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Increased photoreactivity of DOC by acidification: Implications for the carbon cycle in humic lakes

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Abstract

Effects of ultraviolet (UV)-B radiation and acidification on pelagic carbon flux in a humic lake (dissolved organic carbon [DOC] ~ 15 mg C L⁻¹) were studied in a mesocosm experiment during the summer of 2000. Triplicate tanks (107 liters volume, 1 m high) were exposed to natural solar radiation, a daily extra dose of UV-B radiation, or kept dark. One set of tanks was submitted to a decrease in pH (from 5.7 to 4.7), and one set was kept at the natural pH level. During 70 d, water samples were taken regularly from the mesocosms for measurements of DOC, absorbance, dissolved inorganic carbon (DIC), and pH. Additionally, we regularly incubated samples to measure photooxidation rates, primary production, and community respiration. We found an increase in the photooxidation rates in the acidified mesocosms relative to ambient pH. The greater abiotic production of DIC (i.e., photooxidation) in acidified conditions could explain $\sim 27\%$ of the decline in DOC in the same conditions. Laboratory experiments were done to test the effects of pH on the dissolved organic matter (DOM) photoreactivity. At lower pH values, we found both higher abiotic DIC production and specific absorbance fading, relative to neutral pH values in water from a humic lake. In a separate experiment, samples were exposed to prolonged irradiation under laboratory conditions, resulting in complete loss of absorptivity in the wavelengths between 290 and 400 nm. Decreases in DOC in the long-term exposure caused by photochemical mineralization were ~ 45 and 55% of the initial pool for natural pH and acidified samples, respectively, at the end of the experiment. An increase in the dissolved organic matter photoreactivity by acidification could be an important mechanism to explain the increased water transparency and in-lake DOC removal in acid lakes found in several previous studies.

Reductions in stratospheric ozone have resulted in greater amounts of ultraviolet (UV)-B (280–315 nm) radiation reaching the Earth's surface. This effect is expected to increase and persist for several decades, even if present agreements on substitutions of freons and other ozone-destroying chemicals are enforced effectively. UV-B radiation has a direct negative influence on aquatic organisms through DNA damage. On the other hand, UV-B radiation might have indirect, positive effects through food chain alterations (Bothwell et al. 1994) and through photoproduction of bacterial substrates (Mopper et al. 1991; Lindell et al. 1995; Bertilsson and Tranvik 1998, 2000), as well as inorganic nitrogen and phosphorus (Bushaw et al. 1996; Yiyong 1996), from dissolved organic matter.

Although changes in UV-B radiation alone might have environmental consequences in lakes, more severe effects could be expected from interactions between climate change, acidification, and ultraviolet radiation, because drier conditions and acidification could aggravate effects from UV radiation (Schindler et al. 1996; Yan et al. 1996). A decline in dissolved organic carbon (DOC) concentration accompanied by acidification has been observed in several natural systems

(Schindler et al. 1996, 1997; Williamson et al. 1996). Acidification can greatly increase the penetration of damaging UV radiation because of a decrease in DOC concentration, a change in DOC quality, or both, the mechanisms behind which are largely unknown (Donahue et al. 1998). One previous study has provided evidence that there is a negative correlation between pH and photoreactions of dissolved organic matter (Bertilsson and Tranvik 2000). Furthermore, Gennings et al. (2001) demonstrated that additions of acid to stream waters increased photooxidation rates of dissolved organic matter (DOM). However, there are contradictory results from a laboratory study (Gao and Zepp 1998).

A decline in DOC concentration and absorbance in a humic lake is expected to have much less profound effects on UV-B penetration than the same decline of DOC in a clear-water lake because the relationship between attenuation of UV radiation and DOC fits a power model (*see also* Morris et al. 1995; Williamson et al. 1996). Williamson et al. (1996) found that at a DOC concentration >2 mg C L⁻¹, the depth of 1% surface irradiance for UV-B ($\approx 1\%$ UV-B) was <1 m, and small changes in DOC had almost no effect on the 1% attenuation depth. Therefore, humic lakes are expected to be less sensitive to a decrease in DOC than clear-water lakes. Nevertheless, DOC in humic lakes itself is subjected to considerable photochemical degradation, with consequences for the carbon budget of these lakes (Granéli et al. 1996).

During the summer of 2000, we performed a mesocosm experiment to test the combined effects of acidification and increased UV-B radiation on DOC fluxes in a humic lake. We show that acidification led to a small but significant DOC decline, which could be partly explained by an increased photoreactivity of DOC because of acidification. In combination with the mesocosm experiments, laboratory experi-

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ments were also conducted to test the dependence of photooxidation of DOM on pH. The consequences of this increased photoreactivity for carbon budgets are discussed.

Materials and methods

Sampling and experiment setup—Two cubic meters of water from Lake Skärshultsjön (Sweden, lake area = 0.36 km², catchment area = 8 km², retention time = 7 months, water color ~90 mg Pt L⁻¹, Granéli et al. 1996; Lindell et al. 2000) was collected by pumping the water from ~0.5 m depth in mid-June 2000. Water was filtered through a 10- μ m net and distributed into 18, 107-liter-volume cylindrical mesocosms (1.00-m deep by 0.37 m inner diameter). The water surface was ~2 cm from the top of the cylinders. UV-B radiation exposure and pH were manipulated in the mesocosms. Triplicate mesocosms were exposed to either ambient solar radiation (AMB) or a daily extra dose of UV-B (+UVB) or kept dark (Dark). The same light treatments were repeated for water, which was previously submitted to a decrease in pH of one unit (from 5.7 to 4.7) by addition of H₂SO₄ (AMB-pH, +UVB-pH, and Dark-pH). The sides of all mesocosms were covered with a thick paper opaque to radiation.

The mesocosms were placed on the roof of the Ecology Building at Lund University, Sweden (52°N). Three sections of six mesocosms were placed in a line oriented north, where minimal shade from the lamps could be obtained at true midday. In the +UVB treatments, enhancement of UV-B was achieved with fluorescent lamps (Phillips TL12) placed 60 cm above the mesocosms. The lamps were covered with cellulose acetate, which absorbs wavelengths <280 nm. Pseudo-armatures the same size as those used in the +UVB treatments were also placed above the treatments with ambient solar radiation, so the AMB treatments would have the same shade as the +UVB treatments. Dark mesocosms were covered with a thick paper opaque to all radiation.

All mesocosms (except the dark treatments) were covered with Plexiglas (Röhm GS 2458) transparent to UV and photosynthetically available radiation (PAR) to avoid contamination with rainwater and dust from the atmosphere. An opening of 1.0 cm around the mesocosms was left below the Plexiglas to facilitate surface wind action and aeration.

