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Enhanced photochemical loss of organic carbon in acidic waters

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Abstract. Previous studies have shown that (a) a large portion of the annual total organic carbon (TOC) inputs to central Ontario lakes is either lost to sediments or degraded and lost via evasion to the atmosphere, (b) the partitioning of organic carbon between sediments and the atmosphere appears to be a function of acidity and (c) UV irradiation can account for observed long-term loss of TOC from the water column. These findings were extended by examining whether acidity enhances photo-oxidative losses of TOC. Stream waters (initial alkalinities between –97 and 233 μeq l^{-1}) were incubated in UV-transparent containers under incident solar radiation for periods ranging from 14 to 23 days. The highest photo-oxidation rates occurred when alkalinity was negative. Additions of acid and base to stream waters increased and decreased photo-oxidation rates, respectively. The exceptional clarity of atmospherically acidified lakes is usually attributed to increased precipitation of Al-organic carbon complexes but may instead be due to higher photo-oxidation rates of allocthonous organic carbon leading to higher evasion rates of CO_2.

Introduction

We have been studying organic and inorganic carbon fluxes in boreal systems to understand the role of Boreal lakes and catchments in global carbon cycling and to further clarify our understanding of dissolved organic carbon (DOC) dynamics (Dillon & Molot 1997a,b; Molot & Dillon 1996, 1997). Boreal lakes derive their carbon from their catchments, rather than from the atmosphere (Dillon & Molot 1997a; Kling et al. 1991; Cole et al. 1994). Most of the total organic carbon (TOC) input is DOC, with the amount being a function of the extent of peatlands and runoff in the catchment (Dillon & Molot 1997a,b). Much of this carbon is stored in sediments or evaded to the

Table 1. Mean (± standard deviation) carbon mass transfer rates (m yr^{-1}) to sediments, ν_{sed}, and the atmosphere, ν_{atm}, in seven study lakes, 1980–1992. The mass transfer rate is derived from a steady state mass balance model in which (Load – Discharge) = (Atmospheric Loss + Sediment Storage). Annual load, discharge and sediment storage fluxes were measured; atmospheric loss was the difference between discharge and sediment storage. Assuming first order kinetics, Load = [TOC] (q + ν_{toc}) where Load is the TOC load to the lake, [TOC] is the TOC concentration, q is the areal water discharge rate (m yr^{-1}) and ν_{toc} is the TOC mass transfer coefficient (m yr^{-1}). TOC loss from the water column is partitioned between sediments and the atmosphere, hence, $\nu_{\text{toc}} = \nu_{\text{sed}} + \nu_{\text{atm}}$. ν_{sed} and ν_{atm} were calculated from $\nu_{\text{sed}}/\nu_{\text{toc}} = \text{C}_{\text{sed}}/\text{retained TC}$ and $\nu_{\text{sed}}/\nu_{\text{atm}} = \text{C}_{\text{sed}}/\text{C}_{\text{atm}}$ where C_{sed} is the annual storage rate of carbon in sediments, C_{atm} is the annual carbon evasion rate and $\text{C}_{\text{sed}} + \text{C}_{\text{atm}}$ = retained TC (total organic and inorganic carbon inputs less discharge). Data reworked from Dillon and Molot (1997a).

Lake alkalinity	ν_{sed}	ν_{atm}	n
< 20 μeq l^{-1}	0.9 ± 0.1	2.8 ± 0.8	3
> 20 μeq l^{-1}	1.9 ± 0.5	1.0 ± 0.9	4

atmosphere (40 to 70% of annual inputs). The magnitude of carbon stored in lakes sediments in the boreal biome is large, the amount being similar in size to the large carbon pool in peat (Molot & Dillon 1996). However, the mechanisms responsible for transfer of allocthonous organic carbon to sediments and to the atmosphere via evasion of low molecular weight (LMW) gases are poorly understood. Exposure to ultraviolet radiation (UV) assists transformation of allocthonous DOC in lakes into LMW organic and inorganic products that are transferred to the food chain, sediments or the atmosphere; otherwise, DOC remains biologically and chemically recalcitrant (Strome & Miller 1979; Amador et al. 1989; Moran & Hodson 1990; Lindell et al. 1995; Miller & Zepp 1995; Molot & Dillon 1997; Miller & Moran 1997). However, recent studies found that irradiation can reduce bioavailability of autocthonous, labile DOC (Tranvik & Kokalj 1998; Obernosterer et al. 1999).

