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ENVIRONMENTAL PROTECTION BRANCH ENVIRONMENTAL PROTECTION SERVICE PACIFIC AND YUKON REGION

MONITORING ENVIRONMENTAL CONTAMINATION FROM CHLOROPHENOL CONTAMINATED WASTES GENERATED IN THE WOOD PRESERVATION INDUSTRY REGIONAL PROGRAM REPORT 79-24

## Prepared by

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and

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April 1979

### PREFACE

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. Chlorophenols 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 release and contamination of the environment from use of chlorophenols in the wood preservation industry.

In British Columbia, chlorophenols are used for long-term wood preservation as well as for short-term wood pretection against sapstain and mould on freshly cut lumber. For short-term wood protection, sodium salts of tetra and pentachlorophenol are applied by passing the lumber through a spray tunnel or by dipping in a tank. Release of sodium tetra/pentachlorophenate solutions from dip tanks have caused fish mortalities and contamination of the environment in the past.

In order to better define the extent of present release and contamination from spray and dipping operations in British Columbia, the Environmental Protection Service, Pacific and Yukon Region contracted a monitoring study adjacent to selected facilities in Squamish, the lower Fraser River and on the southeast coast of Vancouver Island.

This report was prepared under contract and does not necessarily represent the views or policies of the Environmental Protection Service, Pacific and Yukon Region. Inquiries pertaining to the contents of this report or its availability should be directed to the Environmental Protection Service, Kapilano 100, Park Royal, West Vancouver, B.C. V7T 1A2.

April 27, 1979

Mr. D. Wilson,
Department Fisheries & Environment, Environmental Protection Service,
Kapilano 100 - 4th Floor,
Park Royal South,
West Vancouver, B.C.

Dear Mr. Wilson:

V7T1A2

Re: DSS File No. 07SB.KE 114-8-1935 Monitoring Environmental Contamination from Chlorophenol Contaminated Wastes Generated in the Wood Preservation Industry

It is our pleasure to submit our final report for the above mentioned project.

The study was a joint effort between Can Test Ltd. and E. V. S. Consultants Ltd. Can Test carried out the analytical portion of the program and was supported by E. V. S. Consultants who collected the samples and supplied the interpretation and report writing functions.

We have supplied a number of conclusions and recommendations and I'm sure you will agree that there are some interesting areas for further investigation.

It has been our pleasure working with you on this project.

Yours truly,

CAN TEST LTD (1)

A. Maynard, M.Sc., Assistant General Manager.

E. V. S. Consultants Ltd.

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#### SUMMARY

A field and analytical program was undertaken to investigate the present levels of chlorophenols and chlorobenzene contaminants in selected coastal receiving waters. The study areas were the lower mainland of British Columbia and the lower east coast of Vancouver Island, encompassing fresh water, estuarine, and marine locations, with a reference control site at "contaminant-free" fresh water area and a marine area (Roberts Bank). Samples of sediments, surface water, effluent, and biota (fish, molluscs, and crustaceans) were obtained in field collections for analysis of contaminant levels. Samples were analysed for pentachlorophenol, di-, tri-, and tetra-chlorophenol, pentachloroanisole and chlorinated benzenes, including hexa-chlorobenzene in all samples. It was found that pentachlorophenol was present in the aquatic environment at all sites where PCP formulations were used. Tetrachlorophenol was also detected at similar or greater concentrations at all sites. Other PCP homologues and chlorobenzenes were detected at some sites in the low ppb range (less than 14 ppb). These minor constituents could not be confirmed as degradation products of biological processes. It was probable that these constituents were present as contaminants in the original PCP formulations.

Not all contaminants were present in all tissues. Skeletal muscles often contained penta- and tetra-chlorophenol, but seldom contained other chlorinated products. Livers from prickly sculpins (*cottus asper*) and staghorn sculpins (*leptocottus armatus*) always contained penta- and tetra-chlorophenol at concentrations 1-3 order of magnitude greater than skeletal muscle from the same individuals. Sculpin liver tissue exhibited preferential uptake with bioaccumulation factors (tissue: sediment ratios) of 7-16 for tetrachlorophenol and 19-33 for pentachlorophenol with liver tissue burdens averaging 402 and 448 ppb respectively. Respective maximums of pooled samples were 1600 and 2100 ppb. It was concluded that sculpins were a sensitive monitor for chlorophenol contaminants, and should be given consideration over crabs and clams for biological monitoring purposes.

It was concluded that both tetra- and penta-chlorophenol represent a significant environmental contaminants problem which has been identified by this investigation. Further avenues of investigation are required to determine the mechanisms and extent of PCP contaminations and these areas are briefly outlined.

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#### RESUME

Un programme d'études a été entrepris dans le but de déterminer les niveaux de contamination dus aux rejets de chlorophénols et chlorobenzène dans les eaux cotières du sud de la Colombie-Britanique. La région concernée comprends la zone cotière entre Vancouver et la frontière avec les Etats-Unis, et la partie Sud-Est de la côte de l'ile de Vancouver. Les stations étudiées sont situées respectivement en eau douce, eau salée et eaux saumâtre (estuaires); avec deux stations non contaminées une située en eau douce et une en eau salée.

Des prélèvements de sediments, d'eaux de surface, de rejets polués et d'animaux aquatiques (poissons, mollusques et crustacés) ont été effectués à fin d'analyses.

Tous les prélèvements ont été analysés pour déterminer les niveaux de pentachlorophénol, di-, tri et tetra-chlorophénol, pentachloroanisole et benzène chlorinés ceci inclus les hexa-chlorobenzènes.

Les analyses ont demontré la presence de pentachlorophénol dans l'environement aquatique à toutes les stations ou des combinaisons de PCP sont utilisées a des fin industrielles. Tetrachlorophénol est aussi present a des concentrations similaires ou plus élevées aux mêmes stations. D'autres chlorophénols et chlorobenzènes ont été détecté à certaines stations à des concentrations inferieures a l4 ppb il n'a pas été possible de determiner si ces derniers sont le produit de degradations biologiques. Il est probable que ces contaminants etaient presents originellement dans les composés de P.C.P. Les contaminants analysés n'étaient pas tous présents dans tous les tissus. Les muscles contenaient souvent des Penta- et tetra-chlorophénols, mais trés rarement d'autres composés chlorinés. Les foie de poissons, (*Cottus asper et Leptocottus armatus*) contenaient des concentrations de Penta- et tetra-chlorophenols de un a trois ordres de grandeur superieures aux concentrations contenues dans les muscles des mêmes individus.

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Les tissus du foie de *Cottus* de *Leptcottus* on montré un pouvoir d absorption preferentielle et une accumulation biologique (rapport de tissus-sediment) de 7-16 pour les tetrachlorophénols et 19-33 pour les pentachlorophénols, avec des concentrations moyennes dans les tissus du foie de 402 et 448 ppb respectivement. Les maximum obtenus en groupant les prélèvements ont été de 1600 et 2100 ppb respectivement. Il en a été conclus que *Cottus* et *Leptcottus* sont des espèces sensible a la contamination par les chlorophénols et devraient être considérées comme espèces indicatrices, de préférences aux crabes et aux molluques; pour la surveillance biologique continue des rejéts contaminés.

Nous en avons conclus que les tetra- et Penta Chlorophénols representent un problème sérieux de contamination, lequel a été identifié par cette étude. D autres voies de recherches seront nécéssaires pour déterminer les mecanismes et l'etendue des contaminations dues au PCP, ces sujets sont revus brièvement.

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#### CONCLUSIONS:

Based on the results and findings of this study, it is concluded that:

- 1. Chlorophenols were found in the aquatic environment at all sample sites where penta-chlorophenol was used in industrial processes. It is likely, therefore, that chlorophenols may be found in the aquatic environment wherever they have been used in wood preservation or protection. It is further concluded that these data indicate a potentially serious environmental contaminants problem with respect to the use of penta-chlorophenol.
- 2. Sculpins were the only organisms available in adequate numbers at all sites for body burden comparisons.
- 3. The presence of chlorophenols and chlorophenol homologues in sediments, tissues and water leads to the conclusion that commercial PCP formulations are extensively contaminated with related compounds. Tetrachlorophenol was present in equal or higher concentrations than penta-chlorophenol and must be considered as a major component in establishing environmental criteria for penta-chlorophenol (PCP) formulations.
- 4. Sculpin liver tissue proved to be the most sensitive indicator of chlorophenol contamination.

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#### RECOMMENDATIONS

Based on the conclusions and results of the present study, it is recommended that:

1. Forest industry and related operations presently using pentachlorophenol for wood preservation or wood protection should undertake monitoring programs to determine the extent and levels of penta- and tetra-chlorophenol in the receiving environment. Such studies would provide baseline information on which the effectiveness of control measures could be based. The surveys would also domonstrate the need to control storm water runoff and other non-point source emissions of chlorophenols where necessary.

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- 2. The toxicological effects of the identified chlorophenol body burdens be determined. More specifically, studies should be undertaken to determine the levels to which these contaminants can bioaccumulate before liver dysfunction or histopathologies become evident and pose a threat to the affected species (eg. sculpins). Such studies should involve a combination of laboratory and field sampling work, determining fate and persistence in selected environmental compartments such as sediments, rates of uptake and depuration of chlorophenols, rates of entry to tissues and alterations in liver morphology, biochemistry and histology. Compartmentation of chlorophenols in other body organs (brain, gill, etc.) should also be defined.
- 3. All PCP formulations currently in use should be analyzed to determine the presence and proportions of all major and minor constituents.
- 4. In instances where biological monitoring is desirable to determine the presence of chlorophenols, sculpin species should be considered as a suitable and readily available indicator species inasmuch as their availability, behavorial characteristics and life history are consistent with surveillance requirements. Analysis of whole body homogenates or skeletal muscle alone is not recommended since chlorophenols appear to be a one compartment contaminant accumulating in the liver.

## 1.0 INTRODUCTION

Pentachlorophenol (PCP), a chlorinated hydrocarbon, is used extensively throughout Canada as a wood preservative in lumber and pole yard facilities. Prior to transport, PCP-treated wood products are stockpiled in open facilities in lumber yards or shipping terminals, permitting preservative chemicals to be leached from the treated lumber by rainfall, with eventual possible entry into coastal receiving waters. Pentachlorophenols are among the most acutely toxic chemicals to fish and other aquatic life. However, the fate and effects of chlorophenols are poorly understood and no specific environmental information is available on the presence or extent of chlorophenol contaminants in the Pacific Region. Major users of pentachlorophenols are located on the lower mainstem of the Fraser River and on estuaries of the Fraser, Squamish, Cowichan, Nanaimo, and Somass rivers. This being so, pentachlorophenol poses a potential concern as an environmental contaminant to the commercial and recreational fisheries resources of these areas. To assess this concern, a monitoring program was required in which the collection and analytical methodology would be compatible with the parts per billion level of detection. Based on these requirements, Can Test Ltd. and E.V.S. Consultants Ltd. were contracted to investigate the present levels of chlorophenol and chlorobenzene contaminants in selected coastal receiving waters.

#### 1.1 Objectives

The objectives of this project were as follows:

a) To undertake a sampling program at ll sites where pentachlorophenols are used, with 1 freshwater reference site and 1 saltwater reference site as 'contaminant-free' controls.

- b) To collect and pool biota samples at each site by species, the samples comprising one each of molluscs, flatfish (or sculpins) and crabs (or crayfish).
- c) To collect sediment samples from all sites for chlorophenol analysis.
- d) To collect effluent samples or stormwater run-off samples (as available) and surface water samples from all sites for chlorophenol analysis.
- e) To conduct qualitative and quantitative chlorophenol residue analyses on pooled tissue homogenates, sediment samples, surface water and effluent samples.
- f) To determine the presence of pentachlorophenol, di-, tri-, and tetrachlorophenol, pentachloroanisole, and chlorinated benzenes including hexachlorobenzene in all samples.
- g) To compare the results obtained from the analysis of chlorophenols in tissues, sediments and water from both contaminated and control areas, to assess the presence of metabolites, the accumulation and potential for concern in aquatic organisms.
- h) To write a final report describing the findings of the study and to recommend areas for future research.

# 2.0 DESCRIPTION OF STUDY AREA

There were two principal study areas for this project. The first area of study was the Lower Mainland including the lower mainstem of the Fraser River below the confluence with the Pitt River, Burrard Inlet, the Fraser River Estuary, the Squamish River and the Squamish River Estuary (Fig.1). The second principal area was the lower east coast of Vancouver Island including Victoria Harbour, the Cowichan River Estuary, and the Nanaimo Estuary and Harbour (Fig.2).

#### 3.0 MATERIALS AND METHODS

#### 3.1 Sample Preparation

All instruments, gloves and tinfoil with which biota were to be contacted were washed in pesticide-grade acetone, then washed with pesticide-grade hexane, rinsed with acetone, and finally air-dried. Containers for water, effluent, and sediment samples were pre-treated in a similar fashion.

Depurated whole body tissue of molluscs was removed from the shell and pooled from each sample station for analysis. Similarly, crab chelaped muscle, dorsal muscle tissue and liver tissue from fish were extirpated and pooled from each station for analysis. All tissues for an individual sample station were sorted live according to species, wrapped in tinfoil, placed in plastic bags, frozen and submitted to Can Test for analysis.

