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Research Paper

Photochemical and microbial processing of stream and soil water dissolved organic matter in a boreal forested catchment in northern Sweden

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Abstract. Natural organic matter (NOM) from stream and soil water in a humic-rich headwater catchment in northern Sweden (initial total organic carbon (TOC) concentrations 10–40 mg C L^{-1}) was rapidly degraded by light and microbial activity in an incubation experiment. Concentration losses were 33–50% after 12 days of exposure to 69 W m^{-2} artificial PAR and 16 W m^{-2} UV radiation. Natural, unshaded mid-day solar radiation in the region (68°N 18°E) during the month of june is 159 W m^{-2} for PAR. In contrast to microbial organic carbon removal, TOC exponentially decreased upon radiation, which suggests that TOC is more rapidly oxidized by light than by ambient microbes. Further, rapid decline in TOC concentration implies the presence of a dominant pool of photo-labile compounds (p > 95%). A measured mass balance for carbon identified 50–75% of the degraded TOC as carbon dioxide after 12 days of exposure to light. The observed conversion of organic to inorganic carbon was accompanied by increases in pH and alkalinity, suggesting that photo-degradation of NOM potentially contributes to in-stream buffering capacity. The remaining refractory TOC changed in chemical character, including an altered molecular weight distribution with decreased average weight and a change in the proportions of humics as evidenced by absorbance ratios (A_{254}/A_{420}). Extrapolation of the experiment to natural headwater conditions show that photo-degradation is an important in-stream process that should be considered in calculations of carbon turnover in surface waters because of its influence on both TOC amount and character.

Key words. Photo-degradation; natural organic matter (NOM); headwaters; carbon dioxide; dissolved organic matter (DOM).

Introduction

Allochthonous organic carbon of terrestrial origin and autochthonous carbon is processed by different means in the aquatic environment including biological and chemical oxidation. Allochthonous organic carbon comprises an energy and carbon source for aquatic microbes (Moran and Hodson, 1990), and is the major energy input in many brown water lakes (Tranvik, 1989; Hessen, 1992). The assimilatory cleavage of C-bindings by bacteria results in a stepwise mineralization of organic material and production of carbon dioxide. Photo-oxidation of organic material has been found to produce low molecular weight organic carbon compounds (Kieber et al., 1990; Allard et al., 1994; Bertilsson and Tranvik, 2000) and also re-

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mineralises organic material to carbon monoxide and carbon dioxide (Mopper et al., 1991; Granéli et al., 1996; Miller and Zepp, 1995; Johannessen and Miller, 2001). Most aquatic systems are supersaturated with carbon dioxide (Kling et al., 1992; Cole et al., 1994) and a net source of carbon dioxide to the atmosphere (Cole and Caracao, 2001). The rate of photo-degradation has been found to decrease as the TOC concentration decreases. This has generally been interpreted as the gradual depletion of photo-reactive products, corroborated by the negative correlation between residence time and DOC concentrations in lakes (Lindell et al., 1996). The rate of DOC loss due to solar radiation also is higher in headwater streams compared to waters further downstream (Molot and Dillon, 1997), and dissolved organic matter (DOM) which has been pre-exposed to solar radiation produces less DIC when exposed to UV-radiation (Salonen and Vähätalo, 1994). These studies suggest that as terrestrial organic matter passes through aquatic systems as DOM, exposure to light renders it more photo-refractory over time. There is thus reason to suspect that soil water may contain a large fraction of photo-labile organic material as compared to surface waters which have recently been exposed to light.

There have been many studies on photo-degradation of lake and seawater DOC, but less is known about the potentially accelerated photochemical dynamics of fresh soil water DOC entering headwater streams. Rapid changes in NOM concentration and/or chemical composition/bioavailability could affect microbial productivity, potentially augmenting the rate of carbon loss from headwater streams and help to elucidate the dynamics of organic carbon in soils and headwater catchments (Kalbitz et al., 2000). Hemond (1990) proposed that losses of carbon within headwater streams may be important for the changes in buffering capacity.

Here we present the results of controlled aging of NOM collected at the soil-water interface within a boreal catchment in northern Sweden. The aim of this investigation was to compare the relative contribution of photo-oxidation and bacterial respiration to the oxidation of NOM, as well as to study changes in the chemical properties of apparent molecular weight, absorptivity and acid buffering capacity of NOM caused by these processes.

Methods

Study Site

This study was conducted with water from the 50 ha Svartberget catchment (Fig. 1) in northern Sweden. The catchment is forested with mature spruce and pine on

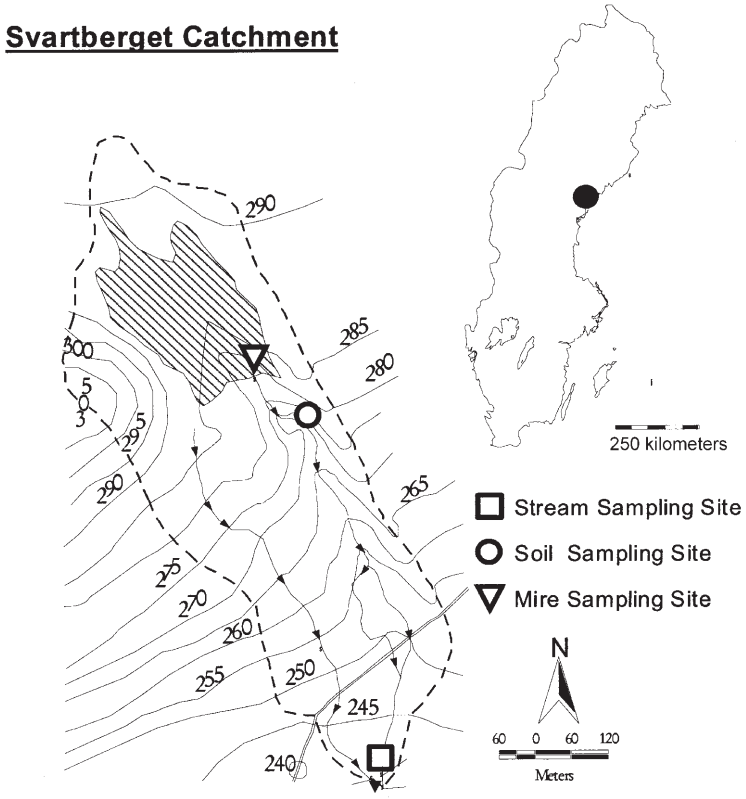

Figure 1. Map of the Svartberget catchment together with an inset map of Sweden. The sampling sites are labelled as follows: mire water (white triangle ▽), soil water (white circle ○) and stream water (white square □). The black shaded area symbolizes the extent of the mire. One of the two streams (black lines with arrows) de-waters the mire and was sampled just above the confluence.