Irradiation levels on a typical cloudless day in South Sweden around noon during the summer are 400, 30, and 0.3 W m⁻² for PAR, UV-A, and UV-B, respectively. Radiation was measured using a Radiometer/Photometer Model IL 1400A (International Light), connected to three different broadband sensors with cut-off filters (PAR: 400–750 nm; UV-A: 320–400 nm; UV-B: 280–320 nm). The extra dose of UV-B was applied every day from 1000 to 1400 h with a constant intensity of 0.15 W m⁻². Because the light source was constant, the percent increment produced by the UV-B lamps was dependent on the weather conditions and time of day. Therefore, the proportional increment in UV-B radiation relative to the ambient level was higher during cloudy days. The average decrease in UV-B radiation in the treatments with only ambient radiation caused by the pseudo-armatures was ~30% relative to ambient UV-B. The decrease in ra-

diation caused by the armatures of the +UVB treatment and the pseudo-armatures in the AMB treatment was calculated by measuring the difference in the incidence of UV-B radiation at noon on a cloudless day at the ground and below the armatures, just above the water surface.

The decrease in pH in the acid treatments was achieved by adding ~22 ml 0.1 N H₂SO₄ directly into the mesocosms. The pH in the mesocosms was monitored every 3–4 d. In order to avoid growth of attached organisms on the walls, the mesocosms were scraped down to the bottom with a brush every third day. After the experiment, the walls of the mesocosms were inspected and no visible algal growth was observed. Every week, ~2 liters of Milli-Q water was added to the mesocosms in order to compensate for losses from evaporation, thus keeping the same water level during the course of the experiment.

For 70 d, water samples were taken regularly from the mesocosms for measurements of DOC, absorbance, dissolved inorganic carbon (DIC), and pH. Additionally, we regularly incubated samples to measure photooxidation, bleaching of DOM, primary production, and community respiration. Light attenuation was measured on one occasion during the last days of the experiment.

Photooxidation rates—After mixing of the water column in the mesocosms, water was taken from the surface with glass bottles (~200 ml) rinsed with acid and Milli-Q water. Half of the water from each treatment was filtered through a 0.2- μ m membrane filter into quartz tubes (inner diameter = 22 mm, length = 145 mm, volume = 40 ml). The remaining unfiltered water from each treatment was used to fill additional quartz tubes in order to measure primary production, as described below. No headspace was left in the tubes. The tubes were previously washed in acid (10% concentration of HCl) and Milli-Q water. Tubes were suspended horizontally at the surface of each mesocosm, with half of the tube above the water and half under the water. Dark controls were incubated in the dark mesocosms. Incubations for photooxidation and primary production measurements were done at days 2, 12, 21, 29, 36, and 48 of the experiment. All incubations were performed between 1000 and 1400 h. On one occasion, a depth profile was done in duplicate mesocosms from each treatment for both photooxidation and primary production. Sampling preparations were done as described above, but tubes were incubated horizontally at the surface and at 10, 20, and 50 cm below the surface for 2 d. Duplicate dark controls were incubated at only one depth.

Community respiration—Community respiration was monitored by measurements of DIC increase. Water was taken from the surface of each mesocosm after mixing of the water column and distributed into two Pyrex glass bottles (50 ml) with ground glass stoppers. DIC was measured immediately in one of the bottles. The other bottle was then incubated in the dark at room temperature (20°C) for 48 h; thereafter, a new DIC measurement was taken. One respiration measurement was taken on days 30, 37, 48, and 68 of the experiment in every mesocosm.

Primary production—Primary production was measured using the ^{14}C -technique. Final specific activity of ^{14}C -bicarbonate added to the quartz tubes was $2.5 \mu\text{Ci ml}^{-1}$. Blanks were achieved by incubating tubes in the dark mesocosms. After incubation, the entire volume of the tubes was immediately filtered through $0.45\text{-}\mu\text{m}$ membrane filters. Filters were fumed with concentrated HCl and 37% formalin for 15 min. Thereafter, filters were placed in vials containing scintillation cocktail and counted in a Beckman scintillation counter (LS 6500). For measurements of primary production, quartz tubes were incubated with water from the mesocosms at the surface. On one occasion, a depth profile was performed with duplicate bottles incubated at the surface, 15, 50, and 100 cm depth. The depth profile data were used to calculate primary production in the mesocosms on an areal basis. The same vertical distribution of primary production was assumed for the occasions when only surface incubations were available.

DOC and DIC—DIC was analyzed with a Shimadzu TOC-5000 total carbon analyzer immediately after termination of photooxidation and community respiration incubations. A minimum of three injections were made for each sample analyzed for DIC and DOC. Photochemical production of DIC was calculated as the concentration of DIC in light minus the concentration in dark tubes at the end of the incubation. Therefore, any eventual production of DIC in the dark is discounted. Autosampling was not used to avoid prolonged contact with the air. DIC was measured immediately after opening the sealed tubes by introducing the inlet tube from the TOC analyzer down to the bottom of the quartz tube. The analysis took a maximum of 10 min and comprised 3–5 measurements of DIC per tube, with no systematic increase in concentration from the first to the last value.

Samples for DOC were taken from each mesocosm on several occasions after mixing of the water column. Water was filtered through $0.2\text{-}\mu\text{m}$ polycarbonate filters into 8-ml pre-combusted (500°C , overnight) glass vials rinsed in acid and Milli-Q water. All samples were analyzed immediately after filtration. Inorganic carbon was purged for 5 min from acidified samples (pH ~ 2 , HCl) before injection into the TOC-5000 total carbon analyzer. We have presented DOC values in relation to the dark control. In that way we could correct DOC values for any systematic variations in the TOC instrument during the experiment (such systematic errors could arise because DOC samples were not run on one occasion, but immediately after every sampling occasion).

Absorbance and UV-B attenuation—Absorbance analyses were performed on $0.2\text{-}\mu\text{m}$ -filtered samples. Absorbance spectra of the samples were obtained with a Beckman DU® 650 spectrophotometer, using 1-cm quartz cuvettes. Wavelengths from 200 to 900 nm were measured. The absorbance spectra between 290 and 700 nm were transformed to the natural log of the absorbance coefficient (m^{-1}) and plotted against wavelength (nm) fitted to an exponential form using a nonlinear least squares fitting routine (Blough and del Vecchio 2002). The slope of this line, usually called the spectral slope S (μm^{-1}), indicates how quickly absorptivity decreases with increasing wavelength. The absorption at 320 nm was

used as a measure of colored dissolved organic carbon (CDOC; Williamson et al. 1999). DOC-specific absorptivity at 320 nm was defined as absorptivity divided by DOC ($\text{m}^{-1} [\text{mg C}]^{-1} \text{L}^{-1}$).

Downwelling underwater irradiance of UV-B was measured with an IL 1400A radiometer (International Light) connected to an UV-B sensor (280–320 nm). Because UV-B radiation was already extinguished after just a few centimeters, we poured water at millimeter intervals from the mesocosms into a shallow container, producing no shadow for the UV-B sensor that was fixed on the bottom of the container.

