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Production, Usage and Atmospheric Emissions of 14 Priority Toxic Chemicals: Appendix 2 to the Proceedings of the Workshop on Great Lakes Atmospheric Deposition

Canada. Department of the Environment. Atmospheric Environment Service

United States. Environmental Protection Service

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Canada. Department of the Environment. Atmospheric Environment Service, United States. Environmental Protection Service, Voldner, E. C., & Smith, L. (1986). Production, Usage and Atmospheric Emissions of 14 Priority Toxic Chemicals: Appendix 2 to the Proceedings of the Workshop on Great Lakes Atmospheric Deposition. *International Joint Commission (IJC) Digital Archive*. https://scholar.uwindsor.ca/ijcarchive/361

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Joint Water Quality Board / Science Advisory Board /
International Air Quality Advisory Board of the International Joint Commission

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of the Workshop on Great Lakes Atmospheric Deposition

Invited Paper by

Eva C. Voldner,
Atmospheric Environment Service,
Environment Canada, Toronto, Ontario and

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CoverPhoto: An aerial view of the Grand Calumet and Indiana Harbor Canal Area of Concern. Credit: *Indiana Department of Environmental Management*

ISBN 1-895085-20-9

Printed on Recycled Paper

DISCLAIMER

This invited paper was prepared as part of the Proceedings of the Workshop on Great Lakes Atmospheric Deposition (October 29-31, 1986). Although the Commission, through its Boards, supported this work, the specific findings, conclusions and/or recommendations do not necessarily represent the views of the International Joint Commission or its Boards.

ABSTRACT

Atmospheric deposition of toxic trace metals and organic compounds to the Great Lakes basins is recognized as a significant contribution to the presence of these toxic chemicals in the Great Lakes Basin Ecosystem. In order to evaluate alternative abatement strategies for toxic contaminants, it is necessary to establish atmospheric source-receptor relationships through atmospheric modeling studies. Emission estimates are required as source term inputs to atmospheric transport models and as order-of-magnitude deposition, relative to other sources of contaminants such as stream discharge to the lakes.

Information on production, usage and atmospheric emissions has been assembled on the 14 priority toxic chemicals designated by the International Joint Commission for initial indepth study. These priority toxic chemicals consist of trace metals, commercial and industrial chemicals or byproducts and organic pesticides.

National and provincial emission totals in Canada and national, regional (census and farm production) and state totals in the United States were compiled. Additionally, commercial sector contributions and historical and projected trends for Canada and the United States were assembled. For some of these chemicals, especially the pesticides, emission estimates are not available. Production and usage information on these were obtained as an initial effort toward developing emission estimates.

Emission estimates for the 14 priority toxic chemicals are not well developed. Emission estimates are available for 1982-1985. However, in most cases, they lack spatial resolution. Estimated emissions for industrial chemicals are uncertain and also lack sufficient spatial resolution. No estimates of emissions of pesticides were found. Information on production and usage patterns, which could potentially be used to develop emission estimates, is scattered among a variety of agencies and not readily available.

A large undertaking of further research on toxic chemical emissions will be required to provide the necessary information on atmospheric emissions and their subsequent deposition in the Great Lakes region. The knowledge and understanding gained as a result of such efforts could contribute to the health of the Great Lakes Basin Ecosystem.

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COMPILATION OF EMISSIONS INVENTORIES

The Great Lakes Water Quality Board has identified a comprehensive list of chemicals of concern to the Great Lakes Basin Ecosystem. Of these, 14 compounds have been classified as "priority" or "fast track" chemicals and singled out for an initial indepth study.

The purpose of this report is to review available information of emissions of these chemicals in North America and to assess their quality and credibility in estimating the impact on the Great Lakes Basin Ecosystem.

Information on past, present and future emissions has been classified by industrial sector and by state, province or region. Annual emissions are presented, with an indication of seasonality where emissions are expected to exhibit a strong seasonal pattern. Information has been obtained through an extensive literature review, through contact with relevant agencies, and through data analysis original to this effort.

Little effort was expended in determining the compatibility of the basic methodologies used by separate investigators in the two countries for estimating emissions. The reader should exercise caution in making direct comparisons between the United States and Canadian emission estimates compiled in this report.

a. Chemicals of Concern

The 14 priority toxic chemicals may be divided into three general groups. These are: trace metals; organic chemicals that are a product or by-product of industry; and organic pesticides.

b. Toxic Contaminant Species

The trace metals include:

- lead;
- mercury;
- cadmium; and
- arsenic.

The industrial organic chemicals include:

- polynuclear aromatic hydrocarbons (PAH) and polycyclic organic matter (POM);
- benzo[a]pyrene (BaP) (a member of PAH);
- polychlorinated dibenzo-ρ-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF); and
- polychlorinated biphenyls (PCB);
- hexachlorobenzene (HCB).

The latter chemical was added to the 14 compounds at the IJC workshop. The discussion of BaP in this report is combined with that for PAH and POM because BaP is a sub-species of PAH and most emission measurements have focused on BaP.

The organic pesticides include:

- Aldrin/Dieldrin;
- DDT;
- Lindane;
- Mirex; and
- Toxaphene.

Mirex and hexachlorobenzene have been used both as pesticides and as industrial chemicals.

c. Estimation of Emissions

Emissions may be estimated by:

- direct source measurements;
- material balance;

1.0 LEAD (Pb)

1.1 PROPERTIES

Elemental Lead (Jacques 1985; Merck 1976) CAS No. 7439-92-1

Density:	11.34 g/mL
Melting Point:	327.43°C
Boiling Point:	1740°C
Vapour Pressure:	1.77 mm Hg @ 1000°C

Alkylated Lead (U.S. EPA 1987; Vershueren 1983; Valaoras 1986)

Tetramethyl lead (TML) CAS No. 75-74-1

$(CH_3)_4Pb$

Solubility:	15 mg/L in seawater, soluble in organic solvents.
Melting Point:	-28°C
Boiling Point:	110°C; flash point 38°C

Tetraethyl lead (TEL) CAS No. 78-00-2

$(C_2H_5)_4Pb$

Solubility:	0.1 mg/L in seawater; 0.8 mg/L at 20°C in distilled water, soluble in organic solvents.
Melting Point:	-137°C
Boiling Point:	200°C; flash point 85°C

1.2 BACKGROUND

A large amount of data exists on the presence of lead in the environment and the history of global lead emissions and deposition has been extensively studied. For example, analysis of pond sediments in the western United States has revealed a 20-fold increase in lead deposition in the last 150 years. These and other results demonstrate the increased use of lead in that region since the onset of the industrial revolution and also emphasize the importance of anthropogenic lead sources relative to natural ones (U.S. EPA 1986a, b).

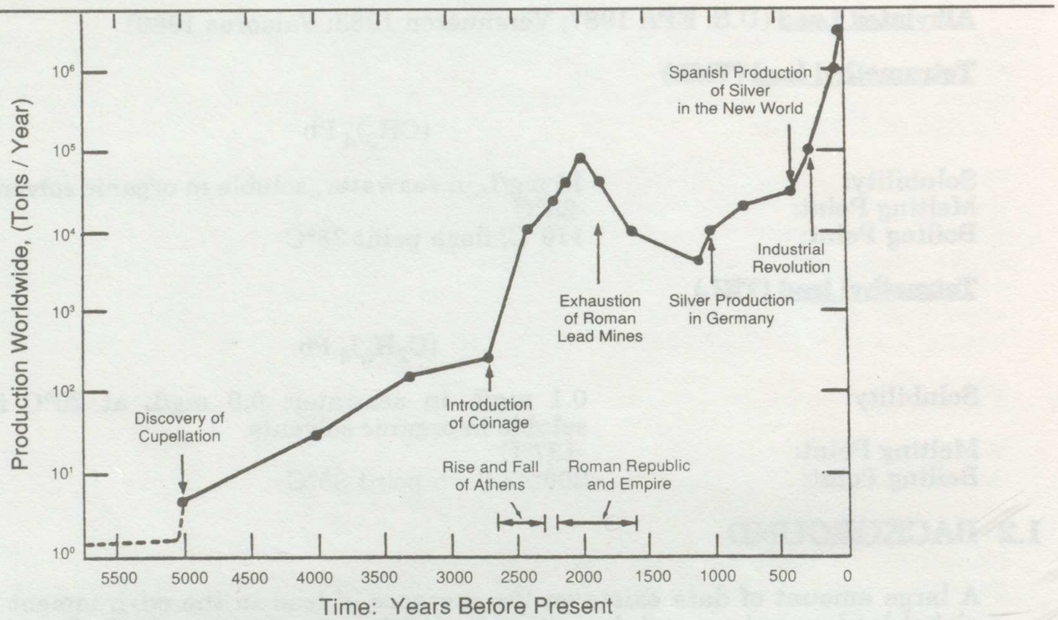
Lead enters the atmosphere from lead-bearing minerals in the lithosphere through both natural and man-made processes. Global atmospheric annual emission of lead has been estimated by Nriagu (1979) at over 470,000 tonnes. Of this 450,000 tonnes or about 95% is anthropogenic, arising from industrial production from combustion of fossil fuels and from disposal of waste, Table 1.1 shows estimates by Nriagu and by Lantzy and MacKenzie (1979). The latter authors estimated global emission to be over 2,000,000 tonnes, to which anthropogenic emission contributed over 99%.

TABLE 1.1 Estimated annual global emissions: natural and anthropogenic (units 1,000 tonnes).

	NATURAL				ANTHROPOGENIC				
	Blown Dust	Wind Volcanic	Other	Total	Fossil Fuel Combus.	Other	Total	Natural +Anthro.	Anthro./ Total
Nriagu	16	6.4	2.1	24.5	287	162	449	473.5	94.8%
Lantzy and MacKenzie	5	0.9		5.9	430	1,600	2,030	2,035.9	99.7%

It has been estimated (U.S. EPA 1986a, b) that global atmospheric lead emissions have increased by a factor of 2,000 since pre-Roman times and that even at that early period, anthropogenic lead emissions may have been three times higher than natural levels. These estimates are based on analysis of polar ice strata (U.S. EPA 1986a,b; Murozumi et al. 1969). With the assumption of constant natural emissions over the centuries, the present anthropogenic emissions may be 6,000 times larger than the natural emissions, a much higher ratio than the estimates by Nriagu (1979) or Lantzy and MacKenzie (1979). Global lead production, analyzed as a response to major economic and political events (U.S. EPA 1986a,b; Settle and Patterson, 1980) is shown in Figure 1.1 in terms of years before the present.

FIGURE 1.1 Historical Change in Global Lead Production in Response to Major Economic and Political Events *(U.S. EPA 1986a).*



Natural sources of lead emissions to the atmosphere include forest fires, volcanic release of aerosols and gases, and weathering of the earth's crustal material with the subsequent entrainment of soil as well as aerosol generation at the sea surface. Estimated annual emissions from volcanic origin have shown considerable variations, i.e. 6,000 tonnes (Nriagu 1979); 1,000 tonnes (Lantzy and MacKenzie, 1979) and 1 tonne (Settle and Patterson, 1980; U.S. EPA 1986a). Estimates were made by Nriagu, Lantzy and MacKenzie, using (different) emission factors based on lead to volcanic dust ratio multiplied by annual volcanic dust produced. Emission factors differed by two orders of magnitude: Nriagu, 6.4 x 10^{-4}; and Lantzy and MacKenzie, 6 x 10^{-6}. Annual volcanic dust fluxes differed by an order of magnitude (Nriagu, 1 x 10^7 tonnes dust/year; Lantzy and MacKenzie, 1.5 x 10^8 tonnes dust/year). Settle and Patterson based their estimate on the measured ratio of lead to sulphur in volcanic emissions of 2 x 10^{-7} and estimated sulphur emissions of 6 x 10^6 tonnes/year.

The remainder of this chapter will focus on anthropogenic lead emissions. In the U.S. economy, lead ranks fifth among metals in terms of tonnage used. Lead or its compounds may enter the environment at any point during mining, smelting, processing, use, recycling, or disposal. Estimates of the dispersal of lead emissions to the environment by principal sources indicate that the major initial recipient is the atmosphere. Lead is emitted primarily in the form of inorganic particulate, though a small fraction (<10%) of the lead emissions resulting from gasoline combustion is released as volatile organic compounds (U.S. EPA 1986a,b).

In recent decades the majority of lead found in the atmosphere has resulted from the combustion of leaded gasoline to which lead was added as an anti-knock agent. Until recently, its contribution was near 80% of the total atmospheric lead input in North America. But this contribution has fallen rapidly in the last few years and is projected to fall further as lead is phased out as a gasoline octane booster. Other significant sources include primary and secondary lead smelting, coal and oil combustion, and solid waste incineration. Emissions from coal combustion and incineration are likely to continue growing at a modest rate.

1.3 NORTH AMERICAN EMISSION RATES

Canada

Estimates of lead emissions in Canada have been obtained from the Canadian Environmental Protection Service (EPS). Reports by Jaques (1985 and 1987) describe the methodology and when appropriate, emission factors used by the EPS to estimate emissions. Although emission estimates refer to 1982, it is unlikely that they differ substantially from 1984 emission rates (Jaques 1987). For information on production, usage and emissions in North America and globally, see also Voldner and Ellenton (1987).

Estimates of lead emissions in 1982 from the various sources in Canada (Jaques 1985) are shown in Table 1.2. Emissions from burning of leaded gasoline in automotive vehicles account for more than 7,000 tonnes annually, which is over 63% of the total. Primary production of metals contributes some 3,500 tonnes or over 30%. This includes the production of lead and zinc, iron and steel and other nonferrous metals. Secondary lead smelters are estimated to emit relatively small amounts of lead, 14 tonnes per year or 0.1% of the total. Of industrial uses, metal foundries and fabricators show the highest annual lead emissions at 212 tonnes (or 2%). Waste incineration accounts for 199 tonnes annually (or 2%) and fuel combustion from stationary sources, 25 tonnes (or 0.2%).

TABLE 1.2 Estimated annual lead emissions in Canada, 1982, by industrial sector and province (Jaques 1985).

												CANADA	
SECTOR	NF	PEI	NS	NB	PQ	ON	MB	SA	AB	BC	NWT	TOTAL	%
INDUSTRIAL PROCESSESS													
• Mining, Milling and Concentrating of Lead Bearing Ores	8		29	281		31	4			259	352	964	8.42
• Primary Lead/Zinc Production				59			76			169		304	2.66
• Primary Copper/Nickel Production					1194	205	305			2		1706	14.88
• Secondary Lead Smelting Industry					5	7	1		<1	<1		14	0.12
• Brass and Brass Foundries				14	<1	1				<1		16	0.14
• Metal Fabricating Industries	<1		<1	<1	18	42	2	<1	5	5		75	0.65
• Metallurgical Coke Production			<1			2	<1	<1		<1		2	0.02
• Primary Iron & Steel Production			36		238	226	12	64	10	14		600	5.23
• Ferroalloy Production					14							14	0.12
• Ferrous Foundries (1980)			<1	<1	34	172	<1		3	2		212	1.85
• Cement Manufacture	<1		<1	<1	3	<1	<1	<1	<1	<1		6	0.05
• Leaded Glass Production				<1	3	5			<1	1		10	0.09
• Leaded Alkyl Manufacture							42					42	0.37
• Storage Battery Production			<1		2	15	1		1	1		20	0.17
• Lead Oxides and Pigment Production	<1		<1	<1	<1	<1	<1	<1	<1			1	0.01
• Tar Sands Operations									20			20	0.17
FUEL COMBUSTION - STATIONARY SOURCES													
• Power Generation	<1	<1	2	1	<1	4	<1	3	3	<1	<1	14	0.12
• Industrial	<1	<1	<1	<1	3	2	<1	<1	<1	<1	1	8	0.07
• Commercial	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	2	0.02
• Residential	<1	<1	<1					<1	<1			1	0.01
FUEL COMBUSION - TRANSPORTATION SOURCES													
• Gasoline-powered Motor Vehicles	100	30	190	170	1390	2230	350	490	1120	910	20	7000	61.05
• Aircraft	3	2	6	1	21	39	20	22	28	29	13	173	1.51
SOLID WASTE INCINERATION													
• Municipal Refuse Incineration					36	23		1		7		67	0.58
• Sewage Sludge Incineration						2				<1		2	0.02
• Waste Oil Incineration	5	2	7	10	53	53						130	1.13
MISCELLANEOUS SOURCES	1		4	2	23	11	2	7	7	6		63	0.55
TOTALS	118	34	276	541	3038	3113	775	578	1199	1408	386	11466	100

<1 values are less than 1 tonne but are included in totals: Neg. - negligible

United States

Table 1.3 shows the estimated 1985 U.S. lead emissions to be over 20,000 tonnes. The U.S. EPA reports annually on estimated lead emissions by the major emitting sectors. Emission estimates for 1985 from this source (U.S. EPA 1987d) were used for some sectors, while emissions for others were calculated independently as a part of this effort (Wilber 1987). Each source category is discussed in the following sections. Geographical distribution is provided, when available, in Table 1.4.

TABLE 1.3 Estimated 1985 U.S. lead emissions by source sector (tonnes/year).

SOURCE	ESTIMATED 1985 EMISSIONS
Transportation	15,400
Coal Combustion*	
Utility	471
Industrial	263
Commercial/Residential	44
Oil Combustion*	
Utility	12
Industrial	8
Commercial/Residential	7
Industrial Processes	2,300
Solid Waste Disposal	2,800
TOTAL	21,305

*high estimates, low estimate 610 tonnes/yr. for these two sectors combined.

1.4 GEOGRAPHIC DISTRIBUTION:

Canada

Geographic distribution of 1982 anthropogenic lead emissions is shown in Table 1.2 for Ontario and Quebec, each accounts for over 33% of the Canadian total. About 70% of the emissions in Ontario is caused by vehicle emissions, while in Quebec primary copper/nickel production and vehicle emissions account for about 40% and 45% each, respectively (Jaques 1985 and 1987). The emission estimates are also available on a 127 x 127 km polar stereographic grid.

United States

The geographic distribution of lead emissions in the U.S. is shown in Table 1.4. The regions with the highest emissions are along the Atlantic and Pacific coasts and around the Great Lakes. The regions are defined in Addendum B.

a. Gasoline Combustion

Consumption of gasoline accounted for 73% of the total lead emissions in 1985. More than 90% of the emissions from combustion are likely to exist in the form of inorganic particulates, primarily lead halides and double salts with ammonium halides (e.g. $PbBrCl.\ 2NH_4Cl$). The remainder of the emissions are in the form of organic lead compounds, such as tetraethyl lead.

Emissions from gasoline combustion were obtained from emission factors and nationwide gasoline usage. The emissions have been disaggregated to geographical regions based on regional gasoline usage (U.S. DOT 1986), as shown in Table 1.5. The regions are defined in Addendum B.

TABLE 1.4 Emission estimates of lead in the United States (tonnes/year).

REGION	TOTAL	REGION	TOTAL
New England	910	East S. Central	1,250
Mid Atlantic	2,520	West S. Central	2,230
East N. Central	3,400	Mountain	1,130
West N. Central	1,330	Pacific	2,450
South Atlantic	3,090	No Distribution found	2,800
		TOTAL	21,110

TABLE 1.5 Geographic distribution of U.S. lead emissions from gasoline combustion (tonnes/year).

REGION	PERCENTAGE OF TOTAL U.S. GASOLINE USED	ESTIMATED EMISSIONS
New England	5	770
Mid Atlantic	12.5	1,925
East N. Central	17	2,618
West N. Central	8	1,232
South Atlantic	18	2,772
East S. Central	7	1,078
West S. Central	13	2,002
Mountain	6	924
Pacific	13.5	2,079
	TOTAL	15,400

b. <u>Coal and Oil Combustion</u>

Lead exists as a trace component in coal and fuel oil. In coal-fired power plants, lead is emitted in the fly ash that becomes enriched in lead in the burning process by as much as 40 times the original lead content of the coal. Emissions from both coal and oil combustion were estimated using the methods described in Addendum A. The "low" value obtained with this method compares well with the value given by the U.S. EPA (1987a,b). Regional values for emissions from this sector are given in Table 1.6.

TABLE 1.6 Regional lead emissions from coal and oil combustion (tonnes/year).

REGION	HIGH ESTIMATE	LOW ESTIMATE
New England	11	9
Mid Atlantic	89	68
East N. Central	221	166
West N. Central	71	54
South Atlantic	141	107
East S. Central	86	65
West S. Central	95	72
Mountain	79	60
Pacific	13	10
TOTALS	806	611

c. Solid Waste Disposal

Lead is emitted from municipal waste incinerators, generally in particulate form. The U.S. EPA (1987a,b) lists national emissions from this sector at 2,800 tonnes/year for 1985. The most current state-by-state data for this sector were available for 1983 from the Hazardous and Trace Emissions System (HATREMS) which gave a U.S. total of 2,300 tonnes/year. These data are shown in Table 1.7.

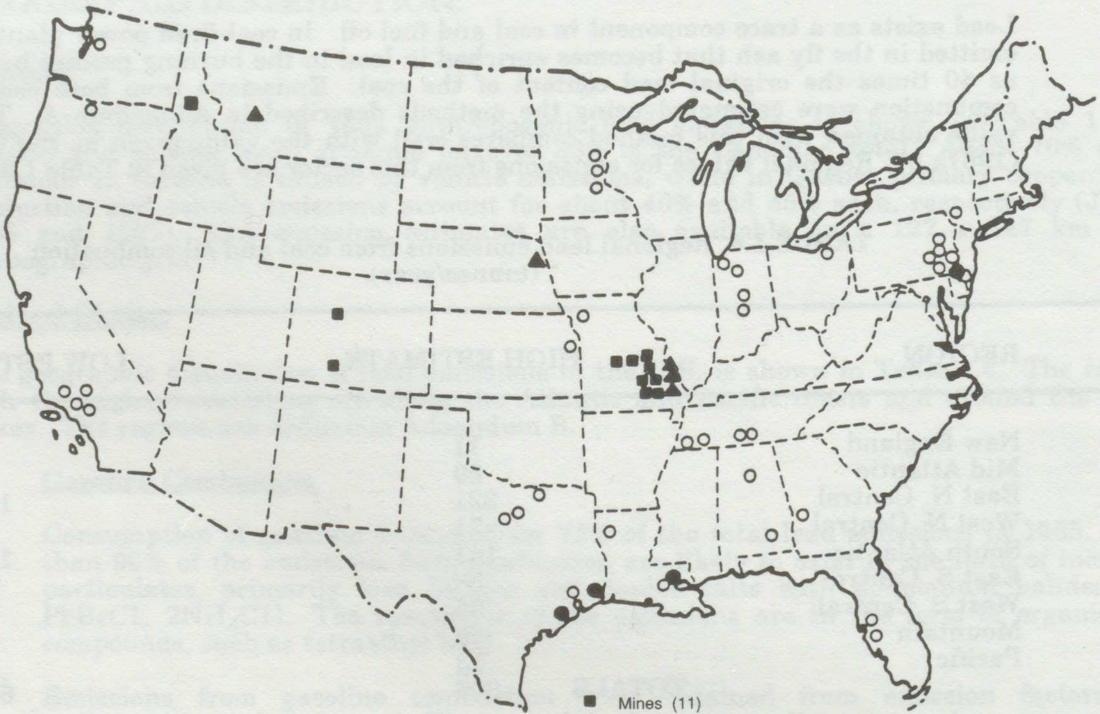
TABLE 1.7 Municipal waste incineration (tonnes/year)
(estimated U.S. lead emissions, from HATREMS).

REGION	TOTAL	REGION	TOTAL
New England	128	East S. Central	86
Mid Atlantic	500	West S. Central	129
East N. Central	550	Mountain	131
West N. Central	264	Pacific	349
So. Atlantic	172	No Regional Data	500
		TOTAL	2,809

d. Industrial Processes

Included in this sector are primary and secondary lead smelters, other lead processing and chemical manufacturing with the majority of the emissions coming from the smelters. Specific state-level data for each of these sectors were not available. Total national emissions from these sources were estimated by the U.S. EPA (1987a,b) to be 2,300 tonnes annually in 1985. Figure 1.2 shows the locations of the major industrial plants.