podzol soils. An 8-ha mire is the source of Kallkällbäcken, one of two main tributaries. Much of the riparian zone, up to 10 m from the stream, is covered by peat 20–80 cm in depth overlying a mineral soil enriched in organic carbon. The site is more fully described by Bishop et al. (1994). Mean stream water TOC is 21 mg L^{-1} (1992–2000), and there is a strong positive correlation between discharge, acidity, and TOC, which together with other evidence indicates that TOC is the controlling factor for stream acidity (Grip and Bishop, 1990; Laudon and Bishop, 1999). Stream TOC is dominated (>95%) by the dissolved fraction (DOC). We collected water on June 13, 1996 at an ambient temperature of 10 °C from three sources within the catchment (Fig. 1), characterized by different concentrations of TOC: water from the mire outlet (high TOC), Kallkällbäcken stream water (intermediate TOC) and superficial soil water (low TOC). Sample water temperatures varied from 4.5–5.5 °C at the time of collection. The soil water sample was taken by collecting water from a small 80 cm deep pool excavated several years earlier at a site two meters from the stream in a peat soil. In order to obtain soil water with minimal recent exposure to light, the stagnant pool was emptied and covered with dark plastic, and the fresh soil water that refilled the pool was collected after one hour. All samples were collected in acid-washed 50 L polyethylene containers that were kept dark and transported within two hours to the laboratory cold room.

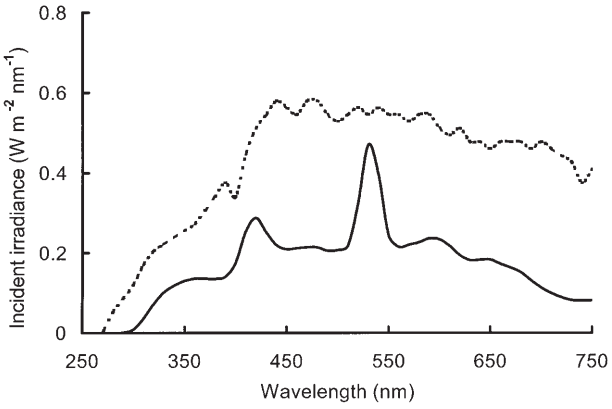

Figure 2. Spectra of ambient open-field solar radiation (hyphenated line) and effective artificial lamp radiation (solid line) passing through the borosilicate sample bottles.

Experimental design

The incubation experiment began approximately 12 hours after the samples had been collected in the field. The samples were filtered (1.2 µm Millipore Opticap prefilter with Milligard media) to remove bacterivores and larger particles (note that this also removes some of the larger bacteria), and then incubated in acid-washed 1-L glass bottles (10 cm diameter) at 15–20 °C for 12 days. The samples were incubated with a headspace volume (initially 150 mL) of ambient air to prevent artefacts of oxygen deficiency during DOM degradation; and thorough mixing of the bottles prior to sampling should assure that oxygen diffusion does not limit C degradation. Equivalent, filter-sterilized (0.2 µm Gelman Maxi Capsule Filter) samples were incubated as abiotic controls.

Parallel incubations were carried out in the dark and under light, using an artificial light source in a climate chamber amounting to 85 W m^{-2} at 280–800 nm, including 0.8 W m^{-2} UVB (290–320 nm), 10 W m^{-2} UVA (320–400 nm), and 69 W m^{-2} PAR (400–700 nm). Open field, long-term (1984–1996) average mean PAR radiation in a meteorological station ca. 400 km north of the catchment (68°N 18°E) is 135 W m^{-2} during the month of June. Incident radiation spectra were measured in the 400–700 nm range using a LICOR LI-190SA quantum sensor at the sample location (1.00 ± 0.05 m from lamps), and extrapolated to the UV region using spectral datasheets from OSRAM, Inc. for the HNS 55 W OFR lamps (Fig. 2). A spectral adsorption curve for the glass sample bottles was established by measurement of transmittance through the glass walls in a scanning spectrophotometer, and this was used to correct incident radiation for adsorption/scattering due to the bottle walls. The average path-length of light through the sample water varied from 8 cm to 3 cm over the course of the experiment due to the removal of water for analyses. Using the Beer-Lambert law and the path-length, the extent of self-shading was calculated for all samples in the light.

All treatments were carried out in duplicate bottles, which were carefully shaken prior to each sampling. Samples were taken after 0, 0.3, 0.8, 2.7, 5.8, and 11.8 days of incubation. The samples were analyzed for TOC, pH, alkalinity, major cation and anion concentration, absorbance at 254 nm and 420 nm, bacterial net production, and apparent molecular size of organic matter. Initial samples were were analysed for bacterial counts.

In a parallel setup, the total carbon balance of the system was studied for selected samples (two replicates for light and dark unfiltered treatment for the mire and one replicate for the unfiltered stream and soil for light and dark treatment, respectively) using gas-tight 500-mL bottles with an initial oxygen headspace volume of ca. 150 mL. Subsamples were taken with a septical syringe and a fresh needle that was pierced through a rubber membrane in the lid. An ascarite syringe was connected to the lid via a t-valve to allow for temporary CO_2-free air exchange during sampling. The samples were then transferred into previously evacuated capsules using new septical needles for each sampling. Carbon dioxide was analyzed in the headspace and selected samples were analyzed for inorganic carbon ($IC_{(aq)}$) and TOC in the water phase. The carbon mass balance in the bottles was then calculated, taking into account the different C pools

($CO_{2(g)}$, $CO_{2(aq)}$, $HCO^-_{3(aq)}$ and TOC), initial volumes, and all changes in both liquid and gas volumes throughout the experiment.

