Risk analysis of dissolved organic matter-mediated ultraviolet B exposure in ...

L A Molot; W Keller; P R Leavitt; R D Robarts; et al

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### PERSPECTIVE / PERSPECTIVE

### Risk analysis of dissolved organic mattermediated ultraviolet B exposure in Canadian inland waters

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**Abstract:** With depleted ozone levels and the possibility that climate change might lower dissolved organic matter (DOM) concentrations, the risk of exposure of fresh waters in Canada to ultraviolet B (UV B) was evaluated. First, the distribution of a UV-B-sensitive zooplankton genus, *Daphnia*, was examined as a function of DOM concentration and maximum depth ( $Z_{max}$ ) in 258 systems. Distribution was not restricted by UV B, although very clear, shallow systems are underrepresented. Secondly, the depth at which 1% of surface radiance at 320 nm occurs ( $Z_{conf...}$ ) was compared with  $Z_{max}$  in over 1000 aquatic systems in 15 ecozones to determine the proportions of optically clear systems ( $Z_{conf...}$ ) and systems that may become clear (i.e., are "at risk") should DOM decrease by 50%. South of the treeline, <6% of systems were clear, with the exception of two ecozones with 10% 20%. The proportion of systems at risk was 0% in most regions, with 5% 9% in four regions. DOM levels appear adequate to prevent extirpation of sensitive taxa like *Daphnia* through direct exposure to UV-B in most regions south of the treeline. However, optically clear and at risk ponds were much more common in the three Artic ecozones, especially the Northern Arctic and Arctic Cordillera.

**Résumé :** Nous avons évalué le risque de l'exposition des milieux d'eau douce canadiens aux ultraviolets (UVB), compte tenu des réductions de la couche d'ozone et de la possibilité que les changements climatiques réduisent les concentrations de matière organique dissoute (DOM). Nous avons d'abord examiné la répartition de *Daphnia*, un genre d'animal zooplanctonique sensible aux UVB, en fonction de DOM et de la profondeur maximale ( $Z_{max}$ ) dans 258 systèmes. La répartition n'est pas restreinte par l'UVB, bien que les milieux peu profonds à cau très claire soient sous

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représentés. Ensuite, nous avons comparé la profondeur à laquelle se retrouve 1 % de la radiance de surface à 320 nm  $(Z_{20,1\%})$  à  $Z_{max}$  dans plus de 1000 systèmes aquatiques dans 15 écozones, afin de déterminer le pourcentage de systèmes optiquement clairs  $(Z_{max} \le Z_{20,1\%})$  et de systèmes qui pourraient devenir clairs (donc à risque) si la concentration de DOM diminuait de 50 %. Au sud de la ligne des arbres, <6 % des systèmes sont clairs, sauf dans deux écozones ou les pourcentages sont de 10 20 %. La proportion de systèmes à risque est de 0 % dans la plupart des régions, sauf dans quatre régions avec des pourcentages de 5–9 %. Les concentrations de DOM semblent suffisantes pour empêcher l'élimination de taxons sensibles, comme Daphnia, par exposition directe aux UV-B dans la plupart des régions au sud de la ligne des arbres. Cependant, les étangs clairs et les étangs à risque sont beaucoup plus nombreux dans les trois écozones arctiques, particulièrement dans le haut-arctique et la cordillère arctique.

[Traduit par la Rédaction]

#### Introduction

Many recent studies have investigated the effects of ultraviolet radiation (UVR; 290-400 nm) on aquatic systems. These have been stimulated in part by increases in summer solar radiation in the UV-B region (290-320 nm) associated with depletion of stratospheric ozone (e.g., see reviews in Hader 1997; de Mora et al. 2000; Helbling and Zagarese 2003). However, estimated increases in erythemal irradiance (a weighted UV-B function) since the early 1980s have only been about 6% 14% in Canada, depending on the region (Kerr et al. 2002). This suggests that ozone depletion is unlikely by itself to have resulted in widespread large-scale extirpation in aquatic systems unless key aquatic organisms are extremely sensitive to UV-B. A complicating factor, however, is that decreases in chromophoric dissolved organic matter (DOM), which strongly absorbs radiation in the UVR region (Scully and Lean 1994), could lead to significant increases in UV-B exposure. Two regional assessments of the risk posed by UV-B to amphibians in ponds in Minnesota and the US Northwest estimated that about 85% of ponds had adequate protection (Diamond et al. 2002; Palen et al. 2002; Peterson et al. 2002). There is, however, no clear pieture of the extent, if any, to which the millions of lakes and ponds in Canada are at risk from UV-B exposure, a term defined operationally below.

Exposure to UV-B varies widely among aquatic systems, mainly because of variation in levels of DOM and its optical properties. It can range from less than 1 mg C-L<sup>-1</sup> in exceptionally clear waters to more than 300 mg C.L. in some saline lakes in the Prairies (P.J. Curtis, unpublished data) (analytical methods for total organic carbon, i.e., hightemperature combustion and UV/persulphate methods, do not discriminate between chromophoric and non-chromophoric DOM). There is some concern that very large decreases in chromophoric DOM might occur as a result of reduced runoff associated with climate change (Leavitt et al. 1997; Schindler et al. 1997; Pienitz and Vincent 2000), producing large increases in underwater irradiance. In fact, increased UV-B exposure from reductions in chromophoric DOM might pose more of a risk to aquatic communities than ozone depletion (Williamson et al. 1996; Pienitz and Vincent 2000; Leavitt et al. 2003). On the other hand, counteractive processes associated with climate warming may affect northern lakes and raise their DOM concentrations (Clair et al. 1999). For example, with climate warming and an expected increase in vegetation at northern latitudes, e.g., the northern shift of the treeline, increased loads of DOM to lakes and

ponds in these areas could occur (Pienitz and Vincent 2000). Attenuation of UVR by chromophoric DOM is discussed in more detail below.

