Environmental factors affecting methyl mercury accumulation in zooplankton

by

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Abstract

Filter-feeding macrozooplankton were collected from 24 lakes in south-central Ontario to examine relationships between environmental factors and methyl mercury accumulation. Zooplankton methyl mercury levels ranged from 19 to 448 $ng \cdot g^{-1}$ dry weight in the study lakes and were highest in zooplankton from acidic brownwater lakes. Water color and lake water pH were the best predictors of methyl mercury levels in zooplankton explaining 73% of the variation. Methyl mercury concentrations were positively correlated with water color and inversely correlated with lake water pH. Water color explained a greater portion of the overall variance in methyl mercury levels, indicating that the supply of mercury from the drainage basin plays a key role in determining methyl mercury concentrations in the lacustrine biota. Zooplankton methyl mercury levels were well correlated with mercury concentrations in smallmouth bass (Micropterus dolomieui) and largemouth bass (Micropterus salmoides) from 11 of the study lakes showing zooplankton to be good indicators of the relative bioavailability of mercury at the base of the food chain.

Résumé

Le zooplancton a été récolté dans 24 lacs du centre-sud de l'Ontario pour examiner les relations entre les facteurs environnementaux et l'accumulation du méthylmercure. La concentration du méthylmercure du zooplancton a varié entre 19 et 448 $ng \cdot g^{-1}$ poids sec et était plus elevée dans les lacs acides à eau brune. La couleur et le pH de l'eau du lac ont expliqué 73% de la variation observée dans la concentration du méthylmercure du zooplancton. La teneur en méthylmercure du zooplancton était positivement corrélée avec la couleur de l'eau et inversement liée au pH. La couleur de l'eau a expliqué une plus grosse proportion de la variation observée ce qui suggère que le bassin hydrologique à un effet très important sur la concentration du méthylmercure dans les biotes lacustres. La concentration du méthylmercure du zooplancton était fortement corrélée avec la concentration du mercure de l'achigan à petite bouche (Micropterus dolomieui) et de l'achigan à grande bouche (Micropterus salmoides) dans 11 des lacs étudiés, ce qui indique que le zooplancton est un bon indicateur de la disponibilité du mercure à la base de la chaîne trophique.

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Preface

The Faculty of Graduate Studies and Research of McGill University requires that the following passage be included in theses containing a manuscript.

"Candidates have the option of including, as part of the thesis, the text of a paper(s) submitted or to be submitted for publication, or the clearly-duplicated text of a published paper(s). These texts must be bound as an integral part of the thesis.

If this option is chosen, ***connecting texts that provide logical bridges between the different papers are mandatory****. The thesis must be written in such a way that it is more than a mere collection of manuscripts; in other words, results of a series of papers must be integrated.*

The thesis must still conform to all other requirements of the Guidelines for thesis Preparation. ***The thesis must include:*** *A Table of Contents, an abstract in English and in French, an introduction which clearly states the rationale and objectives of the study, a comprehensive review of the literature, a final conclusion and summary, and a thorough bibliography or reference list.*

Additional material must be provided where appropriate (e.g., in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

In the case of manuscripts co-authored by the candidate and others, ***the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent.*** *Supervisors must attest to the accuracy of such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all the authors of the co-authored papers.* ***Under no circumstance can a co-author of any component of such a thesis serve as an examiner for that thesis."***

This thesis will be submitted for publication in the Canadian Journal of Fisheries and Aquatic Sciences with Dr. Kalff as co-author. Dr. Kalff provided useful ideas and advice throughout the project and helped with the editing of the manuscript. I was responsible for the data collection, sample preparation and analysis, data analysis and for writing the thesis.

General Introduction

Mercury concentrations in fish in a large number of lakes in Canada, the U.S. and Europe exceed levels considered safe for human consumption (0.5-1.0 $\mu g\ Hg \cdot g^{-1}$ wet weight) (McMurtry et al. 1989; Håkanson et al. 1990; Sorensen et al. 1990; Verta 1990; Lathrop et al. 1991; Wren et al. 1991). Atmospheric deposition of mercury onto lakes and their catchments is thought to be the primary source of mercury to these remote lakes (Mierle 1990; Sorensen et al. 1990; Glass et al. 1991; Swain et al. 1992), and since atmospheric loading to the environment is on the increase (Lindquist 1994), it is unlikely that this problem will be resolved anytime in the near future.

Although only about 1% of the mercury deposited onto lakes and their catchments is methyl mercury (Watras et al. 1994), it is the species of interest with respect to the contamination of the aquatic biota. Methyl mercury is a highly toxic, organic form of mercury that is more readily accumulated by aquatic organisms than inorganic mercury (Olson et al. 1973; deFreitas et al. 1981; Paulose 1987). Methyl mercury is readily bioaccumulated because uptake from food and water is efficient while depuration is slow (Kramer and Neidhart 1975; Phillips and Buhler 1978; Rodgers and Beamish 1982). The principal sources of methyl mercury to non-point source contaminated lakes are: 1) atmospheric deposition of methyl mercury onto the lake surface and drainage basin; 2) methyl mercury in runoff waters- this includes methyl mercury that is deposited onto the drainage basin but not retained there, as well that produced within the drainage basin itself; and 3) methyl mercury produced within the water column and sediments of lakes (Lee and Hultberg 1990; Lee and Iverfeldt 1991; Hultberg et al. 1994; St. Louis et al. 1994; Verta et al. 1994; Watras et al. 1994).

While inorganic mercury can be chemically methylated through a variety of mechanisms (D'Itri 1990), the formation and decomposition or net production of methyl mercury in lakes is largely dependent on the methylation and demethylation of mercury by microbes (Berman and Bartha 1986). A number of factors are thought to influence the net production of methyl mercury by bacteria within a lake including: 1) pH; 2) the availability of inorganic mercury; and 3) environmental factors that affect microbial activity such as temperature, the availability of biodegradable carbon, and redox conditions (Olson and Cooper 1975; Bisogni and Lawrence 1975; Wright and Hamilton 1982; Rudd et al. 1983; Callister and Winfrey 1986; Xun et al. 1987; Steffan et al. 1988; Regnell and Tunlid 1991; Miskimmin et al. 1992; Ramlal et al. 1993). These factors ultimately affect the supply of methyl mercury available for uptake by the biota.

