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ENVIRONMENTAL PROTECTION SERVICE
PACIFIC AND YUKON REGION

HEXACHLOROBENZENE - INDUSTRIAL
AND AGRICULTURAL SOURCES
IN BRITISH COLUMBIA

Regional Program Report: 82-07

By

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FORWARD

This report provides detailed information and discussion of EPS investigations into the industrial and agricultural sources of hexachlorobenzene (HCB) in British Columbia. This study was part of a national survey of sources of environmental contamination by HCB, and results of this study will also be published with results from other EPS regions in a summarized national report on sources of hexachlorobenzene in Canada. Information on the toxicology and environmental dynamics of HCB will be discussed in detail in the national report, and consequently will only be outlined briefly here.

ABSTRACT

The Environmental Protection Service monitored the industrial and agricultural sources of hexachlorobenzene (HCB) in British Columbia. HCB residues were identified in all industrial sectors investigated, but occurred at elevated concentrations only in process sludges (1,270 ppm max.) and in sediments (29 ppm max.) near effluent outfalls of chlor-alkali plants. Levels in marine biota collected near these plants were low (0.026 ppm max.).

Hexachlorobenzene was formed in the electrolytic cells of chlor-alkali plants as a result of chlorine reacting with graphite anode materials. HCB residues were swept out of the cells with the chlorine gas produced in the reaction, and were deposited at various points in the chlorine gas purification train. Effluent releases of HCB from chlor-alkali plants were very low (11×10^{-5} ppm max.), and resulted in measurable contamination only in effluent ponds where HCB residues could accumulate in sediments. Disposal of HCB-contaminated sludges in one landfill site resulted in contamination of adjacent areas apparently through leaching in the landfill site.

Replacement of graphite anodes in chlor-alkali electrolytic cells with dimensionally stable anodes (DSA) has eliminated production of chlorinated benzenes. All plants surveyed have completed electrolytic cell conversion to DSA. Therefore, the chlor-alkali industry is no longer a source of HCB, although previously landfilled sludges and contaminated equipment in chlorine recovery systems may contain HCB residues.

Wood protection facilities using HCB-contaminated chlorophenols were minor sources of HCB contamination.

Agricultural sources of HCB included HCB cereal seed treatments and HCB-contaminated chlorthal herbicides. Neither source was identified as being a major route of entry of HCB into the environment.

RÉSUMÉ

Le Service de la protection de l'environnement (SPE) a surveillé les sources agricoles et industrielles d'hexachlorobenzène (HCB) en Colombie-Britannique. Des résidus de HCB ont été relevés à tous les secteurs industriels examinés, mais ne sont apparus en fortes concentrations que dans les boues industrielles (1270 millionèmes, max.) et les sédiments (29 millionèmes, max.) près des points de déversement d'effluent des usines de chlore et de soude caustique. Les niveaux dans la flore et la faune marines près de ces usines étaient bas (0,026 millionème, max.).

L'hexachlorobenzène se forme dans les cellules électrolytiques des usines de chlore et de soude caustique à la suite de la réaction du chlore aux matériaux des anodes au graphite. Des résidus de HCB sont évacués de la cellule avec le gaz de chlore produit dans la réaction et se déposent en divers points du réseau d'épuration du gaz de chlore. Les décharges d'effluent de HCB des usines de chlore et de soude caustique étaient très faibles (11×10^{-5} millionèmes, max.) et ont donné lieu à une contamination mesurable uniquement dans les étangs d'effluent où les résidus de HCB pouvaient s'accumuler dans les sédiments. L'évacuation de boues contaminées par le HCB dans des lieux de décharge a contaminé des secteurs adjacents, apparamment par lessivage.

Le remplacement des anodes au graphite par des anodes à stabilité dimensionnelle a éliminé la production de benzènes chlorés. Toutes les usines étudiées avaient terminé la conversion. L'industrie du chlore et de la soude caustique n'est donc plus source de HCB, bien que les boues qui ont auparavant été mises en décharge et l'équipement contaminé du système d'épuration du chlore puissent en contenir des résidus.

Les installations de protection du bois, utilisant des chlorophénols contaminés par le HCB sont des sources mineures de contamination.

Les sources agricoles de HCB comprenaient des traitements de semis céréaliers au HCB et les herbicides au chlorthal contaminés par le HCB. Ni l'une ni l'autre ne constitue une voie d'accès importante du HCB à l'environnement.

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CONCLUSIONS

Levels of hexachlorobenzene in British Columbia biota were not elevated or a cause for immediate concern. This conclusion was based, however, on rather limited monitoring information on fish from the Fraser River estuary, and on Great Blue Heron egg collections in various B.C. locations. Nevertheless, these low levels are probably indicative of the limited number of sources of HCB pollution in the province, and the elimination of industrial and agricultural HCB sources by changes in plant processes (ie. conversion from graphite anodes to DSA in chlor-alkali electrolytic cells). by elimination of the direct agricultural use of HCB for cereal seed treatment, and by the limiting of HCB concentrations to low levels in certain pest control products.

Residual HCB concentrations were detected from past agricultural uses of HCB, and from past generation of HCB as a contaminant in chlor-alkali plant processes. Although HCB production has been effectively eliminated in chlor-alkali processes, HCB accumulation may occur in chlorine gas purification equipment in plants that have historically used graphite anodes. Also, landfills containing HCB-contaminated sludges from past chlorine purification processes may release HCB into the environment.

1 INTRODUCTION

1.1 Background to the HCB Problem

In 1978, the Departments of Environment and National Health and Welfare published a List of Priority Substances in the Canada Gazette to be investigated and regulated under the Environmental Contaminants Act (Environment Canada and Health and Welfare Canada, 1978). Chlorinated benzenes including hexachlorobenzene were included in this list as "substances which the government believes may pose a significant danger to the environment or human health and about which further detailed information is required." Among these requirements was information on the industrial sources of chlorinated benzene contamination, in particular, hexachlorobenzene since this was the only chlorinated benzene identified as a problem substance in the Great Lakes.

Hexachlorobenzene (HCB) is a very persistent substance and is not readily degraded by photolysis, hydrolysis, or by other physico-chemical or biological processes in the environment. In this respect, it behaves like several other organohalogen substances such as DDE, PCB, and Mirex (Gilbertson, 1978). Hexachlorobenzene is bioaccumulated in aquatic organisms and when assimilated in the food of mammals, is stored in lipid tissue and excreted very slowly. HCB is dispersive in the environment, and can be transported for great distances adsorbed to suspended sediment in water, or to air particulates. It also sublimates readily and will evaporate if exposed to air, and therefore may be transported as a vapour.

HCB is a toxic compound that causes porphyria, liver enlargement, proliferation of the smooth endoplasmic reticulum, and induction of hepatic microsomal enzymes in laboratory animals (Gilbertson, 1979). HCB has also been shown to be carcinogenic in hamsters and mice, but not in the rat.

Residues of HCB have been reported in human milk from the Netherlands, Australia, Germany, and Sweden (Fishbein, 1979), and have been identified in breast milk from Canadian women. HCB is also a frequent contaminant of human tissues, although levels in Canadian fat tissue appear to be much lower than, for example, PCB residues (Mes et al 1982).

HCB was shown to be the cause of a severe outbreak of a cutaneous type of porphyria involving several thousand people in Turkey in 1955. The porphyria resulted from accidental ingestion of wheat grain seed which had been treated at approximately 2 grams of HCB per kilogram of wheat (Eaman, 1978). The doses of HCB ingested were estimated to have been 1 to 4 mg/kg of body weight for several months to two years. It was concluded that the disease resulted from a metabolic disorder caused by HCB interference with porphyrin metabolism in the liver.

Residues of hexachlorobenzene have been detected in fish and bird species in British Columbia (Appendices 1 and 2). Mean concentrations in fish from the Fraser River and Estuary were less than 10 ppb. The mean HCB concentration in Great Blue Heron eggs collected from five British Columbia locations in 1977/78 was 31 ppb (range 10 to 280 ppb, n= 50). Although hexachlorobenzene residues appear to be widely distributed in some British Columbia biota, the concentrations, based on the recent data, are much lower than levels in Great Lakes' bird and fish species summarized by Gilbertson (1978). For example, 1974/75 collections of herring gull eggs from Lake Ontario contained HCB at a mean concentration of 190 ppb (range 10 to 720 ppb, n= 39). Mean concentrations of HCB in Lake Ontario fish ranged from 30 to 80 ppb in collections obtained during 1977. The lower concentrations in B.C. biota probably indicate both a smaller number of industrial and agricultural sources of hexachlorobenzene, and a lower HCB loading from point sources in British Columbia as compared to the highly industrialized Great Lakes region.

Because of a potential HCB contamination problem in the Great Lakes and elsewhere in Canada, the Departments of Environment and National Health and Welfare through the DOE/NH&W Environmental Contaminants

Committee decided in March 1977 that a program must be developed to determine the sources of HCB to the Canadian environment. A monitoring program of potential HCB sources was initiated by the regional offices of the Environmental Protection Service under coordination by the Contaminants Control Branch, Environmental Protection Service, Ottawa, Ontario. This report outlines the Pacific and Yukon Region investigations into industrial and agricultural sources of hexachlorobenzene.

