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REPORT TO THE VIRTUAL ELIMINATION TASK FORCE

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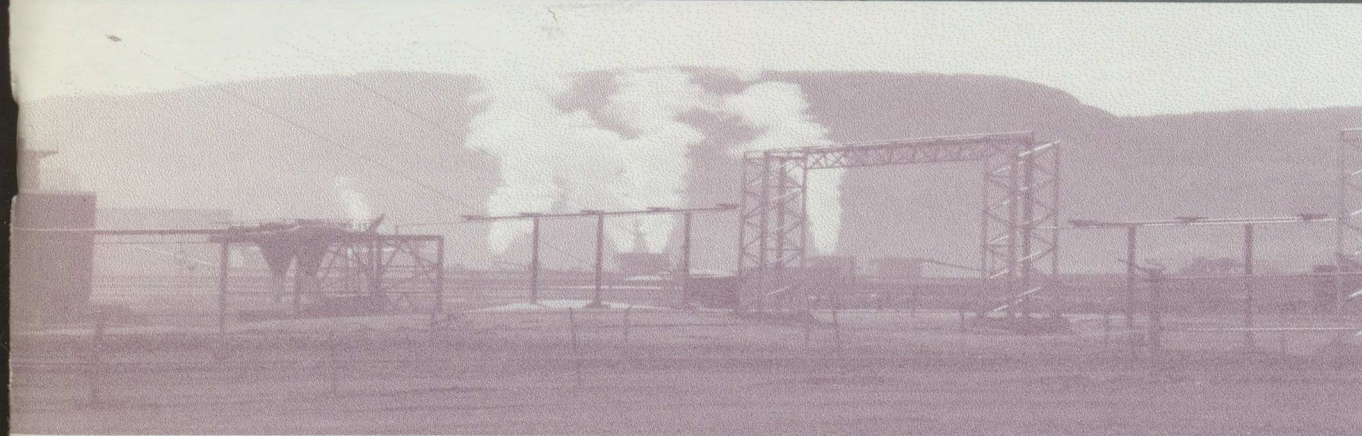
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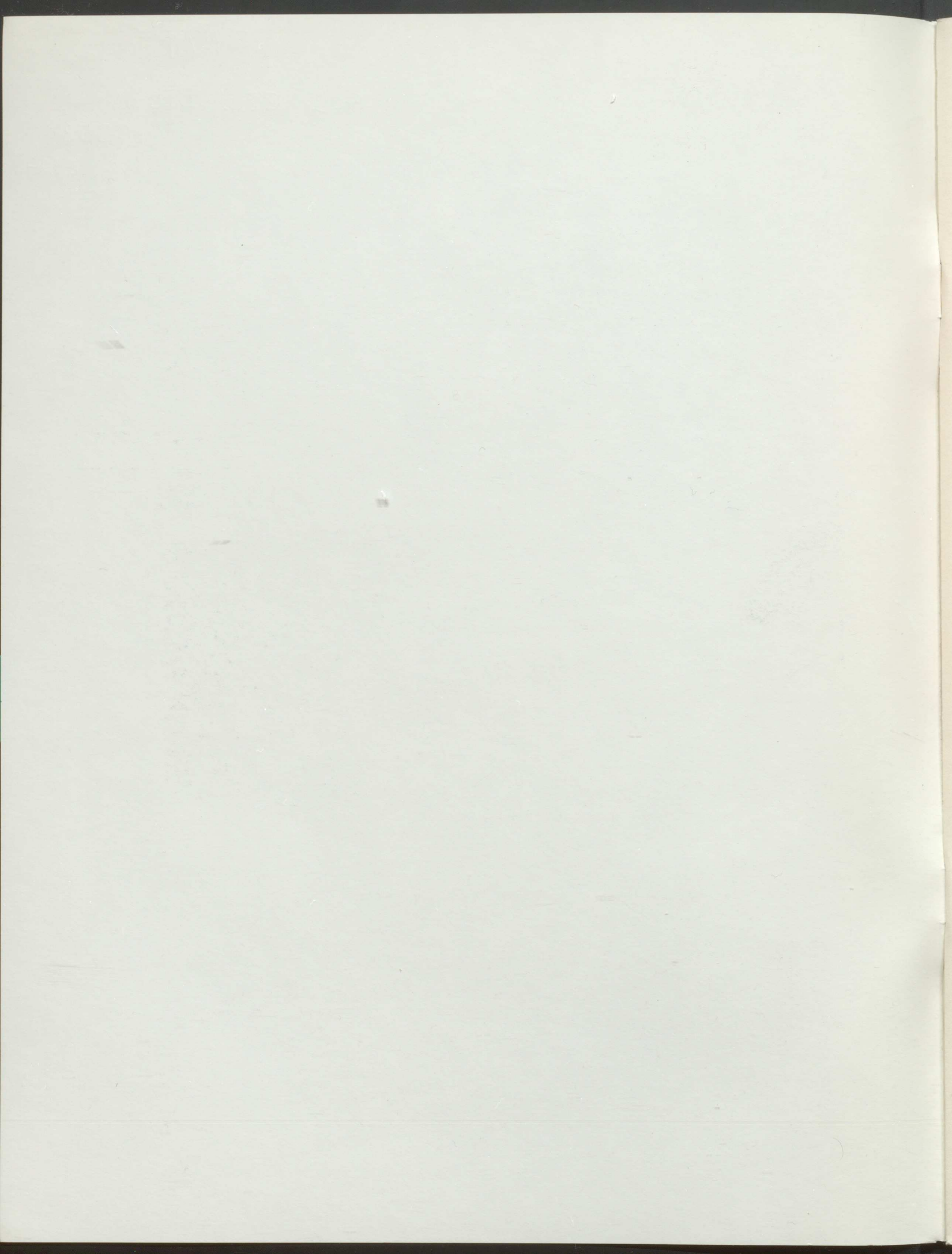
SOURCE INVESTIGATION FOR LAKE SUPERIOR



BY DAVID M. DOLAN,
KEVIN P. MCGUNAGLE,
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AND EVA VOLDNER



International Joint Commission
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BY

DAVID M. DOLAN
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INTERNATIONAL JOINT COMMISSION
WINDSOR, ONTARIO

DECEMBER 1993

ISBN 1-895085-77-2



PRINTED ON RECYCLED PAPER
IN CANADA

DISCLAIMER

The views expressed in this report are those of the authors and are not necessarily those of the Virtual Elimination Task Force or the International Joint Commission.

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ACKNOWLEDGEMENTS

A special thanks to:

- Kathleen Bogan, Emergency Response Division, U.S. Environmental Protection Agency, Washington, D.C.
- J.J. Brickett, Project Officer, Emergency Operations with the Canadian Coast Guard.
- John Menzies, Prevention Division, Environmental Emergencies Branch with Environment Canada.

for their help in retrieving data regarding spills to Lake Superior.

The authors acknowledge the help of Susan Sang, Miriam Diamond and Shirley Thompson from the University of Toronto who performed "reasonableness checks" on the estimated loadings.

The authors also acknowledge the encouragement of Don Mackay of the University of Toronto, Jeff Foran of the ILSI Risk Science Institute and Gayle Coyer of the National Wildlife Federation.

I. INTRODUCTION

Persistent toxic substances enter the ecosystem through a variety of sources and pathways. In their Interim Report (1991) the Virtual Elimination Task Force grouped these into eight categories:

- Municipal point sources.
- Industrial point sources.
- Surface runoff.
- Combined sewer overflows, storm sewers, and treatment plant bypasses.
- Emissions to the atmosphere.
- Contaminated sediment.
- Groundwater.
- Spills from ships and shore-based facilities.

These categories are actually a mixture of sources, pathways and receivers. This report sorts these categories into more rigorous definitions and then examines what is known about each for lead, mercury and polychlorinated biphenyl (PCB) in the Lake Superior basin. Lake Superior was chosen for two reasons:

1. The Commission, in its 5th Biennial Report (1990), suggested that the Lake Superior basin be used as a demonstration area for zero discharge. Further indication of the Commission's interest in the Lake Superior basin was the focus on this basin during the four Zero Discharge Roundtables. In addition, the Virtual Elimination Task Force also used Lake Superior as a study area.
2. Lake Superior does not have the density of sources that the other lakes have so that the necessary effort was less. However, it still has several Areas of Concern with loadings of persistent toxic substances. This allows the linkages between virtual elimination and remedial action plans (RAPs) to be explored and illuminated.

The relative contribution of the pathways of these three toxics are estimated and discussed in the context of the ultimate sources. These loadings are displayed in charts and tables and maps are presented that locate major sources. Table 1 is the summary of the loading estimates made in this report. Some of the estimation methods that were necessitated by lack of actual data are little more than extrapolations of measurements made elsewhere in the Great Lakes basin. While their accuracy is clearly questionable, their utility in gaining a sense of where these substances are coming from is evident. As an independent check on the total load estimates, ambient data are used in conjunction with a mass balance model to "back-calculate" the total loads. This work is done in a separate report (Mackay *et al.* 1992a and 1992b), but the results are used in this report.

The methods used in this report are intended to be general. The approach of using actual measured loadings whenever possible is followed. When data of this nature are not available, then various estimation methods are applied. These are described in detail in the text.

TABLE 1

**SUMMARY ESTIMATES ON SOURCES AND LOADING OF PCBs,
MERCURY AND LEAD TO LAKE SUPERIOR**

CATEGORY	PCB kg/year	Hg kg/year	Pb kg/year
NON-ATMOSPHERIC			
Monitored Tributary	21.6	86.4	9,665
Unmonitored Area	6.2	37.8	5,189
Industry	10.0	39.0	5,124
Municipal	7.7	34.3	2,001
Combined Sewer Overflows	2.3	3.0	619
Direct Runoff	18.1	40.2	7,013
Spills	0.0	2.0	140
Groundwater	0.0	0.0	0
Sub-total	65.9	242.7	29,750
ATMOSPHERIC			
Dry	31.4	282.6	4,655
Wet	124.8	374.4	62,396
Sub-total	156.2	657.0	67,051
TOTAL TO LAKE*	222.1	899.7	96,801
ABSORPTION	136.7**	negligible	0

* Totals may not sum due to rounding.

** This quantity is calculated by the mass balance model and depends on an assumed air concentration and a modeled water concentration. Under current conditions, there is an estimated net diffusive loss of 60 kg/year.

II. SOURCES, PATHWAYS, AND RECEIVERS

TERMINOLOGY

In order to clearly describe the results of a source investigation, it is necessary to define the terms used in the analysis. A source is the origin of the contaminant of interest as a waste product. A pathway is the route by which wastes are delivered to a receiver. A receiver is the physical, chemical and biological system where the contaminant causes undesirable effects. As a contaminant moves from source to pathway to receiver it becomes harder to control. Thus, there is strong interest in control at source or even before the contaminant is used or manufactured. If a compound can be manufactured, used and disposed of in such a way as to result in no release of the compound to the environment, then there is no source of that compound for purposes of this report. Some compounds, such as dioxins and furans are not intentionally manufactured and so the process that results in their formation is also their source. Other compounds, such as the ones focused on in this report (lead, mercury and PCBs) are, or have been, intentionally manufactured and only the waste stream (i.e. air emissions from a lead smelter) from that process would be considered a source. Likewise, only the loss of the compound to the environment while it is in use (i.e. PCB leaking from transformers) would be considered a source. Further, only disposal that results in release (i.e. mercury from batteries in a municipal incinerator) would be a source for purposes of this investigation.

Based on the above, only two of the eight categories identified in the Interim Virtual Elimination Task Force Report are actually "sources." These are atmospheric emissions and spills. Most of the rest are really pathways and one, contaminated sediment, is really a receiver.

SOURCE INVESTIGATION AND MODELING

Before further defining pathways and receivers, it is useful to discuss the relationship between source investigation and modeling, specifically mass balance modeling. As the Virtual Elimination Task Force (VETF) has noted, much of the source information is inadequate and data that do exist are often of limited utility. Mass balance modeling has been used as part of this project in order to provide an independent check on the "reasonableness" of the loadings estimated. Once credible loads have been determined, the model can also be used to investigate alternative load reduction strategies, but the focus here is on the verification aspect.

The definitions of "pathway" and "receiver", then, depend on what is included in the mass balance model. Since the model currently in use includes the waters of Lake Superior, the sediment beneath it and the biota within it, these become the receivers. In modeling terms, the contaminant concentrations in water, sediment and biota (receivers) are the state variables. The rest of the categories defined by the VETF in its Interim Report (municipal and industrial effluents, surface runoff, sewer overflows and bypasses, and groundwater) are actually pathways, or routes, by which the waste compounds are delivered to the receiver. If the model was more inclusive, or if it was focused on a stream, or a sewer, or an industrial facility, the definitions of pathways and receivers would change.

The above definitions will be useful when defining reduction strategies. If sources are defined as above, they immediately suggest remedies (i.e. replace leaking transformers, contain spills, don't incinerate unclassified waste, etc.). Pathways do not suggest remedies other than total elimination. Rather, they are the routes by which sources are delivered to the receivers. Their utility is in load estimation. Collection points such as tributary mouths and pipes often have elevated contaminant levels and are easier to measure. The main objective of the source

investigation project is to use measurements on the pathways to model the effects on the receivers and then to reconcile the pathways with the sources. The results are the relative contribution of the sources of chemicals of concern in terms of categories that suggest remedial steps.

It should be noted that pipes commonly thought of as point "sources" are considered to be pathways for this investigation. This is especially true for municipal effluents which theoretically should not contain any of the compounds of interest. The fact that most sewage effluents are contaminated to some degree is due to the actual sources; industrial sewer users, improper disposal by domestic users and atmospheric deposition within the catchment area. Also, these compounds are not treated to a significant degree and what "treatment" that does occur is incidental. Since the persistent compounds of interest cannot be destroyed by conventional treatment, any removal is really just shifting the problem between media. For example, settling of solids contaminated with mercury in a sewage treatment plant results in sludge contaminated with mercury. Unless this is properly disposed of, the problem remains. See Glass (1990) for a complete description of this cycle.

III. SOURCES

INTRODUCTION

As defined in the previous section, the sources considered here are the origins of the contaminant of interest as a waste product. Since multimedia releases of contaminants often occur, it is difficult to completely separate emissions into air, water and solid waste. In fact, some overlap is unavoidable with two of the chemicals considered in this report, mercury and PCBs, because they are volatile. The sources in this section are categorized as air emissions which contribute to the atmospheric pathway and several other sources which contribute to various water pathways. The distinction is made for convenience of categorization and in many cases is not absolute.

AIR EMISSIONS

The actual sources of persistent toxic substances deposited on the surface of Lake Superior by dryfall or rain/snow are the emissions to the atmosphere by natural and anthropogenic processes. The substances considered in this report, lead, mercury and PCBs have characteristics that make their introduction into the atmosphere somewhat different. Since lead has no appreciable volatility, its main route of input to the atmosphere is combustion. Mercury and PCBs are volatile so that their mere exposure to the atmosphere is an important route. For mercury, there are considerable natural sources, while for PCBs, all sources are manmade.

Atmospheric Sources

Modes of Emissions (Primary and Secondary)

Pollutants originating from anthropogenic and natural sources are introduced into the atmosphere through primary and secondary emissions. Primary emission includes direct emission from industrial stacks, incineration, residential chimneys, transportation and forest fires. For pesticides, it includes losses to the atmosphere through direct application of the pollutant and through volatilization of the pollutant from crop and soil during a relatively short period after application. Secondary emission includes resuspension and volatilization of previously deposited material, volatilization of pesticides entrained in or applied directly to the soil, volatilization from contaminated soils and waters, release from landfills and waste dumps. Pollutants can also be formed through chemical/photochemical reactions.

Region of Concern

Source/Receptor Relationships

Once emitted into the atmosphere, the pollutants are subject to transport, dispersion, physical/chemical/photochemical transformation and are scavenged through wet and dry deposition processes. The distances from actual emissions to removal is a function of effective height of the release, meteorological conditions, properties of the pollutants and the underlying surface.