Studies indicate that a number of interrelated biological and environmental variables influence the accumulation of mercury in aquatic organisms. Biological factors such as age (Bache et al. 1971; Grieb et al. 1990; Lange et al. 1993), size (MacCrimmon et al. 1983; Grieb et al. 1990; Lathrop et al. 1991; Fjeld and Rognerud 1993; Lange et al. 1993) and diet (Phillips et al. 1980; MacCrimmon et al. 1983; Mathers and Johansen 1985; Cabana et al. 1994) have been shown to influence mercury concentrations in fish, while surveys of fish mercury levels indicate that environmental variables such as lake water pH (Wren and MacCrimmon 1983; Cope et al. 1990; Grieb et al. 1990; Wiener et al. 1990; Wren et al. 1991), lake dystrophy (McMurtry et al. 1989; Håkanson et al. 1990; Sorensen et al. 1990; Wren et al. 1991), productivity (Håkanson 1980; Lange et al. 1993) and catchment area relative to lake area (Suns and Hitchin 1990; Lee and Iverfeldt 1991) are also important in influencing mercury accumulation in fish. Although much less is known about the factors affecting the accumulation of mercury in organisms at lower trophic levels in lakes, studies suggest that variables such as feeding habits and life cycle (Parkman and Meilli 1993), density (Sorensen et al. 1990), lake water acidity (Meilli and Parkman 1988; Allard and Stokes 1989; Parkman and Meilli 1993), and water color (Meilli and Parkman 1988; Sorensen et al. 1990; Parkman and Meilli 1993) affect total mercury concentrations in zooplankton and benthic invertebrates.

Studies show that methyl mercury is efficiently transferred up the food chain to higher trophic levels (Boudou and Ribeyre 1981, 1985; Saouter et al. 1989; Watras and

Bloom 1992). In fact, most of the mercury in fish is methyl mercury (Bloom 1989, 1992; Grieb et al.1990). The uptake of methyl mercury by organisms at the base of the food chain is an important step in the transfer of mercury from abiotic to biotic compartments in lakes (Meilli 1991; Meilli 1994), and since diet is a significant source of mercury to fish, it is also an important pathway determining mercury contamination of fish (Meilli 1994). The objective of the present study is to examine relationships between methyl mercury accumulation in filter-feeding macrozooplankton and environmental factors. Filter-feeding macrozooplankton are an important food source for fish and therefore factors that affect their bioaccumulation of methyl mercury ultimately affect mercury concentrations in fish. Since the uptake of methyl mercury by filter-feeding zooplankton is proportional to its availability in the water column and in phytoplankton (Watras and Bloom 1992), I hypothesize that methyl mercury levels in the zooplankton will be well correlated with environmental variables that affect the supply or availability of methyl mercury in the environment.

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Introduction

Although methyl mercury contributes only a small fraction to the total mercury pool in lakes, it is the species of interest with respect to the contamination of the aquatic biota. Methyl mercury is a highly toxic, organic form of mercury that is more readily accumulated by aquatic organisms than inorganic mercury (Olson et al. 1973; deFreitas et al. 1981; Paulose 1987). Moreover, methyl mercury is the fraction of the total mercury pool that is most efficiently transferred up the food chain to higher trophic levels (Boudou and Ribeyre 1981, 1985; Saouter et al. 1989; Watras and Bloom 1992). This point is further substantiated by a number of recent studies that show that virtually all the mercury in fish is methyl mercury (Bloom 1989, 1992; Grieb et al. 1990).

Mercury contamination of fish is a serious problem in a large number of remote lakes in Canada, the U.S. and Europe that do not receive point-source mercury inputs. Atmospheric deposition of mercury onto lakes and their catchments is thought to be the primary source of mercury to these remote lakes (Mierle 1990; Sorensen et al. 1990; Glass et al. 1991; Swain et al. 1992). Even so, mercury levels in fish are highly variable from lake to lake within a single region and differences in the physical and limnological characteristics of lakes and their catchments contribute to this variability. Regional surveys of fish mercury levels indicate that physical and limnological factors such as lake water pH (Wren and MacCrimmon 1983; Cope et al. 1990; Grieb et al. 1990; Wiener et al. 1990; Wren et al. 1991), lake dystrophy (McMurtry et al. 1989; Håkanson et al. 1990; Sorensen et al. 1990; Wren et al. 1991), productivity (Håkanson 1980; Lange et al. 1993) and catchment area relative to lake area (Suns and Hitchin 1990; Lee and Iverfeldt 1991) influence the accumulation of mercury in fish.

While many studies have examined relationships between environmental factors and mercury accumulation in fish, much less is known about the influence of these factors on the bioaccumulation of methyl mercury at lower trophic levels. Since diet is an important source of mercury to fish, and given that methyl mercury is the predominant form of mercury at higher trophic levels, an understanding of the factors influencing the bioavailability of methyl mercury at the base of the food chain would provide important insight into the accumulation of mercury in fish. The purpose of this study is to examine relationships between environmental factors and methyl mercury accumulation in filter-feeding macrozooplankton. Such zooplankton provide an integrated measure of the bioavailability of methyl mercury in the water column and in phytoplankton (Watras and Bloom 1992). Macrozooplankton are also an important food source for fish and therefore factors that affect their bioaccumulation of mercury are directly relevant to the contamination of fish.

Materials and Methods

Study sites

Macrozooplankton were collected from 24 lakes in south-central Ontario (Fig. 1). The lakes were selected from the Ontario Ministry of Natural Resources (MNR) computerized data inventory and the Ontario Acid Sensitivity Data Base (MOE) (Neary et al. 1990), to maximize differences in lake morphometry and water chemistry and minimize distance between lakes. The study lakes were also chosen so as to minimize covariance between water color and pH since these two variables have repeatedly been shown to influence mercury accumulation in fish and often covary in lakes (Meilli 1991). The physical, limnological and biological characteristics of the study lakes are summarized in Table 1. The study lakes are located within 150 km of each other and have no known history of point-source mercury pollution. The geographical area of the study was restricted to control for possible regional differences in mercury and SO_x deposition. All the study lakes are drainage lakes, having either an inflow or an outflow or both.

FIG. 1. Location of the study lakes.

