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Environmental variability in the reactivity of freshwater dissolved organic carbon to UV-B

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Abstract. Reductions in the global stratospheric ozone layer are thought to be increasing the amount of ultraviolet B (UV-B) radiation reaching the planet's surface and may be affecting the chemistry of dissolved organic carbon (DOC) in surface waters. We studied the abundance of chromophores in DOC collected in four different aquatic environments in southwestern Nova Scotia using ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy. We showed a clear seasonal pattern in the distribution of structural carbon related to light-sensitive chromophores. There seemed to be little variation in the UV-B related chemical structure of DOC between lakes and streams, though water from a bog pool showed large differences from the other samples. These patterns of potential UV-B reactivity tend to be dampened however, by variations in DOC concentrations which also occur seasonally.

Introduction

A number of studies show that exposure of aquatic dissolved organic carbon (DOC) to ultraviolet light (UV) in both the UV-A (320–400 nm) and UV-B (280–320 nm) ranges, leads to a number of chemical reactions which can modify features of DOC and generate other by-products. Zepp (1988) reported that aquatic and soil humic substances (which form a large part of DOC) are faded by exposure to both UV and visible light, while Hongve (1994) has shown losses of water color and DOC concentration in waters irradiated for 12 days in the laboratory. Zepp (1988) and Millero and Sohn (1992) summarize these and identify a number of potential reaction pathways leading to various byproducts. They include new oxidized states of DOC and the formation of hydrogen peroxide (H_2O_2). UV oxidation is also used in a number of chemical methods for the analysis of DOC (Koprivnjak et al. 1995) so that increases in ambient levels would be expected to have some impact on naturally occurring DOC.

Photochemical reactions between DOC and UV occur at light sensitive sites on organic molecules called chromophores (Zepp 1988). In DOC, these are mostly conjugated double bonds such as carboxylic acids, aromatic rings, phenolic functional groups associated with aromatic structures and functional groups which contain unbonded electrons (e.g. carbonyls) (Thurman 1985).

There is good evidence that the amount of UV radiation reaching the planet's surface has increased over the last decade (Kerr & McElroy 1993). The effects of UV-B on water chemistry have been relatively well documented for marine systems, though little work has been done assessing how UV affects the chemistry of freshwater systems. Studies by Cooper and Lean (1989), Valentine and Zepp (1993), Cooper et al. (1994) and Scully and Lean (1994) seem to show that though the same chemical reactions elaborated in marine systems are occurring in freshwaters, these are modified by environmental factors which are not yet clearly understood, including the presence of dissolved iron as well as the nature and concentration of dissolved and particulate carbon.

The structure of freshwater DOC is known to vary seasonally and between habitat types because of hydrological and soil biological changes (Clair et al. 1995). We therefore decided to see if these changes in chemical structure could be related to the ability of freshwater DOC to react with UV-B radiation over a seasonal cycle and between different types of aquatic environments. This information could then be used to assess the sensitivity of aquatic ecosystems to the indirect effects of UV-B.

Area and methods

Samples for DOC chemical structure analyses were collected in the Kejimkujik National Park region of southwestern Nova Scotia (Figure 1). The area is underlain by slates and granite. Much of the area is covered with fens or *Sphagnum* bogs. Forest cover is either White or Black Spruce (*Picea glauca, P. mariana*) and mixed hardwood-softwood stands, depending on soil quality and drainage. Sampling was carried out five times (January, March, April, June and November) at four sites representing a continuum of hydrological and seasonal conditions in and around Kejimkujik National Park in 1989. The sites were: Moose Pit Brook, a 17 km^2 first order stream catchment draining a mainly forested area; a 2 ha treed mire (submerged bog) in the Moose Pit Brook basin; Tupper Lake, a small shallow lake fed by Moose Pit Brook and another similar stream, which has a 118 ha surface area and a mean depth of 2.7 m; and the Mersey River at Mill Falls, a fourth order stream with a 297 km^2 catchment size.