Many pollutants released to the atmosphere are persistent, slowly scavenged from the atmosphere and often subject to long distance transport and dispersion. Others may migrate via

FIGURE 1

ATMOSPHERIC REGION OF INFLUENCE AROUND THE GREAT LAKES

Lines of the median location of the air parcel starting points one to five days prior to arrival somewhere in the Great Lakes basin. The three-day line indicates that half of the time the air in the basin would have originated three days earlier within that line and half the time beyond it.

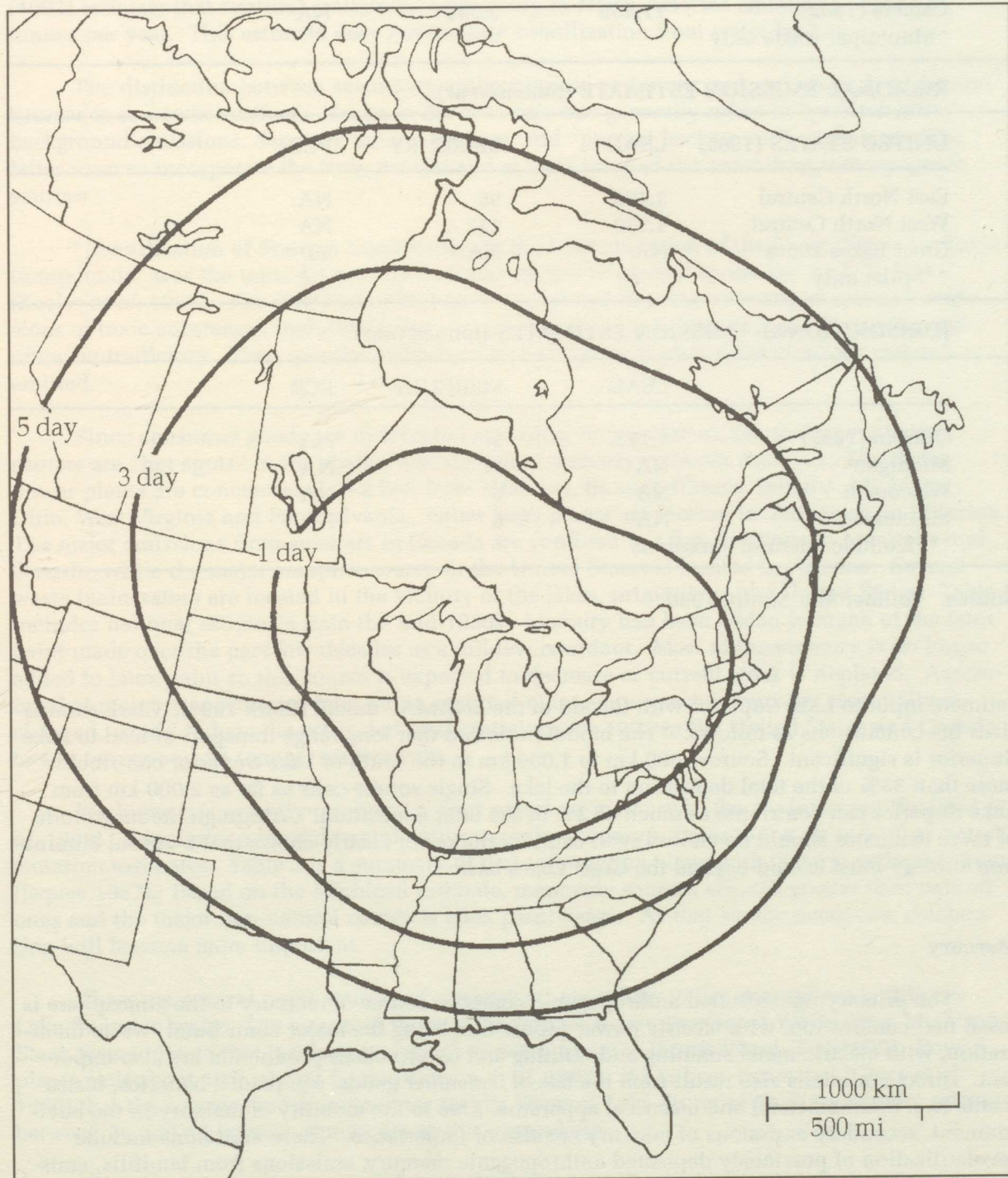


TABLE 2 EMISSION ESTIMATES

NATIONAL EMISSION ESTIMATES (tonnes/year)			
	LEAD	MERCURY	PCBs
United States (1985)	20,900	1,668	5*
Canada (1982)	11,466	3,530	NA
*Municipal waste only			
REGIONAL EMISSION ESTIMATE (tonnes/year)			
UNITED STATES (1985)	LEAD	MERCURY	PCBs
East North Central	3,400	95	NA
West North Central	1,330	112	NA
Great Lakes states	NA	NA	50**
**Spills only			
JURISDICTIONAL EMISSION ESTIMATES (tonnes/year)			
	LEAD	MERCURY***	PCB
Ontario (1982)	3,113	5	NA
Michigan	NA	17	NA
Wisconsin	NA	6	NA
Minnesota	NA	6	NA
***Excludes natural emissions			

Source: Voldner and Smith, 1990

estimate input to Lake Superior with the aid of the ENAMAP model (Clark 1993). Clark summarizes his conclusions as follows: "The model indicated that long-range transport of lead to Lake Superior is significant. Sources 500 km to 1,000 km to the south of Lake Superior contribute more than 33% of the total deposition to the lake. Single source cells as far as 2,000 km from Lake Superior can contribute as much as 2% of the total deposition." Although the magnitude of these estimates should be viewed with caution, the result clearly shows that a virtual elimination strategy must extend beyond the Great Lakes basin.

Mercury

The primary uncontrolled anthropogenic emission source of mercury to the atmosphere is fossil fuel combustion, with electric power production being the major contributor; waste incineration, with electric metal smelting and refining and chloro-alkali production are also important. Direct emissions also result from the use of consumer goods, e.g. paints, batteries, instruments (e.g. thermometers) and electrical apparatus. Due to the mobility of mercury in the environment, secondary emissions of mercury are also of importance. These emissions include revolatilization of previously deposited anthropogenic mercury, emissions from landfills, emissions resulting from mercury discharged from industrial sources into the aquatic and terrestrial ecosystem. These sources are extremely difficult to characterize.

As mentioned previously, natural sources are significant contributors to mercury emissions in North America (and throughout the world). In fact, natural sources are thought to equal

or exceed anthropogenic sources by many investigators. Natural sources include soil, burning vegetation, lakes and oceans, volcanoes and terrestrial mineral deposits (Kurita 1987). Natural emission rates are also difficult to estimate and vary widely. For example, the estimate for Canada by Jaques (1987) of 3,500 tonnes per year is larger than three global estimates made by Slemr and Langer (1992), Lindquist *et al.* (1991) and Nriagu (1990). This frequently quoted Canadian estimate, as well as an estimate of 1,000 tonnes per year in the United States (Van Horn 1975) are considered too high, as they are extrapolated from a few measurements in the mid-1970s. Based on recent measurements of mercury from soils and water bodies Bloxam *et al.* (1992) estimate that "natural emissions" of mercury in North America amount to about 600 tonnes per year. This estimate does not include volatilization from water bodies.

The distinction between secondary anthropogenic emissions and emissions from natural sources is somewhat diffuse. Hence in the literature one generally refers to "pre-industrial" background emissions, denoting natural sources, and "present background" emissions. The latter sources incorporate the truly natural and at least some of the secondary anthropogenic sources.

"Identification of Sources Contributing to the Contamination of the Great Waters by Toxic Compounds" was the topic for a study and peer review workshop sponsored by U.S. EPA (Keeler *et al.* 1993). The study notes that there are several ongoing activities to estimate emissions of toxic substances including mercury and that existing information is incomplete and often contradictory. Thus, present estimates can only serve as an indication of the amount emitted.

Since consumer goods are distributed according to population, the major population centers are "hot spots" in the spatial distribution of mercury in North America. The major power plants are concentrated in a belt from Missouri, through Illinois, Indiana, Michigan, Ohio, West Virginia and Pennsylvania. Other large plants are located in Tennessee and Florida. The major emissions from smelters in Canada are confined to a few locations in Manitoba and Ontario, while the major complex source in the United States is located in Arizona. Several waste incinerators are located in the vicinity of the lakes, primarily in the United States. Table 4 includes national estimates from the mid-1980s. Mercury had been added to much of the latex paint made over the past few decades as a mildew retardant. Most of the mercury is no longer added to latex paint so this source is expected to decrease as current stock is depleted. Assuming that mercury is removed from paint, and that other source sectors remains essentially unchanged, would reduce the estimated total emissions for 1992 in the United States and Canada to 450 tonnes and 26 tonnes, respectively.

Michigan has recently produced a draft report on mercury in the environment (Bedford *et al.* 1992). It includes a breakdown of anthropogenic mercury sources to the air as well as natural emission estimates. Table 5 is a summary of that information along with Ontario estimates from (Jaques 1987). Based on the Michigan estimate, manmade sources are still greater than natural ones and the major non-natural source is latex paint usage. As that source decreases, combustion will become more important.

There are several point sources of mercury air emissions to the atmosphere within the Lake Superior basin. The largest of these is the Copper Range Smelter at White Pine, Michigan. Stack tests indicate that it releases as much as 640 kg/year to the air (Stack Test 1990). Power plants emit about 10% of that figure (Bloxam *et al.* 1992). It has been estimated (Glass *et al.* 1990) that the sewage sludge incinerator for the Western Lake Superior Sanitary District releases between 26 and 46 kg/year of mercury to the atmosphere.

The atmospheric component plays an important role in the biogeochemical cycle of mercury (e.g. Lindquist 1991; Fitzgerald and Clarkson, 1991). As the average atmospheric residence time for total elemental gaseous mercury (assumed to be elemental) has been estimated to be over a year (Fitzgerald *et al.* 1981), inter-continental transport must be considered.

TABLE 3

ESTIMATED AND PROJECTED TRENDS OF LEAD EMISSIONS IN THE UNITED STATES AND CANADA 1970-1995

UNITED STATES (kilotonnes)													
Source Sector	1970	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989		
Transportation		59.4	46.9	46.9	40.8	34.7	15.5	3.5	3	2.6	2.2		
Fuel Combustion		3.9	2.8	1.7	1.7	0.6	0.9	0.5	0.5	0.5	0.5		
Power Generation							0.5						
Industrial							0.3						
Com/Residential								0.1					
Industrial Processes		3.6	3	2.7	2.4	2.3	2.3	1.9	1.9	2	2.3		
Solid Waste Incineration		3.7	3.3	3.1	2.6	2.6	2.6	2.6	2.6	2.5	2.3		
TOTAL	203	70.6	56.0	54.4	47.5	40.2	22.2	8.5	8	7.6	7.3		
CANADA (kilotonnes)													
Source Sector	1970	1978	1982	1985	1986	1987	1988	1989	1990	1991	1994	1995	
Transportation	12.5	9.1	7.2	5.1	3.5	2	1.8	1.5	1.1	0.05	0.05	0.05	
Fuel Combustion			0.023										
Power Generation			0.014										
Industrial			0.008										
Com/Residential				0.003									
Industrial Processes			4			2.9						2.4	
Solid Waste Incineration			0.2										
Miscellaneous			0.063										
TOTAL	19.4	14.5	11.5	9.6	8	6.1		5.6	4.7	4	4	3.8	

TABLE 4

**ESTIMATED EMISSIONS OF MERCURY IN THE UNITED STATES
AND CANADA IN THE MID-1980S**

(tonnes/year)

SOURCE SECTOR	UNITED STATES		CANADA	
	Amount	%	Amount	%
Utility Coal	113	17	3	10
Metal Smelting	51	8	14	45
Incineration	104	16	2	6
Paint Application	202	31	5	16
Other Products	150	23	1	3
Other Sources	30	5	6	19
TOTAL	650	100	31	100

TABLE 5

MERCURY AIR EMISSIONS IN MICHIGAN AND ONTARIO

(tonnes/year)

SOURCE CATEGORY	Michigan	Ontario	
Fuel Combustion			
Coal	4.5	1	
Oil	0.3	-	
Incineration	3.7	1	
Industrial Processes	1.1	1	
Area Sources			
Latex Paint Usage	4.7	2	
Other	2.8	-	
Total Anthropogenic	17.0	5	
Natural	10.9	-	
Total	27.9	-	

Source: Bedford *et al.* 1992
Jaques 1987

The initial speciation of emitted mercury, as well as atmospheric chemistry influences the atmospheric half-life. Primary emitted species are considered to be elemental mercury vapour, divalent (+2) mercury and particulate mercury (Petersen 1992). Although the atmospheric chemistry is not fully understood, in-cloud oxidation of elemental mercury is considered important (e.g. Petersen 1992).

The speciation of emitted mercury, as well as the relative contribution of the total emission from a source are highly dependent on the process, process feed and conditions as well as on where the measurements are taken, e.g. in stack, cooled exhaust (Lindquist *et al.* 1991).

Existing measurements are difficult to generalize and can only serve as an indication of the emission. The factors shown in Table 6 are taken from Petersen (1992).

Little information is available on the size distribution, the physical structure and chemical composition of the particle, which also influence the residence time.

Model calculations by Bloxam *et al.* (1992), where the comprehensive Acid Deposition and Oxidants Model (ADOM) was adapted for simulation of the behaviour of mercury, clearly show high deposition of divalent mercury close to the source, while the other species are removed over longer distances. Studies in Europe show similar results (Petersen 1992). The deposition patterns are very sensitive to the initial speciation. Local strong sources emitting divalent mercury could have a considerable impact on the lakes. As mercury appears to be predominantly emitted as mercury vapour, sources far beyond the lakes could have an impact on the lakes. Sensitivity study shows non-linear response in deposition to changes in emissions (Bloxam *et al.* 1992). A factor of two change in emission resulted in a change in air concentration of elemental and particulate mercury of 40-80% near strong sources. Remote sites experienced a change by 10-20%. Total wet deposition changed by 50-90%. The calculations were based on the inventory by Voldner and Smith (1989).

Although, to elucidate source/receptor relationships clearly requires considerable improvements in emissions inventories, the calculation shows that to achieve "virtual elimination," controls must extend beyond the basin. As the global background concentration is rising, mercury emissions should be controlled on a global basis.

PCB

Although production of PCBs was halted in 1977, over 300 kilotonnes of PCBs are still in use in closed systems. Releases do occur, however, due to fires, spills and leakages. More than 100 kilotonnes have been disposed of in landfills from which leakage and evaporative losses occur. Emissions may also result from incomplete incineration of discarded products. Because of the nature of these sources, emissions are difficult to quantify. Based on limited information, Johnson *et al.* (1992) estimated emissions from the various sources in eastern North America. These estimates, which are shown in Table 7, do not include emissions from diffuse sources such as contaminated soils and water bodies. It has been estimated that 900 tonnes/year of PCBs cycle annually through the atmosphere over the United States. From the areas where PCBs are still in use, leaks and spills occur from which PCBs may evaporate or escape on resuspended particles.

TABLE 6

SPECIATION OF MERCURY AS A FUNCTION OF SOURCE CATEGORY

	Hg	Hg ⁺²	Hg
SOURCE	GAS	GAS	PARTICULATE
	%	%	%
Coal fired power plants	75	20	5
Residential/commercial and industrial fuel combustion	75	20	5
Non-ferrous smelters	90	10	-
Chlor-alkali production	45	45	10
Waste and sewage sludge incineration	20	75	5
Other sources, such as consumer goods, paint application	100	-	-

TABLE 7

PCB EMISSIONS IN EASTERN NORTH AMERICA

SOURCE CATEGORY	ESTIMATED EMISSIONS (kg/year)
Electric Power Generation	337
Industrial Fuel Combustion	113
Subtotal	451
Solid Waste Incineration	
Municipal Waste Incineration	11
Sewage Sludge Incineration	4
Industrial Waste Incineration	7
Comm/Institutional Waste Incineration	3
Waste Oil Combustion	17
Subtotal	42
Open Sources	
Res/Indus./Com. On-Site Incineration	8
Transformers	440
Municipal Refuse-Landfill	69
Subtotal	517
Overall Total	1,010

Source: Johnson *et al.* 1992

PCBs may evaporate slowly from products such as inks and plasticizers into which they were incorporated. For those PCBs currently disposed of or in storage awaiting disposal or incineration, leaks may also occur. The leaks and spills from open sources, especially transformers, appear to be the largest sources to the environment.