Analytical methods

Organic carbon (± 0.3 mg L^{-1}) and $IC_{(aq)}$ (± 0.1 mg L^{-1}) were analyzed using a Shimadzu TOC-5000 analyzer. After the initial filtering no supplementary filtration prior to analysis was undertaken, so values are reported as TOC. Headspace $CO_{2(g)}$ in the closed setup was analyzed using a Perkin Elmer Sigma II gas chromatograph with a methanizer coupled to a FID detector and a column packed with Porapak Q80/100 mesh. Injector, oven and detector temperatures were set at 35, 40 and 350 °C respectively. The average relative standard deviation of the three different CO_2 standards used here were 10%. Apparent molecular weight distribution of DOM was determined through high pressure gel permeation chromatography (Berdén and Bergren, 1990; Mueller et al., 2000) after filtering through a single-use 0.2-µm filter using a TSK-Gel G2000 SW (7.5 × 300 mm) column and a sodium-phosphate buffer at pH 7. The value reported for an individual sample is the apparent molecular weight corresponding to the peak of the observed distribution profile, which should be the most commonly occurring molecular weight of NOM in the sample. For this analysis, NOM was measured as Abs_{254}, using polystyrene sulfonates (PSS) standards of molecular weight varying from 1200–14500 daltons with an average error below 3.5%. True standard deviations of replicate samples are given in a figure below. Absorbance (± 0.005 units) and pH (± 0.05 pH units) were measured with a coupled pH-spectrophotometer flow system using a 1 cm cell. Cation samples were acidified and stored together with anion samples at 4 °C. Cations ($^{44}Ca^{2+}$, $^{25}Mg^{2+}$, $^{23}Na^+$, $^{39}K^+$, $^{27}Al^{3+}$ and $^{57}Fe^{3+}$) were measured using ICP-MS (± 5%), and anions (SO^{2-}_4, NO^-_3, Cl^-) were measured using HPLC ion chromatography (± 5%) for the initial and final samples. Gran acid neutralizing capacity ($Gran_{ANC}$) was determined with a Mettler DL50 automated titrator at 24 ± 1 °C with a precision of 2 µmol L^{-1}. Acid neutralizing capacity (ANC) was calculated by difference from the charge balance of initial concentrations of major cations and anions. Changes in strong organic acid concentration ($\Delta OA = OA_{initial} - OA_{final}$) were calculated as follows:

$$\Delta OA = \Delta ANC - \Delta Gran_{ANC} - \Delta H^+ \quad (1)$$

Strong organic acids are not titrated during the Gran titration procedure. As long as free protons are available every strong organic acid that is oxidized will produce HCO^-_3, consuming free protons without changing $Gran_{ANC}$. As $ANC = Gran_{ANC} + \beta \times TOC$ (Hemond, 1990; Köhler et al., 1999) one may estimate β from the above equation by plotting ΔOA against ΔTOC after accounting for changes in free protons. Bacterial production was measured from ^{3}H-leucine uptake by incubating samples in the dark at in situ temperature as described in Jansson et al. (1999). Bacterial numbers were counted by epifluorescence spectroscopy using DAPI (Porter and Feig, 1980). For each sample, 5–15 fields of 20–200 cells were counted, ensuring that at least 200 bacteria were enumerated per sample. The loss of TOC was used to estimate the degradation of organic matter in the experimental bottles. Bacterial respiration was calculated by integrating the measured production values and assuming a bacterial growth efficiency (BGE) of 20%[1] (del Giorgio et al., 1997). Photo-oxidation of carbon was estimated as the difference between the loss of TOC and the calculated bacterial respiration.

Results

Changes in bulk carbon pool

With few exceptions, all measured parameters were unchanged in the dark over the course of the 11.8 day experiment (linear regression with time, $p > 0.05$ for slope = 0). In general, the 0.2 and 1.2-µm filtered samples did not show significantly different behaviour for any of the analyses performed. Also, several of the 0.2-µm filtered samples showed significant bacterial productivity after 5.7 days of incubation. Since the presence/absence of microbes did not appear to measurably affect the bulk parameters that we measured, the different filtration treatments were pooled for the purposes of further graphical and statistical analysis, yielding four replicates per light/dark treatment.

In light-exposed water, TOC dropped significantly for all sites over the course of the experiment (Fig. 3). All sites showed an exponential decrease in TOC. The streamwater and soil water TOC decreased more quickly at first and then more slowly, while the mire sample decreased consistently throughout the 12-day incubation. Based on analyses of the best-fit exponentials, the size of the refractory pool which would remain after the samples were completely bleached was 7.1 ± 0.2 mg C L^{-1} for soil water, 9.9 ± 0.7 mg C L^{-1} for stream water, and 8.7 ± 7.7 mg C L^{-1} for mire outlet water. The labile pool was estimated at 3.8 mg C L^{-1} (35% of total) for soil water, 10.2 mg C L^{-1} (51% of total) for stream water, and 29.6 mg C L^{-1} (77% of total) for mire outlet water.

[1] Reported values for BGE vary widely. DOM Studies using natural microbial assemblages and streamwater DOM have given values in the 17–31% range (Kaplan and Bott, 1983; Meyer et al., 1987; Mann and Wetzel, 1995). For the purposes of our calculations, we use an intermediate value of 20% determined by del Giorgio et al., (1997) for aquatic systems with low primary productivity.

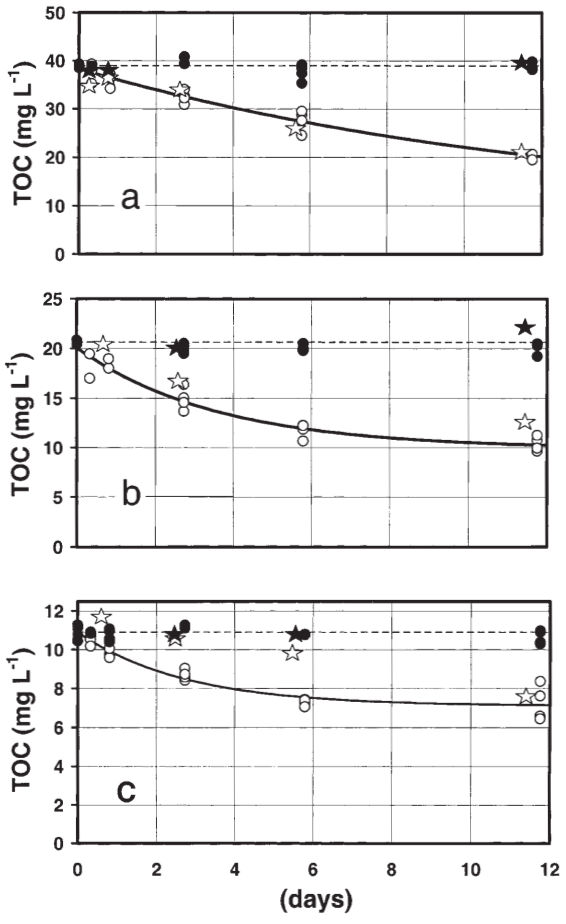

Figure 3. TOC degradation over time for (A) Mire outlet (B) Stream water and (C) Soil water. Dark treatments (black circle ●) showed no significant change over time (slope = 0 shown as dashed line). Light treatments (white circle ○) resulted in exponential decay of TOC over time (best fit exponential shown as solid line). Different filtration treatments are pooled together. The selected measurements done on the closed experiments for the dark experiments (dark star ★) and the light treatment (white star ☆).

