Research Article

The role of fulvic acid composition in the photosensitized degradation of aquatic contaminants

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Abstract. Dissolved organic matter (DOM) chemical composition varies depending upon the source of its precursor materials. Results show that the indirect photodegradation rate coefficients for the compounds sulfadimethoxine (SDM) and triclocarban (TCC) differ depending on the source of fulvic acids used as DOM surrogates. For sulfadimethoxine, little to no enhanced photolysis occurred for the terrestrially derived Suwannee River fulvic acid, but the rate coefficients for triclocarban increased 28%. In contrast, a large photo-enhancement (48% for SDM and 45% for TCC) occurred in the presence of Pony Lake and Old Woman Creek fulvic acids, both of which are derived from predominantly autochthonous material. Conversely, the iron-promoted photodegradation of alachlor occurred more quickly in the presence of Suwannee River fulvic acid than another autochthonous fulvic acid isolated from Lake Fryxell, Antarctica. This pathway is dominated by reaction through hydroxyl radicals generated by the photolysis of the fulvic acids. Taken together, these data provide evidence that autochthonous fulvic acids are more reactive than allochthonous fulvic acids in promoting pathways involving triplet dissolved organic matter intermediates, whereas the latter are more reactive than the former in promoting degradation by some reactive oxygen species (ROS). Thus, more systematic studies are needed to determine the full extent of the linkage between fulvic acid composition and its ability to promote indirect photolytic processes and how the presence of other DOM fractions may affect these reactions.

Key words. Dissolved organic matter; aquatic photochemistry; triclocarban; sulfadimethoxine; alachlor; fulvic acid.

Introduction

Dissolved organic matter (DOM) is a complex, heterogeneous mixture of organic compounds that are ubiquitous to surface waters. The abundant chromophoric moieties in DOM are able to initiate a number of photochemical reactions of environmental significance. These include the production of labile carbon for microbial activity (Moran and Zepp, 1997; Miller et al., 2002; Kaiser and Sulzberger, 2004; Anesio et al., 2005; Kim et al., 2006), screening cell-damaging UV light in the water column (Zepp et al., 1998), and mediating passive and active photochemical processes that can detoxify deleterious substances (Bushmann et al., 2005; Gereke et al., 2001; Lam and Mabury, 2005; Miller and Chin, 2002; Miller and Chin, 2005).

Sunlight irradiated DOM also produces reactive oxygen species (ROS) such as hydrogen peroxide

Table 1. Elemental Analysis and ^{13}C-NMR data for selected fulvic acid samples. Suwannee River Fulvic Acid (SRFA); Pony Lake Fulvic Acid (PLFA); Lake Fryxell Fulvic Acid (LFFA); Old Woman Creek Fulvic Acid (OWCFA).

Fulvic Acid	Source	Distribution of ^{13}C-NMR Signatures of Fulvic Acid Samples[1]					Elemental Analysis					
		Aliphatic (0-60ppm)	Hetero-aliphatic (60-90 ppm)	Aromatic + Phenolic (110-165 ppm)	Carboxyl (165-190 ppm)	Carbonyl (190-220 ppm)	C	H	O	N	S	C:N
SRFA[2]	Terrestrial	33	11	24	20	7	52.4	4.3	42.2	0.7	0.4	72.8
PLFA[3]	Microbial	61	8.4	12	17	1.2	49.6	6.1	37.4	6.5	2.4	7.6
LFFA[4]	Microbial	48	12	12	21	4.0	55	5.5	34.9	3.1	1.3	20.5
OWCFA[5]	Mixed	50	13	15	16	2	-	-	-	-	-	-

[1] The spectral regions for the ^{13}C-NMR signature defined according to Dria and co-workers (2002). The values listed represent the integral of specified ppm region normalized to the total integrated area and are reported as a percent. [2] Solution-state ^{13}C-NMR data from IHSS (Thorn et al, 1989). [3] Solid-state CPMAS ^{13}C-NMR data from IHSS; elemental analysis from R.M. Cory (personal communication). [4] Solution-state ^{13}C-NMR and elemental analysis data for fulvic acid sample isolated from water collected at a depth of 7.5m from McKnight et al. 1991. [5] Solid-state ^{13}C-NMR spectra for Old Woman Creek fulvic acid isolate were acquired in our labs using methods described in Fimmen et al. (2007).

