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Competition between biological and photochemical processes in the mineralization of dissolved organic carbon

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Abstract

The photo- and bioreactive components of dissolved organic matter (DOM) from three different environments were determined during long-term decomposition experiments. Terrigenous DOM was collected from a black-water system, plankton DOM was harvested from phytoplankton cultures, and lake water served as a DOM source with both terrigenous and plankton components. Photomineralization accounted for the removal of 46 and 7% of terrigenous and lake-dissolved organic carbon (DOC), respectively, while no loss in DOC was observed when plankton DOM was exposed to irradiation. Biomineralization accounted for the removal of 27% each of terrigenous and lake DOC and 74% of plankton DOC. Phototransformations of terrigenous and lake DOM resulted in 7% and 2% increases in biodegradable DOC, respectively, while no increase in biodegradable DOC was observed for irradiated plankton DOM. In two different experimental approaches, terrigenous DOM was exposed to sequential and alternating bio- and photodegradation, respectively, to determine the fractions of DOC that were bioreactive and photoreactive. About 15% of terrigenous DOC was susceptible to both biomineralization and photomineralization. These results demonstrate that biological and photochemical processes compete in the mineralization of DOC. Photomineralization of bioreactive DOC is likely an important factor determining the net effect of irradiation on the bioreactivity of DOM.

Photochemical processes have a significant impact on the cycling of dissolved organic matter (DOM) in aquatic environments and thereby affect ecosystem structure and function. Photomineralization and phototransformations directly remove and structurally alter DOM, influencing its biological utilization and fate (see review by Mopper and Kieber 2002). The origin and chemical composition of DOM has a large impact on its photoreactivity and its subsequent bioreactivity (Kieber et al. 1990; Mopper et al. 1991; Miller and Zepp 1995; Graneli et al. 1996; Bertilsson and Tranvik 2000). A net positive effect of irradiation on bioreactivity has been described for DOM originating from aquatic systems with a large input of terrigenous material (see review by Moran and Zepp 1997) and the deep ocean (Mopper et al. 1991; Benner and Biddanda 1998; Obernosterer et al. 1999). In contrast, exposure of surface water from plankton-dominated systems to irradiation has a net negative effect on the subsequent bioreactivity of the DOM (Benner and Biddanda 1998; Obernosterer et al. 1999; Tranvik and Bertilsson 2001). Photomineralization of bioreactive substrates and phototransformations of bioreactive to biorefractory compounds have both been suggested to account for the observed negative effects of irradiation on the bioreactivity of DOM. Even though the exact mechanisms resulting in these contrasting effects of irradiation on DOM bioreactivity have not been elucidated thus far, an inverse relationship between DOM bioreactivity prior to and following exposure to irradiation was established (Obernosterer et al. 2001; Tranvik and Bertilsson 2001).

The photochemical production of bioreactive substrates and the subsequent enhancement of biological utilization of terrigenous dissolved organic carbon (DOC) have lead to the general view that photochemical and biological processes act on different components of DOM. However, there is evidence that bioreactive compounds are also involved in photochemical reactions, either directly or through natural photosensitizers. The bioreactivity of proteins decreased substantially following exposure to irradiation (Keil and Kirchman 1994; Naganuma et al. 1996; Obernosterer et al. 1999). Photomineralization of oxalic acid, a bioreactive photoproduct, was observed by Bertilsson and Tranvik (1998). These results indicate that photochemical processes are potentially important in the removal of bioreactive DOM. If the same substrates are subject to photochemical and biological mineralization, competition between these processes is likely to occur.

In the present study, filtered water from a black-water swamp, a lake, and a phytoplankton culture was exposed to extensive and sequential photodegradation and biodegradation. Rates of photochemical and biological removal of DOC were determined as well as the overall extent of removal by these processes. Major differences were observed among experiments with different types of DOM, indicating that the chemical composition of DOM has a major influence on the extent and pathways of DOC mineralization. The photomineralization of bioreactive DOC was observed, demonstrating these processes compete for some of the same substrates.

Material and methods

DOM sources—The biological and photochemical reactivities of DOM from different environments were investigated.

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Table 1. Characteristics of water samples used for experiments in this study. a_{350} (m^{-1}), absorption coefficient at 350-nm wavelength.