Half-lives were estimated at 1.9 days for soil water, 2.5 days for stream water, and 8.7 days for the mire outlet water (Fig. 3). The entire labile pool appears to have been degraded for the soil water (–33% TOC) and stream water (–50% TOC) after 11.8 days of incubation, but the mire outlet water (–48% TOC) retained some labile material.

Comparison of open and closed systems

Between 50 to 75% of the loss in TOC was recovered as CO_2 in the parallel gas-tight incubations (Fig. 4, Table 1). The results for IC and CO_2 from the closed bottle setup are shown in Table 1, along with mean TOC for all samples. IC measurements done in the gas phase and the calculated concentrations for the liquid phase were summed to produce the reported value and then recalculated relative to the open system using the initial TOC from the open and closed systems. The calculated points of aqueous CO_2 represent results from equilibrium calculations using the appropriate equilibrium constants (Stumm and Morgan, 1980). Total inorganic carbon of the mire sample measured after one day and at the end of the experiment were within 15% of these calculated concentrations. TOC measurements in the closed bottles generally matched well with those made in the "full-experiment" open bottles (Figs. 3, 4). The mass balance that was calculated for the mire and the stream sample indicated that at least 70% of the initial TOC was transformed into aqueous $CO_{2\,(aq)}$ or gaseous $CO_{2\,(g)}$, while CO_2 production explained only 50% of the change in the TOC of the soil sample. A much smaller fraction, approximately 15% of the TOC, was on average left unaccounted for at the end of the experiment. One possible fate for this leftover pool is precipitation of particulates (observed visually in this study, and noted by Kulovaara and Back-

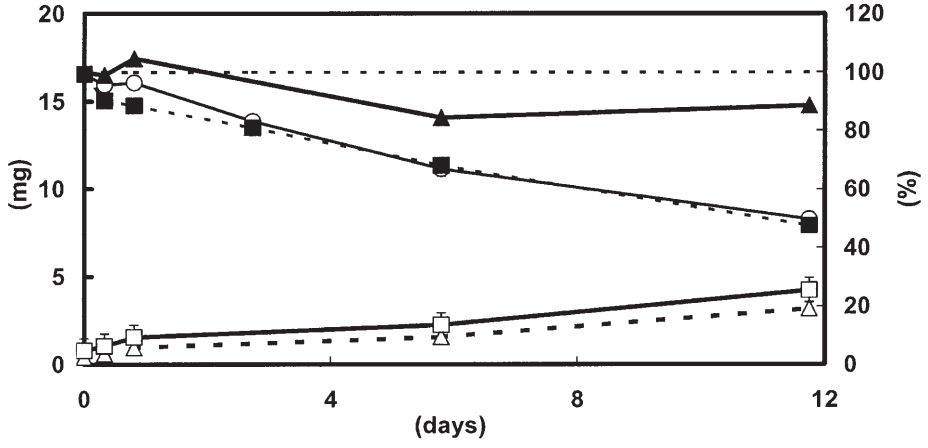

Figure 4. Example of a carbon balance time course, shown for the Mire Light 0.2-µm filtered sample. $CO_{2(g)}$ (white triangle △), $H_2CO_{3(aq)}$ (white square □), and $TOC_{(closed\ system)}$ (white circle ○) are summed to achieve total recovery as % (black triangle ▲). $TOC_{(open\ system)}$ (black square ■) is shown for comparison to $TOC_{(closed\ system)}$.

Table 1. Summary of TOC loss, IC increase, and causes of C transformations throughout the experiment in mg L^{-1} if not mentioned otherwise.

	Light				Dark			
	TOC	IC	IMU	Calc. Photoox.	TOC	IC	IMU	Calc. Photoox.
Mire Outlet Water								
Initial	38.8±0.2	2.7±0.3	0.0	0.0	39.0±0.4	2.7±0.3	0.0	0.0
0.8 days	36.1±1.3	5.9±0.6	0.1±0.0	2.6±1.3	n.d.	2.9±0.3	0.1±0.0	n.d.
2.7 days	32.5±1.3	n.d.	0.2±0.1	6.1±1.3	40.3±0.8	2.9±0.3	0.2±0.1	–1.5±0.8
5.8 days	27.6±2.2	5.9±1.1	0.4±0.2	9.0±2.2	37.6±1.7	3.1±0.3	0.7±0.4	0.7±1.7
11.8 days	20.3±0.7	17.4±2.0	n.d.	n.d.	39.4±0.9	2.9±0.3	n.d.	n.d.
Mean rate of change (mg C L^{-1} d^{-1})	–1.93±0.4	n.d.	0.08±0.04	1.85±0.4	–0.23±0.3	n.d.	0.12±0.06	0.11±0.3
% of TOC drop	100	76	4±2	96±21	100	100	52±26	48±130
Stream Water								
Initial	20.6±0.3	0.6±0.1	0.0	0.0	20.6±0.3	n.d.	0.0	0.0
0.8 days	18.5±0.7	2.1±0.2	0.2±0.1	1.9±0.7	n.d.	n.d.	0.1±0.0	n.d.
2.7 days	14.9±1.1	2.6±0.3	0.9±0.4	4.8±1.4	20.0±0.5	n.d.	0.3±0.1	0.3±0.5
5.8 days	11.8±0.8	5.8±0.6	2.7±1.3	6.1±1.5	20.1±0.4	n.d.	0.8±0.4	–0.3±0.4
11.8 days	10.4±0.3	7.0±0.7	n.d.	n.d.	20.1±0.4	n.d.	n.d.	n.d.
Mean rate of change (mg C L^{-1} d^{-1})	–1.53±0.15	n.d.	0.46±0.23	1.07±0.27	–0.09±0.09	n.d.	0.14±0.07	–0.05±0.11
% of TOC drop	100	73	30±15	70±18	100	n.d.	156±78	–55±122
Soil Water								
Initial	10.9±0.4	4.2±0.4	0.0	0.0	10.9±0.4	n.d.	0.0	0.0
0.8 days	9.9±0.2	4.2±0.4	0.0±0.0	1.0±0.2	10.8±0.3	n.d.	0.0±0.0	0.1±0.3
2.7 days	8.7±0.3	4.1±0.4	0.2±0.1	1.9±0.4	11.2±0.1	n.d.	0.1±0.1	–0.4±0.3
5.8 days	7.3±0.2	6.2±0.6	0.6±0.3	3.0±0.4	10.8±0.0	n.d.	0.3±0.2	–0.2±0.4
11.8 days	7.3±0.2	5.9±0.6	n.d.	n.d.	10.6±0.5	n.d.	n.d.	n.d.
Mean rate of change (mg C L^{-1} d^{-1})	–0.62±0.08	n.d.	0.11±0.06	0.51±0.1	–0.02±0.07	n.d.	0.06±0.03	-0.04±0.08
% of TOC drop	100	48	18±9	82±16	100	n.d.	300±150	–200±400