(H_2O_2) singlet oxygen ($^1O_2$), superoxide (O_2^-), and the hydroxyl radical (OH•) (Blough and Zepp, 1995) as well as other phototransients, e.g., carbon centered radicals and excited triplet states of DOM. In many cases, these transients promote the indirect photo-degradation of organic contaminants (Dimou et al., 2005; Gerecke et al., 2001; Lam and Mabury, 2005; Miller and Chin 2005; Werner et al., 2005; Fisher et al., 2006; Halladja et al., 2007; plus many others). To further complicate matters, DOM also retards contaminant photodegradation by screening reactive wavelengths of light (*e.g.*, Boreen et al., 2004; Walse et al., 2004), and scavenging ROS (Brezonik and Fulkerson-Brekken, 1998) and other photo-generated reactive species such as triplet DOM (^{3}DOM) (Canonica and Laubscher, 2008).

Chemical analysis of DOM materials reveals significant compositional variability between materials of different sources (for examples, see Table 1). In aquatic systems, DOM's composition is determined by the relative contribution and turnover from its precursor materials. These include both terrestrially (allochthonous) and microbially (autochthonous) derived organic matter. Carbon inputs from higher plants containing lignin and tannins dominate the allochthonous DOM chemical signature, whereas autochthonous DOM is derived from the cellular excretions of phytoplankton and bacteria and the turnover of microbial biomass (Aiken et al., 1992). Because of these source differences, DOM end members bear significantly distinct chemical signatures as determined by a variety of analytical techniques such as ^{13}C-NMR (Dria et al., 2002; Kaiser et al., 2003; Mopper et al., 2007), fluorescence (Coble 1996; Cory and McKnight, 2005; McKnight et al., 2001; Schwede-Thomas et al., 2005; Stedmon and Markager, 2005) and absorbance spectroscopy (Del Vecchio and Blough, 2002; Green and Blough, 1994; Stedmon and Markager, 2001; Weishaar et al., 2003), high-

pressure size exclusion chromatography (HPSEC) (Chin et al., 1994; Her et al., 2003), mass spectrometry (Kim et al., 2006; Reemtsma and These, 2005; Reemtsma et al., 2006) and thermochemolysis (Fimmen et al., 2007). Terrestrial DOM has more aromatic moieties (Chin et al., 1994) and lower nitrogen and sulfur functional groups (McKnight et al., 1991; McKnight et al., 1994; Mash et al., 2004) than autochthonous DOM. Finally, terrestrial DOM has a higher molecular weight (both number and weight average) distribution than microbially derived DOM (Chin et al., 1994; Chin et al., 1997). With the exception of special aquatic systems, e.g., "black water" environments that are dominantly comprised of allochthonous materials, DOM from a typical surface water bears chemical characteristics that fall between these two end members.

Differences in chemical composition invariably affect DOM photochemical function. Compositional effects on photo-physical behavior are well documented. For example, the higher aromatic content in terrestrially derived DOM allows it to absorb more light per unit carbon resulting in a larger molar absorptivity (ε) or specific UV absorbance (SUVA) compared to autochthonous DOM (Chin et al., 1994; McKnight et al., 2001). Aromaticity also affects DOM fluorescence signatures. The magnitude of the fluorescence index (FI) (ratio of corrected emission at 470nm:520nm at an excitation of 370 nm) is inversely correlated to the DOM aromatic content and can be used to delineate whether its organic composition is derived predominantly from phytoplankton and bacteria or higher plants (McKnight et al., 2001). Compositional differences may also manifest itself in DOM's photochemical reactivity (Meunier et al., 2005). For example, White (2000) reported that OH• production rates were consistently higher for terrestrially derived DOM relative to autochthonous DOM isolated from Ant-

arctica. Such work suggests differences in DOM source contribution may affect its photochemical reactivity in sunlit surface waters.

To date, a systematic study that examines the role of DOM composition on photosensitized reactions is lacking. We report the results from photodegradation studies conducted on three types of contaminants (Fig. 1), the antibiotic sulfadimethoxine (SDM), the antibacterial agent triclocarban (TCC), and the herbicide alachlor (ALA), in the presence of fulvic acids. Previous work showed that direct photolysis dominates the pathway for sulfadimethoxine (Boreen et al., 2005) while indirect photolytic pathways involving OH• were important in alachlor's fate in sunlit wetland waters (Miller and Chin, 2005). Finally, little is known about the photochemical fate of triclocarban, a common component of personal care products that is a widespread aquatic pollutant in the United States (Halden and Paull, 2005; Heidler et al. 2006). Fulvic acids were used as DOM surrogates and chosen to represent a spectrum of DOM sources: 1) Suwannee River fulvic acid, as an allochthonous end member; 2) either Pony Lake or Lake Fryxell fulvic acid, both of which represent autochthonous DOM end-members from surface waters devoid of any higher plants in Antarctica; and 3) Old Woman Creek a coastal wetland located on the south shore of Lake Erie in northern Ohio, whose DOM is derived from mostly autochthonous materials (Table 1). Evaluating the differences in the contaminants' susceptibility to direct and indirect photochemical reactions in the presence of these select fulvic acids will provide a basis to posit how source composition mediates contaminant photodegradation.