	Sampling date	pH	a_{350} (m^{-1})	DOC (μmol L^{-1})
Rocky Bluff Swamp 1	24 Apr 2001	5.8	71.9	1,288
Rocky Bluff Swamp 2	05 Dec 2001	5.5	35.1	1,069
Lake Murray	20 May 2001	7.0	4.21	324
Phytoplankton cultures		7.0	0.63	68

Water was collected from Rocky Bluff Swamp, a forested, black-water system dominated by vascular plants and situated in the coastal plain near Sumter, South Carolina. Rocky Bluff Swamp is characterized by a relatively low pH, a large component of chromophoric DOM, and high concentrations ($\sim$1 mmol L^{-1}) of DOC; Table 1). The high concentrations of chromophoric DOM and the dense vegetation in Rocky Bluff Swamp limit primary production by algae. We therefore consider the DOM from Rocky Bluff Swamp to be terrigenous. Water was also collected from Lake Murray, a reservoir created in 1930 by damning the Saluda River near Irmo, South Carolina. Lake Murray has a surface area of 43 km^2 and an active plankton community that is a source of DOM in addition to terrigenous DOM supplied by riverine input. The concentration of DOC in Lake Murray is $\sim$300 μmol L^{-1} and the amount of chromophoric DOM is $\sim$10-fold lower than that in DOM from Rocky Bluff Swamp (Table 1). In addition to these sources, plankton DOM was harvested from phytoplankton cultures grown in an artificial freshwater medium (Porcella et al. 1980). The algal growth medium contained carbon at relatively low concentrations (i.e., Na_2EDTA [ethylene diamine tetraacetic acid] 8 μmol C L^{-1}, thiamine 3.5 μmol C L^{-1}, biotin 20 nmol C L^{-1}, and B_{12} 25 nmol C L^{-1} final concentrations) compared with the DOC concentration at the time of harvesting the phytoplankton culture (68 μmol C L^{-1}; Table 1). The freshwater medium was inoculated with a mixed plankton assemblage originating from Lake Murray (inoculum ratio 1 : 1,000) and the phytoplankton cultures were kept in a temperature-controlled incubator (20 $\pm$ 0.1°C) with an 8 : 12 light : dark cycle. The cultures were continuously stirred using magnetic stir bars. The DOM from the phytoplankton cultures was collected during early stationary phase after 12 d of incubation, as described below.

Water was collected from Rocky Bluff Swamp in April and December 2001 and from Lake Murray in May 2001. Water samples were taken in clean polycarbonate carboys and processed within 2 h of collection. Rocky Bluff Swamp samples were filtered through 0.2-μm pore-size Nuclepore QMC polycarbonate cartridge filters and samples from Lake Murray and the phytoplankton cultures were sequentially filtered through precleaned Whatman GF/F and 0.2-μm pore-size cellulose acetate filters.

Photodegradation experiments—Filtered water samples (500 ml) were placed in duplicate in 1-L quartz Erlenmeyer flasks and exposed to irradiation in a solar simulator (Suntest XLS). An equivalent portion of the filtered water was placed in Pyrex flasks and kept in the dark. The solar simulator was equipped with a high-pressure xenon lamp and a special ultraviolet filter with a low wavelength cut-off at 300 nm. The spectrum of the lamp closely resembles the spectrum of natural sunlight. Light intensity during the photodegradation experiments was 765 W m^{-2}. The quartz flasks were submerged in a recirculating water bath maintained at 20 $\pm$ 0.1°C. Irradiated and dark samples were filtered through combusted GF/F filters approximately every 24 h to limit biological activity. Irradiation of the various DOM sources varied from 0.5 d to 8.4 d (Table 2). Absorption measurements (350 nm) were performed at regular intervals during photodegradation. Experiments were terminated when changes in the optical properties were minimal. Photochemical processes could have promoted further changes in the DOM without being recorded in the optical properties at the end of our photodegradation experiment. However, given the low absorption coefficients following extensive photodegradation, we considered DOM phototransformations of minor importance. Besides samples for the optical properties, subsamples for DOC analyses were taken from the irradiated and dark treatments. Subsamples were collected before and after filtration to determine the effect of repeated filtration on the optical properties of the DOM and the DOC concentration. All glassware used for the filtration procedure was soaked in 1 N HCl and subsequently combusted for 5 h at 450°C.

Table 2. Summary of exposure times to photodegradation and biodegradation. PD, photodegradation; BD, biodegradation; PD_BD, photodegradation followed by biodegradation; BD_PD, biodegradation followed by photodegradation; BD_PD_BD, biodegradation followed by photodegradation followed by biodegradation. Samples were exposed to irradiation 24 h per day.