TOC reported is the mean (± s.d. of four replicate bottles, filtration treatments pooled). IC reported is the calculated mean (± s.d. of duplicate bottles for the mire, otherwise 10% of the measurement) of the mass of IC produced from the closed system. IMU is the Integrated Microbial Uptake calculated from microbial productivity measurements made at each time point, using the 1.2-µm filtered samples only and assuming a 20 ± 10% incorporation efficiency (after del Giorgio et al. 1997). Calc. Photoox. is the estimated amount of carbon photo-degraded at a given time point, calculated by subtracting the IMU from the change in TOC. Uncertainty for Calc. Photoox. is propagated from the uncertainty in TOC and IMU measurements. Mean rate of change after 5.8 days is reported for each C pool, both as a bulk number and as a % of the change in TOC. n.d. = not determined.

lund (1993) in a previous study). However, DOC measurements using a single use 0.45 µm Millipore filter in conjunction with TOC on day 11.8 of the experiment suggest that this effect was minor. POC was only 0.6 ± 0.9 mg L^{-1} (5 ± 7% of TOC), with no significant differences between sites or treatments. Furthermore, some of the carbon could have been lost as CO, a known product of DOC photo-degradation (Mopper et al., 1991; Valentine and Zepp, 1993). Miller and Moran (1997) and Gao and Zepp (1998) measured CO production rates of 7–10% as compared to that of CO_2 production.

Both the mire and the soil water were highly supersaturated with carbon dioxide (Table 1). Given the ratio between headspace and water volume used here, half of the IC was in the gas phase while the other half was dissolved in water.

Changes in water chemistry and character of organic matter

The pH increased for all samples in the light treatment (Table 2). The mire sample pH increased from 4.35 to

Table 2. Results for pH and alkalinity (Error of pH measurements of the pooled samples with four replicates show errors below 0.05 pH units and are thus omitted).

Treatment	TIME [days]	Mire		Stream		Soil water	
		pH	ALK [µeq L^{-1}]	pH	ALK [µeq L^{-1}]	pH	ALK [µeq L^{-1}]
Light	0	4.35	–39±1	5.21	12±2	5.03	15±2
	2.7	4.53	n.d.	5.41	n.d.	5.45	n.d.
	5.8	4.76	n.d.	5.82	n.d.	5.77	n.d.
	11.8	4.98	8±4	5.82	51±3	5.78	30±7
Dark (Control)	0	4.35	–38±1	5.21	12±2	5.03	15±2
	2.7	4.49	n.d.	5.32	n.d.	5.42	n.d.
	5.8	4.37	n.d.	5.19	n.d.	5.47	n.d.
	11.8	4.33	–38±2	5.19	9±1	5.47	16±4

n.d. = not determined.

4.98 only in the light, and the stream sample pH increased from 5.21 to 5.82 only in the light, while the soil water sample pH increased in both, light and dark treatments, probably due to degassing of carbon dioxide. The alkalinity was initially low (15 µeq L^{-1}) for all samples but showed large increases in the mire (45 µeq L^{-1}) and the stream water sample (40 µeq L^{-1}) during the experiment (Table 2). The changes in the soil water were small (15 µeq L^{-1}). Changes in $Gran_{ANC}$ were strongly correlated to changes in TOC (Fig. 5), and β (4.9 µmol mg^{-1}) was close to the value (4.6 µmol mg^{-1}) estimated by Hemond (1990). Total iron concentrations were almost constant during the experiment with ca 1.2 ± 0.2 mg L^{-1} in the mire, 0.9 ± 0.2 mg L^{-1} in the stream and 0.4 ± 0.1 mg L^{-1} in the soil water. Absorbance values for the control (dark) samples never changed by more than 4% from the initial value at 254 nm, or by more than 12% from the initial value at 420 nm, with no significant increases or decreases. In the light, all samples decreased consistently in absorbance at both wavelengths (Table 3). The absorbance drop was largest and quickest for the soil water sample, while the mire sample was bleached more slowly. The ratio of A_{254}/A_{420} decreased slightly after light treatment for stream and mire water, but was unchanged for soil water (Table 4). The Abs_{420}/TOC ratio decreased in the light treatment by almost 50% in the soil water but increased by about 20% in both the mire and stream water. SUVA (Abs_{254}/TOC) was not significantly affected by light in the mire and stream samples but dropped by 35% in the soil water sample, mostly late in the incubation, between days 5.8 and 11.8 (Table 4).

The initial apparent molecular weight distribution showed a similar pattern for all three sites, with the bulk of the molecules centered around a peak between 1,300–1,450 daltons (sample spectra for stream water shown in Figure 6). The samples also had a smaller, highly variable peak which eluted very rapidly and gave an apparent peak molecular weight in the 50,000–60,000 range, perhaps representing colloidal material. The primary peak showed clear degradation over time for the light

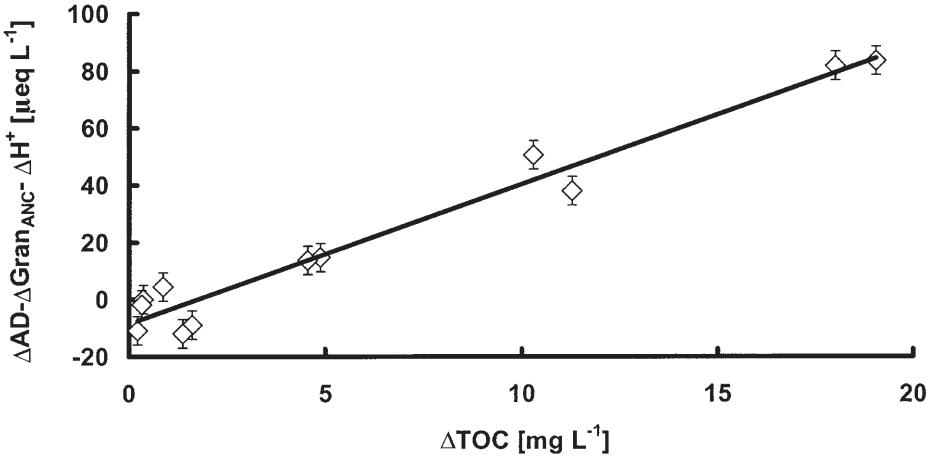

Figure 5. Comparison of changes in buffering capacity (equation 1) plotted against changes in TOC for all light treatments.

