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Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores

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Abstract. Sediment cores were collected from lakes in central and northern Canada and from Hudson Bay to compare current and historic net depositions of mercury. Cores from most locations were enriched in mercury in the upper layers deposited recently relative to deeper, historic layers. The lakes with the greatest enrichments in mercury were located in central/southern Canada. This enrichment was interpreted as being of anthropogenic origin. Mercury inputs at the Experimental Lakes Area (ELA) in northwestern Ontario inferred from a core profile agreed well with inputs calculated independently from precipitation and runoff data. Anthropogenic inputs of mercury to northwestern Ontario were calculated to be about 9 μg m^{-2} y^{-1}. Considering all the locations over the geographic range, the core profiles infer that fluxes of mercury have increased on average by about 2 fold over the past half century. This is consistent with results from other sites in North America and Europe.

Introduction

Numerous studies in central North America and Europe have shown increased concentrations of mercury in lake sediment layers deposited recently as compared with deeper, older layers (Ouellet & Jones 1982; Verta et al. 1989; Swain et al. 1992; Hermanson 1993; Lockhart et al. 1993, 1995; Lucotte et al. 1995; Gubala et al. 1995). Levels of mercury in fish and marine mammals from northern Canada often exceed levels established for the protection of human health. Several lines of evidence have suggested that levels of mercury in some species have increased over pre-industrial levels. Mercury can have natural, geological sources within a watershed but it can also be deposited as a result of human activities which release mercury into the air or water. The objective of this work was to estimate the extent of anthropogenic inputs of mercury to northern locations in Canada and to compare those inputs with natural ones.

Table 1. Locations and limnological data on lakes where cores were collected.

Lake	Latitude (N)	Longitude (W)	Mean depth (m)	Max depth (m)	Lake area (ha, A_0)	Drainage area (ha, A_d)	A_d/A_0
Amituk	75°03′	93°46′	10	42	59	2600	44
Belot	66°53′	126°16′		57	30250	135000	4.5
Buchanan	79°30′	87°30′	ca 40	ca 80	1800	39400	22
Far	63°42′	90°40′	3.6	8.9	3.7	16.6	4.5
Great Bear	65°05′	120°47′	71.7	446	3.1×10^6	11.5×10^6	3.7
Hazen	81°45′	71°30′	ca 85	ca 263	53570	400000	7.5
Kusawa	60°20′	136°22′	54	140	14200	407000	28.7
Lake 375	49°45′	93°47′	12	30	18.9	231	11.1
Laberge	61°11′	135°12′	54	146	20100	2.5×10^6	126
Little Atlin	60°15′	133°57′	1	47	3790		
Lindeman	59°47′	135°03′		58	ca 450		
Ste Therese	64°35′	121°20′		18	11840	1742000	147
Trout	51°15′	93°15′	14	49	34700	71800	2.1
Winnipeg South	50°40′	96°48′					
Winnipeg North	53°12′	99°07′	12	36	2.38×10^6	95.3×10^6	40.1
Yaya	69°12′	134°38′		65	ca 1205		
Hudson Bay Hud 4	55°16′	77°57′			1.2×10^8		
Hudson Bay Fogo 4	58°01′	81°17′					

Materials and methods

The locations and preliminary limnological data for the lakes cored are given in Table 1. Although several cores were taken from most of the lakes, only one from each lake will be discussed. Cores were usually collected in winter through the ice. The Hudson Bay and Lake Winnipeg cores were collected from ships using an oceanographic box corer to obtain a large volume of sediment which was then sub-sampled on the ship by inserting a 10-cm diameter core tube with gentle vaccuum to minimize core compression. Sediment was extruded from core tubes in the field and retained in plastic bags at temperatures just above freezing until analyzed. Upon arrival in the laboratory, sediment was handled as described by Lockhart et al. (1995).

Mean ages of slices were estimated from the regression of unsupported lead-210 against accumulated dry weight. In the case of Lake 375 at the Experimental Lakes Area, the regression method did not describe the data well, and so the "Rapid Steady State Mixing" (RSSM, Robbins 1978) model was used. In the case of Hudson Bay core F4, the "Constant Rate of Supply" (CRS, Oldfield & Appleby 1984) calculation gave the best description of

age structure. Cesium-137 was also determined in each slice and the Pb-210-derived dates were considered credible if the peak activity for Cs-137 occurred during the mid-1960s.