Loss rates of stream TOC incubated under UV (Molot & Dillon 1997) are similar to loss rates measured in long-term mass balance studies in lakes on the Precambrian Shield in central Ontario (Dillon & Molot 1997a) indicating that the magnitude of photo-oxidation is sufficient to account for losses. (This does not imply that photo-oxidation is solely responsible.) UV alone is not sufficient to explain observed variation in mass balance loss rates of TOC and photo-oxidation kinetic constants in lakes, or why partitioning of retained carbon (lake inputs – discharge) between sediments and the atmosphere is a function of lake alkalinity (Dillon & Molot 1997a; Molot & Dillon 1996). The conventional wisdom is that atmospherically acidified lakes are clear because of precipitation of DOC-Al complexes (Effler et al. 1985). This implies an increase in carbon storage in sediments in acidified lakes. However, the ratio of carbon lost to the atmosphere compared to carbon stored in sediments is much higher in acidic lakes (Dillon & Molot 1997a; Molot & Dillon 1996). Moreover, carbon transfer rates to sediments decline when lakes acidify, not increase (Table 1). In this study, we examined whether acidification increases photo-oxidation of TOC.

There are a number of photochemical reaction mechanisms involving organic matter that have been described in the literature in recent years. DOC may be oxidized by direct aborption of radiation (Zepp & Cline 1977) as well as by photo-oxidants. The photo-oxidants are formed in photo-reactions involving direct absorption of UV by DOC, e.g., ligand metal charge transfer (Voelker et al. 1997), nitrate-mediated reactions (Haag & Hoigne 1985; Zepp et al. 1987; Brezonik & Fulkerson-Brekken 1998) and photo-Fenton reactions involving Fe-redox cycling (Moore et al. 1993; Petasne & Zika 1987; Voelker et al. 1997; Waite & Morel 1984).

Photo-Fenton reactions include the reaction of hydrogen peroxide with ferrous iron, Fe^{+2}, to produce the hydroxyl radical, $OH^{\bullet}$. Increasing acidity increases photo-reductive dissolution of Fe and inhibits re-oxidation of Fe^{+2} to Fe^{+3} by O_2 (Waite & Morel 1984), which in turn could produce higher levels of $OH^{\bullet}$ and thus higher DOC photo-oxidation rates. Zepp et al. (1992) observed that photo-formation rates of Fe^{+2} and $OH^{\bullet}$ increased with decreasing pH over the pH range 4.5 to 8.0 within each ligand-probe pair.

Study site

The Dorset Study Area in central Ontario is the site of a long-term study of the impacts of long range atmospheric transport, climate change and cottage development on water quality in forested headwater catchments and seven lakes (e.g., Dillon et al. 1987; Molot et al. 1989; Dillon & Molot 1990; Molot & Dillon 1991; Dillon et al. 1991; Mierle & Ingram 1991; Molot et al. 1992; Dillon & Evans 1993; Molot & Dillon 1993; LaZerte 1993; Nurnberg & Dillon 1993; Dillon & Molot 1996a,b). The twenty study catchments are located in the district of Haliburton-Muskoka on the southern edge of the Precambrian Shield (Figure 1). They range in area from 10 to 456 ha. The streams are first and second order. The catchments are underlain by metamorphic silicate bedrock and are primarily forested (Great Lakes-St. Lawrence forest region) with no upstream lakes. Minor till plains (continuous moraine deposits > 1 m thick but typically less than 10 m) and thin till deposits (< 1 m thick) interrupted by rock ridges are the dominant surficial

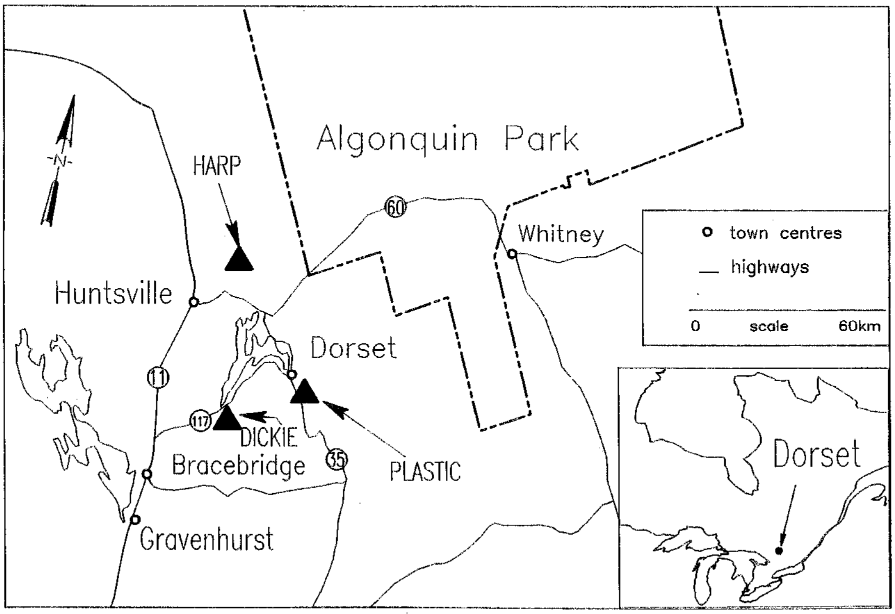

Figure 1. Map showing location of study sites in central Ontario. Blue Chalk lies just to the west of Plastic.

geological characteristics. The most common soils in the study catchments are brunisolic and podzolic. They are found on silicate bedrock, moderate to well drained slopes, generally on coarse grained parent surficial material. Organic soils (peat) lacking well-developed profiles are common, forming in areas saturated with water for a large part of the year. The extent of peatlands ranges from 0 to 25% of the catchment areas. The organic soils may occur as large extensions of lake bays usually overlying a sand deposit, occupy depressions in glacial fluvial deposits, or occupy perched bedrock deposits. Descriptions of physiographic and meteorological features are given in Dillon et al. (1991).