Table 3. Relative changes in absorbance (cm^{-1}) at 420 and 254 nm during the light treatment. Values reported are % of the initial (day 0 = 100%) value, with standard deviations in parentheses (n = 4). Dark samples did not change significantly over time for these parameters.

Wavelength	Site	Initial Abs (100%) (cm^{-1})	Abs after 0.3 days (% of Initial)	Abs after 2.7 days (% of Initial)	Abs after 5.8 days (% of Initial)	Abs after 11.8 days (% of Initial)
420 nm	Mire	0.156 (0.001)	96 (1.8)	91 (2.2)	84 (4.5)	68 (4.4)
	Stream	0.086 (0.003)	90 (2.5)	88 (10)	81 (6.1)	64 (6.3)
	Soil water	0.033 (0.001)	73 (11)	66 (17)	52 (9.2)	35 (15)
254 nm	Mire	1.666 (0.011)	99 (0.7)	88 (1.2)	75 (2.2)	54 (6.2)
	Stream	0.865 (0.004)	97 (0.1)	83 (2.3)	71 (2.3)	54 (2.8)
	Soil water	0.340 (0.016)	92 (3.6)	74 (5.8)	63 (7.6)	41 (5.9)

Table 4. Changes during the light treatment in the ratios of absorbance at 254 and 420 nm relative to each other and to TOC concentration. Standard deviations are reported in parentheses (n = 4). Dark samples did not change significantly over time for these parameters.

Ratio	Site	Initial value	Ratio after 0.3 days	Ratio after 0.8 days	Ratio after 2.7 days	Ratio after 5.8 days	Ratio after 11.8 days
$A_{254\,nm}/A_{420\,nm}$	Mire	10.7 (0.1)	11.1 (0.1)	10.6 (0.1)	10.5 (0.1)	9.7 (0.4)	8.6 (0.4)
	Stream	10.2 (0.3)	10.9 (0.3)	10.6 (0.2)	9.6 (0.8)	9.0 (0.5)	8.7 (0.6)
	Soil water	10.5 (0.7)	13.2 (1.0)	11.4 (0.7)	11.8 (1.4)	12.7 (0.6)	12.5 (1.3)
$A_{420\,nm}$/TOC ($cm^{-1}\,g^{-1}\,L$)	Mire	4.0 (0.0)	4.1 (0.1)	4.2 (0.1)	4.3 (0.2)	4.7 (0.5)	5.1 (0.2)
	Stream	4.0 (0.1)	4.2 (0.5)	4.1 (0.1)	5.0 (0.6)	5.9 (0.4)	5.2 (0.2)
	Soil water	3.0 (0.1)	2.3 (0.2)	2.6 (0.2)	2.5 (0.4)	2.3 (0.2)	1.6 (0.3)
A_{254nm}/TOC ($cm^{-1}\,g^{-1}\,L$)	Mire	42.8 (0.3)	45.0 (2.1)	44.7 (1.5)	45.4 (1.8)	45.6 (4.5)	43.6 (1.4)
	Stream	45.0 (0.7)	46.3 (4.4)	43.9 (1.6)	48.1 (4.1)	52.5 (4.3)	45.4 (3.6)
	Soil water	31.2 (1.2)	29.6 (1.0)	29.6 (0.8)	28.8 (1.5)	29.5 (2.1)	19.4 (2.5)

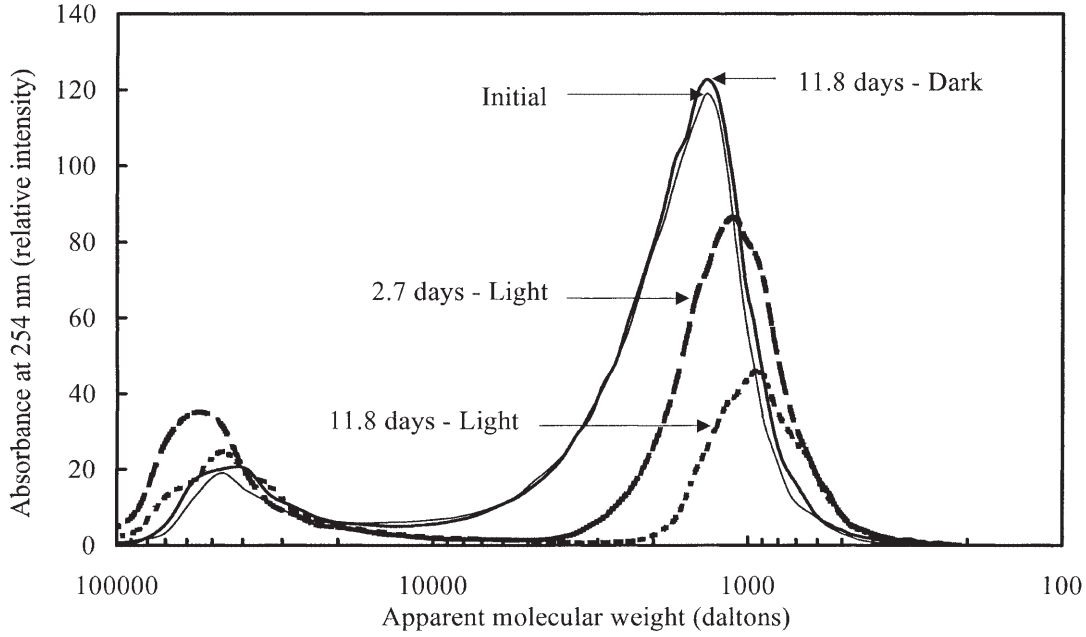

Figure 6. Apparent molecular weight distribution for the stream site at selected time points.