1.2 Source Inventory for HCB

Industrial and agricultural sources of hexachlorobenzene have been reviewed (Mumma and Lawless, 1975; Leah, 1977; Gilbertson, 1978; Eaman, 1978). Hexachlorobenzene has been used directly in industrial processes as a wood preserving agent, as a peptizing agent in the production of nitroso and styrene rubber for tires, as a porosity control agent in the manufacture of graphite anodes, in the manufacture of pyrotechnics, tracer bullets, and other ordnance items, and as a fluxing agent in aluminum manufacture. Hexachlorobenzene is also produced as a contaminant in the production of chlorinated hydrocarbons such as perchloroethylene, ethylene dichloride, trichloroethylene, etc., as a contaminant in production of certain pesticides (notably chlorthal herbicide), and as a contaminant in the production of caustic soda, chlorine, and sodium chlorate by electrolysis using graphite anodes (Mumma and Lawless, 1975).

Hexachlorobenzene was used in Canada as a fungicide for control of smut in cereal seed grains. This use was largely discontinued in 1971, and HCB is not currently used in British Columbia agriculture. However, HCB is present as a contaminant in certain pest control products including chlorthal herbicide formulations, and chlorophenol wood preservatives.

In British Columbia, the chlor-alkali and wood protection industries were determined to be potential sources of hexachlorobenzene. HCB contamination from agricultural sources potentially occurred from HCB cereal seed treatments, and from the use of chlorthal herbicides.

2 INDUSTRIAL SOURCES OF HEXACHLOROBENZENE

2.1 Chlor-alkali Industries

HCB release and contamination of the immediate receiving environment was investigated in three electrolytic chlor-alkali plants manufacturing chlorine gas, caustic soda, and hydrochloric acid, and in two plants manufacturing sodium chlorate. These plants were identified as potential sources of HCB which is produced through attack of chlorine on graphite anodes used in the electrolytic process. HCB is formed by the reaction of chlorine with the graphite and/or hydrocarbon oils which are used as anode coatings. Table 1 outlines the electrolytic processes in the five plants investigated. Appendix 3 provides details on sample collection and analytical methodology for chlorobenzene residue determinations.

2.1.1 Hooker Chemicals Ltd., Nanaimo, B.C. This plant was first surveyed in September of 1977. At that time 80 percent of the anodes were linseed oil impregnated - graphite with the remaining 20 percent having been converted to the dimensionally stable anode (DSA) type. The plant was releasing very low levels of HCB in the final effluent which is a combined stream of process effluent and cooling water (Table 2). However, an elevated level of HCB (10.8 ppm) was detected in a ditch draining the plant yard and solid waste (sludge) landfill area.

Contaminated sludges, landfilled in the plant yard, were the major source of HCB contamination to the drainage ditch. Sludge from the reboiler tank in the chlorine purification train contained up to 1,270 ppm

TABLE 1: ELECTROLYTIC PROCESSES IN PLANTS SAMPLED FOR HEXACHLOROBENZENE

Plant Name & Location	Product Manufactured	Electrolytic Process		
		Cell Type	Anode Type	Process Description
Hooker Chemicals Ltd. Nanaimo, B.C.	chlorine, caustic soda	diaphragm	graphite, linseed oil impregnated (converting to DSA at time of first survey)	electrolysis of brine $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2$
Hooker Chemicals Ltd. North Vancouver, B.C.	chlorine, caustic soda and HCl	diaphragm	dimensionally stable anode (DSA) - titanium alloy (prior to 1975 was graphite)	as above
FMC Chemicals Ltd. Squamish, B.C.	chlorine, caustic soda and HCl	mercury cathode	dimensionally stable anode (DSA) - titanium alloy (prior to 1975 was non- impregnated graphite)	as above
Hooker Chemicals Ltd. Squamish, B.C.	sodium chlorate	open cell	dimensionally stable anode (DSA) - platinum alloy	electrolysis of saturated acidified brine mixed with sodium dichromate $\text{NaCl} + 3\text{H}_2\text{O} \rightarrow \text{NaClO}_3 + 3\text{H}_2$
Erco Industries Ltd. North Vancouver, B.C.	sodium chlorate	open cell	graphite	electrolysis of saturated acidified brine mixed with sodium dichromate

hexachlorobenzene. Elevated HCB levels in the landfilled sludge and drainage ditch were again confirmed in two subsequent surveys conducted in October, 1978 and August, 1980 (Table 2). Surface runoff and leaching from the landfill into the drainage system for a number of years may account for the elevated HCB levels detected in the ditch sediments.

HCB contamination of the adjacent marine environment of Northumberland Channel was low. Sediments and biota from Northumberland Channel were collected and analyzed on two occasions. A composite sample of shoreline sediment collected 400m from the plant contained 2.0 ppb HCB, while a similar composite sample collected 800m from the plant contained no detectable HCB. Small crabs and barnacles collected at the 400m sampling site contained 25.7 and 2.3 ppb HCB respectively. Similar samples collected one year later contained 7.0 ppb (crabs) and 2.0 ppb (barnacles) HCB, while sediments contained 7.0 ppb HCB. Composite samples of oysters, small crabs, and mussels collected 1.2 km from the plant contained no detectable HCB.

In the 1980 survey, sediment samples collected approximately 400m from the plant contained 48.0 ppb HCB. Crabs from the same area contained 19.0 and 6.0 ppb HCB in two samples.

2.1.2 FMC Chemicals Ltd., Squamish, B.C. This plant was surveyed in September of 1977 and again in August of 1978 and 1980. Composite effluent samples taken from the sewer discharge to the effluent pond contained low concentrations of HCB (Table 3). However, sediments near the sewer discharge to the effluent pond contained elevated HCB levels (19.0 to 29.0 ppm). HCB concentrations declined near the pond outlet (3.2 to 5.6 ppm) and final discharge area (0.25 to 0.87 ppm). HCB was not detected in marine sediments immediately adjacent to the plant. Mussels and crustaceans collected approximately 200m from the final outfall also contained no HCB.

In 1979, during a routine maintenance inspection of a chlorine mist eliminator, FMC plant personnel discovered that the fibreglass core in the unit was coated with a white crusty solid. Analysis of this

TABLE 2: LEVELS OF CHLOROBENZENES IN SAMPLING MEDIA FROM THE HOOKER CHEMICAL PLANT AT NAWAJMO, B.C.

Media	Sample Description and Location	Survey No.1	Station No.2	Chlorobenzenes (ppm) 3			Loading ⁴ kg/year
				Hexa-	Penta-	Tetra-	
Effluent	grab sample from outfall	1	6	1.5×10^{-6} (5PPT)			0.05
	4 hr. composite from outfall	2	6	6×10^{-6} (6PPT)	5×10^{-6} (5PPT)		
Water	grab sample from drainage ditch	2	2	1.5×10^{-6} (5PPT)	1.1×10^{-6} (1PPT)	1.1×10^{-6} (1PPT)	
	" " " "	2	5	10×10^{-6} (10PPT)	1.1×10^{-6} (1PPT)	1.1×10^{-6} (1PPT)	
Sediment	composite sample from drainage ditch	1	1 to 4	10.800			
	from drainage ditch near rectifier	2	1	0.090	10.001	10.001	
	from drainage ditch near asbestos storage	2	2	1.750	0.120	0.010	
	from drainage ditch near landfill	2	3	11.100	0.100	0.100	
	" " " "	3	3	7.950			
	from drainage ditch near outlet	2	4	0.920	10.001	10.001	
Soil	from landfilled sludge	1	8	0.108			
	" " "	3	8	12.600	930.00		
Sludge	from reboiler tank	1	7	1,270.0			
	from reboiler tank	2	7	350.0	150.0	150.0	
	from brine mixture	1		0.017			

1. Survey No. 1 was conducted in September 1977, Survey No. 2 in October 1978, Survey No. 3 in August 1980
2. Refer to Figure 1 for sample station locations
3. Limit of HCB detection: Sediment 0.001 ppm
Tissues 0.001 ppm
Water 0.005 ppb
4. Calculated from a flow of 2.7 MIGPD

