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Photodegradation of dissolved organic matter in forested streams of the northern Great Lakes region

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Abstract. Dissolved organic matter (DOM) is an important component of aquatic ecosystems, and it influences a range of physical, chemical, and biological properties. Reactions induced by solar radiation may oxidize DOM to inorganic C or break large molecules into smaller ones. Therefore, photodegradable DOM is removed with exposure to light, and the remaining DOM pool might become less photodegradable as photorecalcitrant DOM accumulates. This possibility has led to speculation that previous light exposure might influence the susceptibility of DOM to photodegradation and that forested low-light streams might have highly photodegradable DOM. To assess this possibility, we measured: 1) the susceptibility of stream DOM to photoreactions and compared our results to studies in other aquatic ecosystems, 2) the relative importance of the ultraviolet (UV) portion of the solar spectrum to DOM photoreactions, and 3) the photoreactivity of DOM collected from streams with and without upstream lakes. We measured DOM properties of stream water exposed for ~56 h to 1 of 3 treatments: full sunlight, sunlight with the UV portion of the spectrum (<400 nm) removed, and a dark control. Exposure to light reduced the UV light-absorbing ability of DOM and, to a lesser extent, its concentration. Most alterations of DOM properties could be attributed to the UV portion of the solar spectrum. We found no evidence that previous light exposure significantly influenced photodegradability of stream DOM. Our results suggest that other DOM-processing agents, such as heterotrophic uptake, can obscure the effect of upstream photoexposure on downstream DOM photodegradability.

Key words: dissolved organic matter, photodegradation, DOM, photodegradability, streams.

Dissolved organic matter (DOM) in aquatic ecosystems is operationally defined by its ability to pass through a filter that excludes particulate matter (0.22–0.45-μm pore size), and it therefore includes a wide range of organic compounds (Wetzel 2001). DOM ranges from simple carbohydrates to complex chains of aromatic rings that exhibit a wide range of physical and chemical properties (Aitkenhead-Peterson et al. 2003, Bertilsson and Jones 2003). DOM heterogeneity leads to physical (e.g., absorbance of light; Frost et al. 2005), chemical (e.g., binding of pollutants; Voets et al. 2004), and biological (e.g., microbial substrate; Biddanda and Cotner 2003) ecological effects. These wide-ranging effects make DOM an important driver of aquatic ecosystem structure and function (Williamson et al. 1999).

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DOM chemistry is altered by exposure to sunlight (Zafiriou 2002). Solar radiation usually reduces the ability of DOM to absorb ultraviolet radiation (UVR; Morris and Hargreaves 1997, Reche et al. 2001), converts significant quantities of DOM into inorganic C (Obernosterer and Benner 2004), and alters the suitability of DOM as a microbial substrate (Tranvik and Bertilsson 2001). Photoreactions of DOM also affect the light environment of lakes. For example, after a summer of photoexposure, UVR transmission depth increased in a Pennsylvania lake (Morris and Hargreaves 1997). In nonturbid streams, UVR penetration through the water column appears to be controlled primarily by DOM properties (Frost et al. 2005). Hence, photo-induced changes in DOM properties may influence the UVR dose to the benthos. In many streams, dense vegetative canopies and relatively high concentrations of DOM reduce UVR doses to the benthos (Frost et al. 2005), suggesting that even modest increases in UVR dose could increase mortality for benthic invertebrates (Bothwell et al. 1994, Kelly et al. 2003). However, the extent and effects of photoexposure on stream DOM have received little study.

Dense canopies along small forested streams (Grant

TABLE 1. Coordinates of streams sampled for experiments 1 and 2. Streams with upstream lakes contain ≥1 lake upstream of the sampling location. Y indicates a stream was used in a given experiment. na = data not available.