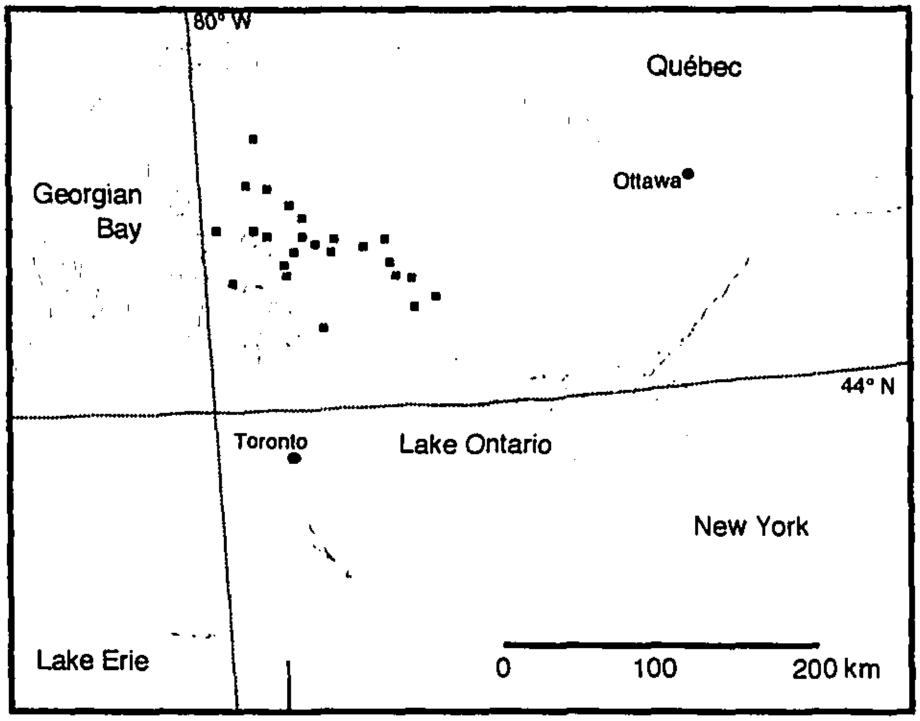

80° W
Québec
Georgian
Bay
Ottawa
44° N
Toronto
Lake Ontario
New York
Lake Erie
0
100
200 km

TABLE 1. Physical, limnological and biological characteristics of the study lakes.

Variable	n	Mean	S.D.	Min.	Max.
Lake area (ha)	24	198	323	12	1377
Maximum depth (m)	24	17.3	14.3	3.4	71.1
Mean depth (m)	24	6.4	4.7	0.7	23.1
Drainage ratio	24	4.4	12.4	0.1	62.1
% Wetland in the catchment	24	10.0	8.7	0	26.0
Surface water temperature (°C)	24	23.5	0.8	21.9	25.0
Lake water pH	24	6.8	0.9	5.4	8.3
Conductivity ($\mu S \cdot cm^{-1}$)	24	60	53	20	224
Water color (mg $Pt \cdot l^{-1}$)	24	72	73	3	231
Total Phosphorus ($\mu g \cdot l^{-1}$)	19	22.0	11.5	7.0	47.4
Chlorophyll-a ($\mu g \cdot l^{-1}$)	19	3.9	2.4	0.8	9.4
% Nitrogen in zooplankton	23	7.5	1.1	5.4	9.4
Zooplankton weight (mg)	24	0.01	0.008	0.001	0.038

Environmental variables

Surface water samples were collected for total phosphorus and chlorophyll-a determinations from the profundal zones of 19 of the study lakes in late May and early June 1993. Total phosphorus concentrations were determined in triplicate using the ascorbic acid modification of the molybdenum blue technique (Strickland and Parsons 1968) following oxidation with potassium persulphate (Menzel and Corwin 1965). Chlorophyll-a concentrations were determined in triplicate for samples collected on Gelman AE glass fiber filters following pigment extraction in 95% ethanol (Bergmann and Peters 1980). Lake water pH, water temperature, oxygen, and conductivity were measured in late July and early August 1993. Temperature and pH profiles were determined with a Hach model 43800 pH meter and electrode with temperature sensor, oxygen profiles were obtained with an Orion model 840 oxygen meter and probe, and conductivity profiles were measured with an Orion model 122 conductivity meter and data standardized to 25°C. Surface water samples were taken from the profundal zone of each lake in late July and early August 1993 for water color determination. The samples were filtered through a 0.45 μm polycarbonate membrane filter (Nucleopore) and stored in dark bottles in a cooler until analyzed. Water color was determined in duplicate in the laboratory by light absorbance at 440 nm. Absorbance coefficients were calculated and converted to platinum color units using the equation of Cuthbert and del Giorgio (1992).

Lake morphometric variables including lake area, maximum depth, and mean depth were obtained from the MNR computerized data inventory. Lake volume was estimated by multiplying lake area by mean depth. Catchment variables were obtained from 1:10,000 base maps or 1:50,000 topographic maps. Drainage area was measured using the cut and weigh method. Percent wetland in the catchment was measured using the dot counting method (Nilsson and Håkanson 1992), from the proportion of the catchment covered by map symbols representing marshes or beaver ponds. Drainage ratio was calculated by dividing drainage area by lake volume.

Zooplankton collection and sample preparation

Zooplankton were collected with a 363 μm mesh plankton net in late July and early August 1993, using vertical hauls at the deepest point in each lake. Great care was taken to avoid contamination during the collection and preparation of the samples. The net was carefully rinsed in lake water before and after each use and stored in a clean plastic container with a lid. Plastic gloves were worn at all times throughout the collection and handling of samples. Once collected, zooplankton were transferred to prewashed Teflon vials that had been acid leached in 20% reagent grade HNO_3 for a week, thoroughly rinsed with distilled, deionized water and stored inside two clean resealable plastic bags. Samples were frozen within 1 hour of collection. In the laboratory, zooplankton samples were hand sorted under a dissecting microscope using acid-cleaned Teflon coated forceps and filter-feeding Cladocera selected for methyl mercury analysis. We chose to restrict our analysis to filter-feeding Cladocera because they feed at approximately the same trophic level in all lakes. It was important to minimize variation in trophic level because it influences methyl mercury levels in the biota and could easily have obscured relationships with environmental variables (Watras and Bloom 1992). Once the Cladocera had been sorted and counted they were freeze-dried for about 24 hours and then weighed on a Mettler AE 100 analytical balance. Their mean individual weight was calculated for each lake by dividing the sample weight by the number of Cladocera per sample. Nitrogen content of the Cladocera was determined for duplicate samples with a Roboprep-CN analyzer. To determine if the taxonomic composition of the zooplankton contributed to the variability in methyl mercury levels we identified a subsample of 200 filter-feeding Cladocera to the genus level. Samples consisted largely of Daphnia spp. and Holopedium gibberum, with Daphnia spp. usually dominating. Since Daphnia spp. were the dominant filter-feeding Cladocera in most lakes the taxonomic composition is given by the proportion Daphnia spp. in each sample. The data revealed that the proportion of Daphnia spp. in the samples did not significantly influence methyl mercury concentrations in the study lakes (r=0.07, P=0.748).

