Biogeochemistry **36:** 1–8, 1997.

The role of DOC in protecting freshwaters subjected to climatic warming and acidification from UV exposure

D. W. SCHINDLER[1] & P. J. CURTIS[2]
[1] *Department of Biological Sciences, University of Alberta, Edmonton, Alberta, Canada T6G 2E9;* [2] *Present address: Division of Science, Okanagan University College, 3333 College Way, Kelowna, British Columbia, Canada V1V 1V7*

Introduction

Dissolved organic carbon (DOC) is known to play a primary role in protecting freshwater organisms from exposure to UV radiation (Scully and Lean 1994). Recent observations in lakes subjected to acidification with strong acids, and to climatic warming and drought have revealed that both perturbations cause DOC to decline, suggesting that climatic warming and acidification were jeopardizing freshwater ecosystems by allowing increasing UV exposure of freshwater communities (Schindler et al. 1996a, b; Yan et al. 1996; Williamson et al. 1996).

From November 4–7, 1994, a small group of freshwater and marine scientists from Canada, the USA and Europe met at the Palisades Center in Jasper National Park, Alberta, Canada, to compare results of their studies of DOC-UV interactions and DOC budgets and characteristics in different regions. Environment Canada and the University of Alberta funded the workshop, which was hosted by Parks Canada. This volume contains a group of papers based on freshwater presentations at the workshop. Here, we present a brief overview of the papers, other recently published studies in this rapidly developing field, and their implications for freshwater ecosystems.

A concern for clear oligotrophic lakes

Because of the negative exponential relationship between DOC and UV absorbance, increasing UV exposure in clear, oligotrophic lakes with low (150–300 uM) natural DOC concentrations is of particular concern if DOC declines (Scully & Lean 1994; Schindler et al. 1996b; Williamson et al. 1996).

Lakes and streams at high altitudes and latitudes generally have catchments that are treeless, and in extreme cases, nearly free of vegetation. Thus, there are few sources of the colored DOC compounds that provide protection from UV (McKnight et al. 1997). Indeed, total DOC in alpine lakes can be 20 μM or less, approaching the limits of detection of even the most rigorous analytical protocols. In such waters, 1% of incident UV radiation can reach depths of several meters, and high UV exposures can occur in shallower waters. The high penetration of UV appears to be due to the scarcity of highly colored aromatic fulvic acid derivatives in runoff from catchments. Such compounds are typically produced by organic soils, which become increasingly scarce at high elevations (McKnight et al. 1997). In North America, there are probably well over 100000 lakes in alpine and arctic regions that are naturally vulnerable to UV because of limited DOC inputs.

In boreal regions, lakes with extremely small catchments (Curtis & Schindler 1997) and lakes acidified by deposition of strong acids are also at risk, regardless of latitude, altitude or vegetation (Schindler et al. 1996b; Yan et al. 1996). Such lakes are numerous. For example, over 20% of the over 1000 lakes surveyed in Ontario have DOC < 300 μM (Neary et al. 1990). Similarly, Williamson et al. (1996) report that a substantial percentage of lakes surveyed as part of the U.S. EMAP program had 1% UV penetration depths of over 4 meters, as the result of low DOC concentrations.

The effects of climatic warming on DOC

DOC in lakes of the Experimental lakes Area (ELA) declined substantially from 1970–1990, a period of substantial climatic warming (1.6 °C). The decline was caused by decreased yield of DOC from the catchment, caused by reduced streamflows, which resulted from increased evaporation and decreased precipitation. Lake waters cleared, allowing greater penetration of all wavelengths of solar radiation. Thermoclines, euphotic zones, and zones of critical UV exposure all increased (Schindler et al. 1990, 1996a, b, 1997). Similar responses of DOC in streams to warming and drought have been observed at Dorset, Ontario (Dillon & Molot 1997 and pers. comm.) The decrease in annual DOC yield occurs despite higher concentrations in storm flows following periods of prolonged drought (Hinton et al. 1997; Schindler et al. 1992). At the ELA, permanent first order streams were dry for up to 150 days during the ice-free season in the drought years of the late 1980s, whereas they had flowed continuously in the ice-free season in the early 1970s (Schindler et al. 1996a).