Other sources of atmospheric PCBs are the emissions from municipal waste landfills and incinerators. Large amounts of PCBs were used in many consumer products, some of which are still in use. The disposal of these products, including capacitors in fluorescent light fixtures, consumer electronics, refrigerators, washing machines, and air conditioners is unrestricted. By 1978, it was estimated that municipal and industrial wastes containing 140 kilotonnes of PCB had been received by United States landfills. Murphy *et al.* (1985) studied the municipal waste-related sources for the Great Lakes region and estimated that the annual PCB emissions from landfills in the United States are between 10 and 100 kg/year.

When municipal waste is incinerated, the temperatures usually do not reach the destruction temperature of PCBs, so any PCBs in the waste are likely to be emitted. Based on measured emissions, Guilford (1977) estimated annual emissions of PCBs from three major Ontario secondary sources of PCBs, two sewage sludge incinerators and one municipal refuse incinerator. Annual emissions were estimated at 3.6, 1.7 and 1.8 kg for the three facilities with an average of 2.4 kg per year, per stack. The Municipal Waste Combustion Study (Federal Register 1988) reports a current national total PCB emission estimate from this sector to be about five tonnes/year.

INDUSTRIAL PROCESSES

Many of the industrial processes that release lead, mercury and PCBs to the Lake Superior ecosystem have been discussed in the previous section as emissions to the air. Primary sources of these chemicals resulting in water effluents are not currently found in the Lake Superior basin. Industrial processes that generate loadings of lead, mercury and PCB to Lake Superior are the result of contact with impurities such as the iron, copper and gold mining operations or spills and breakage such as might occur at electrical utilities. An important source of mercury was chlor-alkali plants which produced caustic soda and chlorine gas, but all facilities in the Lake Superior basin have been closed.

To determine which industrial processes were in use in the Lake Superior basin, facilities reporting under U.S. EPA's National Pollutant Discharge Elimination System (NPDES) and the Ontario Ministry of the Environment's Industrial Monitoring Information System (IMIS) and Municipal/Industrial Strategy for Abatement (MISA) were examined. A total of 73 facilities were found to have effluent flows to the lake for water year 1990 and were thus assumed to be active. Table 8 is a breakdown of the types of activities the industrial facilities are involved in.

Since this report is limited to three parameters, lead, mercury, and PCB, not all of the industrial facilities listed are considered to be sources. Facilities in this list were determined to be a source for the compounds of concern when actual concentration or loading information could be located for the facility or concentration or loading information exists for another Great Lakes facility with the same Standard Industrial Classification (SIC) code. In the United States, the SIC was developed for use in the classification of establishment by type of activity in which they are engaged. A similar classification scheme exists for Canadian facilities. The Canadian industrial classifications have been translated into the United States equivalent for industrial facilities in the Great Lakes basin. Fifty-one of the 73 facilities are known or suspected sources of one or more of the compounds.

Figure 2 shows the final list of sources by industrial category and Figure 3 shows what compound(s) each facility is a source of. Table 9 is a list of the facilities included in Figures 2 and 3.

TABLE 8

INDUSTRIAL ACTIVITIES IN THE LAKE SUPERIOR BASIN

ACTIVITY	NUMBER OF FACILITIES
Mining Related	30
Pulp and Paper	10
Electric Power	8
Fish Hatcheries	6
Railway Related	5
Petroleum Related	4
Wood Products	2
Wood Preserver	1
Other	7

FIGURE 2

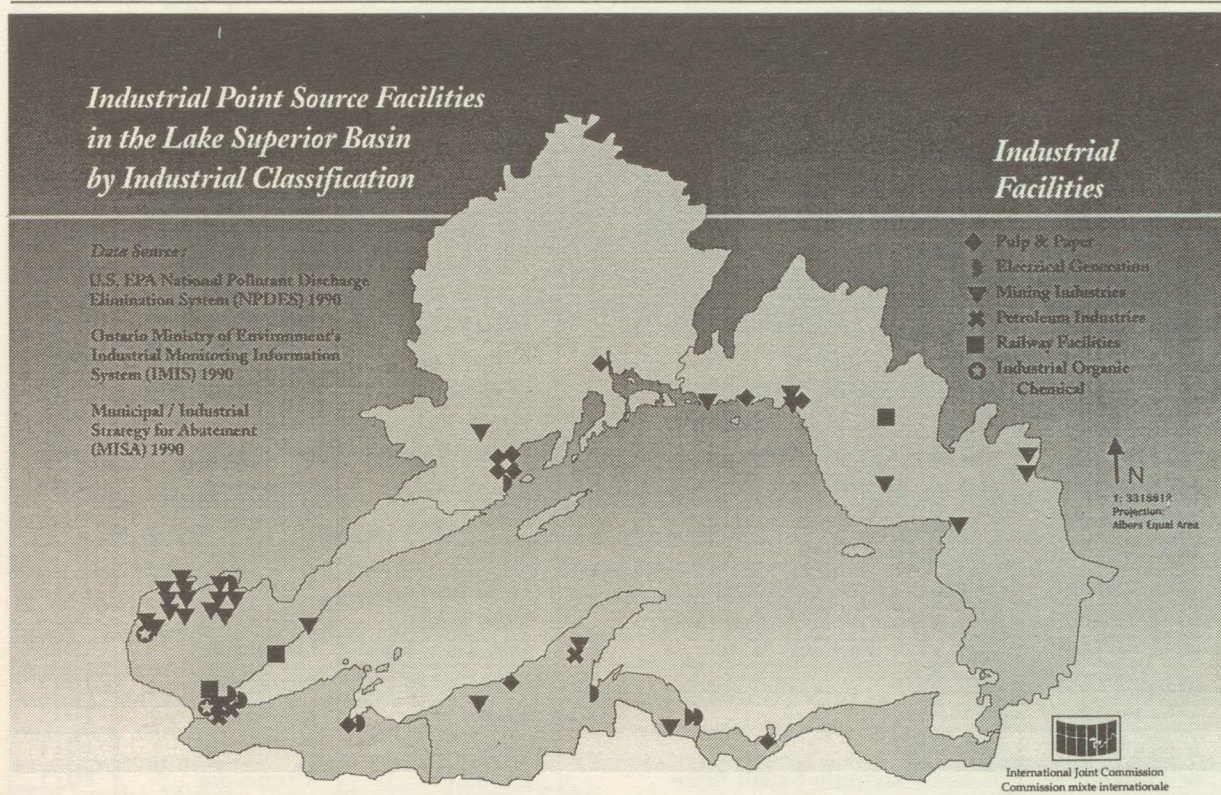


FIGURE 3

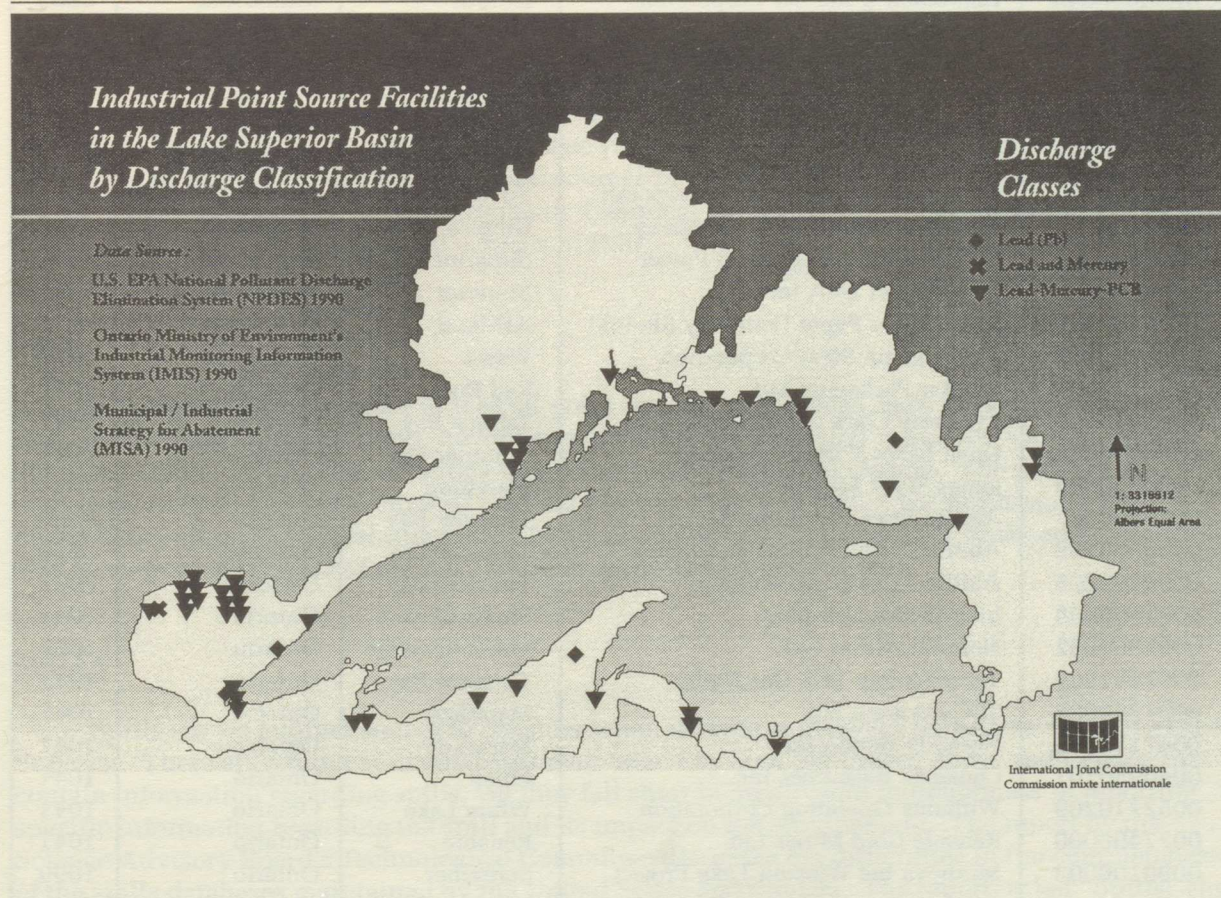


TABLE 9

**POTENTIAL INDUSTRIAL SOURCES OF LEAD, MERCURY OR PCB
IN THE LAKE SUPERIOR BASIN**

NPDES/IMIS	FACILITY NAME	CITY	JURISDICTION	SIC
MI0000892	Kimberly Clark Munising Paper	Munising	Michigan	2621
MI0006076	Marquette Bd. of Power & Light	Marquette	Michigan	4911
MI0006092	UP Power L'Anse	L'Anse	Michigan	4911
MI0006106	Wisconsin Electric Marquette	Marquette	Michigan	4911
MI0006114	Copper Range Company	White Pine	Michigan	1021
MI0006122	Stone Container	Ontonagon	Michigan	2611
MI0041807	Callahan Mining Ishpeming	Marquette	Michigan	1021
MI0044474	Range Oil and Gas Company	South Range	Michigan	5171
MI0045845	Michcan Copper Company	Centennial Hts	Michigan	1021
MN0000361	Duluth, Missabe and Iron Range Co	Two Harbors	Minnesota	4011
MN0000990	Minnesota Power	Hoyt Lakes	Minnesota	4911
MN0001015	Minnesota Power	Duluth	Minnesota	4911
MN0001465	Hibbing Taconite Company	Hibbing	Minnesota	1011
MN0002208	LTV Steel Mining Corporation	Hoyt Lakes	Minnesota	1011
MN0003336	LTV Steel Stephens Mine	Mountain Iron	Minnesota	1011
MN0042536	LTV Steel	Hoyt Lakes	Minnesota	1011
MN0042544	LTV Steel	Hoyt Lakes	Minnesota	1011
MN0042552	LTV Steel	Hoyt Lakes	Minnesota	1011
MN0044482	Eveleth Taconite Expan Mine	Eveleth	Minnesota	1011
MN0044946	Eveleth Taconite Expan Mine	Eveleth	Minnesota	1011
MN0049018	Duluth, Missabe and Iron Range Co	Two Harbors	Minnesota	4011
MN0049760	Hibbing Taconite Company	Hibbing	Minnesota	2869
MN0050644	Haarmann & Reimer Corporation	Duluth	Minnesota	2869
MN0051071	LTV Steel	Hoyt Lakes	Minnesota	1011
MN0051233	U.S. Steel Corporation (East)	Mountain Iron	Minnesota	1011
MN0051241	U.S. Steel Corporation (West)	Mountain Iron	Minnesota	1011
MN0052311	Inland Steel Mining	Virginia	Minnesota	1011
MN0052493	U.S. Steel Corporation	Mountain Iron	Minnesota	1011
MN0055301	Cyprus Northsore Mining Corporati	Silver Bay	Minnesota	1011
WI0002887	Northern States Power Company	Gingles	Wisconsin	4911
WI0003051	Superior Water Light and Power	Superior	Wisconsin	4911
WI0003085	Murphy Oil USA Inc	Superior	Wisconsin	2911
WI0003140	James River Paper Company (de-ink)	Ashland	Wisconsin	2621
0000040105	The Algoma Steel Corporation	Wawa	Ontario	1011
0000140202	Domtar Packaging Ltd.	Red Rock	Ontario	2611
0000830000	Kimberly Clark of Canada	Terrace Bay	Ontario	2611
0000840009	Great Lakes Forest Products	Thunder Bay	Ontario	2621
0000850008	James River Marathon	Marathon	Ontario	2611
0000860007	Abitibi Price (Thunder Bay)	Thunder Bay	Ontario	2621
0000860106	Abitibi Price (Provincial Papers)	Thunder Bay	Ontario	2621
0000860205	Abitibi Price (Fort William)	Thunder Bay	Ontario	2621
0001690908	Inco Metals Company	Shebandowan	Ontario	1041
0001800002	Noranda Mines Ltd	Manitouwadge	Ontario	1081
0001841907	Thunder Bay TGS Ont Hydro	Thunder Bay	Ontario	4911
0031750003	TEC Corunna Ltd	Marathon	Ontario	1041
0042110205	Noranda Hemlo Inc.	Marathon	Ontario	1041
0046950101	Canamax Resources Inc.	Finan	Ontario	1041
0052710209	Williams Operating Corporation	White Lake	Ontario	1041
0077400000	Renabie Gold Mines Ltd.	Renabie	Ontario	1041
0096100003	Minnova Inc Winston Lake Project	Schreiber	Ontario	1099

In addition to regulated facilities, U.S. EPA's Toxic Release Inventory (TRI) was examined. Though the TRI does not indicate that any facilities are releasing lead, mercury, or PCB in the Great Lakes basin, several of the industries are in the same industrial category as facilities reporting releases of these compounds. In all, there were 35 facilities reporting under TRI that are in the Lake Superior basin. Seven of these facilities are permitted under the NPDES program. The TRI also provides information on industries with transfers to sewage treatment plants. A wood products industry, two pulp and paper mills, and an industrial organics facility have releases to the Western Lake Superior Sanitary District. In addition, an electrical components industry discharges to the Hibbing Sewage Treatment Plant (STP), a machine tool accessories facility releases to the Chisholm STP, and an explosives industry has releases to the Marquette STP. The remaining facilities have air emissions or transfer material to other facilities, such as landfills.