#### 3.2 Sample Collection

## 3.2.1 Biota

*Molluscs:* Attempts were made at all sample stations to collect *Macoma* sp. or *Pisidium* sp. in numbers sufficient for analysis. Sediment was collected at low tide by means of a modified Van Veen grab, benthic trawl or shovel, and sieved on site to isolate the organisms. The clams were transported to the laboratory and held live for 24 hours to depurate ingested sediment. They were then frozen in tinfoil and placed in a plastic "zip-loc" bag. The sea water  $(20^{\circ}/_{\circ\circ})$  to be used for depuration was passed through a sand filter for particulate removal and a CUNO<sup>R</sup> activated carbon filter to remove dissolved organics.

Fish: Longlines baited with juvenile trout, herring strips or whole worms were set at each station in an attempt to capture starry flounder (*Platichthys stellatus*) or sculpins (marine, *Leptocottus armatus*; freshwater, *Cottus asper*). Longlines were tended regularly throughout the day and retrieved at the day's end.

Crustaceans: Up to 10 of each of Dungeness crab (Cancer magister), red rock crab (C. productus), or freshwater crayfish (Pacifastacus sp.), were collected at each location using standard commercial crabtrap frames hung with a fine mesh netting to retain the crayfish. Salmon heads or herring were used as bait.

## 3.2.2 Sediments

A modified Van Veen grab or Snapper grab was used to collect subtidal sediments which were transferred directly to wide mouth 225 mL sample bottles. At each site, five sample stations (a-e) were selected for replicate sediment sampling (a-1 and 2, b-1 and 2, etc.). Sediment samples at the two control sites were single grabs at five stations (Appendix I, Figs. 3-14).

## 3.2.3 Effluents and Surface Waters

Where it was possible to locate specific discharges, samples were taken directly from the outfall. Effluent samples were collected by hand in all-glass, l gallon containers. In addition, samples of surface water were obtained at all sites. The samples were stored at  $4^{\circ}$ C prior to analysis.

## 3.3 Analytical Methodology

#### 3.3.1 Extraction of Sediments

Sediment samples were extracted for chlorinated phenols by a modification of the procedure described by Renberg (1974). Approximately

six grams of wet sediment was extracted with dilute sodium hydroxide. The resulting extract was adjusted to pH 8.5, added to three millilitres of an anion ion exchange resin (Sephadex QAE, A-25) and shaken for ten minutes. The liquid phase was removed after centrifugation and three millilitres of benzene plus three millilitres of acidic buffer (0.2M hydrochloric acid/0.2M potassium chloride, 1/1) were added and shaken for five minutes. Following centrifugation the benzene layer was removed for subsequent derivatization and gas chromatographic analysis.

In order to analyze for pentachloroanisole and chlorinated benzenes, a second portion of wet sediment was extracted by a modification of the method described by Environment Canada (1974) for the analysis of organochloride pesticide and PCB's in fish and sediment. The sediment was extracted with hexane-acetone (1:1 v/v) on a rotary shaker, the extraction repeated, and the extracts combined. The resulting extracts were washed with water and the organic phase was dried with anhydrous sodium sulphate and concentrated by evaporation. The concentrate was then "cleaned-up" by column chromatography using Florisil, with the chlorinated benzenes eluting in the first (hexane) fraction and the pentachloroanisole eluting in the second (6% ethyl ether in hexane) fraction. Following concentration of the fractions, elemental sulphur was removed by the use of tetrabutyl ammonium hydrogen sulphate (Jensen et al, 1977) and the extracts analyzed by gas chromatography.

A third portion of sediment was dried to constant weight to allow concentrations to be calculated on a dry weight basis.

## 3.3.2 Extraction of Water

Water and effluent samples were extracted for chlorinated phenols by the procedure described by Renberg (1974). A five hundred millilitre water sample (adjusted to pH 8.5) was passed through a chromatographic column containing five millilitres of ion exchanger (Sephadex QAE, A-25). The ion exchanger was then flushed from the column into a centrifuge tube and washed with organic-free water. The chlorophenols were then eluted by the addition of benzene and acidic buffer. Following centrifugation the benzene layer was removed for subsequent derivatization and gas chromatographic analysis.

A second portion of water was extracted for pentachloroanisole and chlorinated benzenes by a modification of the Environment Canada procedure (1974) for organochlorides and PCB's in waters. A three litre sample of water 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 clean-up was performed using Florisil. The resulting extracts were analyzed by gas chromatography.

### 3.3.3 Extraction of Biota

Tissue samples were extracted for chlorinated phenols by a modification of the method described by Renberg (1974). A five gram sample of tissue was mixed with anhydrous sodium sulphate until dried, and extracted with hexane-acetone. The liquid was removed and a second extraction carried out with hexane-diethyl ether. The liquid was removed, the extracts combined and evaporated carefully to dryness. The residue was taken up in benzene and added to three millilitres of the ion exchanger (Sephadex QAE, A-25) in a centrifuge tube followed by the addition of three millilitres of 0.1M sodium hydroxide. The tube was shaken for five minutes, centrifuged and the liquid removed. The ion exchanger was washed with organic-free water and the

chlorophenols eluted by the addition of benzene and acidic buffer. The resulting benzene extract was derivatized and analyzed by gas chromatography.

A second portion of tissue was extracted for pentachloroanisole and chlorinated benzenes by a modification of the procedure described by Environment Canada (1974) for the analysis of organochloride pesticide and PCB's in fish and sediments. Approximately ten 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 acetonitrite. The resulting extract was then "cleaned-up" by column chromatography using Florisil. The concentrates were then analyzed by gas chromatography.

3.3.4 Analysis of Extracts

All extracts were analyzed by gas-liquid chromatography with electroncapture detection (Nickel-63) using a microprocessor-controlled Hewlett-Packard Model 5840A gas chromatograph. The chromatographic columns used were 3% OV-17, 3% OV-101, 3% OV-225, and 6% OV-210/4% OV-101, all on Chromosorb W-HP.

All injections onto the chromatographic column were carried out using an automatic injector system to ensure reproducibility of results.

Chlorophenol extracts were derivatized to their trimethylsilyl ethers using BSTFA (N, O-bis-(trimethylsilyl)-trifluoroacetamide). Quantitation was carried out by injection of standards derivatized in the same manner.

Pentachloroanisole and chlorinated benzene extracts were analyzed in a similar manner without the need for derivatization.

## 3.3.5 Quality Control

Confirmation of the gas chromatography results were carried out using a second chromatographic column containing a liquid phase of different polarity. Mass spectrometry was not required for further proof of contaminant identity.

A number of blanks and spiked samples were also analyzed and every tenth sample was analyzed in duplicate.

#### 4.0 RESULTS

### 4.1 Sample Collection

The collection dates for each site and material collected (biota, sediments, effluent and surface water) are summarized in Table 1. Figures 1 and 2 indicate the location of sample sites. Appendix I provides the sample station locations and detail of each site. The raw data for analytical results are presented in Appendix II. Raw data on catches, field activities, and sampling conditions are presented in Appendix III, the log of field notes.

With respect to biota, the limited availability of desired species of molluscs, crustaceans and fishes prevented representative collections at every location. Thus for the freshwater stations, the fingernail clam (*Pisidium* sp.) was not obtainable, nor was the starry flounder (*Platichthys stellatus*). The clam *Macoma balthica* was obtained at most saltwater sites, and sculpins were a viable alternate fish at both freshwater and saltwater sites, the principal species being the prickly sculpin *Cottus asper* and the staghorn sculpin *Leptocottus armatus*.

The principal crustacean available at freshwater sites was the crayfish *Pacifactacus leniusculus*, and at saltwater sites adequate numbers of the crabs *Cancer magister* and *Cancer productus* were obtained except at sites X and XI. At site X, the small shore crab *Hemigrapsus nudus* was collected to augment the *Cancer magister*. No alternates were available to augment the two small *Cancer magister* at site XI.

## 4.2 Laboratory Analytical Results

The analytical methodology was selected on the basis of a literature search and the experience in Can Test's laboratory in previous programs.

# 4.2.1 Detection Limits

The detection limits for water, sediment and tissue are listed on the first page of Appendix 2. These limits of quantitation were calculated from in-house data and represent minimum concentrations that can be recovered and detected with confidence, from spiked samples.

## 4.2.2 Contaminant Recovery

The methods were found to achieve favourable results for the analyses of the contaminants under study. Recovery experiments carried out yielded recoveries for pentachlorophenol of 97, 87, and 85 percent for water, sediment and tissue, respectively.

The extraction procedures used for the chlorobenzenes and pentachloroanisole were those of the Water Quality Branch, Inland Waters Directorate of Environment Canada. The methods for the analysis of organochloride pesticides and PCB's were modified for the analysis of hexachlorobenzene and pentachloroanisole. Recovery studies for hexachlorobenzene showed 95, 90, and 89 percent recovery for water, sediment and tissue, respectively, and for pentachloroanisole 87, 90, and 86 percent recovery.

### 4.3 Contaminant Levels

# 4.3.1 Biota

The average concentrations of pentachlorophenol and tetrachlorophenol in the tissues of fish, crabs and molluscs are summarized in Table 3. These two contaminants were predominant in body burdens at all sites.

The liver tissue burdens of both species of sculpins consistently contained the highest levels of chlorophenols, being 1-3 orders of

magnitude higher for penta- and tetra-chlorophenol than average skeletal muscle concentrations from the same individuals or from other species. Skeletal muscle burdens were generally similar between all species of sculpins, crabs, crayfish and clams, ranging from a trace (1-5ppb) to 100 ppb, depending on the site. Hexachlorobenzene (sites Cl, I, II, III, VI and VII), tetrachlorobenzene (site VII) and pentachloroanisole (sites I, II, III, V, VI and VII) were also detected in fish liver tissues but not in any other tissues analyzed.

For all tissues, sites I, VI, VIII and IX contained less than 120 ppb of total chlorinated aromatics, sites III, IV, V, VII, X and XI contained greater than 400 ppb chlorophenols, and site II was intermediate in tissue burdens. Combining these rankings, sites I, II and VIII were least contaminated, sites III, IV, X and XI were the worst contaminated, with sites V, VI, VII, IX being intermediate.

# 4.3.2 Sediments

Average concentrations of the compounds determined in sediment at a particular site were calculated using the upper limit of "trace" or "non-detectable" levels for averaging purposes. Results for sediments and corresponding water data, are summarized in Table 2. Tissue concentrations are summarized in Table 3.

Pentachlorophenol sediment analyses showed wide variability - up to two orders of magnitude - within particular sites (I, VII, IX and XI). Tetrachlorophenol did not vary by more than an order of magnitude, except at I, IV, VII and IX. Trichlorophenol varied to about the same degree as tetrachlorophenol at the same site. Chlorobenzenes were detectable in sediments at sites IV, VII, IX and XI. Sites with generally high pentachlorophenol levels also exhibited detectable amounts of chlorobenzenes and pentachloroanisole, although site IV is an apparent exception. Pentachloroanisole sediment levels were relatively uniform between stations at a given site.

Tetrachlorophenol sediment levels generally exceeded those of pentachlorophenol at all sites (see Table 2). Average trichlorophenol levels were generally less than those of PCP, but the margin was slight at stations VI and VII. XI was the only site where chlorobenzene sediment levels approached or exceeded chlorophenol levels. Pentachloroanisole sediment levels approached PCP levels at sites III, IV and XI.

The pattern for sediment concentrations is different from that of tissue concentrations. For sediments, sites I, II, V, VIII and X have low but detectable levels of pentachlorophenol or it's homologues. Sites VI, VII, IX and XI were an order of magnitude higher in chlorinated aromatics, and the remaining sites (III, IV) were intermediate in detectable levels. Site X was anomalous in having low sediment concentrations but the highest liver tissue burdens.

## 4.3.3 Effluents and Surface Waters

Effluent samples were analyzed from sites VIII, IX, X and XI, pentaand tetra-chlorophenol being identified as the principal chlorinated contaminants. Tetrachlorophenol was consistently present at 2-4 times the concentration of pentachlorophenol. The highest effluent concentrations were obtained at site XI, where effluent concentrations of 2760 ppb and 8270 ppb were obtained for pentachlorophenol and tetrachlorophenol respectively.

Chlorophenols were detected in all surface waters except the control (Cl) and site VII. As with effluent samples, surface waters also exhibited levels of tetrachlorophenol consistently higher than those of pentachlorophenol, with the exception of sites II and XI (Appendix II).

Maximum levels found for the different contaminants in sediment, water, effluent and tissue are presented by site in Table 4a. The number of citations for each site is listed in Table 4b, and on this basis the level of contamination of sites is in increasing order VII, VI, X, XI.

#### 5.0 DISCUSSION

## 5.1 Chlorophenol Levels in Aquatic Environments

Tables 2 and 3 show that, excluding controls, the sediment levels of pentachlorophenol varied from 5.0 to 187.9 ppb, water levels from <0.05 to 7.3 ppb, and tissue levels from <1 to 2100 ppb. The range of results reported by Pierce and Victor (1978), following a pentachlorophenol spill in a freshwater lake, were 4 to 1518 ppb in sediment, 0.1 to 81 ppb in water, and 4 to 325,000 ppb in tissue. Their results were comparable to, but consistently higher than, those reported herein. The fact that spill level maxima in sediments were greater only by a factor of 5, and water values greater by a factor of 10 may reflect possible spill events in the recent past at some of the sites studies here. Further, tissue levels of 2100 ppb pentachlorophenol are directly comparable to the 2500 ppb values detected by Pierce and Victor (1978) in fish tissue collected two months after a pentachlorophenol spill.