FIGURE 1.2 Locations of Major Lead-emitting Industries *(U.S. EPA 1986a,b).*



1.5 EMISSION SEASONALITY

Atmospheric emissions of lead in Canada and the United States do not exhibit a pronounced seasonal bias but are spread fairly evenly throughout the year.

1.6 DATA QUALITY

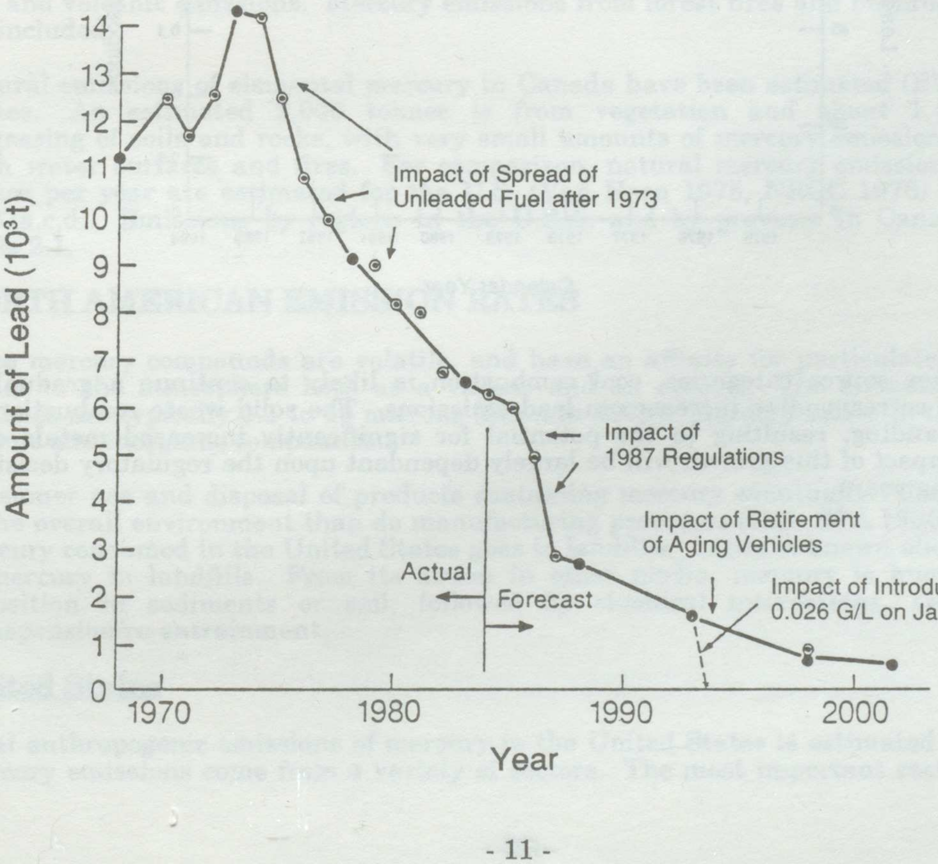
Lead is a criteria pollutant. Emissions from many sources have been estimated by performing emission tests and the largest source category, gasoline combustion, has been extensively investigated. Therefore, the quality of the lead emissions data is judged to be the best of the 14 priority chemicals.

1.7 EMISSION TRENDS

Canada

Trends in automotive lead emissions in Canada from 1933 to 1983, with projections to 2003 are shown in Figure 1.3 (The Royal Society of Canada 1986). Automotive lead emissions in Canada reached a peak in 1973 of over 14,000 tonnes. Regulations introduced in 1973 limited the lead content in gasoline. By 1983 emissions had decreased to just over 6,000 tonnes. As of January 1987, the maximum allowable lead in automotive gasoline is 0.29 g/L. Regulations coming into effect in September 1987, which impose the use of catalytic converters and hence the use of unleaded gasoline on light vehicles, will further reduce lead emissions. Annual lead emissions from automotive gasoline in Canada are projected to drop to less than 2,000 tonnes by the early 1990s and to less than 1,000 tonnes by the year 2000.

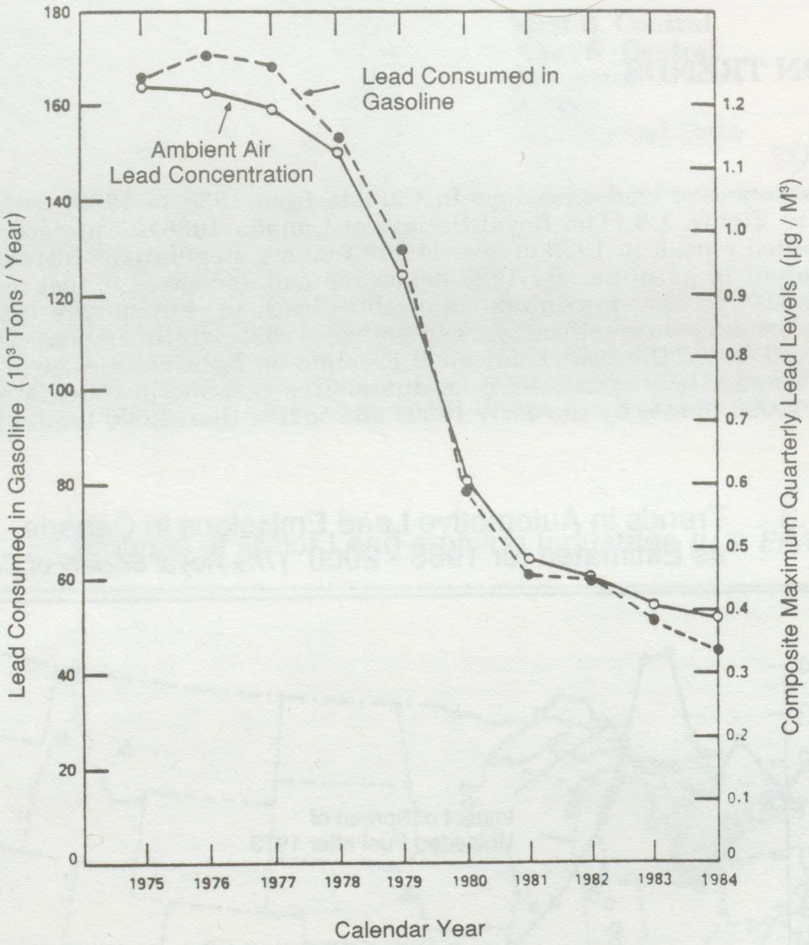
FIGURE 1.3 Trends in Automotive Lead Emissions in Canada as Estimated for 1968 - 2000 *(The Royal Society of Canada 1986).*



United States

Figure 1.4 shows the trends of lead consumed in gasoline and average ambient air concentrations of lead for the period from 1975 to 1984 (U.S. EPA 1986a,b). The amount of lead consumed in gasoline is expected to decrease as both the total amount of leaded gasoline and the amount of lead permitted in each gallon of leaded gas decreases. The U.S. EPA (1986a,b) projected a total gasoline lead consumption of 25,800 tonnes for 1985 and of 1,600 tonnes for 1990.

FIGURE 1.4 Trends in Lead in Gasoline Consumption and Lead Air Concentrations *(U.S. EPA 1986a).*



For the other source categories, coal combustion is likely to continue a gradual increase resulting in corresponding increases in lead emissions. The solid waste combustion sector is rapidly expanding, resulting in the potential for significantly increased metals emissions. The total impact of this growth will be largely dependent upon the regulatory decisions made in the coming years.

2.0 MERCURY

2.1 PROPERTIES (U.S. EPA 1986b; Valaoras 1986)

CAS No. 7439-97-6

Solubility:	0.08 mg/L of water at 30°C; lipid soluble.
Melting Point:	-39°C
Boiling Point:	356°C
Vapour Pressure:	0.002 mm at 25°C

2.2 BACKGROUND

Mercury is a toxic, dense, silvery metal that is in liquid or vapour form at normal temperatures. Mercury compounds have many industrial uses, notably in the chlor-alkali industry, in electrical equipment, and as a paint additive. Past use in the United States and Canada includes pesticides that are now banned except for limited use in fungicides or preservatives.

Though the global cycling of mercury has been a topic of much study in recent years, specific data addressing its anthropogenic sources are still somewhat limited. The primary sources of information for this section for United States are a 1981 U.S. EPA mercury exposure assessment document and a 1984 U.S. EPA NESHAP (National Emission Standard for Hazardous Air Pollutants) document for mercury. A preliminary Canadian emissions inventory for Canada was obtained from the Canadian Environmental Protection Service (Jaques 1987).

Annual global atmospheric emission of mercury from anthropogenic sources has been estimated at 11,000 tonnes by Lantzy and MacKenzie (1979) and at about 20,000 tonnes by the U.S. National Academy of Sciences (1977) and by Sherbin (1979). Estimates of natural source emissions exceed those for anthropogenic emissions.

Natural emissions of mercury include release from soils and vegetation, from forest fires, and from water surfaces. Estimates of global annual natural emissions of mercury vary over several orders of magnitude. Sherbin (1979) cites Weiss et al. (1971) who estimated that annual emissions ranged from 20,000 to 150,000 tonnes. However, Lantzy and MacKenzie (1979) estimated annual natural emissions at only 40 tonnes per year from continental dust flux and volcanic emissions. Mercury emissions from forest fires and burning vegetation were not included.

Natural emissions of elemental mercury in Canada have been estimated (EPS 1981) at 3,500 tonnes. An estimated 2,000 tonnes is from vegetation and about 1,400 tonnes from outgassing of soils and rocks, with very small amounts of mercury emissions estimated from fresh water surfaces and fires. For comparison, natural mercury emissions of about 1,000 tonnes per year are estimated for the U.S. (Van Horn 1975, NRCC 1978) by the U.S. EPA (1987a,c,d). Emissions by regions in the U.S.A. and by province in Canada are shown in Table 2.1.

2.3 NORTH AMERICAN EMISSION RATES

Since mercury compounds are volatile, and have an affinity for particulate matter, mercury occurs in the atmosphere both as a vapour and an aerosol. The diameters of the aerosol particles are typically 0.1 to 10 microns (Sherbin 1979). Mercury exists in the atmosphere as organic and inorganic compounds.

Consumer use and disposal of products containing mercury eventually release more mercury to the overall environment than do manufacturing processes (U.S. EPA 1986b). About 60% of mercury consumed in the United States goes to landfills. Little is known about the movement of mercury in landfills. From its action in other media, mercury is known to cycle from deposition in sediments or soil, followed by chemical interactions, evaporation and/or resuspension/re-entrainment.

United States

Total anthropogenic emissions of mercury in the United States is estimated to be 650 tonnes. Mercury emissions come from a variety of sectors. The most important sectors include fossil fuel combustion, use of paint and electrical equipment, sludge incineration, and nonferrous smelting. A summary of these and other known sources is shown in Table 2.2 and a discussion of each follows.

TABLE 2.1 Geographic distribution of annual natural mercury emissions (tonnes/estimated yearly) in North America.

REGION	TOTAL	REGION	TOTAL
New England	16	Newfoundland	130
Mid. Atlantic	36	Prince Edward Island	<10
East N. Central	46	Nova Scotia	40
West N. Central	96	New Brunswick	50
So. Atlantic	85	Quebec	550
East S. Central	34	Ontario	440
West So. Central	81	Manitoba	230
Mountain	408	Saskatchewan	290
Pacific	216	Alberta	330
		British Columbia	690
		Yukon	220
		North West Territories	550
TOTAL	1,018	TOTAL	3,500

TABLE 2.2 Estimated U.S. mercury emissions by source sector (tonnes/year).

SOURCE	ESTIMATED EMISSIONS	BASE YEAR
Natural	1,018	1976
Hg Mining and Smelting	<1	1983
Fossil Fuel Combustion*		
Utility Coal	113	1985
Industrial Coal	18	1985
Commercial/Residential Coal	1	1985
Utility Oil	1	1985
Industrial Oil	3	1985
Commercial/Residential Oil	3	1985
Copper Smelting	41	1980
Lead Smelting	5	1980
Zinc Smelting	5	1980
Sewage Sludge Incinerators	36	1980
Municipal Waste Incinerators	68	1986
Battery Manufacture	1	1982
Hg Recovery Retorts	<1	1982
Hg Chlor-alkali Plants	3	1983
Use of Consumer Goods	352	1980
Total Man-made Sources	650	
Total Natural and Man-made sources	1,668	

* Values shown for this sector reflect the "high" end of the estimated range.

Canada

For discussions on the compilation of emission inventories, production and usage, see Section 1.3.

Table 2.3 shows the relative emissions by various sectors of the economy in Canada. Total anthropogenic atmospheric emission of mercury in 1982 was approximately 31 tonnes (Jaques 1987). Base metal recovery was the largest contributor to atmospheric emissions at over 45%, followed by fuel combustion at 26%. Thus, over 70% of the emission is from point sources. The third highest source of emissions is paint volatilization, at 16%. Incineration, chlor-alkali plants, agricultural chemicals production and paint manufacturing contribute about 3% each.

TABLE 2.3 Estimated annual mercury emissions (tonnes) in Canada, 1982, by industrial sector and province (Jaques 1987).

SECTOR	NF	PEI	NS	NB	PQ	ON	MB	SA	AB	BC	YUK	NWT	CANADA TOTAL	CANADA %
NATURAL	130	4	35	49	546	438	231	290	326	690	221	546	3500	
INDUSTRIAL PROCESSES														
• Copper/Nickel Production					3		3			<1			6	19.35
• Lead/Zinc Production				<1	1	<1	6			<1			8	25.81
• Chloro-Alkali			<1	<1	<1	<1		<1					1	3.23
• Electrical Equipment Manufacturing					<1								1	Neg.
• Gold Recovery										<1			<1	Neg.
• Instumentation	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1		<1	Neg.
• Agricultural Chemicicals	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1		1	3.23
• Paint Manufacturing	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1		<1	Neg.
• Battery Manufact						<1							<1	Neg.
FUEL COMBUSTION														
• Power Generation	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1		3	9.68
• Petroleum	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1		2	6.45
• Metallurgical Coal			<1			1	<1	<1		<1			3	3.23
• Natural Gas					<1	<1	<1	<1	<1				1	3.23
• Wood	<1	<1	<1	<1	<1	<1	<1	<1		<1	<1		1	3.23
SOLID WASTE INCINERATION														
• Municipal Refuse					1	1		<1		<1			2	2.12
• Sewage Sludge						<1				<1			<1	Neg.
MISCELLANEOUS SOURCES														
• Paint Application	<1	<1	<1	<1	<1	2	<1	<1	<1	<1	<1		5	16.13
• Fluorescent Tube Breakage	<1	<1	<1	<1	1	<1	<1	<1	<1	<1	<1		<1	Neg.
TOTALS														
• Anthropogenic	1	<1	1	1	7	5	10	1	2	2	<1	6	31	100.
• Natural & Anthropogenic	130	5	35	50	560	450	230	290	330	690	220	550	3530	

<1 values are less than 1 tonne but are included in totals: Neg. - negligible

2.4 GEOGRAPHIC DISTRIBUTION

United States

The geographic distribution of estimated anthropogenic mercury emissions in the U.S. is shown in Table 2.4.

a. **Fossil Fuel Combustion**

Rates of mercury emissions from the combustion of fossil fuels were estimated with the methods described in Addendum A. Table 2.5 summarizes the estimates of emissions from coal and oil combustion. The fossil fuel use data are from 1985 (EIA/U.S. DOE 1986).

TABLE 2.4 Regional emission estimates of mercury in the United States (tonnes/year).

UNITED STATES	TOTAL	CANADA	TOTAL
New England	29	East S. Central	58
Mid Atlantic	74	West S. Central	100
East N. Central	95	Mountain	457
West N. Central	112	Pacific	219
South Atlantic	136	No Distribution found	388
TOTAL	446	TOTAL	1,668

TABLE 2.5 Mercury emissions from coal and oil combustion (tonnes/year).

SOURCE	ESTIMATED EMISSIONS	BASE YEAR
New England	2	1
Mid Atlantic	16	13
East N. Central	37	28
West N. Central	11	8
South Atlantic	32	24
East S. Central	19	14
West So. Central	12	10
Mountain	8	6
Pacific	1	1
TOTALS	139	105

b. Mercury-cell Chlor-alkali Plants

Chlorine and caustic are produced in the U.S.A. by the use of electrolytic cells. One type is the mercury cell. Mercury is emitted from this process from two major sources, the hydrogen by-product stream and the end-box ventilation system. The U.S. EPA (1984) notes the test results and year of test for the major chlor-alkali plants. Some of the test data are relatively old, dating back as far as 1973; but emissions from this sector are not significant on either a national or regional level. Hence, their regional distribution is not reported here.

c. Mercury Production

There is currently only one location where mercury is being mined, the McDermitt Mine in Nevada. The U.S. EPA (1984) reports an average emission rate from the mine of 816 g/d, which gives a maximum yearly emission of 0.3 tonne/year.

d. Nonferrous Smelting

Data on current emissions from nonferrous smelting could not be located. The most recent estimates available were for 1980 from the exposure assessment (U.S. EPA 1981a) and did not include individual source estimates. The current emissions total should be significantly lower than the value given here as activities in these industries have decreased since 1980 and emission controls on some plants have increased. This total can be crudely apportioned to the state level according to the known smelter sizes. The results of these approximations are shown in Table 2.6 for copper smelting. Lead and zinc smelter emissions were five tonnes each.

e. Municipal Waste and Sewage Sludge Incineration

These source categories are difficult to characterize because of their continuing rapid growth. The U.S. EPA (1987c) estimated annual emission to the air from municipal waste combustion sources to be 58 tonnes. Table 2.7 shows a regional breakdown of

h. Consumer Use of Mercury-containing Products

United States

Many commercially available products contain mercury. Because of mercury's high volatility, these products release mercury to the atmosphere either during use or after disposal, e.g. paints (in which it is used as a mildew retardant), batteries, and laboratory and dental preparations. As shown in Table 2.8 (U.S. EPA 1981a), emissions from paints dominate. An alternative estimate of mercury emissions from paints used the 1983 mercury content of paint of 209 tonnes and assumed an emission factor of 65% (U.S. EPA 1973). The resulting emissions estimate was 136 tonnes, as contrasted with the U.S. EPA (1981a) estimate of 199 tonnes, which assumed that all mercury in paint eventually volatilizes.

TABLE 2.8 Estimated mercury emissions from use of products which contain mercury (tonnes/year).

SOURCE	ESTIMATED EMISSIONS
Dental Preparations	1
Laboratory Uses	2
Paint	199
Industrial and Control Instruments	7
Electrical Apparatus Use	143
TOTAL	352

Canada

The geographic distribution of estimated anthropogenic mercury emissions as a function of major source sectors is shown in Table 2.3 for Canada in 1982. The central provinces of Manitoba, Ontario and Quebec have the highest emissions, at 33%, 17% and 23%, respectively.

2.5 EMISSION SEASONALITY

Anthropogenic emissions are not believed to exhibit large seasonal variability.

2.6 DATA QUALITY

Natural emission estimates are extrapolated from a relatively sparse data set. As such they contain considerable uncertainty. Anthropogenic emission estimates for the U.S. are of variable quality. Data for the primary smelters are dated and were not estimated with individual source tests, but with average emission factors. For this reason the estimated geographic distribution of emissions from this sector is somewhat uncertain. The estimate for the sludge incinerators is likely to be even less reliable, as this sector has grown significantly since 1980. There is also uncertainty associated with the estimates for fossil fuel sources. Values given for the utility combustion of coal may be somewhat high. The estimates for emissions from consumer goods is also uncertain because the percentage of mercury that actually escapes from each of these products is quite variable, depending in part on whether they are land-filled or incinerated.

The Environmental Protection Service in Canada has compiled mercury emission inventories for 1970 (Sherbin 1979), 1978 (Sheffield 1983), and 1982 (Jaques 1987). These inventories were based on methodologies including measurement, emission factors and professional guesswork. Because the methodologies used in estimating emissions from combustion of petroleum products, from metal recovery and from paint application were significantly different in the two former studies, the values from these years are not comparable (Sheffield 1983) and trends cannot be established. Jaques (1987) cautions that the 1982 inventory is preliminary. Emissions for 1984, however, are not likely to be significantly different from 1982.

2.7 EMISSION TRENDS

No change would be expected for the emission of mercury from natural sources, though it is possible that the use of improved methods or data would change these emission estimates. No projected emission estimates were found for anthropogenic sources in Canada. In the United States, emissions may change in the near future. The municipal waste and sewage sludge incineration sectors are both growing, and this growth could result in increases in the mercury emissions from these sources. The Municipal Waste Combustion Study (Federal Register 1987) projects that mercury emissions from these incinerators could be as high as 148 tonnes by the mid-1990s. Emission regulation decisions expected to be made for these industries in the near future will largely determine the amount of the increase. Mercury emissions are particularly dependent upon the management practices of the incinerators. As destruction efficiencies of organic pollutants increases, the fraction of mercury in the waste which escapes to the flue gas also increases. Another possible source of change is the steady increase in coal combustion over the past few years, which is likely to continue. Lastly, the mercury cell chlor-alkali plants are gradually being replaced by non-mercury methods. Hence, emissions from this source should also be expected to decrease.

A reduction in mercury emissions in Canada has resulted from air pollution control regulation in the chlor-alkali industry. In 1970 this sector was estimated to emit about 24 tonnes (or 32%) of the 75-tonne total. In 1978, the chlor-alkali industry contributed just over two tonnes, or 6% of the 40-tonne total. 1982 emissions are reduced further to just over one tonne, equivalent to 3% of the total. These reductions have been effected by the closing down of the mercury cell processes. Information on trends in other sectors are not reliable because of the change in estimation methodology (Sheffield 1983).

3.0 CADMIUM (Cd)

3.1 PROPERTIES

CAS No. 7440-43-9

Crystal structure: hexagonal pyramids
Melting Point: 321°C
Specific heat: 0.0555 cal g-1 °K-1, solid (25°C)

3.2 BACKGROUND

Cadmium is a soft, silvery-white metal. It occurs in nature as a sulphide, greenockite, closely associated with zinc sulphide ores. It is used mainly in electroplating of other metals or alloys as protection against corrosion.

Cadmium is toxic. Long-term exposure to low cadmium levels leads to its slow accumulation in soft tissues, particularly the liver and kidneys (Health and Welfare and Environment Canada 1983).

Cadmium is a relatively rare element in the earth's crust. Global emissions from natural sources have been estimated by Nriagu (1980) at 830 tonnes, of which 63% (520 tonnes) is from volcanic dust. Other natural sources include vegetation (25%) and windblown dust (12%). It should be noted, however, that the range of these values as given by Nriagu is wide (e.g. windblown dust, whose emission is given as 100 tonnes has a range of 0.1 to 220 tonnes and volcanic particles range from 30 to 780 tonnes). Lantzy and MacKenzie (1979) estimated global natural emissions of cadmium to be 290 tonnes, of which 40 tonnes are from volcanoes and 250 tonnes are from windblown dust.

Anthropogenic cadmium emissions are almost entirely associated with particulates, and in many processes tend to be enriched in the smallest particulate (less than 1 micron). However, in processes which involve extremely high temperatures, cadmium can volatilize and be emitted as a vapor.

3.3 NORTH AMERICAN EMISSION RATES

Canada

For discussions of compilation of emissions in inventories see section 1.3. Annual atmospheric emissions from Canadian sources in 1972 were estimated at about 508 tonnes (EPS 1976). Estimates for 1982 amount to about 322 tonnes (Jaques 1987).

The 1982 estimated emissions, given as provincial contributions, by industrial sector, are shown in Table 3.1 (Jaques 1987). Primary production of copper and nickel contributed the greatest amounts, at over 250 tonnes per year, or 78% of the total. Industrial fuel combustion accounted for about 10% of the total, with emissions of 30 tonnes per year.

3.3 NORTH AMERICAN EMISSION RATES

Canada

For the estimated annual cadmium emissions in Canada by commercial sector and province, see Table 3.1.