PCB

Very little actual point source data exist for PCB. However, based on industrial classification, 44 industrial facilities are believed to be sources of PCB. The industrial classes are Mining, Pulp and Paper, Oil Refining, and Electric Power Generation. One of the reasons for suspecting these industries as sources of PCB is due to the continued use or storage of old electrical equipment. Though the manufacture of PCBs ceased in 1977, there continue to be significant quantities stored and in use throughout the Great Lakes basin, including the Lake Superior basin. Some Great Lakes point source data do exist for the Pulp and Paper industry, the Oil Refining industry, and the Electric Power Generation industry, justifying the inclusion of these facilities as suspected sources. Documentation exists showing the use of electrical equipment containing PCB by the Mining industry (Thompson 1993).

Mercury

As with PCB, very little actual point source data exist for mercury. Most of the suspected industrial point sources of mercury are based upon locating other Great Lakes facilities of the same industrial class for which actual mercury data could be found. Forty-six facilities in the Mining, Pulp and Paper, Oil Refining, Electric Power Generation, and Industrial Inorganic Chemicals industrial classes are suspected sources of mercury to the Lake Superior basin. With the exception of the two Industrial Inorganic Chemical facilities, the suspected sources of mercury are the same as the suspected sources of PCB.

Lead

In general, there are more industrial point source data for lead than for either mercury or PCB. In the Lake Superior basin, however, most of the 50 suspected industrial sources of lead are based upon typical concentrations found for certain industrial classes. The industrial classes that are suspected sources of lead are Mining, Pulp and Paper, Oil Refining, Electric Power Generation, Industrial Inorganic Chemicals, Petroleum Stations, and Railroad Operations. The 46 suspected sources of mercury are also suspected sources of lead.

SPILLS

Spills are yet another source to consider when looking at the ways pollutants can enter Lake Superior. There are a number of databases maintained by both the United States and Canada that contain information regarding spills, yet they fall short in quality and thoroughness in reporting specific information regarding the spill and its impact on the environment. The report by the Science Advisory Board's Technological Committee discusses the difficulties in the completeness of the spills databases maintained by the United States and Canada. The report, titled "Spills: The

Human-Machine Interface, 1988" summarizes two workshops held in 1986 and 1987.

To provide an example of some of the information that can be found, two data bases, one from the United States and one from Canada, were considered. Example retrievals are presented in Tables 10 and 11. The United States data (Table 10) were retrieved from U.S. EPA's Emergency Response Notification System (ERNS) for 1991 - 1992 and the Canadian data (Table 11) from the Canadian Coast Guard (CCG) for 1987 - 1991. There was an additional data search performed on the Environment Canada National Analysis of Trends in Emergencies System (NATES) database, but the last recorded spill in Lake Superior was in 1985.

The data bases, ERNS and CCG, contain information on spills from marine transport as well as over-land transport, although neither records the actual loadings of specific chemicals to the Great Lakes. There are a few cases in the CCG database in which the spill of a known chemical is recorded, such as the sodium hydroxide. But the recording of the various chemicals that make up a material (i.e. components of oil or gasoline) are usually lacking. Many records in the ERNS database are incomplete. The main focus tends to be on the number of spills, amount of material spilled, and action taken. The absence of pertinent information severely hinders the ability to estimate the loadings of mercury, lead, and PCBs. Spills of mercury and PCB on land may be part of air emissions since they are volatile. Direct spills to the lake are important waterborne sources.

LANDFILLS

The Resource Conservation and Recovery Act (RCRA) provides documentation on open dumps that do not comply with U.S. EPA's Criteria for Classification of Solid Waste Disposal Facilities and Practices. Associated with the RCRA is the Resource Conservation and Recovery Information System (RCRIS) that contains listings of all non-compliance open dump and hazardous waste sites. A total of 35 dumps within the United States portion of the Lake Superior basin were detected to be in non-compliance. Table 12 lists these dumps with their associated non-compliance category codes.

The Lake Superior Source Investigation Project concentrates on three parameters consisting of lead, mercury, and PCB. The listings within RCRIS do delineate the potential hazards the dump site has for the environment. They do not estimate loading rates for the three specific parameters of interest.

Environment Canada published a report in 1988 listing all the approved PCB storage facilities in Ontario. The document is titled "Ontario Inventory of Approved PCB Storage Sites". Though these sites are permitted to store PCB, there is the potential for contamination to the area adjacent to them.

Thunder Bay and Algoma Counties occupy the north shore of Lake Superior. In these counties a total of 49 PCB storage sites are located, 39 in Thunder Bay County and 10 in Algoma County. Of these 49 sites, 29 lie within the Superior Basin. Air emissions from these sites are a concern as well as runoff to the lake or a tributary.

HAZARDOUS WASTE SITES

This section identifies the density of recorded hazardous waste sites, for both the United States and Canada, on a county basis. These are sites known to house hazardous materials that are not found in a sanitary landfill. This is available for the entire Great Lakes basin; however, the focus is on those counties that lie within the Lake Superior basin. The lack of accurate coordinates of each site and the large number of sites for some counties eliminated the possibility to determine the exact location of sites that are within the basin for geographical display purposes.

TABLE 10

EXAMPLE ERNS RETRIEVAL 1991-1992

ERNS (EMERGENCY RESPONSE NOTIFICATION SYSTEM) U.S. EPA

Date	Material Spilled	Amount Spilled	County/State	Cause	Action
01/23/91	Waste Oil/ Lubricants	Unknown	Houghton/MI	other	None
04/23/91	Unknown - Material	100.00 gal.	St. Louis/MN	Discharge material from facility.	Water samples taken daily
05/31/91	Hydraulic Oil	2.00 gal.	Douglas/WI	M/V Alpena/ stern tube.	Company crew cleaning up
06/22/91	Oil,Fuel: NO. 6	0.00	Chippewa/MI	other	Vessel bound for Waiska Bay; pollution at this time.
07/04/91	Oil: Diesel	125.00 gal.	Marquette,MI	Car hit truck's fuel tank.	Ditch to Lake Superior was boomed. Oil was collected with sorbent pad.
07/12/91	Unknown Oil	0.00	Marquette,MI	Unknown sheen sighting	None
08/31/91	Gasoline/Auto	9.00 gal.	Lake/MN	21' cruiser washed onto rocks.	None, when weather calms will attempt clean-ups.
02/15/92	Oil, Fuel No. 2	150.00 gal.	St. Louis, MN	Fuel storage tank released fuel into storm sewer.	Applied sorbents and deployed booms to contain the material.
06/09/92	Unknown Oil	0.00	Cook, MN	Unknown sheen sighting, size 10'X40'.	Deployed sorbent boom
09/23/92	Unknown Oil	0.00	Ashland,WI sighting, size unknown.	Unknown sheen	None

TABLE 11

**CANADIAN COAST GUARD, EMERGENCY OPERATIONS BRANCH
SUMMARY REPORTS FOR 1988 - 1991**

1988					
Petroleum		Hazardous Materials		Others	
Source	Total Spills	Source	Total Spills	Source	Total Spills
Ship	1	Ship	0	Ship	0
Shore	0	Shore	0	Shore	0
Mystery	4	Mystery	0	Mystery	1
	Volume Spilled		Volume Spilled		Volume Spilled
Litres	318	Litres	0	Litres	0
Unknown	3	Unknown	3	Unknown	1

1989					
Petroleum		Hazardous Materials		Others	
Source	Total Spills	Source	Total Spills	Source	Total Spills
Ship	6	Ship	0	Ship	0
Shore	3	Shore	4	Shore	0
Mystery	2	Mystery	0	Mystery	1
	Volume Spilled		Volume Spilled		Volume Spilled
Litres	10675	Litres	22500 *	Litres	0
Unknown	5	Unknown	3	Unknown	1

* Sodium Hydroxide spill 22,500 litres, Thunder Bay.

1990					
Petroleum		Hazardous Materials		Others	
Source	Total Spills	Source	Total Spills	Source	Total Spills
Ship	2	Ship	0	Ship	0
Shore	3	Shore	1	Shore	1
Mystery	0	Mystery	0	Mystery	0
	Volume Spilled		Volume Spilled		Volume Spilled
Litres	182	Litres	4091409 *	Litres	1727518 "
Unknown	2	Unknown	0	Unknown	0

* Sodium Sulphide spill 409,149 litres, James River Marathon, Pulp Mill.

" Clarified Effluent spill, 1,727,480 litres, James River Marathon Pulp Mill.

1991					
Petroleum		Hazardous Materials		Others	
No. of Spills	Total Spills	No. of Spills	Total Spills	No. of Spills	Total Spills
Unknown Amnt	1	Unknown Amnt	0	Unknown Amnt	0
Known Amnt	0	Known Amnt	0	Known Amnt	0
Total Amt Known	0	Total Amt Known	0	Total Amt Known	0

Note: The "Others" category includes occurrences such as sewage discharge, garbage, waste water, and unknown substances that are not considered either petroleum or hazardous materials. Reporting format for 1991 did not include break down in regards to source type and volume spilled.

TABLE 12

INVENTORY OF OPEN DUMPS IN THE UNITED STATES

FACILITY	CITY	COUNTY	STATE	CATEGORY
Hulbert Twp. Disp	Hulbert	Chippewa	MI	06-07-09
Morning Star Disp.	Strongs Corner	Chippewa	MI	06-09
Bessemer Dump	Bessemer	Gogebic	MI	06-07-09-11
Ironwood Dump	Ironwood	Gogebic	MI	03-06
Airport Site	Ironwood Twp.	Gogebic	MI	06-07-10
Marenisca Twp. Dump	Marenisco Twp.	Gogebic	MI	06-07-09-11
Bessemer Dump #2	Ramsay	Gogebic	MI	6-7-9-11
Wakefield Dump	Wakefield	Gogebic	MI	06
Eagle River Dump	Eagle River	Keweenaw	MI	06-07-09-11
Laird Twp. Disposal	Laird Twp	Houghton	MI	06-07-09-11
Copper Harbor	Copper Harbor	Keweenaw	MI	06-07-09-11
Lac La Belle	Lac La Belle	Keweenaw	MI	06-11
Gay Dump	Sherman Twp.	Keweenaw	MI	06-07-09
Newberry Disp.	Newberry	Luce	MI	06-07-09
Sand Disposal	Sands	Marquette	MI	09
Skandia W Branch	Skandia	Marquette	MI	07-09
Bergland Dump	Bergland	Ontonagan	MI	06-07-09
Mass Dump	Greenland	Ontonagan	MI	06-07-09
Tri Twp. Dump	Might Twp.	Ontonagan	MI	06-07-09-11
Village of Ontonagon	Ontonagon	Ontonagan	MI	01-03-06-07-09-11
Rockland Dump	Rockland	Ontonagan	MI	01-03-06-07-09-11
Camp Lake Dump	Silver Lake	Ontonagan	MI	06-07-09-11
Trout Creek Dump	Trout Creek	Ontonagan	MI	06-07-09
Grand Portage	Grand Portage	Cook	MN	06-11
McKinley Sanitary	McKinley	St Louis	MN	06
Duluth SLF	Duluth	St Louis	MN	10
Hibbing Dump	Hibbing	St Louis	MN	03-06
Ashland Landfill	Gimsles	Ashland	WI	03-06
Superior Sanitary	Superior	Douglas	WI	03

Code	Category	Code	Category
01	Flood Plains	07	Air
02	Endangered Species	08	Gases
03	Surface Water	09	Fires
04	Ground Water	10	Bird/Aircraft Hazard
05	Application to Food-Chain Cropland	11	Access
06	Disease		

The sources of these data were the U.S. EPA and the Ontario Ministry of the Environment. The United States data were a combination of both the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, also known as Superfund) and the RCRA databases.

In the United States, the CERCLA data base is maintained to provide an automated inventory of abandoned, inactive, or uncontrolled hazardous waste sites that can be utilized to track progress in site clean-ups. The RCRA data base, on the other hand, is maintained to provide control of the transportation, generation, and management of hazardous waste. Table 13 lists the counties within the basin, the number of waste sites, and the calculated value of sites per unit area.

Figure 4 is the map depicting the values found in Table 13. This approach assumes uniformity across the entire county which provides a better understanding of the density of hazardous waste sites rather than the mere number of waste sites in each county. The comparison between the Lake Superior basin and the rest of the Great Lakes shows a low to very low density over most of the basin.

RAW MATERIAL STORAGE

All of the other categories considered in this chapter deal with products and by-products that are either intentionally or accidentally introduced to various pathways. However, since raw materials such as ore and coal are contaminated with many trace metals, the storage and handling of these materials can be a source of lead and mercury. Unless raw materials are completely isolated from the environment during storage, lead and mercury can be washed out during rainfall and mercury may volatilize. An example of the necessity of isolating these materials from the environment is the covering of salt piles used for highway salting.

Many ore and coal piles are not covered while being stored. This is because the raw material is not seriously damaged by the elements and the storage is only temporary. As an example of the magnitude of coal pile runoff at an electric power generating plant, Thompson (1993) estimated lead and mercury loadings from an Ontario Hydro facility in Atikokan, Ontario. Lead loadings were estimated to be 0.22 kg/year, while mercury loadings were estimated at 0.0005 kg/year. These loads would enter the lake via the surface runoff pathway if the coal pile was located on the lake shore or the tributary pathway if the pile was upstream. It is difficult to estimate the total loading in this category because not all raw material storage piles are monitored. Some are probably not sampled at all while others are sampled after mixing with other waste streams on the site.

DOMESTIC USES

This source category includes activities within the home that contribute to loadings of lead, mercury and PCBs. However, major domestic uses have already been considered under air emissions: coal and oil combustion and latex paint usage. There are some domestic activities which contribute significant amounts to loadings which may not result in air emissions (i.e. they would reach the lake by water pathways). This is especially true for mercury. No attempt has been made to estimate the total load to Lake Superior from this source category.

Lead

The two major sources of lead in the home are lead-based paint and plumbing. Both of these are more of a health concern than a loadings problem. For this reason, both of these uses are being phased out and this source should continue to decrease. The short-term problem would be for disposal of unused lead-based paint in municipal refuse collections or sewers. This illustrates the importance of household hazardous waste collection which many communities have implemented.