Methods

Stream waters collected from Dickie 5, Dickie 10, Harp 4, Plastic 1 and Blue Chalk 1 just above the mouths of the streams were exposed to ambient solar radiation in a series of incubations between May and October 1997. We chose to sample headwater streams because allocthonous DOC in lakes has already received such extensive irradiation that what remains is relatively insensitive to UV (Molot & Dillon 1997). Residence times in the Dorset study lakes range from 1.6 to 5.7 years. In contrast, DOC in headwater streams has had little exposure to UV and is much more ‘UV-labile’ (Molot & Dillon 1997).

UV-transparent Teflon bottles or 530 ml sterile polyethylene sample bags (Fisherbrand) containing 300 ml of stream water were placed in shallow water baths (70 × 130 × 9.5 cm deep with a water depth of 3.5 cm) at the Ontario Ministry of Environment’s Dorset Environmental Science Centre in central Ontario (45° 13′N 78° 56′W). The exposed surface of a filled bag was 14 × 7.5 cm with a thickness of 2.5 cm. Bottles were laid on their sides to maximize exposure. Incubation periods ranged from 14 to 23 days. Before use, Teflon bottles were soaked in 95% ethanol saturated with NaOH for at least 12 hours, rinsed with dilute HCl and deionized water and then soaked for 12 hours in de-ionized water. Bags were soaked in de-ionized water for 24 hours. PET (polyethylene teraphthalate) containers were rinsed with deionized water and wrapped in foil as dark controls. Of the 18 stream incubations conducted in 1997, five were conducted with ethanol-treated bottles, nine were conducted with non-ethanol treated bags and two trials used both types of containers. There were no significant differences in first order photo-oxidation constants (see below for definition of constants) between bags and bottles in the latter two trials (t-test at 0.1% level).

All TOC data were corrected for leaching by subtracting the amount of organic carbon found in UV-exposed blanks using deionized water sampled at identical incubation times. When this could not be done, correction factors were applied from the previous experiment. Leaching was minimal in Teflon and PET bottles during the first 13 days (up to 0.1 mg L^{-1} in deionized water under artificial UVB lamps (Sylvania 40 watt) and sunlight. Leaching was higher in bags, reaching 0.8 mg L^{-1} after 18 days and 1.9 mg L^{-1} after 21 days. Only two experiments exceeded 18 days and including the one sample day longer than 18 days did not affect the kinetic calculations.

Transmission of UV through Teflon walls was previously measured using an Optronics OL 752 scanning spectroradiometer (Molot & Dillon 1997). Transmission through bags was determined with a Hewlett-Packard 8452A diode array spectrophotometer with a 1 cm pathlength. Teflon bottles transmitted 45% of incident UVB and 55% of incident UVA (35% of radiation was transmitted at 280 nm and 64% at 400 nm). Bags transmitted 55% of UVB and 61% of UVA (49% of radiation was transmitted at 280 nm and 65% at 400 nm).

Incubations lasted between 14 and 23 days. Three containers from each treatment were removed every three days or four days and unfiltered aliquots were analyzed for TOC using an automated colourimetry UV-acid persulfate digestion method standardized with potassium bithalate. TOC measurements in this study thus include both particulate organic carbon (POC) and DOC.

Stream waters were analyzed for total iron colourimetrically after acid reduction by formation of the ferrous-2,4,6-tri-(2'pyridyl-)-1,3,5-triazine complex. Alkalinity was measured using the Gran titration method. Analytical methods are described in Ontario Ministry of the Environment (1993).

Absorbance was measured in samples collected from Dickie 5 and Dickie 10 in April 2000 and Aldrich humic matter at several pH values. The initial pH values were 4.3 for Dickie 5 and 10 stream waters and 8.4 for Aldrich. pH values were amended with reagent grade H_2SO_4 and NaOH to 3.9 and 5.6 for Dickie 5, 3.9 and 5.9 for Dickie 10 and 4.5 and 6.4 for Aldrich humic matter. Absorption spectra between 200 and 450 nm were used to calculate 'S' values according to $a_\lambda = a_{450}\, e^{S(450-\lambda)}$ where a_λ is the absorbance at wavelength λ and a_{450} is the absorbance at 450 nm (Blough et al. 1993).