United States

The cadmium emission estimates displayed in Table 3.2 are based on Radian Corp. (1985), with the fossil fuel combustion sectors modified as discussed in Addendum A. Fossil fuel combustion is the dominant source, followed by municipal refuse incineration, primary nonferrous smelting, sludge incineration, and iron and steel production. Other sources include rubber tire wear, motor oil combustion, cement manufacturing and fertilizer and fungicide application. These latter sources are considered negligible (U.S. EPA 1981). Fossil fuel combustion occurs at thousands of sources. Individual source-by-source data are not available.

TABLE 3.1 Estimated annual cadmium emissions in Canada by commercial sector and province (Jaques 1987).

SECTOR	NF	PEI	NS	NB	PQ	ON	MB	SA	AB	BC	NWT	CANADA TOTAL	CANADA %
INDUSTRIAL PROCESSES													
• Primary Copper/Nickel Production					144	71	30				2	247	76.71
• Primary Lead/Zinc Production			2	<1	<1	<1	<1			4		7	2.17
• Primary Iron/Steel Production			<1	<1	1	2	<1	<1	<1	<1		3	0.93
• Iron and Steel Foundries		<1	<1	<1	<1	2	<1	<1	<1	<1		2	0.62
• Miscellaneous Sources	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	0.31
STATIONARY FUEL COMBUSTION													
• Power Generation	<1	<1	3	5	<1	1	<1	<1	3	<1	<1	12	3.73
• Commercial	<1	<1	1	<1	<1	3	<1	<1	3	<1	<1	7	2.17
• Industrial	2	<1	1	2	13	7	1	1	<1	3	<1	30	9.32
• Residental	<1	<1	<1	<1	1	1	<1	<1	<1	<1	<1	4	1.25
TRANSPORTATION SOURCES													
• Motor Vehicles	<1	<1	<1	<1	<1	1	<1	<1	<1	<1	<1	2	0.62
• Rail	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	0.31
• Marine	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	0.31
SOLID WASTE INCINERATION													
• Municipal Refuse					1	1		<1		<1		2	0.62
• Sewage Sludge						3		<1		<1		3	0.93
TOTALS	2	1	8	8	164	92	31	2	4	8	2	322	100.

<1 values are less than 1 tonne but are included in totals

TABLE 3.2 Estimated U.S. cadmium emissions by source sector (tonnes/year).

SOURCE	RATE	BASE YEAR
Fossil Fuel Combustion*		
Coal	81	1985
Utility Oil	6	1985
In., Com, Res. Oil	20	1985
Motor Fuels	15	1985
Nonferrous Smelting		
Primary Cadmium	2	1986
Zinc and Zinc Oxide	2	1986
Primary Copper	30	1985
Primary Lead	22	1985
Secondary Copper	1	1984
Secondary Lead	1	1984
Secondary Zinc	<1	1984
Municipal Waste Incineration	10	1986
Sewage Sludge Incineration	10	1984
Iron and Steel Production	10	1984
Cd Pigment Production	1	1985
Cd Stabilizer Production	<1	1985
Ni-Cd Battery Production	<1	1984
TOTAL	211	

* Values shown for this sector reflect the "high" end of the estimated range.

Regional and national emission rates are calculated using emission factors, which are based on average cadmium content in fuel, the nature of the boiler and any emission controls on the boiler, as well as fuel consumption data. This method introduces considerable uncertainty when considering a small number of sources since cadmium content in fuels, and in coals in particular, varies widely by geographic region and can even vary significantly between different veins in the same mine. The uncertainty decreases at the regional and national levels as the analysis incorporates a greater number of sources. The basic approach followed to deal with these complications is described in Addendum A.

Emission rates for smelting processes of copper, lead, zinc and cadmium are generally estimated based on individual source testing.

3.4 GEOGRAPHICAL DISTRIBUTION

Canada

Quebec had the highest annual contribution to the total Canadian emissions, with 164 tonnes (or 50%). Ontario's emissions ranked second, at 92 tonnes (or 29%) and Manitoba followed with 10% (31 tonnes).

United States

The regional distribution of emissions from the primary sectors listed in Table 3.2 are discussed in the following paragraphs and displayed in Tables 3.4 through 3.8. Table 3.3 summarizes the geographic distribution of the U.S. cadmium emissions.

TABLE 3.3 Regional emission estimates of cadmium in the United States (tonnes year).

REGION	TOTAL	REGION	TOTAL
New England	6	East S. Central	15
Mid Atlantic	15	West S. Central	42
East N. Central	37	Mountain	38
West N. Central	25	Pacific	4
South Atlantic	17	No Distribution found	12
		TOTAL	211

a. **Fossil Fuel Combustion**

Fossil fuel combustion is the largest source of emissions of cadmium to the air. It is also one of the most difficult to quantify, as previously described. The resultant estimates obtained by using the methods described in Addendum A are shown in Table 3.4.

b. **Transportation**

The U.S. EPA (1981b) provides a cadmium emission factor for gasoline consumption of 0.30×10^{-7} kg Cd/L. Using a 1985 total gasoline consumption of 107,020 million gallons or 404,530 million litres (U.S. DOT 1986) this results in a national emission of 14.7 tonnes/year. Table 3.5 displays the regional distribution (U.S. DOT 1986). Other transportation sources, such as aviation fuels, were considered negligible compared to the other fossil fuel uses (U.S. EPA 1981b). Diesel and other heavier grade motor fuels were not included in this estimate.

c. **Primary Cadmium Smelters**

The U.S. EPA (1987b) estimates 1986 total annual cadmium emissions, from the four currently operating cadmium smelters, to be 1.8 tonnes per year. Detailed state level emission estimates for this industry are found in Wilber (1987).

TABLE 3.4 Regional cadmium emissions from coal and oil combustion (tonnes/year).

REGION	HIGH ESTIMATE	LOW ESTIMATE
New England	4	4
Mid Atlantic	8	7
East N. Central	21	16
West N. Central	11	9
South Atlantic	11	9
East S. Central	13	10
West S. Central	31	25
Mountain	4	4
Pacific	2	1
TOTALS	105	85

TABLE 3.5 Estimated cadmium emissions from transportation sector.

REGION	1985 GASOLINE USAGE (million gallons/litres)	ESTIMATED EMISSIONS (tonnes/year)
New England	5,311/20,075	1
Mid Atlantic	13,515/51,090	2
East N. Central	18,014/68,093	3
West N. Central	8,679/32,807	1
South Atlantic	19,212/72,620	3
East S. Central	7,286/27,540	1
West S. Central	13,984/52,860	2
Mountain	6,316/23,875	1
Pacific	14,701/404,530	2
TOTALS	107,020/404,530	15

d. **Primary Zinc and Zinc Oxide Smelters**

The five primary zinc and zinc oxide smelters currently operating in the U.S. emit (U.S. EPA 1987b) a total of 2.2 tonnes/year.

e. **Primary Copper Smelters**

Emission estimates for primary copper smelters based on actual source tests and cadmium emission factors combined with production levels from each of the currently operating smelters are given in Table 3.6 (U.S. EPA 1986a,b).

TABLE 3.6 Estimated emissions from primary copper smelters in the United States (tonnes/year).

PLANT LOCATION	ESTIMATED EMISSIONS	PLANT LOCATION	ESTIMATED EMISSIONS
Arizona	0.5	Michigan	0.2
Arizona	2.0	Nevada	5.0
Arizona	0.8	New Mexico	1.9
Arizona	15.8	New Mexico	1.0
Arizona	0.2	Tennessee	0.1
Arizona	0.2	Texas	1.8
Arizona	0.2	Utah	0.9
		TOTAL	30.3

f. Primary Lead Smelters

Data on primary lead smelters were obtained from the U.S. EPA (1986a,b). These are shown in Table 3.7.

TABLE 3.7 Estimated emissions from primary lead smelters in the United States (tonnes/year).

PLANT LOCATION	ESTIMATED EMISSIONS	PLANT LOCATION	ESTIMATED EMISSIONS
Montana	3.4	Missouri	8.7
Missouri	2.0	Texas	6.9
Missouri	0.9	TOTAL	22.0

g. Secondary Nonferrous Smelters

Cadmium emissions from the secondary smelting processes of copper, lead and zinc are comparatively low, under 0.3% of the national total. Hence, geographical allocation of these emissions are not reported here. Secondary smelter emissions are estimated at 0.45 tonnes/year for copper, 0.47 tonnes/year for lead and 0.10 tonnes/year for zinc.

h. Municipal Waste and Sewage Sludge Incinerators

The emissions from incineration processes are difficult to quantify because the cadmium content of the wastes may vary considerably. Furthermore, the use of incinerators is growing rapidly. The number of municipal waste incineration (MWI) units is expected to triple in the next ten years, with the Northeast and Midwest expecting to see the largest growth (Federal Register 1987). The emission estimates shown in Table 3.8 were derived from proportioning total cadmium emissions from this sector (Federal Register 1987) by plant capacities (U.S. EPA 1987c).

TABLE 3.8 Estimated cadmium emissions from municipal waste incinerators in the United States for 1986 (tonnes/year).

REGION	NUMBER OF UNITS	ESTIMATED EMISSIONS
New England	24	1.6
Mid Atlantic	15	2.5
East N. Central	13	1.9
West N. Central	8	0.4
South Atlantic	20	2.7
East S. Central	9	0.6
West S. Central	16	0.4
Mountain	3	0.1
Pacific	3	0.2
TOTALS	111	10.4

Sewage sludge incineration is currently being studied. A state-by-state allocation was not available, although Radian (1985) stated that "the largest concentrations of units are found in the Midwestern and Great Lakes states," and estimated a national total emission of 10.3 tonnes/year.

i. **Iron and Steel Production**

Emissions of cadmium from the iron and steel industry are the result of the use of raw materials which contain cadmium. Since most iron and steel processes operate at temperatures well above the boiling point of cadmium, most of the cadmium is volatilized and emitted with the process off-gases. The most current data are from the Radian (1985) document. Actual state-by-state emission estimates are not available. However, the majority of the plants are located in the area east of the Mississippi River and north of the Ohio River, with the greatest concentration in Illinois, Indiana, Ohio and Pennsylvania (U.S. EPA 1981b). Based on a characterization of the industry and results from averaged emission tests, annual cadmium emissions for this source sector were estimated at 10.3 tonnes/year.

j. **Additional Sources**

Several other industries are known to emit relatively small amounts of cadmium. Among these are cadmium pigment manufacturing, cadmium stabilizer production and nickel-cadmium battery manufacturing. Estimates for the pigment and stabilizer manufacturing plants are taken from U.S. EPA (1986) and for the battery plants from Radian (1985).

3.5 DATA QUALITY

Jaques (1987) states that the Canadian emissions inventory for cadmium is preliminary and should be viewed with caution. He estimates that emissions for 1984 are not likely to differ significantly from 1982 values. Several assumptions went into generating the U.S. cadmium estimates. For the two largest sectors, fossil fuel combustion and municipal waste incineration, there is significant uncertainty for individual plants, e.g. large variability in cadmium contents in fuels and in control efficiencies. Emission estimates reported here therefore place primary emphasis on capturing regional variability in cadmium content in coals at the expense of ignoring what data exist on emission factors as a function of boiler type. Regional variability of cadmium in oil combustion could not be treated.

Estimates for the smaller source categories were based on actual source tests; therefore they should be somewhat more reliable.

3.6 EMISSION TRENDS

No projected emission trends were found in Canada. Changes are expected in a number of the emitting sectors in the USA. Total use of coal increased nearly 20% in the utility sector from 1980 to 1985 (NCA 1987). A continuation of this trend could contribute significantly to annual cadmium emissions. The municipal waste incineration sector is expected to triple in the next ten years. The effect of this growth on future emissions will be determined by pending the effectiveness of emission control decisions.

4.0 ARSENIC (As)

4.1 PHYSICAL PROPERTIES

CAS No. 7440-38-2

(Van Nostrand's Scientific Encyclopedia, 5th Edition and Merck Index, 9th Edition)

Elementary arsenic exists at room temperature in two well-defined crystalline forms: metallic or gray arsenic, the common stable form; and yellow arsenic, the unstable form.

	Gray Arsenic	Yellow Arsenic
Appearance:	steel gray; opaque metallic lustre	yellow, transparent
Crystal Structure:	hexagonal	cubic
Melting Point:	818°C at 36 atm.	transforms to gray form
Vapour Pressure:	380 mm Hg at 1°C	more volatile than gray form

4.2 BACKGROUND

Arsenic is a widely distributed, highly toxic metal. It exists at low concentrations in volcanic gas, sea water and spring water. Arsenic is a by-product in the refining of metal, particularly gold. Arsenic compounds are used as pesticides and as metal alloys. Copper arsenic alloys increase resistance to corrosion and enhance machinability.

Arsenic is found in low concentrations in the natural environment -- less than 4 ppm in agricultural soils, less than 0.3 ppm in river water and less than 0.03 ppm in sea water. Metal-bearing ores contain higher concentrations of arsenic. Certain gold ores may contain up to a few percent (Gagan 1979).

Lantzy and MacKenzie (1979) estimate global natural emission of arsenic to be about 2,800 tonnes (or 3.5%) of total emissions, and 78,000 tonnes to be from anthropogenic sources.

4.3 NORTH AMERICAN EMISSION RATES

United States

The main application of arsenic in the United States (approx. 70%) is for pesticide manufacture. The use of these pesticides, some of which are organic, also accounts for approximately 45% of the estimated releases of arsenic to the air. Other sources of emission include fossil fuel combustion, primary and secondary copper smelting, zinc production and cotton ginning. Most of the arsenic emissions from these sources are in the form of inorganic particulate matter.

Table 4.1 shows the most recent arsenic emissions. Each source type listed will be briefly discussed and geographic distribution information given where available.

Canada

For discussions on compilation of emission inventories and for information on production and usage, see section 1.3.

Table 4.2 shows estimated arsenic emissions by industrial sector and province for Canada (Jaques 1987). The major source of arsenic to the atmosphere in 1982 was the production of base metals, with copper/nickel, iron and steel and lead/zinc production accounting for approximately 60%, 20% and 10%, respectively, of the estimated 471 tonnes/year. Fuel combustion and gold production contributed roughly 7%.

4.4 GEOGRAPHICAL DISTRIBUTION

Distribution of anthropogenic arsenic emissions by provinces for 1982 is shown in Table 4.2. Ontario has the highest arsenic emissions, with over 40% of the total, followed by Quebec at 34% and Manitoba at about 13%. Just under 7% of Canada's arsenic emissions occur in British Columbia (Jaques 1987).

TABLE 4.1 Estimated U.S. arsenic emissions by source sector (tonnes/year).

SOURCE	TOTAL EMISSIONS	YEAR OF RECORD
Coal Combustion *		
Utility	802	1985
Industrial	510	1985
Commer./Resid.	78	1985
Oil Combustion *		
Utility	6	1985
Industrial	9	1985
Commer./Resid.	5	1985
Primary Cu Smelters	312	1985
Primary Pb Smelters	38	1984
Secondary Pb Smelters	7	1984
Zinc Production	9	1984
Arsenic in Pesticides Use	1,500	1979
Arsenic in Chemicals Production	<1	1984
Cotton Gins	3	1985
Glass Manufacturing	33	1984
Arsenic Production	17	1985
Municipal Waste Incineration	3	1986
TOTAL	3,332	

* Values for this sector reflect the "high" end of the estimated range.

TABLE 4.2 Estimated annual arsenic emissions (tonnes) in Canada by industrial sector and province (Jaques 1987).

												CANADA	
SECTOR	NF	PEI	NS	NB	PQ	ON	MB	SA	AB	BC	NWT	TOTAL	%
INDUSTRIAL PROCESSES													
• Primary Copper/Nickel Production					158	77	33			23		291	76.1
• Primary Lead/Zinc Production				4			28			9		41	8.7
• Primary Iron/Steel Production						103						103	21.9
• Metallurgical Processing of Gold						6					9	15	3.2
• Miscellaneous Sources	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	0.2
STATIONARY FUEL COMBUSTION													
• Power Generation	<1	<1	9	<1	2	<1	<1	<1	1	<1	<1	12	2.5
• Commercial	<1	<1	1	<1	<1	<1	<1	<1	3	<1	<1	<1	Neg
• Industrial	<1		<1	<1	2	3	<1	1	<1	3	<1	7	1.5
• Residental	<1	<1	<1	<1	1	1	<1	<1	<1	<1	<1	<1	Neg
TRANSPORTATION SOURCES													
• Marine	<1	<1	<1	<1	<1	<1	<1		<1	<1	<1	1	Neg
SOLID WASTE INCINERATION													
• Sewage Sludge						1		<1		<1		1	0.2
MISCELLANEOUS SOURCES													
• Pesticide Application	<1	<1	<1	<1	<1	<1	<1		<1	<1		1	Neg
TOTALS	1	1	9	4	160	192	61	1	1	32	9	471	100.

<1 values are less than 1 tonne but are included in totals. Neg. = negligible

United States

Regional arsenic emissions in the United States are summarized in Table 4.3.

TABLE 4.3 Regional emission estimates of arsenic in the United States.

REGION	TOTAL	REGION	TOTAL
New England	17	East S. Central	201
Mid Atlantic	234	West S. Central	140
East N. Central	398	Mountain	359
West N. Central	79	Pacific	28
South Atlantic	372	No distribution found	1,504
		TOTAL	3,332

a. **Arsenic Pesticide Use**

The most important source of atmospheric arsenic is the use of arsenical pesticides, including Paris green, calcium arsenate, disodium methanearsenate (DSMA), monosodium methanearsenate (MSMA), cacodylic acid and arsenic acid. Arsenical pesticides have a wide range of applications, but current data on their use has not been found. The 1982 exposure assessment (U.S. EPA 1982b) approximated the atmospheric emissions for 1979 at 1,500 tonnes/year based on 1979 use levels and an emissions factor of 168 kg arsenic emitted per tonne of arsenic applied as pesticide. Application of these pesticides is concentrated in the Southeast, but a detailed geographic pattern was not available.

b. **Fossil Fuel Combustion**

The second largest source of atmospheric arsenic is the combustion of fossil fuels. The emission result from the presence of trace amounts of arsenic in coals and oils. Utilities account for more than a half of the fossil fuel combustion emissions. A multitude of sources and a large variability of arsenic content in the fuels make quantification of emissions from these sources difficult. The approach used here is described in Addendum A. The regional emissions are shown in Table 4.4.

TABLE 4.4 Regional arsenic emissions from coal and oil combustion.
(tonnes/year).

	ESTIMATED			ESTIMATED	
REGION	High	Low	REGION	High	Low
New England	17	14	East S. Central	196	147
Mid Atlantic	219	165	West S. Central	109	83
East N. Central	384	288	Mountain	47	35
West N. Central	72	54	Pacific	9	7
South Atlantic	357	269	TOTALS	1,410	1,062

c. **Primary copper smelters**

At the 14 primary copper smelters currently operating in the U.S., copper ore concentrates typically contain arsenic from 0.4% to 3.8% by weight. It is generally in the form of the mineral arsenopyrite. In the smelting process, arsenic oxidizes to arsenic trioxide, As_2O_3, although some remains in the sulfide form. Both of these compounds are volatile at the high temperatures (up to 1500°C) of the copper smelting processes. The total fraction of arsenic entering with the smelter feed that is volatilized ranges from 40% to nearly 100% (U.S. EPA 1982b). As the gas stream cools, some of the arsenic trioxide or sulfide condenses onto the flue dusts. The cooling and the emission control characteristics of each of the smelters determine the net emissions. About 2.4% of the initial arsenic input escapes as uncontrolled fugitive emissions, mostly in the particulate trioxide form. Table 4.5 summarizes arsenic emissions for this sector (U.S. EPA 1986).

TABLE 4.5 Arsenic emissions from primary copper smelters (tonnes/year).

REGION	TOTAL	REGION	TOTAL
Utah	32	Arizona	43
Nevada	114	Arizona	2
Arizona	14	New Mexico	0
Arizona	30	New Mexico	1
Arizona	35	Texas	20
Arizona	11	Tennessee	0
Arizona	3	Michigan	2
Arizona	4	TOTAL	312

d. Primary and Secondary Lead Smelters

The process of arsenic release to the atmosphere is similar for primary lead and copper smelting. Arsenic is volatilized as arsenic trioxide throughout the lead smelting process, with some arsenic escaping to the atmosphere. For example in an arsenic materials balance for a lead smelter in Missouri, a total of 12.9% of the arsenic entering the smelter could not be accounted for in the collected wastes and product streams and was assumed emitted to the atmosphere. Table 4.6 summarizes the estimated emission of inorganic arsenic from primary lead smelters (U.S. EPA 1985d).

TABLE 4.6 Estimated arsenic emissions from primary lead smelters (tonnes/year).

REGION	TOTAL	REGION	TOTAL
Montana	23	Missouri	2
Missouri	3	Texas	8
Missouri	2	TOTAL	38

e. Zinc Smelters

Zinc and zinc oxide are produced from zinc ores by several different processes, all of which have the potential to emit arsenic. Arsenic is emitted primarily as arsenic trioxide both in vapour and particulate form. These emissions are estimated to total 8.6 tonnes and their geographical distribution can be found in Wilber (1987).

f. Cotton Gins

Arsenic is emitted from cotton gin operations that handle and gin cotton that has been desiccated with orthoarsenic acid. About 98% of all such operations are located in Texas, with the remainder in Oklahoma. In 1985, estimates of the number of such cotton gins ranged from 285 to 320 (U.S. EPA 1985d). Total arsenic released to the atmosphere was estimated to be 2.7 tonnes/year.

g. **Glass manufacturing**

Arsenic can be emitted from a number of glass manufacturing processes. The U.S. EPA (1986a) documented background information for recently promulgated standards and included current (1985) estimates for baseline arsenic emissions from this source. The geographic locations were available for 90% of these emissions and are shown in Table 4.7. Total emissions are estimated to be 33.5 tonnes.

TABLE 4.7 Estimated Arsenic emissions from glass manufacturing (tonnes/year).

REGION	NUMBER OF PLANTS	ESTIMATED EMISSIONS
Rhode Island	1	0.2
New York	2	1.0
Pennsylvania	4	4.0
West Virginia	2	13.3
Ohio	2	1.8
Indiana	1	7.7
Kentucky	2	0.3
Louisiana	1	2.4
NR	12	3.0
	TOTAL	33.5

h. **Arsenic production**

The only primary arsenic production plant operating in 1985 is located in Tacoma, Washington. In 1985 it was estimated to emit 1.3 tonnes/year from its stack (based on a reported emissions of 0.15 kg/hr) and 16.1 tonnes/year (based on a reported rate of 1.84 kg/hr) from various low-level fugitive sources (e.g. roasters, baghouse dust, etc.) for a total of 17.4 tonnes/year. Additional controls on the low-level emissions are likely in the near future and could reduce their emissions to 6.5 tonnes/year, for an overall total of 7.8 tonnes/year.

i. **Municipal waste combustion**

A recently conducted Municipal Waste Combustion Study (U.S. EPA 1987c) reported an estimated emission rate for arsenic from this sector to be 2.7 tonnes/year based on both source tests and applications of emission factors (Federal Register 1987). Wilber (1987) summarizes the geographical distribution of these emissions.

4.5 EMISSION SEASONALITY

Since pesticides application is the dominant source of emissions in the United States, seasonal variations in emissions can be expected. In Canada, however, the emissions, primarily from base metal production, are essentially constant throughout the year.

4.6 DATA QUALITY

Emission estimates for many U.S. industrial sources were based on recent source tests. Hence, these estimates are quite reliable. There may be a few small sources that have not been included. It is probable that the fossil fuel combustion emissions fall within the range given. Emission estimates for pesticide use are highly uncertain. No recent data on pesticide use were found and emission factors are considered to be somewhat unreliable. Jaques (1987) states that in the 1982 Canadian inventory, all sectors have not undergone the same rigorous analyses as those of lead, hence, the inventory should not be used out of context.