The tetrachlorophenol averages (Tables 2 and 3) ranged from 10.0 to 272.1 ppb in sediment, 0.06 to 5.2 in water, and <1 to 1600 in tissue. Pierce and Victor (1978) found, respectively, 3.8 to 339, 0.03 to 2.0, and <1 to 8500 ppb. The levels are quite similar, considering the different circumstances. These results are also consistent with those of Pierce and Victor (1978) in that pentachlorophenol concentration ranges were much greater than tetrachlorophenol and other compounds.

Table 5 examines relationships between contaminant levels in freshwater and saltwater. Saltwater stations had higher average sediment levels, higher water levels and higher sediment/water ratios, with respect to penta- and tetra-chlorophenol content, than freshwater stations. However, because these higher levels occurred in <u>both</u> sediments and water, they are most likely related to mill operations. Relationships to salinity and salting-out phenomena may exist but are likely coincidental in this instance. No data were available on the solubilities of these compounds in saltwater vs. freshwater, although other polychlorinated aromatics such as polychlorinated biphenyls are less soluble in saltwater (Schoor, 1975). The significance of salinity as a major variable clearly warrants more detailed investigation.

The finding that tetrachlorophenol levels in water were consistently higher than pentachlorophenol may indicate a greater water solubility by the former. This would be consistent with the loss of a chlorine atom. It may also simply indicate that tetrachlorophenol was present in the original penta-chlorophenol formulation as a major constituent, a situation which commonly occurs in commercial products (Nilsson, 1978).

It was not possible to relate penta- and tetra-chlorophenol levels in tissue and water at particular sites, partly because of the limited number of data points and partly because water values vary rapidly with time compared to tissue levels which are inherently time-averaged by uptake and depuration rates. Comparison of tissue levels with sediment levels (Table 6) however, indicated a covariance of sediment with skeletal muscle tissue of *L. armatus* and *Cottus asper*. This would be expected if pentachlorophenol compounds may have an extended residence time in sediments (Pierce and Victor, 1978). Liver and chelaped tissue levels showed no trend with sediment level. However, the bioaccumulation factor (tissue : sediment concentration ratio) was 19-38 for pentachlorophenol and 7-18 for tetrachlorophenol.

### 5.2 Analytical Methodology

The analytical methodology selected was consistent with the study objectives of this project. Most of the methodology used was that presently in use in regulatory laboratories. The analysis for chlorophenols however,was based on recently published methodology (Renberg 1974).

The ion exchanger used for the extraction of the chlorophenols in this study was a strongly basic anion exchanger (Sephadex QAE-A25). The functional group was diethyl- (hydroxy-propyl) amino ethyl, with chloride as the counter ion. The use of an ion exchanger allow greater selectivity than solvent extraction as neutral or non-ionic compounds are not bound by the ion exchanger when extracting water samples. It has been shown (Renberg, 1974; Stark, 1969) that high fat content in tissue and gel formation in acidified sediment can seriously affect the separation of chlorophenols by solvent intraction. By utilizing the ion exchanger these problems can be overcome as the acidic substances are effectively removed from the sample by the ion exchanger under alkaline conditions and can then be eluted under acidic conditions.

#### 5.3 Metabolic and Degradation Products of Chlorophenols

Minor constituent chlorophenols were found in fish liver tissue at sites I, II, VI and VII. Measurable chlorophenols increased in sediments as pentachlorophenol concentrations increased (Table 2; Appendix I). However, the present study was not designed to distinguish between the transformations that may occur in PCP *in situ*. It was not possible for example to demonstrate that the range of PCP homologues detected in liver tissue were metabolic byproducts, or simply contaminants in the original PCP formulations. Further, the formulations quite probably varied from one site to the next, which further limited the generalizations that may be applied to the findings  $vis_{-a}-vis$  metabolic degradation products.

The photolysis of PCP in water has been discussed by Wong and Crosby (1978), leading to the proposed photolytic pathway shown in Figure 3. Primary degradation products were chlorinated phenols, tetrachlorodihydroxyl benzenes and non-aromatic fragments such as dichloromaleic acid. Further irradiation produced hydroxylated trichlorobenzoquinones, trichlorodiols, dichloromaleic acid and non-aromatic fragments.

Degradation of PCP by soil micro-organisms led to lower chlorophenols, pentachloroanisole and CO<sub>2</sub> evolution (Kaufman, 1978). The proposed pathway is shown in Figure 4. Kaufman's review tabulated 36 different breakdown products found by other workers, predominantly polychlorinated derivatives of benzoquinones, phenol, anisole, and hydroquinone. The microbial degradation of sodium pentachlorophenate in mixed microbial communities and in an axenic bacterial culture (Reiner *et al.*, 1978) also led to the identification of chlorinated hydroquinones and benzoquinones as metabolites. Figure 5 shows the proposed pentachlorophenol biodegradation in KC-3 bacterial cultures. Lu *et al.*, (1978) evaluated pentachlorophenol degradation in three model ecosystems; aquatic, terrestrial-aquatic and and terrestrial. The principal products are believed to be tetrachlorophydroquinone, pentachlorophenyl acetate, and conjugates.

Kobayashi (1978) found that pentachlorophenol was rapidly absorbed by goldfish, especially in the gall bladder. The pentachlorophenol was quickly excreted, mostly as the pentachlorophenylsulphate conjugate accompanied by a small amount of the unconjugated form. The PCP in the gall bladder was present as the B-glucuronide. A schematic depiction of the metabolic pathway is shown in Figure 6.

Uptake of pentachlorophenol and pentachloroanisole (PCA) by Salmo gairdneri (Lech et al., 1978) was rapid, and the latter compound was retained longer than pentachlorophenol in most tissues. Lech et al. failed to find pentachloroanisole in tissues of trout exposed only to pentachlorophenol, in contradistinction to earlier work which proposed the anisole as a metabolite. The suggestion was that in this previous work pentachloroanisole was formed by microbial processes prior to ingestion (see also Cserjesi and Johnson 1972), and then accumulated. Tissue analysis of pentachloroanisoleexposed trout showed only the compound unchanged, with the exception of traces of the free phenol in liver tissue. Lu *et al.*, (1978) and Koss and Koransky (1978) discussed the biotransformation of hexachlorobenzene (HCB) to pentachlorophenol. Other metabolites of HCB were tetrachlorohydroquinone and sulphur containing compounds. However, none of the work reviewed implicated hexachlorobenzene as a metabolite or degradation product of pentachlorophenol nor is it likely on chemical and biochemical grounds that such a transformation would occur; <u>dechlorination</u> is the norm in such processes. However, small amounts of HCB may be found in commerical PCP (Conklin and Fox, 1978) or may have entered the ecosystems from another source.

Lu (1978) also listed tetrachlorobenzene as a possible metabolite of PCP although this possibility has not been confirmed. It is, therefore, likely that the single finding of tetrachlorobenzene in tissue (at site VII) was derived from an impurity in PCP. This possibility is supported by measurable tissue levels of hexachlorobenzene and measurable sediment levels of hexa-, and tetra-chlorobenzene at the same station.

Pentachloroanisole (PCA) levels in sediment and tissue were measurable at sites I and VII and in water at VII. The average bio-accumulation factor of PCA by tissue from sediment was only about 3 times greater (probably not a significant difference) than for PCP, at site VII, showing little support for the idea that PCA is a metabolite of PCP, and being more consistent with the suggestion (Lech *et al.*, 1978) that PCA is formed prior to ingestion by the aquatic organisms. Pierce and Victor (1978) concluded from their data on water and tissue levels that PCA was accumulated extremely well by tissue, although comparison of their tissue and sediment data would indicate tissue:sediment ratios similar to those reported herein (about 3).

## 5.4 Significance of Bioaccumulation in Sculpins

# 5.4.1 Life History

The prickly sculpin (*cottus asper*) and the staghorn sculpin (*leptocottus armatus*) are important secondary consumers in aquatic food chains. During early post-metamorphic juvenile stages, young sculpins consume a variety of aquatic insect larvae, especially chironomid and trichopteran larvae, molluscs, and other benthic invertebrates. Large sculpins may consume a variety of items such as fish eggs, and young of their own, as well as the young of other species including juvenile salmonids.

A number of species have been reported to prey on sculpins including larger salmonids and water fowl, such as the American merganser. Both species of sculpin may be strongly territorial, and the staghorn sculpin exhibits burrowing behaviour in bottom sediments.

Sculpins are not used directly by man, but it is food of, or predator on, other species which are consumed by man. This feeding pattern, together with the territorial behaviour and availability for capture and anlysis, make the species highly suitable as biological indicators of chlorophenol contaminants. The bioaccumulation factors for liver tissue further indicate excellent level of sensitivity for monitoring purposes, and inclusion of these species of sculpins in future similar inventory programs for environmental contaminants is recommended.

## 5.4.2 Liver Tissue Levels

Preferentially high levels of chlorophenols have been observed in liver tissue from freshwater fishes (Pierce and Victor, 1978). The liver is recognized as the principal body organ responsible for detoxification of xenobiotic chemicals such as pentachlorophenol, and the high chlorophenol concentrations observed would be consistent with this function. To what levels these contaminants can bioaccumulate before liver dysfunction or histopathologies become evident is not known at present.

The high levels of penta- and tetrachlorophenols in sculpin livers, and the apparent lack of metabolic degradation products leads to the conclusion that these particular compounds are bioaccumulative to levels that could be expected to affect the viability of the species concerned, and may offer a threat to man through at least one food web. Data from this study are consistent with the hypothesis that these contaminants may pass relatively unchanged through aquatic environments. Further, the data show that tetrachlorophenol is as persistent as pentachlorophenol, and must be considered as a major component in the environmental control of PCP formulations.

The data indicate potentially serious contaminant problems that require better definition than could be afforded here, with respect to differences in organisms sampled, bacterial mediation, and sediment compartmentation. Technical information is clearly required to demonstrate the toxicological effects the identified body burdens may have. In particular, the rates of uptake and depuration of chlorophenols, routes of entry to tissues and associated food webs, fate and persistence in sediment compartments, and bioaccumulation are among the areas of essential investigation.

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DESCRIPTION OF SAMPLES COLLECTED AND SUBMITTED FOR ANALYSIS TABLE 1.

Surface	Water				<b>1</b>	н	-	п	<b>T</b>	-		-1		
	Effluent									1		1	1	1
	Molluscs +	530											340	
nples	Flatfish	10	_											
No. of Samples	Sculpins			71	70	20	5L,4C	191,50	4L	31	10L		71	JL .
	Sediments		S	10	10	10	10	10	10	10	10	10	10	10
	Crabs	10M*		10P					10M	6M,11P	8M	TOM	2M	2M
	Crayfish				2	10	2							
Date	(1978)	Oct.25	Nov.28	Nov.6,7	Nov.8,9	Nov.8,9	Nov.20	Nov.10	Nov.27	Nov.14,15	VIII Nov.16	Nov.17	Nov.18	Nov.19
Site		CI	C3	н	II II	III	IV	v	١٧	VII	III	IX	x	IX

\* Collected October 20, 1978 M = Cancer magister P = Cancer productus + = Macoma balthica

C = Cottus asper L = Leptocottus armatus

-		SEDIN	IENT	LEVELS				Wat	er Leve	ls
SITE	5CP	4CP	3CP	6CB	5CB	4CB	5CA	5CP	4CP	5CA
CI	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Freshwater										
II	35.0	28.0	N.D.	N.D.	N.D.	N.D.	N.D.	0.28	0.10	N.D.
III	10.8	27.4	2.3	N.D.	N.D.	N.D.	2.6	0.25	1.0	N.D.
IV	18.1	21.9	N.D.	0.73 <sup>,</sup>	N.D.	N.D.	31.1	<0.05	0.30	N.D.
v	5.0	10.0	N.D.	N.D.	N.D.	N.D.	N.D.	<0.05	0.20	.006
<u>Saltwater</u> I	34.7	39.8	N.D.	N.D.	N.D.	N.D.	0.53	0.75	1.3	N.D.
VI	52.8	98.7	52.1	N.D.	N.D.	N.D.	N.D.	2.4	5.2	.020
VII	106.6	272.1	91.0	3.12	1.9	2.76	3.53	<0.01	0.06	.005
VIII	16.0	19.5	N.D.	N.D.	N.D.	N.D.	0.28	<0.05	0.09	N.D.
IX	42.0	65.4	N.D.	N.D.	0.83	0.71	4.31	<0.05	0.06	N.D.
X	13.1	22.8	N.D.	N.D.	N.D.	N.D.	0.58	3.1	3.3	.005
XI	187.9	157.3	37.3	9.19	9.75	64.9	14.89	7.3	0.22	N.D.