UVA and UVB radiation data were incomplete for the experimental period due to lightning strikes and shielding problems so instead, photosynthetically active radiation (PAR) was used to reconstruct UV data using regressions. An Eppley Pyranometer fitted with a KG-3 filter measured PAR in the range 400–700 nm at Dorset (PAR ranged from 12 to 174 Watts m^{-2}). UVB (280–315 nm) was measured at Dorset with a Vital Technology BW-20 sensor. Comparison of average UVB radiation during each incubation period at Dorset with UVB radiation from Environment Canada's Brewer station #014 at Toronto (43° 40′N 79° 23′W) verified the accuracy of the Dorset data. PAR and UVB data were collected between July 31 and November 16, 1997. UVA radiation (315 to 400 nm) from an Environment Canada station at Jacks Lake (44° 42′N 78° 03′W) located 100 km southeast of Dorset was measured on five separate days in May, June and October 1994 using an Optronics OL 752 scanning spectroradiometer.

TOC photo-oxidation is assumed to follow exponential loss with $dC/dt = -k_iC$ where C is the fraction of initial TOC concentration, t is time, k_i is a first order constant (slope of ln C vs time) and i is the light treatment (UV or dark). All loss rates in samples exposed to UV were normalized for changes in the dark and variation in UV intensity by $a_{uv} = (k_{uv} - k_{dark}) / I_{uv}$ where a_{uv} is a broad band constant with units of $m^2\ kJ^{-1}$ and I_{uv} is the average daily intensity of UV between 280 and 400 nm transmitted through the containers (Molot & Dillon 1997). Photo-oxidation in this study thus refers to loss of TOC to inorganic end-products. In four experiments, the initial pH was varied by titrating with reagent grade H_2SO_4 (Baker) or NaOH (BDH).

Results

The ratio of Environment Canada's UVB data for Toronto to UVB data from Dorset (a distance of 200 km) ranged from 0.83 to 1.08 during seven consecu-

Table 2. Mean daily irradiance levels (Watts m^{-2}) during each of the experiments in 1997. UVA and UVB were reconstructed from PAR measurements except September 17–October 16 and September 29–October 19 when UVB was measured directly.

Date	UVB	UVA	PAR
April 5–23	0.24	12.5	102.2
May 5–19	0.20	10.8	87.1
May 24–June 8	0.31	15.4	128.7
June 16–July 4	0.29	12.1	98.4[a]
July 16–August 8	0.33	15.8	132.5[b]
Sept 17–Oct 6	0.14[c]	8.6	66.4[c]
Sept 29–Oct 19	0.13[d]	8.3	63.4[d]

[a] Mean PAR measurement for June 16–22 and July 1–3.

[b] Mean PAR measurement for July 16–August 4.

[c] Mean PAR and UVB measurements for September 17–27 and September 30–October 6.

[d] Mean PAR and UVB measurements for September 30–October 19.

tive 10 day periods beginning July 31, 1997, indicating that the Dorset UVB data were comparable. The mean ratio was 0.96 with a standard deviation of 0.09. Mean daily UVB and UVA (Watts m^{-2}) for each incubation period were determined from mean daily PAR (Watts m^{-2}) for the incubation period using the following regressions:

$$\mathrm{UVB} = -0.028 + 3.06 \times 10^{-5}\mathrm{PAR} \tag{1}$$
$$(R^2 = 0.94;\ n = 92;\ \text{s.e. slope} = 0.000073;\ P < 0.0001)$$
$$\mathrm{UVA} = 1.33 + 0.0013\mathrm{PAR} \tag{2}$$
$$(R^2 = 0.93;\ n = 5;\ \text{s.e. slope} = 0.0176;\ P = 0.0085).$$

Irradiance levels for each of the experiments are shown in Table 2.

Initial TOC, pH and alkalinity for each of the incubations are shown in Table 3. TOC loss ranged from 22% to 72% under exposure to solar radiation in Teflon bottles and bags and 0% to 9% in the dark. Very little organic carbon in stream waters was particulate (for example, the mean POC content in Dickie 10 stream waters was 3.2% of TOC (SD 3.8, range 18.1 to 34.0 mg C L^{-1}, n = 60) although particulate formation during irradiation cannot be excluded (Gao & Zepp 1998). Therefore, loss of TOC during incubation in the order of 22% to 72% can be considered as a net loss of initial DOC to an inorganic product. Alkalinity invariably increased during exposure to solar radiation, an average of 4.8 μeq per mg of TOC lost (std 1.9, n = 12).

Table 3. Initial TOC (mg C L^{-1}), pH, alkalinity (μeq L^{-1}) and iron (mg L^{-1}) for each of the incubations.

