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TOC fluctuations in a humic lake as related to catchment acidification, season and climate

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Abstract. Studies of fluctuations in total organic carbon (TOC) were performed in both the reference basin and the acidified basin of experimental Lake Skjervatjern, in order to separate effects of various catchment and in-lake processes. Nearly five years of catchment acidification did not induce significant changes in TOC. TOC concentrations was not related clearly to precipitation or runoff. In both basins, there was a regular, seasonal pattern with a gradual increase in TOC concentrations from spring to late autumn. Minima in concentrations occurred during periods with frozen ground in winter, irrespective of discharge patterns. The decrease from $\sim$ 10 mg C l^{-1} in autumn to 1–2 mg C l^{-1} in late winter, was only seen in surface layers. Runoff was the major loss route for surface TOC in the lake. Photo-oxidation, bacterial oxidation, and sedimentation combined yielded maximum loss rates of 3% of surface TOC d^{-1}. Below a depth of 1 m 0.5% d^{-1} was lost to these same processes. The surface microlayer had 5–10 times more TOC than the bulk water on average, and could have effects on gas exchange and sub-surface light. Despite the oxidation of TOC, the short residence time of the lake and rapid replacement of TOC from the catchment was the major determinant of lake water TOC.

Introduction

Carbon fixed by photosynthesis in the biosphere re-enters the atmosphere by varying processes at varying timescales. A major return to the atmosphere is caused by respiration. Carbon may be trapped in the biosphere from weeks to months (annual plants) up to hundreds of years (trees), but following decay or burning, a large portion of this carbon is oxidized back to CO_2. Under dry and warm climate, the net flux of carbon to soils may be negligible, while in colder and more humid regions, annual fixation exceeds the oxidation, causing a net accumulation of C. Most northern soils represent large stores of C in the form of humus compounds (Oechel et al. 1993), and this constitutes a major link in the global carbon cycle with quite variable, but normally long turnover rates. The mobility and fate of these compounds are largely dependent on climatic factors. In moist regions, a major portion of the compounds enters rivers, lakes or oceans, largely as DOC, which is oxidized via food chains, photo-oxidation or buried in sediments. Large scale climatic processes affect the input of TOC to aquatic ecosystems (Schindler et al. 1990, 1992, 1996), and may entail important feedbacks to the atmosphere by switching from a positive to a negative net flux of carbon from atmosphere to biosphere, as has happened in the tundra (cf. Oechel 1993). We shall here consider some aspects of humus supply to aquatic environments and the factors governing the fate of this huge carbon reservoir.

Although many TOC components are recalcitrant, humus carbon in aquatic systems supports the growth of heterotrophic bacteria (DeHaan 1977; Hessen 1985; Tranvik 1988), and a major loss route for aquatic humus occurs via bacterial oxidation (Hessen et al. 1990). This process is governed by factors such as molecular size and availability of mineral nutrients. The breakdown of humic substances, fatty acids and other small molecules that can be utilized by bacteria is often initiated by UV radiation (Cooper & Lean 1989; Kieber et al. 1989; de Haan 1993). There is particular concern for the potential increase in UV-B radiation, and its effects on carbon dynamics in the aquatic environment (Mopper et al. 1991). In freshwaters strongly stained by humic matter where UV-B is almost completely blocked in the upper few centimeters (Scully & Lean 1994), the upper layer and particularly the surface film become the sites of most UV-induced effects. For the aquatic bacteria, there are antagonistic effects of UV-light. On one hand, UV promotes molecular degradation, enhances substrate availability, and increases bacterial growth efficiencies (Amador et al. 1989). On the other hand, bacterial metabolism may be inhibited directly by photon flux (Herndl et al. 1993), and indirectly by UV-induced free radicals and strong oxidants (Lund & Hongve 1994). Liberation of adsorbed organic, or chemically bound mineral nutrients from TOC may also be stimulated by short-wave light (Franco & Heath 1982), subsequently stimulating bacterial growth and thus humus degradation (Hessen et al. 1994). Thus, decreasing TOC implies strong feedback on carbon cycling via enhanced photo-oxidation and more active microbial communities. It will also affect the concentrations and fate of inorganic C, and thus gas balance. In addition to UV light, climatic parameters like temperature and rainfall, in a multitude of ways affect mineralization and mobility of organic carbon, and subsequently the release of C into surface waters (Schindler et al. 1992 and this volume).

