluorescence spectra, and in particular the Excitation-Emission Matrix (EEM) technique are extremely useful to characterise many important water components, including humic substances (Baker, 2001). EEM can also be used to monitor the modifications that these compounds undergo, *e.g.* upon microbial and/or photochemical processing (Leenher and Croue, 2003; Mostofa et al., 2011). In this communication we report, for the first time to our knowledge, on the formation of fulvic-like substances upon phenol transformation photoinduced by the triplet sensitizer anthraquinone-2-sulphonate (AQ2S). The latter was used as model compound for the reactivity of organic matter chromophores in the aqueous solution. Such a process provides a new, potentially important pathway for the photoinduced formation of fulvic substances in surface waters, which would have some interesting similarities with the generation of atmospheric HULIS.

## 2. Experimental

*2.1. Reagents and materials.* Anthraquinone-2-sulphonic acid sodium salt (AQ2S, purity grade 97%) and phenol (> 99%) were purchased from Sigma Aldrich. All reagents were used as received, without further purification. Water used was of Milli-Q quality.

*2.2. Irradiation experiments.* The photochemical experiments were carried out on 100 mL aqueous solution (initial AQ2S concentration 0.1 mM), placed in a Pyrex tube reactor. At fixed time intervals during irradiation, 5 mL sample aliquots were taken and used to characterise the fluorescence contours. The irradiation device consisted of six UVA polychromatic lamps ( $\lambda_{\text{max}} = 365$  nm, Philips TL15W) fitted in a cylindrical metal enclosure. The lamps were arranged radially with respect to the reactor and the incident photon flux in solution (between 340 and 400 nm) was  $2.40 \times 10^{-6}$  Einstein  $\text{L}^{-1} \text{s}^{-1}$ , measured by Pyridine PNA actinometry (Dullin et al., 1982). Figure 1 shows the emission spectrum of the lamps, measured with an Ocean Optics SD 2000 CCD spectrophotometer (calibrated by using a DH-2000-CAL Deuterium Tungsten Halogen reference lamp), and the absorption spectra of AQ2S and phenol (molar absorption coefficient,  $\epsilon$ ). The latter were taken with a Varian Cary 3 UV-Vis spectrophotometer, using quartz cuvettes of 1.00 cm optical path length. The same instrument was used to measure absorption spectra of irradiated solutions.

*2.3. Fluorescence measures.* A Varian Cary Eclipse fluorescence spectrophotometer was used, adopting a 5 nm bandpass on both excitation and emission. The fluorescence excitation-emission matrix (EEM) was obtained at 5 nm intervals, for excitation wavelengths from 200 to 500 nm and emission ones from 220 to 600 nm. Identification of fluorescent constituents in water samples was performed on the basis of literature data (Parlanti et al., 2000), using the main fluorescence contours to identify the relevant peaks.

*2.4. Laser flash photolysis measures.* The laser flash photolysis (LFP) system has been described in previous works (*e.g.* Maddigapu et al., 2010). The transient absorption experiments were performed by using the third harmonic ( $\lambda = 355$  nm) of a Quanta Ray Nd:YAG laser system, operating with an output of 60 mJ per pulse. Transient absorption spectra were monitored by means of time-resolved absorption spectroscopy, using a 100 W xenon arc lamp as the light source. The samples were pumped through the cell with a peristaltic pump, replenishing the cell after the required laser pulses. The transient absorbance at each pre-selected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator, and a photomultiplier (1P28). Stock solutions of AQ2S and phenol were prepared in Milli-Q water and an appropriate volume was mixed just before each experiment, to obtain the desired concentration of both species.

