

PRAIRIE PROVINCES WATER BOARD

Report # 1

Biomonitoring at Prairie Provinces Water Board Stations Historic (1993 – 2004) and Future Options

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PPWB fish tissue report Dec 2018

BIOMONITORING AT PRAIRIE PROVINCES WATER BOARD STATIONS, HISTORIC (1993 – 2004) AND FUTURE OPTIONS

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Executive Summary

In response to the 1992 approval and signatures by Ministers of The Agreement on Water Quality, Schedule "E" of the Master Agreement on Apportionment, and the direction provided in the Agreement, the Prairie Provinces Water Board initiated in 1993 biological monitoring at 7 of 11 interprovincial stations. From 1993 to 2004, total mercury, other metals, and organochlorine pesticides were assessed in the muscle of a piscivore and a lower trophic level fish species from each of the seven stations. However, the principal focus of the program was an assessment of mercury concentration in fish muscle evaluated against established tissue objectives. This report provides an overview of the 1993 to 2004 PPWB fish monitoring program, including the methods used during the program, concentrations of mercury in fish, the excursion rates for mercury in fish compared with established objectives, and an overview of mercury concentrations at PPWB stations compared with other locations within the Saskatchewan River basin and northern Canada. Results for the assessment of metals other than mercury and for the organochlorine pesticides are presented in Appendix A.

Walleye had the highest concentration of mercury of all the fish species. For walleye, the mean maximum was 0.798 μ g Hg/g for fish from the North Saskatchewan River (all years combined, N = 30), and the mean minimum was 0.184 μ g Hg/g for fish from the Saskatchewan River (all years combined, N = 30). For walleye, about 40% of the annual and site-specific variation in mercury concentration was related to fish mass. Mean mercury concentration in fish muscle tissue for most other fish populations was also related to fish mass.

The human fish consumption objective of $0.500~\mu g$ Hg/g, which was set for five stations, was exceeded by 53% of walleye, all stations combined. An objective of $0.200~\mu g$ Hg/g, which was set for only two of the seven stations where fish are consumed more frequently in nearby First Nations communities, was exceeded by 68% of walleye. White suckers had low concentrations of mercury, and concentrations in muscle did not exceed objectives at any of the five stations where this fish species was collected.

Mercury muscle tissue for both lower and high trophic level fish species from all PPWB stations were within normally expected concentrations and ranges for the same species from other locations in the prairie provinces and in northern Canada.

Options for a PPWB fish biomonitoring program and a benthic invertebrate monitoring program are presented which include a tissue biomonitoring program for mercury and other metals in fish, and a fish community assessment program at some but not all stations. Details on the approach, methods, and strategy for the options are provided.

INTRODUCTION

In response to the approval by Ministers of Schedule "E" of the Master Agreement on Apportionment in 1992, and the direction provided therein, the PPWB initiated biological monitoring at PPWB stations in 1993. Specifically, the Board determined the concentrations of mercury, other metals, and organochlorine pesticides in fish muscle tissue, compared these concentrations with established PPWB tissue objectives for each parameter, identified excursions of the concentration data that were greater than the established objectives, and recorded these excursions in the annual report of the Board. These activities were completed from 1993 to 2004.

In this report the results of the mercury, other metals and organochlorine pesticides concentration data are summarized for the entire duration of this fish tissue monitoring program (1993 to 2004). The main focus of the original program was to assess mercury concentrations in fish muscle tissue which is the main focus of this report. In addition, options for future monitoring of mercury are provided in the context of the mandate of the Board as outlined in the Master Agreement on Apportionment.

Elemental mercury is the principal form of mercury found in sediment and water and has low toxicity to organisms. Elemental mercury is often monitored in sediments and water downstream of metal and coal mining operations. Methylmercury is a highly toxic form of mercury that bioaccumulates in food chains within aquatic ecosystems. Methyl-mercury is a small percentage of the mercury found in sediments, about half or less of the mercury present in aquatic invertebrates, and about 95% of the mercury found in fish tissues.

High consumption of methyl-mercury in food sources can cause neurological and teratological (embryonic development) effects on vertebrates, including fish and humans (Das et al. 1982; Grandjean et al. 2010). The toxic effects of mercury to humans was known in the early twentieth century. However, widespread assessments of mercury in fish and shellfish began in developed nations in the 1960s after it was determined that the severe and permanent neurological damage to dozens of people living in Minamata, Japan, was caused by mercury (Kurland et al. 1960; Jojima and Jujita 1973). Thereafter, mercury poisoning in humans was diagnosed as Minamata disease. In the Saskatchewan River basin (Sumner et al. 1970; Wobester et al. 1970), and in many other watersheds in North Amercia, the first assessments of mercury in fish were conducted in the late 1960s.

Mercury is a common trace element on the earth and can be found in sediments, soils, and rock. In lakes, pre-industrial and recent concentrations of total mercury

(all forms of mercury) in sediments typically ranges from 0.01 to 0.2 µg/g dry weight (Rada et al. 1989; Rada et al. 1993; Brigham et al. 1998). A detailed assessment of mercury concentrations in sediments in the Bow, Oldman, Red Deer, and South Saskatchewan rivers in Alberta found that mean total mercury concentrations ranged from 0.03 to 0.08 µg/g dry weight with no obvious point source of high concentrations of Hg in sediment (George et al. 1994). In the North Saskatchewan River total mercury concentrations in 108 sediment samples from four reaches ranged from 0.05 to 0.1 µg/g dry weight (Ramamoorthy et al. 1985). Vertical profiles of mercury in lake sediments typically show higher concentrations in the most recent surface sediments. These relatively high concentrations in recently deposited lake sediments are the result of mercury mobilization into the atmosphere from anthropogenic activities followed by longrange transport and deposition onto lakes and lake catchments (Prestbo and Gay 2009). The principal sources of anthropogenic mercury are municipal garbage incineration, electricity generated from burning coal, copper smelting, and artisanal gold extraction (Streets et al. 2009).

Currently, point sources of mercury to the Churchill, Saskatchewan and Assiniboine basins would include municipal waste water discharges, and atmospheric transport of mercury from burning coal to produce electricity. However, exposure of fish to agricultural runoff and urban effluent does not automatically increase mercury burden in fish. In a detailed study of mercury bioaccumulation in a headwater tributary of the South Saskatchewan River, the Oldman River, Brinkmann and Rasmussen (2012) found that agricultural and municipal effluents were either associated with decreased mercury concentration in fish or did not change mercury concentrations relative to reference sites. Oilsands activities in Alberta including mining, extraction, and processing would also contribute mercury primarily to the Churchill River watershed. Historically, copper, lead, and zinc smelting in Flin Flon would have been a source of mercury to the lakes and rivers that ultimately flow to Cumberland Lake which is situated on the mainstem of the Saskatchewan River. In 1962, a chlor-alkali plant began operation in Saskatoon, and from 1963 to 1978 discharged an estimated 22 to 33 tonnes of mercury into the South Saskatchewan River (Harrison and Waite 1988). Peak discharge of mercury from the chlor-alkali plant was 23 kg/day. By 1981, however, effluent regulations and process changes were responsible for reducing mercury discharge to 0.004 kg/day. In the South Saskatchewan River downstream from the plant, Harrison and Waite (1988) reported median total mercury concentrations in sediment of 0.07 µg.g dry weight (range 0.01 to 0.14 µg/g) in 1984-85. At that time, however, relatively high concentrations of total mercury were recorded in Tobin Lake (maximum 0.24 µg/g dry weight).

Relatively non-toxic inorganic elemental mercury is methylated in sediments in aquatic ecosystems by anaerobic bacteria (Furutani and Rudd 1980; Avramescu et al. 2011) to form methyl-mercury which at high concentrations is toxic to organisms. Methyl-mercury is biomagnified upward in the aquatic food chain to organisms such as plankton and invertebrates and then into lower trophic levels

of fish (Lavoie et al. 2013). The highest concentrations of mercury are found in the top piscivores (for example Ramamoorthy et al. 1985; Goldstein et al. 1996; Donald et al. 2015). Water has exceptionally low concentrations of mercury and therefore would not be the main source for methyl-mercury for most organisms. For fish, the principal pathway for mercury uptake is from food (Hall et al. 1997), rather than from water through the gills.

Elemental mercury concentrations in freshwater are usually less than 1 μ g/L. Mercury is difficult to assess in water because of challenges related to eliminating mercury contamination from field and laboratory analytical equipment, and keeping this equipment "clean" during water collection and analysis. Methlymercury concentrations in top piscivores, however, often exceed 1000 μ g/kg or about 1000 times greater than in water. Mercury assessments in fish do not require super, ultra-clean field and analytical methods. Therefore, fish are usually the media of choice when assessing mercury concentrations in the environment.

In the United States, human intake of methyl-mercury is mostly from consumption of marine and freshwater fish and shell fish (Sunderland et al. 2018). For Canadians, the principal source of methyl-mercury would be similar, also fish and shellfish. Because of the relatively simple field and laboratory methods that are used to assess mercury concentrations in fish compared with water, and because of the risk to human health from the consumption of fish, the PPWB monitored mercury in fish at 7 stations from 1993 to 2004. Concentrations of mercury in fish muscle were assessed against the Health Canada guideline for consumption of fish by humans.

History

A multi-media monitoring program was developed by the Committee On Water Quality of the Prairie Provinces Water Board in 1989-1990, wherein the 11 interjurisdictional river reaches would be monitored¹ (PPWB, 1990). The program would collect sediment, water, and biota to assess and report on the ecosystem health for the 11 river reaches. The board planned to partially implement the program in 1990/1991, and eventually execute full implementation of the program, but not until the Federal Treasury Board increased the ceiling for PPWB expenditures, and additional resource allocations were received under the Canada Water Act (PPWB, 1992). However, due to lack of financial resources, the PPWB was forced to delay the program's implementation until the 1991/1992 fiscal year, or until funds became available (PPWB, 1991). The program experienced another delay in the subsequent fiscal year, and was officially implemented in 1993 (PPWB, 1992), although somewhat reduced in scope.

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¹ Note that PPWB's monitoring of the Cold River, on the Saskatchewan/Alberta border, did not begin until 1993. Hence, only 11 interjurisdictional prairie river reaches were monitored before that year.

METHODS

As part of the multi-media monitoring program, the biomonitoring program was implemented to assess the presence of toxic substances in the aquatic environment through chemical analysis of fish tissue. Fish were chosen for the biomonitoring program because of their longevity, which allows them to bioaccumulate specific metals and synthetic organic compounds over multiple years. These toxins can be detected in water at low part per trillion concentrations but can be found at much higher concentrations in fish tissue because they bioaccumulate over time. This allowed for assessment against PPWB objectives and against potential health risks to humans and wildlife. The metals: mercury, cadmium, chromium, nickel, copper, lead, zinc, molybdenum, arsenic, and selenium were assessed. Organics parameters included three dichlorodiphenyl- trichloroethane (DDT) isomers in addition to 32 other chemicals under this category.

Fish were collected from 7 of 11 PPWB stations with mixed-mesh gill-nets under a strategic plan as outlined in Table 1. A lower trophic level fish species such as silver redhorse and white suckers, and a top piscivore, either walleye or northern pike were collected at each station. Gill-nets are not an efficient or effective method for collecting fish in rivers. Consequently, for some stations, fish were collected at a nearby lake (Qu'Appelle River PPWB station – Round Lake; Red Deer River PPWB station – Red Deer Lake, Assiniboine River PPWB station – Lake of the Prairies). Gill-nets were used effectively at specific locations near the PPWB stations on the Saskatchewan River (Big Eddy) and at the lake-like habitat on the Churchill River. With a substantial effort, adequate numbers of fish were also collected with gill-nets from the North Saskatchewan and South Saskatchewan rivers at the Alberta – Saskatchewan boundary.

Table 1. Fish sampled during the PPWB fish monitoring program by river and year.

