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Photoproduction of dissolved inorganic carbon in temperate and tropical lakes – dependence on wavelength band and dissolved organic carbon concentration

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Abstract. We have evaluated photoeffects of UV-B, UV-A and PAR radiation on dissolved organic matter (DOM). Photochemical production of dissolved inorganic carbon (DIC) was measured in sterile lake water from Sweden and Brazil after 6 hours of sun exposure. Tubes were exposed to four solar radiation regimes: Full-radiation, Full-radiation minus UV-B, Full-radiation minus UV-B and UV-A (PAR) and darkness.
In both areas, lakes with most DOC (varying between 3 and 40 mg C l^{-1}) were highly humic, resulting in high UV-B attenuation coefficients (K_d = 5–466 m^{-1}). Under Full-radiation, photooxidative DIC-production varied from 0.09 to 1.7 mg C l^{-1}per 6 h, without UV-B from 0.07 to 1.4 mg C l^{-1} and with PAR only from 0.02 to 0.7 mg C l^{-1}. UV-B radiation explains a minor part (17%) of the photoooxidative DIC-production, while UV-A and PAR have larger effects (39% and 44%, respectively). Photooxidation was proportional to DOC-content and DIC-production was positively related to decrease in DOC and to loss of absorbance at 250 nm. There was no significant difference in DOC and radiation normalized DIC-production between Swedish and Brazilian lakes. The UV-B dose during incubations was approximately 3 times higher in Brazil compared to Sweden, while UV-A and PAR doses were similar. We conclude that DOC from tropical and temperate freshwaters do not seem to differ with respect to sensitivity to photooxidation.

Key words: DOC, humic, lake, photooxidation, ultraviolet, UV-B

Introduction

Dissolved organic carbon (DOC), a major pool of carbon in the biosphere (Thurman 1985), is the main substrate for pelagic bacteria. A more or less large fraction of this DOC is, however, not directly available for bacterial utilization, probably due to unsuitable molecular structure or large molecular size (Thurman 1985). Although much of the DOC is resistant to biological mineralization (Tranvik 1988), there must be other processes that remove DOC from the water since DOC does not behave as a conservative substance (Tranvik 1990; Amon & Benner 1996).

Photodegradation, i.e. the cleavage and ultimate oxidation of DOC to CO_2 under the influence of solar radiation, removes DOC from surface waters. Photodegradation has been shown to affect DOC both in lakes (Strome & Miller 1978; Salonen & Vähätalo 1994; Schindler et al. 1996) and in marine waters (Kieber et al. 1990), and has been indicated as a major process in the mineralization of terrestrially derived DOC in oceanic water (Mopper et al. 1991; Miller & Zepp 1995). It has been shown that purely abiotic photodegradation of DOC can produce CO_2 (Valentine & Zepp 1993; Salonen & Vähätalo 1994; Granéli et al. 1996), CO (Miller & Zepp 1995) and low molecular weight carboxylic acids (Mopper et al. 1991; Wetzel et al. 1995; Bertilsson & Allard 1996). The latter are good bacterial substrates. Thus, photodegradation of DOC could lead to enhanced production of bacterial biomass (Lindell et al. 1995; Wetzel et al. 1995).

Since DOC represents a dynamic component in the interactions between geosphere, hydrosphere and biosphere, it has the potential to influence the global carbon cycle and climate change. Theoretically, the net result of exposure of DOC to solar radiation is an increased DIC-production and a higher turnover rate of DOC through (1), abiotic production of DIC and (2), production of bacterial substrate, increasing bacterial production rate, biomass and rate of respiration, i.e. CO_2 production. Thus, photodegradation of DOC may increase carbon flow. However, this does not take into account direct detrimental effects on bacteria from solar radiation, which have been shown for both marine waters (Herndl et al. 1993) and lakes (Lindell et al. 1996).

The importance of UV-radiation for the decomposition of DOC and especially DHM (dissolved humic matter) was stressed by Strome and Miller (1978). Mopper et al. (1991) suggested that photochemical degradation is the rate-limiting step for the removal of a large fraction of oceanic DOC. According to Kieber et al. (1990) photolysis causes riverine DOC in the sea to break down with a half-life of 5–15 years, much shorter than previously thought. Miller and Zepp (1995) report photochemical production of both CO and CO_2 in water from riverine, near coastal and salt marsh sources; CO_2 production being several times higher than CO production rates. The authors calculated that the half-life of terrestrial DOC in the mixed layer of the ocean would be merely 1.5 years because of photodegradation. Granéli et al. (1996) have shown that measurable quantities of DIC are produced as a consequence of solar radiation acting on DOC in lakes of varying humic content in South

Sweden. The pool of DOC in a moderately humic lake could theoretically be completely mineralized to DIC in a few years due to photodegradation. Somewhat lower rates were found by Salonen and Vähätalo (1994) in a lake in Southern Norway.

It is often thought that the UV-B wavelength band in solar radiation is mainly responsible for photodegradation of DOC and negative effects on pelagic organisms (Kieber et al. 1990; Herndl et al. 1993; de Haan 1993). However, UV-A and even PAR, could have effects on DOC and organisms (Sieracki & Sieburth 1986; Valentine & Zepp 1993; Lindell et al. 1996). Our previous *in situ* measurements indicated that photooxidation occurs deeper in the water column than the penetration of UV-B radiation, and that the surface rate of photooxidation is related to the concentration of DOC in the water (Granéli et al. 1996). However, we had no direct measurements of photooxidation in relation to different wavelength bands (UV-B, UV-A and PAR). It was also unclear whether our rates of photooxidation in South Swedish lakes would be representative for fresh waters in other climatic zones (c.f. Valentine & Zepp 1993; Scully et al. 1996). Beside quantity and quality of solar radiation, photodegradation may also depend on the concentration and the quality of DOC.

In this study, we have investigated photodegradation of DOC due to different wavelength bands (PAR, UV-A and UV-B) in solar radiation and as influenced by DOC concentration in a number of lakes in Brazil and in Sweden. The objective was to establish if there are general patterns in photodegradation of DOC in surface waters comprising a DOC gradient and representing different climates with different spectral composition and intensity of solar radiation. We hypothesized that DOC from tropical freshwaters would be less reactive towards solar radiation than DOC from temperate waters, as the annual solar radiation dose (especially UV-B) is more intense at low latitudes, hypothetically causing DOC to become photo-recalcitrant. Lakes in Brazil and in Sweden were chosen to represent a wide spectrum of DOC/humic content under contrasting climatic conditions.