Stream	Latitude (N)	Longitude (W)	Upstream lakes	Stream order	June 2003 discharge (m^3/s)	Experiment 1	Experiment 2
Baltimore	46°28′44.0″	89°12′06.1″	Absent	2	na	Y	Y
Banner	46°21′41.8″	89°35′50.3″	Absent	1	0.009	Y	Y
Cisco	46°15′12.4″	89°27′09.5″	Present	2	0.020		Y
Manitowash	46°07′15.0″	89°38′23.1″	Present	3	na		Y
Merriweather	46°34′05.6″	89°39′04.1″	Absent	1	na	Y	Y
Nelson	46°23′51.4″	89°37′48.1″	Absent	1	0.007	Y	Y
Tenderfoot	46°15′33.7″	89°32′02.6″	Present	2	1.279	Y	Y
Walton	46°26′12.5″	88°53′19.6″	Absent	1	0.010	Y	
West Branch Ontonagon	46°35′23.3″	89°31′39.7″	Present	3	1.331	Y	
White Sands	46°05′52.4″	89°36′43.6″	Present	3	na		Y

et al. 2002, Frost et al. 2005) and longitudinal inputs of terrestrial DOM that are highly absorptive of light (Elder et al. 2000) should result in stream DOM that has had little exposure to sun. Biddanda and Cotner (2003) proposed that lack of previous exposure to sun (relative to the levels of exposure in lakes, large rivers, and oceans) might leave a high proportion of the DOM pool in northern forested streams susceptible to photodegradation. DOM from northern forested streams has a greater ability to absorb low-wavelength UVR (280–320 nm; UVB) than DOM from temperate lakes, prairie lakes, or wetlands (Frost et al. 2005), and photodegradation is caused mainly by light in these low wavelengths (Kieber et al. 1990, de Haan 1993). Therefore, stream DOM should be highly susceptible to UVR-induced photoreactions.

Upstream features in northern forested streams might influence the degree to which stream DOM is exposed to light. For example, DOM in streams flowing out of lakes might experience considerable upstream photoprocessing as a consequence of in-lake exposure to intense sunlight, whereas DOM from streams with dense canopies might experience low levels of upstream photoprocessing. Thus, DOM might be less susceptible to further photodegradation in forested streams with upstream lakes than in forested streams without upstream lakes. However, other factors (i.e., groundwater inputs, riparian vegetation, bacterial activity) might vary enough among streams to obscure any effect of an upstream lake.

We quantified the photodegradability of DOM from northern temperate forested streams and compared our results to values reported in the literature for other aquatic ecosystems. In addition, we determined the relative effects of full-spectrum and UVR light on photo-induced changes in DOM properties. Last, we evaluated whether upstream lakes altered the extent to which stream DOM could be photodegraded. We hypothesized that photodegradability of DOM would be inversely related to previous exposure to light.

Methods

Study sites

DOM was sampled from 10 streams in northern Wisconsin and the Upper Peninsula of Michigan (Table 1). These streams drain primarily low-gradient watersheds covered by mixed coniferous and deciduous forest. For experiment 1, 7 streams within the larger Ontonagon River watershed were selected randomly to include streams with a variety of watershed characteristics. For experiment 2, 8 streams were selected randomly to include 4 with and 4 without upstream lakes. Streams with upstream lakes were sampled at road crossings ≤1 km downstream of the lake. Five of the streams in experiment 1 also were used in experiment 2. Discharge was measured in each stream by the midsection method using an electromagnetic flow meter (Gore 2006). Additional information on these streams and the surrounding landscape can be found in Frost et al. (2006) and Larson et al. (2007).

Experimental conditions

Approximately 4 L of water were collected from each stream, placed on ice in a cooler, and transported to the University of Notre Dame Environmental Research Center (UNDERC). Water was filtered sequentially through a 0.45-μm glass-fiber filter (Whatman®, Brentford, UK) and a prerinsed 0.22-μm membrane filter (Yoro et al. 1999). Sterile Whirlpak® bags (which transmit the entire solar spectrum) were filled with 200 mL of filtered water and stored at 4°C until the start of the experiment (1 d later for experiment 1; 2 d later for experiment 2). Little or no air was trapped in the bags.

Photoexposure experiments took place outdoors at UNDERC in oval recirculating fiberglass channels

(~40 L volume). Water depth in these channels was ~9 cm, but the Whirlpak® bags floated at the water surface for the duration of the experiments, minimizing shading from the channel edges. The channels were fed by clear ground water (dissolved organic C [DOC] concentration <1 mg C/L) with a replacement rate of >10× daily. All bags were tethered to clay tiles so that replicates maintained similar orientation as they floated. Bags were disturbed enough by the water current to keep their contents well mixed, preventing DOM self-shading. Both experiments began at 1000 h and lasted ~56 h. During this time, bags were exposed to direct sunlight for ~24 h. No direct measurements of UVR dose were made during the experiments, but photosynthetically active radiation (PAR; 400–700 nm) was measured in an open field on the UNDERC property (<1 km from our study site) by a CM3 Pyranometer (Kipp and Zonen, Röntgenweg, Holland). Total PAR received during experiment 1 was 142 moles PAR/m^2, and total PAR received during experiment 2 was 89 moles PAR/m^2.