DOM source	PD irradiation time (days)	BD incubation time (days)	PD_BD incubation time (days)
Rocky Bluff Swamp 2	8.4	111	119.4
Lake Murray	4.9	297	229.9
Phytoplankton cultures	0.5	117	117.5
	BD incubation time (days)	BD_PD irradiation time (days)	BD_PD_BD incubation time (days)
Rocky Bluff Swamp 1	240	6.7	345.7

Biodegradation experiments—Following extensive photodegradation of DOM, both the irradiated treatments and the dark controls were inoculated with a microbial community from the respective aquatic system. Therefore, a 1.5-μm filtrate (Whatman AH filters) of the original water sample was added to the respective 0.2-μm filtrate (1 : 100 inoculum ratio, final volume 1 L), and the biodegradation experiments were subsequently incubated in the dark. The biodegradation experiments with DOM originating from Lake Murray and the phytoplankton cultures were incubated at 20°C and the biodegradation experiments with DOM from Rocky Bluff Swamp 2 were performed in duplicate at 25°C. All bioassay experiments were incubated until no more changes in the

DOC concentration were observed. Subsamples for DOC analyses were GF/F filtered prior to storage (see below). The duration of the biodegradation experiments varied between 111 d and 297 d (Table 2). During both long-term photo- and biodegradation, the water was incubated with a large surface area and headspace to promote aeration.

Rocky Bluff Swamp 1 experiment—In an additional experiment, water collected from Rocky Bluff Swamp (April 2001, Table 1) was filtered through 0.2-μm pore-size Nuclepore QMC polycarbonate filter cartridges and immediately inoculated with a microbial community as described above. The biodegradation experiment was incubated in the dark at 20°C and the decrease in DOC followed over time. When the DOC concentration remained stable (240 d, see Table 2), the water from the biodegradation experiment was filtered through combusted GF/F filters and subsequently exposed to irradiation in the solar simulator at 765 W m^{-2} for 6.7 d (Table 2). Following extensive photodegradation, the GF/F filtrate was reinoculated with a microbial community and incubated in the dark at 25°C for 99 d (Table 2). The bio- and photodegradation experiments were regularly subsampled for DOC and optical properties.

Optical measurements—Absorption at 350-nm wavelength was determined with a Shimadzu 1601 spectrophotometer using a 1-cm, 4-cm, and 10-cm cuvette for samples from Rocky Bluff Swamp, Lake Murray, and the phytoplankton cultures, respectively. Absorbance was measured against Milli-Q water as the blank. Absorption coefficients a_{350} (m^{-1}) were calculated as $a_{350} = (D \times \ln 10)/L$, where D is the absorbance at 350-nm wavelength and L the path length (m) of the cuvette (Hu et al. 2002). Absorption spectra (290–400 nm) were measured using a 1-cm quartz cuvette to determine the spectral slope coefficients (S). The spectral slopes were determined from a least-square linear regression of log-transformed absorption coefficients versus wavelength in this spectral region (Jerlov 1968).

Analysis of dissolved organic carbon—Samples (10 ml) for DOC analyses were acidified with 20% phosphoric acid (pH 2) and stored in combusted, Teflon-capped glass vials in the dark. DOC concentrations were measured using a Shimadzu TOC-5000 carbon analyzer (Benner and Strom 1993) calibrated with potassium hydrogen phthalate.

Results

Effects of irradiation on the optical properties of the DOM—Exposure of water from Rocky Bluff Swamp 2 and Lake Murray to continuous irradiation in the solar simulator resulted in an exponential decrease in a_{350} (m^{-1}) (Fig. 1a,b; Table 3). DOM from the phytoplankton cultures had a comparatively low initial a_{350} (m^{-1}) and exposure to irradiation resulted in a rapid but relatively small decrease in a_{350} (m^{-1}) (Fig. 1c, Table 3). No changes in a_{350} (m^{-1}) were observed for the nonirradiated treatments (Table 3). Repeated filtration of DOM originating from Rocky Bluff Swamp 2 revealed at one time-point, after 2.3 d of continuous irradiation, a 50% decrease in a_{350} (m^{-1}). This filtration-induced loss in a_{350}