Two hundred and thirty litres of water were collected at each site and the dissolved carbon extracted using Reverse Osmosis (RO) following the procedure described by Clair et al. (1991). The concentrated samples were

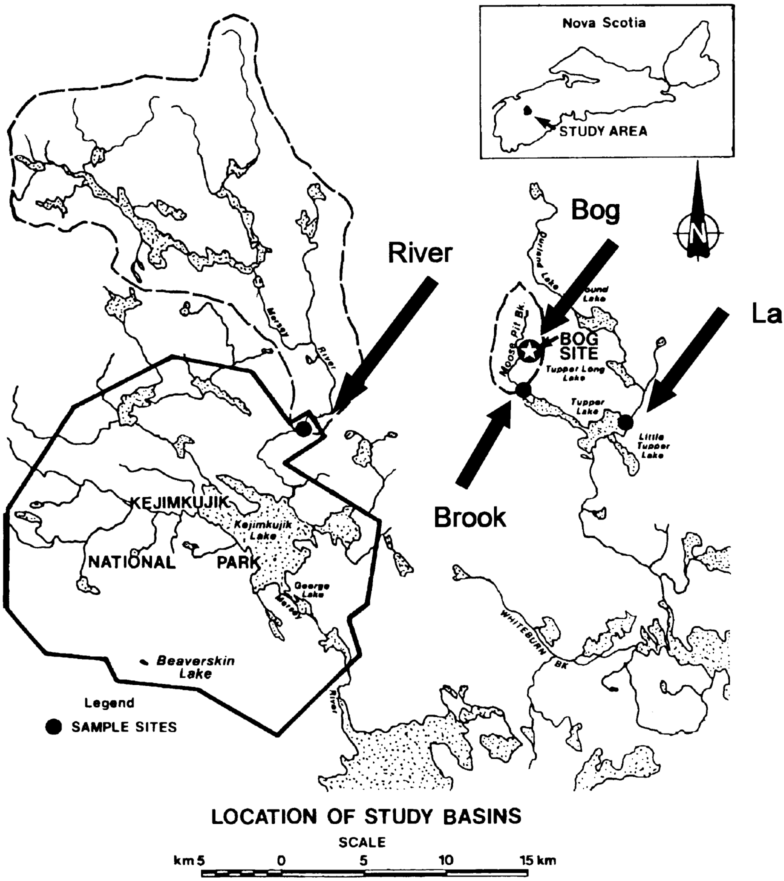

Figure 1. Location of study sites in and near Kejimkujik National Park, Nova Scotia, Canada.

freeze-dried within two weeks to form a powder (Malcolm 1976). The method generally extracted over 95% of dissolved carbon. Over the course of this study, eighteen samples were collected from the sites.

The DOC powder was analyzed using solid-state ^{13}C crosspolarization, magic angle spin, nuclear magnetic resonance spectroscopy (^{13}C CP/MAS NMR). The major advantage of this technique is that it produces well resolved, chemically informative, semi-quantitative spectra from which the percentage of carbon atoms in various functional groups can be estimated. Spectra of the powdered samples were analyzed on a Bruker MSL100 NMR spectrometer operating at 25.18 MHz at 2.35 T. Samples were spun at 4 KHz in a 7 mm (outside diameter) rotor. All spectra were acquired with a 1 msec. contact time and a recycle time of 1.5 sec. Typically 50,000 to 100,000 scans were required to obtain an adequate signal to noise ratio. Though this method is not

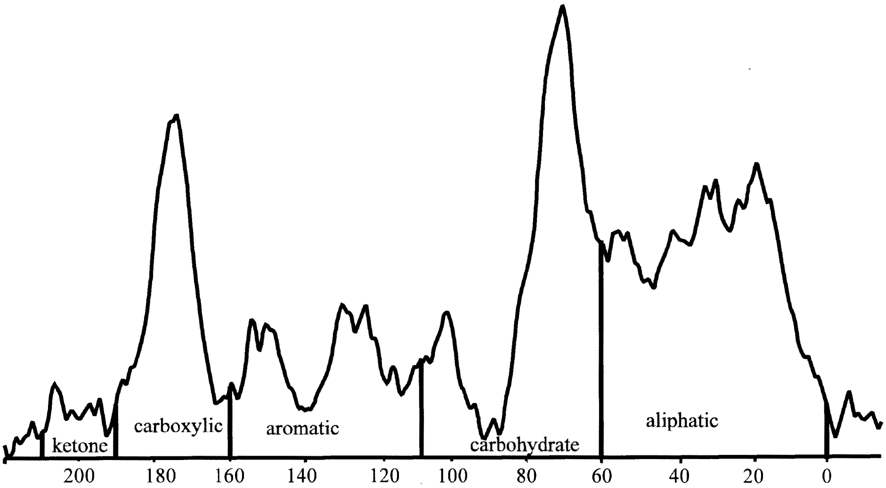

Figure 2. Typical ^{13}C NMR spectrum from a sample. Attribution of portions of the spectrum was done according to Malcolm (1989) and Preston et al. (1990).

quantitative for all carbon types, all samples were analyzed under identical conditions and are considered comparable for the purposes of this study. Preston et al. (1990) report that using similar instrument settings as in this study, the reproducibility of the ratios is within +/–5%.