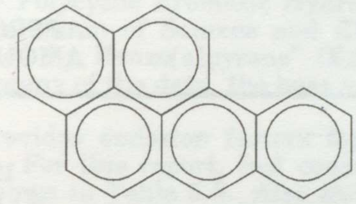
4.7 EMISSION TRENDS

Future changes in arsenic emissions in North America are probable. In the U.S., increased coal combustion will result in a corresponding increase in emissions from this sector. Use of arsenical pesticides has been gradually declining but use of arsenical wood preservatives is likely to continue its current upward trend. According to the Municipal Waste Combustion Study, arsenic emissions from municipal waste incinerators are likely to increase from 2.7 tonnes/year to about 13.0 tonnes/year by the mid 1990s.

Partly due to enhanced pollution control in the gold processing section, there has been a significant decrease in emissions of arsenic and a change in emission patterns since 1972 (Environment Canada 1972). The estimated emissions of arsenic for 1970 were 3700 tonnes as compared to 471 tonnes in 1982. Processing of gold accounted for about 47%, or over 1700 tonnes while in 1982 this sector accounted for less than 1%. Production in 1972 of iron and steel at 900 tonnes (25%) and copper/nickel at 600 tonnes (16%) compares to 103 and about 210 tonnes, respectively, in 1982. No information on future trends was found.

5.0 POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) POLYCYCLIC ORGANIC MATTER (POM)

BENZO[a]PYRENE BaP $C_{20}H_{12}$ CAS No. 50-32-8



5.1 PROPERTIES OF BaP (U.S. EPA 1987d; Vershueren 1983; Strachan 1986)

Solubility:	0.003 mg/L in water
Partition coefficient:	$\log P_{octanol} = 5.97$
Molecular weight:	252
Melting Point:	179°C
Vapour Pressure:	5×10^{-9} torr

5.2 BACKGROUND

Polynuclear aromatic hydrocarbons, or PAHs, are a diverse class of compounds consisting of substituted and unsubstituted polycyclic and heterocyclic aromatic rings. They are often referred to as polycyclic organic matter (POM) (Radian Corp. 1986). A few of the PAH congeners have commercial applications; for example naphthalene is used in mothballs. PAHs are formed primarily through incomplete combustion of organic compounds. Several PAH congeners are carcinogens, the primary one being benzo[a]pyrene, BaP. Therefore, source testing for PAHs focuses on BaP and BaP generally serves as an indicator of PAH or POM. Ratios of BaP:PAH or BaP:POM are quite variable in the literature, depending primarily upon how many PAHs or POMs were tested for. As most studies focus on BaP, the same will be true for this chapter.

Global atmospheric emission of BaP from anthropogenic sources for the period 1966-1969 were estimated by Suess (1976) at 5,000 tonnes per year, of which 1,300 tonnes came from the United States (U.S. NAS 1972).

PAHs may be synthesized by various bacteria and algae, e.g. *Chlorella vulgaris*. The natural production of BaP from various species ranges from 20 to 60 μg BaP produced per kg of dry bacterial biomass (U.S. EPA 1987d). Active volcanoes may be a natural source of PAHs (Il'nitskii et al. 1968, cited in OMOE 1979), but volcanic emissions of PAHs are considered to be relatively minor (NRCC 1983; Suess 1976). Emissions from forest fires have been treated as anthropogenic in this chapter.

5.3 NORTH AMERICAN EMISSION RATES

Canada

Primary atmospheric sources include combustion of fuels for heat and power generation, transportation, solid-waste incineration, industrial processes such as coal and coke processing and petroleum refining. Forest fires may contribute significantly to atmospheric emissions. Miscellaneous combustion sources include agricultural burning and smoking. (NRCC 1983; U.S. EPA 1987c).

Other sources of release to the environment in general include roadbed and asphalt leachate, runoff from greases, domestic effluent, sludge cake from heat treatment plants, wood preservative sludge (U.S. EPA 1987d, and Vershueren 1983). These may in turn be a secondary source to the atmosphere through evaporation or incineration.

Estimated Canadian annual BaP anthropogenic emissions for 1980 (NRCC 1983; Lao et al. 1975) in Table 5.1 are in the range 19 to 22 tonnes. Emissions from forest fires, although noted as a significant source, were not included. Emissions from forest fires and other uncontrolled burning in Ontario, however, were estimated to be 7-100 tonnes in 1976

(NRCC 1983, OMNR 1977). Coke production ranks highest in emissions at 12 tonnes per year which is about 60% of the total, followed by aluminum reduction at four to six tonnes per year, or 25% of the total. Tire wear, with estimated emissions of over one tonne per year, was a significant contributor to these estimates. A brief description of the various source sectors is provided.

TABLE 5.1 Estimated annual emissions of BaP in Canada (tonnes/year).

REGION	APPROXIMATE AMOUNT	PERCENTAGE
INDUSTRIAL PROCESSES		
Coke production	12	60
Aluminum reduction	4 - 6	25
Petroleum catalytic cracking	0.5 - 1	4
FUEL COMBUSTION (STATIONARY SOURCES)		
Utilities, industrial, residential*	0.4	2
TRANSPORTATION		
Cars, trucks, buses	0.4	2
Motorcycles	0.5	2
Tire wear	1.1	5
TOTAL	19 - 22	

*Does not include emissions from wood combustion (NRCC 1983, from Lao et al. 1975)

a. **Industrial Processes**

Coke production contributes significant atmospheric emissions of PAHs, most of which occur from gas leakage during the processing. A review of emissions of PAH from coke ovens appears in a report by the Ontario Ministry of Labour (1982). Up to 60 different PAH congeners have been measured in coke processing (Lao et al. 1975; York Research Corporation 1978). Catalytic cracking in the petroleum industry, aluminum reduction and other processes, such as the manufacture of charcoal and carbon black, are also sources of atmospheric emission of PAHs.

b. **Fuel Combustion**

PAHs are formed from burning wood and fossil fuels. The amount released depends on the efficiency of combustion. It is possible for fossil-fueled power plants with efficient fuel combustion to maintain low emissions of PAHs. Residential combustion of wood in woodstoves and fireplaces is a significant source of PAHs but was not included in the Canadian emissions (NRCC 1983; Peters et al. 1981; Murphy et al. 1985).

c. **Transportation**

PAHs have been identified in the exhaust from cars using leaded and unleaded gasoline and diesel fuel, depending on the type of engine, combustion conditions and emission control devices. Two-cycle engines which operate on an oil/gas mixture, produce more BaP than do four-cycle engines. A further contributor is from wear of tires since carbon black is a reinforcing agent for synthetic rubber (NRCC 1983).

d. **Solid Waste Incineration**

Atmospheric emissions of PAHs from the incineration of solid waste depend on the organic compounds in the waste, the efficiency of operation and the action of pollution control devices. PAHs were identified in fly ash from an electrostatic precipitator of a municipal incinerator by Eiceman et al. (1981), Clement and Karasek (1982) and NRCC (1983).

e. **Other sources**

Forest fires and other open burning of organic matter, such as grass, leaves and bark, were considered to be the most important sources of PAH emissions in Ontario in 1976 (NRCC from OMOE 1979, McMahon and Tsoukalas, 1978).

United States

Primary sources of information include: "An Exposure and Risk Assessment for Benzo[a]pyrene and Other Polycyclic Aromatic Hydrocarbons" (U.S. EPA 1982a); "Polycyclic Aromatic Hydrocarbon Evaluation of Sources and Effects" (NRCC 1983); and "Preliminary Airborne POM as Indicated by Benzo[a]pyrene" (Energy and Environmental Analysis Co. 1978). Unfortunately, for many of the data, the base year is 1978.

The U.S. EPA (1982a) provides emission factors for estimating total BaP emissions from major combustion sources. For this report, fuel consumption for 1985 was used to estimate the U.S. BaP emissions shown in Table 5.2. Also shown are estimates made using emission factors for sources addressed in the EEA (1978) document, but not included in the U.S. EPA (1982a) report, such as incineration and coke production.

TABLE 5.2 U.S. BaP emissions by source sector (tonnes/year).

SOURCE	EMISSION FACTOR	ESTIMATED EMISSIONS
Coal Combustion:		
- Residential/Commercial	1540.00 mg/tonne	8
- Utility	1.60 mg/tonne	1
- Industrial	0.95 mg/tonne	<1
Wood Combustion	0.004 g/kg	560
Prescribed & Agricultural Burning	0.74 mg/kg	40
Wildfire	0.74 mg/kg	20
Gasoline	27 µg/litre	13
Tire wear		1
Coke Production	0.33 mg/kg	9
Coal Refuse Piles		<1
Municipal & Commercial Incineration		1
	TOTAL	655

* Converted to metric units from original reference.

5.4 GEOGRAPHICAL DISTRIBUTION

Canada

The only provincial estimates found were for Ontario. To estimate BaP emissions the Ontario Ministry of the Environment (OMOE) has used U.S. EPA emission factors. Total annual emissions of BaP in 1976 was estimated at 18 tonnes. Major sources were heat and power production, including power plants and residential furnaces, coke and asphalt production, transportation and forest fires for 1976 (OMOE 1979). The calculated emissions for Ontario indicate that forest fires and other uncontrolled burning contribute as much BaP and hence, by inference, PAH, as major industrial and transportation sources. The report also identified motorcycles and snowmobiles, powered by two-cycle engines, as major polluters among mobile sources of PAH. PAH emissions from marine vessels may be significant in localized situations (NRCC 1983) but were not included. Importantly, the report also lacks estimates for emissions from residential fuel combustion.

In 1983 total annual BaP emissions in Ontario were estimated at 12.4 tonnes (OMOE 1985). This is shown in Table 5.3. The largest source is coke production, accounting for 63% of the total. Forest fires are estimated to rank second, contributing 35% of the total. Mobile sources and fuel combustion account for the remaining 2%.

TABLE 5.3. Estimated annual BaP emission in Ontario, 1983.
(Ontario Ministry of the Environment 1985; Voldner 1986).

SOURCE	AMOUNT	APPROXIMATE PERCENTAGE
Coke production	7.8	63.3
Forest fires	4.4	35.2
Mobile sources	0.1	0.9
Fuel combustion	0.1	0.6
TOTAL	12.4	

United States

The regional distribution for U.S. BaP emissions has been estimated for major emitting sectors and summarized in Table 5.4.

TABLE 5.4. Regional emission estimates of BaP in the United States (tonnes/year).

REGION	TOTAL	REGION	TOTAL
New England Mid Atlantic	83	East S. Central West S. Central	
East N. Central West N. Central	76	Mountain Pacific	92
South Atlantic	331	No Distribution found	71
		TOTAL	655

Wood Combustion

A BaP emission factor for wood combustion of 0.004 g/kg was applied to estimates of total U.S. wood combustion for 1983, the most recent year available (Energy Information Administration (EIA)/Department of Energy (DOE) 1984). Table 5.5 shows the geographic breakdown for the consumption and the corresponding emissions. Note that these consumption values include residential fireplaces, primary and auxiliary residential heating as well as commercial, industrial and utility-related uses. No data were found addressing variation in the emission characteristics among these sectors even though the actual emission rates for BaP should be strongly influenced by the temperature at which this fuel is burned. This, in turn, is strongly influenced by the species, aging and physical form of wood burned, the design of the combustion device, amount of excess combustion air, rate of burning, etc. Moreover, organic emissions are also significantly altered by catalytic afterburners, which are frequently used with modern wood-burning stoves. Thus,even though necessitated by a lack of relevant data, use of a single value for the emission factors for this diversity of sources is problematic.

Fossil Fuel Combustion

Using the emission factors from U.S. EPA (1982) and the 1985 coal combustion data from the National Coal Association (1987) and motor fuel usages from the Federal Highway Administration (U.S. DOT 1986), emissions from these combustion sectors were estimated. The results are shown, with approximate geographic distributions, in Tables 5.6 and 5.7.

TABLE 5.5. BaP emissions from wood combustion, 1983 (tonnes/year).

REGION	AMOUNT BURNED	ESTIMATED EMISSIONS
New England Mid Atlantic	20,000,000	80
East N. Central West N. Central	17,000,000	68
So. Atlantic East S. Central West S. Central	81,000,000	324
Mountain Pacific	22,000,000	88
	TOTAL	560

TABLE 5.6. BaP emissions from fossil fuel combustion in the utility, industrial, commercial and residential sectors (tonnes/year).

REGION	TOTAL	REGION	TOTAL
New England	0.2	East S. Central	0.8
Mid Atlantic	1.0	West S. Central	0.2
East N. Central	2.9	Mountain	0.9
West N. Central	1.4	Pacific	0.4
South Atlantic	1.6	TOTAL	9.3

TABLE 5.7. BaP emissions from motor vehicle fuel combustion

REGION	TOTAL GASOLINE CONSUMED (million gallons/litres)	ESTIMATED EMISSIONS (tonnes/year)
New England	5,311/20,075	0.6
Mid. Atlantic	13,515/51,090	1.6
E.N.Central	18,014/68,093	2.2
W.N.Central	8,679/32,807	1.0
So. Atlantic	19,212/72,620	2.3
E.S.Central	7,286/27,540	0.8
W.S.Central	13,984/52,860	1.7
Mountain	6,316/23,875	0.8
Pacific	14,701/55,570	1.8
TOTALS	107,018/404,530	13

Additional Sources

The remaining sources in Table 5.2 were taken directly from U.S. EPA (1982a) and EEA (1978). No recent data were located for prescribed and agricultural burning or for wildfires. A 1985 coke production value was obtained from NCA (1987) and was applied to the emissions factor from EEA (1978).

5.5 EMISSION SEASONALITY

Seasonal variations in BaP emissions are expected to be large. Fuel combustion from residential home heating would be expected to have a bias toward increased amounts in winter. Forest fires, which contribute significantly to atmospheric emissions, occur most often in the summer months. It is expected that emissions from coke production, from power plants and from automobiles will show little seasonal change.

5.6 DATA QUALITY

Emission estimates of BaP and PAHs have large uncertainties. Rates of emissions are usually calculated from emissions factors, defined as statistical averages of the rates of some activity (e.g. combustion, industrial production), divided by the level of that activity (NRCC 1983 from EPS 1981). Emissions factors giving total PAHs based on the amount of BaP have been developed for different source types. The BaP emissions were themselves estimated using emission factors, based on sales figures, usage or population. There are serious difficulties with this method for estimating emission factors (NRCC 1983). An individual source may vary over several orders of magnitude, depending on age, operating conditions and pollution control devices. For national and regional emission estimates, these uncertainties should diminish as the unique conditions of an individual source are averaged over many facilities. Detailed regional estimates are unavailable for Canada. Canadian estimates do not include emissions for residential wood burning, which is expected to be a major source category.

5.7 EMISSION TRENDS

Estimated rates of BaP emissions could change significantly in the coming years. Gradual increases in the use of wood in residential heaters, stoves and fireplaces may continue for several years. The degree to which catalytic afterburners are employed could modify emission trends from this sector. Municipal waste incineration is expected to increase dramatically in the next decade. Coal consumption in the U.S. is also expected to continue its gradual increase over recent years. Current data on prescribed and agricultural burning were unavailable. Wildfires and forest fires vary from year to year.

6.0 POLYCHLORINATED DIBENZO-P-DIOXIN (PCDD) POLYCHLORINATED DIBENZOFURAN (PCDF)

(PCDD) CAS No. 1746-01-6
(PCDF) CAS No. 51207-31-9

6.1 PROPERTIES OF 2,3,7,8-T$_4$PCDD

(U.S. EPA 1987a,d, from Vershueren 1983; Strachan 1986)

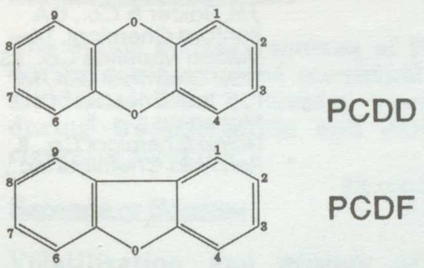
State:	a white crystalline solid
Solubility:	0.2 mg/L
Partition Coefficient:	log $P_{octanol} = 5\text{-}7$
Molecular Weight:	322
Boiling Point:	305°C

6.2 BACKGROUND:

Dibenzo-ρ-dioxin is composed of two benzene rings bonded by two oxygen atoms as shown in Figure 6.1. Chlorinated dioxins (PCDDs) are formed when chlorine is substituted at different positions of the rings resulting in a possibility of 75 different congeners. 2,3,7,8-tetrachloro-dibenzo-ρ-dioxin (2,3,7,8-TCDD) is stable and considered to be one of the more toxic congeners. Hence, it has received considerable attention.

PCDDs are not commercially produced. They form as byproducts in trace amounts during the manufacture of other chlorinated organic chemicals, primarily chlorophenols, as well as during the combustion of a wide range of materials. These include PCBs and other chlorinated organics, as well as municipal and industrial wastes.

Sources of dioxins can be broadly separated into: manufacturing; combustion; chemical disposal; and photochemical processes. However, few quantitative estimates of emissions are available.



Number of Chlorine Atoms	1	2	3	4	5	6	7	8
PCDD Congeners	2	10	14	22	14	10	2	1
PCDF Congeners	4	16	28	38	28	16	4	1

FIGURE 6.1 PCDD and PCDF congeners' triple ring structure (Sheffield 1985).

6.3 NORTH AMERICAN EMISSION RATES AND GEOGRAPHICAL DISTRIBUTION

Little information on PCDDs is presently available. The U.S. EPA is preparing a report "National Dioxin Study - Report to Congress." Preliminary data from this report have been included here.

United States

Four major source categories of PCDDs have been identified. Each is briefly discussed. Location of the principal chemical plants that may release these compounds to the atmosphere is included. Work at U.S. EPA, Office of Air Quality Planning and Standards is currently progressing to better quantify the emissions, particularly from the combustion sources. Preliminary results from these studies are included here.

a. Manufacturing Processes

Most likely, the dominant sources of PCDDs to the total environment are the manufacturing of chlorophenols and their derivatives and the disposal of chemicals containing these wastes (U.S. EPA 1985c). Various dioxin congeners have been found in commercial samples of 2,4,5- and 2,4,6- trichlorophenol (TCP), 2,3,4,6-tetrachlorophenol and pentachlorophenol (PCP), as well as in the herbicides 2,4,5-T and Silvex which are manufactured from TCP. Due to severe restriction on their use, the production and use of these pesticides in recent years have declined significantly. Table 6.1 lists the names and locations of companies that either currently are or have been major producers or formulators of chlorophenols and their derivatives. Little data on these industries and their production levels were found. No estimates regarding the total amounts of dioxins released through the manufacture or use of these contaminated chemicals either industrially or in pesticides, or the land disposal of the contaminated wastes were available. The U.S. EPA speculates that land disposal is the most important route of entry to the environment.

TABLE 6.1 Locations of companies that have been major producers and formulators of chlorophenols and their derivatives.

CHEMICAL AND PRODUCER

2,4-D Acids & Esters
Alco Chemical Corp., PA
* Amvac-Chemical Corp., CA
Chempar, OR
* Diamond Shamrock Corp., AL&OH
Diamond Alkali, NJ
* Dow Chemical USA, MI
Falek-Lankro Corp., AL
GAF, NJ
Guth Corp., IL
Hercules Inc., AR
Imperial Inc., IA
Miller Chemicals, ND
Monsanto Co., IL
North American Phillips, KS
* PBI-Gordon Corp., KS
Rhodia Inc., OR, MN & MO
* Rhone-Poulenc Inc., OR
Riverdale Chemical, MO
Rorer-Amchem, CA and MO
Thompson Chemical, MO
Union Carbide Corp., PA
* Velsicol Chemical, TX
Vertac Inc., AR
Woodbury, FL

2,4,5-T
Chempar, OR
Diamond Shamrock, OH
Dow Chemical USA, MI
Hoffman-Taft Inc., MO
Monsanto Co., IL
North American Phillips, KS
PBI-Gordon Corp., KS
Rhodia Inc., OR and MO
Riverdale Chemical, IL
Rorer-Amchem, PA, CA, MO&AR
Thompson Chemical, MO
Union Carbide Corp., CA & MO
Vertac Inc., AR

2,3,4,6-Tetrachlorophenol
Dow Chemical USA, MI
Sanford Chemical, TX

2,4,5-T DERIVATIVES:
Silvex esters and salts
Dow Chemical USA, MI
North American Phillips Corp.,KS
* Riverdale Chemical Co., IL
Vertac Inc., AR
Ronnel & Erbon
* Dow Chemical USA, MI
Hexachlorophene
Givaudan Corp., NJ

2,4,5-TCP and salts
Diamond Shamrock Corp., OH
Dow Chemical USA, MI
GAF Corp., NJ
Hercules Inc., AR
Hooker Chemical, NY
Merck and Co., NJ
Nalco Chemical Co., IL
North Eastern Pharmac., MO
Roberts Chemical Inc., WV
Rhodia Inc., NJ
Vertac Inc., AR

PCP and Salts
J.H. Baxter & Co., CA
Sanford Chemical, TX
Vulcan Materials Co., KS
Dow Chemical USA, MI
ICC Industries Inc., OH
Monsanto Co., IL
Nalco Chemical Co., IL
* Reichold Chemical Inc., WA

* Company names indicated with an asterisk
were labelled as the major producers of chlorophenols and derivatives in the U.S.

b. **Combustion Sources**

PCDDs have been detected in particulate matter released from several categories of combustion sources. Data are still inconclusive for sources such as coal and gasoline combustion. Formation of PCDDs from the incineration of chlorinated hydrocarbons such as PCBs and chlorinated benzenes, as well as municipal waste incinerators has, however, been repeatedly measured. Stack emissions from one secondary copper smelter which burns plastic coated copper wire have been observed in concentrations as high as 12,000 ng/dscm. In the temperature ranges of 750° - 900°C formation is likely, while above 1,200°C (residence time = 1 second), PCDDs are likely to decompose. Studies of lake sediments in the region of northern Lake Superior yielded temporal data that implied that the earliest flux of PCDDs to the lake occurred around 1940.

Combustion sources of dioxin have been intensively studied in recent years and a comprehensive report on these will be completed soon as a part of the ongoing U.S. EPA National Dioxin Study. Preliminary estimates indicate an annual emission rate of 20 to 50 kg from combustion sources (as 2,3,7,8-TCDD equivalents). Approximately 60%, or 12 to 30 kg annually, of these releases is from municipal waste combustion sources. The summary of the Municipal Waste Combustion Study (Federal Registry 1987) lists a current emissions estimate for combined chlorinated dioxins and dibenzofurans of 24 kg/year.

c. Chemical Waste Disposal

Sites at which chemicals known to be contaminated with PCDDs are either disposed of or are stored awaiting disposal, are also potential sources of PCDDs to the environment. These sites are more likely to be direct sources to land and groundwater receptors rather than to the atmosphere. Once soils become contaminated, however, the potential exists for soil particles to enter the air via wind erosion. It has been estimated that approximately 12,000 tonnes per year of hazardous wastes are produced in the manufacture of chlorophenols and that about 80,000 tonnes result from the manufacture of phenoxy compounds. Some of these compounds have been contaminated with dioxins at levels as high as 100 ppm. Since dioxin is highly persistent, wastes stored decades ago must still be considered to be potential sources of release. Data are insufficient to quantify the PCDDs currently held in storage and in disposal facilities.

d. Photochemical Processes

Certain photochemical processes, such as photolysis of PCP-treated woods, may also lead to the formation of PCDDs, although the amounts from this source are considered to be relatively small. Photolytic dechlorination can also result in the formation of more highly toxic TCDDs from less toxic forms.

Canada

Principal sources of PCDDs and PCDFs in Canada and estimates of PCDDs/PCDFs released to the Canadian environment and to Ontario in particular, are reviewed by Voldner and Ellenton (1987). These will not be discussed here, since the focus is on atmospheric emission.

a. Primary Sources

The major primary sources of PCDDs and PCDFs to the atmosphere are their release during combustion of municipal and industrial waste. Other primary sources include accidental fires of treated wood products, PCB-filled transformers, production spills during transportation and aerial spraying of herbicides, wood stove burning and cigarette smoking.

b. Secondary Sources

Volatilization and erosion of dust from landfill sites and from areas where PCDDs/PCDFs were present as impurities in herbicides, act as secondary sources. The herbicide, 2,4,5-T, is still allowed in Canada for restricted application, primarily in residential, commercial and public use areas. Even where these herbicides have been banned, the applications of earlier years and the persistence in the the soil suggest that a continuing source to the atmosphere may exist over many years due to wind-blown soil following erosion.