Evaluating the extent to which aquatic environments might be "at risk" from UV-B exposure is warranted with the detection of harmful effects of UV-B on some taxa, the restoration of pre-industrial ozone levels still some years away, and the possibility that in chromophoric DOM concentrations might decrease significantly. We explore this topic for Canadian freshwater systems by first examining the eastern North American distribution of a crustacean zooplankton genus, Daphnia, which experimental evidence indicates may be a sensitive indicator of UV-B exposure. The first objective is to determine whether UV-B exposure restricts its distribution. Second, the maximum depth of UV-B transmission (defined here as the depth at which 1% of surface irradiance at 320 nm occurs ( $Z_{320,1\%}$ )) is compared with maximum depths ( $Z_{\text{max}}$ ) for aquatic systems across Canada to determine the extent to which systems are currently optically clear or may become so (at risk) should they lose 50% of their DOM. Discussions of recent variation in incident levels of UV-B and the levels predicted over the short term (years) and long term (decades) across Canada are beyond the scope of this paper.

#### **Methods**

#### UV-B-sensitive indicator organisms

Rather than use the more subtle ecological changes that might occur, such as changes in life-history patterns or energy allocation to UV-protection mechanisms at the expense of growth, we chose instead to analyze the presence/absence of sensitive organisms. Research has shown that some stressors, such as acid deposition and Great Lakes contamination, have led to local extirpation in advanced stages of the problems, thus presence/absence data can be a practical tool for identifying severe damage. Moreover, because presence/absence data are more widely available than other ecological measurements, a larger number of systems can be assessed.

First, the literature was reviewed to identify sensitive indicator organisms. We then analyzed the presence/absence of the indicator taxa with respect to two relevant chemical and physical variables that affect the size of UV-B-free refuges, DOM concentration and  $Z_{\rm max}$ , using several detailed synoptic surveys. The distribution of populations was compared with  $Z_{320.1\%}$ .

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Table 1. List of lake and pond surveys used to analyze dissolved organic matter distributions.

Ecozone	Province	Source <sup>a</sup>		
Atlantic Maritime	Nova Scotia	Clair et al. 2001		
	New Brunswick	T.A. Clair		
Mixedwood Plains	Quebec (Townships)	Y.T. Prairie		
Boreal Shield	Ontario	P.J. Dillon		
	Ontario	D.K. McNicol		
	Quebec (Abitibi)	Y.T. Prairie		
	Newfoundland	Clair et al. 2001		
Prairies				
Saline	Saskatchewan	Arts et al. 2000		
Non-saline	Saskatchewan	Arts et al. 2000		
Non-saline	Alberta	P.J. Curtis		
Taiga Plains	Northwest Territories	Pienitz et al. 1997a		
Hudson Plains	Manitoba	Macrae 1998		
Taiga Shield	Northwest Territories	Pienitz et al. 1997b		
	Northwest Territories	Rühland et al. 2003		
Montane Cordillera	British Columbia	P.R. Leavitt		
	British Columbia	R.N. Nordin		
	British Columbia	Bos and Cumming 2003		
Pacific Maritime	British Columbia	R.N. Nordin		
Boreal Cordillera	Yukon	Pienitz et al. 1997a		
Taiga Cordillera	Yukon	Pienitz et al. 1997a		
Southern Arctic	Yukon, Northwest Territories	Pienitz et al. 1997a, 1997b		
	Northwest Territories	Rühland et al. 2003		
Northern Arctic	Nunavut, Northwest Territories Antoniades et al. 200			
	Nunavut	Michelutti et al. 2002a, 2002b		
	Nunavut	J.P. Smol and M.S.V. Douglas		
Arctic Cordillera	Nunavut	Douglas et al. 2000		

<sup>&</sup>quot;Names of authors of this study are provided if the reference is not cited.

Several criteria were applied to the screening process. (i) Indicator organisms must be widely distributed among aquatic systems. (ii) Survival of indicator organisms must be impaired by UV-B and they must spend at least part of their life cycle in epilimnetic waters during summer daylight hours. For organisms to be useful as a biological indicator in this study, experimental evidence of sensitivity to UV-B must be coupled with evidence of changes in abundance. This is a practical consideration because only abundance data are likely to be widely available. (iii) Responses of indicator populations to UV-B change must be relatively rapid (time scale of weeks or months). (iv) Ideally, indicator organisms should play an important ecological role. (v) Chemical and physical indicators of UV-B exposure must be widely reported to ensure that an adequate number of lakes and ponds in various regions can be assessed.

Collectively, these criteria exclude process measurements such as primary production and DOM-degradation rates, planktonic taxa at the species level (because of wide geographic variation and influence of non-UV-B-related factors), and long-lived taxa even where widely distributed (e.g., fish). Variation in nutrient loading with DOM loading (Dillon and Molot 1997) also precludes using a standing-crop indicator such as chlorophyll a. Certain experimental designs also preclude the use of their results in the search for indicators. For example, Bothwell et al. (1993) pointed out that "conclusions about the long-term ecological impacts of changes in UVB cannot be accurately forecast from short-

term incubation studies". Furthermore, results of studies that remove UV-B through selective use of filters do not necessarily imply that a relationship between a response variable and UV-B intensity can be extrapolated to an increase in UV-B. Organisms must be exposed to UV-B levels above their "ambient" levels, perhaps by incubation in shallower waters or in waters with lower DOM concentration or by supplementation with an artificial source.

#### Distribution of systems at risk in Canada

DOM and  $Z_{\rm max}$  data for aquatic systems across Canada were gathered from a variety of published and unpublished sources (Table 1). The surveys include mostly discrete (one time) measurements, although some means are included (e.g., the Nova Scotia and Newfoundland surveys provided long-term means), as long-term data are usually collected only from a small number of research sites,  $Z_{\rm max}$  was not available from the Ontario Ministry of the Environment (OMOE) and Canadian Wildlife Service (CWS) Ontario surveys and was available for only some of the systems in the Arctic surveys, DOM was measured with either UV/persulfate digestion or high-temperature combustion.

