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Effects of wildfire and clear-cutting in the boreal forest on mercury in zooplankton and fish

SFM Network Project: Water-quality: causes of natural variability and impacts of watershed disturbances in the boreal forest lakes of Québec

By

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EXECUTIVE SUMMARY

We compared the effects of forest logging and wildfire on methylmercury (MeHg) concentrations in bulk zooplankton collected in 38 boreal lakes and on total mercury in northern pike collected in 20 of those lakes. Mean MeHg concentrations were slightly but significantly higher ($p < 0.01$) in zooplankton collected in lakes with recently logged watersheds (135 $ng.g^{-1}$ d.w.) than in lakes with recently burned (97 $ng.g^{-1}$ d.w.) or with undisturbed watersheds (112 $ng.g^{-1}$ d.w.). MeHg levels in zooplankton collected in burned and reference lakes were not significantly different. Multiple regression including all the lakes showed that four variables (dissolved organic carbon, pH, dissolved oxygen and immature zooplankton biomass) explained 43% of the variability in MeHg levels in bulk zooplankton.

Mercury levels in pike normalized to a 560 mm length were significantly higher in logged lakes (3.4 µg.g dry weight $^{-1}$) than in the reference group (1.9 µg.g dry weight $^{-1}$). Pike from burned lakes showed intermediate levels of mercury (2.8 µg.g dry weight $^{-1}$). Mercury levels were above the WHO safe consumption limit in two of the nine reference lakes, in three of the seven burned lakes and in all four logged lakes. Concentrations of mercury were correlated with pH (-), alkalinity (-) and sulfate (+), and with dissolved organic carbon (DOC) (+) or light penetration in lake water (-). The strongest correlation observed was with methyl mercury (MeHg) in zooplankton ($r = + 0.79$). Stepwise multiple regression explained 78% of the variability in mercury in northern pike, and included MeHg in zooplankton, pH and sulfate as independent variables.

The strong association between mercury levels in biota and DOC concentrations in the lakes suggests that the mercury problem can be easily controlled by reducing DOC loads in logged lakes. Simple quantitative relationships based on the harvested area : lake volume ratio, given in Carignan et al. (1999) can be applied in the field to maintain DOC within the range of natural variability in these lakes.

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INTRODUCTION

Mercury contamination of fish is a widespread problem in remote lakes and reservoirs of the boreal forest. Volatile forms of mercury reach these regions through long-range atmospheric transport (Rudd 1995), and after being oxidized to water soluble forms, deposit in lakes or watersheds. In the latter, most mercury accumulates in the upper layer of soil, where it associates with the organic matter (Meili 1991). Significant disturbances in watersheds may therefore influence the transport of mercury to aquatic ecosystems. Wildfire and clear-cutting specifically are two major perturbations affecting the boreal forest. After clear-cutting or low to medium intensity fires, the upper organic layer of the soil becomes more exposed to erosion, and the transfer of particulate and dissolved organic carbon (DOC) to aquatic systems may increase (Hobbie and Likens 1973). Since DOC in forest soil is an important vector of some metals (Shafer et al. 1997), the transfer of these metals, such as mercury, to streams and lakes would also increase. During high intensity fires, on the contrary, most of the organic matter in the forest floor is mineralized (Bormann and Likens 1979) and some elements associated to it, including mercury, may be lost by volatilization.

Although numerous studies have addressed the effects of clear-cutting and fire on the mobilization of nutrients and major ions in forested soils, limited information is available on the transfer of mercury to streams and lakes as a consequence of forest disruption. In this study, we examine the relationships between fire and logging and mercury contamination in zooplankton and fish. Because DOC transfer from logged watersheds to lake water is greater than from burned or undisturbed ones (see Carignan et al. 1999), we hypothesized that zooplankton and fish from lakes with logged watershed would accumulate more Hg than those from lakes with burned or undisturbed catchments. For zooplankton, we focus on the methylated form of mercury (MeHg) because it can be accumulated and bioamplified along the food web. Zooplankton was selected as an indicator of MeHg contamination because these short-lived organisms can readily assimilate bioavailable MeHg from the water column and are expected to respond rapidly to changes in environmental conditions. In predator fish, over 95% the Hg is present as MeHg. We therefore report total mercury concentrations in northern pike (*Esox lucius*), a top predatory fish, which was found in twenty out the thirty-eight lakes. Since methylmercury is bioamplified through the food web, we examine whether mercury levels in fish from logged lakes would also be higher than in burned or reference lakes.