Experiment 1.—Experiment 1 was conducted from 26 to 28 June 2003 using water from 7 streams (Table 1). The experiment consisted of 3 light treatments: dark (D) (3 bags/stream), ambient minus UVR (A–UVR) (4 bags/stream), and ambient (A) (4 bags/stream). Treatment A–UVR was created by covering the bags in one channel with OP3 plastic (CRYO Industries, Parsippany, New Jersey), which excludes wavelengths <400 nm, leaving only the effects of PAR. Treatment A was created by covering the bags in an adjacent channel with OP4 (CRYO Industries), which transmits the entire solar spectrum, to control for any potential effect of plastic (caused by OP3 in treatment A–UVR). Treatment D was created by wrapping bags in aluminum foil before distributing them randomly in both channels. The spectrum of light transmitted by both plastics was confirmed with a fiber-optic spectrometer (S2000; Ocean Optics, Dunedin, Florida).

Experiment 2.—Experiment 2 was conducted from 26 to 28 July 2003 using water from 8 streams. The experiment consisted of 2 light treatments (D and A) and 2 stream-type treatments (with or without upstream lakes; $n = 4$ per stream type). Treatments D and A were created as described above (no A–UVR treatment was necessary for this experiment). For each stream, 2 bags were used for treatment A, and 2 bags were used for treatment D (total of 4 bags per stream). The unit of replication in this experiment was streams within stream type.

DOM properties

Two DOM properties were measured at the end of the experiments: 1) concentration of DOC and 2) ability to absorb light between 280 and 400 nm. A Shimadzu TOC 5000 analyzer (Columbia, Maryland) with potassium hydrogen phthalate standards (ranging from 1 to 35 mg C/L) was used to estimate [DOC] of stream samples. Standards and samples were acidified prior to analysis using concentrated nitric acid and then purged of inorganic C (Sharp et al. 1993). Absorbance was measured using an Ocean Optics S2000 UV-VIS spectrometer (Dunedin, Florida) at ~300 evenly distributed wavelengths between 280 and 400 nm. The UV spectrum has been separated into different bands based on energy and biological relevance (e.g., Morris and Hargreaves 1997). The UVB band refers to all wavelengths between 280 and 320 nm, and the UVA band refers to all wavelengths between 320 and 400 nm. Absorbance was averaged for each wavelength in each band. Beer's Law was used to calculate 1% transmission depths for UVB and UVA. Molar absorptivity (the ability of DOM to absorb light of a given wavelength per mole of DOC) was calculated for each wavelength (Chin et al. 1994) and then averaged to obtain UVB and UVA molar absorptivity.

Light-induced % reduction (%R) of [DOC], UVB and UVA absorbance, absorbance at 320 nm, and UVB and UVA molar absorptivity were calculated by subtracting the treatment D mean from the treatment A mean, dividing the difference by the treatment D mean for each stream and variable, and expressing the value as a percentage. Our use of %R permitted comparison of the per-mole degradability of DOM between different streams with large differences in DOM quantity.

The literature was searched for other studies that included photoexposure experiments using ambient light. The %R values for [DOC] and the absorbance of light at 320 nm observed in those studies were calculated and compared to the %R values obtained in our experiments. The %R values were normalized for exposure time because exposure times differed among studies.

Statistical analyses

Experiment 1.—Multivariate analysis of variance (MANOVA) was done on all DOM properties using light as a fixed factor (3 treatments) because different DOM properties were expected to be related (Zar 1999). Streams were treated as blocks because large among-stream differences in DOM concentration and absorbing ability caused by variation in watershed properties and unrelated instream processes were expected (Zar 1999). The assumptions of homogeneity of variance and normality of data were met after $\ln(x)$ transformation of [DOC]. The MANOVA was significant (Wilks' $p \ll 0.001$), so 1-way analyses of variance (ANOVA) with streams as blocks were used to determine which DOM property was influenced by the light treatments (Zar