Date	Stream	TOC	pH	Alkalinity	Iron
April 5–23/97	DE10	6.2	4.88	–16.1	
May 5–19	DE10	7.4	4.47	–14.1	
	HP4	4.2			
	PC1	5.2			
May 24–June 8	DE10	10.2	4.71	–12.7	
	HP4	3.9	6.3	57.1	
	PC1	8.4	4.63	–19.9	
June 16–July 4	DE10	27.1	4.69	–3.20	1157
	HP4	5.1	6.64	93.3	221
	PC1	20.6	4.76	–5.67	1070
July 16–August 8	DE5	16.4	5.03	3.93	1001
Sept 17–Oct 6	DE5	18.7	4.55	–25.2	731
Sept 29–Oct 19	DE10	29.4	4.56	–17.8	1100
	HP4	6.5	6.88	218.6	552
	PC1	11.1	4.59	–22.6	486
	BC1	2.3	6.60	232.6	124

Loss of TOC was not oxygen-limited. Dissolved oxygen was in Dickie 5 stream water increased from an initial concentration of 2.5 mg L^{-1} to 7.1 mg L^{-1} (measured with a YSI Model 57) during a 21 day incubation in Teflon bottles. TOC losses were not matched by similar increases in dissolved inorganic carbon. Hence, the containers were probably gas-permeable.

All first order rate constants for solar radiation exposures were significantly different from zero at the 0.1% level with R^2 for ln [TOC] versus time ranging from 0.86 to 1.0 suggesting that first order kinetics is an appropriate assumption (Figure 2). K_{uv} was also significantly different from k_{dark} at the 0.1% level (t-test for comparison of slopes). First order constants and standard errors are listed in Table 4.

The highest photo-oxidation rate constants occurred when initial alkalinity was less than zero (Figure 3). The constants, a_{uv}, for the five headwater streams (Dickie 5, Dickie 10, Harp 4, Plastic 1, Blue Chalk 1) ranged from 3.8 to 14.0×10^{-5} m^2 kJ^{-1} in 1997. Similarly, a_{uv} recalculated from previously published data (Molot & Dillon 1997) which included a sixth stream, Chub 2, ranged from 3.1 to 10.9×10^{-5} m^2 kJ^{-1}. In both sets of data, a_{uv} was greater than 6×10^{-5} m^2 kJ^{-1} only when initial alkalinity was less than 0 μeq l^{-1}.

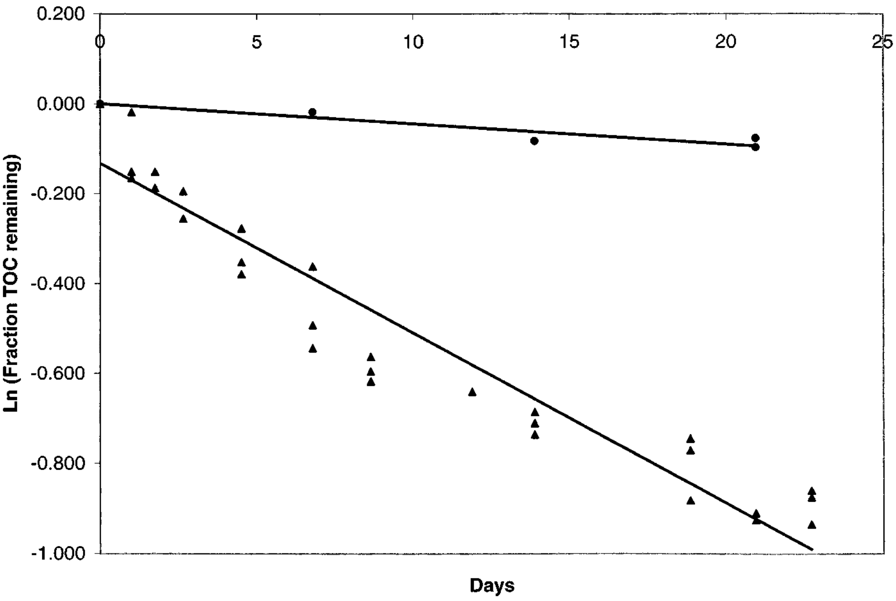

Figure 2. Natural logarithm of TOC remaining corrected for leaching of TOC from container walls as a fraction of the initial TOC versus time in Dickie 5 stream water (▲ exposed to solar radiation in UV-transparent polyethylene bags; ● dark controls) from July 16 to August 8, 1997. The trend lines are best-fit linear regressions.

The apparent relationship between alkalinity and a_{uv} was tested for causality by measuring a_{uv} in stream waters titrated to pH 4 and 6. In each incubation, a_{uv} increased with decreasing pH (Figure 4). Within each of the four experiments, first order slopes were significantly different from each other at the 1% level (t-test). Again, values greater than 6×10^{-5} m^2 kJ^{-1} occurred only when initial alkalinity was less than 0 μeq l^{-1}.

The increase in a_{uv} with decreasing alkalinity was not caused by increased absorption of UV since adding sulfuric acid lowered absorbance in the UV-visible range between 280 and 440 nm in Dickie 10 and Aldrich humic matter (Figure 5). In Dickie 5, absorbance was higher in the acidified sample, but only above 340 nm. Below 340 nm, there was very little difference (0 to 6%) between pH 3.9 and 5.6. The ‘S’ values for untreated Dickie 5 and 10 were 0.0170 and 0.0134 nm^{-1} which are similar to values measured by others (Blough et al. 1993; see Markager & Vincent 2000).

