# University of Alberta

## Mercury in biota from Canadian Rocky Mountain lakes

by

(Lain)

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## Abstract

Methyl mercury (MeHg) is a bioaccumulative and persistent neurotoxin that can cause health problems in fishes and their wildlife and human consumers. National parks in the Canadian Rocky Mountains may be at even greater risk, because Hg "hotspots" in soils have been identified in the vicinity. We sampled invertebrates and fishes from lakes in or nearby Canadian Rocky Mountain National Parks and determined that MeHg and total Hg (THg) concentrations varied within and among invertebrate taxa and fish species. Risk assessments, based on these data, indicated that concentrations of THg (as MeHg) in fish species from some mountain lakes posed a health risk to human and wildlife consumers. We determined that MeHg and THg concentrations in some biota from mountain lakes decreased with elevation and increased with latitude. No significant temporal trend was identified in the concentrations of MeHg in fishes from several mountain lakes. The overall strongest predictors of mean MeHg concentrations in trout were latitude, spring sulphate concentration, mean annual air temperature, concentration of MeHg in zooplankton collected in the spring, and spring dissolved inorganic nitrogen (DIN) concentration. All predictors were significantly and positively related to mean MeHg concentration in trout, with the exception of DIN which was related negatively. We used multiple regression models to predict MeHg concentrations in all other fish-bearing lakes in the Rocky Mountain National Parks and identify other lakes that likely contain fishes with elevated MeHg concentrations. Climate change will likely alter factors that affect MeHg accumulation by aquatic biota. For example, it is predicted that climate change will increase forest fire occurrence in the Canadian Rocky Mountains. We determined that forest fire increased MeHg accumulation by fishes through food web restructuring and increased MeHg inputs. Our results suggest that MeHg contamination of aquatic biota in Rocky Mountain lakes is relatively widespread, temporally persistent and may be exacerbated by climate change. Data collected and model results will aid Parks Canada with monitoring and management objectives.

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# **Table of Contents**

1.0		1
	References	4
2.0	Review of Relevant Literature	8
	Mercury (Hg) Cycling	8
	Health Effects of MeHg	9
	Factors that influence MeHg accumulation by fishes	12
	Factors that affect sources of Hg to a catchment or lake	12
	Factors that affect transport of Hg from a catchment to a lake	13
	Factors that affect in-lake methylation	13
	Factors that affect MeHg bioaccumulation and biomagnification	13
	Forest Fire and Hg	14
	Hg in mountain lakes	16
	Temporal trends of Hg and organochlorine accumulation in fishes	20
	Identification of spatial patterns in Hg using GIS	21
	Climate Change and Hg.	22
	References	23
	and wildlife consumers and seasonal, spatial and temporal trends Introduction	52 52
	Methods	54
	Methods Study Area	54 54
	Study Area	54
	Study Area Field Sampling	54 55
	Study Area Field Sampling Laboratory	54 55 55
	Study Area Field Sampling Laboratory Seasonality Human health risk assessment Wildlife health risk assessment	54 55 55 56
	Study Area Field Sampling Laboratory Seasonality Human health risk assessment	54 55 55 56 56
	Study Area Field Sampling Laboratory Seasonality Human health risk assessment Wildlife health risk assessment Spatial patterns in MeHg and THg concentrations of aquatic biota	54 55 55 56 56 59
	Study Area Field Sampling Laboratory Seasonality Human health risk assessment Wildlife health risk assessment	54 55 56 56 59 61
	Study Area Field Sampling Laboratory Seasonality Human health risk assessment Wildlife health risk assessment Spatial patterns in MeHg and THg concentrations of aquatic biota Temporal trend assessment in fish THg concentration Results	54 55 56 56 59 61 62
	Study Area Field Sampling Laboratory Seasonality Human health risk assessment Wildlife health risk assessment Spatial patterns in MeHg and THg concentrations of aquatic biota Temporal trend assessment in fish THg concentration Results MeHg and THg Concentrations in Aquatic Biota	54 55 56 56 59 61 62 62
	Study Area.Field Sampling.Laboratory.Seasonality.Human health risk assessment.Wildlife health risk assessment.Spatial patterns in MeHg and THg concentrations of aquatic biotaTemporal trend assessment in fish THg concentration.Results.MeHg and THg Concentrations in Aquatic Biota.Benthic invertebrate MeHg and THg concentrations.	54 55 56 59 61 62 62 62
	Study Area.Field Sampling.Laboratory.Seasonality.Human health risk assessment.Wildlife health risk assessment.Spatial patterns in MeHg and THg concentrations of aquatic biotaTemporal trend assessment in fish THg concentration.Results.MeHg and THg Concentrations in Aquatic Biota.Benthic invertebrate MeHg and THg concentrations.Zooplankton MeHg and THg concentrations.	54 55 56 59 61 62 62 62 62

	Wildlife health risk assessment	64
	Spatial patterns of MeHg and THg concentrations in aquatic biota	65
	Effect of Altitude	65
	Effect of Continental Divide	66
	Effect of Latitude	67
	Temporal trend assessment of fish MeHg concentration	68
	Discussion	68
	MeHg and THg Concentrations in Aquatic Biota	68
	Human health risk assessment	69
	Wildlife health risk assessment	70
	Spatial patterns of MeHg and THg concentrations in aquatic biota	71
	Effect of Altitude	71
	Effect of Continental Divide	72
	Effect of Latitude	72
	Temporal trend assessment in fish MeHg concentration	73
	References	73
4.0	Factors that affect total mercury (as MeHg) concentrations in trout	
	from lakes in the Canadian Rocky Mountain National	
	Parks	97
	Introduction	97
	Methods	100
	Study Area	100
	Field Sampling	100
	Laboratory	102
	$\delta^{15}$ N baseline-adjustment	103
	GIS	104
	Data preparation	104
	Creation of catchments	106
	Catchment inside buffer (CIB)	106
	Catchment and catchment inside buffer lake removal	107
	Zonal statistics	107
	Intersections and summarizations	107
	Statistics	108
	Results	109
	Factors that affect sources of Hg to a catchment or lake	109
	Factors that affect transport of Hg within a catchment	110
	Factors that affect MeHg production	111
	Factors that affect MeHg bioaccumulation and biomagnification	112
	Overall factors that affect Hg concentrations in fishes from Rocky	-
	Mountain National Park lakes	112
	Predictive model for all fish-bearing lakes in Rocky Mountain	
	National Parks	113

	Discussion	114	
	Factors that affect sources of Hg to a catchment or lake	114	
	Factors that affect transport of Hg within a catchment	115	
	Factors that affect MeHg production	116	
	Factors that affect MeHg bioaccumulation and biomagnification	117	
	Overall factors that affect Hg concentrations in fishes from Rocky		
	Mountain National Park lakes	118	
	Predictive model for all fish-bearing lakes in Rocky Mountain		
	National Parks	118	
	References	119	
5.0	Forest fire increases mercury accumulation by fishes via food web		
	restructuring and increased mercury inputs	140	
	Introduction	140	
	Methods	142	
	Field Sampling	142	
	Laboratory	142	
	Hg export calculations	144	
	$\delta^{15}N$ baseline-adjustment	144	
	Linear regression	144	
	Results and Discussion	145	
	Conclusion	150	
	References	151	
6.0	Discussion	162	
0.0	Ongoing and Future Research	163	
	References	165	
	Kererences	105	
	Appendix 1	167	
	Appendix 2	169	
	Appendix 3	171	
	Appendix 4	174	
	Appendix 5	177	
	Appendix 6	186	
	Appendix 7	209	
	Appendix 8	221	
	11		

.

# List of Tables

2.1	Catchment characteristics that affect transport of Hg from a catchment to a lake	49
2.2	Interactions with water chemistry parameters that affect in-lake Hg methylation	50
2.3	Biological characteristics that affect MeHg bioaccumulation and biomagnification	51
3.1	Source lakes of the fishes included in this study (University of Alberta: Kelly 2001 and Parker 1997, Environment Canada: Donald 1990s, Parks Canada: Hughson 2003, Pacas 2001, 2002, 2003)	92
3.2	Mammal, bird and reptile species that breed within the study area and consume aquatic invertebrates and fishes	93
3.3	MeHg and THg (range and mean) concentrations of invertebrates from Canadian Rocky Mountain lakes in dry weight	94
3.4	MeHg (range and mean) concentrations of fishes from Canadian Rocky Mountain lakes in wet weight	95
3.5	Changes in MeHg concentrations of lake trout from Canadian Rocky Mountain lakes over time	96
4.1	Difference between waterbodies in ELC and Origin layers and NTDB waterbodies layer, and the number of links used during rubbersheet process to spatially adjust. na=not applicable	135
4.2	Significant results of linear regressions between mean trout MeHg concentrations and factors that affect sources of Hg to a catchment or lake, and correlations between these factors and lake elevation and latitude. Probabilities presented for linear regression models are for the t-statistic for significance of slope, which is equivalent to testing the significance of the correlation between mean trout MeHg concentrations and explanatory variables	136

4.3	Significant results of linear regressions between mean trout MeHg concentrations and factors that affect transport of Hg from catchments to lakes, and correlations between these factors and lake elevation and latitude. Probabilities presented for linear regression models are for the t-statistic for significance of slope, which is equivalent to testing the significance of the correlation between mean trout MeHg concentrations and explanatory variables	137
4.4	Significant results of linear regressions between mean trout MeHg concentrations and factors that affect MeHg production in lakes, and correlations between these factors and lake elevation and latitude. Probabilities presented for linear regression models are for the t-statistic for significance of slope, which is equivalent to testing the significance of the correlation between mean trout MeHg concentrations and explanatory variables	138
4.5	Significant results of linear regressions between mean trout MeHg concentrations and factors that affect MeHg bioaccumulation and biomagnification in aquatic food chains, and correlations between these factors and lake elevation and latitude. Probabilities presented for linear regression models are for the t-statistic for significance of slope, which is equivalent to testing the significance of the correlation between mean trout MeHg concentrations and explanatory variables	139
	Appendix 1 Selected characteristics of Rocky Mountain Park study lakes	167
	Appendix 3Calculated weekly allowable human fish consumptionrates for Rocky Mountain Park study lakes	171
	Appendix 4Calculated monthly allowable human fish consumptionrates for Rocky Mountain Park study lakes	174
	<b>Appendix 5</b> Distribution of wildlife that consume aquatic biota and breed within the Rocky Mountain study area	177
	<b>Appendix 6</b> Mass, energetics and diet of wildlife species that breed and consume aquatic biota in Canadian Rocky Mountain Parks	186
	<b>Appendix 7</b> Literature review of MeHg and THg concentrations and percent MeHg in benthic invertebrates collected from lakes	209
	<b>Appendix 8</b> Literature review of MeHg and THg concentrations and percent MeHg in zooplankton collected from lakes	221

# **List of Figures**

2.1	The mercury (Hg) cycle, A. Biogeochemical Hg cycle including transformations and environmental pathways, and B. Cycle of anthropogenic Hg contamination from industrial sources to health effects of MeHg bioaccumulation in humans	47
2.2	Processes that affect the contaminant distribution over a mountain slope. Day and night differ in wind direction, temperature gradient with elevation, and local source activity (Daly and Wania 2005)	48
3.1	Map of the study area. Fish and invertebrates analysed for Hg were collected from lakes in or near Canadian Rocky Mountain parks (Jasper, Banff, Yoho and Waterton National Parks, Mount Robson Provincial Park, Spray Valley Provincial Park, Shere Lake (near Tête Jaune Cache, BC), and Little Cranberry Lake (near Valemount, BC)) in Alberta and British Columbia, Canada	82
3.2	Human Health Risk Assessment. To assess human health risk, maximum allowable fish consumption rate based on tolerable daily intakes (TDIs) was compared to dashed lines which represent average serving sizes. LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, CI=cisco, MW=mountain whitefish, LNS= longnose sucker, WS=white sucker. Grey vertical boxes indicate fishes that are not allowed to be kept based on Mountain Park fishing regulations	83
3.3	Avian Wildlife Health Risk Assessment. To assess wildlife health risk, the maximum allowable fish consumption rate based on tolerable daily intakes (TDIs) was compared to dashed lines which represent consumption rates. LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, YOY= young of year trout, CI=cisco, MW=mountain whitefish, PW= pygmy whitefish, LNS= longnose sucker, WS=white sucker, BU=burbot, CH= lake chub, SC=torrent sculpin, ST=brook stickleback	84
3.4	Mammalian Wildlife Health Risk Assessment. To assess wildlife health risk, the maximum allowable fish consumption rate based on tolerable daily intakes (TDIs) was compared to dashed lines which represent consumption rates. LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, YOY= young of year trout, CI=cisco, MW=mountain whitefish, PW= pygmy whitefish, LNS=	

- 3.5 Avian Wildlife Health Risk Assessment II. To assess wildlife health risk, THg concentrations in fishes were compared to the Canadian Tissue Residue Guideline of 33 ng/g ww (solid line), and calculated NOAEL and LOAEL) hazard concentrations (HC) (NOAEL HC= upper large dashed line, LOAEL HC=lower small dashed line). LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, YOY= young of year trout, CI=cisco, MW=mountain whitefish, PW= pygmy whitefish, LNS= longnose sucker, WS=white sucker, BU=burbot, CH= lake chub, SC=torrent sculpin, ST=brook stickleback. THg=MeHg... 86

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4.1	Map of the study area. Data were collected from lakes in A. Jasper, and B. Banff and Yoho National Parks in the Rocky Mountains of Alberta and British Columbia, Canada.	129
4.2	Linear regression results for individual factors that were significant predictors of mean trout MeHg concentrations in the overall whole catchment multiple regression model	130
<b>4.3</b>	Linear regression results for individual factors that were significant predictors of mean trout MeHg concentrations in the catchment in 1000 meter buffer around lake multiple regression model	131
4.4	Predicted trout MeHg concentrations for all fish-bearing lakes in Rocky Mountain National Parks (A=Jasper, B=Banff, Yoho, Kootenay, C=Mount Revelstoke, Glacier and Waterton Lakes) based on whole catchment multiple regression model. Green= $\leq$ 50 ng/g THg ww, Orange=50-150 ng/g THg ww and Red=150-400 ng/g THg ww.	132
4.5	Predicted trout MeHg concentrations for all fish-bearing lakes in Rocky Mountain National Parks (A=Jasper, B=Banff, Yoho, Kootenay, C=Mount Revelstoke, Glacier and Waterton Lakes) based on catchment in 1000 meter buffer around lake multiple regression model Green= $\leq$ 50 ng/g THg ww, Orange=50-150 ng/g THg ww and Red=150-400 ng/g THg ww	133
4.6	Snow water equivalents for February snowpack in Canadian Rocky Mountain Parks from 1940 to 2007. Snow samples for this study were collected in February 2001 (dashed line). Data compiled from Alberta Environment Water Supply Outlook Reports: http://www3.gov.ab.ca/env/water/ws/watersupply/historical/histwsindex.html	134
5.1	Map of the study area. The fire, which lasted from 12 July to 31 August 2000, burned 71.5% of the catchment of Moab Lake, as well as 29.3 and 68.4% of the catchments of Lake Creek and Corral Creek respectively. The catchments of Cavell Creek and Corral Creek were not burned	157
5.2	Conceptual diagram demonstrating source attribution of fire-related Hg increase. A baseline-adjusted $\delta^{15}$ N of 7 was chosen because it was common to the 1994, 2001 and 2003 regression lines of invertebrates and lake trout. The difference between the lake trout mercury concentration in 2001 and 2003 was attributed to food web alterations. The difference between lake trout mercury concentration in 1994 and 2001 was attributed to increased Hg inputs and in-lake methylation	158

X

- Mean THg in fish muscle vs. baseline-adjusted  $\delta^{15}N$  for fishes from Moab 5.4 Lake in 1994, 2001, 2003. (A) THg concentration (dry weight). (B) THg (wet weight). CCCG =Canadian Commercial concentration Consumption Guideline; CFCG=Canadian Frequent Consumption Guideline (human health protection). (C) Mean THg for homogenized whole rainbow trout (RT) from Moab Lake versus baseline- adjusted  $\delta^{15}$ N in 1993, 2001, and 2003. ww=wet weight); CRTG= Canadian Tissue Residue Guideline (wildlife health protection). (LT= lake trout, RT=rainbow trout, BLT=bull trout, CI=cisco), Error bars show standard error). We assumed that fish THg concentrations were MeHg concentrations because > 85% of Hg in fish is MeHg (Ullrich et al. 160 2001).....
- 5.5 MeHg and THg export from burned and unburned catchments near Moab Lake, and MeHg and THg concentrations in Moab Lake surface waters. (A and B) Export of MeHg (A) and THg (B) from two burned catchments, L=Lake Creek (29.3% burned) and Co=Corral Creek (68.4% burned), and two unburned catchments, Ca=Cavell Creek and W=Wabasso Creek. (C and D) Seasonal concentrations of MeHg (C) and THg (D) in unfiltered water from Moab Lake in 2000 and 2001...... 161

Appendix 1 Canadian body weight data by age from the 1998-1999National Longitudinal Survey of Children and Youth (Statistics Canada1999) and the Canadian Community Health Survey (Statistics Canada2002, 2005, 2006)......169

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## 1.0 Introduction\*

Methyl mercury (MeHg) is a bioaccumulative and persistent neurotoxin (Schroeder and Munthe 1998) that can cause health problems in fishes (Friedmann et al. 1996, Latif et al. 2001) and their wildlife (Chan et al. 2003) and human (Grandjean et al. 1998, Chan et al. 2003) consumers. MeHg contamination is the main reason (over 90%) for fish consumption advisories in North America (USEPA 1998, CEC 2003). Parks Canada recognizes mercury (Hg) and other airborne pollutants as stresses that affect the ecological integrity of national parks in Canada (Parks Canada 2001). National parks located in the Canadian Rocky Mountains may be at even greater risk, because Hg "hotspots" (soil concentrations over 10 ppb) have been identified in the vicinity (CEC 2003). However, little research has been completed on Hg in Canadian Rocky Mountain Parks.

We sampled invertebrates and fishes from lakes in or near to Canadian Rocky Mountain National Parks to determine total Hg (THg) and MeHg concentrations in aquatic biota (Chapter 3). We determined that some fish species contained MeHg concentrations that could affect the health of wildlife and human consumers. We presented our data to Parks Canada, who in conjunction with Health Canada, established lake-specific fish consumption guidelines for women of reproductive age and children (Parks Canada 2005). Precautionary consumption advice for all other mountain park waters was also implemented because fish MeHg concentrations can change over time and fish MeHg data do not exist for all park waters (Parks Canada 2005). In Chapter 3, we also determined whether seasonal, spatial or temporal patterns existed in MeHg and THg concentrations of aquatic biota from lakes in the Canadian Rocky Mountain parks. Seasonal patterns in MeHg and THg accumulation have been identified for some invertebrate taxa in lakes not located in the Canadian Rocky Mountains (Gorski et al. 2003). Spatial distribution patterns

A review of relevant literature is presented in Chapter 2.

exist in the Canadian Rocky mountains for other airborne pollutants such as organochlorine compounds (OC), which increase with elevation in air (Shen et al. 2004, Shen et al. 2005), snow (Blais et al. 1998), plants (Davidson et al. 2003), amphipods (Blais et al. 2003) and fishes (Demers et al. 2007). Cadmium concentrations in amphipods from Canadian Rocky Mountain lakes also increase with elevation (Varty, unpublished data). Concentrations of MeHg in fishes in areas other than the Canadian Rocky Mountains have been positively correlated to latitude (McMurtry et al. 1989), and recently altitude (Blais et al. 2006). Although long-term decreases in atmospheric Hg (Slemr and Scheel 1998) and sediment Hg accumulation (Greenfield et al. 2005) have been identified over the past few decades in areas other than the Rocky Mountains, MeHg concentrations in fishes from the same areas have not decreased during the same time period (Greenfield et al. 2005).

It would be difficult for Parks Canada to identify specific lakes containing fishes contaminated with MeHg other than those we sampled, because sampling biota for Hg in all park waters is cost, time and logistically prohibitive. Also, MeHg concentrations of fishes from remote lakes, far from point sources are widely variable (Schindler et al. 1995, Allen-Gil et al. 1997, Trip and Allan 2000). Nearby lakes can contain fishes with very low concentrations of MeHg to concentrations that exceed guidelines to protect human and wildlife health (Allan 1999). Many factors can result in among-lake variability in MeHg concentrations of fishes (reviewed in Kelly et al. 2006). These include factors that affect processes within the Hg cycle (e.g. sources of Hg to a catchment or lake, transport of Hg from a catchment to a lake, inlake Hg methylation, and biomagnification and bioaccumulation) (reviewed in Kelly Mountain lakes of differing elevation provide natural gradients in et al. 2006). several factors (e.g., temperature, precipitation, soil, vegetation) that can affect the distribution of MeHg in aquatic biota. In Chapter 4, we identified and modelled (using a Geographic Information Systems (GIS) approach) factors that affect the distribution of MeHg in trout from study lakes. We created another model, based on a subset of variables available for all mountain park lakes, to predict the MeHg concentrations of trout in all other fish-bearing lakes of the Canadian Rocky Mountain National Parks. In addition to the predicted MeHg concentrations of fishes, we utilized fishing pressure data to distinguish which lakes should be a priority to sample for verification of the model/MeHg contamination of trout. The model should aid Parks Canada with fisheries management in the mountain parks.

Forest fire can alter factors that affect the distribution of Hg in aquatic biota. Results from studies on the effects of forest fire on Hg concentrations in biota differ. Studies usually compare MeHg concentrations in biota between lakes in burned catchments and reference catchments (Allen et al. 2005, Garcia and Carignan 2005). In the Canadian Rocky Mountains, forest fire occurrence is expected to increase in the future with climate change (Flannigan et al. 2000, Flannigan et al. 2002, Westerling et al. 2006), and as park managers conduct prescribed burns to renew habitat for wildlife (Weber and Stokes 1998, Spencer et al. 2003). The catchment of one of the original study lakes, Moab Lake, located in Jasper National Park, began to burn in July 2000. David Donald (Environment Canada) analysed samples from Moab Lake for water chemistry parameters in the 1970's and 1990's and archived fish samples in the 1990's, which allowed us to compare pre- and post-fire data. We studied Moab Lake and four nearby creeks (two in burned catchments and two in unburned catchments) and determined that forest fire increased Hg accumulation by fishes in Moab Lake via two mechanisms (Chapter 5); increased inorganic Hg and MeHg inputs from the catchment (~12%) and food web alterations/lengthening of the food chain (~88%).

Results of our research are important for several reasons. We determined that MeHg concentrations in fishes from Canadian Rocky Mountain lakes pose health risks to wildlife and human consumers. Our GIS-based predictive model will help Parks Canada manage fisheries by identifying other lakes in the parks that may contain fishes contaminated with MeHg. We also determined the effects of forest fire on Hg accumulation by fishes. The baseline contaminants data generated through this research will be important in the future as climate change alters factors that affect the distribution of Hg in aquatic biota. Climate change may exacerbate

already problematic MeHg contamination of biota from Canadian Rocky Mountain lakes.

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## 2.0 **Review of Relevant Literature**

The literature on mercury, forest fire and climate change is vast. We examined available literature and integrated our findings to produce a review relevant to mercury in biota from lakes in the Canadian Rocky Mountain Parks.

## Mercury (Hg) Cycling

Elemental gaseous Hg (Hg<sup>0</sup>) has an atmospheric residence time of approximately one year, is subject to long-range transport, and is converted to reactive water soluble ionic Hg (Hg<sup>2+</sup>) through photochemical reactions (Schroeder Hg<sup>2+</sup> is released from the atmosphere to the landscape in and Munthe 1998). precipitation or through dry deposition, where it enters lakes directly or is deposited within a lake's catchment. Methyl mercury (MeHg; CH<sub>3</sub>Hg<sup>+</sup>) is also deposited from the atmosphere in precipitation, but at approximately 1% of THg concentrations (reviewed by Grigal 2002). The vast majority of Hg inputs to catchments are stored in soils and vegetation (Scherbatskoy et al. 1998). Hydrologic events can flush MeHg and Hg<sup>2+</sup> (Lawson and Mason 2001) from soils and wetlands within catchments into lakes where Hg<sup>2+</sup> can be methylated to MeHg by sulfate-reducing bacteria present in sediments (Ramlal et al. 1993) or wetlands (St. Louis et al. 1994). Subsequently, MeHg can enter the aquatic food chain. Both inorganic Hg<sup>2+</sup> and MeHg are accumulated by biota at the base of the aquatic food chain, however, MeHg is more strongly biomagnified than inorganic  $Hg^{2+}$ . Generally, more than 95% of the THg that accumulates in fish is MeHg (Bloom 1992).

Hg present in lake catchments can be both naturally occurring and anthropogenic in origin (Figure 2.1a) (Rasmussen 1998, Trip and Allan 2000). The general cycle of anthropogenic Hg contamination (Figure 2.1a and 2.1b) involves the release of stable gaseous elemental Hg (Hg<sup>0</sup>) to the atmosphere, primarily by high temperature combustion of coal and other fossil fuels (Pacyna and Keeler 1995, Keeler et al. 2006). Atmospheric deposition of Hg has increased 3 to 4-fold since pre-

industrial times (Engstrom and Swain 1997, Fitzgerald et al. 2005). THg and MeHg stored in soils and vegetation pose a serious long-term threat to the health of organisms in both terrestrial and aquatic systems (Lawson et al. 2003). This is because MeHg is a vertebrate neurotoxin that accumulates in organisms and can biomagnify more than a million times through aquatic food chains (Schroeder and Munthe 1998), reaching concentrations toxic to upper trophic levels.

#### Health Effects of MeHg

MeHg contamination is responsible for over 90% of the fish consumption advisories in North America (USEPA 1998, CEC 2003). Lakes located near to one another can contain fishes with very low concentrations of MeHg to concentrations that exceed Health Canada's commercial consumption guideline for human health of 0.5  $\mu$ g/g wet weight (ww) (Allan 1999), Health Canada's frequent consumption guideline of 0.2  $\mu$ g/g ww (Evans et al. 2005b), or the United States Environmental Protection Agency (USEPA) federal human health screening value of 0.3  $\mu$ g/g ww.

A significant positive relationship exists between MeHg concentrations in human blood and fish consumption rates (Hightower and Moore 2003, Mahaffey et al. 2004). Long-term exposure to MeHg through the consumption of fishes can permanently damage human neurologic, renal, and cardiovascular systems (Chan et al. 2003, Park and Johnson 2006). In adults, low dose exposure is related to paresthesias (a loss of sensation in hands and feet) (Fitzgerald and Clarkson 1991), and sensory and motor impairment (Park and Johnson 2006) due to nervous system damage. Severe exposure to MeHg in adults leads to irreversible brain damage, including the destruction of neuronal cells (Fitzgerald and Clarkson 1991). Several well known examples of human mercury poisoning via fish consumption exist, including Minimata, Japan (Watanabe and Satoh 1996) and the English-Wabigoon river system in northern Ontario, Canada (Wheatley et al. 1997).

MeHg crosses the placenta during pregnancy and accumulates in the blood, brain and other tissues of the fetus (Park and Johnson 2006). Health effects from fetal MeHg exposure are also dose-dependent. Symptoms can range from subtle motor function, language and memory deficits (Grandjean et al. 1998) to nervous system disorders, loss of hearing and vision, mental retardation and cerebral palsy (Chan et al. 2003, Park and Johnson 2006). In-utero MeHg exposure inhibits fetal cell division and neuronal migration (Fitzgerald and Clarkson 1991). Thus, fetuses (through women of child bearing age) and children are at the greatest risk of health effects from consumption of MeHg contaminated fishes.

The Canadian and American federal guidelines discussed previously are applied generally and do not specifically take into account the serving sizes of fish consumed, the exposure duration (# of fish meals per unit time), the mercury concentration of consumed fishes, or the body weight of the consumer for particular population groups. In Canada, the general Hg guidelines are only applicable for commercially sold fishes, and do not apply to self-caught freshwater fish. Upon request, when data are available, waterbody-specific risk assessment calculations are completed by Health Canada for sport fish consumption by male adults, women of child bearing age and children. The calculation results are provided as advice to provincial and territorial governments and Parks Canada, who use the results to determine if a consumption advisory is necessary. Advisories are usually expressed as a number of fish meals per month that should not be exceeded for a particular waterbody by adult males or women of childbearing age and children. Recently, the waterbody-specific or regional calculation approach to risk assessment has become more widely used (USEPA 1989, USEPA 1997, Huggett et al. 2001, Jewett et al. 2003). Unfortunately, fish consumers often do not heed or are not aware of government implemented consumption advisories, which puts their health at risk (Burger and Gochfeld 2006).

Piscivorous wildlife consistently consume whole fishes, so the Canadian Tissue Residue Guideline (CTRG) to protect wildlife consumers of aquatic biota has been established at 0.033  $\mu$ g/g ww, a much lower concentration than human health guidelines. Many fishes from remote lakes contain MeHg concentrations of concern for piscivorous wildlife (*e.g.*, Common Loons (*Gavia immer*)) (Trip and Allan 2000). Concentrations of MeHg below 0.5  $\mu$ g/g ww can cause reproductive and

behavioural effects in piscivorous birds (Chan et al. 2003). Exposure of piscivorous mammals to MeHg through fish consumption can be accompanied by weight loss, neurological disorders, and impairment of sensory and motor skills (Chan et al. 2003). MeHg exposure can also inhibit biochemical production of enzymes, immunoresponse and be genotoxic to piscivorous mammals (Wolfe et al. 1998). Reproductive effects of MeHg exposure in piscivorous mammals include fetal development problems that cause either physical or behavioural deficits after birth or death of the fetus (Wolfe et al. 1998).

The use of waterbody or regionally specific prey fish Hg data and speciesspecific toxicity data to assess health risks for piscivorous wildlife has recently become popular (Yeardley et al. 1998, Morrissey et al. 2005, Hinck et al. 2006). Studies either compare dietary Hg exposure to a tolerable daily intake (TDI) or calculated wildlife criteria values. Published wildlife criteria values are generally specific to the northeastern United States. For example, calculated wildlife criteria values are  $0.02 \,\mu\text{g/g}$  ww for piscivorous birds (Yeardley et al. 1998) or  $0.03 \,\mu\text{g/g}$  ww for Belted Kingfishers (*Ceryle alcyon*) (Lazorchak et al. 2003). The wildlife criteria value calculated for piscivorous mammals is  $0.1 \,\mu\text{g/g}$  ww (Yeardley et al. 1998), or  $0.1 \,\mu\text{g/g}$  ww for River Otters (*Lutra canadensis*) and  $0.07 \,\mu\text{g/g}$  ww for American Mink (*Mustela vison*) (Lazorchak et al. 2003).

Risk assessment of MeHg exposure on the health of fishes has not been widely published. However, a wholebody tissue threshold-effect level (t-TEL) of 0.2  $\mu$ g/g ww has recently been calculated for the protection of the health of juvenile and adult fishes (Beckvar et al. 2005). The value was calculated based on sublethal endpoints such as growth, reproduction, development and behaviour (Beckvar et al. 2005). Even small quantities of MeHg can affect embryo production (Latif et al. 2001), inhibit growth and gonadal development (Friedmann et al. 1996), and can have genotoxic effects on fishes (Easton et al. 1997). Dietary mercury exposure (at concentrations currently occurring in northern US lakes) has been found to alter fish predator avoidance behaviour, which likely increases the vulnerability of MeHg

contaminated fishes to predation (Webber and Haines 2003). This has serious implications for transfer of MeHg to fish consumers (Webber and Haines 2003).

### Factors that influence MeHg accumulation by fishes

MeHg concentrations in fishes from remote lakes, not subject to point source pollution, vary widely (Schindler et al. 1995, Allen-Gil et al. 1997, Trip and Allan 2000). There are many factors that could result in among-lake variability in fish Hg concentrations. These include factors that affect the following processes within the Hg cycle: 1.) *sources of Hg to a catchment or lake*; 2.) *transport of Hg from a catchment to a lake*; 3.) *In-lake Hg methylation*; and 4.) *biomagnification and bioaccumulation of MeHg*. Complex interactions of all of these factors produce highly variable Hg concentrations in fishes collected among species and in different lakes.

### Factors that affect sources of Hg to a catchment or lake

Catchment geology (*e.g.*, weathering of metamorphic, intrusive or volcanic rocks, biotite rich granites, and black shales) has been identified as a source of Hg contamination to lakes (Lawson and Mason 2001, Vaidya and Howell 2002, Loukola-Ruskeeniemi 2003, Page and Murphy 2003, Lockhart et al. 2005). However, atmospheric deposition is usually the principal source of Hg (Swain et al. 1992, Wang et al. 2004). Large-scale studies in the United States have recently linked atmospheric deposition of inorganic Hg<sup>2+</sup> to MeHg concentrations in mosquitoes (Hammerschmidt and Fitzgerald 2005) and freshwater fishes (Hammerschmidt and Fitzgerald 2006). A mesocosm study using mercury isotopes verified the results of the large scale study by demonstrating that methylation and bioaccumulation respond proportionally to atmospheric Hg<sup>2+</sup> loading (Orihel et al. 2006, 2007).

Climatic variables can influence both rates of rock weathering and quantities of contaminants deposited to an area. The cold condensation effect, which is the evaporation of volatile chemicals in warm areas and subsequent deposition in cold regions, is hypothesized to be responsible for increased concentrations of Hg at high latitudes and altitudes far from point sources (Mackay et al. 1995). Temperature decreases can cause greater condensation of the vapour phase and increased precipitation volume. Therefore, temperature may be related negatively and precipitation volume positively to the quantity of Hg deposited to the landscape. Consequently, Hg concentrations in fishes have been positively correlated to latitude (McMurtry et al. 1989), and recently altitude (Blais et al. 2006). Ultra-violet (UV)-mediated photo-reduction of Hg<sup>2+</sup> in snow and subsequent re-volatilization to the atmosphere (Amyot et al. 2003, Lalonde et al. 2003) can also affect the quantity of Hg deposited in remote catchments.

### Factors that affect transport of Hg from a catchment to a lake

High flow events, which cause seasonal flooding of large areas of normally dry land and erosion (Balogh et al. 2006, Belger and Forsberg 2006), are important for transport of MeHg and Hg<sup>2+</sup> from a catchment to a lake (Balogh et al. 1997, 1998, 1998b, 2004, 2005, Lawson and Mason 2001, Wang et al. 2004). Catchment characteristics also affect the mobility of Hg (Table 2.1). Physiogeographic variables (e.g. topography, geology, soil type and land use) are often grouped and expressed as 'ecoregions' which explain some variability in the MeHg concentrations of fishes (Allen-Gil et al 1995).

#### Factors that affect in-lake Hg methylation

In-lake MeHg production can be affected by water temperature (Reinert et al 1974, Bodaly et al. 1993, Ullrich et al. 2001), and photodegradation of MeHg in water (Sellers et al. 1996, Hammerschmidt et al. 2006, 2006b). MeHg production is enhanced under anaerobic conditions (*i.e.*, sediments and wetlands) (reviewed Ullrich et al. 2001). Interactions with water chemistry parameters also affect in-lake Hg methylation (Table 2.2).

## Factors that affect MeHg biomagnification and bioaccumulation

Biomagnification and bioaccumulation of MeHg in fishes may be influenced by the concentration of MeHg and THg in water (Fitzgerald and Clarkson 1991,

Paterson et al. 1998), lake productivity (Kidd et al 1999, Essington and Houser 2003, Kamman et al. 2005, Mailman et al. 2006b), and interactions between MeHg and other trace elements in water (*e.g.*, Hg declines when Zn, and Cd are present (Chen et al. 2001)). Many biological characteristics also affect biomagnification and bioaccumulation of MeHg in aquatic systems (Table 2.3). Fishing pressure can decrease MeHg concentrations in fishes (Verta 1990, Lindqvist 1991, Evan et al. 2005, Mailman et al. 2006).

#### Forest Fire and Hg

Landscape disturbance can affect Hg dynamics (Munthe and Hultberg 2004) by altering factors that affect Hg source, transport, methylation and accumulation processes. Forest fire potentially modifies complex interactions that control MeHg accumulation by fishes. For instance, forest fire releases Hg<sup>0</sup> to the atmosphere (Veiga et al. 1994, Artaxo et al. 2000, Brunke et al. 2001, Friedli et al. 2001, Friedli et al. 2003 and 2003b, Sigler et al. 2003, Harden et al. 2004, DiCosty et al. 2006, Engle et al. 2006, Hall et al. 2006, Biswas et al. 2007), which can deposit elsewhere and become a source of Hg to lakes and their catchments. The removal of Hg and/or MeHg from soils and vegetation within a catchment by fire (Amirbahman et al. 2004, Harden et al. 2006, Turetsky et al. 2006, Biswas et al. 2007) affects the quantity and availability of Hg for runoff. In the Rocky Mountains, the fire-related release of Hg from soils is associated with fire severity (*e.g.*, 22.3% and 81.2% loss of soil Hg during low and high severity fires, respectively) (Biswas et al. 2007).

Forest fire impacts or eradicates soils and vegetation within catchments, which affects nutrient (Gresswell 1999) and likely Hg transport (Caldwell et al., 2000, Grigal 2002). For example, fire-related alterations to soil properties lead to increased erosion, overland flow and stream peakflows (Ice et al. 2004, Shakeby and Doerr 2006). Increased runoff after fire may also occur due to decreased evapotranspiration (Bayley et al. 1992).

Post-fire alterations to lake and stream water temperature and chemistry (e.g. DOC, SO<sub>4</sub><sup>2-</sup>, pH, nutrients) have been widely documented (Gresswell 1999, Carignan et al. 2000, Lamontagne et al. 2000, Planas et al. 2000). Increases in water temperature (Reinert et al 1974, Ullrich et al. 2001), DOC (Driscoll et al. 1995, Watras et al. 1998, Ullrich et al. 2001),  $SO_4^{2-}$  (Chen et al 2005) and decreases in pH (Driscoll et al. 1995, Watras et al. 1998, Ullrich et al. 2001) can increase in-lake Hg methylation (Caldwell et al. 2000). Fire-mobilized nutrients (usually nitrogen and sometimes phosphorus) (Gresswell et al. 1999, Carignan and Steedman 2000, Carignan et al. 2000, McEachern et al. 2000) can enhance lake productivity (Spencer et al. 2003), which can result in increased phytoplankton (Planas et al. 2000, Charette and Prepas 2003) and crustacean zooplanton biomass (Patoine et al. 2000, 2002). Increased lake productivity can reduce Hg bioaccumulation (Kidd et al. 1999, Essington and Houser 2003, Herendeen and Hill 2004, Kamman et al. 2005) through increased phytoplankton and zooplankton biomass (i.e., biodilution), enhanced fish growth rates (*i.e.*, growth dilution), or increased sedimentation of particles (Gunnarssom et al. 1995, Mailman et al. 2006).

MeHg concentrations in biota are known to increase with increasing trophic position, as indicated by  $\delta^{15}N$  (Cabana and Rasmussen 1994, Cabana et al. 1994, Kidd et al. 1995). Forest fire results in small increases in baseline-adjusted  $\delta^{15}N$  (0.5-1.8‰) of aquatic biota (Spencer et al. 2003, Allen et al. 2005, Garcia and Carignan 2005, Mihuc and Minshall 2005), which should occur concurrent with increased MeHg accumulation by biota. However, some have attributed these increases in  $\delta^{15}N$  to increased inputs of inorganic nitrogen from the burned catchment (Allen et al. 2005, Garcia and Carignan 2005), rather than food web alterations. Hg content is also related to food source, as indicated by  $\delta^{13}C$  (Power et al. 2002). Forest fire results in small depletions of  $\delta^{13}C$  (~1.0 ‰) (Spencer et al. 2003, Allen et al. 2005).

Few have studied the effects of forest fire on the biogeochemical cycling of Hg and no studies investigate the effects of forest fire on concentrations of metals or other persistent bioaccumulative toxicants such as organochlorine pesticides and PCBs in biota. Studies on the effects of forest fire on Hg accumulation by aquatic

organisms have differing results. When lakes in burned and unburned catchments in Quebec were compared, MeHg concentrations in zooplankton were not elevated in lakes from burned catchments (Garcia and Carignan 1999, Garcia et al. 2006), and increased MeHg concentrations in fishes from lakes in burned catchments were not statistically significant (Garcia and Carignan 2000, Garcia and Carignan 2005). However, fishes and zooplankton from lakes located in partially burned catchments contained the highest MeHg concentrations measured in the study (Garcia and Carignan 2005, Garcia et al. 2006). Forest fire was also related to elevated reservoir sediment MeHg and THg concentrations (Caldwell et al. 2000), likely because increased fire-related loading of ionic Hg<sup>2+</sup> and DOC stimulated methylation of Hg<sup>2+</sup> (Regnell et al. 1997, Lee et al. 2000). In the boreal plain of Alberta, concentrations of MeHg in invertebrates from lakes in burned and unburned catchments were similar for all taxa, with the exception of the odonate Cordulia shurtleffi, which contained elevated MeHg concentration in lakes from burned catchments (Allen et al. 2005). Conversely, Hg concentrations declined in invertebrates and fishes from a lake sampled before and after a severe fire, despite small increases in the  $\delta^{15}N$  of some invertebrate species (Allen et al 2005). Future research will likely clarify reasons for the variability in study results to date.