The influence of pH on the photoreactivity of DOM under laboratory conditions—Water from the studied lake was collected on the same occasion as for the mesocosm experiments and manipulated to different pH values. Acidification was achieved by addition of H_2SO_4 , whereas increase in pH was achieved by NaOH additions. Four different pH values were established: one value of decreased pH (pH 4.5), one of natural pH (pH 5.7), and two of increased pH (pH 6.8 and 8.6). The water was poured into 40-ml quartz tubes and irradiated with UV-B + UV-A lamps or incubated without radiation for 24 h. The UV radiation source consisted of a bank of eight fluorescent tubes (UVA-340, Q-Panel) emitting UV-B ($\sim 2 \text{ W m}^{-2}$), UV-A (23 W m^{-2}), and negligible PAR ($< 5 \text{ W m}^{-2}$), as determined using a Model IL 1400A radiometer with broadband sensors (International Light). Dark conditions were achieved by wrapping the tubes with aluminum foil. The tubes were incubated at 19°C in a temperature-controlled room. DIC production and the absorptivity characteristics of the water were analyzed after irradiation as mentioned above.

Long-term photobleaching and DIC production of natural pH and acidified lake water—Water collected from Lake Skärshultsjön in May 2001 (~ 5 liters) was filtered through 142-mm Gelman GF/E and $0.2\text{-}\mu\text{m}$ membrane filters. Water was distributed into two acid- and Milli-Q-rinsed glass bottles, and pH was decreased in one of the bottles (from 5.8 to 4.8), by addition of $0.1 \text{ N H}_2\text{SO}_4$. Water from each pH treatment was distributed into quartz tubes (inner diameter = 40 mm, length = 200 mm, volume = 190 ml). Quadruplicate quartz tubes were exposed to UV-A + UV-B radiation (see above) or kept in dark as controls for 15 d.

Dissolved inorganic carbon and absorbance spectra were measured every 3–4 d, consuming a total volume of ~ 10 ml from each quartz tube. After each sample was removed, the remaining water from each quartz tube was bubbled with air to avoid any possibility of oxygen limitation for photo-oxidative processes. Water was also filtered through $0.2\text{-}\mu\text{m}$ filters and exhaustively rinsed with Milli-Q water to eliminate bacterial regrowth during the exposure. The volume used in the analyses for DIC and absorbance spectra was compensated with $0.2\text{-}\mu\text{m}$ -filtered water from each pH treatment kept in darkness. During the last two samplings, dissolved organic carbon was also measured and the remaining water after analyses was bubbled, $0.2\text{-}\mu\text{m}$ filtered, and poured into smaller quartz tubes (volume = 40 ml). Therefore, no replacement of water was necessary during the last

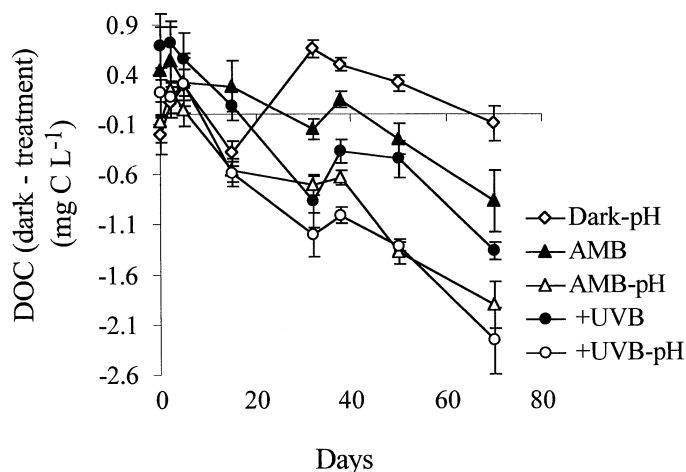


Fig. 1. Difference in DOC concentration between the dark and the other treatments. Dark, AMB, and +UVB are mesocosms in dark conditions, exposed to ambient levels of solar radiation, and with an extra dose of UV-B radiation, respectively. -pH is for acidified treatments (\pm SE, $n = 3$).

two samplings. The water was irradiated until no more photobleaching or DIC production could be observed (i.e., ~15 d). Oxygen concentration was monitored after every measurement of DIC and absorbance and before each new incubation with an oxymeter-type Oxy Guard, Handy MK III.

Results

Mesocosm experiment—The summer in southern Sweden during the year 2000 was characterized by low temperatures and a high number of cloudy days: 51 d out of a total of 70 had less than 7 h of sunshine (maximum sunshine for that period of the year is around 16 h). The water temperature in the mesocosms correlated strongly with the daily mean air temperature (slope = 1.01, $r^2 = 0.92$). Except during the first day of the experiment, the water temperature never exceeded 20°C.

Mean initial DOC concentration in the mesocosms was 16.1 mg C L⁻¹, with no significant differences between acidified and nonacidified treatments (t -test, $P > 0.1$). In the AMB and +UVB treatments, a decline in DOC concentration was detected during the course of the experiment (Fig. 1). Although small, significant differences were found between acidified and nonacidified light-exposed mesocosms (repeated ANOVA, $P < 0.01$). On average, the DOC concentration was 0.9 mg C L⁻¹ lower in the acid treatments relative to nonacid mesocosms at the end of the experiment. Differences between acidified and nonacidified mesocosms could already be detected 15 d after acidification. Concerning differences among the light treatments, mesocosms exposed to ambient radiation or to +UVB had, on average, lower DOC concentration than mesocosms in darkness. No significant differences in DOC concentration were found between AMB and +UVB mesocosms ($P > 0.1$, post hoc, Tukey test).

Absorptivity at 320 nm was significantly lower in the acidified mesocosms exposed to light relative to nonacidified

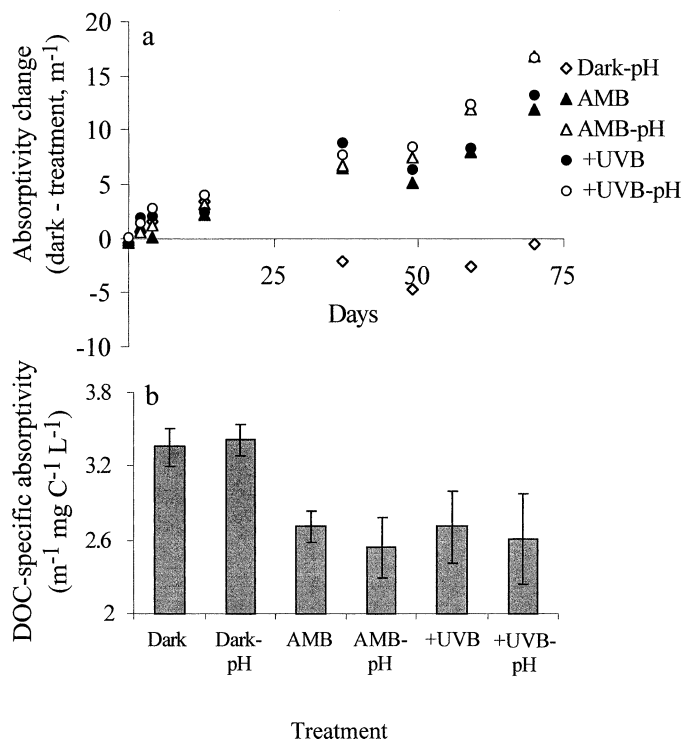


Fig. 2. (a) Absorptivity changes at 320 nm relative to the dark treatments and (b) the DOC-specific absorptivity at 320 nm (\pm SD, $n = 3$) at the end of the experiment.