Methods

Chemicals and DOM
Ultrapure deionized water used in this study was obtained from a Milli-Q water system (Millipore Corp., Bedford MA). Sulfadimethoxine sodium salt (99 %) was purchased from MP Biomedicals, Inc (Solon, OH), while triclocarban (99.5 %) and alachlor (99.5 %) were obtained from Chem Services (West Chester, PA). All other reagents (buffers, reactants, and mobile phases) were purchased from Mallinckrodt, Aldrich Chemicals or Fisher Scientific. Suwannee River (SRFA) and Pony Lake fulvic acids (PLFA) were obtained from the International Humic Substances Society (IHSS). Lake Fryxell fulvic acid (LFFA) was obtained from Dr. George Aiken (USGS) and, like PLFA, was isolated from a water body in Antarctica. Unlike SRFA, these two Antarctic fulvic acids are derived entirely from microbial
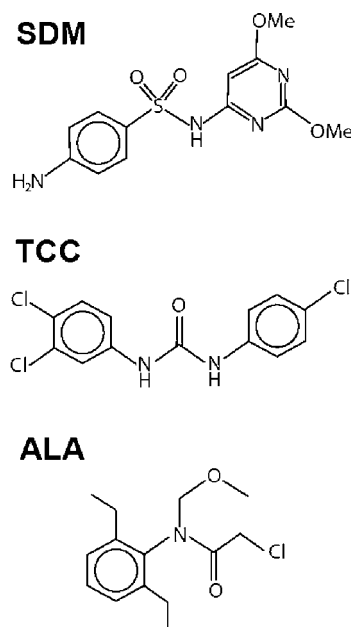

Fig. 1. Chemical structure of sulfadimethoxine (SDM), triclocarban (TCC) and alachlor (ALA).

precursors and share similar structural components (Table 1) (McKnight et al., 1994). Old Woman Creek fulvic acid (OWCFA) isolate was collected in September 2005. All fulvic acids were isolated using the XAD-8 chromatographic procedures detailed in Thurman and Malcolm (1981).

Analytical protocols
SDM, TCC, and ALA concentrations were determined by reversed-phase high-pressure liquid chromatography (HPLC) with UV detection that was externally calibrated (Waters). The SDM peak was resolved using a Restek Ultra IBD column (150 x 4.6 mm), eluted with a mobile phase of acetonitrile and 1 mM ammonium acetate (NH_4Oac) (30:70 % v/v at 1 mL/min), and detected at a wavelength of 260 nm. TCC was separated using a Waters Novapak C-18 column (3 x 150 mm), detected at 257 nm, and eluted using a methanol/water (80:20 % v/v) mobile phase. ALA was analyzed according to the published procedure in Miller and Chin (2005).

Absorbance scans from 200–600 nm of fulvic acid solutions were collected on a Varian Cary 1 UV-VIS spectrophotometer and baseline corrected to Mill-Q water. A fluorescence assay (Miller and Kester, 1988) was adapted to measure hydrogen peroxide production rates in fulvic acid solutions using a standard additions method. Irradiated fulvic acid solutions were spiked with a buffered (0.25 M Tris, pH 8.8) fluorescent reagent containing 0.255 mM recrystallized (p-hydroxylphenyl)acetic acid (POHPAA) and

0.16 mg mL^{-1} horseradish peroxidase (Sigma Type IV). The resultant fluorescent dimer was detected at λ_{excit}=313 nm; λ_{emit} = 402 nm (Cary Eclipse, Varian Instruments). Total iron was measured using graphite furnace atomic absorption that was externally calibrated according to the procedure outlined in Miller and Chin (2005). Total organic carbon analysis was measured on a Shimadzu TOC-5000 carbon analyzer calibrated with potassium hydrogen phthalate standards.

Photolysis experimental protocols
Solutions of 1.0 μM SDM, 0.5 μM TCC or 5 μM ALA were prepared in Milli-Q water, filtered (0.45 μM) natural water samples, or in solutions of fulvic acids (nominally 10 mg C L^{-1} for SDM solutions, 5 mg C L^{-1} for TCC solutions and 8 mg C L^{-1} for ALA solutions). Solution pH was adjusted to 8.0, 7.0, and 3.6 respectively with NaOH or HCl. For ALA experiments, an aliquot of Fe (III) from an acidified 0.01 M H$_2$SO$_4$ (trace metal grade) stock solution of FeCl$_3$ 6H$_2$O was added to splits of buffered (5 mM phosphate) fulvic acid solution resulting in total iron (Fe$_T$) in the range of 0–50 ppb to investigate photo-Fenton pathways.