Groundwater appears to be a particularly important source of highly colored refractory DOC in catchments of the Precambrian Shield, probably because of its passage through wetlands and wet organic soils. Carbon-14 dates from groundwater and streams at baseflow in eastern Ontario indicate that DOC in such waters predates bomb tests, and is probably at least 100 years in average age (Schiff et al. and Hinton et al. 1997). However, due to the importance of stormflows, when more recently-formed soils are flushed, young carbon (average age $<$40 years, as evidenced by its nearly complete labelling with bomb ^{14}C) made up the greater proportion of carbon released from catchments to lakes, even when wetlands containing very old carbon were the source (Schiff et al. 1997). Obviously, DOC is very refractory in the soil environment.

The UV reactivity of DOC also varies seasonally, both as a function of DOC concentration and of the proportion of reactive chromophoric carbon. Highest overall reactivities were observed in the summer months, when exposure to incident UV would also be greatest (Clair & Sayer 1997).

Hinton et al. (1997) show the extreme difficulty of accurately measuring DOC yields from streams. Concentrations in catchments from eastern Ontario increased by 100 to over 400% during storms. Missed storms can cause important errors in DOC budgets, for 50% of annual DOC exports occurred during the upper 10% of the annual flow regime.

In addition to decreased DOC inputs, in-lake DOC removal increased in the ELA lakes during the 1970–1990 period, presumably because longer water residence times allowed greater exposure to photolyzing radiation, microbial action, and flocculation processes (Schindler et al. 1997; Dillon & Molot 1997). The increasing penetration of UV as DOC declined also constitutes a potential positive feedback mechanism, that might be expected to accelerate DOC removal.

In-lake processes remove colored organic compounds much more rapidly than uncolored ones, probably by a combination of photodegradation and photobleaching (Curtis & Schindler 1997; Dillon & Molot 1997). While the relative importance of different removal mechanisms isn’t known, they are probably interdependent. For example, although the breakdown of DOC appears to be initiated by photolysis, the resulting smaller molecules such as fatty acids, appears to stimulate oxidation by microbial action (Wetzel 1992; Wetzel et al. 1995). The observation of Hessen et al. (1997) that DOC declined from spring to fall, but continued to decline under winter ice and snow, reaching minima in late winter, supports the conclusion that processes other than photolysis are important in DOC removal. On the other hand, Molot and Dillon (pers. comm.) showed that photodegradation could account for a large part of the DOC losses from Precambrian Shield lakes of eastern Ontario. Further study is needed to resolve these differences in conclusions.

Forest fires appear to cause declining DOC input by mineralizing organic matter in soils and vegetation, although the effects are short-lived and generally much less important than reduced water flows (Schindler et al. 1997).

The end-point of climatic warming and drought appears to be reached in closed-basin lakes. Peculiarly, DOC in such lakes rises as a function of salinity. In contrast to other lake types, DOC is nearly colorless and highly refractory, probably as the result of centuries of photodegradation and photobleaching (Curtis & Adams 1995). The penetration of UV radiation in these systems is much higher than would be expected from DOC concentrations. Many are also very shallow, and aquatic communities may be vulnerable to high UV. The effects of high UV exposure in such communities are still unknown.

A double whammy: The effects of acidification and drought on DOC

It is well known that DOC declines and transparency increases in lakes as they acidify (reviewed by Driscoll & van Dreason 1993; see also Williamson et al. 1996; Yan et al. 1996). The disappearance of DOC in acidified lakes is much more rapid than in circumneutral lakes of the same region (Dillon & Molot 1997; Schindler et al. 1996b, 1997). Mass balance budgets (Dillon & Molot 1997; Molot & Dillon 1996) indicate that much of the lost DOC can be accounted for by release of CO_2 to the atmosphere, although this remains to be confirmed by direct measurements of gas exchange.

In addition to the direct effects of drought on the yield of DOC from catchments, drought causes increased inputs of strong acid pulses, which result from reoxidation of previously-deposited and reduced sulfur in catchments (Bayley et al. 1992; Lazerte 1993) and littoral lake sediments (Yan et al. 1996).

It is noteworthy that the drought-induced acid pulses depend on sulfur reduced and deposited in catchments and sediments in the past. These processes protected lakes and streams to some degree from acidic deposition at the time. However, the above studies have shown that reduced sulfur deposits in shallow lake sediments and wet soils can be an acidification “time bomb” under climatic warming, delaying recovery of lakes and streams from acidification (Keller et al. 1992; Dillon et al. 1987; Dillon et al. in press). In contrast, addition of strong acids to catchments appears to have little short-term effect on DOC yields (Hessen et al. 1997; S. E. Bayley, unpublished data).