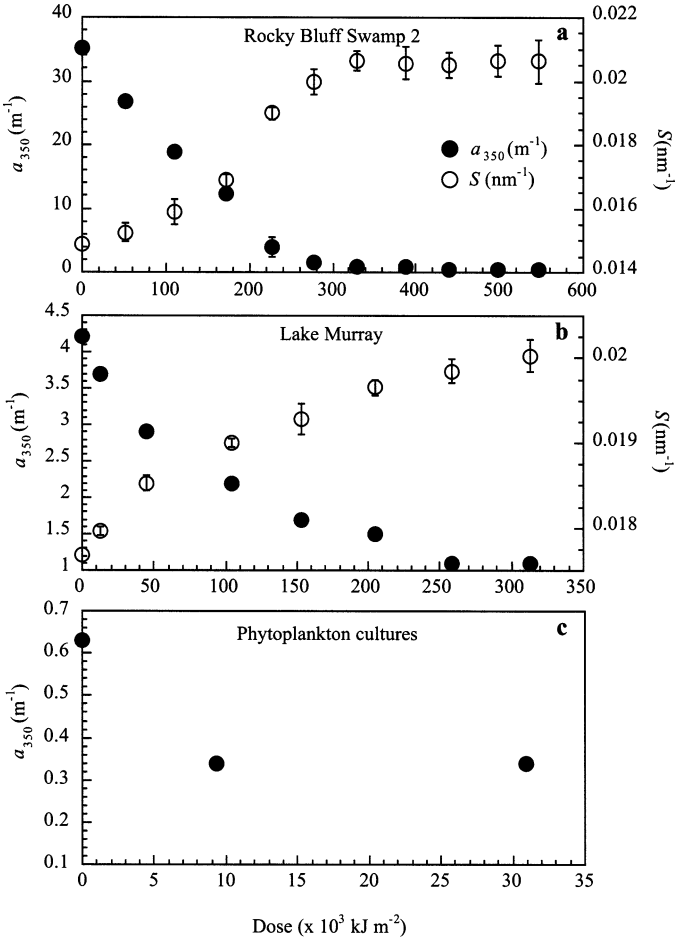

Fig. 1. Changes in a_{350} (m^{-1}) and spectral slope coefficients during photodegradation of DOM originating from (a) Rocky Bluff Swamp, (b) Lake Murray, and (c) phytoplankton cultures. Mean values ± mean deviations of duplicate incubations are shown. a_{350} (m^{-1}), absorption coefficient at 350-nm wavelength; S (nm^{-1}), spectral slope coefficient.

(m^{-1}) accounted for 17% of the initial a_{350} (m^{-1}). A similar filtration-induced loss of a_{350} (m^{-1}) for irradiated riverine DOM was reported by Gao and Zepp (1998). We did not observe similar losses in the dark controls, and we therefore considered the loss in a_{350} (m^{-1}) in the irradiated treatments an indirect contribution (e.g., photo-induced precipitation) to the overall decrease in a_{350} (m^{-1}) during photodegradation. Repeated filtration did not affect the a_{350} (m^{-1}) of DOM from Lake Murray and the phytoplankton cultures. The initial DOC-normalized a_{350} (m^{-1}) varied between 0.0093 and 0.0328 μmol DOC^{-1} L and was 2.5- and 3.5-fold higher for DOM originating from Rocky Bluff Swamp 2 than for DOM from Lake Murray and the phytoplankton cultures, respectively (Table 3).

In the irradiated treatments from Rocky Bluff Swamp 2 and Lake Murray, the decrease in a_{350} (m^{-1}) was accompanied by an increase of the spectral slope coefficient by 38% and 14%, respectively (Fig. 1a,b; Table 3). In the dark controls, an increase in the spectral slopes by 5% and 1% was observed for DOM from Rocky Bluff Swamp 2 and Lake

Table 3. Initial and final optical properties for photodegradation experiments with water from Rocky Bluff Swamp, Lake Murray, and phytoplankton cultures. a_{350} (m^{-1}), absorption coefficient at 350 nm; L, irradiated treatment; D, dark control; a_{350} (m^{-1})*, DOC-normalized absorption coefficient (μmol DOC^{-1} L); S (nm^{-1}), spectral slope coefficient; n.d., not determined. Mean values ± mean deviations of duplicate incubations are shown.

	a_{350}(m^{-1})				S (nm^{-1})		
		Final				Final	
	Initial	L	D	a_{350}(m^{-1})*	Initial	L	D
Rocky Bluff Swamp 2	35.1	0.37±0.01	34.80±0.39	0.0328	0.0149	0.0206±0.0007	0.0156±0.0004
Lake Murray	4.21	1.11±0.00	4.21±0.03	0.0129	0.0178	0.0203±0.0002	0.0180±0.0003
Phytoplankton cultures	0.63	0.34±0.01	0.63±0.01	0.0093	n.d.	n.d.	n.d.
Rocky Bluff Swamp 1	30.1	1.46±0.00	n.d.	0.0319	0.0152	0.0208±0.0002	n.d.

Murray, respectively. The initial spectral slope coefficients varied by a factor of 1.2 between Rocky Bluff Swamp 2 and Lake Murray, and extensive irradiation resulted in values that were similar for these waters (Table 3).

In the Rocky Bluff Swamp 1 experiment, irradiation following extensive biodegradation also resulted in an exponential decrease in a_{350} (m^{-1}) (Table 3). Concurrently, an increase in the spectral slope coefficient was observed during exposure to irradiation, resulting in a final value similar to those observed for extensively irradiated DOM from Rocky Bluff Swamp 2 and Lake Murray (Table 3).