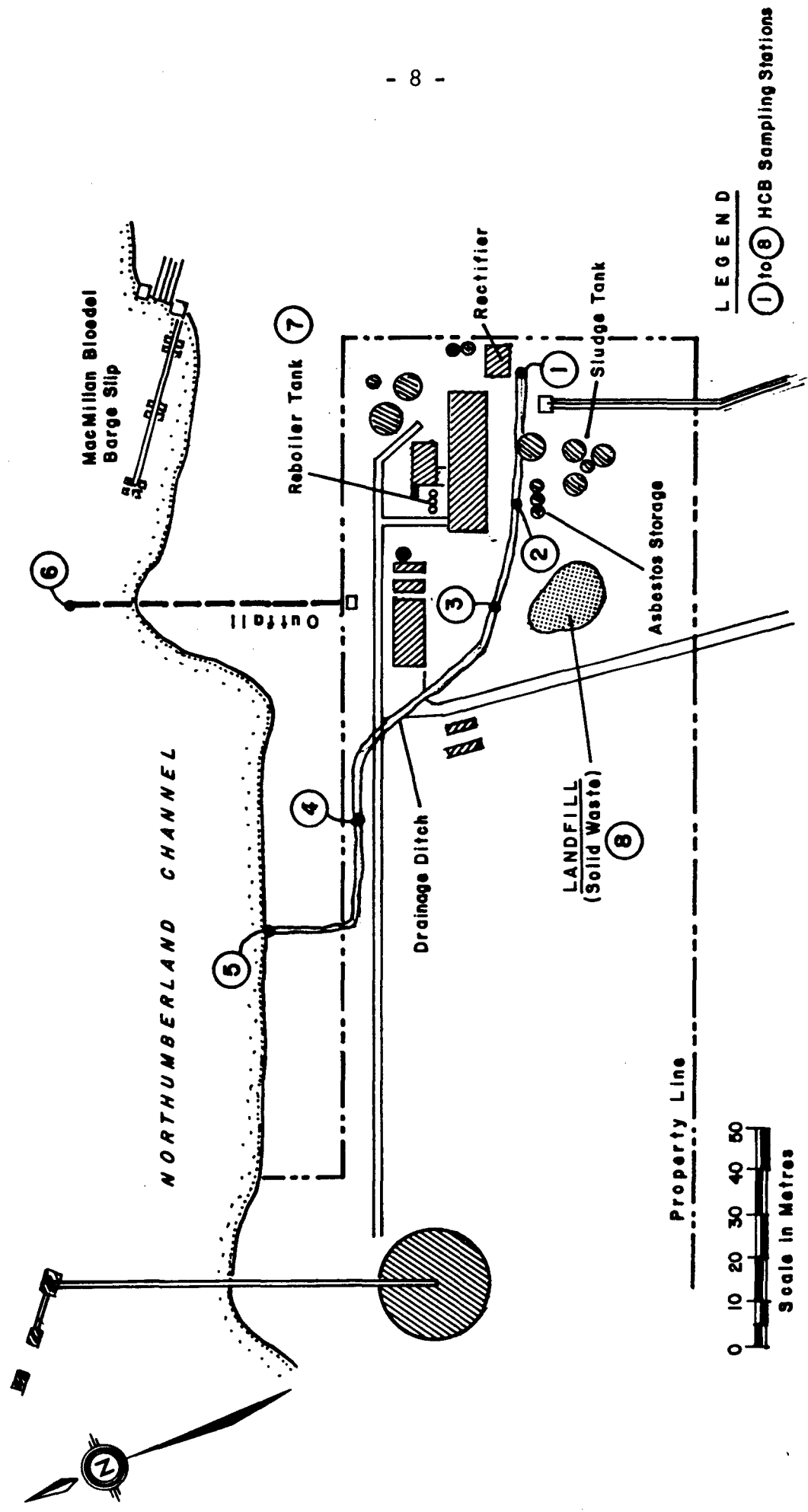


FIGURE 1 SITE PLAN OF HOOKER CHEMICALS (NANAIMO) CHLOR-ALKALI PLANT

TABLE 3: LEVELS OF CHLOROBENZENES IN SAMPLING MEDIA FROM THE FMC CHEMICAL PLANT AT SQUAMISH, B.C.

Media	Sample Description and Location	Survey No.1	Station No.2	Chlorobenzenes (ppm)			Loading ³ kg/year
				Hexa-	Penta-	Tetra-	
Effluent	grab sample from inlet to effluent pond	1	1	5x10 ⁻⁵ (50PPT)			0.18
	3½ hr. composite	2	1	1.4x10 ⁻⁵ (14PPT)			
	grab sample from outlet from effluent pond	1	2	11x10 ⁻⁵ (110PPT)			
	grab sample from pond discharge to sea	1	3	4x10 ⁻⁵ (40PPT)			
	" " " " " "	1	3	1.9x10 ⁻⁵ (19PPT)			
Sediment	near inlet to effluent pond	1	4	19.000			0.22
	" " " " " "	3	4	29.000	0.90		
	near outlet from effluent pond	1	5	5.600			
	" " " " " "	3	5	3.240	0.18		
	near pond discharge to sea	1	6	0.250			
	" " " " " "	2	6	0.870	0.057		
	" " " " " "	3	6	0.260	0.020		
	from abandoned effluent pond	3	6	1.890	0.099		
	near plant at high tide line	1	8	10.001			
	" " " " " "	3	8	0.015	0.003		
	" " " " " "	1	9	10.001			
Soil	near plant at very low tide	2	10	0.005			
	" " " " " "	2	11	0.005			
	from sludge disposal area	1	7	0.005			
" " " " " "	3	7	0.170	0.065			

1. Survey No. 1 was conducted in September 1977, Survey No. 2 in August 1978, Survey No. 3 in August 1980
2. Refer to Figure 2 for sample station locations
3. Calculated from a flow of 7.8 MIG PD.

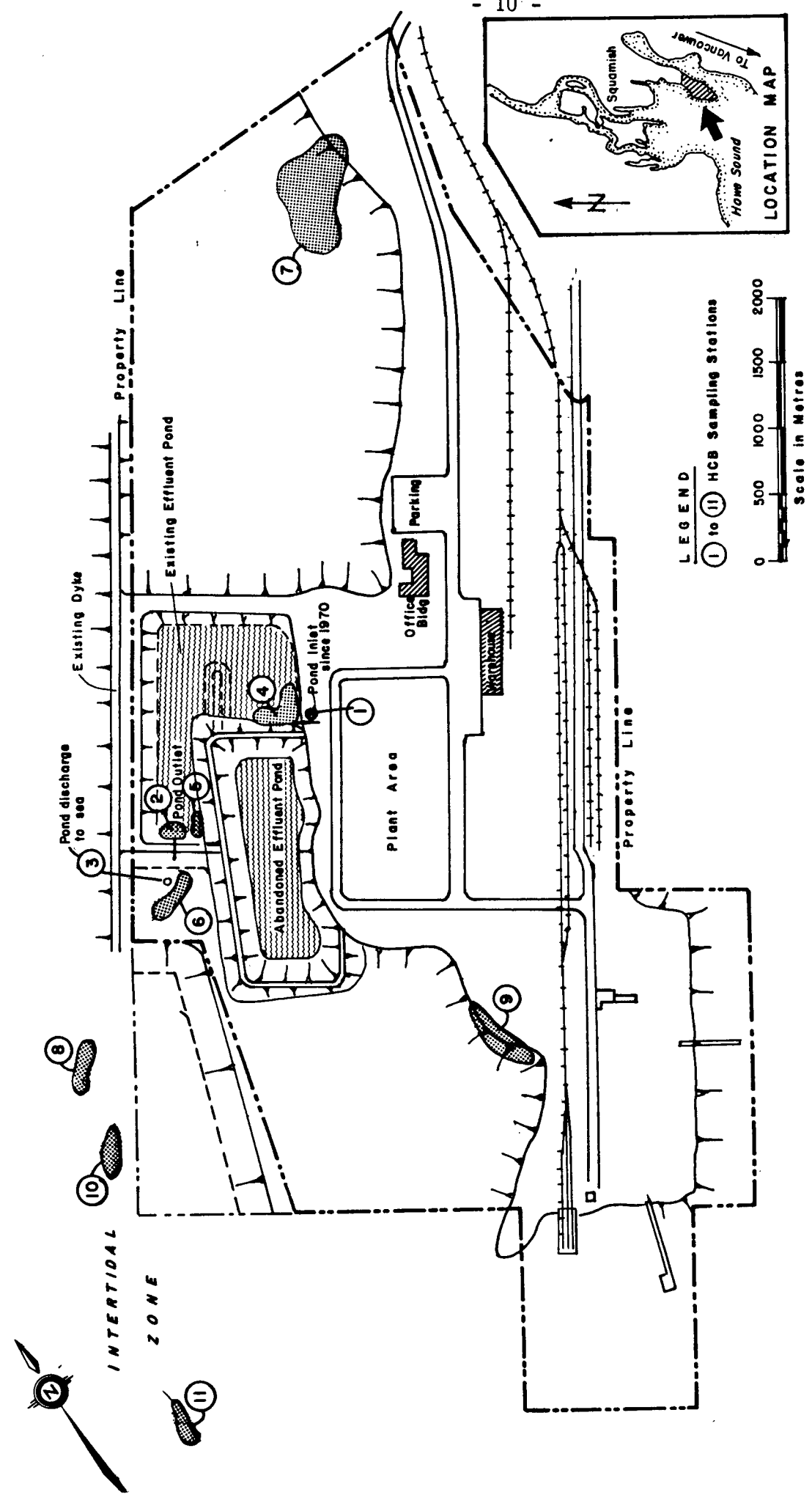


FIGURE 2 SITE PLAN OF FMC CHEMICALS (SQUAMISH) CHLOR-ALKALI PLANT

material at an analytical laboratory demonstrated that this deposit was 99.99% HCB. In order to recover the HCB it was necessary to slurry the solid in concentrated sulphuric acid. The slurry was then pumped into 45 I.G. steel drums, sealed, and labelled in preparation for transport to the United States. A total of 19 drums were shipped to an Oregon hazardous waste landfill operated by Chem-Security Systems Inc. Eleven drums were two-thirds full of the H_2SO_4 - HCB slurry, and four drums contained the contaminated fibreglass packing material from the mist eliminator.