For each site we estimated a 'focusing factor' based on the flux of Pb-210 measured in the core and the flux estimated from the nearest soil profile we had. Soil samples were collected at a few sites believed to be neither erosional nor depositional. Each slice was analyzed for Pb-210 and Ra-226 and the excess Pb-210 and its flux (Bq m^{-2} yr^{-1}) to the site were calculated.

Mercury in sediment was analyzed as described earlier by boiling a small amount of sediment (0.1–0.5 g) with 8 mL of aqua regia and bringing the volume to 50 mL with distilled water followed by flameless atomic absorption (Hendzel & Jamieson 1976).

A recent and an historic flux of mercury (μg m^{-2} y^{-1}) was calculated for each core. The recent flux was taken arbitrarily as the average flux for those slices estimated to have been deposited since 1950; the deepest slice used in the calculation of a recent flux did not date exactly to 1950 and so the slice dating closest to 1950 was the deepest one included in the average. The historic flux was calculated by averaging the fluxes calculated from the deepest 5 slices in which mercury was determined.

Results and discussion

Pb-210 and Cs-137 profiles for a selection of the lakes are shown in Figure 1. The quality of the dating was generally good as judged by the exponential declines with depth in excess Pb-210. Cs-137 peaks were placed in the mid-1960s with a few exceptions (Table 2). We were unable to date the Buchanan Lake core using Pb-210. The Cs-137 profile in this core, however, showed a sharp sub-surface maximum (Figure 1) allowing us to estimate recent dates by making the assumption that the Cs-137 peak occurred in 1963, the time of maximum bomb fallout. Far Lake, a very small lake on the west coast of Hudson Bay, had a spike in Cs-137 activity in the top slice. This core was collected in May, 1988, and the top slice probably received some Cs-137 from Chernobyl since trace amounts of Cs-134 were also detected in that slice.

Sedimentation rates and methods used to calculate them are listed in Table 2. Pb-210 deposition varied with the most northerly sites having the lowest fluxes. In all cases except Yaya Lake, the flux of Pb-210 to the sediment was greater than the flux to the nearest soil profile collected and we attributed this difference to sediment focusing. The focusing factor for each site was estimated by dividing the flux of Pb-210 to the sediment by the flux to the nearest soil sample. These factors ranged from less than 1 for Lake Kusawa to about 5 for Lindeman Lake in northern British Columbia (Table 2).