Finally, acidification may further interfere with TOC metabolism and concentrations by altering the chemical properties of catchments and lakes. This is of particular relevance for humic lakes, where decreased TOC (or water color) following acidification is attributed to increased inputs of Al or

$Fe(OH)_3$ and subsequent flocculation and sedimentation (Yan 1983; Effler et al. 1985; Schindler et al. 1992).

Here we try to reveal some of the processes by which acidification effects TOC by studying TOC-fluctuations in the streams draining reference and acidified catchments to the experimental, humic Lake Skjervatjern.

Material and methods

The experiments were performed in the Lake Skjervatjern catchment, western Norway. The area receives in excess of 2500 mm precipitation annually, and is only marginally influenced by anthropogenic acidification. The lake was divided by a plastic curtain in 1989. The catchment of one basin has been acidified since late summer 1990 (A-basin), while the other half has been kept as an untreated reference basin (B-basin). The outlet was divided in two by the curtain, so that each half of the catchment has an independent water flow. The acidified basin has a volume of 9 000 m^3 and a catchment area of 2.7 ha, versus 58 000 m^3 and 6.2 ha in the reference basin. Theoretical retention time is 1.6 months in the A-basin versus 4.5 months in the B-basin, thus there are consistent hydrological differences between the two halves. The acidified catchment received sulfuric acid and ammonium-nitrate, approximately 4.2 g sulfate m^{-2} y^{-1} and 1.3 g ammoniumnitrate m^{-2} y^{-1} respectively, from a set of sprinklers on top of trees in the catchment. Acid doses for sulfur and nitrogen were similar to those received over the most polluted areas of southern Norway (Gjessing 1994). From 1991 on, there are also continuous records of outlet discharge and precipitation, temperature and solar irradiance. TOC, UV-absorbance (254 nm) and color (mg Pt) were monitored from both outlets every fortnight from 1988 onwards. The samples were also analyzed for nitrogen and phosphorus, aluminium fractions and major anions and cations. Vertical profiles of lake chemistry, including TOC, UV-absorbance (254 nm) and DIC (CO_2) were also measured a number of times in each basin. CO_2-balance was assessed from primary production measurements (Brettum 1994), dark respiration measurements (Hessen et al. 1994) and measurements of photo-oxidation (Salonen et al. 1994). C-flux to sediments were calculated from sediment traps in both basins. Small vial traps were used in 1991 and 1992, while larger, standardized sediment traps were applied in 1993. The traps were emptied once or twice each month during summer, filtered on precombusted GF/F-filters, and analyzed for particulate organic matter (POC). Measurements from the shallow, acidified basin were obscured by resuspended sediments and omitted from further analysis. TOC was measured as total carbon by combustion in a Dohrman DC-190 analyzer on unfiltered samples. POC was analyzed on washed, pre-ignited GF/F-filters on a Carlo-Erba elemental analyzer. The values reported in text is largely on dissolved form, since particulate C normally constituted less than 10% of total carbon. Water for CO_2-analysis was stored in gas-proof serum vials, acidified with phosphoric acid. Head-space CO_2 was analyzed on an infrared gas analyzer.

Surface microlayer samples were obtained in early and late July, in August and September to reveal if there were seasonal or diurnal patterns in surface microlayer concentrations of TOC that could affect light penetration and gas exchange. The samples were taken by using a remote controlled surface slick sampler, fitted with a rotating drum with a hydrophilic Teflon surface (Södergren 1984).