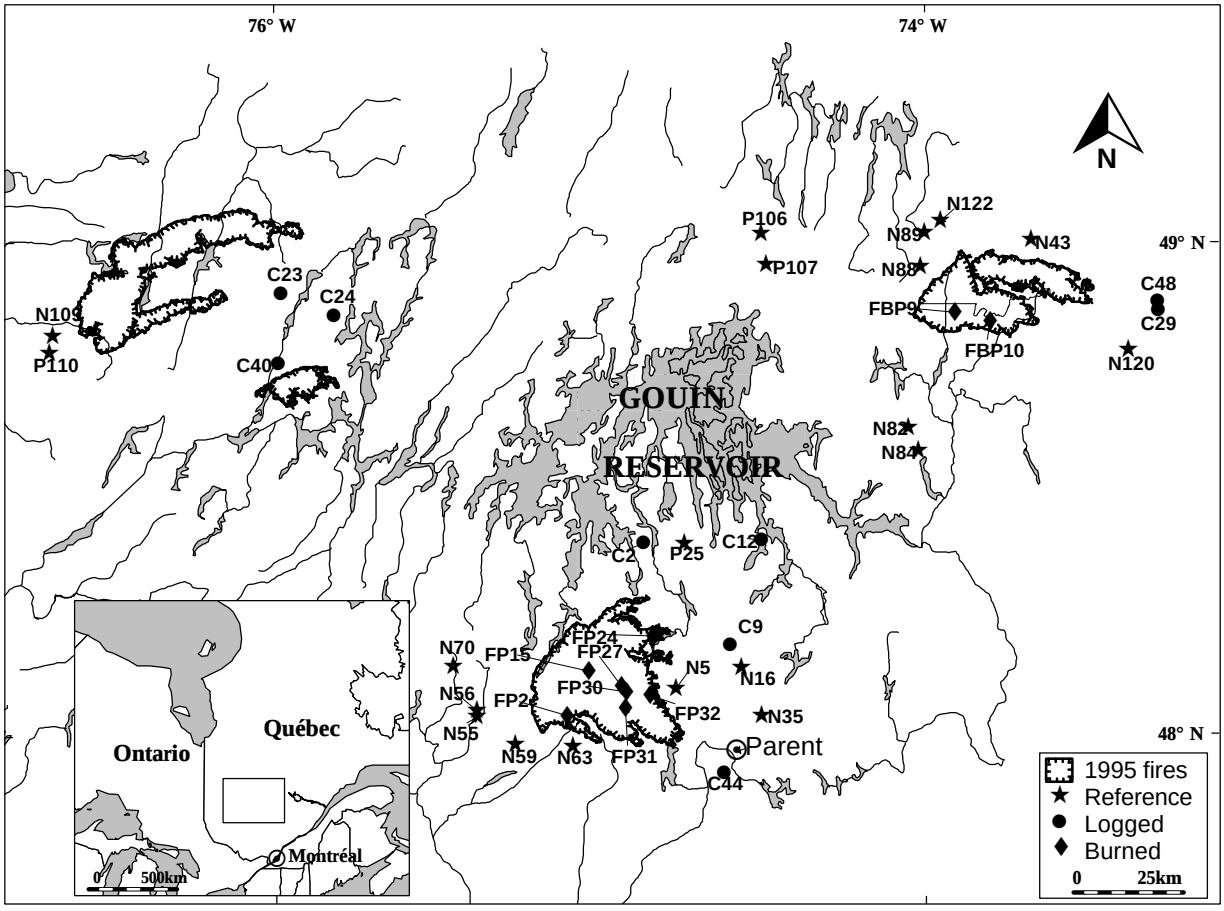
MATERIALS AND METHODS

Study site

The study was conducted in 38 headwater lakes located in a 40,000 km^2 region of central Quebec, Canada, surrounding Gouin Reservoir (Figure 1). All the lakes are located on the Canadian Shield, where the bedrock consists mainly of granite and gneisses, and is covered by

thin glacial tills. Soils are mostly humo-ferric podzols (Clayton et al. 1978). The lakes overlap the transition zone of the boreal mixed and coniferous forests. Wetlands (bogs, marshes, beaver ponds) are sometimes present, but their importance does not exceed 5% of the drainage area of the study lakes. Logged lakes had 8 to 96% of their watershed clear-cut. In burned lakes 50 to 100% of the catchments were affected by high intensity fires. All logging and fires occurred during 1995, approximately one year before sampling started. The lakes were also chosen in order to minimize differences in morphometric properties between treatments (Table 1). Further details regarding lake selection, morphometry, chemistry and severity of impacts by fire can be found in Carignan et al. (1999).

Figure 1. Location of the study sites.



Water chemistry

The lakes were sampled in June, July and September 1996. All chemical analyses were performed on duplicate integrated samples of the euphotic zone (1 % of the incident light) taken with a flexible PVC tube. Samples were processed as described in Carignan et al. (1999).

Zooplankton

Zooplankton was collected near the deepest point in each lake from vertical hauls using a one meter diameter 200 μm mesh net, on the same dates as the water sampling. Subsamples for MeHg analysis were transferred into polypropylene bottles, immediately frozen and after freeze-dried. Zooplankton for taxonomic identification was narcotized with carbonated water and preserved in 4% formaldehyde. Because of the large mesh net used, the samples consisted almost exclusively of adult specimens and the larger forms of copepodites (stages IV and V). Zooplankton (5-ml subsamples) was counted and identified to the genus level, with the exception of cyclopoids and calanoids copepods. In these two suborders, only the predator calanoid *Epischura* spp was identified, the other individuals were only discriminated as adults and immature specimens. The predators *Chaoborus* spp and *Leptodora* ssp were counted in the entire sample. On the basis of feeding habits, adult individuals from the different taxa and *Chaoborus* spp were separated in three groups : filter-feeders (most Cladocera and calanoids), omnivores (cyclopoids) and predators (*Chaoborus*, *Leptodora* and *Epischura*). A fourth group comprised immature forms of Cladocera and copepodites. Dry weight for biomass estimation was obtained from Pinel-Alloul et al. (unpublished data) for all taxa except *Chaoborus* spp, the dominant predator. Because of size variation of the latter species, biomass was directly measured for each sample by drying the individuals (24 hours at 50^0C) and weighing them on a Cahn microbalance ($\pm$ 0.001 mg). Results were expressed as % of total biomass.

MeHg analysis in zooplankton

Determination of MeHg followed aqueous phase ethylation, Tenax trap collection, isothermal gas chromatography separation and cold vapor atomic fluorescence detection (CVAFS), using a modification of the method described in Bloom (1989). Subsamples (0.1g) of finely ground bulk zooplankton were digested overnight at room temperature into 10 ml of 25% KOH in methanol. The digestates (250 μl) were transferred to a reaction vessel and diluted with 150 ml of tap water. pH was adjusted to 4.9 with an acetate buffer (2 M sodium acetate in 2 M acetic acid) and 100 μl of 1% sodium tetraethylborate was then added for ethylation. Duplicate subsamples of each digestate were analyzed and averaged. The average coefficient of variation and the detection limit (3 X SD) for a 0.1g sample were 8 % and 4.8 ng $Hg.g^{-1}$ d.w., respectively. Analytical blanks averaged 7.8 ng $Hg.g^{-1}$ d.w. Certified reference materials (DORM-1 - National Research Council of Canada) were run each 4 or 5 samples, and recoveries averaged 0.692 $\pm$ 0.045 $mg.kg^{-1}$ (n = 25), which corresponds to 94.7 $\pm$ 6.2% of the certified value (0.731 $\pm$ 0.060 $mg.kg^{-1}$). MeHg measures in zooplankton samples from one burned lake were discarded due to analytical problems.