treatments exposed to light, and differences between acid and nonacid mesocosms were not found in the dark treatments (Fig. 2a). DOC-specific absorbance at 320 nm showed no differences between acid and nonacid mesocosms, indicating that the lower absorptivity at 320 nm found in the acid mesocosms exposed to light, compared to the nonacid mesocosms, mainly was due to the lower amounts of DOC found in the acid mesocosms (Fig. 2b).

During the experiment, we observed changes in the shape of the absorbance spectra, as represented by the spectral slope (S ; the absolute value of the slope using a nonlinear regression of $\ln[a]$ vs. λ for 290–700 nm). Differences in the spectral slope between acid and nonacid treatments suggest that the absorptivity at different wavelengths was influenced in different ways by acidification. Therefore, changes in wavelengths other than 320 nm are not only due to the modifications in DOC concentration. An increase in the spectral slope was observed in all treatments exposed to solar radiation, compared to the dark treatment (Fig. 3a). Generally, acidified treatments showed lower spectral slopes than nonacidic treatments, whereas no differences were found between AMB and +UVB, or between AMB-pH and +UVB-pH. In the PAR region of the spectrum, we found significantly higher absorbance values in the acidified mesocosms relative to the nonacid treatments, which could partially explain the lower spectral slopes in those treatments (Fig. 3b).

The depth of UV-B attenuation ($\approx 1\%$) in the dark mesocosms was ~6.4 cm. Exposure to ambient solar radiation and to an extra dose of UV-B increased the depth of 1% UV-B attenuation in the acid and nonacid-treated mesocosms

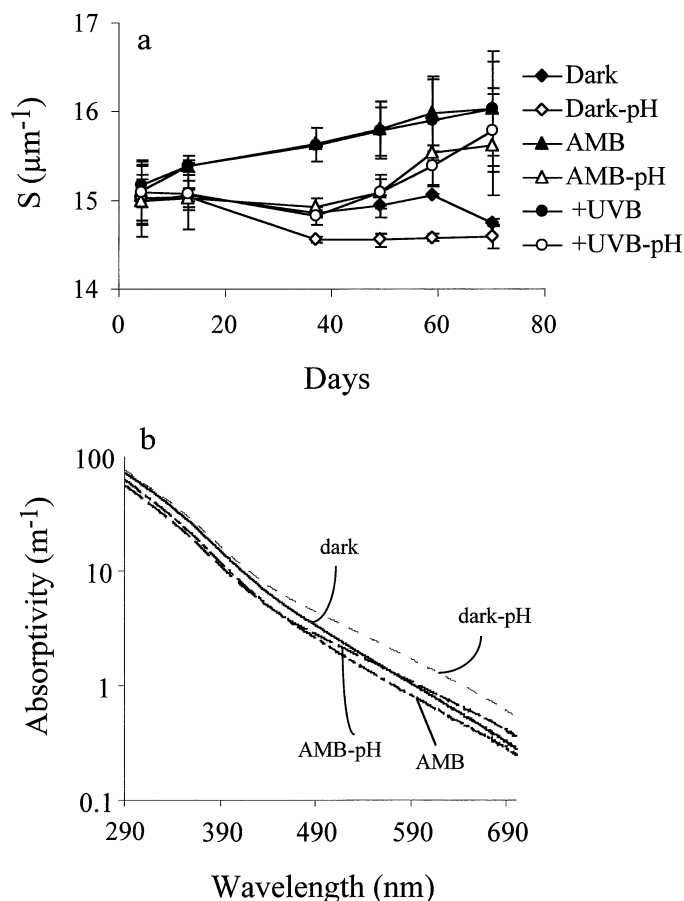


Fig. 3. (a) Spectral slopes (\pm SD, $n = 3$) during the mesocosm experiment and (b) log-normal plot of the spectral dependence of the absorption coefficient for some treatments at the last sampling.

by ~ 1.6 cm, after 60 d. The depth of UV-B attenuation was not altered significantly, either by acidification or by an extra dose of UV-B during the 2-month period of this study (two-way ANOVA, $P > 0.1$).

We found high rates of photooxidation in the beginning of the mesocosm experiment for all treatments compared to the later part of the experimental period (Fig. 4). Differences among treatments were also detected. Highest photooxidation rates were found in the acid treatment with an extra dose of UV-B, and the lowest photooxidation was found in the nonacid treatment with only ambient solar radiation. However, differences between mesocosms with AMB and +UVB could not be detected after 28 d (Fig. 4a). The rate of photooxidation normalized to global radiation during the day of the incubation decreased logarithmically with time (Fig. 4b). A depth profile of photooxidation rates was measured on one occasion. We observed higher rates of DOC photoreactivity in acidified treatments than in nonacidified mesocosms. Higher photooxidation rates in the acidified treatments persisted below the influence depth of UV radiation (i.e., down to 50 cm, Fig. 5a), where a negligible DIC production should have been observed. This might indicate a systematic error in the DIC measurements between acidified and nonacidified treatments. We had dark controls for every pH treatment in both mesocosm and laboratory ex-