2.1.3 Erco Industries Ltd., North Vancouver, B.C. This sodium chlorate plant was not an important source of HCB (Table 4). Both effluents and sediments from the sewer outlets, including the sewer lagoon, did not have elevated HCB concentrations.

2.1.4 Hooker Chemicals Ltd., North Vancouver, B.C. HCB concentrations in effluents from this plant were low. Soil from the sludge disposal landfill contained low concentrations of HCB (Table 5).

2.1.5 Hooker Chemicals Ltd., Squamish, B.C. Sludge from this sodium chlorate plant did not contain detectable HCB.

2.2 Wood Protection Facilities

In 1978, a contract study was initiated for the sampling and analysis of sediments, fish, and effluents for chlorophenol contamination associated with wood protection facilities in the lower Fraser River and southeastern Vancouver Island (Environmental Protection Service, 1979). Levels of tetra-, penta-, and hexachlorobenzene were determined in addition to penta-, tetra-, and trichlorophenol. Table 6 summarizes the locations and media which contained detectable chlorobenzene residues. Most plants listed utilized either spray or dip-tank facilities for protection of export lumber against sapstain and mould.

TABLE 4: LEVELS OF CHLOROBENZENES IN SAMPLING MEDIA FROM THE ERCO CHEMICAL PLANT AT NORTH VANCOUVER, B.C.

Media	Sample Description and Location	Survey No.1	Station No.2	Chlorobenzenes (ppm)			
				Hexa-	Penta-	Tetra-	
Effluent	grab sample from east sewer outlet	1	1	1.5x10 ⁻⁶ (5PPT)			
	grab sample from south sewer outlet to lagoon	1	2	1.5x10 ⁻⁶ (5PPT)			
	grab sample from lagoon outlet	1	3	2.9x10 ⁻⁵ (29PPT)			
Water	grab sample from mud wash tank	1	4	0.129			
Sediment	near east sewer outlet	1	1	0.028			
	from south sewer lagoon	1	5	0.035			
	from lagoon discharge to Burrard Inlet	1	6	0.001			
	from mud wash tank	1	4	0.293			

1. Survey conducted in October 1977.
2. Refer to Figure 3 for sample station locations.

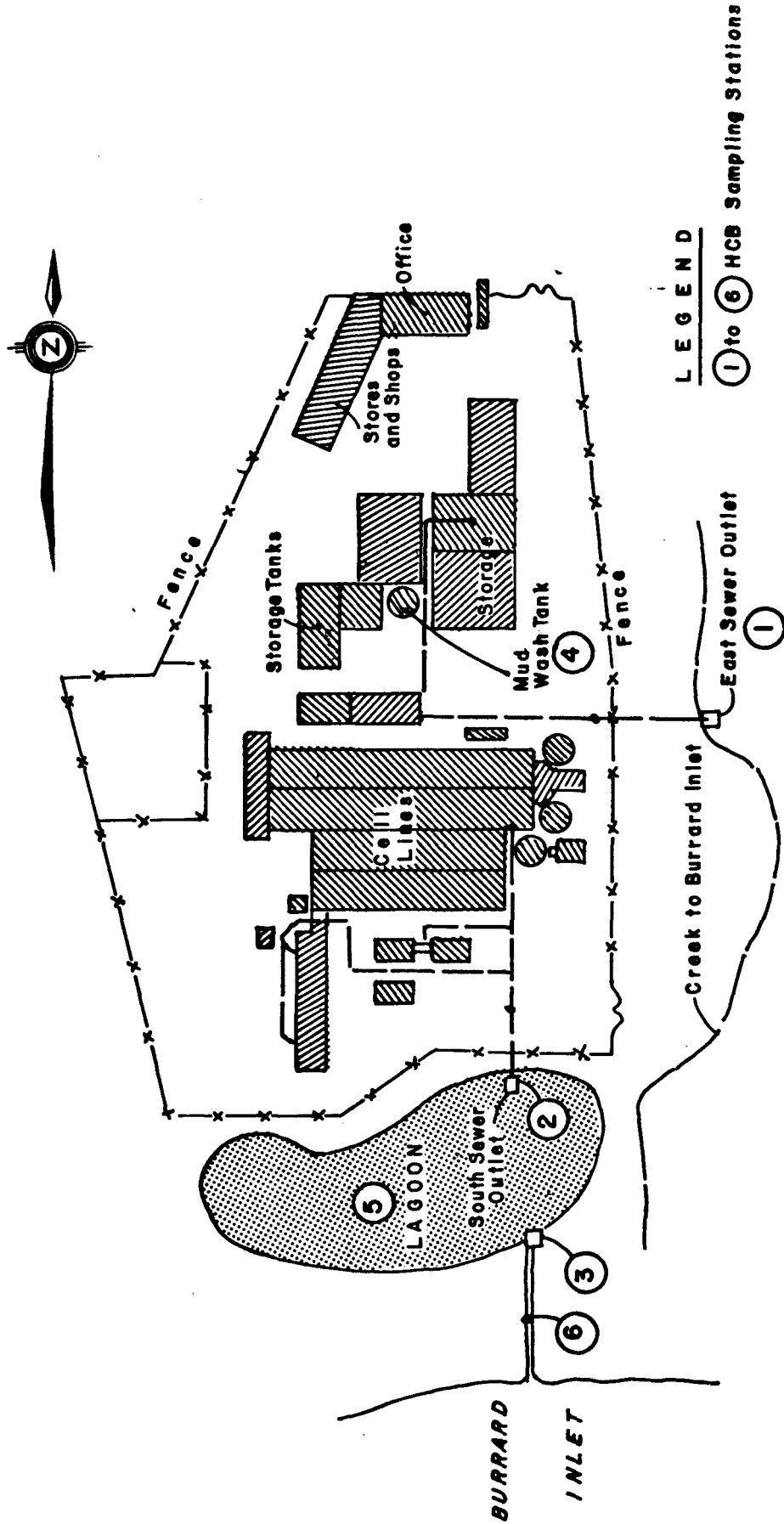
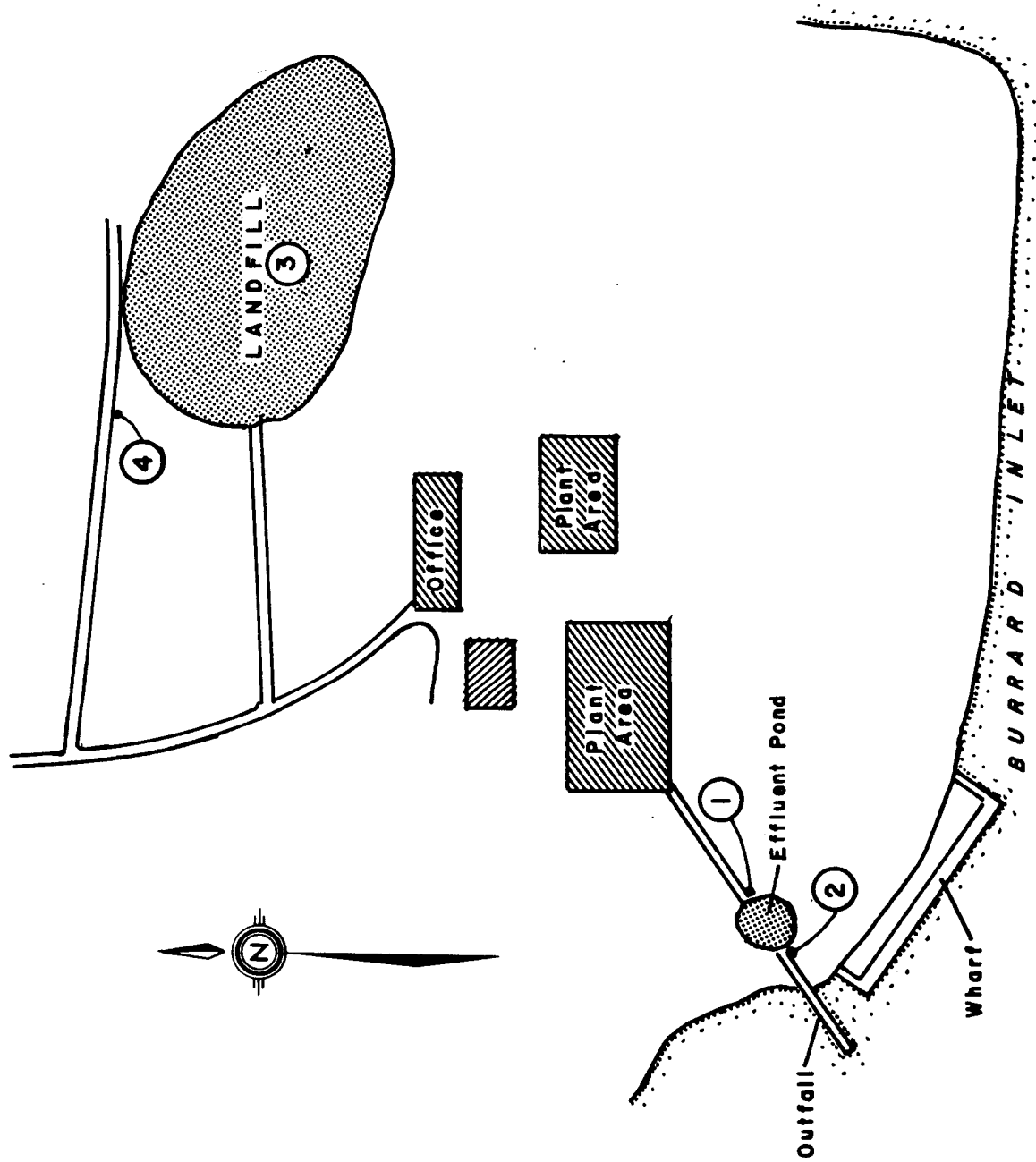


FIGURE 3 SITE PLAN OF ERCO INDUSTRIES (NORTH VANCOUVER)
SODIUM CHLORATE PLANT

TABLE 5: LEVELS OF CHLOROBENZENES IN SAMPLING MEDIA FROM THE HOOKER CHEMICAL PLANT AT NORTH VANCOUVER, B.C.

