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INVITED REVIEW

Photochemical, microbial and metal complexation behavior of fluorescent dissolved organic matter in the aquatic environments

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Chemical properties and reactivity of fluorescent dissolved organic matter (FDOM) are examined in this paper. They are key issues to understand the biogeochemical processes in the aquatic environments. Typically, FDOM undergoes photochemical transformation and is recalcitrant to microbial degradation, except for the aromatic amino acids that are microbiologically degraded under dark conditions. Experimental results demonstrate that the fluorescence intensity of various FDOM components is depleted upon irradiation (in the hours to 70 days time scale), approximately by 20–85% for fulvic acid, by 12–95% for fluorescent whitening agents (FWAs) or commercial detergents, and by 5–60% for trytophan. Microbial degradation is able to decompose the amino acid tryptophan and similar compounds, by approximately 13–24% in unfiltered river waters, 67% in unfiltered sewerage samples, and 11% in filtered river samples. The photoreactivity of FDOM is greatly decreased when passing from freshwater (river and lakes) to marine waters, but deep waters in lakes or marine environments are often more sensitive to photodegradation processes than surface waters. The high reactivity of FDOM toward photodegradation could be understood on the basis of its (however complex) chemical structure, considering that many FDOM components can undergo photoionization or otherwise photosensitized oxidation under sunlight. The controlling factors to the photochemical and microbial degradation of FDOM for a variety of waters are extensively discussed. One of the important functions of FDOM is the formation of complexes with transition metals in the aquatic environments, and this review discusses the mechanisms by which FDOM interacts with metals. Further investigations on FDOM, namely the identification of still unknown FDOM components, the metal-FDOM interactions as well as the photochemical and microbial reactivity will give invaluable information on the DOM dynamics in the aquatic environments.

Keywords: photodegradation, microbial degradation, metal complexation, fulvic acid, humic acid

INTRODUCTION

Solar radiation is vital for life on Earth. It maintains all the physical, chemical, chemoautotroph and biological processes of dissolved organic matter (DOM) or fluorescent dissolved organic matter (FDOM) in natural waters. The major known FDOM components in the aquatic environments are fulvic and humic acids, aromatic amino acids (tryptophan, tyrosine and phenylalanine), and components of fluorescent whitening agents (FWAs) or household detergents such as diamino stilbene (DAS1) and distyryl biphenyl (DSBP). These species have been identified as FDOM components using excitation-emission matrix spectroscopy (EEMS) (Komaki and Yabe, 1982; Coble, 1996, 2007; Yamashita and Tanoue, 2003a; Mostofa *et al*., 2005a; Wu *et al*., 2005; Hudson *et al*., 2007) as well as chromatographic methods (Kramer *et al*., 1996; Yamashita and Tanoue, 2003a; Managaki and Takada, 2005). Solar irradiation of natural waters causes alterations in the optical and chemical properties of the FDOM and typically decreases its ability to absorb sun-

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Table 1. Photochemical and microbial changes of fluorescence intensity (FI) of fulvic acid-like (peak C), fluorescent whitening agents (FWAs)-like (peak W) tryptophan-like or protein-like (peak T) substances as a result of photoirradiation experiments conducted on standard substance and natural waters

Type of samples/Locations	Filtration size/type	Irradiation time	Solar intensity	Changes in peak C or peak W		Changes in FI of peak T		References
				Photoirradiation	Microbial	Photoirradiation	Microbial	
	(μm)	(h/days)	(MJm^{-2})	%	%	%	%	
Suwannee River Fulvic Acid, SRFA: 1 mg L^{-1}	MQ water	10 h (Xe lamp)	nd	–42	(+)0.1	na	na	Mostofa and Sakugawa, UD
SRFA: 1 mg L^{-1}	MQ water	3 h (Xe lamp)	nd	–19	nd	na	na	Mostofa and Sakugawa, UD
SRFA: 1 mg L^{-1} + 50 μM NO_2^-	MQ water	3 h (Xe lamp)	nd	–22	nd	na	na	Mostofa and Sakugawa, UD
SRFA: 3 mg L^{-1}	MQ water	3 h (Xe lamp)	nd	–23	nd	na	na	Mostofa and Sakugawa, UD
SRFA: 5 mg L^{-1}	MQ water	3 h (Xe lamp)	nd	–20	nd	na	na	Mostofa and Sakugawa, UD
Suwannee River Humic Acid: 1 mg L^{-1}	MQ water	10 h (Xe lamp)	nd	(+)70	nd	na	na	Mostofa and Sakugawa, UD
Suwannee River Humic Acid: 3 mg L^{-1}	MQ water	3 h (Xe lamp)	nd	–17	nd	na	na	Mostofa and Sakugawa, UD
Suwannee River Humic Acid: 5 mg L^{-1}	MQ water	3 h (Xe lamp)	nd	(+)5	nd	na	na	Mostofa and Sakugawa, UD
Standard Tryptophan: 1 mg L^{-1}	MQ water	10 h (Xe lamp)	nd	na	na	–63	–0.1	Mostofa and Sakugawa, UD
Standard Tryptophan: 3 mg L^{-1}	MQ water	3 h (Xe lamp)	nd	na	na	–23	nd	Mostofa and Sakugawa, UD
Standard Tryptophan: 5 mg L^{-1}	MQ water	3 h (Xe lamp)	nd	na	na	–20	nd	Mostofa and Sakugawa, UD
Standard DSBP: 1 mg L^{-1}	MQ water	10 h (Xe lamp)	nd	–94	(+)0.1	na	na	Mostofa and Sakugawa, UD
Standard DSBP: 3 mg L^{-1}	MQ water	3 h (Xe lamp)	nd	–73	nd	na	na	Mostofa and Sakugawa, UD
Standard DSBP: 5 mg L^{-1}	MQ water	3 h (Xe lamp)	nd	–60	nd	na	na	Mostofa and Sakugawa, UD
Standard DAS1: 1 mg L^{-1}	MQ water	10 h (Xe lamp)	nd	–93	nd	na	na	Mostofa and Sakugawa, UD
Fulvic acid, extracted from Göta River: 6.3 mg L^{-1}	NaOH + MQ water	13 (UV-B lamp)	nd	–32	na	na	na	Lepane *et al*., 2003
Humic acid, extracted from Göta River: 6.5 mg L^{-1}	NaOH + MQ water	13 (UV-B lamp)	nd	(+)4	na	na	na	Lepane *et al*., 2003
Fulvic acid, extracted from Göta River: 6.3 mg L^{-1}	NaOH + MQ water	9 (dark)	nd	na	(+)8	na	na	Lepane *et al*., 2003
Humic acid, extracted from Göta River: 6.5 mg L^{-1}	NaOH + MQ water	9 (dark)	nd	na	(+)6	na	na	Lepane *et al*., 2003
Aldrich fulvic acid component	Deionized water	13 (irradiated)	nd	–(26–41)	na	na	na	Winter *et al*., 2007
Aldrich humic acid component	Deionized water	13 (irradiated)	nd	–(21–45)	na	na	na	Winter *et al*., 2007
Kago upstream, Japan (35°N)	0.45	12 (irradiated)	192	–74	na	np	np	Mostofa *et al*., 2005b
Kago upstream, Japan (35°N)	0.45	12 (dark)	192	na	(+)3	np	np	Mostofa *et al*., 2005b
Kago upstream, Japan (35°N)	0.45	13 (irradiated)	176	–72	na	np	np	Mostofa *et al*., 2007b
Kago upstream, Japan (35°N)	0.45	13 (dark)	176	na	(+)15	np	np	Mostofa *et al*., 2007b
Nishi-Mataya upstream, Japan (35°N)	0.45	13 (irradiated)	176	–84	na	np	np	Mostofa *et al*., 2007b
Nishi-Mataya upstream, Japan (35°N)	0.45	13 (dark)	176	na	(+)6	np	np	Mostofa *et al*., 2007b
Nishi-Mataya upstream, Japan (35°N)	0.45	12 (irradiated)	192	–78	na	–40	na	Mostofa *et al*., 2007b
Nishi-Mataya upstream, Japan (35°N)	0.45	12 (dark)	192	na	(+)5	na	np	Mostofa *et al*., 2007b
Yasu River, Japan (35°N)	0.45	13 (irradiated)	176	–80	na	–59	na	Mostofa *et al*., 2007b
Yasu River, Japan (35°N)	0.45	13 (dark)	176	na	(+)14	na	(+)6	Mostofa *et al*., 2007b