The solid state ^{13}C NMR spectra were divided into specific chemical shift regions corresponding to particular organic carbon functional groups present in the concentrate (Figure 2) using the classifications reported by Preston et al. (1990). The region between 0 and 60 parts per million (ppm) is assigned to aliphatic carbons and includes signals from lipids and fatty acids. The region between 60 and 110 ppm contains mostly carbohydrates with an oxygen substituted aliphatic carbon maximum at 73 ppm and di-oxygen substituted carbons at 104 ppm. The aromatic region is between 110 and 160 ppm and includes the phenolic region between 140 and 160 ppm. Proton-bearing aromatic carbons show a maximum near 130 ppm. The carboxyl region between 160 and 190 ppm includes signals from carboxylic acid esters and amides and includes those present in lipids and amino acids. Carbonyl signals from ketones and aldehydes are observed in the region between 190 and 210 ppm.

Work summarized by Thurman (1985) and MacCarthy and Rice (1985) shows that the main humic substance structures containing chromophores are the aromatic, phenolic, carboxyl and carbonyl, all of which are found at the upper portions of the NMR scans. Despite the presence of chromophores in these structures, it is not yet possible to quantify their amounts. Nevertheless, we used the NMR spectra to provide a relative indication of the abundance of chemical structures which can contain chromophores. For the purpose of this paper, the NMR spectral information were divided into two classes, the proportion of the spectra showing structures most likely containing chromophores (aromatic, phenolic, carboxylic and carbonyl fractions, between 110 and 210 ppm) and the proportion showing structures with few double bonds and thus a lower chance of containing chromophores (aliphatic and carbohydrate fractions, between 0 and 110 ppm).

Results and discussion

Results of the NMR analysis showed clear patterns of UV-reactive structure abundances of DOC in the environments we studied (Figure 3). Carbon not belonging to chromophoric structures (aliphatic & carbohydrate C, Figure 3) comprised at least 64% of the total in all samples, though its proportion in the stream, river and lake was greater in the April and June sampling than in the fall and winter. Bog water non-chromophoric C tended to remain relatively stable at between 75 and 80% of total for the three sampling times when the site was not frozen (the site could not be sampled in the winter).

Conversely, carbon belonging to chromophoric groups (Figure 3) was lower in April and June and relatively higher in November, January and March. Clair et al. (1995) suggested that interactions between diagenetic C processes in soils and hydrological transport or that some other diagenetic factors, unrelated to photochemistry, such as bacterial decomposition or adsorptive processes were probably responsible for the seasonal differences in the DOC structure of waters reaching the streams and lakes via soils. The Bog water DOC was relatively non-chromophoric compared to the other sites perhaps because the diagenetic processes described above occur at different rates, under different conditions or are bypassed completely.

In order to see how these variations in DOC affected the total reactivity of the surface waters to UV-B, DOC concentrations of the waters (Figure 4) were multiplied by the % chromophoric carbon content. Our results (Figure 4) show relatively low and similar concentrations of chromophoric carbon during the January, March and April samplings at the stream, river and lake. In June and November however, concentrations of reactive chromophore sites increase sharply in the brook samples, to values of 10 mg L^{-1}. The increase was less sharp, but was still obvious in the river water (to 4 mg L^{-1}), and less so again in the lake waters. This suggests that because of higher summer DOC concentrations, the UV-B reactivity of stream and river water is greater from late spring to late fall than for the remainder of the year. This should