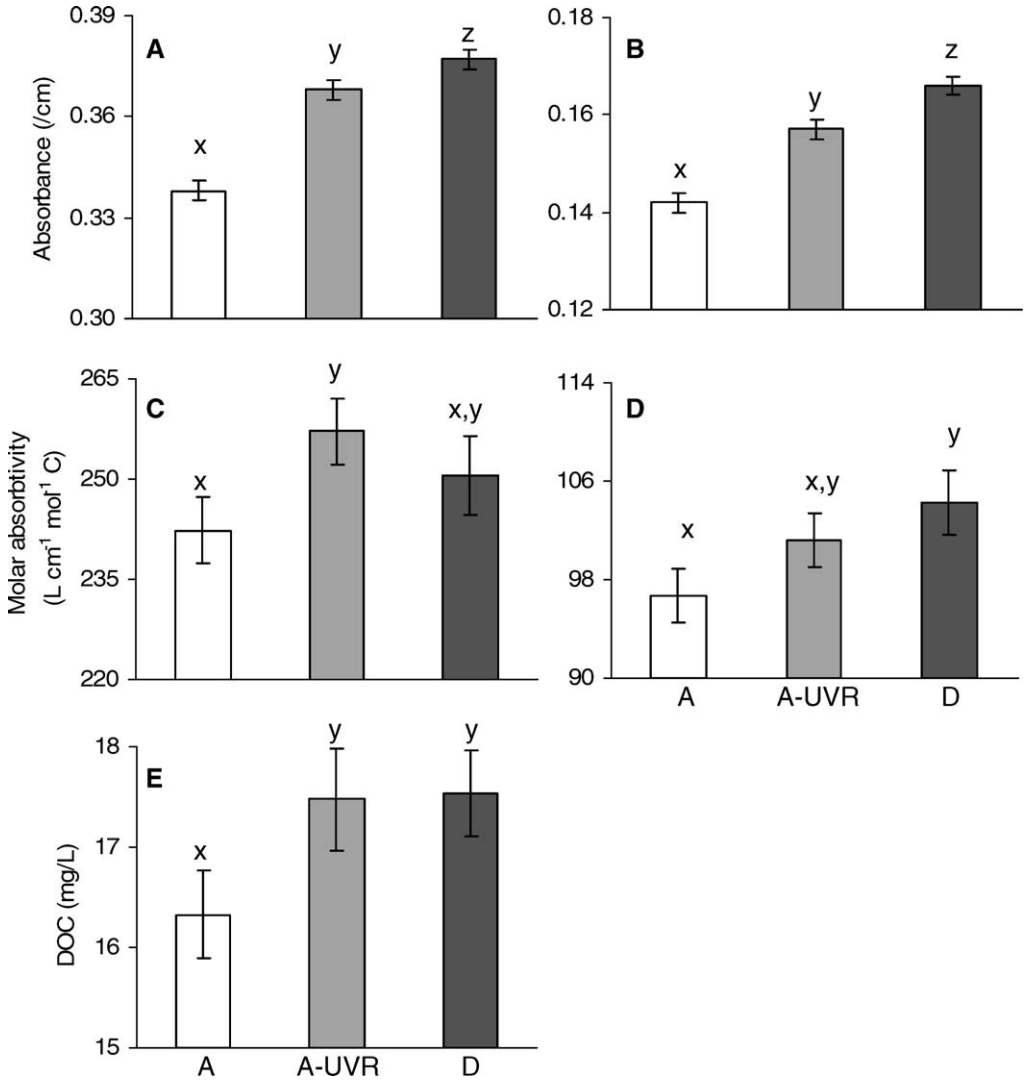

FIG. 1. Adjusted (for differences among streams) mean (±1 SE) absorbance of ultraviolet B (UVB) (A) and ultraviolet A (UVA) (B) radiation, molar absorptivity of UVB (C) and UVA (D), and concentration of dissolved organic C (DOC) (E) in stream water following exposure to different light treatments (ambient [A], ambient minus ultraviolet radiation [A–UVR], and dark [D]). Bars with the same lower-case letters are not significantly different (Tukey's $p < 0.05$).

1999). Tukey's tests were used to identify differences among treatment means for each DOM property. Adjusted means (and associated error) were calculated by removing variation caused by differences in DOM properties among streams and are presented in the figures. All statistical analyses were done using SYSTAT (version 10; SPSS, Chicago, Illinois).