Acidification and climatic warming also cause thermoclines to deepen in small lakes, as the result of increased buoyancy of deepwater caused by penetration of solar energy deeper into the water column (Schindler et al. 1996a; Dillon et al. 1984). The volume of summer habitat available for coldwater organisms is thus reduced. Conversely, larger and warmer epilimnions increase the habitat for warmwater organisms, and can be expected to decrease the development times and shorten the life cycles of many invertebrates.

Climatic change, acidification and UV exposure

The most common concern about stratospheric ozone depletion has been the increase in incident UV that has been predicted to have numerous effects on aquatic ecosystems (Williamson & Zagarese 1994). However, the decreased in DOC and resulting increase in transparency caused by climatic warming and drought, or acidification, can cause much greater increases in exposure of aquatic ecosystems to UV radiation than predicted declines in stratospheric ozone at northern latitudes (Schindler et al. 1996b; Yan et al. 1996; Williamson et al. 1996). Because of the negative exponential nature of the relationship between DOC and UV penetration, there must be concern for UV damage when DOC concentrations in lakes decrease to below about 300 uM. Such values are common in softwater lakes of eastern North America, and predominant in arctic and alpine areas.

In the past, climate warming, acidification, and UV have been treated as if they had distinct, separate effects on aquatic ecosystems. It is now clear that these three major stresses caused by man's alteration of the atmosphere cannot be studied in isolation.

Other effects of declining DOC

Increased exposure to UV light and decreasing coldwater habitats are not the only concerns if DOC declines. DOC also has important effects on the cycle of many metals. For example, Driscoll et al. (1995) noted that both methyl mercury and total mercury in remote Adirondack lakes increased with increasing DOC. Similar obervations were made by Mierle and Ingram (1991) and Lindqvist et al. 1991). These observations are consistent with the catchment budgets at ELA (St. Louis et al. 1994), where wetlands yielded nearly 100-fold more total and methyl mercury that adjacent upland catchments, for wetlands are far more important sources of DOC than uplands (Urban et al. 1988; Driscoll et al. 1995).

Conversely, both forms of mercury also increased in acidified Adirondack lakes (Driscoll et al. 1995), whereas DOC declined, suggesting that acidification limited the bioavailability of mercury or otherwise decoupled the DOC-Hg relationship. It is possible that acidification affects the ratio of methylation to demethylation (Xun et al. 1987; Ramlal et al. 1985; Miskimmin et al. 1992), or that the deeper thermoclines in acidified lakes cause methylation to increase relative to demethylation as described by Ramlal et al. 1993 and Bodaly et al. 1993).

Further complicating the changes to mercury cycling caused by DOC decline is the observation of Sellers et al. (1996) that methyl mercury can be photooxidized directly to Hg°, the primary form of mercury lost to the atmosphere. Both UV and short wavelength visible light appear to stimulate the reaction. Previously, the reduction of divalent mercury to Hg° was believed to be the only pathway of importance.

Also of concern is the formation of a number of reactive chemicals as the result of DOC-UV interactions, including OH^-, H_2O_2, superoxides, formaldehyde and carbon monoxide (Cooper et al. 1989; Kieber et al. 1990). In addition to facilitating other chemical transformations, these chemicals can reach concentrations high enough to be toxic on their own.

Flocculation with DOC may also affect the cycle of many elements, causing them to precipitate or coprecipitate (Jackson and Schindler 1985; Weilenmann et al. 1989; Urban et al. 1990).

In summary, the DOC-mediated interactions between climatic warming, acidification, increased UV, and biological changes in aquatic ecosystems are many, cumulative, and complex. The papers in this volume represent an important first step in understanding the rates and biogeochemical mechanisms involved.