Photomineralization of DOC—Concentrations of DOC decreased exponentially during irradiation of water samples from Rocky Bluff Swamp 2 and Lake Murray (Fig. 2a,d). A total of 46% and 7% of the initial DOC concentrations in Rocky Bluff Swamp 2 and Lake Murray water, respectively, was removed and presumably photomineralized (Table 4). No decrease in the DOC concentration was observed during irradiation of water from the phytoplankton cultures (Fig. 2g). In the dark controls, the concentrations of DOC were 1,060 μmol L^{-1}, 324 μmol L^{-1}, and 68 μmol L^{-1} at the end of the photodegradation experiments with Rocky Bluff Swamp 2, Lake Murray, and plankton samples, respectively. In contrast with the filtration-induced changes in a_{350} (m^{-1}), no effect of repeated filtration on the concentration of DOC was detectable.

Biomineralization of DOC—Long-term biodegradation prior to and following photodegradation resulted in an exponential decrease in DOC concentrations in all experiments (Fig. 2). In the first 2 weeks of the biodegradation experi-

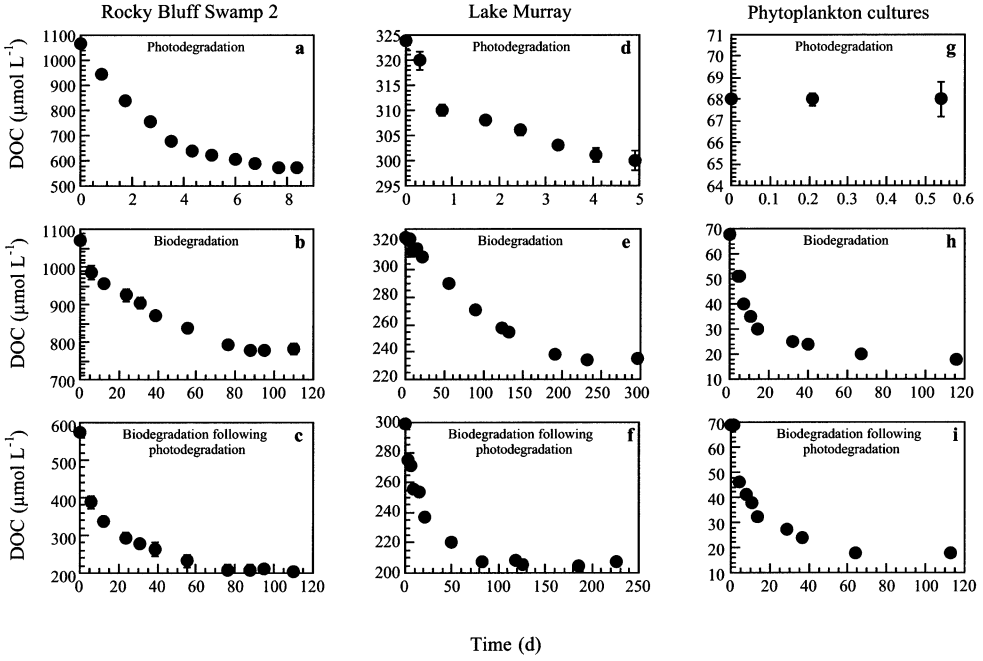

Fig. 2. Decreases in DOC concentrations during (a, d, g) photodegradation, (b, e, h) biodegradation, and (c, f, i) biodegradation following photodegradation of DOM originating from Rocky Bluff Swamp, Lake Murray and the phytoplankton cultures. All photodegradation experiments and the Lake Murray and phytoplankton culture biodegradation experiments were performed at 20°C. Rocky Bluff Swamp biodegradation experiments were performed at 25°C. Mean values ± mean deviations of duplicate incubations are shown.

Table 4. Initial and final concentrations of DOC from long-term decomposition experiments and the concentrations of DOC removed due to photodegradation and biodegradation. Abbreviations as in Table 2.

Treatment	Rocky Bluff Swamp 2	Lake Murray	Phytoplankton cultures	Rocky Bluff Swamp 1
		DOC (μmol L^{-1})		
Initial	1,069	342	68	1,288
PD	495	24	0	n.d.
BD	289	89	50	343
PD_BD	369	94	50	n.d.
BD_PD	n.d.	n.d.	n.d.	402
(PD_BD)-(BD)	80	5	0	n.d.
BD_PD_BD	n.d.	n.d.	n.d.	284
Final	205	206	18	259
		% of initial DOC		
Reactive DOC	81	36	74	80
Nonreactive DOC	19	64	26	20

ments, 11%, 2%, and 56% of the initial DOC concentration of Rocky Bluff Swamp 2, Lake Murray, and the phytoplankton cultures, respectively, were mineralized (Fig. 2b,e,h). For comparison, in the first 2 weeks of the biodegradation experiments following photodegradation, 22%, 15%, and 56% of the initial DOC concentration of Rocky Bluff Swamp 2, Lake Murray, and the phytoplankton cultures, respectively, were mineralized (Fig. 2c,f,i). Biomineralization removed a total of 27% of the DOC in the Rocky Bluff Swamp 2 and Lake Murray experiments, and 74% of the DOC in the phytoplankton cultures (Table 4). Irradiation resulted in a net increase in the biodegradable DOC component by 7% and 2% of the initial DOC concentrations in Rocky Bluff Swamp 2 and Lake Murray experiments, respectively (Table 4). No increase in the biodegradable DOC component was observed following irradiation of DOM from the phytoplankton cultures (Table 4).

