Environmental Protection Service

Environment Canada

Pacific and Yukon Region

REGIONAL ENVIRONMENTAL CONTAMINANTS SEMINAR - SUMMARY OF PROCEEDINGS

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PREFACE

This seminar was organized to present studies on monitoring of environmental contaminants in British Columbia. Seminar topics cover a variety of contract studies supported through the federal Environmental Contaminants Contract Fund, as well as in-house monitoring and research by certain federal government agencies, and a contract study for the City of Seattle.

The Environmental Contaminants Contract Fund is a $750,000 annual allotment to Environment Canada specifically intended to assist in the implementation of the Environmental Contaminants Act. The fund has supported environmental sampling and analytical studies to determine sources and levels of contaminants in the environment, literature reviews on priority chemical substances, and development of codes of practise and testing protocols for priority chemical substances.

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PRIORITY POLLUTANTS - GUIDELINES FOR THE DESIGN OF MONITORING STUDIES

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Following the "NRDC Consent Decree" of June 1976, the U.S. Environmental Protection Agency published a list of toxic chemicals whose discharge into the aquatic environment the EPA intends to curtail. These toxic chemicals, now numbering 129 compounds, are commonly known as Priority Pollutants. The purpose of this paper is to summarize the aquatic fate of the 129 Priority Pollutants based on the current state of knowledge, categorize these pollutants based on their potential threat to the environment and suggest a simplified but comprehensive environmental sampling design that is based on the environmental compartment(s) in which each pollutant is most likely to accumulate or be of most significance.

Priority Pollutants are first ranked into ten chemical classes and are then ranked into five categories of importance based on their chemical behaviour and biological significance in the aquatic environment. Based on this information, the most appropriate environmental compartment (water, sediment, or biota) is indicated for sampling each pollutant. Since it is both difficult and expensive to survey for the full complement of 129 Priority Pollutants in all possible environmental compartments, the use of this selective rationale can reduce monitoring programs to manageable proportions. Moreover, this rationale permits analysis of environmental compartments on a sequential basis so that the sequence can be extended in a cost-effective manner if contaminants persist in a given compartment.

METHYLATION OF ARSENIC IN MARINE SEDIMENTS AND INTERSTITIAL WATERS OF RUPERT INLET, B.C.

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The incidence and production of organoarsenic compounds in sediments and overlying waters of a Vancouver Island inlet, which has been perturbed by mine tailing discharge, were studied in a two-phase study. In Phase I, 2 sediment samples from Rupert Inlet, one sample from adjoining Holberg Inlet and one from Quatsino Sound were obtained for pore water sampling and analysis for total carbon and arsenic concentrations. Overlying waters were obtained at each station. Pore waters and overlying waters were analysed for As(III), As(V), $CH_3AsO(OH)_2$ (monomethylarsonic acid) and $(CH_3)_2AsO(OH)$ (dimethylarsinic acid) using vapor phase chromatography and flameless atomic absorption techniques. No As was detectable in overlying waters at concentrations below one $\mu g\ L^{-1}$. In pore waters As(III), As(V) and the two methylarsenic compounds were found in concentrations up to approximately 5 $\mu g\ L^{-1}$ in two samples only where both dissolved As and organic carbon were in higher concentrations that at the other two stations.

In phase II the capability of sediment microorganisms to methylate added As(III), as arsenite, and $(CH_3)_2As$ as $(CH_3)_2AsO(OH)$ under anaerobic conditions was examined. When As(III) was added, amounts of $(CH_3)AsO(OH)_2$ ranging from 599 to 1167 $\mu g.L^{-1}$ were produced. Concentrations of $(CH_3)_2AsO(OH)$ produced ranged from 22 to 50 $\mu g.L^{-1}$ after four weeks incubation at 15^{o}. Variations in production for the four sediment samples used were not great. Dimethylarsenic acid added to

each of the four sediment samples was rapidly reduced regardless of nutrient levels. Amounts remaining after 4 weeks incubation ranged from 1 to 2 percent of the amount added. The study indicated that organoarsenic derivatives exist in pore waters at concentrations considerably above those in sea water. From the limited data, a relationship between the arsenic, organic carbon and the methylarsenic concentrations exists. The importance of release of arsenic from tailings to pore waters requires further investigations.