 $Z_{320,1\%}$  was compared with  $Z_{\rm max}$  to determine the extent to which systems are currently optically clear or may become so (at risk) should they lose 50% of their DOM,  $Z_{320,1\%}$  was chosen because deeper waters are virtually UV-B-free (see Attenuation of UVR penetration by chromophoric DOM below). Relative proportions of optically clear systems and

Table 2. Regression	equations for	$ln(K_{\lambda})$ as	functions	of $ln(DOM)$	and ln(POM)	between 320
and 550 nm.						

Eq.	λ (nm)	Intercept	Slope			P > F	
			ln(POM)	ln(DOM)	$R^2$	POM	DOM
4	550	-2.29	0.54	0.75	0.88	< 0.0001	0.008
5	380	-0.35	0.42	1.03	0.92	< 0.0001	0.014
6	360	-0.23	0.32	1.14	0.92	< 0.0001	0.047
7	340	0.16	0.33	1.08	0.91	< 0.0001	0.051
8	320	0.38	0.30	1.11	0.91	< 0.0001	0.077

**Note:** Data are from Scully and Lean (1994).  $K_{\lambda}$  is the attenuation coefficient for wavelength  $\lambda$ , DOM is dissolved organic matter, and POM is particulate organic matter.

systems at risk were analyzed on a regional basis using the terrestrial ecozone classification adopted by Environment Canada in which 15 major ecosystems are defined on the basis of broad, common characteristics such as major plant formations (www.ccea.org/ecozones/terr.html).

The vast majority of the sampled sites (over 7200) were from two surveys of the Boreal Shield ecozone in Ontario (some sites were sampled in both surveys), with 791 sites sampled in 14 other ecozones across Canada. There are insufficient sampled sites from the Taiga Plains and Taiga Cordillera, with five and six sites, respectively. Hence, results for these ecozones should be treated with caution until additional data are available. Finally, some of the limnological surveys south of the treeline may have ignored small, shallow ponds (<1.0 m maximum depth), which could bias the results for regions where they are numerous. The exceptions to this are the Prairies survey of lakes and ponds in Saskatchewan, which includes 18 ponds (Arts et al. 2000), the CWS survey of lakes and ponds in the Boreal Shield in Ontario, which includes an unknown number of ponds (D. McNicol, unpublished data), and the Atlantic Maritime survev in Nova Scotia (six ponds) (Clair et al. 2001). By definition, a greater proportion of ponds than lakes should be at risk because of the shallow nature of the former.

#### Results

Attenuation of UVR Penetration by chromophoric DOM

The attenuation of incident radiation of a specific wavelength is described by exponential decay with depth:

(1) 
$$dE_{\lambda,Z}/dZ = -K_{\lambda}$$

(2) 
$$E_{\lambda,Z} = E_{\lambda,0} \exp(-K_{\lambda}Z)$$

where  $E_{\lambda,Z}$  is the solar-radiation intensity at wavelength  $\lambda$  at depth Z below the surface, and  $K_{\lambda}$  is the attenuation coefficient for wavelength  $\lambda$ . The depth at which 1% of surface radiation for a given wavelength occurs (e.g., 99% attenuation) is given by

(3) 
$$Z_{\lambda,1\%} = -\ln(0.01)/K_{\lambda} = 4.61/K_{\lambda}$$

 $K_{\lambda}$  is a function of photon absorption by water and its constituents and photon scattering by particles (Vincent et al. 2001). UV-B is strongly absorbed by chromophoric DOM relative to light in the visible region (400–700 nm) (Crump et al. 1999; Markager and Vincent 2000).

The effect of chromophoric DOM and particulate matter on attenuation of solar radiation is illustrated with stepwise regressions developed using  $K_2$  and DOM and particulate organic matter (POM) data for 14 lakes along a latitudinal gradient between 41 and 51 N (from Scully and Lean 1994). Attenuation coefficients for six wavelengths are reported between 300 and 400 nm. The attenuation coefficient at 550 nm was estimated by extrapolating the linear relationship between  $\lambda$  and  $\ln K_{\lambda}$  for each lake. Regressions for attenuation coefficients at 320, 340, 360, 380, and 550 nm as functions of DOM and POM concentrations are shown in Table 2. These equations are used in the risk-assessment sections that follow. We make several assumptions here: (i) the relationship between  $\ln K_{\lambda}$  and  $\lambda$  is linear between 300 and 550 nm. within each lake, (ii) POM is an indicator of the level of suspended sediments, and (iii) the ratio of coloured to uncoloured DOM is relatively constant among the 14 lakes, though this is not strictly true for coloured Precambrian Shield waters (Molot and Dillon 1997a). A fuller discussion of the latter is included below.

Irradiance in the visible region penetrates much deeper than irradiance in the UV-B region at all concentrations of total organic matter (TOM = DOM + POM),  $Z_{320,1\%}$  exceeds 6 m when TOM < 2 mg C·L<sup>-1</sup> and is restricted to depths <1 m when TOM > 7 mg C·L<sup>-1</sup>,  $Z_{580,1\%}$  exceeds 70 m when  $TOM < 2 \text{ mg C-L}^{-1}$  and is restricted to depths <13 m when  $TOM > 7 \text{ mg C-L}^{-1}$ . Note that the depth of relative penetration depends only on the absorption and scattering properties of the water body and not on absolute irradiance, whereas absolute irradiance depends on absolute surface irradiance. as well as the absorption and scattering properties. A decrease in DOM will therefore significantly affect irradiance at a given depth at constant surface irradiance. For example, if DOM in a lake declines from 3 to 2 mg  $C \cdot L^{-1}$  with 0.2 mg C-L<sup>-1</sup> POM, then  $K_{320}$  will decrease from 3.05 to 1.95 m<sup>-1</sup>.  $Z_{320.1\%}$  will increase from 1.51 to 2.36 m and the irradiance at 320 nm at 1.51 m will increase 5.3-fold. Similarly, the irradiance at 300 nm at 1.51 m will increase 1.23-fold, an increase much larger than the estimated increase of 6%-14%in crythemal UV-B (Kerr et al. 2002).