Media	Sample Description and Location	Survey No. ¹	Station No. ²	Chlorobenzenes (ppm)			
				Hexa-	Penta-	Tetra-	
Effluent	grab sample from inlet to effluent pond	1	1	L5x10 ⁻⁶ (5PPT)			
	grab sample from outfall to Burrard Inlet	1	2	L5x10 ⁻⁶ (5PPT)			
Soil	from sludge disposal landfill (0-15cm deep)	1	3	0.095			
	" " " (15-45cm deep)	1	3	0.302			
	" " " (0-45cm deep)	1	3	L0.001			
	from outside landfill (0-45cm deep)	1	4	L0.010			

1. Survey conducted in September 1977.
2. Refer to Figure 4 for sample station locations.



LEGEND

① to ④ HCB Sampling Stations

FIGURE 4 SITE PLAN OF HOOKER CHEMICALS (NORTH VANCOUVER) CHLOR-ALKALI PLANT

Chlorobenzene levels in fish tissue and sediment adjacent to wood protection facilities were low, and chlorobenzenes were not detected in most effluent samples. However, at the MacMillan Bloedel Ltd. Port Alberni sawmill facilities, low levels of chlorobenzenes (78 ppt hexa-, 50 ppt penta-, and 420 ppt tetrachlorobenzene) were detected in effluent samples that contained high levels of penta- and tetrachlorophenol (2760 ppb and 8270 ppb respectively). The highest sediment chlorobenzene concentrations were also detected at this site (Table 6).

2.3 Discussion of Industrial Sources of HCB

2.3.1 Chlor-alkali plants Hexachlorobenzene residues were identified in all industrial sectors investigated, but occurred at elevated levels only in the chlor-alkali industry. Chlor-alkali plants that have historically used graphite anodes produced elevated quantities of HCB which concentrated in process sludges from chlorine purification, or in sediments near effluent outfalls.

Disposal of HCB-contaminated sludges in landfill sites can result in contamination of adjacent areas through rainwater runoff and leaching in the landfill site. The elevated HCB concentrations in the drainage ditch sediments at the Hooker Chemical plant, Nanaimo, B.C. show that HCB residues were escaping from the landfilled sludges. In addition, HCB residues may be released into the ambient air over the landfilled sludges due to the tendency of HCB to sublime from soil into ambient air (Leah, 1977). The tendency of HCB residues to sublime from the landfill would vary with the depth of soil cover over the sludge waste. However, since airborne levels of HCB were not determined over these landfills, it is difficult to speculate on the importance of this source of release.

Elevated HCB concentrations in effluent pond sediments at FMC chemicals, Squamish, B.C. indicate that small, but continuous past effluents loadings have contaminated this area with HCB residues, but not

TABLE 6: LEVELS OF CHLOROBENZENES IN SEDIMENTS AND FISH TISSUES NEAR WOOD PROTECTION FACILITIES ON THE LOWER FRASER RIVER AND SOUTHEAST COAST OF VANCOUVER ISLAND¹

Sample Description	Location	Chlorobenzenes (ppb)			
		Hexa-	Penta-	Tetra-	
Sediment	Seaboard Terminals, N. Vancouver	all trace (5) ²			
	Domtar Chemicals, Coquitlam	all trace (2)			
	Canadian White Pine, Burnaby	tr. to 1.9 (6)			
	B.C. Forest Products, Victoria	tr. to 21.0 (6)	1.4 to 4.2 (7)	1.4 to 20.0 (5)	
	Cipa Lumber & Dormans, Nanaimo		2.1 to 3.0 (3)	tr. to 1.8 (6)	
MacMillan Bloedel, Port Alberni		tr. to 39.0 (9)	4.4 to 78.0 (4)	tr. to 340.0 (10)	
Liver Tissue					
Staghorn Sculpin	Seaboard Terminals, N. Vancouver	15.0 (7) ³			
Prickly Sculpin	Crown Zellerbach, Coquitlam	8.0 (7)			
Staghorn Sculpin	Empire Mills, Squamish	54.0 (4)			
Staghorn Sculpin	B.C. Forest Products, Victoria	5.2 (3)			14.0 (3)

1. Adapted from Environmental Protection Service (1979) Appendix 2

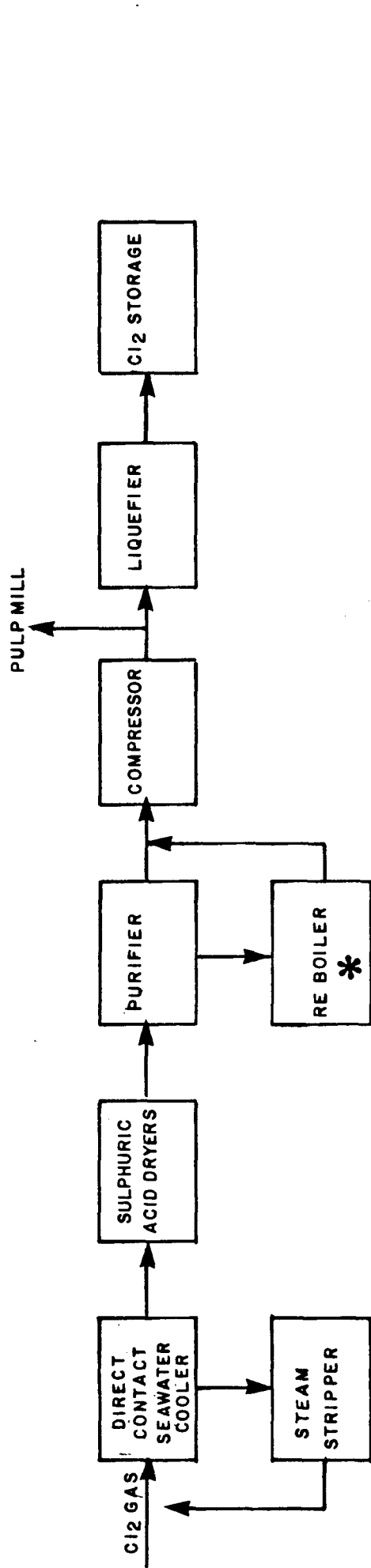
2. Numbers in brackets refer to the number of individual sediment samples containing the range of chlorobenzenes reported. A total of 10 samples were collected and analyzed at each location.

3. Numbers in brackets refer to the number of fish from which liver samples were pooled for analysis.

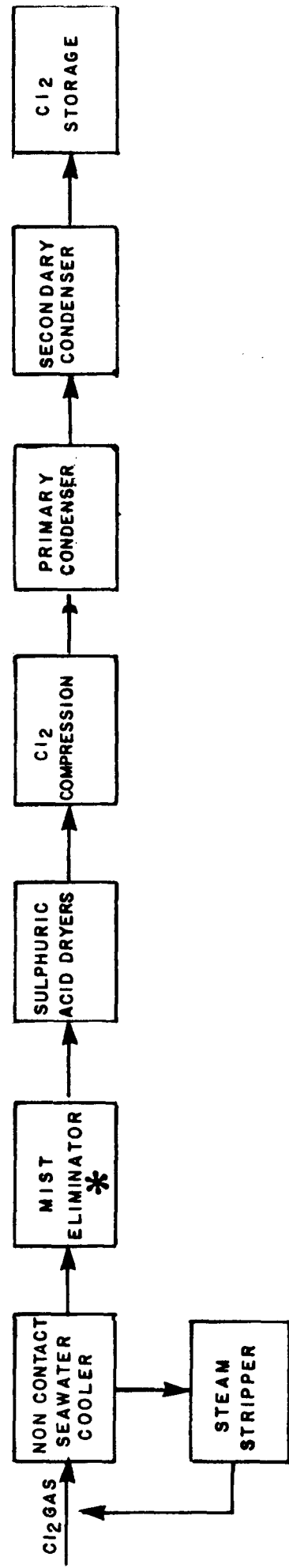
the adjacent marine receiving environment. Similarly, the marine environment of Northumberland Channel adjacent to the Hooker Chemical plant at Nanaimo was not contaminated with HCB residues. Therefore, effluent releases from these chlor-alkali plants appeared to result in measurable contamination only in small areas immediately adjacent to outfalls in effluent holding ponds, where HCB residues could accumulate in sediments.