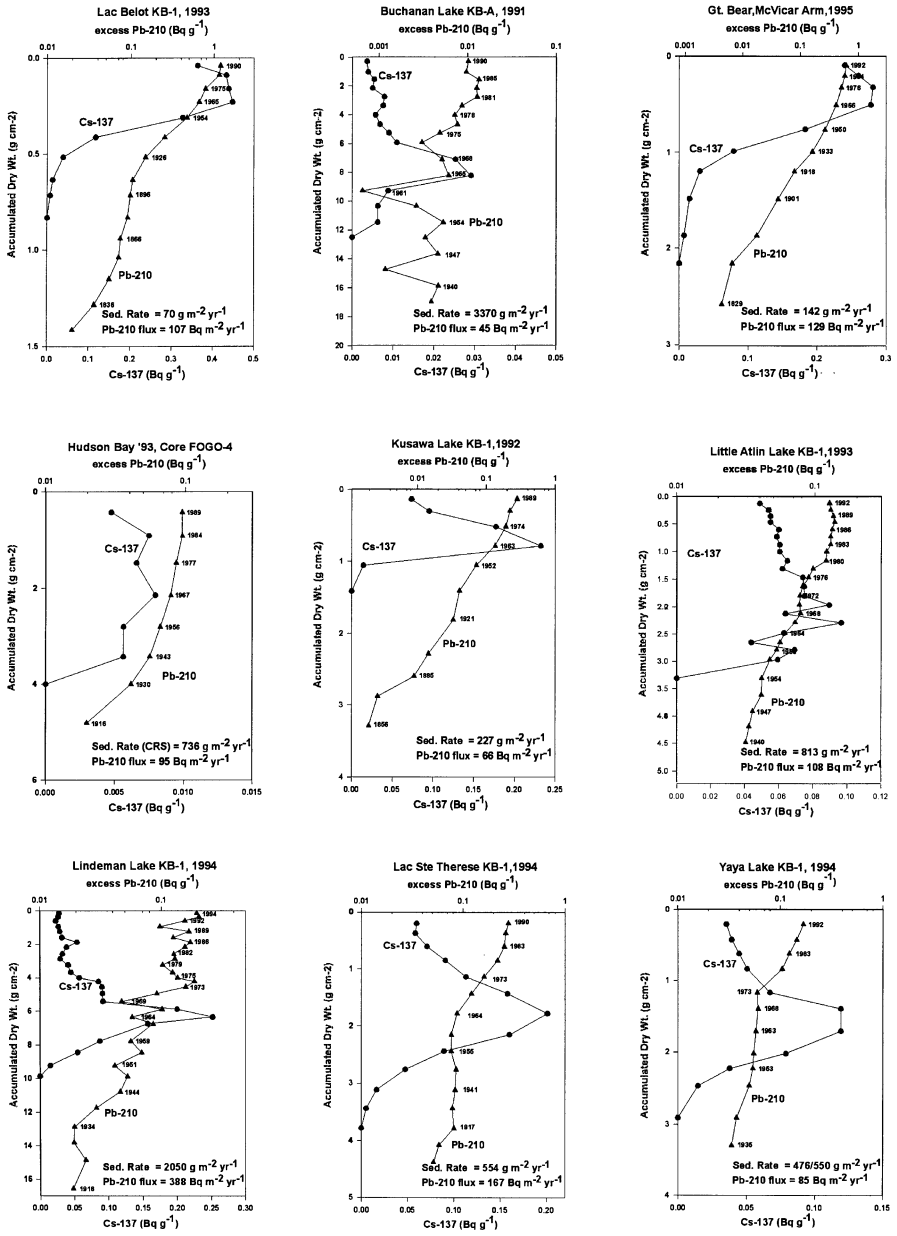

Figure 1. Down-core profiles of lead-210 and cesium-137 for a selection of the lakes studied.

The down-core profiles in concentrations of mercury are shown in Figure 2. Mercury concentrations in the recent slices ranged from 23 to 155 ng g^{-1} (dry wt), in agreement with a range of 20 to 175 ng g^{-1} reported by Friske

Table 2. Core data used to calculate sedimentation rates and focusing factors.

Site	Core	Dating calc.	Fit of Cs-137	Sediment core Pb-210 flux Bq m^{-2} y^{-1}	Expected Pb-210 flux from soil data Bq m^{-2} y^{-1}	Focus factor	Recent sedimentation rate g m^{-2} y^{-1}	Historic sedimentation rate g m^{-2} y^{-1}
Amituk	KB1	Linear	Poor	179	60[1]	3.0	235	334
Belot	KB1	Linear	Good	107	50[2]	2.1	70	70
Buchanan	KBA	Cs-137					2930	
Far	BCA	Linear	Good	131	60[1]	2.2	77	77
Great Bear	KB1	Linear	Good	129	50[2]	2.6	142	142
Hazen	BCB	Linear	Poor	11	7[4]	1.6	498	498
Kusawa	KB1	Linear	Good	66	80[5]	0.8	227	227
Lake 375	BCA	RSSM	Poor	320	175[3]	1.8	187	187
Laberge	KB3	Linear	Good	114	80[5]	1.4	999	999
Little Atlin	KB1	Linear	Good	108	80[5]	1.4	813	813
Lindeman	KB1	Linear	Good	388	80[5]	4.9	2050	2050
Ste Therese	KB1	Linear	Good	167	50[2]	3.3	638	638
Trout	TL12	Linear	Good	406	175[3]	2.4	264	264
Winnipeg South	NAM 7A	Linear	Good	195	175[3]	1.1	1000	1000
Winnipeg North	NAM 2A	Linear	Good	216	175[3]	1.3	750	750
Yaya	KB1	Linear	Good	85	50[2]	1.7	476	550
Hudson Bay	Hud 4	Linear	Good	272	60[1]	4.5	1180	1180
Hudson Bay	Fogo 4	CRS	Fair	95	60[1]	1.6	736	736

Calculated from soil profiles from Saqvaqjuac[1] = 60 Bq m^{-2} y^{-1} (Far Lake); Lac Belot[2] = 50 Bq m^{-2} y^{-1}; Experimental Lakes Area[3] = 175 Bq m^{-2} y^{-1} (Lake 375); Lake Hazen[4] = 7 Bq $m^{-2}y^{-1}$; Lac Laberge[5] = 80 Bq m^{-2} y^{-1}.