# TABLE 2. AVERAGE SEDIMENT AND WATER CONCENTRATIONS IN PPB FOR CHLORINATED PHENOLS, CHLORINATED BENZENES, AND PENTACHLOROANISOLES

## \* KEY

5 CP = Pentachlorophenol 4 CP = Tetrachlorophenol

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- 4 CP = letrachioropheno
- 3 CP = Trichlorophenol
- 6 CB = Hexachlorobenzene
- 5 CB = Pentachlorobenzene
- 4 CB = Tetrachlorobenzene
- 5 CA = Pentachloroanisole

	ſ																					25
			Mean	8	8			260	147	35	49	448	402	15	11							L'
•			XI	8	1-5							640	430	84	34							
•			x	17	2							2100	1600	1-5	8	<b>1</b> 2	12					
-			XI	1-5	6.6	ı	1	ı	ı	1	1	- 2	- 1	ı	1	ı	1	1	ł	ł	,	
	THE		1111	16	20							1-5	29	1-5	10							
•			111	1-5	1-5	7	1-5					210	470	13	8							
•	OROPHE		١N	41	8							35	63	1-5	6							
•	[RACHL(		^					1-5	82	12	2	470	480	5	8							
	ND TET		IV					300	96	74	10	100	74	1-5	1-5					I-5	1-5	
	HENOL A	•	111					600	320	14	80							ć1	1-5			
	ILOROPI		11					140	89	40	100							ŝ	ć1			
	PENTACE		I	1	ı	1-5	9	I	ı	1	ı	24	69	1-5	9			ı	ι	1	'	oheno1
	IN PPB OF PENTACHLOROPHENOL AND TETRACHLOROPHENOL IN AND MOLLUSCS.		ant * CI													1-5	15					tetrachlorophenol
	CONCENTRATIONS OF FISH, CRABS		Contaminant *	5CP	4CP	5 CP	4CP	5CP	4CP	5CP	4 C P	5 CP	4CP	SCP	4CP	5CP	4CP	5CP	4CP	5 CP	4CP	4CP =
	AVERAGE CONCENTRA TISSUES OF FISH,		Tissue	er muscle		tus muscle		liver		muscle		liver		muscle				sp. pincers		tail		pentachlorophenol,
	TABLE 3		Species ,	Cancer magister		Cancer productus muscle		Cottus asper				L. armatus				Macoma sp.		Pacifastacus sp.				* 5CP = penta

Contaminant	Sedir	nent	Water	Effluent	Tissu	ıe
Pentach1oropheno1		(XI)	7.3 (XI)	2760 (XI)	2100	
Tetrachlorophenol		(VII)	5.2 (VI)	8270 (XI)	1600	(X)
Trichlorophenol		(VII)	<0.01	<0.01	<1	
Hexachlorobenzene	39	(XI)	.012 (XI)	.078 (XI)	4	(VI)
Pentachlorobenzene	78	(XI)	.019 (XI)	.050 (XI)	0.1	
Tetrachlorobenzene	340	(XI)	.017 (XI)	42 (XI)	14 (1	VII)
Pentachloroanisole	100	(IV)	.02 (VI)	.09 (X)	8.3	(I)

TABLE 4a MAXIMUM LEVELS OF CONTAMINANTS DETECTED IN PPB BY SITE

Site	Number of Citations
XI	13
x	3
VI ) ) VII )	2
I ) ) IV )	1

TABLE 4b NUMBER OF MAXIMUM VALUES CITED PER SITE

	SED.     SCP WATER     WATER SED.     RATIOS SED.     MATER WATER     RATIOS SED.     MATER WATER     SED.     MATER WATER     SED.     MATER WATER     SED.     MATER WATER       35     .28     28     .1     125     220     4CP     5CP     5CP     5CP     5CP     5CP <th>SED.         SCT WATER         WATER SED.         MATER MATER         MATER SED.         MATER MATER         MATER SED.         MATER MATER         SED.         WATER WATER         SED.         WATER WATER         SED.         WATER WATER         SED.         WATER WATER         SED.         WATER         SED.         SED.         WATER         SE</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th>****</th> <th></th> <th></th> <th></th> <th></th> <th></th>	SED.         SCT WATER         WATER SED.         MATER MATER         MATER SED.         MATER MATER         MATER SED.         MATER MATER         SED.         WATER WATER         SED.         WATER WATER         SED.         WATER WATER         SED.         WATER WATER         SED.         WATER         SED.         SED.         WATER         SE								****					
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	3 $2$ $2$ $1$ $12$ $280$ $1$ $12$ $280$ $1$ $12$ $214$ $1.0$ $43$ $27.4$ $1.0$ $43$ $27.4$ $1.0$ $43$ $27.4$ $1.0$ $43$ $27.4$ $1.0$ $43$ $27.4$ $1.0$ $43$ $27.4$ $1.0$ $43$ $27.4$ $1.0$ $23$ $362$ $73$ $33$ $362$ $73$ $33$ $362$ $73$ $33$ $362$ $73$ $33$ $362$ $73$ $33$ $362$ $73$ $33$ $362$ $213$ $33$ $362$ $213$ $33$ $362$ $213$ $33$ $362$ $213$ $33$ $362$ $213$ $33$ $362$ $216$ $46$ $31$ $31$ $22$ $31$ $392$ $216$ $31$ $392$ $216$ $31$ $312$ $212$ $312$ $129$ $312$ $129$ $312$ $129$ $129$ $129$ $129$ $129$ $129$ $129$ $129$ $129$ $129$					CP	RAT SED. 5CP	I OS WATER 4CP		SED. 5CP	Į	AVERAGE WATE 5CP		M/S
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				187.9	7.3	157.3	.22	.26	715	~~				~~	370
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# TABLE 7. STATION OPERATION CHARACTERISTICS

Station	Operation	PCP Treatment	Receiving Environment
I	export terminal	dip	saltwater
II	lumber mill	spray and dip	freshwater
III	lumber mill	pressure	freshwater
IV	lumber mill	spray	freshwater
v	formulator	-	freshwater
VI	lumber mill	dip	saltwater
VII	lumber mill	spray and on-line dip	saltwater
VIII	lumber mill	spray	saltwater
IX	lumber mill	spray	saltwater
	lumber mill	dip	saltwater
x	lumber mill	dip	saltwater
XI	lumber mill	spray	saltwater

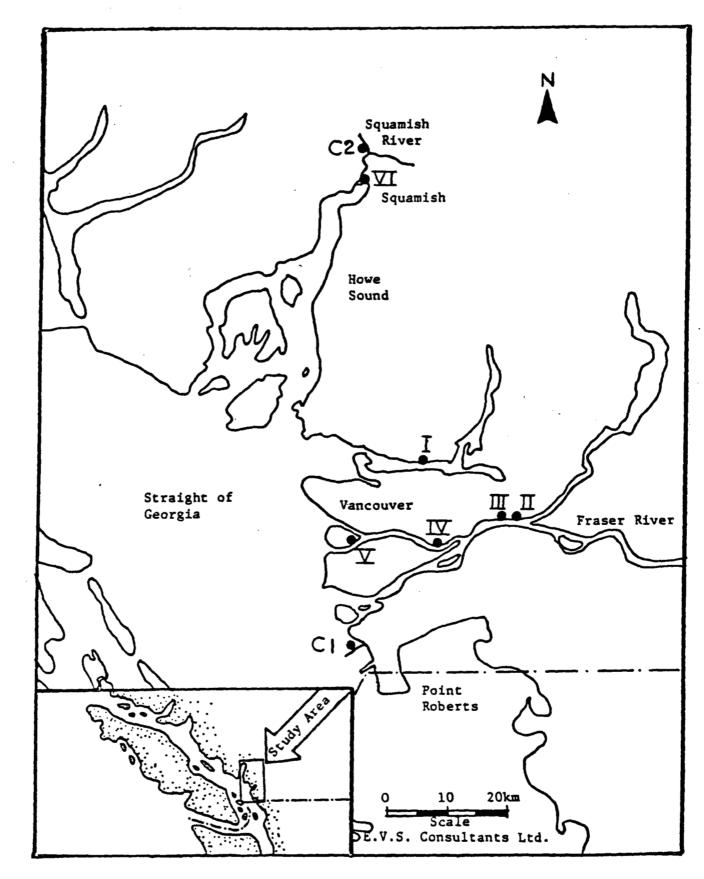
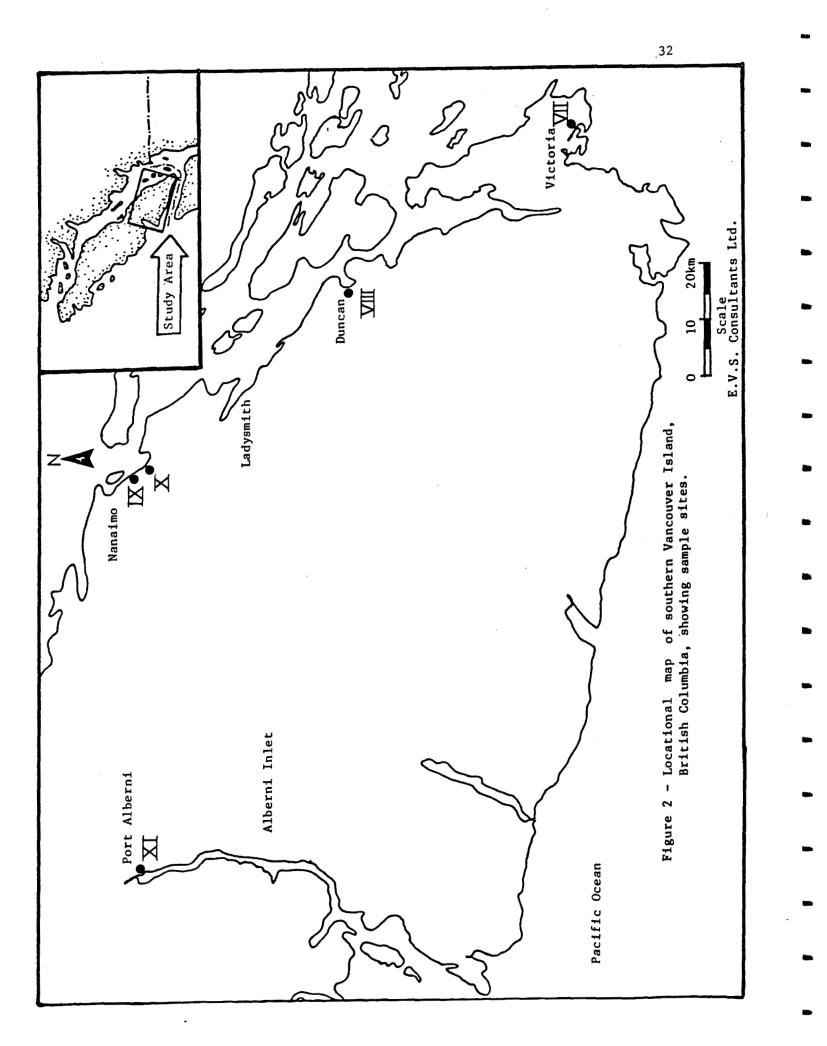


Figure 1 - Locational map of the Lower Mainland, British Columbia, showing sample sites.

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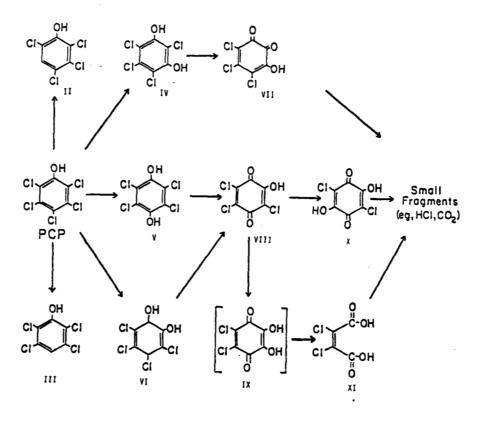


Figure 3. Proposed photolysis pathway for pentachlorophenol (PCP) (Wong and Crosby, 1978).

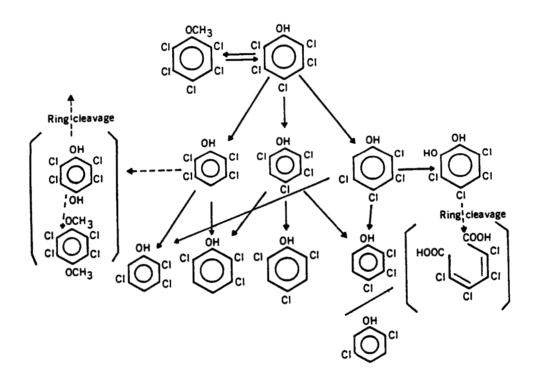


Figure 4. Proposed pathway of pentachlorophenol degradation in soil (Kaufmann, 1978).

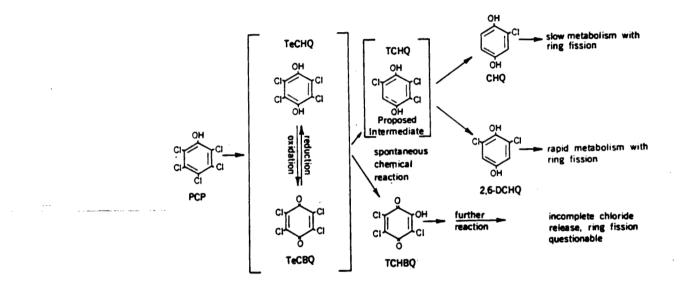


Figure 5.

e 5. Hypothetical pathway for the biodegradation of pentachlorophenol by the bacterial culture, KC-3 (Reiner <u>et al</u>, 1978).

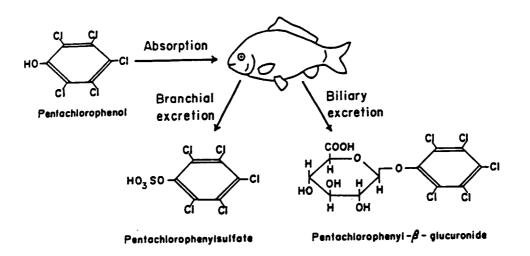


Figure 6. A schematic view of the major detoxification pathways for pentachlorophenol in fish (Kobayashi, 1978).

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## APPENDIX I

Locational maps showing sample sites and sample stations for sediments, effluents and biota.