Materials and methods

DIC is here defined as the sum of dissolved CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}. We studied photooxidative production of DIC in filter-sterilized water incubated in UV-transparent quartz tubes in full natural solar radiation and with various filters for 6 hours, ±3 hours around true noon, close to summer solstice conditions.

Studies on rates of photooxidative DIC-production were made in 5 oligotrophic lakes close to the limnological field station at Aneboda (the Einar

Naumann laboratory, 57°07′ N, 14°34′ E), ca. 30 km north of Växjö in southern Sweden (Table 1) and in 4 coastal lakes close to Macaé in Brazil (22°21′ S, 41°46′ W), ca 150 km NE of Rio de Janeiro. A sample was also obtained from Rio Negro, upstream of Manaus in the Brazilian Amazon region (3°9′ S, 60°0′ W). Lakes were chosen to represent a spectrum from clear-water to highly humic conditions, both in Sweden and in Brazil. Another criterion was a low inorganic carbon content in order to facilitate detection of changes in DIC after exposure to solar radiation (Granéli et al. 1996). However, some of the Brazilian lakes had comparatively high DIC content, probably due to marine influence, since several of these lakes were separated from the sea with a sand bar only. Photooxidation experiments with Swedish lake water samples were done from July 9 to 12, 1995 and for Brazilian samples from January 20 to 29, 1996, i.e. during periods for both areas with close to maximal potential solar radiation. Experiments were performed only on clear and sunny days.

For the Swedish lakes water was taken from the epilimnion using a 2 m long, 50 mm i.d. Plexiglas tube, which was emptied into a 10 l polyethene container. For the Brazilian lakes water was filled from ca 0.5 m depth into 1 l polyethene containers. Until water was used for measurements of photooxidation (within 1–7 days) it was stored in darkness at room temperature (Sweden) or in a refrigerator (Brazil). Water was passed stepwise through 142 mm Gelman A/E and 0.2 μm membrane filters (Supor-200$^{\mathrm{TM}}$, Gelman Sci.) into 10 l Pyrex bottles using a peristaltic pump (Sweden). Finally, the water was sterile-filtered under low vacuum ($<$300 mbar) into quartz or borosilicate tubes (Ø = 40 mm, l = 200 mm, volume = 190 ml) using 0.2 μm VacuCap$^{\mathrm{TM}}$ filters (Gelman Sci.). For the Brazilian experiments water was prefiltered through 47 mm Whatman GF/F filters and 47 mm 0.2 μm membrane filters (Schleicher & Schuell BA 83) before being filled into quartz or borosilicate tubes (Ø = 22 mm, l = 145 mm, V = 37 ml) using VacuCap$^{\mathrm{TM}}$ filters (Gelman Sci.). Before use, tubes were washed in dilute hydrochloric acid (1:10), rinsed in deionized water and autoclaved. Borosilicate tubes were wrapped in aluminium foil and used for dark exposure.

Tubes were positioned horizontally on steel wire platforms. Platforms were placed on supports in children's plastic swimming pools with the tubes half immersed in water, ensuring that no shading occurred. One set of tubes from each lake was exposed to full solar radiation, a second set was covered with UV-transparent Plexiglas (Röhm GS 2458 Plexiglas, $\geq$ 90% transmittance at wavelengths $\geq$ 300 nm) covered with Mylar foil (Du Pont de Nemours$^{\circledR}$; quality Mylar D$^{\mathrm{TM}}$, cut-off at 318 nm), excluding UV-B radiation, and a third set of tubes was covered with Plexiglas transparent to visible light only, (Röhm GS 233 Plexiglas, $<$1% transmittance of UV-B;

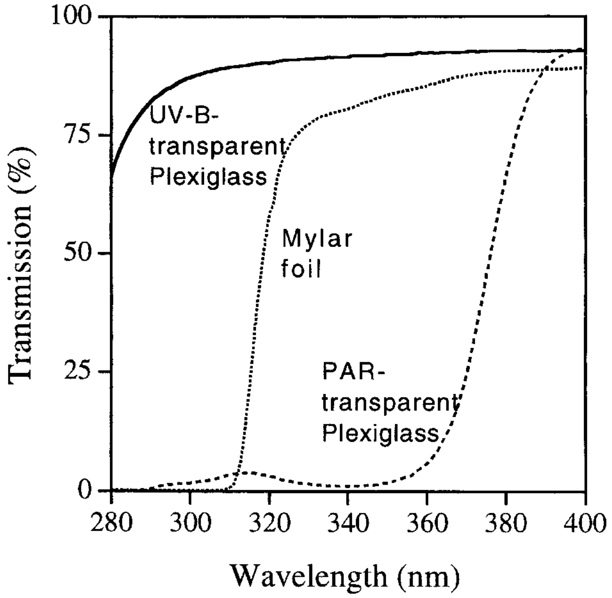

Figure 1. Transmission of filters for screening out UV-B (<320 nm) or both UV-B and UV-A (<400 nm) of natural solar radiation. UV-transparent Plexiglas was used as support to the Mylar foil.

28% transmittance of UV-A {average per wavelength 320–400 nm} almost all UV-A transmittance was at wavelengths >370 nm) (Figure 1). A fourth set of tubes was covered with aluminum foil as a dark reference, i.e. solar radiation mediated DIC-production was calculated from DIC in solar exposed samples minus DIC in dark samples. Incubations were made from −3 to +3 hours around true noon, i.e. total incubation time was 6 hours. During incubation, temperature in the pool was checked frequently and cold water or ice was added to maintain the temperature in the pool at +22±2 °C (Sweden) or at +35±3 °C (Brazil). To check for differences in DIC-production between tubes of different diameter, lake water from two Swedish lakes with contrasting humic content (Fiolen and Skärshultsjön) were sterile-filtered as above, exposed in narrow tubes (the type used in Brazil) and in wider tubes (used in the Aneboda experiments) to full natural solar radiation 6 hours around noon during a cloudless day in the beginning of July 1997. For each tube type (narrow and wide) and radiation treatment (full and dark) 4 replicates were used.