Results

TOC-fluctuations in the lake

The annual fluctuations in lake surface (runoff) TOC concentration show a remarkable regularity, with a short winter minimum below 2 mg TOC l^{-1} during periods with frozen ground, and a gradual increase from about 4 mg TOC l^{-1} in early spring to nearly 10 mg TOC l^{-1} in late autumn (Figure 1). Apparently, the winter minimum in TOC occurred only at the surface. To test the representativeness of the runoff samples for the whole water column, a number of vertical TOC profiles were analyzed. Vertical profiles coinciding with the pronounced winter minima showed that there was no depression below 1 m depth. In summer, concentrations of TOC in the surface and deeper layers (1–3 m) were well correlated, although surface TOC was still poorly correlated with TOC of 4 meters (Figure 2 and Table 1). This calls for some precautions with regard to generalization of patterns in lake TOC based on surface samples.

There were no consistent differences in TOC-concentrations between the two basins, in spite of different hydrology, retention times and the nearly five years of acidification treatment. The five year included a range of climate extremes, including the unusually mild, but moist winters in 1991 and 1992. There was no correlation between TOC and runoff on a day-to-day comparison for the years 1991–92 ($r^2 < 0.05$; Figure 1). Neither did a calculation on cross-correlation based on 14 d averages of runoff yield any significant relation with TOC and runoff. For all years, TOC was stable or decreased slightly from May to July, then rose sharply to a maximum in late autumn. The June-July depression in TOC was not related to solar irradiance at any clearcut manner (Figure 3). However, there was a pronounced correlation between seasonal UV-absorbance and TOC, with an apparent bleaching of