				Fish sa	ampling			
	1993	1994	1995	1996	1997	1999	2003	2004
	,		,		,		,	
Assiniboine River at Lake of the Prairies	V		1		√		V	
Churchill River			$\sqrt{}$		$\sqrt{}$			
North Saskatchewan River at Lea Park								
Qu'Appelle River at Round Lake								
Red Deer River at Red Deer Lake			V		V		V	
Saskatchewan River above Carrot River				V				V
South Saskatchewan River at HWY 41		V		V		V		V

Muscle tissue from the dorsal part of the fish was collected for mercury analysis every second year over a five year period (1993 to 1997) and again in 2003 and 2004 (Table 1). Composite samples of muscle tissue for metals and organochlorine pesticides were taken from the same 10 fish sampled for mercury. The target sample for mercury analysis was 10 fish per trophic category over a range of fish size. In practice, however, the number of fish caught and sampled varied from 2-30 depending on the particular station and year.

Gill-nets were used to catch fish at every site. Table 2 illustrates how fish catches were summarized into tables, which included details such as net mesh size, net set and lift times, fish mortalities and releases, etc. A relatively limited range in gill-net mesh sizes was used to catch fish, and consequently the catch included a relatively narrow range of fish mass and length. Sampling of fish of different mass from the same site would provide and improve the types of data needed to assess relationship between mercury concentration and fish mass.

Muscle tissue from a total of 523 fish were assessed for mercury during the PPWB biomonitoring program. Walleye and northern pike represented the piscivores; and white suckers, shorthead redhorse suckers, and longnose suckers represented the lower trophic level fish species. For the 523 fish, the sample counts by species were, in descending order: 187 walleye, 127 white suckers, 121 shorthead redhorse suckers, 78 northern pike, and 10 longnose suckers. Also, when counting the total number of samples taken per station, one finds that approximately 23% of the total samples were taken from the Assiniboine River (Lake of the Prairies), and that the number of fish sampled at this location was double that of any of the other stations, with the exception of the Churchill River where 18% of all the samples of fish were collected.

After removal from the nets, the fish were processed either immediately upon arrival at shore, or as soon as an appropriate location could be found. Recorded field data included the species, round (total weight) and muscle sample weight, sex, fork length and total length. The fork length was occasionally omitted from the field data, and when large numbers of fish were caught at one lake, only a portion of the total fish were recorded. For example, in 1997, only 38 of the 290 fish caught at Round Lake were recorded. The fork length was recorded using a Wildco plastic fish measuring board. All of the field data were then entered into a table that also included the following information: site, species, date, PPWB code, length, weight, sex, and weights of samples for mercury, other metals, and organics, as well as a designated replicate sample or composite. A Sartorius PT6 electronic field balance was used to measure the total round weight and morsel weight. When opening and filleting the fish, a clean cutting board was used as a surface. To ensure accurate results, acetone and hexane were used to pre-wash all surfaces and tools used in the processing of fish. Fish samples were frozen on dry ice in cases where processing was performed in the field and the fish samples

were then transported back to Regina. Upon arrival to Regina, the frozen samples were placed in a cryo-freezer at -60° C. All samples were stored in this freezer until they were shipped to the Burlington lab on dry ice. The fish tissue samples were then homogenized by the Department of Fisheries and Oceans and forwarded, for chemical analysis, to the National Laboratory for Environmental Testing (NLET), also in Burlington. The fish tissue samples were analysed in Burlington by Cold Vapour Atomic Florescence Spectroscopy.

Table 2 is an example of the field sheet for a fish sampling trip summary (Biomonitoring Report: Fish, 1997)

Table 2. Example of a field sheet. Net set data, released fish and CPUE (catch per unit effort) data for PPWB fish collected in 1997. Note the Round Lake sets were overnight sets (set 03/09, lift 04//09), while all others were same-day sets and lifts. Hours fished and Total were rounded to the nearest hour.

Site	Net	Set	Lift	Hours fished	White sucker	Redhorse sucker	Walleye	Northern pike	Perch	Rock bass	Bullhead	Goldeye	Total	Total mortality	Total catch	CPUE fish/hr
				Horica	Sucitor	Sucker		Releas	ed	bass				mortanty	Caton	11311/111
Round Lake	55 M, var	14:00	08:45	19	1				26							
Round Lake	30 M, 4 in	12:45	10:10	22					1							
Round Lake	60 M, 3 in	13:07	11:10	22	23		3		3							
Round Lake	60 M, 4 in	13:30	13:30	24	8	2			1	3	1					
TOTAL				87	32	2	3	1	31	3	1		73	290	363	4.2
Lake of Prairies	30 M, 4 in	13:30	15:30	2	6			2								
Lake of Prairies	55 M, var	13:55	16:00	2	10	3		1	18							
TOTAL				4	16	3		3	18				40	23	63	15.8
Churchill River	55 M, Var	07:30	13.30	6	1	7		3								
Churchill River	60 M, 3 in	08:00	14:45	6	3	22										
Churchill River	30 M, 4 in	08:30	15:15	7		5										
Churchill River	60 M, 4 in	09:00	15:30	6												
TOTAL				25	4	34		3					41	60	101	4.8
Red Deer Lake	60 M, 4 in	09:30	11:40	2								1				
Red Deer Lake	60 M, 3 in	10:00	11:15	1								3				
Red Deer Lake	30 M, 4 in	10:01	12:40	3												
TOTAL				6								4	4	25	29	4.8

River, Lake and Station Information

Fish were sampled from seven interjurisdictional river reaches at or near established PPWB water quality monitoring stations. Table 3 gives the absolute location (longitudinal and latitudinal coordinates), ecozone and ecoregion of each station. The following river descriptions provide information into the origin of the rivers, flow direction, and the location of the water quality monitoring stations relative to the fish monitoring stations.

Assiniboine River

The Assiniboine River originates approximately 54km northwest of the Town of Preeceville, Saskatchewan. The river flows in a southeasterly direction for 192 km until it crosses the Manitoba border. The fish monitoring program was conducted at Lake of the Prairies which is downstream of the water quality monitoring station and is on the Saskatchewan – Manitoba border.

Table 3. Fish collection locations (degrees, minutes, seconds) and the biogeographic divisions of the PPWB stations.

	Fish Sampling Plan								
Site	Latitude N	Longitude W	Ecozone	Ecoregion					
Assiniboine River at Lake of the Prairies	51º 13' 47.348"	101º 31' 35.997"	Boreal Plains	Boreal Transition					
Churchill River	56° 36' 29.016"	102º 11' 44.016"	Boreal Shield	Churchill River Uplands					
North Saskatchewan River at Lea Park	53° 36 '05.004"	110º 00' 29.988"	Prairies	Boreal Transition					
Qu'Appelle River at Round Lake	50° 32' 24.518"	102º 22' 23.135"	Prairies	Aspen Parkland					
Red Deer River at Red Deer Lake	52º 56' 59.183"	101º 21' 33.516"	Boreal Plains	Mid Boreal Lowland					
Saskatchewan River above Carrot River	53° 50' 30.012"	101º 20' 03.984"	Boreal Plains	Mid Boreal Lowland					
South Saskatchewan River at HWY 41	50° 44' 15.000"	110º 05' 44.016"	Prairies	Mixed Grassland					

Churchill River

The Churchill River originates from the Beaver River in eastern Alberta, and extends 1600 km before entering Hudson Bay. The PPWB water quality and fish monitoring sites for this river were located near Wasawakasik Lake at the Saskatchewan – Manitoba border.

North Saskatchewan River

The water quality and fish monitoring stations were at similar locations near the interprovincial boundary.

Qu'Appelle River

Approximately 290 km from the headwaters of the Qu'Appelle River at Lake Diefenbaker is the confluence of the Qu'Appelle and Assiniboine rivers. The Qu'Appelle River monitoring station is located at Welby, Saskatchewan, approximately 100 km southeast of Yorkton, Saskatchewan. The fish monitoring station at Round Lake was upstream of the water quality monitoring station.

Red Deer River near Erwood River

The PPWB's Water Quality monitoring station for the Red Deer River (Saskatchewan – Manitoba border) is located near Erwood. The fish monitoring station at Red Deer Lake was downstream of the water quality monitoring station.

Saskatchewan River

The Saskatchewan River originates near Prince Albert, Saskatchewan, at the confluence of the South and North Saskatchewan rivers. The PPWB monitoring site for this river is located upstream of the river's confluence with the Carrot River. A traditional "First Nations" fishing site at "big eddy" on the Saskatchewan River provides an ideal location for catching fish. The "big eddy" on the Saskatchewan River is a few kilometres upstream of the water quality monitoring station.

South Saskatchewan River

The South Saskatchewan River is a northeasterly flowing river and originates at the confluence of the Oldman and Bow rivers. Its origin is approximately 30 km west of Medicine Hat, Alberta. The PPWB monitoring station for this river is located in Alberta along Highway #41. Both the water quality and fish monitoring sites were at locations near the interprovincial boundary.

The Biomonitoring Program and PPWB Annual Reports

For the fish tissue monitoring program, concentrations of mercury and other chemicals were compared to established PPWB objectives and the results of the comparison were

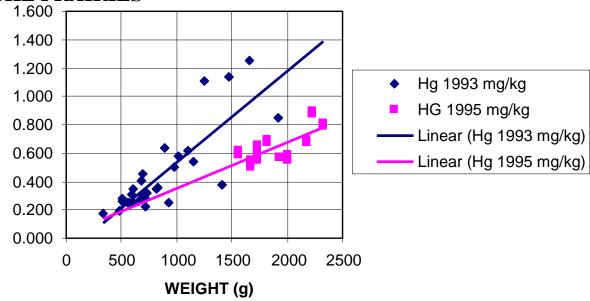
presented in the annual reports of the Board (PPWB 1994 to PPWB 2004). In the context of reporting water quality and biomonitoring results, an objective for a given parameter refers to a concentration value set to protect a particular water use such as for agricultural use or protection of aquatic life. For example, an objective of 200 mg/L for dissolved sodium might be used to protect the source of drinking water supplies, and an objective of $0.2~\mu g/g$ for mercury in fish tissue might be used to provide guidance on fish consumption. Any given sample that has a concentration greater than or equal to an objective is reported as an excursion of that objective.

For the purpose of the annual reports, the fish tissue mercury concentration results were recorded as an average of the fish samples taken per species, while composite sample results were reported for the remaining metals. Individual fish tissue mercury concentrations were also compared with the PPWB fish tissue mercury objectives (Table 4), and were reported as the percent of samples greater than the objective. While few lower trophic level fish species had mercury concentrations that exceeded the objective 0.2 μ g/g or 0.5 μ g/g, piscivores often exceeded the objective at some locations. A secondary objective of the biomonitoring program as indicated in the PPWB annual reports was to make recommendations on maximum human fish consumption in meals per week.

When average mercury concentration for a fish species from a PPWB station exceeded the objective, the PPWB annual report recommended a maximum consumption rate. In some cases, especially when the mercury concentration average for a fish species was well above the objective, the average was compared to results from studies that had been conducted on the same rivers but in earlier periods, from 1980 until approximately 1990, by provincial agencies (Manitoba Environment and Saskatchewan Environment). This comparison was made to determine if concentrations of mercury in fish muscle during the PPWB monitoring program were higher than historic concentration values. This was never the case, as historic average concentrations of mercury were higher for piscivores collected from the same rivers.

In 1997 and 1998, the relationships between fish tissue mercury concentrations and fish weight for fish caught from 1994 to 1996 were calculated and presented in the annual report of the PPWB. In general, fish tissue mercury concentrations were directly proportional to fish weight, as shown in Figure 1.





Objectives and Excursions

The annual report of the PPWB provides an annual summary of excursions of water quality parameters against established objectives for 12 interprovincial rivers. During the 1990s, the annual report of the Board also included assessment of 8 objectives that were based on concentrations of chemicals in fish tissue. Objectives that identify health risk to wildlife that consume fish and objectives that identify health risk to people that consume fish were used.