Type of samples/Locations	Filtration size/type	Irradiation time	Solar intensity	Changes in peak C or peak W		Changes in FI of peak T		References
				Photoirradiation	Microbial	Photoirradiation	Microbial	
	(μm)	(h/days)	(MJm^{-2})	%	%	%	%	
Kurose River (Izumi site), 34°N	0.20	6 (irradiated)	118.5	−77	na	−10	na	Mostofa and Sakugawa, UD
Kurose River (Izumi site), 34°N	0.45	6 (dark)	118.5	na	(+)6	na	(+)4	Mostofa and Sakugawa, UD
Kurose River (Izumi site), 34°N	unfiltered	6 (irradiated)	118.5	−77	na	−5	na	Mostofa and Sakugawa, UD
Kurose River (Izumi site), 34°N	unfiltered	6 (dark)	118.5	na	nd	na	−17	Mostofa and Sakugawa, UD
Kurose River (Hinotsume site), 34°N	0.20	10 (irradiated)	152.5	−76	na	−21	na	Mostofa and Sakugawa, UD
Kurose River (Hinotsume site), 34°N	0.45	10 (dark)	152.5	na	nd	na	−11	Mostofa and Sakugawa, UD
Kurose River (Hinotsume site), 34°N	unfiltered	10 (irradiated)	152.5	−81	na	−19	na	Mostofa and Sakugawa, UD
Kurose River (Hinotsume site), 34°N	unfiltered	10 (dark)	152.5	na	nd	na	−13	Mostofa and Sakugawa, UD
Nanming River, (Near Institute), 26°N	unfiltered	3 h (irradiated)	nd	−27	na	−32	na	Mostofa *et al*., 2010
Drain Samples, (Near Institute), 26°N	unfiltered	3 h (irradiated)	nd	−34	na	−50	na	Mostofa *et al*., 2010
Commercial detergent sample	MQ water	3 h (irradiated)	nd	−88	na	np	na	Mostofa *et al*., 2010
River water + commercial detergent	unfiltered	10 (dark)	nd	na	(+)21	na	−24	Mostofa *et al*., 2010
Drain samples, (Near Institute), 26°N	unfiltered	10 (dark)	nd	na	(+)8	na	−67	Mostofa *et al*., 2010
Commercial detergent sample	MQ water	10 (dark)	nd	na	(+)14	na	np	Mostofa *et al*., 2010
River water + DSBP	river water	12 h (summer period)	nd	−31	na	nd	nd	Poiger *et al*., 1999
River water + DAS1	river water	12 h (summer period)	nd	−12	na	nd	nd	Poiger *et al*., 1999
Mackenzie River, 68°N	0.20	72 h (summer)	nd	−(13–45)	nd	nd	nd	Osburn *et al*., 2009
Mackenzie River, 68°N	0.20	72 h (spring)	nd	−33	nd	nd	nd	Osburn *et al*., 2009
Mackenzie River, 68°N	0.20	72 h (autumn)	nd	−(1–10)	nd	nd	nd	Osburn *et al*., 2009
Laramie River-DOM, 41°N	river water	72 h (sunlight)	nd	−23	na	nd	nd	Brooks *et al*., 2007
Chimney Park Wetland-DOM, 41°N	river water	72 h (sunlight)	nd	−7	na	nd	nd	Brooks *et al*., 2007
Lake Biwa, 35°N: surface water (2.5 m)	0.10	12 (irradiated)	137	−36	na	−18	na	Mostofa *et al*., UD
Lake Biwa, 35°N: surface water (2.5 m)	0.10	12 (dark)	137	na	(+)31	na	(+)68	Mostofa *et al*., UD
Lake Biwa, 35°N: surface water (70 m)	0.10	12 (irradiated)	137	−48	na	−7	na	Mostofa *et al*., UD
Lake Biwa, 35°N: surface water (70 m)	0.10	12 (dark)	137	na	0	na	(+)5	Mostofa *et al*., UD
Lake Biwa, 35°N: surface water (2.5 m)	<5 kDa	12 (irradiated)	137	−16	na	(+)4	na	Mostofa *et al*., UD
Lake Biwa, 35°N: surface water (2.5 m)	<5 kDa	12 (dark)	137	na	(+)102	na	(+)51	Mostofa *et al*., UD
Lake Biwa, 35°N: surface water (70 m)	<5 kDa	12 (irradiated)	137	−50	na	−19	na	Mostofa *et al*., UD
Lake Biwa, 35°N: surface water (70 m)	<5 kDa	12 (dark)	137	na	(+)20	na	(+)28	Mostofa *et al*., UD
Four Lakes (45°N)	0.45	6 h (summer)	nd	−(22–31)	−(0–4.5)	nd	nd	Garcia *et al*., 2005
Fulvic acid, Mill Creek: surface water, 43°N	0.45	6 h (summer)	nd	−(48–79)	na	−(81–88)	na	Garcia *et al*., 2005
Fulvic acid, Bannister Lake: surface water, 43°N	0.45	6 h (summer)	nd	−(75–83)	na	np	na	Garcia *et al*., 2005
Fulvic acid, Lake Erie: surface water, 42°N	0.45	6 h (summer)	nd	−(74–77)	na	−(72–82)	na	Garcia *et al*., 2005
Fulvic acid, Sanctuary Pond: surface water, 41°N	0.45	6 h (summer)	nd	−(71–79)	na	np	na	Garcia *et al*., 2005
Humic acid, Luther Marsh: surface water, 43°N	0.45	6 h (summer)	nd	−(64–65)	na	na	na	Garcia *et al*., 2005

Table 1. (continued)

Type of samples/Locations	Filtration size/type	Irradiation time	Solar intensity	Changes in peak C or peak W		Changes in FI of peak T		References
				Photoirradiation	Microbial	Photoirradiation	Microbial	
	(μm)	(h/days)	(MJm^{-2})	%	%	%	%	
Humic acid, Mill Creek: surface water, 43°N	0.45	6 h (summer)	nd	–(91–100)	na	na	na	Garcia *et al*., 2005
Humic acid, Bannister Lake: surface water, 43°N	0.45	6 h (summer)	nd	–71	na	na	na	Garcia *et al*., 2005
Humic acid, Lake Erie: surface water, 42°N	0.45	6 h (summer)	nd	np	na	na	na	Garcia *et al*., 2005
Humic acid, Sanctuary Pond: surface water, 41°N	0.45	6 h (summer)	nd	–(63–81)	na	na	na	Garcia *et al*., 2005
Satilla Estuary	0.20	70 (irradiated)	nd	–61	na	–45	na	Moran *et al*., 2000
Satilla Estuary	0.20	70 (irradiated)	nd	–67	na	–37	na	Moran *et al*., 2000
Satilla Estuary	0.20	51 (dark)	nd	na	–12	na	(+)112	Moran *et al*., 2000
Satilla Estuary	0.20	51 (dark)	nd	na	–1	na	(+)23	Moran *et al*., 2000
Estuary, Beaufort Sea, 69°N	0.20	72 h (summer)	nd	–(47–60)	nd	nd	nd	Osburn *et al*., 2009
Estuary, Beaufort Sea, 69°N	0.20	72 h (spring)	nd	–33	nd	nd	nd	Osburn *et al*., 2009
Estuary, Beaufort Sea, 69°N	0.20	72 h (autumn)	nd	–19	nd	nd	nd	Osburn *et al*., 2009
Shelf, Beaufort Sea, 69–70°N	0.20	72 h (summer)	nd	–(67–75)	nd	nd	nd	Osburn *et al*., 2009
Shelf, Beaufort Sea, 70°N	0.20	72 h (spring)	nd	–(46–61)	nd	nd	nd	Osburn *et al*., 2009
Shelf, Beaufort Sea, 70–71°N	0.20	72 h (autumn)	nd	–(29–84)	nd	nd	nd	Osburn *et al*., 2009
Gulf, Beaufort Sea, 70°N	0.20	72 h (spring)	nd	–66	nd	nd	nd	Osburn *et al*., 2009
Gulf, Beaufort Sea, 70–71°N	0.20	72 h (autumn)	nd	–(50–61)	nd	nd	nd	Osburn *et al*., 2009
Gulf, Beaufort Sea, 70–71°N	0.20	72 h (winter)	nd	–(21–67)	nd	nd	nd	Osburn *et al*., 2009
Baltic Sea: Arkona, 55°N; Kotla, 60°N; Oulu, 65°N	0.20	48 h (UV-A lamp)	nd	65 ± 7	na	26 ± 9	na	Stedmon *et al*., 2007a
Autochthonous DOM (comp 2): Arkona, 55°N; Kotla, 60°N; Oulu, 65°N	0.20	48 h (UV-A lamp)	nd	69 ± 6	na	na	na	Stedmon *et al*., 2007a
Unidentified DOM (comp 4): Arkona, 55°N; Kotla, 60°N; Oulu, 65°N	0.20	48 h (UV-A lamp)	nd	54 ± 6	na	na	na	Stedmon *et al*., 2007a
Unidentified DOM (comp 6): Arkona, 55°N; Kotla, 60°N; Oulu, 65°N	0.20	48 h (UV-A lamp)	nd	(+)(252–2740)	na	na	na	Stedmon *et al*., 2007a
Baltic Sea, BY15: 0–30 m depth	0.20 (unfiltered)	5	nd	–(44–52)	nd	nd	nd	Skoog *et al*., 1996
Baltic Sea, BY15: 100–240 m depth	0.20 (unfiltered)	5	nd	–(58–65)	nd	nd	nd	Skoog *et al*., 1996
Baltic Sea, BY32: 0–50 m depth	0.20 (unfiltered)	12	nd	–(61–70)	nd	nd	nd	Skoog *et al*., 1996
Baltic Sea, BY32: 0–50 m + Chloroform	0.20 (unfiltered)	12	nd	–(59–81)	nd	nd	nd	Skoog *et al*., 1996
Baltic Sea, BY32: 100–190 m depth	0.20 (unfiltered)	12	nd	–(73–75)	nd	nd	nd	Skoog *et al*., 1996
Baltic Sea, BY32: 100–190 m + Chloroform	0.20 (unfiltered)	12	nd	–(83–84)	nd	nd	nd	Skoog *et al*., 1996
Baltic Sea, F15: 0–50 m depth	0.20 (unfiltered)	4	nd	–(48–49)	nd	nd	nd	Skoog *et al*., 1996
Baltic Sea, F15: 0–50 m depth	0.20 (unfiltered)	4	nd	–50	nd	nd	nd	Skoog *et al*., 1996
Baltic Sea, F15: 0–50 m depth	0.20 (filtered)	4	nd	–(50–51)	nd	nd	nd	Skoog *et al*., 1996
Baltic Sea, F15: 100 m depth	0.20 (filtered)	4	nd	–56	nd	nd	nd	Skoog *et al*., 1996
Mediterranean Sea, 42°N: Canet lagons	0.20 (filtered)	8 h (summer)	nd	–22	(+)8	nd	nd	Abboudi *et al*., 2008
Mediterranean Sea, 42°N: Leucate lagons	0.20 (filtered)	8 h (summer)	nd	–9	(+)0.4	nd	nd	Abboudi *et al*., 2008
Mediterranean Sea, 42°N: Coastal waters (SOLA)	0.20 (filtered)	8 h (summer)	nd	–34	–2	nd	nd	Abboudi *et al*., 2008
Seawater, Gotland Deep: 40 m, 57°N	0.45	13 (UV-B lamp)	nd	–32	nd	nd	nd	Lepane *et al*., 2003