## Hg in mountain lakes

Mountain lakes of varying elevation, not impacted by point source pollution, are ideal for studying factors that affect the distribution of MeHg in aquatic biota because they provide steep environmental gradients over short distances (Daly and Wania 2005). In addition, mountain-specific meteorology can affect contaminant distribution in several ways (Figure 2.2). Large-scale winds, created from circulation among high and low pressure systems can be modified or channelled by mountains. These terrain-forced winds cause airflow to be blocked, carried over or around mountain barriers, or forced through mountain passes (Daly and Wania 2005). Different wind patterns access different contaminant sources. For example, diurnal wind systems can be created by temperature differences between mountains and

surrounding plains (Daly and Wania 2005). These winds vary in scale, moving several meters to several hundred kilometres, and can carry air from the plains into the mountains during the day and reverse during the night (Daly and Wania 2005). During the day, high temperatures favour evaporation of contaminants in the lowlands (Daly and Wania 2005). As air masses rise upslope, adiabatic cooling, enhanced cloud formation and subsequent precipitation occur, leading to enhanced contaminant deposition at high elevations (Figure 2.2) (Daly and Wania 2005). During the night, low temperatures prevent contaminant evaporation along the entire gradient. Therefore, downslope winds contain less contaminants, resulting in a steady transfer of contaminants upslope (Daly and Wania 2005).

The form of precipitation can affect the quantity of contaminants deposited to high elevation catchments. Snow is generally a more effective scavenger of contaminants than rain, and in the Rocky Mountains, 60-70% of precipitation is snow (Daly and Wania 2005). High rates of snow deposition can lead to large releases of contaminants in snowmelt (Daly and Wania 2005). However, Hg concentrations in snow could decrease due to UV-mediated photo-reduction of Hg<sup>2+</sup> and subsequent re-volatilization to the atmosphere (Amyot et al. 2003, Lalonde et al. 2003). This could explain why most Hg deposition at high altitudes occurs during summer months (Allan 1999, Mast et al. 2003, Miller et al. 2005). High altitude mountain areas have 2-5 fold greater wet Hg deposition rates than surrounding lowlands (Allan 1999). This results from large quantities of precipitation, typical of the Rockies, with moderate Hg concentrations (Mast et al. 2003), and cloud water Hg deposition which is twice as high as rainfall at high elevations (Lawson et al. 2003, Malcolm et al. 2003). High alpine lakes may be particularly sensitive to airborne pollutants because catchments contain thin soils with little vegetative cover. Thus, catchments have limited ability to prevent contaminants from entering surface waters through runoff (Blais et al. 2005, Daly and Wania 2005).

Similar distribution patterns have been identified for Hg, organochlorines and trace metals in mountain ecosystems. Hg concentrations in mosses and lichens increase with increasing altitude (Evans and Hutchinson 1996), and a recent study in

France identified the same trend in fishes (Blais et al. 2006). High elevation coniferous forests assimilate more Hg<sup>0</sup> per gram of foliage than lower elevation deciduous forest, and particulate carbon transported to mountain aquatic systems during snowmelt consists mostly of leaf litter that provides a source of MeHg to lakes (Miller et al. 2005). Persistent organic pollutants in snow, vegetation, amphipods (Gammarus lacustris) and fishes in the Rockies (reviewed in Blais 2005, Hageman et al. 2006, Demers et al. 2007) also increase with elevation. These distribution patterns have been identified in other mountainous regions for organochlorines in air, precipitation, water, foliage, soils, sediments and biota (e.g., California, Japan, various mountain ranges in Europe, Africa, South America) (reviewed by Daly and Wania 2005). High altitude lakes are known to contain fishes with elevated concentrations of trace metals such as Cd and Pb (Kock et al. 1995), and amphipod Cd concentrations have been shown to increase with altitude in the Canadian Rockies (Varty, unpublished data). Metal (Pb, Cd, Cu, Zn, Cr, Fe, Mn, Mo and S) concentrations increase in moss with elevation in European mountains (Soltés 1992 and 1998, Zechmeister 1995). Thus, several different contaminants increase in concentration with elevation in a variety of media.

Catchment characteristics (*e.g.*, vegetation, soils etc.) change with altitude and can affect transport of nutrients and other compounds resulting in water chemistry (*e.g.*, pH, alkalinity, conductivity, total phosphorus and total nitrogen) gradients with elevation (Larson et al. 1999). Lake productivity (Schindler 1990), species richness (Schindler 1990), and the growth rate of aquatic biota (Donald et al. 1980, Daly and Wania 2005) decrease with altitude. Low lake productivity should favour enhanced contaminant concentrations in organisms (Kidd et al 1999, Essington and Houser 2003, Daly and Wania 2005, Kamman et al. 2005, Mailman et al. 2006b). Also, organisms in high elevation lakes are longer-lived (Donald and Alger 1986), have higher lipid storage (Daly and Wania 2005), and have slower metabolism and excretion of contaminants (Daly and Wania 2005). These factors may enhance MeHg and other contaminant accumulation by organisms, which would pose a threat to

wildlife predators of aquatic biota in mountain systems (*e.g.*, birds of prey, carrion-feeding birds, lynx, cougars, wolves, and bears) (Daly and Wania 2005).

Alternatively, some characteristics of mountain lakes could limit MeHg accumulation by biota. UV radiation increases with elevation (Blumthaller et al. 1997) and may be responsible for high rates of photo-reduction of Hg<sup>2+</sup> in high altitude lakes (Krabbenhoft et al 2002). Furthermore, food chains in mountain lakes tend to be short, which should limit accumulation of contaminants by aquatic biota (Campbell et al. 2000, Daly and Wania 2005). Rognerud et al. (2002) found low Hg concentrations in fishes from European high altitude lakes, which they attributed to low sediment fluxes of Hg, low net production of MeHg, and short food chains. Low water temperatures, DOC concentrations and organic matter content of sediments in high elevation lakes could contribute to low methylation rates (Rognerud et al. 2002). Demethylation could be favoured due to high transparency and low water temperatures, which could also result in reduced MeHg concentrations in these lakes (Rognerud et al. 2002). Determining the effects of counteractive factors on MeHg accumulation by mountain lake biota requires further research.

Forest fires have been suppressed in Rocky Mountain parks for over 100 years (Weber and Stokes 1998), causing mature forest ecosystems to contain pools of nutrients and Hg equivalent to many years of deposition. The Rockies will be exposed to increased landscape disturbance as park managers conduct prescribed burns to renew habitat for wildlife (Murray et al. 1998, Weber and Stokes 1998, Spencer et al. 2003). Climate change is also expected to increase forest fire occurrence and the area burned in this region (Stocks et al. 1998, Flannigan et al. 2000, Dale et al. 2001, Flannigan et al. 2002, Stocks et al. 2003, Gillett et al. 2004, Flannigan et al. 2005, Westerling et al. 2006). Increased forest fire frequency in the Rockies will have implications for the distribution of contaminants in aquatic biota.

The USEPA has identified a need for further research on mountain lakes in the United States which are likely Hg-sensitive ecosystems (Krabbenhoft et al. 2002). However, few studies explore the transfer of pollutants in alpine lake food chains

(Daly and Wania 2005). Three studies have been completed on Hg in mountain lakes from national parks of the western United States (Watras et al. 1995, Krabbenhoft et al. 2002, Mast et al. 2005). In Canada, the State of Protected Heritage Areas Report (Parks Canada 2001) identified airborne pollutants, such as Hg and organochlorine pesticides and PCBs, as ecological stresses affecting the ecological integrity of national parks across Canada. Banff and Jasper National Parks in Alberta, and Yoho National Park and Mt. Robson Provincial Park in British Columbia are part of the Rocky Mountain Parks World Heritage Site designated by the United Nations Educational, Scientific, and Cultural Organization (UNESCO). The management plans for these national parks include actions to deal with identified stresses. Although there have been some studies on organochlorine airborne pollutants in these parks, little if any research on Hg has been completed. Hence, the key action identified in management plans is baseline data collection (Parks Canada 1997, Parks Canada 2000).

#### Temporal trends of Hg and organochlorine accumulation in fishes

Long-term decreases in atmospheric Hg (Slemr and Scheel 1998) and sediment (Greenfield et al. 2005) Hg accumulation have been identified over the past few decades. However, MeHg concentrations in fishes in the same areas have not decreased during the same time period (Greenfield et al. 2005, Muir et al. 2005). MeHg concentrations of fishes have not changed or have slightly declined temporally in several locations, while organochlorine (OC) concentrations have declined rapidly in the same fishes (Lake Ontario: French et al. 2006, San Francisco Bay: Greenfield et al. 2005, Canadian arctic review: Evans et al. 2005b). Declines in OC concentrations of fishes occurred coincident with decreasing sediment OC concentrations. The declines in OC concentrations of sediments and fishes have been attributed to bans on production and use (French et al. 2006). In the arctic, decreases in OC concentrations have also been related to climate variability (changes in water temperature, seasonal ice, primary productivity, fish growth rates and fish condition factor) (Ryan et al. 2005). Oscillations in OC concentration over time in Lake Ontario fishes have been linked to the stocking of other fish species, nutrient abatement programs, climate and introduced species (French et al. 2006). The lack of a long-term decrease in fish MeHg concentrations likely is because Hg bioavailability is related to interannual variation in fish ecology, watershed loading, contaminated sediment exposure, and net methylation rates (Greenfield et al. 2005). In addition, results of a Hg isotope study to determine the fate of newly deposited Hg in aquatic systems indicate that accumulation of ambient MeHg predominates in all organisms. This suggests that changes in Hg loading will affect MeHg concentrations in fishes and other biota, but steady state may not occur for 10-30 years (Paterson et al 2006).

### Identification of spatial patterns in Hg using GIS

Studies of factors that affect the distribution of contaminants in biota often include large numbers of variables, making spatial analyses difficult (Page and Murphy 2003). These variables can include different point (*e.g.* a water or snow sample) and polygon (*e.g.* geology or wetland area) data, which complicate the examination of relationships between variables (Page and Murphy 2003). Geographic Information Systems (GIS) allow all available contaminants data and related data to be incorporated into a common dataset, which can be used to examine relationships among variables and to complete spatial analyses. GIS has been used to relate water quality to land use practices (Tong and Chen 2002) and to simultaneously monitor multiple metal concentrations in mosses and/or soils (Schröder and Pesch 2005, Grammatica et al. 2006).

GIS has been utilized in a few recent Hg studies to determine relationships between Hg and other variables. GIS has also been used to predict Hg concentrations based on relationships with other variables. Kejimikujik National Park in eastern Canada, contains Common Loons (*Gavia immer*) and fishes with extremely high concentrations of MeHg, that could not be accounted for by atmospheric deposition alone (Page and Murphy 2003). Statistical and GIS analyses determined that certain geology types are major sources of Hg in the park (Vaidya

and Howell 2002, Page and Murphy 2003). Kramar et al. (2005) used MeHg concentrations in loons, with precipitation, land cover, topography and hydrology data, in a GIS-based statistical model to predict Hg concentrations in loons at a watershed scale. Another GIS-based predictive model was recently created using THg and MeHg surface water data for the northeastern United States and maritime Canada (Dennis et al. 2005). These results demonstrate the usefulness of a GIS based approach for Hg studies, particularly for projects with a modelling or monitoring component.

# **Climate Change and Hg**

High altitude ecosystems, particularly alpine lakes, are expected to exhibit increased vulnerability to climate change and even slight environmental changes could substantially affect ecosystem function (Daly and Wania 2005, Macdonald 2005). In the Rocky Mountains, alterations to precipitation and temperature regimes are expected to affect vegetation, hydrology, biogeochemical fluxes and cycles, and lake heat budgets (Hauer et al. 1997). Mean annual temperature data for Banff, Jasper and Valemount show an increasing trend over the past ~100 years (Luckman 1990, Luckman and Seed 1995), and increased precipitation is expected with climate change in the Canadian Rocky Mountains (Evans and Clague 1997).

Climate change will likely alter many factors that affect sources, transport, methylation and accumulation of Hg (Macdonald 2005). For example, climate warming may result in longer ice-free seasons (Evans et al. 2005b), which should profoundly affect the limnological characteristics of lakes (Schindler and Smol 2006), increase algal productivity (Outridge et al. 2005), alter phytoplankton and zooplankton community structure (Strecker et al. 2004), cause shifts in the distribution of other aquatic organisms (Schindler 1997), and increase growth rates and survival of fishes in alpine lakes (Schindler and Smol 2006). Further, as previously stated, climate change is expected to increase forest fire occurrence and the area burned in mountainous regions of western North America (Stocks et al. 1998, Flannigan et al. 2000, Dale et al. 2001, Flannigan et al. 2002, Stocks et al. 2003,

Gillett et al. 2004, Flannigan et al. 2005, Westerling et al. 2006). All of these climate change induced alterations have implications for Hg cycling.

Grigal (2003) predicted that climate change related alterations to forest structure could cause loss of soil carbon and release of large stores of Hg to the atmosphere. Some Hg discharge in runoff could also occur (Grigal et al. 2003), which would release Hg stored in catchments to aquatic systems (Evans et al. 2005). However, Lee et al. (2000) have shown that warmer and drier climatic conditions decrease catchment outputs of both inorganic and MeHg to aquatic systems. It has also been speculated that climate warming could enhance accumulation of MeHg by fishes (Evans et al. 2005, Macdonald et al. 2005), by increasing the availability of MeHg (Muir et al. 2005). Enhanced MeHg availability in aquatic systems with climate warming could be due to warmer water temperatures and increased methylation rates (Evans et al. 2005, Macdonald et al. 2005), an increase in the ratio of methylation to demethylation because of increased photoreduction of Hg<sup>2+</sup> to Hg<sup>0</sup> (Schindler 1997, 2001, Macdonald et al. 2005), or enhanced organic matter content of sediments (due to increased lake productivity) which would favour increased methylation rates (Outridge et al. 2005). It is evident that climate change will affect Hg dynamics in the future, but how and why changes will occur is still unclear. Baseline and long-term data sets will be required to tease apart the effects of climate change on Hg accumulation by fishes.

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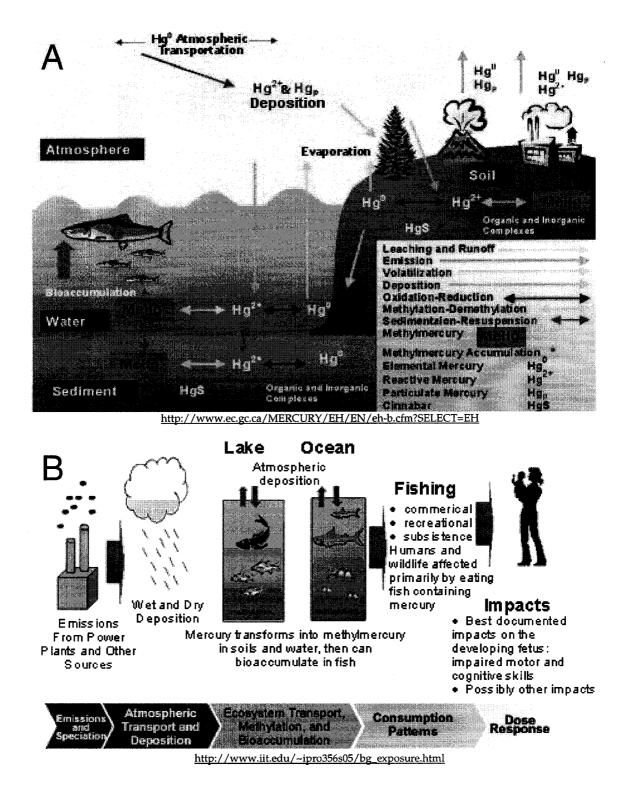
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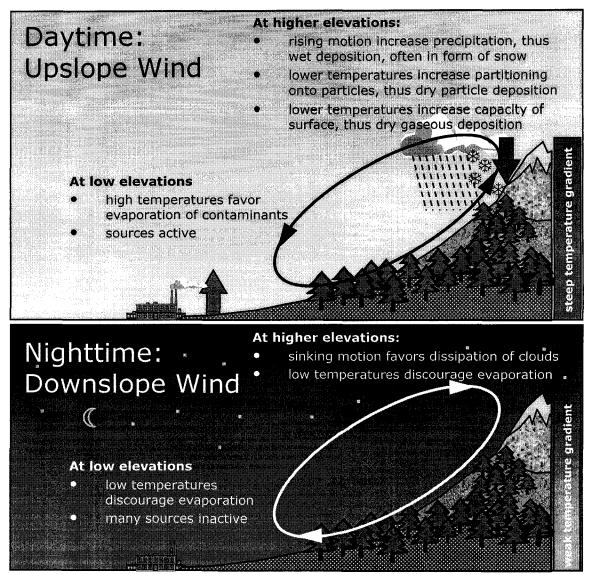
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**Figure 2.1** The mercury (Hg) cycle, A. Biogeochemical Hg cycle including transformations and environmental pathways, and B. Cycle of anthropogenic Hg contamination from industrial sources to health effects of MeHg bioaccumulation in humans.





**Figure 2.2** Processes that affect the contaminant distribution over a mountain slope. Day and night differ in wind direction, temperature gradient with elevation, and local source activity (Daly and Wania 2005).

<u>Table 2.1</u>	Catchment characteristics that affect transport of Hg from a catchment	
	to a lake	

Factor	Reference
Aspect	Grigal 2002
Slope	Dennis et al. 2005, Kainz and Lucotte 2006
Soil type	Shanley et al. 2005
Vegetation type	Hurley et al. 1995, St. Louis et al. 2001, Ericksen et al. 2003, Kramar et al. 2005, Shanley et al. 2005
Litter, leaf, or needle inputs	Balogh et al. 2003, Miller et al. 2005
% wetland	Hurley et al. 1995, St. Louis et al. 1996, Grigal 2002, Balogh et al. 2004 & 2005, Branfireun et al. 2005
Lake area	Bodaly et al. 1993, Evans et al. 2005
Catchment area	Hakanson et al. 1988, Stemberger and Chen 1998, Grigal 2002, Kamman et al. 2005
Catchment volume	Grigal 2002
Catchment area to lake area ratio	Vaidya and Howell 2002

<u>Table 2.2</u>	Interactions with water chemistry parameters that affect in-lake Hg
	methylation

Factor	Reference
Dissolved organic carbon (DOC)	Driscoll et al. 1995, Watras et al. 1998, Ullrich et al. 2001
рН	Wren and MacCrimmon 1983, Wiener et al. 1990, Winfrey and Rudd 1990, Watras et al. 1998, Ullrich et al. 2001, Burgess and Hobson 2006
salinity	Ullrich et al. 2001
alkalinity	Hakanson et al. 1988, Spry and Wiener 1991
Calcium (Ca+)	Allard and Stokes 1989
Magnesium (Mg+)	Allard and Stokes 1989
Sulphate (SO4 <sup>2-</sup> )	Chen et al. 2005
Conductivity	Allard and Stokes 1989
Nutrient availability	Ullrich et al. 2001
Lake productivity	Rose et al. 1999

# Table 2.3Biological characteristics that affect MeHg bioaccumulation and<br/>biomagnification

Factor	Reference
Positive interactions with other trace elements within fishes	Zn: Chen et al. 2000
Negative interactions with other trace elements within fishes	Se: Burger et al. 2001, Belzile et al. 2006 Ag: Ribeyre et al. 1995
Phytoplankton density, biomass and community structure	Lithner et al. 2000, Skei et al. 2000, Pickhardt et al. 2002, Gorski et al. 2006,
Zooplankton density, biomass and community structure	Stemberger and Chen 1998, Pickhardt et al. 2002, Chen and Folt 2005, Pickhardt et al. 2005
MeHg concentration in prey	Mathers and Johansen 1985, MacCrimmon et al. 1983, Borgmann and Whittle 1992, Hall et al. 1997, Stafford and Haines 2001, Houck and Cech 2004, Kainz et al. 2006
Trophic position/food chain length (δ <sup>15</sup> N)	Cabana and Rasmussen 1994, Cabana et al. 1994, Kidd et al. 1995, Evans et al. 2005
Source of carbon ( $\delta^{13}$ C)	Power et al. 2002
Fish age	MacCrimmon et al. 1983, Grieb 1990, Stafford et al. 2004, Evans et al. 2005
Fish length	Grieb 1990, Stafford et al. 2004, Burgess and Hobson 2005
Fish weight	Wren et al. 1983, Grieb 1990, Stafford et al. 2004, Burgess and Hobson 2005
Fish condition factor	Scott and Armstrong 1972, Suns and Hitchins 1990, Cizdiel et al. 2002 & 2003
Fish growth rate	MacCrimmon et al. 1983, Verta 1990, Borgmann and Whittle 1992, Doyon et al. 1998, Greenfield et al. 2001, Stafford and Haines 2001, Essington and Houser 2003, Stafford et al. 2004, Simoneau et al. 2005, Surette et al. 2006, Swanson et al. 2006

# 3.0 Methyl and total mercury concentrations in aquatic biota from lakes in the Canadian Rocky Mountains: implications for human and wildlife consumers and seasonal, spatial and temporal trends

# Introduction

We sampled 44 lakes near or within Canadian Rocky Mountain parks to determine seasonal methyl mercury (MeHg) and total mercury (THg) concentrations in invertebrates and THg (as MeHg) concentrations in fishes. Subsequently, we investigated whether MeHg concentrations in fishes posed a health risk to human and wildlife consumers. We also identified whether spatial patterns (*i.e.*, elevation, latitude, continental divide) in MeHg and THg concentrations in aquatic biota existed. Finally, we ascertained if MeHg concentrations in fishes changed over time in three of the lakes.

MeHg is a bioaccumulative and persistent neurotoxin that can affect the health of fishes (Friedmann et al. 1996, Latif et al. 2001) and their wildlife (Chan et al. 2003) and human (Grandjean et al 1998, Chan et al. 2003) consumers. MeHg contamination is responsible for over 90% of the fish consumption advisories in North America (USEPA 1998, CEC 2003). Mercury (Hg) and other airborne pollutants affect the "ecological integrity" of national parks in Canada (Parks Canada 2001). Hg "hotspots" (soil concentrations over 10 ppb) have been identified in the vicinity of the Canadian Rocky Mountains, indicating that parks in this area may be at even greater risk of Hg contamination. However, little research has been completed on Hg in Canadian Rocky Mountain parks.

In mountain ecosystems other than the Canadian Rockies, spatial distribution patterns are similar for Hg (Evans and Hutchinson 1996, Blais et al. 2006), other trace metals (Šoltés 1992 and 1998, Kock et al. 1995, Zechmeister 1995) and organochlorine compounds (OCs) (reviewed by Daly and Wania 2005, Demers et al. 2007). Decreased temperatures at high elevations can cause greater condensation of the vapour phase of Hg and OCs and increased precipitation volume, which should 52 cause increased deposition of contaminants with elevation (Mackay et al. 1995), and latitude (McMurty et al. 1989). Hg concentrations in moss and lichen increase with increasing altitude (Evans and Hutchinson 1996), and a recent study in France identified the same trend in fishes (Blais et al. 2006). High altitude lakes are known to contain fishes with elevated concentrations of trace metals including Cd and Pb (Kock et al. 1995), and trace element concentrations (Pb, Cd, Cu, Zn, Cr, Fe, Mn, Mo and S) in moss increase with elevation in European mountains (Šoltés 1992 and 1998, Zechmeister 1995). OCs increase with elevation in air, precipitation, water, foliage, soil, sediment and biota in mountainous regions (*e.g.*, California, Japan, and various mountain ranges in Europe, Africa and South America) (reviewed by Daly and Wania 2005). Thus, many contaminants exhibit increases in concentrations with elevation in a variety of media.

In the Canadian Rocky Mountains, several studies have shown that spatial distribution patterns exist for OCs, which increase with elevation in air (Shen et al. 2004, Shen et al. 2005), snow (Blais et al. 1998), vegetation (Davidson et al. 2003), amphipods (Blais et al. 2003) and fishes (Demers et al. 2007; a subset of the fishes collected for this study). Cadmium concentrations in amphipods also increase with elevation in Canadian Rocky Mountain lakes (Varty, unpublished data). However, no research on spatial patterns of Hg distribution in the Canadian Rocky Mountains had been completed prior to this study. Within the Canadian Rocky Mountains, lakes located on the windward side of the continental divide in British Columbia would be exposed to greater quantities of precipitation and may be more at risk of contamination than Alberta lakes on the leeward side (Gadd 1996). Alberta lakes would encounter less precipitation due to the rain shadow effect (Gadd 1996). Positive relationships between Hg and latitude have been identified previously outside the Canadian Rocky Mountains (McMurty et al. 1989).

Over the past few decades, decreases in atmospheric Hg concentrations (Slemr and Scheel 1998) and sediment (Greenfield et al. 2005) Hg accumulation have been documented. However, Hg concentrations in fishes from the same areas have not decreased during the same time period (Greenfield et al. 2005, Muir et al. 2005).

Concentrations of MeHg in fishes have slightly declined or remained constant over time in Lake Ontario (French et al. 2006), the Canadian Arctic (Evans et al. 2005), and San Francisco Bay (Greenfield et al. 2005). The lack of long-term decreases in fish MeHg concentrations is likely because Hg bioavailability is related to inter-annual differences in fish ecology, watershed loading, contaminated sediment exposure and net methylation rates (Greenfield et al. 2005). In addition, results of a Hg isotope study to determine the fate of newly deposited Hg in aquatic systems indicate that accumulation of ambient MeHg predominates in all organisms (Paterson et al. 2006). Reductions in Hg loading are expected to affect MeHg concentrations in fishes and other biota, but steady state may not occur for 10-30 years (Paterson et al. 2006).

We hypothesized that MeHg and THg concentrations in aquatic biota would vary among lakes, and that concentrations of MeHg in fishes from some lakes might exceed guidelines for the protection of human and wildlife health. We also predicted that spatial patterns in MeHg and THg concentrations of aquatic biota would exist and that MeHg concentrations in fishes would not vary substantially over time (~5-10 years).

## Methods

#### Study area

Fish and invertebrates analysed for Hg were collected from 44 lakes in or near Canadian Rocky Mountain parks (Jasper, Banff, Yoho and Waterton National Parks, Mount Robson Provincial Park, Spray Valley Provincial Park, Shere Lake (near Tête Jaune Cache, BC), and Little Cranberry Lake (near Valemount, BC)) in Alberta and British Columbia, Canada (Figure 3.1). These lakes ranged in elevation from 760 to 2520 meters above sea level. Selected characteristics of study lakes (*i.e.*, longitude, latitude, elevation, catchment area, lake area, mean depth, maximum depth and water chemistry parameters) are presented in Appendix 1.

# Field sampling

Lakes were sampled during the late summer/early fall of 2000 and spring/early summer of 2001. Zooplankton samples were collected by repeatedly hauling a conical 140 µm mesh net vertically through the water column in the pelagic zone from 1 meter above the lake sediments to the lake surface. Bulk samples of the zooplankton community were frozen for THg and MeHg analyses. Benthic macroinvertebrates were collected using sweep nets and weighted mesh colonization traps in the littoral zone. Invertebrates were sorted, rinsed and frozen. In 2000 and 2001, small fishes were captured by minnow traps set overnight and baited with dogfood. In August 2001, stretched multi-mesh monofilament "test mesh" gillnets (1, 1.5, 2, 3, 4") and a combination of single mesh Swedish-style gillnets (1.5, 2 and 3") were set perpendicular to shore. The nets were used to collect a maximum of 30 fish of each species over the size range present at each study lake. Brian Parker (University of Alberta) and David Donald (Environment Canada) provided archived frozen fish tissue samples collected from lakes in the study area in the 1990s which supplemented field sampling that occurred in 2001. Archived samples were collected using multi-mesh gillnets. Ward Hughson and Charlie Pacas (Parks Canada) collected fishes from other lakes in the study area in 2001, 2002 and 2003. In 2003, Parks Canada used a multi-mesh test net set overnight to collect fishes. Fishes were identified (Nelson and Paetz 1992, Scott and Crossman 1998) to species, and frozen. The source of fishes analysed in this study is available in Table 3.1.

# Laboratory

Benthic macroinvertebrate were grouped by Order for THg and MeHg analyses (*i.e.*, many individuals of the same Order were included in one sample). Zooplankton and benthic macroinvertebrate samples were freeze-dried for 48 hours. Freeze-dried samples were powdered using an acid-washed glass mortar and pestle. Hg analyses were conducted at the University of Alberta Low-Level Mercury Analytical Laboratory (http://www.biology.ualberta.ca/facilities/mercury/). Fish dorsal muscle samples and freeze-dried invertebrates were digested with 7:3 HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> in closed Teflon bombs. THg was determined by BrCl oxidation, SnCl<sub>2</sub> reduction, purge and trap, and cold vapour atomic fluorescence spectrometry (CVAFS) (modified (USEPA 1996, Olson et al. 1997)). The analytical detection limit was 0.1-0.3 ng/g. Fish samples were not analysed for MeHg, because >85% of Hg in fish is MeHg (Ullrich et al. 2001). To determine MeHg concentrations in freeze-dried zooplankton and macroinvertebrates, samples were digested in a KOH-methanol solution, ethylated, and separated by gas chromatography with CVAFS. Detection limits were 0.1-0.3 ng/g dry weight. All Hg analyses included spike recoveries, duplicates, blanks and National Research Council (Canada) certified reference materials (DORM-2), which were prepared alongside the original samples as matrix matched biomaterial.

# Seasonality

We used Wilcoxon signed ranks tests to compare MeHg and THg concentrations and %MeHg in zooplankton and benthic invertebrate samples collected from the same lakes throughout our study area in different seasons (*i.e.*, spring and late summer/early fall). The nonparametric equivalent of the paired t-test was used because of: 1) small sample sizes and 2) variations from normality that were not corrected by data transformations.

### Human health risk assessment

We compared Hg concentrations in fishes from the lakes to Health Canada's commercial consumption guideline of 0.5  $\mu$ g/g ww (Allan 1999), Health Canada's frequent consumption guideline of 0.2  $\mu$ g/g ww (Evans et al. 2005b) and the United States Environmental Protection agency (USEPA) federal human health screening value of 0.3  $\mu$ g/g ww (USEPA 2000). We then calculated risk based on human health risk assessment methods used by Health Canada (Health Canada Bureau of Chemical Safety, personal communication, Health Canada 2007) and the USEPA (USEPA 2000).

We calculated the maximum allowable daily fish consumption rate (MADFCR) as follows:

$$MADFCR = \frac{TDI \times BW}{fish [Hg]}$$
(1)

where:

MADFCR= Maximum Allowable Daily Fish Consumption Rate (kg/day) TDI= Tolerable Daily Intake (µg/kg bw/day) BW= body weight (kg) Fish [Hg] = fish Hg concentration (µg/kg)

We used the same TDIs as Health Canada's Bureau of Chemical Safety. The provisional tolerable weekly intake was divided by seven to calculate the provisional tolerable daily intake of 0.47  $\mu$ g/kg bw/day. This TDI is used for the general public (*i.e.*, adult men and post-reproductive women). A provisional TDI for sensitive sub-groups of 0.20  $\mu$ g/kg bw/day was used for women of reproductive age, infants and children. The United States reference dose (RfD) of 0.1  $\mu$ g/kg bw/day was not used in this risk assessment.

Health Canada and the USEPA use mean body weights based on age classes (Health Canada: adults=60 kg, children 5-11=26.4 kg, children 1-4=14.4 kg, USEPA: adults=70 kg, children <6=14.5 kg). We used Canadian body weight data from the 1998-1999 National Longitudinal Survey of Children and Youth (Statistics Canada 1999) and the 2000-2001, 2003 and 2005 Canadian Community Health Survey (Statistics Canada 2002, 2005, 2006). We compared body weight data for Albertans, British Columbians and Canadians of the same age, and compared adult male and female body weights over time (2000-2005) (Appendix 2). We used Canadian data from the 1998-1999 National Longitudinal Survey of Children and Youth (Statistics Canada 1999) and the 2000-2001 Canadian Community Health Survey (Statistics Canada 2002) in the risk assessment because these studies took place within a three year period that coincided closely with fish sampling conducted in the parks. We used Canadian national body weight data, rather than data specific to Alberta and British Columbia. Although the body weight data for the children were similar, this decision could slightly underestimate the risk to adult British Columbians and

overestimate the risk to adult Albertans, who are under and over the national body weight average respectively at certain age classes. Based on Appendix 2, we used the following age classes for the risk assessment: children 2-3, 4-8, females 13-19, 20-50 and 51+ and males 13-19, 20-50 and 51+. We used the lowest mean body weight for each age class so that risk within an age class would not be underestimated.

We used fish mercury concentrations from samples collected for this study (Table 3.1). We speculated that people would normally not consume small fishes from mountain park lakes, so only Hg concentrations of fishes greater than 200 mm were included in this risk assessment.

MADFCRs are generally compared to consumption rates (kg/day) to assess risk. To estimate meal size, it first must be determined whether serving size data are based on cooked or uncooked fish mass. Cooking fish decreases the mass through loss of moisture content, but does not decrease the quantity of mercury in the fish (Morgan et al. 1997, Burger et al. 2003). We found that the loss of mass due to cooking trout fillets was ~20%. This indicates that if the Hg concentration in an uncooked fish fillet was 400 ng/g, the Hg concentration after cooking would be  $\sim$ 480 ng/g. We used uncooked portion sizes, because the concentrations of Hg from our study were determined in uncooked fishes. Uncooked fish serving size information was collected from three Edmonton, Alberta restaurants (i.e., Joey's Only, Backhome Fish and Chips and Brit's Fish and Chips) and USEPA 2000. We calculated the mean portion sizes for each age class. In this risk assessment, we used uncooked portion sizes of 75g for a child 2-3, 113g for a child 4-8, 141 g for a child 9-12, 170 g for a female 13-19, 20-50 and 51+ and 227 g for a male 13-19, 20-50 and 51+. Consumers are generally more aware of cooked serving sizes, because it represents what they actually eat. Our uncooked portion sizes convert to cooked portion sizes as follows: 57 g for a child 2-3, 91 g for a child 4-8, 119 g for a child 9-12, 140 g for a female 13-19, 20-50 and 51+ and 176 g for a male 13-19, 20-50 and 51+. Health Canada generally uses cooked fish portion sizes of 75-125 g for children and 150 g for adults (Health Canada Bureau of Chemical Safety, personal communication). However, meals consumed by anglers at a waterbody are likely larger than restaurant portions or

serving sizes recommended by Canada's Food Guide. The USEPA (2000) indicates that an uncooked portion size of 227 g for adults is not representative of higher end exposure.

Consumption guidelines and consumption advice are generally presented to the public in fishing regulations as maximum allowable meals per month. To calculate weekly or monthly maximum allowable fish consumption rates, we used the following equation (USEPA 2000):

$$MAFCR = \frac{MADFCR \times T}{MS}$$
(2)

where:

MAFCR= Maximum Allowable Fish Consumption Rate (meals/week or month) MADFCR=Maximum Allowable Daily Fish Consumption Rate (kg/day) T= Time Averaging Period (days/week or month) MS = Meal size (kg)

The MADFCR is calculated using equation 1. The time averaging period used was 7 days/week or 30.44 days/month. We used the meal sizes described previously.

The calculated results for the weekly and monthly allowable fish consumption rates are available in Appendix 3 and 4.

#### Wildlife health risk assessment

We determined the distribution of mammal, bird and reptile species that consume aquatic invertebrates and fishes and breed in the study area (Table 3.2). We used field guides (Fisher 1997, Fisher et al. 2000), wildlife inventories from the ecological land classification of each park (Holroyd and Van Tighem 1983, Wallis et al. 1996, Wallis et al. 2002), background reports (British Columbia Ministry of the Environment 2006), birding checklists (Friends of Jasper National Park 2005, Parks Canada 2007, Mount Robson Bird Blitz 2006), mammal checklists (Parks Canada), and discussions with local naturalists (Mike McIvor, personal communication) or park employees (Wayne Van Velzen, Area Supervisor, Mount Robson Provincial 59 Park, personal communication and Gail Ross, British Columbia Ministry of the Environment, personal communication). Appendix 5 provides the distribution of these wildlife species by park, and Appendix 6 details the mass, energy requirements and diet of each species potentially at risk.

We chose the same six piscivorous species for this risk assessment as those used in the USEPA (1997) Mercury Study Report to Congress (*i.e.*, Belted Kingfisher (*Ceryle alcyon*), Common Loon (*Gavia immer*), Osprey (*Pandion haliaetus*), Bald Eagle (*Haliaeetus leucocephalus*), River Otter (*Lutra canadensis*) and American Mink (*Mustela vison*)). We used three methods of risk assessment: 1) comparison of fish Hg concentrations from lakes to the Canadian Tissue Residue Guideline to protect wildlife consumers of aquatic biota (0.33  $\mu$ g/g ww MeHg), 2) calculation of the MADFCR for each wildlife species and comparison to consumption rates, and 3) calculation of Hazard Concentrations based on the no observable adverse effects level (NOAEL) and low effects adverse effects level (LOAEL) (as used in Hinck et al. 2006).

To calculate the MADFRC, we used a TDI of 21 µg/kg bw/day for avian species and 18 µg/kg bw/day for mammalian species (USEPA 1997). These TDIs are much greater than TDIs for humans because they are based on serious health effects such as reproductive failure, rather than subtle health effects (USEPA 1997) which are difficult to measure in wildlife species. Literature values for the body weight of the six wildlife species were utilized (USEPA 1997, Warrington 2001). We determined the size of fish that each of the six piscivorous wildlife species would generally consume. Belted Kingfishers consume fish up to 150 mm (Environment Canada 2003), Common Loons eat fishes from 50-300 mm (Flick 1983, Barr 1996), Osprey prey upon fishes 110-350 mm in length (Environment Canada 2003), Bald Eagles consume fishes between 230 and 380 mm (Buehler 2000), River Otters eat fishes between 20 and 500 mm, and American Mink prey upon fishes 150-200 mm in length (Environment Canada 2003). Only Hg concentrations from fishes of relevant size were included in the risk assessment for each of the wildlife species. This study determined THg (as MeHg) concentrations in dorsal muscle although wildlife

species would likely consume whole fish. Trudel and Rasmussen (2001) assumed that THg concentrations measured in dorsal muscle were equal to THg concentrations in whole fish (based on Lockhart et al. 1972, Becker and Bigham 1995, Post et al. 1996), whereas other studies indicate that THg concentrations in whole fish are less than THg concentrations in fish muscle (Goldstein et al. 1996, Harris and Bodaly 1998, Peterson et al. 2005). If dorsal muscle THg concentrations overestimate whole fish THg concentrations, this wildlife risk assessment could slightly overestimate potential risk. We compared the MADFRC to consumption rates from the literature (Warrington 2001) to assess risk.

To calculate Hg Hazard Concentrations (HC), we used the method described in Hinck et al. (2006):

#### HC (µg Hg/kg)= <u>NOAEL or LOAEL (µg/kg bw/day) x BW (kg)</u> consumption rate (kg/day)

Body weight and consumption rate data were derived from the same literature sources described above. NOAEL and LOAEL data were collected from Sample et al. (1996).

#### Spatial patterns in MeHg and THg concentrations of aquatic biota

Linear regression was used to determine whether altitude influenced Hg concentrations in biota. Some data varied slightly from a normal distribution but transformation did not normalize the data. Regression is robust for slight violations of some assumptions (Zar 1999); therefore, untransformed data were used and residuals were checked for normality and homoscedasticity. The *p* values presented for linear regressions are for the t-statistic for significance of slope ( $\approx$ regression coefficient). This is equivalent to testing the significance of the correlation between the independent and dependent variables. We used the ESRI (2007) ArcGIS 9 ArcMap 9.2 ArcScene function to create three dimensional figures based on MeHg and THg concentrations in biota. Catchments were extruded based on the MeHg or

THg concentration of the featured biota, allowing for spatial distribution patterns (*i.e.*, continental divide, latitudinal) to be easily identified. Spatial patterns of Hg in biota were identified statistically using Mann Whitney U-test (because of small sample sizes). MeHg concentrations of fishes were presented at a standardized fish age to eliminate the possible effect of increasing MeHg concentrations with increasing age. ANCOVAs were not utilized for standardization because there was no relationship between age and MeHg concentration in fishes within many lakes. If relationships between MeHg concentrations in fishes and age were significant, MeHg was adjusted for age using linear regression. Mean MeHg concentration in fishes were used when no significant relationship between age and MeHg concentrationship between age and MeHg concentrationship between age and MeHg concentrationship between age and MeHg concentration. Mean MeHg concentration in fishes were used when no significant relationship between age and MeHg concentration in fishes existed within lakes. Age was used because fish populations can grow slowly in high elevation lakes (Donald and Alger 1986), indicating that fish length may not be a reliable measure of exposure for fishes from mountain lakes.