Objectives for mercury, arsenic, lead and dichlorodiphenyltrichloroethane (DDT) were used to assess risk to human health from consuming muscle tissue (fillets) of fish. These objectives were adopted from Health Canada's (HC's) Food and Drug Regulations.

Objectives for DDT were used to assess risk to wildlife (mammals and birds). These were adopted from objectives established by the Canadian Council of Ministers of the Environment (CCME).

Fish Tissue Objectives for Mercury

Methyl-mercury is the dominant form of mercury in fish, with methyl-mercury 80% to 95% of total mercury (Donald 2016 and references therein). As noted by the Environmental Protection Agency (EPA), impaired neurological development is the primary health effect of methyl-mercury. More specifically, methyl-mercury can adversely affect attention, thinking, language, memory, visual spatial skills and fine motor skills. These symptoms are most prominent in children whose mothers consumed shellfish and fish while the child was in her womb. Other adverse effects include lack of coordination, and impaired speech, walking, hearing, and peripheral vision (EPA, 2012a).

The PPWB's current mercury objectives for fish muscle tissue is 0.2 μ g/g. The standard objective provided by Health Canada (HC) is 0.5 μ g/g (with the exception of escolar, orange roughie, marlin, fresh and frozen tuna, shark, and swordfish, which have an objective of 1.0 μ g/g). During the fish sampling program, the lower PPWB mercury objective of 0.2 μ g/g was adopted to reduce the risk of mercury toxicity to the two most sensitive fish consumers of the human population: women of childbearing age and children under 12 years old. The 0.2 μ g Hg/g also provides protection for individuals who consume fish frequently, more than 2 meals a week. As stated by the Government of Manitoba (G of M), who has also adopted HC's objective (0.5 μ g/g), sensitive members of the population should only consume 0.2 μ g of mercury per kilogram of the individual's weight (0.2 μ g/kg bw) a day (G of M, 2007). Therefore, assuming that the sensitive group consumes up to 8 meals of fish per month, fish tissue mercury levels should not exceed 0.2 μ g/g. However, as presented in past annual reports, the PPWB adopted two fish tissue objectives for mercury (0.2 μ g/g and 0.5 μ g/g).

Of the monitored rivers, the Saskatchewan River and the Churchill River were assigned the 0.2 μ g/g objective, while the less conservative objective was assigned to the remaining 5 five rivers (Table 4). The lower 0.2 μ g/g Hg in fish muscle tissue is also used as the human health objective to protect those individuals who consume large quantities of fish regularly. Individuals from First Nations in northern settlements are known to consume fish frequently. The Opaskwayak Cree First Nation settlement is at "big eddy"; near the location of the PPWB fish sampling station on the Saskatchewan River. The Wapaskakimaw Indian Reserve settlement, near Sandy Bay, is at the location of the PPWB fish sampling station on the Churchill River.

Table 4. Increary half hadde objectives ascallingast in VVD / lilliaat Nepoli	Table 4. Mercur	v fish tissue objective	es used in past PPWB Annual Rep	oorts.
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	Fish tissue objective
Assiniboine River at Lake of the Prairies	0.5 μg/g
Churchill River	0.2 μg/g
North Saskatchewan River at Lea Park	0.5 μg/g
Qu'Appelle River at Round Lake	0.5 μg/g
Red Deer River at Red Deer Lake	0.5 μg/g
Saskatchewan River above Carrot River	0.2 μg/g
South Saskatchewan River at HWY 41	0.5 μg/g

RESULTS AND DISCUSSION

Mercury Concentrations by River and Fish Trophic Position

Walleye had the highest average concentration of mercury compared to all other fish species. (Averages were calculated for each species for all years at each station for all years combined.) Walleye from the North Saskatchewan River had the greatest average concentration of mercury, 0.798 μ g/g (N = 30 fish collected from 1994 to 2004), followed by the South Saskatchewan, Assiniboine (Lake of the Prairies) and Churchill rivers, which had average concentrations of 0.763 μ g/g, 0.481 μ g/g, and 0.446 μ g/g, respectively (Tables 5, 6, 7 and 10). The Saskatchewan River had the lowest mean concentration for mercury for walleye, 0.184 μ g/g. Northern pike from Red Deer Lake had the lowest overall concentration of mercury of the piscivores, 0.104 μ g/g (Table 9).

Both walleye and northern pike were assessed for mercury at two stations, Churchill River and Round Lake (Table 7 and 11). At these locations, the concentration of mercury in muscle was similar for the two fish species (Churchill River: walleye 0.446 μ g Hg/g, northern pike 0.463 μ g Hg/g; Round Lake: walleye 0.216 μ g Hg/g, northern pike 0.253 μ g Hg/g).

Lower trophic level fish species had lower concentrations of mercury than piscivores at all stations (Figures 2 to 8). However, concentrations of mercury in lower trophic levels species were relatively high at some stations. For example, redhorse suckers taken from North Saskatchewan and South Saskatchewan rivers had average mercury concentrations of 0.442 $\mu g/g$ and 0.262 $\mu g/g$, respectively. These concentrations were greater than the average concentrations of mercury in piscivores taken from the Qu'Appelle (Round Lake), Saskatchewan River, and Red Deer Lake

(Red Deer River). The lowest concentration of mercury was found in shorthead redhorse collected from Red Deer Lake, 0.051 µg/g.

Excursion from Objectives

The North Saskatchewan River had a high total excursion rate for mercury in walleye with 80% having concentrations > 0.500 μ g/g (Table 5). The South Saskatchewan River, which was second, had an excursion rate of 76.5% for walleye followed by the Assiniboine (Lake of the Prairies) where the objective excursion rate for walleye was 43.4%. Northern pike either rarely exceeded the 0.500 μ g Hg/g objective (3.3%, Qu'Appelle River at Round Lake) or did not exceed the objective (0%, Red Deer River at Red Deer Lake).

The excursion rate for walleye from the Churchill River was 97.6%, and 100% for northern pike. This station had a low concentration objective of 0.200 µg Hg/g to protect a segment of the human population that would be at risk from consuming excessive quantities of mercury in fish. This same objective was used for the Saskatchewan River. However, the excursion rate for walleye from this river was much lower, 26.7%. For the Saskatchewan and Churchill rivers, the excursion rate for lower trophic level species was from 0% to 18%, respectively.

Mercury concentrations in muscle from low trophic level fish species generally did not exceed the PPWB mercury objective (Saskatchewan River, Red Deer Lake, Lake of the Prairies, Round Lake) or the excursion rates were far less than samples taken from piscivores (North Saskatchewan River 10% to 33.3%; South Saskatchewan River 6.7%; Churchill River 18%). The Churchill River had a large difference between excursion rates for the two trophic levels. Piscivores exceeded the objective 97.6% of the time and lower trophic level species exceeded the objective 18.8% of the time, a difference of 78.8% (Table 7).

For the five stations with the historic mercury objective of $0.500~\mu g/g$ combined, 53% of walleye exceeded that objective (62 of 116 fish), while 1 % of northern pike (1 of 70 fish), 3% of shorthead redhorse (3 of 89 fish), and none of the white sucker exceeded the objective (0 of 90 fish). Using the current objective of $0.200~\mu g$ Hg/g for these same five stations, 93% of walleye exceeded that objective (108 of 116 fish), and 26% of northern pike (18 of 70 fish), 18% of shorthead redhorse (16 of 89 fish), and 11% of white sucker exceeded the current objective (10 of 90 fish). Interestingly, at the lower objective of $0.200~\mu g$ Hg/g, there were no white sucker that exceeded the objective (0 of 37 fish) from the Churchill and Saskatchewan rivers. These summary concentration data when compared with other locations in northern Canada indicate that the mercury burden in fish at PPWB stations is within normally expected concentrations and ranges (McCarthy et al. 1997; Evans et al. 2005).

Mercury Concentration versus Fish Mass

An analysis of all of the fish data collected from 1994 to 2004 showed that mercury concentration and mass were significantly related for most fish species, at most but not all of the stations (Table 12; Figures 2-8). The relationship between mercury concentration and fish mass was significant (p < 0.05) for all of the 6 walleye populations, 2 of 3 northern pike populations, 3 of 6 shorthead redhorse populations, 3 of 5 white sucker populations, and for the longnose sucker population (Table 12). In addition to the relationship between mercury concentration and fish mass, other studies have found significant positive relationships between mercury concentration and fish length and fish age (for example Ramamoorthy et al. 1984; Goldstein et al. 1996; Donald et al. 2015).

The largest fish caught in a given year and station, however, did not always have the greatest mercury concentration. For instance, the largest fish caught at all PPWB stations combined was a northern pike take from the Assiniboine River (Lake of the Prairies) in 1995. This fish weighed 9923 g and was over twice the weight of the largest fish sampled from any of the other stations. However, the mercury concentration in this fish (0.741mg/kg) was far less than the maximum concentration for walleye caught from the North Saskatchewan River (1.67 μ g Hg/g), South Saskatchewan River (1.47 μ g Hg/g) and Lake of the Prairies (1.250 μ g Hg/g).

The significant direct relationship between mercury concentration and fish mass for individual populations was also evident for walleye for all stations combined (Figure 9). This assessment of 187 walleye from 6 stations indicates that fish mass accounts for about 40% of the variation in mercury concentration among PPWB stations for this species ($r^2 = 0.43$, p < 0.01). However, for shorthead redhorse, the relationship between mercury concentration and fish mass for all stations combined was not significant (p > 0.05, Figure 10). It is intriguing, nevertheless, that the trend pattern for mercury concentration and mass may be different for lake populations of redhorse suckers compared with populations from rivers (Figure 10).

Table 5. Mercury concentration in muscle tissue of walleye, white sucker, and shorthead redhorse from the North Saskatchewan River from 1994 to 2004 including fish mass, and percent excursions greater than the historic PPWB objective of 0.500 µg Hg/g and the current objective of 0.200 µg Hg/g.

North Saskatchewan	River									
	Mercury (μg/g) Mass (g)									
Species	Year	Percent								
		Mean	SD	Range	Excu	rsions	Mean	SD	Range	N
					>0.5 µg	>0.2 µg				
Walleye	1994	0.639	0.173	0.360-0.840	70%	100%	1182	495	299-1739	10
•	1996	1.018	0.226	0.822-1.540	100%	100%	1257	1170	564-4172	10
	2004	0.738	0.413	0.407-1.670	70%	100%	1012	291	590-1501	10
	All years	0.798	0.324	0.360-1.670	80%	100%	1150	734	299-4172	30
Longnose sucker	1994	0.251	0.205	0.040-0.600	12.5%	50%	812	332	274-1201	8
· ·	2004	0.434	-	0.396-0.472	0%	100%	858	-	430-1286	2
	All years	0.288	0.197	0.040-0.600	10%	40%	821	356	274-1286	10
Shorthead redhorse	1996	0.422	0.155	0.222-0.699	33.3%	100%	1045	261	721-1551	9

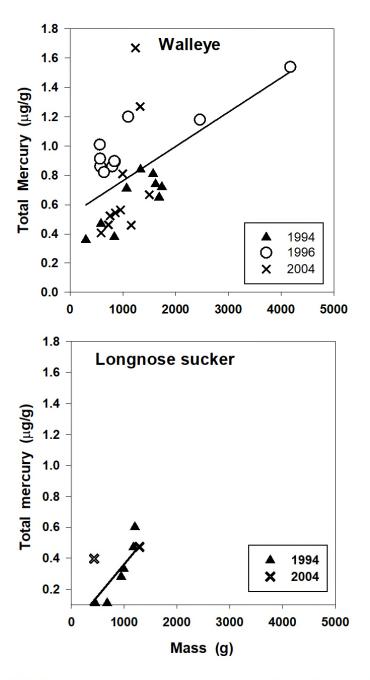


Figure 2. Relationship between total mercury concentration (μ g/g ww) and mass (g) for walleye and longnose sucker from the North Saskatchewan River. Walleye: Y = 0.235 M + 528; Longnose sucker: Y = 0.409 M - 48.