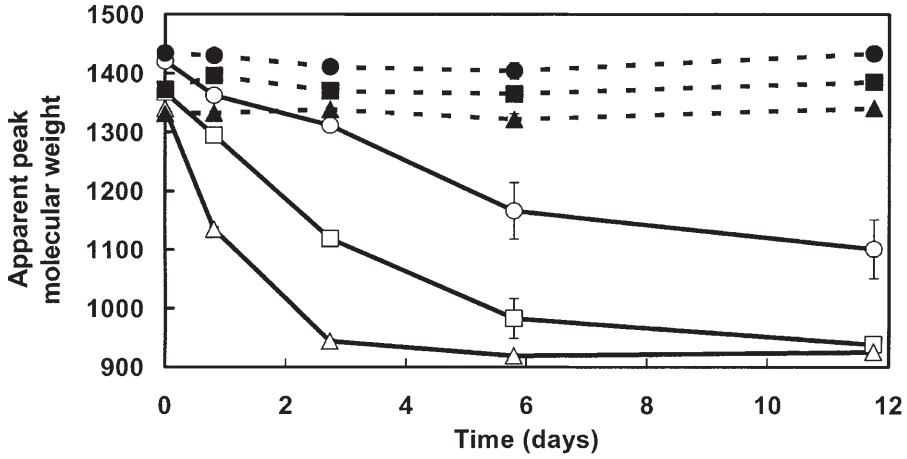

Figure 7. Summary of peak apparent molecular weight for all samples over the course of the incubation: Mire-Light (white circle ○), Mire-Dark (black circle ●), Stream-Light (white square □), Stream-Dark (black square ■), Soil water-Light (△), Soil water-Dark (black triangle ▲). Error bars represent standard deviation of four samples (0.2-µm and 1.2-µm filtered samples averaged).

treatment, having a decrease in both area (correlated to TOC concentration) and in peak molecular size. The pattern exhibited by the stream water sample (Fig. 6) was mimicked fairly closely by the soil water and mire outlet samples. In the dark, the molecular weight distribution retained its original configuration, even after 11.8 days. The apparent molecular weight showed an exponential decrease in the light treatment for all water samples (Fig. 7). The mire water initially had the highest abundance of high molecular weight compounds and the soil water the lowest. The differences between the peak of the weight fractions of the initial samples were smaller than approximately 100 daltons. The light treatment accentuated differences in apparent molecular weight, with the mire peak molecular weight approximately 200 daltons heavier than the soil water and stream samples after 11.8 days in the light. As with TOC concentrations, the most rapid initial drop in molecular weight was observed in the soil water, followed by the stream water, while the mire outlet showed a more gradual, almost linear response.

Microbial activity

The Bacterial numbers in the 1.2-µm filtered samples were initially 1.0×10^6 mL^{-1} in the stream and mire water, and 3.1×10^6 mL^{-1} in the soil water. Table 1 presents the integrated microbial uptake (IMU) for both the dark and light treatments, calculated from net production measurements at each time-point for the 1.2-µm filtered samples. The calculation of IMU relies on several conversion factors and an assumed value for bacterial growth efficiency (BGE). The direct comparison between samples depends upon the assumption that the conversion factors (including BGE) do not change substantially between samples or over the course of the experiment. The uncertainty in BGE was taken into account in the error terms reported in Table 1. The value of 20% that we used for BGE is on the low end of reported values for natural stream water DOM and microbial assemblages (e.g., Kaplan and Bott, 1983; Meyer et al., 1987; Mann and Wetzel, 1995) and thus should overestimate the contribution of microbes to the observed oxidation of TOC. Assuming that the calculated IMU values are accurate relative to one another, the light treatment resulted in a 240% increase in microbial production in the stream water, a 110% increase in the soil water, and a 30% reduction in the mire water. When normalized to TOC concentration, microbial C uptake was highest in the stream water in the light (2.8% d^{-1}) and lowest in the mire outlet water (0.2% d^{-1} and 0.3% d^{-1} for light and dark, respectively). Microbial respiration calculated from productivity measurements in the 1.2-µm filtered samples accounted for about 30% of the organic carbon loss in the stream water sample, but only 4% and 18% in the mire and soil water, respectively (Table 1). For all samples in the light, photodegradation of TOC exceeded calculated microbial respiration by at least two-fold.

Discussion

Our results show that, as hypothesized, soil water, first-order streamwater, and mire-runoff NOM is highly photo-labile. DOC measurements after 12 days never indicated a greater loss than 1.5 mg C L^{-1} for the dark samples. The photo-oxidation rates in our experiment are comparable or higher than those found in other investigations (Granéli et al., 1996; Amon and Benner, 1996; Bertilsson et al., 1999; Molot and Dillon, 1997). Bano

et al. (1998) found that organic carbon originating from mires is rapidly degraded by light due to the high phenolic component, which could explain the large photolabile pool in our mire water sample (Table 1). In both, the mire and the stream water, more than 60% of the total organic C are contained in the more hydrophobic type phenolic-rich DOM adsorbed by XAD-8 (Bertilsson et al., 1999). The soil water, which was originally hypothesized to contain a relatively large pool of labile organic carbon, had the lowest mean loss rate of TOC, and the smallest labile pool, both in size and as a % of the total TOC pool (Fig. 3, Table 1). However, although the labile pool is small in the soil water, it degrades very rapidly, and the photo-degradation rate per initial DOC concentration is very similar between the mire water and the soil water (cf. Table 1).

There was a clear difference in the time response of the loss rates between the organic material leached from the different environments within this headwater catchment (Fig. 3). The soil water and stream water samples contained a highly labile TOC pool that was rapidly depleted, with a half-life on the order of two days (see Fig. 3). The size of this labile pool is larger for the stream water than for the soil water. Higher initial loss rates could be due to differences in chemical composition or pH dependant iron-mediated photo-mineralisation (e.g., Faust and Zepp, 1993). In contrast, the mire sample showed a nearly linear decrease in the loss rate, which suggests that the mire contains a very large (estimated at 77% of total) pool of photo-labile TOC, but it is not as rapidly degraded as the stream or soil photo-labile material. The longer half-life (9 days) of the mire photo-labile pool may be partly due to self-shading caused by the initial high TOC concentration. As in natural systems, light was absorbed more readily in our experiment by more highly-absorbing (coloured) waters. Therefore, due to self-shading, the average parcel of mire water received less radiation in our light treatment than does the stream water, which in turn receives less than the soil water. Based on the Beer-Lambert law (and taking into account sample bleaching and volume changes over the course of the experiment), self-shading reduced incident irradiance at 420 nm by an average of 7% for the soil water sample, 17% for the stream water sample, and 28% for the mire water sample. The mire water has by far the highest absorbance of the three sites, and bleaches more slowly than the other two sites, both at 254 nm and 420 nm (Table 3). Small light doses seem to be a requisite for changes in Abs_{420}/TOC and Abs_{254}/TOC, and the less humic material in the soil water is more prone to fast degradation. While there was a significant decrease in Abs420/TOC over time (Table 4), Abs_{254}/TOC did not change, implying that it potentially could have been used as a tracer for the TOC mass balance throughout the experiment.

