



A comprehensive structural evaluation of humic substances using several fluorescence techniques before and after ozonation. Part I: Structural characterization of humic substances

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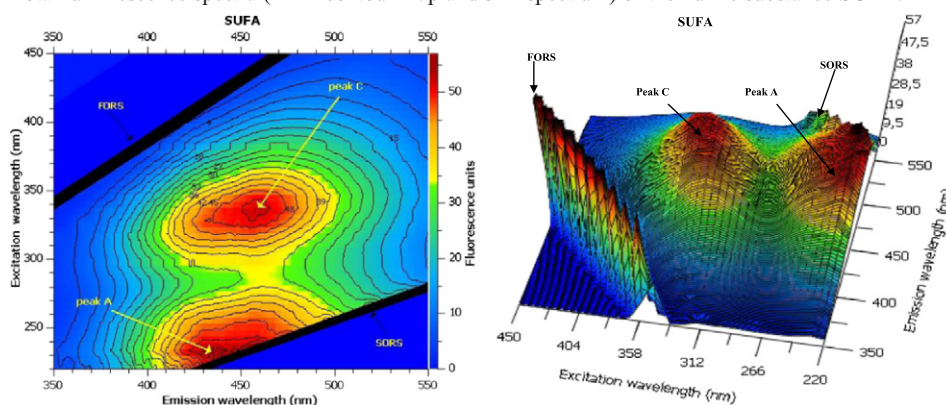
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HIGHLIGHTS

- TLS, SFS, ESF, fluorescence index and $\lambda_{0.5}$ are useful to characterize humic substances.
- EEM spectra of natural humic substances show 2 peaks: A (230/437 nm) and C (335/460 nm).
- Synchronous spectra allowed the identification of a protein-like peak ($\lambda_{syn} = 290$ nm).
- Good correlations were obtained between ¹³C NMR aromaticity and fluorescence index and $\lambda_{0.5}$.
- ALHA shows fluorescence spectra completely different to those of natural humic substances.

GRAPHICAL ABSTRACT

Total luminescence spectra (EEM contour map and 3-D spectrum) of the humic substance SUFA.



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ABSTRACT

The main objective of this work (Part I) is to conduct a comprehensive structural characterization of humic substances, using all the current fluorescence techniques: emission scan fluorescence (ESF), synchronous fluorescence spectroscopy (SFS), total luminescence spectroscopy (TLS or EEM) through the use of both 2-D contour maps and 3-D plots, fluorescence index and the $\lambda_{0.5}$ parameter. Four humic substances were studied in this work: three of them were provided by the International Humic Substances Society (Suwannee River Fulvic Acid Standard, Suwannee River Humic Acid Standard and Nordic Reservoir Fulvic Acid Reference) and the other one was a commercial humic acid widely used as a surrogate for aquatic humic substances in various studies (Aldrich Humic Acid: ALHA). The EEM spectra for the three natural aquatic substances were quite similar, showing two main peaks of maximum fluorescence intensity: one located in the ultraviolet region and centered at around Ex/Em values of 230/437 nm (peak A) and another one in the visible region, centered at around 335/460 nm (peak C); however, the EEM spectrum of ALHA is completely different to those of natural aquatic humic substances, presenting four poorly resolved main peaks with a high degree of spectral overlap, located at 260/462, 300/479, 365/483 and 450/524 nm. The synchronous spectra at $\Delta\lambda = 18$ and 44 nm (especially at $\Delta\lambda = 18$ nm) allowed the identification of a protein-like peak at λ_{syn} around 290 nm, which was not detected in the EEM spectra; as it happened with EEM spectra, the synchronous spectra of ALHA are quite different from those of the aquatic humic substances, presenting a higher number of bands that suggest greater structural

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complexity and a higher degree of polydispersity. Good correlations were achieved between ^{13}C NMR aromaticity and both fluorescence index and $\lambda_{0.5}$ parameter. The different spectra presented by ALHA compared to those shown by the natural aquatic humic substances for all the fluorescence techniques studied suggest an important structural difference between them, which cast doubt on the use of commercial humic acids as surrogates for natural humic substances.

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1. Introduction

Aquatic natural organic matter (NOM) composition clearly depends on the environmental source (Aiken and Costaris, 1995); a range of organic compounds are found in natural waters, from low molecular weight hydrophilic acids, carbohydrates, proteins and amino acids to higher molecular weight compounds such as humic substances (fulvic and humic acids) (Choudry, 1984). Most of the NOM found in natural waters are humic substances (30–50%) (Pernet-Coudrier et al., 2011; Thurman, 1985), which result from elutriation of the surrounding soils and from microbiological, chemical and photochemical reactions (humification process) that occur during the degradation and polymerization of vegetable organic matter in water (Galapate et al., 1997; Langlais et al., 1991; Rodríguez et al., 2012a). Humic substances compete for adsorption sites with target compounds in activated carbon adsorption (Rodríguez et al., 2011), contribute to the fouling of membranes, form soluble complexes with many heavy metal ions and organo-pollutants, promote the formation of bio-film in water distribution pipelines and are known precursors for disinfection by-products in chlorination (Allpike et al., 2005; Liu et al., 2008; Zhou et al., 2000).