Fish

Northern pike was captured in 20 lakes that includes included 9 reference lakes (N43, N55, N56, N59, N63, N88, N89, N107 and N122), 4 lakes which had 11 – 72% (average = 43%) of their catchment harvested in 1995 (C2, C9, C24 and C40), and seven lakes which had between 50% and 100% (average = 90%) of their catchment burned by high-intensity fires in 1995 (FP2, FP15, FP24, FP30, FP32, FBP9 and FBP10). The fish were collected during the summers of 1996 or 1997 using overnight sets of experimental nets. Seven lakes were sampled again during the summer of 1998. Between 6 and 23 specimens distributed in different length classes were collected in each lake, totaling 312 individuals. Total length, weight and sex were recorded for all fish.

Total Hg analysis in fish

A boneless, skinless fillet of dorsal muscle tissue was removed from each individual, frozen and freeze-dried. Samples were acid-digested and analyzed for total mercury by cold vapor atomic absorption spectrophotometry. Duplicate samples, analytical blanks and certified reference material (DORM-2, National Research Council of Canada) were analyzed as part of quality control. Concentrations are reported as micrograms per gram of dry weight. A conversion factor of 0.24 was used to estimate concentration on a wet weight basis.

Statistical analyses

Differences in MeHg level in zooplankton as well as environmental and biological differences among the three treatments and sampling dates were tested using repeated measures analysis of variance. Pearson correlation coefficients between MeHg contents in zooplankton and environmental and biological variables were calculated separately for logged, burned and control lakes. Between-treatment differences in these correlation coefficients were tested with ANCOVA. Multiple regressions were used to model the relationships among MeHg in zooplankton and the set of variables for the three treatments and for the three sampling periods. To normalize the data and reduce heteroscedasticity, the values were log-transformed where required.

Mercury levels in fish from each lake were regressed against fish weight and total length. Regressions using total length were significant for most lakes and showed the highest correlation coefficients. Length was therefore selected as the covariate to compare mercury contamination of pike from different lakes and treatments. In all but one lake, the regression equations were used to estimate the mean mercury values for a standard length of 560 mm, which corresponded to the catches' mean total length. For each treatment, the average mercury concentration was the arithmetic mean of the values estimated for the standard length. A reference lake with no significant relationship between mercury concentration and length was excluded from our

analysis. This lake had the smallest sample size (N = 6) and a mean total length for pike (594 mm) higher than the standardized length.

Between-year differences in mercury accumulation as a function of total length for the seven lakes sampled twice were tested with ANCOVA. Whenever differences between the two years were not significant, the two samples of a same lake were pooled and then mercury contents were regressed against fish length. One-way analysis of variance was used to compare mean mercury levels among the three groups of lakes for the standardized total length. In order to detect variations in mercury levels between sexes, linear regressions of mercury on length were estimated for males and for females from each lake, and mercury contents for the standardized length were estimated. Mean mercury concentrations in both sexes were then calculated for the three treatments. Pearson correlation coefficients were calculated between mercury in fish and physico-chemical variables. Stepwise multiple linear regression was used to model the relationships between mercury in fish and environmental and biological variables. The significance level for all the statistical analysis was set at 0.05. Normality of residuals and homoscedascity were verified for each analysis, with values being log transformed where required.

DATA ANALYSIS

Environmental factors

The most conspicuous effect of forest logging on water quality was the increase in dissolved organic carbon (DOC), which was greater in logged lakes than in the other two treatments (see Fig. 2b and Carignan et al. 1999). This result can not be attributed to differences in landscape form, such as the presence of wetlands, which are rich sources of DOC (Mulholland and Kuenzler 1979), because the percent of wetlands in the study lakes was very low. Furthermore, our lakes were selected in order to minimize morphometric variations (Table 1). A strong relationship between DOC and light attenuation coefficient and Secchi transparency ($r = +0.90$ and -0.85, respectively) indicated that the DOC found in our lakes was highly colored, being thus of terrestrial origin.

Concentrations of sulfate and nitrate nitrogen were substantially higher ($P < 0.01$) in burned lakes compared to the other two treatments. Concentrations of chlorophyll *a* were significantly distributed following the pattern : fire > logged > control lakes ($P < 0.01$). Except in June, levels of total phosphorous were identical in burned and cut lakes, and both showed higher concentrations than reference lakes ($P < 0.01$). Concentrations of dissolved oxygen in lake water were similar for logged, burned and reference lakes. There were no significant differences neither in lake water pH, alkalinity and temperature among the three treatments, but temperature in June was significantly lower than that from July and September ($P < 0.01$).

Zooplankton composition

Zooplankton biomass consisted predominantly of filter-feeders (Table 2), and the relative biomass of immature zooplankton and of the three adult groups (filter-feeders, omnivores and predators) was equivalent in the three treatments ($P > 0.10$). The biomass of immature zooplankton, however, differed for the three sampling periods ($P < 0.01$). Samples collected in June presented the greatest proportion of immature zooplankton, whereas samples from July had the smallest ratio of young forms.

Mercury levels in zooplankton

MeHg concentrations in bulk zooplankton ranged from 35 to 377 $ng.g^{-1}$ d.w. This range was similar to those found by Back and Watras (1995) and Westcott and Kalff (1996) in herbivorous taxa (1 to 479 $ng.g^{-1}$ d.w. and 19 to 448 $ng.g^{-1}$ d.w., respectively). A narrower range (50 to 200 $ng.g^{-1}$ d.w.) was reported in bulk zooplankton from undisturbed lakes of midnorthern Quebec (Plourde et al. 1997).

Figure 2. Mean dissolved organic carbon concentration (DOC) in water (a), and (b) mean MeHg levels in zooplankton from logged (N = 9), burned (N = 9) and reference lakes (N =20). Values represent averages for each sampling period. Error bars represent ± 1 SE of the mean.