# Analysis of Daphnia presence/absence as a function of DOM and $Z_{\rm max}$

A review of studies of UV-B-impact studies on amphibians, fish, phytoplankton, zooplankton, macrophytes, and littoral-zone algae suggests that there is only one indicator so far that meets all of the criteria. Species of the cladoceran crus-

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**Table 3.** Summary of lakes and ponds from four surveys with maximum depth < 17 m and DOM < 5 mg C·L<sup>-1</sup> used to analyze *Daphnia* distributions.

Source	No. of lakes and ponds	Region	
Norman Yan, Ontario Ministry of the Environment <sup>a</sup>	18	Muskoka-Haliburton, Ontario	
Bill Keller, Laurentian University <sup>a</sup>	151	Algoma and Sudbury, Ontario	
Don McNicol, Canadian Wildlife Service <sup>a</sup>	8	Sudbury, Ontario	
US Environmental Protection Agency Environmental Monitoring	81	Northeastern USA	
and Assessment Program, Eastern Lake Survey <sup>b</sup>			

"DOM measured by acidifying samples, flushing with  $N_2$  to remove inorganic C, then oxidizing with a UV digester in acid persulfate media.  $CO_2$  is colorimetrically detected.

tacean genus *Daplinia* appear sensitive to UV-B (Zagarese et al. 1994; Zellmer 1998; Grad et al. 2001) and UV-A (320–400 nm) (Rautio and Korhola 2002*a*), showing decreased survival when exposed. *Daplinia* was the most UV-B-sensitive of several zooplankton taxa tested (Cywinska et al. 2000). Significant in-situ mortality was observed after 2 days of exposure at and above 73% of surface radiation at 320 nm but not at 63% (Zagarese et al. 1994). Survival of *Daplinia magna* was impaired after 4 and 8 h of exposure to UVR at DOM concentrations \$1 mg C4. \(^1\), while 5 mg C4. \(^1\) provided complete protection from 4 but not 8 h of exposure (Hessen and Faerovig 2001).

There are several mitigating factors that may affect tolerance to UV-B, such as calcium level, pigment production, temperature, and behaviour. Hessen and Alstad Rukke (2000). found that low calcium concentrations can increase Daphnia sensitivity to UV-B. Declining calcium levels in some areas of eastern North America related to atmospheric deposition (Keller et al. 2001) may, therefore, complicate risk assessment. Some Daphnia produce melanin, a photoprotective pigment that absorbs UV-B (Hessen et al. 2002). Melanin concentration in subarctic lakes was a function of DOM concentration, increasing sharply below 3 mg C-L<sup>-1</sup> (Rautio and Korhola 2002b) Daphnia were absent from subarctic ponds with  $DOM < 5 \text{ mg C-L}^{-1}$ , and in ponds with  $DOM > 5 \text{ mg C-L}^{-1}$ , melania levels were higher than those in lakes with similar DOM concentrations, perhaps because deep-water refuges were not available. Elevated temperatures increased UV-B tolerance in Daphnia catawba; however, the temperature effect was species-specific (Williamson et al. 2002).

Daplinia migrate downwards to avoid UV-B (Leech and Williamson 2001), the extent of migration being an inverse function of pigmentation (Rhode et al. 2001). Less-pigmented animals could survive in clear waters provided that a deepwater refuge is available for shelter during daylight hours. The corollary of this is that Daplinia should be absent from clear waters without a refuge. Evidence supporting this supposition comes from a study of shallow ponds (<0.5 m depth) in Finnish Lapland (Rautio and Korhola 2002b). Daplinia were absent from ponds with DOM < 5 mg C·L<sup>-1</sup>, perhaps because the ponds are too shallow to provide refuge from UV-B, although other factors associated with low DOM concentration, such as higher temperature (Rautio and Korhola 2002a) or increased visibility to predators, possibly have an effect.

Daplinia are very common and are often an important contributor to crustacean zooplankton biomass on the Cana-

dian Shield (Yan et al. 1988). Loss of *Daphnia* would therefore lead to significant ecological changes. Based on their sensitivity to UV-B and their contribution to zooplankton biomass, *Daphnia* were explored as a potential biological indicator. On a cautionary note, the possibility exists that more UV-tolerant *Daphnia* species would supplant more sensitive daphnids; therefore, combining all *Daphnia* species may result in a loss of information.

Data on pH. *Daplmia* sp. abundance,  $Z_{\rm max}$ , and DOM concentration from four surveys of lakes and ponds were pooled (Table 3). *Daplmia* spp. abundance data were available for 258 sites in Ontario and the northeastern USA in which DOM < 5 mg C·L. and maximum depth < 17 m. These sites were used to explore whether a relationship existed between *Daplmia* presence/absence and DOM concentration and  $Z_{\rm max}$ .

DOM concentration was plotted against  $Z_{max}$  using symbols to indicate whether Daphnia were present or absent (Fig. 1). Acidic sites with pH < 5.3 were included because Daplmia have been observed in acidic lakes (Keller et al. 1992; Clair et al. 2001; N.D. Yan, unpublished data). For comparison, depths at which 1% of surface irradiance occurs for 320, 340, 360, and 380 nm and  $10^{6}e$  for 320 nm are shown. If a lake or pond appears to the left of an extinction curve, say the 1% curve for 320 nm, then it is shallower than  $Z_{320,1\%}$  and therefore irradiance at  $Z_{max} > 1\%$ .  $Z_{max}$  in most lakes and ponds is below the depths that receive 1% and 10% of 320 nm. Only 14 acidic systems have small refuges or none at all, yet Daphnia are present in 5 of these. There is no strong evidence of any region in which Daphnia are excluded (Fig. 1). Hence, there does not appear to be a minimum level of DOM needed to protect Daphnia from extirpation, although systems with DOM < 1 mg C/L  $^{\pm}$  and  $Z_{\rm max}$  < 4 m are rare in the surveys. This implies that the effeets of UV-B on distributions of other organisms will be difficult to detect unless they are much more sensitive to UV-B or are unable to escape to refuges.