The correlation between a_{uv} and total iron was poor (r = –0.01) which is not unexpected. Correlations were higher but negative when the results were separated into two groups by alkalinity (r = –0.47 and –0.61 for alkalinity < 0 and > 0, respectively). Total Fe levels ranged an order of magnitude from

Table 4. First order rate constants (10^{-2} day^{-1}), standard errors (in brackets) and incubation lengths (days).

Date	Stream	k_{uv}	k_{dark}	Incubation length
April 5–23/97	DE10	9.5* (2.60)	–0.28 (0.05)	18
May 5–19	DE10	3.8* (0.29)	0.34 (0.21)	14
	HP4	3.6* (0.80)	–0.08 (0.11)	14
	PC1	5.8* (0.60)	–0.06 (0.14)	14
May 24–June 8	DE10	6.6* (0.75)	0.63 (0.13)	15
	HP4	4.9 (0.56)	0.21 (0.13)	15
	PC1	5.0 (0.34)	0.12 (0.07)	15
June 16–July 4	DE10	3.3* (0.40)	0.27 (0.15)	18
		3.5 (0.56)		18
	HP4	4.1 (0.30)	0.40 (0.24)	18
	PC1	6.1 (0.24)	0.10 (0.38)	18
July 16–August 8	DE5	3.8* (0.75)	0.45 (0.12)	23
		3.8 (0.19)		23
Sept 17–Oct 6	DE5	3.1 (0.14)	0.33 (0.34)	17
Sept 29–Oct 19	DE10	3.3 (0.29)	0.25 (0.06)	20
	HP4	1.8 (0.41)	0.15 (0.03)	20
	PC1	4.4 (0.78)	0.24 (0.06)	20
	BC1	2.4 (0.15)	0.23 (0.57)	20

*Samples containers were Teflon bottles. All other experiments used bags.

174 to 1670 μg l^{-1}. If photo-Fenton reactions are important in these waters and if they are limited by iron availability, then only a fraction of total iron is photo-reducible.

Discussion

Photo-oxidation rate constants increased markedly as alkalinity fell below 0 μeq l^{-1} which is consistent with mass balance observations showing greater atmospheric loss of carbon from acidic waters (Dillon & Molot 1997a) and is consistent with the photo-kinetic mechanisms outlined earlier. Zepp et al. (1992) observed that photo-formation rates of Fe^{+2} and $OH^{\bullet}$ increased with decreasing pH over the pH range 4.5 to 8.0 within each ligand-probe pair. In contrast, increasing the pH from 4 to 7 increased the DIC formation rate by 50% in acidic, coloured, DOC-rich river water in the southeastern U.S.

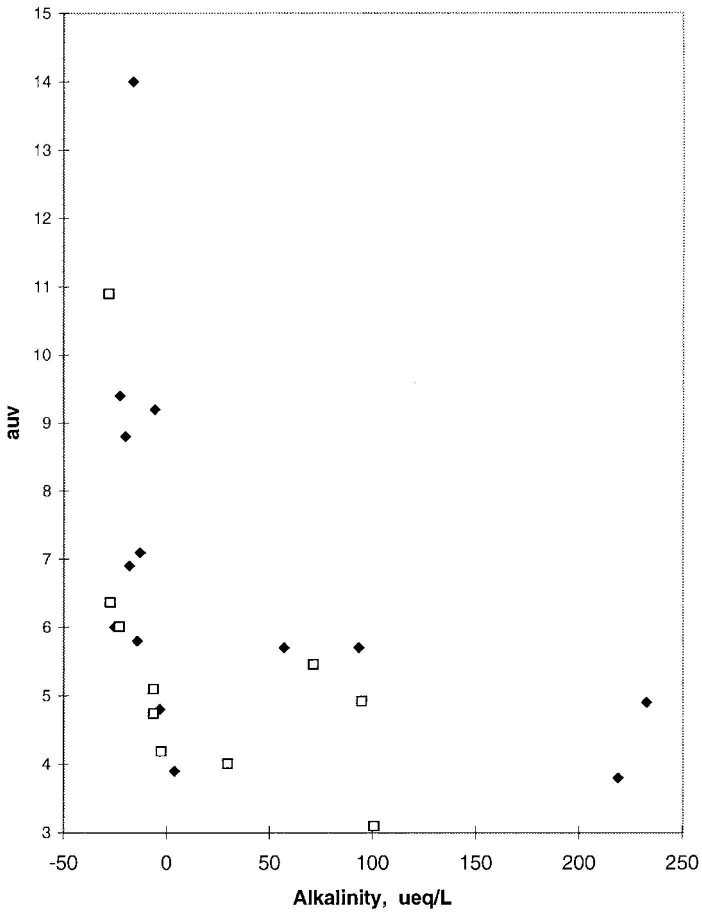

Figure 3. Photo-oxidation constants, a_{uv} (10^{-5} m^2 kJ^{-1}), versus initial alkalinity (μeq l^{-1}). Symbols: ◆ this study; ☐ data reworked from Molot and Dillon (1997). All values are dark-corrected.

during three day incubations. The pH effect was eliminated when a strong iron chelator, fluoride, was introduced (Gao & Zepp 1998).