TABLE 13

NUMBER OF HAZARDOUS WASTE SITES IN THE LAKE SUPERIOR BASIN

STATE	COUNTY	TOTAL AREA km ²	TOTAL AREA mi ²	# WASTE SITES	DENSITY	
					#/km ²	#/mi ²
Michigan	Alger	2,394	924	3	0.0013	0.0032
Michigan	Baraga	2,372	916	5	0.0021	0.0055
Michigan	Chippewa	3,828	1,478	17	0.0044	0.0115
Michigan	Gogebic	2,953	1,140	4	0.0014	0.0035
Michigan	Houghton	2,694	1,040	2	0.0007	0.0019
Michigan	Iron	3,131	1,209	7	0.0022	0.0058
Michigan	Keweenaw	903	349	1	0.0011	0.0029
Michigan	Luce	2,445	944	2	0.0008	0.0021
Michigan	Marquette	4,844	1,870	19	0.0039	0.0102
Michigan	Mackinac	2,642	1,020	8	0.0030	0.0078
Michigan	Ontonagon	3,448	1,331	6	0.0017	0.0045
Michigan	Schoolcraft	3,188	1,231	17	0.0053	0.0138
Minnesota	Aitkin	5,185	2,002	1	0.0002	0.0005
Minnesota	Carlton	2,268	876	8	0.0035	0.0091
Minnesota	Cook	4,195	1,620	1	0.0002	0.0006
Minnesota	Itasca	7,559	2,919	5	0.0007	0.0017
Minnesota	Lake	5,979	2,308	1	0.0002	0.0004
Minnesota	Pine	3,686	1,423	4	0.0011	0.0028
Minnesota	St. Louis	17,451	6,738	36	0.0021	0.0053
Wisconsin	Ashland	2,568	991	1	0.0004	0.0010
Wisconsin	Bayfield	3,914	1,511	0	0	0
Wisconsin	Douglas	3,407	1,315	6	0.0018	0.0046
Wisconsin	Iron	2,090	807	1	0.0005	0.0012
Wisconsin	Vilas	2,662	1,028	1	0.0004	0.0010
Ontario	Algoma	50,907	19,655	9	0.0002	0.0005
Ontario	Thunder Bay	113,435	43,798	10	0.0001	0.0002

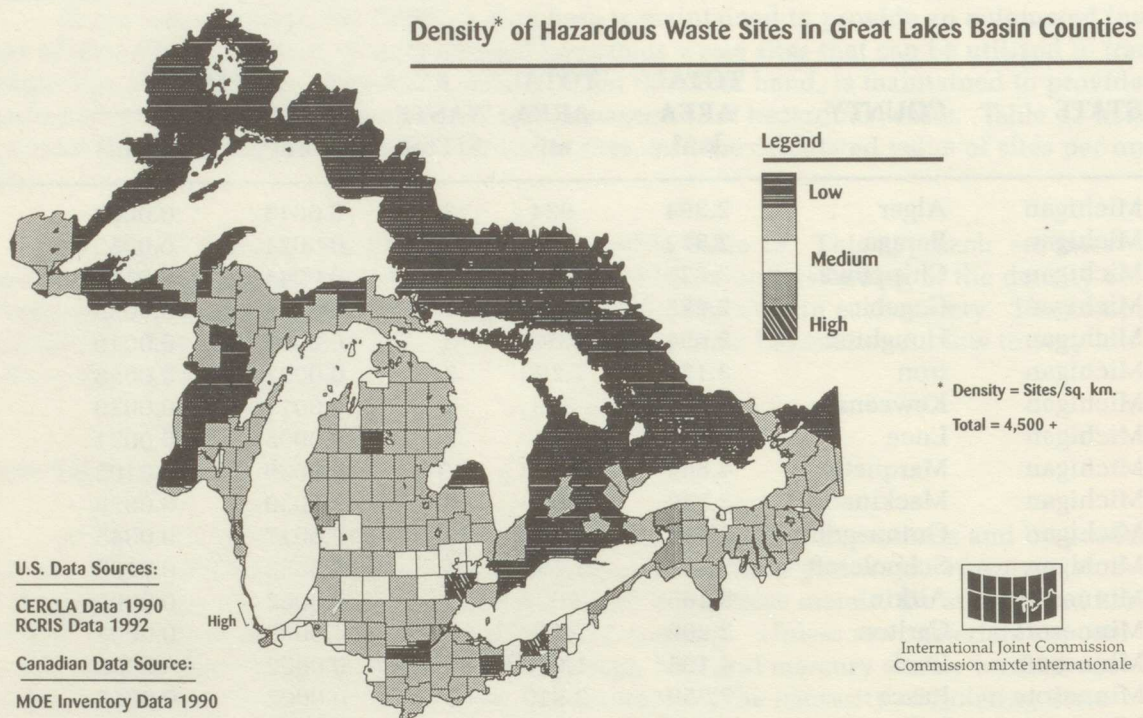
Source:

Stats Canada 1991 census, U.S. CERCLA updated 1990;

U.S. RCRIS updated 1992;

Canada, Ontario Inventory MOE - Health and Welfare updated 1990.

FIGURE 4



Mercury

Besides fuel combustion and latex paint usage, there are several domestic uses of mercury. These include instruments such as thermometers, electrical apparatus such as switches and mercury arc lamps, mirrors, batteries, dental amalgams, lubricants, caulks and coatings. The route by which most of the mercury from these uses would enter the lake is by atmospheric transport and deposition, but batteries, in particular, would enter through the municipal waste stream (sewers or garbage collection). Glass *et al.* (1990) estimate that 150-300 g of mercury are contained in about 100 tons of processed garbage in Duluth. Reimann (1986) reports that over 50% of the mercury in European domestic garbage comes from used batteries.

PCBs

There are no known current domestic uses of PCBs.

AGRICULTURAL USES

Mercury is the only substance of the three considered here that has a significant agricultural use. It is used as a slimicide and an ingredient in some agricultural chemicals. It is also a contaminant in wood preservatives. The main route for entry to the lake would be air transport but the potential exists for contribution to surface runoff. No attempt has been made to estimate the total loading to Lake Superior from this source category.

IV. PATHWAYS

INTRODUCTION

This section describes the pathways by which contaminants reach the lake. It includes the estimates of loadings made as well as alternatives in some cases. The methodology of estimation is briefly described.

A further distinction for pathways is necessary between direct and indirect routes. Again, these are defined in terms of the mass balance model, so what follows is relevant to the current model. Direct pathways result in the delivery to a receiver of a waste compound without any intermediate routes. For example, if a municipal sewage treatment plant has a pipe or outfall directly to the waters of Lake Superior, then that effluent is a direct pathway. Indirect pathways may have two or more routes to the receiver. A similar sewage plant may have an outfall to a creek which flows into a river which flows to Lake Superior. The outfall would then be an indirect pathway. One very important reason to make this distinction is to avoid double counting. For example, if one sums all municipal effluents and all tributary inputs, double counting would occur because some of the effluents discharge to tributaries.

ATMOSPHERIC DEPOSITION

Deposition of contaminants to the lake surface from the atmosphere is an extremely important pathway for the Great Lakes. Deposition can be either wet (rainfall or snowfall) or dry (fallout of particles) and is measured as a flux (loading per unit area). Strachan and Eisenreich (1988) have shown that atmospheric deposition is the major pathway for many contaminants to the upper Great Lakes, especially Lake Superior. They have recently revised their flux estimates (Eisenreich and Strachan, 1992) using the most recent data and more sophisticated estimation methods. PCBs, mercury and lead continue to be input to Lake Superior primarily by atmospheric deposition. The estimates of flux have been lowered somewhat; however, the process of volatilization of PCBs and mercury was previously thought to be a net loss from the lake and more recent information indicates that there might be a net gain from absorption. This process is handled by mass balance modeling and is discussed in the chapter on receivers. The loads to Lake Superior for PCBs, mercury and lead from the atmospheric pathway are based on Eisenreich and Strachan (1992) and are summarized in Tables 14 and 15.

Dry particle deposition is estimated by:

$$F_{\text{dry}} = C_{T, \text{air}} \Phi V_d SA f_d$$

where F_{dry} is the load in kg/year for dry particle deposition

$C_{T, \text{air}}$ is the total air concentration of chemical

Φ is the fraction of chemical in the particle phase

V_d is the dry particle deposition velocity = 63,000 m/year

SA is the lake surface area = $8.21 \times 10^{10} \text{ m}^2$

f_d is the fraction of the year not raining or snowing = 0.9

For PCB, the estimates are made seasonally because of the variability of C_T , air and Φ with season.

Wet deposition is estimated by:

$$F_{\text{wet}} = C_{T, \text{rain}} P SA$$

where F_{wet} is the wet-only load in kg/year

$C_{T, \text{rain}}$ is the total concentration of chemical in rain

P is the annual precipitation intensity = 0.76 m/year

and

SA is as above

For comparison purposes, the fluxes in $\mu\text{g}/\text{m}^2/\text{year}$ are also shown in Table 14.

TABLE 14

**ATMOSPHERIC DEPOSITION ESTIMATES FOR LAKE SUPERIOR
FOR LEAD, MERCURY AND PCB**

	LEAD	MERCURY	PCB
$C_{T, \text{air}}$ (ng/m ³)	1	2	Seasonal*
Φ	1	0.03	Seasonal*
$C_{T, \text{rain}}$ (ng/L)	1,000	6	2
F (kg/year)			
- Dry	4,655.07	282.63	31.42 [†]
- Wet	62,396.00	374.38	124.79
- Total	67,051.07	657.01	156.21
Flux ($\mu\text{g}/\text{m}^2/\text{year}$)			
- Dry	56.70	3.44	0.38
- Wet	760.00	4.56	1.52
- Total	816.70	8.00	1.90

* See Table 15

[†] Mean of seasonal loads from Table 15

TABLE 15

SEASONAL AIR DEPOSITION FOR PCBs

	SUMMER	FALL	WINTER	SPRING
$C_{T, \text{air}}$ (ng/m ³)	0.4	0.2	0.1	0.2
Φ	0.01	0.03	0.11	0.03
F_{dry} (kg/year)	18.62	27.93	51.21	27.93

MUNICIPAL EFFLUENTS

In order to estimate loadings from municipal effluents two sources of information were examined. In the United States, municipal facilities obtain a permit through the National Pollutant Discharge Elimination System (NPDES). A NPDES permit specifies effluent limits and monitoring requirements. In Canada, municipal facilities go through a Certificate of Approval (CofA) process in which monitoring requirements and performance are set. There are 67 permitted or approved municipal sewage treatment facilities in the Lake Superior basin. Eighteen are lagoons, seven provide primary treatment, and 42 provide secondary or better treatment. A list of municipal facilities may be found in Table 16 and are shown geographically in Figure 5. Sewage treatment plants are not sources of contaminants, but pathways. Inputs are received from actual sources such as industrial facilities and household waste, as well as from other pathways such as urban runoff. Only one facility, the Western Lake Superior Sanitary District, has self-monitoring data for water year 1990 for the three parameters of concern, lead, mercury, and PCB. Alternative methods for estimating the loadings for the remaining facilities were employed.

Lead

The first method used to estimate lead loadings from municipal treatment plants was to determine typical concentrations and apply them to each facility's flow. The typical concentration was determined by computing the average effluent concentration of all sewage treatment plants in the Great Lakes basin. Because many of the individual values were coded as "less than," a maximum likelihood estimation was employed. The computed average concentration, 23.2 $\mu\text{g/L}$, was assigned as the typical concentration for facilities providing secondary treatment. The Municipal Pretreatment Task Force Report (1990) contains percent removal information for lagoons, primary facilities, and secondary facilities. The percent removal information was used to calculate factors that were then used to determine typical concentrations for lagoons, 26.4 $\mu\text{g/L}$, and primary facilities, 28.5 $\mu\text{g/L}$. When actual lead data did not exist for a facility, the typical concentrations were multiplied by the facility flow to estimate the load. The total lead load from municipal treatment plants was calculated to be 3,255.5 kg/year. This value may be biased high as some data that are not flagged are suspected of being "less than" the reported value.

Influent lead concentration data were also available for many municipal treatment plants in the Great Lakes basin. The average influent lead concentration was estimated with the maximum likelihood estimator and alternative effluent concentrations were calculated from Municipal Pretreatment Task Force's published percent removals. The calculated effluent concentrations are 15.5, 17.7, and 19.1 $\mu\text{g/L}$ for secondary treatment, lagoons, and primary treatment, respectively. When actual lead data did not exist the alternative concentrations were used to estimate the load. The resulting total load is 2,435.3 kg/year. This estimate, using influent lead concentrations, is probably better than the typical concentrations calculated from the effluents because there were relatively fewer flagged data in the set of influent concentrations.

A third method was also used to estimate lead loadings from municipal facilities. The suspended solids loadings were calculated and used as a basis for estimating the loadings of lead. The Municipal Pretreatment Task Force reported two typical sludge concentrations for lead (221.7 mg/kg and 313.0 mg/kg).

As part of the permit requirements, suspended solids and flow are monitored for most permitted facilities. The self-monitoring data were used to calculate annual solids loading rates. When the solids load data were not available, the monthly concentration and flow were multiplied to determine a monthly load. The annual average was computed by averaging the monthly loads. The method used to calculate the solids loads is identical to that used by the IJC (Rathke and McRae, 1989) to calculate annual phosphorus loads from municipal treatment plants. Once the solids loads were calculated for each facility, a sludge concentration of 300.0 mg/kg was applied to estimate the loading rate for lead and resulted in an estimated loading of

TABLE 16

**MUNICIPAL FACILITIES IN LAKE SUPERIOR BASIN
WITH TREATMENT TYPE**

NPDES/IMIS	FACILITY NAME	CITY	JURIS	TREATMENT TYPE
MI0020044	Munising WWTP	Munising	Michigan	Secondary
MI0020061	Portage Lake Authority WWTP	Hancock	Michigan	Secondary
MI0020125	Gogebic-Iron WW Authority WWTP	Ironwood	Michigan	Secondary
MI0020133	L'Anse WWTP	L'Anse	Michigan	Secondary
MI0020231	Newberry WWTP	Newberry	Michigan	Secondary
MI0020559	Ontonagon WWTP	Ontonagon	Michigan	Primary
MI0021202	South Range SD	South Range	Michigan	Secondary
MI0021296	Negaunee WWTP	Negaunee	Michigan	Secondary
MI0021423	USAF-K1 Sawyer AFB WWTP	Gwinn	Michigan	Secondary
MI0021440	Wakefield WWSL	Wakefield	Michigan	Lagoon
MI0023531	Marquette WWTP	Marquette	Michigan	Secondary
MI0024309	Watersmeet Township WWTP	Watersmeet	Michigan	Primary
MI0024554	USDA-Black River Rec Area WWTP	Ironwood	Michigan	Secondary
MI0036714	Interior Township WWSL	Trout Creek	Michigan	Lagoon
MI0037133	Marenisco Township WWTP	Marenisco	Michigan	Secondary
MI0043192	Superior Township WWSL	Brimley	Michigan	Lagoon
MI0044423	Ishpeming Area WWTP	Ishpeming	Michigan	Secondary
MI0045853	USDI-Isle Royale NP WWTP	Rock Harbor	Michigan	Secondary
MI0047554	Keweenaw Bay Tribe WWSL	Baraga	Michigan	Lagoon
MI0047562	Keweenaw Bay Tribe WWSL	Baraga	Michigan	Lagoon
MN0020010	Grand Marais WWTP	Grand Marais	Minnesota	Secondary
MN0020117	Chisholm WWTP	Chisholm	Minnesota	Secondary
MN0020125	Gilbert WWTP	Gilbert	Minnesota	Secondary
MN0020206	Hoyt Lakes WWTP	Hoyt Lakes	Minnesota	Secondary
MN0020494	Aurora WWTP	Aurora	Minnesota	Primary
MN0020711	Meadowlands WWSL	Meadowlands	Minnesota	Secondary
MN0021610	Biwabik WWSL	Biwabik	Minnesota	Secondary
MN0022250	Two Harbors WWTP	Two Harbors	Minnesota	Secondary
MN0022969	Buhl-Kinney WWTP	Buhl	Minnesota	Secondary
MN0023337	Eveleth WWTP	Eveleth	Minnesota	Lagoon
MN0023442	Floodwood WWTP	Floodwood	Minnesota	Secondary
MN0024031	McKinley WWTP	McKinkley	Minnesota	Primary
MN0024899	Silver Bay WWTP	Silver Bay	Minnesota	Secondary
MN0030163	Virginia WWTP	Virginia	Minnesota	Lagoon
MN0030627	Hibbing - North WWTP	Hibbing	Minnesota	Secondary
MN0030643	Hibbing - South WWTP	Hibbing	Minnesota	Lagoon
MN0040754	Beaver Bay WWTP	Beaver Bay	Minnesota	Secondary
MN0040835	Mountain Iron WWTP	Mountain Iron	Minnesota	Secondary
MN0049786	Western Lake Superior SD	Duluth	Minnesota	Secondary
MN0052230	Knife River SD	Knife River	Minnesota	Secondary
WI0020311	Mellen WWTP	Mellen	Wisconsin	Lagoon
WI0022306	Montreal WWTP	Montreal	Wisconsin	Lagoon
WI0022675	Washburn WWTP	Washburn	Wisconsin	Secondary
WI0025593	Superior WWTP	Superior	Wisconsin	Secondary
WI0028941	Knight WWTP	Ironbelt	Wisconsin	Secondary
WI0029637	Pikes Bay SD	Bayfield	Wisconsin	Secondary
WI0029653	Bayfield WWTP	Bayfield	Wisconsin	Secondary
WI0029670	Port Wing WWTP	Port Wing	Wisconsin	Secondary
WI0029947	Pence WWTP	Pence	Wisconsin	Primary