nd, not detected; na, not applicable; np, no significant fluorescence peak observed in samples; UD, unpublished data.
(–) and (+) means a decrease in fluorescence and an increase in fluorescence, respectively, of the respective peaks.

light, a phenomenon known as photobleaching (Senesi, 1990a; Yamashita and Tanoue, 2003b; Wu *et al*., 2005; Hudson *et al*., 2007).

The photochemical degradation of FDOM and its consequences on natural waters are significantly dependent on the spectral range of sunlight under consideration, namely the UV-A (315–400 nm), UV-B (280–315 nm) or visible light (400–700 nm). Depending on the wavelength, there are significant variations as far as sunlight penetration in the water column is concerned (Scully *et al*., 1996; Morris and Hargreaves, 1997; Reche *et al*., 1999). DOM is typically able to absorb UV radiation in sea and lake water (Kirk, 1994; Morris *et al*., 1995), thereby controlling the penetration of UV in the deep water layers.

It has been demonstrated that photoirradiation reduces the fluorescence intensity by decomposing fulvic and humic acids (Moran *et al*., 2000; Wu *et al*., 2005), tryptophan-like component (Moran *et al*., 2000; Mostofa *et al*., 2007b), and FWAs or household detergents (Poiger *et al*., 1999; Mostofa *et al*., 2005a, 2010) in natural waters. On the other hand, microbial degradation has been observed to either enhance or decrease the fluorescence intensity in natural waters. This is mainly the consequence of the complex interactions between micro-organisms and fulvic and humic acids (Moran *et al*., 2000; Ma and Green, 2004; Mostofa *et al*., 2007a), detergent components (Table 1) and tryptophan-like compounds (Moran *et al*., 2000; Baker and Inverarity, 2004; Mostofa *et al*., 2007b; Table 1). The photochemical and microbial processing of FDOM yields a variety of photo- and microbial transformation intermediates in natural waters (Amador *et al*., 1989; Allard *et al*., 1994; Amon and Benner, 1996; Kramer *et al*., 1996; Ma and Green, 2004; Table 1 and references therein). Moreover, the fluorescence properties are often affected by the FDOM interactions with transition metals through formation of organo-metal complexes. The fluorescence intensity can be either enhanced or quenched depending on the system under study and the under experimental conditions (Cabaniss, 1992; Esteves da Silva *et al*., 1998). Due to the varied chemical structure of humic substances (fulvic and humic acids), aromatic amino acids and components of FWAs or household detergents, it is interesting to examine the photochemical, microbial and chemical reactivity of FDOM in the aquatic environments.

A review by Leenheer and Croué (2003) discusses the fluorescence properties of various fluorophores as fragments of natural organic matters (NOM). Another review by Hudson *et al*. (2007) has been focused on the effects of metal ions on DOM fluorescence, and has discussed the fluorescence quenching or enhancing properties of humic and fulvic acids with different concentration levels of metals. It has also addressed the photodegradation issue, providing useful information about the decrease of fluorescence intensity that may be related to photoproducts, chemical structure, DOM source, and incident irradiance. Another recent review by Coble (2007) covered the topic of marine optical biogeochemistry, discussing the chemical properties connected with chromophoric or colored dissolved organic matter (CDOM) absorbance, as well as its fluorescence characteristics.

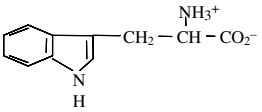
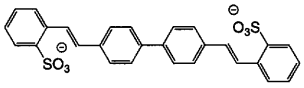
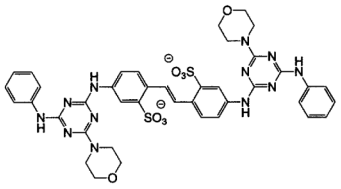
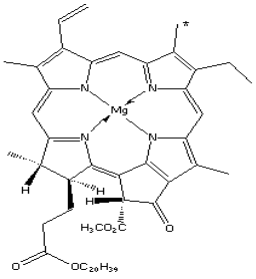
This review will give a general overview of the changes of the fluorescence properties because of the photochemical and microbial degradation of FDOM of different origin. The chemical reactivity will also be discussed, with the aim of understanding the biogeochemical activity of DOM in freshwater and marine environments. The photochemical and microbial reactivity of FDOM and its mechanism of chemical interaction with transition metals are discussed, with a particular focus on the photochemical, biological and geochemical aspects in freshwater and marine environments.

Chemical Properties of FDOM

The most common FDOM components studied in natural waters are fulvic acid-like, humic acid-like, tryptophan-like, and FWAs-like (DAS1 and DSBP) compounds. However, it is important to compare the chemical properties of these FDOM species with chlorophyll that is also fluorescent (Ex/Em = 431/670 nm for chlorophyll *a* (Chl *a*) and 435/659 nm for chlorophyll *b*; Moberg *et al*., 2001). The chemical structure and molecular weight of the different FDOM components are described in Table 2. The molecular structure of fulvic acid is not yet known because of the complicated chemical composition and relatively large molecular size. A quantitative study on stream fulvic acid (FA) showed that the functional groups found in Ogeechee stream FA samples are 6.4 meq (millequivalents) g^{-1} of carboxylic acids and 1.6 meq g^{-1} of phenolic hydroxyl groups. The percentages of aliphatic and aromatic C were 63% and 17%, respectively (Malcolm, 1985). The analysis of standard International Humic Substance Society (IHSS) fulvic acid have allowed the identification of the molecular structure as benzene-containing carboxyl, methoxylate and phenolic groups, hydroxycoumarin-like structures, fluorophores containing Schiff-base derivatives as well as chromone, xanthone, and quinoline ones (Senesi, 1990a; Leenheer and Croué, 2003). The tryptophan-like compounds consist of aromatic amino acids and have been observed in sea and river water. Their chemical structure is relatively simple (Table 2a).

The molecular structure of distyryl biphenyl (DSBP): 4,4′-bis[(2-sulfostyryl)biphenyl] is presented (Table 2b). Its photochemical decomposition is considered to be caused by an oxidative cleavage of the double bond, fol-

Table 2. Molecular structure and molecular weight of some fluorescent organic substances (data source: Mostofa et al., 2009a)

Components	Molecular structure	Molecular weight (Dalton)
Fulvic acid (IHSS):	Polymeric structure (Not yet identified)	2310 (Chin *et al*., 1994)
Tryptophan: (a)		204
Distyryl biphenyl, DSBP: (b)		562
Diaminostilbene, DAS1: (c)		924
Chlorophyll *a*: (d)		893

lowed by the production of various aldehydes such as 2-sulfonic acid benzaldehyde, 4-aldehyde-4′-(2-sulfostyryl)biphenyl(4-benzaldehyde-2′-sulfonic acid-stilbene) and 4,4′-bisaldehyde biphenyl (Guglielmetti, 1975; Kramer *et al*., 1996). The molecular structure of diaminostilbene-type (DAS1) compounds: 4,4′-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2′-stilbenedisulfonate is described in Table 2c. The photodegradation of DAS1 yields alcohols, aldehydes and some unidentified products. It is reported that the degradation of DSBP decreases in the presence of DOM, but the degradation of DAS1 is not hindered by the presence of DOM in natural waters (Kramer *et al*., 1996).

The chemical structure of Chl *a* is depicted in Table 2d, including its molecular formula ($C_{55}H_{72}MgN_4O_5$) and molecular weight (893.49). Chlorophyll *b* (molecular formula $C_{55}H_{70}MgN_4O_6$ and molecular weight 906.51) exhibits the same chemical structure as Chl *a*, replacing only one methyl group (–CH_3, marked with an asterisk (*)) with an aldehyde one (–CHO). Photo-experiments conducted on sedimentary chloropigments using ^{14}C-labeled algal cells in combination with field observations showed that a major fraction of Chl *a* would be rapidly degraded to various soluble colorless compounds. Only a minor fraction of Chl *a* (~30–40%) was degraded to pheophytin a (Klein *et al*., 1986; Bianchi *et al*., 1988; Sun *et al*., 1993).