Although absorption of UV decreased with pH in Dickie 5 and 10 stream waters (Figure 5), photo-oxidation rate constants were higher in acidic waters (Figure 3). The chromophoric (UV absorbing) properties of organic compounds are attributed to double bonds involving carbon, nitrogen and oxygen whereas saturated compounds are usually transparent to UV (Larson & Weber 1994). Thus, absorbance in the UV region appears influenced by the type and number of double bonds. While decreasing the pH in Dickie stream samples to 3.9 was unlikely to make or break double bonds significantly, it

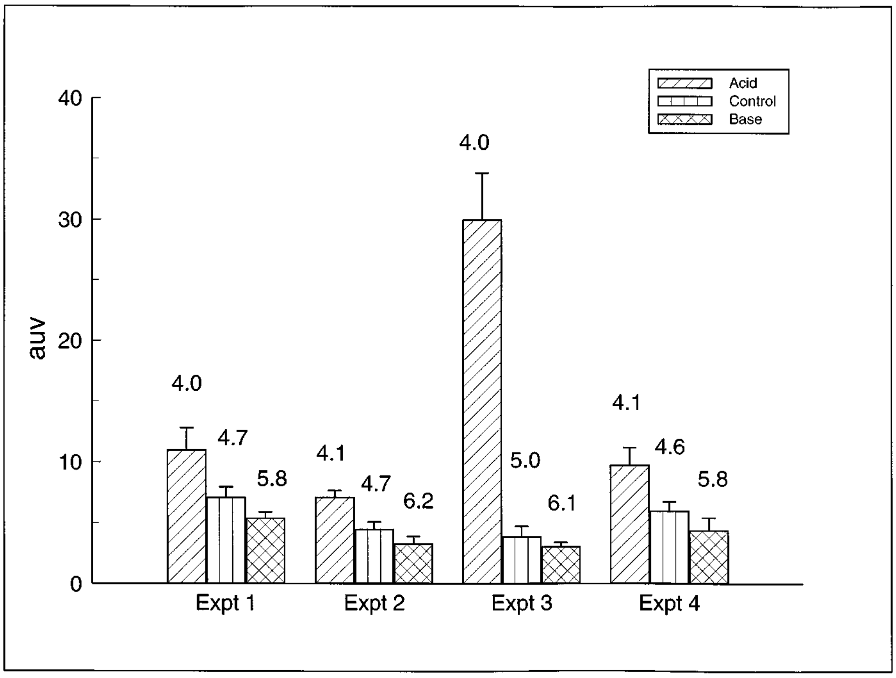

Figure 4. Effect of adding acid and base on the photo-oxidation constants, a_{uv} (10^{-5} m^2 kJ^{-1}). All values are dark-corrected. Bars are standard errors. Dates for experiments 1- 4 are May 24–June 8 (Dickie 10), June 16–July 4 (Dickie 10), July 16–August 8 (Dickie 5) and September 17–October 6 (Dickie 5), 1997, respectively. Initial pH for the base, control, and acid treatments are indicated on the graph. Initial alkalinities (μeq l^{-1}) for acid, control and base treatments, respectively are: experiment #1: –97.3, –12.7, 37.3; experiment #2: –79.5, –3.2, 109.7; experiment #3: –98.4, 3.9, 61.7; experiment #4: –82.8, –25.1, 47.1.

did lower UV absorption between 280 and 440 nm in Dickie 10 and 280 and 340 nm in Dickie 5. Whatever the mechanism that caused the decrease in absorption, it was more than compensated for by another mechanism which increased photo-oxidation rates in acidic waters, perhaps the photo-Fenton mechanism (Voelker et al. 1997). The effect of pH on UV and visible absorption in a range of stream and lake types warrants more investigation.

If the loss rate of allocthonous DOC is higher in acidic waters, then one would expect to find less UV-sensitive (i.e., photo-bleachable) DOC in more acidic lakes. In a recent study of twenty four North American lakes (Reche et al. 1999) there was a very poor but slightly negative correlation between photobleaching rate constant (loss of absorbance at 440 nm) and pH in the pH range 4 to 7 (r = –0.38) which is similar to the range of pH values in this study. Above pH 7 photobleaching increased sharply with pH.