#### Temporal trend assessment in fish MeHg concentration

Hg concentrations in lake trout collected from the same lake in different years were compared using ANCOVA, with THg as the dependent variable, year as the factor, and fish length as the covariate. If the assumption of homogeneity of slopes was not justified, ANCOVA was not used. Instead, THg concentrations of fishes over the same size range from each year were compared using a two sample t-test.

#### Results

### MeHg and THg Concentrations in Aquatic Biota Benthic invertebrate MeHg and THg concentrations

Concentrations of MeHg in benthic invertebrates from Rocky Mountain lakes varied widely (Table 3.3). Mean MeHg concentrations of Amphipoda, Trichoptera, Ephemeroptera and Diptera were lower than those of Odonata and Plecoptera (Table 3.3). When compared to MeHg concentrations of benthic invertebrates from the literature (Appendix 7), mean MeHg concentrations of benthic invertebrates from Rocky Mountain lakes were generally at the lower end of the range.

THg concentrations in benthic invertebrates were variable, and exhibited the same trend among taxa as MeHg concentrations (Table 3.3). Mean THg concentrations of benthic invertebrates were within range or slightly lower than other published values (Appendix 7). The percent MeHg (percentage of THg that is MeHg) was variable among and within taxa (Odonata:  $\bar{x} = 57.337\% \pm 6.770$  SE (range=27.354 – 94.531%), Plecoptera:  $\bar{x} = 45.954\% \pm 5.576$  SE (range=18.265 – 64.257%), Trichoptera:  $\bar{x} = 30.315\% \pm 5.656$  SE (range=4.724 – 73.762%), Ephemeroptera:  $\bar{x} = 22.508\% \pm 4.232$  SE (range=4.929 – 40.153%), Amphipoda:  $\bar{x} = 34.546\% \pm 5.451$  SE (range=7.256 – 99.079%)).

MeHg and THg concentrations and percent MeHg in Odonata and Amphipoda did not differ seasonally between spring and late summer/early fall (Odonata: MeHg Z=0.944, p=0.345, THg Z=-0.943, p=0.345, %MeHg Z=0.947, p=0.345, Amphipoda: MeHg Z=-0.700, p=0.484, THg Z=-0.415, p=0.678, %MeHg Z=0.140, p=0.889). Paired samples of Ephemeroptera were available for three lakes, but the data were insufficient for statistical analysis using the Wilcoxon Signed Ranks test.

#### Zooplankton MeHg and THg concentrations

Zooplankton MeHg and THg concentrations varied throughout the study area (0.020 - 67.73 and 19.01 - 138.0 ng/g dw, respectively) (Table 3.3). Mean MeHg and THg concentrations of zooplankton from Rocky Mountain lakes were at the low end of the range of values reported in the literature (Appendix 8). Percent MeHg in zooplankton ranged from 0.042 - 93.526% within this study, with a mean of  $33.102\% \pm 3.498$  SE.

Spring MeHg concentrations in zooplankton were significantly lower than late summer/early fall MeHg concentrations (*Z*=-2.272, *p*=0.023, spring  $\bar{x}$  =15.391 ng/g dw, late summer/early fall  $\bar{x}$  =24.580 ng/g dw). THg concentrations in zooplankton exhibited the same trend as MeHg concentrations (*Z*=-2.934, *p*=0.003, spring  $\bar{x}$  =36.888 ng/g dw, late summer/early fall  $\bar{x}$  = 68.095 ng/g dw). No seasonal difference in percent MeHg of zooplankton was detected (*Z*=0.178, *p*=0.859).

#### Fish MeHg concentrations

MeHg concentrations of the 12 fish species collected ranged from 0.006  $\mu$ g/g ww in white sucker to 1.563  $\mu$ g/g ww in lake trout (Table 3.4). Brook trout, cutthroat trout, bull trout, mountain whitefish, white sucker and torrent sculpin had lower MeHg concentrations than brook stickleback, lake chub, longnose sucker, cisco, rainbow trout and lake trout (Table 3.4).

#### Human Health Risk Assessment

MeHg concentrations in some fishes collected from lakes within the Canadian Rocky Mountains were greater than Health Canada's commercial consumption guideline of 0.5 µg/g ww, Health Canada's frequent consumption guideline of 0.2 µg/g ww, and the USEPA federal human health screening value of 0.3 µg/g ww. Of the 12 fish species collected, only cutthroat trout, mountain whitefish, white sucker and torrent sculpin were without individuals that exceeded at least one of the guidelines or screening value (Table 3.5). However, only the mean MeHg concentrations of cisco (0.395  $\pm$  0.041 µg/g ww) and lake trout (0.201  $\pm$  0.013 µg/g ww) were over the guidelines or screening value.

Health Canada and the USEPA use calculated risk assessments to assess noncommercial or recreational fisheries. Comparison of the calculated maximum allowable fish consumption rate to realistic human consumption rates indicate that all age groups of both males and females would be at risk of exceeding their TDI by consuming fishes from some lakes in the study area (Figure 3.2). Weekly and monthly allowable fish consumption rates (available in Appendix 3 and 4) indicate that humans who consume fish from some lakes on a regular basis are likely at increased risk of health effects from MeHg exposure through fish consumption.

#### Wildlife health risk assessment

Individual fish of all 12 species analysed contained THg concentrations greater than the Canadian Tissue Residue Guideline of 0.033  $\mu$ g/g ww MeHg.

Generally, over 85% of the THg in fishes is MeHg (Ullrich 2001), therefore wildife species consuming fishes from Canadian Rocky Mountain lakes are likely at risk. Comparison of maximum allowable fish consumption rates (calculated for several bird and mammal species) with consumption rates found in the literature revealed that wildlife consuming fishes from the lakes are at risk of exceeding their TDI (Figure 3.3 and 3.4). Hazard concentrations, calculated based on NOAEL and LOAEL (Figure 3.5 and 3.6), also indicate that the consumption of some fish species from mountain park lakes could impact the health of several wildlife species due to MeHg exposure.

# **Spatial patterns of MeHg and THg concentrations in aquatic biota** Effect of Altitude

Linear regressions indicated that MeHg and THg concentrations in benthic invertebrates from Rocky Mountain lakes did not increase with elevation (Odonata: p=0.302, Plecoptera: p=0.897, Ephemeroptera: p=0.732, Amphipoda: p=0.294). MeHg decreased with elevation in Trichoptera (elevation explained 40.1% of the variation in Trichoptera MeHg concentration, p=0.011) and zooplankton collected in late summer/early fall (elevation accounted for 29.2% of the variation in zooplankton MeHg, p=0.004). Spring zooplankton MeHg concentration were not related to altitude (p=0.128).

No significant relationship between THg concentration and altitude was identified for any of the invertebrate taxa studied (Odonata: p=0.143, Plecoptera: p=0.164, Trichoptera: p=0.693, Ephemeroptera: p=0.235, Amphipoda: p=0.307, late summer/early fall zooplankton: p=0.710, spring zooplankton: p=0.130). MeHg concentrations in fishes were also unrelated to lake elevation within the study area, as identified by linear regression (brook trout age 6: p=0.501, lake trout age 6: p=0.159, rainbow trout age 5: p=0.108, all trout p=0.065).

Percent MeHg in invertebrates was generally unrelated to altitude (Odonata: p=0.547, Plecoptera: p=0.243, Ephemeroptera: p=0.693, Amphipoda: p=0.392, spring zooplankton: p=0.188), with the exception of a negative relationship in Trichoptera

(elevation explained 41.1% of the variation in Trichoptera %MeHg, p=0.013) and late summer/early fall zooplankton (elevation accounted for 52.6% of the variation in zooplankton %MeHg, p=0.0001).

#### Effect of the Continental Divide

When lakes were separated for analysis based on the British Columbia – Alberta provincial boundary (*i.e.*, the continental divide) and MeHg, THg and percent MeHg in invertebrates were compared, few differences were revealed. Trichoptera from lakes in British Columbia contained more MeHg than those from Alberta lakes (U=3.0, p=0.030). In addition, zooplankton collected in late summer/early fall from Alberta lakes contained greater percent MeHg than zooplankton from lakes in British Columbia (U=21, p=0.022). Mann-Whitney U tests revealed no difference in fish MeHg concentrations between provinces (brook trout age 6: p=0.881, lake trout age 6: p=0.112, rainbow trout age 5: p=0.355, all trout p=0.465).

When linear regression was used to determine if MeHg, THg and percent MeHg in invertebrates was related to elevation by province, few significant relationships were identified. In Alberta lakes, MeHg concentrations in Trichoptera and zooplankton collected in spring and early summer/late fall were negatively related to altitude (Trichoptera: 35.4% or variation explained, p=0.041, spring zooplankton: 19.4% of variation accounted for, p=0.019, late summer/early fall zooplankton: 26.9% of variation explained, p=0.05). Percent MeHg in zooplankton was also negatively related to elevation in Alberta Rocky Mountain lakes (spring: 31.9% of variation accounted for, p=0.018, late summer/early fall: 57.7% of variation explained, p=0.0001). Comparison of MeHg concentrations in fishes from Alberta lakes with altitude revealed similar trends (rainbow trout: 51.6% of variation accounted for, p=0.037, all trout: 39.1% of variation explained, p=0.015). In lakes located in British Columbia, MeHg concentrations in zooplankton collected in late summer/early fall were negatively related to elevation sin zooplankton collected in late

explained, p=0.043). The same trend was evident in Trichoptera THg concentrations from British Columbian lakes (THg: 96.7% of variability accounted for, p=0.017).

#### *Effect of Latitude*

ESRI Arc Scene figures only reveal distributional patterns in MeHg and THg concentration of aquatic biota with latitude. MeHg concentrations of zooplankton collected in spring (Figure 3.7) and late summer/early fall increased with latitude. A similar trend was identified in MeHg concentrations of Trichoptera and Odonata, as well as THg concentrations in zooplankton, Trichoptera and Odonata. However, MeHg and THg concentrations varied or decreased with latitude in Amphipoda, Ephemeroptera and Plecoptera (Figure 3.8, MeHg). THg concentrations of MeHg in brook trout, rainbow trout, lake trout and all trout (Figure 3.9) increased with latitude throughout the study area.

Division of lakes by latitude into northern (Jasper National Park and Mount Robson Provincial Park) and southern (Banff National Park and Yoho National Park) regions and subsequent statistical comparison of MeHg, THg and percent MeHg revelealed some latitudinal differences. Zooplankton collected in spring and late summer/early fall contained more MeHg in northern lakes (spring: U=126, p=0.031, late summer/early fall: U=146, p=0.001). Percent MeHg in zooplankton collected in late summer/early fall and Trichopterans was also greater in the northern portion of the study area than in the south (U=33, p=0.066). This trend was also identified in fish MeHg concentrations (lake trout age 6 U=36, p=0.032, rainbow trout age 5 U=9, p=0.050, all trout U=89, p=0.007).

Few significant relationships were revealed when linear regression was used to determine if MeHg, THg and percent MeHg of invertebrates were related to elevation with latitude. In northern lakes, MeHg concentrations in Trichoptera were negatively related to altitude (Trichoptera: 70.1% of variability was explained, p=0.002). THg concentrations in Trichoptera and Amphipoda were negatively related to elevation in northern Rocky Mountain lakes (Trichoptera: 44.1% of variability was accounted for, p=0.036, Amphipoda: 64.4% of variation explained,

p=0.018). Percent MeHg in zooplankton collected during late summer/early fall in northern lakes was also negatively related to altitude (53.6% of variation accounted for, p=0.001). The same trend was evident in Amphipoda collected from southern lakes (61.4% or variation explained, p=0.037).

#### Temporal trend assessment of fish MeHg concentrations

MeHg concentrations in lake trout from Lake Minnewanka (Banff National Park) and Pyramid Lake (Jasper National Park) did not change significantly between 1991 and 2003 (Minnewanka - ANCOVA: F=2.908, p>0.05, Pyramid –two sample t-test (THg): t=-2.066, p>0.05, two sample t-test (fork length): t=-0.514, p>0.05). THg concentrations in lake trout collected from Bow Lake (Banff National Park) were also not significantly different when compared between 1991 and 1995 (ANCOVA: F=3.867, p>0.05).

#### Discussion

#### MeHg and THg Concentrations in Aquatic Biota

MeHg and THg concentrations of benthic invertebrate taxa and bulk zooplankton were generally at the lower end of the range of published values for freshwater lakes (Table 3.3, Appendix 7 and 8). However, MeHg and THg concentrations (see range Table 3.3) in invertebrates from some Rocky Mountain lakes were similar to those in geographic areas that likely receive greater atmospheric deposition of mercury from industrial sources. Within the study area, some lakes contained invertebrates of the same taxa with MeHg and THg concentrations and percent MeHg over one order of magnitude greater than other lakes. MeHg and THg concentrations and percent MeHg in Odonata and Amphipoda did not change seasonally. Similarly, MeHg and THg concentrations and percent MeHg in Odonata remained quite constant throughout the ice-free season in Lake Ritchie, Isle Royale National Park, USA (Gorski et al. 2003). However, MeHg and THg concentrations in Trichoptera and Ephemeroptera changed seasonally in Lake Ritchie (Gorski et al. 2003). Analysis at higher taxonomic resolution (*i.e.*, species or genera rather than Order, Sub-order, or Family) would be more costly, but would likely allow seasonal patterns to be more easily resolved by decreasing within-sample variability (*i.e.*, diet, habitat, etc.) that may affect MeHg and THg concentrations. Seasonal differences were identified in MeHg and THg concentrations (*i.e.*, lower in spring than in late summer/early fall) of bulk zooplankton, but no differences were revealed for percent MeHg. In Lake Superior, the opposite trend was identified for seasonal MeHg and THg concentrations of bulk zooplankton (Back et al. 2003). Among and within-lake variability of MeHg and THg concentrations and percent MeHg in some invertebrates from Rocky Mountain lakes may be due to many factors that affect Hg cycling and accumulation by aquatic organisms.

In the next chapter, we will identify factors that affect MeHg concentrations in trout from Rocky Mountain lakes. For example, positive relationships generally exist between fish MeHg concentrations and fish age, length or weight. MeHg concentrations are often standardized to a specific fish age, length or weight to allow for among lake comparison. The standardized age, length or weight usually varies by study, causing among- study comparisons of MeHg concentrations in fishes to be difficult. This is the basis for not including such comparisons within this chapter.

#### Human Health Risk Assessment

Comparison of fish MeHg concentrations to human health guidelines and calculated risk assessments indicate that MeHg concentrations in some fish species from some lakes pose a risk to human health. The MeHg concentrations in fishes determined for this study were provided to Parks Canada. Parks Canada, in conjunction with Health Canada, implemented consumption guidelines for several lakes within the Rocky Mountain National Parks, and consumption advice for all waterbodies in the Parks that contain fishes (Figure 3.10) (Parks Canada 2005). Information in Parks Canada fishing regulations indicate that children under 15 should limit consumption to three meals of 75 grams per month, and women of reproductive age should consume no more than four meals of 113 grams per month

(Parks Canada 2005). Consumers should compare the serving sizes that they actually eat to those used in guidelines, because consuming larger portions would increase risk. Serving size information from our study indicates that serving sizes usually exceed those used in the guidelines (i.e., average serving sizes of cooked fish may be closer to the following - children: 2-3 years- 57 g, 4-8 years- 91 g, 9-12 years-119 g, women: 140 g and men 176 g cooked). At Lake Minnewanka in Banff National Park, unpublished 2000 creel survey data (Pacas, Parks Canada) revealed that recreational fishers kept ~48% of fish they caught and guided fishers retained 21% of their catch. Generally, fishers kept 907 g (or 2 lb.) fish for later consumption (Pacas, Parks Canada). In addition, of the 108 day fishing season, there was evidence that some individuals fished 100 days. Although creel sensus data are not available for all Rocky Mountain Park lakes, the fishing pressure at Lake Minnewanka is likely exceptional. However, available creel census data, the operation of guiding companies in Jasper and Banff National Parks, and the presence of commercially and privately owned boats at some lakes suggest that people within the study area are fishing and likely consuming fishes that could pose a risk to their health.

#### Wildlife health risk assessment

Wildlife that feed on fishes while breeding on or near Rocky Mountain lakes are also at risk, based on comparison of fish MeHg concentration data from this study to the Canadian tissue residue guidelines and the results of calculated risk assessments. Wildlife species that are piscivorous generally consume fishes more consistently than humans, which substantially increases their risk. However, migratory birds that breed on mountain park lakes during summer months and over-winter elsewhere may be at lower risk if fishes at their wintering grounds contain less MeHg. The small body mass of the piscivorous offspring of these birds may increase their risk, particularly in areas where small forage fishes such as lake chub and brook stickleback contain high concentrations of MeHg. Some piscivorous wildlife, such as American Mink, consume fishes of a small size range (150-250 mm),

which were not particularly well represented in this study. Risk assessments for wildlife species that consume aquatic invertebrates rather than, or in addition to fishes are ongoing. Birds such as Prairie Falcons (*Falco mexicanus*), Peregrine Falcons (*Falco peregrinus*), Gyrfalcons (*Falco rusticolus*) and Great Horned Owls (*Bubo virginiansus*) that feed on shore birds or waterfowl within the study area (Fisher 1997) are likely at increased risk of accumulating high concentrations of mercury based due to biomagnification. Birds that prey upon flying insects that emerge from waterbodies in the study area may also be at risk (*e.g.*, Black Swift (*Cypseloides niger*), Tree Swallow (*Tachycineta bicolor*) and Marsh Wren (*Cistothorus palustris*)) (Fisher 1997).

# **Spatial patterns of MeHg and THg concentrations in aquatic biota** Effect of Altitude

Our results contrast the findings of studies of Hg in mosses, lichens (Evans and Hutchinson 1996) and fishes (Blais et al. 2006) in mountainous areas, and trace metals (Kock et al. 1995, Soltés 1992 and 1998, Zechmeister 1995) and OCs (reviewed by Daly and Wania 2005) in a variety of media from other mountain ranges and the Canadian Rockies. MeHg concentrations in aquatic invertebrates and fishes and THg concentrations and percent MeHg of aquatic invertebrates were not positively related to elevation in our lakes. In fact, MeHg concentrations and percent MeHg of some invertebrates (e.g., Trichoptera, zooplankton collected in late summer/early fall) were related negatively to altitude. There are several possible explanations for among-study differences in results. The majority of Hg in soils and Hg deposited from the atmosphere to the landscape is in the form of ionic Hg<sup>2+</sup> (Grigal 2002, 2003), which must be chemically transformed to neurotoxic and bioaccumulative MeHg before biomagnifying in aquatic food webs. Many trace metals and OCs are toxic and bioaccumulative in their deposited form, and are deposited in greater quantities at higher elevations. Conditions for methylation of  $Hg^{2+}$  are not ideal at high elevations (e.g., low water temperatures, low DOC), and even if Hg<sup>2+</sup> is deposited in greater amounts at higher altitudes, ultra-violet (UV)-mediated photo-reduction of

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deposited Hg<sup>2+</sup> could re-volatilize Hg<sup>0</sup> to the atmosphere (Amyot et al. 2003, Lalonde et al. 2003). Also, photodegradation of MeHg in water is likely increased in high elevation mountain lakes (Sellers et al. 1996, Hammerschmidt et al. 2006, 2006b). Krabbenhoft et al. (2002) found low concentrations of MeHg in water from high altitude mountain lakes, which was attributed to photo-demethylation. Lower elevation lakes are likely exposed to better conditions for in-lake methylation for a longer period of time than high elevation lakes, due to longer ice-free seasons. This could explain the negative relationships between elevation and MeHg concentrations in some aquatic invertebrate taxa from Rocky Mountain lakes.

#### Effect of Continental Divide

Decreased methylation rates and increased photo-reduction in high elevation lakes could also explain the lack of effect from the continental divide. Although Trichoptera from British Columbian lakes contained greater concentrations of MeHg than those in Alberta lakes (as expected due to increased precipitation west of the continental divide), this relationship did not exist for any other taxon. Negative relationships between elevation and MeHg and THg concentration or percent MeHg in aquatic biota were amplified when provincial subsets of the data were analysed.

#### Effect of Latitude

Latitudinal trends in MeHg and THg concentrations and percent MeHg of aquatic biota were evident within the study area. Other studies have identified positive relationships between MeHg concentrations in fishes and latitude over a larger geographic scale (McMurty et al. 1989). Many factors could be responsible for the latitudinal patterns identified, including climate, geology and rate of atmospheric deposition. The reasons for these patterns will be explored in Chapter 4.

#### Temporal trend assessment in fish MeHg concentration

The lack of temporal trend in MeHg concentrations of fishes in Rocky Mountain Park lakes was similar to findings in the Canadian arctic (Evans et al. 2005b), Lake Ontario (French et al. 2006), and San Francisco Bay (Greenfield et al. 2005). Lack of long-term decreases in fish MeHg concentrations is likely because Hg bioavailability is related to watershed loading, contaminated sediment exposure and net methylation rates (Greenfield et al. 2005). Results of a Hg isotope study indicate that declines in Hg loading will lead to decreases in MeHg concentrations in fishes and other biota, but not for 10-30 years (Paterson et al. 2006). However, in the Rocky Mountain National Parks, climate warming is causing glacial melt which is likely a source of legacy pollutants, and conditions for in-lake Hg methylation may improve with climate warming (Evans et al. 2005). Glacial melt could conversely decrease Hg methylation potential by causing lakes to become colder, more turbid and less Furthermore, climate change is expected to increase forest fire productive. occurrence in mountainous areas of western North America (Weber and Stocks 1998, Westerling et al. 2006), which will likely lead to increases MeHg accumulation by fishes (Kelly et al. 2006, Chapter 5). Baseline and long-term data sets, such as the data from this chapter and Chapter 4, will be necessary for monitoring and determining the effects of climate change on Hg accumulation by fishes.

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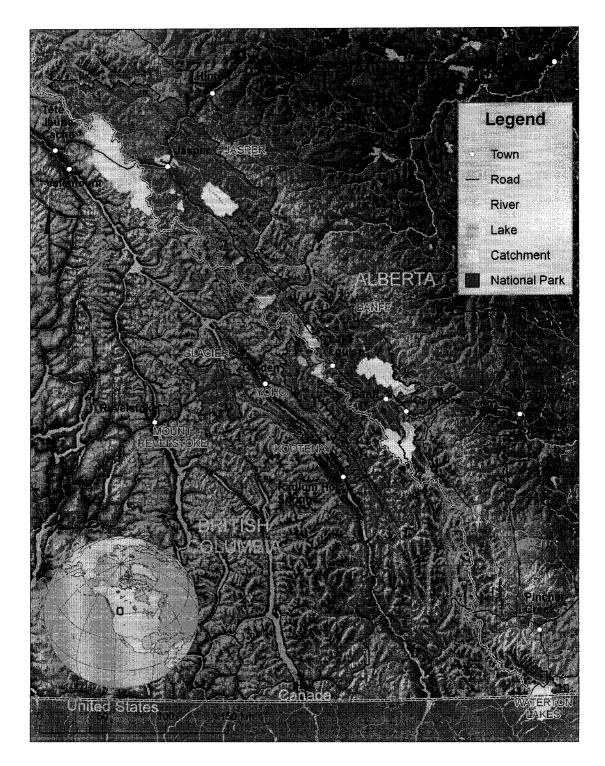
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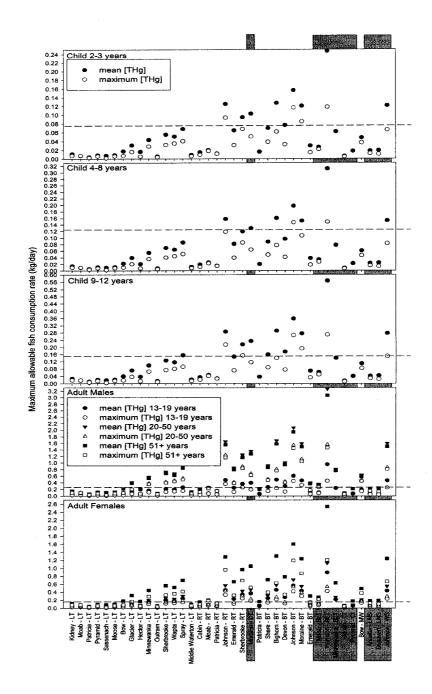
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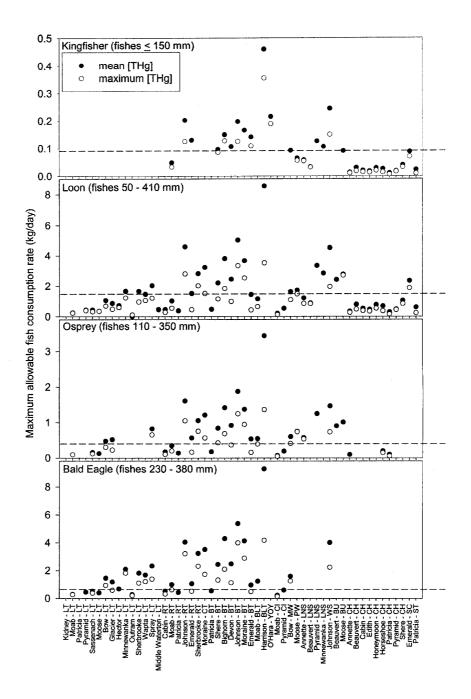
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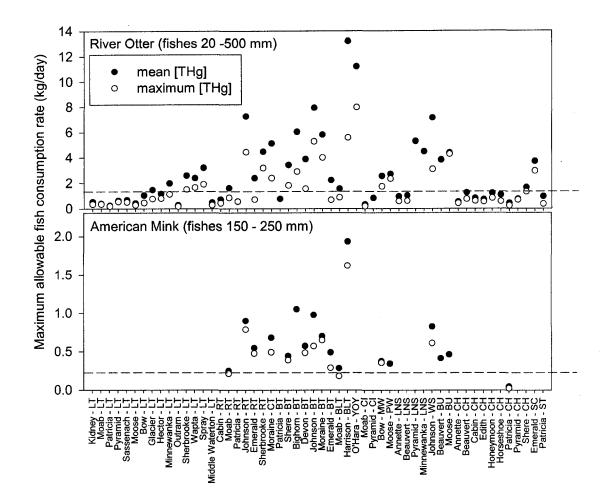
**Figure 3.1** Map of the study area. Fish and invertebrates analysed for Hg were collected from lakes in or near Canadian Rocky Mountain parks (Jasper, Banff, Yoho and Waterton National Parks, Mount Robson Provincial Park, Spray Valley Provincial Park, Shere Lake (near Tête Jaune Cache, BC), and Little Cranberry Lake (near Valemount, BC)) in Alberta and British Columbia, Canada.



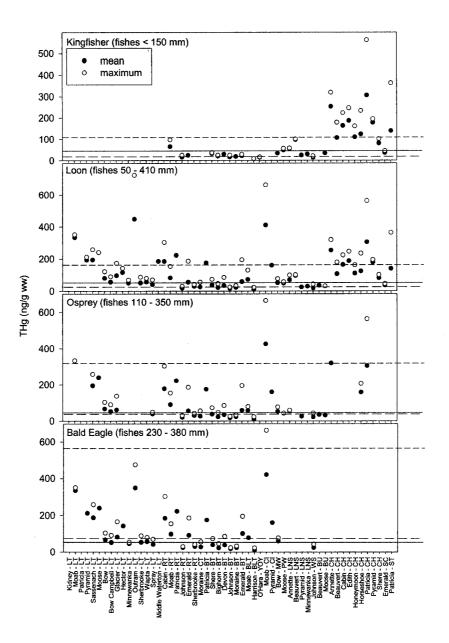
**Figure 3.2** Human Health Risk Assessment. To assess human health risk, maximum allowable fish consumption rate based on tolerable daily intakes (TDIs) was compared to dashed lines which represent average serving sizes. LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, CI=cisco, MW=mountain whitefish, LNS= longnose sucker, WS=white sucker. Grey vertical boxes indicate fishes that are not allowed to be kept based on Mountain Park fishing regulations.



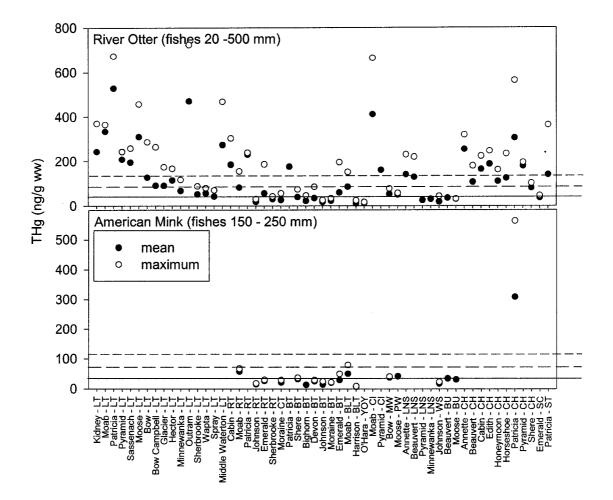
**Figure 3.3** Avian Wildlife Health Risk Assessment. To assess wildlife health risk, the maximum allowable fish consumption rate based on tolerable daily intakes (TDIs) was compared to dashed lines which represent consumption rates. LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, YOY= young of year trout, CI=cisco, MW=mountain whitefish, PW= pygmy whitefish, LNS= longnose sucker, WS=white sucker, BU=burbot, CH= lake chub, SC=torrent sculpin, ST=brook stickleback.



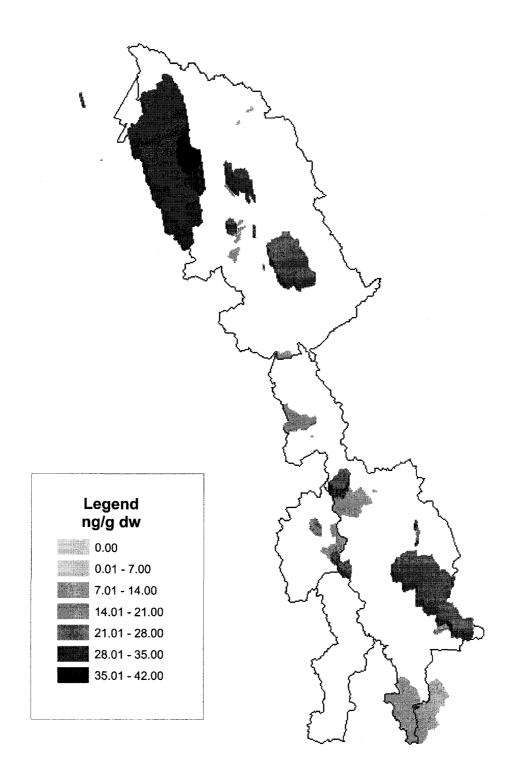
**Figure 3.4** Mammalian Wildlife Health Risk Assessment. To assess wildlife health risk, the maximum allowable fish consumption rate based on tolerable daily intakes (TDIs) was compared to dashed lines which represent consumption rates. LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, YOY= young of year trout, CI=cisco, MW=mountain whitefish, PW= pygmy whitefish, LNS= longnose sucker, WS=white sucker, BU=burbot, CH= lake chub, SC=torrent sculpin, ST=brook stickleback.



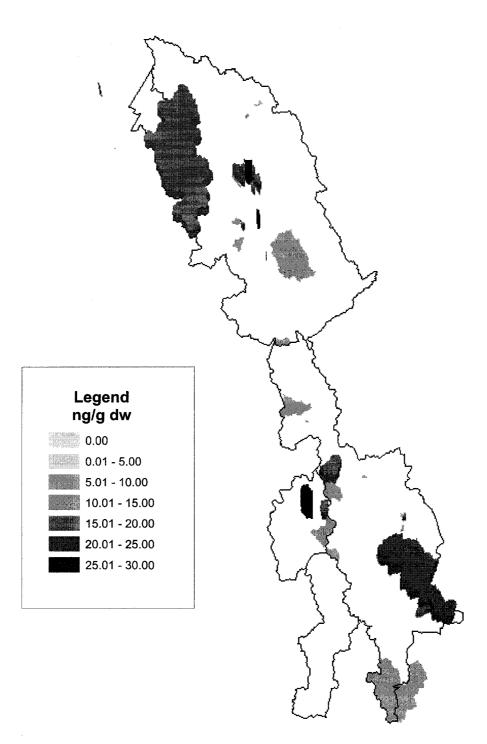
**Figure 3.5** Avian Wildlife Health Risk Assessment II. To assess wildlife health risk, THg concentrations in fishes were compared to the Canadian Tissue Residue Guideline of 33 ng/g ww (solid line), and calculated NOAEL and LOAEL) hazard concentrations (HC) (NOAEL HC= upper large dashed line, LOAEL HC=lower small dashed line). LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, YOY= young of year trout, CI=cisco, MW=mountain whitefish, PW= pygmy whitefish, LNS= longnose sucker, WS=white sucker, BU=burbot, CH= lake chub, SC=torrent sculpin, ST=brook stickleback. THg = MeHg.



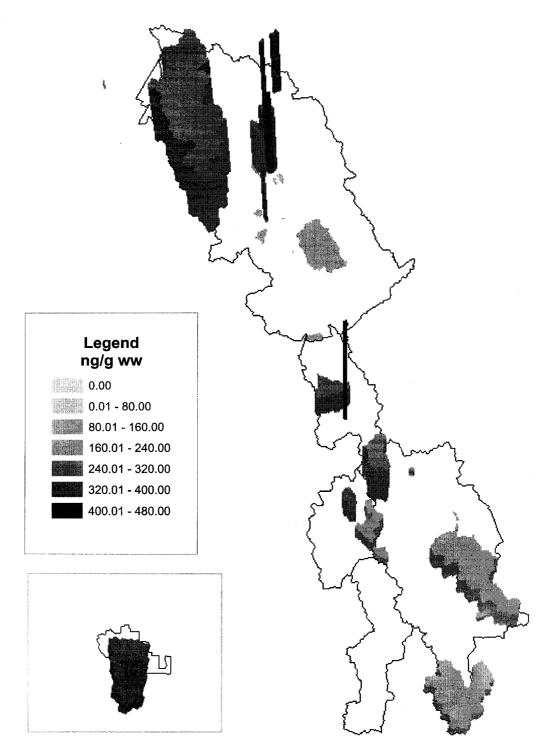
**Figure 3.6** Mammalian Wildlife Health Risk Assessment II. To assess wildlife health risk, THg concentrations in fishes were compared to the Canadian Tissue Residue Guideline of 33 ng/g ww (solid line), and calculated NOAEL and LOAEL) hazard concentrations (HC) (NOAEL HC= upper large dashed line, LOAEL HC=lower small dashed line). LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, YOY= young of year trout, CI=cisco, MW=mountain whitefish, PW= pygmy whitefish, LNS= longnose sucker, WS=white sucker, BU=burbot, CH= lake chub, SC=torrent sculpin, ST=brook stickleback. THg=MeHg.



**Figure 3.7** ESRI Arc Scene images of MeHg concentrations in zooplankton (ng/g dw) collected in spring throughout the study area. Figure 3.1 provides the names of depicted national parks.



**Figure 3.8** ESRI Arc Scene images of MeHg concentrations in Amphipoda (ng/g dw) collected from lakes throughout the study area. Figure 3.1 provides the names of depicted national parks.



**Figure 3.9** ESRI Arc Scene images of MeHg concentrations in trout (ng/g dw) collected from lakes throughout the study area. Figure 3.1 provides the names of depicted national parks. Inset is Waterton Lakes National Park, which is located south of the main study area.

#### Fish Consumption Advisory (Mercury) Mountain Parks

Parks Canada has been advised that elevated mercury concentrations have been found in fish in some Mountain National Park waters. Therefore, Parks Canada, in consultation with Health Canada, has established consumption guidelines for women of reproductive age and children (see table one).

Mercury in the parks can come from natural sources (e.g. soils and sediments) or sources outside the Mountain Parks (e.g. transported through the atmosphere). It can be passed up the food chain and become concentrated in top predators (e.g. Lake trout, Northern pike). Mercury is a toxin that can affect human health, which is why Health Canada has developed fish consumption guidelines based on the mercury concentration of fish tissue.

Mercury data does not exist for all fish species in all park waters and fish mercury concentrations may change over time. To be precautionary, anglers may wish to apply the following guidelines to all sport fish caught in park waters (see table two).

#### Table 1: Consumption guidelines

		Women of re- productive age	Children (under 15yrs)
Lake	Species	# of 113 g (4 oz.) servings**	# of 70 g (2.5 oz.) servings**
Moab - JNP	Cisco*	7/month	5/month
Patricia -JNP	Lake Trout	4/month	3/month
Sassenach - JNP	Lake Trout	4/month	3/month
Bow - BNP	Lake Trout	4/month	3/month
Hector - BNP	Lake Trout	4/month	3/month
Outram - BNP	Lake Trout	4/month	3/month

# Table 2: Precautionary consumption advice for game fish in waters not mentioned above

	Women of reproductive age	Children (under 15yrs)
Species	# of 118 g (4 oz.) servings**	# of 70g (2.5 oz.) servings**
Game fish - general	4/month	3/month

\* Please note that consumption advice has been given for a species which is not legal to possess. Anglers should check the Catch & Possession Limits of these Fishing Regulations to ensure that all fish which are kept are legal to possess. Cisco closely resemble mountain whitefish; there are no Mountain whitefish in Moab Lake.

\*\* A 100g serving is approximately the size of a deck of standard playing cards.

**Figure 3.10** Mercury consumption guidelines and precautionary consumption advice provided in Parks Canada Mountain Park Fishing Regulations (http://www.pc.gc.ca/pn-np/ab/banff/visit/visit14b\_E.asp), as a result of this study.