Methyl mercury determinations

Methyl mercury levels in zooplankton were determined by aqueous phase ethylation, gas chromatograph (GC) separation and cold vapour atomic fluorescence detection (CVAFS) using a technique modified from Bloom (1989). Zooplankton (0.1 g) were digested with 2 ml 25% KOH in methanol for 3 h at 70°C. An aliquot (500 μl) of the digestate was then diluted with 200 ml of water, neutralized to pH 4.9 with acetate buffer, and ethylated with 100 μl of sodium tetraethylborate. The sample was allowed to react for 20 minutes and was then purged with argon onto a Tenax® trap. The use of a Tenax® trap instead of a graphitized carbon column allowed rapid desorption of trapped mercury species at lower temperature (275°C) and direct coupling to the GC (Van Tra et al., submitted). Separation of the volatile alkyl derivatives was achieved by isothermal (90°C) GC separation rather than cryogenic GC separation. Eluted species were thermally decomposed (900°C) and the resulting elemental mercury measured by CVAFS. The detection limit (3xSD) for a 0.1 g sample was 3.9 ng $Hg \cdot g^{-1}$ dry weight. Certified standard tissues and blanks were analyzed every five samples. Samples were subsequently corrected for reagent contamination. Analysis of 0.1 g samples of National Research Council of Canada DORM-1 (0.731$\pm$ 0.060 $mg \cdot kg^{-1}$) yielded 0.788 $\pm$ 0.053 $mg \cdot kg^{-1}$ (n=8). Samples analyzed in triplicate for three of the study lakes had a mean coefficient of variation of 14%$\pm$ 4%. This variation was considered acceptable and therefore data for the remaining lakes are the result of one determination.

Statistical analyses

To examine relationships between environmental factors and methyl mercury accumulation Pearson correlation coefficients were calculated between methyl mercury levels in the Cladocera and environmental variables. Variables significantly correlated with methyl mercury levels were entered into a stepwise multiple regression and the best-fitting model determined by the coefficient of determination and the standard error of the estimate. Separate analyses were conducted to determine if relationships between methyl mercury levels in zooplankton and environmental variables were different in clearwater (n=14) than in brownwater lakes (n=10). The level of significance for statistical tests was set at $P \leq 0.05$. Variables were logarithmically transformed where necessary to linearize relationships between the dependent and independent variables. All statistical analyses were performed using SYSTAT version 5.1 for the Macintosh (Wilkinson 1990).

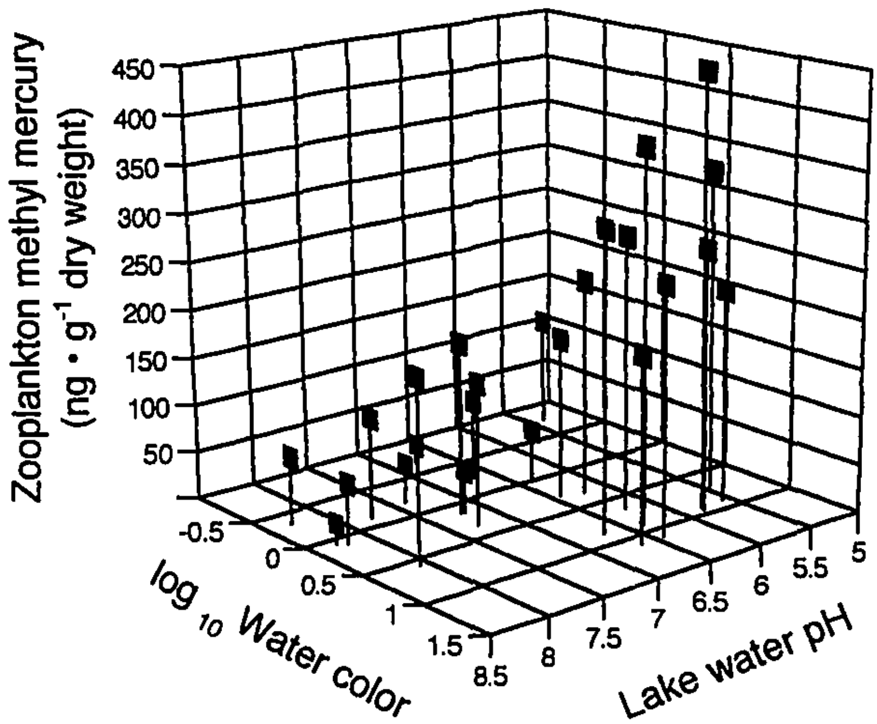
Results

Methyl mercury levels in the Cladocera ranged from 19 to 448 $ng \cdot g^{-1}$ dw in the study lakes. This range is similar to that reported for zooplankton collected from Swedish lakes with a 250 μm plankton net (35 to 400 $ng \cdot g^{-1}$ dw) (Meilli 1991). Methyl mercury levels were highest in Cladocera from brownwater acid lakes and lowest in those from clearwater alkaline lakes (Fig. 2). Zooplankton from brownwater lakes were significantly more contaminated (mean=289, n=10) than those from clearwater lakes (mean=95, n=14) (Student's t-test, P=0.0001).

Zooplankton methyl mercury levels were significantly correlated with lake area (-), maximum depth (-), mean depth (-), $\log_{10}$ drainage ratio (+), %wetland in the catchment (+), lake water pH (-), $\log_{10}$ conductivity (-), $\log_{10}$ water color (+), total phosphorus (+), and $\log_{10}$ zooplankton weight (-) (Table 2). Water temperature, chlorophyll-a and % nitrogen in zooplankton did not significantly influence methyl mercury levels. As there were significant intercorrelations between a number of the predictor variables (Table 3), the analysis was limited to subsets of variables that did not share a high degree of covariance.

Water color and lake water pH were the best predictors of methyl mercury levels in zooplankton explaining 73% of the variation (Table 4). Methyl mercury levels increase

FIG. 2. Three-dimensional scatter plot of the relationships among methyl mercury levels in zooplankton, log_{10}water color, and lake water pH.



Zooplankton methyl mercury
(ng • g-1 dry weight)
450
400
350
300
250
200
150
100
50
-0.5
0
0.5
1
1.5
log 10 Water color
8.5
8
7.5
7
6.5
6
5.5
5
Lake water pH

TABLE 2. Pearson correlation coefficients for methyl mercury levels in zooplankton and environmental variables.

Variable	n	r	P
Lake area	24	-0.432	0.035
Maximum depth	24	-0.482	0.017
Mean depth	24	-0.449	0.028
$\log_{10}$ Drainage ratio	24	0.515	0.010
% Wetland in the catchment	24	0.428	0.026
Surface water temperature	24	0.120	0.577
Lake water pH	24	-0.598	0.002
$\log_{10}$ Conductivity	24	-0.530	0.008
$\log_{10}$ Water color	24	0.788	0.000
Total phosphorus	19	0.724	0.000
Chlorophyll-a	19	0.331	0.166
% Nitrogen in zooplankton	23	0.287	0.185
$\log_{10}$ Zooplankton weight	24	-0.559	0.005

TABLE 3. Correlation matrix of environmental variables significantly related to methyl mercury levels in zooplankton. Only correlation coefficients with <u>P</u>≤0.05 are shown. LA=lake area, Zmax=maximum depth, Zmean=mean depth, DR=log_{10} drainage ratio, %WET=%wetland in the catchment, pH=lake water pH, COND=log_{10} conductivity, COL=log_{10} water color, TP=total phosphorous, and WGT= log_{10} zooplankton weight.