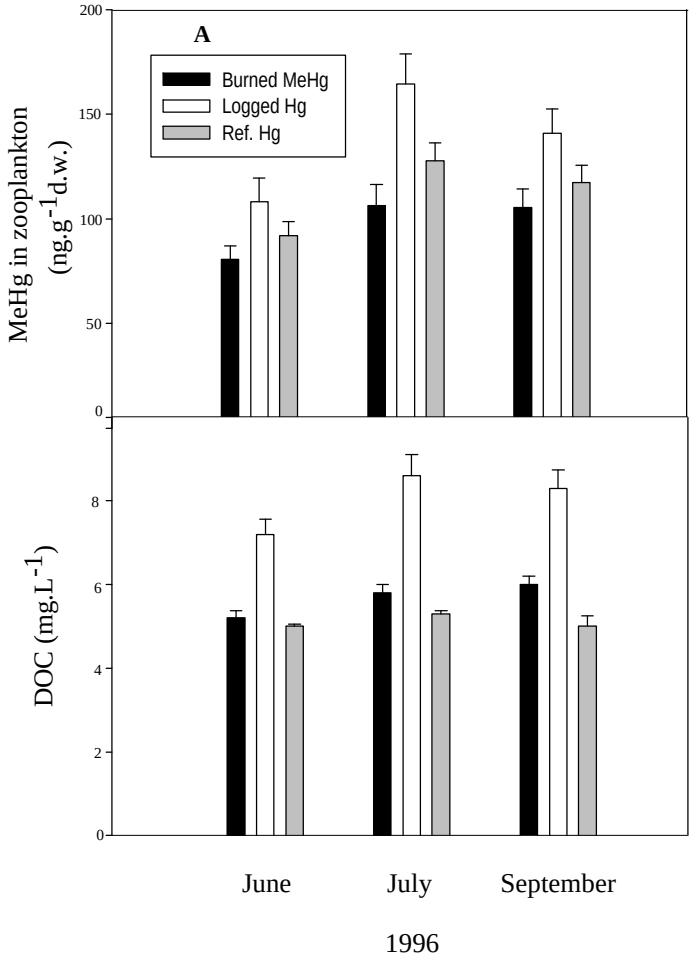


Table 1. Chemical and morphometric characteristics of the study lakes and of their catchments (N = number of observations for the three sampling periods; Med = median).

	Reference				Logged				Burned			
	N	Med.	Mean	SD	N	Med.	Mean	SD	N	Med.	Mean	SD
Lake area (km^2)	20	0.4	0.5	0.2	9	0.3	0.6	0.7	9	0.4	0.4	0.1
Drainage area (km^2)	20	1.9	2.2	1.3	9	2.6	2.2	3.0	9	3.1	5.3	6.2
Drainage ratio	20	4.3	5.3	3.0	9	7.5	6.9	3.2	9	8.2	11.4	11.6
Maximum depth (m)	20	11.5	12.4	4.0	9	13.0	13.8	6.1	9	14.0	17.1	7.8
Mean depth (m)	20	4.1	4.5	1.5	9	4.4	4.7	1.6	9	5.2	5.7	1.8
Slope (%)	20	8.0	9.2	3.1	9	7.0	8.2	2.8	9	8.1	9.7	2.9
Lake water pH	60	6.6	6.6	0.3	27	6.6	6.5	0.5	27	6.7	6.7	0.4
Alkalinity ($\mu eq.L^{-1}$)	60	46.1	54.0	28.8	27	48.3	56.0	32.0	27	58.2	68.0	41.8
DOC ($mg.L^{-1}$)	60	5.1	5.1	1.4	27	7.1	8.0	3.9	27	5.5	5.7	1.7
Total phosphorus ($\mu g.L^{-1}$)	60	6.6	7.0	2.2	27	9.2	9.8	3.5	27	10.7	10.9	4.0
Chlorophyll *a* ($\mu g.L^{-1}$)	60	1.9	2.0	0.8	27	2.2	2.4	0.8	27	2.9	3.1	1.1
NO_3-N ($\mu g.L^{-1}$)	60	1.1	6.5	12.5	27	1.1	3.7	7.8	27	10.0	76.6	139.0
SO_4-S ($mg.L^{-1}$)	60	0.9	0.9	0.2	27	0.9	0.8	0.2	27	1.7	1.7	0.4
Dissolved oxygen ($mg.L^{-1}$)	60	8.1	8.1	1.1	27	7.9	7.8	1.2	27	7.6	7.7	1.4

The three treatments showed different MeHg levels in zooplankton. In logged lakes, MeHg concentrations averaged 135 $ng.g^{-1}$ d.w. and were significantly higher ($P< 0.01$) than those from reference and burned lakes (Figure 2a). This result is in agreement with those of Rask et al. (1994), who found that mercury concentrations in zooplankton increased after clear-cutting of the watershed of a small humic lake. Burned lakes exhibited the lowest mean levels of MeHg (97 $ng.g^{-1}$ d.w.) in zooplankton, but did not differ significantly from reference lakes (112 $ng.g^{-1}$ d.w.).

The distribution of MeHg in zooplankton (Figure 2a) essentially reflected that of DOC among the three groups of lakes (Figure 2a). Thus, the highest levels of both MeHg and DOC were observed in logged lakes, whereas no significant difference was found between burned and reference lakes. It is known that mercury and MeHg accumulate in the upper layer of forest floors, where they bind to humic compounds. For this reason, dissolved and particulate humic matter from exposed soils are considered as important carriers of Hg to lakes and streams (Mierle and Ingram 1991). Since DOC in lake waters essentially consists of humic substances, the similar distribution of MeHg in zooplankton and DOC among treatments during the three sampling periods suggests a relationship between the uptake of MeHg by the zooplankton and the transfer of humic matter to aquatic ecosystems, as indicated by the significant positive correlation observed between MeHg levels in zooplankton and DOC in the three groups of lakes (Table 3). Co-transport is, however, one of the mechanisms through which DOC can mediate higher biotic MeHg levels in lakes. Input of DOC may stimulate the microbial activity and the production of MeHg (McMurtry et al. 1989), and may also decrease the rates of photodegradation of MeHg in lakes (Sellers et al. 1996). In burned lakes, however, and in contrast with logged lakes, DOC loading did not increase even if soil exposure was accentuated after fire. Several reasons may explain why perturbation by fire did not cause an increase in MeHg concentration in zooplankton. Fire may have changed soil-Hg speciation, Hg may have been lost by volatilization, and the nutrient and productivity pulse following fire may have diluted the Hg associated to the biota.