Reactive and nonreactive components of DOC—The combined effect of extensive photodegradation and subsequent biodegradation resulted in the removal of 81% and 36% of the initial DOC in Rocky Bluff Swamp 2 and Lake Murray water, respectively (Table 4). The reactive component from the phytoplankton cultures accounted for 74% of the initial DOC and was exclusively attributable to biomineralization (Table 4).

Rocky Bluff Swamp 1 experiment—In a different experimental approach, the potential bio- and photomineralization of DOC from Rocky Bluff Swamp was determined by sequential exposure to biological and photochemical degradation. In the first 2 weeks of biodegradation, 7% of the DOC was mineralized. The lower percentage of DOC initially biomineralized in the Rocky Bluff Swamp 1 experiment as compared with the Rocky Bluff Swamp 2 experiment (11%; Fig. 2b) could be attributable to the 5°C lower incubation temperature in the Rocky Bluff Swamp 1 experiment. The total biodegradable DOC component during the Rocky Bluff Swamp 1 experiment accounted for 27% of the initial DOC concentration, equivalent to Rocky Bluff Swamp 2 experiment (Table 4). Irradiation of the nonbiodegradable DOM component resulted in a 31% decrease in the initial (prior to biodegradation) DOC concentration (Table 4). Reinoculation following biodegradation and subsequent photodegradation resulted in the biomineralization of an additional 22% of the initial (prior to bio- and photodegradation) DOC (Table 4). Overall, 80% of the initial DOC was removed during sequential bio- and photodegradation (Table 4).

Bioreactive and photoreactive DOC components of terrigenous DOM—Based on a comparison of photo- and biomineralization of terrigenous DOC determined in the two ex-

Table 5. Contributions of photomineralization and biomineralization of DOC during Rocky Bluff Swamp 1 and 2 experiments and calculations of the percentages of DOC removed by biological, photochemical, or both processes. Abbreviations as in Table 2.

Rocky Bluff Swamp 2	% of initial DOC	Rocky Bluff Swamp 1	% of initial DOC	Calculation	% of initial DOC	Mechanisms of removal
BD	27	BD	27	BD_PD	31	Photomineralization
PD	46	BD_PD	31	(PD_BD)-(BD_PD_BD)	13	Biomineralization
PD_BD	35	BD_PD_BD	22	(PD)-(BD_PD)	15	Biomineralization or photomineralization
				BD_PD_BD	22	Biomineralization due to phototransformation
Relative DOC	81		80			
Nonreactive DOC	19		20			

perimental approaches, we calculated the percentages of DOC that are photoreactive, bioreactive, and both photo- and bioreactive (Table 5). A total of 31% of the DOC could be photomineralized but was resistant to biomineralization. The component that could be removed biologically but that was resistant to photomineralization accounted for 13% of the DOC. Based on the difference between DOC photomineralization prior to and following extensive biodegradation, we calculated that 15% of the DOC could be removed photochemically or biologically (Table 5). Phototransformations of bioresistant DOC produced photoproducts that were biomineralized and accounted for 22% of the DOC (Table 5).

Discussion

Phototransformations of the optical properties of DOM—Spectral slope coefficients describe the change in the absorption of DOM as a function of wavelength. It has been suggested that spectral slopes provide rough estimates of the molecular weight distribution of DOM, based on an inverse relationship between the spectral slope coefficient and molecular weight (Carder et al. 1989; Pages and Gadel 1990; Mopper et al. 1996). Previous studies report that values of spectral slopes are greater for oligotrophic (0.02–0.03) than for coastal waters (0.01–0.02) (see review by Blough and Del Vecchio 2002). The increase in the spectral slope from coastal to offshore waters has been attributed to phototransformations of terrigenous DOM (Vodacek et al. 1997). Initial spectral slopes for Rocky Bluff Swamp (0.0149–0.0152) are in the lower range of values reported for coastal waters and they are comparable with those determined for the Satilla River in the southeastern United States (0.0137–0.0152; Moran et al. 2000).