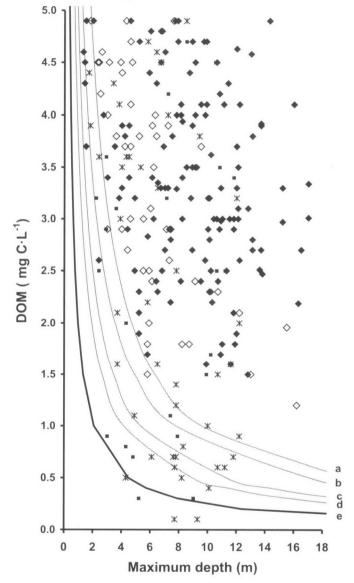
## Analysis of aquatic systems at risk in Canada based on DOM and $Z_{\rm max}$ distributions

In a worst case scenario, we assume that some taxa cannot tolerate even small amounts of UV-B at 320 nm (>1% of surface irradiance). Theoretically, these organisms should be excluded from systems in which  $Z_{\rm max} < Z_{\rm C0,F}$ , and may be excluded from deeper systems if the refuge below  $Z_{\rm C0,F}$ , is unsuitable habitat. In this study, we consider a system to be optically clear if its DOM is such that irradiance at  $Z_{\rm max}$  is

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<sup>&</sup>lt;sup>b</sup>Analytical method for DOM described in Hillman et al. (1986). Data are available on-line at www.epa.gov/docs/emap/html/datal/surfwatr/data/napap/els.html.

**Fig. 1.** Dissolved organic matter (DOM; mg C·L<sup>-1</sup>) and maximum depth,  $Z_{\text{max.}}$  (m), for 258 Ontario and US Environmental Monitoring Assessment Program Eastern Lake Survey sites. The broken lines are the depths at which 1% of surface irradiance at 320, 340, 360, and 380 nm occurs, assuming a particulate organic matter concentration of 0.4 mg C·L<sup>-1</sup> (eqs. 5–8; see Table 2) ( $\diamondsuit$ , Daphnia absent > pH 5.3;  $\spadesuit$ , *Daphnia* present > pH 5.3; \*, *Daphnia* absent < pH 5.3;  $\blacksquare$ , *Daphnia* present < pH 5.3). Curves are as follows:  $Z_{380,1\%}$  (a),  $Z_{360,1\%}$  (b),  $Z_{340,1\%}$  (c),  $Z_{320,1\%}$  (d), and  $Z_{320,10\%}$  (e). The curve for  $Z_{320,1\%}$  is almost identical with the curve for  $Z_{360,10\%}$ .



greater than 1% of surface irradiance at 320 nm. Because shorter wavelengths have higher extinction coefficients, relative irradiance levels for wavelengths < 320 nm are less than 1% at  $Z_{320,1\%}$ . Hence, waters deeper than  $Z_{320,1\%}$  are essentially UV-B-free. Also,  $Z_{320,1\%}$ , is very similar to  $Z_{360,10\%}$ , which means that waters above  $Z_{320,1\%}$ , will receive significant levels of UV-A > 360 nm. Note that atmospherically acidified lakes may still be clearer than their historical values in spite of recovery (Gunn et al. 2001).

Next, we define systems at risk as those that will become optically clear should they lose 50% of their DOM. However, DOM levels vary with time, and thus there is the danger that organisms in systems with low DOM concentrations may be temporarily exposed to UV-B. For example, the chromophoric portion of DOM can vary diurnally (Gibson et al. 2001) and seasonally (Clair et al. 1996; Morris and Hargreaves 1997; Laurion et al. 2000). The most plausible explanation is that as DOM ages it becomes more photobleached. This is consistent with the decline in colour–DOM ratios observed between headwater streams and lake outflows (Molot and Dillon 1997a).

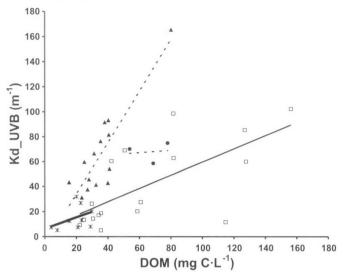
Variation in allochthonous loading will affect DOM concentrations. Mean annual DOM varied <1 mg C L<sup>-1</sup> in three central Ontario lakes (regional runoff 0.4–0.6 m-year <sup>1</sup>) over a 12-year period from 1980 to 1992; 1.7-1.9 mg  $C \cdot L^{-1}$  in Blue Chalk Lake, 3.9-4.6 mg C·L<sup>-1</sup> in Crosson Lake, and 4.7-5.6 mg C·L 1 in Dickie Lake (P.J. Dillon, unpublished data). In any given year the maximum deviation from the long-term mean was between 7% and 11%. Thus, in a lake with a long-term mean DOM of 3.7 mg C·L<sup>-1</sup>, the concentration may decline to 3.3 mg C·L<sup>-1</sup> in some years, and in a lake with a long-term mean DOM of 1.7 mg C-L<sup>-1</sup>, it might decline to 1.6 mg C·L<sup>-1</sup> in some years. The DOM concentration varied more in other regions; in Lake 239 in northwestern Ontario (regional runoff 0.2 m·year <sup>1</sup>) (Schindler et al. 1997), DOM ranged from a high of about 8.6 mg C·L <sup>1</sup> in 1982 to a low of about 5.2 mg C·L<sup>+</sup> in 1984, a decline of 3.4 mg C·L<sup>-1</sup> in 2 years. In Kejimkujik Lake in southwestern Nova Scotia (regional runoff 1 m·year <sup>1</sup>), DOM ranged from 3.0–13.0 mg  $C L^{-1}$  with a mean of 6.9 mg  $C L^{-1}$  between 1983 and 1999, although 91% of the samples were between 3 and 8.3 mg C·L<sup>-1</sup> (Clair et al. 2001). Shallow systems can also exhibit large seasonal variation; in 11 of 13 wetland sites studied at St. Denis, Saskatchewan, DOM concentrations increased from spring to fall by an average of 64% (Waiser and Robarts 2004). Specific absorptivity in Prairie ponds decreases during the summer, even as DOM increases (Waiser and Robarts 2004).