& Coker (1995) for a large number of Canadian lake and stream sediment samples. Most of the lakes showed increases in concentrations of mercury in slices near the sediment surface, as has been described for numerous sites in North America and Europe (Ouellet & Jones 1982; Verta et al. 1989; Swain et al. 1992; Hermanson 1993; Lockhart et al. 1993, 1995; Lucotte et al. 1995; Gubala et al. 1995).

The recent flux to a core site is interpreted as the total flux comprising all inputs to the sites from both natural, geological processes originating both inside and outside the basin and also from any anthropogenic sources. Recent fluxes of mercury ranged from 2.1 μg m^{-2} y^{-1} at Lac Belot to 114 μg m^{-2} y^{-1} in the South Basin of Lake Winnipeg (Table 3). The historic fluxes calculated from the deepest sections of the cores are taken to be the natural inputs resulting from all processes operating at the times the deep sections were deposited. Historic fluxes ranged from 1.1 μg m^{-2} y^{-1} at Far Lake on

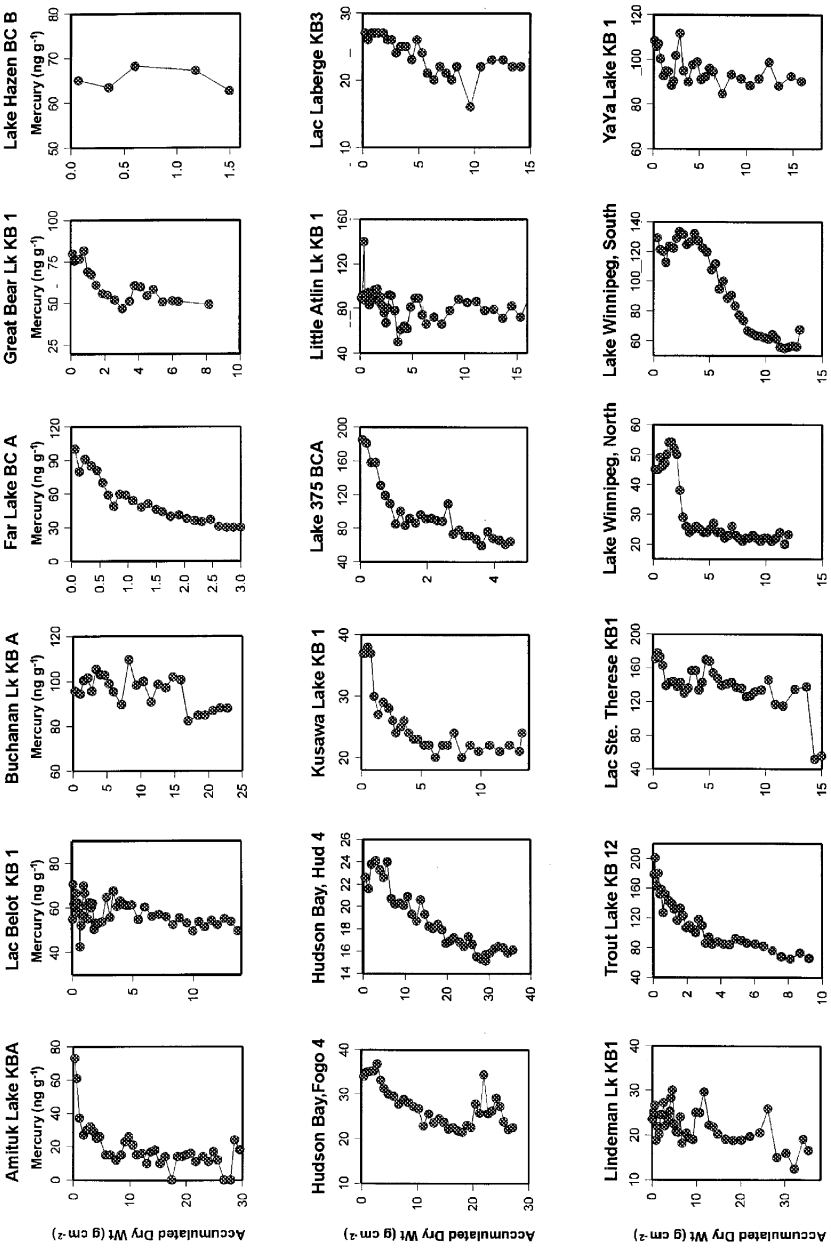

Figure 2. Down-core profiles of mercury concentrations in sediments from lakes in central and northern Canada.

the west coast of Hudson Bay to 52.7 μg m^{-2} y^{-1} in the South Basin of Lake Winnipeg (Table 3). Since both recent and historic fluxes incorporate a natural, geological component, there is no reason to expect them to be comparable from lake to lake over a broad range of geological settings. The historic flux was subtracted from the recent or total flux to obtain a value for the excess of the recent over the historic flux; this value has been interpreted as the flux attributable to anthropogenic activities (Table 3). This interpretation implies negligible vertical redistribution of mercury throughout the sediment column after deposition, as has been indicated in other studies (Gobeil & Cossa 1993; Porcella 1996). Only at Yaya Lake in the Mackenzie River Delta was the recent flux (28 μg m^{-2} y^{-1}) smaller than the historic flux (29.8 μg m^{-2} y^{-1}) and so there was no measurable increase in recent time. All the other sites had the recent flux greater than the historic flux. Ignoring Lake Winnipeg, the anthropogenic fluxes ranged from undetectable at Yaya Lake to 9.3 μg m^{-2} y^{-1} at Trout Lake in northwestern Ontario (Table 3, Figure 3).