	COL	TP	pH	WGT	COND	DR	Zmax	Zmean	%WET	LA
COL										
TP	0.824***									
pH		-0.601**								
WGT	-0.548**	-0.663**								
COND		-0.450*	0.911***							
DR	0.819***	0.678***		-0.611**						
Zmax	-0.492*	-0.505*	0.440*			-0.615***				
Zmean	-0.496*	-0.546*				-0.642***	0.974***			
%WET	0.486*	0.467*				0.444*	-0.482*	-0.518**		
LA			0.559**		-0.673***		0.401*			

* $P \leq 0.05$, ** $P \leq 0.01$, and *** $P \leq 0.001$

TABLE 4. Stepwise multiple regression of methyl mercury levels in zooplankton on environmental variables. Model r^2= 0.73, Intercept= 449.64, SE_{est}=65.61, P= 0.0001.

Independent variable	n	Partial r^2	Std. partial r	Slope	Partial F	P
$\log_{10}$ Water color	24	0.62	0.668	146.35	30.74	0.0001
Lake water pH	24	0.11	-0.352	-47.41	8.55	0.008

with water color and decline with increasing lake water pH. The standardized partial correlation coefficients point to water color having a much greater affect on methyl mercury accumulation in zooplankton than lake water pH. The data scatter around the line of best fit was not correlated with any of the other environmental variables measured.

Discussion

The results of this study show that methyl mercury levels in zooplankton increase with increasing water color and decline with increasing lake water pH and that water color influences methyl mercury concentrations in the study lakes to a greater extent than lake water pH. These results are consistent with previous studies that have shown that mercury levels in fish and other aquatic organisms are positively correlated with water color or dissolved organic carbon (DOC) concentration in lake water (Meilli and Parkman 1988; McMurtry et al. 1989; Sorensen et al. 1990; Håkanson et al. 1990; Wren et al. 1991; Parkman and Meilli 1993), and inversely correlated with lake water pH (Cope et al. 1990; Grieb et al. 1990; Wiener et al. 1990; Watras and Bloom 1992; Parkman and Meilli 1993).

Few studies have examined the effects of environmental factors on methyl mercury accumulation in aquatic invertebrates in relatively pristine lakes. Watras and Bloom (1992) evaluated the effects of lake water pH on the availability of methyl mercury in the water column and biota of an experimentally acidified lake basin. They found that acidification resulted in significant increases in methyl mercury concentrations in the water column, in phytoplankton and in zooplankton. Their results clearly show that environmental factors influence both the availability of methyl mercury in the environment and the bioaccumulation of methyl mercury by zooplankton and other lacustrine organisms. Meilli (1991) too found significant correlations between methyl mercury concentrations in zooplankton and water color and lake water pH in 18 lakes in central and southern Sweden. However, these two variables explained considerably less of the variation in methyl mercury concentrations in the Swedish lakes than in the present study, despite similar ranges in water color and lake water pH. This may be because the lakes sampled in the Swedish study encompass two regions that vary with respect to climate, hydrology, and mercury deposition, and because the zooplankton included predaceous as well as filter-feeding crustacean zooplankton.

Several hypotheses have been proposed to explain elevated mercury levels in the biota from brownwater lakes. It has been suggested that mercury levels are high because humic substances that are largely derived from catchments (Rasmussen et al. 1989), mobilize mercury from the drainage basin (Lee and Hultberg 1990; Lee and Iverfeldt 1991; Mierle 1990; Mierle and Ingram 1991), that the abiotic methylation of inorganic mercury by humic substances in highly organic soils may increase the supply of methyl mercury to lakes (Lee et al.1985; Lee and Hultberg 1990), and that humic substances may stimulate the in-lake production of methyl mercury (McMurtry et al. 1989; Wren et al. 1991; Miskimmin et al. 1992), or enhance the retention of methyl mercury by lakes (Miskimmin 1991). Lastly, it has been hypothesized that mercury levels are high in the biota from brownwater lakes because these lakes receive water from wetlands that are sources of methyl mercury (St. Louis et al. 1994).

While mercury levels in fish and other aquatic organisms have been found to be positively correlated with water color or DOC concentration in studies on drainage lakes, the opposite trend has been observed in fish from seepage lakes. Grieb et al. (1990) found mercury levels in yellow perch to be inversely correlated with DOC concentration in seepage lakes. They attributed this negative relationship to a reduced bioavailability of mercury resulting from its complexation with organics. Their findings together with those of Miskimmin et al. (1992), who showed experimentally that increased concentrations of DOC in lake water result in decreased specific rates of net methylation, suggest that humic substances inhibit the in-lake production of methyl mercury. Since humic substances appear to inhibit rather than stimulate the in-lake production of methyl mercury it is unlikely that this mechanism alone could account for elevated mercury levels in the biota from brownwater lakes.

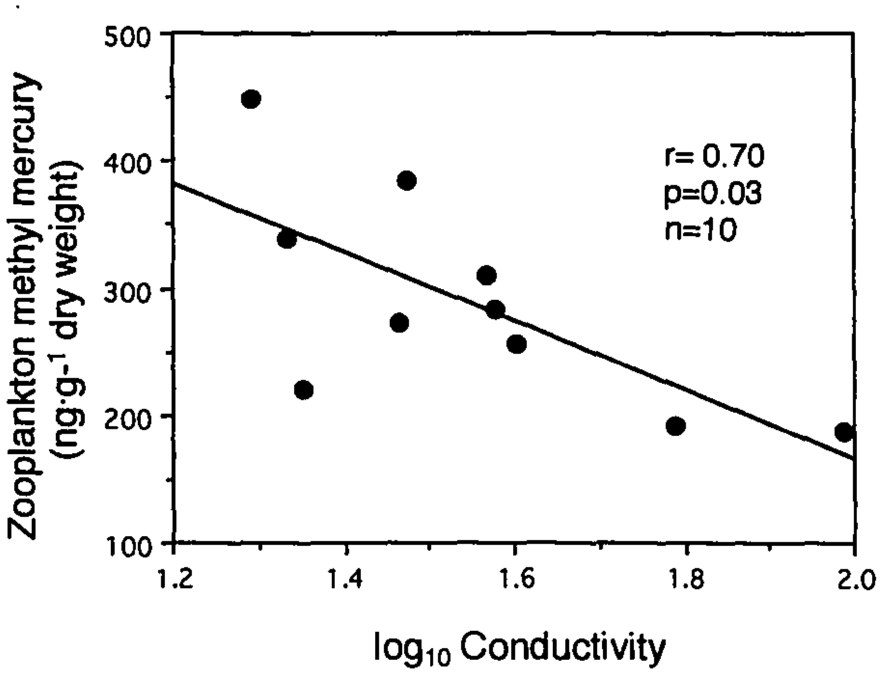
Correlational evidence indicates that mercury entering lakes from the drainage basin is associated with humic substances (Lee and Hultberg 1990; Lee and Iverfeldt 1991; Mierle 1990; Mierle and Ingram 1991), and that the concentration of humic substances in runoff from the drainage basin and in lake water is positively correlated with mercury concentrations in fish (McMurtry et al. 1989; Sorensen et al. 1990; Håkanson et al. 1990; Wren et al. 1991; Lee and Iverfeldt 1991). Furthermore, the drainage ratio has been found to be well correlated with mercury loading from the drainage basin (Swain et al. 1992), while mercury concentrations in fish have been shown to be positively correlated with the drainage ratio (Suns and Hitchin 1990). Lastly, the present study shows that methyl mercury levels in filter-feeding macrozooplankton are also positively correlated with the concentration of humic substances in lake water and with the drainage ratio (Table 2). Together, these results provide strong evidence for the notion that humic substances influence mercury levels in the biota through their role in the export of mercury from the drainage basin. That methyl mercury levels in the zooplankton were also positively correlated with the percent wetland in the catchment is particularly interesting in light of recent work by St. Louis et al.(1994) who demonstrated the wetland portions of catchments to be net sources of methyl mercury but net sinks of total mercury. The positive relationship observed between methyl mercury levels in the Cladocera and the percent wetland in the catchment supports the idea that terrestrial sources of methyl mercury contribute significantly to the contamination of the lacustrine biota.