Solutions of SDM or TCC were placed into (14×100 mm) long quartz reaction tubes that were sealed with Teflon tape wrapped O-rings and clamped shut. ALA solutions were conducted in Pyrex tubes (13×100 mm). Samples were irradiated in a Suntest CPS+ (Atlas Devices) solar simulator with a 500W Xe lamp (T = 25 °C) for SDM and TCC or a 450W Xe Arc lamp housed in a borosilicate water-jacketed immersion well (λ > 290 nm) in a merry-go-round reactor (T= 40 °C) for ALA. A radiometer and/or p-nitroanisole/pyridine chemical actinometry (Dulin and Mill, 1982) were used to monitor irradiance to ensure that the photon flux did not vary significantly (> 5 %) during the photolysis experiments. Dark controls wrapped in aluminum foil were run concurrently.

Samples were irradiated over three half-lives to determine the order of the kinetics. Rate coefficients for contaminant degradation were determined using a nonlinear least-squares fit of the observed data. In all cases, data conformed to a pseudo-first order kinetics model (R^2 > 0.97).

Inner-filter corrections were applied to predict direct photolysis rate coefficients in fulvic acid solutions (Leifer, 1988). An overall screening factor, $S_{\Sigma\lambda}$, was calculated according to the method presented in Miller and Chin (2002) to compensate for the light absorbed by fulvic acids in the absorption envelope of either the contaminant or photoreaction (i.e., production of H$_2$O$_2$ or OH$^{\bullet}$) of interest. Wavelength specific screening factors (S$_\lambda$) were calculated from the equation,

$$S_\lambda = \frac{1 - 10^{-a_\lambda l}}{2.303 a_\lambda l},$$

where a$_\lambda$ (cm^{-1}) is the wavelength specific attenuation coefficient, l (cm) is the pathlength of the tubes used in photochemical experiments and was determined experimentally to be 1.1 and 0.9 cm for Pyrex tubes and the quartz tubes, respectively (Leifer, 1988). S$_{\Sigma\lambda}$ were determined by taking the ratio of the integrated area of a plot of S$_\lambda$ versus wavelength (nm) and dividing by theoretical area of the plot if no inner filtering occurred (i.e., S$_\lambda$ = 1.0 for all wavelengths). The direct photolysis rate coefficients in fulvic acid solutions (k$_{dp}$ (hr^{-1})) were predicted from the equation, k$_{dp}$ = S$_{\Sigma\lambda}$ × k$_{milliQ}$, where k$_{milliQ}$ (hr^{-1}) is the direct photolysis rate coefficient experimentally determined in Milli-Q water controls. S$_\lambda$ was calculated for SDM and TCC for the region of 290–350 nm; for alachlor experiments, from 290–375 nm. For H$_2$O$_2$ production, wavelengths of 290–320 nm were used because exposure of natural waters to light in this range is associated with the largest production of H$_2$O$_2$ (Scully et al., 1996). Under conditions of constant irradiance and solutions with low contaminant concentrations, the observed first-order rate coefficient for the contaminant degradation (k$_{obs}$ (hr^{-1})) is the sum of the contributions from both direct and indirect photolytic pathways, assuming the pathways behave independently. The contribution from indirect pathways (k$_{ip}$ (hr^{-1})) on contaminant degradation in the DOM solutions was calculated from k$_{obs}$ by subtracting the inner filter corrected direct photolysis rate coefficient (k$_{dp}$) (Table 2; Miller and Chin, 2002).

Results and discussion

Photodegradation of SDM and TCC in the presence and absence of DOM
Our data showed that both sulfadimethoxine and triclocarban undergo both direct and indirect photolysis at a pH of 8 and 7, respectively (Table 2). Contaminants did not degrade in the dark controls over the course of the experiments. Direct photolysis accounted for > 50 % of the degradation in all cases and was the dominant degradation pathway for SDM and TCC. Nonetheless, nearly all fulvic acids used in this study enhanced the degradation of both target compounds by indirect photolytic pathways. SRFA showed the lowest reactivity for SDM and TCC, promoting the reactions by 19 % and 28 %, respectively, even though it had the greatest ability to absorb light (based upon SUVA and ^{13}C-NMR analyses). Given the error in k$_{obs}$ for the SDM-SRFA experiment, the 19 % contribution by SRFA was shown to be

Table 2. Observed pseudo-first order photodegradation rate coefficients (k_{obs}) and predicted contributions from the direct and indirect photolysis of sulfadimethoxine and triclocarban in presence of DOM.