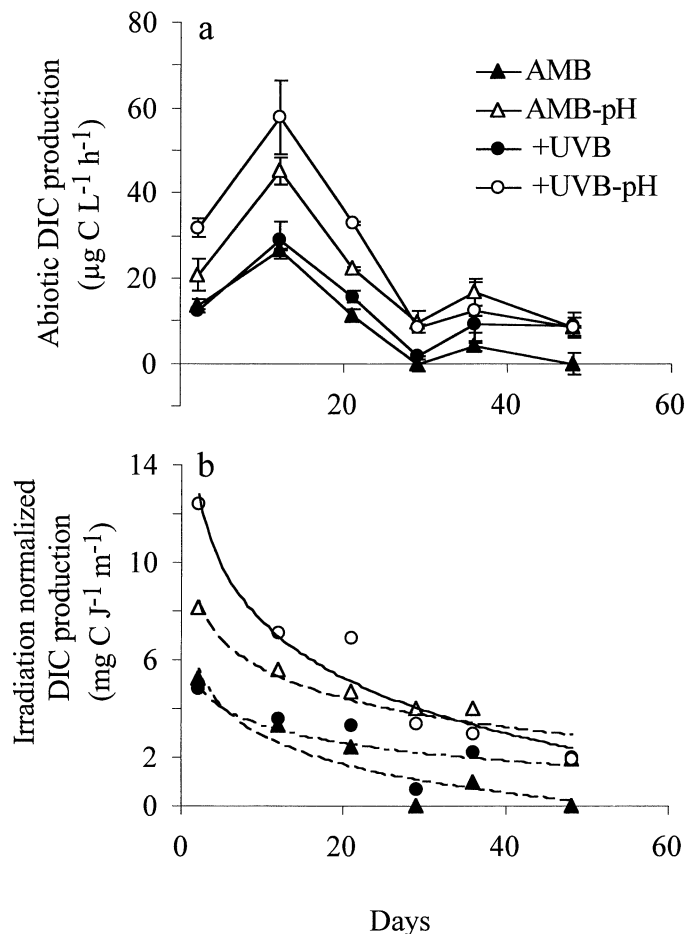


Fig. 4. (a) Photooxidation rates (\pm SD, $n = 3$) and (b) photooxidation rates normalized to the amount of global radiation during the mesocosm experiment.

periments. However, if there was a systematic error between DIC measurements in acidified and nonacidified treatments, this error should have been the same for all depths during the depth profile experiment. We observed that the difference in abiotic DIC production between acidified and nonacidified treatments was $\sim 12 \mu\text{g C L}^{-1} \text{ d}^{-1}$ at a depth of 50 cm, whereas this difference was $\sim 74 \mu\text{g C L}^{-1} \text{ d}^{-1}$ at the water column surface. Therefore, we believe that any eventual systematic error in DIC measurements between acidified and nonacidified treatments was small enough to not invalidate our results (i.e., that acidification increased photooxidation rates of DOC). In order to avoid any bias in our measurements of DIC between acidified and nonacidified treatments, we reconstructed the depth profile of photooxidation rates, subtracting for each treatment the values obtained at 50 cm depth for that treatment (Fig. 5b). Furthermore, we used the average value from each depth of all treatments by considering surface values as 100% and 50 cm depth as zero, to calculate the photooxidation extinction with depth (Fig. 5c). This means that we used a conservative estimation of the photooxidation on an areal basis in the acidified treatments. We used an exponential function with a nonlinear least squares fitting routine to describe the photooxidation atten-

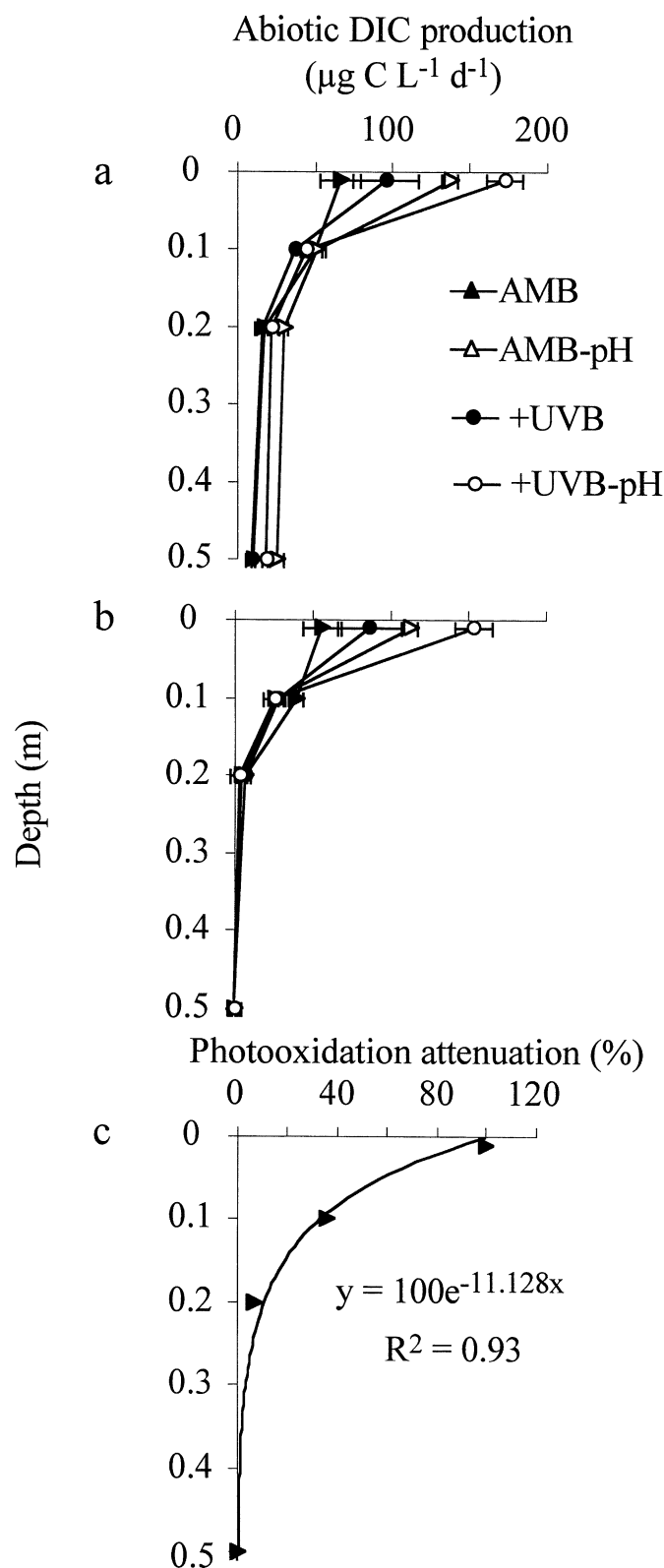


Fig. 5. (a) Photooxidation rates as a function of depth in the different light treatments during the mesocosm experiment and (b) photooxidation rates as a function of depth, where values in each treatment and depth were discounted from values obtained at 50 cm depth. Mean \pm SD ($n = 2$). (c) Exponential function between photooxidation decay (average of all treatments, $n = 4$) and depth. The exponential function was built with a nonlinear least squares fitting routine.

Table 1. Minimum–maximum (mean) values for all incubations of primary production and respiration in the mesocosm experiments ($n = 18$ and 12 for primary production and respiration, respectively). Results are calculated on an areal basis. A depth profile was done for the primary production, whereas incubations for respiration were done in samples collected after mixing water in the mesocosms.