Several mechanisms have also been proposed to explain the relationships observed between mercury concentrations in the biota and lake water pH. These mechanisms, all of which involve the effects of pH on in-lake processes, include the increased production of methyl mercury in the water column and surface sediments at low pH (Furutani and Rudd 1980; Xun et al. 1987), a decreased loss of volatile mercury from lake water at low pH

(Rada et al. 1987), and an increased uptake of both organic and inorganic mercury by aquatic organisms at low pH (Rodgers and Beamish 1983; Saouter et al. 1989; Ponce and Bloom 1991). The importance of pH in influencing methyl mercury levels in zooplankton is highlighted not only by the fact that pH explained a significant proportion of the overall variance in methyl mercury levels (Table 2), but also by the fact that conductivity, a variable closely linked to lake water pH (Table 3), explained much of the among lake variance in methyl mercury concentrations in the brownwater lakes (Fig. 3). Methyl mercury levels in the zooplankton from brownwater lakes were not significantly related to water color, showing that variables related to lake water acidity become more important when interlake differences in mercury loading from the drainage basin are reduced.

In drainage lakes, such as those sampled here the supply of mercury from the drainage basin has been estimated to be about 40-75% of the total annual load (Iverfeldt and Johansson 1988; Mierle 1990; Sorensen et al. 1990; Mierle and Ingram 1991). The present study shows that in such lakes both water color and lake water pH significantly influence the accumulation of methyl mercury in zooplankton. Nevertheless, water color, which appears to represent mercury loading from the drainage basin, outweighs the in-lake effects of lake water pH on methyl mercury accumulation. More precisely, the standardized partial correlation coefficients of water color and lake water pH (Table 4) show that the effects of water color on methyl mercury levels in zooplankton are 1.9 times more important than those of lake water pH. This means, for example, that if methyl mercury levels in zooplankton increase or decrease by 40% per unit change in water color, methyl mercury levels would increase or decrease by 22% for a similar change in pH. It is however worth noting that the relative importance of water color and lake water pH will shift depending on the magnitude of differences in the supply of mercury from the drainage basins, and on the relative importance of catchment inputs of mercury in comparison to other sources. Thus, where catchment inputs of mercury are minor, as in seepage lakes with their typically small drainage basins (Watras et al. 1994;

FIG. 3. Relationship between methyl mercury levels in zooplankton from brownwater lakes and log_{10} conductivity.



Zooplankton methyl mercury (ng·g-1 dry weight)
500
400
300
200
100
1.2
1.4
1.6
1.8
2.0
r= 0.70
p=0.03
n=10
log10 Conductivity

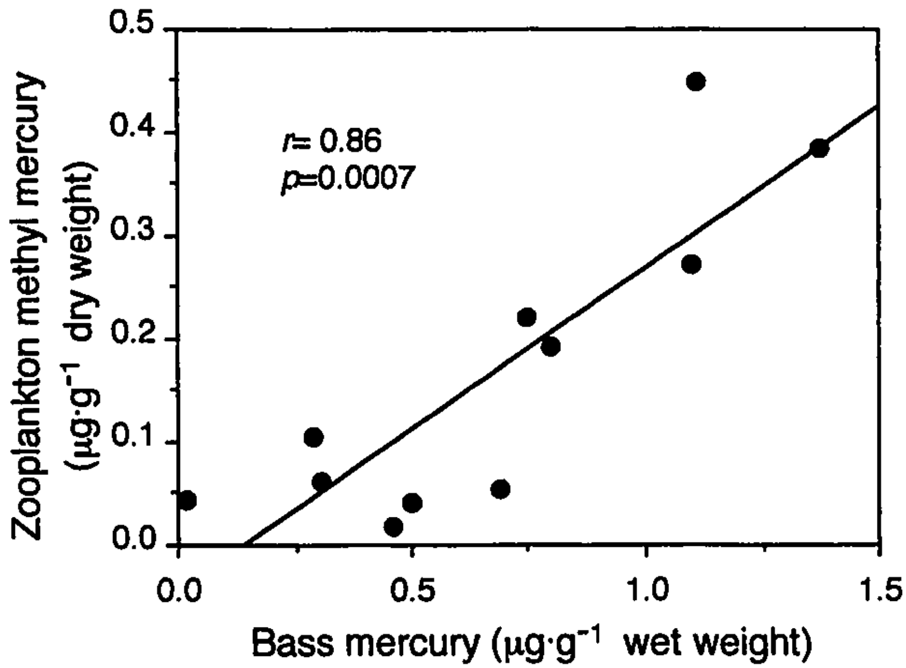
Verta et al. 1994), lake water pH has been found to be the variable of importance in influencing mercury levels in the biota (Grieb et al. 1990; Bloom et al. 1991).