### 3. Results and discussion

Figure 2 reports the EEM spectra of: 2A) 0.1 mM AQ2S as prepared; 2B) 0.1 mM phenol as prepared; 2C) 0.1 mM AQ2S after 8 h irradiation; 2D) 0.1 mM AQ2S + 0.1 mM phenol after 8 h irradiation. AQ2S alone shows no fluorescence, while phenol shows its typical fluorescence peaks at excitation/emission wavelengths  $Ex/Em = 200-230 \text{ nm}/ 280-330 \text{ nm}$  and  $250-280 \text{ nm}/ 280-330 \text{ nm}$  (Bosco et al., 2006). The peaks at  $Em \sim 580 \text{ nm}$  represent second harmonics of phenol fluorescence emission and are a mere instrumental effect. Irradiation of phenol alone did not modify its EEM spectrum, coherently with the fact that this compound does not absorb radiation above 300 nm. Therefore, phenol would not undergo direct photolysis under the adopted experimental conditions.

When AQ2S was irradiated alone (2C), three weak to very weak signals or groups of signals appeared at  $Ex/Em = 200-240/400-450 \text{ nm}$ ,  $280-350/400-450 \text{ nm}$  and  $200-500\text{nm}/540-600 \text{ nm}$ . They are most likely due to AQ2S phototransformation intermediates, possibly the hydroxyderivatives. Indeed, the evolution of AQ2S triplet state upon reaction with water produces transient adducts with water (where water is attached to either the aromatic ring or an oxygen atom), which either yield back ground-state AQ2S, or evolve into AQ2S-OH isomers (Maurino et al., 2008; Maddigapu et al., 2010; Bedini et al., in press). To support this, we observed the formation of a broad absorption band in the 350-550 nm range (that is, right in the range of EEM excitation wavelengths), which is fully compatible with the occurrence of  $\alpha$  and  $\beta$ -hydroxy-AQ2S (Loeff et al., 1983; see also Figure SM1).

Irradiation of 0.1 mM AQ2S + 0.1 mM phenol gave quite different results (2D). In addition to the fluorescence of AQ2S intermediates and the residual one of phenol (after 8 h irradiation, phenol was present at about 10% of its initial concentration), a new strong signal appeared with a maximum at  $Ex/Em = 250-300/330-400 \text{ nm}$ . Such a signal could be compatible with previously reported data attributed to marine-like (“M-like”) fulvic acids (Parlanti et al., 2000), which show similar excitation maximum range, but emission maximum shifted at 380-420 nm.

Interestingly, compounds that show fluorescence in this region are formed upon irradiation of terrestrial fulvic acids (C-like), the photodegradation/photobleaching of which produces a blue shift in both the excitation and emission wavelengths (Mostofa et al., 2007). The blue shift might be caused by a photoinduced decrease of molecular weight and/or aromaticity degree of fulvic acids upon irradiation.

In the present case, the observed peak is red-shifted (at least as far as the emission wavelength is concerned) compared to that of phenol. Such an effect could likely be ascribed to an increase of the

molecular weight of the transformation intermediates compared to the starting compound (Mostofa et al., 2011). This is a reasonable hypothesis, considering that phenol dimers (dihydroxybiphenyls and phenoxyphenols) have been detected as intermediates of AQ2S-sensitised phenol transformation (Maurino et al., 2008). Such compounds may be formed upon dimerization of the phenoxy radical (Neta and Grodkowski, 2005), and Figure 3 provides evidence for the formation of such a transient species upon laser irradiation of AQ2S in the presence of phenol. Indeed, the difference of transient spectra obtained after excitation of AQ2S with and without phenol shows a transient species absorbing from 360 up to 420 nm, with  $\lambda_{\text{max}} \sim 400$  nm. It is compatible with the formation of phenoxy radical (Gadosy et al., 1999). Further irradiation of phenol dimers is then expected to produce higher oligomers, as recently proposed by Net and coworkers (2010). Several papers report on the possible formation of atmospheric HULIS upon photoinduced oligomerization of phenolic compounds (Net et al., 2010). Here we show that a similar process would produce compounds that could be classified as “M-like” fulvic material on the basis of their EEM spectra. Considering that AQ2S is a good proxy for naturally occurring triplet sensitizers (Maddigapu et al., 2011), the described process could be operational in natural waters under irradiation.

#### 4. Conclusions

The sensitised transformation of phenol upon irradiation of AQ2S produces fluorescent material that can be classified as “M-like” fulvic substances. The likely formation pathway involves phenol oligomerization, initially started by its oxidation to the phenoxy radical. This primary process would then be followed by dimerisation of phenoxy and, possibly, by similar reactions involving phenol dimers.