MeHg concentrations in zooplankton also significantly correlated to other chemical characteristics of the lakes (Table 3). Some of the most significant correlations were with : dissolved oxygen (-) in the three groups of lakes, temperature (+) in logged and burned lakes, and pH (-) and SO_4^{2-} (+) in logged lakes. MeHg levels in zooplankton has been reported to be correlated with some morphometric variables, such as lake area, maximum and mean depth, and the ratio between drainage area and lake volume (Westcott and Kalff 1996). In this sense, one could expect that differences in MeHg levels among logged, burned and reference lakes would be due to variations in the morphometry rather than to differences in the treatments themselves. Among the morphometric variables, MeHg in zooplankton showed only a significant positive correlation with the ratio of the drainage area to lake volume (DA/VOL) or to lake area (DA/LA) in logged lakes (Table 3). Both ratios were also significantly correlated to DOC (Pearson coefficient = 0.93 for DA/VOL, and 0.59 for DA/LA). Although some authors have pointed the epilimnetic sediment as an important site of mercury methylation (Ramlal et al. 1993), no significant relationship was observed between MeHg levels and the ratio of surface of epilimnetic sediment to lake volume (SES/VOL).

Table 2. Pearson correlation coefficients observed between MeHg in zooplankton and environmental and biological characteristics of the study lakes and watersheds.

	Logged		Burned		Reference		Pooled lakes	
	N	r	N	r	N	r	N	r
Lake area	9	n.s.	9	n.s.	20	-0.33*	38	-0.28**
Drainage ratio	9	0.54**	9	n.s.	20	n.s.	38	0.31***
Slope	9	n.s.	9	n.s.	20	0.36**	38	n.s.
Mean depth	9	n.s.	9	-0.41*	20	n.s.	38	n.s.
Latitude	9	n.s.	9	-0.52**	20	-0.21*	38	-0.20*
Longitude	9	0.63***	9	n.s.	20	0.29**	38	0.33***
Alkalinity	27	n.s.	27	-0.42*	57	n.s.	111	-0.32***
pH	27	-0.49**	27	-0.70***	57	n.s.	111	-0.42***
Temperature	27	0.43*	27	0.52**	57	n.s.	111	n.s.
Chlorophyll *a*	27	n.s.	27	n.s.	57	n.s.	111	n.s.
Total P	27	n.s.	27	n.s.	57	0.27*	111	0.22*
DOC	27	0.58**	27	0.58**	57	0.32*	111	0.52***
SO_4^{-2}-S	27	0.43*	27	n.s.	57	n.s.	111	0.21*
NO_3-S	27	n.s.	27	n.s.	57	n.s.	111	n.s.
Filters-feeders	27	0.59**	27	n.s.	57	n.s.	111	0.24*
Omnivores	27	n.s.	27	0.42*	57	n.s.	111	n.s.
Predators	27	n.s.	27	n.s.	57	n.s.	111	n.s.
Immature ind.	27	n.s.	27	n.s.	57	-0.25**	111	-0.26**

Note : n.s. = not significant (P > 0.05) ; * P < 0.05 ; ** P < 0.01 ; *** P < 0.001.
Except for morphometric variables, *N* represents three sample periods by lake.

Seasonal variations

Significant differences in MeHg concentrations in zooplankton were found between the three sampling dates. For the three groups of lakes, MeHg levels were significantly lower in June, then peaked in July, and decreased in September. Seasonal variation in MeHg levels in aquatic biota has also been reported by other authors (Meili and Parkman 1988 ; Bodaly et al. 1993). Such variations may reflect changes in the supply of dissolved and particulate material from the drainage area. Meili and Parkman (1988) observed that both total mercury in mesoplankton and DOC in lake water varied seasonally. In their work, total mercury levels in mesoplankton were lower immediately after snow-melt and increased during the summer, whereas DOC concentrations were highest in the spring. In our study, MeHg concentrations in zooplankton also were lower after snow-melt than in the subsequent periods. DOC concentrations, however, did not vary significantly from one month to another. Assuming that DOC represents an important vector of mercury for lake water (Meili 1991), these results suggest a lag period between Hg loading to the lakes from their watersheds during snowmelt, and its availability to aquatic organisms as MeHg. Other studies indicate that the rate of bacterial methylation of mercury in the sediment and in the epilimnion increases with temperature (Matilainen et al. 1991, Ramlal et al.

1993). These findings may explain why our logged and burned lakes showed a weak but significant positive correlation between MeHg in zooplankton and water temperature (Table 3).

Another explanation for the seasonal variation in MeHg levels in aquatic biota takes into account the life stage of sampled individuals. In their investigations, Parkman and Meili (1993) noted that the low mercury concentrations in zoobenthos coincided with the annual appearance of a new generation of those invertebrates. In our study, although biomass of immature zooplankton was higher in June, it represented less than 5.5% of the entire zooplankton biomass, and thus is not expected to influence MeHg levels in bulk zooplankton.

Regression models of MeHg concentrations in zooplankton

DOC was the most important predictor of MeHg, and, along with dissolved oxygen, was a common variable in our regressions (see Garcia and Carignan 1999). Other investigations have demonstrated that mercury and MeHg accumulation in zooplankton (Westcott and Kalff 1996 ; Meili and Parkman 1988) and in fish (McMurtry et al. 1989) increases with DOC or water color. Humic substances may, however, interfere with the availability of mercury for methylation and MeHg uptake by the biota (Grieb et al. 1990, Miskimmin et al. 1992). Thus, the relationship between MeHg bioavailability and DOC are far from being well understood.