Mercury levels in fish in a given lake can be reasonably well predicted from levels in other organisms within that lake (Stokes et al. 1983; Cope et al. 1990; Sorensen et al. 1990; Meilli 1991; Allard and Stokes 1989; Wren et al. 1991). This may be because the fish are either directly or indirectly feeding on the other organisms, or simply a result of the fact that they share the same environment and are as such exposed to similar ambient mercury levels (Wren et al. 1991). I compared methyl mercury levels in zooplankton to mercury concentrations in largemouth and smallmouth bass for 11 lakes in which data were available from the Ontario Mercury Data Base (MOE 1993). Mercury levels in the bass were indeed well correlated with methyl mercury levels in zooplankton from the same lakes (Fig. 4). Since adult largemouth and smallmouth bass feed primarily on fish, aquatic insects and crayfish (Scott and Crossman 1973), it is highly unlikely that they are trophically linked to profundal zooplankton. Thus we can conclude that filter-feeding macrozooplankton reflect the relative bioavailability of mercury at different trophic levels within these lakes. This makes them an easy to obtain and convenient measure of the bioavailability of mercury at the base of food chains that is useful in studies that must account for differences in the bioavailability of mercury among lakes.

Conclusions

Methyl mercury levels in filter-feeding macrozooplankton varied 24 fold across the study lakes and 73% of this variation was accounted for by differences in water color and lake water pH. Water color explains a greater portion of the overall variance in methyl mercury levels, indicating that the supply of mercury from the drainage basin plays a key role in influencing the accumulation of methyl mercury in the lacustrine biota. Furthermore, this study provides a first demonstration that the effects of water color outweigh those of lake water pH in influencing methyl mercury levels in the biota at or near

FIG. 4. Relationship between methyl mercury concentrations in zooplankton and mercury concentrations in largemouth or smallmouth bass in 11 Ontario lakes.



0.5
0.4
0.3
0.2
0.1
0.0
Zooplankton methyl mercury (µg·g⁻¹ dry weight)
r= 0.86
p=0.0007
0.0
0.5
1.0
1.5
Bass mercury (µg·g⁻¹ wet weight)

the base of the food chain. Methyl mercury concentrations were highest in zooplankton from acidic brownwater lakes, supporting the notion that the pool of bioavailable mercury is particularly large in this type of lake. Finally, zooplankton methyl mercury levels were well correlated with mercury concentrations in fish showing filter-feeding zooplankton to be good indicators of the relative bioavailability of mercury at the base of the food chain in lakes.

Summary

The purpose of the study was to examine relationships between environmental factors and methyl mercury accumulation in filter-feeding macrozooplankton. The results of this study show that methyl mercury accumulation is strongly influenced by water color and lake water pH. These two variables together explained 73% of the variance in methyl mercury concentrations in zooplankton across the study lakes. Zooplankton from brownwater lakes were significantly more contaminated than those from clearwater lakes suggesting that the bioavailability of mercury is enhanced in the former. The effects of water color on methyl mercury accumulation appear to be primarily related to the supply of mercury from the drainage basin. In contrast, the effects of lake water pH appear to be principally linked to in-lake processes. Water color explained a greater portion of the overall variance in methyl mercury levels suggesting that the supply of mercury from the drainage basin plays an important role in determining methyl mercury concentrations in the lacustrine biota. Methyl mercury concentrations in the filter-feeding Cladocera were well correlated with mercury levels in smallmouth and largemouth bass in 11 of the study lakes showing zooplankton to be good indicators of the bioavailability of mercury at the base of the food chain.

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Appendix A

Physical and limnological characteristics of the study lakes

Lake	Latitude	Longitude	Lake area (km^2)	Lake volume ($m^3 \times 10^5$)	Z max (m)	Z mean (m)	Catchment area (km^2)	Drainage area (km^2)	Drainage ratio
Pearceley	45.42	79.3	0.441	1.9	9.2	4.2	0.66	0.22	0.4
Fogal	45.11	79.53	0.118	0.3	5	2.2	0.87	0.75	3.4
Meadow	45.22	79.35	0.739	1.9	7.9	2.6	4.21	3.47	2.2
Moot	45.09	79.1	0.462	1.2	7.9	2.6	5.55	5.09	4.6
Fawn	45.1	79.15	0.867	2.9	7.9	3.4	12.72	11.85	4.3
Healey	45.05	79.11	1.189	3.3	7	2.8	5.72	4.53	1.7
Crosson	45.05	79.02	0.568	4.6	23.5	8.1	2.11	1.54	0.5
Fox	45.23	79.2	1.366	7.8	12.2	5.7	9.57	8.2	1.2
Leonard	45.04	79.27	1.93	13.1	18.3	6.8	5.91	3.98	0.5
Leech	45.03	79.06	0.82	5.2	13.7	6.3	3	2.18	0.6
Lowe	44.55	79.15	0.194	0.3	3.4	1.3	15.65	15.46	62.1
Brandy	45.07	79.31	1.048	3.7	7.5	3.5	34.41	33.36	9.4
Spring	45.01	79.08	0.258	1.7	18.9	6.6	0.72	0.46	0.4
Ryde	44.54	79.15	0.817	4.8	12.8	5.9	9.46	8.64	2
Clear	45.02	79.01	0.963	11.4	29.6	11.8	1.93	0.97	0.2
Bark	44.56	78.28	1.679	7.7	12.2	4.6	10.22	8.54	1.3
Looncall	44.44	78.09	0.864	4.8	15.5	5.6	4.7	3.84	1
Cavendish	44.44	78.17	0.235	2.5	25.9	10.6	4.23	4	1.7
Boshkung	45.04	78.44	7.164	165.5	71.1	23.1	21.2	14.03	0.1
Pine	45.07	78.35	1.118	8.5	20.4	7.6	16.67	15.55	2
Pencil	44.48	78.21	0.766	6.4	21.3	8.4	13.66	12.89	2.1
Gloucester Pool	44.51	79.42	13.766	95	30.5	6.9	88.52	74.75	0.9
Salmon	44.49	78.27	1.716	19.4	30.5	11.3	6.28	4.56	0.3
Mitchell	44.35	78.57	8.511	6	3.7	0.7	22.14	13.63	3.7