Secchi-depth and a radiation profile were recorded for each lake (excluding Rio Negro). Downward irradiance was measured with an IL 1400A radiometer (International Light$^{\text{TM}}$) connected to three different sensors with cut-off filters (PAR: 400–750; UV-A: 320–400; UV-B 280–320 nm). Because UV-B radiation was already extinguished after a few centimetres in the more humic lakes, lake water was poured into a wide container with low walls and the sensor was fixed on the bottom. Water level was increased in mm intervals. Vertical attenuation coefficients were calculated for each wavelength band (PAR, UV-A and UV-B) by fitting straight lines to ln-transformed radiation data over depth for each of the five lakes in Sweden and the four in Brazil ($r^2 = 0.79$ to 0.97). The UV-B sensor has a response centre at about 313 nm, and measures UV-radiation in the 300–320 nm wavelength band (Kirk et al. 1994). Vertical attenuation coefficients (representing the 300–320 nm band) calculated from measurements with this instrument are in reasonable agreement with values calculated from more advanced radiometers and spectroradiometers (Kirk et al. 1994). Attenuation values from Swedish lakes were obtained in 1994, during the same time of the year as sampling in 1995 (Granéli et al. 1996) and are presented here for comparison to the Brazilian lakes.

Solar radiation was also measured above water during the day at approximately hourly intervals, from 10 am to 16 pm, during the days of incubation. The low sensitivity of the sensor over part of the UV-B band results in almost nine fold less energy being detected in total solar UV-B radiation compared to more advanced instruments (unpubl. res). Thus, the UV-B radiance should only be used for relative comparisons between Sweden and Brazil.

After incubation, tubes were retrieved (protected by black plastic) and brought immediately ($<$5 min) to the laboratory for DIC-analysis. At least 3 DIC-measurements were made for each tube, resulting in a CV of less than 2% (see Granéli et al. 1996). DIC-calibration was carried out using standard solutions in serum bottles.

Dissolved organic carbon was analysed by transferring 0.2 μm sterile filtered water into acid rinsed, precombusted (+500 °C, overnight) glass vials with screw caps. The DOC-vials were placed in a refrigerator when analysis was made within a few days or, in case of later analyses, immediately frozen. DOC was analysed by the Pt-catalysed high-temperature combustion method using a Shimadzu TOC-5000 total carbon analyzer.

A portion of the water in the tubes was used for measurements of absorbance at 250, 365 and 430 nm on a Beckman DU®650 (Sweden) or a Shimadzu UV-210A (Brazil) spectrophotometer using 1 or 5 cm quartz cuvettes.

Mean DIC-values for each treatment (tubes exposed to PAR + UV-A + B; PAR + UV-A; PAR and darkness) were calculated. We assume an increase in DIC in solar radiation treatments compared to dark controls to represent photooxidative DIC-production from DOC (Granéli et al. 1996). The difference between Full-radiation and Mylar covered treatments is the effect of UV-B radiation and the difference between Mylar and Plexiglas covered treatments represents the effect of UV-A. Similarly, the difference between Full-radiation and Plexiglas depicts the effect on photooxidative DIC-production of UV-A + UV-B together. Plexiglas minus dark treatment values represent PAR effects (see Figure 1).

For comparison, we have used values for photooxidation from an *in situ* study done in 1994 in the same Swedish lakes as in the present study, and under similar solar radiation and temperature conditions. The 1994 study used essentially the same methods as in the present study (Granéli et al. 1996), the difference being that tubes were incubated *in situ* at different depths and without any filters (only dark and Full-radiation). Tubes incubated at the surface in the lakes are equivalent to the 1995 Full-radiation treatments, except that incubation time was from dawn until dusk. Wherever necessary, we have recalculated these values to a 6-hour period around true noon using the relation between solar radiation doses during the incubation periods. This ratio (full solar radiation dose during 6 hours around true noon in relation to a whole day of solar radiation from dawn until dusk) is approximately 0.75 for surface incubated samples in southern Sweden.

Statistical analyses have been performed on log-transformed data (ANOVA with Fisher's PLSD post-hoc test, and linear regression).

Results

Secchi depth varied between 1.5 and 7.6 m for the Swedish lakes and between 0.3 and 1.6 m for the Brazilian lakes. DOC-content was 2.9 to 15.3 mg l^{-1} in Sweden and 9.9 to 41.8 in Brazil (Table 1). These DOC values are for the sterile-filtered water used in the experiments, and may thus be lower than the in situ values due to precipitation during storage/handling or retention of DOC on filters. Absorbance at 250 nm was positively related to DOC ($p < 0.0001$, $n = 15$) (Figure 2A). Absorbance ratio 250/365 decreased with increasing DOC-concentration ($p < 0.0001$, $n = 15$). Initial DIC-concentration was not related to DOC ($p = 0.1$, $n = 10$).

Solar radiation intensity of all three wavelength bands decreased exponentially with depth in all lakes ($p < 0.001$). Vertical attenuation coefficients (K_d) in the five Swedish lakes, ranging from 0.4 to 2.6 $m^{-1}$for PAR, 1.2 to 3.9 m^{-1} for UV-A, and 4.53 to 150 m^{-1} for UV-B, as well as in the four Brazilian lakes (1.6 to 6.65 m^{-1}, 1.6 to 5.3 m^{-1} and 92.4 to 466 m^{-1}, respectively) were positively related to DOC ($p < 0.001$ for PAR, UV-A and UV-B, respectively, df = 8). UV-B radiation was effectively attenuated by DOC. In the most clear lake (Klintsjön) the 10% depth for UV-B measured with our radiometer was 0.51 m, but in the most humic lake (Comprida) the corresponding depth was only 0.5 cm (Table 1).