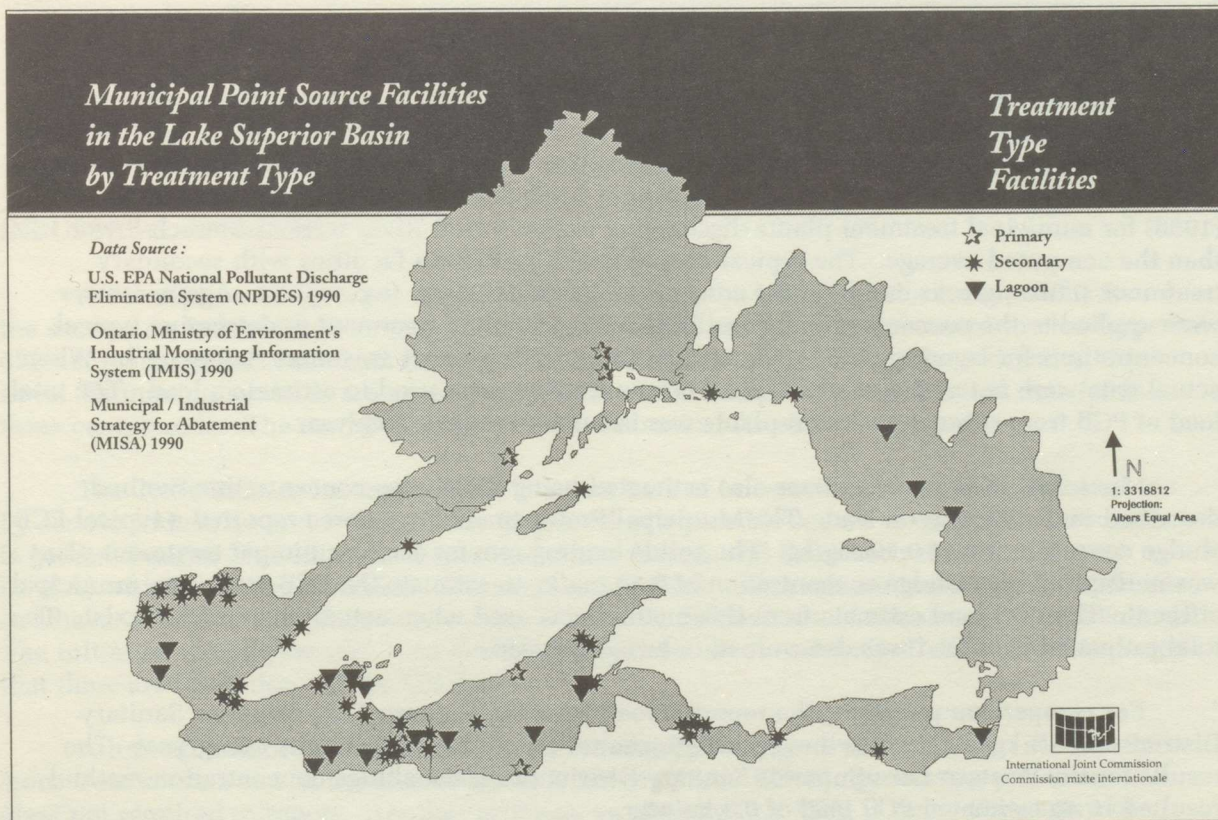
TABLE 16 - CONT'D

NPDES/IMIS	FACILITY NAME	CITY	JURIS	TREATMENT TYPE
WI0030431	Superior WWTP	Superior	Wisconsin	Secondary
WI0030759	Madeline SD	LaPoint	Wisconsin	Lagoon
WI0030767	Ashland WWTP	Ashland	Wisconsin	Secondary
WI0031615	Drummond SD	Drummond	Wisconsin	Lagoon
WI0031704	Saxon SD	Saxon	Wisconsin	Secondary
WI0031747	Anderson SD	Upson	Wisconsin	Secondary
WI0032069	Clover SD	Clover	Wisconsin	Lagoon
WI0035131	Grandview SD	Grandview	Wisconsin	Lagoon
WI0036544	Bad River Indian Reservation WWSL	Odanah	Wisconsin	Lagoon
WI0061336	Bell SD	Cornucopia	Wisconsin	Lagoon
0010000454	Wawa WWSL	Michipicoten	Ontario	Lagoon
0010002112	Schreiber WPCP	Schreiber	Ontario	Secondary
0010002522	White River WWSL	White River	Ontario	Lagoon
0020000471	Marathon WPCP	Marathon	Ontario	Secondary
0020000514	Nipigon WPCP	Nipigon	Ontario	Primary
0020001817	Red Rock WPCP	Red Rock	Ontario	Primary
0020001988	Manitouwadge WWSL	Manitouwadge	Ontario	Lagoon
0020004805	Thunder Bay WPCP	Thunder Bay	Ontario	Primary

ABBREVIATIONS:

- SD - SANITARY DISTRICT
- WPCP - WATER POLLUTION CONTROL PLANT
- WWSL - WASTE WATER SEWAGE LAGOON
- WWTP - WASTE WATER TREATMENT PLANT

FIGURE 5



1,547.5 kg/year. Actual data were used for the Western Lake Superior Sanitary District.

For comparison purposes, the reported load from the Western Lake Superior Sanitary District was 770.9 kg/year, which is identical to the results from the typical influent concentration method. The results for the Western Lake Superior Sanitary District using the sludge concentration method resulted in an estimated lead load of 194.5 kg/year.

Mercury

Available mercury effluent concentration data were not of sufficient quality to apply the first method described above, determining a typical effluent concentration. However, influent concentration data were available for many Great Lakes facilities and an average, or typical, influent concentration was calculated. The percent removal information from the Municipal Pretreatment Task Force report was used to calculate typical effluent concentrations for lagoons, 0.10 µg/L, primary treatment, 0.16 µg/L, and secondary treatment, 0.13 µg/L. As in the case of lead, the typical concentrations were used in estimating loadings when actual data did not exist. The estimated mercury loading was 37.8 kg/year.

Municipal mercury loadings were also estimated using the sludge concentration method described above. The Municipal Pretreatment Task Force reported typical sludge concentrations of 3.2 mg/kg and 4.1 mg/kg for mercury. The solids loading rate for each municipal treatment plant was multiplied by a sludge concentration of 4.0 mg/kg to estimate the mercury load from municipal effluent. The mercury load estimate from this method was used when actual data did not exist. The total estimated mercury load was determined to be 34.5 kg/year.

For comparison purposes, the reported load from the Western Lake Superior Sanitary District was 24.1 kg/year, while the typical concentration method resulted in 6.5 kg/year. The results for the Western Lake Superior Sanitary District using the sludge concentration method resulted in an estimated mercury load of 2.6 kg/year.

PCB

Effluent PCB concentrations for municipal facilities in the Great Lakes basin were retrieved and a typical concentration was calculated. The calculated concentration, however, was two orders of magnitude higher than the concentration reported by the Municipal Pretreatment Task Force. Concentrations reported in the Upper Great Lakes Connecting Channel Report (1988) for municipal treatment plants discharging to the Detroit River were also much lower than the computed average. The typical concentration of PCB in facilities with secondary treatment, 0.020 µg/L, is based on the concentrations in the latter two reports. Again, factors were applied to the concentration for facilities with secondary treatment to determine typical concentrations for lagoons, 0.038 µg/L, and facilities with primary treatment, 0.044 µg/L. When actual data were not available, the typical concentrations were used to estimate a load. The total load of PCB from sewage treatment plants was calculated to be 8.3 kg/year.

Municipal PCB loadings were also estimated using the sludge concentration method described in the section on lead. The Municipal Pretreatment Task Force reported a typical PCB sludge concentration of 0.39 mg/kg. The solids loading rate for each municipal treatment plant was multiplied by a sludge concentration of 0.39 mg/kg to estimate the PCB load from municipal effluent. The PCB load estimate from this method was used when actual data did not exist. The total estimated PCB load was determined to be 6.5 kg/year.

For comparison purposes, the reported load from the Western Lake Superior Sanitary District was 5.5 kg/year, while the typical concentration method resulted in 1.0 kg/year. The results for the Western Lake Superior Sanitary District using the sludge concentration method resulted in an estimated PCB load of 0.3 kg/year.

Summary

Table 17 contains a summary of the load estimates. As one can see, the loading rates for mercury and PCB are very comparable for the two methods. The lead loading rate calculated using the typical concentration is about 1-1/2 times the rate using the sludge concentration method. Because of the relatively low amount of industrial activity in the Lake Superior basin, the typical influent concentration that was calculated may be a little high. There are not sufficient data to verify this.

The one municipal facility that has data for the three parameters is the Western Lake Superior Sanitary District, Duluth, Minnesota. This facility has numerous industrial inputs, including two paper mills and an organic chemical plant, and accounts for a significant portion of the loading from municipal effluent for all three parameters. The loading rates are: lead 770.9 kg/year, mercury 24.1 kg/year, and PCB 5.5 kg/year.

The loading rates from municipal effluents would be much better if actual monitoring data were available. In the United States, there is a trend toward including more monitoring requirements in NPDES permits when they are issued or renewed. The Municipal/Industrial Strategy for Abatement (MISA) program in Canada may also provide a mechanism in which actual loading rates will be available for many more compounds. Until such time as quantitative loading rates are available, estimation techniques will be required.

TABLE 17

ESTIMATED TOTAL MUNICIPAL LOADS OF LEAD, MERCURY AND PCB kg/year

COMPOUND	TYPICAL CONCENTRATION METHOD	SLUDGE CONCENTRATION METHOD
Lead	2,435.3	1,547.5
Mercury	37.8	34.5
PCB	8.3	6.5

INDUSTRIAL EFFLUENTS

A description of the types of industries located in the Lake Superior basin can be found in the section on Industrial Processes. The purpose of this section is to document the loading rates of lead, mercury, and PCB from industrial facilities and the methodology for estimating those rates. Estimation methods are necessary because of the limited amount of actual data for these three compounds. The methods employed were identical for each compound.

The Toxic Release Inventory (TRI) is a data base of information based upon submissions by certain industries and was therefore inspected as a possible source of data. The information is gathered under Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA) which requires manufacturing companies which use or release certain toxic chemicals and have 10 or more employees to report information on the use and release of those chemicals. The initial reporting year was 1988 and annual updates are now required. It has been reported that there are limitations of the TRI data.

A limited number of industrial classes are required to report under SARA Title III. Emissions from sources not in the classes are thus not reported. Electric generating plants are in a class not required to report. Another problem, as cited by U.S. EPA, is that enforcement of

reporting requirements is lax. It is estimated that only two thirds of the facilities required to file a report actually did file a report. A more serious problem, though, is data errors. The errors can be in the estimations made by the manufacturers or in the data entry process.

The first two limitations may help to explain why there are no releases reported for lead, mercury, or PCB in the 1990 TRI data base for United States counties in the Lake Superior basin. The three Lake Superior states, Michigan, Minnesota, and Wisconsin, were examined for emissions of the compounds of interest. There were 142 facilities that filed a report for lead. Twelve did not list an emission or transfer, only the presence of the material. One-hundred-two facilities reported an emission, 100 a transfer, with 60 reporting both an emission and a transfer. Only four facilities in the three states filed a report for mercury. Two reported air emissions, and the other two reported releases to sewage treatment plants. Four facilities in the three states filed reports for PCB. Three stated that they transferred amounts to other offsite locations. The other facility reported storage of a quantity of PCB. These limitations prohibited direct use of TRI data in estimating loadings in the Lake Superior basin.

The above mentioned limitations affect the quantity of data available. Data errors, on the other hand, affect the quality of the data. For example, one facility that reported a release of lead to the waters of the Great Lakes and monitored lead as part of their NPDES permit demonstrates the problems that can be encountered with the quality of the load estimation. The facility reported that, in 1988, they discharged between 100 and 500 pounds of lead. TRI reports a release of 250 pounds for this range. When the release is divided by actual facility flow and corrected for units, the concentration in the effluent of the facility was calculated to be over 40,000 $\mu\text{g/L}$. Self-monitoring data indicate a concentration range of 5 to 50 $\mu\text{g/L}$. The difference is three to four orders of magnitude. Similar calculations for another facility found that TRI estimates were one order of magnitude higher than the facility's self monitoring data. Of course, the comparisons could not be made for all facilities in the TRI data base. These examples are not to say that all estimates in TRI are of poor quality, only to show that there are some data that are of questionable quality. This caused concern for using TRI data in a quantitative sense for estimating typical concentrations for industrial categories. When one significantly large number is in error the average can be greatly affected. This, in turn can cause the load estimation to be greatly overstated. For this reason, only actual self-monitoring data were used in calculating typical concentrations for various industrial classes.

The first step in calculating the water year 1990 loading rates for lead, mercury, and PCB from self-monitoring information was to retrieve the available point source data. United States data from the NPDES program are available from the Permit Compliance System (PCS). Monthly self-monitoring data from each facility with an NPDES permit are contained in PCS. Canadian self-monitoring data are available from the Industrial Monitoring Information System (IMIS) and the MISA program. Monthly loads were calculated and averaged for lead, mercury, and PCB for each Lake Superior industrial facility with available data. As stated earlier, the number of facilities for which actual loadings could be calculated was limited.

To estimate the loadings for other facilities, industrial category information was used. Both the United States and Canada have standard industrial classification schemes. The classification code for Canadian facilities in the Great Lakes basin has been translated to the equivalent United States code, allowing for direct comparison. A list of all the industrial classes in the Lake Superior basin was developed (see Table 18). For each of these classes, all Great Lakes facilities of the same class were examined for available lead, mercury, and PCB data. When data were available, the effluent concentrations were averaged to determine a typical concentration for the class. In most cases, a maximum likelihood estimator was used to calculate the average because the data included censored (less than) values. The typical concentrations of Great Lakes facilities for industrial classes in the Lake Superior basin are listed in Table 18. Once the typical concentrations were calculated, facility flows were multiplied by the concentration to estimate the loading rate for each of the three chemicals. The above method, however, was not suitable for electric generating facilities. The contaminant loading rates are not associated with the non-contact cooling water but with other process water for which individual flow rates are

usually not available. Detailed information from the Thunder Bay Thermal Generating Station was used to estimate typical loading rates for electric generating facilities (Thompson 1993). Total annual loads for the three compounds from this facility were assigned as typical loads for each electric generating facility. The final load estimation tables are a combination of actual and estimated loading data.

The estimated loading of PCB from Lake Superior industrial effluent is 21.85 kg/year. Most of the load can be attributed to continued use of old electrical equipment containing this compound, especially for the mining and electric generation industrial sectors. Table 19 contains the estimated loadings of lead, mercury and PCB summarized by industrial sector. It is worth noting that the majority of industrial loadings of mercury in the Lake Superior basin are from the mining industry and related activities. This industry also contributes a significant portion of the industrial lead loadings. The majority of the industrial lead loading is from the pulp and paper industry due to the high volumes of process water discharged.