Biogeochemical Functions Caused by Photochemical and Microbial Activity in the Aquatic Environments

The photochemical effects or solar radiation can produce various modifications in natural waters, which can be discriminated as:

1) Photo-induced generation of free radicals, which are involved into the photodegradation of FDOM or DOM in aqueous media. The free radicals sources include: (i) Photolysis of NO_2^- and NO_3^- ions to •OH (Vione *et al*., 2006; Minero *et al*., 2007); (ii) Generation of free radical species such as superoxide ion (O_2^-), hydrogen peroxide (H_2O_2), organic peroxides (ROOH) and hydroxyl radical

(•OH) by photolysis of CDOM or FDOM in waters (Cooper *et al*., 1988; Moore *et al*., 1993; O'Sullivan *et al*., 2005; Mostofa and Sakugawa, 2009); (iii) Photo-induced production of •OH by the photo-Fenton (Zepp *et al*., 1992; White *et al*., 2003) as well as the photo-ferrioxalate/H_2O_2 reactions (Safarzadeh-Amiri *et al*., 1997; Southworth and Voelker, 2003).

2) Production of new organic substances by photochemical and microbial assimilation of particulate organic matter and high-molecular weight DOM or FDOM. These processes have a deep impact on the carbon cycling and include: (i) Photochemical degradation of chlorophyll *a* with production of new organic substances; this process is typically occurring in the photic layer of natural lake and seawater (Rontani, 2001; Cuny *et al*., 2002); (ii) Photo-assimilation or degradation of algal biomass in surface waters under natural sunlight, which may produce new DOM or FDOM species in the aquatic environments (Henrichs and Doyle, 1986; Thomas and Lara, 1995; Biddanda and Benner, 1997; Carrillo *et al*., 2002; Rochelle-Newall and Fisher, 2002; Fu *et al*., 2010; Mostofa *et al*., 2009b); (iii) Microbial assimilation or degradation of algal biomass or phytoplankton; *in vitro* experiments have shown that under dark incubation these processes may produce new DOM or FDOM (Biddanda and Benner, 1997; Rochelle-Newall and Fisher, 2002; Yamshita and Tanoue, 2004, 2008; Stedmon and Markager, 2005; Fu *et al*., 2010; Mostofa *et al*., 2009b); (iv) Photochemical transformation of high-molecular weight DOM into low-molecular weight organic substances; in some cases the process can lead to complete mineralization (Dahlén *et al*., 1996; Moran and Zepp, 1997; Ma and Green, 2004; Vähätalo and Järvinen, 2007).

3) Photochemical degradation can regulate water-quality parameters. In particular: (i) Photochemical degradation modifies the physical, chemical and optical properties of water (Moran *et al*., 2000; Vähätalo *et al*., 2000; Twardowski and Donaghay, 2002; Kopáček *et al*., 2003; Mostofa *et al*., 2005a, 2007a, 2007b), the DOM molecular structure (Kramer *et al*., 1996; Kulovaara, 1996; Bertilsson and Allard, 1996) as well as its molecular weight (Allard *et al*., 1994; Twardowski and Donaghay, 2002; Kaiser and Sulzberger, 2004); (ii) Photodegradation processes can affect the acidity-alkalinity balance and the consumption of dissolved oxygen at the epilimnion level in both lacustrine and oceanic environments (Amon and Benner, 1996; Gao and Zepp, 1998; Kopáček *et al*., 2003); (iii) Photochemical degradation decreases the absorbance of CDOM (and/or FDOM), which can result in water discoloration (Reche *et al*., 1999 and references therein) and increases the water-column transparency. A notable consequence is the increased penetration of photosynthetically active radiation (PAR, 400–700 nm) but also of damaging UV radiation (280–400 nm) in the water column (Laurion *et al*., 2000 and references therein). These effects have also an influence on the photodegradation of deep-water DOM (Siegel and Michaels, 1996; Morris and Hargreaves, 1997); (iv) Photochemical processes can induce the degradation of organic pollutants or contaminants. A wide variety of photogenerated transients is involved (•OH, $CO_3^{-\bullet}$, $^1O_2$, ^{3}CDOM*), but the hydroxyl radical is the reactive species that is less likely to produce secondary pollutants. Therefore, •OH-induced processes are most likely to achieve efficient decontamination. The photo-Fenton reaction or photo-ferrioxalate/H_2O_2 reactions are particularly effective to this purpose (Safarzadeh-Amiri *et al*., 1997; Brezonik and Fulkerson-Brekken, 1998; Southworth and Voelker, 2003); (v) Photochemical degradation of DOM can interact with eutrophication by increasing the phosphate concentration upon decomposition of organic phosphorus present in DOM (Carpenter *et al*., 1998; Reche *et al*., 1999; Kim *et al*., 2006; Li *et al*., 2008 and references therein); (vi) Production of CO_2 as well as other dissolved inorganic carbon (DIC) species upon photochemical degradation of DOM can potentially influence the carbon cycling, and may have an impact on climate change (Salonen and Vähätalo, 1994; Granéli *et al*., 1998); (vii) The decomposition of DOM affects directly or indirectly the distribution of trace elements in natural waters (Kieber *et al*., 1989; Kopáček *et al*., 2003).

4) Photochemical degradation of DOM can be beneficial to the water ecosystem and provides energy for microbial loops. Its effects include: (i) Supply of nutrients, which are naturally important for plankton productivity in natural waters (Kirchman *et al*., 1991; Salonen *et al*., 1992; Wetzel, 1992; Kim *et al*., 2006); (ii) Increase in the pool of bioavailable carbon substrates, which are essential foods for microorganisms (Lindell *et al*., 1996; Wetzel *et al*., 1995; Bertilsson and Allard, 1996; Benner and Biddanda, 1998); (iii) Photo-production of reactive species by CDOM or FDOM, such as hydrogen peroxide (H_2O_2), organic peroxides (ROOH) and hydroxyl radical (•OH). These species can contribute damage to macromolecules such as DNA, proteins and lipids (Samuilov *et al*., 2001; Blokhina *et al*., 2003; Zhao *et al*., 2003; O'Sullivan *et al*., 2005).

Photochemical Behavior of FDOM in the Aquatic Environment

Photochemical degradation significantly changes the optical properties (excitation-emission wavelengths and fluorescence intensity) of the FDOM in the aquatic environments (Fig. 1; Table 1 and references therein). This photochemical effect can decrease the fluorescence intensity (FI) of fulvic acid-like (peak C), FWAs-like (peak

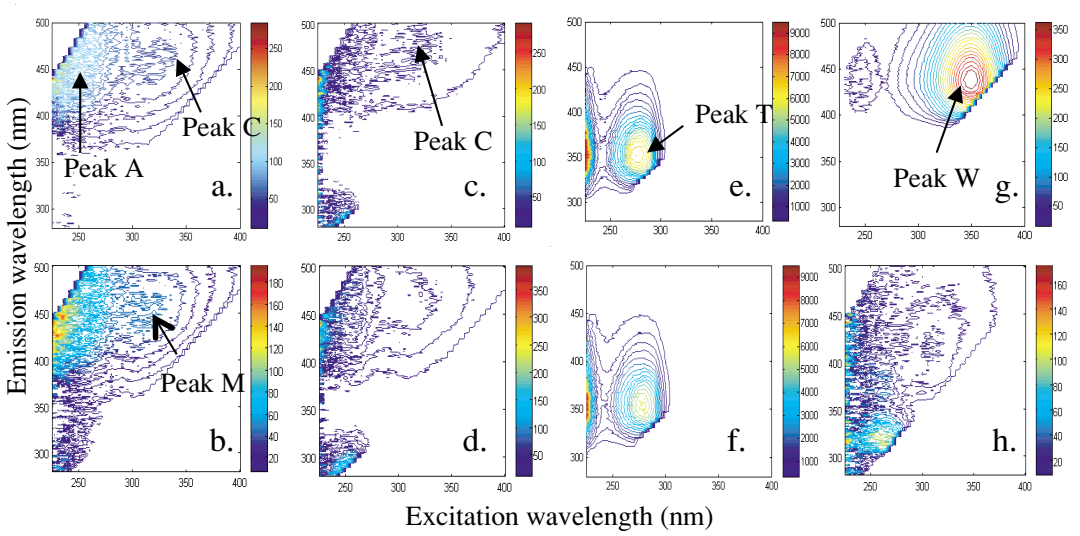


Fig. 1. Photochemical changes in the excitation-emission peak and fluorescence intensities of various standard irradiated samples using a solar simulator: Suwannee River Falvic Acid (a: 0 h and b: 10 h), Suwannee River Humic Acid (c: 0 h and d: 10 h), trypophan (e: 0 h and f: 10 h), and Distyryl biphenyl or DSBP (g: 0 h and h: 20 h).