Experiment 2.—MANOVA was used to compare %R values for [DOC], UVB and UVA absorbance, absorbance at 320 nm, and UVB and UVA molar absorptivity between streams with or without upstream lakes. No blocking among streams was necessary for this analysis because data were presented as %R (normalized across streams). The MANOVA was not significant (Wilks' $p = 0.19$), so subsequent univariate ANOVAs were not done.

Results

Experiment 1

Overall, DOM properties of stream water in treatments A and A–UVR differed significantly from those in treatment D (MANOVA, Wilks' $p \ll 0.001$). This overall effect reflected significant differences among treatments in each individual DOM property. UVB and UVA absorbance differed significantly among all treatments, with the highest absorbance in treatment D and the lowest in treatment A (ANOVA, UVB: $F_{2,77} = 51.12$, $p \ll 0.001$; UVA: $F_{2,77} = 35.71$, $p \ll 0.001$; Fig. 1A, B). UVB molar absorptivity was highest in treatment A–UVR and lowest in treatment A

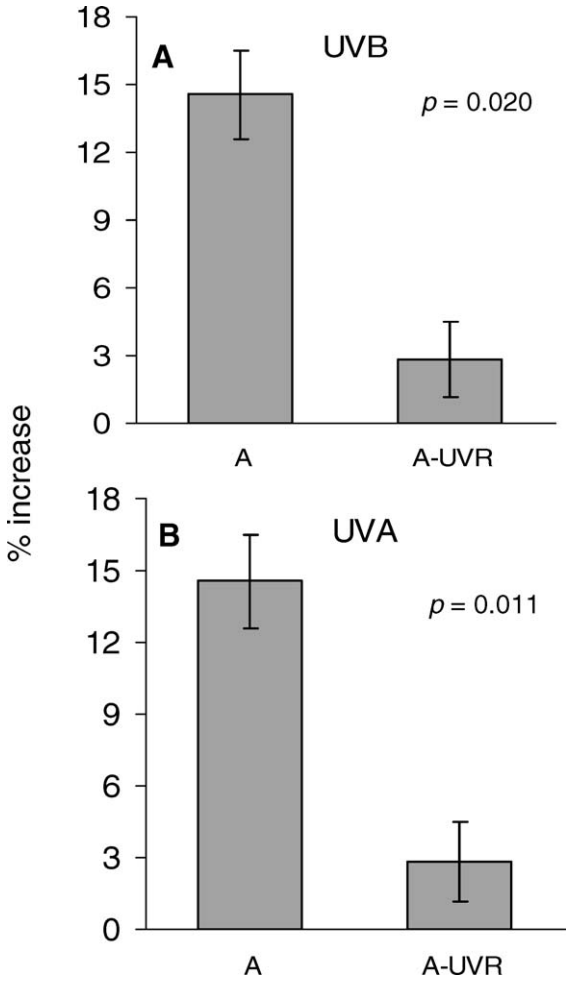

FIG. 2. Mean (±1 SE) % increase in the 1% transmission depth (1%T) of ultraviolet B (UVB) (A) and ultraviolet A (UVA) (B) radiation in stream water exposed to ambient (A) and ambient minus ultraviolet radiation (A–UVR) light relative to 1%T of stream water kept in the dark. The 1%T depth was calculated from absorbance data using Beer's Law; $n = 7$ different stream sources of dissolved organic matter (DOM).

(ANOVA, $F_{2,74} = 4.04$, $p = 0.022$; Fig. 1C). UVA molar absorptivity was significantly lower in treatment A than in treatment D and intermediate in treatment A–UVR (ANOVA, $F_{2,74} = 5.58$, $p = 0.0058$; Fig. 1D). [DOC] was significantly lower in treatment A than in treatments A–UVR and D, which were nearly identical (ANOVA, $F_{2,74} = 4.32$, $p = 0.0173$; Fig. 1E). The differences in degrees of freedom among these separate ANOVAs reflect the loss of 3 DOC samples caused by mishandling.

The 1% transmission depths for UVB and UVA differed significantly among treatments (ANOVA, UVB: $F_{2,74} = 5.50$, $p = 0.020$; UVA: $F_{2,74} = 6.80$, $p = 0.011$; Fig. 2A, B). The UV portion of the solar spectrum caused, on average, 97.7% of observed increases in 1% transmission depths, but among-stream variation existed (Table 2, Fig. 2A, B). Absorbance in some streams actually increased in treatment A–UVR (causing negative Δ1%T UVB; Table 2). Values for %R for streams in our experiments were within the ranges of values from other studies (Table 3).