Formation of fulvic substances showing fluorescence in the wavelength interval of interest has been observed upon irradiation of surface waters. The phenomenon has been attributed to photoinduced fragmentation of humic and fulvic substances (“top-down” pathway; Mostofa et al., 2007). Here we show that compounds with very similar EEM spectra can be formed upon oligomerisation of phenolic species (“bottom-up” pathway). The two opposite pathways (fragmentation *vs.* oligomerization) are closely reflected in the trends of the relevant EEM spectra: a blue-shift has been observed upon photoinduced fragmentation of humic and fulvic acids, and a red shift is seen here in the transformation of phenol into “M-like” compounds. Because phenol oligomerization would obviously produce phenol-like substances, here we show that there could be a partial overlap between phenol-like and fulvic-like substances in environmental waters.

The “bottom-up” pathway described here has similarities with the formation of atmospheric HULIS, which takes place upon oligomerization of smaller molecules. It allows the hypothesis that partially similar processes could take place in surface and atmospheric waters. In surface waters, however, additional reactions would be operational (fragmentation of larger compounds) that might at least partially account for the difference in photoactivity between atmospheric and surface-water chromophoric organic matter. Interestingly, atmospheric chromophoric compounds are less photoactive than those found in surface waters (Albinet et al., 2010). Indeed, further research will be required to assess the relative importance of the “bottom-up” and the “top-down” pathways to the formation of humic and fulvic compounds in environmental waters.