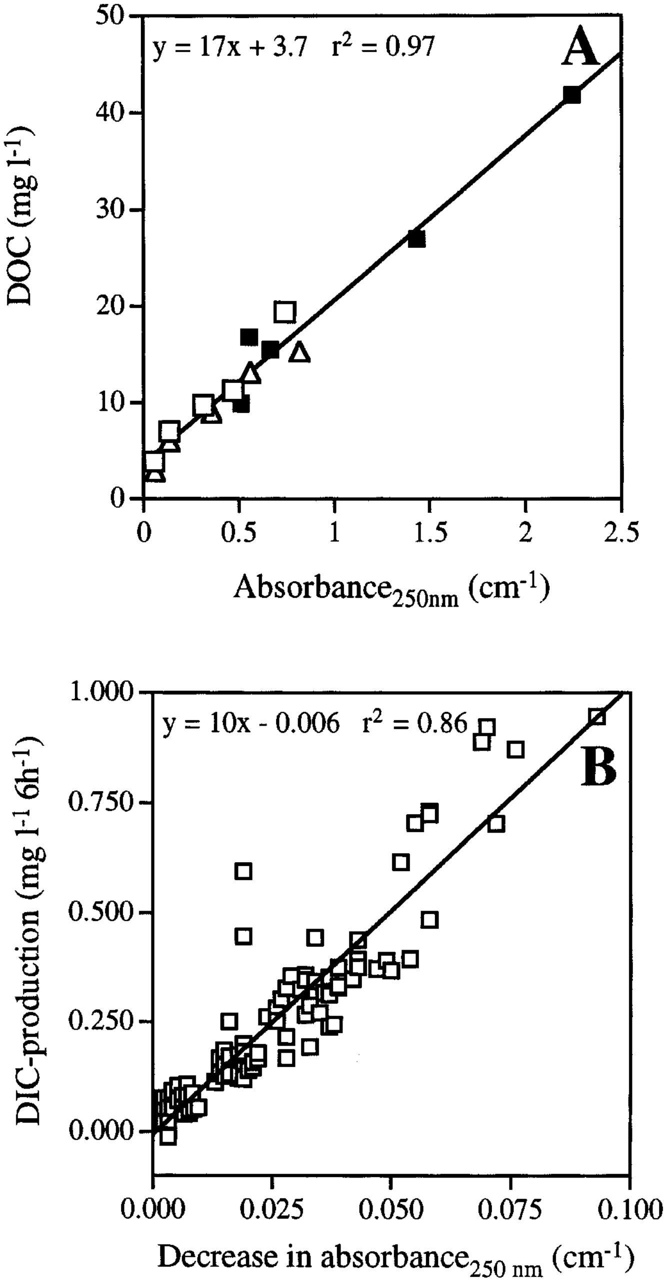

Figure 2. DOC-concentration in relation to absorbance at 250 nm in Swedish lakes 1994 (open squares) and 1995 (open triangles) and Brazilian lakes 1996 (filled squares) (A). DIC-production relative to loss of absorbance at 250 nm in Swedish lakes 1995 and Brazilian lakes 1996 (B).

Table 1. Characteristics of the investigated lakes in Sweden and Brazil. DOC, DIC and absorbance represent data of dark exposed samples, thus not strictly representing *in situ* values. Attenuation coefficients and depth corresponding to 10% (in parantheses) of surface solar radiation is given. (ND = not determined).

Lake	DOC $(\mathrm{mg\ l^{-1}})$	DIC $(\mathrm{mg\ l^{-1}})$	Abs Abs (430 nm)	Secchi depth (m)	K_dPAR $(\mathrm{m^{-1}})$	K_dUVA $(\mathrm{m^{-1}})$	K_dUVB $(\mathrm{m^{-1}})$
Klintsjön	2.9	0.155	0.001	7.6*	0.44* (5.2 m)	1.24* (1.9 m)	4.53* (0.51 m)
Fiolen	6.0	0.456	0.005	5.5*	0.55* (4.2 m)	1.91* (1.2 m)	22.4* (0.10 m)
Stråken	9.0‡	1.078	0.018	2.9*	1.28* (1.8 m)	1.67* (1.4 m)	34.3* (0.067 m)
Skärshultsjön	13.1	0.181	0.039	1.9*	2.05* (1.1 m)	1.36* (1.7 m)	69.3* (0.033 m)
Lindhultsgöl	15.3	3.905	0.063	1.5*	2.56* (0.90 m)	3.89* (0.59 m)	150* (0.015 m)
Rio Negro	9.9	0.551	0.049	nd	nd	nd	nd
Carapebus	16.8	9.677	0.024	1.6	1.63 (1.4 m)	1.60 (1.4 m)	92.4 (0.025 m)
Cabiunas	15.5	4.448	0.092	0.9	2.83 (0.82 m)	2.39 (0.96 m)	180 (0.013 m)
Coca Cola	27.0	2.280	0.213	0.4	6.65 (0.35 m)	5.03 (0.46 m)	119 (0.019 m)
Comprida	41.8	0.808	0.223	0.3	5.80 (0.40 m)	5.34 (0.43 m)	466 (0.0049 m)

* Data from Granéli et al. (1996)

‡ Value based on an average of a few uncontaminated samples of the whole serie.

PAR and UV-A integrated over the incubation period (±3 hours around true noon), were similar for Sweden and Brazil, 17% and 8% more in Brazil, respectively, while UV-B doses during sample incubation in Brazil were 3.33 times those in Sweden (integrated solar energy by using best fitted curve to data of hourly solar radiation intensity values, 5th degree polynomial, $R^2 > 0.9$) (Figure 3).

Photochemical DIC-production in wide tubes containing clear Fiolen water was significantly higher compared to production in narrow tubes (Mann-Whitney U-test, $p < 0.05$, $n = 4$), although in absolute numbers the difference was small, 0.025 mg DIC l^{-1} $6h^{-1}$ (0.062 versus 0.037). This is in the range of the standard deviation of DIC measurements for replicate tubes of the same diameter, 0.01–0.03 mg DIC l^{-1} (Graneli et al. 1996). Mean photochemical DIC-production in wide tubes containing humic Skärshultsjön water was lower compared to that of narrow tubes (0.364 versus 0.390 mg DIC l^{-1}), but this difference (0.026 mg DIC l^{-1}) was not significant ($p > 0.05$, $n = 4$). We conclude that even if there was a significant difference in DIC-production between narrow and wide tubes, this difference was small (on the order of the standard deviation of DIC measurements for replicate tubes) and there was no consistent tendency for either an under- or overestimation of DIC production in narrow compared to wide tubes.