In the present study, spectral slopes increased during irradiation resulting in final values for both Rocky Bluff Swamp and Lake Murray water that are comparable with values reported for offshore waters (0.0203–0.0208). The irradiation-induced increase in the spectral slope coefficient observed in the present and previous studies (Moran et al. 2000; Del Vecchio and Blough 2002) could be indicative of an increase in low-molecular-weight photoproducts. Direct evidence for photo-induced changes of the molecular size distribution of terrigenous DOM was demonstrated by Opsahl and Benner (1998). These authors observed that phototransformations of riverine dissolved lignin, which is primarily of high molecular weight, resulted in highly oxidized, mainly low-molecular-weight lignin photoproducts. These irradiation-induced changes of riverine dissolved lignin were consistent with the composition of oceanic dissolved lignin (Opsahl and Benner 1998; Benner and Opsahl 2001). Results from the present study are consistent with previous suggestions (Vodacek et al. 1997) that photochemical processes play an important role in altering the optical properties of terrigenous DOM, resulting in material that is optically similar to marine DOM. The observed irradiation-induced changes in the optical properties of DOM likely reflect alterations in the composition of DOM (Opsahl and Benner 1998).

Photoreactivity of different DOM sources—Terrigenous DOM had the largest photoreactive component among the sources investigated in the present study. A greater fraction of terrigenous DOM was photoreactive than bioreactive. Photochemical processes have been identified previously as potentially important for the degradation of terrigenous DOM (Kieber et al. 1989; Miller and Zepp 1995; Amon and Benner 1996; Graneli et al. 1996; Opsahl and Benner 1998; Moran et al. 2000). The significance of photomineralization is likely attributable to the chemical composition of terrigenous DOM, in particular to the high concentrations of aromatic carbon. In contrast, there was no measurable photomineralization of plankton DOC in the present study, indicating phototransformations were minimal. The low a_{350} (m^{-1}) values and the lack of DOC photomineralization of plankton DOM also indicate that the artificial freshwater medium used in these experiments did not contain a significant amount of photoreactive compounds. Indirect phototransformations of plankton DOM could be more significant in natural waters containing photosensitizers (Tranvik and Kokalj 1998). Lake water contained terrigenous and plankton DOM, and photomineralization removed 7% of the DOC.

Bioreactivity of different DOM sources—In the present study, 74% of plankton DOC was removed during long-term biodegradation. A much smaller percentage (27%) of terrigenous and lake DOC was biomineralized. The bioreactive nature of plankton DOM is also indicated by the high yields of carbohydrates in DOM from phytoplankton cultures (Biddanda and Benner 1997; Biersmith and Benner 1998). About 25% of plankton DOC was nonreactive, a result that is consistent with previous long-term degradation experiments with plankton DOC (Fry et al. 1996; Meon and Kirchman 2001).

Most previous studies have focused on the initial rates of biodegradation to characterize the bioreactivity of DOM from different aquatic environments. The present study, however, was designed to determine initial rates as well as the total bioreactive DOC component. In a cross-system overview, Sondergaard and Middelboe (1995) estimated that ~1% and ~14% of the DOC of black-water systems and lakes, respectively, are removed during short-term (1–2 weeks) biodegradation experiments. In the present study, ~10% and ~2% of the DOC in a black-water swamp and lake were biomineralized in this time period. This could be attributed to environmental variability as well as to differences in experimental conditions, such as the presence or absence of grazers and incubation temperature. In the present study, the initial rates of DOC biomineralization varied by a factor of five between terrigenous and lake DOM, but the extent of biomineralization was equivalent, indicating that removal of DOC during short-term incubations may not be indicative of the bioreactive fraction.

Coupled photochemical and biological mineralization of DOC—In combination, biological and photochemical processes removed ~40–80% of the DOC from the various systems. Thus, all systems included DOC components that were resistant to photochemical and biological degradation over periods of months to a year. Most (~65%) of the DOC in

lake water was resistant to biological and photochemical degradation. Lake Murray receives terrigenous and plankton DOM that is likely similar in composition and reactivity to that in Rocky Bluff Swamp and the phytoplankton cultures. However, unlike Rocky Bluff Swamp, Lake Murray surface waters are exposed to daily irradiation and the terrigenous DOM is extensively photodegraded. Plankton DOM produced in surface waters of Lake Murray is exposed to rapid biodegradation. Thus, the reactive components of DOM in Lake Murray are continuously being removed and the nonreactive components slowly accumulate and become dominant. Based on the results presented herein, the bioreactive and photoreactive components of DOC entering Lake Murray are largely removed within the residence time of water in Lake Murray, which is about 1 yr (Campbell and Dean 1976).

This study demonstrates that similar fractions of terrigenous and plankton DOC are reactive during extensive bio- and photodegradation. The primary mechanisms for the remineralization of these chemically distinct substrates are fundamentally different and can be spatially and temporally uncoupled. However, assuming terrigenous DOM is exposed to solar irradiation during its transport to and residence in the ocean, there is no evidence in this study to suggest it would accumulate to a greater extent than phytoplankton DOM produced in the ocean.