Sample	DOC[1] (mgC L^{-1})	pH	$S_{\Sigma 290-350}$ [2]	k_{obs}[3] $\times 100$ (hr^{-1})	Half-life (hrs)	k_{dp}[4] $\times 100$ (hr^{-1})	k_{ip}[5] $\times 100$ (hr^{-1})	% DP[6]	% IP[6]
Sulfadimethoxine									
Control	NA	8.00	NA	5.75 ± 0.3	12.05	5.75	NA	100	0
SRFA	10	8.00	0.847	6.00 ± 0.5	10.51	4.87	1.13 ± 0.6	81	19
OWCFA	10	8.00	0.862	9.08 ± 0.5	7.02	4.95	4.13 ± 0.6	55	45
PLFA	10	8.00	0.927	10.28 ± 0.5	6.20	5.33	4.95 ± 0.6	52	48
Triclocarban									
Control	NA	7.00	NA	2.86 ± 0.3	24.24	2.86	NA	100	0
SRFA	4.97	7.00	0.920	3.64 ± 0.3	19.04	2.63	1.01 ± 0.4	72	28
OWCFA	4.94	7.00	0.924	4.64 ± 0.5	14.94	2.64	2.00 ± 0.6	57	43
PLFA	4.69	7.00	0.965	5.08 ± 0.3	13.64	2.76	2.32 ± 0.4	55	45

[1] Average DOC from triplicate injections (CV < 2%) . [2] Light screening factor for wavelengths 290-350 nm. [3] k_{obs} represents the observed pseudo first-order rate degradation coefficient measured from a least squares fit of degradation kinetics. [4] k_{dp} represents the rate coefficient predicted for contribution of direct photolysis to the overall degradation of the target contaminant in a given DOM solution. [5] k_{ip} represents the rate coefficient predicted for contribution of indirect photolysis to the overall degradation of the target contaminant. [6] The percentage contribution of direct photolysis (%DP) and indirect photolysis (%IP) to the overall observed degradation.

not statistically significant, an observation consistent with that reported by Boreen et al. (2005) for the photolysis of SDM in Lake Josephine, MN water. In contrast, the autochthonous PLFA exhibited the highest reactivity toward these two compounds, which was counterintuitive since microbial fulvic acids tend to absorb less light than allochthonous material. Finally, we observed similar photo-enhanced degradation of SDM and TCC in the presence of fulvic acid isolated from Old Woman Creek, which is a temperate highly eutrophic wetland. While DOM from this site does have allochthonous components, much of the material is derived from autochthonous sources (Miller and Chin, 2005).

One might attribute these differences in fulvic acid photoreactivity to inner-filter effects, and we compensated for the indirect photolysis rate coefficients for light screening by dividing k_{ip} by the screening factor ($S_{\Sigma 290-350}$). This correction step, however, did not change this trend, and our kinetic data unequivocally showed SDM and TCC transformation by photosensitization for all the fulvic acids with the exception of SDM in SRFA solutions (Table 2). For TCC, this study is the first to our knowledge to report that direct and indirect photolysis may be important in the fate of this compound in the aquatic environment.

Additional experiments suggested that the indirect pathway for SDM and TCC could be mediated by excited DOM triplet states. To assess the role of ^{3}DOM in the photodegradation of these two compounds, experiments were conducted in argon-sparged solutions to eliminate competitive scavenging by dioxygen. For both TCC and SDM, measured rate constants increased by a respective 42% and 64% in PLFA, which is indicative of a ^{3}DOM oxidation pathway. Carbon-centered radicals could also account for these effects, however, life times of such species

compared to ^{3}DOM are too short to be responsible for the observed results. The addition of isopropanol (an effective OH$^\bullet$ scavenger) to SDM-PLFA solutions resulted in no significant quenching (k_{obs} of 0.103 ± 0.005 hr^{-1} vs. 0.095 ± 0.003 hr^{-1}). TCC, however, reacted to some degree by the hydroxyl radical pathway because isopropanol partially quenched the reaction (29% for PLFA, 28% for OWCFA, and 22% for SRFA).

Several studies corroborate the finding that fulvic acid triplet states promote the indirect photolysis of contaminants (Canonica and Freiburghaus, 2001; Gerecke et al., 2001; Boreen et al., 2005; Fisher et al., 2006), although the nature of the interaction and possible quenching pathways remain largely uncharacterized. Quantum yields for the triplet formation of Laurentian and Armadale fulvic acids were high, ranging from 0.79–0.28 and from 0.82 to 0.35, respectively, for the pH range of 2.0–9.5 (Bruccoleri et al., 1993). The respective decrease and increase in quantum yields at higher pH values and ionic strength suggests that the fulvic acid conformation (i.e., coiled vs. uncoiled) was important in facilitating intersystem crossing. Given the compositional differences in source materials, quantum yields for triplet formation may be very different across the DOM source spectrum as observed by Halladja and co-workers (2007) for soil humic and fulvic acids. To date, it is difficult to identify the specific chemical moieties responsible for the observed photochemical enhancement because we have not studied the transformation pathways in detail and our data set is insufficiently large for a rigorous statistical analysis. Nonetheless, our results merit further investigation.