C.E.P.E.X. STUDY OF THE FATE, PATHWAYS AND TOXIC EFFECTS OF TETRAETHYLLEAD AND PCBS IN THE MARINE ENVIRONMENT

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The fate, pathways and toxic effects of tetraethyllead and PCBs were studied in two separate controlled experiments utilizing the C.E.P.E.X. (Controlled Ecosystem Pollution Experiment) techniques.

The C.E.P.E.X. experiment for PCBs was conducted in August, 1978 and for tetraethyllead in October, 1978 in Saanich Inlet, B.C. In each set of experiment, three plastic enclosures of 60,000 liters volume each were launched simultaneously by divers to capture the sea water, together with a natural phytoplankton population. One enclosure was used as control and the other two spiked with approximately 5 and 50 ppb. (parts per billion) of Arochlor^{R} 1254 mixed with ethanol and a dispersant, Corexit 9527 in the August study and of tetraethyllead in methanol for the October study. Nutrients were added to stimulate the phytoplankton bloom. An extensive sampling schedule was carried out on a large number of chemicals and biological parameters in the ecosystems: seawater concentrations of the contaminant (PCBs or tetraethyllead), particulates, chlorphyll , a primary productivity by C-14 uptake salinity, nutrients (phosphate, nitrate, silicate), phytoplankton and zooplankton populations and detritus sediments.

Results showed that at the 50 ppb. level of tetraethyl lead, most of the zooplankton and phytoplankton activities were destroyed within 48 hours, and 5 ppb. level reduced the populations and growth rates considerably. In the case of PCBs, there appeared to be a delay in the timing of the blooms of phytoplankton in the 5 and 50 ppb. enclosures by a few days for diatoms, and at the 50 ppb. level, a shift in the species composition from domination by diatoms to that by the micro-flagellates after 12 days. For zooplankton, the growth was suppressed temporarily by PCBs at the 5 ppb. level but was inhibited

severely at the 50 ppb. level with low recovery later. Detritus sedimentation appeared to be the major controlling factor in removal of PCBs or tetraethyl-lead from seawater, after adsorption onto surfaces of living and/or dead cells. In the case of PCBs, there was evidence of PCBs released back to the sea water column during the remineralization phase. In the case of tetrethyllead, evaporative loss to the atmosphere and transformation into other forms of organic and inorganic lead compounds might be possible routes, although such routes would not be significant for PCBs.

HYDROCARBONS IN KITIMAT HARBOUR AND ITS SEAWARD APPROACHES AND A STATISTICAL CORRELATION WITH A PECULIAR INFILTRATIVE HYALINOCYTIC CONDITION IN MUSSELS

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A more than two orders of magnitude increase in benthic sediment concentrations of polycyclic aromatic hydrocarbons (PAHs) is observed between sites remote from Kitimat Harbour and sites in the harbour itself. A similar increase is observed in benthic sediment concentrations of non-polar, aliphatic/alicyclic hydrocarbons (NPHs). The distribution of the two classes of hydrocarbons within the harbour indicates that their principal sources are not the same. The PAHs are predominantly distributed along the west side of the harbour with the maximum concentrations in the northwest corner. The NPHs are predominantly distributed across the harbour with the maximum concentrations in the northeast corner. The probable sources, modes of transport and fluxes of hydrocarbons will be discussed.

Histopathological examination of mussels and clams has revealed a infiltrative hyalinocytic condition where nearby surface sediment concentrations of PAHs are elevated. The condition was not observed in mussels from Alberni Inlet where sediment concentrations of PAHs are not elevated. The nature of the condition will be described and the possibility of a causal relationship between the condition and PAHs will be discussed.

IDENTIFICATION BY GC-MS ANALYSES OF HALOGENATED ORGANICS AND PCBS IN TISSUES OF FRASER RIVER ESTUARY AQUATIC ORGANISMS

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Samples of crabs, flounders, clams (Macoma sp.), and salmonids were taken from two sites at Sturgeon Banks at different distances from the outfall of Iona Island sewage treatment plant in August and November 1978. Equivalent samples were collected from a control station at Roberts Bank. A sediment sample was also collected at each station in the November sampling. All samples were frozen and shipped by air express to Radian Corpn. in Austin, Texas for chemical analysis

Composite samples of ground tissue (50 g) or sediment were mixed with an equal weight of anhydrous sodium sulphate and extracted in a column with hexane/methylene chloride. The crude extracts were split into base/neutrals and acid fractions by extraction with aqueous ammonia. The base-neutrals fractions were chromatographed on Florisil and analysed by GC. Acid fractions were analysed by GC both before and after methylation with diazo methane. Selected acid and base/neutral fractions were analysed by GC-MS. Appropriate blank samples were prepared using all laboratory procedures and these also were analysed. Gas chromatographic analyses of all fractions included the use of a Hall specific conductivity detector for halogenated compounds and a flame ionization detector (FID) for total organics.