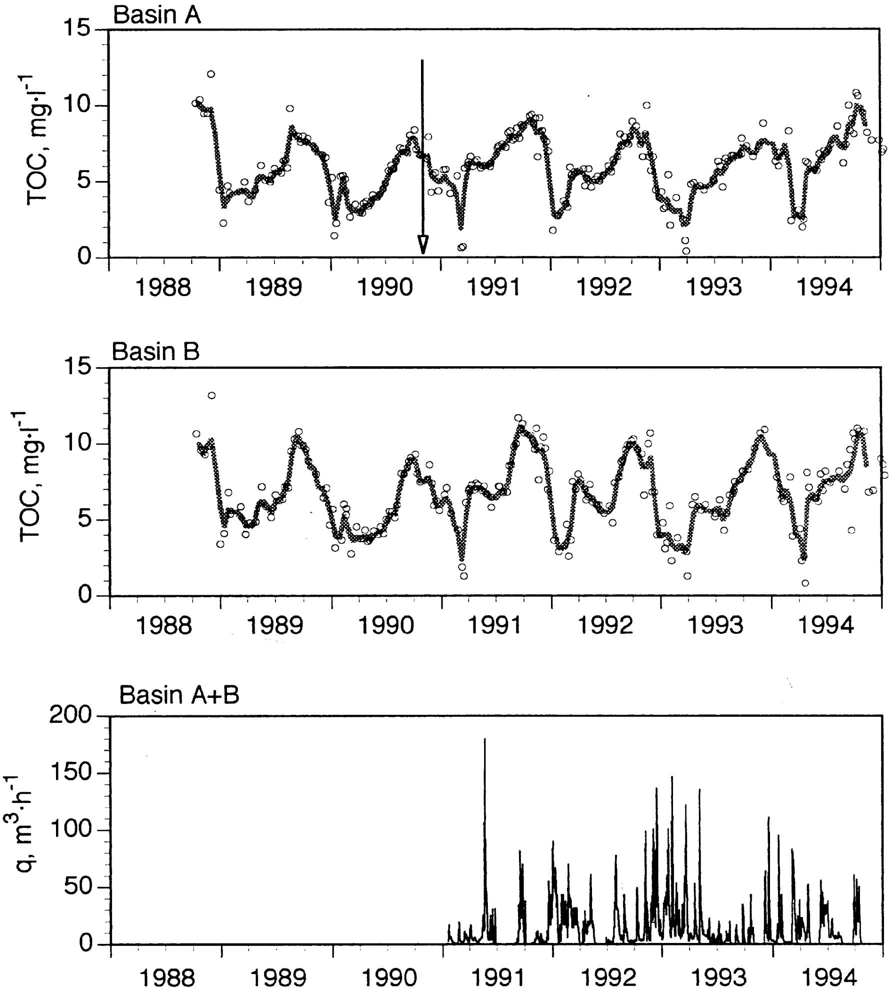

Figure 1. Seasonal variations in the concentrations of TOC in the outlet of Lake Skjervatjern. TOC is the sum of particulate carbon (< 10% of TOC) and dissolved organic carbon (DOC). Curves are smoothed by 14 d time-weighted averages. Discharge in lower panel. below.Onset of acidification in the A-basin is indicated with an arrow.

chromophores during summer (Figure 4). This trend was most visible in the A-basin, but both basins gave a similar, seasonal response.

Carbon budget and loss processes

The lake was fed by a number of seepage vents, preventing a calculation of C influx. The major loss route was the outflow, which had peaks of 10 kg C d^{-1}, (Figure 5), but normally less than 2–3 kg d^{-1}. Assuming that losses of TOC to

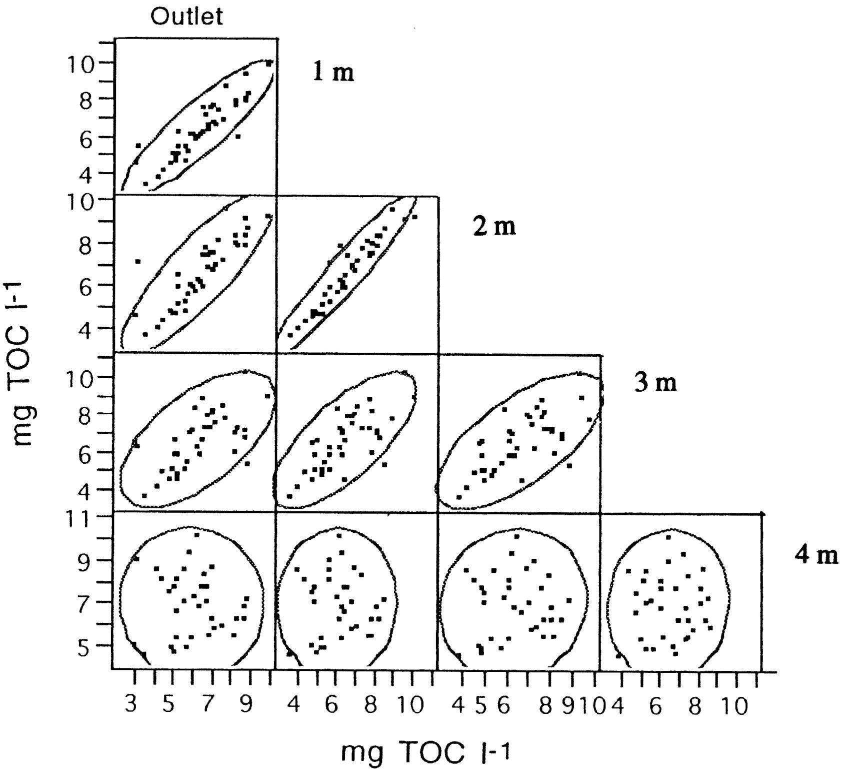

Figure 2. Scattergram of correlation between TOC at surface (runoff) and consecutive depths for the A-basin. Contour lines are fitted 95% bivariate normal density ellipses. Each square represents the correlation between various depths.

Table 1. Pairwise correlation between various depths from surface to bottom of the A-basin (upper) and the B-basin.