Table 3. Effect of iron level on the measured rate coefficients for the photoinduced degradation of alachlor in allochthonous (SRFA) and autochthonous (LFFA) DOM samples.

Sample	Fe Added (ppb)	DOC [1] (mg C L^{-1})	$\varepsilon(M^{-1}cm^{-1})$ [2]		$\Sigma S_{290\text{-}375}$ [3]	Fe_{Total} (ppb)	k_{obs} [4] $\times 10^3$ (hr^{-1})
			280nm	320nm			
Fe Control	0	0.17 ± 0.04			NA [5]	2.94 ± 0.17	1.86 ± 1.03
	2	NA				6.26 ± 0.21	5.54 ± 0.48
	5	NA				9.15 ± 0.39	8.89 ± 0.81
	10	NA				13.36 ± 0.42	12.1 ± 1.09
	20	NA				22.29 ± 1.05	24.0 ± 1.05
	30	NA				27.68 ± 0.20	35.4 ± 2.04
	40	NA				32.1 ± 0.22	39.7 ± 2.24
	50	NA				36.22 ± 0.41	48.2 ± 2.05
SRFA	0	7.94 ± 0.04	343	190	0.86	1.82 ± 0.15	12.1 ± 1.39
	2	7.93 ± 0.01				4.02 ± 0.39	14.4 ± 0.99
	5	8.00 ± 0.08				8.88 ± 0.15	19.3 ± 2.02
	10	7.98 ± 0.05				13.8 ± 0.15	26.5 ± 2.43
	20	8.07 ± 0.07				23.0 ± 0.11	34.1 ± 1.45
	30	8.15 ± 0.04				33.07 ± 0.40	41.7 ± 1.65
	40	8.20 ± 0.25				43.23 ± 0.20	45.6 ± 3.15
	50	8.16 ± 0.08				53.37 ± 0.69	49.1 ± 3.50
LFFA	0	8.15 ± 0.05	157	69	0.94	2.71 ± 0.08	14.6 ± 7.42
	2	8.06 ± 0.04				4.49 ± 0.40	15.0 ± 0.82
	5	7.98 ± 0.03				7.33 ± 0.23	19.0 ± 1.19
	10	8.20 ± 0.02				12.81 ± 0.07	21.4 ± 1.38
	20	8.20 ± 0.03				23.59 ± 0.01	26.3 ± 1.60
	30	8.02 ± 0.06				34.01 ± 0.41	30.7 ± 1.24
	40	8.09 ± 0.07				43.81 ± 0.34	33.2 ± 1.62
	50	8.18 ± 0.05				55.00 ± 0.64	36.1 ± 1.67

[1] Measured dissolved organic carbon (DOC), where ± values are one standard deviation for replicate samples. [2] Molar absorptivity (ε). [3] Light screening factor. [4] The values for k_{obs} are reported ± 95% CI. [5] NA, not applicable or parameter not measured or calculated for this sample.

Photodegradation of ALA: Effect of fulvic acid source on ROS transformations

The photodegradation of alachlor in surface waters occurs primarily through attack by the hydroxyl radical (Wilson and Mabury, 2000; Miller and Chin, 2005). Measured indirect photolysis rate coefficients were highest in waters with high nitrate levels (on the order of 1 mM) and in samples having their pH adjusted to 4, due to increased OH$^\bullet$ production under these conditions (Miller and Chin, 2005). The observed increased reactivity at lower pH was attributed to an enhancement of a mechanism in which OH$^\bullet$ is produced directly from DOM (Vaughan and Blough, 1998) and/or through an iron-mediated mechanism, presumably the photo-Fenton pathway (Southworth and Voelker, 2003). The DOM composition may be important in several steps of either pathway because 1) the nature of the DOM complexes with iron may influence the photo-Fenton pathway, 2) irradiated DOM is the source of H_2O_2 needed to complete the Fenton cycle, and 3) the composition of DOM may affect how much of the produced OH$^\bullet$ can be scavenged by the DOM.

To test the role of fulvic acid composition in a photo-Fenton pathway, ALA photodegradation was measured in buffered solutions that contained either SRFA or LFFA and incremental iron additions at environmentally relevant levels (ppb). As a control, ALA degradation was also measured in solutions treated in the same manner in the absence of fulvic acid (Table 3). The dark and direct photolytic reactions were found to be statistically insignificant during the course of the experiments (25 hrs) (data not shown). The iron control (no DOM) showed that the measured rate coefficients (k_{obs}) were correlated ($R^2 = 0.98$) to the amount of Fe_T (Fig. 2) and suggested that low levels of Fe (~3 ppb) are enough to facilitate the photochemical degradation reaction of ALA *in the absence of the* DOM. Although a truly "iron-free" solution could not be achieved under our laboratory conditions (trace contamination from buffers and reagents used was 2.94 ppb Fe_T), the plot shows that iron will not be important below the level determined from the X-intercept (2.78 ppb Fe_T) of the extrapolated line.