DIC-production varied between 0.088 and 1.694 mg C l^{-1} in Full-radiation, 0.066 to 1.386 mg C l^{-1}in Full-radiation minus UV-B (i.e. exposed to PAR + UV-A) and 0.016 to 0.735 mg C l^{-1} in Full-radiation minus UV-A and UV-B (i.e. exposed to PAR only) (Figure 4). DIC-production differed significantly between exposures Full, PAR + UV-A, PAR and dark) in every case ($p < 0.0001$), except for the Full vs PAR+UV-A and PAR vs Dark exposures ($p > 0.05$) of the two oligohumic lakes, Klintsjön and Fiolen, and in the most humic Swedish lake, Lindhultsgöl, as well as in Rio Negro water, between Full vs PAR+UV-A ($p > 0.05$).

DIC-production was positively related to the DOC-content of the water for all three solar radiation treatments (Figure 5), both when the lakes from each area were tested separately (Sweden: $p < 0.0001$, df = 24; Brazil: $p < 0.0001$, df = 19) and when values from Brazil and Sweden were pooled ($p < 0.0001$, df = 44) (Figure 5). The individual slope coefficients of the two areas differed significantly from each other in Full radiation treatment, but not in PAR+UV-A and PAR only exposure (T-test between slopes). X-intercepts for linear regression were positive, 2.9, 2.3 and 3.3 mg DOC l^{-1} for the pooled data set of samples exposed to Full solar radiation, PAR + UV-A and PAR only, respectively (Figure 5). Photooxidative DIC-production per unit DOC and wavelength band did not differ significantly between the two areas ($p > 0.05$) although there was a tendency for DIC-production per unit DOC to be

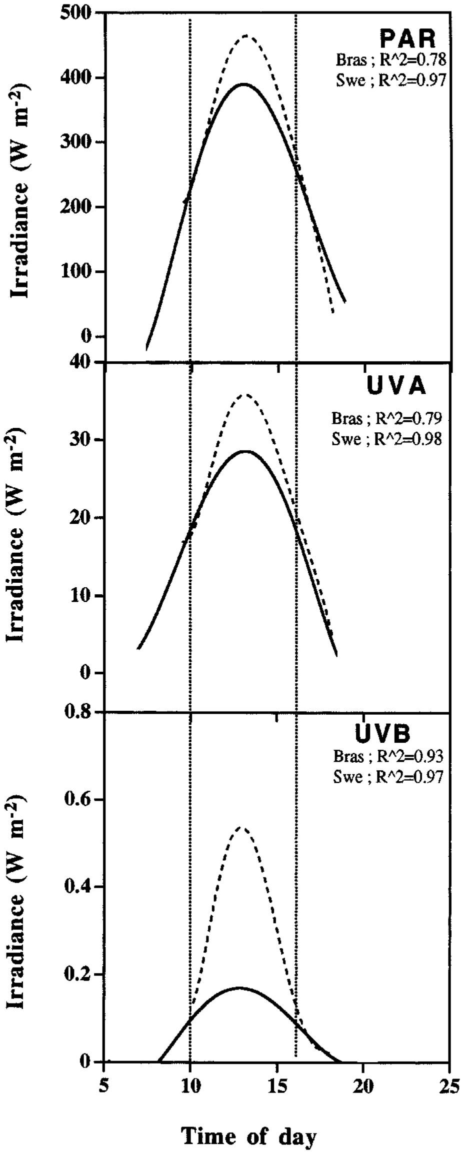

Figure 3. Mean intensities of PAR, UV-A and UV-B radiation from natural solar radiation at ground level during days of incubation in Sweden (solid line) and Brazil (dashed line). Vertical dashed lines illustrate time interval for exposure of samples (10 AM to 4 PM, summer time). Values were obtained with an International Light 1400A radiometer; especially for UV-B irradiance only relative comparisons between regions should be made (see Materials and Methods).