In this study, a simplifying assumption is that temporal variation in chromophoric DOM concentration is relatively small in low-DOM systems (<5 mg C·L<sup>-1</sup>), which are the primary systems of interest, while it is acknowledged that the risk analysis below might have to be revisited if this assumption proves to be dramatically violated. We also assume that regional variation in the chromophoric content of DOM is not significant in low-DOM systems. Data from Scully and Lean (1994) suggest that regional variation in chromophoric content is not large. However, other studies have shown that attenuation of UVR can vary regionally, in part because vegetation affects the chromophoric content of DOM. In the Tyrolian Alps in Europe, specific absorptivity at 320 nm was lowest among lakes with poor soil cover and highest among lakes with forest cover (Laurion et al. 2000). Regional differences in the chromophoric content of DOM are suggested by differences in specific UV-B attenuation (broadband UV-B attenuation coefficient  $(K_a)/DOM$ ) between Prairie and non-Prairie freshwater lakes (Scully and Lean 1994; Arts et al. 2000). However, specific UV-B attenuation in non-Prairie lakes sampled by Scully and Lean (1994) is similar to that in Prairie ponds (Arts et al. 2000).

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Fig. 2. Ultraviolet B (UV-B) attenuation coefficients  $(K_d)$  versus DOM in Saskatchewan lakes and ponds (data from Arts et al. 2000) (\*, non-saline lakes;  $\square$ , saline lakes;  $\blacktriangle$ , non-saline ponds;  $\bullet$ , saline ponds).



Saline systems are quite different from freshwater systems (Fig. 2) (Arts et al. 2000; Waiser and Robarts 2000). Most prairie saline systems have much lower specific attenuation than freshwater systems and high DOM concentrations (>20 mg C·L<sup>-1</sup>) (Fig. 2). None of the 3 saline ponds and only 2 of the 17 saline lakes surveyed by Arts et al. (2000) in Saskatchewan had a  $K_{\rm d}$  value < 10 m<sup>-1</sup>, which is the maximum value in the freshwater, low-DOM lakes (<5 mg C·L<sup>-1</sup>) measured by Scully and Lean (1994). Although saline ponds have lower specific absorptivity and thus a higher proportion of non-chromophoric DOM (Arts et al. 2000; Waiser and Robarts 2000), their much higher DOM levels result in significant UV-B attenuation.

We operationally define systems at risk here as systems that are not now optically clear but in which loss of 50% of DOM would result in  $Z_{320,1\%} \ge Z_{\rm max}$ . We are now in a position to estimate the number of systems in ecozones across Canada that are naturally optically clear or at risk of becoming optically clear should DOM decrease.

Data were collected from all 15 ecozones across Canada (Table 4). The number of sites with complete data varied dramat cally from 5 in the Taiga Plains ecozone to over 500 in the Boreal Shield ecozone. All ecozones are represented by at least 24 sites except the Taiga Cordillera (5) and Taiga Plains (6). Results from the latter two ecozones should therefore be treated with caution.

Median DOM concentrations varied dramatically among ecozones, ranging from 1.1 mg C-L $^{\rm T}$  on Victoria Island in the Northern Arctic to 14.7 mg C-L $^{\rm T}$  in the Boreal Cordillera, with the exception of the Prairies (Table 4). Median Prairie non-saline and saline concentrations were 39 and 59.8 mg C-L $^{\rm T}$  in Saskatchewan and 46 and 120 mg C-L $^{\rm T}$  in Alberta, respectively.

The proportion of systems currently deemed optically clear is quite low (<6%) in most regions south of the treeline, with 10%-20% in the Montane Cordillera (Kamloops, Prince George, and Continental Divide regions) and Pacific Maritime ecozones (Table 4). Optically clear

ponds are more common in the Hudson Plains and Southern Arctic ecozones (0% 13%) and are the norm in the Northern Arctic and Northern Cordillera ecozones (31% 100%). Community structure in these clear systems may, perhaps, reflect the effects of UV-B exposure. If, however, a sensitive aquatic biota was able to tolerate, say, no more than 10% of surface radiation at 320 nm rather than 1%, then the proportion of optically clear systems would be smaller.

The proportion of systems deemed to be at risk was 0% in most regions south of the treeline and between 5% and 9% in the Boreal Shield (Ontario and Newfoundland), Atlantic Maritime (Nova Scotia), and Montane Cordillera ecozones along the Continental Divide (Table 4). The proportion of ponds at risk ranged from 0% to 28% in the Southern Arctic and from 11% to 62% in the Northern Arctic. No systems at risk occurred at Cape Herschel on Ellesmere Island in the Arctic Cordillera because all ponds were optically clear. These estimates are based on a worst case scenario in which it is assumed that there exist very sensitive organisms incapable of tolerating more than 1% of surface irradiance at 320 nm. If these sensitive organisms are able to tolerate up to, say, 10% of surface irradiance at 320 nm, then the proportion of systems at risk (i.e., systems without refuge below  $Z_{320,10\%}$ ) would be smaller.

There is a note of caution regarding wetlands; many of these shallow systems can lose considerable water volume and therefore depth as a result of strong evaporation. Consequently, deeper water refuges from harmful UV-B may disappear with relatively low DOM concentration, especially in very dry years.

DOM < 5 mg C4.  $^{+}$  in a large fraction of systems on the Boreal Shield in Ontario (53% and 39% in the OMOE and CWS surveys, respectively). Because depth data are not available, we take these estimates to represent the upper bounds for the proportion of systems at risk. The actual proportion is likely much less, as indicated by the small proportions of Boreal Shield systems at risk in the Algoma, Sudbury, and Muskoka Haliburton regions of Ontario, the Abitibi region of Quebec, and Newfoundland (5%, 0%, and 6%, respectively).