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## TABLE

## KEY TO LABELS APPLIED TO SAMPLE SITES

<u>Site</u>	Location
C1	Roberts Bank (control site #1)
C2	Squamish River (control site #2)
I	Seaboard (Burrard Inlet)
II	Crown Zellerback (Fraser River)
III	Domtar (Fraser River)
IV	Canadian White Pine (Fraser River)
V	Later's Chemical (Fraser River)
VI	Empire Mills (Squamish)
VII	BCFP (Gorge Inlet, Victoria)
VIII	Doman's (Cowichan)
IX	Dorman, Cipa (Nanaimo)
X	Mayo (Nanaimo)
XI	Somass (Port Alberni) Alberni Pacific (Port Alberni)

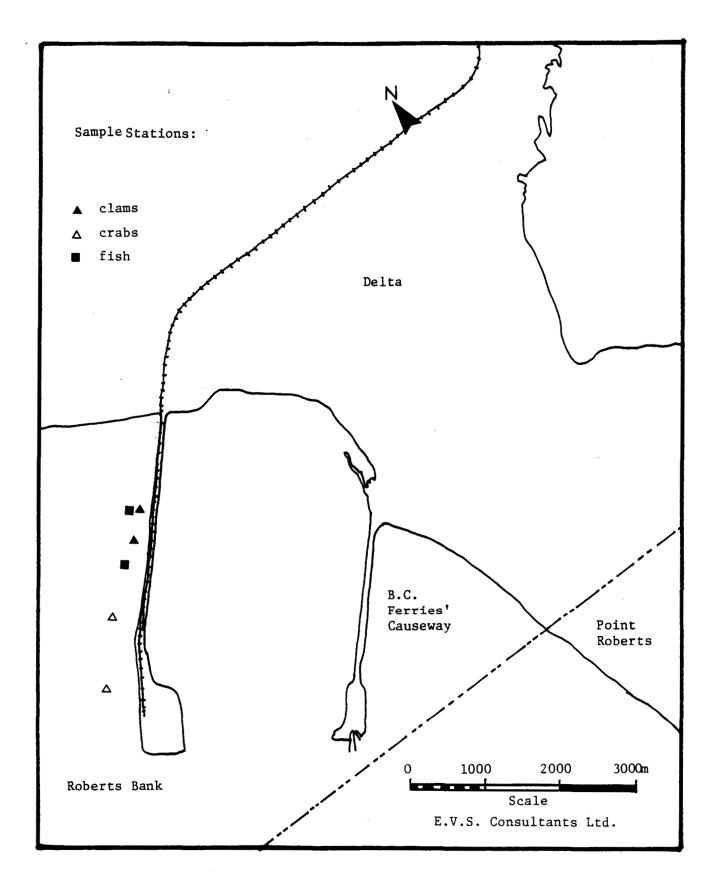


Figure 3 - Location of Site Cl on Roberts Bank showing sample stations for sediments and biota.

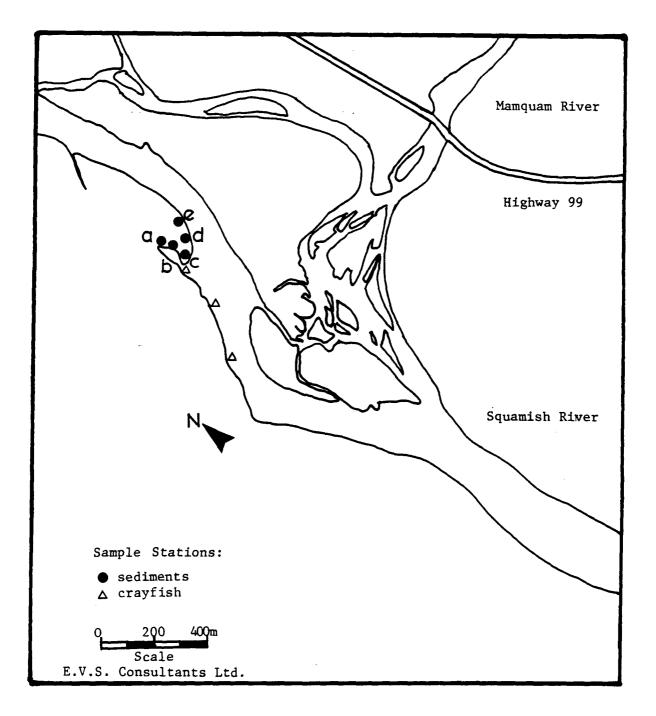


Figure 4 - Location of Site C2 on the Squamish River, showing sample stations for sediments and crayfish.

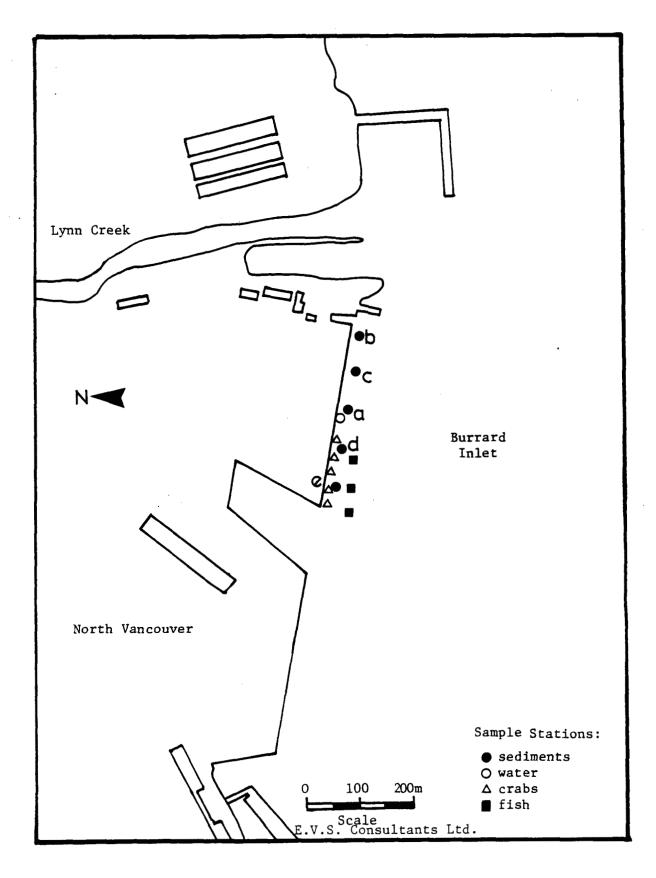


Figure 5 - Location of Site 1, North Vancouver, B.C., showing sample stations for sediments, water and biota.

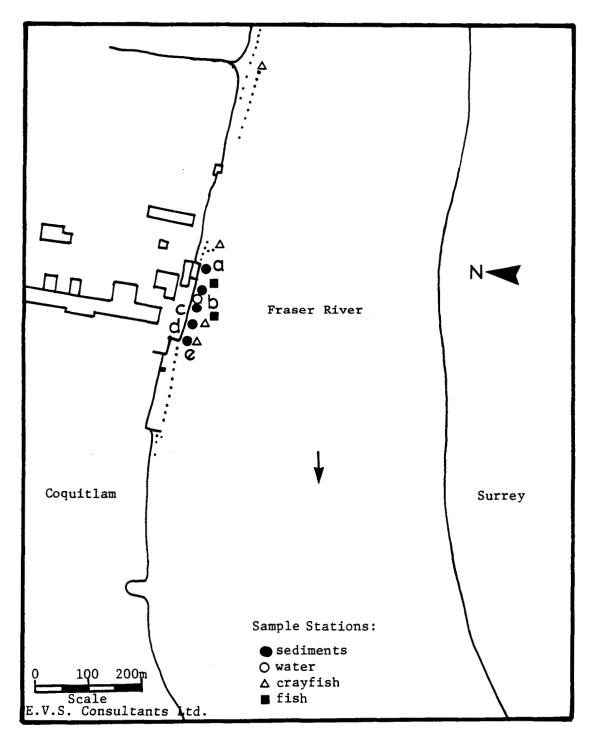


Figure 6 - Location of Site II on the Fraser River, Coquitlam, B.C., showing sample stations for sediments, water and biota.

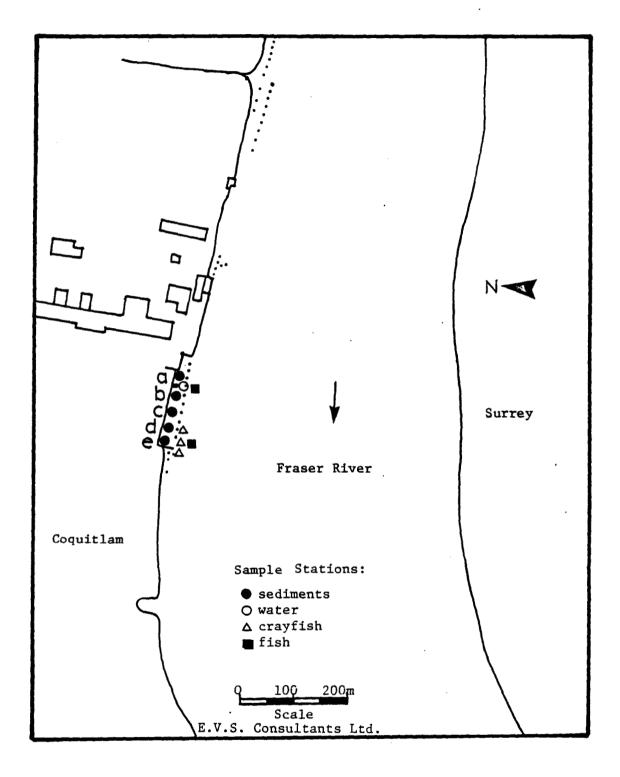


Figure 7 - Location of Site III on the Fraser River, Coquitlam, B.C., showing sample stations for sediments, water and biota.

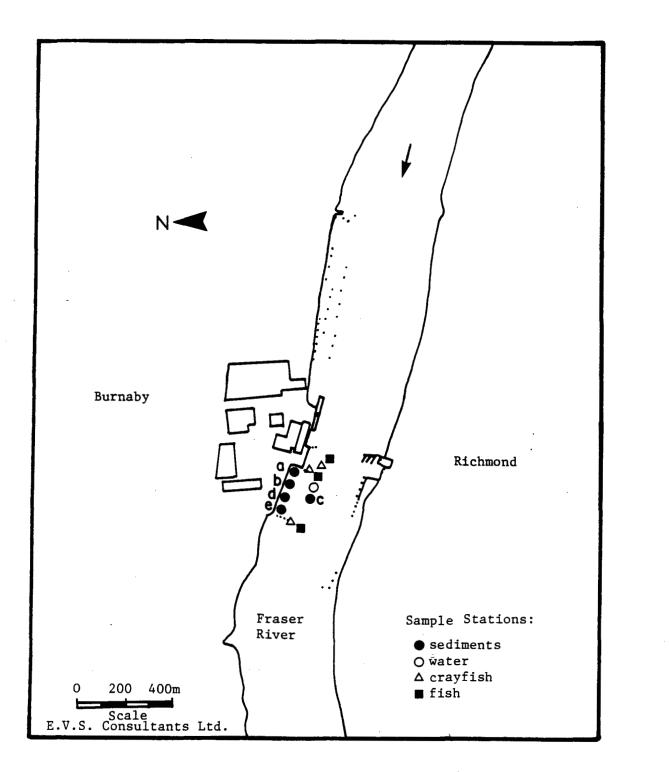


Figure 8 - Location of Site IV on the Fraser River, Burnaby, B.C., showing sample stations for sediments, water and biota.

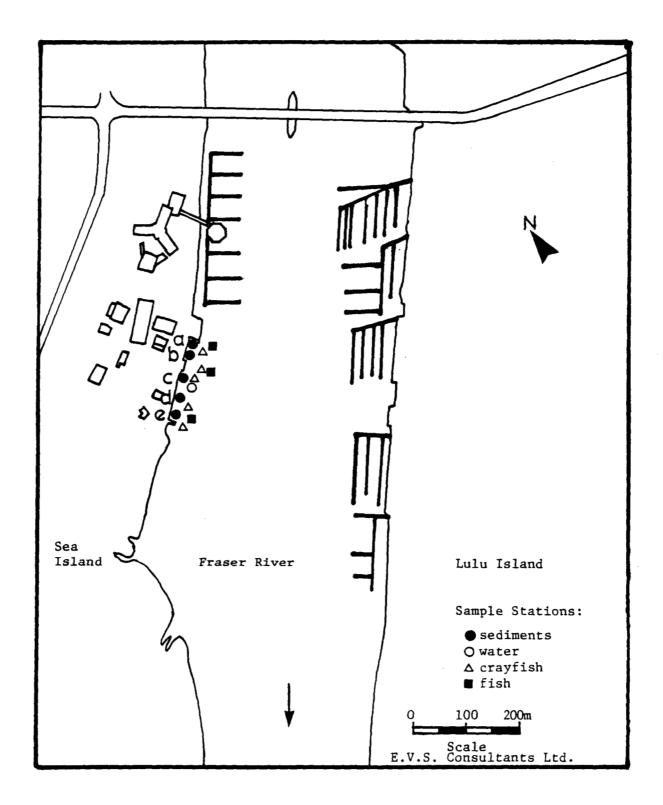


Figure 9 - Location of Site V on the Fraser River, Richmond, B.C., showing sample stations for sediments, water and biota.