We also observed in all our models that MeHg concentration in zooplankton was inversely related to dissolved oxygen in lake water. This result is in agreement to the fact that methylation of inorganic mercury in lakes increases under low oxygen conditions (Cossa et al. 1994). On the other hand, the inverse correlation between MeHg and chlorophyll *a* found in the alternative model for burned lakes may be an effect of dilution (Watras and Bloom 1994).

Even if our lakes covered a small range of pH, a negative correlation between this variable and MeHg levels in zooplankton was observed, as previously reported in other studies (Westcott and Kalff 1996 ; Watras and Bloom 1992). Several mechanisms have been proposed to explain why the acidity of lake water increases Hg accumulation in biota. High H^+ concentrations would affect the speciation of mercury, the rates of methylation and demethylation, as well as the physiology of the organisms (Winfrey and Rudd 1990). Laboratory studies showed that under circumneutral conditions a slight reduction in pH increases the rate of MeHg accumulation in fish (Ponce and Bloom 1991).

MeHg in zooplankton from logged and burned lakes was also significantly correlated with sulfate, and both MeHg and SO_4^{-2} showed a significant inverse collinearity with latitude. Although these results suggest a possible influence of long range atmospheric transport from industrial regions, such a correlation was not found in reference lakes.

Mercury levels in northern pike

Mean mercury concentrations in 560 mm-northern pike ranged from 0.89 to 6.10 µg.g dry weight^{-1}. This range was wider than that observed by Bodaly et al (1993) for pike of similar standard size in six Canadian Shield lakes, but it was narrower than the range of concentrations reported by Parks et al (1994) for 42 pristine lakes in northern Minnesota, USA. Mercury in pike from logged lakes averaged 3.4 µg.g dry weight $^{-1}$, and was significantly higher than in reference lakes (mean concentration of 1.9 µg.g dry weight^{-1}) (Figure 3). The average mercury concentration in pike from burned lakes (2.8 µg.g dry weight^{-1}) was intermediate between the levels observed in logged and in reference lakes, but the differences were not significant. When a lake (C40) with only 11% of its watershed harvested was excluded from the comparisons, mean mercury levels in logged lakes decreased slightly (3.3 µg.g dry weight $^{-1}$), but the standard error of the mean increased by 20%. As a consequence, the difference between logged and reference lakes became significant only at the $P = 0.12$ level. In all logged lakes and in three burned lakes, average mercury concentrations in pike, on a wet weight basis, were higher than the health advisory limit for human consumption of 0.5 µg.g wet weight.$^{-1}$(WHO). This limit was exceeded only in two of the reference lakes.

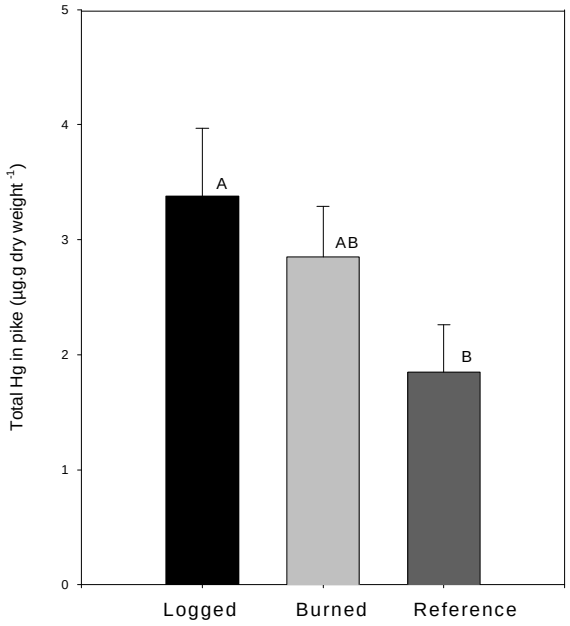
As for zooplankton, differences in mercury contents in fish from logged and reference lakes may be attributed in part to variations in mercury inputs associated to the loading of terrestrial DOC, as a positive correlation was observed between DOC and mercury contents in pike (Tables 3 and 4). Mercury levels in pike from burned lakes were lower than in fish from logged lakes, as found for zooplankton. Variables other than DOC were also significantly correlated to mercury in pike. These were pH (-), alkalinity (-) and sulfate (+), light attenuation (-), and methyl mercury levels in zooplankton (+).

Even if the pH range of the study lakes was relatively small (5.9 to 6.8), mercury in pike was significantly related to pH. An experimental study by Ponce and Bloom (1991) has shown that, under circumneutral conditions, a slight decrease in pH can increase MeHg uptake by fish. In the field, this inverse correlation, as well as the correlation between mercury in fish and other variables related to acidity, such as alkalinity and sulfate, has been widely reported (Jensen 1988).

Regression models for pike

MeHg in zooplankton, sulfate and pH explained 78% of the variance in mercury concentrations in pike (Table 5). MeHg in zooplankton alone explained 58% of the variations (Figure 4). When MeHg was removed from the set of variables, pH and sulfate remained in the model, and DOC was included. The alternative regression model (Table 5) was highly significant, but its R^2 was reduced to 0.65. Lake pH explained a larger amount of the variation in mercury than sulfate and DOC in this regression.

Figure 3. Average levels of total mercury in 560 mm northern pike from logged (N = 4), burned (N=7) and reference lakes (N = 8). Bars represent standard errors.



Influences of size, sex and age of pike on mercury levels

Total length correlated better with mercury than did weight. Correlations between mercury and length were significant in all but one lake, whereas correlations with weight were not significant in seven lakes. Linear regressions between mercury contents and length showed higher R^2 (average = 0.85) than regressions where weight was used as the independent variable to estimate mercury concentrations (average R^2 = 0.69). These observations are consistent with those of many other studies on northern pike (Bodaly et al 1993, Rask and Metsala 1991, Scott and Armstrong 1972). Length is less subject to major daily fluctuations than total body weight for species that feed on large preys.