Experiment 2

The %R values for [DOM] and absorption properties of DOM did not differ significantly between streams with or without upstream lakes (MANOVA, Wilks' $p = 0.193$; Fig. 3). However, %R values for DOM properties differed considerably among individual streams. For example, %R for UVB molar absorptivity was 36% for water from Baltimore Creek and only 2.9% for water from Banner Creek (both streams without upstream lakes). In general, the presence of upstream lakes did not influence the photodegradability of DOM.

Discussion

Photodegradability of stream DOM

Like Biddanda and Cotner (2003), we predicted that stream DOM would be highly susceptible to photodegradation because of limited prior exposure to light. As expected, both [DOM] and absorption ability were significantly reduced by exposure to light. [DOM] did not decline as much as absorbance did, resulting in lower molar absorptivity of the remaining DOM. Other studies have shown similar effects of light on DOM (e.g., Osburn et al. 2001a, De Lange et al. 2003), and the magnitude of those effects appears to be similar across different aquatic ecosystems. One explanation for this result is that all (or nearly all) DOM might be photodegradable. If so, then the %R of DOM by light should not change as [DOM] declines. However, 2 lines of evidence suggest that this explanation is not the case. First, natural DOM does not appear to be completely photodegradable when exposed to high light (and high UVR) doses from artificial light sources (e.g., Kohler et al. 2002, Brinkmann et al. 2003b). Golden (2004) collected DOM from a stream used in our study and found measurable DOM even after exposure to extremely high doses of artificial light. Second, some natural DOM appears to be photorecalcitrant, as evidenced by high [DOC] in some hydrologically closed high-salinity northern Great Plains lakes (Arts et al. 2000). Therefore, natural DOM does not appear to be completely photodegradable.

Another possible explanation is that DOM that is

TABLE 2. Calculated 1% transmission depths (1%T) for ultraviolet B radiation (UVB) in stream water kept in the dark (D) and change (Δ; relative to water in treatment D) in 1%T of UVB in stream water exposed to ambient (A) and ambient minus ultraviolet radiation (A–UVR) in experiment 1. Δ1%T caused by UVR is the difference between Δ1%T in treatments A and A–UVR expressed as absolute and % difference.

		Δ1%T UVB (cm)		Δ1%T UVB caused by UVR	
Stream	1%T UVB (cm)	A	A–UVR	(cm)	(%)
Baltimore	40.2	6.17	1.07	5.10	82.6
Banner	5.30	0.68	0.15	0.53	77.8
Merriweather	8.12	0.86	0.09	0.77	89.5
Nelson	6.25	0.61	0.13	0.48	78.6
Tenderfoot	77.44	10.01	0.38	9.63	96.2
Walton	13.65	0.82	–0.14	0.96	117.6
West Branch Ontonagon	37.33	3.33	–1.39	4.71	141.6
Mean (±1 SE)	**26.90 ± 10.07**	**3.21 ± 1.38**	**0.04 ± 0.28**	**3.17 ± 1.32**	**97.7 ± 9.0**

photodegraded to a photorecalcitrant form is subsequently removed by some other DOM-processing agent, such as heterotrophic uptake. Photodegradation can alter bacterial uptake of DOM (Tranvik and Bertilsson 2001, Amado et al. 2006), but no research has investigated this phenomenon relative to longitudinal gradients in streams. Longitudinal fluctuations in the canopy density and, subsequently, light intensity might allow a synergistic processing effect between bacterial uptake and photodegradation as DOM moves downstream (Frost et al. 2005). For example, light in unshaded stream reaches may photodegrade DOM to more photorecalcitrant forms that are subsequently taken up by bacteria in shaded reaches where bacteria are not inhibited by UVR (Sommaruga et al. 1997, Jeffery et al. 2000, Amado et al. 2006). An analogous vertical gradient in UVR dose would allow simultaneous processing in the well-mixed waters of streams with high DOM.

A final possible explanation is that some hidden factor might be controlling DOM photodegradation. For example, conversion of DOM to inorganic C requires a source of dissolved O_2. We did not control for differences in initial dissolved O_2 content among streams, and, therefore, differences in dissolved O_2 could have confounded our other analyses. However, water was filtered before the experiments, and

TABLE 3. Photodegradability of dissolved organic matter (DOM) (measured as % reduction [%R] of absorbance at 320 nm or concentration of dissolved organic C [DOC] after exposure to light) in different sources of water. Mean (±1 SE) %R is shown for streams from our study (northern forested streams). Other DOM sources are shown without error, as they represent a single DOM source. Exposure time varied considerably among studies (56 h to 10 d). Therefore, we normalized the %R for exposure time by dividing by the hours of exposure in each study.