Depth	Outlet	A1	A2	A3
A1	0.887			
A2	0.855	0.949		
A3	0.616	0.729	0.684	
A4	0.031	0.026	0.081	0.045

Depth	Outlet	B1	B2	B3	B4	B6
B1	0.829					
B2	0.787	0.952				
B3	0.714	0.879	0.928			
B4	0.651	0.774	0.812	0.783		
B6	0.461	0.587	0.647	0.581	0.831	
B8	0.378	0.509	0.578	0.525	0.764	0.969

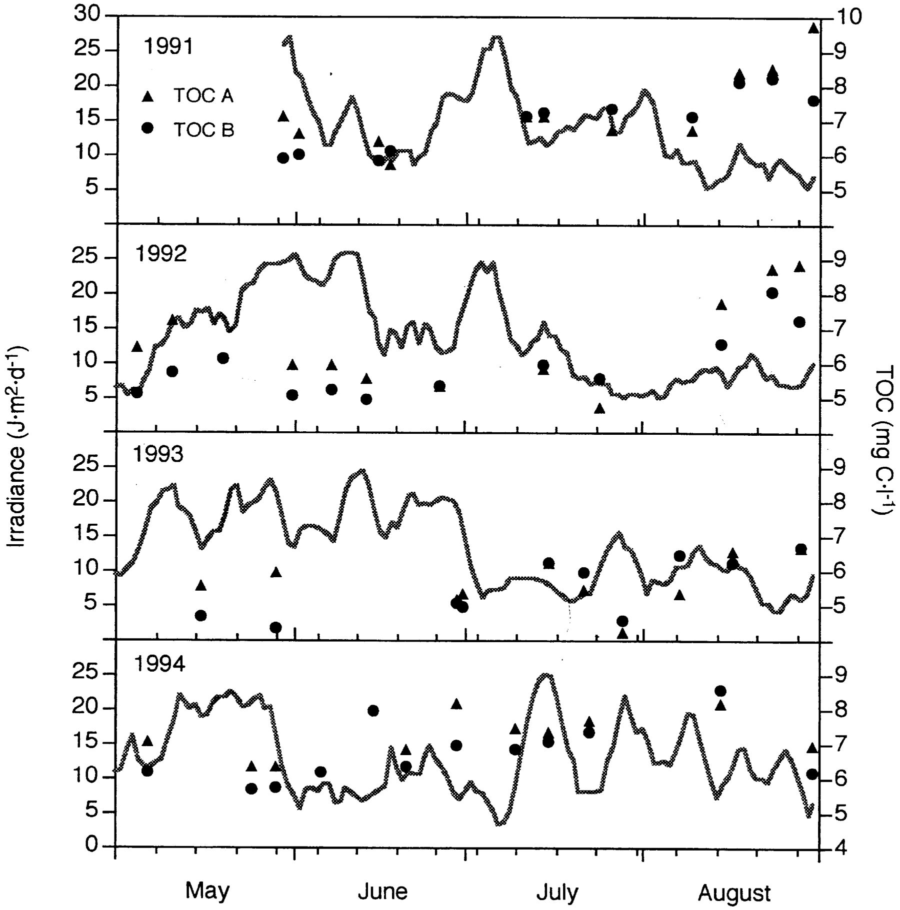

Figure 3. Smoothed solar irradiance (line) based on daily averages measured on site, related to TOC-concentrations in the outlet of the two basins during the four years of study.

in-lake processes were negligible, annual export of TOC was approximately 1000 and 440 kg C from the A and B-basin, respectively. For the B-basin, where the most appropriate run-off data exist, actual time integrated export was 546 kg averaged over the years 1991–1994, implying a loss rate of 45% to sediments and oxidation processes.

Sedimentation flux varied considerably between the small traps, less so in the larger traps. Based on all 10 recordings during 1991–1993, total sedimentation amounted to 165 ± 176 mg C m^{-2} d^{-1} over the upper 2 meters, while data from the larger traps yielded an average of 43 ± 11 mg C m^{-2} d^{-1}. There were no clearcut seasonal trends. Owing to the great variability and the possibility of sediment resuspension, these numbers should be