Effect of irradiation on initial rates and extent of biomineralization—The photochemical production of low-molecular-weight compounds and the subsequent stimulation of bacterial metabolism can account for a substantial increase in the initial rates of DOC biomineralization (see review by Moran and Zepp 1997). In the present study, irradiation of DOM from different sources had widely varying effects on subsequent initial rates of biomineralization. Irradiation resulted in two- and sevenfold increases in the initial rates of DOC biomineralization in Rocky Bluff Swamp and Lake Murray water, respectively. In contrast, irradiation had no effect on the initial rates of DOC biomineralization in plankton DOM. Prior to irradiation, lake DOM had the lowest initial rates of biomineralization of the three DOM sources and plankton DOM had the highest initial rates. These results are consistent with previous observations suggesting that the effect of irradiation on the bioreactivity of DOM is inversely related to the initial DOM bioreactivity prior to irradiation (Benner and Biddanda 1998; Obernosterer et al. 2001; Tranvik and Bertilsson 2001).

Irradiation had a much larger effect on the initial rates of biomineralization of DOC than on the overall fraction of DOC that was mineralized. Phototransformations of terrigenous DOM increased the percentage of biodegradable DOC in swamp water from 27% to 35%. The biodegradable DOC components of lake DOM were 27% and 29% prior and following photodegradation, respectively, and phototransformations of plankton DOM had no effect on the percentage of biodegradable DOC. Similar effects of extended photodegradation on DOC mineralization were observed for DOM from the Satilla River (Moran et al. 2000). Up to 30% of riverine DOC was photomineralized and phototransformations increased the percentage of biodegradable DOC from 10% to 16% (Moran et al. 2000).

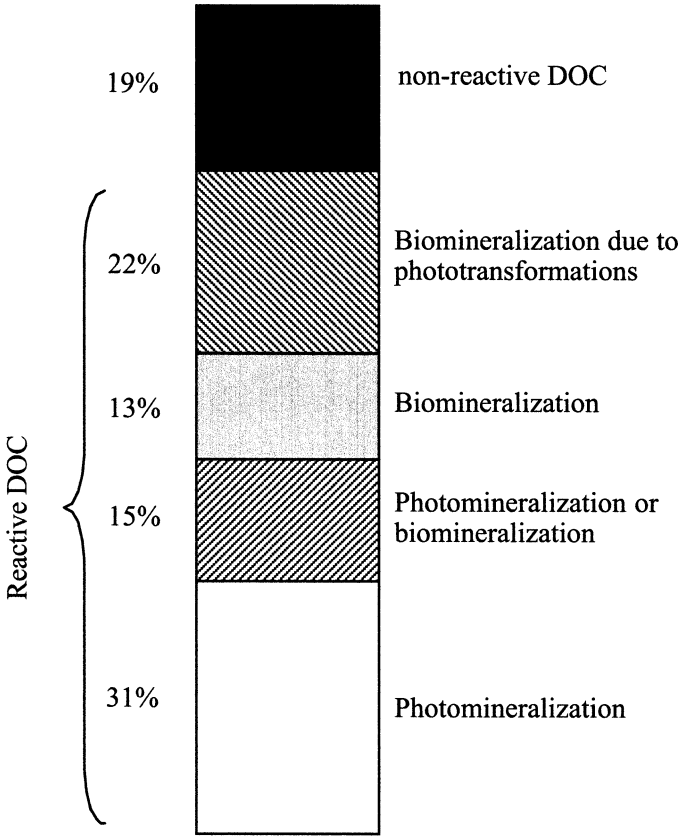

Fig. 3. Percentages of terrigenous DOC removed by biological, photochemical, or both processes. The calculation of the bioreactive and photoreactive DOC fractions is described in Table 5.

Competition between biological and photochemical processes—Components of terrigenous DOM are susceptible to both biomineralization and photomineralization (Fig. 3). These processes compete for the same substrates, and it appears that the intensity, spectral composition, and duration of light exposure largely determines the outcome of this competition. It is interesting to note that about half of the bioreactive, terrigenous DOC was also susceptible to photomineralization, while only about one third of the DOC that could be photomineralized was also bioreactive. Thus, photomineralization has the potential to remove a large fraction of bioreactive DOC and could account for observed decreases in bacterial activity following irradiation of DOM from some environments. The relative significance of photomineralization and biomineralization of DOC is source dependent. Nevertheless, competition between these processes likely occurs in a variety of aquatic environments and is an important factor determining the net effect of photochemical processes on the bioreactivity of DOM. Photomineralization of DOC removes the primary carbon and energy source supporting microbial food webs and thereby alters the structure and function of aquatic ecosystems in ways that are not yet fully recognized.

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