The size of the refractory TOC pool appears to be remarkably similar between the different sites, varying only from 7.1 ± 0.2 mg C L^{-1} for soil water to 9.9 ± 0.7 mg C L^{-1} for stream water (Fig. 2). Note that the estimate of the refractory pool for the mire water (8.7 ± 7.7 mg C L^{-1}) has a large uncertainty due to the near-linearity of the decay curve. The fraction of the TOC which is labile (35–77%), mostly due to photo-degradation, is large and variable compared to the size of the microbially labile pools in other studies (reviewed in Søndergaard and Middelboe, 1995).

Most of the TOC lost was mineralised to carbon dioxide (Table 1). While photo-oxidation was shown to be high compared to several other studies, it does not account for the photo-production of low molecular weight organic substances such as carboxylic acids. Bertilsson and Tranvik (2000) estimated that 34% of the new C production, calculated as the sum of organic acids and DIC produced, may be in form of these compounds, thus significantly increasing the total effect of radiation on DOC processing. Their results on DIC and carboxylic acid production during an experiment with 8 h of mild UV irradiation corresponded to an average of 4.7% (average of 38 lakes studied) of the total DOC pool. Corresponding (12 h treatment) values recalculated from our data (from day 0.8, Table 1) show that photo-oxidation ranged between 4.2 and 5.8% of the initial DOC concentration. Similar degradation rates were reported by Granéli et al. (1996), and by Granéli et al. (1998) for samples exposed to natural radiation with slightly higher PAR during 18 hours.

Due to the fact that the experiment was carried out using glass containers which excluded UVB radiation below 290 nm, most of the photo-degradation observed can be attributed to PAR and UVA radiation. According to Granéli et al. (1998), 20% of the DOC degradation is due to UVB while other researchers (Salonen and Vähätalo, 1994, Bertilsson and Tranvik, 2000) have found that natural UVB may be responsible for up to 50% of the photo-oxidation of natural DOC, suggesting that our observed photo-oxidation rates would have been slightly higher if higher UVB had not been excluded by the glass bottles used.

The pH increase in the experimental bottles manifests the change from a NOM dominated buffer system to a carbonate buffer system, due to the degradation of both strong and weak organic acids. The loss of organic acids is strongly correlated to changes in buffer capacity. Initially, and throughout the whole experiment, pH was depressed by CO_2 as none of the samples were in equilibrium with atmospheric CO_2 (Table 1). If equilibration to atmospheric carbon dioxide had occurred, samples exposed to the light would have achieved pH 5.1 (mire), 6.5 (stream) and 5.8 (soil water) after 12 days. This demonstrates the large potential effect on pH caused by

the losses of DOC. Organic acid related alkalinity (Fig. 5) allowed us to determine the strong acid component as 4.9 µeq mg^{-1} organic carbon, very close to the value of 4.6 reported by Hemond (1990). This suggests that there was no significant change in the acid-base character of the TOC.

The TOC in our water samples exposed to light not only bleached and lost TOC, but also underwent a decrease in the apparent average molecular weight accompanied by a slight shift in the MW distribution (Fig 4). These results are similar to results observed during other photo-degradation studies (Allard et al., 1994; Amador et al., 1989; Hongve, 1994). The measurement is termed "apparent" because the size exclusion chromatography method that we used may be subject to various artefacts due to variations in the chemistry of the measured NOM such as hydrophobic interaction with the column retarding the passage and decreasing apparent molecular weight, complexation reactions, or the presence of iron or aluminium colloids. However, under careful conditions this method has yielded values for natural fulvic acids in general agreement with accepted molecular weights (Chin et al., 1994). The low apparent molecular weight for the initial stream, mire and soil water in our experiment suggests that the samples are probably composed largely of fulvic acids (Thurman, 1985), similar to findings by Cole et al. (1984). The rapid decrease in the soil water organic carbon molecular weight (or increase in hydrophobicity) matches the rapid decrease in TOC. The change in organic carbon molecular weight of the soil water levelled off after 2.7 days, which could indicate that the photo-labile pool has been degraded and the organic matter has reached an equilibrium with respect to molecular size and photo-reactivity. The effective size of organic molecules affects their chemical and biological availability, and different size-fractions of DOC sponsor different bacterial growth rates and growth efficiencies (Amon and Benner, 1996; Tranvik, 1990; Kieber et al., 1990).

In our experiment bacterial respiration was only to a small extent responsible for the loss of organic carbon during the incubations, and photo-oxidation was the major cause of organic carbon loss from the systems. We estimated that of the observed TOC losses, 70 ± 18% in the stream, 82 ± 16% in the soil water, and 96 ± 21% in the mire outlet water could be attributed to direct photomineralization by light (Table 1).

Although our results give similar degradation rates (Table 1) to other studies from the same location (Bertilsson et al., 1999), the relative importance of light in our experiments may not be directly comparable to natural conditions. Both the shading of streams by vegetation and the attenuation of light with water depth increases the relative importance of microbial degradation (Jonsson et al., unpublished). Light-induced changes in character may still be important, as character changes can effect the microbial processing of DOC (Lindell et al., 1995; Bertilsson and Tranvik, 1998; Obernosterer and Herndl, 2000). It is also worth pointing out that the bacterial community present in the three studied waters might not be equally well adapted to the oxic conditions used in our experimental setup.

Although the experiment was designed to have "sterile" and „non-sterile" treatments, several of the sterilized treatments began to exhibit bacterial production after 5.8 days. In the data analysis, we have generally pooled the two filtration treatments together (e.g., Fig. 3), and all samples may be thought of as "live", i.e., containing bacteria. We acknowledge that our bacterial productivity measurements are subject to some uncertainty due to the potential effect of bacterial grazing owing to passage of bacteriophages in the filtration procedure (Wikner et al., 1999, and ref. therein), and as such, the bacterial productivity measurements were only used until 5.8 days.

Conclusions

The average hydrological residence time of water in the main stream channel is about 12 hours, implying that only minor changes in stream TOC occur within the watershed, and the majority of these changes could be photochemically induced. The light-induced degradation of fresh NOM is an important process on the time scale of days and thus is an important within-stream process. Organic carbon originating from different sources shows different stability with respect to biological and photochemical degradation. Photo-oxidation was responsible for 70–96% of TOC lost in headwater samples subjected to both light (predominantly PAR and UVA) and natural microbial assemblages. The majority of TOC lost was oxidized to CO_2 for all sites. This shifted the pH buffer system from DOM control to HCO_3^- control. The light treatment changed the character of the remaining TOC as indicated by apparent molecular weight distributions and absorbance ratios. An important questions to study in the future is: How important is light-induced carbon degradation in relation to other TOC decreasing mechanisms like precipitation/adsorption or coagulation? Another logical follow-up would be to more clearly separate the microbial and photochemical processes so that they could be examined individually.

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