Appendix A
Physical and limnological characteristics of the study lakes

Lake	% Wetland	Lake Elevation (m)	Spring secchi (m)	Summer secchi (m)	Spring pH	Summer pH	Spring colour (abs @ 440 nm)	Summer colour (abs @ 440 nm)
Pearceley	10	358.5	•	8.6	•	5.35	•	0.17
Fogal	24.5	213	2.2	2.4	5.77	5.5	5.84	5.69
Meadow	26	318.5	1.4	1.3	5.58	5.56	5.12	7.91
Moot	18.5	350.6	1.6	1.5	5.78	5.8	5.5	8.34
Fawn	18.5	289.9	1.2	1.6	5.77	5.82	7.51	8.92
Healey	11.6	304.9	•	2.4	•	6.22	•	4.46
Crosson	7.7	335.4	2.6	2.9	6.42	6.23	2.58	2.14
Fox	3.7	297.9	1.5	1.5	5.87	6.37	6.42	8.13
Leonard	0	182.9	2.8	5.2	6.33	6.38	0.51	1.01
Leech	0	320.1	2.6	3.7	6.34	6.41	1.9	1.9
Lowe	9.8	253	•	1	•	6.42	•	12.63
Brandy	6.3	236	1.4	1	6.79	6.64	7.63	12.68
Spring	0	•	5.5	5.9	6.1	6.67	0.96	0.56
Ryde	16	243.9	•	2.4	•	6.69	•	7.23
Clear	0	330.5	9.9	7.4	6.51	6.78	0.14	0.22
Bark	17.9	343	4.4	3.9	6.63	7.18	1.95	1.34
Looncall	16.1	350.6	4.1	4.4	7.21	7.2	1.07	1.31
Cavendish	0	294.5	•	3.6	•	7.29	•	2.2
Boshkung	0	•	5.5	5.3	6.87	7.38	0.24	0.63
Pine	0	317.1	3.9	5.2	7.07	7.77	1.01	0.75
Pencil	24.1	323.2	3.2	2.8	7.32	8.08	3.58	3.75
Gloucester Pool	6.2	197.9	3.2	3.8	8.11	8.22	1.76	1.25
Salmon	7.5	322	10.4	8.1	8.09	8.28	0.29	0.45
Mitchell	14.3	256.4	•	•	8.08	8.28	0.74	1.14

Appendix A

Physical and limnological characteristics of the study lakes

Lake	Spring colour (Pt. mg/l)	Summer colour (Pt. mg/l)	Spring total phosphorous (ug/l)	Spring chl-a (ug/l)	Mixing depth (m)	Hypolimnetic O_2 (mg/l)
Pearceley	•	3	•	•	8	•
Fogal	106	103	23.8	8.2	2	0.1
Meadow	93	144	34.4	9.4	4	•
Moot	100	152	47.4	3.3	3	0.3
Fawn	137	162	40.2	3.7	3	0.9
Healey	•	81	•	•	4	4.8
Crosson	47	39	31.9	6.2	3	5.1
Fox	117	148	26.1	3.1	6	•
Leonard	9	18	16.5	6.8	5	8
Leech	34	34	16.6	3.7	4	4.6
Lowe	•	230	•	•	2	6.6
Brandy	139	231	37.1	2.6	3	0.9
Spring	17	10	11.1	1.8	4	9.6
Ryde	•	132	•	•	4	2.9
Clear	2	4	7	0.8	6	11.3
Bark	35	24	18.5	2.8	5	•
Looncall	19	24	18.4	7.3	5	•
Cavendish	•	40	•	•	3	•
Boshkung	4	11	14	2.9	8	9.6
Pine	18	13	11.4	2.7	6	5.4
Pencil	65	68	11.6	2	6	•
Gloucester Pool	32	23	17	3	7	9.5
Salmon	5	8	10.3	1.3	8	•
Mitchell	13	21	25.2	2.6	•	10.8

Appendix A

Physical and limnological characteristics of the study lakes

Lake	Surface H_2O tempmperature (°C)	Epilimnetic H_2O tempmperature (°C)	Mean H_2O column tempmperature (°C)	Conductivity@ 25 °C (µs/cm^2)	Lake type
Pearceley	22.2	21.3	21.3	21	ca
Fogal	24.6	23.6	20.9	21.5	ba
Meadow	21.9	21.7	15.2	22.5	ba
Moot	24.2	22.7	18.3	19.5	ba
Fawn	23.9	23.2	18.1	29.2	ba
Healey	22.3	22.3	20.7	37.7	bcn
Crosson	25	23.8	10.6	22.8	intcn
Fox	22.8	22.6	15	29.7	bcn
Leonard	24.2	23.4	15.4	35.9	ccn
Leech	22.4	22	13.4	33.7	ccn
Lowe	23.3	23.2	23.2	40.1	bcn
Brandy	24	23.1	19.3	61.5	bal
Spring	23.8	23.1	13.6	45.3	cal
Ryde	23.5	23.2	15.1	37.1	bal
Clear	23.2	22.8	11.2	32.3	cal
Bark	22.8	22.6	17.3	33	cal
Looncall	24.2	22.2	13.7	43.8	cal
Cavendish	24.2	23	10.2	50.4	intal
Boshkung	22.8	22.6	•	55.2	cal
Pine	23.6	23.1	14.8	71.1	cal
Pencil	24.1	22.5	9.7	96.8	intal
Gloucester Pool	24.1	23.6	18.6	224.2	cal
Salmon	23.2	23.1	10.1	171.5	cal
Mitchell	23.3	23.3	23.3	153.3	cal

Appendix B

Characteristics of the zooplankton populations sampled

Lake	Zooplankton MeHg (ng/g dw)	Mean individual zooplankton weight (mg dw)	% Daphnia	C:N	% N	% C
Pearceley	113	0.008	95	9.0	6.4	57.9
Fogal	338	0.007	20	7.9	7.7	60.8
Meadow	221	0.011	100	5.7	8.6	49.2
Moot	448	0.002	70	8	7.1	56.8
Fawn	271	0.001	70	6.3	8.3	52.2
Healey	283	0.003	100	6.3	8	50.5
Crosson	225	0.012	40	6.4	8.4	54
Fox	384	0.005	100	7.6	9	68.1
Leonard	55	0.038	0	6.6	8.9	58.3
Leech	171	0.014	90	7.8	6.9	53.9
Lowe	256	0.001	100	6.4	9	58
Brandy	192	0.004	100	7.6	7.3	55.6
Spring	83	0.015	95	7.8	7.2	56.3
Ryde	309	0.009	100	7.9	6.8	53.8
Clear	19	0.009	75	12.0	6	72
Bark	44	0.008	5	6.6	9.4	62.4
Looncall	142	0.014	50	9.1	6.8	62.1
Cavendish	148	0.013	95	8.9	6.6	58.6
Boshkung	40	0.007	80	6.9	8	55.3
Pine	105	0.006	95	8.5	7	59.4
Pencil	164	0.018	100	8.0	7.2	57.4
Gloucester Pool	62	0.010	95	10.2	5.4	55.1
Salmon	70	0.019	100	8.1	6.0	48.5
Mitchell	20	0.011	100	•	•	•

Appendix C

Mercury data for the study lakes with either smallmouth or largemouth bass

Lake	Zooplankton MeHg ($\mu g/g$ dry weight)	Mean bass Hg ($\mu g/g$ wet weight)	Mean bass weight (g)	Bass sample size
Meadow	0.221	0.750	876	10
Moot	0.448	1.110	1000	18
Fawn	0.271	1.100	604	14
Fox	0.384	1.375	784	42
Leonard	0.055	0.690	573	12
Brandy	0.192	0.800	475	19
Clear	0.019	0.460	818	5
Bark	0.044	0.020	294	4
Boshkung	0.040	0.500	784	16
Pine	0.105	0.290	473	17
Gloucester Pool	0.062	0.306	•	•