Volatilization of 2,3,7,8-T_4CDD has been demonstrated (OMOE 1985 citing Young 1983). The rate of volatilization depends on the concentration of the chemical and meteorological conditions such as temperature, wind speed and vapour pressure. One estimated emission rate (OMOE 1985, citing Thibodeaux 1983) given for a 2,3,7,8-T_4CDD concentration of 1,300 pg/g of soil over an area of 753 m_2, was 120 - 1,200 g per year.

Volatilization from water surfaces is a secondary source of PCDDs/PCDFs to the atmosphere.

Estimates of PCDDs entering the atmosphere from combustion vary among investigators. NRCC (1981) estimated primary emissions for Canada of PCDDs from combustion of municipal incinerators to 6.6 kg per year of particulates, of which Ontario emissions amounted to 2.2 kg per year. Estimated Ontario emissions of PCDDs by OMOE (1985) are much higher. For three installations, two municipal incinerators and one sewage sludge incinerator, estimated emissions of PCDDs are 7 kg per year, including both particulates and gaseous material. Significant additional emissions are expected from other incinerators, including hospitals and other major buildings (OMOE 1985). The Ontario estimate (OMOE 1985) of PCDD+PCDF emissions from municipal incinerators is about 30 kg per year, with an additional 100 kg per year of PCDD+PCDF from other combustion sources. Sheffield's estimates of atmospheric emissions from municipal and sewage sludge incinerators in Canada are 2 to 17 kg PCDDs and 2 to 28 kg PCDF, respectively, per year.

Primary emission amounts from spray drift in the application of herbicides is unknown.

Secondary atmospheric emissions due to volatilization from landfills and from spills and leakages of chemicals contaminated with PCDDs and PCDFs cannot yet be quantified. The estimated releases of PCDDs and PCDFs to the general environment provide an indication of the amounts of PCDDs and PCDFs which are available for secondary emission.

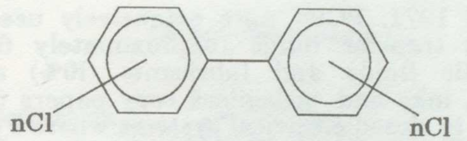
6.4 EMISSION SEASONALITY

Since emissions of PCDDs and PCDFs are largely unquantified, their seasonality is not reliably established. The major factors which could produce seasonal variation in emissions are the effect of winter freezing in temporarily immobilizing releases from soils and chemical dump sites and the lack of herbicide applications during winter months.

6.5 DATA QUALITY

No reliable emission inventories are available for the United States and Canada. There is scattered information on sources. The U.S. EPA is conducting a comprehensive study of PCDDs and PCDFs, including sampling of combustion sources (Andren, pers. comm.). The results of this and related assessment efforts will be contained in a forthcoming report to the Congress. Large uncertainties exist because of the difficulty in estimating emission factors.

7.0 POLYCHLORINATED BIPHENYL (PCB)



7.1 PROPERTIES (U.S. EPA 1979a; Vershueren 1983)

CAS No. 1336-36-3

Solubility: 0.04 - 0.2 ppm, water solubility decreases with increasing chlorination.
Vapour Pressure: relatively low; decreases with increasing chlorination.

PCBs are chlorinated hydrocarbons manufactured by the controlled chlorination of the biphenyl molecule. Chlorine replaces hydrogen at two or more sites, so that more than 200 compounds are possible (Sonzogni and Swain, 1984). These vary from oily liquids to white crystalline solids and hard, non-crystalline resins.

7.2 MANUFACTURING HISTORY

PCBs were first produced commercially in 1929 at the Swann Research plant in Anniston, Alabama (U.S. EPA 1979a). This plant was subsequently sold to Monsanto which operated the plant until 1971. Monsanto also manufactured PCBs at Sauget, Illinois until 1977. PCBs were marketed under the trade name Aroclor. The only other known manufacturer of PCBs in the United States was Geneva Industries of Houston, Texas, which operated from 1972 to 1974.

The total amount of PCBs produced in the United States over the period 1930 to 1975 exceeds 600,000 tonnes (U.S. EPA 1987a). During this time imports amounted to just over one tonne and exports to 68 tonnes.

In Table 7.1 the U.S. production of PCB, its domestic sales for use in transformers and large capacitors, and its export to the Organization for Economics and Cultural Developments countries are shown for the period 1955 to 1980. The estimates were made by the Monsanto Chemical Co. (Bletchly 1983b). The production peaked between 1965 and 1969. The accumulated production for 1955 to 1980 is estimated at 476,000 tonnes.

TABLE 7.1 PCB production and sales and exports: United States 1955-1980
(kilotonnes; after Bletchly 1983b).

YEARS	PRODUCTION	DOMESTIC SALES[1] TRANSFORMERS AND LARGE CAPACITORS	EXPORT TO O.E.C.D. MEMBER COUNTRIES[2] TRANSFORMERS AND LARGE CAPACITORS
1955-59[3]	68	37	0
1960-64	95	36	1
1965-69	166	55	4
1970-74	114	53	5
1975-79	33	19	2
1980	0	0	0
TOTALS	476	200	12

[1] assuming 50% of quantities given by Monsanto as domestic sales for capacitors went into large capacitors.
[2] assuming 50% of exports went to OECD countries and up to 1971, 40% of these went into transformer and large capacitors but from 1972 that became 65%.
[3] figures for 1955-59 calculated by extrapolating Monsanto's data for 1957-1959 (Bletchly 1983b).

While PCBs apparently have never been produced in Canada, an estimated 40,000 tonnes of PCBs were imported between 1929 and 1977, the year when U.S. production ceased. An additional 3,000 tonnes of PCBs are estimated, as of 1983, to have entered Canada in manufactured electrical ballasts in fluorescent and high intensity discharge lighting fixtures.

7.3 USE HISTORY

From the early 1930s until 1971, PCBs were extensively used. Products included closed system electrical and heat transfer fluids (approximately 60% of total uses), various plasticizers (25%), hydraulic fluids and lubricants (10%) and many others such as flame-retardants, adhesives, inks and carbonless copy papers (5%). After 1971, uses were restricted almost completely to closed electrical systems where PCBs functioned as insulators, coolants or dielectrics. Nearly all large capacitors made before 1977 contained PCBs.

Total sales to manufacturers of transformers and capacitors is reported at about 400,000 tonnes or 70% of production since their introduction into commerce. Sales for the manufacture of plasticizers, hydraulic oils and lubricants, heat transfer fluids, carbonless copy paper and petroleum additives accounted for about 130,000 tonnes, or about 20% of production. (U.S. EPA 1987a).

A general approximation of the status as of 1982 for the estimated total of 640,000 tonnes of PCBs manufactured in the U.S. is given in Table 7.2 (Miller 1982).

TABLE 7.2 Estimated total (tonnes) PCBs manufactured in the U.S.A.

CURRENT STATUS	PERCENTAGE OF TOTAL	AMOUNT (tonnes x 10^3)
Destroyed	3	20
Exported	11	70
Buried in landfills	21	140
Still in service*	54	340
Circulating through the environment	11	70
	TOTAL	640

* Mostly in electrical transformers and capacitors.

Of the 40,000 tonnes of PCB fluids imported into Canada, the Environmental Protection Service (EPS) has identified the locations of 24,300 tonnes (61% of the total). The distribution by product in the 1985 inventory is shown in Figure 7.1. The major portion, 17,650 tonnes (44.1% of the total) is contained in transformers and capacitors presently in service. The known amount in storage awaiting disposal is 6,500 tonnes (16.3% of the total). Another 150 tonnes is in other electrical or mechanical equipment. There are 15,700 tonnes of PCBs unaccounted for in the inventory, or 39% of the total. An estimated 3,000 tonnes of PCBs in lighting fixtures distributed throughout the country are not included in the EPS inventory. This amounts to 7.5% and would reduce the fraction unaccounted for to 32%.

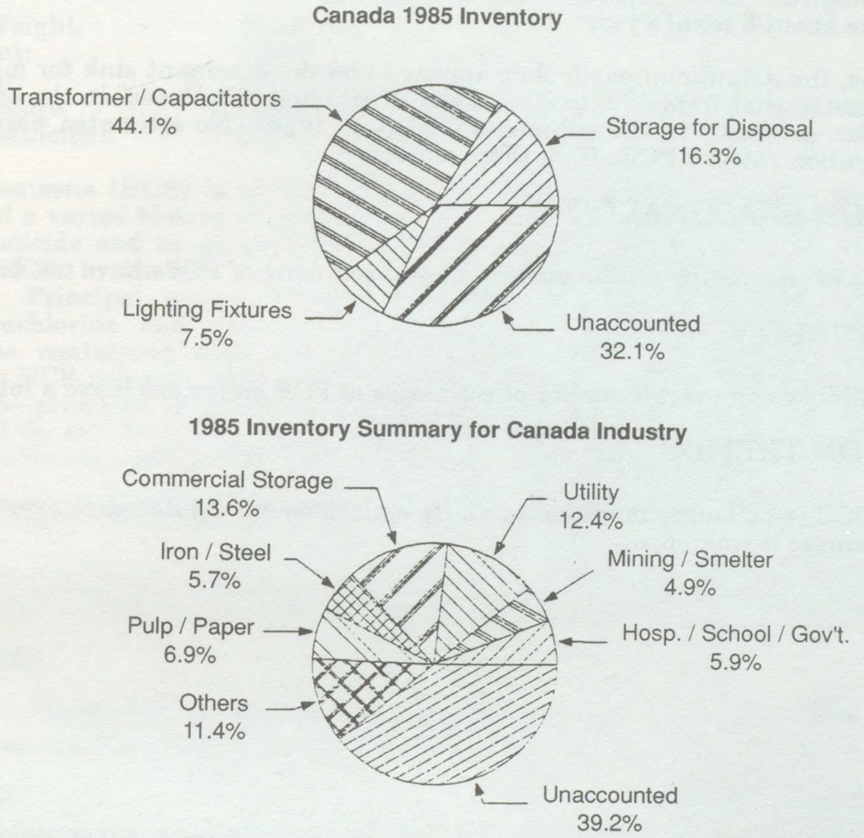
Distribution of PCBs by industry is shown in Figure 7.1. Next to the percentage of PCBs unaccounted for (39%), commercial storage facilities and utilities account for 14% and 12%, respectively, followed by the forestry/pulp and paper industry, at 7%.

Distribution of known PCB liquids by province is as follows: Ontario, 39.4%; Alberta, 23.1%; Quebec, 20.6%; and British Columbia, 7.0%.

7.4 DISCUSSION OF SOURCES TO THE ENVIRONMENT

Their ubiquitous past use has led to widespread distribution of PCBs in the environment, causing great environmental concern due to their extreme persistence, bioaccumulation and adverse health effects. 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.

FIGURE 7.1 Distribution of PCBs in Canada (1985) by application and by industrial sector *(Brien 1986).*



40,000 tonnes imported into Canada 1929 - 1977

It has been estimated that 900 tonnes/year of PCBs cycle annually through the atmosphere over the U.S. This estimate was based on an averaged PCB air concentration of 0.05 ng m^{-3} in rural areas, 5 ng m^{-3} in urban areas, a mixing height in the atmosphere of 2 km and an average residence time of one week (Murphy et al. 1985). From the areas where PCBs are still in use, leaks and spills occur from which PCBs may evaporate or escape on resuspended particles. PCBs may evaporate slowly from products, such as inks, plasticizers, etc., 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 current U.S. uses, which must be reported to the National Reporting Center, appear to be the largest source to the environment. In the Great Lakes states, for example, a statistical analysis of the available data estimated that in an average year about 50 tonnes of PCBs are released to the environment through accidental spills (Valaoras 1986).

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, air conditioners, etc., is unrestricted. By 1978, it was estimated that municipal and industrial wastes containing 140 kilotonnes of PCB had been received by U.S. 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 U.S. 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 1987) reports a current national total PCB emission estimate from this sector to be about 5 tonnes/year.

The oceans, the Atlantic in particular, appear to be the dominant sink for many PCBs. It has been estimated that from 50% to 80% of the PCBs currently "loose" in the environment are in the Atlantic, primarily in the sediments (Valaoras 1986). No estimates were found regarding the evaporation rates of PCBs from these waters.

7.5 EMISSION SEASONALITY

The effects of seasonality on the environmental recycling of PCBs have not been determined.

7.6 DATA QUALITY

The availability and overall quality of estimates of PCB emissions leave a lot to be desired.

7.7 EMISSION TRENDS

Because PCB is no longer manufactured, its emissions should decrease over time, but the rate of this decrease is unknown.

8.0 HEXACHLOROBENZENE

8.1 PROPERTIES (Vershueren 1983) CAS No. 118-74-1

Molecular Weight:	284.8
Melting Point:	228°C
Boiling Point:	322-326°C
Vapour Pressure:	1.089×10^{-5} mm Hg
Partition Coefficient:	$\log P_{octanol}=6.18$

Hexachlorobenzene (HCB) is a fully chlorinated, six-membered aromatic carbon compound that has had a varied history of production and use. In the past it has been manufactured for use as a pesticide and as an industrial chemical. Currently, however, the largest source of release of HCB to the air appears to be from the manufacture of certain chlorinated compounds. Principal among these compounds are perchloroethylene, trichloroethylene, carbon tetrachloride and chlorinated benzenes. In addition, five pesticides have been identified as containing HCB as an inadvertently-produced impurity, resulting in the potential for HCB release, both in their manufacturing process and in their use. HCB is also thought to be produced during certain combustion processes as it has been detected in both flue gas and fly ash from municipal waste incinerators. These diverse sources have resulted in hexachlorobenzene's wide distribution throughout the environment.

8.2 TABULATION OF THE UNITED STATES EMISSION RATE

The following summary description of U.S. sources of hexachlorobenzene is abstracted from a U.S. EPA report: "Exposure Assessment for Hexachlorobenzene" (U.S. EPA 1985).

a. Solvents

TABLE 8.1 Estimated releases (tonnes) of HCB to the air, 1984.

SOURCE		ESTIMATED RELEASES
Manufacture of chlorinated solvents		3.4 - 11.3
Manufacture of other chlorinated compounds		.003
Municipal incineration		.06 - .45
Pesticide Use *		
PCNB		5.7
chlorothalonil		1.7
DCPA		6.5
Picloram		.09
Pentachlorophenol		3.4
Historical sources		**
	TOTAL	20.9 - 29.1

* These pesticide figures were estimated as "total" releases to air, land and water.

** Could not be quantified.

As shown in Table 8.1, the largest probable atmospheric source of HCB is from the manufacture of chlorinated solvents, in particular carbon tetrachloride, trichloroethylene and perchloroethylene. Air emissions from these processes are the result of the disposal of HCB-contaminated wastes, since HCB is readily separated during purification steps. The amount of release was estimated using a measured range of concentrations of HCB in the waste, an approximation of the amount of HCB produced and the assumption that 2% of the wastes are land-filled and 98% are incinerated, with a destruction efficiency of 99.9% (U.S. EPA 1985). These approximations are summarized in Table 8.2.

TABLE 8.2 Estimated air release of HCB from chlorinated solvents.

SOLVENT	PRODUCTION (kilotonnes)	CONC. OF HCB IN WASTE (percentage)	AMT. OF HCB PRODUCTION (kilotonnes)	EST. AIR RELEASE (tonnes)
Carbon tetrachloride	313	10-65	1.3-8.4	1.3-8.2
Trichloroethylene	6	5-20	0.1-0.5	0.1-0.5
Perchloroethylene	260	20-25	2.1-2.6	2.0-2.5
			TOTAL	3.4-11.3

b. Other Chlorinated Compounds

In addition to the solvents, the manufacture of several other chlorinated chemicals, including several pesticides, is known to result in inadvertent production of HCB. The pesticides will be addressed below. The other compounds include benzylchloride, ethylchloride, phthalic anhydride, chlorine, hexachlorocyclo-pentadiene (HEX) and phthalocyanine dyes and pigments. A large number of additional compounds are also suspected of producing HCB in their manufacture. The U.S. EPA (1985) estimated that in 1984 a total of 16,670 tonnes/year of HCB-containing waste was generated by these non-solvent processes with an estimated total quantity of generated HCB of 2.6 tonnes/year. Assuming that 99.5% of these wastes were incinerated with a 99.9% destruction efficiency, 2.6 kg of HCB would have been released to the air in 1984 from these sources.

No source-by-source analyses were done for these plants. Table 8.3 lists the locations of facilities that in 1985 were producing chemicals whose manufacture was known to generate HCB.

TABLE 8.3 Locations of facilities producing chemicals whose manufacture is known to generate HCB, 1985.

COMPANY	LOCATION	PRODUCTS*
Diamond Shamrock Corp.	Deer Park, TX	Perc
Dow Chemical	Freeport, TX	Perc, TCE, pic, CT
Dow Chemical	Pittsburgh, CA	Perc, CT
Dow Chemical	Plaquemine, LA	Perc, CT
E.I. DuPont de Nemours & Co., Inc.	Corpus Christie, TX	Perc, CT
KemaNord, Inc.,	Columbus, MS	Chlorine
Kerr McGee Chemical Corp.	Hamilton, MS	Chlorine
Kerr McGee Chemical Corp.	Henderson, NV	Chlorine
LCP Chemical & Plastics	Moundsville, WV	CT
Monsanto Company	Sauget, IL	CBs
Occidental Chemical Corp.	Montague, MI	HEX
Occidental Chemical Corp.	Tacoma, WA	Chlorine
Occidental Chemical Corp.	Taft, LA	Chlorine
PPG Industries Inc.	Lake Charles, LA	Perc, TCE
PPG Industries Inc.	Natrium, WV	CBs
Reichold Chemicals Inc.	Tacoma, WA	PCP
SDS Biotech Corp.	Greens Bayou, TX	dacthal, c.thal
Southland Corp.	Green Meadows, NJ	CBs
Standard Chlorine Chem.	Delaware City, DE	CBs
Stauffer Chemical Co.	LeMoyne, AL	CT
Velsicol Chemical Co.	Memphis, TN	HEX
Vulcan Materials Co.	Gelsmar, LA	Perc, CT
Vulcan Materials Co.	Wichita, KS	Perc, CT, PCP

Perchloroethylene (Perc); trichloroethylene (TCE); carbon tetrachloride (CT);
chlorine; pentachlorophenol (PCP); picloram (pic);
chlorothalonil (c.thal.); hexachlorocyclopentadiene (HEX);
dacthal; and chlorinated benzenes (CBs).

c. Contaminated Pesticides

HCB has been found in the technical grade product of five currently used pesticides and it is suspected of being produced as an impurity in others as well. The U.S. EPA (1985a) made estimates for the total environmental releases of HCB from the use of these pesticides based on approximate HCB contamination levels and current annual use levels. These estimates are shown in Table 8.4 as are the geographic use areas, where available. No data were found on the release of HCB from the plants that manufactured these pesticides, though these releases are assumed to be small.

TABLE 8.4 Estimated release of HCB from use of contaminated pesticides.

PESTICIDE	AVERAGE (percentage)	ESTIMATED TOTAL USE HCB 1985 (million kg)	ENVIRON. RELEASES (tonnes)	STATES OF MOST USE	WHERE PRODUCED
PCNB	0.5	1.1	5.7	AR, LA, MS, AL TN, GA, WA, ID	Mexico
Chlorothalonil	0.05	3.4	1.7	GA, AL, VA, NC, CA, ID, ND, WA, MI, MN, FL, TX.	Texas
DCAA	0.3	2.2	6.5	N/A	Texas
Picloram	0.02	0.5	.09	N/A	Texas
PCP	0.01	33.6	3.4	N/A	Washington Kansas

d. Municipal Waste Incineration

As mentioned, HCB has been detected in both flue gas and fly ash of municipal waste incinerators. This is believed to be the result of incinerating products that contain chlorine, though small amounts of HCB may also be present initially in the waste. Using a simple methodology based on municipal incineration data and a range of reported flue gas HCB concentrations of 1.4 to 11 μg m^{-3}, the U.S. EPA (1985) estimated a total release of HCB to the air of 57 to 454 kg/year. Almost all of this HCB is thought to be in the flue gas. No geographic distribution was estimated. Municipal incinerators are located throughout the country, with the largest concentrations in the northeast and the upper midwest.

e. Historical Sources

HCB is very persistent in the environment, hence, sites where HCB and chemicals contaminated with HCB were previously manufactured, used, or disposed of must also be considered potential sources of HCB to the ambient atmosphere. The U.S. EPA (1985a) has a thorough discussion of many of these sites, including Superfund sites known to contain HCB wastes. Due to the large uncertainty involved, no numerical estimations were made for these HCB releases.

8.3 EMISSIONS FROM CANADIAN SOURCES

Since HCB was not included among the 14 priority chemicals, no emissions of HCB in Canada were compiled.

8.4 MONITORING IN THE GREAT LAKES

Eisenreich et al. (1981) reported a mean air concentration of HCB in the Great Lakes Basin Ecosystem of 0.2 ngm^{-3} and a mean concentration in precipitation of 2 ngL^{-1}. From these data, the total deposition of HCB to Lake Superior was estimated to be 1.7 metric tons per year. Strachan (1985) reported for 1983 a volume-weighted rain concentration of 0.075 ngL^{-1} and a subsequent deposition from rain and snow to Lake Superior of 3.7 kg/year. Dry deposition was "... estimated to be at least as great as the contribution from wetfall." Other than noting that Eisenreich's results indicated precipitation rate an order of magnitude too high, no definitive explanation could be found for the large differences between these two otherwise similar studies.

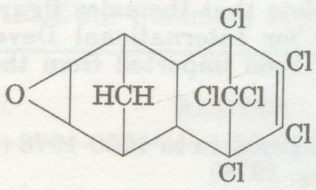
8.5 FUTURE EMISSIONS

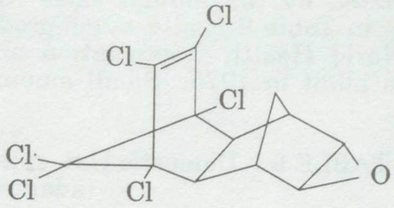
HCB emissions for a few sectors are likely to change significantly in the near future. For example, stricter controls on the amount of HCB contaminant permitted in pesticides are being implemented. In 1988, the allowable level of HCB contamination in PCNB drops from 0.5% to 0.1%. If usage remains constant, this will result in a decrease in the estimation of total HCB release from 5.7 tonnes to 1.1 tonnes per year.

Because municipal waste incineration is growing rapidly, emissions from this sector can be expected to increase. The size of this increase will depend upon the regulatory decisions made for municipal incinerators over the next few years.

9.0 DIELDRIN/ALDRIN

$C_{12}H_8Cl_6O$



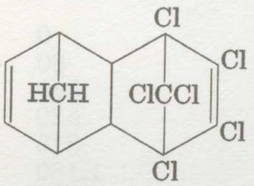


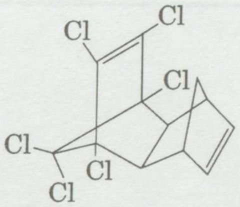
1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene

DIELDRIN

CAS No. 60-57-1

$C_{12}H_8Cl_6$





1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene

ALDRIN

CAS No. 309-00-2

9.1 PROPERTIES OF DIELDRIN/ALDRIN

(U.S. EPA 1987a; Vershueren 1983; Strachan 1986)

Solubility:	0.1 mg/L
Partition coefficient:	log $P_{octanol} = 4.86$
Molecular weight: 381	
Melting Point:	176°C
Boiling Point:	356°C
Vapour Pressure:	1×10^{-7} torr

9.2 BACKGROUND

Dieldrin originated in 1948 by J. Hyman & Co. During the 1960s and early 1970s, the organochlorine insecticides Aldrin and Dieldrin were two of the most widely used pesticides in the United States. Their primary use during that time was for control of corn pests, although they were also used by the citrus industry. Aldrin and Dieldrin are members of the same group of cyclic hydrocarbons called cyclodienes and are considered together here. Aldrin is rapidly converted to Dieldrin in the environment by several processes, including photodegradation. Although Aldrin was used in greater quantities than Dieldrin, most environmental samples show the presence of Dieldrin rather than Aldrin.