Table 6. Mercury concentration in muscle tissue of walleye and shorthead redhorse from the South Saskatchewan River from 1994 to 2004 including fish mass, and percent excursions greater than the historic objective of $0.500 \mu g Hg/g$ and the current objective of $0.200 \mu g Hg/g$.

South Saskatchewan	River									
			Mei	rcury (µg/g)		Mass (g)				
Species	Year				Per	cent				
		Mean	SD	Range	ange Excursions		Mean	SD	Range	Ν
					>0.5 µg	>0.2 µg				
Walleye										
	1996	0.783	0.348	0.540-1.470	100%	100%	1742	1572	217-4566	6
	2004	0.750	0.353	0.332-1.220	60%	100%	1491	1022	315-3024	10
	All years	0.763	0.340	0.332-1.470	76.5%	100%	1585	1211	217-4566	16
Shorthead redhorse*	1994	0.267	0.127	0.130-0.470	0%	60%	843	471	335-1931	10
	1996	0.315	0.133	0.137-0.546	10%	70%	967	151	798-1258	10
	2004	0.205	0.147	0.070-0.505	10%	30%	881	631	337-2565	10
	All years	0.262	0.139	0.070-0.546	6.7%	53%	897	450	335-2565	30

^{*}may include silver redhorse

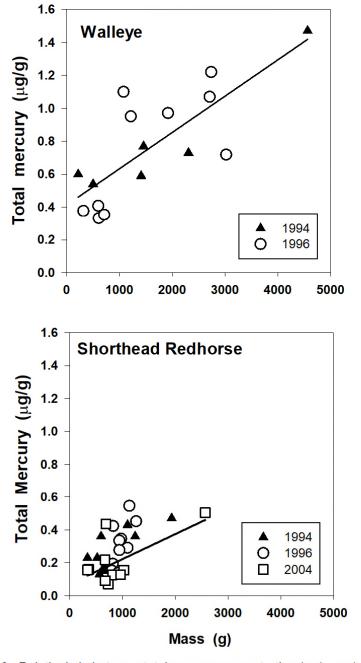


Figure 3. Relationhsip between total mercury concentration (μ g/g ww) and mass (g) for walleye and shorthead redhorse from the South Saskatchewan River. Walleye: Y = 0.220 M + 414; Shorthead redhorse: Y = 0.185 M + 96.

Table 7. Mercury concentration in muscle tissue of northern pike, walleye, white sucker, and shorthead redhorse from the Churchill River from 1993 to 2003 including fish mass, and percent excursions greater than the historic and current PPWB objective of 0.200 µg Hg/g.

Churchill River									
			M	lercury (µg/g)		<u>-</u>			
Species	Year				Percent				
		Mean	SD	Range	Excursions	Mean	SD	Range	N
Northern pike	1993	0.463	0.325	0.271-1.250	100%	1194	628	485-2508	8
Walleye	1993	0.467	0.169	0.341-0.789	100%	621	385	292-1598	10
,	1995	0.432	0.091	0.288-0.568	100%	519	178	283-850	10
	1997	0.471	0.089	0.384-0.733	100%	774	49	697-865	12
	2003	0.408	0.196	0.176-0.808	90%	623	108	485-747	10
	All years	0.446	0.139	0.176-0.808	97.6%	641	227	283-1598	42
White sucker	1993	0.096	0.039	0.041-0.152	0%	773	212	473-1027	10
Shorthead redhorse	1995	0.108	0.058	0.016-0.210	10%	746	326	341-1244	10
	1997	0.222	0.087	0.146-0.429	33.3%	828	128	608-1151	12
	2003	0.139	0.053	0.072-0.233	10%	729	98	542-855	10
	All years	0.160	0.084	0.016-0.429	18.8%	771	204	341-1244	32

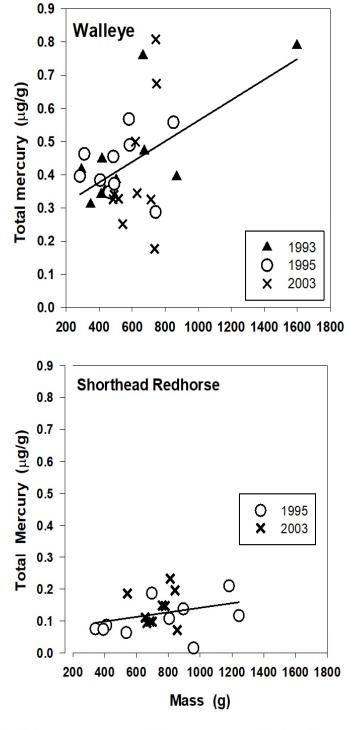
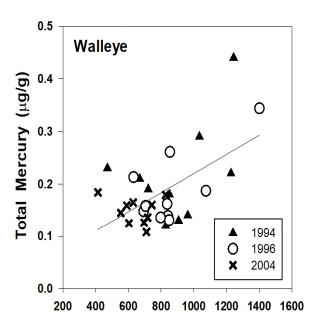


Figure 4. Relationship between total mercury concentration (ug/g ww) and mass for walleye and shorthead redhorse from the Churchill River. Walleye: Y = 0.303 M + 252; Shorthead redhorse: not significant.

Table 8. Mercury concentration in muscle tissue of walleye and white suckers from the Saskatchewan River from 1994 to 2004 including fish mass, and percent excursions greater than the historic and current objective of 0.200 µg Hg/g.

			N/	lercury (µg/g)	Mass (g)				
Species	Year			J (1 0 0)					
		Mean	SD	Range	Excursions	Mean	SD	Range	N
Walleye	1994	0.215	0.094	0.120-0.440	50%	892	241	472-1243	10
	1996	0.188	0.068	0.131-0.344	30%	868	223	632-1401	10
	2004	0.149	0.025	0.108-0.184	0%	649	116	414-828	10
	All years	0.184	0.072	0.108-0.440	26.7%	803	224	414-1401	30
White sucker	1994	0.048	0.024	0.020-0.098	0%	953	234	508-1443	10
	1996	0.062	0.044	0.023-0.162	0%	1004	191	697-1292	10
	2004	0.082	0.037	0.040-0.142	0%	1012	274	624-1338	7
	All years	0.071	0.037	0.020-0.162	0%	986	223	508-1443	27



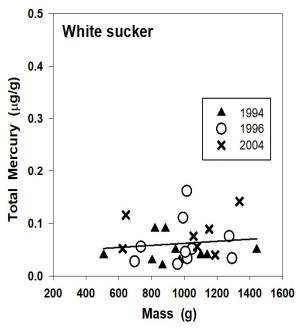


Figure 5. Relationship between total mercury concentration (μ g/g ww) and fish mass (g) for walleye and white sucker from the Saskatchewan River. Walleye: Y = 0.183 M + 38; White sucker: not significant.

Table 9. Mercury concentration in muscle tissue of northern pike, white sucker, and shorthead redhorse from Red Deer Lake (Red Deer River) from 1993 to 2003 including fish mass, and percent excursions greater than the historic PPWB objective of 0.500 µg Hg/g and the current objective of 0.200 µg Hg/g.

Red Deer Lake (Red	Deer River)									
	Mercury (μg/g)						Mass (g)			
Species	Year		SD	Range	Percent Excursions			SD	Range	N
		Mean					Mean			
					>0.5 µg	>0.2 µg				
Northern pike	1993	0.099	0.016	0.076-0.124	0%	0%	1074	317	491-1515	10
·	1995	0.069	0.017	0.039-0.096	0%	0%	870	523	260-1781	10
	1997	0.106	0.030	0.051-0.146	0%	0%	887	318	615-1479	10
	2003	0.143	0.073	0.078-0.303	0%	20%	1000	272	681-1484	10
	All years	0.104	0.048	0.039-0.303	0%	5%	958	366	260-1781	40
White sucker	1993	0.044	0.020	0.013-0.078	0%	0%	1046	316	661-1621	10
	2003	0.033	0.011	0.015-0.045	0%	0%	682	251	316-1034	10
	All years	0.039	0.017	0.013-0.078	0%	0%	864	335	316-1034	20
Shorthead redhorse	1995	0.042	0.022	0.021-0.078	0%	0%	830	238	549-1176	10
	1997	0.061	0.021	0.018-0.094	0%	0%	701	171	501-1072	10
	All years	0.051	0.023	0.021-0.094	0%	0%	766	212	501-1176	20

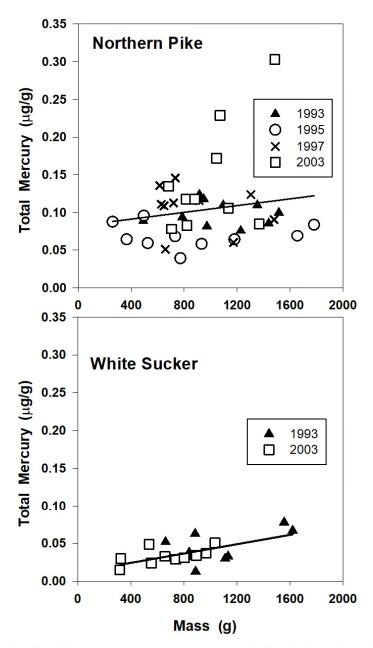


Figure 6. Relationship between total mercury concentration (μg/g ww) and mass (g) for northern pike and white sucker from Red Deer Lake. Northern pike: not significant; White sucker: Y = 0.031 M + 12.

Table 10. Mercury concentration in muscle tissue of walleye, white sucker, and shorthead redhorse from Lake of the Prairies (Assiniboine River) from 1993 to 2003 including fish mass, and percent excursions greater than the historic PPWB objective of $0.500 \mu g Hg/g$ and the current objective of $0.200 \mu g Hg/g$.

Lake of the Prairies (Assiniboine	River)								
		•	rcury (µg/g)	Mass (g)						
Species	Year	Percent								_
		Mean	SD	Range	Excursions		Mean	SD	Range	Ν
					>0.5 µg	>0.2 µg				
Walleye	1993	0.444	0.290	0.171-1.250	26.7%	93%	855	375	328-1921	30
·	1995	0.650	0.123	0.504-0.899	100%	100%	1918	261	1555-2325	10
	1997	0.581	0.147	0.412-0.896	60%	100%	1478	405	1035-2406	10
	2003	0.321	0.154	0.205-0.599	20%	100%	953	478	503-1898	10
	All years	0.481	0.249	0.171-1.250	43.4%	97%	1152	556	503-2406	60
White sucker	1993	0.144	0.074	0.028-0.292	0%	27%	1275	373	339-2151	30
	1995	0.153	0.045	0.097-0.246	0%	20%	1354	127	1162-1561	10
	1997	0.060	0.015	0.046-0.088	0%	0%	843	183	560-1252	10
	All years	0.129	0.070	0.028-0.292	0%	20%	1205	355	339-2151	50
Shorthead redhorse	2003	0.066	0.044	0.026-0.138	0%	0%	1249	399	790-1820	10

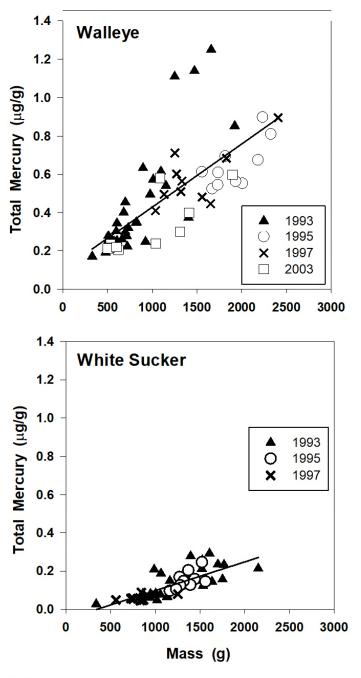


Figure 7. Relationship between total mercury concentration (μ g/g ww) and mass (g) for walleye and white sucker from Lake of the Prairies. Walleye: Y = 0.329 M + 102; White sucker: Y = 0.150 M - 51.