References

Bayley SE, Behr RS & Kelly CA (1986) Retention and release of sulfur from a freshwater wetland. Water Air Soil Pollut. 31: 101–114

Bayley SE, Schindler DW, Parker BR, Stainton MP & Beaty KG (1992) Effect of forest fire and drought on acidity of a base-poor boreal forest stream: similarities between climatic warming and acidic precipitation. Biogeochemistry 17: 191–204

Bodaly RA, Rudd JWM, Fudge RJP & Kelly CA (1993) Mercury concentrations in fish related to size of remote Canadian Shield lakes. Can. J. Fish. Aquat. Sci. 50: 980–987

Clair TA & Sayer BG (1997) Environmental variability in the reactivity of freshwater dissolved organic carbon to UV-B. Biogeochem. 36: 89–97

Cooper WJ, Zika RG, Petanse RG & Fischer AM (1989) Sunlight-induced photochemistry of humic substances in natural waters: Major reactive substances: Influences on fate and treatment of pollutants. Adv. Chem. Ser. 219. Amer. Chem. Soc.

Curtis PJ & Adams HE (1995) Dissolved organic matter quantity and quality from freshwater and saline lakes in east-central Alberta. Biogeochem. 30: 59–76

Curtis PJ & Schindler DW (1997) Hydrologic control of dissolved organic matter concentration and quality in low-order Precambrian Shield lakes, Experimental Lakes Area, northwestern Ontario. Biogeochem. 36: 125–138

Dillon PJ & Molot LA (1997) Dissolved organic and inorganic carbon mass balances in central Ontario lakes. Biogeochem. 36: 29–42

Dillon PJ, Molot LA & Futter M (1996) The effect of El Nino-related drought on the recovery of acidified lakes. Int. J. Monit. Assess. (in press)

Dillon PJ, Reid R & de Grosbois E (1987) The rate of acidification of aquatic ecosystems in Ontario, Canada. Nature 329: 45–48

Dillon PJ, Yan ND & Harvey HH (1984) Acidic deposition: effects on aquatic ecosystms. Critical Reviews in Environmental Control 13, no. 3: 167–194

Driscoll CT, Blette V, Yan C, Schofield CL, Munson R & Holsapple J (1995) The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. Water, Air Soil Pollut. 80: 499–508

Driscoll CT & Van Dreason R (1993) Seasonal and long-term temporal patterns in the chemistry of Adirondack lakes. Water Air Soil Pollut. 67: 319–44

Hessen DO, Gjessing E, Knulst J & Fjeld E (1997) TOC fluctuations in a humic lake as related to catchment acidification, season and climate. Biogeochem. 36: 139–151

Hinton MJ, Schiff SL & English MC (1997) The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochem. 36: 67–88

Jackson TA & Schindler DW (1985) The biogeochemistry of phosphorus in an experimental lake environment: evidence for the formation of humic-metal-phosphate complexes. Int. Ver. Theor. Angew. Limnol. Verh. 19: 211–221

Keller W, Pitblado JR & Carbone J (1992) Chemical responses of acidic lakes in the Sudbury, Ontario, area to reduced smelter emissions, 1981–1989. Can. J. Fish. Aquat. Sci. 49: 25–32

Kieber RJ, Zhou X & Mopper K (1990) Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: Fate of riverine carbon in the sea. Limnol. Oceanogr. 35: 1503–1515

Lazerte B (1993) The impact of drought and acidification on the chemical exports from an minerotrophic conifer swamp. Biogeochem. 18: 153–175

Lindqvist O, Johansson K, Astrup M, Andersson A, Bringmark L, Hovsenius G, Håkanson L, Iverfeldt Å, Meili M & Timm B (1991) Mercury in the Swedish environment – recent research on causes, consequences and corrective measures. Water Air Soil Pollut. 55 (1/2)

McKnight DM, Harnish R, Wershaw RL, Baron JS & Schiff S (1997) Chemical characteristics of particulate, colloidal, and dissolved organic material in Loch Vale Watershed, Rocky Mountain National. Biogeochem. 36: 99–124

Mierle G & Ingram R (1991) The role of humic substances in the mobilization of mercury from watersheds. Water Air Soil Pollut. 56: 349–357

Miskimmin BM, Rudd JWM & Kelly CA (1992) Influence of dissolved organic carbon, pH, and microbial respiration rates on mercury methylation and demethylation in lake water. Can. J. Fish. Aquat. Sci. 49, no. 1: 17–22

Molot LA & Dillon PJ (1996) Storage of terrestrial carbon in boreal lake sediments and evasion to the atmosphere. Global Biogeo. Cycles (in press)

Neary BP, PJ Dillon, JR Munro JR & Clark BJ (1990) The acidification of Ontario Lakes: An assessment of their sensitivity and current status with respect to biological damage. Ontario Ministry of Environment, Dorset Research Centre, Dorset, Ontario