The suspension of the registration of Aldrin and Dieldrin was ordered in 1974, effectively halting further production (by 1975) and use (by 1976) of these products. The only exception since that time has been the importation from Europe of small quantities of Aldrin products solely for the purpose of subsurface soil injection for termite control (U.S. EPA 1980). A similar regulation is in effect in Canada.

Information concerning the manufacturing history of Aldrin and Dieldrin is limited. As summarized by the U.S. Federal Register: "In May 1952, Shell Chemical Company [became the sole manufacturer and distributor for Aldrin and Dieldrin]. From 1952 until 1967, Shell sold only technical Aldrin and Dieldrin [all manufactured at its plant in Denver, CO] to pesticide formulators who manufactured it into emulsifiable concentrate, dust, wettable powder and granular formulations. Beginning in 1967, Shell started selling formulated product [and by] 1972, only 11% of the total Aldrin and Dieldrin sold was sold as a technical product for use in non-Shell branded formulations," (Federal Register 1974).

No comprehensive manufacturing data could be found for Shell's Denver plant. It is known (Midwest Research Institute [MRI] 1974) that the approximate annual plant capacity was 9,000 tonnes and that the estimated production of Aldrin in 1972 was about 5,100 tonnes. It is also known that liquid wastes at the plant went to an evaporation basin from which Aldrin and Dieldrin volatilized. While annual manufacturing figures are unavailable, they can be approximated by the annual sales figures published in the Federal Register. These are displayed in Table 9.1 with other production data. Note that the sales figures exclude sales to the World Health Organization and the Agency for International Development. Shell closed its plant in 1975. Small amounts have since been imported from the Shell plant in England.

TABLE 9.1 Domestic U.S. sales of Aldrin and Dieldrin in 1950-1973 (tonnes) (adapted from Fed. Reg. 1974).

	ALDRIN		DIELDRIN	
YEAR	SALES	AQ. USE	SALES	AQ. USE
1950	660		0	
1951	1,500		80	
1952	370		340	
1953	560		520	
1954	910		810	
1955	2,000		1,180	
1956	2,950		1,650	
1957	1,100		1,220	
1958	2,240		1,400	
1959	2,530		1,370	
1960	3,640		1,200	
1961	4,510		1,260	
1962	4,950		1,360	
1963	5,530		1,220	
1964	5,500	5,070	930	430
1965	6,490		820	
1966	8,780	6,710	870	330
1967	8,220		670	
1968	6,220		610	
1969	4,500		550	
1970	4,050		340	
1971	5,280	3,600	320	150
1972	5,370*		340	
1973	4,500		NR	
1974			**	

* MRI (1974) reports a 1972 usage of 5,800 tonnes domestically and an export of 100 tonnes.
** U.S. DA reports 0.1 kilotonnes of Dieldrin imported in 1974, but none in 1975-1977 (U.S. DA 1977 and 1978).

From 1981 to 1985 Aldrin was imported from Shell International and sold in termite control products at a rate of about 500-700 tonnes of active ingredient per year. Most of this usage was in the South and Southeast U.S. and most of these applications are expected to have been underground injections.

Since exports of Dieldrin and Aldrin were generally small, one estimate showed that only 2.3% of the 1972 production of Aldrin was exported (MRI 1974), the sales and production values given above can probably also be viewed as rough approximations of domestic use.

9.3 USAGE

Canada

Available information for Aldrin and Dieldrin usage in Canada is shown in Table 9.2. In 1968, 82 tonnes of Aldrin and 2.7 tonnes of Dieldrin were used in Canada. Usage in Ontario was reported as 12.2 tonnes and in Manitoba, 0.2 tonnes. Canadian usage of Aldrin decreased to 57.6 tonnes in 1969 and to 19.6 tonnes in 1970. No data were obtained for total Canadian Dieldrin usage in these years. Ontario consumption of Dieldrin in 1969 was 0.4 tonnes; Aldrin usage is unknown. In 1969 Manitoba's reported usage of Aldrin/Dieldrin was zero; 1969 and 1970 Aldrin consumptions were .05 and 0.1 tonne; Dieldrin consumption was zero in 1970 and .005 tonne in 1971.

TABLE 9.2 Summary of pesticide usage (tonnes) in Canada (Voldner 1986).

YEAR	ALDRIN	DIELDRIN	LINDANE	DDT
		CANADA		
1968	83	3	16	831
1969	58		3	894
1970	20		3	287
1971			3	137
		ONTARIO		
1968	12	<1	<1	134
1969		<1	1	210
1970			<1	34
1971			1	39
1972				
1973				
1974			<1	
		MANITOBA		
1967		<1		3
1968	<1	0		5
1969	0	0		1
1970	<1	0		3
1971	<1	<1		1

United States

Estimated annual farm use, including regional distribution of Aldrin and Dieldrin is available from the U.S. DA for 1964, 1966, 1971 and 1976. These estimates do not cover "non-agricultural" uses, such as the control of termites. The average rate of application for these pesticides was 0.04-0.89 kg/hectare for soil treatment and 0.005-0.095 kg/hectare for treatment of foliage. A summary of the use data and their geographic distribution is given in Table 9.3 (page 54).

9.5 NORTH AMERICAN EMISSIONS

As in the case of other insecticides, release to the atmosphere occurs during aerial spraying and from volatilization from soil, plants and water surfaces after application. Because the chemicals are persistent, the contaminated soil can act as a source of atmospheric emissions for several years after cessation of treatment. When the soil is turned over in cultivation, airborne dust will carry the chemicals. A 1967 study found air concentrations of Dieldrin and Aldrin of 8.0 - 29.0 ng m^{-3} at a number of sites across the U.S.A. Edwards (1973) also found evidence that Dieldrin had been transported long distances, possibly thousands of miles, in the air.

Aldrin is rapidly converted to Dieldrin in the environment. Thus, most environmental residues show Dieldrin, not Aldrin. The estimated half life of Dieldrin in soils varies from five to 25 years, depending upon the nature of the soil and its microbial flora (U.S. EPA 1972).

9.6 EMISSION SEASONALITY

Since emissions of Dieldrin are unknown, their seasonality cannot be established.

TABLE 9.3 Geographic distribution of Aldrin and Dieldrin agricultural usage in the United States (tonnes).

REGION FOR CROP USE	1964 Aldrin	1964 Dieldrin	1966 Aldrin	1966 Dieldrin	1971 Aldrin	1971 Dieldrin	1976 Aldrin
Northeast		72	14	20		3	
Lake States	345	31	325	44	42		15
Corn Belt	3,900	57	5,897	18	3,380		344
No. Plains	223	23	189	2	112		30
Appalachia	485	21	151	10	18	3	
Southeast	86	95	36	118	19	3	5
Delta States			6	<1	16	72	
So. Plains		33	8	75	<1	15	
Mountains		80	50	28	5	7	
Pacific	11	8	28	5	1	44	
Livestock			1	<1	6	2	
Other	12	5	3	9	3	3	—
TOTALS	5,066	426	6,710	329	3604	151	393
% of Total Sales	92	46	76	4	68	47	

9.7 DATA QUALITY

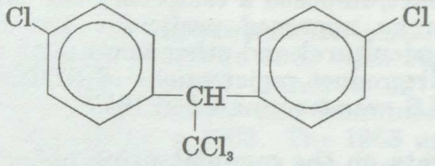
Not applicable.

9.8 DISCUSSION OF CURRENT TRENDS

In their discussion, Strachan and Eisenreich (1988) state: "Use of Dieldrin has been limited for many years yet it continues to appear at unchanged levels in samples from the Great Lakes. The observed levels are usually low and approaching [the limits of] detectability." It is reasonable to assume that the environmental recycling of Dieldrin will decline over time if no new material is introduced. However, the introduction of fresh material is possible as the long-range transport of Aldrin and Dieldrin can occur from Latin America. In 1978, 1,100 tonnes were used there, and projected use in 1988 amounts to 925 tonnes (Burton and Philogene, 1985).

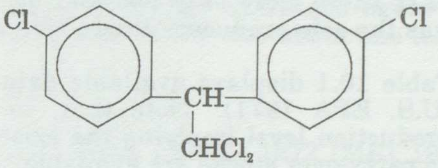
10.0 DDT AND METABOLITES

$C_{14}H_9Cl_5$



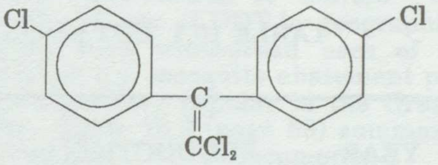
DICHLORODIPHENYLTRICHLOROETHANE (DDT) **CAS No. 50-29-3 (Merck 9th Ed. 1976)**

$C_{14}H_{10}Cl_4$



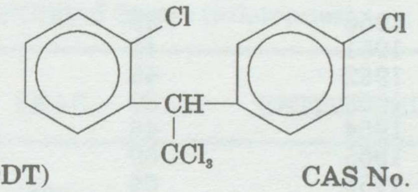
DICHLORODIPHENYLDICHLOROETHANE (DDD) **CAS No. 72-54-8**

$C_{14}H_8Cl_4$



DICHLORODIPHENYLDICHLOROETHYLENE (p,p'-DDE) **CAS No. 72-55-9**

$C_{14}H_9Cl_5$



o,p'-DICHLORODIPHENYLTRICHLOROETHANE (o,p'-DDT) **CAS No. 789-02-6**

10.1 PHYSICAL PROPERTIES (U.S. EPA 1971; Merck 1976; Vershueren 1983)

State:	a waxy solid	
Solubility:	DDT	0.031-0.0034 mg/L at 25°C
	DDD	0.160 mg/L at 24°C
	p,p'-DDE	0.065 mg/L at 24°C
Partition coefficient:	DDT	log Poctanol = 6.19 at 20°C
	DDD	log Poctanol = 5.99
	p,p'-DDE	log Poctanol = 4.28
Molecular weight:	DDT = 355	
	DDD = 320	
	DDE = 318	
Melting Point:	DDT = 109°C	
	DDD = 112°C	
	DDE = 89°C	
Vapour Pressure:	DDT = 1.9×10^{-7} mm Hg	
	DDD = 10.2×10^{-7} torr	
	DDE = 6.2×10^{-6} torr	

10.2 BACKGROUND

The organochlorine pesticide DDT (Dichlorodiphenyltrichloroethane) was one of the first synthetic chemicals to be produced in large quantities and widely dispersed in the environment. It was used extensively throughout many parts of North America, including the Great Lakes region. Its use began in 1947 and continued for more than 20 years. Recognized as an inexpensive, persistent, wide-spectrum insecticide, its use reached a peak around 1959 in the U.S. In the 1960s its usage gradually declined due to the development of resistence to DDT by many insect species, the introduction of effective replacement insecticides and increasing concern about its extreme persistence and its effect on nontarget species. By the end of the 1960s, widespread distribution of DDT throughout the Great Lakes Basin Ecosystem had already been documented. The U.S. Court of Appeals directed, in 1969, the U.S. Department of Agriculture to ban the use of DDT in the Great Lakes basin. The following year the U.S. EPA was established and under an order from the same court, imposed a temporary ban on DDT in the form of a cancellation of DDT's registration as an approved pesticide. The EPA ordered in 1972, full suspension of DDT use for agricultural and other non-health related purposes. Under the Canadian Pest Control Act, all product registrations of DDT were discontinued effective 1986 and manufacture in the U.S. was terminated in 1977.

Data on the manufacturing history of DDT are somewhat limited and none was found for Canada. There were several producers of DDT in the United States in the early 1960s; by 1971 there were only two and by 1974 the Montrose Chemical Co. plant in Torrance, CA, was the sole producer. Production after 1972 was for the export market.

Table 10.1 displays available data on the production and export of DDT in North America (U.S. EPA 1971). Note that, in 1970 for example, export figures exceed the reported production level implying the existence of stocks carried over from previous years. No data on carry-over stocks are available.

TABLE 10.1 DDT production estimates and exports for the United States (kilotonnes).

YEAR	PRODUCTION	EXPORT
1950	23	
1951	48	
1952	45	
1953	39	
1954	45	
1955	59	
1956	64	
1957	56	
1958	66	
1959	72	
1960	74	
1961	75	
1962	74	
1963	78	
1964	55	
1965	64	41
1966	64	41
1967	47	37
1968	63	50
1969	56	37
1970	27	32
1971	20	NA
1972		NA
1973		NA
1974		27
1975		31
1976		11
1977	0	<1

NA = Not available.

Information regarding the emission of DDT from manufacturing plants is scarce. Archer et al. (1978) proposed an emission factor from the Montrose plant in California of 0.33 kg DDT particulate/tonne produced. Based on a 1974 production estimate of 27,000 tonnes, emission of 9 tonnes DDT particulate for 1974 are obtained. This amount is in good agreement with estimates made by the Montrose company for their 1974 emissions (U.S. EPA 1978c).

Information on emissions from other DDT manufacturing sites or from sites of DDT product formulation was not found. No information could be found on the use of and evaporation from holding tanks or ponds, or on closure procedures at these plants as they shut down.

DDT has a vapor pressure high enough to ensure direct losses from plants and soil into the atmosphere which can carry residues worldwide (Woodwell et al. 1971). It gets into the atmosphere via both direct volatilization and wind erosion of small particles from treated soils. Suspended DDT is available for deposition back to land and water surfaces. Woodwell et al. (1971) estimated a mean residence time of 4.5 years for DDT on land. Other factors considered in this estimate are its removal by harvest of organic matter, water runoff and chemical degradation.

10.3 USAGE

Canada

The DDT consumption in Canada for the period 1968 to 1971 is shown in Table 9.2, together with Canadian consumption of other pesticides. The peak year was 1969 with 894 tonnes used; 1968 consumption was 831 tonnes. Usage decreased to 287 tonnes in 1970 and to approximately 140 tonnes in 1971. DDT consumption in Ontario and Manitoba is also shown in Table 9.2. Ontario usage peaked at over 200 tonnes in 1969. The 1968 usage was about 130 tonnes. There was declining consumption in 1970 and 1971 to less than 40 tonnes per year. Manitoba's consumption was considerably less than Ontario's. In Manitoba, usage rose from three tonnes in 1967 to five tonnes in 1968, then decreased again to three tonnes in 1970. In 1969 and 1971, Manitoba's consumption of DDT was about one tonne.

United States

Table 10.2 summarizes annual DDT usage in the U.S. from 1950 to 1972 (MRI 1974; U.S. EPA 1971). Usage peaked in 1959, with an application of about 36 kilotonnes and declined steadily thereafter. Information on the geographic distribution is limited. U.S. DA documents for 1964, 1966 and 1971 detail the agricultural uses of DDT by geographic region (regions defined in Addendum B). However there were widespread uses of DDT in applications that were not recorded as agricultural uses; e.g. mosquito abatement programs and various forest pest programs. These programs were very popular in the Great Lakes region, although specific estimates are not available. Table 10.3 (page 58) summarizes the geographic distribution data for agricultural usage from the U.S. DA documents.

TABLE 10.2 Estimated DDT use in the United States (kilotonnes).

YEAR	ESTIMATED USE
1950	27
1951	32
1952	32
1953	28
1954	20
1955	27
1956	34
1957	33
1958	30
1959	36
1960	32
1961	29
1962	30
1963	27
1964	23
1965	24
1966	20
1967	18
1968	14
1969	14
1970	11
1971	6
1972	0

10.4 ATMOSPHERIC EMISSIONS

DDT entered the atmosphere directly in the past from aerial spraying. It also volatilizes from soils, plants and from water surfaces. Attached to suspended particulate matter, it can be transported long distances (Edwards 1973). An estimate of the amount that could have been volatilized from southern cotton soils is 110 tonnes per year (U.S. EPA 1987d).

Since DDT is a persistent chemical, emissions from soils can extend over a long period of time. The half-life of DDT is greater than ten years. On sandy soil it is 15 years. On certain agricultural soils a half-life of 35 years was determined as an upper limit (U.S. EPA 1987a).

Volatilization of DDT from water surfaces can be a source to the atmosphere, particularly when the DDT is concentrated in surface slicks. Winds and surface turbulence tend to increase the water-to-air transfer (Edwards 1973). A further source of emission is the disposal of wastes containing DDT, by landfill or by incineration. Present DDT emissions may arise from application of pesticides which are contaminated with DDT, such as Dicofol and chlorobenzilate.

TABLE 10.3 Geographical distribution of DDT agricultural use (tonnes of active ingredient).

USE	REGION	1964	1966	1977
CROPS	Northeast	455	334	142
	Lake States	232	195	1
	Corn Belt	278	164	4
	N. Plains	5	18	
	Appalachia	1,263	835	452
	Southeast	5,700	4,932	3,179
	Delta States	3,114	3,236	2,170
	S.Plains	2,143	1,228	375
	Mountains	351	540	19
	Pacific	927	482	25
LIVESTOCK	All Regions	291	230	111
OTHER	All Regions	485	81	34
TOTALS		15,247	12,275	6,511
Percentage of Overall Total		53%	63%	100%

10.5 EMISSION SEASONALITY

The seasonality of emissions from environmental recycling has not been determined. Little progress has been made in establishing what part of the more than 500,000 tonnes of DDT used in Canada and the U.S. since 1950 remains circulating through the environment, or in determining how much longer it will continue to do so. Environmental levels have decreased since the time of its peak use, but the overall rate of decrease seems to imply that DDT residues could be at detectable levels for decades. New material can arrive through atmospheric transport from areas of current use south of the United States. It has been estimated that nearly 16,000 tonnes of DDT were used in Latin America in 1978 and that as much as 11,000 tonnes will be used there in 1988 (Burton and Philogene 1985).

11.0 LINDANE
1,2,3,4,5,6-HEXACHLOROCYCLOHEXANE

11.1 PROPERTIES OF GAMMA-HCH (Worthing 1983; Merck 1976) CAS No. 58-89-9

$C_6H_6Cl_6$

Common names:	γ-HCH; γ-BHC
State:	colourless crystals
Melting Point:	112°C
Vapour Pressure:	0.14 mm Hg @ 40°C
Solubility:	insoluble in water, 1.4 mg/L in salt water >50 g/L in acetone, benzene, ethanol

LINDANE AND α-HCH

11.2 BACKGROUND INFORMATION

Lindane is the common name given to the γ-isomer of hexachlorocyclohexane or HCH. It has also been commonly referred to as γ-BHC (benzene hexachloride). Use of Lindane is allowed, albeit restricted in the United States and Canada to specialized applications, predominantly in closed systems. Production of Lindane in the U.S. was first reported in 1950, reaching a peak in the mid-1950s and was discontinued in 1976 (U.S. EPA 1985a). Since then, all Lindane used in the U.S. has been imported with the main producers located in West Germany, France and Japan (U.S. EPA 1985b).

Lindane acts as a stomach poison by contact and has some fumigant action. It is effective against a wide range of soil-dwelling and phytophagous insects. It is used as a foliar spray, in soil applications, as a seed treatment, and in baits for rodent control. It is frequently combined with fungicides or other insecticides when intended for seed treatment (Worthing 1983). When used as a fungicide on seeds and lumber, it is often applied in closed, automatic systems. Reports on its health effects have conflicted and more studies have been ordered by the U.S. EPA before its use is further restricted or banned (U.S. EPA 1985c).

Gamma-HCH is readily converted in the environment to the alpha-isomer in the atmosphere, and the beta isomer in fish and mammals (Strachan and Eisenreich, 1988). Since α-HCH has no commercial use or production in the North America, its presence in the environment is attributed to the conversion of γ-HCH after its entry into the environment or from its presence in technical grade γ-HCH as an impurity. According to Strachan and Eisenreich (1988), Lindane and its alpha isomer are "... the most prominent of all the atmospherically observed organic contaminants."

11.3 MANUFACTURING DATA

Lindane production in the U.S. began about 1950. From the period between 1956 and 1976, the only known U.S. producer was the Hooker Chemical and Plastics Corporation in New York. Production was discontinued in 1976 and since then Lindane has been imported. Hooker's production volumes were not available.

11.4 USE DATA

United States

United States information is limited regarding use patterns of Lindane. Eckerman (1984) provides approximate usages by type of treatment for 1976 and 1982 as shown in Table 11.1. Though no geographical distribution was given, the "hardwood lumber" uses are considered to be mainly in the southeast; the "seed treatment" are mainly on small grain crops in the north-central states, such as North Dakota and Minnesota; and the "livestock" uses are primarily on cattle and hogs in the midwest. These three uses constitute almost 90% of the total. Since 1982, use has slowly declined for these types. Other use information is summarized in Table 11.2.

TABLE 11.1 Lindane usage (tonnes) by application in 1976 and 1982 (Eckerman 1984).

SITE	1976	1982
Hardwood lumber	91	54
Seed treatment	193	121
Forestry	2	1
Livestock	64	56
Ornamentals	8	5
Pecans	15	9
Pets	14	8
Structures	<1	<1
Household	6	3
Cucurbits	5	3
Avocadoes	3	2
TOTALS	400	268

TABLE 11.2 U.S. DA data on agricultural Lindane usage (tonnes).

CROP REGION	USE (ACTIVE INGREDIENTS) 1964	1966	1971	1976
Northeast	10	20	3	NA
Lake states	11	26	<1	NA
Corn belt	3	8	<1	NA
No. plains	<1	<1	1	NA
Appalachia	83	1		NA
Southeast	213	77	19	NA
Delta states	4		49	NA
So. plains	54	24		NA
Mountain	1	18		NA
Pacific	54	4	8	NA
Livestock	177	133	189	80
Other	6			
TOTALS	617	312	269	80

Import Data Reported in U.S. DA "Pesticide Review, 1978."

	1974	1975	1976	1977
Reported amount imported	1,600	2,900	13,100	152,000

NA = Data Not Available.

Canada

As shown in Table 9.2 (page 53), Lindane usage in Canada was 16 tonnes in 1968, decreasing to three tonnes in each of 1969, 1970 and 1971. Ontario usage during the years 1968 to 1974 was less than 1 tonne annually. Reported usage of Lindane in Ontario in 1983 was 110 kg (McGee 1984). Current usage in Canada as a whole is unavailable.

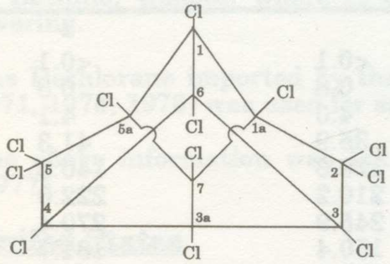
11.5 EMISSIONS

Lindane has a relatively high vapour pressure and has been shown to readily volatilize from soils and other surfaces under a wide range of conditions (U.S. EPA 1985a). Lindane used in livestock treatment is generally in a powder or dust form. Thus these particles have potential for atmospheric transport. Wood and seed applications are generally sprays in closed systems. Residues on their surfaces could volatilize readily, while the fraction incorporated more deeply into the wood or seeds could be expected to be released more slowly. Measurements (Strachan and Eisenreich, 1988) indicate that Lindane is widespread in the atmospheric compartment. No emissions inventory of Lindane, however, was found.

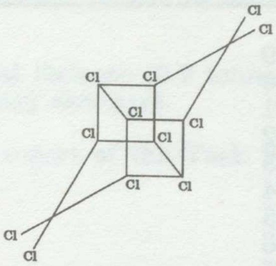
11.6 DISCUSSION OF CURRENT TRENDS

The use of Lindane has gradually decreased in recent years. No significant change in its use pattern is expected in the near future unless further regulatory restrictions are imposed. Greater restrictions upon its use are a possibility if the results of further toxicity and carcinogenicity tests suggest that Lindane poses a human health risk. These would therefore be expected to affect the rate at which Lindane enters the Great Lakes. Atmospheric transport from other countries is possible. Burton and Philogene (1985) project that the use of "benzene hexachloride" in 1988 in Latin America will be 4,700 tonnes of active ingredient.