Table 11. Mercury concentration in muscle tissue of northern pike, walleye, shorthead redhorse and white sucker from Round Lake from 1993 to 2003 including fish mass, and percent excursions greater than the historic PPWB objective of 0.500 µg Hg/g and the current objective of 0.200 µg Hg/g.

Round Lake (Qu'Appe	elle River)									
		Mercury (μg/g)					Mass (g)			
Species	Year	Percent								
		Mean	SD	Range	Excu	rsions	Mean	SD	Range	N
					>0.5 µg	>0.2 µg				
Northern pike	1993	0.151	0.082	0.066-0.336	0%	20%	772	772	161-2049	10
Northern pike	1995	0.131	0.143	0.009-0.471	0%	40%	2009	1750	184-4759	10
	1997	0.394	0.104	0.242-0.584	10%	100%	1494	975	641-3317	10
	All years	0.253	0.151	0.009-0.584	3.3%	53%	1425	1302	161-4759	30
Walleye	2003	0.216	0.082	0.134-0.357	0%	40%	568	141	423-846	10
Shorthead redhorse	1993	0.054	0.022	0.027-0.105	0%	0%	924	196	721-1313	10
	2003	0.143	0.055	0.069-0.247	0%	20%	895	240	541-1317	10
	All years	0.099	0.061	0.027-0.247	0%	10%	910	214	541-1317	20
White sucker	1995	0.042	0.039	0.002-0.117	0%	0%	1058	534	258-1866	10
	1997	0.065	0.034	0.037-0.130	0%	0%	1270	250	932-1657	10
	All years	0.053	0.038	0.002-0.130	0%	0%	1164	421	258-1866	20

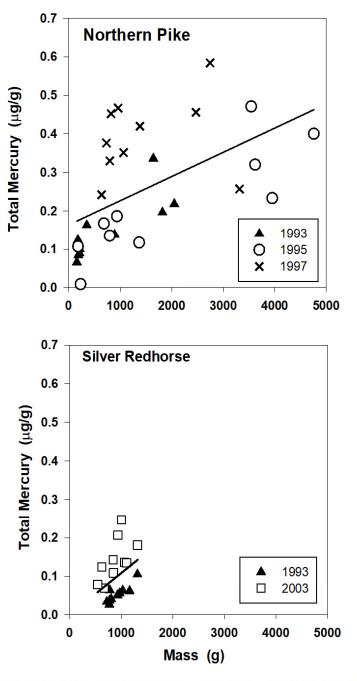


Figure 8. Relationship between total mercury concentration (μ g/g ww) and mass (g) for northern pike and shorthead redhorse from Round Lake. Northern pike: Y = 0.063 M + 164; shorthead redhorse: not signicant.

Table 12. Relationship between mercury concentration in ng/g and fish mass in grams for PPWB stations with the catch for all years combined. Significant relationships (p < 0.10) are shaded in grey.

Location	Fish species	Hg ±SE = a ±SE • Mass in g + b ±SE	N	r²	р
North Saskatchewan	Walleye	Y ±279 = 0.235 ±0.071 • M + 528 ±96.0	30	0.28	p < 0.01
	Longnose sucker	Y ±141 = 0.409 ±0.132 • M - 48 ±117.2	10	0.55	p < 0.05
	Shorthead redhorse	$Y \pm 128 = 0.376 \pm 0.173 \bullet M + 29 \pm 185.7$	9	0.40	p < 0.10
South Saskatchewan	Walleye	Y ±218 = 0 .220 ±0.047 • M + 414 ±91.9	16	0.61	p < 0.001
	Shorthead redhorse	Y ±113 = 0.185 ±0.047 • M + 96 ±46.8	30	0.36	p < 0.001
Churchill	Northern pike	$Y \pm 190 = 0.434 \pm 0.114 \cdot M - 56 \pm 152.3$	8	0.71	p < 0.01
Ondroniii	Walleye	Y ±122 = 0.303 ±0.084 • M + 252 ±57.0	42	0.25	p < 0.01
	White sucker	Y ±25 = 0.145 ±0.040 • M - 16 ± 31.9	10	0.62	p < 0.01
	Shorthead redhorse	not significant	32	0.05	p >0.10
Saskatchewan	Walleye	Y ±61 = 0.183 ±0.051 • M + 38 ±42.2	29	0.33	p < 0.01
	White sucker	not significant	27	0.02	p > 0.10
Red Deer Lake	Northern pike	not significant	40	0.03	p > 0.10
	White sucker	Y ±13 = 0.031 ±0.009 • M + 12 ±8.5	20	0.38	p < 0.01
	Shorthead redhorse	not significant	20	0.13	p > 0.10
Lake of the Prairies	Walleye	Y ±171 = 0.329 ±0.040 • M +102 ±51.1	60	0.54	p < 0.001
Lake of the France	White sucker	Y ±46 = 0.150 ±0.018 • M - 51 ±23.0	50	0.58	p < 0.001
	Shorthead redhorse	$Y \pm 15 = 0.104 \pm 0.013 \cdot M - 64 \pm 16.5$	10	0.89	p < 0.001
-					
Round Lake	Northern pike	Y ±129 = 0.063 ±0.018 • M + 164 ±35.1	30	0.30	p < 0.01
	Walleye	$Y \pm 60 = 0.420 \pm 0.143 \cdot M - 22.2 \pm 83.3$	10	0.52	p < 0.05
	Shorthead redhorse	not significant	20	0.14	p > 0.10
	White sucker	not significant	20	0.03	P > 0.10

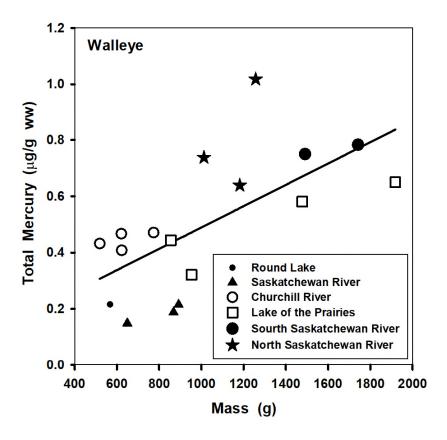


Figure 9. Relationship between fish mass and total mercury concentration in dorsal muscle tissue of walleye from 18 separate catches taken from 1993 to 2004 from six PPWB stations (y = 0.0004 X + 0.1104, $r^2 = 0.43$, p < 0.01, n = 188 walleye).

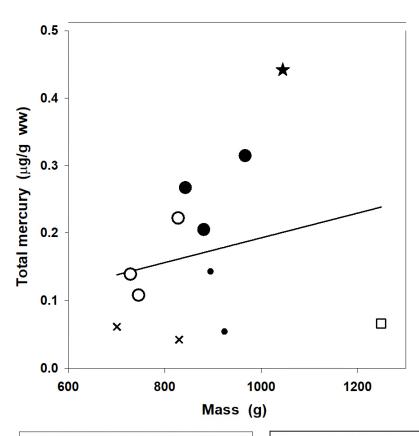


Figure 10. Scatter plot between fish mass and total mercury concentration in dorsal muscle tissue for shorthead redhorse from 12 separate catches from 6 stations taken from 1994 to 2004. The relationship between mass and mercury was not significant (p > 0.05).

- Red Deer Lake
- ☐ Lake of the Prairies
- Round Lake
- South Saskatchewan River
- North Saskatchewan River
- O Churchill River

Mercury in Walleye from the Saskatchewan River Basin, 1969 – 2009

Other studies have measured and assessed mercury concentrations in walleye from multiple locations along the North Saskatchewan and Saskatchewan rivers from near the headwaters in Alberta to the Saskatchewan – Manitoba border (Table 13). In general, concentrations in walleye from the upper reaches of the North Saskatchewan River (Edmonton and upstream) were about 0.50 µg Hg/g. Concentrations in walleye downstream of Edmonton to Tobin Lake in Saskatchewan were about double that value, about 1.15 µg Hg/g. The lowest concentrations of mercury in walleye (about 0.18 µg Hg/g) were recorded for fish caught at the PPWB station at the Pas, Manitoba.

Mercury concentrations varied for the walleye taken from the South Saskatchewan River basin, ranging from about 0.2 μ g Hg/g (Lemsford,1985) to 3.3 μ g Hg/g (Hague, 1972 (Table 14). The walleye were collected from the Oldman and Red Deer rivers, as well as the South Saskatchewan River to the confluence with the North Saskatchewan River.

Long-term trend assessment of mercury in fish is challenging and often compromised because of inconsistencies in species, differences in mass/age of fish collected over time, and at times the small number of fish collected (small sample size). Nevertheless, mercury concentration in walleye probably declined in Tobin Lake from 1969 to 1982 (Table 13). A change in the operation of a chlor-alkali plant in Saskatoon in 1978 to meet effluent regulations has been attributed to much of the decline in mercury in walleye at Tobin Lake (Harrison and Waite 1988).

In 1982, mean concentration of mercury for walleye collected downstream of Edmonton to the Alberta – Saskatchewan border was 0.646 µg/g (range 0.140 to 1.20 µg/g, N = 35) for fish with mass ranging from about 300 to 1000 g. For walleye collected from 1994 to 2004 from the Alberta – Saskatchewan border adjusted for the same mass (fish in the records with mass from 300 to 1000 g), mean concentration of mercury was 0.674 µg/g (SD = \pm 0.227, range 0.360 to 1.010 µg Hg/g, N 16). Assuming a similar standard deviation for mercury in walleye collected in 1982 and again in 1994 to 2004, there was no significant difference in the mean concentration of mercury in walleye for these two time periods (t = 0.41, p < 0.01).

Table 13. Concentrations of total mercury (wet weight) in walleye muscle tissue from the North Saskatchewan and Saskatchewan rivers from upstream to downstream.

Location	Year	Mercu	ıry (µg/g)	Ма	ss (g)	N	Source
		Mean	Range	Mean	Range		
	•	•		skatchev	wan River	•	
Drayton Valley	1984	0.368	0.23-0.62	964	550-1670	8	Moore et al. 1986
Devon	1984	0.597	0.27-0.89	928	830-1150	4	Moore et al. 1986
Edmonton	1973	0.480	0.21-0.69			3	Munson 1978
Edmonton	1974	0.340	0.17-0.88			20	Munson 1978
Edmonton	1975	0.690	0.21-0.98			8	Munson 1978
Edmonton	1976	0.590	0.16-0.89			5	Munson 1978
Edmontona	1982	0.369	0.23-0.63			8	Ramamoorthy et al. 1985
Edmonton ^b	1982	0.645	0.14-1.20			35	Ramamoorthy et al. 1985
Edmonton ^b	2016	0.362	0.20-0.91	831	27-3989	19	Alberta Health
AB-SK Border	1969	1.0	0.60-1.40			2	Wobeser et al. 1970
AB-SK Border	1992	0.533	0.51-0.55	-	-	3	PPWB
AB-SK Border	1994	0.639	0.36-0.84	1182	299-1739	10	PPWB
AB-SK Border	1996	1.018	0.82-1.54	1257	564-4172	10	PPWB
AB-SK Border	2004	0.738	0.41-1.67	1012	590-1501	10	PPWB
Battleford	1969	0.9	0.60-1.30			3	Wobeser et al. 1970
Prince Albert ^b	1969	2.1	1.40-2.80			2	Wobeser et al. 1970
Cecil	1985	0.532	0.28-0.84	805	50-2150	10	Saskatchewan
Cecil	1986	0.532	0.38-0.99	713	325-1550	10	Saskatchewan
			Saska	atchewan	River		
Gronlid	1975	0.885	0.4- 1.23	1134	312-2070	10	Saskatchewan
Tobin Lake	1969	2.700	2.60-2.70			2	Wobeser et al. 1970
Tobin Lake	1974	1.140	0.67-2.01			23	Munson 1978
Tobin Lake	1975	0.920	0.41-1.47			7	Munson 1978
Tobin Lake	1978	1.080				16	SEPS*
Tobin Lake	1979	1.860				11	SEPS*
Tobin Lake	1980	1.560				15	SEPS*
Tobin Lake	1981	0.760				12	SEPS*
Tobin Lake	1982	0.720				10	SEPS*
The Pas	1994	0.215	0.12-0.44	892	472-1243	10	PPWB
The Pas	1996	0.188	0.13-0.34	868	632-1401	10	PPWB
The Pas	2004	0.149	0.11-0.18	649	414-828	10	PPWB

^a – upstream; ^b – downstream; *unpublished data, Saskatchewan Environment and

Public Safety

Table 14. Concentrations of total mercury (wet weight) in walleye muscle tissue from the South Saskatchewan River from upstream to downstream.

