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Organic matter source discrimination by humic acid characterization: Synchronous scan fluorescence spectroscopy and Ferrate(VI)

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HIGHLIGHTS

- Synchronous scan fluorescence spectroscopy to distinguish humic acid source.
- Use of Ferrate(VI) to dramatically enhance spectroscopic discrimination of source.
- Use of intensity ratios of SSF peaks to further enhance source discrimination.

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ABSTRACT

In this study, seven soil and sedimentary humic acid samples were analyzed by synchronous scan fluorescence (SSF) spectroscopy. The spectra of these humic acids were compared to each other and characterized, based on three major SSF peaks centered at approximately 281, 367 and 470 nm. Intensity ratios were calculated based on these peaks that were used to numerically assist in source discrimination. All humic acid samples were then reacted with Ferrate(VI) and were again analyzed with SSF. Upon the addition of Ferrate(VI) SSF spectra were obtained which more readily differentiated humic acid source. This method will assist geochemists and water management districts in tracing sources of organic matter to receiving water bodies and may aid in the elucidation of the chemical nature of humic acids.

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1. Introduction

Humic substances are the most prevalent source of natural organic matter in soils, sediments, and natural waters and contribute to the brownish-yellow color of natural waters, consisting of complex heterogeneous mixtures formed by the decomposition of surrounding plant, animal, and microbial matter (Calace et al., 2000; Hsu and Hatcher, 2006). The chemical composition of humic substances will therefore vary with source of input and depositional environment. Because humic substances are ubiquitous in nature, represent a large fraction of the organic matter present in soils and sediments and their chemical structures reflect both precursor material and environmental conditions, developing a method to differentiate between humic substances from different environments would be a significant contribution to organic matter source determination.

With respect to aquatic or terrestrial organic matter source determinations, a biomarker is typically a compound or a set of compounds whose structure or compositional distribution can be correlated with origin. Historically, biomarkers are molecular fossils (Belicka et al., 2002; White et al., 2008) associated with specific organisms or specific sets of organisms, the basic structures of which remain relatively intact throughout diagenetic processes. Belicka et al. (2009) described the importance of understanding carbon source input and output and how this balance may be perturbed by global climate change and how important source input is to constructing meaningful carbon budgets. Fluxes of marine and terrestrial organic matter to marine systems, for instance, the Arctic Ocean, a large repository for terrestrial organic matter runoff (Rachold et al., 2004), might change with altered organic carbon supply and cannot be understood without the discrimination between more rapidly metabolized carbon from aquatic biomass, and more recalcitrant terrestrial carbon (Belicka et al., 2009). Typically biomarkers have most commonly consisted of lipids (*n*-alkanes, sterols, fatty acids, terpenoids, etc.) which may be enhanced by carbon isotopic composition data and C/N ratios. This study proposes to use humic acids, a major fraction of soil and sedimentary organic matter, analyzed by fluorescence as an alternate method for organic matter source discrimination.

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Numerous studies have been done to characterize humic acids from different sources. Previous studies generally concur that terrestrial humic acids contain more highly condensed aromatic systems than do their sedimentary counterparts based most often on 13CNMR and fluorescence spectroscopy (Millero and Sohn, 1992; Sharpless and McGown, 1999). However, visual inspection of such spectra alone emphasizes the challenge of differentiating between soil (terrestrial) and sedimentary humic acids isolated from various locations. Senesi et al. (1991a), for instance, emphasized the red shift that is found for both emission and excitation peaks in the fluorescence spectra of a series of samples progressing from dissolved fulvic acid, sedimentary humic acid, leonardite and soil humic acid and finally to paleosol humic acid. Sierra et al. (2005) concluded that a combination of excitation/emission matrix (EEM) fluorescence, regular emission and excitation spectra and synchronous scan fluorescence provided valuable information on organic matter sources and degree of humification for humic and fulvic acids.

Studies by Kalbitz et al. (1999) and Milori et al. (2002), have shown the benefits of using an intensity ratio to determine the degree of humification in soils. This study demonstrates how intensity ratios may have the possibility of also serving to numerically aid in humic acid source differentiation. Furthermore, Ferrate(VI) addition, monitored by synchronous scan fluorescence, may provide a more distinct parameter for the characterization and differentiation of humic acids from various sources. Although studies exist which have examined the possibility of characterizing humic acids qualitatively and quantitatively by using synchronous scan fluorescence spectroscopy (Senesi et al., 1989, 1991a, 1991b; Långvik et al., 1994; Ahmad and Reynolds, 1995) or by studying humic acid oxidation products (Ertel and Hedges, 1984; Ertel et al., 1984), none were found which coupled synchronous scan fluorescence with oxidation by Ferrate(VI). The purpose of this study was to determine whether synchronous scan fluorescence spectroscopy, coupled with Ferrate(VI) oxidation, might serve as an enhanced and relatively inexpensive means to compare humic acids from different environments. If successful, this method could not only benefit geochemists and water management districts in tracing sources of organic matter to surrounding water reservoirs, but might also prove useful in elucidating the chemical nature of humic acids.