#### Discussion and conclusions

This study suggests that DOM levels are adequate to prevent large-scale loss of *Daphnia* and perhaps other similarly sensitive taxa from direct exposure to UV-B at current incident levels in most regions below the treeline in Canada. In contrast, a large proportion of ponds in the Canadian Arctic are either optically clear or at risk. These conclusions are based on two approaches: (1) a comparison of  $Z_{max}$  with  $Z_{320.1\%}$  in conjunction with the presence/absence of Daph. nia, and (2) biogeochemical estimates of the numbers of "optically clear" and "at-risk" systems across Canada. Although we tentatively conclude that UV-B-induced extirpation of *Daphnia* and similarly sensitive taxa is probably not a major concern south of the treeline, even if a 50% loss of DOM should occur, generalizing this to conclude that loss of DOM will not affect species richness requires that (i) additional chemical and morphometric data be collected. especially from shallow ponds south of the treeline, and (ii) additional sensitive taxa be identified to which a

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**Table 4.** Percentages of surveyed lakes and ponds that are optically clear and at risk in Canadian ecozones.

		Median DOM	Clear	At risk
	N	$(mg\ C{\cdot}L^{-1})$	(%)	(%)
Atlantic Maritime				
Nova Scotia <sup>a</sup>	45	5.8	4	7
New Brunswick	11	3.4	0	0
Mixedwood Plains	33	6.1	0	0
Boreal Shield				
Ontario <sup>b</sup>	2744	4.7		53 <sup>c</sup>
Ontario <sup>b</sup>	4488	5.8		39 <sup>c</sup>
Ontario <sup>d</sup>	499	3.7	6	5
Quebec	42	8.7	0	0
Newfoundland <sup>a</sup>	16	4.3	0	6
Prairies	10	1.5	O	O
Saline <sup>e,f</sup>	20	59.8	0	0
Saline <sup>g</sup>	17	120	0	0
Non-saline <sup>f</sup>	24	39	0	0
Non-saline <sup>g,h</sup>	8	46	0	0
Boreal Plains	0	-10	O	O
Alberta <sup>g</sup>	1	18	0	0
Wood Buffalo Park <sup>i</sup>	30	36.0	0	0
Wood Burraio Fark	5	3.6	O	O
Taiga Plains <sup>h</sup>	5	13.1	0	0
Taiga Shield	$11^h$	5.7	0	0
Taiga Siliciu	38	24.5	0	0
Montane Cordillera	66 <sup>j</sup>	1.5	14	9
Wolltaile Coldillera	$61^k$	12.3	10	0
	50 <sup>l</sup>	11.4	0	0
Pacific Maritime <sup>m</sup>	60	3.2	20	0
Boreal Cordillera <sup>h</sup>	24	14.7	0	0
Taiga Cordillera <sup>h</sup>	6	8.3	0	0
Hudson Plains <sup>n</sup>	38	9.4, 13.0	13	8
Southern Arctic	$37^h$	6.3	0	0
Southern Arctic	18	2.3	6	28
Northern Arctic <sup>o</sup>	10	2.5	0	20
Axel Heiberg Island				
Ponds	26	3.9	89	11
Lakes	12	2.3	0)	11
Victoria Island	12	2.3		
Ponds	28	1.5	100	
Lakes	6	1.1	100	
Banks Island	0	1.1		
Ponds	32	7.0	52	33
Lakes	9	3.4	32	33
Prince Patrick Island,	9	5.4		
Mould Bay				
Ponds	32	6.9	31	62
Lake	1		31	02
Arctic Cordillera <sup>o</sup>	1	3.5		
Ellesmere Island, Cape	37	4	100	0
Lifesificie Island, Cabe	21	-4	100	U

**Note:** A clear lake is one with a DOM concentration such that irradiance at maximum depth,  $Z_{\text{max}}$ , > 1% of surface irradiance at 320 nm. A lake is at risk if it is not now optically clear but would become so upon losing 50% of its DOM. *N* is the total number of surveyed systems. "Multiyear means.

Percentage of all lakes with DOM < 5 mg C·L<sup>-1</sup> because maximum depths are not recorded.

<sup>2d</sup>Data from CWS, Yan, and Keller zooplankton surveys (see Table 3). <sup>e</sup>The lowest DOM concentration in saline lakes and ponds is 22.1 mg C·L⁻¹. In a non-saline lake, DOM of 12.2 mg C·L⁻¹ would provide similar UV-B attenuation.

/Sites from Saskatchewan. Maximum depths are not available. However, depths at which 1% UV-B penetration occurs are much less than probable maximum depths (<90 cm in lakes and <15 cm in ponds), implying that refuges exist and systems are not at risk from UV-B.

\*Sites from Alberta. Mean depths ranged from <1 to 2.5 m. Includes saline and moderately saline systems.

<sup>h</sup>Maximum depth estimated as  $Z_{\text{max}} = 2.88 \times \text{mean depth} + 0.60$ ,  $R^2 = 0.82$ . The regression was derived from data for 33 Ontario lakes (Molot et al. 1992).

<sup>1</sup>DOM concentrations are means. Thirty lakes are classified as muskeg and sinkhole and 5 lakes as Canadian Shield lakes. Depths are not reported (Moser et al. 1998).

All lakes from the Continental Divide region.

<sup>k</sup>All lakes from the Prince George and Kamloops regions.

<sup>1</sup>Most sites are north of Prince George within approximately 300 km. Three of the northeastern lakes may be in the Boreal Plains ecozone (Bos and Cumming 2003).

<sup>m</sup>Of the 60 lakes, 56 are on Vancouver Island.