Humic substances are complex mixtures of high to low molecular weight species, so they are polydisperse systems with a specific distribution of molecular weights (Cabaniss et al., 2000; Myllykangas et al., 2002; Rodríguez and Núñez, 2011); fulvic and humic acids make up the two main fractions of humic substances and they can be distinguished by their different solubility at pH 1: the precipitated fraction is humic acid and the part remaining in solution is fulvic acid. Fulvic acids always represent the larger fraction (the fulvic acid/humic acid mass ratio is generally around 9:1) and are more soluble than humic acids, since they have a lower average molecular weight and a higher acidity (especially carboxylic acidity) than humic acids (humic acids are often in colloidal form due to their large size), whereas humic acids show more aromaticity and UV absorbance and have more color than fulvic acids (Andrews and Huck, 1996; Langlais et al., 1991; Rodríguez and Núñez, 2011); moreover, humic acids generally have a greater trihalomethane formation potential (Rodríguez et al., 2012b) and are more readily coagulated by aluminum and iron (III) salts than fulvic acids (Rodríguez et al., 2012a).

The following analytical techniques are prominent among those used for the characterization of humic substances (Rodríguez and Núñez, 2011): high performance size-exclusion chromatography (HPSEC) for the study of the distribution of molecular weights (Chin et al., 1994; McDonald et al., 2007), elemental analysis (EA) (Langlais et al., 1991), organic acidity analysis (Chandrakanth and Amy, 1996), nuclear magnetic resonance (NMR)—both ^1H NMR (Kim et al., 2006; Ma et al., 2001) and ^{13}C NMR (Mao et al., 2007; McDonald et al., 2007; Muller et al., 2004; Thorn et al., 2010; Tsuda et al., 2010), Fourier-transform infrared (FTIR) (Chen et al., 2002; Chiang et al., 2009; Kim et al., 2006; Ma, 2004) and UV/Vis spectroscopy (Rodríguez and Núñez, 2011).

In addition to those techniques, fluorescence techniques have also been used in the study of humic substances (Kalbitz et al., 2000). Fluorescence spectroscopy provides important information on the chemical nature of the humic substances: the position, shift and intensity of fluorescence peaks can be correlated to structural information such as functional groups (electron-donating/withdrawing groups), polycondensation, aromaticity, heterogeneity and dynamic properties related to their intramolecular and intermolecular interactions (Chen et al., 2003; Mobed et al., 1996; Zhang et al., 2008); moreover, it is a simple, rapid, sensitive and non-destructive method requiring only a small volume of

aqueous sample at a low concentration (usually <20 mg/L) (Swietlik and Sikorska, 2004). There are several fluorescence techniques, from the simplest and conventional emission (emission scan fluorescence—ESF) to the most recent and complete synchronous fluorescence spectroscopy (SFS) and total luminescence spectroscopy—TLS (also known as excitation–emission matrix—EEM). SFS presents several advantages over conventional ESF: it provides better sensitivity and improved peak resolution (Chen et al., 2002) as well as additional information on structural signatures of humic macromolecules (Chen et al., 2003); it also offers a potentiality to reduce overlapping interferences and a possibility for each fluorescent component to be identified in a specific spectral range (Miano and Senesi, 1992; Peuravuori et al., 2002). TLS (in which repeated emission scans are collected at numerous excitation wavelengths) is at present the most complete technique, as it provides unique “finger prints” (in the form of an excitation–emission matrix) for single compounds or a mixture of fluorescent components (Alberts et al., 2002; Chen et al., 2003; Coble, 1996; Henderson et al. 2009; Her et al., 2003; Hudson et al., 2008; Peiris et al., 2011; Sierra et al., 2005). Even though the various structural units present in the humic macromolecules can have very variable effects on the wavelength and intensity of fluorescence, some general behaviors may be described (Coble, 1996; Peuravuori et al., 2002; Senesi, 1990; Swietlik and Sikorska, 2004): the fluorescence intensity decreases with increasing molecular size of the humic macromolecule; electron-withdrawing groups (COOH) decrease and electron-donating groups (OH, NH_2 , OCH_3) increase the fluorescence intensity in aromatic compounds; carbonyl-containing substituents, hydroxyl, alkoxy and amino groups tend to shift fluorescence maxima to longer wavelengths (red-shift), whereas a blue-shift (fluorescence maxima shift towards shorter wavelengths) can be caused by a reduction in the degree of the π -electron system (such a decrease in the number of aromatic rings), by a reduction of conjugated bonds in a chain structure or by a conversion of a linear ring system to a non-linear system and finally, the presence of fluorescence bands (peaks) at long wavelengths with low intensity can be attributed to linearly condensed aromatic rings and other unsaturated bond systems capable of a high degree of conjugation within the humic macromolecule (Peuravuori et al., 2002).

Direct fluorescence TLS measurement of natural waters is not suitable for studying humic and fulvic acids individually, since their fluorescence in most cases overlap (Baker, 2001; Hudson et al., 2008; Sierra et al., 2005), making an accurate identification of humic acids in the presence of fulvic acids difficult (the comparatively weaker fluorescence signals of the less abundant humic acids are overshadowed by the stronger fluorescence signals of the more abundant fulvic acids) (Peiris et al., 2011); that is why isolated humic and fulvic acids have been used in this study.

The main objective of this work is to conduct a comprehensive structural characterization of humic substances, employing all the current fluorescence techniques: emission scan fluorescence (ESF), synchronous fluorescence spectroscopy (SFS) and total luminescence spectroscopy (TLS or EEM) through the use of both 2-D contour maps and 3-D plots. In addition to the three earlier techniques, other fluorescence-related parameters have been studied, such as the fluorescence index (Chen et al., 2003; Kim et al., 2006; McKnight et al., 2001) and the $\lambda_{0.5}$ parameter (Kim et al., 2006), both related with the aromaticity of humic substances.

Humic substances provided by the International Humic Substances Society (IHSS), which are considered as reference materials at an

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