TABLE 18

TYPICAL CONCENTRATIONS OF LEAD, MERCURY AND PCB FOR INDUSTRIES IN THE GREAT LAKES BASIN

SIC CODE	DESCRIPTION	Pb (µg/L)	Hg (µg/L)	PCB (µg/L)
921	Fish Hatcheries	-	-	-
1011	Metal Mining (Iron Ores)	17.0	0.310	0.135
1021	Metal Mining (Copper Ores)	10.4	0.180	0.135
1041	Metal Mining (Gold Ores)	36.0	0.204	0.135
1081	Metal Mining Services	9.8	-	-
1099	Metal Mining (Other)	13.7	0.135	0.135
1311	Crude Petroleum and Natural Gas	-	-	-
1499	Non-metallic Minerals	-	-	-
2435	Hardwood Veneer and Plywood	-	-	-
2493	Reconstituted Wood Products	-	-	-
2611	Pulp Mills (Bleached Kraft)	19.2	0.030	0.02
2611	Pulp Mills (Non-bleached)	19.2	0.030	0.006
2621	Paper Mills	19.2	0.030	0.006
2869	Industrial Organic Chemicals	6.0	0.340	-
2911	Petroleum Refining	17.1	0.066	0.05
3296	Mineral Wool	-	-	-
3312	Blast Furnaces, Steel Works, Rolling Mills	15.9	0.984	-
3398	Metal Heat Treating	-	-	-
4011	Railroads, Line-Haul Operations	25.0	-	-
4013	Switching and Terminal Establishments	-	-	-
5171	Petroleum Bulk Stations and Terminals	16.7	-	-
8211	Elementary and Secondary Schools	-	-	-
8412	Museums and Art Galleries	-	-	-
8731	Accounting/Auditing/Bookkeeping Services	-	-	-
9511	Air/Water Resource/Solid Waste Management	-	-	-
9512	Land, Mineral, Wildlife, Forest Conservation	-	-	-
		Pb (kg/year)	Hg (kg/year)	PCB (kg/year)
4911	Electric Services	4.2354	0.4056	0.1096

TABLE 19

LEAD, MERCURY AND PCB LOAD ESTIMATES BY INDUSTRIAL SECTOR

INDUSTRIAL SECTOR	LEAD ESTIMATE (kg/year)	MERCURY ESTIMATE (kg/year)	PCB ESTIMATE (kg/year)
Mining and Related	1,849.3	35.72	16.93
Pulp and Paper	4,829.7	26.08	4.00
Industrial Organic Chemicals	25.4	1.44	-
Petroleum	12.5	0.05	0.04
Railroad	10.1	-	-
Electric Generation	33.9	3.24	0.88
Totals	6,760.9	66.53	21.85

SURFACE RUNOFF

Runoff or overland movement of water to a receiver or other pathway is mainly originated by rainfall. Other contributions are due, for example, to snow and ice melt, street cleaning, and lawn watering. This runoff, which has an initial contaminant concentration (see atmospheric deposition section), picks up additional amounts of contaminants due to contact with sources on its way to a receiver or other pathway such as a sewer or tributary. One of the major sources that increase the concentration of lead, mercury and PCB in runoff is atmospheric emissions that have deposited on the surface, are scoured by the water movement, and become either dissolved or suspended in the runoff. Other sources that increase runoff concentrations are onland spills and exposed material storage sites. Coal piles are a good example of the latter and these will be sources of lead and mercury (as well as other metals) to runoff as discussed earlier.

It is difficult to quantify how much loading is contributed to surface runoff by spills and material storage. However, the major source of contaminated runoff can be estimated by assuming that the flux deposited directly on the lake is the same as that deposited on land within the basin. From the atmospheric deposition section, above, the fluxes to the lake for PCBs, mercury and lead are 1.91, 8.0 and 817 $\mu\text{g}/\text{m}^2/\text{year}$. Therefore, the mass of the contaminants that could eventually be conveyed to the lake via surface runoff is the flux multiplied by the land area of the Lake Superior basin (total area minus lake surface area). This area, referred to as the drainage basin area is 127,700 km^2 or $12.77 \times 10^{10} \text{m}^2$. Therefore, the load of PCB, mercury and lead deposited on land is 244, 1,022 and 104,000 kg/year , respectively.

There are several points that should be made about these estimates. First, major fractions of these loads can be attenuated in the basin (primarily through binding with soil particles) and therefore may not be delivered to the lake for years or decades. For mercury, the fraction attenuated has been estimated to be 0.9 (Mierle 1990). Also, some of the load of these contaminants falls on water bodies within the basin and is either conveyed to the lake via tributaries or lost from the system to bottom sediments. Lake Nipigon, for example, may represent a significant sink for these contaminants. Urban runoff represents a special case and it is considered under the section entitled CSOs, storm sewers and bypasses.

These load estimates can be apportioned among the river basins in the Lake Superior drainage basin (on an area basis) and used to compare to load estimates from tributaries. If a tributary estimate were higher than what could be explained by deposition and subsequent runoff, it is indicative of active point sources (or spills) within the river basin. An example of this type of comparison may be found in the section on tributaries.

GROUNDWATER

The significance of the groundwater pathway to Lake Superior is still unclear. There have been studies conducted that have concentrated on estimating actual flow and seepage of groundwater and its effect on surface water, but all have concentrated on Lakes Michigan, Erie, or Ontario. Questions such as, is discharge uniform across the entire lake bottom, or is it concentrated along the nearshore zones still need to be pursued. In order to answer these questions more emphasis must be put towards collecting field data over a larger area.

In many cases, studies have modeled groundwater flow to surface water using sampling data taken from small areas. Utilizing this procedure for Lake Superior would prove inadequate due to the lake's massive size and diverse bottom characteristics. An example of a small-area study for Lake Superior is reported by Thompson (1993). Mercury loadings due to groundwater seepage at the Domtar Landfill in Red Rock were estimated to be 0.0007 kg/year.

Studies that have reported groundwater flow to the Great Lakes are Anderson and Miller, 1983; Cartwright *et al.* 1976; and Siegle *et al.* 1990.

At present the groundwater contribution to Lake Superior is assumed to be zero for the substances in this study.

CSOs, STORM SEWERS AND BYPASSES

These pathways are often grouped together because they are the major means for municipalities to deal with excess storm water. Combined sewer overflows (CSOs) are significant contributors of pollutants to lakes and streams. This is due to the connections between sanitary sewers and storm sewers. If rainfall or snowmelt causes the total volume of flow to a wastewater treatment plant to exceed the design flow, the sewers overflow to local water bodies before damage can occur to the plant. Besides any contaminants present in the stormwater, CSOs contain sewage, some of which can be industrial in nature as is described above.

If storm sewers are separate, as in some municipalities, they will be composed only of surface runoff and will be routed to lakes and streams. These will still be pathways for contaminants but are unlikely to be at high levels. Storm sewers could still be a pathway for spills if they occur nearby.

Bypasses refer to the practice of routing stormwater and sewage to a water body from a wastewater treatment plant with partial or no treatment. This is normally done in an emergency to protect the plant from surges, although bypasses may be planned when equipment is down. Bypasses have similar quality characteristics to CSOs, unless they receive partial treatment. If bypasses are a regular occurrence, then they become significant pathways for contaminants. In 1989, the only Ontario municipalities in the Lake Superior basin to report a bypass were Marathon and Red Rock. A total of 340 m³ of untreated sewage was discharged (MOE 1991).

Since these pathways are primarily found in urban and industrial areas and since only 1% of the Lake Superior basin is residential/industrial, these pathways are not viewed as major contributors to contaminant loadings to Lake Superior. Further, only pipes that are located on the lakeshore or downstream of a sampling station need be considered. Pathways that meet these criteria are centered in Thunder Bay, Ontario and Duluth-Superior, Minnesota-Wisconsin.

In order to estimate the contaminant loads from these pathways, estimates from Schroeter and Associates (1991) have been used (Table 20). This report contains estimates for Canadian municipal wastewater (STP), CSOs and runoff. The runoff estimates include both storm sewers and overland runoff. Since similar information on CSOs and runoff is not available on the United States side, the ratios for the Canadian data were applied to the United States STP loads to estimate these components. Bypasses were assumed to be insignificant.

The CSO and runoff loadings were estimated as follows. Because these loadings are related to the size of a municipality, the estimates are based on the municipal effluent flow rate. First, a decision was made whether to estimate a CSO loading. As Table 20 indicates, the smaller towns do not have CSOs. An arbitrary cutoff of 3,800 m³/day (1 million U.S. gallons per day) was used to decide whether or not to include a CSO estimate. Then, if the municipality had a flow greater than the cutoff, the ratios for Thunder Bay in Table 20 between CSO load and STP load and between runoff load and STP load for each contaminant were used to obtain estimates. Similarly, if the flow was below the cutoff, the ratios for Marathon in Table 20 between runoff load and STP load for each contaminant were used. To avoid double counting, the municipalities with direct discharges to Lake Superior were separated and the sums of their CSO and runoff estimates were used as the total loadings from these pathways.

TRIBUTARIES

Tributaries that enter Lake Superior are significant pathways for contaminants, probably next in importance to atmospheric deposition to the lake surface. Concentrations and loadings measured at or near the mouths of these tributaries are representative of all of the activities and processes that have taken place upstream. Many of the other pathways, such as effluents, runoff, groundwater and CSOs are contributory to the flow of the tributaries.

Unfortunately, most tributaries are not well-monitored for contaminants. This is due to two related reasons -- logistics and cost. Contaminant concentrations in most tributaries vary seasonally, thus it is necessary to sample throughout the year to obtain a representative estimate for the annual average loading. Also, analytic chemistry for contaminants in water is expensive. In fact, the sensitive analytic methods needed for most Lake Superior streams are very difficult to operate on a production basis. Therefore, estimation methods were needed for most tributaries to Lake Superior (Table 21). Most of the data needed to calculate tributary loading rates are in the U.S. EPA's national database, STORET. United States flow data are collected by the U.S. Geological Survey (USGS) and transferred to STORET semi-annually. Canadian flow data are collected by Water Survey of Canada. They provide a tape for updating STORET once a year. Concentration data are collected by the Great Lakes states, USGS, and the Ontario Ministry of the Environment.

Initial inspection of available lead, mercury, and PCB data revealed that loading rates for these compounds could not be calculated using standard methodology. Most concentration data were flagged as "less than" the reported concentration. In fact, the only load that could be calculated is lead for the St. Louis River. For the remainder of the loads that were estimated, the available data could only provide an upper limit on the actual load.

TABLE 20

STORMWATER AND CSO CONTAMINANT LOADINGS* (kg/year)

	PCBs	MERCURY	LEAD
THUNDER BAY			
STP	1.06	1.56	874.0
Runoff	1.66	0.59	1,460.0
CSOs	0.33	0.16	304.0
RED ROCK			
STP	0.03	0.05	25.3
Runoff	0.13	0.05	117.0
CSOs	0	0	0
MARATHON			
STP	0.01	0.01	9.4
Runoff	0.19	0.07	164.0
CSOs	0	0	0

*As estimated by Schroeter and Associates (1991).

TABLE 21

TRIBUTARY LOADING DATA

TRIBUTARY NAME	# SAMPLES	JURIS-DICTION	AREA km ²	SUSPENDED SOLIDS kg/year	FLOW m ³ /sec	PCB kg/year	Hg kg/year	Pb kg/	EFFECTIVE CONCENTRATIONS		
									PCB ng/L	Hg ng/L	Pb µg/L
Ontonagon	3	Michigan	3,530	24,486,938	26.004	1.22	4.90	489.74	1.49	5.97	0.60
Tahquamenon	4	Michigan	2,180	3,252,442	25.537	0.16	0.65	65.05	0.20	0.81	0.08
St. Louis	9	Minnesota	9,453	50,369,234	63.769	2.52	10.07	2,036.15	1.25	5.01	1.01
Michipicoten	8	Ontario	5,307	32,412	64.409	0.16	0.65	64.82	0.08	0.32	0.03
Magpie	7	Ontario	1,930	891,002	14.016	0.04	0.18	17.82	0.10	0.40	0.04
White	11	Ontario	5,524	1,934,683	50.625	0.10	0.39	38.69	0.06	0.24	0.02
Pic	49	Ontario	2,347	139,394,559	32.487	6.97	27.88	2,787.89	6.80	27.21	2.72
Black	48	Ontario	2,240	60,199,122	16.341	3.01	12.04	1,203.98	5.84	23.36	2.34
Little Pic	10	Ontario	1,357	1,936,143	3.674	0.10	0.39	38.72	0.84	3.34	0.33
Nipigon	12	Ontario	24,579	78,898,072	308.882	3.94	15.78	1,577.96	0.40	1.62	0.16
Black Sturgeon	12	Ontario	2,639	9,297,864	12.488	0.46	1.86	185.96	1.18	4.72	0.47
McIntyre	6	Ontario	148	173,156	0.789	0.01	0.03	3.46	0.35	1.39	0.14
Neebing	5	Ontario	205	330,617	1.130	0.02	0.07	6.61	0.46	1.86	0.19
Kaministikwia	34	Ontario	7,796	22,298,179	57.248	1.11	4.46	445.96	0.62	2.47	0.25
Goulais	6	Ontario	1,945	5,463,941	22.829	0.27	1.09	109.28	0.38	1.52	0.15
Bad	8	Wisconsin	2,580	14,666,832	17.979	0.73	2.93	293.34	1.29	5.17	0.52
Bois Brule	8	Wisconsin	311	1,248,264	4.065	0.06	0.25	24.97	0.49	1.95	0.19
Montreal	7	Wisconsin	700	847,092	5.672	0.04	0.17	16.94	0.24	0.95	0.09
Nemadji	7	Wisconsin	1,088	12,903,736	10.26	0.65	2.58	258.07	1.99	7.98	0.80
SUM				431,833,070		21.59	86.37	9,665.43			

Concentrations applied to solids loads - PCB - 0.05 µg/g, Hg - 0.2 µg/g, Pb - 20.0 µg/g

Because of the quality of concentration data, an alternate method of estimating loading rates was used. The first step in the process was to calculate suspended solids loading rates. Next, factors were applied to the suspended solids loading quantities to estimate the lead, mercury, and PCB loading rates. The factors are based upon concentrations found on particulate matter.

For each tributary, flow and suspended solids data were retrieved from STORET. Beale's Ratio Estimator (Dolan *et al.* 1981) was used to calculate suspended solids loading rates. The methods used are the same as those used to determine phosphorus loadings as reported in Appendix B (Rathke and McRae, 1989) and other IJC reports. Stratified estimates were calculated for individual tributaries when sampling indicated a relation between flow and concentration.

Once the suspended solids loading rates were calculated for each tributary, a separate factor was used to estimate the loading rates for lead, mercury, and PCB. For lead the factor is based upon 20 $\mu\text{g/g}$ of lead on particulate matter; for mercury, 0.2 $\mu\text{g/g}$; and for PCB, 0.05 $\mu\text{g/g}$. These factors were obtained from data on contaminants in suspended particulates from Lake Superior Areas of Concern. The final values were agreed on in the peer review described earlier, but they are consistent with typical data from these areas. The one exception, noted above, is the lead loading rate for the St. Louis River. The rate was estimated by processing lead concentration data and flow data through Beale's Ratio Estimator. When this load was compared to the estimates that would have been used for the St. Louis, it was twice as large. In other words, a factor of 40 $\mu\text{g/g}$ would have to be applied to the suspended solids load of the St. Louis River in order to agree with the measured results. This is reasonable agreement considering the nature of the approach and the characteristics of the St. Louis River basin.

Since the current project is more focused on the tributary contribution on a whole lake basis, a comparison as suggested in the surface runoff section for the entire Lake Superior drainage basin was used. For ease of computation, the fraction attenuated was assumed to be 0.9 for all three chemicals. In Table 22, estimates made from tributaries are compared to estimates made assuming 10% of the fallout from the atmosphere on the basin reaches the lake plus indirect industrial and municipal effluents.

This comparison shows reasonably good agreement and is encouraging, since the sources of data for the estimates were different. The values used cannot be greatly in error, or this type of agreement would not be obtained.

TABLE 22

COMPARISON OF TRIBUTARY ESTIMATES VS. BASIN RUNOFF PLUS EFFLUENT ESTIMATES

(kg/year)

	TRIBUTARY	RUNOFF & EFFLUENTS
Lead	14,850	12,470
Mercury	124	133
PCB	27.8	36.9

Tributary Estimate = Monitored Tributary + Unmonitored Area
 Runoff + Effluents = Basin Runoff from Atmospheric Fallout
 + Indirect Industrial + Indirect Municipal

V. RECEIVERS

AMBIENT WATER

The waters of Lake Superior receive the impact of loadings to it in the form of increases in concentration over background or natural levels. The amount of a substance contained in the lake may be estimated and changes can be tracked through time. Because lead, mercury and PCBs are all to some extent hydrophobic all of the chemicals loaded to the lake will not be in the dissolved phase, but measurable concentrations will be found in the sediment or biota.