The two lakes in northwestern Ontario (Trout Lake and Lake 375) had total inputs of 17 and 16 μg m^{-2} y^{-1} of which 9 μg m^{-2} y^{-1} was estimated to be of anthropogenic origin (Table 3). Swain et al. (1992) studied small lakes in Minnesota and Wisconsin and calculated an historic flux of 3.7 μg m^{-2} y^{-1} and a recent flux of 12.5 μg m^{-2} y^{-1}, which suggests an anthropogenic component of about 8.8 μg m^{-2} y^{-1}. Mierle (1990) measured an input of 18.1 μg m^{-2} y^{-1} of mercury from precipitation and streams into Harp Lake in south-central Ontario which compares closely with our total mercury flux calculations of 16 and 17 μg m^{-2} y^{-1} (Table 3). The figures obtained here for the sites in northwestern Ontario are consistent with independent estimates of fluxes of mercury to lakes in the wider geographic region of central North America (Swain et al. 1992).

In the instance of Lake 375 at the Experimental Lakes Area we can test the fluxes of mercury calculated from the core against an hypothetical mass balance based on independent studies by St. Louis et al. (1996) on nearby watersheds. The input of mercury from precipitation to the Experimental Lakes Area is about 30.8 mg ha^{-1} y^{-1} and the area of Lake 375 is 18.9 ha and so the wet deposition to the lake surface is about 582 mg y^{-1}. Dry deposition of mercury can be estimated at about half the wet deposition, adding an additional 291 mg y^{-1}. The catchment of Lake 375 is approximately 115.9 ha of upland plus a sub-catchment of 80.6 ha which contains another lake (Lake 373). Upland terrain at the ELA retains mercury deposited to it and delivers an average of only 35% to the lakes, and so inputs to lake 375 from upland runoff add an additional 1877 mg y^{-1}. Inputs to Lake 373 can be calculated in the same way given that the area of the lake and its sub-catchment are 27.3 and 53.3 ha respectively. The wet and and dry inputs to the lake can

Table 3. Estimates of fluxes of mercury to the upper parts of the cores deposited since the 1950s (recent flux) as compared with fluxes to the deepest slices in the same cores (historic flux). The anthropogenic flux is taken as the difference between the recent flux and the historic flux.