# Table 3.1Source lakes of the fishes included in this study (University of Alberta:<br/>Kelly 2001 and Parker 1997, Environment Canada: Donald 1990s,<br/>Parks Canada: Hughson 2003, Pacas 2001, 2002, 2003)

Species	Kelly 2001	Parker 1997	Donald 1990s	Hughson 2003	Pacas 2001, 2002, 2003
Lake Trout (Salvelinus namaycush)	Moab, Patricia		Bow, Glacier, Hector, Kidney, Middle Waterton, Minnewanka, Moose, Outram, Pyramid, Sassenach, Sherbrooke, Spray, Wapta	Moab, Pyramid	Minnewanka
Rainbow Trout (Oncorhynchus mykiss)	Emerald, Johnson, Patricia, Sherbrooke		Cabin,	Moab	
Cutthroat Trout (Oncorhynchus clarki)	Moraine				
Brook Trout (Salvelinus fontinalis)	Emerald, Johnson, Moraine, Patricia, Shere	Bighorn			Devon
Bull Trout (Salvelinus confluentus)	Harrison, Moab			Moab	Minnewanka
YOY Trout	O'Hara				
Cisco (Coregonus artedi)				Moab, Pyramid	
Mountain Whitefish (Prosopium williamsoni)			Bow		
Pygmy Whitefish (Prosopium coulteri)	Moose				
Longnose Sucker (Catostomus catostomus)	Minnewanka, Pyramid		Annette, Beauvert		
White Sucker (Catostomus commersoni)	Johnson				
Burbot (Lota lota)	Moose				
Lake Chub ( <i>Couesius</i> plumbeus)	Annette, Beauvert, Cabin, Edith, Honeymoon, Horseshoe, Patricia, Pyramid, Shere				
Torrent Sculpin (Cottus rhotheus)	Emerald				
Brook Stickleback (Culaea inconstans)	Patricia				

Mammals	Birds	Reptiles
American Mink	Common Loon	Western Terrestrial
Northern River Otter	Pied-billed Grebe	(Wandering) Garter Snake
Common Muskrat	Red-necked Grebe	Common (Red-sided) Garter
Common Water Shrew	American Bittern	Snake
Black Bear	Great Blue Heron	
Grizzly Bear	Gadwall	
	Mallard	
	Blue-winged Teal	
	Northern Shoveler	
	Green-winged Teal	
	Canvasback	
	Ring-necked Duck	
	Lesser Scaup	
	Harlequin Duck	
	Bufflehead	
	Barrow's Goldeneye	
	Hooded Merganser	
	Ũ	
	Common Merganser	
	Osprey Bold Eagle	
	Bald Eagle Sora	
	American Coot	
	Sandhill Crane	
	Solitary Sandpiper	
	Spotted Sandpiper	
	Wilson's Snipe	
	Ring-billed Gull	
	California Gull	
	Black Tern	
	Great Horned Owl	
	Belted Kingfisher	
	American Dipper	
	Northern Waterthrush	
	Yellow-headed Blackbird	

# Table 3.2Mammal, bird and reptile species that breed within the study area and<br/>consume aquatic invertebrates and fishes

	n	MeHg (ng/g dw)		THg (ng/g dw)	
		range	Mean + SE	range	Mean + SE
Odonata	15	8.213 - 80.85	35.52 + 7.380	21.95 - 159.5	60.95 + 13.24
Plecoptera	9	7.326 - 51.29	31.62 + 5.324	40.57 - 92.66	67.77 + 7.555
Diptera	4	4.184 - 26.94	12.60 + 7.208		
Trichoptera	14	2.910 - 44.98	11.91 + 2.948	13.47 - 63.06	42.00 + 4.341
Ephemeroptera	9	1.628 - 33.41	12.51 + 3.884	17.64 - 77.18	43.71 + 7.644
Amphipoda	24	1.012 - 27.45	11.79 + 1.636	13.92 - 58.18	40.12 + 3.510
Zooplankton	44	0.020 - 67.73	19.10 + 3.201	19.01 - 138.0	61.74 + 5.992

Table 3.3MeHg and THg (range and mean) concentrations of invertebrates<br/>from Canadian Rocky Mountain lakes in dry weight

Species	n	MeHg (µg/g ww) range	MeHg (µg/g ww) mean + SE
cisco	16	0.160 - 0.663	0.395 + 0.041
lake trout	208	0.028 - 1.563	0.201 + 0.013
lake chub	124	0.015 - 0.563	0.152 + 0.009
brook stickleback	10	0.030 - 0.363	0.134 + 0.032
longnose sucker	26	0.025 - 0.267	0.132 + 0.013
rainbow trout	55	0.011 - 0.303	0.082 + 0.010
mountain whitefish	9	0.033 - 0.077	0.052 + 0.006
brook trout	155	0.009 - 0.195	0.035 + 0.002
torrent sculpin	14	0.012 - 0.045	0.028 + 0.003
cutthroat trout	26	0.015 - 0.056	0.026 + 0.002
bull trout	40	0.003 - 0.152	0.024 + 0.005
white sucker	43	0.006 - 0.043	0.019 + 0.001

<u>Table 3.4</u>	MeHg (range and mean) concentrations of fishes from Canadian
	Rocky Mountain lakes in wet weight

<u>Table 3.5</u>	Changes in MeHg concentrations of lake trout from Canadian Rocky
	Mountain lakes over time

Lake	Time period	Trend	Statistic
Lake Minnewanka	1991 - 2003	no change	ANCOVA F=2.908, p>0.05
Bow Lake	1991 – 1995	no change	ANCOVA F=3.867, p>0.05
Pyramid Lake	1991 – 2003	no change	Two-sample t-test Fork length t=-0.514, p>0.05, THg t=-2.066, p>0.05

# 4.0 Factors that affect total mercury (as MeHg) concentrations in trout from lakes in the Canadian Rocky Mountain National Parks

# Introduction

Total mercury (THg) (as methyl mercury (MeHg)) concentrations in fishes increase with latitude in lakes of the Canadian Rocky Mountain Parks (Chapter 3). Generally, THg concentrations in fishes are considered to be equivalent to MeHg concentrations because the majority of THg in fishes is in the methylated form (Ullrich et al. 2001). Concentrations of MeHg in fishes from numerous lakes are a risk to the health of human and wildlife consumers (Chapter 3). We investigated factors that affect MeHg accumulation in fishes to determine those responsible for the variability in MeHg concentrations in trout (*i.e.*, Lake Trout (*Salvelinus fontinalis*), Rainbow Trout (*Onchorhynchus mykiss*), Cutthroat Trout (*Onchorhynchus clarki*), Brook Trout (*Salvelinus fontinalis*), Bull Trout (*Salvelinus confluentus*)) among lakes in the Canadian Rocky Mountain Parks. We then created a statistical model to predict MeHg concentrations in trout species from all fish-bearing lakes in the Rocky Mountain National Parks.

Many factors can lead to among-lake variability in MeHg concentrations of fishes, including those that affect processes within the Hg cycle. For example, factors can affect sources of Hg to a catchment or lake and transport of Hg from a catchment to a lake. Within lakes, factors can affect in-lake MeHg production and MeHg biomagnification and bioaccumulation within aquatic food chains (reviewed in Kelly et al. 2006). Sources of Hg to a catchment or waterbody can include atmospheric deposition (Swain et al. 1992) and catchment geology (Vaidya and Howell 2002). Climate can influence both contaminant deposition and rates of rock weathering. For example, the cold condensation effect (*i.e.*, evaporation of volatile chemicals in warm areas and deposition in cold regions) has been hypothesized to cause increased concentrations of Hg at high latitudes and altitudes far from point sources (Mackay et al. 1995). Generally, the quantity of Hg deposited to the 97

landscape is related negatively to temperature and positively to precipitation volume (Mackay et al. 1995). However, ultra-violet (UV)-mediated photo-reduction of ionic Hg<sup>2+</sup> and revolatilization to the atmosphere (Amyot et al. 2003, Lalonde et al. 2003) may decrease quantities of Hg deposited.

Within catchments, soil and vegetation type (Shanley et al. 2005), slope (Dennis et al. 2005), aspect (Grigal 2002), lake area (Bodaly et al. 1993), catchment area (Hakanson et al. 1988, Stemberger and Chen 1998) and the catchment area to lake area ratio (Vaidya and Howell 2002) can affect Hg transport to a lake. Ecoregions, or grouped physiogeographic variables (*e.g.*, topography, geology, soil type and land use), have also explained some variability in the MeHg concentration of fishes (Allen-Gil et al. 1995). Precipitation events that generate runoff are important for transportation of MeHg and ionic  $Hg^{2+}$  from catchments to lakes (Balogh et al. 1997, Lawson and Mason 2001). These events can cause seasonal flooding which mobilizes Hg stored in areas of normally dry land (Balogh et al. 2006, Belger and Forsberg 2006).

Within lakes, increases in water temperature, dissolved organic carbon (DOC) and sulphate ( $SO_4^{2-}$ ), and declines in pH can increase in-lake Hg methylation (Ullrich et al. 2001). Salinity (Ullrich et al. 2001), alkalinity (Hakanson et al. 1988), calcium, magnesium and conductivity (Allard and Stokes 1989) have also been related to Hg accumulation by fishes. In-lake photodegradation of MeHg to Hg<sup>0</sup> can release Hg from a lake back to the atmosphere (Sellers et al. 1996, Hammerschmidt et al. 2006), decreasing the quantity of MeHg available for bioaccumulation and biomagnification.

The concentrations of MeHg and THg in water (Fitzgerald and Clarkson 1991, Paterson et al. 1998) and MeHg in prey of aquatic organisms (Mathers and Johansen 1985, Hall et al. 1997) can influence MeHg bioaccumulation and biomagnification. Increased lake productivity can reduce Hg biomagnification (Kidd et al. 1999, Essington and Houser 2003) by means of biomass (Chen and Folt 2005, Pickhardt et al. 2005) and growth dilution (Simoneau et al. 2005). This causes fishes in nutrient-enriched lakes to have lower concentrations of Hg than fishes from

reference lakes (*i.e.*, Essington and Houser 2003), although food chains are the same length. Thus, zooplankton density and biomass are negatively related to MeHg accumulation by fishes (Stemberger and Chen 1998, Pickhard et al. 2002). Conversely, increased MeHg bioaccumulation may occur because of increases in food chain length (MeHg is positively correlated with nitrogen stable isotope ratio;  $\delta^{15}$ N) (Cabana and Rasmussen 1994, Kidd et al. 1995). MeHg accumulation in fishes is inversely related to  $\delta^{13}$ C (Power et al. 2002) and condition of fishes (Scott and Armstrong 1972, Suns and Hitchins 1990), and positively related to fish age (MacCrimmon et al. 1983, Grieb 1990), length (Grieb 1990) and weight (Wren et al. 1983).

Lakes within mountainous areas, such as the Canadian Rockies, are ideal for studying factors that affect the accumulation of MeHg in fishes because mountains provide steep environmental gradients (Daly and Wania 2005). For example, mountain meteorology, such as colder temperatures and greater precipitation volume, can enhance contaminant deposition at high elevations (Blais et al. 1998, Daly and Wania 2005). Catchment characteristics (*e.g.*, vegetation and soils) change with altitude and can affect transport of nutrients and other compounds, resulting in water chemistry (*e.g.*, pH, alkalinity, conductivity, total phosphorus and total nitrogen) gradients with elevation (Larson et al. 1999). Lake productivity (Schindler 1990), species richness (Schindler 1990) and the growth rate of aquatic biota (Donald et al. 1980, Daly and Wania 2005) decrease with altitude. This, in conjunction with longer life-cycles (Donald and Alger 1986) and slower metabolism and excretion of contaminants (Daly and Wania 2005), should enhance Hg concentrations in aquatic biota from high elevation lakes.

Alternatively, some characteristics of mountain lakes could limit MeHg accumulation by aquatic biota. UV radiation increases with elevation (Blumthaller and Ambach 1990, 1992, 1997) and may be responsible for high rates of photo-reduction of ionic Hg<sup>2+</sup> in high altitude lakes (Krabbenhoft et al. 2002). Furthermore, mountain lake food chains tend to be short, which can restrict contaminant biomagnification (Campbell et al. 2000, Daly and Wania 2005). Rognerud et al.

(2002) found that high altitude lakes in Europe contained fishes with low Hg concentrations. They attributed this to low sediment fluxes of Hg, low net production of MeHg, and short food chains. Methylation rates in high altitude lakes likely are low because of decreased water temperatures, low DOC concentrations and decreased organic matter content of sediments (Rognerud et al. 2002). Demethylation of MeHg could be favoured because of high transparency and low temperatures of alpine lake water (Rognerud et al. 2002). Our study determined which factors were important for accumulation of MeHg by fishes from Rocky Mountain lakes.

It would be cost, time and logistically prohibitive to identify all Mountain Park lakes (other than those sampled) that contain fishes with elevated concentrations of MeHg (*i.e.*, 319 lakes in the parks contain fishes). Our predictive model distinguished which lakes should be a priority for sampling to verify the model and predicted MeHg contamination in fishes. Fishing pressure data provided by Parks Canada allowed for the identification of lakes where consumption of fishes could pose a risk to human health. Therefore, our predictive model should aid Parks Canada with fisheries management in Mountain Parks.

### Methods

# Study Area

Study lakes were located in Jasper, Banff, and Yoho National Parks in the Rocky Mountains of Alberta and British Columbia, Canada (Figure 4.1A and B). Selected characteristics of study lakes (*i.e.*, longitude, latitude, elevation, catchment area, lake area, mean depth, maximum depth and water chemistry parameters) are presented in Appendix 1.

#### Field Sampling

Lakes were sampled in late summer/early fall 2000 and spring 2001. At each lake, surface water temperature and Secchi depth were recorded. Water samples

were collected for THg, MeHg (using ultra-clean sampling protocol (St. Louis et al. 1996)) and water chemistry. A 140 µm mesh net was hauled vertically through the water column to capture zooplankton. Animals were preserved in formalin for enumeration and frozen for Hg analyses. An Ekman dredge was used to collect sphaeriid clams. Fishes were collected using gillnets in the 1990s and early 2000s (see chapter 3 Methods). Specimens were identified, measured, weighed and frozen. Benthic macroinvertebrates were collected near-shore by using sweep nets and weighted mesh colonization traps. Invertebrates were sorted, rinsed, and frozen.

Epilimnetic surface water samples were processed within one hour of collection. THg water samples were acidified with concentrated trace metal-grade HCl equivalent to 0.2% of the sample volume. MeHg water samples were frozen. Unfiltered water for alkalinity, pH, conductivity, ammonia  $(NH_4^+)$ , nitrite + nitrate  $(NO_2^{-2} + NO_3^-)$ , total phosphorus (TP), turbidity and silica  $(SiO_2)$  was kept cool until analysis. Water was filtered prior to analysis for anions (sulfate  $(SO_4^{2-})$ , chloride (Cl-)), cations (sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>)), dissolved organic carbon (DOC), colour (abs 350), total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP). Chlorophyll *a* and particulates (for CHN) were collected on Whatman (Maidstone, England) GF/F filters and frozen.

Snow samples were collected from a subset of 19 accessible lakes in February 2001. Sampling sites were chosen far from each lake's shoreline. A plastic shovel was used to dig a pit that exposed the snowpack from its surface to lake ice. The layer of snow that was in contact with the shovel was removed using an acid-washed Teflon scraper. An acid-washed Teflon knife and scoop were used to transfer an integrated sample of the snowpack into acid-washed 2L Teflon jars. Samples remained frozen until analysis. Near each pit, five snow cores were obtained. The depth and weight of the cores were measured for determination of snow density and snow water equivalents (to convert THg and MeHg concentrations to areal deposition).

# Laboratory

Water analyses were completed at the University of Alberta Limnology Services Unit (http://www.biology.ualberta.ca/facilities/limnology/). Benthic macroinvertebrates were grouped by Order (Clifford 1991). Zooplankton were identified to copepod Order and cladoceran Family (Edmondson 1959), and enumerated to determine community structure. A stereomicroscope was used to measure zooplankton, and zooplankton biomass was calculated using length-weight regressions (McCauley 1984). Wet weight zooplankton biomass was also determined. Fishes were aged by using otoliths. Growth rates were determined by dividing fish age by length or growth and condition factor (K) was calculated as:

$$K = \frac{W \times 10^5}{L^3}$$

where W=weight (g), L=length (mm) and 10<sup>5</sup> is a scaling factor applied to bring K close to 1 (Barnham and Baxter 1998, Nash et al. 2006). Fish stomach contents were identified. Invertebrate and fish muscle samples were freeze-dried for 48 hours. Freeze-dried samples were powdered using an acid-washed glass mortar and pestle.

Hg analyses were conducted at the University of Alberta Low-Level Mercury Analytical Laboratory (http://www.biology.ualberta.ca/facilities/mercury/). THg in unfiltered water was determined by BrCl oxidation, SnCl<sub>2</sub> reduction, purge and trap, and cold vapour atomic fluorescence spectrometry (CVAFS) (modified (USEPA 1996, Olson et al. 1997)). The analytical detection limit was 0.05 ng/L. For MeHg in unfiltered water, samples were distilled and ethylated, followed by gas chromatography separation with CVAFS (Horvat et al. 1993, Olson et al. 1997). The detection limit was 0.02 ng/L. Snow samples were melted in the laboratory, and analysed as water. Fishes and freeze-dried invertebrates were digested with 7:3 HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> in closed Teflon bombs and analyzed for THg the same as water samples. Detection limits were 0.1-0.3 ng/g. For MeHg, zooplankton and macroinvertebrates were digested in a KOH-methanol solution, ethylated, and separated by gas chromatography with CVAFS. Detection limits were 0.1-0.3 ng/g dry weight. All Hg analyses included spike recoveries, duplicates, blanks and 102

National Research Council (Canada) certified reference materials (DORM-2), which were prepared alongside the original samples as matrix-matched biomaterial.

Freeze-dried fish tissue was analysed for a suite of trace elements by ICP-MS at the National Laboratory for Environmental Testing (NLET) in Burlington, Ontario, Canada.

Freeze-dried fish tissue was analysed for stable isotopes at the University of Ottawa G.G. Hatch Isotope Laboratories. Samples were weighed in tin capsules ~0.3-0.5 mg) and combusted in an automated elemental analyzer (CE Elantech Inc., Lakewood, NJ) CE-1110 coupled to a Finnigan Mat Delta<sup>PLUS</sup> Isotope Ratio mass spectrometer; (Thermo Scientific, Waltham, MA) with a Conflow III interface. Water was removed by magnesium perchlorate trap. Helium was the carrier gas. Stable isotopes are expressed in "delta" notation ( $\delta$ ):

 $\delta R \% = [(R_{sample}/R_{standard})-1] \times 1000$ 

where R=<sup>15</sup>N/<sup>14</sup>N or <sup>13</sup>C/<sup>12</sup>C (Peterson and Fry 1987). A normalized calibration curve based on NBS-22 and IAEACH-6 for carbon and IAEA-N-1 and IAEA-N-2 for nitrogen were used to calculate  $\delta^{15}$ N and  $\delta^{13}$ C. Standards were from the National Institute of Standards and Technology (NIST). An internal laboratory standard (caffeine) was run every 10th sample to correct for drift in values. Precision was 0.2% for nitrogen and 0.3% for carbon (based on analyses of 20 replicates). Comparable methods were used for 1990s samples at the Environment Canada Laboratory in Saskatoon (Saskatchewan, Canada).

#### $\delta^{5N}$ baseline-adjustment

Baseline  $\delta^{15}N$  variability must be removed by baseline-adjustment before organism  $\delta^{15}N$  values can be compared among lakes (VanderZanden and Rasmussen 1999, Post 2002). Sphaeriid clams (collected in 1990s-2000s) were used as baseline organisms, and their  $\delta^{15}N$  was subtracted from invertebrate and fish  $\delta^{15}N$ .

# GIS

#### Data preparation

National Topographic Data Base (NTDB) waterbodies, toponymy, watercourses, and geonames were merged using ESRI's ArcGIS 9.2 ArcMap. These data included 57 1:50000 National Topographic Service (NTS) mapsheets (082G01, 082H04, 082J11, 082J12, 082J13, 082J14, 082K09, 082K16, 082M01, 082N01, 082N02, 082N03, 082N04, 082N05, 082N06, 082N07, 082N08, 082N09, 082N10, 082N14, 082N15, 082N16, 082O03, 082O04, 082O05, 082O06, 082O11, 082O12, 082O13, 083C02, 083C03, 083C04, 083C05, 083C06, 083C07, 083C10, 083C11, 083C12, 083C13, 083C14, 083D08, 083D09, 083D10, 083D14, 083D15, 083D16, 083E01, 083E02, 083E03, 083E04, 083E05, 083E06, 083E07, 083E08, 083F03, 083F04, 083F05). The digital map sheets are available free of charge at http://www.geogratis.ca/geogratis/en/index.html. The waterbodies were then dissolved by ENTITYNAME and TYPE, and a spatial join with toponymy was performed and subsequently cross-checked with geonames to add additional names and verify lake locations. This also required accessing the Toporama website (http://atlas.nrcan.gc.ca/site/english/maps/topo/map). Lake waterbodies attached to river polygons were edited based on Landsat imagery using the cut polygon features task.

Excel spreadsheets provided by Parks Canada that indicated which park lakes contained fish and spatial lake information and an excel spreadsheet identifying study lakes were spatially joined to waterbodies. This distinguished study lakes and lakes with fish throughout the study area. A numeric ID for each lake was derived by adding a new LAKE identification field that was calculated equal to OBJECTID. These data were exported to a FishLakes geodatabase. All lake features were converted to lines and merged with watercourses to create continuously connected streams. These data were exported to the FishLakes geodatabase. All lakes with fish were selected and exported as TheFishLakes to the FishLakes geodatabase.

Digital elevation models (DEM) provided by Parks Canada, were defined and projected as needed to NAD83 UTM Zone 11 with a common cell size of 30 m. The

DEMs were mosaicked into one main DEM. The DEM was smoothed using FocalMean = mean\_dem (which reduces extreme differences due to the presence of cells with errors). Slope and aspect layers were created using 3D Analyst Tools. Aspect was reclassified by coding all north aspects as the number 2. X and Y coordinates were created within the geographic extent of the study area (X coordinates = \$\$XMAP and Y coordinates= \$\$YMAP). All Ecological Land Classification (ELC) layers provided by Parks Canada were projected to NAD83 UTM Zone 11 if needed. They were renamed to ELC\_\*.shp, and spatially adjusted as required. The ELC for Waterton Lakes National Park was created by merging separate ecoregions. A SOURCE text field was added to indicate original shapefile names.

All ELC shapefiles were exported to the FishLakes geodatabase. All origin (stand age) layers provided by Parks Canada were projected to NAD83 UTM Zone 11 if necessary and renamed to origin\_\*.shp. The origin layers were spatially adjusted as required. Origin layers for Jasper National Park were unioned and a new burn date was calculated. The BURN\_DATE field was used in subsequent analyses. Rubbersheet was used to spatially adjust ELC and origin layers to the NTDB waterbodies layer. The differences between waterbodies in the ELC and Origin layers and the NTDB data as well as the number of links added during the rubbersheet process can be found in Table 4.1. Next, the Geographic Survey of Canada digital geology map 1712a (Wheeler and McFeely 1991) was imported to the FishLakes geodatabase. The slope layer was then used to create surface area grids, which were used to calculate 3D surface area of lake catchments through zonalstats SUM (surface = Sqr(\$\$CELLSIZE) / COS([slope] DIV DEG). The DEM for the southern portion of the study area had some errors that resulted in extreme slopes for scattered cells, therefore, the 'smoothed' DEM from FocalMean was used. Climate grids (McKenney et al. 2001, 2006, 2006b) accessed through the Great Lakes Forestry Centre (http://www.glfc.cfs.nrcan.gc.ca/landscape/climate\_models\_e.html) were projected to NAD1983\_UTM\_Zone11 using a 90 m cell size and snapped to the mosaicked main DEM and study area extent.

# Creation of catchments

The DEMs were reconditioned using ArcHydro Tools DEM Reconditioning  $\rightarrow$  Fill Sinks  $\rightarrow$  Flow Direction to create a flow direction layer for each DEM. The reconditioning raised the vertical units of the DEM to avoid negative values. The DEM that included Jasper National Park and Mount Robson Provincial Park was raised 311 units. The DEM for Banff, Kootenay and Yoho National Parks was raised 1020 units. The DEM for Mount Revelstoke and Glacier National Parks was raised 518 units. The Waterton Lakes National Park DEM did not need to be raised. The features in TheFishLakes layer were converted from polygon to lines and the attributes were preserved. TheFishLakes were selected by the DEMGRID field and converted from feature to raster using the NAME field. The extent and cell size used was the same as DEMGRID. Each raster lakes outline layer and the corresponding flow direction layer was then added to ArcMap and statements created in Excel the were copied and pasted into raster calculator (e.g., C:\WorkSpace\ErinK\FL\lakes\n\W1.shp=GridShape(Watershed([fdr],

Select([rlakesn], 'value = 1')), NOWEED). Each set of watersheds were then merged and joined by attributes (GRID\_CODE to VALUE) with the raster lakes outline layer and (NAME to NAME) with TheFishLakes. The data were exported to delete extraneous fields and make the joins permanent. Next, the raster lakes outline layer was merged with the FishLakes and dissolved using NAME, STUDY, FISH, PARKS, PROVINCE and DEMGRID to multipart. All of these layers were exported to the FishLakes geodatabase. A new field named SPLIT was added, and overlapping features were assessed and coded from 1 to 7. Incomplete features were coded 99.

# Catchment inside buffer (CIB)

TheFishLakes layer was buffered by 1000 m and named TheFishLakesBuffer. The catchments and TheFishLakesBuffer were intersected to produce a CatchBuffer layer. A select by attributes NAME=NAME\_1 was preformed, and then the layer was dissolved by NAME, STUDYLAKE, FISH, PROVINCE, PARK, LAKE, DEMGRID, SPLIT and BUFF\_DIST. All layers were exported to FishLakes geodatabase.

# Catchments and catchment inside buffer lake removal

Catchments were unioned with TheFishLakes to create CatchLakes. Then, a select by attributes "NAME" <> "NAME\_1" was performed. The layer was dissolved by NAME, STUDYLAKE, FISH, PROVINCE, PARK, LAKE, DEMGRID, and SPLIT to produce CatchmentErase. CIB and TheFishLakes were unioned, and the selection and dissolve (with the addition of BUFF\_DIST) procedures were repeated. All layers were exported to the FishLakes geodatabase.

#### Zonal statistics

Catchments, CatchmentsErase, CIB and CIBErase layers were SPLIT and exported to separate geodatabases. SPLIT Catchments and CIB were converted to rasters (90 m cell size snapped to the main DEM) for use with the projected climate grids. Batch grid control was used for SPLIT CatchmentsErase and CIBErase on the slope layer and reclassified aspect layer. Batch grid control was also used for SPLIT catchments and CIB on x and y coordinate layers and 3D surface areas. Finally, batch grid control was utilized for TheFishLakes on the DEMs to determine lake elevation. The ZonalStats function in raster calculator was used on projected climate grids. The results were appended and climate output tables were exported to the geodatabase and .dbf files.

## Intersections and summarizations

Catchments were intersected with ELC, origin and GSC layers and the results were saved to geodatabases. Results for catchments that were not completely contained within Parks were selected and deleted for ELC and origin layers that were not available outside the parks. Areas were summarized by NAMES and fields of interest (*e.g.*, ECOSITE, BURN\_YEAR and TECHUNIT) and the ELC layers were joined to a table of values for each ecosite (e.g. soil type, vegetation type, etc.) found

within a study lake catchment. The table was created from print versions of the ELC (Holland and Coens 1982, Achuff et al. 1997). Data were then exported to .dbf files.

#### **Statistics**

Data for all trout species (brook trout, bull trout, cutthroat trout, rainbow trout and lake trout) were grouped together to increase sample size because there is generally little variability in feeding behaviour among trout species from mountain All fish related data (i.e., length, weight, growth rate, condition factor, lakes. baseline-adjusted  $\delta^{15}N$ ,  $\delta^{13}C$  and other metal concentrations in trout) were ageadjusted to 6 year old trout. ANCOVAs were not utilized for standardization because there was no relationship between age and fish-related variables within many lakes. If relationships between fish-related variables and age were significant, they were adjusted for using linear regression. The mean for each fish variable was used when no significant relationship between age and fish-related variables existed within lakes. Age was used because fish populations can grow slowly in high elevation lakes (Donald and Alger 1986), indicating that fish length may not be a reliable measure of exposure for fishes from mountain lakes. All data were tested for normality visually by plotting histograms and using the Wilks-Shapiro test, which is the best alternative when sample size is small (Zar 1999). Linear regression was used to determine whether relationships existed between THg concentration in trout and explanatory variables. Models that excluded lake trout (which generally had higher MeHg concentrations than other species) were also completed, but were not included in this thesis for the sake of brevity. The *p* values presented for linear regressions are for the t-statistic for significance of slope. This is equivalent to testing the significance of the correlation between the independent and dependent variables. Plots of residuals were visually inspected for homogeneity of variances. Regression models were not detrended for spatial patterns, however, relationships of elevation and latitude with significant explanatory variables for THg concentrations in fishes were explored using Pearson product moment correlations (because significant linear relationships were identified by previous linear regression

analyses and scatterplots indicated linear relationships). Backward stepwise multiple regressions (with alpha-to-enter and alpha-to-remove set to 0.05) were completed on variables that would affect: 1) sources of Hg to a catchment or lake, 2) transport of mercury within a catchment, 3) MeHg production and 4) MeHg bioaccumulation and biomagnification. Collinearity of variables within each model was eliminated by creating correlation matrices and removing variables that correlated to the variable in question with a correlation coefficient greater than 0.7. Catchment data was extracted for the whole catchment and catchment within a 1000 m buffer around the study lake, to determine if variables closer to the lake were more important. Variables that were significant predictors in each of the four models were included in an overall backward stepwise regression model. Separate models including only variables available for all park lakes were calculated and solved for each lake that contained trout species in the Canadian Rocky Mountain Parks. Maps of the predicted THg concentrations for all lakes with trout were created using ESRI's ArcGIS 9.2 ArcMap.

# Results

#### Factors that affect sources of Hg to a catchment or lake

Linear regressions completed on MeHg and THg concentration in snow, areal MeHg and THg snow deposition, geologic variables, air temperature, precipitation, elevation, y-coordinate (latitude) and x-coordinate (longitude) revealed several factors that significantly explained variability in mean MeHg concentrations of trout (Table 4.2). Mean annual air temperature, %uPW, % morainal, % glacial parent material and latitude were positively related to mean MeHg concentrations of trout. Percent colluvium A, B, or C, lake elevation and x-coordinate (longitude) were negatively related to mean MeHg concentrations of trout. In Chapter 3, linear regression indicated that MeHg concentrations in trout were not significantly related to lake elevation (p=0.065). The differing results are because only data from lakes within Jasper, Banff and Yoho National Parks were used in this chapter because ecological land classification data were not available outside the national parks. The

multiple regression model that included data for the whole catchment explained 55.7% of variability in mean trout MeHg concentration (F=10.076, p=0.001). The equation was:

 $\bar{x}$  trout [MeHg] = -3425.228 + 29.236 \*  $\bar{x}$  annual air temperature + 0.001 \* latitude The multiple regression equation that included data extracted from the catchment within a 1000 meter buffer around lakes explained 44.4% of the variability in trout MeHg concentration (*F*=13.564, *p*=0.002):

 $\bar{x}$  trout [MeHg] = -5877.297+1046.029 \* latitude

Factors related to sources of Hg that significantly explained variation in mean MeHg concentration of trout were also correlated with both lake elevation and latitude (Table 4.2). Although mean annual precipitation was not significantly related to mean MeHg concentrations of trout, it significantly correlated with both lake elevation and latitude (Table 4.2).

# Factors that affect transport of Hg within a catchment

Linear regression conducted on lake area, catchment area, catchment area to lake area ratio, aspect, slope, ecosite, ecosection, ecoregion, soil and vegetation variables determined that many factors related to the transport of Hg within a catchment significantly explain variation in mean MeHg concentrations of trout (Table 4.3). Aspect, % talus, % alpine, % alpine tundra, and % unvegetated were negatively related to mean MeHg concentrations in trout. Catchment area to lake area ratio, % Bryant 2 ecosite, % Sawback 1 ecosite, % water, % Bryant ecosection, % lower subalpine, % calcareous soil, % medium textured soil, % coarse fragments, % rapid to well draining soils, % eutric brunisol, % Englemann spruce and subalpine fir and % Englemann spruce, subalpine fir, feathermoss and false azalea were positively related to mean MeHg concentrations of trout. The multiple regression model for data from the whole catchment was significant (F=18.088, p=0.0001), and explained 78.3% of the variability in mean MeHg concentrations of trout:

 $\bar{x}$  trout [MeHg] = 191.219 – 22.008 \* aspect + 1252.227 \* catchment area:lake area +

6.171 \* % eutric brunisol

The multiple regression model that included only data from the portion of the catchment located within a 1000 meter buffer around the lake explained 62.0% of the variability in mean MeHg concentration of trout (F=8.174, p=0.002):

 $\bar{x}$  trout [MeHg] = 240.639 – 26.770 \* aspect+ 5.317 \* %BY2 (Bryant 2 ecosite) + 1.689 \* % coarse fragments 20-50

Several factors associated with the transport of Hg within a catchment (that significantly explained variability in mean MeHg concentrations of trout) were also correlated with lake elevation and latitude (Table 4.3).

#### Factors that affect MeHg production

Linear regressions performed on water temperature, and water chemistry variables (*e.g.*, DOC, pH, salinity, alkalinity, Ca<sup>2+</sup>, Mg<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, conductivity, nutrients and chlorophyll *a*) indicated that factors that affect in-lake Hg methylation significantly explained variation in mean MeHg concentrations of trout (Table 4.4). Spring dissolved inorganic nitrogen (DIN) (DIN=NH<sub>4</sub><sup>+</sup> + NO<sub>2</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>) concentration was related negatively, while spring dissolved organic carbon (DOC) concentration, late summer/early fall and spring concentrations of sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>) and magnesium (Mg<sup>2+</sup>), and spring conductivity were related positively to mean MeHg concentrations of trout. The multiple regression model for factors that affect MeHg production was significant (*F*=4.987, *p*=0.027), and explained 45.4% of variation in mean MeHg concentration of trout:

 $\bar{x}$  trout [MeHg] = 138.435 + 1.488 \* spring [SO<sub>4</sub><sup>2-</sup>] – 1.409 \* spring [DIN] Spring DOC concentration, late summer/early fall K<sup>+</sup> concentration and spring K<sup>+</sup> concentration were correlated with both lake elevation and latitude. Late summer/early fall chlorophyll *a*, spring water temperature and spring turbidity were not significantly related to mean MeHg concentrations in trout. However, these factors were correlated with lake elevation and latitude.

# Factors that affect MeHg bioaccumulation and biomagnification

Linear regressions executed on MeHg and THg concentrations in lake water, lake productivity indicators, zooplankton density and wet weight (ww) biomass, MeHg in invertebrates (*i.e.*, prey), trout baseline-adjusted  $\delta^{15}N$ ,  $\delta^{13}C$ , age, length, weight, condition factor, growth rate and concentrations of other metals in trout determined that many of these factors were significantly related to mean MeHg concentrations in trout (Table 4.5). Measures of zooplankton density, spring zooplankton MeHg concentration, baseline-adjusted  $\delta^{15}N$  of trout, trout length, weight, and growth rate, arsenic (As), copper (Cu), nickel (Ni) and palladium (Pd) concentrations of beryllium (Be) and antimony (Sb) were negatively related to mean MeHg concentrations in trout from lakes in the Canadian Rocky Mountain Parks . A significant regression model (*F*=14.288, *p*=0.002) that explained 86.0% of the variability in mean MeHg concentrations of trout was calculated for factors that affect biomagnification and bioaccumulation:

 $\bar{x}$  trout [MeHg] = -164.861 +4.594 \* spring [MeHg] of zooplankton + 14.846 \* baselineadjusted  $\delta^{15}$ N of trout + 1.238 trout growth rate (g/yr)

Some factors that were related significantly to mean MeHg concentrations of trout were also correlated with lake elevation and latitude (Table 4.5). Concentrations of selenium (Se) in trout were not significantly related to mean MeHg concentrations in trout, but were negatively correlated with latitude (Table 4.5).

# Overall factors that affect Hg concentrations in fishes from Rocky Mountain National Park lakes

Overall multiple regression models that included factors that were significant in previously described multiple regressions for each catchment level and in-lake process in the Hg cycle were calculated. The model that included data from the entire catchment explained 98.7% of the variability in mean MeHg concentration of trout (F=58.284, p=0.004):

 $\bar{x}$  trout [MeHg] = -7230.403 + 40.035 \*  $\bar{x}$  annual air T + 0.001 \* latitude + 2.843 \*

 $[SO_4^{2-}] + 2.750 * spring [MeHg] of zooplankton$ 

Figure 4.2 provides plots of the individual linear regressions for significant explanatory variables in the overall whole catchment multiple regression model. The model that included catchment data located within the 1000 m buffer around the lake was significant (F=91.688, p=0.002) and explained 99.2% of the variation in mean MeHg concentrations of trout.

 $\bar{x}$  trout [MeHg] = -5684.217 + 1.524 \* [SO<sub>4</sub><sup>2-</sup>] – 2.109 [DIN] +0.001 \* latitude + 4.313 \* spring [MeHg] of zooplankton

Individual linear regressions for significant explanatory variables from the overall multiple regression model for buffered catchments are presented in Figure 4.3.

# Predictive model for all fish-bearing lakes in Rocky Mountain National Parks

Only a subset of factors (*i.e.*, geology, climate, elevation, x-coordinate (longitude), latitude, ecoregion, aspect, slope, lake area, catchment area, soil and vegetation) were available for all fish-bearing lakes in the Rocky Mountain National Parks. The whole catchment model created to predict MeHg concentrations in fishes from all fish-bearing lakes was significant (*F*=11.076, *p*=0.001), and explained 58.1% of the variability in mean MeHg concentrations of trout from lakes:

 $\bar{x}$  trout [MeHg] = 371.094 + 32.232 \*  $\bar{x}$  annual air T – 29.507 \* aspect

Figure 4.4 includes a map of MeHg concentrations predicted by this model. The buffered catchment model explained 62.1% of the variation in mean MeHg concentrations of trout (F=8.174, p=0.002):

 $\bar{x}$  trout [MeHg] = 253.854 – 28.139 \* aspect + 5.301 \* BY2 (Bryant 2 ecosite) + 1.515 \* % coarse fragments 20-50

A map of the predicted MeHg concentrations generated from the buffered catchment model is presented in Figure 4.5.

# Discussion

#### Factors that affect sources of Hg to a catchment or lake

Atmospheric deposition of Hg is usually the principle source of Hg to lakes (Swain et al. 1992, Wang et al. 2004). Recent studies in the United States have linked atmospheric deposition of inorganic Hg to MeHg concentrations in mosquitoes (Hammerschmidt and Fitzgerald 2005) and freshwater fishes (Hammerschmidt and Fitzgerald 2006). A mesocosm study using Hg isotopes verified these results by demonstrating that methylation (Orihel et al 2006) and bioaccumulation (Orihel et al. 2007) respond proportionally to atmospheric Hg<sup>2+</sup> loading. In our study, concentration of MeHg and THg in snow, and areal deposition of MeHg and THg in snow were not related to mean MeHg concentrations in trout. However, snow sampling for this study occurred in 2001, an anomalously low snowpack year (Figure 4.6), which may account for this result.

Catchment geology (*i.e.*, the weathering of metamorphic, intrusive or volcanic rocks, biotite-rich granites and black shales) has also been identified as a source of Hg (Lawson and Mason 2001, Vaidya and Howell 2002, Page and Murphy 2003). Mean MeHg concentrations of trout in Canadian Rocky Mountain lakes were related positively to the proportion of sedimentary, metamorphic and volcanic rocks within catchments (Table 4.2). The proportion of morainal and glacial parent material present in a catchment was also positively related to mean MeHg concentrations in trout. These results indicate that geology affects MeHg concentrations in trout from lakes of the Canadian Rocky Mountain Parks.

Climatic variables can affect rates of atmospheric deposition and rock weathering. Rates of atmospheric deposition should increase with decreasing temperature and increasing precipitation volume. As expected, annual air temperature was negatively correlated with lake elevation, and annual precipitation was positively correlated with lake elevation. Mean MeHg concentrations in trout were positively related to mean annual air temperature. This could be due to increased Hg methylation and MeHg accumulation potential in warmer lakes. Inlake MeHg production increases with temperature (Reinert et al. 1974, Bodaly et al. 1993, Ullrich et al. 2001).

Multiple regression analyses indicated that latitude and mean annual air temperature were the best predictors of mean MeHg concentrations in trout. Models were similar for data from whole catchments and buffered catchments. Previously, fish MeHg concentrations have also been positively correlated to latitude (McMurty et al. 1989), which was attributed to increased precipitation volume and decreased temperatures.

# Factors that affect transport of Hg within a catchment

Daly and Wania (2005) indicated that meagre soils and vegetative cover in catchments of high elevation lakes increase the risk of airborne contaminants reaching surface waters. Mean MeHg concentrations in trout from Rocky Mountain lakes were negatively related to lake elevation and the proportion of alpine, alpine tundra, talus and unvegetated catchment (Table 4.3). Although precipitation volume is enhanced at high elevations, UV radiation increases with elevation (Blumthaller et al. 1997) and may be responsible for increased photo-reduction of atmospherically deposited Hg<sup>2+</sup> in snow. This would decrease the quantity of ionic Hg<sup>2+</sup> available for transport to lakes. Mean MeHg concentrations were positively related to proportions of soil and vegetation types, particularly rapid to well drained soils. Transport of THg and MeHg from catchments to lakes is likely enhanced in catchments containing rapid draining soils. A positive relationship between catchment area to lake area ratio and mean MeHg concentrations in trout was identified. Runoff becomes increasingly more important than deposition as catchment area to lake area ratios increases (Vaidya and Howell 2002). This indicates that runoff is likely an important transport mechanism in alpine systems, similar to other ecosystems (Balogh et al. 1997, Lawson and Mason 2001). Mean MeHg concentrations in trout were negatively related to aspect. This demonstrates that lakes within catchments with a western aspect contain fishes with greater MeHg concentrations than fishes from lakes in catchments without a western aspect. These catchments would experience warmer conditions and faster snowmelt runoff. Relationships with physiogeographic variables were reflected in the positive relationships between mean MeHg concentration in trout and ecosites (Table 4.3). The positive relationship between mean MeHg concentrations in trout and xcoordinate (longitude) is an artifact of park and lake location. Northern lakes are located east of southern lakes (Figure 4.1A and B).

Multiple regression models determined that aspect, catchment area to lake area ratio, % eutric brunisol, %Byrant 2 ecosite, and % coarse fragments 20-50 were the best predictors of mean MeHg concentration in trout. Predictors differed between whole catchment and buffered catchment models, with the exception of aspect.

# Factors that affect MeHg production

As expected, mean MeHg concentrations in trout from lakes in Rocky Mountain Parks were positively related to DOC and cation concentrations in lake water (Table 4.4). Many others studies have identified DOC as an important factor in the Hg cycle, for both transport and MeHg production (Driscoll et al. 1995, Watras et al. 1998, Ullrich et al. 2001). Some cations and anions have previously been shown to affect in-lake Hg methylation (Allard and Stokes 1989), which explains the positive relationship between mean trout MeHg concentrations and conductivity, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> (Table 4.4). DIN concentrations were negatively associated with mean MeHg concentrations in trout, however the mechanism for this relationship is unclear. No other nutrients were related significantly to mean MeHg concentrations in trout. Chlorophyll a concentration was also unrelated to MeHg concentrations in trout, but was related negatively to elevation (Table 4.4). The same trend was identified in spring water temperature and turbidity. Thus, conditions for MeHg production in high altitude Rocky Mountain lakes are poor. Lakes are cold, unproductive, and low in DOC. Also, MeHg produced in alpine lakes may be photo-reduced to Hg<sup>2+</sup> and released from lakes to the atmosphere at an increased rate (Krabbenhoft et al. 2002) due to enhanced UV exposure. Demethylation could also be favoured because of the high water transparency and low temperatures of high altitude lakes (Rognerud et al. 2002). These results are likely linked to the negative relationship between mean MeHg concentration in trout and lake elevation. A multiple regression model indicated that  $SO_4^{2-}$  and DIN concentrations were the best predictors of mean MeHg concentrations in trout.