Similar to the SDM and TCC experiments, both fulvic acid solutions in the absence of amended iron showed enhanced ALA degradation above the iron control. Unlike SDM and TCC, however, there was no statistical difference between the rate coefficients for SRFA and LFFA solutions. The dissimilarity between ALA and the SDM/TCC systems is not surprising

given that argon sparging of ALA-fulvic acid solutions showed no effect on measured rate coefficients (Miller and Chin, 2005), precluding the direct involvement of DOM triplets or oxygen in the mechanism. When the iron content was increased, the measured rate coefficient for ALA degradation increased proportionately for SRFA and LFFA solutions and leveled off at higher levels of Fe_T. The divergence of the SRFA curve from the LFFA data with increasing iron dosage suggests that solutions containing LFFA were less effective at producing $OH^\bullet$ than those containing SRFA (Fig. 2). Indeed, regression analysis on the linear region of the curves yields a slope for SRFA ((1.06 ± 0.06) $\times 10^{-3}$ $hr^{-1}ppb^{-1}$; n = 5; $R^2 = 0.99$), which is twice that of LFFA ((0.51 ± 0.04) $\times 10^{-3}$ $hr^{-1}ppb^{-1}$; n = 6; $R^2 = 0.97$). Inner-filter effects arising from fulvic acid attenuation play a minor role because the LFFA solutions were less reactive even though their screening factors were smaller (Table 3). The decrease in reactivity for both fulvic acids at high Fe_T amendments is consistent with scavenging of $OH^\bullet$ by DOM.

As with SDM and TCC, these results show that system reactivity depends on fulvic acid source. Although scavenging of $OH^\bullet$ is important at higher Fe_T levels, this process does not explain the divergence of the curves in Figure 2. SRFA is a slightly more efficient (~5%) scavenger of hydroxyl radicals than LFFA (Westerhoff et al., 1999), and the influence of this process on the hydroxyl radical steady-state concentration should be indistinguishable from error of the experiments. The divergence could be explained by the fulvic acid solutions having different H_2O_2 production rates. Thus, the composition of the fulvic acid could play a critical role in the amount of $OH^\bullet$ that can be produced by the photo-Fenton process.

When measured, the H_2O_2 production rates in solutions of SRFA were consistently higher than those from PLFA and OWCFA (Fig. 3). The initial production rate of hydrogen peroxide (measured within the first hour) was at least 50% larger for SRFA than either PLFA or OWCFA, which were statistically indistinguishable (Table 4). Inner-filter-effects are insufficient to explain the magnitude of these differences. If SRFA is producing more H_2O_2 per mg C L^{-1} of fulvic acid (and thus more $OH^\bullet$) than LFFA, the larger steady-state H_2O_2 concentration may explain the faster ALA kinetics observed for the SRFA solutions. The trend observed in H_2O_2 production for these materials is opposite from the trends observed for SDM and to a lesser extent, TCC, and one may conclude from the evidence that fulvic source composition is as important for the generation of ROS as well as ^3DOM.
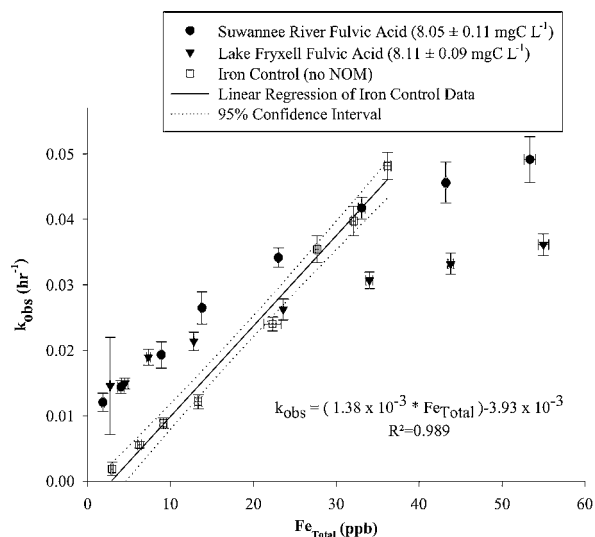

Fig. 2. Effect of Fe_{Total} (ppb) on the measured rate coefficient for the photoinduced degradation of alachlor in fulvic acid (pH = 3.60).