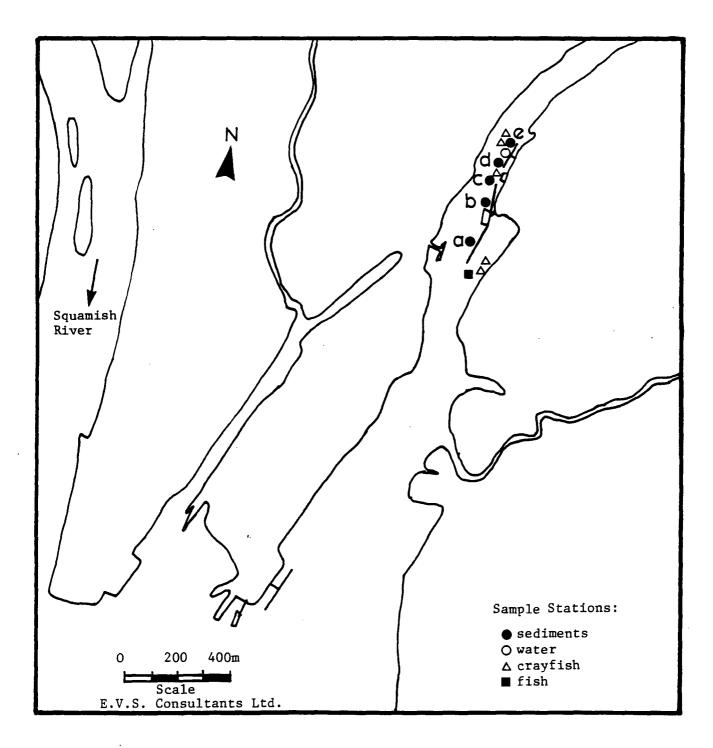


Figure 10 - Location of Site VI on the Squamish River delta, Squamish, B.C., showing sample stations for sediments, water and biota.

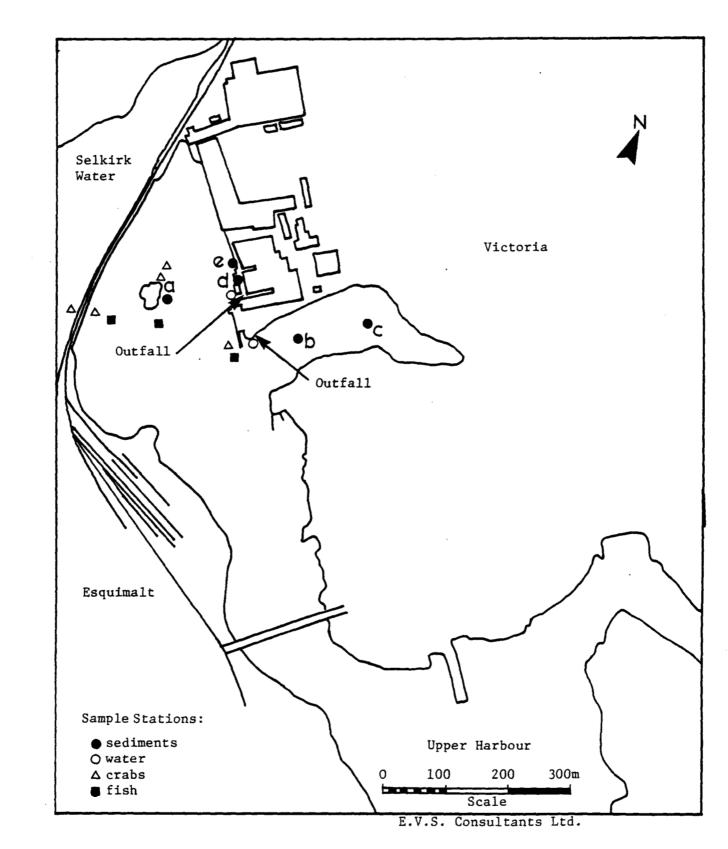
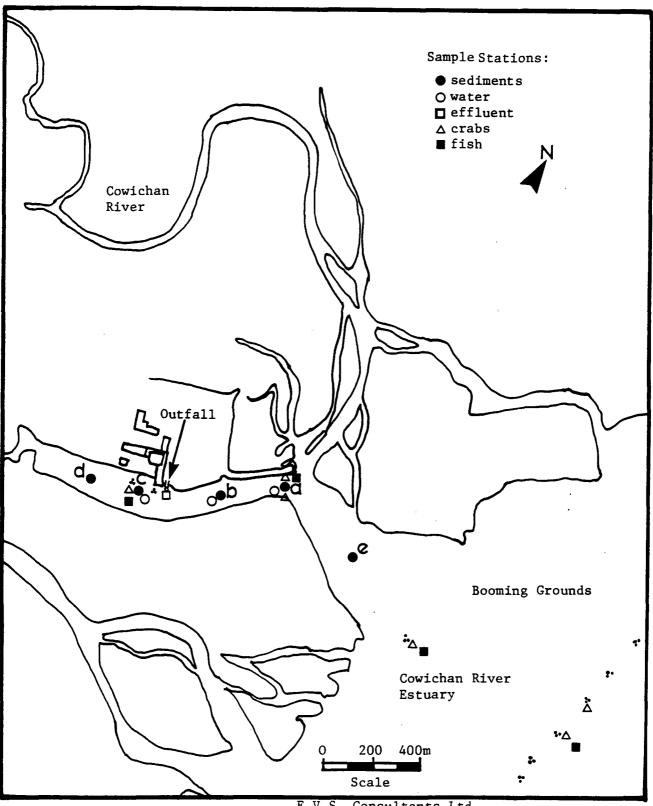


Figure 11 - Location of Site VII Victoria, B.C., showing sample stations for sediments, water and biota.



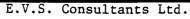


Figure 12 - Location of Site VIII at Cowichan Bay, B.C., showing sample stations for sediments, water, effluent and biota.

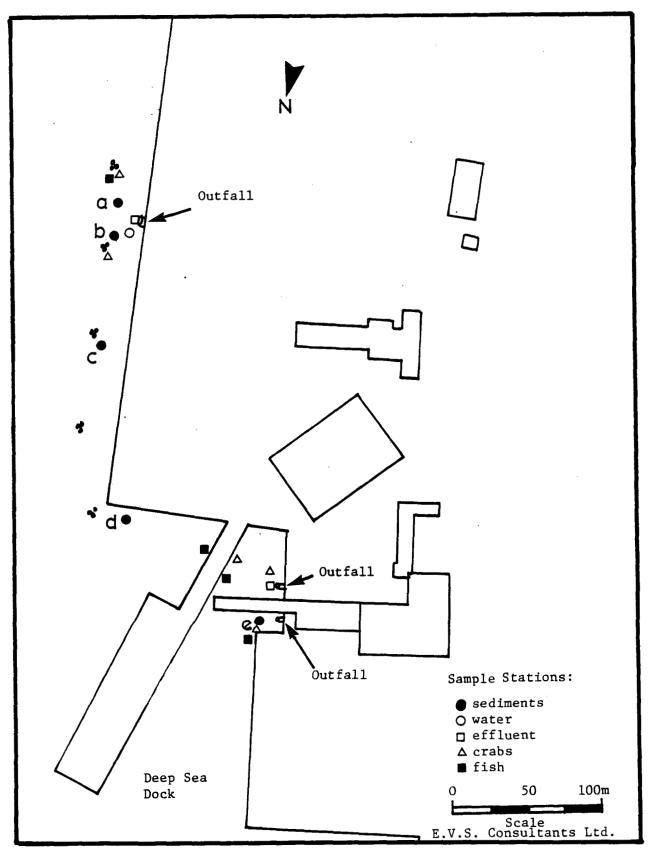


Figure 13 - Location of Site IX, Nanaimo, B.C., showing sample stations for sediments, water, effluent and biota.

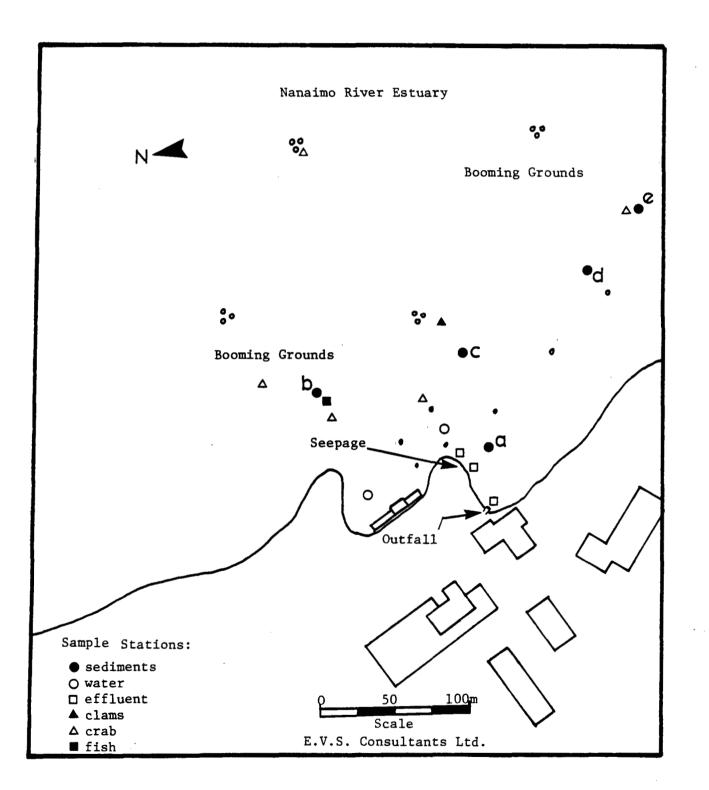


Figure 14 - Location of Site X, Nanaimo, B.C., showing sample stations for sediments, water, effluent and biota.

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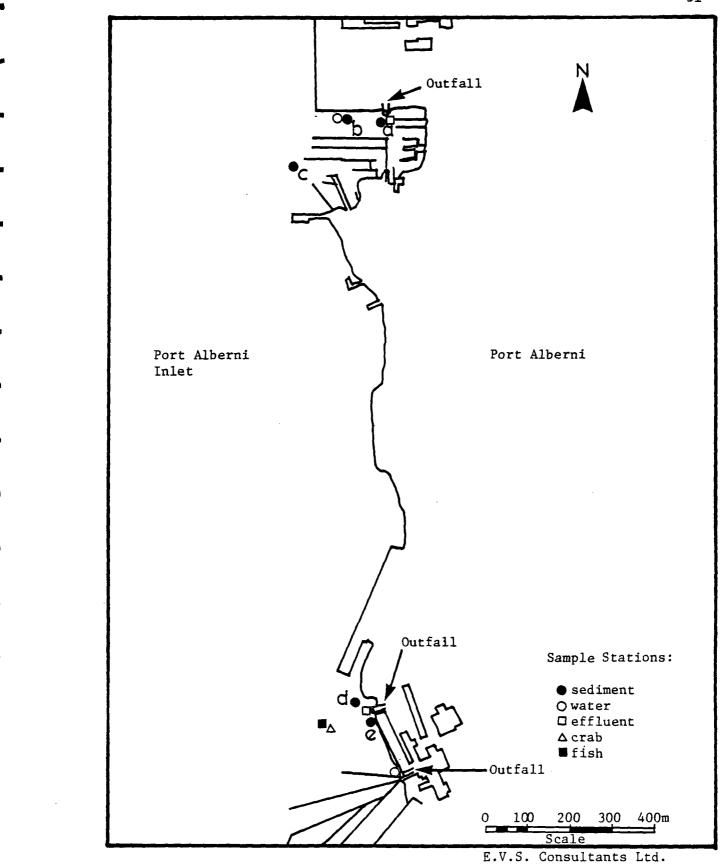


Figure 15 - Location of Site XI, Port Alberni, B.C., showing sample stations for sediments, water, effluent and biota.

## APPENDIX II

Results of replicate analyses for chlorophenols, chlorobenzenes, and pentachloroanisole in sediments, water and biological tissues.

## APPENDIX 2

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## Analytical Results:

1. Sediments

expressed as ppb (microgram per kilogram) on a dry weight basis.

2. Water/Effluent

expressed as ppb (microgram per liter) on an as received basis.

3. Tissue

expressed as ppb (microgram per kilogram) on an as received or wet weight basis.