Location	Year	Mercu	ıry (μg/g)	M	ass (g)	N	Source
		Mean	Range	Mean	Range		
		•	Red Dee	r Rive	r		
Dickson Damb	1983	0.656	0.35-0.91	880	440-2470	10	Alberta Environment
Dickson Damb	2014	0.732	0.52-0.99	1479	873-2261	8	Alberta Health
Dickson Dam ^b	2015	0.575	0.22-1.30	1815	705-4346	11	Alberta Health
Blindman River	2006	0.799	0.48-1.40	1520	416-2520	7	Alberta Health
Hwy 585	2014	0.850	0.52-1.28	2620	1150-4664	6	Alberta Health
Drumheller	2015	1.173	0.43-2.12	3014	550-4957	7	Alberta Health
			Oldman	River			
Lethbridge	1983	0.555	0.32-0.73	960	65-1320	11	Alberta Environment
		0 4		•			
			n Saskato				
Medicine Hat	2006	0.609	0.35-1.16	889	493-2200	14	Alberta Health
A D. O. (D.)	1001	0.700	0.54.4.47	704	50 4500		DDIAID
AB-SK Border	1994	0.783	0.54-1.47	701	53-4566	6	PPWB
AB-SK Border	1996	0.750	0.33-1.22	1491	315-3024	10	PPWB
AB-SK Border	2004	0.337	0.23-0.45	494	356-631	2	PPWB
Lamatand	4070	4.000	0.40.0.04	040	075 0700	40	Caalvatahawan
Lemsford	1979	1.386	0.13-2,64	910	275-2700	10	Saskatchewan
Lemsford	1985	0.199	0.03-0.93	658	325-1400	10	Saskatchewan
Lemsford	1986	0.440	0.10-0.93	1419	500-3600	8	Saskatchewan
Lake Diefenbaker	2008-09	0.494		1325		50	Donald et al. 2015
Zako Biorombakor	2000 00	0.101		1020		- 00	Boriaia ot all 2010
Warman	1986	0.820	0.44-1.54	1071	400-2050	6	Saskatchewan
Warman	1988	1.205	0.71-2.00	1769	850-3500	8	Saskatchewan
Hague	1972	3.263	2.0-4.8	1145	652-1531	8	Saskatchewan
Fenton	1975	1.686	0.73-3.20	732	425-1049	5	Saskatchewan
Fenton	1977	1.379	0.69-2.28	620	85-1219	8	Saskatchewan
Fenton			0.48-3.12	942	200-2950	9	Saskatchewan
1900 1.400		1.400	J. 70°J. 12	J-72	200 2000	3	Casitatoricwari
]	I	1	l			

^b - downstream

BIOMONITORING - DUTIES OF THE BOARD

The Agreement on Water Quality, Schedule "E", (1992) of the 1969 Master Agreement on Apportionment provides the Prairie Provinces Water Board with a Water Quality Mandate and with Duties. The Mandate of the Prairie Provinces Water Board is "to foster and facilitate interprovincial water quality management among the parties that encourages the protection and restoration of the aquatic environment". The Mandate is a process-oriented statement and does not give the Board any specific information on what should or should not be monitored in the aquatic environment. The direction that is provided to the Board on what should be monitored is given in the Duties of the Board. However, the Mandate statement clearly indicates that the water quality management activities of the Board need to be taken in a broader context to include protecting the aquatic environment and not simply protecting water quality alone.

Section 8 of the Agreement provides specific information on the monitoring activities that should be undertaken by the Board. Section 8a of the Duties of the Board directs the Board to monitor "the quality of the aquatic environment" (defined as, "all things upon or in water including all bottom substrates and physical, chemical, and biological constituents"). Note, this statement does not direct the Board to put an emphasis on water chemistry monitoring. Moreover, the "all things" phrase suggests that much more than water chemistry should be monitored.

Section 8e of the Duties of the Board further emphasises the importance of taking a broader view of water quality management by directing the Board to take a "preventive and proactive ecosystem approach to interprovincial water quality management". In the Agreement, by definition, "ecosystem" means "a community of animals, plants, and microbes and its interrelated physical and chemical environment".

Clearly, the Board has a mandate under the Agreement to facilitate interprovincial water management by monitoring biological components of interprovincial rivers at interprovincial borders, to establish biological objectives for these stations, and to determine long-term trends for these aquatic ecosystems based on biological variables assessed against established biological objectives.

At present, the Board has well established programs to conduct long-term monitoring of the physical (discharge) and chemical components of the aquatic environment (rivers) at interprovincial borders. However, monitoring of the chemical environment is not a substitute for biological monitoring that would enhance water management in prairie provinces watersheds.

Historical Biological Monitoring and Assessment

Shortly after the Agreement on Water Quality (Schedule "E") was signed in 1992 by the federal and provincial governments, the Board initiated biological monitoring at interprovincial stations. By 1992, the Board had decided that mercury monitoring and assessment in fish tissue would address the "biological" and "ecosystem" monitoring directives as outlined in the Agreement. That year, a fish monitoring program was designed, stations were selected, field methods were evaluated, and some fish were caught and assessed for mercury. From 1993 to 2004, mercury in muscle tissue of a piscivore and a lower trophic level fish species was monitoring and assessment at seven PPWB stations. Only three or four of the seven stations were assessed for mercury each year, with the station return frequency varying from two to six years.

An important result of the mercury monitoring program was that mercury concentrations in fish muscle tissue, particularly for piscivores, frequently exceeded the Health Canada guideline for fish consumption by humans at most stations. However, the concentration data from the study also found that, when compared with other locations in northern Canada, the mercury levels in fish at PPWB stations were similar to these other locations in both concentrations and ranges (McCarthy et al. 1997; Evans et al. 2005).

From 2000 to 2005, a biological assessment was completed for the benthic invertebrate fauna for each of eleven PPWB stations once. The dominant substrate at each station was described and details on the invertebrate assemblage provided. Taxonomic richness, mayfly-stonefly-caddisfly richness, abundance and other metrics of the invertebrate assemblage were calculated for each station.

An important result of the benthic invertebrate assessment was that abundance and diversity of aquatic invertebrates at PPWB stations was highly variable and probably depended on substrate type. Cobble substrates supported high diversity and abundance of invertebrate while sandy substrates were much less favourable for most aquatic invertebrate species.

Provincial Agency Monitoring of Mercury in Fish

In all three prairie provinces, fisheries agencies assess mercury concentration in sport fish (primarily mid- to large- walleye and northern pike) in lakes and rivers. Then, fish consumption guidelines are established for each location based on the mass of the fish caught by anglers, the mercury concentration in the muscle tissue of the fish (fillets), and Health Canada mercury concentration limits set to protect humans from toxic burdens of mercury. Currently, fish collected by provincial agencies for mercury analyses are taken opportunistically such as during sport fish stock assessments. No provincial agency currently assesses mercury in fish at or near PPWB stations, although in the past, mercury was opportunistically assessed for the Qu'Appelle River station at Round Lake (1978, 1979, 1981, 1983,1984,1993, 1999,

2010) during sport-fish stock assessments. However, mercury concentrations in fish have been determined at other locations on interprovincial rivers of interest to the PPWB (Tables 13 and 14). These assessments are typically associated with short-term studies. No provincial agency monitors mercury in fish from any location on interprovincial rivers that is long-term and has an established return frequency.

Long-term monitoring of mercury in fish at PPWB stations would not duplicate or be redundant with programs to assess mercury in fish from rivers and lakes by provincial agencies.

Designing a Biological Monitoring Program

Because of the large number of aquatic species of algae, invertebrates, and fish that inhabit a reach in any given river, biological monitoring programs typically focus on a specific component of the ecosystem. Selection of a specific component or species to monitor is the challenge. A number of criteria have been identified that can be used during the process of selection of biota for monitoring (Johnson et al. 1993; Stribling 1994; Banff-Bow Valley Study 1995; Cash et al. 1996). Important selection criteria include:

- 1. relevance to the public
- 2. cost of measurement and assessment
- 3. sensitivity to stresses such as climate change, invasive species, toxic chemicals, and eutrophication.
- 4. established and relatively simple field protocols.

Selection criteria such as cost and public relevance of a biological monitoring program are important for promoting and perhaps ensuring long-term sustained monitoring. Senior managers who are responsible for making financial decisions related to monitoring programs may have little knowledge of the relevance and benefits of environmental monitoring. A monitoring program that is mainly "science" based may receive less support than a monitoring program that is publicly relevant, although the latter would have a scientific design and approach. Moreover, should the Board at any time in the future wish to undertake public consultation, a monitoring program that has a publicly relevant component would be readily understood.

Taking into consideration the criteria listed above, the physical characteristics of PPWB stations, and some basic and preliminary information on the biological characteristics of PPWB stations, the following options for a biological monitoring program are proposed. A monitoring program at PPWB stations would contribute to the requirements of the Agreement to use an ecosystem approach to monitor biological variables and assess these variables against established objectives.

PPWB BIOMONITORING: OPTIONS and RECOMMENDATIONS

Options, approaches, and recommendations for biomonitoring at PPWB stations are provided below.

1. OPTION

Methyl-mercury, total mercury, and other metals could be monitored in the dorsal muscle tissue of fish (walleye - 20 fish, two lower trophic level species – 10 fish each) in the Churchill and Saskatchewan rivers, Lake of the Prairies and Cold Lake every three to five years using mixed mesh nets (equal length panels of 25, 38, 50, 78, 100, 125, 150, 125, 150, 200, 250, and 300 mm mesh). Details on each fish assessed for mercury including mass, length, and gender should be recorded. Concentrations of mercury detected in fish could then be compared against one or more of established guidelines, thresholds, and objectives for mercury including:

- a. CCME (2001) guideline 0.033 µg Hg/g in whole fish to protect wildlife that consume fish (mink, otter, osprey, and bald eagle).
- b. threshold effects concentration $0.320~\mu g$ Hg/g in muscle tissue set to protect the health of fish (Beckvar et al. 2005; adjusted in Donald 2016).
- c. CCME guideline 0.200 µg Hg/g to protect humans that consume fish frequently, more than one meal per week, as well as children and women of child-bearing age.
- d. CCME guideline $0.500~\mu g$ Hg/g to protect humans that consume fish occasionally.

Rationale:

- Section "E" of the Master Agreement (2003) instructs the Board to establish objectives, monitor "the quality of the aquatic environment", and assess the established objectives against chemical, physical, and biological variables using a "proactive ecosystem approach". Ecosystem according to the Agreement is "a system made up of a community of animals, plants, and microbes". A mercury monitoring program of the fish community at PPWB stations would contribute to the requirements of the Agreement to use an ecosystem approach to monitor biological variables and assess these variables against established objectives for wildlife and fish health, and for human consumption of fish.
- Fish are abundant and can be caught with gill-nets at these four station efficiently at relatively low cost.
- Mercury concentrations in water are typically exceptionally low, and therefore, mercury assessment in water requires ultra-clean field and laboratory techniques.
 Only "clean" field and laboratory techniques are required when sampling fish tissue.
 Moreover, mercury only becomes an environmental and an ecosystem concern once it has been methylated and bioaccumulated upward in the food chain.