#### Factors that affect MeHg bioaccumulation and biomagnification

Contrary to other studies, concentrations of MeHg and THg in lake water and lake productivity were not related to mean MeHg concentrations in trout. Crustacean zooplankton density (i.e., copepod density in particular) was positively related to mean trout MeHg concentrations. Other studies indicate that lake productivity (Kidd et al. 1999, Essington and Houser 2003), zooplankton density (Stemberger and Chen 1998, Chen and Folt 2005) and fish growth rate (MacCrimmon et al. 1983, Verta et al. 1990) are negatively related to MeHg accumulation by fishes. In lakes of the Canadian Rocky Mountain Parks, zooplankton density and fish growth rate were positively related to mean MeHg concentrations of trout. This may be due to the relatively small range in productivity of mountain lakes. Increased zooplankton density and growth rates could be an indicator of better prey resources and increased consumption rates in oligotrophic mountain lakes. Spring MeHg concentrations of zooplankton, baseline-adjusted  $\delta^{15}N$  of trout, and fish length and weight were positively related to mean MeHg concentrations in trout as expected based on other studies (Mathers and Johansen 1985, MacCrimmon et al. 1983, Hall et al. 1997). Contrary to published results (Ribeyre et al. 1995), concentrations of Ag were positively related to mean MeHg concentrations in trout. However, as expected, relationships between concentrations of other metals and mean MeHg concentrations of trout were evident. A multiple regression model determined that the best predictors of MeHg accumulation in trout were spring MeHg concentration of zooplankton, baseline-adjusted  $\delta^{15}N$  of trout, and trout growth rate.

# Overall factors that affect Hg concentrations in fishes from lakes of the Canadian Rocky Mountain National Parks

Results of overall whole catchment and buffered catchment multiple regression models were similar. Thus, whole catchment models which are logistically easier to create, can be used without loss of information and predictive power. The best overall predictors of mean MeHg concentrations were spring MeHg concentrations,  $SO_4^{2-}$  concentrations, mean annual air temperature, DIN concentration and latitude. Correlations of explanatory variables with lake elevation (previously discussed) and latitude indicate that environmental gradients existed within our study area. Contrary to expectation, lake catchments in the northern portion of the study area were warmer and received less precipitation than lakes in southern catchments. High latitude catchments also contain increased proportions of sedimentary, volcanic and metamorphic rock, and well drained soils. Northern catchments had increased catchment area to lake area ratios, DOC, cation and chlorophyll *a* concentrations, zooplankton density, concentrations of MeHg in zooplankton collected in the spring, and weights of trout. Many of these factors can increase MeHg accumulation by fishes.

# Predictive model for all fish-bearing lakes in Rocky Mountain National Parks

Multiple regression models created for prediction of trout MeHg concentrations could only include variables available for all lakes. This reduced the amount of variation in mean trout MeHg concentrations that could be explained. However, the results of the models provided in Figure 4.4 and 4.5 should aid Parks Canada with fisheries management. Model results indicate that trout from Park lakes other than those we sampled are at risk of MeHg contamination (Figure 4.4 and 4.5). The predicted MeHg concentrations of trout from the whole catchment model were greater than the predicted values generated by the buffered model. Figures 4.4 and 4.5 distinguish which lakes should be a priority for sampling to verify the model/MeHg concentrations in fishes. Priority lakes were identified

based on fishing pressure data provided by Parks Canada. As Parks Canada samples more lakes, trout MeHg concentrations can be added into the model which should increase its predictive power. All catchment variables were extracted for all fish-bearing lakes, so modeling can be completed for other purposes (*e.g.*, factors that affect other contaminants in fishes and/or their consumers).

Climate change will likely influence many factors that affect sources, transport, methylation and accumulation of MeHg (Macdonald 2005) and consequently Hg cycling in mountain lakes. For example, climate change may result in longer ice-free seasons (Evans et al. 2005), which should profoundly affect the limnological characteristics of lakes (Schindler and Smol 2006), increase algal productivity (Outridge et al. 2005), alter phytoplankton and zooplankton community structure (Strecker et al. 2004), cause shifts in the distribution of other organisms (Schindler 1997), and increase growth and survival of fishes in alpine lakes (Schindler and Smol 2006). Furthermore, climate is expected to increase forest fire occurrence and the area burned in the mountains of western North America (Westerling et al. 2006). The implications of increased forest fire for MeHg accumulation by fishes are discussed in the following chapter (Chapter 5). Model results and baseline data from this chapter and Chapter 3 will be useful for monitoring the effects of climate change.

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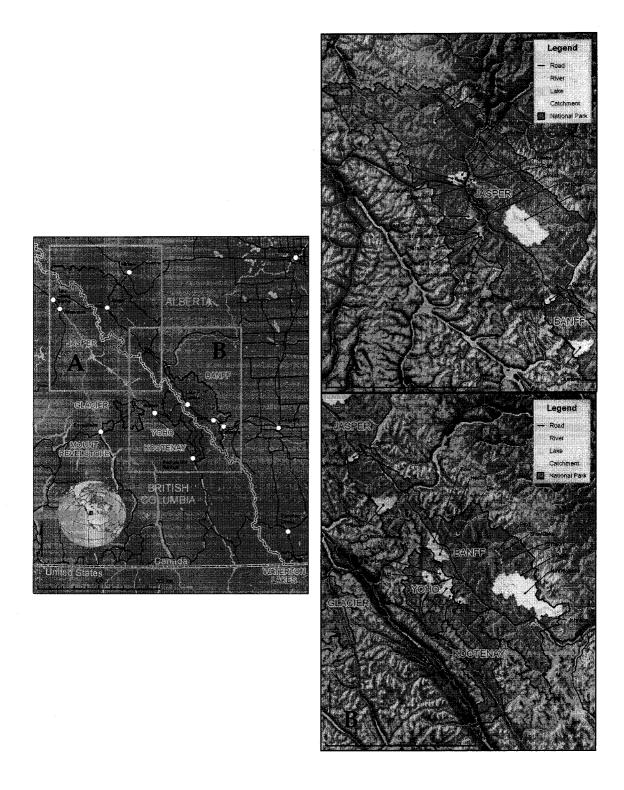
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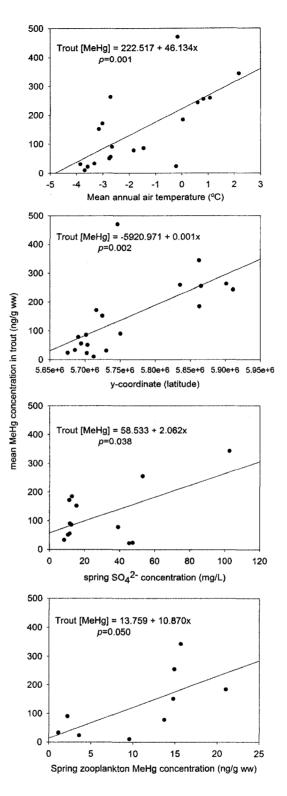
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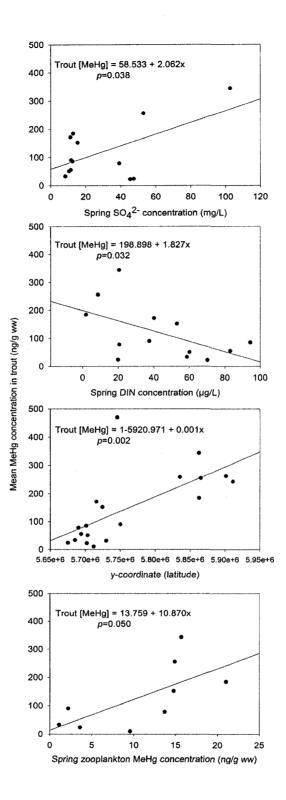
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**Figure 4.1** Map of the study area. Data were collected from lakes in A. Jasper, and B. Banff and Yoho National Parks in the Rocky Mountains of Alberta and British Columbia, Canada.



**Figure 4.2** Linear regression results for individual factors that were significant predictors of mean trout MeHg concentrations in the overall whole catchment multiple regression model.



**Figure 4.3** Linear regression results for individual factors that were significant predictors of mean trout MeHg concentrations in the catchment in 1000 meter buffer around lake multiple regression model.

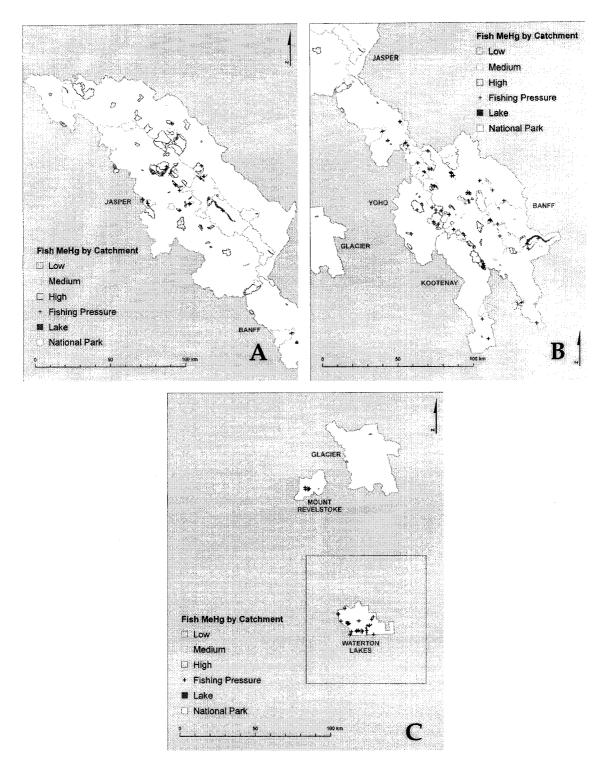


Figure 4.4 Predicted trout MeHg concentrations for all fish-bearing lakes in Rocky Mountain National Parks (A=Jasper, B=Banff, Yoho, Kootenay, C=Mount Revelstoke, Glacier and Waterton Lakes) based on whole catchment multiple regression model. Green=≤50 ng/g THg ww, Orange=50-150 ng/g THg ww and Red=150-400 ng/g THg ww.

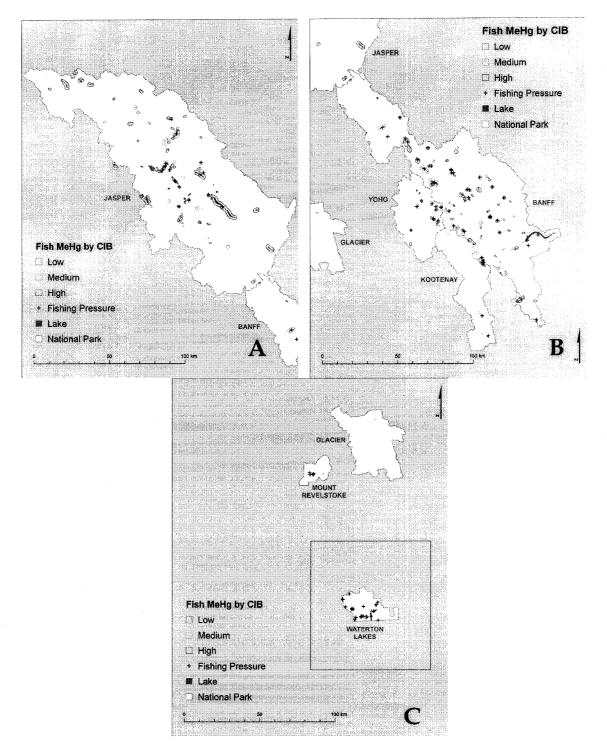
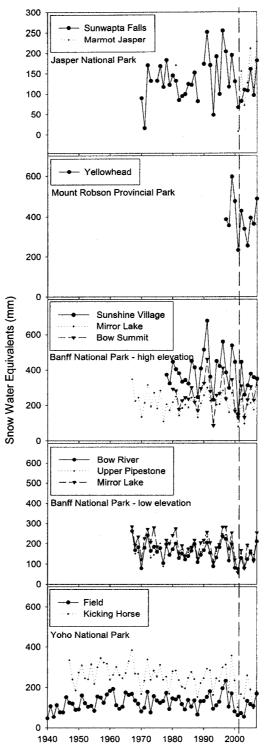


Figure 4.5 Predicted trout MeHg concentrations for all fish-bearing lakes in Rocky Mountain National Parks (A=Jasper, B=Banff, Yoho, Kootenay, C=Mount Revelstoke, Glacier and Waterton Lakes) based on catchment in 1000 meter buffer around lake multiple regression model. Green=≤50 ng/g THg ww, Orange=50-150 ng/g THg ww and Red=150-400 ng/g THg ww.



# Figure 4.6

Snow water equivalents for February snowpack in Canadian Rocky Mountain Parks from 1940 to 2007. Snow samples for this study were collected in February 2001 (dashed line). Data compiled from Alberta Environment Water Supply Outlook Reports: http://www3.gov.ab.ca/env/water/ws/watersupply/historical/histwsindex.html

Table 4.1Difference between waterbodies in ELC and Origin layers and NTDB<br/>waterbodies layer, and the number of links used during rubbersheet<br/>process to spatially adjust. na=not applicable

	ELC (meters difference)	Origin (meters difference)	Number of links to Rubbersheet		
Jasper National	na	na	na		
Park					
Banff National	85	85	1742		
Park					
Kootenay National	129	223	204		
Park					
Yoho National	118	288	213		
Park					
Mount Revelstoke	94	94	193		
and Glacier					
National Park					
Waterton Lakes	40	55	205		
National Park					

**Table 4.2** Significant results of linear regressions between mean trout MeHg concentrations and factors that affect sources of Hg to a catchment or lake, and correlations between these factors and lake elevation and latitude. Probabilities presented for linear regression models are for the t-statistic for significance of slope, which is equivalent to testing the significance of the correlation between mean trout MeHg concentrations and explanatory variables.

Linear Regression with $\bar{x}$ trout [MeHg]				Correlation with lake elevation		Correlation with latitude		
Explanatory Variable	+ or -	<i>p</i> =	% variation in trout [MeHg] explained	r=	<i>p</i> =	r=	<i>p</i> =	
		Who	le catchment					
x annual air temperature	+	0.001	46.1	-0.848	0.0001	0.625	0.004	
% uPW (Windermere) sedimentary, volcanic, metamorphic rock; quartz-feldspar-grit, sandstone, siltstone, shale, limestone, greenstone, marble	+	0.042	22.2	-0.503	0.028	0.526	0.021	
% morainal	+	0.031	24.7	-0.710	0.001	-0.473	0.041	
% colluvium A, B or C; solifluction &/or eroded	-	0.049	21.0			0.582	0.009	
% glacial parent material	+	0.012	31.8	-0.804	0.0001	-0.522	0.022	
Lake elevation (m)	-	0.029	25.2					
x-coordinate (longitude)	-	0.001	49.8	0.503	0.028	-0.953	0.001	
y-coordinate (latitude)	+	0.002	44.5					
Catchment in 1000m buffer around lake								
Lake elevation (m)	-	0.029	25.2					
x-coordinate (longitude)	-	0.001	49.7	0.488	0.034	-0.956	0.001	
y-coordinate (latitude)	+	0.002	44.4			1		
x annual precipitation (mm)				0.667	0.001	-0.550	0.015	

Table 4.3Significant results of linear regressions between mean trout MeHg<br/>concentrations and factors that affect transport of Hg from catchments<br/>to lakes, and correlations between these factors and lake elevation and<br/>latitude. Probabilities presented for linear regression models are for<br/>the t-statistic for significance of slope, which is equivalent to testing<br/>the significance of the correlation between mean trout MeHg<br/>concentrations and explanatory variables.

Linear Regression with $\bar{x}$ trout [MeHg]			Correlation with lake elevation		Correlation with latitude		
Explanatory Variable	+ or -	<i>p</i> =	% variation in trout [MeHg] explained	r=	<i>p</i> =	r=	<i>p</i> =
· · · · · · · · · · · · · · · · · · ·		Who	le catchment		•	•••••••••	· · · · · · · · · · · · · · · · · · ·
Aspect	-	0.003	41.4			-0.564	0.012
Catchment area:lake area	+	0.003	42.4	Ţ		0.509	0.026
% Bryant 2 ecosite	+	0.005	37.5				
% Sawback 1 ecosite	+	0.029	24.9				
% Talus	-	0.025	26.2			-0.522	0.022
% Water	+	0.007	35.4			0.455	0.050
% Bryant ecosection	+	0.027	25.8				
% Lower subalpine	+	0.028	25.2	-0.620	0.005		
% Alpine	-	0.044	21.8			-0.496	0.031
% Calcareous soil	+	0.041	22.4	-0.765	0.0001		
% Medium textured soil	+	0.019	28.2	-0.765	0.0001		
% of coarse fragments 20- 50	+	0.010	33.0	-0.698	0.001	0.567	0.010
% rapid to well draining soils	+	0.003	42.2	-0.750	0.0001	0.484	0.036
% eutric brunisol	+	0.003	42.5				
% Alpine tundra	-	0.028	25.5				
% Englemann spruce – subapline fir	+	0.045	21.6	-0.472	0.041		
% Engelmann spruce- subalpine fir/feathermoss (C13) & Engelmann spruce- subalpine fir/false azalea (C14)	+	0.032	24.2				
% unvegetated	-	0.029	25.0	0.902	0.0001		
	Catchm	ent in 1(	000m buffer aro	und lake			
Aspect	-	0.006	36.8				
% Bryant 2 ecosite	+	0.006	37.7				
% Medium textured soil	+	0050	20.3	-0.526	0.021		
% of coarse fragments 20- 50	+	0.029	25.2	-0.553	0.014	0.541	0.017

Table 4.4Significant results of linear regressions between mean trout MeHg<br/>concentrations and factors that affect MeHg production in lakes, and<br/>correlations between these factors and lake elevation and latitude.<br/>Probabilities presented for linear regression models are for the t-<br/>statistic for significance of slope, which is equivalent to testing the<br/>significance of the correlation between mean trout MeHg<br/>concentrations and explanatory variables.

Linear Regression with $\bar{x}$ trout [MeHg]				Correlation with lake elevation		Correlation with latitude	
Explanatory Variable	+ or -	<i>p</i> =	% variation in trout [MeHg] explained	r=	<i>p</i> =	r=	<i>p</i> =
Spring [DIN] ( $\mu$ g/L)	-	0.032	30.8				
Spring [DOC] (mg/L)	+	0.042	28.2	-0.441	0.019	0.402	0.034
Spring [SO <sub>4</sub> <sup>2-</sup> ] (mg/L)	+	0.032	30.6				
Late summer/early fall [Na] (mg/L)	+	0.006	45.8				
Spring [Na <sup>+</sup> ] (mg/L)	+	0.005	47.0				
Late summer/early fall [K <sup>+</sup> ] (mg/L)	+	0.011	40.3	-0.412	0.029	0.437	0.020
Spring [K <sup>+</sup> ] (mg/L)	+	0.011	40.1	-0.425	0.024	0.429	0.023
Late summer/early fall [Mg <sup>2+</sup> ] (mg/L)	+	0.027	32.2				
Spring [Mg <sup>2+</sup> ] (mg/L)	+	0.013	39.0				
Spring conductivity (µS/cm)	+	0.005	26.4				
Late summer/early fall chlorophyll <i>a</i> (µg/L)				-0.420	0.026	0.392	0.039
Spring water temperature (°C)				-0.750	0.0001	0.458	0.014
Spring turbidity (NTU)				-0.468	0.012		

Table 4.5Significant results of linear regressions between mean trout MeHg<br/>concentrations and factors that affect MeHg bioaccumulation and<br/>biomagnification in aquatic food chains, and correlations between<br/>these factors and lake elevation and latitude. Probabilities presented<br/>for linear regression models are for the t-statistic for significance of<br/>slope, which is equivalent to testing the significance of the correlation<br/>between mean trout MeHg concentrations and explanatory variables.

Linear Regression with $\bar{x}$ trout [MeHg]				Correlation with lake elevation		Correlation with latitude	
Explanatory Variable	+ or -	<i>p</i> =	% variation in trout [MeHg] explained	r=	<i>p</i> =	r=	<i>p</i> =
Cladoceran + copepod density (#/L)	+	0.013	41.3			0.515	0.009
Copepod density (#/L)	+	0.002	56.1			0.440	0.029
Spring zooplankton [MeHg] (ng/g)	+	0.044	37.9	-0.420	0.046	0.533	0.009
Trout baseline-adjusted $\delta^{15}N$	+	0.006	35.4				
Trout fork length (mm)	+	0.024	22.0	-0.541	0.008		
Trout weight (g)	+	0.001	40.8			0.432	0.045
Trout growth rate (g/yr)	+	0.022	22.6	-0.549	0.007		
Trout [Ag] (µg/g)	+	0.002	60.5			-0.636	0.019
Trout [Be] (μg/g)	-	0.047	33.8				
Trout [Cu] (µg/g)	+	0.007	46.8				
Trout [Ni] (µg/g)	+	0.049	28.6				
Trout [Pd] (μg/g)	+	0.016	59.1			0.635	0.050
Trout [Sb] (µg/g)	-	0.046	29.1				
Trout [Se] (μg/g)			·	L		-0.459	0.060

# 5.0 Forest fire increases mercury accumulation by fishes via food web restructuring and increased mercury inputs<sup>+</sup>

## Introduction

Recent findings indicate that fishes from lakes in partially burned catchments contain greater mercury (Hg) concentrations than fishes from reference catchments (Garcia and Carignan 2005). Increased methyl Hg (MeHg) concentrations in fishes can result in serious health problems for consumers (Fitzgerald and Clarkson 1991). In this study, we compared pre- and post-fire data to identify mechanisms responsible for post-fire increases in MeHg concentrations of fishes.

Concentrations of MeHg in fishes are a complex function of MeHg and inorganic mercury inputs to waterbodies and in-lake processes such as MeHg production, biomagnification and bioaccumulation. For example, inputs of Hg to a waterbody can be influenced by atmospheric deposition (Swain et al. 1992), geology (Vaidya and Howell 2002), soil and vegetation type (Shanley et al. 2005) and large precipitation events (Lawson and Mason 2001). Increases in water temperature, dissolved organic carbon (DOC), and sulfate (SO<sub>4</sub><sup>2-</sup>), and declines in pH can increase in-lake Hg methylation (Ullrich et al. 2001). Increased lake productivity can reduce Hg biomagnification (Kidd et al. 1999, Essington and Houser 2003), by means of biomass (Chen and Folt 2005, Pickhardt et al. 2005) and growth dilution (Simoneau et al. 2005). This causes fishes in nutrient-enriched lakes to have lower concentrations of Hg than fishes from reference lakes (Essington and Houser 2003), although food chains are the same length. Conversely, increased Hg bioaccumulation may occur because of enhanced Hg inputs to lakes (Fitzgerald and Clarkson 1991), or increases in food chain length (nitrogen stable isotope ratio;  $\delta^{15}N$ ) (Cabana and Rasmussen 1994, Kidd et al. 1995a). As a result, MeHg concentrations in fishes from adjacent lakes that are not subjected to point-source pollution can

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range from very low to those that exceed guidelines to protect the health of human and wildlife consumers (Allan 1999).

Forest fire potentially modifies complex interactions that control MeHg accumulation by fishes. For instance, forest fire alters soil and vegetation within burned catchments, which can affect nutrient transport (Gresswell 1999), and postfire impacts on water chemistry (i.e., nutrients, DOC, SO<sub>4</sub><sup>2-</sup>, pH) and water temperature have been documented (Gresswell 1999). Fire-mobilized nutrients (usually N and sometimes P) (Carignan and Steedman 2000) can enhance lake productivity (Spencer et al. 2003). Forest fire also causes small increases in  $\delta^{15}N$  of aquatic organisms (Spencer et al. 2003, Allen et al. 2005, Garcia and Carignan 2005), which some attribute to increased inputs of inorganic nitrogen from the catchment (Allen et al. 2005, Garcia and Carignan 2005), not food web alterations. Few have studied the effects of forest fire on the biogeochemical cycling of Hg. Fires are known to release Hg from forested catchments to the atmosphere, where longdistance transport occurs (Friedli et al. 2003, Sigler et al. 2003). Elevated Hg concentrations in sediment (Caldwell et al. 2000) and fishes (Garcia and Carignan 2005) have been identified in waterbodies located in catchments partially burned by forest fire, but mechanisms causing enhanced Hg accumulation by fishes have not been previously identified.

Mature forest ecosystems contain pools of nutrients and Hg equivalent to many years of deposition, particularly when subjected to fire suppression. In North America, forest fire has been suppressed for over 100 years; however, prescribed burning has recently become a popular counteractive management option (Weber and Stocks 1998). Prescribed burning (Weber and Stocks 1998, Spencer et al. 2003) and climate change are expected to increase forest fire occurrence (Flannigan et al. 2000, Flannigan et al. 2002).

We intensively studied Moab Lake (1240 meters above sea level, area =21.4 hectares (ha), mean depth =8.6 m, undeveloped catchment) and proximate streams in Jasper National Park (Alberta, Canada) (Figure 5.1) after a 1120 ha forest fire burned 72% of Moab Lake's 342 ha catchment between 12 July and 31 August 2000.

Our study demonstrates that forest fire and climate change are linked in previously unanticipated ways to factors that control MeHg concentrations in fishes.

#### Methods

## Field sampling

Moab Lake and creeks were sampled biweekly in 2000 and monthly in 2001. Lake sampling included measuring water temperature, and collecting water samples for THg, MeHg (using ultra-clean sampling protocol (St. Louis et al. 1996)), and water chemistry. A 140 µm mesh net was hauled vertically to capture zooplankton. Animals were preserved in formalin for enumeration and frozen for Hg analyses. Fishes were gillnetted in the 1970s, 1994, 2001, and 2003. Specimens were identified, measured, weighed and frozen. Benthic macroinvertebrates were collected by using sweep nets and weighted mesh colonization traps. Invertebrates were sorted, rinsed, and frozen. At creeks, temperature, depth, and width were recorded. Flow was measured using a Price AA current meter (Scientific Instruments, Inc., Milwaukee, WI). Water samples for Hg analyses were collected in Teflon bottles and processed the same as lake samples. THg water samples were acidified with concentrated trace metal-grade HCl equivalent to 0.2% of the sample volume. MeHg water samples were frozen. Unfiltered water for ammonia, nitrate + nitrite and total phosphorus was kept cool until analysis. Water was filtered for  $SO_4^{2^2}$ , DOC, total dissolved nitrogen, and total dissolved phosphorus. Whatman (Maidstone, England) GF/F filters for chlorophyll *a* and water for nitrogen analyses were frozen.

## Laboratory

Water analyses were completed at the University of Alberta Limnology Services Unit (http://www.biology.ualberta.ca/facilities/limnology/). Benthic invertebrates were identified to Order and enumerated. Fishes were aged using otoliths. Growth rates were determined from length-age regressions. Fish stomach contents were identified. Benthic invertebrate, bulk zooplankton and fish muscle samples were freeze-dried for 48 hours. Whole fish were homogenized using a stainless steel grinder. Fish samples were weighed before and after freeze-drying. Freeze-dried

samples were powdered using an acid-washed glass mortar and pestle. Hg analyses were conducted at the University of Alberta Low-Level Mercury Analytical Laboratory (http://www.biology.ualberta.ca/facilities/mercury/).

THg in unfiltered water was determined by BrCl oxidation, SnCl<sub>2</sub> reduction, purge and trap, and cold vapour atomic fluorescence spectrometry (CVAFS) (modified (USEPA 1996, Olson et al. 1997)). The analytical detection limit was 0.05 ng/L. For MeHg in unfiltered water, samples were distilled and ethylated, followed by gas chromatography separation with CVAFS (Horvat et al. 1993, Olson et al. 1997). The detection limit was 0.02 ng/L. Fishes and freeze-dried invertebrates were digested with 7:3 HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> in closed Teflon bombs and analyzed for THg the same as water samples. Detection limits were 0.1-0.3 ng/g. For MeHg, zooplankton and macroinvertebrates were digested in a KOH-methanol solution, ethylated, and separated by gas chromatography with CVAFS. Detection limits were 0.1-0.3 ng/g dry weight. All Hg analyses included spike recoveries, duplicates, blanks and National Research Council (Canada) certified reference materials (DORM-2), which were prepared alongside the original samples as matrix matched biomaterial.

Freeze-dried invertebrates and fishes were analysed for stable isotopes at the University of Ottawa G.G. Hatch Isotope Laboratories. Invertebrate were treated with HCl to dissolve shells and/or surficial carbonates, oven dried at 60°C and reground with a mortar and pestle. Samples were weighed in tin capsules (~1-2 mg for invertebrates and ~0.3-0.5 mg for fish) and combusted in an automated elemental analyzer (CE Elantech Inc., Lakewood, NJ) CE-1110 coupled to a Finnigan Mat Delta<sup>PLUS</sup> Isotope Ratio mass spectrometer; (Thermo Scientific, Waltham, MA) with a Conflow III interface. Water was removed by magnesium perchlorate trap. Helium was the carrier gas. Stable isotopes are expressed in "delta" notation ( $\delta$ ):

$$\delta R \% = [(R_{sample}/R_{standard})-1] \times 1000$$

where  $R=^{15}N/^{14}N$  or  $^{13}C/^{12}C$  (Peterson and Fry 1987). A normalized calibration curve based on NBS-22 and IAEACH-6 for carbon and IAEA-N-1 and IAEA-N-2 for 143

nitrogen were used to calculate  $\delta^{15}$ N and  $\delta^{13}$ C. Standards were from the National Institute of Standards and Technology (NIST). An internal laboratory standard (caffeine) was run every 10th sample to correct for drift in values. Precision was 0.2‰ for nitrogen and 0.3‰ for carbon (based on analyses of 20 replicates). Comparable methods were used for pre-fire samples at the Environment Canada Laboratory in Saskatoon (Saskatchewan, Canada).

#### Hg export calculations

THg and MeHg exports from catchments were calculated from THg and MeHg concentrations, streamflow data from September 1st to October 13th 2000 and 2001, and catchment areas. Dates were chosen based on available 2000 streamflow data. Hg concentrations and streamflow values between sampling dates were interpolated from the sampling dates before and after.

#### $\partial^{5}N$ baseline-adjustment

Nutrient inputs may cause baseline  $\delta^{15}N$  variability, which must be removed by baseline-adjustment before among-year comparison. Sphaeriid clams (collected in 1997, 2000 and 2001) were used as baseline organisms, and their  $\delta^{15}N$  was subtracted from invertebrate and fish  $\delta^{15}N$ .

#### Linear regression

Invertebrate MeHg and baseline-adjusted  $\delta^{15}N$  (BA $\delta^{15}N$ ) were extrapolated for 1994 and 2003. Data from 2000 before the post-fire runoff event were used for 1994 (with 1997 sphaeriid clams as baseline), and data from fall 2001 were used for 2003. Only lake trout were included with invertebrates in regression analyses because muscle Hg data were available for 1994, 2001 and 2003. Linear regression models were created for 1994, 2001, 2003, and other proximate lakes. Some data varied slightly from a normal distribution but transformation did not normalize the data. Other assumptions of linear regression were met. Regression is robust for slight violations of some assumptions (Zar 1999); therefore, untransformed data were used. Slopes and elevations of regression lines were compared by using t-tests (Zar 1999). A BA $\delta^{15}N$  of 7 (common to regression lines for 1994, 2001, 2003) was chosen, and the difference between the lake trout Hg concentration in 2001 and 2003 was

attributed to food web restructuring, whereas the difference between the lake trout Hg concentration in 1994 and 2001 was attributed to increased catchment inputs and in-lake methylation (Figure 5.2).

## **Results and Discussion**

Nutrient concentrations increased post-fire when compared with pre-fire Moab Lake data from the 1970s (Donald and DeHenau 1981) and 1990s. Nitrate + nitrite increased 9-fold from  $\leq 2.0 \ \mu g/L$ , total dissolved nitrogen increased 2-fold from 89  $\mu g/L$ , total phosphorus increased 4-fold from 5.0  $\mu g/L$ , and total dissolved phosphorus increased 5-fold from 1.0  $\mu g/L$ . All nutrient concentrations continued to increase in 2001, and may persist for several years (Carignan and Steedman 2000, Spencer et al. 2003).

Nutrient enrichment caused increases in measures of lake productivity. Phytoplankton chlorophyll *a* was 1.5-fold greater (from 0.9  $\mu$ g/L) post-fire. Zooplankton density was 1.6- to 3.0-fold higher in 2000 and 2001 than in the 1990's (13.2 crustaceans/L). Conductivity, a surrogate for productivity (Trippel and Beamish 1989), doubled from 113  $\mu$ S/cm after the fire. Fire-associated nutrient loading can stimulate aquatic primary productivity (Carignan and Steedman 2000, Spencer et al. 2003), and cause increased abundance of zooplankton (Carignan and Steedman 2000) and likely benthic invertebrates (Clarke et al. 1997). Post-fire fish growth rates were 12-30% greater than in the 1970's (Donald and DeHenau 1981). Enhanced lake productivity increases fish growth rates (Donald and Anderson 1982, Trippel and Beamish 1989), which may lead to earlier age of piscivory in lake trout (*Salvelinus namaycush*) (Donald and Anderson 1982, Trippel and Beamish 1989).

Increased fish growth in Moab Lake after the fire can be explained by dietary alterations. Before the fire, all fish species primarily consumed invertebrates (Figure 5.3). Fishes switched from feeding on *Hyalella* (a detritivore) before the fire to *Mysis* (a zooplanktivore) in 2001 after the fire. In 2003, rainbow trout (*Oncorhynchus mykiss*), lake trout, bull trout (*Salvelinus confluentus*), and cisco (*Coregonus artedi*) consumed young rainbow trout, likely because of fire-related increases in rainbow

trout recruitment from enhanced lake productivity and/or increased water temperatures in spawning streams. Forest fire can increase stream water temperatures by consuming forest canopy and riparian vegetation, resulting in a loss of shading (Ice et al. 2004). Strong year classes of rainbow trout in mountain lakes are related to warmer summer temperatures, probably because warm water causes egg development and hatching times to decrease (Donald and Alger 1986). However, a degree-day analysis indicated that enhanced recruitment was not because of year-to-year summer temperature variability, and recruitment was not unusual in other nearby lakes. Lake trout also preyed on cisco post-fire in 2003. These dietary shifts altered the stable isotope composition of fishes.

The nitrogen stable isotope ratio ( $\delta^{15}$ N) is commonly used as a continuous measure of trophic position (Peterson and Fry 1987, Post 2002). Baseline  $\delta^{15}$ N, measured in long-lived sphaeriid clams, increased from 0.15‰ before the fire to 2.58‰ in 2001. This increase was probably due to consumption of more autochthonous food sources (Spencer et al. 2003) (indicated by a decline in sphaeriid clam  $\delta^{13}$ C from –22.2 to –29.8 from 1997 to 2001), and/or a positive shift in  $\delta^{15}$ N in runoff from burned areas. Others have shown that organisms from fire-impacted waterbodies were significantly enriched in  $\delta^{15}$ N when compared to reference waterbodies (Spencer et al. 2003, Garcia and Carignan 2005).

We observed significant increases in the BA $\delta^{15}$ N of lake trout (1994  $\bar{x}$  =7.25, 2001  $\bar{x}$  =9.13, 2003  $\bar{x}$  =12.6; Tukey Test,  $p \le 0.05$ ), rainbow trout (1994  $\bar{x}$  =4.22, 2001  $\bar{x}$  =5.59, 2003  $\bar{x}$  =9.47; Tukey Test,  $p \le 0.05$ ), and bull trout (2001  $\bar{x}$  =6.85, 2003  $\bar{x}$  =8.68; Mann-Whitney U Test,  $p \le 0.05$ ) within Moab Lake (Figure 5.4A). Increases in BA $\delta^{15}$ N reflect increased post-fire consumption of *Mysis* and enhanced piscivory by all fish species (Figure 5.3). Increases in BA $\delta^{15}$ N of fishes is representative of a longer food chain. Productivity has been hypothesized to explain food chain length variability (Post et al 2000); however, little empirical supporting evidence exists and has generally been collected through multi-lake studies over a productivity gradient (Post et al. 2000). In our study, a fire-related increase in lake productivity led to a longer food chain, which supports the productivity hypothesis. The length of a food 146

chain is important because it affects the structure of aquatic communities and concentrations of contaminants in biota (Kidd et al. 1995b, Post et al. 2000).

MeHg concentrations of organisms from Moab Lake were correlated with BAδ<sup>15</sup>N (r=0.900, Figure 5.4A, 5.4B), as expected (Cabana and Rasmussen 1994, Kidd et al. 1995a). Hg in rainbow trout muscle increased significantly after fire (2001  $\bar{x}$ =68.0 ng/g wet weight (ww), 2003  $\bar{x}$  =140 ng/g ww; Mann-Whitney U Test,  $p \le 0.05$ ). By 2003, rainbow trout muscle Hg concentration and BA $\delta^{15}$ N approached those of more piscivorous bull trout (Figure 5.4A). A significant increase in the Hg concentration of lake trout muscle was also observed (1994  $\bar{x}$  =215 ng/g ww, 2001  $\bar{x}$ =250 ng/g ww, 2003  $\bar{x}$  =391 ng/g ww; Tukey Test,  $p \le 0.05$ ). Enhanced piscivory caused increased Hg concentrations in lake trout (MacCrimmon et al. 1983). Pre-fire bull trout were not available for Hg analyses, but muscle Hg concentrations increased 1.2-fold from 2001 ( $\bar{x}$  =90.1 ng/g ww) to 2003 ( $\bar{x}$  =105 ng/g ww). The increase was not statistically significant (Mann-Whitney U Test,  $p \ge 0.05$ ). In 2003, cisco (not normally a piscivorous species) began to eat fishes (Figure 5.3), which could further increase Hg accumulation by lake trout that consume them. Young rainbow trout were present in stomachs of lake trout pre-fire and several species post-fire, indicating they are preferred prey. Whole-body Hg concentrations of rainbow trout were 5-fold greater in 2003 than in 1994 (1994  $\bar{x}$  =69.21 ng/g ww, 2001  $\tilde{x} = 151.82 \text{ ng/g ww}, 2003 \tilde{x} = 318.6 \text{ ng/g ww}; \text{Tukey Test}, p \le 0.05)$  (Figure 5.4C).

Regressions of MeHg concentration and BA $\delta^{15}$ N (invertebrates and lake trout only) were highly significant for 1994, 2001 and 2003 (p=0.0001). BA $\delta^{15}$ N explained 70.8% of the variation in Hg in 1994, 84.8% in 2001, and 88.5% in 2003. The slope of the regression line for 1994 was not significantly different from 2001 (t=-0.882, v=27, p=0.001), or other nearby lakes (t=-0.839, v=41, p=0.001), indicating similar Hg bioaccumulation rates. The slope of the regression line for 2003 was significantly steeper than for 1994 (t=-3.779, v=24, p=0.001), 2001 (t=-3.013, v=29, p=0.01), and other lakes (t=-3.779, v=38, p=0.001), suggesting enhanced Hg bioaccumulation in 2003. When lake trout MeHg concentrations from regression lines are compared

among years at a BA $\delta^{15}$ N of 7 (common to regression lines for 1994, 2001 and 2003), ~88% of the MeHg increase can be attributed to restructuring of the food web.