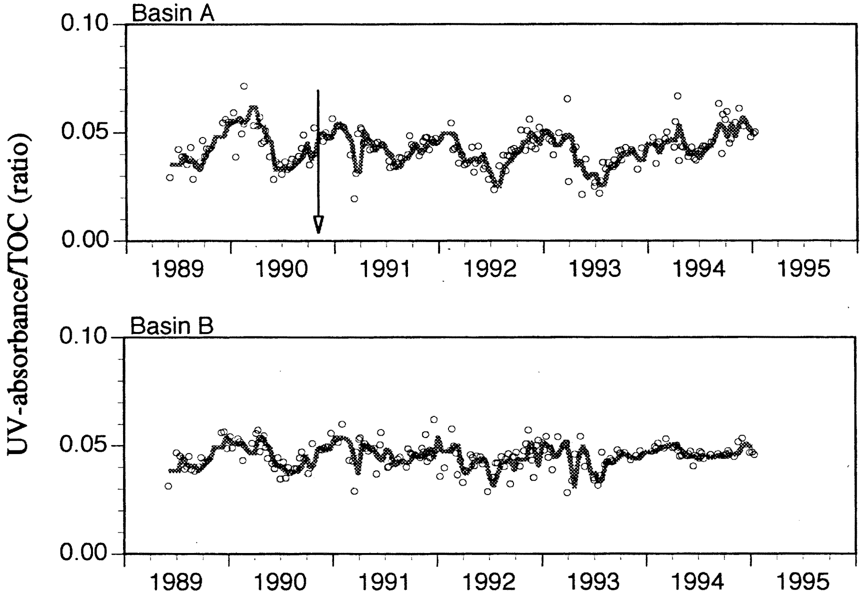

Figure 4. Seasonal fluctuations in UV-absorbance/TOC ratio in the A-basin (upper panel) and B-basin. Arrow indicated onset of acidification. Curves smoothed by 14 d time-weighted averages.

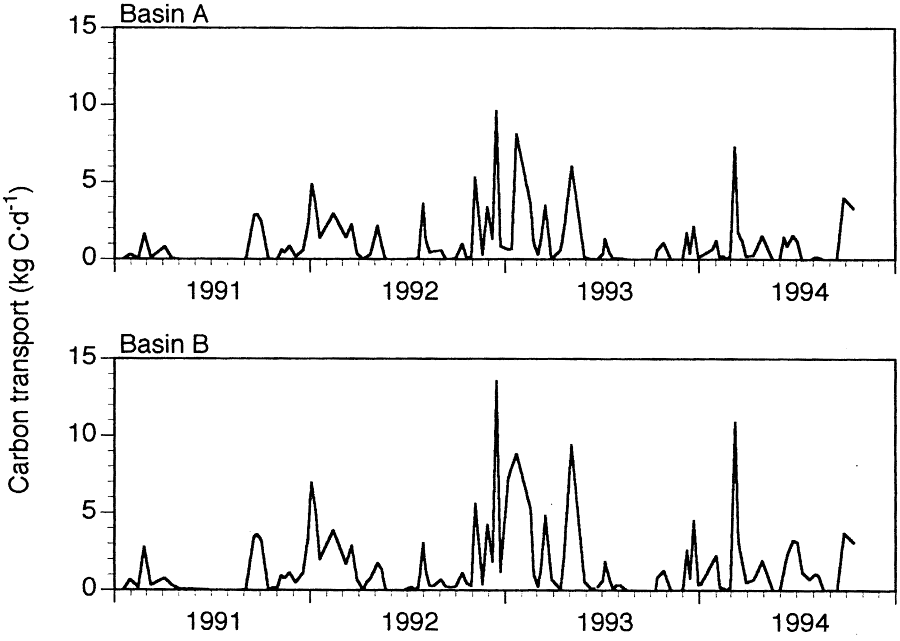

Figure 5. Carbon export as kg C d^{-1} from the outlets of the two basins.

Table 2. Diel variations in TOC in the surface microlayer of humic lake Skjervatjern (mg C l^{-1}).