- PPWB stations on the Saskatchewan and Churchill rivers are adjacent to First Nation reserves (Opaskwayak Cree First Nation settlement; Wapaskakimaw Indian Reserve settlement, respectively). Fish are caught at these locations with gillnets and are consumed frequently. Lake of the Prairies falls within the mandate of the Board because it is an "inter-provincial lake on or intersecting the common boundary between the Provinces of Saskatchewan and Manitoba" (section 1c, Schedule B, Master Agreement on Apportionment). Similarly, Cold Lake, on the Alberta Saskatchewan border, falls within the mandate of the Board for the same reason.
- Water quality parameters are typically integrated within catchments over days to months. Mercury (but not necessarily other metals) is integrated in fish tissues over years to decades in long life-span species making an annual assessment of mercury concentration in fish mostly redundant.
- A common characteristic of river ecosystems, including interprovincial rivers of interest to the PPWB, is the propensity of the fish species they support to make long distance movements of several hundred kilometres each year. Therefore, these accumulate and integrate tissue chemical concentrations over significant reaches of mainstem rivers, much the same as the chemical constituents in water. Fish species found at PPWB stations that are highly migratory probably include goldeye, mooneye, shorthead redhorse, and silver redhorse.
- Standard and specified gill-nets of multiple mesh sizes are critical to the success of a long-term mercury monitoring program for fish. The size of a fish captured in a gill-net is highly influenced by mesh size, and fish size (mass) is directly correlated with mercury concentration. Thus, long-term trend assessments of mercury concentration in fish are a challenge to undertake unless the same size of fish (same mesh size used) are captured over successive years. Moreover, the size of fish consumed by wildlife, typically < 500 g (caught in mesh sizes < 100 mm), is different from the size of fish consumed by humans > 500 g (caught in mesh sizes > 100 mm). And, all small- and large-bodied fish species can be captured using a wide range of multiple mesh-sizes, and then assessed against objectives and "threshold effects" concentration for methyl-mercury in muscle.

2. OPTION

Methyl-mercury, total mercury, and other metals be monitored in the dorsal muscle tissue of a top predator (walleye or northern pike - 20 fish each and two lower trophic level species – 10 fish each) in Red Deer Lake (Red Deer River) and in Round Lake (Qu'Appelle River) three to five years using mixed mesh nets. Concentrations of mercury detected in fish should then be compared against established guidelines, thresholds, and objectives.

Rationale:

– The Red Deer and Qu'Appelle rivers at the established PPWB water quality monitoring stations appear to be poor habitat for large bodied fish species and cannot be fished with gill-nets effectively. Nearby lakes provide optimal fish habitat where large numbers of fish can be collected with gill-nets efficiently.

3. OPTION

Methyl-mercury, total mercury, and other metals be monitored in the dorsal muscle tissue of a top predator (walleye - 20 samples and two lower trophic level species – 10 samples each) in the North Saskatchewan, South Saskatchewan, and Red Deer (Alberta – Saskatchewan border) rivers every three to five years using a boat mounted electrofisher. Fish could be collected by consultants who both own the required equipment and have employees trained to operate the specialized electrofishing equipment. The fish, once collected, could be processed by Environment Canada employees. Concentrations of mercury detected in fish should then be compared against established guidelines, thresholds, and objectives.

4. OPTION

Monitor and assess aquatic invertebrates at PPWB stations using CABIN field protocols except for the Churchill and Saskatchewan rivers. At these two stations, an Ekman grab should be used because of discharge and depth considerations. Invertebrate samples should be taken under low flow conditions in the fall each year. Initially, results from an aquatic invertebrate monitoring program would be descriptive (for example, "high diversity" at South Saskatchewan River), with a long-term goal of assembling a data-base that would permit developing station specific and statistically relevant objectives.

A modified CABIN:

– the CABIN approach to assessing invertebrate communities uses a "reference condition" to evaluate "test" sites against the reference condition (Reynoldson et al. 1999). Test sites that lie within a 90% probability ellipse are deemed equivalent to reference. Those sites that lie outside the 99.9% ellipse are very different and are probably impaired. The first years of a PPWB biomonitoring program for invertebrates would be to establish the reference condition for each station. Once the reference condition was established (minimum three years), each successive year would be tested ("test site") against the reference. Should a test pass for a given station in a given year (within the 90% probability ellipse), then the invertebrate data for that year would be added to the reference condition database. The power of a modified CABIN approach to detecting change and impairment to invertebrate communities would increase with each passing year. Furthermore, the "reference condition" could be used by the Board as the established biological objective.

 a station specific PPWB objective for a modified CABIN approach to biomonitoring could state that, "the invertebrate community is similar to the reference condition, remaining within the 90% probability ellipse.

Rationale:

- Benthic invertebrate monitoring provides an assessment of aquatic quality conditions integrated over months because benthic invertebrate species typically have a life-span of one year and for some species, two or more years. A single water quality sample taken each month may miss short-term toxic chemical discharges to interprovincial rivers. However, this type of discharge might be detected by a change in the abundance or species richness of a benthic invertebrate community that was sensitive to and affected by the toxic discharge and was monitored by PPWB.. However, detecting short-term discharges of chemicals toxic to invertebrate populations could be a challenge with a once-per-year monitoring program, as would identifying the specific cause.
- Benthic invertebrate monitoring has the potential to identify long-term cumulative affects of to aquatic ecosystems from multiple environmental stressors that may not be identified from monitoring water quality.
- CABIN field protocols are the established method for collecting aquatic invertebrates for Environment and Climate Change Canada. Currently, and probably in the future, employees of ECCC will have the appropriate training and experience to collect relevant invertebrate samples from PPWB stations.
- For each PPWB station, a modified CABIN monitoring program when fully implemented would identify changes to aquatic invertebrate communities, provide numeric targets or objectives for invertebrate communities, and restoration targets for invertebrate communities should they be needed in the future.
- The biological pilot study showed that the invertebrate communities among PPWB stations were highly variable and were probably influenced by substrate, winter discharge, and the overall different hydrological conditions of the rivers throughout the year. Thus, invertebrate community objectives established in the future would be station specific, and in this respect, similar to the water quality objectives established for PPWB stations.

1. RECOMMENDATION

The physical and biological characteristics of each of the PPWB stations be described in a single document (station description document).

After five decades of monitoring, the physical and chemical environments at PPWB stations are mostly described and understood. Of the physical, chemical, and

biological components of the ecosystem at PPWB stations, however, only the biological component remains poorly understood and not well documented.

The first step in designing a biological monitoring program for PPWB stations is to describe in as much detail as possible the biological components of each of the PPWB stations. Once the biological components (plants, invertebrates, fish) are identified, one or a few of the biological components should be considered and selected for long-term monitoring.

A station description document with details on the biological components of the ecosystem provides the Board with the information it requires to undertake "protection and restoration of the aquatic environment" as stated in the Agreement under the Water Quality Mandate. To protect the "ecosystem", the Board needs to know details of the physical, chemical and biological components and characteristics of each of the PPWB stations.

For example, the station description for the physical and biological characteristics of the South Saskatchewan River might be presented in a report as follows:

SOUTH SA	ASKATCHEWAN RIVER	R at Hwy 41	
Physical	Discharge (mean)	165 m ³ /s	
	Substrate	boulder/cobble	
Biological	Fish Assemblage	interprovincial boundar is dominated by goldey suckers, including shor redhorse. Walleye are Lake sturgeon, an enda (COSEWIC), is uncomi	van River at or near the y*. The fish assemblage e, and by redhorse thead redhorse and silver the dominant piscivore. Angered fish species mon, but regularly the site. The fish species

A	Aquatic invertebrates ⁺	The South Saskatchewan Riv highest diversity of aquatic invident highest richness of mayflies-s caddisflies (EPT) compared with stations. However, density of relatively low (3227/m²). The Lampsilis siliquoidea, is abundant these invertebrate metrics indiaquatic environment. The spe	vertebrates and the toneflies- vith all other PPWB invertebrates is freshwater clam, dant. Generally, icate a high quality
		aquatic invertebrate assembla	age include:
		EPT richness	14
		Chironomidae richness	126
		Density (number/m²)	3277
		EPT abundance	550
		EPT %	0.17
		Chironomidae abundance	1683
		Oligochaeta abundance	699

^{*} data from PPWB fish collections, Nelson and Paetz 1992, Donald et al. 2015.

2. RECOMMENDATION

Fish should not be monitored for mercury or other metals in the Beaver, Battle, and Carrot rivers.

Rationale:

 The Beaver, Battle, and Carrot rivers provide poor habitat for fish, and it would be a challenge to collect a suitable number of fish for mercury analyses at these stations.

3. RECOMMENDATION

If the PPWB proceeds with a mercury biomonitoring assessment program for fish, a PPWB fish species diversity objective could be established for each relevant station. A detailed record on the number of individuals of each species would be recorded

⁺ data from PPWB biological pilot study

ensuring that fish species that are taxonomically challenging are correctly identified. These catch records should be assembled into a standard table for each catch at each station and each year. Once the fish community has been described from a minimum of three years, the data could be converted into a "species richness" index metric and that value used as a numeric fish community objective. For example, the Shannon-Wiener Diversity Index (calculated from the number of individuals of each species, the total number of individuals of all species, and the number of species) could be used to set a numeric objective for the fish community for those stations with a relatively high diversity of fish (North Saskatchewan, Red Deer (Alberta), South Saskatchewan, Saskatchewan, and Churchill rivers).

Rationale:

- A fish community monitoring program at PPWB stations would contribute to the requirements of the Agreement to use an ecosystem approach to monitor biological variables and assess these variables against established objectives.
- The activity of collecting a suitable number of fish for mercury analysis by an unbiased catch method typically results in large numbers of other fish species being caught. A detailed record of the total catch provides a valuable record of one component of the aquatic ecosystem that could be assessed against an established narrative objective.

4. RECOMMENDATION

If a fish monitoring program is implemented, it should be led by an aquatic biologist with both training and field experience in assessing fish populations.

Rationale:

- PPWB stations support a diversity of fish with some species being very similar in general appearance. For example, fish taxonomic training is required to identify species such as silver redhorse and shorthead redhorse, sauger and walleye, mooneye and goldeye.
- To determine long-term trends in metal concentrations in fish, and compare concentrations of metals between and among stations, specific and consistent fisheries related field sampling techniques and taxonomic identifications are required.

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Appendix: Arsenic, Lead, and DDT

Arsenic

Arsenic in fish is found in a much more stable form than the arsenic present in groundwater World Health Organization (WHO, n.d.). Nevertheless, arsenic in fish is monitored, since fish consumption constitutes one of the pathways of arsenic ingestion. Acute adverse effects of arsenic include diarrhea, vomiting, and abdominal pain. Long-term effects include skin lesions and pigmentation loss (WHO, n.d.).

The current PPWB objective for arsenic is 3.5 mg/kg, following the Drug and Food Regulations developed by Health Canada.

Lead

Lead accumulates in fish tissue and can cause lead poisoning in humans. Early symptoms of lead poisoning consumption are very general and, thus, this medical condition is difficult to identify in its early stages. As identified by the EPA, early symptoms of lead poisoning are: irritability, reduced attention span, insomnia, persistent fatigue, loss of appetite, and constipation or stomach discomfort. If not treated, which is often the case, adults and children can experience distinguishable symptoms. The former group can experience increased blood pressure, poor muscle coordination, reproductive problems, and vision impairment. The latter group can experience kidney and liver damage, hyperactivity, behavioral problems, and even death. Both groups can experience hearing loss (EPA, 2012b).

The current PPWB lead objective is 0.5 mg/kg, as per Health Canada's Drug and Food Regulations.

Consumption of Fish by Humans: DDT

The National Pesticide Information Center [NPIC], a representative of the EPA, reports that DDT can lead to dizziness, headaches, incoordination, confusion, lethargy, tremors, fatigue, vomiting, nausea, and a prickling sensation in the mouth (NPIC, 1999).