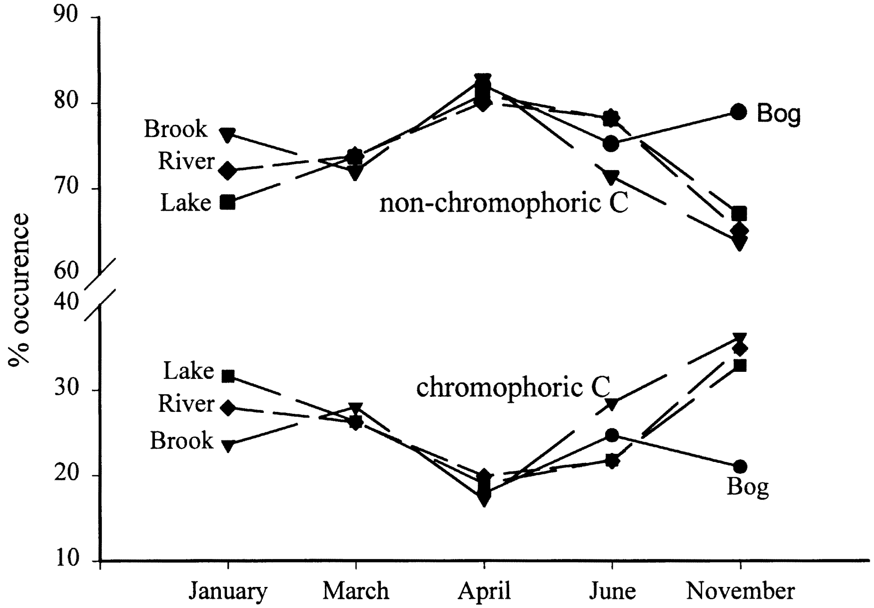

Figure 3. Percent occurrence of carbon in chromophoric and non-chromophore C structures at four sites in the study area. The circles are Bog samples; inverted triangles, Brook; squares, Lake; and diamonds, rivers.

lead to higher free radical concentrations and other related chemical changes (Zepp 1988).

Because much of the earlier work which studied interactions between UV-B and DOC was done in marine systems, we found it useful to compare freshwater conditions with marine to get an idea of potential differences in organic – UVB interactions between the two types of environments. An important consideration is that freshwater DOC concentrations are usually an order of magnitude greater than marine values. While higher concentrations should lead to more potential chemical reactions, UV-B penetration should also be attenuated more quickly than in marine situation, so that the actual UV-B chemical influence in freshwaters compared to marine water is not necessarily greater.

Also important in comparing UV-B effects between freshwater and marine systems is that the origins of the DOC are different in the two environments. Apart from coastal and estuarine situations, most marine DOC is of phytoplankton origin which is generally non-aromatic (Stuermer & Payne 1976; Wilson et al. 1983). They show marine DOC to be mostly carbohydrate in structure and completely derived from phytoplankton exudates. DOC from this study and in most small streams, rivers and lakes is mostly of terrigenous

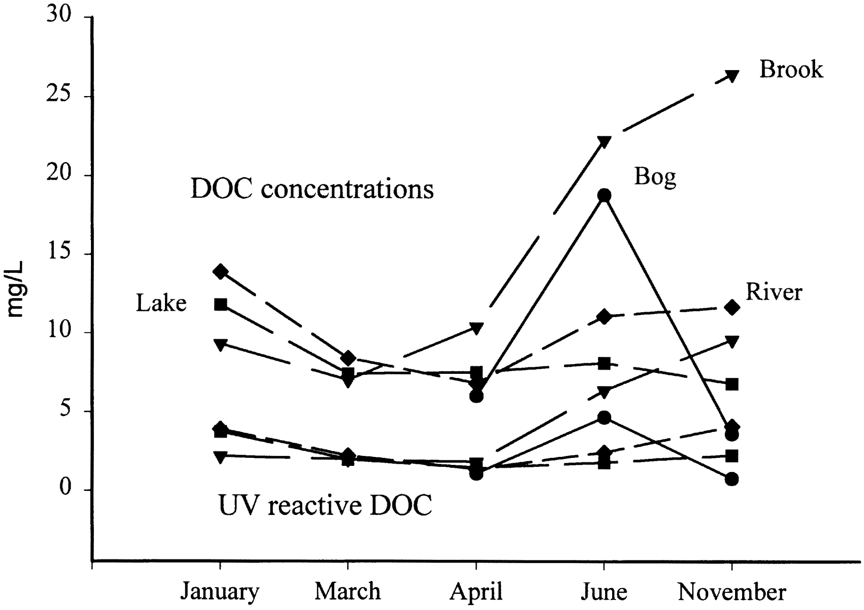

Figure 4. DOC concentrations at the sampling times (upper group) and the portion of that DOC which can be assigned to chromophores (lower group). The circles are Bog samples; inverted triangles, Brook; squares, Lake; and diamonds, rivers.

origin and contains more aromatic structures. Because of the difference in composition due to different source materials, we expect UV-B interactions to be more intense in freshwater than in marine ecosystems.

Finally, the oceans are stable hydrologically compared to most freshwaters. This allows greater marine DOC compositional stability than in freshwaters, where rapid changes in water and DOC sources can occur. Structures which contain chromophores, and thus which are potentially reactive with UV light, vary seasonally in relative concentration and their abundances are dependent on the origin of DOC and redox conditions of the soils where they are formed and temporarily stored (Orem & Hatcher 1987).

In conclusion, our results suggest that in slower moving sytems, such as small ponds or shallow lakes, UV-B may be much more important in affecting DOC chemistry than in relatively more dynamic sites. The greater variability and chemical complexity of freshwaters must lead to greater variations in UV-B related DOC chemistry than marine systems. More work now needs to be done to understand the magnitude of these changes and their impact on ecosystems.

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