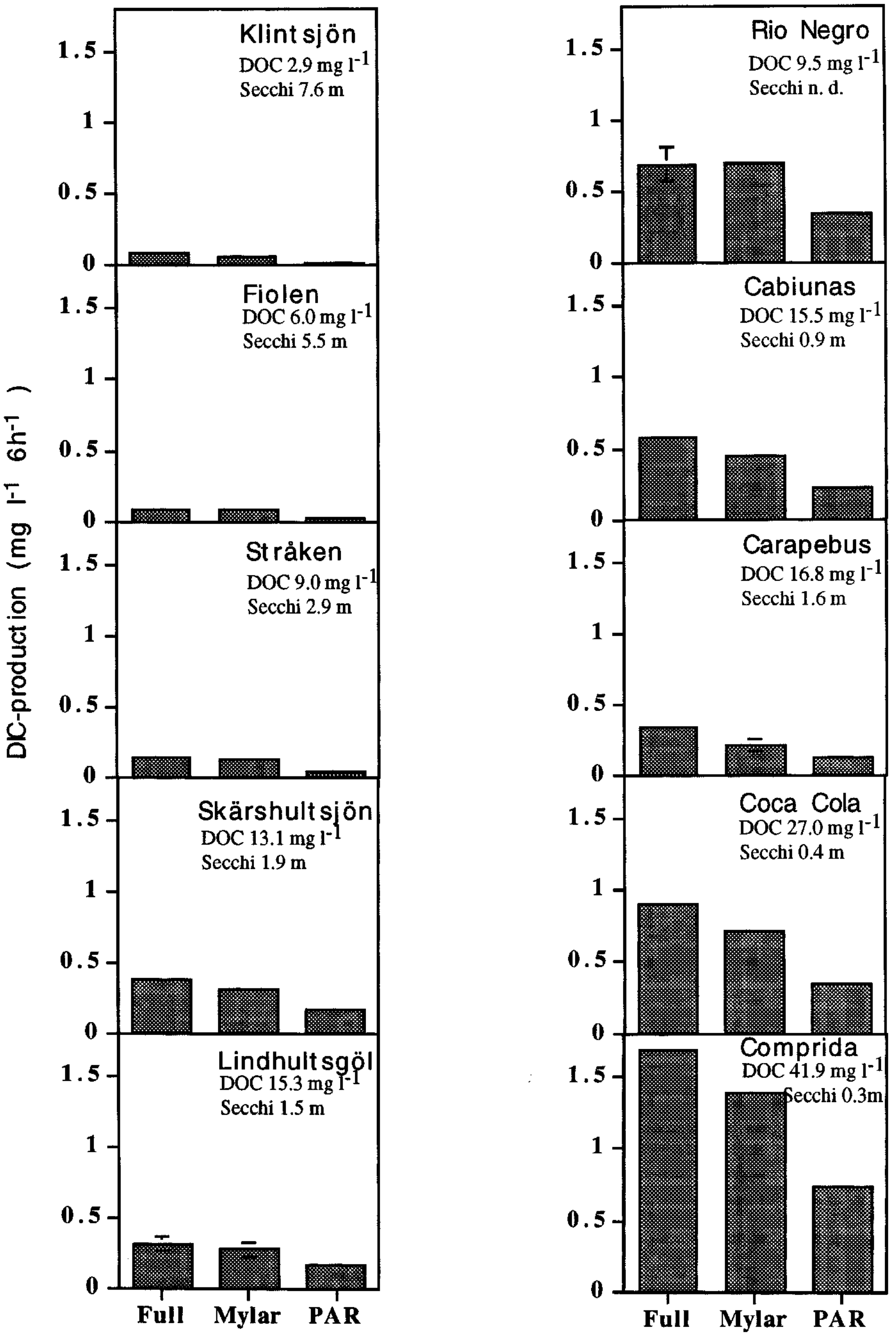

Figure 4. Abiotic photooxidative DIC-production in samples exposed to different wavelength bands of solar radiation during cloudless days ±3 hours around true noon for water from different lakes in Sweden (left) and Brazil (right).

somewhat higher in Brazil (Figure 6). DIC-production was positively related to decrease in absorbance at 250 nm ($p < 0.0001$, $R^2 = 0.819$, df = 113) (Figure 2B) but not to changes in the 250/365 ratio ($p > 0.05$).

Since there was no significant difference between the Swedish and the Brazilian waters with respect to the proportions of total DIC-production caused by the various wavelength bands of solar radiation (Figure 6), relative DIC-production data of all lakes at both locations were pooled (Figure 7). The individual effects from UV-B, UV-A and PAR in the pooled data set represented 17%, 39% and 44%, respectively, of the total DIC-production (Figure 7).

DOC-decrease could not be measured with the same precision as DIC-increase (see also Granéli et al. 1996). Thus, for individual lakes, although the tendency was a decrease in DOC concomitant with the increase in DIC, the differences in DOC between treatments were not generally statistically significant ($p > 0.05$). The greatest differences were found for Full-radiation exposures vs Dark, where 50% of the different lakes showed significant differences ($p < 0.05$). Using all treatments and pooling data from both Sweden and Brazil, we found a positive relation between DIC-production and DOC-consumption ($p < 0.0001$, $R^2 = 0.3$, df = 98).

Discussion

Our hypothesis that DOC from tropical freshwaters would be less reactive towards solar radiation than DOC from temperate waters was not substantiated. Per mg DOC there was actually a somewhat larger DIC-production in the Brazilian waters, compared to the Swedish, although this difference was not statistically significant (Figure 6). The amount of UV-B radiation per day close to summer solstice conditions was substantially higher (approximately 3 times) in Brazil compared to Sweden. Higher UV-B radiation in Brazil compared to Sweden could result in a higher DIC-production per unit DOC carbon. On the other hand, prolonged UV-B-radiation could also result in photoresistant DOM, being refractory towards further photodegradation. If we normalize UV-B-induced DIC-production per unit DOC to the amount of UV-B radiation in Sweden, the two areas show equal photosensitivity (Figure 6A) and there is also no differences between Brazil and Sweden with respect to UV-A-induced photooxidation (Figure 6B). Only PAR-normalized values showed higher mean DIC-production per DOC in Brazil, although not significant (Figure 6C). These results confirm findings by Valentine and Zepp (1993), who showed remarkably similar photoproduction of CO in natural waters from different areas, and the conclusions of Scully et al. (1996) who

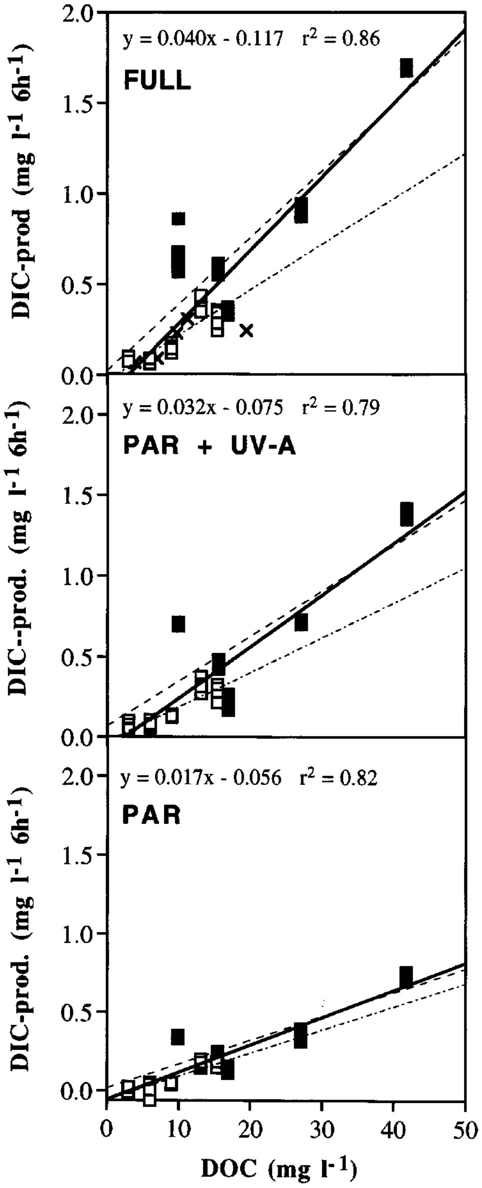

Figure 5. DIC-production relative to initial DOC-content of water exposed to different wavelength bands in Sweden (open symbols) and Brazil (dark symbols). Correlation based on the complete data set (*n* = 45). The dashed lines indicate the individual areas (Sweden - - - -, and Brazil - - - -). Also shown for full-radiation are values (x) from Aneboda lakes 1994 (*n* = 5) (see text).