Site	Core	Time interval used to calculate recent mercury concentration	Mean Hg concentration in slices since 1950s ng g^{-1} dry wt	Recent flux of Hg μg m^{-2} y^{-1}	Mean Hg concentration in deepest 5 slices ng g^{-1} dry wt	Historic flux of Hg μg m^{-2} y^{-1}	Excess of recent flux over historic flux of Hg μg m^{-2} y^{-1}
Amituk	KB1	Since 1957, slices 1–4	49.5	3.9	16.4, slices 31–37	1.8	2.1
Belot	KB1	Since 1954, slices 1–5	62.8	2.1	53.1, slices 42–46	1.8	0.3
Buchanan	KBA	Since 1950, slices 1–16	98.8				
Far	BCA	Since 1949, slices 1–4	89.0	3.1	31.6, slices 21–25	1.1	2.0
Great Bear	KB1	Since 1950, slices 1–5	77.9	4.3	52.1, slices 17–23	2.8	1.5
Hazen	BCB	Since 1963, slices 1–5	65.3	23			
Kusawa	KB1	Since 1951, slices 1–5	35.8	10	22, slices 25–29	6.2	3.8
Lake 375	BCA	Since 1953, slices 1–6	155	16	67, slices 25–29	7.0	9.0
Laberge	KB3	Since 1951, slices 1–12	25.8	18.4	22.4, slices 22–26	16.0	2.4
Little Atlin	KB1	Since 1950, slices 1–22	87.8	51	78.6, slices 38–42	45.6	5.4
Lindeman	KB1	Since 1951, slices 1–23	23.1	9.6	15.8, slices 36–40	6.6	3.0
Ste Therese	KB1	Since 1953, slices 1–10	152	29	130, slices 29–33	25.1	3.9
Trout	TL12	Since 1952, slices 1–10	159	17	69.6, slices 32–36	7.7	9.3
Winnipeg South	7A	Since 1949, slices 1–15	125	114	58.0, slices 34–38	52.7	61.3
Winnipeg North	2A	Since 1952, slices 1–13	45.0	26	22.0, slices 38–42	12.7	13.3
Yaya	KB1	Since 1951, slices 1–10	98.4	28	92.1, slices 24–28	29.8	
Hudson Bay	H4	Since 1949, slices 1–6	23.0	6.0	16.2, slices 34–38	4.2	1.8
Hudson Bay	F4	Since 1955, slices 1–5	35.2	16.2	24.9, slices 31–35	11.4	4.7