DOM source	%R	%R/h exposure	Study
Absorbance at 320 nm			
Northern forested streams	10.3 ± 1.2	0.18 ± 0.02	Experiment 1, our study
Lake Trebol	15.9	0.07	Zagarese et al. 2001
Lacawac Bog[a]	28.8	0.17	Osburn et al. 2001a,
	30	0.18	De Lange et al. 2003
Lake Lacawac	51.6	0.27	De Lange et al. 2003
Lake Giles	36.49	0.19	De Lange et al. 2003
Lake Waynewood	42.82	0.25	Morris and Hargreaves 1997
[DOC]			
Northern forested streams	6.4 ± 3.04	0.11 ± 0.05	Experiment 1, our study
Lacawac Bog[a]	16	0.10	Osburn et al. 2001a,
	25	0.15	De Lange et al. 2003
Lake Lacawac	13	0.07	De Lange et al. 2003
Lake Giles	12	0.06	De Lange et al. 2003
Lake Waynewood	17	0.10	Morris and Hargreaves 1997
Leaf leachate	2.3–3.4[b]	0.04–0.07[b]	Tietjen et al. 2005

[a] Sampled twice in different studies
[b] Range

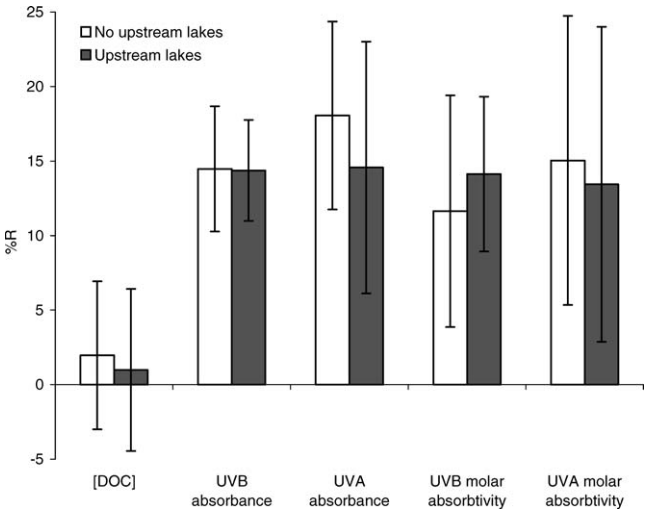

FIG. 3. Mean (±1 SE) % reduction (%R) in 5 properties of dissolved organic matter (DOM) caused by exposure to light of DOM from 4 streams with and 4 streams without upstream lakes. The large error bars within each category (relative to error bars in Fig. 1) are a result of high among-stream variation, which was removed from data in Fig. 1.

filtration might have saturated the water with O_2. Other factors, such as the concentration of Fe or NO_3^-, can strongly influence photodegradation of DOM (Zafiriou 2002, Brinkmann et al. 2003a, Golden 2004). Moreover, daily solar radiation varies by region, time of year, and weather. Thus, unmeasured factors could have caused variation in our study and others (e.g., Graneli et al. 1998, De Lange et al. 2003) that prevented detection of differences in DOM photodegradability between lakes and streams.

Photodegradation might influence UVR penetration into the water column and, potentially, to the benthos in stream reaches where DOM, instead of cloud cover, turbidity, or riparian vegetation, controlled the UVR dose (Xenopoulos and Schindler 2001, Frost et al. 2005). We observed significant changes in UVR penetration despite relatively short exposure periods (cf. Morris and Hargreaves 1997, Osburn et al. 2001a). Most of our study streams were shallow 1st- to 3rd-order streams where even modest increases in the depth of UVR penetration had the potential to expose the stream benthos to greater UVR doses. This potential is important because UVR has detrimental effects on numerous aquatic organisms (Hader et al. 1998) and can cause trophic cascades in the stream benthos (Bothwell et al. 1994, Kelly et al. 2003).