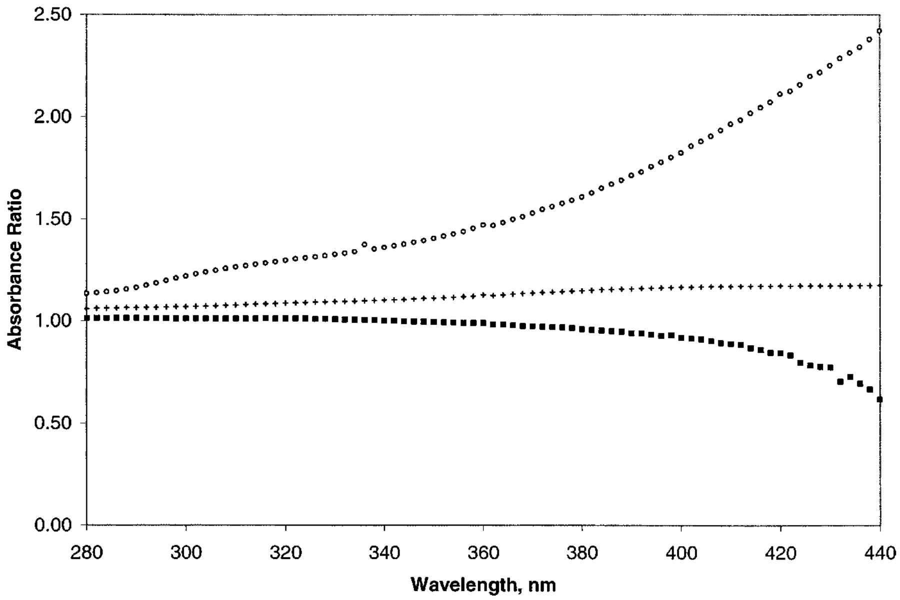

Figure 5. Effect of pH on absorbance, plotted as the ratio of absorbance at two pH values versus wavelength, in Dickie 5 (■) and Dickie 10 (○) stream waters and a solution of Aldrich humic matter (+). The absorbance at the more acid value is the numerator. The pH values used were 5.6/3.9 for Dickie 5, 5.9/3.9 for Dickie 10 and 8.5/4.5 for Aldrich humic. For reference, absorbance at 400 nm in untreated samples was 0.30 in Dickie 5, 0.27 in Dickie 10 and 0.75 in Aldrich humic.

Some of the irradiated TOC may have been microbially consumed and respired because the experiments were not performed under sterile conditions. Bacteria can consume humic material at a relatively low rate (Moran & Hodson 1990). It is widely accepted that microbes consume low molecular weight (LMW) photo-products (e.g., Amador et al. 1989; Lindell et al. 1995; Moran & Zepp 1997; Miller & Moran 1997; Bertilsson & Tranvik 1998) although a recent study found that irradiation can reduce bioavailability of labile, autocthonous marine DOC (Obernosterer et al. 1999). However, the importance of microbial consumption *in situ* relative to direct photo-mineralization of allocthonous DOC to CO_2 is still unknown. In the only published study on relative importance that we know of, bacterial consumption rates of several LMW photo-products were lower than LMW production rates and thus photo-products accumulated in short-term incubations (Bertilsson & Tranvik 1998). In two small, oligotrophic brown-water lakes in the Dorset study area pelagic heterotrophic bacterial production was 13% and 16% of that produced by phytoplankton between May and November, 1994 (Ferguson 1998) and 28% and 31% of the estimated allocthonous

TOC inputs retained by the lakes on an annual basis. Retained TOC was estimated as ν_{toc} [TOC] where ν_{toc} is the mass balance loss coefficient set equal to 3.3 m yr^{-1} (Dillon & Molot 1997a). Clearly, a large portion of the autocthonous and allocthonous TOC pools were not utilized by the pelagic microbial community.

If we assume that microbial consumption rates are high and that they are able to consume all LMW photo-products before being mineralized to CO_2, then the consumption rates would be rate limited by photo-oxidation. Thus, photo-oxidation mechanisms are still important to understanding the dynamics of the allocthonous carbon fraction in lakes which is not directly susceptible to microbial degradation, with the caveat that microbes may accelerate or delay transformation of LMW photo-products to CO_2 and thus affect a_{uv}. Microbial consumption may explain some of the variation in a_{uv}.

Molot and Dillon (1997) found that TOC photo-oxidation rates in incubations lasting up to 11 days were similar to loss rates measured in long-term (12 year) mass balance studies, suggesting that photo-oxidation has the potential to remove most of the allocthonous TOC although other mechanisms may also remove TOC. The results presented here indicate that allocthonous DOC loss in lakes is strongly influenced by the intensity of UV and pH. The effects of DOC quality and availability of photo-reducible (i.e., reactive) Fe are not known at this time but may explain some of the variation in a_{uv}. Zuo and Jones (1997) found that the rate of photochemical formation of CO increased non-linearly with dissolved iron and with iron additions. This study also supports the argument made elsewhere that lake DOC concentrations are susceptible to several regional and global human stresses (Schindler 1998): acidification and ozone depletion will accelerate DOC loss while the effects of climate change will be more variable.

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