As discussed in the atmospheric deposition section, above, another mechanism by which PCB and mercury enter the lake, absorption, depends on both the air concentration of chemical and the lake concentration. Because none of these concentrations are well known, absorption is estimated by a model. The air concentrations from Tables 14 and 15 are used as well as the modelled lake concentration. The values estimated for this mechanism are in Table 23.

TABLE 23

AMBIENT VALUES USED TO ESTIMATE ABSORPTION LOADING

	PCB	MERCURY
Air Concentration	0.3 ng/m ³	2 ng/m ³
Lake Concentration	0.173 ng/L	0.842 ng/L
Absorption Loading	137 kg/year	negligible

SEDIMENT

Each of the substances considered here can adsorb to sediment particles. These particles can be either suspended in the water column or settled on the lake bottom. The amount adsorbed to particles is determined partly by the amount dissolved in water and partly by the mass of sediment available. The concentration of contaminants on particles can be determined by centrifuging water samples to separate particles or by coring the lake bottom to bring up sediment for analysis.

Virtually all of the pathways discussed above contain suspended sediment. Depending on the physics of the lake system, these sediments can settle out, remain suspended or adsorb or desorb contaminants. Those sediments that have been loaded in from previous years that settle out are called "in-place" sediments and are available to contaminate (or re-contaminate) the water column and/or biota by releasing their chemical burdens. The rate at which this occurs is difficult to estimate without a mathematical model and it may be easier to treat "in-place" sediment as part of the lake than as part of the loading to the lake.

BIOTA

Plankton, benthos, mussels and fish all are in contact with water and sediment and thus are also receivers. Because some chemicals bioconcentrate or bioaccumulate up the food chain, higher trophic levels contain much of the contaminant mass. Samples of these biota, analyzed

for bioaccumulative contaminants, reveal significant information about the loadings of contaminants to the lake. PCBs are readily bioaccumulated, especially by biota with high lipid content. When mercury and lead are alkylated, significant bioaccumulation occurs. Natural methylation of mercury occurs in lakes and mercury has been observed to accumulate throughout the food chain.

Contaminant	Source	Concentration
PCBs	Industrial	High
Mercury	Natural	Medium
Lead	Industrial	Low

The bioaccumulation of contaminants in the food chain is a complex process. It is influenced by many factors, including the lipid content of the organisms, the persistence of the contaminants, and the rate of excretion. PCBs are highly persistent and have a high lipid content, which makes them particularly prone to bioaccumulation. Mercury and lead, when alkylated, also bioaccumulate significantly. Natural methylation of mercury occurs in lakes, and mercury has been observed to accumulate throughout the food chain.

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VI. BALANCES

SOURCES VS. PATHWAYS

Table 1 is the main summary for loadings of lead, mercury and PCBs directly to Lake Superior for all known sources. A comparison with the sources chapter, especially for air emissions indicates that much less material is actually reaching the lake in a year than is released to the environment. For lead, the estimate of 97 tonnes per year loaded to Lake Superior can be compared to the Ontario air emission estimate of 3,113 tonnes per year or the West North Central United States estimate of 1,330 tonnes per year. While it is encouraging that less than 10% of the lead released actually reaches the lake, some of the loading is only attenuated by the basin and will be brought in as runoff in future years. Of course, some lead will never reach the lake if it becomes incorporated in lake and stream bottom sediments or is transported out of the basin by air currents. Similar comparisons can be made for mercury and PCBs.

RECEIVERS VS. PATHWAYS

Unlike the balance of sources vs. pathways, it is possible to determine with reasonable certainty the fate of the chemicals loaded to the receivers via the pathways. This is due to the homogenous nature of the offshore waters of Lake Superior which make up the bulk of the water mass. Relatively few samples of the water, sediment and biota can be used to indicate the fate of the contaminants. The mass in these compartments of the lake can be "balanced" with the inputs from the pathways. Because the pathways are influenced by so many diffuse sources and are often difficult to estimate, the results of a balance with the receivers can be used to "adjust" the loading estimates to a total that "supports" the observed contaminant concentration in the receivers. This is best accomplished using a mass balance model such as the fugacity model used in this project. The loads in Table 1 were reconciled with a mass balance model at a workshop held in Toronto in December 1992 (Mackay *et al.* 1992b). The model is described in a separate report (Mackay *et al.* 1992a).

VII. RELATIVE CONTRIBUTIONS

Detailed knowledge of the relative significance or importance of sources leads to optimal management actions to control them. As has been pointed out in this report, more information is known about pathways than about actual sources. However, information about relative contributions of pathways can lead to appropriate management actions.

Figures 6, 7 and 8 are pie charts for lead, mercury and PCBs relative contributions of pathways. It is obvious that the major contributing pathway for each of these substances is atmospheric deposition. In addition, airborne contaminants are probably contributing to the other pathways, especially runoff and tributaries. This leads to a consideration of management options for controlling air emissions. Figure 9 is the pie chart for mercury air emissions in Michigan. Actions have already been taken to eliminate mercury use in latex paint. Fuel combustion and solid waste incineration should be considered next in terms of their relative contribution. Combustion of coal releases a variety of contaminants including lead and mercury as well as sulphur. It has long been recognized that a shift from coal to oil and gas would reduce air emissions of toxics. However, the economics of such a shift have so far been prohibitive.

Incineration of solid wastes containing lead, mercury and PCBs only succeeds in transferring the problem from one medium to another. If this practice is continued then management actions need to be taken to reduce the contaminant content of solid waste. This is desirable no matter how the solid waste is disposed of.

The question of natural sources of mercury for air emissions should be considered further. Many anthropogenic activities increase natural emissions such as mining and forestry practices. Vegetation picks up mercury from the soil and air and releases it back to the environment when it is burned or decomposed. Pulp and paper mills and sawmills release mercury from trees. It is a matter of speculation, but natural emissions of mercury should be decreased when anthropogenic sources are better controlled.

FIGURE 6

LEAD LOADINGS TO LAKE SUPERIOR

Total Loading = 96,801 kg/year

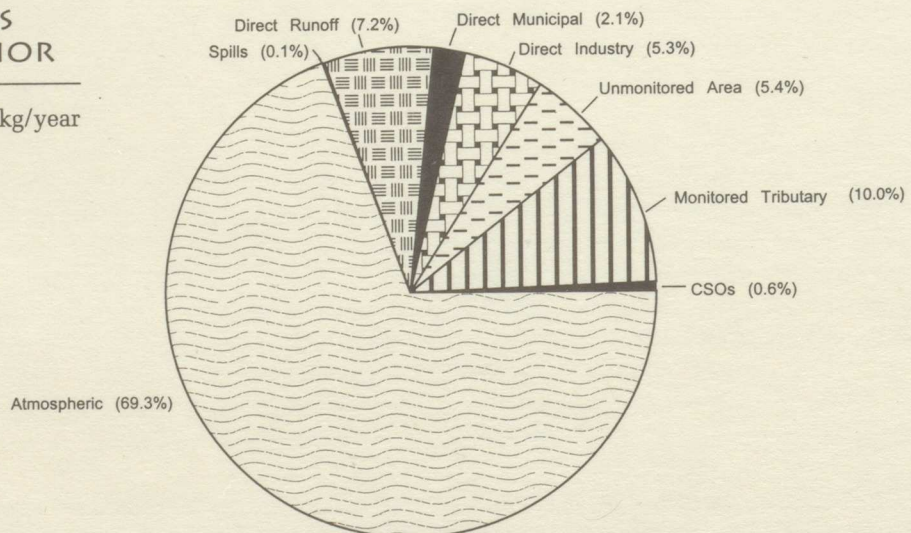


FIGURE 7

MERCURY LOADINGS TO LAKE SUPERIOR

Total Loading = 899.7 kg/year

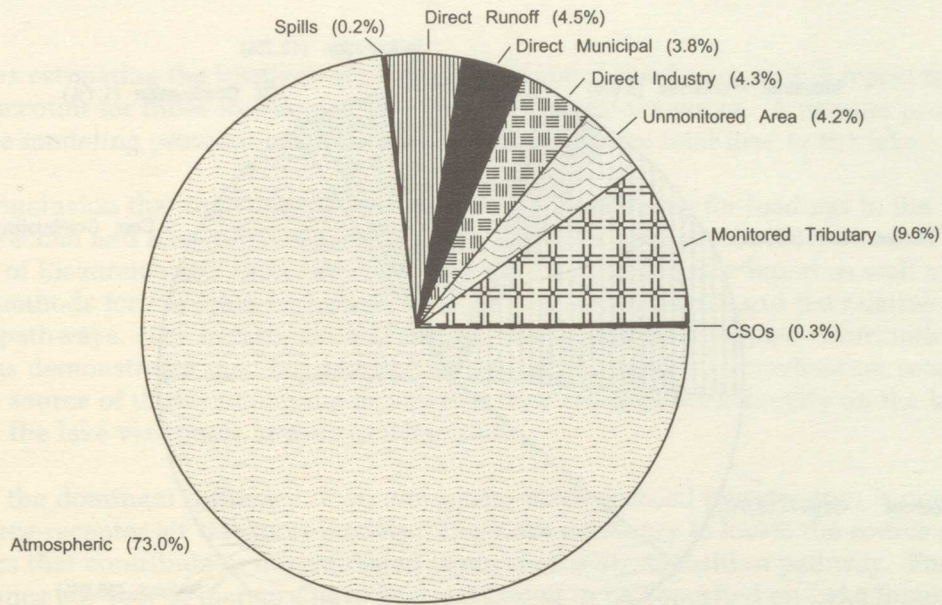


FIGURE 8

PCB LOADINGS TO LAKE SUPERIOR

Total Loading (Including Absorption) = 358.7 kg/year

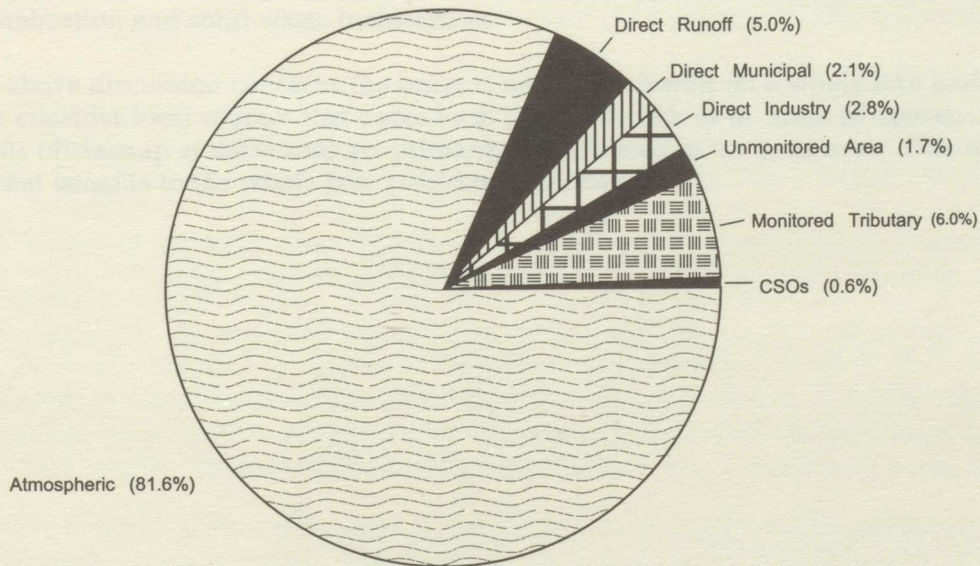
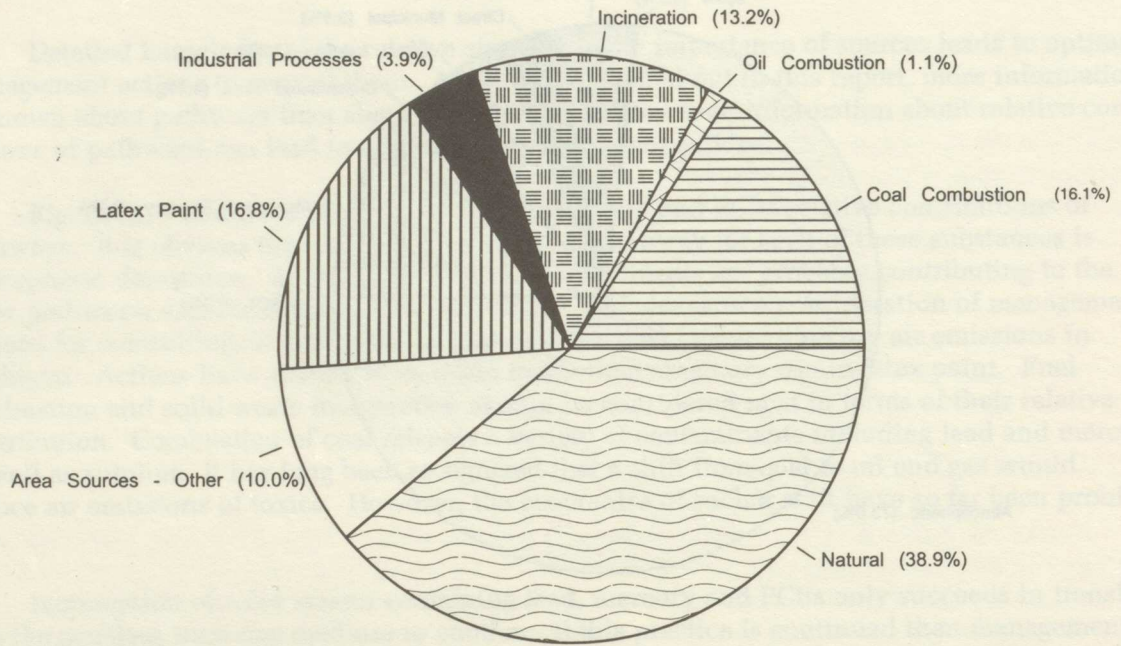


FIGURE 9

MERCURY AIR EMISSIONS IN MICHIGAN

Total Loading = 27.9 tonnes/year



VIII. CONCLUSIONS

Besides estimating the loadings of contaminants into Lake Superior, this report has attempted to account for those loadings in terms of their ultimate sources. A parallel project using mass balance modeling provides an independent estimate of the total load to the lake.

The conclusion that the atmosphere is the dominant pathway for loadings to the lake is not new. Strachan and Eisenreich reported this in 1988 and have been widely cited. The most recent work of Eisenreich and Strachan (1992) has been utilized in this report as well as various estimation methods for the other pathways to refine the load estimates and the relative contributions of the pathways. The investigation of sources to explain the estimated contribution of the pathways has demonstrated qualitatively that air emissions, especially combustion processes are the ultimate source of these contaminants, whether they are deposited directly on the lake or washed into the lake via runoff, sewers or tributaries.

Given the dominant influence of air emissions, more detailed investigation is not feasible without source-receptor air transport models. These are necessary to locate the source area of the emissions that contribute to the estimated loads via the air deposition pathway. For example, 0.66 tonnes per year of mercury have been estimated to be deposited on Lake Superior from the atmosphere and 0.5 tonnes per year have been measured being emitted from the Copper Range Smelter in White Pine, Michigan. How much of that mercury emitted is deposited on the Lake Superior basin versus contributions from power plants and solid waste incineration throughout North America is still unknown.

Without source-receptor modeling, a simplified approach is needed to identify appropriate management actions. Since the Great Lakes Water Quality Agreement goal for lead, mercury and PCBs (as well as other persistent toxic substances) is virtual elimination, a reduction towards zero of all sources is called for. Since reductions in air emissions benefit other regions beyond the Great Lakes, reciprocal reductions in other regions would be probably necessary to substantially reduce loadings. This approach may succeed for Great Lakes specific activities like copper smelting, but a more national (or international) approach would probably be needed for coal combustion and solid waste incineration.

The above discussion concerns the impacts on Lake Superior on a whole lake basis. It does not consider local sources that cause local problems such as in Areas of Concern. The benefits of cleanup at these sites are primarily experienced in the local area. This report indicates that benefits to the whole lake would be secondary.

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