Treatment	Primary production ($\text{mg C m}^{-2} \text{ d}^{-1}$)	Respiration ($\text{mg C m}^{-2} \text{ d}^{-1}$)
Dark	—	54–89(67)
Dark-pH	—	53–73(55)
AMB	152–403(247)	118–171(145)
AMB-pH	128–307(213)	117–144(127)
+UVB	103–459(226)	135–224(180)
+UVB-pH	121–344(218)	134–177(147)

uation with depth. Data on photooxidation rates on an areal basis were used further to calculate the total DOC photomineralization from solar radiation during the course of the mesocosm experiment (see Discussion). The low rates of photooxidation at depths <20 cm are in agreement with UV radiation profiles in such high DOC waters. Light extinction coefficients at 305, 320, 340, and 380 nm and at PAR in lake Skärshultsjön were measured during the summer of 2001 with a radiometer (model PUV 500, Biospheric Instruments, data not shown). These data indicated that $>90\%$ of radiation at UV-A and UV-B wavelengths is extinguished, whereas $\sim 20\%$ of PAR radiation is left at 50 cm compared to surface levels.

Community respiration was roughly constant within a treatment during the course of the experiment (Table 1). DIC content was lower in the acidified dark treatments than in dark ambient-pH treatments (Fig. 6a). DIC content in light-exposed mesocosms decreased from $\sim 545 \mu\text{g DIC L}^{-1}$ in the beginning of the experiments to $\sim 200 \mu\text{g DIC L}^{-1}$ after 40 d (Fig. 6b). Although the DIC content decreased in both acidified and nonacidified light treatments, the values were slightly higher in the acidified mesocosms than in the nonacidified treatments. No significant differences were found between AMB and +UVB-exposed mesocosms. DIC content was high in the beginning of the experiments, when primary production was still low and photooxidation was highest. Conversely, DIC decreased during the experiment, when the ratio between production of organic matter by primary producers (i.e., uptake of DIC) and photooxidation was highest. After day 50 of the experiment, zooplankton growth, mainly *Bosmina*, was observed in the mesocosms and was probably the explanation for the DIC increase in the light-exposed mesocosms. Lower primary production after day 48 coincided with the appearance of zooplankton in the mesocosms (data not shown).

We did not observe any significant treatment effect on primary production between +UVB and AMB or between acidified and nonacidified treatments, although there was a trend toward higher primary production in the nonacidified treatments (repeated ANOVA, $P > 0.1$; Table 1). Average primary production measured at the surface of the mesocosms was $\sim 8.5 \pm 3.7 \mu\text{g C L}^{-1} \text{ d}^{-1}$.

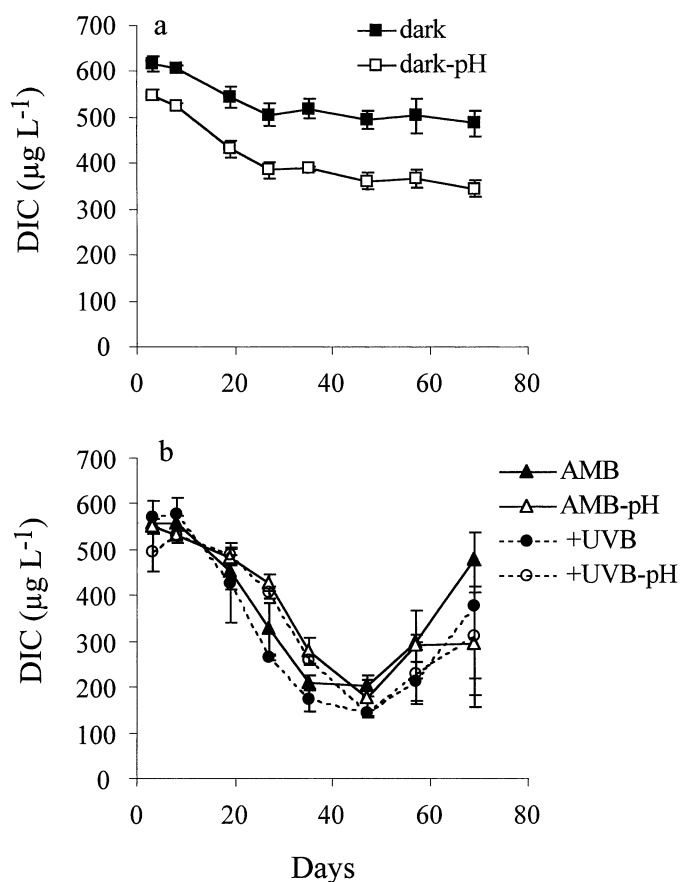


Fig. 6. DIC in the (a) dark and (b) light-exposed treatments during the course of the mesocosm experiment. Results are mean \pm SD ($n = 3$).

Photoreactivity of DOM under artificial radiation—Although we could not observe differences in the absorptivity characteristics between nonacidified and acidified mesocosms in the beginning of the experiment, we detected a small but significant difference in this variable for pH-manipulated 0.2- μm -filtered lake water during the laboratory experiments when comparing only dark treatments (ANOVA, $P < 0.01$). After irradiation, we detected both greater photooxidation and greater photobleaching at lower pH than at higher pH values (Table 2).

Exposure of lake water to prolonged irradiation under laboratory conditions resulted in complete loss of absorptivity in the wavelengths between 290 and 400 nm (i.e., the same spectral interval as the action spectrum of the lamps used in

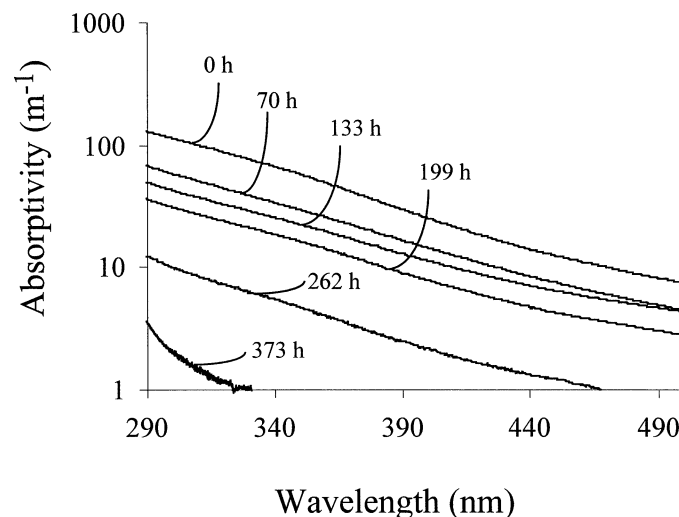


Fig. 7. A log-normal plot of the spectral dependence of the absorption coefficient during the long-term exposure of 0.2- μm -filtered natural pH water in laboratory conditions.

this experiment) in acidified and nonacidified treatments (Fig. 7). In dark controls, the decrease in absorptivity at 320 nm was $\sim 7\%$, which was probably due to repeated filtration through the 0.2- μm filters (Fig. 8a). Decreases in DOC caused by photochemical mineralization by the end of the experiments were ~ 45 and 55% of the initial pool for natural pH and acidified samples, respectively, corrected for losses in the dark (data not shown). The concentration of DIC increased continuously and approached an asymptotic value of 11.9 and 12.7 mg DIC L^{-1} for the natural pH and acidified treatments, respectively. The differences in DIC production between natural pH and acidified water were similar to the differences in DOC losses found between these two treatments (i.e., $\sim 0.8 \text{ mg C L}^{-1}$).