The ratio between males and females was 0.7, 1.1 and 1.3, respectively in logged, burned and reference lakes. The unbalanced number of males and females could lead to an underestimation of mercury levels in pike from logged lakes and an overestimation in the reference group. According to Olsson (1976), adult male northern pike have a higher metabolic turnover per unit length and probably a higher rate of mercury accumulation than females. Olsson observed that male pike longer than 500 mm had higher mercury levels than females of a similar length. In our study, mercury levels in 560 mm-male pike were slightly but not significantly lower than in females in burned lakes (Table 6). No difference was found between males and females in the logged and reference lakes. Thus, adult male and female northern pike accumulated mercury at the same rate in the three treatments.

Temporal trends of mercury in pike

Seven of the lakes were sampled twice. Slight temporal trends in mercury accumulation in pike were detected, but, except for one reference lake (N55), the slopes of the regressions of mercury against length did not differ significantly from one year to another for a same lake (Table 7, ANCOVA, $P > 0.05$). In one of the two logged lakes revisited in 1998 (C9), the standardized mercury concentrations increased by about 20%, whereas it remained the same in the other lake (C2). In burned lakes, an average decrease of 14% was observed. In two reference lakes mercury concentrations in pike almost did not vary from one year to another. The most conspicuous variation occurred in a third reference lake (N55), where, for unknown reasons, mercury increased by 77% from 1997 to 1998.

Differences between logged and reference lakes were observed as early as one to three years after harvesting. Short lag time (2 to 3 years) after impoundment have been reported for pike (Bodaly et al 1984). Both results indicate a relatively rapid response of northern pike to changing mercury loads. A study in Finland showed that accumulation of mercury in the youngest perch, that feeds mostly on zooplankton, occurred only one year after logging (Rask et al 1994), but no signs of the effects of harvesting were recorded for pike. Bodaly and Fudge (1999) reported that a forage fish, finescale dace (*Phoxinus neogaeus*), also responded quickly to

flooding, showing the highest mercury concentrations in the first two years following impoundment.

Figure 4. Linear relationship between Hg concentration in pike and MeHg concentration in zooplankton.

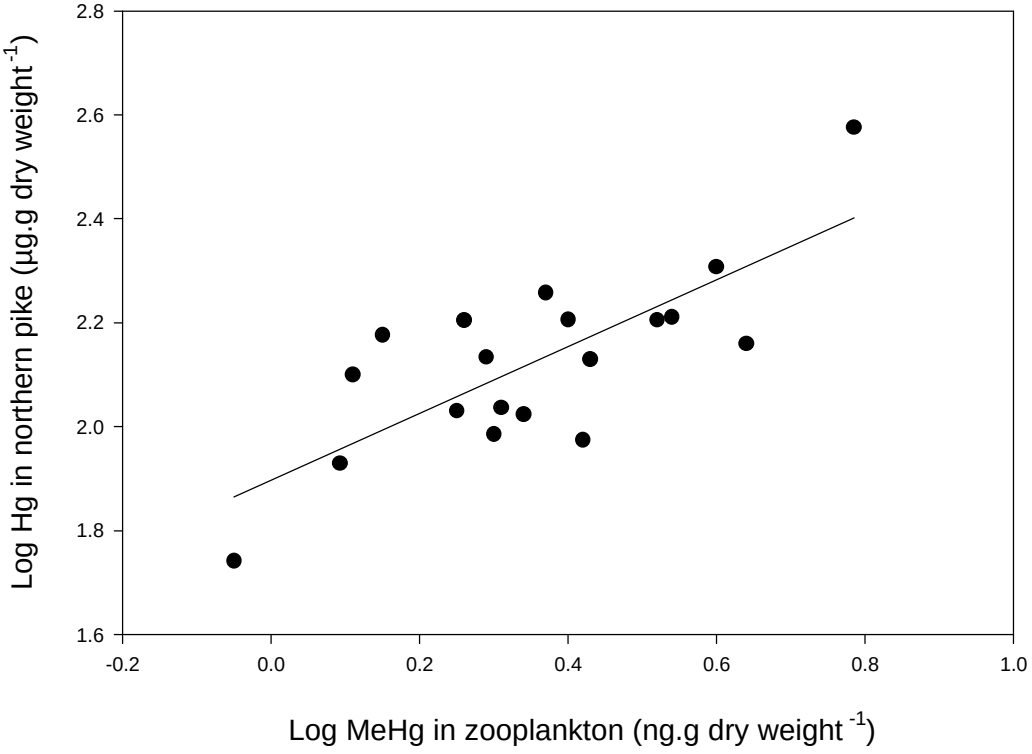


Table 3. Physichal, chemical and morphometric characteristics of the study lakes and of their catchments.

	Reference (N = 8)				**Burned (N = 7)**				logged **(N = 4)**			
	Mean	SE.	Min	Max	Mean	SD.	Min	Max	Mean	SD.	Min	Max
Lake area (km^2)	0.4	0.1	0.1	0.7	0.4	0.1	0.2	0.6	3.1	1.0	1.0	5.9
Drainage area (km^2)	2.2	0.5	0.5	4.5	5.2	2.5	0.6	19.7	9.0	3.1	5.3	6.2
AD/AL	5.9	1.3	2.8	15.5	12.6	4.9	3.4	41.0	8.6	2.3	3.5	14.4
Slope (%)	10.7	1.1	6.9	16.6	10.5	1.3	7.7	18.0	8.2	1.0	5.7	10.3
PH	6.6	0.1	6.3	7.0	6.5	0.2	5.7	7.2	6.1	0.2	5.9	6.6
Alkalinity ($\mu eq.L^{-1}$)	66.1	10.1	32.0	110.0	66.4	15.6	17.2	146.1	34.7	7.8	15.3	47.6
DOC ($mg.L^{-1}$)	5.5	0.5	3.6	9.2	6.2	0.6	4.0	8.0	7.5	1.3	4.2	11.1
Light attenuation coef (m^{-1})	1.0	0.1	0.7	1.7	1.1	0.1	0.6	1.8	1.5	0.4	1.0	2.5
Secchi depth (m)	3.7	0.3	2.2	5.1	3.1	0.5	2.1	5.6	2.9	0.6	1.6	4.2
Chlorophyll-*a* ($\mu g.L^{-1}$)	1.9	0.1	1.1	2.3	3.2	0.4	1.6	4.7	2.0	0.3	1.3	2.7
Total phosphorus ($\mu g.L^{-1}$)	6.7	0.5	4.7	9.5	11.7	1.0	8.4	15.3	9.1	1.2	6.9	12.4
Total nitrogen ($\mu g.L^{-1}$)	226.1	13.8	149.5	294.0	311.1	31.4	217.0	440.0	237.3	29.4	160.0	303.0
Ca^{2+} ($mg.L^{-1}$)	1.7	0.2	1.2	2.5	2.1	0.2	1.4	2.7	1.6	0.2	1.2	2.0
SO_4-S ($mg.L^{-1}$)	0.8	0.1	0.6	1.2	1.6	0.1	1.1	2.1	0.9	0.0	0.8	1.0
MeHgZoop ($ng.g\ d.w^{-1}$)	124.6	12.3	55.1	160.6	151.8	38.0	94.2	376.7	176.8	9.9	160.5	203.0