"Mean depths measured in 37 of 38 ponds were <0.6 m on 19 June 1995. DOM ranged from 4.8 to 42.6 mg C·L<sup>-1</sup> on 19 June 1995 and 13 August 1997, respectively. Maximum depth is estimated as  $2.88 \times Z_{mp} + 0.60$ .

 $Z_{\rm mn}$  + 0.60. "Proportions based only on those systems where approximate depth is recorded.

presence/absence analysis can be applied. Moreover, this study does not address the possibility that UV-B affects systems in subtler ways than extirpation. Exploration of the extent of subtle effects will require experimental identification and then widespread measurement of appropriate indicators across Canada.

An assessment of 136 ponds and small lakes in the US Pacific Northwest suggested that DOM levels are sufficient to protect developing amphibian eggs from UV-B in 85% of the sites (Palen et al. 2002). Similarly, an assessment of wetlands in northern Minnesota (a region similar to the Boreal Shield ecozone) also showed that DOM provided adequate protection to the northern leopard frog, Rana pipiens, in most wetlands (Ankley et al. 2002; Diamond et al. 2002; Peterson et al. 2002). The latter assessment was based on experimentally determined dose-response relationships for developing eggs (removed from their egg masses) and tadpoles. While experimental exposure to full sunlight reduced tadpole survival and caused malformation of tadpoles, the modeling component showed that DOM provided sufficient protection in 21 of 26 wetlands, assuming a worst case scenario (that tadpoles remain within the top 10 cm of the water column). However, tadpoles probably reduce their exposure to UV-B by spending part of the day in the shade or hiding under natural objects in situ rather than remaining within the top 10 cm of the water column (as per the experimental protocol). Even very clear ponds have refuges, at least in forested areas, and thus may support frog populations. Furthermore, in a review of studies of the effects of UV-B on developing amphibian eggs, Licht (2003) found possible negative effects for 9 species and no significant effects for 25 species. Three of the 31 species tested exhibited either possible effects or no significant effects, depending on the study. Licht (2003) also argued that experimental proto-

<sup>&</sup>lt;sup>b</sup>Some lakes are duplicated in the Canadian Wildlife Service (CWS) and Ontario Ministry of Environment surveys. Maximum depths are not available.

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cols can sometimes generate unrealistic conditions. Therefore, the percentage of wetlands in the US Pacific Northwest and northern Minnesota that provide adequate protection to developing amphibians is probably underestimated.

This study did not assess the extent to which DOM may decrease. Significant regional variation in response to climate change is predicted by the Canadian General Circulation Model, especially north of the treeline and on the Prairies (Canadian Centre for Climate Modelling and Analysis 2003). Hence, the probability of experiencing decreasing DOM and increasing exposure is not constant among ecozones. In general, DOM export from catchments to surface waters will decrease if there is a reduction in peatland area (Dillon and Molot 1997). This, in turn, may occur if there is a significant long-term reduction in runoff.

We express a word of caution at a time when the search for sentinel indicators of ecosystem health is in full swing; our study suggests that obtaining experimental evidence of sensitivity of organisms to a stressor should not lead us to automatically conclude that these organisms are effective indicators or that significant ecological impacts will occur in nature. Instead, the existence of experimental evidence should lead us to hypothesize that an organism is affected in situ, and then to test this hypothesis as we did here. In some cases, an organism's unexpected resilience in situ may mean that behaviours or characteristics that provide protection have been overlooked in experimental studies.

There are two issues worth mentioning. (1) This study defined risk incurred through increased UV-B exposure only in terms of loss of DOM. If risk is to be more fully defined by loss of DOM, then a suite of indicators should be expanded to include other impacts associated with loss of DOM, such as changes in heating and visible-light penetration to name just two. Loss of DOM would lead to a larger, clearer epilimnion and smaller hypolimnion in lakes deep enough to stratify (Gunn et al. 2001). An empirical formula recently developed to predict optimal lake trout (Salvelinus namayeush) habitat in Ontario (Dillon et al. 2003) predicts that a decline in DOM from 8 to 7 mg C-L<sup>-1</sup> would result in the depth at which 10 °C occurs at the end of the summer  $(Z_{10-C})$  becoming 0.2 m deeper but a decline from 3 to 2 mg  ${
m C4L^{-1}}$  would result in  $Z_{10-C}$  becoming 1.9 m deeper. As is the case with UV-B, systems with relatively low DOM are more at risk of heating from loss of DOM (Gunn et al. 2001), and as we have shown here, most ecozones outside the Prairies have large numbers of low-DOM (<3 mg C4. <sup>1</sup>) systems. (2) Owing to variation in the proportions of chromophoric and non-chromophoric DOM, we recommend that future surveys also measure underwater radiation transmission in addition to DOM. Because direct measurement of in situ irradiance requires expensive equipment not available in many laboratories, we recommend instead measuring absorbance of unfiltered surface samples throughout the UVR and visible regions (a path length > 1 cm will be needed for longer wavelengths and clear waters).

Although there are no guidelines for judging what percent loss is acceptable, current critical load targets for acid deposition in North America provide a model. Critical load targets are based on the desirability of maintaining 95% of lakes in each deposition region above the critical pH thresh-

old of 6; that is, 5% of lakes will not be protected (Jeffries 1997). Using this criterion, DOM levels in most regions south of the treeline appear to be adequate to protect aquatic systems from significant species losses, with the possible exception of 5% 9% of systems in Nova Scotia and Newfoundland and along the Continental Divide. However, DOM levels are probably not adequate to protect 95% of systems north of the treeline.

This should not be construed to suggest that UV research is no longer necessary. In fact, there is a consensus that less dramatic UVR-mediated impacts are quite important. For example, UV-A induces photorepair (Quesada et al. 1995) and may inhibit photosynthesis (Callieri et al. 2001). UV-A is also responsible for the majority of photooxidative loss of DOM (Molot and Dillon 1997b). Our understanding of these roles is only emerging, therefore process based ecological research on both UV-B and UV-A should continue. Future research may shape our understanding of how aquatic organisms have evolved to cope with UVR and the extent to which subtler impacts occur.

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