Discussion

DOC decline and increased photoreactivity of DOC under acidified conditions—Differences in DOC between acidified and nonacidified mesocosms were detected only among light-exposed mesocosms, indicating that the decrease in DOC observed in acidified lakes might at least partly be due to a pH effect on photooxidation, as we found that photooxidation was higher in the acid treatments relative to the nonacid mesocosms. DOC losses in the mesocosms because of photooxidation were calculated as follows. (1) Photooxi-

Table 2. Absorbance characteristics and dissolved inorganic carbon production (i.e., photooxidation; \pm SD, $n = 3$) in UV-exposed and dark controls under different pH conditions in the laboratory experiment after 24 h.

pH	Absorptivity, 320 nm (m^{-1})			Slope (λ , 290–700 nm) (μm^{-1})		DIC production ($\mu\text{g C L}^{-1} \text{ h}^{-1}$)
	Dark	UV	Bleaching (%)	Dark	UV	
4.5	40.5 \pm 0.4	25.9 \pm 1.0	36	15.58 \pm 0.01	16.22 \pm 0.12	31.8 \pm 1.5
5.7	42.8 \pm 0.2	31.3 \pm 0.8	27	15.27 \pm 0.03	15.54 \pm 0.06	28.7 \pm 1.3
6.8	43.3 \pm 0.2	33.5 \pm 0.3	23	15.14 \pm 0.02	15.39 \pm 0.02	23.7 \pm 1.4
8.6	44.0 \pm 0.2	33.8 \pm 0.3	23	15.04 \pm 0.08	15.79 \pm 0.18	18.4 \pm 0.8

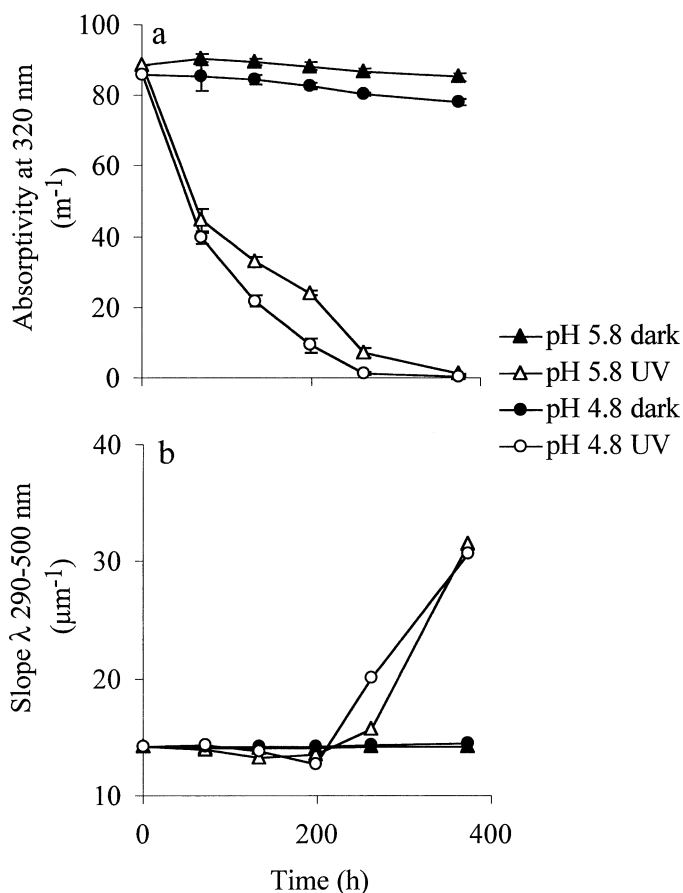


Fig. 8. (a) Absorptivity at 320 nm \pm SD ($n = 4$) and (b) spectral slopes in ambient and decreased pH conditions for dark and UV-exposed samples, during the long-term laboratory experiment.

dation in the surface water of the mesocosms was measured on six occasions (Fig. 4a). (2) Measured values were normalized by global radiation for the respective days (Fig. 4b). (3) Normalized values were fitted to a logarithmic curve with relation to time. (4) Photooxidation for each day of the mesocosm experiment was then calculated using the logarithmic curve, multiplying by the global radiation for that day. Global radiation data was obtained from the Swedish Meteorological and Hydrological Institute (SMHI). (5) For the calculation of photooxidation on an areal basis, we assumed that the shape of the curve for photooxidation extinction with depth was constant for the whole period of the experiment, and the same for all treatments (Fig. 5c). We assumed that photooxidation rates were approaching zero at 50 cm depth (*see also* fig. 2d in Granéli et al. 1996). (6) Finally, total photooxidation was calculated for the whole period of the experiment by summing photooxidation for each day. Based on these calculations, we conclude that the difference in the abiotic production of DIC (i.e., photooxidation) between acid and nonacid treatments could explain ~27% of the DOC difference between these treatments (Table 3).

Photooxidation is not the only process responsible for removal of DOC from the mesocosms. Respiration can also be an important mechanism in DOC removal. However, res-

Table 3. Difference in DOC concentration in relation to the dark (i.e., dark minus treatment) at the final sampling of the experiments and total photooxidation calculated for the entire experiment (*see text* in the discussion for how photooxidation was calculated). Rows labeled "Difference" show the difference between acidified and nonacidified treatments.

Treatment	DOC loss relative to the dark ($\text{g C m}^{-2} 70 \text{ d}^{-1}$)	Photooxidation ($\text{g C m}^{-2} 70 \text{ d}^{-1}$)
AMB	0.86	0.18
AMB-pH	1.90	0.41
Difference	0.84	0.23
+UVB	1.35	0.28
+UVB-pH	2.25	0.52
Difference	0.90	0.24

piration is not likely to be responsible for the lower amounts of DOC and higher DIC in the acidified treatments, since we found higher respiration rates in the nonacidified treatments. Besides photooxidation and respiration, another process that could have influenced our DOC results was the input of DOC by primary production. This is probably an important source of DOC in our mesocosms, but based on our measurements of primary production at the surface, we could only observe a small trend toward higher primary production in the nonacidified mesocosms relative to the acidified treatments.