The first major post-fire runoff event in September 2000 mobilized a large short-term pulse of MeHg and total Hg (THg) (Figure 5.5A and 5.5B). This pulse of Hg was unexpected because fire-related volatilization of Hg to the atmosphere removes substantial amounts of Hg from soils (Harden et al. 2004) and vegetation (Friedli et al. 2003), and decreased concentrations of Hg in soil have been identified even 50 years post-fire (Amirbahman et al. 2004). However, increased THg and MeHg concentrations in sediments close to an inflow draining a burned area of a New Mexico reservoir's catchment were attributed to sediment methylation of THg bound to organic matter and MeHg in runoff (Caldwell et al. 2000), but Hg inputs were not measured. Two streams near Moab Lake, in burned catchments, had peak MeHg concentrations of 0.14 and 0.13 ng/L and THg concentrations of 102.4 and No pre-fire data were available, however, the MeHg and THg 21.4 ng/L. concentrations from the streams in burned catchments were greater than those from two nearby streams in unburned catchments. In a high elevation catchment in Rocky Mountain National Park, Colorado, stream MeHg peaked at 0.048 ng/L just after snowmelt and were generally at or below their detection limits (<0.040 ng/L) for the rest of the season (Mast et al. 2005). THg concentrations in the same streams ranged from 0.8 to 13.5 ng/L. Concentrations of both MeHg (<0.040 ng/L) and THg (~1.0 ng/L) were lowest during September and October (Mast et al. 2005). Near Moab Lake, MeHg and THg exports to water were greater from burned catchments (x =0.33 mg MeHg/ha, 29.7 mg THg/ha) than unburned catchments ( $\bar{x}$  =0.04 mg MeHg/ha, 1.52 mg THg/ha) in 2000. The exports from burned catchments were greater than the total annual export from high elevation catchments in Colorado (0.13 mg MeHg/ha and 6.5-23.4 mg /ha THg) (Mast et al. 2005), although our export estimates were only for a 43 day period in September and early October. MeHg and THg exports decreased in both burned and unburned catchments close to Moab Lake from 2000 to 2001 (Figure 5.5A and 5.5B). Fire may release previously soilbound MeHg for export in burned catchments. Increased Hg exports from burned 148

and unburned catchments in 2000 may be indicative of local fire-related Hg deposition resulting from smoke and ash. Ash contains substantially lower MeHg and THg concentrations than unburned soil and vegetation because of volatilization (vegetation = 97% loss of THg and 94% loss of MeHg; soil= 79% loss of THg and 82% loss of MeHg) (Mailman and Bodaly 2005), and much greater concentrations of THg than MeHg (Mailman and Bodaly 2005). Soil fertilization stimulates MeHg production in forest soils (Amirbahman et al. 2004, Matilainen et al. 2001). In this study, unburned catchments and unburned areas of burned catchments were likely subjected to nutrient deposition from the fire. This nutrient deposition could enhance methylation of both in-situ and newly deposited fire-related THg, which would increase MeHg export from burned and unburned catchments. Thus, both burned and unburned (to a lesser extent) catchments may suffer deleterious effects from fire-related increases in MeHg and THg export.

Export of MeHg and THg from the burned watershed caused a short-term increase in MeHg and THg concentrations in Moab Lake water during the autumn of 2000 (Figure 5.5C and 5.5D). The mean MeHg and THg concentrations in Moab Lake between August and mid-October 2000 were 0.10 and 2.72 ng/L respectively. Peak concentrations were 0.13 ng/L MeHg and 6.66 ng/L THg. August to mid-October mean concentrations declined to 0.03 ng/L MeHg and 0.55 ng/L THg in 2001. The 2000 mean concentrations were also higher than mean concentrations in 36 other lakes in the Canadian Rockies (August to September 2000  $\bar{x} = 0.06$ , range=0.02-0.15 ng/L MeHg,  $\bar{x}$  =0.68, range=0.36-2.24 ng/L THg, May to July 2001  $\bar{x}$ = 0.05, range=0.02-0.15 ng/L MeHg,  $\bar{x} = 0.49$ , range=0.21-2.88 ng/L THg), and in 90 high-altitude lakes located in 8 Mountain National Parks in the United States (September 1999  $\bar{x} = 0.05$ , range=0.01-0.73 ng/L MeHg and  $\bar{x} = 1.07$ , range=0.27-14.09 ng/L THg) (Krabbenhoft et al. 2002). Although direct evidence exists of increased MeHg and THg inputs to Moab Lake after fire, the possibility that in-lake methylation was stimulated by fire cannot be ruled out. The first pulse of MeHg in 2000 (Figure 5.5C) coincided with fire-related changes in water chemistry (e.x. SO<sub>4</sub> concentration was 8.5 mg/L before the fire, 32.71 mg/L at the time of the first MeHg 149

pulse in 2000, and remained ~16-18 mg/L to the end of 2001). The second MeHg pulse in 2000 occurred at the same time as a large rain event (Figure 5.5C). A small, short-lived peak in MeHg in invertebrates from Moab Lake (20-60ng/g dw) coincided with the second fire-related peak in water MeHg concentration in September 2000. The overall increase in mass of MeHg and THg in Moab Lake water between July and mid-October was greater in 2000 (0.23 g MeHg, 13 g THg) than in 2001 (0.07 g MeHg, 0.6 g THg).

Although the baseline-adjusted rates of MeHg bioaccumulation in 1994 and 2001 were not significantly different, the elevation of the regression line (invertebrates and lake trout only) for 2001 was significantly higher than for 1994 (*t*=-2.199, *v*=28, *p*=0.05). When lake trout MeHg concentrations from regression lines are compared among years at a BA $\delta^{15}$ N of 7, ~12% of the MeHg increase is due to fire-enhanced Hg inputs to Moab Lake and/or increased in-lake methylation. However, if the pulse of Hg from the burned catchment occurred in summer, rather than in autumn, Hg bioaccumulation could increase more than observed at Moab Lake because warmer water temperatures, greater nutrient concentrations, increased DOC and SO<sub>4</sub><sup>2-</sup> could enhance production and uptake of fire-related MeHg.

## Conclusion

We conclude that forest fire caused increased Hg accumulation by fishes in a partially burned catchment by means of two mechanisms. Food web restructuring was more important than increased Hg inputs and MeHg production at Moab Lake. We hypothesize that fire characteristics (i.e., fire severity, proportion of catchment burned, and timing and intensity of runoff) influence nutrient and contaminant release from burned catchments, altering the relative importance of the two Hg accumulation mechanisms. This hypothesis provides an explanation for the differing results from studies conducted in severely and/or fully burned catchments (Garcia and Carignan 1999, Garcia and Carignan 2000, Allen et al. 2005). The post-fire changes in Hg cycling observed in this study are likely not unique to Moab Lake.

persist for several years (Carignan and Steedman 2000) in partially burned catchments. We recently observed elevated THg concentrations in streams in other burned catchments in the Canadian Rocky Mountains, indicating increased post-fire Hg inputs (E.N.K., D.W.S., U. Silins, M. Wagner, and J. Graydon, unpublished data). In some lakes, forest fires could cause MeHg concentrations in fishes to exceed guidelines that protect the health of fish-eating birds and mammals, including humans (Garcia and Carignan 2005). Hg in fishes often remains high for many years after Hg inputs have ceased (Ullrich et al. 2001). In North America, Hg contamination is already the most frequent reason for fish consumption advisories (USEPA 1998). If climate change and prescribed burning increase forest fires in the future in North America (Weber and Stocks 1998, Flannigan et al. 2000, Flannigan et al. 2002, Spencer et al. 2003), and the average annual area of forest burned continues to increase in Asia, Europe, the Caribbean, Oceania, South America and some parts of Africa as it did from 1990 to 2000 (FAO 2005), fish Hg contamination could become more widespread.

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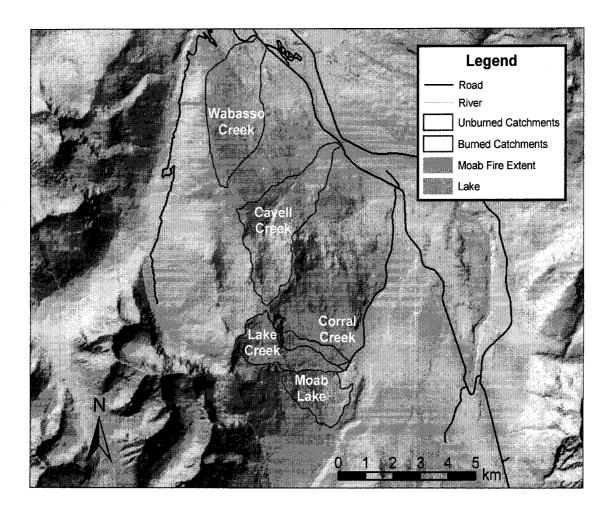
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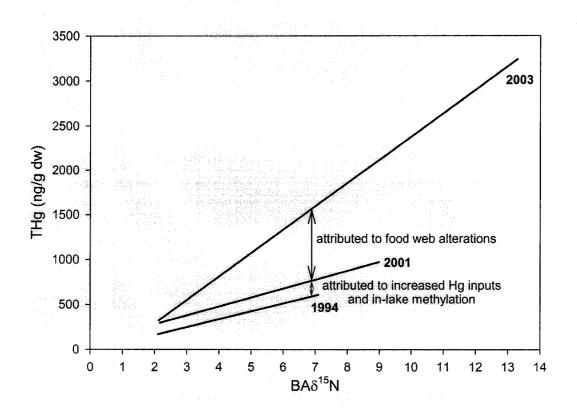
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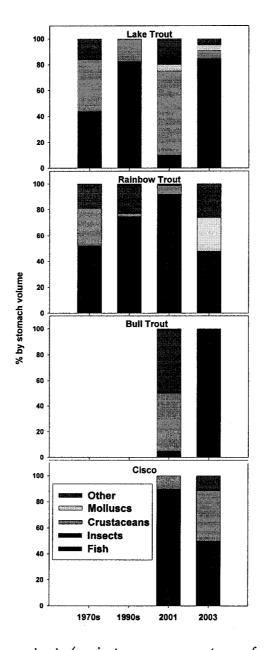
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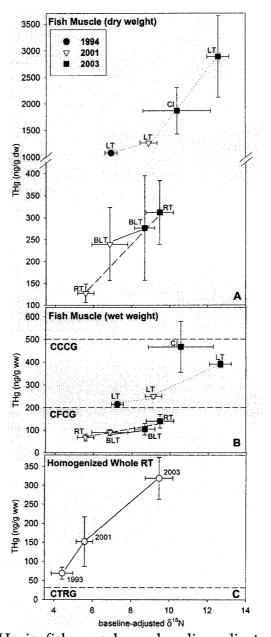
**Figure 5.1** Map of the study area. The fire, which lasted from 12 July to 31 August 2000, burned 71.5% of the catchment of Moab Lake, as well as 29.3 and 68.4% of the catchments of Lake Creek and Corral Creek respectively. The catchments of Cavell Creek and Corral Creek were not burned.



**Figure 5.2** Conceptual diagram demonstrating source attribution of fire-related Hg increase. A baseline-adjusted  $\delta^{15}N$  of 7 was chosen because it was common to the 1994, 2001 and 2003 regression lines of invertebrates and lake trout. The difference between the lake trout mercury concentration in 2001 and 2003 was attributed to food web alterations. The difference between lake trout mercury concentration in 1994 and 2001 was attributed to increased Hg inputs and in-lake methylation.



**Figure 5.3** Stomach contents (main taxa as percentage of stomach volume) of lake trout, rainbow trout, bull trout and cisco from Moab Lake in 1979 (Donald and DeHenau 1981), 1993, 2001, and 2003 (*n*=1 to 26). In lake trout stomachs, both rainbow trout (1993/2003) and cisco (2003) were identified, in rainbow trout, bull trout and cisco stomachs the species of prey fish was rainbow trout/unidentifiable. Crustaceans included *Daphnia* (which were only present in cisco), Amphipoda, and *Mysis*; insects included Odonata, Trichoptera, Diptera, Ephemeroptera, and Hemiptera; molluscs included Pelecypoda and Gastropoda; and other included terrestrial items such as adult insects, ants, spiders, semi-aquatic mammals and unidentifiable matter.



**Figure 5.4** Mean THg in fish muscle vs. baseline-adjusted  $\delta^{15}N$  for fishes from Moab Lake in 1994, 2001, 2003. (A) THg concentration (dry weight). (B) THg concentration (wet weight). CCCG =Canadian Commercial Consumption Guideline; CFCG=Canadian Frequent Consumption Guideline (human health protection). (C) Mean THg for homogenized whole rainbow trout (RT) from Moab Lake versus baseline- adjusted  $\delta^{15}N$  in 1993, 2001, and 2003. ww=wet weight); CRTG= Canadian Tissue Residue Guideline (wildlife health protection). (LT= lake trout, RT=rainbow trout, BLT=bull trout, CI=cisco), Error bars show standard error). We assumed that fish THg concentrations were MeHg concentrations because > 85% of Hg in fish is MeHg (Ullrich et al. 2001).

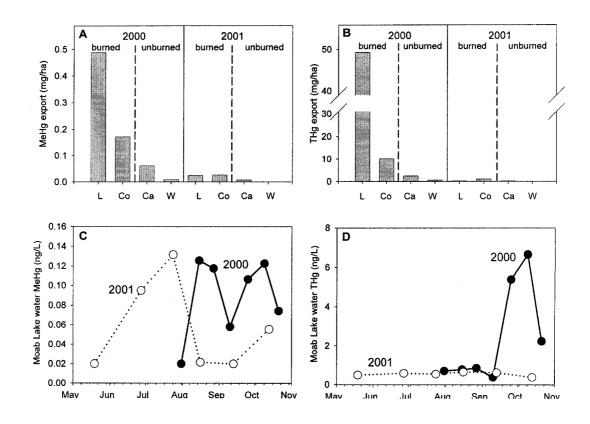


Figure 5.5 MeHg and THg export from burned and unburned catchments near Moab Lake, and MeHg and THg concentrations in Moab Lake surface waters. (A and B) Export of MeHg (A) and THg (B) from two burned catchments, L=Lake Creek (29.3% burned) and Co=Corral Creek (68.4% burned), and two unburned catchments, Ca=Cavell Creek and W=Wabasso Creek. (C and D) Seasonal concentrations of MeHg (C) and THg (D) in unfiltered water from Moab Lake in 2000 and 2001.

# 6.0 Discussion

In Chapter 3, we determined that methyl mercury (MeHg) and total mercury (THg) concentrations in aquatic invertebrates and THg (as MeHg) concentrations in fish species varied widely among lakes sampled in the Canadian Rocky Mountains. Risk assessments indicated that MeHg concentrations of some fish species from a number of lakes posed a risk to human and wildlife health. Based on these results, Parks Canada (in conjunction with Health Canada) implemented consumption guidelines for several lakes and consumption advice for all fish-bearing mountain park waters (Parks Canada 2005). MeHg and THg concentrations in some biota decreased with elevation and increased with latitude. Seasonal changes in MeHg and THg concentration of some biota were also identified. No temporal trend was evident in MeHg concentrations of fishes from several Rocky Mountain lakes.

Many factors lead to among-lake variability in MeHg concentrations of fishes, including those that affect sources, transport, MeHg production and bioaccumulation and biomagnification of MeHg (reviewed in Kelly et al. 2006). In Chapter 4, we used multiple regression models to reveal the best predictors of mean MeHg concentrations in trout. Overall, these were latitude, spring sulphate concentration, mean annual air temperature, concentration of MeHg in zooplankton collected in the spring, and spring dissolved inorganic nitrogen (DIN) concentration. These predictors were all significantly and positively related to mean MeHg concentration in trout, with the exception of DIN which was related negatively. Together, these explained a high proportion of the variation in mean MeHg concentrations of trout. Negative relationships between MeHg concentations in trout and elevation were likely due to poor conditions for MeHg production (*i.e.*, cold temperatures, decreased lake productivity, and low DOC concentrations) in high altitude lakes. Mean MeHg concentrations in trout were positively related to latitude, likely because northern catchments were

warmer than southern catchments, contained increased proportions of sedimentary, volcanic and metamorphic rock and well drained soils. Northern catchments also had increased catchment area to lake area ratios, DOC concentrations, cation and chlorophyll *a* concentrations, zooplankton density, concentrations of MeHg in zooplankton collected in the spring, and weight of trout. Many of these factors can increase MeHg accumulation by fishes. Multiple regression models were used to predict MeHg concentrations in all other fish-bearing lakes in the Rocky Mountain National Parks and to identify other lakes that likely contain fishes with elevated MeHg concentrations. Results of the predictive model must be verified, but indicate that other lakes are at risk of MeHg contamination. Baseline data and model results should aid with monitoring and management of aquatic ecosystems in Canadian Rocky Mountain Parks.

Climate change will likely alter factors that affect MeHg accumulation by aquatic biota. In the Canadian Rocky Mountains, forest fire occurrence is expected to increase in the future with climate change (Flannigan et al. 2000, Flannigan et al. 2002, Westerling et al. 2006), and as park managers conduct prescribed burns to renew habitat for wildlife (Weber and Stokes 1998, Spencer et al. 2003). In Chapter 5, we determined that forest fire increased Hg accumulation by fishes in Moab Lake via two mechanisms. These mechanisms were increased inorganic Hg<sup>2+</sup> and MeHg inputs from the catchment (~12%) and food web alterations/lengthening of the food chain (~88%). These results are likely not unique to Moab Lake (see last paragraph of Discussion). Greater MeHg concentrations in fishes have been identified in lakes within partially burned catchments when compared to fishes from lakes in reference catchments in Quebec (Garcia and Carignan 2005). In some lakes, forest fire may cause MeHg concentrations in fishes to exceed guidelines that protect the health of human and wildlife consumers.

#### **Ongoing and Future Research**

Several analyses are ongoing, and new research has begun based on the results of this project. Analyses of factors that affect trace element accumulation 163

within lakes and risk assessments for wildlife species that include aquatic invertebrates in their diet are in progress. We determined the concentrations of trace elements other than Hg in invertebrates and fishes (some of these data were included in analyses in Chapter 4). Preliminary results indicate that some trace element concentrations in fishes (*e.g.*, arsenic, selenium, copper and zinc) may pose a health risk to human and/or wildlife consumers. Trace element concentrations in fishes will be analysed for spatial distribution patterns, and multiple regression analyses will be used to find the best predictors. We identified elevated selenium concentration in southeastern Banff National Park and Spray Lakes reservoir. Barbra Fortin's M.Sc. project focusses on determining the mechanisms and geographic extent of selenium contamination in fishes in this area. Sarah Lord, another M.Sc. student, is studying contaminants in piscivorous birds throughout the Canadian Rocky Mountains and utilizing data and modeling results from this project.

Although some previous research has shown that forest fires influence Hg accumulation by fishes, no studies have evaluated the effects of forest fire on OC accumulation by fishes. Elevated concentrations of OCs have been identified in fishes from some lakes in the Canadian Rocky Mountain Parks (Donald et al. 1993, Campbell et al. 2000, Demers et al. 2007). We established that forest fire caused OC concentrations to decline as MeHg concentrations increased in the same fishes from Moab Lake. While developing a hypothesis to explain this occurrence, we discovered that our method for source attribution in Chapter 5 likely underestimated the importance of fire-related Hg inputs for increased Hg accumulation by fishes. We used the hypothesis to create a framework, useful for managers, which predicts the effect of forest fire on contaminants. All research completed thus far on the effects of forest fire on contaminant accumulation by fishes fits within our framework (*e.g.*, Allen et al 2005, Garcia and Carignan 1999, 2000, 2005). A manuscript on this research is currently in preparation.

We sampled Moab Lake in 2006 to determine the longer-term effects of forest fire on contaminant accumulation. Samples were analysed for Hg, OCs and trace

elements. We also analysed archived invertebrate and fish samples from the 1990s, 2000, 2001, and 2003 for trace elements. This will allow us to determine the effects of forest fire on accumulation of other trace elements in aquatic biota.

When fishes from lakes in burned catchments were compared to fishes from reference catchments, increased Hg accumulation by fishes after forest fire was identified without food web alterations/lengthening of the food chain (Garcia and However, the increased Hg<sup>2+</sup> and MeHg inputs mechanism Carignan 2005). (causing increased MeHg concentrations in fishes) has only been identified at Moab Lake. We compared Hg in stream water and fishes from reference, burned, and burned and salvage logged catchments in the Crowsnest Pass, to verify the generality of the Hg input mechanism and to study the effects of forest fire and salvage logging on Hg in stream biota. The effects of forest fire, and forest fire and salvage logging on Hg in stream biota have not been previously studied. Several studies indicate that logging increases Hg accumulation by biota from lakes, such as zooplankton (Garcia and Carignan 1999) and fishes (Garcia and Carignan 2000, Garcia and Carignan 2005). We determined that the increased Hg input mechanism did apply to streams affected by fire and those affected by fire and salvage logging. The effects of forest fire on Hg accumulation by stream fishes fit within the management framework we developed.

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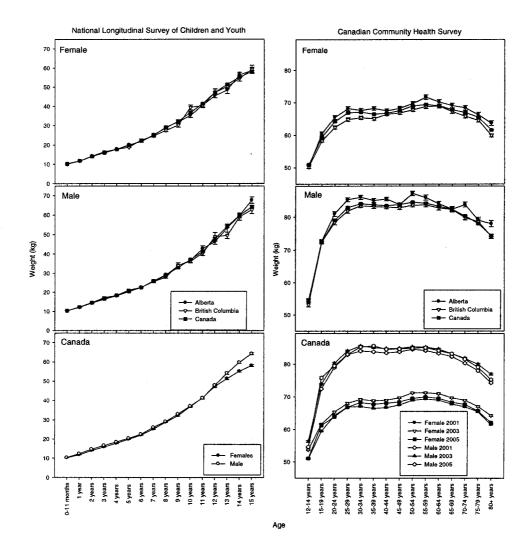
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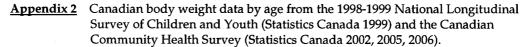
[						Mean	Max				}		1					1		[]
	Longitude		Elevation	Catchment	Lake area	depth	depth		Secchi		DOC	тр	TN	Cond	cı-	SO <sub>4</sub> 2-	Nat	K.	Ca2+	Mg2+
Lake Name	(-)	Latitude	(m.a.s.l)	area (m³)	(m²)	(m)		T (°C)	(m)					(uS/cm)			1			(mg/L)
	(-)	Latitude	(111.4.5.1)	area (m <sup>3</sup> )	(m²)	(m)	(m)	1(0)	(m)	pН	(mg/L)	(µg/L)	(µg/L)	(µS/cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Annette	118.048093	52.901891	1016	861870	271626	6.60	23.00	19.00	9.00	8.41	0.88	3.80	175.86	283.50	1.91	26.07	2.94	0.49	34.90	15.20
Beauvert	118.059582	52.882421	1023	4593850	351825	6.80	25.00	14.00	10.00	8.32	0.91	1.90	130.43	247.20	2.47	24.54	2.67	0.44	32.30	12.00
Bighorn	115.648082	51.464636	2355	1083630	15380	3.09	9.20	9.80	1.80	8.18	0.44	1.70	163.39	293.20	0.20	84.05	0.37	0.32	37.30	14.10
Bow	116.456778	51.669123	1934	78069600	3094963		51.00	10.50	2.50	8.18	0.61	4.20	78.49	164.70	0.37	15.12	0.64	0.17	20.10	8.42
Cabin	118.131662	52.878348	1218	19471000	348732	8.30	20.50	11.50	4.25	7.84	3.61	5.60	255.55	141.90	0.23	11.87	2.55	0.64	16.00	6.68
Caledonia	118.161861	52.867144	1167	9576960	151615	4.70	11.00	12.00		7.76	3.39	5.80	216.13	114.20	0.18	9.66	2.05	0.54	13.30	5.08
Caveli	118.061311	52.698070	1711	16635100	129281			4.25	3.75	7.15	0.42	1.20	208.76	90.80	0.22	19.27	0.77	0.30	9.98	4.09
Devon	116.237210	51.724993	2288	3897640	27986					8.12	0.75	2.60	105.62	179.40	0.23	28.87	0.57	0.55	22.90	8.84
Edith	118.039446	52.912150	1021	14615600	539134	5.10	18.00	16.00	8.00	8.30	1.42	2.90	140.58	309.00	1.53	30.92	3.87	0.65	37.30	17.20
Emerald	116.530644	51.443195	1292	48884900	1029516		28.00	13.00	4.00	8.22	0.62	3.60	141.61	204.60	0.33	12.22	0.42	0.09	26.90	10.20
								10100			0.02			201100						Į
Fryatt	117.921067	52.542602	2508	1467580	48827			1.00	1.75	8.01	0.19	1.70	113.67	112.70			2.75	0.10	16.30	5.20
Geraldine 3	117.942759	52.592691	1883	26374400	322974	20.10	31.00	8.50	3.50	7.79	0.34	1.80	94.32	126.20	0.13	22.92	1.10	0.22	15.80	5.79
Geraldine 5	117.948848	52.570490	1984	12652000	174541	13.40	25.00	7.50	3.25	7.73	0.33	1.50	80.18	105.10	2.89	11.75	0.49	0.16	13.20	4.70
Geraldine H	117.933005	52.558753	2295	1101060	36824			3.50	2.25	8.13	0.19	2.30	92.28	119.50	4.56	10.42	2.10	0.15	13.10	6.74
Geraldine T	117.959447	52.577505	2096	3650260	31390			4.00	2.75	7.96	0.18	2.60	88.95	166.30	0.21	8.27	0.40	0.21	19.90	8.22
Glacier	116.861073	51.920908	1420	129174000	2368733		38.00	8.00	1.25	8.08	0.45	4.90	138.29	136.90	0.33	10.92	0.53	0.16	20.80	4.83
Harrison	115.810616	51.554481	2232	4324060	50946	5.40	10.70	11.00	8.50	8.37	1.04	2.60	186.41	287.20	0.15	51.62	1.00	0.25	38.70	12.90
Hector	116.362174	51.585411	1740	81677600	5548798		87.00	11.50	2.70	8.14	0.78	1.90	98.42	151.70	0.26	10.82	0.58	0.17	18.90	7.58
Honeymoon	117.677762	52.556509	1397	600779	170141	2.10	7.00	10.00	3.75	8.36	7.82	5.80	764.16	177.50	0.49	0.00	1.14	0.55	27.00	6.63
Horseshoe	117.865589	52.698152	1244	1106050	80474	10.69	31.50	10.00	12.00	8.19	0.96	1.50	174.26	256.00	0.52	65.26	1.80	1.20	26.60	13.90
Johnson	115.483611	51.196191	1407	16346300	156061			15.00	1.75	8.27	1.47	6.80	85.23	341.20	0.60	50.69	1.43	0.58	45.40	16.70
Kidney	118.350100	53.354170	1378	7658980	614265	4.00	12.00									<b> </b>		1		†

Appendix 1 Selected characteristics of Rocky Mountain Park study lakes

Minnewanka	115.390034	51.256034	1468	685728000	22334906		99.00	13.00	10.50	8.38	0.97	4.30	86.29	335.00	0.48	58.21	1.16	0.41	47.10	15.40
O'Hara	116.330667	51.355773	1985	17159600	303098		38.10	10.00	3.50	7.59	0.51	3.80	108.50	117.00	0.25	16.32	0.35	0.10	12.80	6.54
Little Cranberry	119.253447	52.794603	802	652992	51184			20.00	2.50	7.39	11.40	14.00	831.07	136.40	0.81	0.83	1.46	2.91	24.10	1.92
Lower Geraldine	117.929051	52.616157	1604	33026900	124817	3.30	6.00	12.00	4.00	7.86	0.37	1.50	99.83	119.40	1.05	16.48	0.54	0.21	14.90	5.30
Maligne	117.536948	52.662257	1659	508516000	20582030	38.30	96.00	10.00	3.25	8.16	0.65	2.30	259.07	201.10	5.75	31.48	4.00	0.54	29.20	8.22
Middle Waterton	113.875916	49.057084	1259		4418767		27.00													
Moab	117.959129	52.661579	1204	3215250	213518	8.60	18.00	17.00	5.25	7.81	1.80	4.10	118.82	125.90	0.28	14.25	1.31	0.25	16.70	5.84
Moose	118.909900	52.953804	1025	1859780000	13809708		83.00	13.00	1.50	7.69	0.49	2.60	104.67	113.50	0.33	16.28	0.62	0.15	14.20	5.15
Moraine	116.185060	51.321531	1849	32556100	391970			7.00	4.75	8.04	0.45	2.50	157.77	136.60	0.25	10.36	0.36	0.09	16.60	6.83
Outram	116.810031	51.864873	1436	1930150	90864		12.00													
Patricia	118.103221	52.904270	1180	3091680	645282	12.00	40.00	16.00	6.25	8.81	7.33	5.40	543.51	611.70	2.36	99.97	24.10	5.11	19.10	60.80
Pipit	115.862380	51.616884	2209	3175270	80210	12.60	20.60	8.00	6.50	8.26	0.56	2.60	144.46	210.90	0.29	14.38	1.37	0.21	30.10	10.20
Pyramid	118.095654	52.923041	1191	31070900	1241874	8.70	19.00	15.50	7.50	8.20	3.78	3.20	151.11	256.30	0.27	51.25	2.89	1.05	30.20	12.50
Sassenach	118.397270	53.256645	2017	5749280	177958	6.20	16.00												-	
Sherbrooke	116.386857	51.456819	1801	24175700	361314		12.00	8.00	2.25	8.06	0.42	1.90	98.91	168.30	0.22	14.10	0.67	0.12	23.00	8.22
Shere	119.604352	53.034655	760	436888	66430			17.25	2.75	7.88	9.65	7.60	691.75	110.70	0.24	0.43	1.36	1.36	19.20	1.72
Snowflake	115.832943	51.597949	2313	2704080	58082	6.10	13.00	8.20	5.00	8.31	0.69	4.90	138.51	228.30	0.20	21.05	1.57	0.27	29.10	11.60
Spray	115.357967	50.917842	1688	578951000	19141012	13.50	65.40					4.00		· · · · · ·						<u> </u>
Sunwapta	117.235043	52.214560	1923	36477400	128095			3.00	0.25	8.40	0.35	9.30	119.45	104.40	0.21	7.52	0.36	0.13	17.20	4.11
Wapta	116.349514	51.439038	1584	104920000	191363		8.20	8.50	4.00	8.12	0.73	3.70	107.57	170.70	1.20	13.22	0.96	0.11	20.60	8.86
Yellowhead	118.540071	52.862087	1099	141310000	2366088			14.00	4.50	7.84	1.12	0.90	204.99	167.20	0.67	25.44	1.06	0.16	15.60	11.00

H=Headwater, T=Tributary, Max=Maximum, DOC=Dissolved Organic Carbon, TP=Total Phosphorus, TN=Total Nitrogen, Cond=Conductivity, Cl=Chloride, SO<sub>4</sub>=Sulphate, Na=Sodium, K=Potassium, Ca=Calcium, Mg=Magnesium





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Fish	ar se la ser esta de s	Child			- 10 M <sup>11</sup> - 11 - 11 - 11 - 11 - 11 - 11 - 11	Ad	lult		
meals per				13-19	years	20-50	years	51+	years
week	2-3 years	4-8 years	9-12 years	Male	Female	Male	Female	Male	Female
7 or >	RT - Johnson BT – Johnson, Moraine BLT - Harrison	RT - Johnson BT – Johnson, Moraine BLT - Harrison	RT – Johnson, Sherbrooke BT – Bighorn, Johnson, Moraine BLT – Harrison WS - Johnson	RT – Johnson, Sherbrooke BT – Bighorn, Johnson, Moraine BLT – Harrison WS - Johnson	RT – Johnson, Sherbrooke CT - Moraine BT – Bighorn, Johnson, Moraine BLT – Harrison WS - Johnson	LT – Glacier, Minnewanka, Sherbrooke, Spray, Wapta RT – Emerald, Johnson, Moab, Sherbrooke CT - Moraine BT – Bighorn, Devon, Johnson, Patricia, Moraine, Shere BLT – Harrison, Minnewanka, Moab CI – Pyramid MW – Bow WS - Johnson	LT – Spray, Wapta RT – Johnson, Sherbrooke CT _ Moraine BT – Bighorn, Johnson, Moraine, Shere BLT – Harrison, Minnewanka MW – Bow WS – Johnson	LT – Minnewanka, Sherbrooke, Spray, Wapta RT – Emerald, Johnson, Moab, Sherbrooke CT - Moraine BT – Bighorn, Devon, Johnson, Moraine, Shere BLT – Harrison, Minnewanka, Moab CI - Pyramid MW – Bow WS – Johnson	LT – Glacier, Minnewanka, Sherbrooke, Spray, Wapta RT – Emerald, Johnson, Moab, Sherbrooke CT - Moraine BT – Bighorn, Devon, Johnson, Moraine, Patricia, Shere BLT – Harrison, Minnewanka, Moab CI - Pyramid MW – Bow WS - Johnson
6	RT - Sherbrooke BT – Bighorn WS - Johnson		CT - Moraine	CT - Moraine	LT - Spray BT - Shere MW - Bow	BT - Emerald	LT – Sherbrooke RT – Emerald BT – Devon	LT – Glacier BT – Emerald, Patricia	BT – Emerald
5	CT - Moraine	RT - Sherbrooke BT - Bighorn WS - Johnson	LT - Spray	LT - Spray BT - Shere	LT – Sherbrooke, Wapta RT - Emerald BT – Devon BLT - Minnewanka	RT - Patricia LNS - Annette	LT – Minnewanka	RT – Patricia LNS – Annette	RT – Patricia LNS – Annette, Beauvert

Appendix 3 Calculated weekly allowable human fish consumption rates for Rocky Mountain Park study lakes

4	LT - Spray BT - Shere	CT - Moraine	LT – Sherbrooke, Wapta RT – Emerald BT – Devon, Shere BLT - Minnewanka MW - Bow	LT – Sherbrooke, Wapta RT – Emerald BT – Devon BLT - Minnewanka MW - Bow	LT - Minnewanka	RT - Cabin LNS - Beauvert	BLT – Moab	RT – Cabin LNS - Beauvert	RT – Cabin
3	LT – Minnewanka, Sherbrooke, Wapta RT – Emerald BT – Devon BLT - Minnewanka MW - Bow	LT – Sherbrooke, Spray, Wapta BT – Devon, Shere BLT - Minnewanka MW – Bow	LT - Minnewanka BT – Emerald BLT - Moab	LT - Minnewanka	RT – Moab BLT - Moab CI - Pyramid	LT – Bow, Kidney, Moab, Moose	LT – Glacier RT – Moab BT – Emerald, Patricia CI - Pyramid	LT – Bow, Kidney, Moab	LT – Bow, Kidney, Middle Waterton, Moab, Moose, Pyramid
2	LT – Glacier RT - Moab BT - Patricia BLT – Moab CI - Pyramid	LT - Minnewanka RT – Emerald BLT - Moab	LT – Glacier RT – Moab BT - Patricia CI - Pyramid	LT - Glacier RT – Moab BT – Emerald, Patricia CI - Pyramid LNS - Annette	LT - Glacier RT - Patricia BT – Patricia, Emerald LNS – Annette, Beauvert	LT – Hector, Middle Waterton, Outram, Pyramid CI - Moab	RT – Cabin, Patricia LNS – Annette, Beauvert	LT – Hector, Middle Waterton, Moose, Outram, Pyramid CI – Moab	LT – Hector, Outram CI – Moab
1	LT – Bow, Kidney, Moab RT – Cabin, Patricia BT - Emerald LNS – Annette, Beauvert	LT - Glacier RT – Cabin, Moab, Patricia BT – Emerald, Patricia LNS – Annette, Beauvert CI - Pyramid	LT – Bow, Kidney, Middle Waterton, Moab, Moose, Pyramid RT – Cabin, Patricia LNS – Annette, Beauvert	LT – Bow, Hector, Kidney, Middle Waterton, Moab, Moose, pyramid RT – Cabin, Patricia LNS - Beauvert	LT – Bow, Hector, Kidney, Middle Waterton, Moab, Moose, Pyramid RT - Cabin	LT – Patricia, Sassenach	LT – Bow, Hector, Kidney, Middle Waterton, Moab, Moose, Outram, Pyramid CI – Moab	LT – Patricia, Sassenach	LT – Patricia, Sassenach
0.5	LT – Hector, Middle Waterton, Moose, Pyramid	LT – Bow, Kidney, Middle Waterton, Moab, Moose, Pyramid	LT – Hector CI - Moab	LT - Outram	LT -Outram CI - Moab		LT - Patricia		

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h, LNS= longnose	LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, CI=cisco, MW=mountain whitefish, LNS= longnose ucker. WS=white sucker	ut, CI=cisco, MW	3LT=bull tro	'=brook trout, I	throat trout, BT	v trout, CT=cut	.T=lake trout, RT=rainbov ucker, WS=white sucker	LT=lake tr sucker, WS
						CI - Moab		
						Sassenach	CI - Moab	
					Sassenach	Patricia,	Sassenach	
			Sassenach	Sassenach	Patricia,	Outram,	Patricia,	
	LT - Sassenach		LT – Patricia,	- Outram, LT - Patricia,	LT – Outram,	LT – Hector,	LT – Outram,	< 0.5

Fish		Child	1			Ac	lult	· · · · · · · · · · · · · · · · · · ·	
meals per month				13-19	years	20-50	years	51+	years
	2-3 years	4-8 years	9-12 years	Male	Female	Male	Female	Male	Female
16 or >	LT - Spray RT – Johnson, Sherbrooke CT - Moraine BT – Bighorn, Johnson, Moraine, Shere BLT – Harrison WS - Johnson	RT – Johnson, Sherbrooke CT - Moraine BT – Bighorn, Johnson, Moraine BLT – Harrison WS - Johnson	LT – Sherbrooke, Spray, Wapta RT – Emerald, Johnson, Sherbrooke CT - Moraine BT – Bighorn, Devon, Johnson, Moraine, Shere BLT – Harrison, Minnewanka MW – Bow WS – Johnson	LT – Sherbrooke, Spray, Wapta RT – Emerald, Johnson, Sherbrooke CT - Moraine BT – Bighorn, Devon, Johnson, Moraine, Shere BLT – Harrison, Minnewanka MW – Bow WS - Johnson	LT – Minnewanka, Sherbrooke, Spray, Wapta RT – Emerald, Johnson, Sherbrooke, CT – Moraine BT – Bighorn, Devon, Johnson, Moraine, Shere BLT – Harrison, Minnewanka MW – Bow WS - Johnson	LT - Glacier, Minnewanka, Sherbrooke, Spray, Wapta RT - Cabin, Emerald, Johnson, Moab, Patricia, Sherbrooke CT - Moraine BT - Bighorn, Devon, Emerald, Johnson, Moraine, Patricia, Shere BLT - Harrison, Minnewanka, Moab CI - Pyramid MW - Bow LNS - Annette, Beauvert WS - Johnson	LT – Minnewanka, Sherbrooke, Spray, Wapta RT – Emerald, Johnson, Sherbrooke CT - Moraine BT – Bighorn, Devon, Johnson, Moraine, Shere BLT – Harrison, Minnewanka, Moab MW – Bow WS - Johnson	LT - Glacier, Minnewanka, Sherbrooke, Spray, Wapta RT - Emerald, Johnson, Moab, Patricia, Sherbrooke CT - Moraine BT - Bighorn, Devon, Emerald, Johnson, Moraine, Patricia, Shere BLT - Harrison, Minnewanka Moab CI - Pyramid MW - Bow LNS - Annette, Beauvert WS - Johnson	LT - Glacier, Minnewanka, Sherbrooke, Spray, Wapta RT - Cabin, Emerald, Johnson, Moab, Patricia, Sherbrooke CT - Moraine BT - Bighorn, Devon, Johnson, Emerald, Moraine, Patricia, Shere BLT - Harrison, Minnewanka, Moab MW - Bow LNS - Annette, Beauvert WS - Johnson
15	MW - Bow			LT - Minnewanka			RT - Moab	RT - Cabin	
14	LT - Wapta	LT – Spray	LT – Minnewanka		BLT - Moab	LT - Kidney	CI - Pyramid		LT – Bow, Kidney, Moab
13	LT - Sherbrooke RT – Emerald BT – Devon BLT –	BT – Shere				LT – Bow, Moab	LT – Glacier BT - Patricia	LT – Bow, Kidney	

Appendix 4 Calculated monthly allowable human fish consumption rates for Rocky Mountain Park study lakes

	Minnewanka	T	1				T	<u> </u>	1
12		LT – Wapta BLT – Minnewanka, MW – Bow			RT - Moab		BT - Emerald	LT - Moab	
11	LT – Minnewanka	LT - Sherbrooke RT – Emerald BT – Devon	BLT – Moab	BLT - Moab	LT – Glacier CI - Pyramid	LT – Middle Waterton, Moose, Pyramid			LT – Middle Waterton, Moose, Pyramid
10		LT - Minnewanka		RT - Moab	BT - Patricia		RT - Patricia LNS - Annette	LT – Middle Waterton, Moose, Pyramid	LT - Hector
9	BLT – Moab		RT – Moab CI - Pyramid	CI - Pyramid	BT - Emerald	LT - Hactor	LNS - Beauvert	LT - Hector	
8	· · · · · · · · · · · · · · · · · · ·		LT – Glacier BT - Patricia	LT - Glacier BT – Emerald, Patricia	RT - Patricia LNS - Annette	CI - Moab	RT - Cabin		CI - Moab
7	LT – Glacier RT – Moab BT - Patricia CI – Pyramid	BLT – Moab	BT – Emerald		LNS - Beauvert	LT - Outram		LT - Outram CI - Moab	LT - Outram
6	BT – Emerald	LT – Glacier, RT – Moab CI - Pyramid	LNS – Annette	RT – Patricia LNS – Annette	RT - Cabin		LT – Bow, Kidney, Moab		
5	RT – Patricia LNS - Annette	BT – Emerald, Patricia	RT – Cabin, Patricia LNS – Beauvert	RT - Cabin LNS - Beauvert	LT – Bow, Kidney, Moab	LT - Patricia	LT – Hector, Middle Waterton, Moose, Pyramid	LT - Patricia	LT – Patricia
4	RT – Cabin LNS - Beauvert	RT – Patricia LNS – Annette, Beauvert	LT – Bow, Kidney, Moab	LT – Bow, Kidney, Moab	LT – Hector, Middle Waterton, Moose, Pyramid		CI - Moab		
3	LT Bow, Kidney, Moab, Moose	LT – Bow, Kidney RT - Cabin	LT – Hector, Middle Waterton, Moose, Pyramid	LT – Hector, Middle Waterton, Moose Pyramid	LT - Outram CI - Moab	LT - Sassenach	LT - Outram	LT - Sassenach	LT - Sassenac