Time of day Date:	Skjervatjern 2 July 1994	Skjervatjern 24 July 1994	Skjervatjern 11 Aug 1994	Skjervatjern 22 Sept 1994
04:00	–	40.0	24.0	18.0
05:00	71.4	56.3	80.7	29.7
07:00	58.4	58.7	179	36.0
08:00	42.4	110	186	30.0
09:00	66.1	144	192	35.2
10:00	35.2	129	775	45.5
11:00	100	180	421	30.1
12:00	46.2	114	128	28.0
13:00	66.1	178	94.5	36.5
14:00	64.8	63.9	42.1	39.7
15:00	–	119	251	66.4
16:00	44.8	80.6	43.7	63.3
17:00	–	57.5	–	39.8
18:00	16.5	84.6	–	60.0
19:00	–	62.2	–	49.1
20:00	73.9	–	–	–
21:00	53.0	30.8	–	–
22:00	27.8	38.4	–	–
23:00	44.7	30.6	–	–
24:00	64.6	47.9	–	–
02:00	–	45.0	–	–

interpreted cautiously, yet they indicate that a maximum loss rate of 1.5% of TOC d^{-1} (but as much as 10–20% of POC) via sedimentation. The loss rate of TOC to respiration and photo-oxidation were recorded more occationally, yet with smaller fluctuations. These two oxidation processes combined yielded a maximum loss rate of nearly 100 mg C m^{-3} d^{-1} (see discussion) implying a turnover of approximately 1.5–2% d^{-1} of summer TOC also for oxidation losses.

Effects on surface film

The surface film was well developed in the lake. The enrichment ratio (TOC conc. in surface film relative to bulk water) normally ranged from 5 to 10. There were pronounced fluctuations in surface microlayer density (Table 2), and with a clear tendency for higher surface TOC around noon in calm and bright days like that of 24th of July.

Discussion

The first five years of acid treatment yielded no observable effects on TOC contrasting previous reports on increased transparency and decreased TOC (or water color) following acidification (Yan 1983; Effler et al. 1985). Decreased TOC is not, however, a unifying response on acidification in all lakes (Schindler et al. 1992), but in general where catchment acidification causes increased mobility and concentrations of metals in lake water, TOC retention may be expected to increase. These first years of treatment could still be a transient situation, however, and conclusions on acidification and TOC are still premature. The regular seasonality in TOC concentrations indicates some inherent patterns associated with catchment properties. There are contrasting reports on seasonal variation in TOC, and how this correlates with hydrology (Schindler et al. 1992, 1996). In humid regions like that of Lake Skjervatjern, which receives approximately 2500 mm precipitation annually, and with drainage areas dominated by water saturated bogs, increased rainfall largely has a diluting effect on TOC concentrations. In dry areas, or after periods of drought, rainfall could have the opposite effect, soil stores of water soluble, humic matter would be flushed into surface waters (Schindler et al. 1992, 1996). While TOC in Lake Skjervatjern did not reflect seasonal fluctuations in hydrology, it is likely that interannual trends would be significant. Increased summer temperatures, reduced ground water flow, and reduced runoff would most likely yield decreased lake TOC first because soil respiration would increase, and secondly because of longer water residence time and increased losses by oxidation or sedimentation processes. The remarkable winter depression of surface TOC, which occurs during periods of ice-cover and frozen soils suggests that winter warming could yield increased levels of TOC in surface and runoff waters. In-lake processes will become increasingly important with increasing residence times, due to increased bacterial activity.

The UV-B mediated photo-oxidation in such brown waters would be restricted to the surface film and the top few centimeters of bulk water (Scully & Lean 1994). Due to mixing, the effects may propagate to deeper layers, and there are claims that photo-oxidation is a major cause of low oxygen levels in humic lakes (Lindell & Rai 1994). Salonen et al. (1994) found a pronounced UV-B mediated mineralization at the very surface of Lake Skjervatjern, but very low photodegradation below 10 cm. At the surface, maximum mineralization from photo-oxidation exceeded 100 mg C m^{-3} d^{-1} on a sunny mid-summer day, decreasing to less than 25 mg C m^{-3} d^{-1} below 10 cm depth. In comparison, average epilimnetic microbial oxidation in the same lake was 30–40 mg C m^{-3} d^{-1} (Hessen 1992). Integrated over the water column, and over the season, it is evident that direct photo-oxidation in these waters is of minor importance relative to the microbial degradation.