The PPWB fish tissue objective for DDT is 5.0 mg/kg, following HC's Drug and Food Regulations.

Consumption of Fish by Wildlife: DDT

DDT accumulates in animals and plants, and is found to cause health problems in animals at high trophic levels of the food chain. DDT is known to alter cellular

metabolism, liver and neural function, and reduce fertility. Also, it is carcinogenic, mutagenic, and has adverse effects on growth, reproduction, and immunocompetence.

Since total DDT is a mixture metabolites, including DDD and DDE, the objective for total DDT was derived using the most toxic isomer to birds and mammals. For example, in avian consumers of aquatic biota, soft egg shells are the most sensitive endpoint of DDT, which causes soft and thin shells

The objectives calculated by CCME were 14.0 μ g/kg and 94.0 μ g/kg for birds and mammals, respectively. Therefore, CCME adopted the lowest objective, 14.0 μ g/kg, which was later adopted by the PPWB.

Excursions of Objectives for Arsenic, Lead, and DDT

There were no excursions of the PPWB objectives for arsenic, lead, and DDT from 1994 to 2004. Both arsenic and lead concentrations were consistently well below objective. The highest detected arsenic concentration was 0.06 mg/kg from a 1993 Red Deer River white sucker composite sample, while the highest lead concentration was 0.47 mg/kg from a 1993 Churchill River walleye composite sample. While the maximum arsenic concentration was well below the PPWB objective, 3.5 mg/kg, the maximum lead concentration approached the 5.0 mg/kg objective. Moreover, none of the DDT isomers were detected, and therefore it can be concluded that total DDT did not exceed the objective.

Concentration Results for Parameters Without PPWB Objectives

Metals

Metals that were regularly above detection limits are nickel, copper, zinc, and selenium, which had average concentrations of 0.0384 mg/kg, 0.405 mg/kg, 4.09 mg/kg and 0.328 mg/kg, respectively. Cadmium occasionally had concentrations above the detection limit and had an average of 0.0117 mg/kg. The remaining metals, i.e. chromium and molybdenum, regularly had concentrations below the detection limits. The metals data are in Table 15.

Organochlorine Pesticides

From this group of parameters, 1,2-dichlorobenzene and endrin are the only parameters whose results were ever above the detection limit. For the results of the former parameter that were above the detection limit, the average concentration was 2.46 ng/g, while that of the latter parameter was 0.92 ng/g.

Table 15. Metal concentrations in the muscle of fish from PPWB stations. Composite samples were typically equal mass portions of muscle tissue from 10 fish combined into a single sample (L = less than; > less than).

Year	Fish species	chromium	copper	zinc	arsenic	selenium	cadmium	lead	nickel	molybdenum	Sample
		μg/g	µg/g	μg/g	μg/g	µg/g	µg/g	μg/g	µg/g	μg/g	
Nort	h Saskatchew	an River									
1994	Walleye	L.2	0.25	3.5	L.05	0.36	L.01	L.05	L.02	L5	individual
1996	Walleye	L.2	0.48	6.36	L.05	0.31	0.016	L.05	-	-	composite
1994	Longnose sucker	L.2	0.5	4.91	L.05	0.24	L.01	L.05	L.02	L5	individual
2004	Longnose sucker	0.02	0.8	3.4	0.001	0.3	0.002	0.01	0.01	0.001	composite
1996	Shorthead redhorse	L.2	0.29	4.04	L.05	0.29	0.016	L.05	-	-	composite
Sout	th Saskatchewa	an River									
1994	Walleye	0.33	0.22	3.63	L.05	0.69	L.01	L.05	0.062	L5	individual
1996	Walleye	L.2	L.2	3.76	L.05	0.57	0.017	L.05	-	-	composite
2004	Walleye	0.001	0.1	0.4	0.001	0.1	0.0001	0.001	0.005	0.001	composite
2004	Walleye	0.02	0.5	4	0.001	0.6	0.005	0.01	0.04	0.001	individual
2004	Walleye	0.01	0.4	4.2	0.01	0.6	0.002	0.01	0.005	0.001	individual
2004	Walleye	0.02	0.4	3.3	0.001	0.6	0.002	0.001	0.005	0.001	individual
2004	Walleye	0.01	0.4	3.9	0.001	0.8	0.002	0.01	0.01	0.001	individual
	Walleye	0.001	0.4	4.7	0.001	0.9	0.002	0.001	0.005	0.001	individual
2004	vvalleye	0.00.	_								

Year	Fish species	chromium	copper	zinc	arsenic	selenium	cadmium	lead	nickel	molybdenum	Sample
		μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	
Sout	th Saskatchewa	an River									
2004	Walleye	0.05	0.5	3.6	0.001	0.6	0.001	0.01	0.05	0.01	individual
1994	Shorthead redhorse	0.22	L2	3.45	L.05	0.48	L.01	L.05	L.02	L5	individual
1996	Shorthead redhorse	L.2	0.38	4.4	L.05	0.52	0.014	L.05	-	-	composite
2004	Shorthead redhorse	0.02	0.5	3.7	0.001	0.5	0.002	0.01	0.01	0.001	composite
Chu	rchill River										
1993	Northern pike	L 0.2	L 0.2	6.48	L 0.05	0.18	L 0.01	0.05	0.034	L 1.0	composite
1993	Walleye	L 0.2	0.36	3.86	L 0.05	0.19	L 0.01	0.47	0.084	L 1.0	composite
1995	Walleye	L.2	0.24	3.68	L.05	0.14	L.01	L.05	-	-	composite
1997	Walleye	<0.2	0.3	4.1	<0.05	0.2	<0.01	<0.05	-	-	replicate composite
1997	Walleye	<0.2	0.3	4.2	<0.05	0.21	0.01	<0.05	-	-	replicate composite
1997	Walleye	<0.2	0.3	5.5	<0.05	0.21	0.01	<0.05	-	-	replicate composite
2003	Walleye	0.012	0.3	3.41	0.001	0.2	0.0001	0.003	0.005	0.002	composite
2003	Walleye	0.013	0.39	3.75	0.001	0.18	0.0022	0.005	0.005	0.002	composite
1993	White sucker	L 0.2	0.29	3.09	L 0.05	0.24	L 0.01	0.05	0.03	L 1.0	composite
1995	Shorthead redhorse	0.36	0.36	4.48	0.05	0.14	0.021	L.05	-	-	composite
1997	Shorthead redhorse	<0.2	0.4	4	<0.05	0.32	0.02	< 0.05	-	-	replicate composite

1997	Shorthead redhorse	<0.2	0.4	3.9	0.06	0.15	0.01	<0.05	-	-	replicate composite
1997	Shorthead redhorse	<0.2	0.4	3.9	0.05	0.16	0.01	<0.05	-	-	replicate composite
Year	Fish species	chromium	copper	zinc	arsenic	selenium	cadmium	lead	nickel	molybdenum	Sample
		μg/g	µg/g	µg/g	μg/g	μg/g	µg/g	µg/g	µg/g	μg/g	
Sas	katchewan Rive	er									_
1994	Walleye	0.27	L.2	3.31	L.05	0.31	L.01	L.05	0.045	L5	individual
1996	Walleye	L.2	0.25	4.21	L.05	0.32	0.011	L.05	-	-	composite
2004	Walleye	0.01	0.6	3.6	0.001	0.4	0.002	0.01	0.01	0.001	composite
1994	White sucker	L.2	0.25	3.13	0.05	0.3	L.01	L.05	L.02	L5	individual
1996	White sucker	L.2	0.49	4	0.06	0.32	0.017	L.05	-	-	composite
Dad	Danil ala										
Kea	Deer Lake										
1993	Northern pike	L 0.2	0.2	5.01	L 0.05	0.38	L 0.01	L 0.05	0.132	L 1.0	composite
1995	Northern pike	L.2	0.28	5.18	L.05	0.31	0.016	L.05	-	-	composite
1997	Northern pike	<0.2	0.4	5.2	0.05	0.14	0.01	< 0.05	-	-	composite
4000											
1993	White sucker	L 0.2	0.28	3.92	0.06	0.33	L 0.01	L 0.05	L 0.02	L 1.0	composite
2003	White sucker	0.022	0.45	4.39	0.001	0.32	0.0001	0.002	0.005	0.005	composite
2003	White sucker	0.008	0.26	7.93	0.001	0.43	0.0001	0.001	0.005	0.001	composite
1005	Charthand radharas	1.2	0.25	4.02	I OF	0.24	L 01	1.05			aampasita
1995	Shorthead redhorse	L.2	0.35	4.03	L.05	0.34	L.01	L.05	-	-	composite

Year	Fish species	chromium	copper	zinc	arsenic	selenium	cadmium	lead	nickel	molybdenum	Sample
		μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g	
Lake	e of the Prairie	s									
1993	Walleye	L 0.2	0.22	3.8	L 0.05	0.36	L 0.01	L 0.05	0.031	L 1.0	replicate composite
1993	Walleye	L 0.2	0.32	3.6	L 0.05	0.35	L 0.01	L 0.05	0.026	L 1.0	replicate composite
1993	Walleye	L 0.2	0.23	3.62	L 0.05	0.35	L 0.01	L 0.05	0.051	L 1.0	replicate composite
1995	Walleye	0.31	0.31	4.13	L.05	0.32	L.01	L.05	-	-	replicate composite
1995	Walleye	L.2	0.31	4.29	L.05	0.36	L.01	L.05	-	-	replicate composite
1995	Walleye	L.2	0.3	4.32	L.05	0.37	0.01	L.05	-	-	replicate composite
1997	Walleye	<0.2	0.2	4	<0.05	0.39	0.02	<0.05	-	-	composite
1993	White sucker	L 0.2	0.48	3.99	0.05	0.29	L 0.01	L 0.05	0.057	L 1.0	replicate composite
1993	White sucker	L 0.2	0.64	4.09	L 0.05	0.3	L 0.01	L 0.05	0.33	L 1.0	replicate composite
1993	White sucker	L 0.2	0.46	3.59	0.05	0.31	L 0.01	L 0.05	0.023	L 1.0	replicate composite
1995	White sucker	L.2	0.47	3.57	L.05	0.23	0.013	L.05	-	-	replicate composite

1995	White sucker	L.2	0.48	3.75	L.05	0.21	L.01	L.05	-	-	replicate composite
1997	White sucker	<0.2	0.3	4.1	< 0.05	0.34	0.01	<0.05	-	-	composite
2003	Shorthead redhorse	0.01	0.59	4.09	0.001	0.33	0.0001	0.027	0.005	0.001	composite
2003	Shorthead redhorse	0.027	0.75	4.24	0.001	0.36	0.0001	0.011	0.005	0.004	composite

Year	Fish species	chromium	copper	zinc	arsenic	selenium	cadmium	lead	nickel	molybdenum	Sample
		μg/g	μg/g	μg/g	µg/g	μg/g	μg/g	μg/g	μg/g	μg/g	
	Roun	d Lake									
1995	Northern Pike	L.2	0.2	5.22	L.05	0.23	L.01	L.05	-	-	composite
1997	Northern Pike	<0.2	<0.2	4	<0.05	0.25	0.1	<0.05	-	-	composite
1993	Shorthead redhorse	L 0.2	0.46	3.66	0.05	0.22	L 0.01	L 0.05	0.03	L 1.0	composite
2003	Shorthead redhorse	0.019	0.34	4.23	0.001	0.34	0.0001	0.001	0.005	0.007	composite
2003	Shorthead redhorse	0.018	0.18	4.43	0.001	0.41	0.0001	0.015	0.005	0.002	composite
1995	White sucker	L.2	0.29	3.97	L.05	0.26	0.012	L.05	-	-	composite
1997	White sucker	<0.2	0.3	3.6	<0.05	0.31	0.02	<0.05	-	-	composite