Mumma and Lawless (1975) reviewed the potential sources of hexachlorobenzene pollution in industrial processes. They concluded that either diaphragm or mercury electrolytic cells in chlor-alkali industries have the potential for production of HCB-contaminated chlorine gas when graphite anodes were used. The hexachlorobenzene produced in these cells would tend to escape with the hot and wet crude chlorine gas since HCB sublimates readily and is volatile in water vapour even at low temperatures (Mumma and Lawless, 1975). In both the diaphragm and mercury cells, the crude chlorine gas is dried and purified prior to being liquified. In certain purification processes, chlorinated hydrocarbons (ie. HCB) can be separated from the chlorine gas and remain as components of the "heavy ends" from product distillation. As noted earlier, HCB is produced as a contaminant in chlor-alkali electrolytic cells by reaction of chlorine with graphite anode materials. Dimensionally stable anodes (DSA) are usually made of titanium or platinum alloys (see Table 1) free of materials such as carbon or oils that will react with chlorine. Therefore replacement of graphite anodes with DSA will eliminate production of chlorinated benzenes (Mumma and Lawless, 1975).

At the Hooker Chemical plant (Nanaimo, B.C.), chlorine gas liberated at the anode is cooled with direct contact seawater and then dried by scrubbing with sulphuric acid (Figure 5). The chlorine gas is then further purified in a chlorine fractionation tower (purifier) where chlorine liquid is combined with the gas in order to absorb the less volatile, high molecular weight chlorinated organic materials. The liquid chlorine is revaporized in the reboiler and chlorinated organics remain as a liquid sludge in the reboiler tank.



CHLORINE RECOVERY SYSTEM AT HOOKER CHEMICALS LTD., NANAIMO, B.C.



CHLORINE RECOVERY SYSTEM AT FMC CHEMICALS LTD., SQUAMISH, B.C.

FIGURE 5 FLOW SHEET OF CHLORINE RECOVERY PROCESSES AT THE HOOKER CHEMICAL (NANAIMO) AND FMC CHEMICAL (SQUAMISH) CHLOR-ALKALI PLANTS (* shows point where HCB residues were found in the process)

As indicated previously (Table 2), the reboiler tank sludge was heavily contaminated with hexachlorobenzene residues. The reboiler would likely be the major area of HCB accumulation within the chlorine recovery system, removing all high molecular weight substances prior to chlorine compression or liquifaction for storage. HCB levels in the reboiler tank sludge at Hooker Chemicals (Nanaimo, B.C.) declined between the first (September, 1977) and second (October, 1978) surveys (Table 2). At the time of the first survey, this plant was beginning the process of changing over to DSA (vide. page 4), and had progressed, but not completed the conversion by the second sampling of the reboiler sludge. Technical information received from Hooker Chemicals (Nanaimo, B.C.) indicated that organic sludge was no longer being generated in the reboiler system since the complete conversion to DSA. Therefore, HCB contamination in and around this plant was from waste disposal prior to DSA conversion.

The chlorine recovery process at FMC Chemicals (Squamish, B.C.) is similar to the system at Hooker Chemicals (Nanaimo, B.C.), but does not include the additional chlorine purification and recovery of chlorinated organics in a fractionation/reboiler process (Figure 5). As noted previously (vide. page 6), an internal fibreglass core of a chlorine mist eliminator was coated with crystallized HCB. Again it appears that the HCB formation was due to the reaction of chlorine with the graphite anodes in the electrolytic cells, and that the deposit had accumulated over a nine year period prior to the plant changing over to DSA. During this period, the mist eliminator was removing HCB from the chlorine gas although the efficiency of this system is not known.

Two types of graphite anodes were used, linseed oil impregnated (formerly at Hooker, Nanaimo) and non-impregnated graphite (formerly at FMC, Squamish). The impregnated anodes decompose and produce an organic sludge through the oxidation and chlorinolysis of graphite and the oleic acid glycerides and other unsaturated fatty acids which make up the linseed oil. These oxidation and chlorinolysis processes produce chlorinated benzenes. The non-impregnated type do not produce the same organic sludge,

but are subject to oxidation and chlorinolysis of graphite which also produces chlorinated benzenes. It is possible that linseed oil impregnated graphite anodes produced greater quantities of HCB, although this cannot be substantiated by comparison of residue data from plants using the two types of anodes.

The low level of HCB residues detected in the effluents of both the Hooker and FMC plants probably resulted from residual HCB contamination in the plant system subsequent to the anode changeover. However, since effluents are probably not the major conduit of HCB wastes, these very low concentrations were probably not exceeded even when the plants were using graphite anodes.

2.3.2 Other Industrial Sources of HCB The two sodium chlorate plants monitored (Erco Industries, North Vancouver and Hooker Chemicals, Squamish) were not important sources of HCB. These plants do not have a diaphragm in the electrolytic cells and the electrodes are closely spaced to allow mixing of the products, so that although electrolysis yields chlorine at the anode and sodium hydroxide at the cathode, good mixing of these products results in the formation of sodium hypochlorite and then sodium chlorate (Mumma and Lawless, 1975). Therefore, although both plants have graphite anodes, the mixing of the electrolysis products probably reduces the amount of chlorine available to attack the graphite anodes producing HCB residues.

Wood protection facilities were also a minor source of HCB contamination. The chlorophenolate solutions used for wood protection were the likely source of HCB residues detected in trace amounts in sediments and biota adjacent to treatment facilities. Chlorophenols are produced by the chlorination of phenol and chlorobenzenes can be expected as a reaction by-product, and as a contaminant of the end product. Therefore, the dip-tank or spray solutions of chlorophenols would contain only trace quantities of chlorobenzenes. However, these concentrations were apparently sufficient to result in trace contamination of the receiving environment near the wood treatment mills.

3 AGRICULTURAL SOURCES OF HEXACHLOROBENZENE

3.1 Cereal Seed Treatments with HCB

HCB cereal seed treatments were applied primarily in the Peace River region of British Columbia. Twenty-four areas of this region were monitored for HCB residues in the soil (Figure 6). Six of the twenty-four sampling areas had detectable HCB residues ranging from 1.3 to 2.2 ppb. Soil sampled near a former grain treatment plant contained 260 ppb HCB.

Hexachlorobenzene seed treatments were last applied in the Peace River area between 10 and 15 years ago. As noted in Section 1.2, agricultural use of HCB in Canada was largely discontinued in 1971, and there are no current registrations of pest control products having HCB as the active ingredient. It is possible that HCB was used from time to time after 1971 since importation of HCB seed treatment fungicides for a farmers own use was allowed by Agriculture Canada until March, 1977. However, the low levels of HCB detected in Peace River soils probably indicate that residues have dissipated greatly in the last decade. Agricultural use of HCB as a seed treatment fungicide does not appear to constitute a lasting or continuous source of HCB in the Peace River area, or in other parts of Canada (Eaman, 1978).

3.2 Use of HCB-Contaminated Herbicides

A number of herbicides registered for use in Canada have contained varying levels of HCB as a contaminant in the technical product. The triazine herbicides (atrazine, propazine, simazine) and chlorthal have been reported to be contaminated with HCB. Atrazine was reported to contain 0.025 to 0.25 ppm HCB, while chlorthal contained 0.3 percent HCB after 1971, and up to 10 percent HCB prior to 1971 (Mumma and Lawless, 1975).

Chlorthal is presently registered under the federal Pest Control Products Act as a selective pre-emergence herbicide for control of