In general, small concentrations only (part per billion) of chlorinated organics were observed. PCB's in the form of Aroclor 1254 were identified in many of the samples. No other chlorinated compounds were identified with certainty except 1,2-dichlorobenzene in one sediment sample and pentachlorophenol in one flounder, each from Sturgeon Bank. GC analysis indicated the tentative identification of 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and p-chloro-m-cresol in many of the acid extracts but there were too many lipid interferences to allow comfirmation by GC-MS.

The U.S. EPA Priority Pollutants were analysed for in nine base-neutral fractions, two acid fractions and three methylated acid fractions. The Radian computer software program allowed the identification of 11 Priority Pollutants including phthalate esters, PCB's and polynuclear aromatic hydrocarbons in spite of high levels of interfering compounds.

Further work is underway to analyse three Iona Island sewage samples by the Radian procedures. Also a flounder extract containing some unknown chlorinated organics is being re-examined after more sophisticated cleanup. It is hoped that this will permit mass spectral identification of these unknowns.

MONITORING ENVIRONMENTAL CONTAMINATION FROM CHLORPHENOL CONTAMINATED WASTES GENERATED IN THE WOOD PRESERVATION INDUSTRY

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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 precesses. 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 investigations are required to determine the mechanisms and extent of PCP contaminations and these areas are briefly outlined.

REVIEW OF A PCB SPILL FROM CANADIAN CELLULOSE LTD. INTO PORPOISE HARBOUR, PRINCE RUPERT, B.C.

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In January, 1977, a transformer at the Canadian Cellulose pulp and paper mill near Prince Rupert, B.C., malfunctioned and deposited approximately 800 litres of polychlorinated biphenyl (PCB) fluid into the storm sewer system and consequently into the marine waters of Porpoise Harbour. The initial monitoring program indicated that sediments in the immediate vicinity of the spill contained excessively high levels of contamination. Analyses showed that levels of up to 8000 ppm were detected in the sediments collected directly off the storm sewer outfall. Subsequent monitoring in the spill area indicated even higher levels of sediment contamination (up to 74,000 ppm). Consequently, charges were laid by the Environmental Protection Service under Section 33 (2) of the Fisheries Act.

This presentation will discuss the levels of contamination in sediments and biota immediately following the spill, initial clean-up measures taken to contain the PCBs, and the ultimate in-situ containment of contaminated sediments within the spill area to prevent the further spread of contamination. The results of the 1978 and 1979 annual post-containment monitoring in Porpoise Harbour will also be described as will the major highlights and the outcome of the prosecution.

APPENDIX - SUMMARIES OF OTHER STUDIES SUPPORTED THROUGH THE ENVIRONMENTAL CONTAMINANTS CONTRACT FUND

1. "Analysis of Organic Environmental Contaminants in Fish from the Lower Fraser River"

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Scientific Authorities : O. Langer and D. Wilson, Environmental Protection Service, Environment Canada.

Most of the available information on organic contaminant levels in Fraser River fish species was obtained in a Westwater Research Centre fish sampling program conducted in 1972 and 1973. The majority of the samples, analyzed in 1973, determined muscle tissue levels of chlorinated pesticides and PCBs. In 1978, funding obtained from the Environmental Contaminants Contract Fund permitted the balance of the samples collected in 1973 to be analyzed for a wide range of industrial and agricultural organic contaminants.

PBBs, PCTs, and Mirex were not detected in any samples. PCBs were detected with greater frequency and at higher concentrations than were any other contaminants. Residue levels were highest in coarse fish species such as Largescale suckers (up to 3695 ppb) and Northern squawfish (up to 1894 ppb). Most species from the Fraser River contained PCB tissue concentrations between 100 and 900 ppb. Residue levels and incidence of occurrence in several species were higher in the more industrially developed estuarine portions of the river than further upstream, indicating that past and current industrial activity in this vicinity has contributed to significant PCB contamination in the Fraser River.