W), and tryptophan-like (peak T) compounds, which are commonly observed in field observations of natural waters (Hayase and Shinozuka, 1995; Vodacek *et al*., 1997; Mostofa *et al*., 2005a, b; Yamashita *et al*., 2007; Yamashita and Tanoue, 2008; Borisover *et al*., 2009; Fu *et al*., 2010). They have been observed FI losses of fulvic acid-like substance of 72–84% upon 12–13 days of irradiation; in the case of household detergents or FWAs components, the observed FI losses after up to 10 days irradiation have been 12–81% in rivers, 34% in drain samples and 60–94% in Milli-Q water (Table 1). In lake water after 12 days irradiation, the losses of fulvic acid-like FI have been 36% at the surface (2.5 m) and 48% in deeper waters (70 m) for DOM fractions of <0.1 μm. In the case of DOM molecular-weight fractions below 5 kDa, the corresponding losses have been 16% in surface waters (2.5 m) and 50% in deeper waters (70 m). The low FI decrease in the case of surface-water DOM with molecular weight below 5 kDa may be explained by the fact that the corresponding samples have been collected during an ongoing summer stratification period (September). Therefore, the photosensitive DOM fractions had probably already undergone photochemical decomposition before sample collection. The higher FI decrease observed for deep-water DOM may be accounted for by the fact that deep waters undergo photochemical degradation processes to a lesser extent because of the reduced sunlight irradiance compared to surface waters (Laurion *et al*., 2000). As a consequence, deep-water samples may contain significant amounts of photosensitive DOM components, which have not been degraded in the natural environment and can undergo photochemical decomposition when irradiated in the laboratory (Table 1). For similar reasons, photochemical DOM mineralization is very difficult to be observed in surface lake water samples and is much easier upon irradiation of groundwater (Vione *et al*., 2009).

In estuarine water it has been observed a FI decrease in fulvic acid-like substances of 61–67% during 70 days irradiation (Table 1). In unfiltered seawater samples from the Baltic Sea irradiated for 4–5 days, the corresponding FI decrease has been of 44–52% at the surface (0–50 m) and 56–65% in the deeper layers (100–240 m). In some cases the decrease has been more marked, i.e., 61–70% at the surface (0–50 m) and 73–75% in the deeper layer (100–190 m). Interestingly the addition of chloroform significantly enhanced photodegradation, yielding a fulvic-acid like FI decrease of 59–81% in surface samples (0–50 m) and of 83–84% in deep-water ones (Table 1). The mechanism behind the increase FDOM photodegradation upon addition of chloroform may be the production of phosgene in the presence of O_2 ($CHCl_3 + O_2 + hv \rightarrow COCl_2 + HCl$). Phosgene is highly reactive toward the degradation of the fluorophores, such as the amino groups ($RNH_2 + COCl_2 \rightarrow RN{=}CO + 2HCl$) or carboxylic acids ($RCO_2H + COCl_2 \rightarrow RC(O)Cl + HCl + CO_2$). Such processes would contribute to the decrease of DOM fluorescence in natural waters (Shriner *et al*., 1943; Mostofa *et al*., 2009a).

The results of photodegradation of protein- or tryptophan-like components (peak T) have shown a FI decrease of 5–59% in rivers, 50% in sewerage drain samples, 7–88% in lakes and 37–45% in estuaries (Table 1). The decrease of tryptophan-like FI was low (59%) in rivers compared with fulvic acid (80%) (Mostofa *et al*.,

2007b). This suggests that tryptophan-like components are less susceptible to photodegradation than fulvic and humic acids in the aquatic environments.

Photochemical degradation of Mediterranean Sea samples (8 h sunlight exposure) showed a decrease in the fluorescence of fulvic acid-like or humic-like fluorophores (peak C), in the range of 9–22% for lagoon water and approaching 34% for coastal water (Table 1). Similarly, photochemical degradation of waters collected from Mackenzie River and Beaufort Sea (Estuary, Shelf and Gulf) demonstrates that the degradation of fulvic acid-like fluorophores (peak C) is usually higher during summer irradiation than in spring, autumn and winter (Table 1). The photodegradation of fulvic acid-like fluorophore (peak C) was relatively higher in Beaufort Sea samples (47–60% in Estuary during summer; 67–75% in Shelf during summer; 66% in Gulf during spring; 72 h irradiation) than in Satilla Estuary (61–67%, 70 days), Baltic Sea (44–52% in surface waters, 4–5 days), and Gotland Deep seawater (32%, 13 days) (Table 1). The high photodegradation of fulvic acid-like substances in Beaufort Sea samples has been explained by the occurrence of two phenomena. Firstly, in many cases a significant fraction of the fulvic acid-like substances are of autochthonous-origin, which makes them highly susceptible to photodegradation. Secondly, in the case of the Beaufort Sea the fulvic acid-like substances have allochthonous origin as they mainly derive from riverine input. Photochemical degradation of these compounds is poorly effective due to low water temperature in the Beaufort Sea (–0.54 to 21.81°C in Estuary, –1.36 to 9.23°C in Shelf, and –1.68 to 0.12°C in Gulf samples) (Osburn *et al*., 2009). Therefore, unaffected allochthonous fulvic acid-like substances are highly susceptible to degradation upon laboratory irradiation. The case of the Beaufort Sea may be a particular one, however, because it has been reported that DOM (or FDOM) components are produced from microbial assimilation of phytoplankton biomass or organic matter in natural waters (Rochelle-Newall *et al*., 1999; Parlanti *et al*., 2000; Rochelle-Newall and Fisher, 2002; Yamashita and Tanoue, 2004; Stedmon *et al*., 2007a, b; Mostofa *et al*., 2009b; Fu *et al*., 2010).

The fluorescence of various standard organic substances and of extracted fulvic and humic acids is generally decreased by photochemical degradation under sunlight. It has also been suggested that the FI of these substances undergoes a lower decrease when their initial concentration is higher (Table 1). It has been found that the FI decrease because of photochemical degradation was 42% for Suwannee River Fulvic Acid (SRFA) at 1 mg L^{-1} and 10 h irradiation, 23% for SRFA at 3 mg L^{-1} and 3 h, and 20% for 5 mg L^{-1} and 3 h. It has also been observed a FI decrease of 63% for tryptophan at 1 mg L^{-1} and 10 h, 23% for 3 mg L^{-1} and 3 h, and 20% for 5 mg L^{-1} and 3 h. In the case of distyryl biphenyl (DSBP) the FI decrease was 94% for 1 mg L^{-1} and 10 h, 73% for 3 mg L^{-1} and 3 h, 60% for 5 mg L^{-1} and 3 h. For diaminostilbene (DAS1) it has been observed a 93% decrease at 1 mg L^{-1} initial concentration and 10 h irradiation under a solar simulator (Table 1). Further studies will be required to ascertain the dependence of the photochemical degradation on the concentration of various FDOM components. However, it has been shown that the FI decrease shows large variations for different FDOM components under irradiation. This suggests that photodegradation rate/degree depends on the chemical nature of organic substances and on irradiation time.

Parallel factor (PARAFAC) analysis on Excitation Emission Matrix (EEM) spectra of irradiated Baltic Sea samples demonstrated that Component 2 (presumably autochthonous DOM) is photochemically more degradable ($69 \pm 6\%$, $n = 3$) than Component 1 (fulvic acid-like, $65 \pm 7\%$, $n = 3$), although the authors did not carry out a clear identification of these components (Stedmon *et al*., 2007a; Table 1). The image of Component 2 is similar to fluorescent matter identified in microbial assimilations of algal biomass collected from surface lake waters. Component 1 is similar to fulvic acid undergoing photobleaching (Mostofa *et al*., 2010). Component 3 did not undergo decomposition due to solar effects, and an increase in fluorescence was observed that was similar to extracted Göta River humic acid and standard SRHA (Stedmon *et al*., 2007a; Table 1). Unfortunately, this point was left obscure in the cited paper. The longer emission wavelength of Component 3 is also similar to SRHA reported in earlier studies (Mostofa *et al*., 2005a). Moreover, Component 5 (tryptophan-like) was less degradable ($26 \pm 9\%$, $n = 3$) than the unidentified Component 4 ($54 \pm 6\%$, $n = 3$, probably autochthonous DOM) as well as Components 1 and 2 (Stedmon *et al*., 2007a; Table 1). The significant increase of the fluorescence of the unidentified Component 6 may derive from the photoproducts of DOM, and possibly from the aromatic compounds originated upon photoirradiation of fulvic and humic acids (Corin *et al*., 1996; Schmitt-Kopplin *et al*., 1998).

As a result of photochemical degradation, the decrease of the fluorescence of fulvic acid-like, FWAs-like and tryptophan-like components and of their photochemical reactivity may greatly vary in a variety of natural waters. This may lead to hypotheses about several characteristic chemical and optical features of FDOM, which can be listed as follows: 1) In upstream and downstream rivers the fluorescence is predominantly caused by fulvic and humic acids, but in some polluted downstream rivers there is a significant contribution from components of FWAs or household detergents. The latter species are highly susceptible to photochemical degradation upon irradiation in the laboratory (Baker, 2002; Mostofa *et al*., 2005a;

Table 1 and references therein). In contrast, in the surface layer of lakes and oceans the fluorescence of various FDOM components is rapidly depleted by exposure to natural sunlight (Hayase and Shinozuka, 1995; Mostofa *et al*., 2005b; Yamshita and Tanoue, 2008; Fu *et al*., 2010). As a consequence, the FDOM sampled from these environment is relatively less susceptible to undergo further photochemical degradation in the laboratory (Table 1 and references therein). 2) High losses of fulvic acid-like FI have been observed upon irradiation of water samples from the deeper layers of lakes and seas. They are more pronounced compared to surface water. A reasonable explanation could be the higher occurrence of fulvic or humic acids in the deeper layers (Mopper *et al*., 1991; Table 1 and references therein). 3) Photo-induced losses of fulvic acid-like FI are gradually reduced in the passage from river to lake, estuary and sea water (Vodacek *et al*., 1997; Yamashita and Tanoue, 2003b; Mostofa *et al*., 2005b, 2007a; Cory *et al*., 2007). The cause might be linked to the prior losses of FI in stagnant lake or seawaters by photodegradation. In contrast, photodegradation in rivers is less effective due to continuous transport of water. The photodegradation changes the excitation-emission spectra by introducing a shift to the shorter wavelengths. This might constitute evidence of the alteration of existing fluorophores or of the appearance of new fluorescent organic substances (Fig. 1; Mostofa *et al*., 2009a). Examples of fluorescent substances arising from FDOM photodegradation could be salicylic acid (Ex/Em = 314/410 nm), 3-hydroxybenzoic acid (Ex/Em = 314/423 nm), and 3-hydroxycinnamic acid (Ex/Em = 310/407 nm). These molecules are characterized by fluorescence at relatively short wavelengths (Mostofa *et al*., 2009a and references therein).