Several mechanisms have been suggested to explain the observed DOC reduction during acidification of some natural lakes, such as a decrease in the dissociation and solubility of humic materials with the addition of H^+ (Krug and Frink 1983), an increase in microbial decomposition because of increased nutrient availability (Schindler et al. 1992), and removal of DOC by coagulation with aluminum (Schindler et al. 1992). In this study, we have shown that greater photooxidation under acidified conditions can explain a substantial part of the DOC reduction upon acidification. However, we do not exclude one or a combination of the above-mentioned mechanisms as an additional explanation for the DOC reduction in acidified waters.

Interestingly, photooxidation was greater in the acidified treatments receiving ambient solar radiation than ambient pH treatments with an extra dose of UV-B (Table 3). Therefore, acidification of humic lakes might have a greater effect on abiotic DOC mineralization and phototransformations than stratospheric ozone depletion alone. Morris and Hargreaves (1997) showed in their study that DOC in an acid lake was more sensitive to bleaching relative to DOC in more alkaline lakes. An inverse correlation between photoproduction of DIC and lake pH has been found by Bertilsson and Tranvik (2000). Dillon and Molot (1997) found a higher ratio between CO_2 evasion to the atmosphere and carbon storage in the sediment for acid lakes ($\text{pH} < 5.8$) compared to more neutral lakes ($\text{pH} > 6.0$), which they attributed to high DOC mineralization including photoproduction of DIC or a decrease in DOC production. More recently, Gennings et al. (2001) observed an increase in the photooxidation rates of stream waters (DOC concentration between 10.2 and 27.1

mg C L⁻¹) after additions of acid. This is in agreement with the idea that acid deposition, which can alter DOC photoreactivity, could be at least as important as stratospheric ozone depletion for long-term changes in carbon cycling in aquatic ecosystems.

Gao and Zepp (1998), on the other hand, found an increase in DIC production of 50%, with an increase in pH from 4 to 7, an effect which disappeared when fluoride was added to mask the effect on photooxidation from iron. This result is in contradiction to our study, and even if we had low iron content in our water (which was probably not the case for the humic water), this would, according to the findings of Gao and Zepp (1998), not have increased DIC production when pH was decreased. In our laboratory experiments, we could verify the dependence of DOM photoreactivity on pH. DOC decline through abiotic mineralization to DIC and color bleaching increased when pH was decreased (Table 2). These processes contribute to a transparency increase in humic lakes. Even under prolonged UV exposure until complete bleaching of DOM, we could observe that the final amount of DIC produced in the experiments was greater under acidified conditions. The greater direct photochemical mineralization of DOC in the acidified treatments was in agreement with the greater decrease in DOC concentration relative to the nonacidified treatments.

Changes in the absorptivity characteristics of DOM from acidification—Acidification can change the structure of CDOM in several ways. Acidification affects the spectra of DOM by causing a change in absorption maxima (λ_{\max}) and absorptivity from protonation of carboxyl and hydroxyl groups (Bloom and Leenheer 1989). Under laboratory conditions, we found a significant inverse correlation between absorbance spectral slope and pH in the samples kept in the dark (Table 2). However in the mesocosm experiments, we could not find any increase in the spectral slope in the acidified treatments. Indeed, we found significant decreases in the spectral slope in the acidified treatments compared to the nonacid-treated mesocosms during the course of the experiment (Fig. 3a). New DOM produced by the phytoplankton and other microbial communities might have a stronger effect on the spectral slope of DOM than changes caused by acidification. The increase in the spectral slope we found in the mesocosms exposed to light relative to the dark treatments corroborates the idea that autochthonous DOM has a higher spectral slope than allochthonous material (Green and Blough 1994; Whitehead et al. 2000). The observed difference in the spectral slopes between acid and nonacid treatments is difficult to explain. We did not measure a significant difference in the primary production between these treatments. However, we did not have information on the qualitative differences of phytoplankton or DOC exudate production between acid and nonacid treatments and its consequences for the spectral slopes. We found high primary production values in the mesocosms, and new production of DOC of autochthonous origin probably balanced some of the removal of DOC through photomineralization and respiratory processes. Moreover, in natural samples, sequential photochemical and biological degradation could have opposite effects on the spectral slope (Moran et al. 2000), which could

have confounded the results in the mesocosms. An increase in the spectral slope could be caused by acidification (Table 2) or increased influence of phytoplankton DOM in the bulk DOM pool (Carder et al. 1989), whereas a decrease in the spectral slope could be by biological degradation of DOM (Moran et al. 2000; *but see also* Pages and Gadel 1990).

Both a decrease (Morris and Hargreaves 1997; Gao and Zepp 1998) and an increase (Vodacek et al. 1997; Moran et al. 2000; Whitehead et al. 2000) in the spectral slope has been reported following photooxidation. During the long-term exposure experiment, we detected a decrease in the spectral slopes during the first 260 h of irradiation (Fig. 8b). However, after ~90% of the initial absorbance had faded, a substantial increase in the spectral slopes was observed, and values were similar to those of other studies reported for waters with low influence of terrestrial DOM (Green and Blough 1994; Vodacek et al. 1997).

Implications to the carbon budget of humic lakes—We found slightly higher DIC contents in acid than nonacid treatments in the mesocosms that were exposed to solar radiation. Conversely, significantly lower amounts of DIC were found in acidified relative to nonacidified treatments in the mesocosms that were kept in darkness. Because of the increase in photooxidation in the acid treatments, the importance of abiotic production compared to the biotic production of DIC (i.e., respiration) increased in the acid treatments compared to the nonacid mesocosms. It is worth a mention that we did not find higher total planktonic respiration in acid than nonacid treatments, although higher bacterial respiration could be expected because acidification might cause a higher photoproduction of labile DOM, in the same way as photoproduction of DIC was higher in the acidified treatments. The absolute values of the contribution of photooxidation to the total inorganic pool of DIC in situ is somewhat underestimated in our experiments because (1) the shadow from the mesocosm walls probably decreased photooxidation rates during the earlier and later parts of the day and (2) experimental conditions in such mesocosms probably improve biological growth and respiration. If we assume that photooxidation affects DOM of allochthonous origin almost exclusively (values extracted from Table 3) and that respiration in the dark mesocosms represented the respiration rates of DOM of allochthonous origin (values extracted from Table 1 multiplied by 70 d), then the contribution of photooxidation to the allochthonous DOM mineralization was up to 4.5 and 10.5% in nonacidified and acidified conditions, respectively. One should consider that these estimations were done for the first meter of the water column, meaning that the contribution would be much less for lakes with mean depth >1 m.

During the long-term incubation, we were able to photooxidize DOM until complete disappearance of CDOM under acidified and nonacidified conditions. Results from this experiment suggest that the higher photooxidation rates found under acidified conditions could result in a final lower percentage of DOM that is resistant to photooxidation. Finally, our study suggests that, in humic lakes, increased photochemical reactivity of DOC by acidification could be one important mechanism for in-lake DOC removal in acid lakes.

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