$$k_{obs} = (1.38 \times 10^{-3} * Fe_{Total}) - 3.93 \times 10^{-3}$$
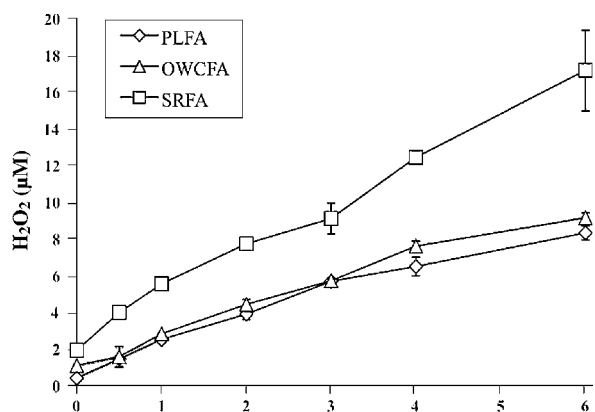$$R^2 = 0.989$$

Fig. 3. Comparison of the photochemical H_2O_2 production in reconstituted Pony Lake (PLFA), Old Woman Creek (OWC) and Suwannee River (SRFA) fulvic acids. For solution conditions please refer to Table 4.

Implications and conclusions

To date very few studies have considered how DOM source composition may have an impact on its ability to promote the photosensitized degradation of organic contaminants. Most studies focus on uncharacterized DOM in water samples collected from a specific water body or have used fulvic and humic acids from the International Humic Substances Society or other suppliers. Natural waters from locations worldwide have been used to investigate the photochemical fate of a number of contaminants. The advantage to this method is its simplicity and unbiased representation of the entire organic carbon pool in the water sample. Unfortunately, the DOM in these waters typically remains uncharacterized and, in some cases, other chemical species in the sample (nitrate, pH, presence

Table 4. Description of sample matrices used to reconstitute fulvic acid isolates to study the effect of source composition on the photochemical production of hydrogen peroxide.

Fulvic Acid	pH	DOC[1] (mg C L^{-1})	NaCl (M)	Na$_2$SO$_4$ (M)	R$_{H2O2}$[2] (μM/hr/mg C L^{-1})	S$_{\Sigma290\text{-}320}$[3]	R$_{H2O2}$[4] (μM/hr/mg C L^{-1})
Pony Lake	7.99	8.88 ± .22	4.7 × 10^{-2}	1.10 × 10^{-2}	0.24 ± 0.01	0.906	0.265
Old Woman Creek	8.03	9.54 ± .10	9.31 × 10^{-4}	3.12 × 10^{-4}	0.18 ± 0.04	0.830	0.217
Suwannee River	7.95	10.06 ± .24	9.31 × 10^{-4}	3.12 × 10^{-4}	0.36 ± 0.03	0.818	0.440

[1] DOC (in mg C L^{-1}) reported ± one standard deviation. [2] Hydrogen peroxide production rates (R$_{H2O2}$) were determined from a least squares fit of the initial rates data and normalized to the DOC (in mg C L^{-1}) to account for differences in carbon level. [3] Screening factor for wavelengths 290-320 nm. [4] Compensation for inner filter effects on production rates was performed by dividing production rate by screening factor calculated at a wavelength of 320 nm for these DOM solutions.

of metals) could influence photodegradation, making it difficult to delineate DOM's exact role in the contaminant's fate (Wilson and Mabury 2000; Miller and Chin, 2005).

The other common approach to study DOM's role as a photosensitizer is to use a solution containing a subset of the organic matter pool such as the fulvic acids used in this study. Fulvic acids represent a fraction (20–50 %) of the DOM pool and, unlike a using a whole water sample, are stable in its lyophilized state. In addition, evidence in the literature show that the fulvic acid fraction of DOM typically accounts for the dominant share of light absorption (McKnight et al., 2001). While fulvic (and to a lesser extent humic acids) are useful for inter-comparative studies, the results are applicable to that specific isolate and cannot be used to interpret overall DOM photoreactivity from other water bodies.

DOM mediated indirect photolysis of organic compounds can occur via a number of possible pathways and is in part driven by the contaminant's chemical reactivity. However, there exists a paucity of data that examines the role of DOM composition on photosensitized reactions. In this study, the indirect photolysis of SDM and TCC was consistent with a predominantly triplet DOM mediated pathway, and promoted to a greater extent by autochthonous fulvic acid. In contrast, ALA underwent degradation by OH$^\bullet$ generated from irradiated fulvic acid in the presence of low levels of iron (ppb), and the allochthonous material was more reactive. Our results demonstrate the need to conduct more systematic studies that investigate the role of DOM composition in the photosensitized degradation of organic contaminants.

Acknowledgments

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