12.0 MIREX



$C_{10}Cl_{12}$



1,1a,2,2,3a,4,5,5a,5b,6-Dodecachloro octahydro-1,3,4-metheno-1H-cyclo-butapentalene

12.1 PHYSICAL PROPERTIES (U.S. EPA 1987a)

CAS No. 2385-85-5

Solubility:	0.20 mg/L at 24°C
Partition Coefficient:	$\log P_{octanol} = 6.89$
Molecular Weight:	550
Melting Point:	485°C (sealed tube)
Vapour Pressure:	6×10^{-6} torr

12.2 BACKGROUND INFORMATION

Mirex is highly persistent (Strachan and Eisenreich, 1988). It has been used both as a pesticide and in industrial chemical preparations. Industrial use, under the trade name Dechlorane, exceeds pesticide use by a factor of three.

Mirex was used as a pesticide during the period from 1961 to 1978, primarily for the control of the imported fire-ant in the southeastern United States. Its presence in the Great Lakes region, however, is associated primarily with two manufacturing plants that discharged Mirex into rivers that drain into Lake Ontario. Data are scarce that address potential atmospheric sources of Mirex including atmospheric transport from areas of heavy use in the southeastern United States and the use, disposal and incineration of various plastic materials that incorporate it as a fire retardant.

After a number of legal actions, the manufacturing of products containing Mirex was effectively banned in 1977. Existing stocks of Mirex products were not to be sold, distributed or used in the U.S. after June 1978 (U.S. EPA 1985c). In Canada, under the Environmental Contaminants Act, the Mirex regulation prohibiting all commercial manufacturing and processing of Mirex came into effect in December 1978 (Pascoe 1986).

12.3 MANUFACTURING DATA

Mirex was primarily produced in the U.S. by the Hooker Chemicals and Plastics Corporation in New York, the Nease Chemical Company in Pennsylvania, and Hexagon Laboratories in New York. Hooker manufactured technical Mirex from 1959 to 1968. After that time Hooker bought and processed Mirex from Hexagon Laboratories of New York, New York and from the Nease Company which manufactured Mirex from 1966 to 1974. Only sales data of Mirex and Dechlorane by Hooker Chemicals from 1969 to 1975, are available. These are shown in Table 12.1 (Task Force on Mirex 1977; U.S. EPA 1978c).

Mirex bait used to control fire ants was manufactured at an Allied Chemical Company plant in Aberdeen, Mississippi. In 1975 Allied transferred the plant to the state of Mississippi, the heaviest user of Mirex, which operated the plant until the 1977 ban on use. Production in 1976 was estimated to be about 9,000 tonnes of bait containing 0.15% Mirex (U.S. EPA 1978c).

The manufacture of products containing Dechlorane was another potential source of Mirex to the environment. For example, Armstrong Cork Company of New York, a known user of Dechlorane in the 1960s, discharged wastes into the Oswego River, which flows into Lake Ontario. Elevated levels of Mirex were subsequently found in the Lake Ontario sediments near the area where the Oswego discharges into the lake. Estimates on atmospheric releases of Mirex from any of these plants were not found.

TABLE 12.1 Hooker Chemicals and Plastics sales of Mirex and Dechlorane, 1959-1975 (tonnes sold).

YEAR	MIREX	DECHLORANE	TOTAL
1959		<0.1	<0.1
1960		0.8	0.8
1961	0.1	4.0	4.1
1962	5.4	35.9	41.3
1963	11.6	129.3	140.9
1964	11.8	210.2	222.0
1965	24.5	245.9	270.4
1966	31.4	150.4	181.7
1967	33.0	72.4	105.3
1968	28.2	126.4	154.6
1969	46.3	32.8	79.1
1970	26.3	20.7	47.0
1971	13.6	37.2	50.9
1972	61.6	54.5	116.1
1973	51.3		51.3
1974	36.3	1.3	37.6
1975	18.2	4.7	22.9
TOTALS	400	1,127	1,526

12.4 USAGE

Canada

The amount of Mirex imported into Canada in the years 1963 to 1968 is shown in Table 12.2, by company and province. The chief importers were in Ontario. Inmont Presstite in Georgetown, Ontario, imported 130.2 tonnes of Dechlorane between 1963 and 1968 to use in the manufacture of an expanding rubber-based sealant for the automotive industry. There is a large discrepancy between this amount of Mirex reported by Hooker to the New York State Department of Conservation and the amount reported by Inmont to the Ontario Ministry of the Environment (U.S. EPA 1978c; Task Force on Mirex 1977; Ralston, unpublished). The sealant was sold to General Motors in the form of a tape and to Chrysler in the form of a paste.

TABLE 12.2 Canadian Dechlorane imports by company and province, 1963 to 1976 (tonnes; U.S. EPA, taken from the Report of the Task Force on Mirex 1977).

COMPANY	1963	1964	1965	1966	1967	1968	TOTAL 1963-68
ONTARIO							
Garlock Inc.,Toronto	<0.1						<0.1
Kayson Plastics,Preston	3.5	1.8	4.7		1.7	2.0	13.8
H.B. Morningstar Corp., Weston		0.1					0.1
Northern Electric, Kingston			1.4				1.4
Inmont Presstite, Georgetown	5.7	23.5	39.8	37.8	21.5	1.8	130.8
Parr Paint and Colour, Rexdale		<0.1	0.2				0.2
Western University, London	.	.	.	<0.1	.	.	<0.1
TOTALS	9.2	25.3	46.1	37.8	23.2	3.9	145.5
QUEBEC							
Dept. of National Defense*, Val Cartier							
H.B. Fuller, Boucherville		0.01	0.04				0.05
Penguin Knitting Mills, Montreal	.	.	.	0.03	.	.	0.03
TOTALS	0.00	0.01	0.04	0.03	0.00	0.00	0.08
BRITISH COLUMBIA							
J.W. Johnson, Surrey	0.06	.	.	.	.	.	0.06
TOTAL	0.06						0.06

* Further Imports: 1972, 0.01; 1975, 0.11; 1976, 0.11; totalling 0.22 tonnes.

Kayson Plastics Division used 13.8 tonnes of Dechlorane as a flame retardant in polypropylene, which was sold to Sigma Tools, Scarborough and Polobak Plastics, Downsview, for manufacturing parts for television picture tubes.

Northern Electric, Kingston, shipped their imported Dechlorane (1.4 tonnes) to their plant at Lachine, Quebec, where it was used as a fire retardant in the manufacture of cable covering.

The Dechlorane imported by the Department of National Defense (0.2 tonnes total, during 1971, 1975, 1976) was used for smoke generation in military exercises.

The above information was taken from the U.S. EPA report of the Task Force on Mirex (1977).

United States

As a pesticide Mirex was used primarily in the south to control the fire ant. The states with the heaviest infestation include Mississippi, Arkansas, Alabama, North Carolina, South Carolina, Florida, Georgia, Louisiana and Texas. A summary of estimated use of Mirex of over 200 tonnes for fire ant control for the years 1962 to 1975 is found in Table 12.3. Mirex was also used to control several other pests over more localized areas including termites, western harvester ants and the Texas leaf-cutting ants, though no totals were available for these uses. These amounts are not included in Table 12.3.

TABLE 12.3 Mirex used in the U.S. for fire-ant control (U.S. EPA 1978a).

YEAR	TOTAL ACRES/HECTARES	TOTAL (TONNES)
1962	163,388/66,009	<1
1963	1,523,469/615,481	3
1964	2,230,542/901,139	4
1965	359,903/145,401	6
1966	6,290,570/2,546,000	11
1967	10,417,187/4,216,006	18
1968	13,208,746/5,346,070	23
1969	11,557,182/4,677,139	20
1970	16,025,737/6,486,249	26
1971	11,609,907/4,698,123	20
1972	1,165,153/471,519	19
1973	14,184,017/5,740,438	24
1974	13,611,289/5,508,139	23
1975	12,112,616/4,902,483	21
	TOTAL	216

12.5 FATE AND TRANSPORT

Mirex has a very low solubility in water and a high affinity for fats and oils. As with the other organochlorine pesticides, these properties result in storage in animal fats and bioaccumulation in higher organisms.

Mirex was sprayed aerially, as particulate bait which should have settled quickly. The evaporation rate of Mirex is low and little volatilization from the ground was expected (U.S. EPA 1978a). Thus, atmospheric transport is unlikely and Strachan and Eisenreich (1988) comment that it is "... unlikely that [Mirex] is an atmospheric problem." This conclusion is supported by the fact that while Mirex is found in the water and sediments of Lake Ontario, "... it is not found elsewhere in the Great Lakes ... ." Mass balance budgeting of Mirex in the Great Lakes Basin Ecosystem would appear to largely depend on determining the rate at which it is covered by settling and uncovered by resuspension of suspended matter in Lake Ontario and its rate of export down the St. Lawrence River (Strachan and Eisenreich, 1988).

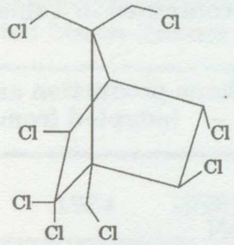
12.6 DISCUSSION OF CURRENT TRENDS

There is no evidence of current emissions of Mirex to the atmosphere. No estimates were found of emission from use, disposal and incineration of products into which it is incorporated.

13.0 TOXAPHENE

CAS No. 8001-35

$C_{10}H_{10}Cl_8$



also: Camphechlor

13.1 PROPERTIES (Merck 1976; Vershueren 1983)

Toxaphene is a complex mixture composed of more than 177 congeners with differing chemical properties. It is produced through chlorination of camphene. Technical grade Toxaphene has an average chlorine content of 67 to 69% (Rice and Evans, 1984). Bidleman and Christiansen (1979) report a vapour pressure of only 3×10^{-7} mm Hg at 20°C. Other reported vapour pressures are in the range of 0.17 to 0.4 mm Hg (Rice and Evans, 1984; Brooks 1974). This variability in measured vapour pressures arises because each congener has its own vapour pressure and because Toxaphene composition varies with the manufacturer and probably between batches (Rice and Evans, 1984).

Toxaphene ranges from relatively soluble to practically insoluble in water (Merck 1976). Rice and Evans (1984) discuss reported solubilities of Toxaphene ranging from 400 μg/L (Sanborn et al. 1976) to 1,000 μg/L at room temperature (Korte et al. 1979), attributing the differences to the Toxaphene analyzed or the temperature at which tests were conducted. Solubility reported by U.S. EPA (1986b) and Vershueren (1983) is 740 μg/L.

The estimated log (octanol-water coefficient) for Toxaphene reported by Rice and Evans (1984) and Magnuson et al. (1979) is 6.44. The U.S. EPA (1987d) reports a value of 5.28 (Vershueren 1983). Its melting point is 65-90°C (Merck, 1976).

Rice and Evans (1984) conclude that Toxaphene is relatively volatile and water-soluble and that, because of its relatively high octanol-water partition coefficient, it is very soluble in lipids and tends to accumulate in the fats of organisms.

13.2 BACKGROUND

Toxaphene became commercially available in 1948 and has been used in a variety of forms including emulsifiable concentrates, wettable powders, dusts and granular baits. Toxaphene was the most heavily used pesticide in the U.S. during the 1960s and 1970s, particularly after the banning of DDT. Annual applications exceeded 10,000 tonnes in the 1960s increasing to over 35,000 tonnes in the early 1970s.

Toxaphene has been used against insect pests on cotton, tobacco, forests, grains, ornamental plants and livestock; most heavily in the southern United States (U.S. EPA 1986b). In the sixties and early seventies, the predominant use of Toxaphene was as an insecticide on cotton. This use gradually declined as other more effective cotton insecticides became available in the mid-to-late seventies. By 1980 Toxaphene was also registered as a herbicide for control of sicklepod on soybeans in Arkansas, Alabama, Georgia, Mississippi, North Carolina and Tennessee. This became its largest single use by 1981 (Vlier-Zygadlo 1986). In the 1950s and early sixties Toxaphene was used in several states for rough fish control in lakes and ponds, but this use was discontinued when unexpectedly high persistence was discovered in some lakes (U.S. EPA 1986b).

Toxaphene usage in Canada appears to have been negligibly small, since only a limited amount of Toxaphene was used for scabies treatment on livestock (Health and Welfare Canada 1977).

The U.S. EPA cancelled the registration of Toxaphene for all but a few limited uses in December 1982. Use of existing stocks was allowed under increasingly stringent restrictions through December 1986. Under the Canadian Pest Control Products Act, all product registrations of Toxaphene were discontinued by 1983.

13.3 MANUFACTURING DATA

Toxaphene has not been produced in Canada (Health and Welfare Canada 1977). Toxaphene had a number of different producers in the U.S., but comprehensive data on plant locations and production amounts are not available. A summary of the available data on the manufacture of Toxaphene is contained in Table 13.1 (MRI 1974).

TABLE 13.1 Toxaphene production and use (tonnes) in the United States (adapted from MRI 1974).

YEAR	PUBLISHED PRODUCTION ESTIMATES	PRODUCERS	PUBLISHED USE ESTIMATES	USE ESTIMATES FOR YEARS WITHOUT DATA
1964		H	17,700	
1965		H		16,800
1966	29,500	H	15,700	
1967		H		15,500
1968		H,S	15,000	
1969		H		14,500
1970	22,700	H,S,T	14,100	
1971	34,500	H,S,T	13,900	
1972	34,000	H,T	25,900	
1973		H,T		32,300
1974	50,000	H,T,R		38,500
1975	50,000	H,T,R,V		38,900
1976	29,500	H,T,R,V	13,900	
1977		H,V,		10,500
1978	19,100	H,V		9,100
1979		H,V		7,500
1980		H,V		5,900
1981	10,000	H,V	7,230	
1982			4,100	
1983	0		2,000	
1984	0		2,000	
1985	0		2,000	
1986	0		0	
	Total Estimated Use 1964-1986		320,000	

H = Hercules (GA); S = Sonford (TX); R = Riverside (TX); V = Vertac (MS); T = Tenneco (NJ)

Table 13.1 shows that through most of the 1960s the primary producer was Hercules, Inc., which manufactured Toxaphene at its plant in Georgia. By 1974 there were three additional producers, Tenneco Chemicals in New Jersey; Riverside Chemicals in Texas (previously operated by the Sonford Corp.); and Vicksburg Chemical in Mississippi.

Little information was found on emissions of Toxaphene from the manufacturing process, although emissions undoubtedly occurred. While virtually no actual emissions testing was performed for these plants, attempts were made to estimate emission factors. Archer et al. (1978) proposed an average emissions factor for Toxaphene production of 0.28 kg/tonne, based primarily on evaporation from holding ponds and lagoons.

13.4 USAGE

United States

Information on the historical use patterns of Toxaphene is incomplete. However, because Toxaphene had very few non-agricultural applications, U.S. DA data that reports its agricultural use for selected years is a reasonable surrogate for its total use for those years.

Data on total Toxaphene used nationally and/or regionally were found for the years 1964, 1966, 1971, 1976 and 1981. Data for the missing years were estimated by interpolation (see Table 13.1). From 1964 to 1982 there was a marked reduction in usage of Toxaphene in the southern states as shown in Table 13.2. Note that there are inconsistencies in the distributions because the same regional distribution was not applied to all data. The regions are displayed in Addendum B.

TABLE 13.2 Geographical allocation of Toxaphene use in the United States (tonnes).

	YEAR					
	1964	1966	1971	1972	1976	1981
North Central						
W.N. Central				230		460
E.N. Central				230		45
Corn Belt	590	180	80		270	
No. Plains	<1	3	40		25	
Lake States	24	50	20		5	
Northeast	1	2			125	70
West	830	900	700	2,050	750	210
So. Plains	2,300	2,260	1,220	4,550	170	650
South						
Delta States	4,660	3,300	4,900	10,900	4,600	
Southeast	5,230	6,230	6,990		6,880	4,720
Appalachian	1,900	1,150	1,000		1,140	
Non Ag. Use				450		1,080
TOTALS	155,000	14,100	14,900	26,400	14,000	7,200

Canada

Toxaphene usage in Canada appears to have been negligibly small since only a limited amount of Toxaphene was used for scabies treatment on livestock (Health and Welfare Canada 1977).

13.5 NORTH AMERICAN EMISSION RATES

Rice and Evans (1984) state that atmospheric deposition is probably the major source of Toxaphene to the Great Lakes. Evidence that atmospheric transport is a major means of distribution of Toxaphene may be drawn from Bidleman and Olney's (1974) conclusion that Toxaphene is a major atmospheric contaminant. This is supported by modeling of emissions and transport of Toxaphene (Voldner and Schroeder, 1986). Presence of Toxaphene in ambient air and in precipitation have been reported by Eisenreich et al. (1980) in the Great Lakes region. Further, Murphy (1984) notes that the atmosphere is the only source of the significant concentrations of chlorinated hydrocarbons, including Toxaphene, in fish in Siskiwit Lake, on Isle Royale in Lake Superior.

Other pathways such as riverine discharge to the Great Lakes are possible. The use of Toxaphene for rough fish control in states bordering the Great Lakes (Lee et al. 1977) is one example of aquatic sources of Toxaphene.

Primary emissions of Toxaphene to the atmosphere can occur through loss to the air at manufacturing sites; through leakages and spills during transportation; and through loss to the air during application to crops by aerial or ground-based spraying. Toxaphene has been applied as an emulsion in water, or as a dust. Off-target drift during application and volatilization from foliage and from the soil immediately following spraying constitute primary emissions of Toxaphene.

Experimental evidence (Mickle et al. 1984; Crabbe et al. 1984; Crabbe and McCoolye 1985) have shown immediate off-target drift of pesticides during spraying of up to 50%. While this is not directly applicable to Toxaphene, it serves to support the experimental evidence discussed below:

Ground-based Spraying: Harper et al. (1983) reported that in an experiment conducted on cotton fields in Mississippi during August-September 1976, about 55% of Toxaphene and 70% of DDT were lost within a few hours of application by ground equipment, either during initial spraying or through volatilization within a few hours of application. About 50% of the deposited Toxaphene was lost after 4.7 days in "midseason" and 10.8 days in late season. The volatilization rate from foliage increases with wind speed and leaf temperature.

Aerial Spraying: Willis et al. (1980) found, in two similar experiments in the same region in 1974, that less than 10% and 20%, respectively, of the Toxaphene applied by aerial spraying to cotton could be accounted for. Possible reasons for this loss were given. These include losses through drift, evaporation and initial volatilization, as well as sampling and analysis errors. About 25% of the Toxaphene was lost through volatilization and 15% through washoff. Volatility rates were found to be high when wind speeds and leaf humidity were high. Approximately 85% of the remaining Toxaphene deposited on the foliage was in the upper half of the canopy.

Volatilization from plant foliage and soil: Seiber et al. (1979) noted a 60% loss of Toxaphene during a 28-day period following aerial spraying to cotton fields in California. Loss was attributed primarily to volatilization from the plant canopy and from the soil, with residues declining more slowly in the soil. Nash et al. (1977), experimenting with Toxaphene application to cotton in an enclosed agro-ecosystem, found 25% volatilization over a 90-day period during which Toxaphene was applied weekly for six weeks.

Secondary sources of Toxaphene to the atmosphere include volatilization from soil and by entrainment of soil particles with adsorbed Toxaphene during soil cultivation, for an extended period of months or even years following application. This has been discussed by Seiber et al. (1979) and by Rice and Evans (1984). Reported Toxaphene half-lives, summarized by U.S. EPA (1987d) vary from a few months to more than ten years. Potential loss routes such as leaching, degradation, volatilization and particle resuspension were suggested. Reported persistence figures for Toxaphene by the U.S. EPA (1987d) include the following: six years at an application rate of 140 ppm in soil; for more than 11 years with 50% loss; and for 14 years with 55% loss at 100 ppm.

From the foregoing discussion, it is clear that Toxaphene is transferred to the atmosphere in significant quantities. No emission inventory for Toxaphene is available. Toxaphene usage patterns, in combination with typical volatilization rates, could serve as a surrogate for a crude emission inventory. Emissions would be derived from factors depending on the times, locations and types of application. However, the lack of required detail in the available data bases would result in large uncertainties difficult to quantify. Voldner and Schroeder (1986) have attempted to estimate emissions of Toxaphene for 1976 and 1979-80, respectively, based on use patterns.

As a high degree of volatility so strongly affects Toxaphene's fate and transport characteristics, it is not surprising that airborne transport of Toxaphene over several-hundred kilometers has been observed. The work of Rice et al. (1986) states: "Long-range transport of Toxaphene by way of the air is well documented, both by direct observation of Toxaphene in air at remote sites and by inference from finding the material in organisms at sites remote from the use of this material [including] Great Lakes fish, Antarctic cod and Arctic char." Bidleman and Olney (1974) reported an average of 0.6 ng m^{-3} in air samples from the North Atlantic, more than 1,600 km from the nearest known use. Air mass trajectory modeling was used to show that Toxaphene transport to Bermuda could be linked to the southeastern region of the United States. Rice et al. (1986) monitored atmospheric concentrations of Toxaphene in the Summer and Fall of 1981 in four locations between Greenville, Mississippi and northern Lake Michigan. Their results suggest that the Cotton Belt was a source of Toxaphene to Lake Michigan. The authors estimated a total Toxaphene input to Lake Michigan of 3,360 to 6,720 kg for 1981. This is supported by results obtained through mathematical simulation of emission, transport and deposition by Voldner and Schroeder (1986).

In 1983, however, Strachan (1985) did not detect Toxaphene (with a detection limit of approximately 0.2 ng/L) in a few rain samples taken over Lake Superior. Strachan commented that these observations "must be considered in light of the widely-held view that [Toxaphene] arrives in this lake via atmospheric transport." As a proposed explanation, he states that "... very little Toxaphene was used in aerial spraying programs in the U.S. during 1983. It would seem, therefore, that the 1982 ban on most uses of Toxaphene has been effective, at least in reducing atmospheric deposition in the Lake Superior region."

13.6 EMISSION SEASONALITY

For the period of heavy usage, ample evidence exists that emissions were seasonally dependent, as discussed below. Time of treatment and number of applications vary with type of infestation, crop and region. Most applications occurred between late June and early September. Livestock was generally treated throughout the year (Eichers et al. 1978).

Rice and Evans (1984) reported on atmospheric measurements that suggest a seasonal dependence of emissions of Toxaphene. Examples of Toxaphene measurements in air that showed seasonal variation include those by Arthur et al. (1976) who reported levels of Toxaphene in air over the Mississippi Delta in September at 900 ng m^{-3}, decreasing in winter and increasing again to about 10 ng m^{-3} in February when the fields were tilled. Harder et al. (1980) reported Toxaphene concentrations of over 150 ng/kg in rainwater sampled over South Carolina in June-August of 1977-1978. They remained high during September and October, but falling below detection limit (i.e. less than 1 ng/kg) during winter and spring. Rice et al. (1986) found air concentrations in Mississippi, Missouri and Michigan higher in summer than in fall, during the period August to November 1981.

13.7 QUALITY OF EMISSION DATA

The release of Toxaphene to the atmosphere through volatilization and resuspension processes is strongly dependent upon the type of application, the local weather and the soil conditions at the site of application, and thus, reliable means are not available to develop credible emission inventories.

13.8 TRENDS IN EMISSIONS

Emissions in North America are likely to have been high during the 1970s. After Toxaphene was delisted in 1983, emissions probably underwent a sharp decline. Volatilization from soil and resuspension of contaminated soil particles would have been the principal remaining emission sources. Sources in Latin America and Mexico appear to have been relatively constant from 1978 until 1988.

Toxaphene use in Latin America exceeded 17,000 tonnes in 1978. Projected use in 1988 is 11,000 tonnes. Usage in Mexico in 1978 exceeded 22,000 tonnes with a projected use in 1988 of 20,000 tonnes (Burton and Philogene, 1985; Maltby 1980).