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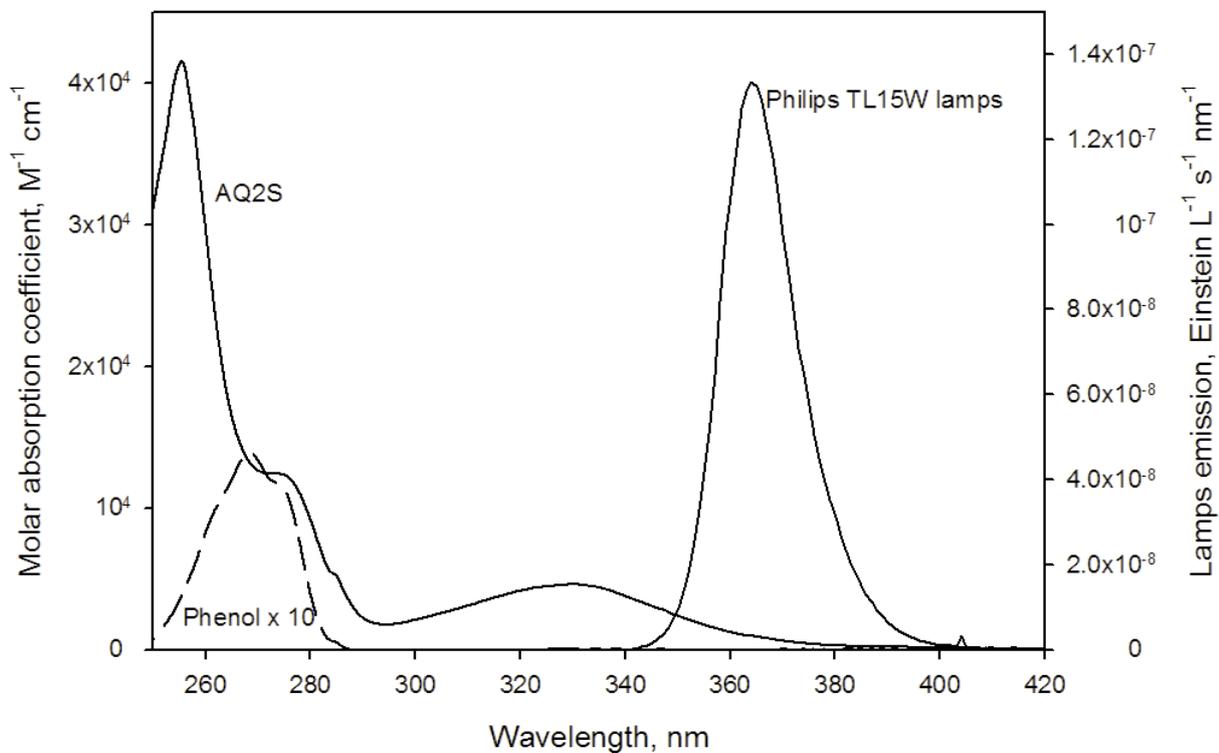
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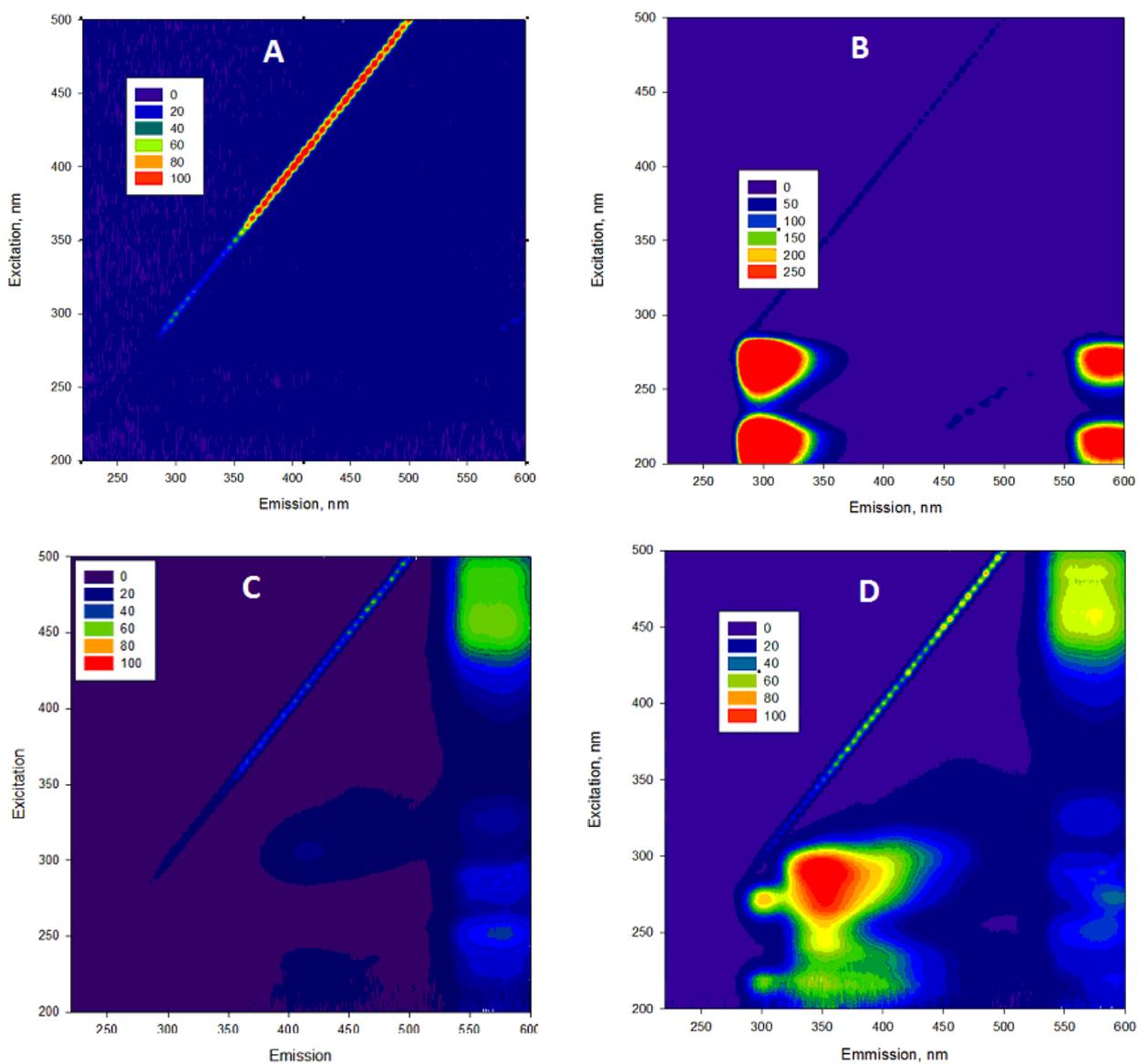
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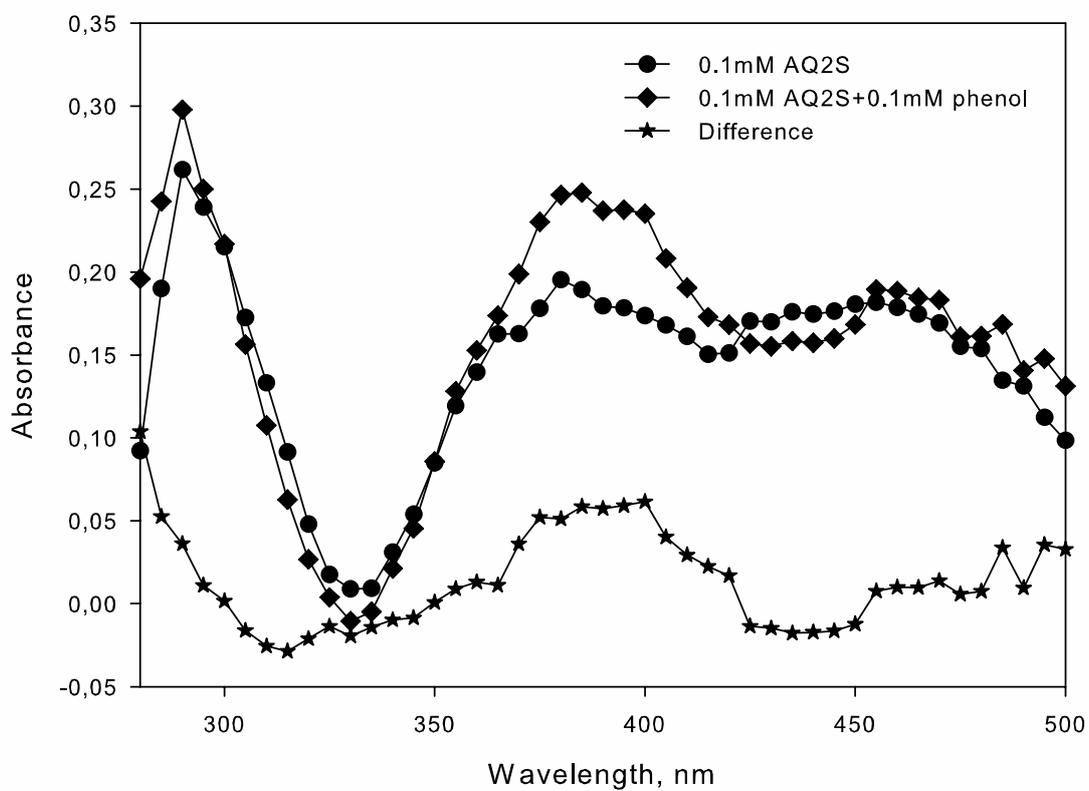
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**Figure 1.** Absorption spectrum (molar absorption coefficient  $\epsilon(\lambda)$ ) of AQ2S and Phenol in Milli-Q water, and emission spectrum of the six lamps (Philips TL15W) adopted for the irradiation experiments.



**Figure 2.** 3D fluorescence excitation-emission matrix of: as-prepared 0.1 mM AQ2S (A) and 0.1 mM phenol (B), without irradiation; 0.1 mM AQ2S alone after 8-h irradiation (C); and 0.1 mM AQ2S + 0.1 mM phenol after 8-h irradiation (D). The linear features correspond to the signal obtained when excitation equals the emission wavelength (Rayleigh scattering).



**Figure 3.** Absorption spectra obtained upon 355 nm excitation of 0.1 mM AQ2S, with and without 0.1 mM phenol, at the natural pH and at ambient temperature in aqueous solution, 90 ns after the laser pulse.