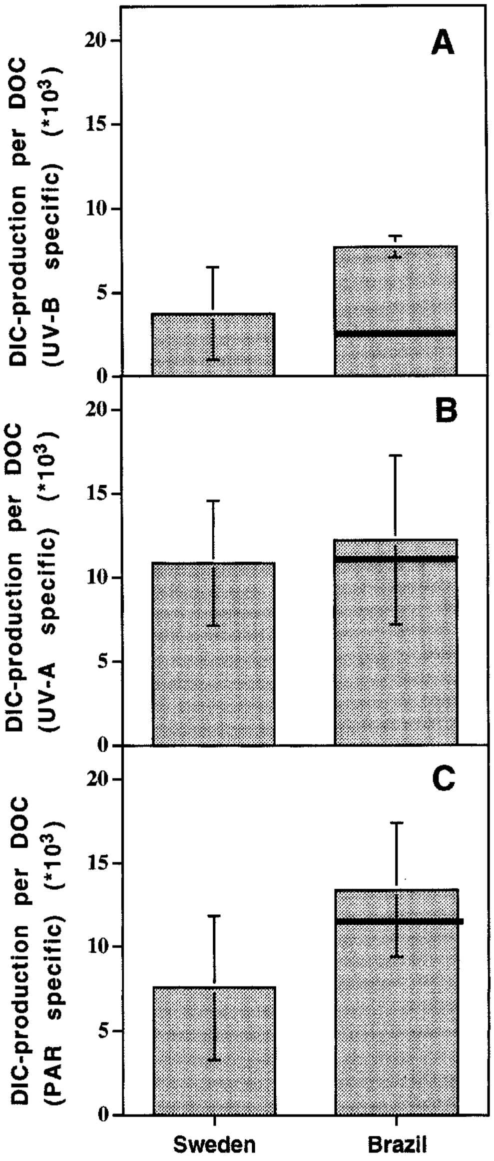

Figure 6. DOC-specific and wavelength band dependent DIC-production of lake water from Sweden ($n = 5$) and Brazil ($n = 5$). Error bars are ±1x SD. Horizontal lines on bars for Brazilian lakes are DIC-production values recalculated to the solar radiation energy as received by the Swedish samples during a 6-hour incubation, i.e. representing DIC-production in Brazil when assuming exposure to solar energy as in Sweden. No differences are significant, neither for original values, nor for radiation-normalized values.

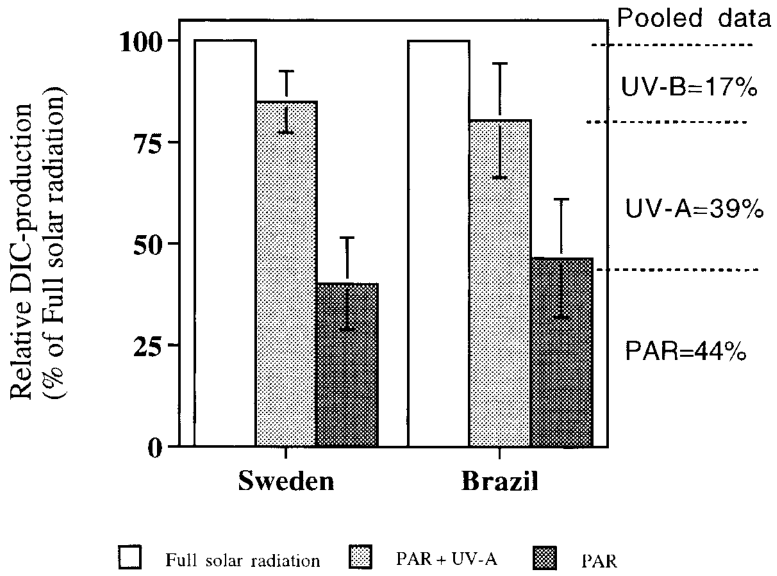

Figure 7. Relative (in relation to production in Full-radiation) DIC-production of sterile filtered lake water from Sweden (n = 5) and Brazil (n = 5) in Full-radiation, Full-radiation minus UV-B (Mylar shielding) and PAR (Plexiglas shielding). Error bars are ±1x SD. Numbers on right-hand side of graph indicate mean contribution from each wavelength band based on the pooled data set (n = 10).

state that the photooxidative production of H_2O_2 does not differ in lake waters from a 43–75° N gradient.

A higher DOC-and radiation normalized DIC-production of Brazilian samples (only found for PAR, but not statistically verified, Figure 6) may be due to the use of narrow quartz tubes in Brazil. In the wide tubes, which were used only in Sweden, one might expect part of the water volume to be unaffected by solar radiation due to high attenuation, especially in highly humic lakes. However, we found no such effect when we compared the two types of tubes.

It is possible that DOM in areas experiencing highly variable solar radiative conditions (e.g. temperate zones) exhibit annual cycles with high DOM photosensitivity during spring, since solar radiation is low during winter and rapidly increases in spring and low photosensitivity in late summer/fall. However, tropical areas are also subjected to annual cycles (rainperiods etc). The residence-time of water in the Brazilian lakes used in the present study is not well defined, due to location in sandy areas with no visible riverine influences. Presumably, these lakes are mainly ground water fed. During the period preceeding our measurements precipitation was high, which may have caused new humic matter to enter the lakes from the catchment area. Precipitation before the experimental period in Sweden was on the other hand low, implying low recent allochthonous DOM input to these lakes. Thus, different DIC-production normalized to solar radiation and DOC between lakes in this study may, except for initial differences in the quality of the organic matter being produced in or delivered to the lakes, be due to solar radiation and runoff conditions during a several-month period preceeding the measurements of photooxidation. However, it is remarkable that the magnitude of photooxidative DIC-production normalized to unit solar radiation and DOC were so similar in lakes of widely contrasting humic content (a measure of degree of allochthonous influence on DOC) situated in very different climate zones (Figure 6).