Ramlal PS, Rudd JWM, Furutani A & Xun L (1985) The effect of pH on methyl mercury production and decomposition in lake sediments. Can. J. Fish. Aquat. Sci. 42: 685–692

Ramlal PS, Kelly CA, Rudd JWM & Furutani A (1993) Sites of methyl mercury production in remote Canadian Shield lakes. Can. J. Fish. Aquat. Sci. 50: 972–979

St. Louis, VL, JWM Rudd, CA Kelly, KG Beaty, NS Bloom & RJ Flett (1994) Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. Can. J. Aquat. Sci. 51: 1065–1076

Schindler, DW, KG Beaty, EJ Fee, DR Cruikshank, ED DeBruyn, DL Findlay, GA Linsey, JA Shearer, MP Stainton & MA Turner (1990) Effects of climatic warming on lakes of the central boreal forest. Science 250: 967–970

Schindler, DW, SE Bayley, PJ Curtis, BR Parker, MP Stainton & CA Kelly (1992) Natural and man-caused factors affecting the abundance and cycling of dissolved organic substances in Precambrian Shield lakes. Hydrobiologia 229: 1–21

Schindler, DW, SE Bayley, BR Parker, KG Beaty, DR Cruikshank, EJ Fee, EU Schindler & MP Stainton (1996a) The effects of climatic warming on the properties of boreal lakes and streams at the Experimental Lakes Area, Northwestern Ontario. Limnol. Oceanogr. 41(5) (in press)

Schindler DW, Curtis PJ, Parker BR & Stainton MP (1996b) Consequences of climatic warming and lake acidification for UVb penetration in North American boreal lakes. Nature 379: 705–708

Schindler DW, Curtis PJ, Bayley SE, Beaty KG, Parker BR & Stainton MP (1997) Climate- and acidification induced changes in the dissolved organic carbon budgets of boreal lakes. Biogeochem. 36: 9–28

Schiff S, Aravena R, Trumbore SE, Hinton MJ, Elgood R & Dillon PJ (1997) Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: Clues from ^{13}C and ^{14}C. Biogeochem. 36: 43–65

Scully NM & Lean DRS (1994) The attenuation of ultraviolet radiation in temperate lakes. Arch. Hydrobiol. Beih. Ergebn. Limnol. 43: 135–144

Sellers P, Kelly CA, Rudd JWM & MacHutchon AR (1996) Photodegradation of methylmercury in lakes. Nature 380: 694–697

Urban NR, Bayley SE & Eisenreich SJ (1988) Export of dissolved organic carbon and acidity from peatlands. Water Resour. Res. 25: 1619–1628

Urban NR, Gorham E, Underwood JK, Martin FB & Ogden JG III (1990) Geochemical processes controlling concentrations of AL, Fe, and Mn in Nova Scotia lakes. Limnol. Oceanogr. 35: 1516–1534

Weilenmann U, O’Melia CR & Stumm W (1989) Particle transport in lakes: Models and measurements. Limnol. Oceanogr. 34: 1–18

Wetzel RG (1992) Gradient-dominated ecosystems: sources and regulatory functions of dissolved organic matter in freshwater ecosystems. Hydrobiologia 229: 181–198

Wetzel RG, Hatcher PG & Bianchi TS (1995) Natural photolysis by ultraviolet irradiance of recalcritrant dissolved organic matter to simple substrates for rapid bacterial metabolism. Limnol. Oceanogr. 40: 1369–1380

Williamson, CE, Stemberger RS, Morris DP, Frost TM & Paulsen SG (1996) Ultraviolet radiation in North American lakes: attenuation estimates from DOC measurements and implications for plankton communities. Limnol. Oceanogr. (in press)

Williamson CE & Zagarese HE (1994) The impact of UV-B radiation on pelagic freshwater ecosystems. Arch. Hydrobiol. Beih. Ergebn. Limnol. 43: IX–XI

Xun L, Campbell NER & Rudd JWM (1987) Measurements of specific rates of net methyl mercury production in the water column and surface sediments of acidified and circumneutral lakes. Can. J. Fish. Aquat. Sci. 44: 750–757

Yan ND, Keller W, cully NM, DRS Lean DRS & Dillon PJ (1996) Increased UV-B penetration in a lake owing to drought-induced acidification. Nature 381: 141–143