2	LT – Hector,	LT – Hector,	LT - Outram	LT - Outram	LT - Patricia	LT – Patricia,	
	Middle	Middle	CI – Moab	CI - Moab		Sassenach	
	Waterton,	Waterton,					
	Outram,	Moab, Moose,					
	Pyramid	Pyramid					
	CI – Moab	-					
1	LT – Patricia,	LT – Outram,	LT - Patricia	LT – Patricia,	LT - Sassenach		
-	Sassenach	Patricia		Sassenach			
		CI - Moab					
0.5		LT - Sassenach					

LT=lake trout, RT=rainbow trout, CT=cutthroat trout, BT=brook trout, BLT=bull trout, CI=cisco, MW=mountain whitefish, LNS= longnose sucker, WS=white sucker

<u>Appendix 5</u>	Distribution of wildlife that consume aquatic biota and breed within	in the Rocky Mountain study area

				Distributio	n		
Common Name	Scientific Name	Field Guides	Jasper	Mount Robson	Banff	Yoho	Waterton
MAMMALS	··········						<b>.</b> .
American Mink	Mustela vison	All of study area		X	Х	X	X
Northern River Otter	Lontra canadensis	All of study area	X	X	X	X	X
Common Raccoon	Procyon lotor	Only in Waterton					
Black Bear	Ursus americanus	All of study area	Х	X	х	X	X
Grizzly Bear	Ursus arctos	All of study area	Х	X	X	X	X
Common muskrat	Ondatra zibethicus	All of study area	X	X	x	x	X
Common water shrew	Sorex palustris	All of study area	X	X	X	X	X
BIRDS		···· • · · · · · · · · · · · · · · · ·					
Common Loon	Gavia immer	Common breeder and migrant throughout study area	Х	x	Х		x
Pied-billed Grebe	Podilymbus podiceps	Uncommon summer resident and migrant throughout study area	Х	x	X	x	x
Horned Grebe	Podiceps auritus	Fairly common spring and fall migrant throughout study area		X			
Red-necked Grebe	Podiceps grisegena	Uncommon breeder and common migrant throughout study area	Х	x	Х		x
Eared Grebe	Podiceps nigricollis	Common breeder and fairly common spring and fall migrant throughout study area		X			
Western Grebe	Aechmorphorus occidentalis	Common spring and fall migrant throughout		X			

		study area					
American Bittern	Botaurus lentiginosus	Uncommon breeder throughout, known to			Х	X	
		nest in Banff and Yoho National Parks					
Great Blue Heron	Ardea herodias	Uncommon migrant and summer visitor throughout the study area		х	Х	X	
Gadwall	Anas strepera	Uncommon migrant and rare visitor throughout study area		х			X
American Widgeon	Anas americana	Common migrant and uncommon summer resident throughout the study area	x	х			x
Mallard	Anas platyrhynchos	Abundant summer resident, abundant migrant and common winter resident throughout study area	x	X	X	x	x
Blue-winged Teal	Anas discors	Common migrant and uncommon breeder throughout study area	X	Х	Х		X
Cinnamon Teal	Anas cyanoptera	Uncommon migrant throughout study area		x			
Northern Shoveler	Anas clypeata	Uncommon migrant throughout study area		Х	Х		X
Northern Pintail	Anas acuta	Uncommon to common migrant and uncommon breeder throughout study area	X	х			
Green-winged Teal	Anas crecca	Common migrant and uncommon breeder	х	Х	Х	X	X

		throughout study area					
Canvasback	Aythya valisineria	Rare migrant in study		Х			Х
· · · · · · · · · · · · · · · · · · ·		area					
Redhead	Aythya americana	Rare migrant in study		Х			
·····		area					
Ring-necked duck	Aythya collaris	Fairly common breeder	х	Х	x	X	X
		and migrant					
		throughout study area					
Lesser Scaup	Aythya affinis	Locally common	X	Х	X	X	Х
		breeder and					
		uncommon to common					
		migrant throughout					
		study area					
Harlequin Duck	Histrionicus histrionicus	Regular but local	X	Х	X	X	X
-		breeder throughout					
		study area, more					
		common in Alberta and					
		British Columbia					
Surf Scoter	Melanitta perspicillata	Common spring and		X			
		uncommon fall					
		migrant, occasionally					
		non-breeding birds					
		summer throughout					
		study area					
White-winged Scoter	Melanitta fusca	Common spring and		x			
		uncommon fall					
		migrant, occasionally					
		non-breeding birds					
		summer throughout					
		study area					
Bufflehead	Bucephala albeola	Common spring	X	Х	X	X	Х
		migrant and					
		uncommon breeder					
		throughout study area					

Common Goldeneye	Bucephala clangula	Common migrant throughout study area		Х			X
Barrow's Goldeneye	Bucephala islandica	Uncommon to common breeder and migrant throughout study area	Х	Х	Х	х	Х
Hooded Merganser	Lophodytes cucullatus	Uncommon spring migrant and summer visitor throughout the study area	x	х	Х		Х
Red-breasted Merganser	Mergus serrator	Rare migrant throughout study area					
Common Merganser	Mergus merganser	Common migrant and breeder and winter resident on open water throughout study area	x	x	X	X	X
Ruddy Duck	Oxyura jamaicensis	Uncommon migrant and summer resident throughout study area	Х	х			
Turkey Vulture	Cathartes aura	Rare throughout study area					
Osprey	Pandion haliaetus	Common breeder and migrant throughout study area	х	х	Х	X	x
Bald Eagle	Haliaeetus leucocephalus	Locally common migrant and breeder, winter resident at open waters throughout study area	x	x	X	X	
Virginia Rail	Rallus limicola	Very uncommon migrant throughout study area			.,		
Sora	Porzana carolina	Locally common summer breeder throughout study area	х	Х	Х	x	X

American Coot	Fulica americana	Fairly common summer breeder	Х	Х	Х	Х	Х
		throughout study area			-		
Sandhill Crane	Grus canadensis	Common in Waterton		X			X
		rare elsewhere					
		throughout study area					
American Avocet	Recurvirostra americana	Uncommon to rare					
		migrant throughout					
		study area					
Greater Yellowlegs	Tringa melanoleuca	Common migrant and	Х	X			
		uncommon summer					
		breeder throughout					
······		study area					
Lesser Yellowlegs	Tringa flavipes	Uncommon migrant		X			
		throughout study area					
Solitary Sandpiper	Tringa solitaria	Uncommon migrant	Х	X	х	Х	
		and summer resident					
		throughout study area					
Spotted Sandpiper	Actitis macularia	Common migrant and	Х	Х	х	x	Х
		summer breeder					
<u> </u>	Calification	throughout study area		X			
Semipalmated	Calidris pusilla	Uncommon fall		X			
Sandpiper		migrant on eastern					
Least Sandpiper	Calidris minutilla	slopes Rare spring migrant		x			
Least Sandpiper	Culturis minutitu	and common fall		^			
		migrant throughout					
		study area					
Baird's Sandpiper	Calidris bairdii	Common fall migrant	·	X			
		in Jasper, rare spring					
		migrant throughout					
		study area					
Long-billed Dowitcher	Limnodromus scolopaceus	Uncommon to common	·····.	X			
-		fall migrant and rare					

		spring migrant throughout Rockies					
Wilson's Snipe	Gallinago delicata	Locally common migrant and summer	Х	Х	Х	Х	X
		breeder, rare winter					
		resident throughout					
······		study area					
Wilson's	Phalaropus tricolor	Common migrant and		X			
Phalarope		local summer breeder					
		throughout study area					
Red-necked Phalarope	Phalaropus lobatus	Uncommon fall		X			
		migrant and rare spring					
		migrant throughout					
		study area					
Bonaparte's Gull	Larus philadelphia	Uncommon to common		X			
		visitor and migrant					
		throughout study area					
Ring-billed Gull	Larus delawarensis	Uncommon migrant		X	Х		
		and summer visitor					
		throughout study area					
California	Larus californicus	Uncommon migrant		X	x		
Gull		and summer visitor					
		throughout study area					
Herring Gull	Larus argentatus	Rare but regular		x			
		migrant throughout					
		study area					
Common Tern	Sterna hirnudo	Uncommon migrant		X			
		throughout study area					
Forster's Tern	Sterna forsteri	Rare migrant and					
		summer visitor					
		throughout study area					
Black Tern	Chlidonias niger	Uncommon migrant		X			X
	_	and local breeder in					
		southern Canadian					

		Rockies, rare through rest of study area			, . ,		
Great Horned Owl	Bubo virginiansus	Uncommon to common year round resident throughout study area	х	х	Х	Х	X
Belted Kingfisher	Ceryle alcyon	Uncommon to common spring, summer and fall breeder, rare winter resident throughout study area	X	X	X	X	X
American Dipper	Cinclus mexicanus	Locally common year round throughout study area	Х	x	Х	X	x
Northern Waterthrush	Seiurus noveboracensis		Х	Х	Х	X	X
Yellow-headed Blackbird REPTILES	Xanthocephalus xanthocephalus	Rare migrant throughout study area	X	Х			X
Western Terrestrial (Wandering) Garter Snake	Thamnophis elegans vagrans	Throughout study area				X	X
Common (Red-sided) Garter Snake	Thamnophis sirtalis parietalis	Not in Banff and Jasper		Х			x

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# **Appendix 6** Mass, energetics and diet of wildlife species that breed and consume aquatic biota in Canadian Rocky Mountain Parks

	Scientific Name	Mass	Energetics	Diet	References
MAMMALS		1		· · · · · · · · · · · · · · · · · · ·	l
American Mink	Mustela vison	Adults: 0.8 – 2.3 kg		Muskrat, frogs, fish, waterfowl and their eggs, mice, voles, rabbits, snakes, crayfish and other aquatic invertebrates	Fisher et al. 2000
Northern River Otter	Lontra canadensis	Adult: 4.5 – 11 kg 140 g at birth		majority of diet includes crayfish, turtles, frogs, and <b>fish</b> , sometimes birds and eggs, small mammals (e.g. mice, young muskrats, young beaver), insects and earthworms, often chase fish under winter ice	Fisher et al. 2000
Common Raccoon	Procyon lotor	Adult: .4 – 14 kg 57 g at birth		Omnivore; fruit, nuts, berries, insects, clams, frogs, <b>fish</b> , eggs, young birds and rodents	Fisher et al. 2000
Black Bear	Ursus americanus	Adult: 40 – 270 kg Young leave den at 2 – 3 kg		When not influenced by humans, up to 95% of diet is plant based (e.g. leaves, buds, flowers, berries, fruits and roots), sometimes <b>fish</b> , young hooved mammals, insects, bees and honey, carrion and human garbage	Fisher et al. 2000
Grizzly Bear	Ursus arctos	Adult: 110 – 530 kg		70-80% of diet is plant material (e.g. leaves, stems, flowers, roots and fruits), also eats other mammals (e.g. ground squirrels, marmots, mice, young hooved mammals, bighorn sheep), fish, insects and carrion	Fisher et al. 2000
Common muskrat	Ondatra zibethicus	Adult: 0.8 – 1.6 kg		Diet in summer includes various emergent plants (e.g. cattails, rushes, sedges, irises, water lilies and pondweeds), a few frogs, turtles, mussels, snails, crayfish, occasional <b>fish</b> ; diet in winter is submerged vegetation	Fisher et al. 2000
Common water shrew	Sorex palustris	Adult: 8.9 – 19 g		Majority of the diet is aquatic insects, spiders, snails, other invertebrates and small fish up to half their size	Fisher et al. 2000
BIRDS					
Common Loon	Gavia immer			• Fish, large aquatic invertebrates and larval and adult amphibians	Fisher et al. 1997
		<b>Adult:</b> Throughout range: 1.6- 8.0 kg	Chick - 1 week =90 kcal - At fledging, 11	<ul> <li>Primarily fish 10-70 g up to 300 g + (e.g., lake whitefish, cisco, brook trout, rainbow trout, lake chub, sucker, stickleback, etc.)</li> </ul>	McIntyre and Barr 1997

		Minnesota: M: 2.52-4.2 kg F: 1.62-3.86 kg Eastern Ontario: M: 5.46 kg avg. (4.77-6.13 kg) F: 4.5 kg avg. (3.38-4.65 kg) Northwestern Ontario: M: 4.4 Kg F: 3.54 Kg Chick: 93.9 g (71.4- 108.5g) week 1: 137 g, week 2: 291 g, week 3: 562 g, week 4: 944 g, week 5: 1422g, week 6: 1894 g, week 7: 2363 g, week 8: 2662 g, week 9: 2988 g, week 10: 3016 g, week 11: 3288 g, week 12: 3444 g	weeks after hatching = 1086 kcal Into second year: average 900 g/d or 1214 kcal)	<ul> <li>Leeches are occasionally an important food source</li> <li>Small chicks: invertebrates, fish, and vegetation. Fish 1-2 g of fish 1 day after hatching, 3 g at week 1, up to 10 g at week 2.</li> <li>Fledged juveniles and adults eat similar sized fish</li> </ul>	
Pied-billed Grebe	Podilymbus podiceps	Adult:	Adult: 75-150 g/d	<ul> <li>Aquatic invertebrates, small fish, larval amphibians and infrequently water plants</li> <li>Fish (carp, cyprinids, catfish, sculpins, sticklebacks),</li> </ul>	et al.
		M: $474.0 g \pm 60.6$ (321-568g) Females: 358.0 g $\pm$ 51.0 (253-479 g) Chicks: day 1: 12.5 g, day 2: 13.9 g, day 3: 23.7 g, day 7: 37.5 g, day 13: 92.2 g, day 23: 186 g, day 26: 211.6 g		<ul> <li>crustaceans (crayfish), aquatic invertebrates Hemiptera, Coleoptera, Hirudinea) and aquatic invertebrate larvae (Odonata), frogs, tadpoles, salamanders</li> <li>Chicks eat 1-2 2.5 cm fish /hr day 1, two 2.5 cm fish/hr days 2-5, one 10 cm fish/hr days 6-15 and one 11.25 cm fish/2h or four 5cm fish/2hr days 16-45</li> </ul>	1999
Horned Grebe	Podiceps auritus			• Aquatic invertebrates, crustaceans, molluscs, small fish and larval and adult amphibians 1997	et al.

		327.2 – 528.5 g M: 436, 485, 432, 479 g F: 351, 433 g Chicks: day 1: 14-20 g	500 g horned grebe requires 100 g fish/day	<ul> <li>Aquatic invertebrates and larvae in summer, fish and crustaceans (especially amphipods and crayfish) and polychaetes in winter</li> <li>Opportunistically exploits locally abundant or super abundant prey</li> <li>Stomach contents average from all seasons: 34.6% fish, 46% insects, remainder largely crustaceans, small frogs, salamanders, leeches and tadpoles</li> <li>Chicks eat same diet as adults 7.5-7.8 food items/min, up to 465/hour</li> </ul>
Red-necked Grebe	Podiceps grisegena	M: 873.5 <u>+</u> 124 g F: 785.4 <u>+</u> 97g	Estimated that 840 g individual would require 156 g of fish/day Captive adults fed a mixed diet of aquatic insects and fish consumed about 180 g of food/day	<ul> <li>Small fish, aquatic invertebrates and amphibians</li> <li>Fish, crustaceans, aquatic invertebrates, occasionally amphibians</li> <li>Main diet of young during first few weeks is invertebrates (Odonata), which are then replaced by fish</li> <li>Recorded diet items include fish up to 19 cm long (brook stickleback, sculpins, , clams, crustaceans (amphipods), aquatic (Zygoptera, Anisoptera, Ephemeroptera, Trichoptera, Corixidae, Notonectidae, Coleoptera, Dytiscidae, Gyrinidae, Haliplidae,Hydrophilidae) and terrestrial invertebrates, leeches, frogs, salamanders and tadpoles</li> <li>Fish comprised 21.6 – 91.7% of diet on a nesting lake, while 8.3 – 77.8% was insects</li> </ul>
Eared Grebe	Podiceps nigricollis			Aquatic invertebrates, crustaceans, molluscs, small fish, and larval and adult amphibians     1997
Western Grebe	Aechmorphorus occidentalis			Small fish and aquatic invertebrates     Fisher et     1997
American Bittern	Botaurus lentiginosus	571 g M: 372 g Fat F: 482 g	Captive bird ate 23.9 g (dry weight) of food (mice) per day.	<ul> <li>Small fish, amphibians and aquatic invertebrates</li> <li>Insects (Odonata, Belastomatidae, Dytiscidae), amphibians, small fish (suckers, sticklebacks, perch etc.), mammals (meadow voles), frogs, tadpoles, salamanders, garter snakes and crayfish</li> </ul>

Great Blue	Ardea herodias		Metabolic rate: 56 kcal/d	<ul> <li>Stomach contents: 23% insects, 21% frogs and salamanders, 21% fish, 19% crayfish, 10% small mammals, 5% snakes, and small quantities of crabs, spiders, and unidentified invertebrates</li> <li>Chicks given regurgitated partly digested fish, frogs, tadpoles, snakes, crayfish and mice</li> <li>Small fish, amphibians, small mammals, aquatic invertebrates</li> </ul>	Fisher et al. 1997
Heron		Adult BC: M: 2.48 kg F: 2.11 kg Eastern Canada & US: M and F: 2.23 kg Oregon: 2.09 kg Juvenile (July) 1.76 kg (Aug-Dec) 1.98 kg Yearling (Jun-Jan) 2.22 kg	Estimated mean ( <u>+</u> SE) egg-laying: 1,163 kJ ( <u>+</u> 555) Incubation: 1,197 kJ ( <u>+</u> 194), small chicks: 4,264 kJ ( <u>+</u> 764) large chicks: 1,598 kJ ( <u>+</u> 151)	<ul> <li>invertebrates and reptiles, occasionally scavenges</li> <li>Predominantly fish, also amphibians, invertebrates, reptiles, mammals and birds</li> <li>Voles 24-40% of nestling diet</li> </ul>	Butler 1992
Gadwall	Anas strepera	Adult: M: 966 g (726-1043), 968 $g \pm 9.8$ (790-1250) F: 835 g (635-1043), 866 $\pm 14.4$ (720-980) Immature: M: 857 g (590-1043), 924 $g \pm 18.4$ (715-1100) F: 776 g (499-953), 805 $\pm$ 24.5 (685-920) Newly hatched ducklings: M: 30.8 g $\pm$ 2.68 F: 30.5 g $\pm$ 2.37	Requirements for protein during egg- laying causes an increase in invertebrate consumption for females, females consume 10% more animal food and 8 % less plant food during breeding	<ul> <li>Aquatic vegetation, aquatic invertebrates, tadpoles and small fish</li> <li>Submerged aquatic vegetation, seeds, aquatic invertebrates</li> <li>Pondweed, naiad, widgeon grass, water milfoil, algae, seeds of pondweed, smartweed, bulrush and spike rush</li> <li>Important invertebrate foods include Anostraca, Cladocera, and Chironomidae</li> <li>Adult diet consist of 23-46% animal and 42-54% plant during breeding season</li> <li>Adult breeding season foods: filamentous algae, 25.3%, Anostraca crustaceans (17.3%), widgeon grass (12.7%), chironomid midges (8.6%), Dytiscid beetles (3.8%)</li> <li>Duckling diet: slender pondweed (37%), filamentous algae (19%), grass seeds (11%), duckweed (7%), flies</li> </ul>	Fisher et al. 1997 LeSchack et al. 1997

				<ul> <li>(4%), coontail (3%), muskgrass (3%), beetle larvae (3%)</li> <li>Ducklings &lt;21 days primarily feed on invertebrates (midge larvae and adults, beetles and Cladocerans), plant matter increases and by 21 days becomes 90% of diet</li> </ul>	
American Widgeon	Anas americana	Yukon Territory M: 797.0 g $\pm$ 58 (675- 950) F: 672.0 $\pm$ 67 (555-790) Ducklings: 24 g $\pm$ 1.3 at 1 day, 54 g $\pm$ 6.2 at day 7, 139 $\pm$ 20.2 at day 14, 259 $\pm$ 33.9 at day 21, 382 $\pm$ 20.9 at day 28, 433 $\pm$ 37.8 at day 35	M: 2.3 – 3.1 kcal/g ash free weight F post- reproductive: 3.5 kcal/g dw	<ul> <li>Aquatic vegetation, infrequently aquatic invertebrates</li> <li>Shift toward greater quantities of seeds, fruits and substantial shift to more invertebrates (Odonata, Coleoptera, Diptera, Trichoptera, Gastropods and crustaceans such as Ostracoda, Daphinidae, Diaptomidae) during breeding season</li> <li>Female diet 36.4% animal matter, flies (10.3%), Trichoptera (9.6%), Odonata (6.3%), crustaceans (5.0%), snails (3.6%)</li> <li>Female diet remains high in animal matter (22.9-36.1%) through incubation and brood rearing</li> <li>Ducklings consume 97% animal matter (62% surface invertebrates, 35% aquatic invertebrates) through day 10</li> <li>By day 20, plant matter is 89% of diet</li> </ul>	Fisher et al. 1997 Mowbray 1999
Mallard	Anas platyrhynchos	Adult M: 1264 g $\pm$ 14 Breeding F: Prelaying: 1200 g $\pm$ 78 Laying: 1301 g $\pm$ 115 Incubation: 967 g $\pm$ 44 Duckling 31.8 g $\pm$ 27.2 - 40.6 day 1, 66 g $\pm$ 9.7 week 1, 148 g $\pm$ 14.4 week 2, 288 $\pm$ 24.6 week 3, 388 g $\pm$ 46 week 4, 453 g $\pm$ 58.4 week 5, 683 $\pm$ 46.8 wk 6	290 kcal/day Basal metabolic rate: 3.1-3.9 kcal/hr Calculated cost of incubation: 23.9 kcal/d	<ul> <li>Aquatic vegetation, aquatic invertebrates, larval amphibians and fish eggs</li> <li>During breeding season, eats mostly animal foods (70%)(Chironomidae and other Diptera, Odonata, and Trichoptera larvae, aquatic invertebrates such as snails and Mysis, and earthworms)</li> <li>Ducklings &lt;25 d eat mostly animal foods (90%) (invertebrates, small crustacean, molluscs and fish eggs, especially chironomids)</li> <li>Vegetation constitutes 99% of food items in ducklings &gt;45 d old</li> </ul>	Fisher et al. 1997 Drilling et al. 2002

Blue-winged Teal	Anas discors	Adult: M: 376-427 g F: 352-431 g Juvenile: M: 388-513 g F: 382-431 g Hatchlings: 18.1 $g \pm 0.32$ 87 g at 7 days 111 g at 14 days 205 g at 21 days 258 g at 28 days 301 g at 35 days 298 g at 42 days	490 kJ and 258kJ of energy/d at temps 0° C and 25° C, respectively	<ul> <li>Aquatic vegetation and aquatic invertebrates</li> <li>Aquatic invertebrates, seeds, vegetation</li> <li>Animal matter dominates diet of breeding females</li> <li>Principle foods of male and female breeding adults includes aquatic insects (65%, &gt;70% Chironomid larvae), snails (16%), crustaceans (9%), Pelecypoda (7%), seeds (3%)</li> </ul>	Fisher et al. 1997 Rowher et al. 2002
Cinnamon Teal	Anas cyanoptera			Aquatic vegetation and aquatic invertebrates	Fisher et al. 1997
Northern Shoveler	Anas clypeata	Adult: M:558g $\pm$ 40 - 572 g $\pm$ 21 In spring, 641g $\pm$ 58 after prebasic molt F: 630 g $\pm$ 8 pre-laying, 653g $\pm$ 7 laying, 442 g $\pm$ 39 - 474 g $\pm$ 29 incubating depending on success Duckling: 22.7 g $\pm$ 1.43 at 1 day, 53 g $\pm$ 6.6 at 1 week, 135g $\pm$ 23 at 2 weeks, 242 g $\pm$ 23 at 3	700 g Northern Shoveler needs 204 kcal of energy/d Vascular plants 0.2 kcal/g dw, 910 g/d to meet energy requirements Cladocera 0.8 kcal/g DW, 233 g/day to meet energy requirements	<ul> <li>Aquatic vegetation, aquatic crustaceans and insect larvae</li> <li>Small aquatic invertebrates and seeds</li> <li>In summer, adult males east mostly Cladocera (Daphnia and related genera) (69%), and some seeds (22%), chironomid larvae and pupae (6%) and Corixidae</li> <li>Laying females consume 99% animal matter, Crustacea (54%), and Mollusca 40%</li> <li>Ducklings feed on zooplankton, aquatic invertebrates and duckweed</li> </ul>	Fisher et al. 1997 DuBowy 1996

		weeks, 303 g ± 27.2 at 4 weeks, 370 g ± 43.1 at 5 weeks	Insects 2.3-3.2 kcal/g DW, 60-80 g/d to meet energy requirements		
Northern Pintail	Anas acuta			• Aquatic vegetation, aquatic invertebrates and larval amphibians	Fisher et al. 1997
Green-winged Teal	Anas crecca			Aquatic invertebrates, larval amphibians, aquatic vegetation	Fisher et al. 1997
		Adult M: 320 -370 g F:270 – 340 g Duckling: 15.1 g <u>+</u> 0.29 at 1 day		<ul> <li>Seeds of sedges and grasses (77%) and aquatic vegetation, aquatic insects and larvae, (Chiromidae 15%, Physidae 5%) molluscs and crustaceans during breeding</li> <li>Few studies of diet during breeding</li> <li>Opportunistically feed on food items that are abundant</li> <li>Downy young consume mainly animal matter, such as insect larvae (80-90% of duckling diet until 14 d)</li> </ul>	Johnson 1995
Canvasback	Aythya valisineria			Aquatic vegetation and occasionally aquatic     invertebrates	Fisher et al. 1997
		Adult: M: 1238.4 – 1482 g F: 1216 – 1348 g, higher mass during breeding Duckling: 44.7 g at 1 day, 69.2 g at 5 days, 133.1 g at 14 days, 252.2 g at 22 days, 400.5 g at 29 days, 732.5 g at 37 days, 911.6 g at 48 days, 960.0 g at 59 days	370 kcal/bird/day wintering birds in Chesapeake Bay	<ul> <li>Consume both plant (seeds, buds, leaves, rhizomes, tubers and root stalks of aquatic plants) and animal matter (Gastropoda, Odonata, Ephemeroptera, Diptera, Trichoptera) during breeding season</li> <li>Diptera are 63-66% of animal diet</li> <li>Pre-laying and laying females consume 47.7 and 57.1% animal diet respectively</li> <li>In NV, 77.7% of diet animal matter, with Trichoptera, Odonata, and Gastropoda making up 88% of the diet</li> <li>Ducklings consume 87% animal diet between 10 and 43 days (42% Gastropoda, 27% Trichoptera, 12% Odonata)</li> <li>At another lake, diet from &lt;7 days to 63 days is 94%animal matter, primarily Trichoptera and Diptera</li> </ul>	Mowbray 2002
Redhead	Aythya americana			Aquatic vegetation and occasionally aquatic invertebrates	Fisher et al. 1997

Ring-necked duck	Aythya collaris	Adult: Arrival on breeding grounds in Minnesota M: $745g \pm 59.7$ F: $730.4 g \pm 60.7$ Breeding M: $721g \pm 47.5$ F: $789.1 g \pm 67.4$ Mass declines through	Captive M: 65.6 kcal/.male/day Captive F:69.3 kcal/female/day Daily winter energy expenditure 123 -169 kcal/bird/ay	<ul> <li>Aquatic vegetation and aquatic invertebrates</li> <li>Terrestrial and aquatic plant seeds and tubers, and aquatic invertebrates</li> <li>Animal food consumption greatest in downy young (98%) and attending female (92%)</li> <li>Important animal food items are benthic (Oligochaeta, Hirudinea, Chironomidae, Gastropoda and Pelecypoda) or associated with vegetation (Odonata, Trichoptera)</li> <li>During periods of rapid ovarian follicle growth, diet insludes 16 25% Odonate 14 16% Distance 21 24%</li> </ul>	Fisher et al. 1997 Hohman and Eberhardt 1998
Lesser scaup	Aythya affinis	mass declines through incubation and brood rearing Ducklings: 29.3 g $\pm$ 0.38 at one day	Kai/ Diru/ ay	<ul> <li>includes 16-25% Odonata, 14-16% Diptera, 21-34% Trichoptera, 7-10% Gastropoda and Pelecypoda, 5-7% Hirudinea</li> <li>During incubation and brood rearing, females consume 11-56% Trichoptera, 9-40% Hirudinea, 11- 21% Gastropoda and Pelecypoda, 6% Diptera, 5% Odonata, and 11% cow lily seeds</li> <li>Diet of downy young contains 98% animal material in Minnesota, 43% Trichoptera, 48% Diptera</li> <li>Consumption of animal matter decreases as ducklings mature</li> <li>Aquatic invertebrates, mostly amphipods and insect</li> </ul>	Fisher et al.
<b>r</b>		Adult: Breeding: Northwest Territories: M: 706 g $\pm$ 7 F: 735 g $\pm$ 12 Manitoba: M: 716 g $\pm$ 7, F: 736 g $\pm$ 12 Ducklings: 2980 g $\pm$ 1.55 SD at 1 day (26-34.20 g), 61 g $\pm$ 8 by 7 days, 128 g	Metabolizable energy intake averages 5575 kcal during first 7 weeks Food intake by captive ducklings increases from 6.7g/duck/day during first week to peak of 52.5 g/duck/day in 5 <sup>th</sup> week	<ul> <li>Predominately aquatic invertebrates (insects, crustaceans and molluscs</li> <li>Seeds and aquatic vegetation important in some areas</li> <li>Aquatic invertebrates preyed upon include Amphipoda, Diptera, Hemiptera, Hirudinea</li> <li>Juvenile diet dominated by Amphipoda (49%), Mollusca (39%), Diptera (8%)</li> <li>Amphipoda increases in dietary importance as ducklings age</li> </ul>	1997 Austin et al. 1998

		<u>+</u> 19 by 14 days, 192 g <u>+</u> 29 by 20 days			
Harlequin Duck	Histrionicus histrionicus			• Aquatic invertebrates, mainly caddisfly and stonefly larvae, fish eggs	Fisher et al. 1997
		Adults M: 490-760 g F: 470-670 g Ducklings: 22-27 day old ducklings gained 66 g (60-70g) in 10 days	Winter: diet quality 2.72 kcal/d dry mass <u>+</u> 0.18 SE	<ul> <li>Diet is entirely animal matter</li> <li>At breeding grounds consumes larval (Diptera, Trichoptera, Plecoptera, Ephemeroptera)and adult aquatic insects and fish roe</li> <li>In Icelandic breeding grounds adulta, 98.5% Diptera, , 0.1% caddisfly larvae (duckling diet similar)</li> <li>Throughout year, 63% crustaceans (Amphipoda), 24.7% molluscs (Gastropoda), 10.2% insects, 2.4% fish (sculpins and salmonids)</li> </ul>	Robertson and Goudie 1999
Surf Scoter	Melanitta perspicillata			Aquatic invertebrates such as damselfly, dragonfly, mayfly and caddisfly larvae, occasionally aquatic vegetation	Fisher et al. 1997
White-winged Scoter	Melanitta fusca			Aquatic invertebrates such as crustaceans, stonefly and caddisfly larvae, and snails	Fisher et al. 1997
Bufflehead	Bucephala albeola		· · ·	• Aquatic invertebrates such as water boatmen, mayfly and damselfly larvae, snails, crustaceans, sometimes small fish and aquatic vegetation	Fisher et al. 1997
		Adults; M: 465 g <u>+</u> 48 F: 337 g <u>+</u> 45 g Juvenile : 23.8 g <u>+</u> 2.1		<ul> <li>Aquatic invertebrates (insects, crustaceans, molluscs), and some seeds</li> <li>Freshwater: Odonata, Chironomidae larvae, Corixidae, Ephemeroptera, Trichoptera, Amphipoda</li> <li>Diet of young is 92-100% animal matter, mostly invertebrates (Odonates, Coleoptera Corixidae, Trichoptera, Amphipoda, Cladocera and Copepoda)</li> </ul>	Gauthier 1993
Common Goldeneye	Bucephala clangula			Aquatic invertebrates such as crustaceans, aquatic vegetation and small fish	Fisher et al. 1997
		North America: adult males: range 938-1400 g, females: 585-1133 g,	At 1-Kg, adults estimated to expend approx. 70	<ul> <li>Aquatic invertebrates (insects, molluscs, crustaceans), sometimes small fish or fish eggs</li> <li>Vegetation typically comprises less than 25%</li> </ul>	Eadie et al. 1995

		immature males: 636- 1227 g, females: 545- 1182 g Europe and Asia: adult males: 888-1245 g, females: 500-860 g Duckling: $38.1 \text{ g} \pm 0.4$ one day	kcal/d at basal metabolic rate, Caloric content of invertebrate prey is 1.18 kcal/g ww, therefore 59 g required for self maintenance, estimates for Ephemeroptera, Trichoptera, Odonata average 0.035 g ww/prey item 1 day old duckling BMR = 206 cal/g/d Daily maintenance = 7.2 kcal	<ul> <li>Crustceans (32%), Insects (28%) and molluscs (10%) were predominant, fish (4%)</li> <li>Crustaceans include amphipods, insects include Trichoptera, Corixidae, Odonata, Ephemeroptera, Coleoptera</li> <li>At breeding grounds, adults eat mostly Odonata and Trichoptera</li> <li>Young eat primarily animal matter (Coleoptera, Trichoptera, Odonata, Corixidae and Ephemeroptera</li> </ul>
Barrow's Goldeneye	Bucephala islandica	Adult: M: 1075 – 1320 g F: 580-870 g Duckling: 39.9 g <u>+</u> 0.18 (30-49 g)	At 1-Kg, adults estimated to expend approx. 70 kcal/d at basal metabolic rate, Caloric content of invertebrate prey is 1.18 kcal/g ww, therefore 59 g required for self maintenance, estimates for Ephemeroptera, Trichoptera, Odonata average 0.035 g ww/prey	<ul> <li>Aquatic invertebrates such as damselfly and dragonfly larvae and nymphs, crustaceans and some aquatic vegetation</li> <li>Aquatic invertebrates, including insects, molluscs, and crustaceans, also fish eggs and a small &lt;20% quantity of vegetation (seeds and tubers)</li> <li>At interior BC lakes, Crustacea (31.6%), Trichoptera (11.1%), Odonata (6%), Corixidae (3.4%), Gastropoda (0.4%), fish (0.3%), other insects (3.3%), seeds (3.9%) and tubers (39.4%) were consumed</li> <li>Also consume Ephemeroptera, Notonecta and Diptera</li> <li>On breeding grounds adult diet contains more insects (78%), particularly Odonata, Trichoptera, Corixidae, and Diptera larvae, Crustacenas, molluscs and seeds are also consumed</li> <li>Juvenile diet is similar to adult diet at breeding grounds, 78-85% insects</li> </ul>

			item 1 day old duckling BMR = 206 cal/g/d Daily maintenance = 7.2 kcal		
Hooded Merganser	Lophodytes cucullatus	Adults M:: 680 g (595-879g ) F: 554 g (453-652 g) Duckling: 31 g at 1 day		<ul> <li>Small fish, aquatic invertebrates such as caddisfly and dragonfly larvae, snails, amphibians and crayfish</li> <li>Primarily aquatic invertebrates, fish and crustaceans (crayfish in particular)</li> <li>44% fish, 22% crayfish, 13% aquatic insects, 10% other crustaceans, 6% amphibians, 4% vegetation, and &lt;1% mollluscs</li> <li>Odonata and Trichoptera were consumed</li> <li>Ducklings consume primarily invertebrates including Notonectidae, Corixidae, Dytiscidae, Odonata</li> </ul>	Fisher et al. 1997 Dugger et al. 1994
Red-breasted Merganser	Mergus serrator			Small <b>fish, aquatic invertebrates</b> , fish eggs and crustaceans	Fisher et al. 1997
Common Merganser	Mergus merganser			• Small fish such as trout, carp, suckers, perch and catfish, young consume aquatic invertebrates	Fisher et al. 1997
		Adult: M: 1,264-2,160 g, F: 898-1,770 g, Duckling: 46.2 g at day	Captive birds consumed 178-689 g/d, with an average of 450 g/d, In Scotland, birds ate 480-522 g/d Mean daily energy expenditure was 1939 kJ/d $\pm$ 184 SE BMR= 638 $\pm$ 37 SE Ducklings at 170 g required 270 g/day BMR AT 46.2 g= 151 cal/g/day	<ul> <li>Primarily small fish, also aquatic invertebrates such as insects, molluscs, crustaceans and worms, frogs, small mammals, birds and plants</li> <li>Consume salmon (<i>Salmo</i> spp. And <i>Oncorhynchus</i> spp.), trout, suckers, sculpin, sticklebacks, chub and cyprinids</li> <li>Generally, fish consume most abundant suitably sized prey</li> <li>During breeding season may also consume Trichoptera, Ephemeroptera, Notonectidae, Diptera, Gerridae, Odonata, Coleoptera, sponges, spiders, caterpillars, and Gastropoda</li> <li>Downy young eat mostly aquatic invertebrates (Trichoptera, Ephemeroptera, Notonectidae, Diptera, Gerridae, Odonata), but begin to consume fish at 12 d</li> </ul>	Mallory and Metz 1999

Ruddy Duck	Oxyura jamaicensis			Aquatic vegetation and aquatic invertebrates	Fisher et al. 1997
Turkey Vulture	Cathartes aura			Carrion such as ungulates, carnivores, rabbits, fish, domestic animals and rodents	Fisher et al. 1997
Osprey	Pandion haliaetus	Adult: M=1425-1475 g F=1725-1950 g Young: 50.3 g ± 10.3 SE	In Africa, 649-858 kJ/d for a 1.3 kg M, 1252-2387 kj/d for a 2 kg F In Idaho, 794g/d for adult and 2 young or 1048 for adult and 3 young In Massachusetts, M, F and 3 young (20-30 days old) was 1250g/d, with 400 g (or 1507 kJ) for the M Adult: 1197 kJ BMR=3.2kcal/h/kg Fledging young 1063 kJ/d, 92 g/h	<ul> <li>Fish, averaging 1 kg. make up 98% of the diet</li> <li>Fish at least 99% of prey items recorded (suckers, whitefish, trout and salmon such as cutthroat and rainbow trout, chub)</li> <li>Fish captured usually weigh 150-300 g (range 50-300 g), and are 25-35 cm</li> <li>In Idaho 11-30 cm fish captured</li> <li>Young consume fish</li> </ul>	Fisher et al. 1997 Poole et al. 2002
Bald Eagle	Haliaeetus leucocephalus	Adult: Alaska: M: 4.23 kg (3.68-4.86), F;:5.35 Kg (4.64-6.41) Juvenile: 80 g at 6 days, 260 g at 8 days and 477 g at 9 days	489g/d of fish to maintain body weight of adult, adults consumed 522g/d of salmon	<ul> <li>90% of diet is fish, birds and mammals, likely waterfowl and carrion</li> <li>Preys on fish, waterfowl, small mammals, consumes carrion</li> <li>Generally chooses aquatic habitat for foraging and prefers fish (&gt;75%)</li> <li>Prefers large fish (340-380 mm) during breeding season, otherwise, little size selection</li> <li>Eats terrestrial (hares) and aquatic mammals (muskrats), reptiles and amphibians, crustaceans and a variety of birds (waterfowl such as gulls and Great</li> </ul>	Fisher et al. 1997 Buehler 2000