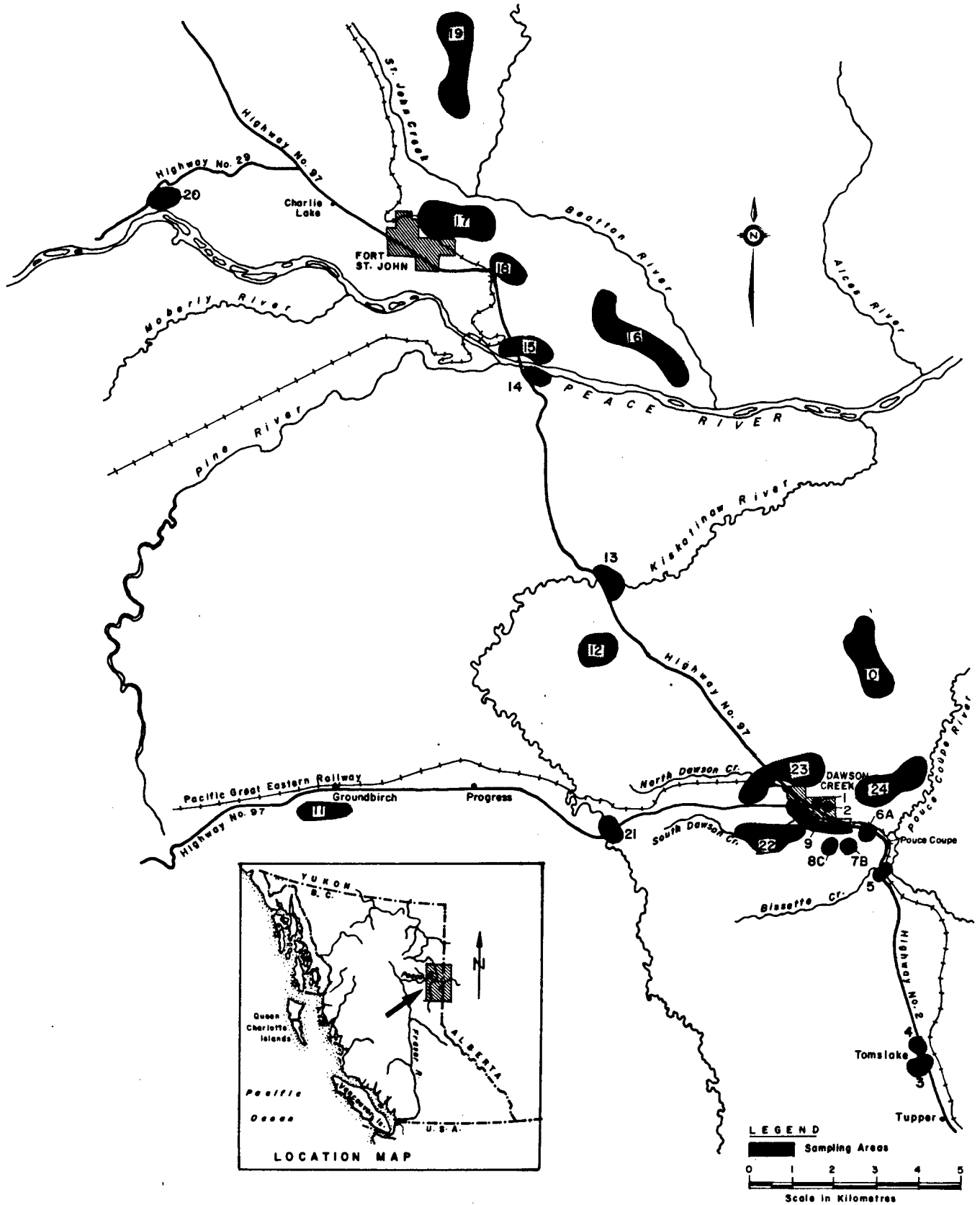


FIGURE 5 HEXACHLOROBENZENE SURVEY IN THE PEACE RIVER REGION, B. C.

certain annual grasses and broadleaved weeds on mineral soils. There are eight products being sold in Canada, five formulated as granules and three as wettable powders (Agriculture Canada, 1979). Diamond Shamrock Inc. is the major manufacturer of chlorthal and distributes the herbicide under the trade name of Dacthal.

To determine historical HCB contamination in areas where Dacthal had been used, soil samples were obtained in October of 1977 from three B.C. Forest Service nurseries where detailed records had been kept of Dacthal applications. Two fields were sampled at a Duncan, B.C. nursery, one that had been treated at 25.2 kg Dacthal/hectare in 1971 and another at 26.9 kg Dacthal/hectare in 1972. HCB levels were 9.4 ppb in the 25.2 kg/ha field and 5.4 ppb in the 26.9 kg/ha field. At another Vancouver Island nursery, 3.6 ppb HCB was detected in soil treated at 23.5 kg Dacthal/hectare in 1971. Finally, in a Surrey, B.C. nursery, fields were sampled that had been treated with Dacthal at 9.2 kg/ha in 1971, 17.9 kg/ha in 1972, and 30.3 kg (total)/ hectare in 1972-1973. HCB levels here were respectively 19.1 ppb, 4.7 ppb, and 17.5 ppb.

In British Columbia, Dacthal W75 (75% wettable powder) is recommended for weed control in mineral soils for the production of broccoli, brussel sprouts, cabbage, cauliflowers (applied at 13 to 16 kg/ha), and dry bulb onions (applied at 6.7 to 17.9 kg/ha). Two vegetable growing areas in south Vancouver and Burnaby were selected for soil and sediment monitoring. Soil in an onion growing area of south Vancouver contained 2.3 ppb HCB, but sediments in drainage ditches adjacent to the field contained 24.0 and 54.0 ppb HCB. Sediments in ditches draining vegetable growing areas of south Burnaby contained less than 5 ppb HCB in nine sampling sites. Cabbage, corn, lettuce, and onions are grown in this area, so it was likely that Dacthal had been used at sometime in the past.

The concentrations of HCB residues in the soils and sediments at the B.C. Forest Service nurseries and vegetable growing areas are commensurate with the levels expected in Dacthal formulations containing

0.3 percent or less of HCB. In order to better define HCB content in Dacthal formulations sold in British Columbia, samples were obtained from two B.C. formulators. One lot from Van Waters and Rogers Ltd. formulated prior to 1973 contained 5.6 percent HCB while a second lot, formulated in 1973, contained 8.0 percent HCB. Two samples from Dacthal formulated by Green Valley Fertilizer and Chemical Co. in 1976 contained respectively 8.4 and 9.0 percent HCB.

These very high HCB levels in Dacthal products were surprising in light of the low concentrations of HCB detected in Dacthal-treated soils. The Pesticides Section of Agriculture Canada in Ottawa indicated that the product labels submitted for review with the analytical results were of an old format (probably pre - 1974) and that it was not possible to determine when the chlorthal active ingredient was actually made. Dacthal was described as a "low volume, slow moving product" with tail ends of old production appearing in commerce for some years after the introduction of a purified material.

Agriculture Canada analyzed a Dacthal W75 sample obtained from Diamond Shamrock in 1978. This sample contained 0.19 percent HCB which was similar to another analysis on the same product by EPS Quebec Region (0.105 percent HCB content). In 1980, Diamond Shamrock informed Agriculture Canada that when chlorthal was formulated as a 75% wettable powder, the maximum HCB content would be 0.225 percent. However, the current production was running near the 0.1 percent level of HCB.

HCB does not appear to be a significant environmental contaminant from either its past use as a cereal seed treatment, or as a constituent of chlorthal herbicide formulations. The elimination of HCB cereal seed treatments in 1971, and the action taken to lower HCB content in chlorthal herbicides greatly reduced HCB loading into the environment from agricultural sources.

REFERENCES

- Agriculture Canada, Compendium of Pest Control Products Registered in Canada. Pesticides Section, Plant Products Division, Agriculture Canada, Ottawa. Publication 1654 RP/79, (1979).
- Environment Canada, Health and Welfare Canada. Environmental Contaminants Act List of Priority Chemicals. Canada Gazette Part I, May 20, 1978, p. 3011.
- Environmental Protection Service. Monitoring Environmental Contamination from Chlorophenol Contaminated Wastes Generated in the Wood Preservation Industry. EPS Pacific and Yukon Region, Regional Program Report 79-24, (1979).
- Eaman, M.J. Review of the Status of Hexachlorobenzene in Canada. Beak Consultants Ltd. Unpublished report for the Contaminants Control Branch, Ottawa (1978).
- Fishbein, L. Potential Industrial Carcinogens and Mutagens. Studies in Environmental Science 4. Elsevier Scientific Publishing Company (1979).
- Garrett, C.L. Toxic Organic Contaminants. Canada/British Columbia Fraser River Estuary Study Water Quality Report Series, (1980).
- Gilbertson, M. Hexachlorobenzene - Background Document on the situation in Canada for the DOE/NH&W Environmental Contaminants Committee. Contaminants Control Branch, Environmental Impact Control Directorate, Environmental Protection Service, Ottawa (1978).

Gilbertson, M. Sources of Hexachlorobenzene in Canada. Report to the DOE/NH&W Environmental Contaminants Committee. Contaminants Control Branch, Environmental Impact Control Directorate, Environmental Protection Service, Ottawa (1979).

Leah, T.D. Hexachlorobenzene - A Survey of Environmental Levels in the Ontario Region. Unpublished report for the Contaminants Branch, EPS, Ontario Region (1977).

Mes, J., D.J. Davies, and D. Turton. Polychlorinated Biphenyl and Other Chlorinated Hydrocarbon Residues in Adipose Tissue of Canadians. Bull. Environ. Contam. Toxicol. 28: 97-104 (1982).

Mumma, C.E. and E.W. Lawless. Survey of Industrial Processing Data. Task I - Hexachlorobenzene and Hexachlorobutadiene Pollution from Chlorocarbon Processing. U.S. Department of Commerce National Technical Information Service Report PB-243 641 (1975)

Service de la protection de l'environnement. L'Hexachlorobenzene dans l'environnement vue d'ensemble du probleme au Quebec. SPE Region du Quebec. Dossier SPE 4405-H25 (1979).