Note: MeHgZoop, methyl mercury in zooplankton.

Table 4. Pearson correlation coefficients observed between mean mercury concentrations in 560 mm northern pike and environmental and biological characteristics of the study lakes and watersheds (N = 19).

	r
Lake area (LA)	ns
Drainage area (DA)	ns
DA/LA	ns
Slope	ns
Alkalinity	- 0.50**
pH	- 0.61***
DOC	+ 0.39*
Light penetration	- 0.47*
Secchi depth	ns
Chlorophyl *a*	ns
TP	ns
TN	ns
Ca^{2+}	ns
SO_4^{2-}	+ 0.30*
MeHgZoop.	+ 0.79***

Note : ns = not significant (P > 0.05) ; * P < 0.05 ; ** P < 0.01 ; *** P < 0.001. SES, surface of epilimnetic sediment; MeHgZoop, methyl mercury in zooplankton.

Table 5. Multiple regression models for mercury concentrations in northern pike (N = 19 lakes).

(1) Log (Hg) = 3.72 (± 1.19) + 0.60 (± 0.13) log(MeHgzoop)*** + 0.46 (± 0.13) log(SO_4^{2-})** – 0.34 (± 0.14) pH*

R^2 = 0.78, SE_{est} = 0.20, *P* = 0.0000, N = 19 lakes

(2) Log (Hg) = 0.14 (± 1.35) - 0.57 (± 0.16) pH** + 0.55 (± 0.16) log(SO_4^{2-})** + 0.45 (± 0.20) log(DOC)*

R^2 = 0.65, SE_{est} = 0.26, *P* = 0.0001, N = 19 lakes

Note : * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$. MeHgzoop, Methyl mercury concentrations in zooplankton.

Table 6. Average mercury concentrations and standard error in male and female 560 mm-northern pike from logged (N = 3), burned (N = 7) and reference lakes (N =7).

	Hg in 560 mm-male pike (µg.g dry weight $^{-1}$)	Hg in 560 mm-female pike (µg.g dry weight $^{-1}$)
Logged lakes	3.2 ± 0.6	3.0 ± 0.9
Burned lakes	2.3 ± 0.3	2.8 ± 0.7
Reference lakes	1.7 ± 0.3	1.8 ± 0.6

Table 7. Temporal trends in average levels of total mercury in 560 mm-northern pike from logged, burned and reference lakes.

Lake	Treatment	Hg in pike caught in 1996 (µg.g dry weight $^{-1}$)	Hg in pike caught in 1997 (µg.g dry weight $^{-1}$)	Hg in pike caught in 1998 (µg.g dry weight $^{-1}$)
C2	harvesting		3.3 ± 0.15	3.2 ± 0.14
C9	harvesting	2.4 ± 0.10	2.8 ± 0.0.14	
FP24	fire	2.6 ± 0.23		2,2 ± 0.20
FBP10	fire		2.2 ± 0.19	2.0 ± 0.14
N55	reference		1.2 ± 0.21	2.3 ± 0.12
N63	reference	2.0 ± 0.14		1.9 ± 0.22
N107	reference		2.7 ± 0.21	2.8 ± 0.12

MANAGEMENT APPLICATIONS

Several studies have shown that the problem of elevated mercury levels in predator fish (pike, walleye, salmonids) is endemic in softwater boreal boreal lakes. Our result indicate that mercury levels in the biota are further increased when a major proportion a lakes' watershed is harvested. The effect of logging appears important enough to increase mercury levels in northern pike above the limit for safe consumption recommended by the World Health Organization. In comparison, fire had a lesser effect on mercury levels. Both perturbations are therefore not comparable in terms of effects on aquatic resources.

Our results also indicate that mercury levels in the biota of logged lakes increase as a result of higher loading of organic matter (DOC) and DOC-bound mercury in these lakes. The relationships between DOC loading in lakes and the degree of harvesting (see reports by Carignan et al., 1999 and Lamontagne et al., 1999), and between methylmercury levels in zooplankton and DOC concentrations are statistically very robust. Because methylmercury concentrations are amplified in the food chain, the high mercury levels observed in pike were expected. It should be noted, however, that pike was found in only four of the logged lakes. Because of the limited number of lakes where this species was present, the association between logging and mercury contamination in pike was only marginally significant. If proven correct through further studies, this effect should be taken into consideration in future forestry practices.

Because mercury contamination is linked to high DOC concentrations in these lakes, controlling DOC in logged lakes should also reduce the associated mercury problem. Carignan et al. (1999) have provided a quantitative relationship linking DOC to an impact factor defined as the harvested area in the watershed : lake volume ratio. They have found that DOC will not exceed the range of natural variability, and that excess DOC (and presumably mercury) problems can be avoided if this ratio does not exceed 0.5. This guideline can easily be applied in the field to potentially sensitive lakes by limiting harvest size in a given pass.

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