The results of this study are presented and discussed as part of an EPS

Pacific Region report prepared for the Canada-British Columbia Fraser River Estuary Study.

2. "Study to Evaluate and Monitor the Use of Polychlorinated Biphenyls (PCBs) in Electrical Equipment"

Contractor: Stothert Engineering Ltd.
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Scientific Authority: D. Wilson, Environmental Protection Service, Environment Canada.

This study evaluated the conditions of PCB-filled electrical equipment and potential for accidental release of PCB in large British Columbia industries. Equipment maintenance, spill control, storage and disposal procedures, and potential escape routes of PCB from the plants to the environment were determined and inspection reports prepared.

A handbook for PCB users was also developed covering uses, storage, handling, shipping and disposal procedures for PCB wastes and equipment. Personnel safety, equipment maintenance methods, spill prevention and containment plans, and substitute chemicals for PCB were among the many topics covered.

3. "EPS-Pacific Region Mercury Overview"

Contractor: multi-contracts

Scientific Authority: O. Langer, Environmental Protection Service, Environment Canada.

The report is intended to provide an overview of mercury contamination in British Columbia and the Yukon Territory, based on the compilation and interpretation of data supplied by various sources. In many instances, the reported data is plotted on regional maps so to give a geographical representation.

Elevated mercury levels occur most frequently in aquatic organisms,

fish-eating birds, and sediments from the more heavily urbanized areas around Vancouver and Victoria and from regions of extensive natural mineralization, such as Pinchi Lake. Localized incidents of mercury contamination have also been demonstrated in the receiving environments of industrial operations such as mines, smelters, pulp mills, and a mercury cell chlor-alkali plant. In most instances, the occurrence of high level of environmental contamination have been attributed to industrial mercury releases prior to recently implemented government regulations and pollution control measures; however, some industrial facilities in B.C. continue to discharge significant amounts of mercury to the atmosphere and receiving waters.

No major areas of mercury contamination have been identified in the Yukon Territory. Preliminary sampling programs, however, have indicated the presence of elevated concentrations in surface waters, sediments, and fish from various Yukon water systems. While contamination in the Yukon has not been attributed to industrial mercury releases, it is likely that the past widespread activity of placer mines combined with natural releases have contributed to the contamination of some aquatic systems.

4. "Identification of Heavy Metals in Organisms within an Area of the Fraser River Estuary Receiving a Major Municipal, Industrial and Stormwater Discharge"

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Scientific Authority: I.K. Birtwell
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Concentrations of heavy metals were measured in sediments and marine organisms from two mudflat areas in the Fraser River estuary, British Columbia. The Sturgeon Bank mudflat was influenced by the combined municipal, industrial and storm water discharge from the Iona Island sewage treatment plant. The second mudflat, Roberts Bank, was used as a control area.

Metal levels in sediments reached their highest levels at sites closest of the Iona Island sewage treatment plant outfall. Of the metals analyzed, only mercury and arsenic showed levels indicating contamination in animal tissues. However, elevated levels of these metals were also found in samples from the control site, indicating other sources of metal contamination to the estuary. Concentrations of mercury in sediments and biota, and concentrations of arsenic in biota showed seasonal fluctuations of over one order of magnitude. High detection limits precluded assessment of cadmium and lead as heavy metal contaminants.

Mercury levels were significantly ($p<0.05$) higher in clams, Macoma balthica and flounder, Platichthys stellatus collected from sites on Sturgeon Bank than specimens taken from the control area. However, the mercury content of crabs (Cancer magister) in the two areas was not always significantly different, although values approached 0.5 µg/g wet weight. These findings indicated the potential for an environmental contaminants problem in both study areas. Metal levels in chinook salmon (Oncorhynchus tshawytscha) were generally low. Concentrations of mercury in tissues did not reach 0.5 µg/g wet weight in any of the samples. Arsenic did exceed the recommended level of 5.0 µg/g wet weight for commercial seafood organisms in some samples of both crabs and flatfish.

Results were discussed with respect to a literature review on the effects of heavy metals with emphasis on mercury and arsenic. Recommendations for the direction of future studies included studies of temporal fluxes in heavy metal levels, physio-chemical and biological factors affecting the availability and uptake of metals by marine organisms, and improved analytical practices.