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APPENDICES

APPENDIX 1: HEXACHLOROBENZENE RESIDUES IN FISH FROM THE FRASER RIVER/ESTUARY¹

SPECIES	HCB Concentrations ² at Various Locations in the Fraser River/Estuary				
	North Arm	South Arm	Upper Estuary	Chilliwack Area	Hope Area
Staghorn sculpin	8.0 ± 7.1 (2)	3.6 ± 1.2 (5)	4.8	4.8 (1)	
Northern squawfish	4.5 ± 2.4 (2)	7.9 ± 3.5 (4)	3.3 ± 0.1 (2)	2.6 ± 0.4 (2)	1.4 ± 0.3 (2)
Dolly varden	5.2 ± 2.8 (3)	6.1 ± 1.1 (3)		3.9 ± 3.5 (1)	17.0 (1)
Largescale sucker	2.0 ± 0.6 (2)	1.9 ± 1.9 (2)	5.5 ± 1.8 (2)	3.1 ± 2.5 (2)	4.5 ± 4.9 (2)
Peamouth chub	1.6 ± 1.5 (2)	6.2 ± 2.1 (2)	1.6 ± 1.6 (2)	4.5 ± 2.7 (2)	2.4 ± 0.1 (2)
White sturgeon	8.3 ± 3.8 (2)	7.2 ± 5.4 (2)	4.4 ± 2.4 (3)	9.1 ± 8.6 (3)	
Cutthroat trout	9.9 ± 10.0 (2)			6.0 ± 3.4 (4)	4.1 ± 2.5 (2)
Black crappie	3.3 ± 2.4 (5)			5.5 (1)	
Rainbow trout		1.4 ± 0.4 (2)		1.9 ± 0.2 (2)	2.2 ± 0.3 (2)

1. Adapted from Garrett (1980) Appendix 3.

2. Concentrations in ppb wet weight (muscle tissue) presented as a mean and standard deviation. Number of samples analyzed are shown in brackets.

APPENDIX 2: HEXACHLOROBENZENE RESIDUES IN BIRDS FROM VARIOUS LOCATIONS IN BRITISH COLUMBIA
 [Mean \pm S.D. (Range)]¹

LOCATION	DATE	NO. OF SAMPLES	SPECIES	TISSUE	HCb CONCENTRATION (ppb wet weight)
Boundary Bay	1968	2	Glaucous Winged Gull	muscle	23.0 \pm 4.2 (20-26)
Bonilla Island	1970	3	Glaucous Winged Gull	eggs	7.0
Beach Grove	1968	1	Great Blue Heron	brain	12.0
Cleland Island	1970	1	Pigeon Guillemot	egg	131.0
	1970	1	Tufted Puffin	egg	129.0
	1970	10	Glaucous Winged Gull	eggs	46.0
	1970	10	Leach's Petrel	eggs	62.0
Coquitlam	1977	12	Great Blue Heron	eggs	46.7 \pm 74.3 (10-280)
Crescent Beach	1977	11	Great Blue Heron	eggs	23.6 \pm 9.2 (20-50)
Fraser Delta	?	1	Short Eared Owl	brain	14.0
	?	1	Short Eared Owl	muscle	19.0
Lucy Island	1970	10	Rhinoceros Auklet	eggs	29.0
	1970	10	Glaucous Winged Gull	eggs	9.0
Mandarte Island	1970	10	Glaucous Winged Gull	eggs	9.0
	1970	3	Double Crested Cormorant	eggs	304.0
	1970	10	Pelagic Cormorant	eggs	9.0
Mittlenatch Island	1970	10	Pigeon Guillemot	eggs	72.0
	1970	10	Glaucous Winged Gull	eggs	6.0
	1970	10	Pelagic Cormorant	eggs	131.0
Moore Islands	1970	4	Cassin's Auklet	eggs	23.0
	1970	1	Rhinoceros Auklet	egg	18.0
McGillivray Slough	1977	2	Great Blue Heron	eggs	25.0 \pm 21.1 (10-40)
Pender Harbour	1978	12	Great Blue Heron	eggs	31.7 \pm 11.1 (10-50)

continued.....

APPENDIX 2: HEXACHLOROBENZENE RESIDUES IN BIRDS FROM VARIOUS LOCATIONS IN BRITISH COLUMBIA
 [Mean \pm S.D. (Range)]

LOCATION	DATE	NO. OF SAMPLES	SPECIES	TISSUE	HCB CONCENTRATION (ppb wet weight)
Point Roberts	1977	13	Great Blue Heron	eggs	23.8 \pm 15.6 (10-60)
Queen Charlotte Is.	?	2	Ancient Murrelet	whole bird	5.0 \pm 4.2 (2-8)
	?	2	Cassin's Auklet	whole bird	2.0 \pm 0.0 (2-2)
	?	2	Rhinoceros Auklet	whole bird	10.5 \pm 9.2 (4-17)
	1971	2	Tufted Puffin	whole bird	9.5 \pm 3.5 (7-12)
	?	1	Common Murre	whole bird	16.0
	1971	1	Sooty Shearwater	whole bird	13.0
Sea Island	1968	10	Dunlin	muscle	15.0 \pm 13.2 (3-38)
	1968	3	Killdeer Plover	muscle	26.0 \pm 7.8 (21-35)
	1968	2	Robin	muscle	30.5 \pm 2.1 (29-32)
Skedans Island	1970	2	Pigeon Guillemot	eggs	15.0
	1970	10	Glaucous Winged Gull	eggs	11.0
	1970	2	Fork-Tailed Petrel	eggs	271.0
Stevensons Islets	1970	10	Glaucous Winged Gull	eggs	18.0

1 Canadian Wildlife Service, Pacific and Yukon Region, unpublished data.

APPENDIX 3: SAMPLE COLLECTION TECHNIQUES AND ANALYTICAL METHODOLOGY FOR
CHLOROBENZENE RESIDUE DETERMINATIONS IN ENVIRONMENTAL
SAMPLES

1 SAMPLE COLLECTION TECHNIQUES

1.1 Sample Preparation

All sampling instruments, glassware, and tinfoil used to obtain and store samples for residue analysis were washed in pesticide grade acetone, pesticide grade hexane, and then heated to dryness in an oven.

All biota collected at each sample station were sorted live according to species, wrapped in tin foil and submitted to the analytical laboratory. Whole body tissues of small crabs, mussels, and oysters were removed from the shell and pooled from each sample station for analysis.

1.2 Sample Collection

1.2.1 Sediments and Soils. Surface sediments and soils were sampled with a steel trowel to a depth of approximately 10 cm. Five subsamples were obtained at each sample station and pooled for analysis. A long-handled scoop was used to sample surface sediments in chlor-alkali plant effluent ponds. Surface soils in the Peace River area were also sampled with a steel trowel, but in this case 10 subsamples were obtained in each of the twenty-four sampling areas. These subsamples were also pooled for analysis.

1.2.2 Effluents. Samples were collected in one gallon glass bottles. Both grab and composite sampling was conducted. Initial surveys on all five plants were grab samples, while 3.5 and 4.0 hour composite samples were respectively collected in subsequent surveys from two chlor-alkali plants (FMC Chemicals, Squamish and Hooker Chemicals, Nanaimo).

1.2.3 Other Samples. Biota were sampled as described in Section 1.1 above. Process sludges were obtained on two occasions from the reboiler tank at Hooker Chemicals, Nanaimo and placed in glass jars for HCB analysis.

2 ANALYTICAL METHODOLOGY

2.1 Extraction and Cleanup Procedures

All samples were analyzed by CanTest Ltd. The methodology outlined here is reproduced from the EPS report on monitoring of chlorophenol and chlorobenzene contamination near wood protection facilities (Environmental Protection Service, 1979).

2.1.1 Extraction of Sediments and Soils. Wet sediments or soils were extracted with hexane-acetone (1:1 v/v) on a rotary shaker, the extraction repeated, and the extracts combined. The combined extracts were washed with water and the organic phase dried with anhydrous sodium sulphate and concentrated by evaporation. The concentrate was then cleaned up by column chromatography using Florisil. Hexane was used to elute the chlorinated benzenes from the column, and following concentration of the cleaned extract, the sample was analyzed by gas liquid chromatography. A second portion of sediment from each sample was dried to a constant weight to allow concentrations to be calculated on a dry weight basis.

2.1.2 Extraction of Effluents. A three litre sample of effluent was extracted with hexane using a magnetic stirrer. The layers were allowed to separate and the hexane dried with anhydrous sodium sulphate. Following concentration of the extract, column chromatography cleanup was performed with Florisil and the cleaned up extract analyzed by gas liquid chromatography.

2.1.3 Extraction of Biota. Approximately 2 grams of tissue was mixed and dried with anhydrous sodium sulphate. Extraction was carried out with petroleum ether, the extraction repeated, and the extracts combined and evaporated to dryness. Lipid material was then removed by liquid-liquid extraction using acetonitrile. The extracts were then cleaned by column chromatography on Florisil and concentrated for analysis by gas liquid chromatography.

2.2 Analysis of Extracts

All extracts were analyzed by gas-liquid chromatography with electron-capture detection (Nickel-63) using a microprocessor-controlled Hewlett-Packard Model 5840A gas chromatograph. The chromatographic columns consisted of 3% OV-17, 3% OV-101, 3% OV-225, and 6% OV-210/49% OV-101, all on chromosorb W-HP. An automatic injector system was used to ensure reproducibility of the results. Quantification of results was carried out by injection of known quantities of chlorobenzene standards.

2.3 Quality Control

Confirmation by gas-liquid chromatography was done by using different columns containing liquid phases of varying polarity. A number of blanks and spiked samples were also analyzed, and every tenth field sample was analyzed in duplicate.

2.4 Detection Limits

Limits of HCB detection were 0.001 ppm for tissues and sediments and 0.005 ppb for water.