On the other hand, photochemical degradation or assimilation of algae can produce new DOM or FDOM in the aquatic environments (Thomas and Lara, 1995; Rochelle-Newall and Fisher, 2002; Hiriart-Baer and Smiith, 2005; Fu *et al*., 2010; Mostofa *et al*., 2009b). It has been shown that the fluorescence intensity of FDOM is gradually increased upon 6 h sunlight irradiation in the presence of re-suspended algal biomass, collected by filtration of water (~0 m depth) from Lake Hongfeng (China) using GF/F filters during the summer season (Mostofa *et al*., 2009b). These results imply that photochemical processes play an important role both in the decomposition of FDOM and in its production. These processes play a key role in the biogeochemical cycles in the aquatic environments.

Controlling factors and impacts of DOM fluorescence loss upon photochemical degradation

The photochemical degradation of FDOM depends on the several factors in the aquatic environments: (i) The nature or the quality of the organic components of DOM; (ii) The concentration or the quantity of the organic DOM components; (iii) The pH of the sample solution that may affect the photo-induced generation of •OH, a strong oxidizing agent that is involved in the photodegradation of DOM (Bertilsson and Tranvik, 2000; Kwan and Voelker, 2002; Wu *et al*., 2005). pH also influences the photoactivity of Fe species that take part to DOM photomineralization (Vione *et al*., 2009); (iv) The presence and quantity of Fe in the water samples that may provide •OH through photo-Fenton reaction ($H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \bullet OH + OH^-$) or induce DOM transformation though irradiated Fe-DOM complexes (Miles and Brezonik, 1981; Zepp *et al*., 1992; Southworth and Voelker, 2003; Wu *et al*., 2005); (v) The concentration of O_2 that can assist in the production of •OH or H_2O_2 (Miles and Brezonik, 1981); (vi) The occurrence of NO_2^- and NO_3^-, further sources of •OH that may enhance the photoinduced decrease of DOM fluorescence (Table 1; Mack and Bolton, 1999). For example, addition of NO_2^- to standard SRFA slightly enhanced the decrease of fluorescence, which reached 22% with 1 mg L^{-1} SRFA + 50 μM NO_2^- upon 3 h irradiation compared to 19% with 1 mg L^{-1} SRFA after 3 h. Irradiation took place under a solar simulator (Table 1); (vii) The light intensity (UV-B, UV-A and PAR: photosynthetically active radiation) is a key factor in the photochemical reactions and controls the production of reactive transients that correspondingly enhance the photodegradation processes (Granéli *et al*., 1998; Bertilsson and Tranvik, 2000; Qian *et al*., 2001; Garcia *et al*., 2005; Randall *et al*., 2005). Interestingly, the decrease of fluorescence upon addition of NO_2^- that is a major •OH source (Mack and Bolton, 1999) was relatively limited (3%). This finding would be compatible with SRFA photooxidation primarily occurring because of the photo-induced generation of •OH ($H_2O_2 + h\nu \rightarrow 2\bullet OH$, Wang *et al*., 2001) from H_2O_2 originated from SRFA. It can be noted that the production rate of H_2O_2 from SRFA is 69×10^{-12} M s^{-1} (Mostofa and Sakugwa, 2009) and a relatively low level of H_2O_2 dosage can accelerate the photochemical degradation of humic acid in aqueous media (Wang *et al*., 2001). This hypothesis is in agreement with the assumption that a major production pathway of •OH by DOM under irradiation is constituted by the preliminary production of H_2O_2. It is also in agreement with by the results of field observations that the DOM fluorescence decreases with an increase of H_2O_2 concentration over the course of the day in marine surface waters (Obernosterer *et al*., 2001). An alternative possibility is that also other species different from •OH may induce the transformation of DOM. Interestingly, the generation rate of •OH was largely unable to account for the photoinduced mineralization of acidified lake-water or filtered groundwater DOM (Vione *et al*., 2009).

The decreases in FI of various FDOM samples reflect the sequential degradation and mineralization of the corresponding fluorophores or functional groups in the chemical structure of FDOM (Amador *et al*., 1989; Bertilsson and Allard, 1996; Corin *et al*., 1996). Photochemical degradation firstly modifies the fluorescence properties, and in particular the excitation-emission wavelengths (peaks A and C) of fulvic acid in the aquatic environments (Moran *et al*., 2000; Mostofa *et al*., 2007a, b). From the photochemical degradation of bog DOM and International Humic Substances Society Nordic fulvic acid, it has been highlighted the losses of carbohydrates, secondary alcohols, protonated and substituted aromatic compounds, carboxyl, amide, ester, ketone and quinines, with no changes in aliphatic carbons (Osburn *et al*., 2001 and references therein). Photochemical changes in FDOM correspond to a decrease in the dissolved organic carbon (DOC) concentration (Moran *et al*., 2000; Vähätalo and Wetzel, 2004; Garcia *et al*., 2005; Brooks *et al*., 2007; Mostofa *et al*., 2007b; Osburn *et al*., 2009) and to the generation of photoproducts. These processes can be summarized as: 1) Conversion of high molecular weight into low molecular weight DOM, which is generally observed in experimental and field observations of natural waters (Corin *et al*., 1996; Morris and Hargreaves, 1997; Wu *et al*., 2005; Lou and Xie, 2006; Yoshioka *et al*., 2007 and references therein); 2) Formation of microbiologically labile organic substances, which is commonly observed in the epilimnion of natural waters (Moran and Zepp, 1997; Bertilsson and Tranvik, 1998, 2000); 3) Formation of CO, CO_2 and dissolved inorganic carbon (DIC, which is usually defined as the sum of dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}), which are generally observed upon photodegradation of DOM (Valentine and Zepp, 1993; Granéli *et al*., 1998; Miller and Moran, 1997; Bertilsson and Tranvik, 2000; Ma and Green, 2004); 4) Formation of N-containing (NH_4^+ or NO_2^-) and P-containing inorganic compounds, which may typically be produced by degradation of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) in the epilimnion of natural waters (Bronk, 2002; Zhang *et al*., 2004; Kim *et al*., 2006; Vähätalo and Järvinen, 2007; Li *et al*., 2008 and references therein); 5) Energy changes (±), such as supply (+) or consumption (–) of energy because of the photodegradation of DOM, with (+) representing the photochemical formation of biologically labile compounds and (–) the abiotic mineralization of DOM (Wetzel, 1992; Tranvik, 1992; Hedges *et al*., 2000).

Photochemical degradation properties of fulvic and humic acids

It is shown that the fluorescence of SRFA dissolved in Milli-Q water is photochemically decreased under simulated sunlight (by 42% in 1 mg L^{-1} SRFA for 10 h, 23% for 3 mg L^{-1} and 3 h, 20% for 5 mg L^{-1} and 3 h, and by 22% with 1 mg L^{-1} SRFA + 50 μM NO_2^- for 3 h) (Table 1). The extracted fulvic acid from Göta River showed a decrease in fluorescence (32%) in alkaline samples (6.3 mg L^{-1} fulvic acid in 0.5 M NaOH solution) after 13 days UV-B irradiation (Table 1). A 6-hour summer sunlight exposure of fulvic and humic acids extracted from Lake, Pond and Marsh showed that the decrease of humic acid fluorescence was relatively higher (64–100%) compared to fulvic acid (48–83%) (Table 1). It is reported that the fluorescence of humic acid is highly depleted in acidic samples, and undergoes a more pronounced decrease compared to fulvic acid even at higher pH (Wu *et al*., 2005). Correspondingly, photoirradiation can decompose 35% of extracted Nordic Reference humic acid (NoHA) and 24% of extracted Nordic Reference fulvic acid (NoFA) from humus-rich pond water in photoexperiments conducted using a solar simulator (Corin *et al*., 1996). The reported results suggest that the photochemical degradation of humic acid is pH and concentration dependent, but the reason behind this phenomenon is still unknown. However, the relatively high photolability of humic acid can be in agreement with the high level of aromaticity (30–51%), in particular when compared to fulvic acid (14–21%) (Gron *et al*., 1996; Malcolm, 1985; Wu *et al*., 2005).