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

SUMMARY

Under the United States - Canada Great Lakes Water Quality Agreement, the presence of toxic contaminants in the Great Lakes Basin Ecosystem is an issue of major concern. Atmospheric input of toxic trace metals and organic compounds to the Great Lakes basin is recognized as a significant contribution and in some cases, the dominant contribution, to the presence of these toxic chemicals in the Great Lakes Basin Ecosystem. Fuller knowledge of this atmospheric contribution is essential for establishing the cause-effect relationship between inputs to the lake and the state of health of the aquatic ecosystem. Rational management of this valuable ecosystem requires such scientific understanding.

A fundamental component of the atmospheric system depositing to the Great Lakes is the emissions of the relevant toxic chemicals. Characterizing these emissions with adequate resolution in space and time is an elusive goal, but progress toward this goal is necessary if better scientific understanding is to lead to better management decisions. Information has been assembled on emissions and usage of the 14 priority toxic chemicals designated by the International Joint Commission for an initial, in-depth study. These chemicals include trace metals, commercial and industrial chemicals or by-products, and organic pesticides.

A summary of the information on emissions and usage, obtained from various agencies and through an extensive literature survey is shown in the summary table. The year of the most recent emission data found and the availability of national and regional totals for the United States and national and provincial totals for Canada are shown. Also, the availability sectorial emission data is indicated. As indicated, relatively complete emission estimates are available for only the metals, i.e. lead, mercury, cadmium and arsenic, with limited emission data reported for PAH and PCDDs/PCDFs for both countries and for hexachlorobenzene in the United States. For the remaining priority chemicals, where essentially no emission information is available, the acquisition of data on usage and production/sales is a preliminary step toward estimating emissions.

SUMMARY TABLE
Emissions and usage information retrieved.

	Pb	Cd	Hg	As	BaP	PAH	PCDD PCB	DIELDRIN PCDF	ALDRIN	DDT	LINDANE	MIREX	TOXA-PHENE	HCB
U.S.A.														
Total	1985	1985	1985	1985	1983									1984
Sector	X	X	X	X	X									X
Region	X	X	X	X										
Trends	X													
Quality	1	2	2	2	3	3	3	3	3	3	3	3	3	3
CANADA														
Total	1982	1982	1982	1982	1980			X						1984
Sector	X	X	X	X	(1983)			X						1984
Region	X	X	X	X	Ont.			Ont.						
Trends	X													
Quality	1	2	2	2	3	3	3	3	3	3	3	3	3	3
CONSUMPTION/ PRODUCTION/SALES														
U.S.A							X		X	X	X	X	X	X
Canada		X					X		X	X	X	X		
STORAGE							X							
SPILLS							X							

Quality Indicators: 1. Marginally acceptable. 2. Questionable. 3. Unacceptable or non-existent.

a. Lead, Mercury, Cadmium and Arsenic

The most complete emission data is for lead. Data for each of the metals have been obtained for 1985 in the United States and for 1982 in Canada. Data include provincial totals in

Canada and regional (census) totals in the United States for each of the primary emitting sectors. Historical and projected emissions of lead were also acquired and indications of probable future changes in emission levels for the other metals were made.

b. PAH, BaP, PCBs, PCDDs/PCDFs and HCB

PAH and BaP are undesired by-products of combustion. The limited estimates found for them vary among authors because of differing emission factors, the incomplete nature of their data, and the strong dependence of these emissions on process conditions.

Estimated emissions of PCBs are not available. Data are presented on the historical production and sales of PCBs and amounts in use and in storage.

Estimates on the release of PCDDs/PCDFs to the North American environment include limited emissions data. The quality of estimated emissions was judged to be poor due to conflicting estimates among authors. Production information on PCDDs/PCDFs is not relevant because these chemicals are undesirable by-products. Information has been presented on production and usage of chemical precursors of PCDDs/PCDFs.

Emission estimates for hexachlorobenzenes were assembled for the United States. Although these estimates cover the major emitting sectors, they are quite uncertain and their geographical allocations were not quantified.

c. Pesticides

Pesticide emission estimates are not available. Since emissions are related to the amount and method of application of these chemicals to crops and livestock, historical production and usage data have been obtained for the United States and Canada.

CONCLUSIONS

Relatively comprehensive emission information is available in the United States and Canada for the four trace metals. The information is, on the whole, recent (mid 1980s) and available as provincial totals in Canada and regional (census) for the United States' major emission sectors. There are some historical and projected emission data. For most of the other chemicals, little reliable current emission information exists. Indeed for many of the chemicals, notably the organic pesticides, no emission data are available. In order to estimate emissions, production and usage data must be combined with emission factors. Detailed information on pesticide usage at the county level in the United States is currently being developed under contract for U.S. EPA. The Province of Ontario is funding a study to estimate emissions of pesticides from Ontario and the states bordering the Great Lakes. Emission factors relevant to the current application of pesticides are a function of the method of application and meteorological conditions, such as wind speed, vertical temperature profiles and humidity. On the other hand, emission factors relevant to the cycling through environmental compartments of pesticides previously applied are dependent upon soil type, conditions and vegetative cover, as well as meteorological conditions. At present, credible emission factors have not been developed to represent the wide variety of conditions encountered for organic pesticides.

It should be noted that although most of the pesticides on the priority list are currently banned in Canada and the United States, in some cases, such as DDT, metabolites may be present in pesticides that are still in use. Further, pesticides that are banned in the United States and Canada are frequently used in Mexico and other Latin American countries, as well as in some Asian countries. Hence, primary emission sources of these organic pesticides continue to add to their global background.

For industrial chemicals including PAH and BaP, measurements have revealed that emission rates are strongly dependent upon the type of emission process, the nature of the precursors and conditions under which emission takes place. Most emission factors rely upon a small number of measurements which may not adequately characterize the wide range of conditions under which these substances are released.

In closing, it should be noted that the development and refinement of emission inventories for many toxic substances released to the atmosphere (and land and water environmental compartments) in the United States could be greatly facilitated in the future by reporting requirements in the "Superfund Amendments and Reauthorization Act" (SARA). SARA was enacted in October 1986 (99th Congress). Section 313 (Title III) of SARA requires that facilities employing ten or more persons covered by Standard Industrial Classification Codes 20 through 39, and satisfying other threshhold requirements, must annually report their releases of certain toxic chemicals to the atmosphere and other environmental media. The list of chemicals covered contains more than 300 compounds, some of which are relevant to the IJC's priority list. The first reporting of toxic releases under Section 313 is due July 1, 1988. Except where a claim of divulging a trade secret can be maintained, all such reports will be assessed and indicated improvements in reporting made. Over the next few years, a particularly rich data base for studying atmospheric (and other media releases of toxic substances) will become available. The potential value of these data cannot be overemphasized.

RECOMMENDATION

Efforts to compile emission inventories for toxic substances are severely constrained by the availability of representative emission data and the completeness of these data. SARA Title III reporting requirements could substantially alleviate these problems in the U.S.A. over the next few years for many substances. Even so, substantial research and measurement programs are required to lift these constraints for some toxic substances of concern. The benefits to be gained from these undertakings include enhancing our ability to prioritize the relative importance of atmospheric sources in the management of these chemicals in the Great Lakes Basin Ecosystem and providing necessary input information to the scientific study of the transport and fate of these chemicals.

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ADDENDA

A. Summary of the Methods Used to Estimate Emissions from Coal and Oil Combustion for the Toxic Emission Database for the International Joint Commission

B. Census and Farm Production Regions of the Contiguous United States

Woodwell, G.M., P.P. Craig and H.A. Johnson, 1971. "DDT in the biosphere: Where does it go?" Science 174(4014):1101-1107.

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A. SUMMARY OF THE METHODS USED TO ESTIMATE EMISSIONS FROM COAL AND OIL COMBUSTION FOR THE TOXIC EMISSIONS DATABASE FOR THE INTERNATIONAL JOINT COMMISSION

NOTE: The values quoted in addendum A have been converted to metric units for use in the body of this report in order to facilitate comparison with other data.

COAL COMBUSTION

1. Determine metal concentrations for each region.

a. From Coal Data 1987 (NCA 1987), for each coal use (census) region, calculate the percentages of its total which came from each coal-producing region.

New England	100%	Appalachian
Mid Atlantic	100%	Appalachian
East North Central	48.5% 34.1% 7.0% 10.4%	Appalachian + Illinois Basin + Northern Plains + Rocky Mountains
West North Central	1.1% 19.6% 7.7% 33.3% 38.3%	Appalachian + Illinois Basin + Interior Basin + Rocky Mountains + Northern Plains
South Atlantic	88.7% 11.3%	Appalachian + Illinois Basin
East South Central	60.1% 37.9% 2.0%	Appalachian + Illinois Basin + Rocky Mountains
West South Central	40.8% 2.8% 56.4%	Interior Basin + Northern Plains + Rocky Mountains
Mountain	92.2% 7.8%	Rocky Mountains + Northern Plains
Pacific	34.0% 66.0%	Rocky Mountains + Northern Plains

b. Use metal contents for each coal production region, as given in Mead et al. (1986).

REGION	CADMIUM	ARSENIC	MERCURY	LEAD*
	(parts per million)			
Appalachian	0.13	22.2	0.24	8.3
Interior Basin	5.47	16.3	0.14	8.3
Illinois Basin	2.89	14.9	0.21	8.3
Northern Plains	0.30	6.33	0.11	8.3
Rocky Mountains	0.35	4.72	0.09	8.3

* No regional variation data available.

c. Using these figures, calculate a weighted average trace metal concentration for each coal use region, e.g. Cadmium for the South Atlantic region

Cadmium concentration = (0.13 ppm)(0.887) + (2.89 ppm)(0.113)
= 0.44 ppm

The resulting concentrations are:

REGION	CADMIUM	ARSENIC	MERCURY	LEAD*
	(parts per million)			
New England	0.13	22.2	0.24	8.3
Mid Atlantic	0.13	22.2	0.24	8.3
E.N. Central	0.70	14.7	0.20	8.3
W.N. Central	1.22	8.4	0.13	8.3
So. Atlantic	0.45	21.4	0.24	8.3
E.S. Central	1.18	19.1	0.24	8.3
W.S. Central	2.44	9.6	0.11	8.3
Mountain	0.35	4.9	0.10	8.3
Pacific	0.32	5.8	0.10	8.3

* No regional variation data available.

2. Calculation of Emission Factors

In each case, a high and low value for an uncontrolled emission factor will be calculated. The high value will be based on the assumption that 100% of the trace metal content is emitted in the flue gas and/or fly ash and so is calculated simply by converting the ppm values to pounds per short (2,000 pound) ton. In the case of mercury this is probably a good assumption, while for the other metals it should result in an overestimation. The low value of the range will be based on the assumption that an average of 25% of the trace metal content remains in the bottom ash and is calculated by taking 75% of the high value.

Control efficiencies are then applied to both the high and low values, with respect to these economic sectors:

SECTOR	ASSUMED CONTROL EFFICIENCY Cd, As, Pb	Hg
Utility	91%	50%
Industrial	75%	0%
Commercial/Residential	0%	0%

The resultant emission factors, which compare fairly well with those in Mead et al. (1986), are shown in the following tables. These numbers are then multiplied by the region's coal use amounts for each economic sector, for 1985, as found in NCA (1987), which are given in units of short (net) tons per year. Since the emission factors are in lbs. per short ton, it is possible to avoid making additional assumptions about the heat content of the coal, which also varies regionally.

Most other documents addressing these emissions rely upon actual source tests of various types of boilers and develop average emission factors, using the distribution of the various types of boilers (Radian, 1984). Unfortunately it was not possible to use the boiler type data and also account for the regional variability in the coal and metal content, since the concentrations of the metal in the coal used in each test was not given. For this report, it was decided that reviewing this regional variability should be the overriding priority.

Emissions factors from coal combustion (2,000 pounds/ton).

	UTILITY		INDUSTRIAL		COMMERC./RESID.	
REGION	High	Low	High	Low	High	Low
CADMIUM						
New England	0.000023	0.000017	0.000065	0.000049	0.000260	0.000195
Mid Atlantic	0.000023	0.000017	0.000065	0.000049	0.000260	0.000195
E.N. Cent.	0.000126	0.000095	0.000350	0.000263	0.001400	0.001050
W.N. Cent.	0.000216	0.000162	0.000600	0.000450	0.002400	0.001800
South Atlantic	0.000081	0.000061	0.000225	0.000169	0.000900	0.000675
E.S. Cent.	0.000216	0.000162	0.000600	0.000450	0.002400	0.001800
W.S. Cent.	0.000441	0.000331	0.001225	0.000919	0.004900	0.003675
Mountain	0.000063	0.000047	0.000175	0.000131	0.000700	0.000525
Pacific	0.000057	0.000043	0.000160	0.000120	0.000640	0.000480
ARSENIC						
New England	0.003996	0.002997	0.0111	0.008325	0.044400	0.0333
Mid Atlantic	0.003996	0.002997	0.0111	0.008325	0.044400	0.0333
E.N. Cent.	0.002646	0.001984	0.00735	0.005512	0.029400	0.02205
W.N. Cent.	0.001512	0.001134	0.0042	0.00315	0.016800	0.0126
South Atlantic	0.003852	0.002889	0.0107	0.008025	0.042800	0.0321
E.S. Cent.	0.003438	0.002578	0.00955	0.007162	0.038200	0.02865
W.S. Cent.	0.001728	0.001296	0.0048	0.0036	0.019200	0.0144
Mountain	0.000882	0.000661	0.00245	0.001837	0.009800	0.00735
Pacific	0.001044	0.000783	0.0029	0.002175	0.011600	0.0087
MERCURY						
New England	0.000043	0.000032	0.00012	0.00009	0.00048	0.00035
Mid Atlantic	0.000043	0.000032	0.00012	0.00009	0.00048	0.00035
E.N. Cent.	0.000036	0.000027	0.0001	0.000075	0.0004	0.00005
W.N.Cent.	0.000023	0.000017	0.000065	0.000048	0.00026	0.000195
South Atlantic	0.000043	0.000032	0.00012	0.00009	0.00048	0.00036
E.S.Cent.	0.000043	0.000032	0.00012	0.00009	0.00048	0.00036
W.S. Cent.	0.000019	0.000014	0.000055	0.000041	0.00022	0.000165
Mountain	0.000018	0.000013	0.00005	0.000037	0.0002	0.00015
Pacific	0.000018	0.000013	0.00005	0.000037	0.0002	0.00015
LEAD						
All regions	0.001494	0.001120	0.00415	0.003112	0.0166	0.01245

OIL COMBUSTION

1. Determination of emission factors.

Here, uncontrolled emission factors for each metal for both residual and distillate oil combustion were taken directly from Mead et al. (1986) and are shown below.

Since oil combustion generates no bottom ash, it is assumed that 100% of the trace metals present are in the uncontrolled emissions. Industrial, commercial and residential oil combustion are assumed uncontrolled and presently, the most up-to-date use figures which include both regional and residual versus distillate breakdowns are found in Mead et al. (1986) and are for 1982. More current numbers will be used if they are available. The utility sector is assumed to use 100% residual oil and an overall control efficiency of 20% was assumed for this industry. This is based on EPA (1981), which estimates 60% of this sector to be uncontrolled and 40% to be controlled with an average efficiency of 50%, resulting in a new emission factor of 12.6 lb/10^{12} BTU (80% of 15.7) Fuel use data for this sector is for 1985 and was obtained from DOE/EIA (1986).

Uncontrolled Emission Factor (pounds = 10^{12} BTU).

	RESIDUAL OIL		
METAL	Uncontrolled	Controlled	DISTILLATE OIL
Cadmium	15.7	12.6	10.5
Arsenic	19.0	15.2	4.2
Mercury	3.2	2.6	3.0
Lead		28.0*	8.9**

* Lead figures were given for: utility (*) and for industrial, commercial and residential (**) usages.

COMPARISON BETWEEN THIS AND OTHER DOCUMENTS

As mentioned, this approach differs somewhat from several other published reports, which will be discussed here, using cadmium emissions as the example. The documents Survey of Cadmium Emission Sources (EPA 1981) and Methodology for Estimating Exposure to Arsenic, Beryllium, Cadmium and Nickel from Coal and Oil Combustion (Radian Corp. 1984), estimate the following emission factors.

COAL COMBUSTION (pounds = 10^{12} BTU).

	EPA 1981	Radian 1984	This report*
Utility	11.1	3.9	7.4
Industrial	73	7.7	20.4
Commercial/Residential	76	41/31	82.6

* assume 11,500 BTU/lb. average heat content for purposes of comparison.

OIL COMBUSTION (pounds = 10^{12} BTU).

	E P A 1981			THIS REPORT*	
	Res.	Dist.	RADIAN 1984	Res.	Dist.
Utility	95	3.9	16	12.6	
Industrial	121	4.9	14	15.7	10.5
Commercial/Residential	121	4.9	41/43	15.7	10.5

* adapted from Mead et al. (1986)

EPA (1981) is consistently higher than the other documents, especially the oil combustion factors, which were more than seven times greater. Mead et al. (1986) figures were chosen here since they appeared to be based on the largest number of tests.

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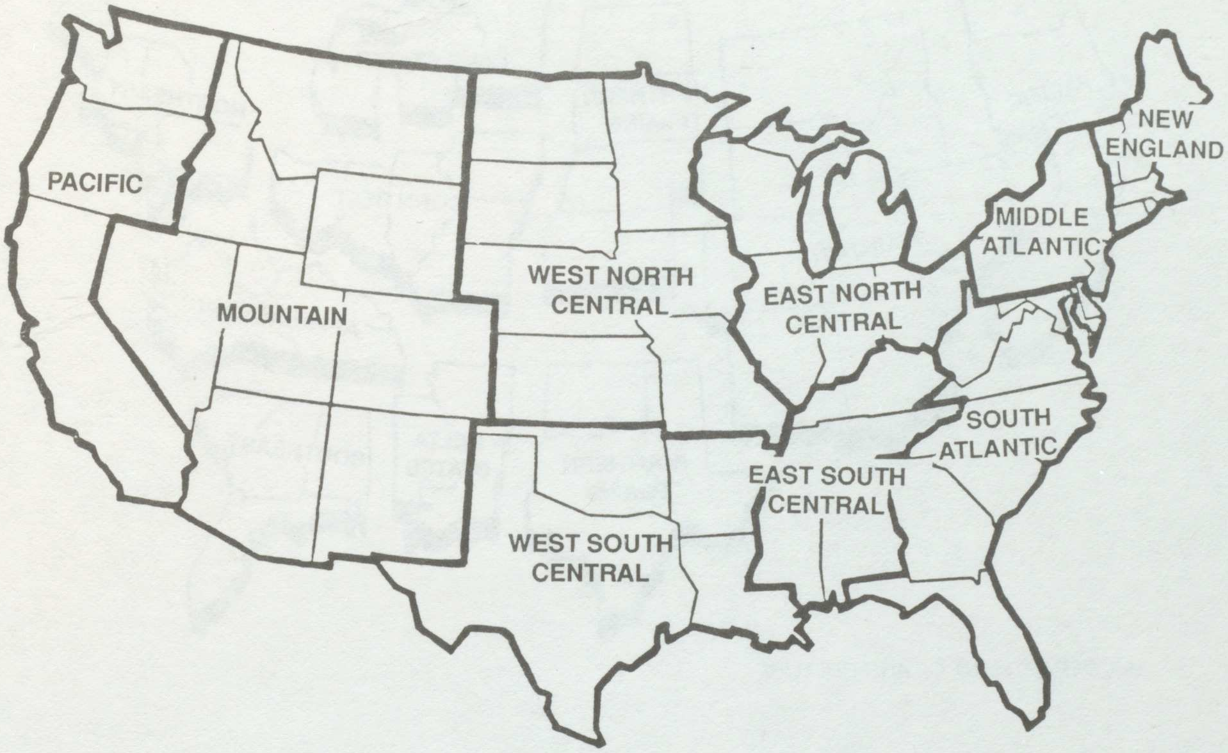
B. CENSUS AND FARM PRODUCTION REGIONS OF THE CONTIGUOUS UNITED STATES



Census Regions of the Contiguous United States

PACIFIC

- California
- Oregon
- Washington

MOUNTAIN

- Arizona
- Colorado
- Idaho
- Montanat
- Nevada
- New Mexico
- Utah
- Wyoming

WEST NORTH CENTRAL

- Iowa
- Kansas
- Minnesota
- Missouri
- Nebraska
- North Dakota
- South Dakota

WEST SOUTH CENTRAL

- Arkansas
- Louisiana
- Oklahoma
- Texas

EAST NORTH CENTRAL

- Illinois
- Indiana
- Michigan
- Ohio
- Wisconsin

EAST SOUTH CENTRAL

- Alabama
- Kentucky
- Mississippi
- Tennessee

NEW ENGLAND

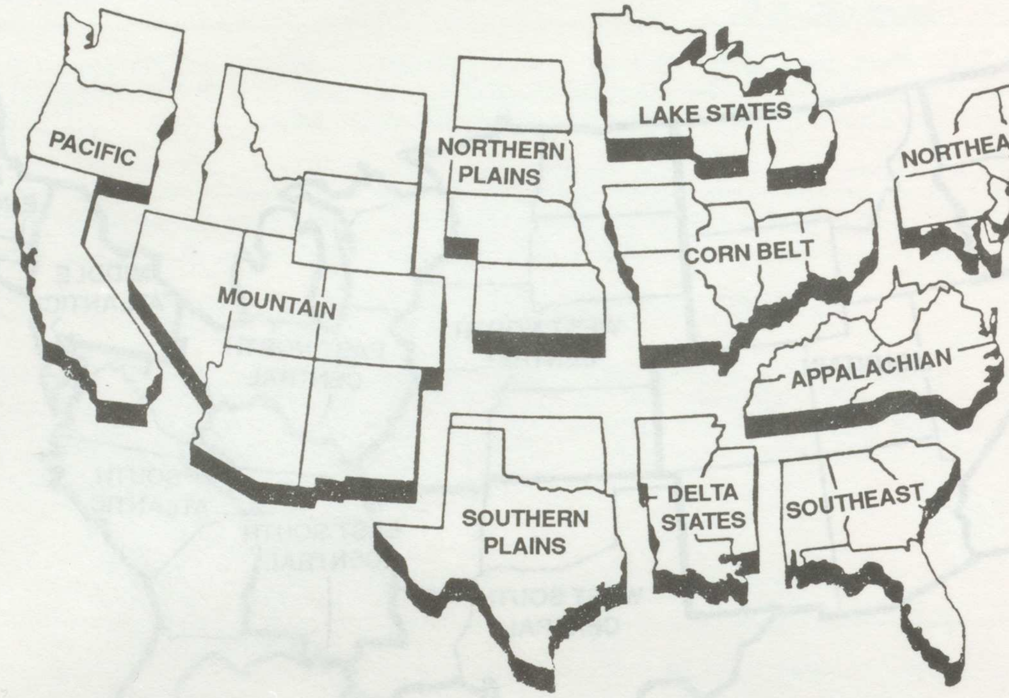
- Connecticut
- Maine
- Massachusetts
- New Hampshire
- Rhode Island
- Vermont

MIDDLE ATLANTIC

- New Jersey
- New York
- Pennsylvania

SOUTH ATLANTIC

- Delaware
- District of Columbia
- Florida
- Georgia
- Maryland
- North Carolina
- South Carolina
- Virginia
- West Virginia



U.S. DEPARTMENT OF AGRICULTURE

Farm Production Regions of the Contiguous United States

PACIFIC

California
Oregon
Washington

MOUNTAIN

Arizona
Colorado
Idaho
Montana
Nevada
New Mexico
Utah
Wyoming

NORTHERN PLAINS

Kansas
Nebraska
North Dakota
South Dakota

SOUTHERN PLAINS

Oklahoma
Texas

LAKE STATES

Michigan
Minnesota
Wisconsin

CORN BELT

Illinois
Indiana
Iowa
Missouri
Ohio

DELTA STATES

Arkansas
Louisiana
Mississippi

NORTHEAST

Connecticut
Delaware
Maine
Maryland
Massachusetts
New Hampshire
New Jersey
New York
Pennsylvania
Rhode Island
Vermont

APPALACHIAN

Kentucky
North Carolina
Tennessee
West Virginia
Virginia

SOUTHEAST

Alabama
Florida
Georgia
South Carolina