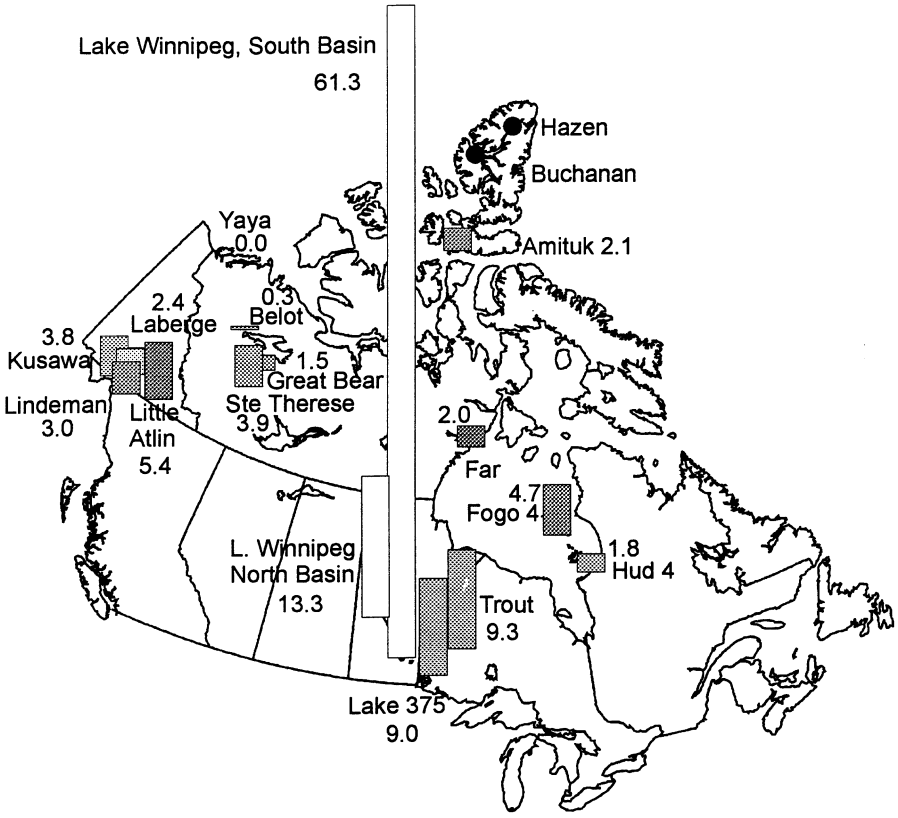

Figure 3. Estimated anthropogenic loadings (μg m^{-2} y^{-1}) of mercury to lakes in central and northern Canada.

be estimated as 2107 mg y^{-1}; the proportion of this exported to Lake 375 is expected to be of the order of 35%, (based on unpublished calculations by V. St. Louis for the nearby watershed of Lake 240) which would add an extra 737 mg y^{-1} to the input budget of Lake 375. Adding these contributions, the total input to Lake 375 is estimated at 3488 mg y^{-1} of which about 65% would be retained in the lake which is equal to 2267 mg y^{-1} or 12 μg m^{-2} y^{-1}. The estimated total flux to the lake from the core was 16 μg m^{-2} y^{-1} (Table 3) of which 9 μg m^{-2} y^{-1} was estimated to be of anthropogenic origin. The input from precipitation of 12 μg m^{-2} y^{-1} was slightly larger than the anthropgenic component of 9 μg m^{-2} y^{-1} estimated from the core, and this difference may indicate that about one quarter of the atmospheric loading was of natural origin. Further experiments are being conducted to calibrate flux measurements obtained from cores against mass balance estimates using Lake 240 at the ELA.

If the anthropogenic fluxes are driven by air concentrations of mercury, then we might expect them to be more uniform regionally than the historic fluxes or the total recent fluxes. With the exception of Lake Winnipeg, this was the case (Table 3, Figure 3). Most of the sites have little or no industrial activity or centres of human population within the drainages. Lake Winnipeg, however, drains a large area containing industrial activity, extensive agricultural land and several million people. As a result, inputs to Lake Winnipeg should reflect both atmospheric loadings and diverse anthropogenic contributions from within the watershed. The South Basin of Lake Winnipeg has few major catchments upstream from the lake while the North Basin has several hydroelectricity dams and Cedar Lake and the South Basin intervening, all of which should regulate inputs of particulate materials and probably mercury. If the anthropogenic flux at the most southerly locations is about 9 μg m^{-2} y^{-1} as indicated by Trout Lake and Lake 375 (Table 3), then the anthropogenic input to the South Basin of Lake Winnipeg (61 μg m^{-2} y^{-1}, Table 3), is too high to be accounted for by atmospheric inputs. Even the North Basin had an anthropogenic flux of 13.3 μg m^{-2} y^{-1}, a value above the range indicated from the other lakes.

In summary, sediment core profiles from lakes over a wide geographic range in Canada inferred increases in the deposition of anthropogenic mercury to lakes in central and northwestern Canada. Over the range of remote lakes studied, the anthropogenic component of inputs of mercury ranged from undetectable in the Mackenzie Delta up to about 9 μg m^{-2} y^{-1} in northwestern Ontario. Anthropogenic deposition to the lakes in northwestern Ontario agreed with independent studies in north/central U.S.A. The anthropogenic flux calculated from a core at the Experimental Lakes Area was very similar to that calculated from mass balance studies on nearby lakes. Anthropogenic contributions to lakes in the Northwest Territories and Yukon were smaller than to those from northern Ontario. Lake Winnnipeg was an exception with much higher anthropogenic loadings than those exhibited by isolated lakes, probably as a result of the extensive human activity within the watershed.

The core results are consistent with other core studies, the mass balance study, and other independent lines of evidence, all of which indicate increased loadings with mercury during the past century relative to historical loadings.

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