The rate constants for the decrease in fluorescence and for DOC loss are significantly higher for humic than for fulvic acid, as resulted in photoexperiments carried out at different pH levels on extracted humic and fulvic acid from upstreams (Wu *et al*., 2005). Thus, photodegradation of the humic acid fraction is significantly higher than the fulvic acid fraction and is more sensitive to pH. Interestingly, the higher photolability of humic compared to fulvic acid correlates well with the higher production rate of H_2O_2 upon irradiation of Suwannee River humic Acid (179×10^{-2} M s^{-1}) than for Suwannee River fulvic Acid (69×10^{-2} M s^{-1}) (Mostofa and Sakugawa, 2009). This might imply that the production of H_2O_2 is a primary step for the photochemical degradation of DOM in aqueous solution. Humic acid could thus be the primary target of DOM photodegradation in natural waters (Wu *et al*., 2005). In contrast, fulvic acid is photochemically more stable than humic acid in aqueous media and may play a vital role in biogeochemical processes due to its longer lifetime in natural waters.

It can be noted that the fluorescence intensity of humic acid is increased by irradiation in some particular cases. Thus, increases have been observed of *ca*. 70% for Suwannee River Humic Acid (SRHA) (1 mg L^{-1}, 10 h), 5% for SRHA (5 mg L^{-1}, 3 h), and 4% in alkaline samples (6.5 mg L^{-1} Göta River humic acid in 0.5 M NaOH) (Table 1). The reason behind such a phenomenon may be the generation of aromatic photoproducts upon irradiation of humic acid (Corin *et al*., 1996). Some of these

photoproducts may show the fluorescence at peak C-region, for example 3-hydroxybenzoic acid at Ex/Em = 314/423 nm, 3-Hydroxycinnamic acid at Ex/Em = 310/407 nm, and methyl salicylate at Ex/Em = 366/448 nm (Mostofa *et al*., 2010). This may produce an increase of humic acid fluorescence. Weak light intensity may prolong the lifetime of humic acid and its aromatic photoproducts, which may result in a fluorescence increase. On the other hand, intense and prolonged irradiation may decompose humic acid and its photoproducts rapidly (Corin *et al*., 1996), which causes a decrease in fluorescence.

Microbial Behavior of FDOM in the Aquatic Environments

The microbial degradation under dark incubation would usually change the fluorescence properties of fulvic acid-like (peak C), FWAs-like (peak W) and tryptophan-like components (peak T) in natural waters (Moran *et al*., 2000; Ma and Green, 2004; Mostofa *et al*., 2007b; Yamshita and Tanoue, 2008; Mostofa *et al*., 2010). Fulvic acid-like FI is typically increased in rivers (3–15%) and FWAs-like FI is often increased, by 14% for commercial detergents in MQ waters, by 8% in drain samples and by 21% in river waters plus commercial detergents after 6–13 days dark incubation (Table 1). In lake water under dark incubation, the increase of fulvic acid-like FI was higher (it reached up to 31% in molecular fractions <0.1 μm and 102% in <5 kDa) in surface waters than in deeper DOM fractions (where the corresponding increases were 0% and 20%). In estuarine water, a little decrease (1–12%) of fulvic acid-like FI was observed during a 51 days incubation period (Table 1). Microbial degradation carried out on Mediterranean Sea samples showed an increase of DOM fluorescence after 8 h dark incubation of 0.4–8% in lagoon water, and a fluorescence decrease of 2% in coastal water (Table 1). Upon microbial processing, the fluorescence of standard SRFA, tryptophan and DSBP did not change significantly upon 10 h incubation (Table 1). Similarly, a fluorescence increase after a 9-day incubation period has been detected in fulvic (8%) and humic acid (6%) extracted from Göta River (Table 1). These results may lead to the hypothesis that there are several characteristic chemical and optical features of fulvic acid and FWAs in natural waters, which can be classified as: 1) fluorescent compounds, especially humic substances in stream, are typically unable to experience microbial degradation. Fluorophores of humic substances are mostly aromatic molecules associated with functional groups having extensive π-electron systems. They show fluorescence properties and are highly recalcitrant to microbial degradation (Geller, 1986; Münster, 1991). 2) In rivers, commercial detergents or FWAs-like components typically undergo an increase in fluorescence after microbial degradation. Such a behavior is similar to that of fulvic acid under dark incubation in the aquatic environments. 3) Under dark incubation, the increase of fulvic acid-like FI is typically higher in surface lake water compared to the deeper layers. This finding allows the hypothesis that surface photo-bleached fulvic acid is highly labile to microbial changes, which can lead to a significant increase in fulvic acid-like FI. However, the mechanism behind the increase in fulvic acid-like fluorescence is not well documented and should be the focus for future research.

Microbial degradation shifts the fluorescence peak position (Ex/Em) of fulvic acid-like component from shorter to longer wavelength regions in natural waters (Moran *et al*., 2000; Mostofa *et al*., 2005a, 2007b). This might be caused by a decrease in aliphatic carbon or an increase of aromaticity or π-electron systems in fulvic acid (Senesi, 1990a, b). Microbial changes in fluorescence characteristics are relatively less efficient than those caused by the photochemical processes (Table 1; Moran *et al*., 2000; Ma and Green, 2004; Mostofa *et al*., 2007a).

On the other hand, microbial degradation or assimilation of algal biomass or phytoplankton, observed in *in vitro* experiments or under dark incubation may produce new DOM or FDOM (Rochelle-Newall and Fisher, 2002; Yamshita and Tanoue, 2004, 2008; Stedmon and Markager, 2005; Fu *et al*., 2010; Mostofa *et al*., 2009b). From the experimental results, it is shown that the fluorescence intensity of microbiologically produced FDOM is gradually increased after 20 days dark incubation at room temperature or upon resuspension of algal biomass, which was collected through filtration of surface lake waters (~0 m) of Lake Hongfeng (China) using GF/F filters during the summer season (Mostofa *et al*., 2009b). Microbial processes are vital in biogeochemical processes, and they simultaneously cause production and degradation of FDOM in the aquatic environments.

The fluorescence of tryptophan-like components under dark incubation is typically decreased, approximately by 13–24% in unfiltered river waters, by 67% in unfiltered sewerage drain samples, and by 11% in filtered river samples. However, an increase in tryptophan-like FI is often observed in filtered river samples (4–6%), in lake water in the molecular fractions <0.1 μm (68% in surface water and 5% in deep water) and <5 kDa (51% in surface water and 28% in deep water), and in estuaries (23–112%) (Table 1). From these results it can be concluded that there are several characteristic phenomena concerning microbial degradation of tryptophan-like components in natural waters. First, tryptophan-like components are microbiologically labile but microbial degradation is a relatively slow process whilst photodegradation is rapid (Moran *et al*., 2000; Baker and Inverarity, 2004; Mostofa *et al*., 2007b). Second, an increase in tryptophan-like FI in fil-

tered samples and a decrease in unfiltered samples can be rationalized considering that the filtration processes may deactivate or hinder the bacterial activity. However, if the FI decrease in unfiltered samples may be due to the microbial degradation of tryptophan, the reason for the FI increase in filtered samples might be the result of the binding of tryptophan-like component with humic substances (Volk *et al*., 1997). Interestingly, an increase of fulvic acid-like FI is typically observed under dark incubation (Moran *et al*., 2000; Mostofa *et al*., 2007b) and in deep lake or seawaters (Hayase and Shinozuka, 1995; Mostofa *et al*., 2005b). Finally, photo-bleached tryptophan-like DOM is resistant to microbial processes in natural waters. It has been shown that 70% of the dissolved amino acids (DAA) and dissolved carbohydrates (DCHO) associated with the humic fraction are consumed by microbial degradation in natural waters (Rosenstock and Simon, 2003).

Complexation of Metal Ions with FDOM

Metal ion (M) complexes with dissolved organic matter (DOM) to form M-DOM species is an important biogeochemical phenomenon that is frequently detected in natural waters. The major organic substances studied in M-DOM complexation are fulvic acid, humic acid, tryptophan, cysteine, selenoprotein P, the Schiff base 2-[4-dimethylaminocinnamalamino]-benzoic acid, phenols, polyphenols, etc. (Powell *et al*., 1993; Yalçin *et al*., 1998; Sidenius *et al*., 1999; Wu and Tanoue, 2001a, b; Cao *et al*., 2004). The major transition metals examined in M-DOM complexation are Fe, V, Ce, Th, U, Mo, Cu, Mn, Ni, Co, Cr, Zn, Pb, Cd, Al, Ca, Hg, UO_2(II) (Esteves da Silva *et al*., 1998; Yalçin *et al*., 1998; Sidenius *et al*., 1999; Shin *et al*., 2001; Wu *et al*., 2004a, b; Yamashita and Jaffé, 2008). The complexes formed by all the studied organic substances exhibit fluorescence properties, thus they are included in FDOM. Therefore, the functional groups or fluorophores in FDOM are susceptible to show their fluorescent properties as well as to interact with metals via complex formation. The interaction of metals with DOM (M-DOM) and with FDOM (M-FDOM) are thus closely associated, and the fluorescence intensity of M-FDOM is either enhanced or quenched compared to the original FDOM (Cabaniss, 1992; Esteves da Silva *et al*., 1995; Lu and Jaffé, 2001; Wu *et al*., 2004a, b).