The 250/365 nm absorbance ratio has been implied as a rough estimate of the proportion of smaller versus larger organic molecules in natural waters (Strome & Miller 1978). This ratio showed a decrease relative to DOC-content, which can be interpreted as an increasing proportion of larger molecules with increasing DOC, possibly implying a higher proportion of dissolved humic matter, in this case of terrestrial origin (Tranvik 1990). These larger humic molecules may have greater capacity for photooxidation due to a larger relative amount of chromophores. There was however, no consistent pattern in the rate of photooxidation per unit DOC (Figure 6).

DIC-production under similar solar radiation conditions increased more or less linearly with initial DOC-content of samples (Figure 5). There was no large difference in this relationship between waters from the two areas, for any of the three wavelength bands. Since there are no data from other studies to compare with, the generality of this relationship for other fresh or marine waters is unknown. The data set from the Aneboda lakes 1994, where we made in situ incubations at various depths, using the same type of tubes as for the lake waters investigated in the present study (Granéli et al. 1996), fits well into the relationship after recalculations to 6 h incubations instead of dawn to dusk (Figure 5).

If a linear relationship is assumed between photooxidative DIC-production and DOC-concentration, a positive X-intercept of 2–3 mg DOC l^{-1} is found (Figure 5). A positive intercept implies that below a certain threshold DOC should be resistant to photooxidation, at least in natural solar radiation. Although this may be possible, e.g. due to some residual DOC with very low light absorption characteristics, it is perhaps more likely that the relation is not linear for low DOC-concentrations. Further investigations in the lower end of the natural DOC-concentration spectrum are necessary (Scully & Lean 1994), especially since a large fraction of surface waters, e.g. marine waters, are found in this DOC-concentration region. Furthermore, it has recently been suggested that small molecules may constitute a recalcitrant pool of organic matter, being less available for bacteria than large molecules (Tranvik 1990; Amon & Benner 1996) and possibly also resistant to photolysis/photooxidation.

DIC-production is accompanied by a decrease in absorbance at 250 nm, implying a decrease in DOC (Figure 2B). Using values of DIC-production from Aneboda 1994 (Granéli et al. 1996) as well as the values for Aneboda 1995 and Brazil 1996, measured with three different incubation procedures (in situ from dawn to dusk, in large and small quartz tubes ±3 hours around true noon, respectively) and absorbance values measured with three different spectrophotometers, it is found that a unit change in absorbance is equivalent to approximately 10 mg DIC (see Figure 2B). The relationship between absorbance at 250 nm and DOC-concentration for the same samples imply that a unit change in absorbance is equivalent to approximately 17 mg DOC (Figure 2A). Although this is more than the increase in DIC for the same decrease in absorbance, the agreement is still reasonable given the use of different protocols and instruments and also considering that solar radiation may produce smaller organic molecules, which may not have the same absorbance per unit DOC as the original material.

One of the most striking findings in this study was that photooxidation of DOC to DIC was not effected exclusively by UV-B radiation despite the optimal exposure conditions (samples submerged only to half the diameter of tubes, sunny days etc). PAR had the largest effect (44%) and UV-A (39%) was also more important than UV-B (17%) (Figure 7). The importance of PAR compared to UV-radiation (44% versus 56%) may be partly explained by the interference of longwave UV-A penetrating the PAR-Plexiglas filter and affecting the PAR treatments (Figure 1). Approximately 50% of the UV-A radiation >370 nm is included in the PAR treatment and, hence, the calculated importance of PAR may be somewhat exaggerated. The minor relative effect of UV-B in natural solar radiation compared to UV-A and PAR on DIC-production is in agreement with results of Valentine and Zepp (1993) and Scully et al. (1996) for photochemical oxidation of DOC to CO and photochemical production of H_2O_2, respectively.

The relative importance of the different wavelength bands is based on measurements representing water at the very surface of the lake, down to a few cm depth, depending on water characteristics. UV-B is attenuated much faster in the water column than is PAR and UV-A (Kirk et al. 1994; Scully & Lean 1994). PAR and UV-A vertical attenuation coefficients, as measured with the International Light radiometer, were similar, while attenuation coefficients for UV-B were 20–60 times larger than for PAR and UV-A (Table 1). This means that UV-B only affects a thin layer of the lake water, some few centimeters in humic lakes (Valentine & Zepp 1993). If the 10% depth of surface radiation is taken as a limit for significant photoeffects, then the lakes in Brazil and Sweden investigated by us would be affected by UV-B between less than a cm (Comprida) and 0.5 m (Klintsjön), by UV-A between 0.2 and 2.0 m and by PAR between 0.4 and 5.2 m (Table 1). Incident solar energy flux on a lake surface at the latitude of south Sweden (56° N) is approximately 90% PAR and 10% UV-radiation, of which only 0.5% is UV-B (Fredrik & Lubin 1994; Nielsen 1996). Thus, the total energy of UV-A is 20 times more than UV-B (Kirk et al. 1994). Although the energy per photon is higher for shorter wavelengths and UV-B is effectively absorbed by DOC, the small total energy in UV-B and the rapid attenuation in the water column, indicates that longer wavelengths may be more important for photoeffects in the water column of lakes. UV-B does not dominate photooxidation even at the surface, as shown in this study. Thus, one probably cannot expect any dramatic increases in photodegradation of DOC in lakes from ozone thinning since (I), UV-B has a small part in photooxidation, both at the surface and in the water column and (II), stratospheric ozone thinning does not affect UV-A and PAR radiation (Frederick & Lubin 1994), which according to this study, are most responsible for photooxidation. However, direct UV-B-effects on organisms (Herndl et al. 1993) and in combination with other environmental changes, e.g. acidification (Schindler et al. 1996), may still be of great importance in affecting aquatic ecosystems.

This study shows that photooxidation of DOC to inorganic carbon occurs in lakes of widely varying DOC-content, in both temperate and tropical climates. Photooxidation for a given solar radiation dose is proportional to DOC-concentration. Both UV-B, UV-A and PAR cause production of DIC from DOC, but UV-B has the smallest effect.

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