				Blue Herons)	
				Young consume fish	
Virginia Rail	Rallus limicola			Aquatic invertebrates and aquatic vegetation	Fisher et al. 1997
Sora	Porzana carolina	Adults: M: 88 g $\pm$ 14.3 (71.7- 105.6g), F: 71.9 g $\pm$ 6.6 (65.0- 78.2g) Young: 6.35 g at hatching (5.0 - 7.5g), 47.6 g at 14 d, 43 g at 25 d, 76.5 g at 39 d		<ul> <li>Aquatic vegetation, aquatic invertebrates and molluscs</li> <li>Seeds of wetland plants and aquatic invertebrates</li> <li>Seeds are the predominate food (wild or cultivated rice, smartweeds, sedges, bulrushes, and grasses), also feed on duckweeds and pondweeds</li> <li>Adults, larvae, and pupae of Coleoptera, Diptera, Hemiptera, Odonata and Gastropoda</li> </ul>	Fisher et al. 1997 Melvin and Gibbs 1996
American Coot	Fulica americana			Aquatic vegetation, aquatic invertebrates, sometimes     tadpoles and fish	Fisher et al. 1997
		Adults: M: 724 g (576-848g) F: 560 g (427-628 g) Young: 19-22 g at haching, 55.9g at 19d, 223.1 g at 36 d, 447-492g at 71-73 d	BMR of adult F laying coot= 185 kJ/bird/d Total time activity budget of young coots 270-870 kJ/bird/day and increases with age	<ul> <li>Aquatic and terrestrial vegetation, aquatic invertebrates (molluscs, crustaceans, insects and their larvae), fish, tadpoles and some carrion</li> <li>Generally vegetation predominates, but during breeding season animal matter becomes important particularly to young</li> <li>In order of decreasing importance, Coleoptera, Odonata, Hemiptera, Orthoptera, Diptera, Gastropoda, Pelecypoda, Arachnidia, Amphipoda and other Crustacea, salamander larvae, tadpoles, fish</li> </ul>	Brisbin and Mowbray 2002
Sandhill Crane	Grus canadensis			Aquatic invertebrates and aquatic vegetation, frequently amphibians, reptiles, small mammals and nesting birds	Fisher et al 1997
		Adults: <i>G.c rowani</i> M: 4.80 kg <u>+</u> 0.39		<ul> <li>Cultivated grains are major food items whenever available.</li> <li>During breeding season in Alaska, breeding cranes</li> </ul>	Tacha et al

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		F: 4.11 kg $\pm$ 0.25 G.c. pratensis M: 4.67 kg $\pm$ 0.34 F: 4.07 kg $\pm$ 0.34 Chicks: 114.2 g at hatching, 315 g at 12-13 days,		<ul> <li>consume berries and small mammals</li> <li>In Michigan berries and insects are consumed during the summer</li> <li>Nonmigrator birds consume larval and adult insects, snails, reptiles, amphibians, nesting birds, small mammals, seeds and berries</li> <li>In Wisconsin, diet of adults and young include invertebrates and some small mammals and reptiles during brood rearing</li> </ul>	1992
American Avocet	Recurvirostra americana			Aquatic invertebrates, such as crustaceans	Fisher et al. 1997
Greater Yellowlegs	Tringa melanoleuca			Aquatic invertebrates, will eat small fish	Fisher et al. 1997
Lesser Yellowlegs	Tringa flavipes			Aquatic invertebrates, will eat small fish and tadpoles	Fisher et al. 1997
Solitary Sandpiper	Tringa solitaria	Adults 48.4 g <u>+</u> 8.6 SD (31.1-65.1 g) Adult M 5-7 g lighter than adult F		<ul> <li>Aquatic invertebrates such as water boatmen and damselfly nymphs</li> <li>Diptera, Coleoptera, Odonata, Notonectidiae and Arachnidae, Annelida, cyprinids, tadpoles, Trichoptera, Gastropoda</li> <li>In winter, consumers terrestrial invertebrates, soil or litter invertebrates and aquatic invertebrates</li> </ul>	Fisher et al. 1997 Moskoff 1995
Spotted Sandpiper	Actitis macularia			Terrestrial and aquatic invertebrates	Fisher et al. 1997
Semipalmated Sandpiper	Calidris pusilla	Adulta: Breeding incubation: 27.5 g $\pm$ 2.1, Chicks: 4.4 g $\pm$ 0.04	Chironomid larvae=20 kJ/g dw Small Diptera, tipulids, and coleopterans=21.9- 23.9 kJ/g dw	<ul> <li>Aquatic invertebrates such as crustaceans</li> <li>Benthic invertebrates (small arthropods, molluscs, and annelids) in fresh or saltwater, also some terrestrial invertebrates such as insects and spiders</li> <li>Diet during breeding in Manitoba: Diptera Chronomidae (60%), arachnids (20%), &lt;10% plant seeds, Gastropoda, Coleoptera</li> <li>During breeding season in Alaska: Chironomid larvae (60%), Diptera and Tipulidae (15%), Arachnidae (15%)</li> </ul>	Fisher et al. 1997 Gratto- Trevor 1992

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Least Sandpiper Baird's Sandpiper Long-billed Dowitcher	Calidris minutilla Calidris bairdii Limnodromus scolopaceus			<ul> <li>and Coleoptera</li> <li>Chicks forage by pecking at small adult Diptera when very young, and predominately insect larvae when older</li> <li>Aquatic invertebrates such as amphipods, flies and gastropods</li> <li>Aquatic invertebrates, particularly larval mosquitoes and flies, terrestrial beetles and grasshoppers</li> <li>Aquatic invertebrates such as larval flies and worms</li> </ul>	Fisher et al. 1997 Fisher et al. 1997 Fisher et al. 1997
Wilson's Snipe	Gallinago delicata	Adult: Newfoundland M: 90-97 g (May to Aug) F: 96-118 g (May to Aug) Chicks: 10.8 – 11.0 g		<ul> <li>Aquatic invertebrate larvae</li> <li>Larval insects, Crustacea, Oligochaeta, Mollusca</li> <li>Stomachs can contain up to 66% vegetation, but little energy is obtained from plants</li> <li>Larval and sometimes adult invertebrates: Diptera, primarily Tipulidae and Tabanidae, Coleoptera, Odonata, Hemiptera, Hymenoptera, Ephemeroptera, Lepidoptera, Trichoptera, Annelida, Crustaceans, Gastropoda</li> <li>Rarely eats small lizards, salamanders, frogs, fish and nesting birds</li> </ul>	Fisher et al. 1997 Mueller 2005
Wilson's Phalarope	Phalaropus tricolor			Aquatic invertebrates	Fisher et al. 1997
Red-necked Phalarope	Phalaropus lobatus			Aquatic invertebrates	Fisher et al. 1997
Bonaparte's Gull	Larus philadelphia			Aquatic invertebrates, small fish and tadpoles, terrestrial and flying invertebrates	Fisher et al. 1997
Ring-billed Gull	Larus delawarensis			Garbage, arthropods, rodents earthworms, scavenger, aquatic invertebrates and fish	Fisher et al. 1997
		Adults: Ontario	No data from wild birds.	<ul> <li>Fish, insects, earthworms, rodents and grain</li> <li>Mostly fish, such as alewives, smelt, nine-spined stickleback, yellow perch and arthropods such as</li> </ul>	Ryder 1993

		M: 566 g $\pm$ 42 (485-650 g) F 471 g $\pm$ 46 (375-59g0) Alberta M: 533 g $\pm$ 25 F: 463 g $\pm$ 11 Chicks: Ontario 41.4 g $\pm$ 3.6 Alberta 38.5 g $\pm$ 4.4	Full grown, hand- reared immatures: 69 g/d, calorific value 1,948 kJ	<ul> <li>Coleptera, Diptera, Odonata, Hemiptera, Lepidoptera in eastern populations</li> <li>Grains, insects and rodents consumed by western populations</li> <li>Food of young: Ontario: mostly insects fish, Alberta: insects, rodents, refuse, bird remains and plants</li> </ul>	
California Gull	Larus californicus	Adult: M: 841.0 g $\pm$ 103.3 (653- 1045) F; 710.0 g $\pm$ 91.2 (568- 903) Young: 50.9 g $\pm$ 0.8 SE at hatching		<ul> <li>Terrestrial invertebrates, aquatic invertebrates</li> <li>Small mammals, fish, birds, garbage and invertebrates such as Orthoptera, Ephemeroptera, Odonata (adults and nymphs), earthworms and brine shrimp</li> <li>Adult and chick diets do not vary widely</li> </ul>	Fisher et al. 1997 Winkler 1996
Herring Gull	Larus argentatus			Aquatic invertebrates and small fish, terrestrial insects and worms, scavenges dead fish and garbage, eats other birds young	Fisher et al. 1997
Common Tern	Sterna hirnudo			Small fish and aquatic invertebrates	Fisher et al. 1997
Forster's Tern	Sterna forsteri			Small fish and aquatic invertebrates	Fisher et al. 1997
Black Tern	Chlidonias niger	Adults: On breeding range at various regions: (May- Aug): M: $64.3 \text{ g} \pm 3.8 (59-71\text{ g})$ F: $62.9 \text{ g} (58.3-67.5)$		<ul> <li>Terrestrial flying invertebrates, aquatic invertebrates, fish</li> <li>Insects and freshwater fish are consumed on breeding grounds</li> <li>Odonata, Ephemeroptera, Trichoptera, Coleoptera, Lepidoptera, Diptera, Hemiptera, Amphipoda and small molluscs</li> <li>Eats small fish such as cyprinids where available</li> </ul>	Fisher et al. 1997 Dunn and Agro 1995

		Chicks: 7.25 g newly hatched, 8.1 <u>+</u> 1.2 g at 14 days		<ul> <li>Rarely consume frogs, lizards and eggs</li> <li>Parents feed chicks fish and invertebrates</li> </ul>	
Great Horned Owl	Bubo virginiansus			• Voles, mice, hares, squirrels, skunks, pocket gophers, grebes, grouse and <b>fish</b>	Fisher et al. 1997
		Adult: M: 1304 g, F:1706 g Young; 347 g at hatching, 1000 g an 25 days F, 800g at 29 days M	Mean values for captive owls were ~26.6 g/kg/d Metabolic energy requirements averaged 141.9 kcal/kg/d	<ul> <li>Wide range of prey: scorpions, small rodents, hares and rabbits, ducks, geese and herons</li> <li>90% mammals, 10% birds, and a smaller number of amphibians, reptiles, fish , insects and other invertebrates</li> <li>Main foods include rabbits and hares, coots and other waterfowl</li> </ul>	Houston et al. 1998
Belted Kingfisher	Ceryle alcyon	Adult: Minnesota Spring (May-June) M: 143.6 g (138-150 g) F: 151.6 g (138-169 g) Young: 9-13 g	Average daily consumption of a 130 g adult captive kingfisher= 55-61 k/cal	<ul> <li>Small fish, aquatic invertebrates and tadpoles</li> <li>Consume mostly fish, and some molluscs, crustacean, insects, amphibians, reptiles, young birds, small mammals and berries</li> <li>Fish diet consists of what is available in shallow water or near the surface, trout, stickleback</li> <li>Fish generally &lt;10.2 cm, fish longer than 12. 7 cm prove difficult for bird to swallow</li> <li>Central New York: fishes and crayfishes</li> <li>Michigan: trout constituted 29-80% of fishes taken from streams, but only 175 of fishes from lakes</li> <li>Very young fed regurgitated fish, as grow older whole fish</li> </ul>	Fisher et al. 1997 Hamas 1994
American Dipper	Cinclus mexicanus	Adult: C. m mexicanus: Alberta M: 60.0 g (63.5-67.0g), F: 53.6 g (48.5-62.5g)		<ul> <li>Aquatic invertebrates, small fish and fish eggs</li> <li>Feeds mostly on aquatic stream insects and insect larvae occasionally other invertebrates and small fish, fish eggs and flying insects</li> <li>Primarily forages in fast flowing water of streams</li> <li>Consumes all major stream insects, mostly larval</li> </ul>	Fisher et al. 1997 Kingery 1996

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		Young: 10 g (10-25 g) at day 3, 55 g (40-55g) at day 16, 46-54 g at day 23		Trichoptera, Ephemeroptera, Plecoptera, and Diptera, sometime Coleoptera, Odonata, and Oligochaetes Occasionally consumes small fish (trout $\leq 10$ cm, arctic grayling $\leq$ 7cm and sculpins Will take tadpoles Prefers large obvious prey such as Trichoptera Young fed similar diet	
Northern Waterthrush	Seiurus noveboracensis		•	Terrestrial invertebrates, aquatic invertebrates, small fish	Fisher et al. 1997
		Adult: Breeding: 16.1 -19.6 g Young: 1.9 g at hatching, 3.0 g at 1 day, 5.6 g at 3 days, 7.2 g at 4 days, 9.7 g at 5 days. 14 g at 6 days, 13.5 g at 9 days	•	During breeding season consume mostly larval and adult insects, Arachnids and Gastropods New York and Connecticut: Coleoptera (families - Dytiscidae, Hydrophilidae, Halipidae, Carabidae, Chrysomelidae and Rhynchophora)., Diptera larvae and adults of Mycetophilidae and Tipulidae, Lepidoptera larvae, adult Odonata, Neuroptera larvae, adult Plecoptera, Ephemeroptera, Sialidae nymphs, adult Formicidae, Megaloptera, Gastropoda, Hirundinea, Isopoda, Chilopoda, Oligochaeta, and salamanders New York: Diptera adults (50.5%), Coleopterans (40%), Lepidoptera larvae, Plecoptera, Gastropoda, Hirudinea	Eaton 1995
Yellow- headed Blackbird	Xanthocephalus xanthocephalus		•	Seeds, <b>aquatic invertebrates</b> such as beetles, snails and dragonflies, terrestrial insect larvae	Fisher et al. 1997
		Adult: Alberta: M: 96.64g <u>+</u> 5.23 F; 50.70 <u>+</u> 3.78 Young: 3.3 g (2.6 – 3.6 g) at hatching, F:30-40g and M 45-55g at 10 days		Throughout breeding season consumes aquatic invertebrate prey and feeds it to nestlings, consume cultivated grains and seeds during post breeding In Utah, Odonata, Coleoptera, Lepidoptera, Diptera, Hymenoptera, Arachnidia and seeds Young feed on emergent aquatic insects, particularly Odonates (60-90% of diet), and Gastropoda, Hydrachnidia, Diptera, Orthoptera and Arachnidia	Twedt and Crawford 1995

Western	Thamnophis		Amphibians, fish, invertebrates, rodents, s	mall birds, http://www.
Terrestrial (Wandering)	elegans vagrans		and carrion	pc.gc.ca/pn- np/ab/banff docs/herp/c
Garter Snake				ap5/natcul7a _E.asp#WanderingTerrestr alGarterSnak
			<ul> <li>Slugs, small mammals, fish, small amphibi birds, and other snakes</li> </ul>	bcreptiles.ca/ nakes/westte rgarter.htm
		Maximum length of 1.06 m	• Slugs, snails, leeches, earthworms, fish, am small mammals (e.g. voles)	Iph.ca/reptil s/fresh/repti e/accounts/ olubridae/w ndering/acc unt.htm
Common (Red-sided) Garter Snake	Thamnophis sirtalis parietalis		<ul> <li>Amphibians, slugs, earthworms, fish, smal rodents</li> </ul>	ll birds, and <u>http://en.w</u> ipedia.org/v <u>ki/Common</u> <u>Garter_Snak</u>
		Adults range from 0.46 – 1.3m	<ul> <li>Adults consume slugs, frogs, toads, salama tadpoles, and insects, occasionally will con mammals, birds, fish and other reptiles</li> <li>Young eat mainly earthworms</li> </ul>	

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Study Location	· ·	MeHg	THg	% MeHg	Reference
Lake 239, Experimental	Ambient concentrations	ng/g dw		· · · · · · · · · · · · · · · · · · ·	Paterson et al. 2006
Lakes Area,	Ceratopogonidae	81 ± 37 SD			
Northwestern Ontario,	Chironomidae	47 ± 17 SD, 38± 18 SD			
Canada	Ephemeroptera	41 <u>+</u> 16 SD, 44 <u>+</u> 6 SD			
	Hydracarina	220 ± 194 SD, 53 ± 15 SD			
	Pisidiidae	44 <u>+</u> 60 SD, 13 <u>+</u> 4 SD			
Wetland lakes 979 and	1993	ng/g dw			Hall et al. 1998
632, Oligotrophic lake	L979	0.0			
240, Experimental Lakes	Amphipoda				
Area, Northwestern	Ĥyalella azteca	78.2 <u>+</u> 12 SE (65.9-90.5)			
Ontario, Canada	Ephemeroptera				
	Siphlonurus sp.	87.1			
	Trichoptera				
	Limnephilidae	47.7 <u>+</u> 16 SE (19.0-107.8)			
	Odonata				
	Aeshnidae	79.8 ± 17 SE (49.7-121.4)			
	Corduliidae	59.4			
	Other Odonata	79.3 <u>+</u> 5 SE (69.6-87.5)			
	Total Odonata	77.1 ± 9 SE (49.7-121.4)			
	Hemiptera				
	Belostomatidae				
	Lethocerus americanus	107.7			
	Gerridae				
	Gerris sp.	108.6			
	Notonectidae				
	Notonecta sp.	159.6 ± 134 SE (25.9-293.4)			
	Coleoptera				
	Dytiscidae				
	Dytiscus sp.	118.2			
	Gyrinidae				
	<i>Gyrinus</i> sp.	34.6 <u>+</u> 9 SE (25.5-43.7)			
	Dineutus sp.	39.8 <u>+</u> 4 SE (35.6-44.0)			
	Total Gyrinidae	55.4 ± 13 SE (25.5-107.9)			

Appendix 7 Literature review of MeHg and THg concentrations and percent MeHg in benthic invertebrates collected from lakes

	Total collectors/shredders	60.3 <u>+</u> 12 SE (47.7-87.1)	 	
	Total predators	82.9 ± 13 SE (25.5-293.4)		
	L632	_ 、 /		
	Amphipoda			
	Ĥyalella azteca	57.4 <u>+</u> 21 SE (11.7-126.9)		
	Trichoptera			1
	Limnephilidae	37.6 ± 15 SE (1.3-124.8)		
	Odonata			
	Aeshnidae	77.3 <u>+</u> 6 SE (34.6-182.0)		
	Corduliidae	87.3 <u>+</u> 8 SE (48.4-139.5)		
	Other Odonata	72.6 ± 9 SE (7.6-116.1)		
	Total Odonata	79.1 ± 4 SE (7.6-182.0)		
	Hemiptera			
	Belostomatidae			
	Lethocerus americanus	310.6 <u>+</u> 74 SE (139.6-600.0)		
	Corixidae	155.8 ± 22 SE (113.1-184.2)		
	Gerridae			
	Gerris sp.	142.2 <u>+</u> 47 SE (94.7-189.7)		
	Notonectidae			
	Notonecta sp.	182.3 <u>+</u> 25 SE (65.7-264.9)		
	Nepidae			
	Ranatra sp.	233.7		
	Coleoptera			
	Dytiscidae			
	Dytiscus sp.	204.7 <u>+</u> 33 SE (96.5-487.2)		
	Gyrinidae			
	<i>Gyrinus</i> sp.	55.0 <u>+</u> 17 SE (38.5-71.6)		
	Dineutus sp.			1
	Total Gyrinidae	55.0 <u>+</u> 17 SE (38.5-71.6)		1
	Total collectors/shredders	46.7 <u>+</u> 13 SE (1.3-127.0)		
	Total predators	125.0 <u>+</u> 11 SE (7.6-600.0)		
	L240			
	Odonata			
	Total Odonata	52.6 ± 11 SE (14.2-112.1)		
	Hemiptera			
	Gerridae	118.6 <u>+</u> 7 SE (86.5-136.3)		
······································	•	· · · · · · · · · · · · · · · · · · ·		<u> </u>

	Gerris sp.				
	Coleoptera				
	Gyrinidae	57.0 ± 6 SE (32.8-82.9)			
	Total Gyrinidae	86.5 <u>+</u> 14 SE (14.2-136.3)			
	Total predators				
Mouse and Ranger	June to August 1992			· · · · · ·	Wong et al. 1997
Lake, Muskoka, south-	Mouse		ng/g dw		5
central Ontario, Canada	Gastropoda		938.7 + 92.0 SE		
	Amphipoda		98.2 + 22.9 SE		
	Chironomidae (<1 m)		177.2 <u>+</u> 18.1 SE		
	Chironomidae (1-4.9 m)		116.4 <u>+</u> 9.0 SE		
	Chironomidae (5-9 m)		97.2 + 17.1 SE		
	Chaoboridae		73.9 <u>+</u> 10.4 SE		
	Trichoptera		92.4 <u>+</u> 9.6 SE		
	Ephemeroptera		151.0 ± 162 SE		
	Odonata		135.7 <u>+</u> 4.5 SE		
	Ceratopogonidae		162.4 + 31.0 SE		
	Ranger		· · · · · <u></u> · · · · · -		
	Gastropoda		609.9 <u>+</u> 53.4 SE		
	Amphipoda		157.6 <u>+</u> 20.4 SE		
	Chironomidae (<1 m)		110.3 <u>+</u> 9.7 SE		
	Chironomidae (1-4.9 m)		131.1 <u>+</u> 19.3 SE		
	Chironomidae (5-9 m)		132.9 <u>+</u> 12.4 SE		
	Chaoboridae		82.4 + 18.7 SE		
	Trichoptera		70.5 <u>+</u> 7.6 SE		
	Ephemeroptera		128.4 <u>+</u> 17.2 SE		
	Odonata		112.7 <u>+</u> 3.7 SE		
	Ceratopogonidae		99.7 <u>+</u> 2.4 SE		
	Coleoptera		$206.4 \pm 56.0$ SE		
	Oligochaeta		163.7 <u>+</u> 2.0 SE		
Lake Superior, Ontario,	Pelagic:				Back et al. 2003
Canada	Chironomidae	August: 7.9 ng/g dw			
	Amphipoda	August: 31.9 ng/g dw			
	Mysis relicta	August: 17-54.01 ng/g dw			
Lake Laflamme,	Libellulla sp. (Odonata)		~140 ng/g dw		Sarica et al. 2005
southern Quebec,	Hyallela azteca		~40 ng/g dw		

Canada					
Duncan Lake, northern	Coleoptera			and a second	Tremblay et al. 1996
Quebec, Canada	Dytiscidae	107.3	175	61.3	
	Ephemeroptera				
	Leptophlebiidae				
	Leptophlebia spp.	13.5	129	10.5	
	Heteroptera				
	Corixidae				
	Sigara spp.	124.3	256	48.6	
	Odonata				
	Corduliidae				
	Somatochlora spp.	102.2	136	75.1	
	Trichoptera				
	Phryganeidae				
	Agrypnia sp.	61.4	124	49.5	
	Limnephilidae				
	Grammotaulius spp.	56.3	120	46.9	
	Asynarchus spp.	28.5	143	19.9	
5 lakes, northern	Detcheverry	ng/g dw	ng/g dw		Verdon and Tremblay
Quebec, Canada	Mollusca	25 ± 9 SD	78 <u>+</u> 22 SD	32	1999
	Diptera	$101 \pm 36 \text{ SD}$	495 <u>+</u> 260 SD	21	
	Ephemeroptera	$205 \pm 141 \text{ SD}$	275 ± 108 SD	74	
	Trichoptera	214 <u>+</u> 70 SD	305 <u>+</u> 98 SD	71	
	Heteroptera	139	140	100	
	Rond-de-Poêle				
	Mollusca	$13 \pm 2 \text{ SD}$	92 <u>+</u> 18 SD	14	
	Diptera	$175 \pm 75 \text{ SD}$	$403 \pm 100 \text{ SD}$	44	
	Ephemeroptera	$185 \pm 145 \text{ SD}$	$207 \pm 133$ SD	86	
	Trichoptera	$153 \pm 63 \text{ SD}$	232 ± 75 SD	70	
	Des Voeux	_	-		
	Mollusca	32	42	77	
	Diptera	157 <u>+</u> 109 SD	227 + 120 SD	66	
	Ephemeroptera	98	200	48	
	Trichoptera	97	124	78	
	Sérigny				
•	Mollusca		354		

	Diptera	318 <u>+</u> 308 SD	532 ± 284 SD	51	
	Ephemeroptera	718	845	85	
	Trichoptera	151 <u>+</u> 39 SD	390 <u>+</u> 90 SD	38	
	Jobert	—	_		
	Mollusca	40 <u>+</u> 6 SD	62	63	
	Diptera	$382 \pm 151$ SD	441 <u>+</u> 209 SD	78	
6 lakes, northern	Heteroptera	410 ng/g dw	793 ng/g dw		Tremblay and Lucotte
Quebec, Canada	Diptera	12 ng/g dw	17 ng/g dw		1997
11 lakes, northern	Des Voeux	ng/g dw	ng/g dw		Tremblay et al. 1996
Quebec, Canada	Ephemeroptera	0.0	0.0		, , , , , , , , , , , , , , , , , , ,
	Leptophlelbia sp.	14	49 (37-61)	38	
	Odonata				
	Somatochlora and	90	121	74	
	Cordulia			. –	
	Heteroptera				
	Gerris sp. and	102 (30-189)	147 (106-200)	66 (22-94)	
	Sigara sp.			(	
	Trichoptera				
	Limnephilidae	32 (14-49)	143 (42-244)	27 (20-34)	
	Diptera				
	Chironomidae	34	151	22	
	Detcheverry				
	Ephemeroptera				
	Leptophlelbia sp.	39	69 (61-76)	41	
	Odonata				
	Somatochlora and	76 (74-78)	167 (116-217)	51 (34-67)	
	Cordulia	- ( )			
	Heteroptera				
	Gerris sp. and	92 (69-119)	129 (66-129)	64 (58-72)	
	Sigara sp.	,		(/	
	Trichoptera				
	Limnephilidae	20 (11-30)	59 (34-117)	36 (22-51)	
	Coleoptera			\ /	
	Gyrinus sp.	42 (34-55)	65 (56-69)	65 (49-80)	
	Diptera	( )	( /	( )	
	Chironomidae		105 (85-124)		

Duncan				
Ephemeroptera				
Leptophlelbia sp.	34 (12-67)	99 (31-216)	35 (10-60)	
Odonata	. ,			
Somatochlora and	81 (59-127)	107 (34-171)	73 (47-92)	- -
Cordulia				
Heteroptera				
Gerris sp. and	129 (59-410)	227 (67-793)	58 (30-74)	
Sigara sp.				
Trichoptera				
Limnephilidae	46 (20-102)	104 (50-178)	47 (19-79)	
Coleoptera			·	
<i>Gyrinus</i> sp.	61 (35-107)	81 (22-175)	63 (44-84)	
Diptera				
Chironomidae	70 (39-88)	65 (17-196)	43 (42-44)	
Evans area				
Ephemeroptera				
Leptophlelbia sp.	196 (142-289)	241 (180-355)	81 (75-86)	
Odonata				
Somatochlora and	167 (136-198)	217 (201-233)	76 (67-86)	
Cordulia				
Coleoptera	68	405	17	
<i>Gyrinus</i> sp.				
Diptera		194		
Chironomidae				
Jobert				
Odonata	64	80	80	
Somatochlora and				
Cordulia				
Trichoptera	25 (16-34)	90 (79-100)	28 (20-34)	
Limnephilidae				
Coleoptera	77	108	71	
<i>Gyrinus</i> sp.				1
Lake 136				
Trichoptera	9	85 (79-91)	10	
Limnephilidae				
Lake 150	···	l		l

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			a	
Ephemeroptera				
<i>Leptophlelbia</i> sp.	54 (34-74)	84 (65-102)	62 (52-72)	
Heteroptera				
<i>Gerris</i> sp. and	137 (80-176)	207 (98-359)	70 (57-84)	
Sigara sp.				
Trichoptera				
Limnephilidae	43 (10-101)	141 (30-219)	46 (10-58)	
Coleoptera				
<i>Gyrinus</i> sp.	74 (54-93)	104 (86-122)	70 (63-76)	
Diptera				
Chironomidae	56	166 (147-184)	31	
Laporte				
Ephemeroptera				
Leptophlelbia sp.		217		
Odonata				
Somatochlora and		217 (147-276)		
Cordulia				
Heteroptera				
Gerris sp. and		277 (275-279)		
Sigara sp.				
Trichoptera				
Limnephilidae		133		
Diptera				
Chironomidae		137 (112-162)		
Matagami		( ,		
Ephemeroptera	23	55	43	1
Leptophlelbia sp.				1
Heteroptera	112	151	74	
Gerris sp. and				
Sigara sp.				
Trichoptera	9	45	20	
Limnephilidae	-		_0	1
Coleoptera	210 (168-251)	192 (79-281)	84 (78-90)	
<i>Gyrinus</i> sp.	()			
Diptera		106		
Chironomidae		100		
· · · · · · · · · · · · · · · · · · ·			· · · · ·	1

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	Opinica				
	Ephemeroptera	89	164	54	
	Leptophlelbia sp.				
	Odonata		149		
-	Somatochlora and				
	Cordulia				
	Heteroptera	117 (93-140)	151 (136-166)	76 (68-85)	
	Gerris sp. and	. ,			
	Sigara sp.				
	Coleoptera	88	129 (93-164)	93	
	Gyrinus sp.				
	Diptera		95		
	Chironomidae				
5 lakes, west-central	Odonata				Allen et al. 2005
Alberta, Canada	Corduliidae				
	Cordulia shurtleffi		38 <u>+</u> 6 SE ng/g dw		
	Aeshna spp.		83 <u>+</u> 36 SE ng/g dw		
	Trichoptera				
	Phryganeidae		14 <u>+</u> 1 SE ng/g dw		
	Notonecta spp.		172 <u>+</u> 18 SE ng/g		
	Gammarus lacustris		dw		
			27 <u>+</u> 4 SE ng/g dw		
5 lakes Fort Simpson,	Benthos		0.7 – 41.4 ng/g ww		Evans et al. 2005
Northwest Territories,			00		
Canada					
22 lakes in Maryland	Composite				Albers and Camardese
and 12 lakes in Maine,	Maryland				1993
USA	Coleoptera, Hemiptera and		300 ng/g dw		
	Odonata		(100-800)		
	Maine				
	Coleoptera, Hemiptera,		300 ng/g dw		
	Odonata, Megaloptera,		(200-600)		
	Trichoptera,				
	Ephemeroptera	· · · · · · · · · · · · · · · · · · ·			
15 lakes, Vilas County,	Chironomidae	5 ng/g dw	114 ng/g dw	5	Watras et al. 1998

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Wisconsin, USA		(3-7)	(95-133)	(4-5)	
Flathead Lake,	Chironomids	8.8 ng/g ww			Stafford et al. 2004
Montana, USA*	Mysis	9.6 ng/g ww			
Lake Washington,	Mysis	15 <u>+</u> 2 ng/g ww			McIntyre and Beaucham
Washington, USA	Trichoptera	6 <u>+</u> 0.6 ng/g ww			2007
Lake Ritchie, Isle Royale	Trichoptera	ng/g dw			Gorski et al. 2003
National Park, USA	May	20.4	43.5	46.9	
	June	22.4	62.4	35.9	
	July	11	26.5	41.5	
	August	10.1	19.4	52.1	
	Odonata - Anisoptera				
	May	46.4	63.5	72.9	
	June	48.7	69.4	70.2	
	July	53.1			
	August	52.6, 41.6	87.3, 91.5	60.2, 45.5	
	Odonata - Zygoptera				
	May	20.5	44.5	46.1	
	Ephemeroptera –				
	Heptageniidae				
	June	14.4	58.1	24.8	
	July	20.4			
	August	42, 8.5	88.6	9.6	
	Ephemeroptera –				
	Hexagenia				
	May	7.8	61.7	12.6	
	June	16.4	90.5	18.1	
	August	18.6			
8 Headwater lakes,		20-6000 ng/g dw			Meili 1991
Sweden		0.0			
8 Headwater lakes,	Bottentjärn	ng/g dw	ng/g dw		Parkman and Meili 199
Sweden	Odonata	316	501	63	Tremblay et al. 1996
	Trichoptera				, j
Acidic Dystrophic:	Limnephilidae	88	163	54	

Bottentjärn,	Diptera				
Skärhultssjön	Chaoborus	79 (58-100)	218 (211-225)	35 (27-43)	
	Skärhultssjön	,, (00 100)		00 (2, 10)	
Neutral Dystrophic:	Odonata	352	423	83	
Blacksåstjärn, Löjesjön	Trichoptera				
	Limnephilidae	54 (25-66)	209 (56-443)	38 (15-55)	
Mesotrophic:	Blacksåstjärn				
Loppesjön, Gårdsjön	Odonata	299 (124-372)	358 (201-446)	78 (62-84)	
	Löjesjön				
Oligotrophic:	Odonata	234	337	69	
Stensjön ,	Trichoptera				
Holmeshultasjön	Limnephilidae	62	109	56	
	Diptera				
	Chaoborus	39	60	66	
	Loppesjön				
	Odonata	104	152	68	
	Trichoptera				
	Limnephilidae	45	93	48	
	Diptera				
	Chironomidae	9.5	33	29	
	Gårdsjön				
	Odonata	296	371	80	
	Trichoptera				
	Limnephilidae	27	114	24	
	Diptera				
	Chironomidae	21 (16-27)	380 (311-427)	12 (4-9)	
	Stensjön				
	Trichoptera				
	Limnephilidae	38	123	31	
	Diptera				
	Chironomidae	55 (38-67)	386 (165-667)	19 (6-35)	
	Holmeshultasjön				
	Trichoptera				
	Limnephilidae	217	299	73	
	Diptera				
	Chironomidae	24	252	10	

\_ 218

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Study Location		MeHg	THg	% MeHg	Reference
5 lakes, northern Quebec, Canada	53 μm mesh (size fractions 53, 100, 200, 500 μm)	10 – 150 ng/g dw	25 – 350 ng/g dw	<b>~~</b>	Masson and Tremblay 2003
5 lakes, northern Quebec, Canada	150 μm mesh (size fractions 210 μm)	97.3 <u>+</u> 39.2 SD ng/g (34.0 – 156.8)			Montgomery et al. 2000
3 lakes, northern Quebec, Canada	210 µm mesh				Tremblay et al. 1998
	Duncan Lake Detcheverry Lake Rond-de-Poêle Lake Hazeur Lake Des Voeux Lake	23 ng/g dw 43 ng/g dw 18 ng/g dw 82 ng/g dw 34 ng/g dw	223 ng/g dw 190 ng/g dw 85 ng/g dw 432 ng/g dw 166 ng/g dw		
Natural lakes, northern Quebec, Canada	190 µm mesh	20 – 140 ng/g dw	75 – 180 ng/g dw		Kainz et al. 2002
Lake Lusignan, Quebec, Canada	53 μm mesh (size fractions 53, 100, 202, 500 μm)	5 – 105 ng/g dw	45 – 200 ng/g dw		Kainz et al. 2002
9 reference lakes, central Quebec	200 µm mesh	122.3 <u>+</u> 38.9 SD 55.1 - 160.6 ng/g dw			Garcia and Carignan 2000
5 lakes, northern Quebec, Canada	Detcheverry Des Voeux Sérigny Jobert	ng/g dw 104 <u>+</u> 27 SD 96 136 183 <u>+</u> 83 SD	ng/g dw 595 <u>+</u> 234 SD 104 336 <u>+</u> 37 SD 308 <u>+</u> 30 SD	18 89 45 57	Verdon and Tremblay 1999
24 lakes, Ontario and Quebec, Canada	225 µm mesh		107.6 <u>+</u> 76.2 SD (25.5 – 376.9)		Tremblay et al. 1995
24 lakes, south-central, Ontario	363 µm mesh Cladocera		July-August 19 – 448 ng/g dw		Westcott and Kalff 1996
Lake Superior, Ontario, Canada	153 µm mesh	April: 32 – 46 ng/g dw August: 15 – 25 ng/g	April: 78 – 113 ng/g dw August: 22 – 67 ng/g		Back et al. 2003

Appendix 8 Literature review of MeHg and THg concentrations and percent MeHg in zooplankton collected from lakes

		dw	dw		
Lake 239, Experimental Lakes Area, Northwestern Ontario, Canada	150 μm mesh	Ambient concentrations 108 <u>+</u> 26, 58 <u>+</u> 20 ng/g dw			Paterson et al. 2006
Lake 110 and Lake 227, Experimental Lakes Area, Northwestern Ontario, Canada	150 μm mesh	Oligotrophic Lake 110 146 <u>+</u> 6.4 ng/g dw Eutrophic Lake 227 35.3 <u>+</u> 8.8 ng/g dw			Kidd et al. 1999
2 lakes on southern Vancouver Island, Canada	64 μm mesh (size fractions 100, 200, 500 μm) macrozooplankton	105 <u>+</u> 9 ng/g dw			Kainz and Mazumder 2005
5 lakes Fort Simpson, Northwest Territories, Canada			1.5 – 10 ng/g ww		Evans et al. 2005
Max Lake, Wisconsin, USA	Individual Cladocera (1 mm Daphnia or Holopedium)	20 ng/g ww (12-28)	56 ng/g ww (36-92)	29	Watras and Bloom 1992
Mud Lake, Wisconsin, USA	Daphnia	41 - 61 ng/g ww	71 – 89 ng/g ww		Back et al. 1995
15 lakes, Vilas County, Wisconsin, USA	20 cm diameter net with 153 µm mesh				Watras et al. 1998
	All zooplankton	53 ng/g dw (6 - 161)	83 ng/g dw (33 – 206)	57 (11 – 83)	
	Crustacea	54 ng/g dw (13 - 143)	78 ng/g dw (23 – 179)	70 (52 – 83)	
	Cladocera	73 ng/g dw (35 - 148)	110 ng/g dw (50 - 197)	70 (50 - 87)	
ATT ( ) , ) , ) , () , () , () , () , ()	Daphnia	65 ng/g dw	81 ng/g dw	80	

	Holopedium Bosmina Copepoda	(41 - 112) 88 ng/g dw (47 - 184) 65 ng/g dw (29 - 88) 45 ng/g dw (13 - 132)	(54 - 143) 130 ng/g dw (64 - 251) 105 ng/g dw (46 - 158) 60 ng/g dw (23 - 144)	(76 - 87) $68$ $(57 - 83)$ $67$ $(50 - 90)$ $71$ $(52 - 97)$	
	Diaptomus Cyclopoida	(13 - 132) 52 ng/g dw (14 - 132) 28 ng/g dw (9 - 46)	(25 - 144) 67 ng/g dw (19 - 144) 46 ng/g dw (12 - 84)	(52 - 97) 76 (50 - 97) 62 (50 - 90)	
12 lakes, north central Wisconsin, USA	20 cm diameter net with 153 μm mesh				Back and Watras 1995
	Herbivorous Taxa	1 -479 ng/g dw			
	Daphnia pulex, D. galeata mendotae, D. ambigua	1 - 211 ng/g dw			
	Holopedium gibberum	40 -419 ng/g dw			
	Bosmina longirostris	479 ng/g dw			
	Diaptomus oregonensis & D. minutus	22 – 66 ng/g dw			
	Omnivorous Taxa				
	Mesocyclops edax	24 – 30 ng/g dw			
Devil's Lake, Sauk County, Wisconsin, USA	Daphnia	1994: 275 ng/g dw 1995: 133 ng/g dw 1996: 163 ng/g dw			Gorski et al. 1999
20 lakes, northeastern USA	45-202 μm	<u> </u>	3610 <u>+</u> 1840 ng/g dw (26-29400)		Chen et al. 2000
	>202 µm		1200 <u>+</u> 437 ng/g dw		

			(28-7480)		
53 lakes, Minnesota, USA	80 µm mesh Wisconsin style net		90 ng/g dw (10 - 210)		Sorensen et al. 1990
12 lakes, northeastern Minnesota, USA	300 µm mesh		53 – 300 ng/g dw		Monson and Brezonik 1998
Lake Ritchie, Isle Royale National Park, USA	112 μm mesh Cyclopoid Daphnia g. m. Ceriodaphnia Calanoid Bosmina Bulk zooplankton	79.4 ng/g dw 31.4 ng/g dw 41.0 ng/g dw 27.7 ng/g dw ND 32.2 <u>+</u> 0.4 SE – 75.1 <u>+</u> 0.1 SE ng/g dw	181.8 ng/g dw 102.6 ng/g dw 68.3 <u>+</u> 7.27 SE ng/g dw 44.6 <u>+</u> 17.8 SE ng/g dw 132.9 150.7 <u>+</u> 9.8 SE – 256.9 <u>+</u> 7.1 SE ng/g dw	43.7 30.6 60 62.1 18.1 – 35.6	Gorski et al. 2003
Lake Washington, Washington, USA	153 μm mesh (bulk zooplankton), 1 mm mesh (mysids, <i>Daphnia</i> , <i>Leptodora</i> )	9 <u>+</u> 0.9 ng/g ww (Daphnia) 5 <u>+</u> 1.8 ng/g ww (Leptodora)	4 <u>+</u> 0.4 ng/g ww (bulk zooplankton)		McIntyre and Beauchamp 2007
8 Headwater lakes, Sweden		70-700 ng/g dw			Meili 1991
Lake Balaton, Hungary	300 µm mesh	1 -13 ng/g dw	14 – 42 dw	17%	Nguyen et al. 2005
Lake Malawi, Africa	71 µm mesh		3.0 <u>+</u> 1.6 ng/g ww		Kidd et al. 2003
4 New Zealand Lakes		4 - 36 ng/g ww			Kim and Burggraaf 1999

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