Paramagnetic metal ions can typically produce a quenching in the fluorescence intensity of EEM spectra (Esteves da Silva *et al*., 1998; Shin *et al*., 2001; Hays *et al*., 2004; Wu *et al*., 2004b). Both excitation and emission wavelength maxima gradually increase upon addition of metal aqueous solution to the organic ligands (Wu *et al*., 2004c). Kinetic changes of excitation and emission wavelengths of the fluorescence maxima suggest the occurrence of two major binding sites on fulvic acid, fast and slow, having half-lives of 1.3–3.9 and 34.7–69.3 s, respectively (Wu *et al*., 2004c). However, there are at least three binding sites on fulvic acid that have been observed with time-resolved fluorescence measurements (Cook and Langford, 1995; McGown *et al*., 1995; Kumke *et al*., 1998). For three fluorophores in fulvic acid, the lifetimes and emission wavelength maxima have been identified as follows: ~50 ps (392 nm), ~430 ps (465 nm), and 4.2 ns (512 nm) (Cook and Langford, 1995).

Trivalent Al^{3+} and Be^{3+} can enhance the fluorescence response as a result of complexation with fulvic acid (Esteves Da Silva *et al*., 1995; Lakshman *et al*., 1996) and isolated natural organic matter (Smith and Kramer, 1999). However, the formation of M-FDOM complexes greatly varies in stream, river, lake and sea water, depending on several factors such as water quality parameters (DOC concentration, pH, salinity, ionic strength, anions and cations) and solar radiation (Esteves da Silva *et al*., 1998; Lu and Jaffé, 2001; Wu and Tanoue, 2001a, b; Wu *et al*., 2004b).

The mechanism for complexation between transition metals and FDOM

To better elucidate the M-FDOM complex formation and its significance in natural waters, it is essential to evaluate the underlying mechanisms that, however, have not been well documented in earlier studies (Shin *et al*., 2001; Wu *et al*., 2004b; Hudson *et al*., 2007). The mechanism behind the M-FDOM complexes may possibly be the formation of a strong π-electron bond between the fluorophore or functional group of FDOM and the *d*-orbitals of the transition metal. The π-electron bonding system can be formed in two ways: First, by donation of electrons from the fluorophore (F:) of FDOM to the empty *d*-orbitals of the transition metal (M^{n+}).

$$F: + M^{n+} \rightarrow F:M^{n+}.$$

This type of π-electron bonds in metal-FDOM complexes can greatly reduce the electron density of the fluorophore. The latter (F:) causes the *d*-orbitals to be either stabilized or destabilized. A stabilizing effect from a fluorophore lowers the energy of the interacting *d*-orbitals, which can considerably decrease the electron transfer probability and decrease the fluorescence intensity as a consequence. It is generally known that the transition metals are excellent Lewis acids and accept electron density from many molecules or ions that act as Lewis bases. As an alternative, upon M-FDOM formation the probability of an electron transfer is enhanced if a destabilizing effect from a fluorophore raises the energy of the *d*-orbitals. This effect subsequently leads to an increase in the fluorescence intensity of the fluorophore in the M-FDOM complex.

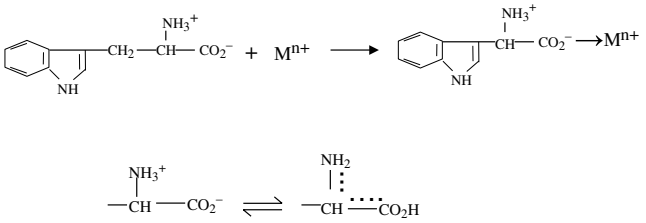


Fig. 2. The mechanism of the chemical bonding between tryptophan and trasition metal (M), above; resonance configulation of [–CH(NH$_2$)–COOH], below.

The mechanism of the interactions leading to M-FDOM formation can be clarified by considering tryptophan as an example that can is schematically depicted in Fig. 2.

In this mechanism, the functional group or fluorophore [–CH(NH$_2$)–COOH] existing in the chemical structure of tryptophan (Table 2a) may electronically bind with metal ions, creating a strong π-electron bond with the *d*-orbitals of transition metal ions (Fig. 2). Because the [–CH(NH$_2$)–COOH] group has a strong affinity toward a resonance configuration (Fig. 2), there is a high probability of electron donation from this fluorophore to the *d*-orbitals of transition metal ions. The π-electron bonding system would greatly reduce the electron density of the fluorophore in tryptophan, which results in a lower probability of electron transition of that fluorophore and decreases as a consequence the fluorescence intensity of tryptophan after complexation with the metal ions. On the other hand, an increase in fluorescence intensity of the FDOM in M-FDOM complexed may arise from enhanced probability of electron transition of the fluorophore due to M-FDOM complexation.

Controlling factors of the complexation

It has been shown that the number-averaged molecular weight (M_n) of the FDOM-bound complexes for the transition metals follows the order Cu > Ni > (Co, Cr, Zn) > Pb > Cd (Wu *et al*., 2004b). This is in agreement with the Irving-Williams series, and the order (Fe, V, Ce) > Th > U > Mo is followed by the FDOM-bound complexes of other metals with a given ligand (Irving and Williams, 1953; Winzerling *et al*., 1992), fulvic acid (Wu *et al*., 2002) and proteins (Sidenius *et al*., 1999). The order of complex formation of the transition metals to bulk FDOM in natural waters depends on several associated effects such as: (i) fluorophores with high electron density will merely compete for the metal ions with stabilizing effects of *d*-orbitals; (ii) among the transition metals, the size or atomic radius generally decreases with increasing nuclear charge, because the electrons that experience a greater nuclear charge are pulled more strongly towards the nucleus. However, the last few elements (Cu, Zn, Ag, Cd, Pt, Au, Hg, etc.) in each row of the *d*-block are slightly larger than those preceding them because in these cases the electron-electron repulsions caused by the filling of the *d*-orbitals outweigh the increasing nuclear charge. Therefore, the two competing effects of nuclear charge and electron-electron repulsion affect the chemical binding of the *d*-orbital metals with the fluorophores. As one moves across a period, the increasing nuclear charge is usually more significant than the electron-electron repulsion. These combined effects make Cu and other metals of the same row more susceptible to complexation with FDOM than the transition metals of the second and third rows. Moreover, the ground states for Sc, Ti, Fe, Co, and Ni are ferromagnetic because of the presence of one unpaired electron, while V, Cr, and Mn are antiferromagnetic (Iota *et al*., 2007; Tung and Guo, 2007). It can be proposed that the unpaired electron of ferromagnetic transition metals would easily form a bond with an electron donated by FDOM, which is not possible for antiferromagnetic metals. This hypothesis can account for the rapid complexation of the ferromagnetic transition metals compared to the antiferromagnetic elements.

Importance of the complexation between transition metals and FDOM

The M-FDOM complexes control the speciation of metals and influence their toxicity, bioavailability and transport in the aquatic environment (Bidoglio and Stumm, 1994; Wu *et al*., 2004a). Complex formation might also be an important factor in the production of free radicals that are strong oxidizing agents in the photodegradation of DOM, e.g., through the photo-Fenton reaction (Zepp *et al*., 1992; Southworth and Voelker, 2003). The M-FDOM complexation has been applied in petrochemical industry and in the production of chemicals for the extraction, separation and recycling of metal ions from aqueous and organic phases, where the M-FDOM complex is selectively dissolved.

SCOPE OF THE FUTURE CHALLENGES

This review shows that the fluorescence of major FDOM components such as fulvic acid, humic acid, tryptophan, fluorescent whitening agents (DAS1 and DSBP) and some household detergents are photochemically decomposed in natural waters. FDOM is often microbiologically recalcitrant to a decrease in fluorescence under dark incubation, except for the tryptophan-like component. It is reported that autochthonous DOM typically shows fluorescence at peak C- and A-regions, which is a similar behavior as humic-like and fulvic acid-like components (Fulton *et al*., 2004; Yamashita and Tanoue, 2004; Stedmon *et al*., 2007a; Yamashita and Jaffé, 2008; Fu *et al*., 2010). Recently, PARAFAC modeling has been ap-

plied to the identification of various fluorescent components and of their characteristic changes (optical and chemical) upon photochemical and microbial degradation in seawater (Stedmon *et al*., 2007a). These researchers did not distinguish between the photochemical, microbial and metal-complexation processing of the autochthonous DOM (fulvic acid-like or humic-like substances) nor its differentiation with terrestrial fulvic acid, which should be a key focus for future research. It has also been shown that the fluorescence of humic acids does not decrease photochemically in alkaline samples, but it is quickly depleted in acidic waters. The mechanism behind these phenomena is a major concern for future research. Finally, a few studies have been conducted on the photochemical, microbial and metal-complexation behavior of FDOM in the aquatic environments. It should be important to conduct the experiments in underdeveloped regions, particularly in Asia, Africa, and Latin America where freshwaters are highly contaminated with untreated sewerage and industrial effluents. Application of PARAFAC modeling to photochemical and microbial processing as well as metal complexation of FDOM and its photoproducts may pave the way to understand the optical FDOM nature and its chemical characteristics. It would be a major leap forward in understanding the FDOM biogeochemical functions in the natural aquatic ecosystem.

Due to global warming, an increase in water temperature may significantly enhance the photochemical processes. This could correspondingly impact on microbial processes as well as other key biogeochemical functions in natural aquatic ecosystem. However, there is no study conducted to examine the temperature effect on the photochemical, microbial and metal-complexation features of FDOM, which might be an interesting issue for future study. Finally, photochemical and microbial changes of FDOM are fundamental to find out the links with other chemical changes, such as DOC mineralization and structural changes of DOM in natural waters.

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