2. Experimental methods

All HAs used in this study were extracted in our laboratory from soils and sediments, the sources of which are summarized in Table 1. Procedures for extraction and purification of HA samples are described in detail elsewhere (Sohn and Hughes, 1981). Humic acid solutions were prepared from the eight different humic acids used in this study by weighing 15–16 mg of solid humic acid and dissolving it in 100 mL of 5 mM phosphate buffer (Na_2HPO_4; initial pH∼9). The solutions were diluted to yield concentrations of 30–40 mg L^{-1} HA. Upon Addition of HA to buffer and subsequent dilution, the pH for all diluted samples ranged from 7 to 8, making these analyses very environmentally relevant as this is the pH range for most natural waters.

Potassium ferrate (K_2FeO_4) of high purity was prepared by the wet method (Luo et al., 2011). Two Fe(VI) concentrations (∼250 μM and ∼1000 μM) in 5 mM Na_2HPO_4/1 mM $Na_2B_4O_7{\cdot}10H_2O$) were used for each sample to study the effect of varying the concentration on the reaction with the humic acid. The concentrations were determined by adjusting the Fe(VI)/buffer concentrations until ultraviolet–visible (UV–Vis) absorbance values of ∼0.288 and ∼1.15 (250 and 1000 μM respectively), were obtained at 510 nm in a 1-cm quartz cuvette (ε at 510 nm is 1150 $M^{-1}cm^{-1}$ for Fe(VI)). The phosphate/borate buffer provides a stable matrix for Fe(VI) and prevents coagulation of Fe (III) hydroxides (reaction product of Fe(VI)) which can interfere with spectroscopic analysis of the reaction mixture. Also, this buffer has a pH ∼9.0, which upon HA addition, results in a solution of desired pH (7.0–8.0) for modeling natural waters. Solutions of Fe(VI) were prepared fresh daily and concentrations were continuously monitored by UV–Vis spectroscopy.

Synchronous scan fluorescence (SSF) spectra were collected using the diluted HA samples (15–20 mg L^{-1}) on a J-Y/Horiba SPEX Fluorolog spectrophotometer. A 1-cm quartz cuvette was used and was acid-washed and rinsed with distilled water between trials. Synchronous scans were conducted over a range of 250–520 nm while keeping a constant wavelength difference of 55 nm. In this study, parameters similar those described by Milori et al. (2002) were used for preliminary trials in addition to the following conditions which were chosen based on the observance of reproducible spectra and maximum differentiation of peaks. Increment and integration times of 1.0 nm and 0.3 s were used, respectively along with slit widths for both the excitation and emission monochromators of 7 nm. All spectra were analyzed for the presence and location of peaks and if/how the fluorescence intensity of those peaks changed after reaction with Fe(VI).

Fe(VI) solutions were initially scanned before HA addition and no detectable fluorescence was observed. Subsequently 1.5 mL of humic acid solution was placed in the cuvette and 1.5 mL of the ∼1000 μM (first trial) or ∼250 μM (second trial) Fe(VI) solution was added to the cuvette. A 1:1 volume ratio of humic acid and Fe(VI) cuts each of the initial concentrations in half. Thus, the final concentrations of humic acid and Fe(VI) were 15–20 mg L^{-1} (depending on the sample solubility) and either 500 μM or 125 μM, respectively. Immediately after Fe(VI) addition, fluorescence monitoring began. Spectral readings were taken approximately every 2.5 min (based on the time needed to complete a scan) for 20 min, or until no further change in fluorescence was observed, to track the change in humic acid fluorescence as a function of wavelength and time after the addition of Fe(VI). After every trial, the quartz cuvette was soaked in concentrated nitric acid

Table 1
Summary of humic acid sample source.

Type	Abbreviation	Location	Location Description
Soil	S2	Melbourne, Florida	Florida Institute of Technology's Dent's Botanical Garden, which consists mainly of Live Oak, Cabbage Palmetto, and Basswood
Soil	CO	Colorado	8600 feet above sea level from an instream excavated pond that was surrounded by an environment of grasses, aspen, Ponderosa pine, Douglas fir, and Engelmann spruce
Marine Sedimentary	HA4	Sebastian Inlet, Florida	4.5 miles offshore from inlet
Marine Sedimentary	M2	Atlantic Ocean, off the Florida coast	23 miles off the eastern Florida coast at a depth of 275 meters (27°2′N, 79°48′W)
Estuarine Sedimentary	MC	Mullet Creek, Florida	Indian River Lagoon, Intertidal channel between mangrove islands at a salinity of 25 ppt
Estuarine Sedimentary	KBN5	Kings Bay, Florida	Salinity range from 0–10 ppt depending on tidal fluctuations and freshwater input
Freshwater Sedimentary	SR	Sebastian River, Florida	Electrical conductivity of 0 established this as freshwater environment

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