## Limits of Quantitation

1.	chlorophenols:	sediment & tissue - 5 ppb
		water - 0.05 ppb
2.	chlorobenzenes:	sediment & tissue - 0.5 ppb
		water - 0.005 ppb
0		

3. pentachloroanisole: sediment & tissue - 0.5 ppb water - 0.005 ppb

#### Abbreviations used in the Following Tables

tr = present but below limit of quantitation

ND = not detected (approximately 1/4 of limit of quantitation)

UN DN DN	UN UN UN			Tetra- Tri Hexa- Penta-
		-		Penta- Tetra-
	tus armatus - muscle (N=10) ND tus armatus - liver (n=10) ND		 	Tissue       (µg kg <sup>-1</sup> wet wt)         Tissue       (µg kg <sup>-1</sup> wet wt)         Cancer magister - chelaped muscle       NI         Cancer magister - chelaped muscle       NI         Leptocottus armatus - muscle (N=10)       NI         Leptocottus armatus - liver (n=10)       NI

Pentachloro anisole 55 Q Tetra-Q (ppb) Chlorobenzenes Penta-QN PARAMETERS Hexa-g Tri Ð Chlorophenols Tetra-Penta-g Sediment (µg kg<sup>-1</sup> dry wt) SAMPLE IDENTIFICATION SAMPLE STATION C2 Water (µg kg<sup>-1</sup>) و م د ج ه

SAMPLE SITE 1							
SAMPLE IDENTIFICATION			PAR	AMETER	S (ppb)		
WWW HE TOURING TON	Ch10	ch1oropheno1s			Chlorobenzenes	zenes	Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
Sediment (µg kg- <sup>1</sup> dry wt)							
a1 2	240 90	280	QN	t t r	Q Q	29	1.5
b1 2	10 ND	ON N	QN NN			D Q	0 QN
c1 2	QN	QQ		Q Q		QN QN	tr tr
d1 2	QQ	QN	200	tr ND			t t
e1 2	QQ	QN NN	QN	tr ND			ND tr
Water (µg L <sup>-1</sup> )	0.75	1.3	- N	QN	QN	QN	tr
Tissue (µg kg- <sup>1</sup> wet wt)		· · · ·					
<b>a</b> 1	tr	9	ON .	tr	DN	QN	QN
Cancer productus -miccle (n=/)	24	69	ND	15	QN	QN	8.3
(N=10) Algorithe (N=10)	tr	9	ND	ND	QN	UN	Ŭ

			PARA	METERS	(ddd)		
SAMPLE IDENTIFICATION	Ch1 or	orophenols			Chlorobenzenes		Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
Sediment (µg kg <sup>-1</sup> dry wt)							
a1 2	70 30	30	Q Q N	<u>n</u> n	QN	QN	tr
b1 2	40 30	40 20	QN	QN	ON ND	QN	tr
c1 2	20	30	Q Q	QNQ	QN	QN	QN
d1 2	70	20	QN	QNQ	QN	QN	QNN
e1 2	01	20	QN	QN	QN	QN	QNN
Water (µg L <sup>-1</sup> )	0.28	0.10	ON N	ND	ND	DN	tr
Tissue (µg kg <sup>-1</sup> wet wt)							
Pacifastacus sp. pincer muscle (n=7)	QN	QN	QN	ND	QN	QN	QN
Cottus asper - muscle (n=7)	40	100	QN	DN	QN	DN	QN
Cottus asper - liver (n=7)	140	68	ND	8	QN	DN	tr
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SAMPLE SITE III							
S AMDI E TRENTIELEATION			PARA	METER	S (ppb)		
	Chlor	18			Chlorobenzenes	tenes	Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
Sediment (µg kg <sup>-1</sup> dry wt)							
a1 2	20 10	30 30	10 tr	QN	QQ	QN	QN
b1 2	20 30	50 40	QN	ND tr	O O N	QN	Q O
c1 2	7 tr	9 30	QN	tr ND	QN NN N	QN QN	tr d
d1 2	ND tr	0 00	QN QN	QN QN	QN	QN	5 Q."
el 2	tr t	8	QN	QN	QN	QN	) Qr
Water (µg L <sup>-1</sup> )	0.25	1.0	ND	QN	DN N	QN QN	/ DN
Tissue (µg kg <sup>-1</sup> wet wt)							
Pacifastacus sp. pincer muscle(n=10)	ND	tr	QN	tr	Q	QN	CN
Cottus asper - muscle (n=2)	14	80	QN	QN	QN	QN	2 ×
Cottus asper - liver (n=2)	600	320	QN	ŨN	QN	QN	tr c

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			PARA	AMETERS	(dqd)		
SAMPLE IDENTIFICATION	Ch1	orophenols			Chlorobenzenes	enes	Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
Sediment (µg kg <sup>-1</sup> dry wt)							
a1 2	QN	17 19	Q Q Q	QN	QN N N	QN	14 2
b1 2	32 tr	10	Q N N N	1.4			13 - 2
c1 2	t r	15	QN	1.3 0.9	Q Q	QQ	51 51 44
d1 2	32 0	90 23	Q Q N	l.9 tr	Q Q N N	QQN	100 14
el 2	t t r	tr	QQN	QN	QQ		tt
Water (µg L <sup>-1</sup> )	t.	0.30	ON	QN	DN	QN	QN
Tissue (µg kg <sup>-1</sup> wet wt)							
	t	t	QN	Q	ND	QN	QN
Leptrocottus armatus-muscle (n=6)	tr	tr	QN	QN	QN	ND	ND
Cottin anno	100	74	QN	ŊŊ	QN	QN	ND
-liver	/4	10	QN	QN	QN	ND	QN
united asper	300	96	QN	QN	QN	ND	QN

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SAMPLE SITE V							
			PARA	METERS	(dqq)		
SAMPLE IDENIFICATION	Chlor	Chlorophenols			Chlorobenzenes	enes	Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
Sediment (µg kg <sup>-1</sup> dry wt)							
al 2	tr	თ.თ.	QN	t ND	QQ	QN	nn N
b1 2	tr t	11	QN	QN	QN QN	QQ	992
c1 2	tr	tr	QN QN	QN	ON QN	QN	QQ
d1 2	tr	12 8	QN CN	QN ND	QN	QN QN	QQ
e1 2	tr	15 14	QN	QN	QN	QN	QN QN
Water (µg L <sup>-1</sup> )	tr	0.20	QN	QN	QN	QN	0.006
Tissue (µg kg <sup>-1</sup> wet wt)							
Cottus asper -muscle (n=5)	12	2 2	QN	QN	QN	ÛN	C N
Cottus asper -liver (n=5)	tr	82	QN	QN	QN	QN QN	
41	5	80	QN	UN	ND	QN	DN D
veptocottus armatus-liver (n=19)	470	480	QN	ŊŊ	QN	DN	QN

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SAMPLE SITE VI							
			PARA	METERS	(dqq)		
SAMPLE IDENTIFICATION		Chlorophenols			Chlorobenzenes	enes	Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
Sediment (µg kg <sup>-1</sup> dry wt)							-
a1 2	57 58	78 76	24 19	QN	QN	QN	QN
b1 2	80 58	220 79	150 140	QN	QN	D D N	ND t
c1 2	27 14	79 83	35 36	QN	ON N	QN	Lt.
d1 2	16 58	46 68	5 ]5	Q N N N	QN	QN	
e1 2	76 84	78 180	100 40	ON N N	QN	QN QN	QN QN
Water (µg L <sup>-1</sup> )	2.4	5.2	ŊD	ON	tr	QN	0.020
Tissue (µg kg <sup>-1</sup> wet wt)							
Leptocottus armatus -muscle (n=4)	tr	6	ND	ND	DN	QN	QN
Leptocottus armatus -liver (n=4)	35	63	ND	54	ND	QN	tr
Cancer magister-chelaped muscle(n=10)	DN	8	QN	tr	DN	DN	QN
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SAMPLE SITE VII							
			PARI	AMETER	S (ppb)		
SAMPLE IDENTIFICATION	Chiol	Chiorophenols			Chlorobenzenes	zenes	Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
Sediment (µg kg <sup>-1</sup> dry wt)							
a1 2	tr 14	<sup>6</sup> 50	26 34	QQ	QN	QN ND	QN
b1 2	76 59	120	140 160	ND 2.6	ND 1.4	ND 2.1	1.6 6.6
c1 2	56 45	68 58	110	3.8 2.4	2.4 1.6	1.8	4.0
d1 2	160	140 96	160 tr	tr	4.2 3.1	QN	5.2 7.6
e1 2	500	1600 480	tr 170	21 DN	3.0	20 1.8	tr 6.2
Water (µg L <sup>-1</sup> )	QN	ND	- UN	ND	QN	QN	0,005
Tissue (µg kg <sup>-1</sup> wet wt)							
Cancer magister -chelaped muscle(n=6	6) tr	tr	QN	DN	QN	QN	QN
Cancer productus-chelaped muscle(n=1	2	tr	QN	QN	QN	QN	QN
Leptocottus armatus - muscle (n=3)		8	QN	QN	QN	QN	tr
Leptocottus armatus - liver (n=3)	_	470	DN	5.2	QN	14	20

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P A R A M         Chiorophenols         P A R A M           Chiorophenols         Chiorophenols         ND           Penta-         Tetra-         Tri-           ND         20         ND           ND         20         ND           tr         17         ND           tr         13         ND           tr         11         ND           tr         11         ND           53         20         ND           tr         17         ND           tr         11         ND           tr         11         ND           tr         17         ND           0.069         ND         ND           tr         0.069         ND           atr         0.069         ND           b         1.2         ND           atr         0.069         ND           b         1.2         ND	SAMPLE SITE VIII							
IDENTIFICATIONChiorophenols(ug kg <sup>-1</sup> dry wt)Penta-Tetra-(ug kg <sup>-1</sup> dry wt)ND20ND17NDtr17NDtr19NDtr11NDtr11NDtr11NDtr11NDtr11NDtr11NDtr11NDtr11NDtr11NDtr11NDtr17NDtr17NDtr17NDtr17NDtr17NDtr17NDtr12NDtr0.09NDtr1.2NDg kg <sup>-1</sup> wet wt)16tr1620tr1620tr1620				A R	Σ	(dqq)		
( $\mu g \ kg^{-1} \ dry \ wt$ )       Penta-       Tetra-       Tri-         ( $\mu g \ kg^{-1} \ dry \ wt$ )       ND       20       ND         ND       17       ND       20       ND         tr       17       ND       17       ND         tr       13       ND       17       ND         tr       13       ND       17       ND         tr       11       ND       75       44       ND         tr       11       ND       75       44       ND         tr       11       ND       75       44       ND         tr       17       ND       17       ND       ND         tr       17       11       ND       17       ND         g kg^{-1}       Met wt)       0.56       1.2       ND       ND         g/ister - chelaped muscle(n=8)       16       20       ND       ND	SAMPLE IDENTIFICATION	Chlor	ophenols			Chlorobenzenes	cenes	Pentach loro
$ (\mu g \ kg^{-1} \ dry \ wt) $ $ ND 20 ND 18 ND 18 ND 17 ND$		Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
$ \begin{array}{cccccccc} & & & & & & & & & & & & & & & $	(µg kg <sup>-1</sup>							
tr 17 ND tr 18 ND tr 19 ND tr 11 ND 75 44 ND 75 44 ND 17 ND	a1 2	QN QN	20 18	Q Q Q N	QN NN	DN ND	Q Q	ON ON
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	b1 2	tr	17 18	Q Q Q N	QN	DN ND	QQ	ON N
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	c1 2	tr	61	Q N Q N	QN	QN	QN	QN NN
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	d1 2	tr 75	11 44	ON ON	QN NN	QN ND	QQ	ON N
$f_{1} L^{-1}$ ) tr 0.09 ND 0.56 1.2 ND 0.56 1.2 ND ND ND ND ND ND ND ND ND ND ND ND ND N	e1 2	53 tr	20	ON ON	QQ	<u>n</u> n	QN	0N 1.9
If tr 0.09 ND 0.56 1.2 ND ND 0.56 1.2 ND ND ND 0.56 1.2 ND ND ND ND 0.56 1.2 ND ND ND 00000000000000000000000000000	Water (µg L <sup>-1</sup> )							
=8) 16 20	Water Effluent	tr 0.56	0.09	QN N	QN	Q Q N	QQ	QN
=8) 16 20								
	Cancer magister - chelaped muscle(n		20	QN	QN	· DN	QN	QN
tr 10	Leptocottus armatus - muscle (n=10)		0[	QN	DN	QN	QN	QN
			29	ND	QN	QN	QN	QN

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. SAMPLE SITE IX							
SAMPLE TDENTIETCATTOM			PARA	METERS	(ddd)		
	Ch107	Chlorophenols			Chlorobenzenes	zenes	Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
Sediment (µg kg <sup>-1</sup> dry wt)							
al 2	tr 77	15 46	QN	QN	2.5	1.8	17 6.3
b1 2	26 29	22	QN	QN	3 ND	1.8 tr	4.4 5.2
c1 2	tr 34	20	QN	QN	QN QN	t t	1.7
d1 2	49 170	100 290	QN	QN QN	QN	QN	2.2
e1 2	ND 24	66 59		QN QN	QN	QN	QN
Water (µg L <sup>-1</sup> ) Water Effluent	tr 225	0.06 530	QN N	t t	Q N Q N	QN	QQ
<u>Tissue</u> (µg kg <sup>-1</sup> wet wt) Cancer magister-chelaped muscle(n=10)	ţ	6.6	QN	ŊŊ	D DN		2. 2
							2

			PARA	METER	S (ppb)		
SAMPLE IDENTIFICATION		Chlorophenols			Chlorobenzenes	zenes	Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
<u>Sediment</u> (µg kg <sup>-1</sup> dry wt)					-		
a1 2	67 27	71 50	QN	Q N N N	Q N N	QN	
b1 2	tr	e 01	ON ND	QN			tr g
c1 2	tr ND	E 6	QN	QN	Q Q N	QQN	tr tr
d1 2	tr ND	24 18	QN	QN	QQ	QN	0.5
e1 2	ON OI	14	QN	QN QN	QQ	QN	1.2
<u>Water</u> (µg L <sup>-1</sup> ) Water Effluent	3.1 ND	3.3	QQ	QN	QQ	QN	0.090
Tissue (µg kg <sup>-1</sup> wet wt)							
<i>Macoma</i> sp. tissue (n=340)	ND	12	QN	QN	QN	QN	Ŋ
Leptocottus armatus-muscle (n=7)		8	QN	ND	Ņ	QN	QN
Leptocottus armatus-liver (n=7) Cancer Magister-chelaped muscle(n=2)	2100 17	1600	Q Q	QN	Q Q	QN N	QN

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DAMPLE DILE XI							
SAMPLE THENTIFICATION			PARI	AMETERS	(ppb)		
	Chior	Chlorophenols			Chlorobenzenes	tenes	Pentachloro
	Penta-	Tetra-	Tri-	Hexa-	Penta-	Tetra-	anisole
Sediment (µg kg- <sup>1</sup> )						5	
al 2	42 130	120	6	ND 2.3	- 25 4.4	<del>م</del> در	1.9
b1 2	20 46	130	20	23 39	78 12	340 270	34
c1 2	0 UN	98 54	]4 96	25 tr	QN	tr	9.6 4
d1 2	100 590	140 58	27 14	tr	QN	tr	6.1
e1 2	490 390	360 370	80 85	tr	QN	tr	14
Water (µg L <sup>-1</sup> )							
Water	7.3	0.22	QN	0.012	0.019	210.0	G
Effluent	2760	8270	QN	0.078	0 050		
Tissue (µg kg- <sup>1</sup> wet wt)					0000	0.42	0.024
Leptocottus armatus_muscle (n=1)	84	34	ŪN	QN	ŰN	ÛN	2
Leptocottus armatus-liver (n=2)	640	430	QN	QN	e Q	QN ON	
Cancer magister chelaped muscle(n=2)	α	\$	4				

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# APPENDIX III

Log of field notes for the lower mainland and Vancouver Island Survey.