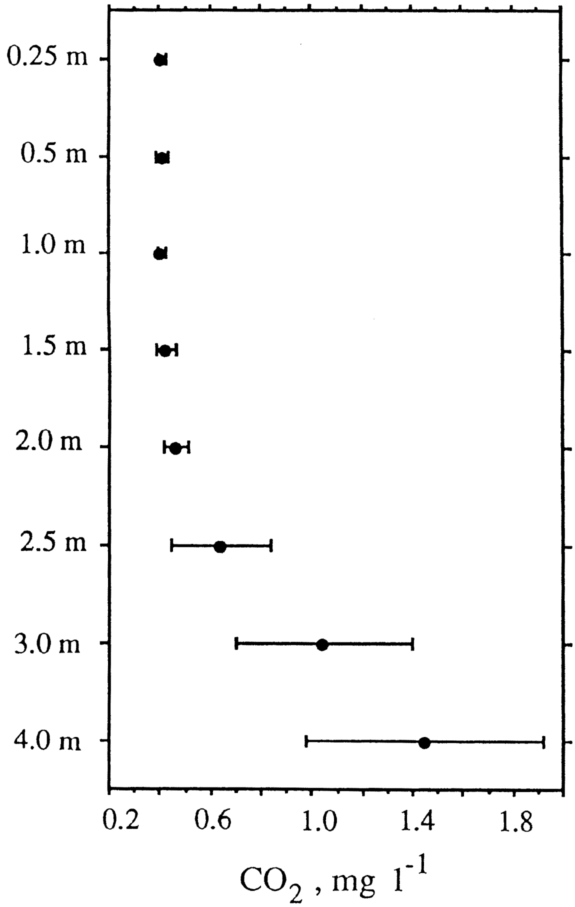

Figure 6. The CO_2 depth profile of the B-basin for the May-August period during 1992 and 1993. Average with SD of 10 measurements.

Since photo-oxidation promotes bacterial degradation, however, its overall importance is probably greater than indicated from the direct, abiotic CO_2 production alone. These mineralization processes combined imply a maximum loss rate of epilimnetic TOC close to 0.02 d^{-1}, and could thus be a major sink for surface TOC. Deeper in the water column, losses to respiration of $\sim$ 35 μg C l^{-1} d^{-1} imply a turnover of TOC about 0.005 d^{-1}. Detectable primary production were restricted to the top 2 m, and had occasional surface peaks exceeding 100 mg C m^{-3} d^{-1}, but had normally an abrupt decrease from around 50 at the surface towards zero at 2 m (Brettum 1994). This would imply nearly balance between respiration and fixation close to the surface, with excess CO_2 producton below 0.5 m. This is reflected in the vertical CO_2-

profiles (Figure 6) and does not support to the hypothesis that photo-oxidation is a major reason for low O_2 in humic lakes.

Inland waters may be pronounced CO_2 conduits to the atmosphere (Kling et al. 1991), carbon mineralized in humic surface waters may return to the atmosphere (Hessen et al. 1990). Gaseous exchange would be mediated by the surface microlayer (Emerson 1975). The thickness and constitution of this “boundary layer” was also a major determinant of the downwelling UV-B flux in this lake (unpubl. data). Our data suggest a positive relation between surface film thickness and light (and calm conditions), and effects of changed climate and UV-B could affect this microhabitat and by that the entire carbon dynamics of the lake.

Drought and decreased precipitation cause increased retention of TOC in lakes, and hence increased losses via sedimentation and oxidation. In lakes with long residence times, short-wave light and bacterial oxidation combined may cause minimum concentrations in surface water TOC in summer, but in this humid catchment with a residence time of only few months, TOC-supply from recent terrestrial production and vernal litterfall overwhelm in-lake processes, yielding a remarkably regular seasonal pattern.

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