Solar wavelengths that cause DOM photodegradation

Other researchers have found strong effects of UVR on DOM properties. For example, Osburn et al. (2001b) found that UVB plus UVA caused >76% of the change in the spectral-weighting function (a measure of DOM absorbance). Graneli et al. (1998) reported that photo-induced dissolved inorganic C (DIC) production (a result of DOC breakdown) was caused mostly (56%) by UVB and UVA. Morris and Hargreaves (1997) found that UVR was responsible for >50% of the change in DOM absorbance properties. Our results were notable because virtually all (97.7%) of the effects of light on DOM absorbance were caused by the UV portion of the solar spectrum, although stream-to-stream variation was considerable. DOM did not appear to be more photodegradable in ambient light in our streams than in other ecosystems, but it did appear to be more susceptible to UVR than in other ecosystems.

When averaged across all streams, PAR caused a small, but statistically significant, decline in DOM absorbance. However, this effect varied tremendously among streams. In some streams, PAR actually appeared to increase DOM absorbance, possibly because of increases in humic-like DOM (Kieber et al. 1997, Benner and Biddanda 1998). Photohumification typically has been observed in marine ecosystems where photooxidation of more common organic compounds, followed by condensation and transformation, is a presumed source of marine humic material (Kieber et al. 1997). A similar explanation was invoked by Reche et al. (2001) to explain changes in the spectral properties of freshwater DOM.

Differences among methods could explain some of the variation in the effect of PAR observed among our study and other photoexposure studies. Most other researchers (e.g., Morris and Hargreaves 1997, Graneli et al. 1998, Osburn et al. 2001a) exposed water to light for much longer periods (6–10 d) than we did (56 h). How this longer exposure time might influence the importance of PAR relative to UVR is unknown. Furthermore, differences in light intensity (caused by latitude, cloud cover, etc.) on a per-day or per-hour basis could lead to differences in the amount of UVR or PAR exposure (Xenopoulos and Schindler 2001). Other studies with longer exposure times might have integrated wide variations in the PAR:UVR ratio that our study did not capture.

Effects of upstream lakes on DOM properties

We hypothesized that the presence of upstream lakes would reduce DOM photodegradability because of greater previous photoexposure in upstream lakes (with long water-retention times) than in streams. However, we did not observe a lake effect. Graneli et al. (1998) compared photodegradation in lakes from temperate and tropical latitudes and hypothesized that the

relatively UVR-rich tropical solar spectrum would cause DOM to be photorecalcitrant. However, as also reported elsewhere (Valentine and Zepp 1993, Scully et al. 1996), photodegradation did not differ between lakes from different latitudes. We avoided the potential confounding factors present when comparing aquatic ecosystems in different latitudes, but our results also indicated that previous exposure to solar radiation was not a strong predictor of the photodegradability of DOM.

There are several possible nonexclusive explanations for this result. One explanation is that none (or almost none) of the DOM pool is photorecalcitrant. In this case, the proportional change in DOM caused by light would be similar regardless of previous light exposure. However, photorecalcitrant DOM has been reported in other experiments (e.g., Kohler et al. 2002) and in natural ecosystems (Arts et al. 2000). Another possibility is that lakes might not cause differences in upstream light exposure. We find this possibility unlikely given the more intense radiation on open water than on streams, the longer water-residence time in lakes than in streams, and the timing of our experiments, which followed a summer of exposure to light in the lakes but not in the shaded streams.

A more likely possibility is that DOM is subjected to multiple production and processing agents that obscure the effects of upstream light exposure. For example, we sampled up to 1 km downstream of lakes. If most of the DOM leaving the lake were removed or if large new DOM inputs were added over that distance, then the imprint of the lake would diminish, and the history of DOM exposure to light might not differ between lake-outflow streams and other streams. Uptake of DOM in streams varies widely because of differences among DOM sources. Labile DOM sources are removed very quickly (Wiegner et al. 2005). Heterotrophic uptake might be strongly influenced by photodegradation, possibly leading to rapid uptake of photodegraded DOM (Tranvik and Bertilsson 2001). As a result, watershed DOM inputs, such as those from riverine wetlands, could replenish the photodegradable DOM pool. A combination of frequent DOM inputs and preferential removal of photodegraded DOM would make detection of the effects of upstream exposure to light difficult. We hypothesize that photorecalcitrant DOM is removed or altered by other DOM-processing agents in streams, thereby limiting the effect of previous light exposure on DOM photodegradability.

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