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# APPENDIX . LOG OF FIELD NOTES FOR THE LOWER MAINLAND AND VANCOUVER ISLAND

#### I. FIELD NOTES - LOWER MAINLAND

. Point Roberts Control Site

Friday, October 20, 1978 Site C1

Cave and Munday, using SCUBA, obtained crab along the causeway running transects parallel to the shoreline. Crab caught at the edges and within eel grass beds. 10 *Cancer magister* obtained.

Wednesday, October 25, 1978

Cave and Munday arrived at the Point Roberts Bank coal port causeway at 0930 h after mobilizing equipment at the laboratory. Sediment samples were taken comprising sample sites a-e. Only one sediment sample was taken per site, therefore 5 samples were submitted for analyses. The following species were collected:

> 10 Platichthys stellatus (Starry flounder) 530 Macoma sp. (clams)

. Seaboard Terminals (Burrard Inlet)

Monday/Tuesday, November 6/7, 1978 Site I

On the morning of Nov. 6, crab/prawn traps and longlines were set alongside the dock at this facility. A discharge pipe was located centrally along the front of the dock. This pipe receives surface drainage from the storage yard. However, no discharge was noted at the time of sampling. A surface water sample was taken. Sediments were collected in replicate at evenly spaced intervals along the front of the facility. A total of 10 sediment samples were collected. The following species and numbers were collected:

> 10 Cancer productus (crab) 7 Leptocottus armatus (staghorn sculpin)

. Crown Zellerbach (Fraser River)

Wednesday/Thursday, November 8/9, 1978, Site III

Cave and Munday arrived at this facility at approx. 0900 h and commenced sampling. Storm sewers were noted at several locations. However, none were suitable for sampling since they did receive plant effluent. A surface water sample was taken near one of the storm sewers. The following species and numbers were collected:

> 7 Pacifastacus sp. (crayfish) 7 Cottus asper (prickly sculpin)

#### . Domtar (Fraser River)

Wednesday/Thursday, November 8/9, 1978, Site III

This facility was sampled during the same time interval as that of Station II. No discernable effluent or surface water discharge pipes were observed. A surface water sample was taken in front of the preservation area at the log haul-out area. The following species and numbers were collected:

10 Pacifactacus sp. (crayfish)
2 Cottus asper (prickly sculpin)

## . Later's Chemical (Fraser River)

Friday, November 10, 1978, Site V

Cave and Munday arrived at this sample station at 0915 h and after launching the boat, traps and longlines were set. Sediments were taken in replicate at 5 sites evenly spaced alongside the facility. No discharge pipes were noted and a surface water sample was taken. The following species and numbers were caught:

> 19 Leptocottus armatus (staghorn sculpin) 5 Cottus asper (prickly sculpin)

. Canadian White Pine (Fraser River)

Monday, November 20, 1978 Site IV

Cave and Coustalin left E.V.S. at 0800 h and proceeded to CWP for sampling. Checked in at mill, J. Pillsbury previously contacted. Proceeded with sampling by setting crab/prawn traps and longlines in a.m. Afternoon spent collecting 10 sediment samples along the dock and 1 surface water sample. No preservation activity evident at dockyard adjacent to sampling area. Areas used for loading of cut lumber to barges with storage area in this vicinity. Once the sediments were collected trawls made for benthos proved unsuccessful in isolating *Macoma*. At days end the following species were caught:

- 2 Pacifactacus sp. (crayfish)
- 6 Leptocottus armatus (staghorn sculpin)
- 4 Cottus asper (prickly sculpin)

. Empire Mills (Squamish)

Monday, November 27, 1978, Site VI

Cave and Munday departed North Vancouver 0900 h to Squamish. After checking into hotel, proceeded to Empire Mills and established contact with Mr. Seimens, Mill Manager. After brief discussions with Mr. Seimens, we made a brief tour of the mill to choose sampling locations. Crab/prawn traps were set along with one longline. Following lunch, ten sediment samples were taken on the docks on Empire Mills foreshore. In the vicinity of sawdust and chip barges the bottom was littered with wood waste making sampling very difficult. Sediment which was obtained proved to be black and anoxic. An effluent sample was taken during the course of sediment sampling following which the crab traps and longlines were checked, rebaited and replaced. Due to the anoxic nature of the sediments along the channel, it was deemed senseless to attempt collection of benthos. Just prior to dark (1600 h) the longline and crab traps were recovered yielding the following:

- 10 Cancer magister (crab)
- 4 Leptocottus armatus (staghorn sculpin)
- 1 Cottus sp. (species unidentified)

. Squamish River, Control Site Tuesday, November 28, 1978, Site C2

Having made a brief reconnaissance of the Squamish River with respect to boat launching facilities on the previous day the boat was lugged down to the river between 9 and 10 o'clock and loaded. We ran upstream to above the confluence of the Mamquam and Squamish rivers and placed our crayfish traps. Five sediment samples were collected. Large numbers of chum salmon were observed to be migrating upstream during this period. At approximately 1430 h the crayfish traps were recovered and yielded no crayfish. At approximately 4 o'clock, following unloading of the boat and packing of equipment, we returned to the lab, North Vancouver.

#### II. FIELD NOTES - VANCOUVER ISLAND

. B.C. Forest Products Ltd. (Victoria)

Tuesday, November 14, 1978, Site VII

Left E.V.S. at 9 a.m. and caught 10 a.m. ferry to Victoria. Met Mr. J.W. Warr (P. Eng.), Mill Manager, of B.C. Forest Products Ltd., Victoria, located at Selkirk Water. Waited for approval to commence sampling. Approval received 5 p.m. In evening, benthic samples attempted. Plenty of clam shells, very few live ones. No *Macoma* sp., too sandy/gravelly. Out of approximately 15 sediment screenings obtained only 2 live clams. Set crab traps and longlines. Mr. Warr suggested we check PCB records since they routinely sample the mill.

Wednesday, November 15, 1978

Mr. Jack Clark showed us (via Mr. D. Marshall, Production Manager) around the mill. PCP bought as a 24% solution, diluted as 50:1. Used at a rate of 250 gal/day as diluted. PCP used at a rate of \$45,000 per annum. Greenchain has diptank arrangement, as does the timberdeck. Spray boxes - used in planer mill. Surface drains shown near PCP treatment areas.

Sewer locations and hookups not exactly known. However, two outfall areas shown, one by the pipeshop, the other by log sort/ booming area, beneath pilings. Latter discharge impossible to get to due to pilings and other obstructions. Mr. Clark felt that a lot of the drainage water from the mill site was going directly to the Victoria sewage treatment plant and that the 2 outfalls may simply contain coolant water. Pulled traps and lines and the following species and numbers were collected:

- 7 Cancer magister (crabs)
- 11 Cancer productus (crabs)
- 3 Leptocottus armatus (staghorn sculpin)

Sediment sample - attempted to get sediment samples by outfall by pipeshop. No sample obtainable due to bark debris and rock. Therefore, had to move to middle of channel to obtain a sample. Sediments at sample site "d" were taken behind J. Redikopp's office (log-sort) near hidden outfall. Adjacent to railway tracks, sediments from site "e" were sampled to assess seepage from mill yard.

Took a composite water sample near the pipeshop area outfall and by sediment sample site "d". The former outfall not visible due to high tides. Drove to Cowichan Bay/Duncan late that evening.

# . Doman Forest Products (Cowichan Bay)

Thursday, November 16, 1978, Site VIII

Mr. Warrenden not in. Mr. Wes Sheard showed us around the plant -PCP treatment on greenchain and planer mill. All are sprayers (3 units), one of which has not been in operation for a while. No signs of floordrains in vicinity of units. All units well containerized. Deep concrete wells retain any spillage. Outfalls shown on attached map. Two outfalls drain at or are near preservation areas. One was found; the other, below the jackladder, was not visible due to high water and wood debris. Mr. Sheard said it was somewhere down there. Other outfalls were not flowing. With traps caught the following:

- 8 Cancer magister (crabs)
- 15 Leptocottus armatus (staghorn sculpin) 3 Crangon sp. (shrimp)

Dredge used to sample intertidal areas outside the booming ground. After 1 1/2 h of dredging only 12 *Macoma* obtained. Sediments difficult to obtain due to bark debris. Both effluent and surface water sample obtained.

## . CIPA Lumber and G.W. Dorman's Ltd. (Nanaimo)

#### Friday, November 17, 1978, Site IX

In morning, approached contacts at CIPA, Dorman's and also Mayo (sampling planned for Saturday). At CIPA met Al Hopkins (Supervisor) and had one of his assistants show us the mill site. Has sprayer systems for the application of preservative (greenchain). Drainage systems shown. Due to rain, outfall was flowing well and effluent sample taken (composited with that of the outfall off the large Harbour Commission lumber storage yard). Both effluents very silty. On the N.H.C. assembly wharf map supplied by D. Wilson a storm drain was indicated to the <u>north</u> of the jackladder. However, the storm drain outfall is actually located to the south of the ladder. The outfall indicated by Wilson receives water from cooling systems within the plant.

Obtained approval from G.W. Dorman's Ltd. from Mr. Dorman himself. Spillage was conceivable getting to the outfall of the Harbour Commission storage yard from the Dorman's site.

Obtained approval and instructions from Mr. Hilton for Mayo.

Set traps and longlines at CIPA - Dorman before 10 a.m. Sediments taken on the north side of the jack-ladder (sample site "e") *C. magister*, *C. productus* and *Cymatogaster aggregata* (shiner perch). Also took a sample of *Mytilus edulis* from pilings, as well as *Crassostrea gigas*. Hooks on longlines were picked clean of bait by crab and did not catch any fish. The following numbers were caught:

6 Cancer productus (crab)

13 Cancer magister (crab)

50 Cymatogaster aggregata (shiner perch)

20 Mytilus edulis (mussel)

4 Crassostrea gigas (oyster)

No clams were obtainable. Both a composite surface water sample and a composite effluent sample were taken.

. Mayo Forest Products Ltd.

Saturday, November 18, 1978, Site X

After picking up longlines at CIPA - Dorman site (used worms) proceeded to the Mayo site, adjacent to the booming ground in the Nanaimo River estuary. Very shallow area adjacent to study site. Not very suitable for *Cancer* sp. Traps and longlines put in place at 9 a.m. Because of shallow depth one crab trap was placed approx. 1 km from the site to obtain deep enough water. The following species and numbers were collected:

- 2 Cancer magister (crab)
- 20 Hemigrapsus nudus (crab)
- 7 Leptocottus armatus (staghorn sculpin)
- 2 Ammodytes hexapterus (sandlance)
- 1 Apodichthys flavidus (gunnel)
- 1 Platichthys stellatus (Starry flounder)

A trap located near the dozer-dock caught the last 4 species and, in addition, *H. nudus*. 350 *Macoma* plus approx. 10 other clams were obtained from a sandbar 200 m east of the study site.

Effluent samples were composited from 2 seepage areas immediately south of the light-tower and from an outfall (pipe) delivering a darkly stained effluent. In addition, a surface water sample was taken. Placement of booms impaired sample collection to some extent. Heavy deposits of bark and wood debris by the dozer dock prevented us from obtaining proper sediment samples in that area. No fish were noted at any time in the study area other than a number of salmon carcasses (coho and chinook).

Drove to Port Alberni that evening.

. Alberni Pacific Division and Somass Division, MacMillan Bloedel Ltd., Port Alberni

### Sunday, November 19, 1978, Site XI

Contacted maintenance personnel (Dave Clements) at A.P.D. via R. Wiltse and was shown preservative areas and points of effluent discharge. Have sprayer systems for the application of PCP. Effluent discharge adjacent (east site) to the dozer dock not visible due to tide level and presence of pilings below the dock. Therefore, a surface water sample was taken as close to the discharge as possible as well as from surface waters near the Somass Div. A large and accessible 1.5 m diameter culvert was sampled in addition. A sample from this latter culvert was composited with that of a sample of outfall effluent at the Somass Division flowing into the fisherman's docks. This effluent collected surface drainage from areas adjacent to the three greenchains.

Traps and longlines were placed in several strategic locations. Only the trap located near the barge 80 m offshore the A.P.D. wharf caught biota. Sediments proved biologically unproductive black ooze, sulphurous in odor with wood wastes at all sample sites. Species and numbers cuaght were:

> 2 small Cancer magister (crab) 1 small Leptocottus armatus (staghorn sculpin)