STUDY OF THE RATE OF UPTAKE AND BIOACCUMULATION OF CONTAMINANTS FROM MARINE SEDIMENTS FOR OCEAN DUMPING

Prepared For

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Project 478



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February 29, 1984

Our File: 478

Mr. H. Nelson Environmental Protection Service 3rd Floor - Kapilano 100 Park Royal South West Vancouver, B.C. V7T 1A2

Dear Mr. Nelson:

RE: Study of the Rate of Uptake and Bioaccumulation of Contaminants from Marine Sediments for Ocean Dumping

We are pleased to provide our final report on the above project following your review. Our findings show bioaccumulation of cadmium and lead in clams exposed to False Creek sediments, and uptake of lead from Vancouver Harbor sediments. Mercury was not accumulated from any of the test substrates. The rate of uptake and achievement of a "steady state" condition with respect to bioaccumulation was highly variable for cadmium and lead and was dependent on the sediment tested. Generally, the rate of uptake and bioaccumulation of cadmium was much faster than for lead.

We trust that this report completes our present assignment to your satisfaction.

Yours very truly,

E.V.S. CONSULTANTS

P.M. Chapman, Ph.D.

Vice-President

PMC/si Encls.



TABLE OF CONTENTS

		Page No.
Title Page Letter of Transmittal Table of Contents List of Figures List of Tables Summary Acknowledgements		i ii v v v vi
1.0	INTRODUCTION	1
1.1	Objectives	2
2.0	METHODS	2
2.1 2.1.1 2.1.2 2.1.3 2.2 2.2.1 2.2.2 2.3 2.3.1.1 2.3.1.2 2.3.1.3 2.3.2 2.3.2.1 2.3.2.2 2.3.2.4 2.3.3 2.3.3.1 2.3.3.2	Field Methods Sediment Collection Clam Collection Worm Collection Laboratory Methods Bioaccumulation Studies - Experimental Setup Expertimental Sampling Analytical Methods Seawater Cadmium and Lead Mercury Precision and Accuracy Sediment Total Cadmium and Lead Total Mercury Precision and Accuracy Particle Size and Total Organic Carbon Tissues Cadmium and Lead Mercury Precision and Accuracy Statistical Analysis	2 2 2 3 3 4 4 6 7 7 7 8 8 8 9 10 10 11 11
3.0	RESULTS AND DISCUSSION	12
3.1 3.2 3.3 3.4 3.4.1 3.4.2	Water Quality and Sediment Monitoring During Bioassays Precision and Accuracy of Trace Metal Analysis Characteristics of Test Sediments Release of Metals from Test Sediments Cadmium Lead	12 13 13 14 14
3.4.3 3.5	Mercury Bioaccumulation	16 17



3.5.1	Cadmium	17
3.5.2	Lead	18
3.5.3	Mercury	20
3.5.4	Rate of Uptake and Achievement of Steady State Condition	21
3.6	Sediment Toxicity	22
4.0	CONCLUSIONS	24
5.0	RESEARCH NEEDS	25
6.0	REFERENCES CITED	27



LIST OF FIGURES

Figure		
I	Concentrations of dissolved metals in seawater overlying test sediments.	
2	Mean $\pm SE$ values for tissue metal concentrations in \underline{M} . $\underline{balthica}$ exposed to test sediments.	
3	Mean $\pm SE$ values for tissue metal concentrations in N . virens and C . capitata exposed to test sediments.	
	LIST OF TABLES	
<u>Table</u>		
1	Physical Characterization of Test Sediments	
2	Chemical Characterization of Test Sediments	
3	Cadmium, Lead and Mercury in Seawater	
4	Values for Tissue Metal Concentrations in Macoma balthica	
5	Values for Tissue Metal Concentrations in <u>Nereis</u> <u>virens</u> and <u>Capitella</u> <u>capitata</u>	
6	Summary of One Way ANOVA by Site for Clam Tissue Metal Concentration for Each Month Sampled	
7	Summary of One Way ANOVA by Month for Clam Tissue Metal Concentration for Each Site Sampled	
8	Percent Mortality of Bioassay Species in Test Sediments During Bioaccumulation Experiment	
	LIST OF APPENDICES	
A-I	Accuracy and Precision of Seawater Analyses	
A-2	Accuracy and Precision of Sediment Analyses	
A-3	Accuracy and Precision of Tissue Samples	



SUMMARY

McGreer, E.R. and B.J. Reid. 1983. Study of the rate of uptake and bioaccumulation of contaminants from marine sediments for ocean dumping. Report prepared for Environmental Protection Service, West Vancouver by E.V.S. Consultants, North Vancouver, B.C., 29 p.

Bioaccumulation of cadmium, lead and mercury by two species of marine polychaete worms (Nereis virens, Capitella capitata), and a clam (Macoma balthica) was assessed during prolonged laboratory exposures to four marine sediments. N. virens and C. capitata were exposed for two and three month periods respectively, and \underline{M} . $\underline{balthica}$ for six months. The three sediments tested each represented a different industrialized area: a harbor drydock/ship repair facility (Vancouver Harbor); a heavily industrialized embayment (False Creek); and an area receiving pulp mill effluent discharge (Powell River). A fourth sediment collected from an area with no known sources of contamination (Bedwell Bay) served as a reference. Cadmium was readily released into interfacial seawater above all test sediments. Bioaccumulation of cadmium was greatest in C. capitata (16 µg/dry g) exposed to sediments from False Creek. Lead bioaccumulated to the highest mean concentration (37.7 µg/dry g) in M. balthica exposed to sediments from Vancouver Harbor. Vessel antifouling paint and runoff were considered as possible sources of the bioavailable lead at the Vancouver Harbor site. The rate of uptake and achievement of a steady state condition with respect to bioaccumulation was highly variable for both metals and was dependent on the sediment tested. Generally, the rate of uptake and subsequent bioaccumulation of cadmium was much faster (I month) than for lead (4 months). Mercury was not released into seawater, and did not bioaccumulate significantly from any of the test sediments.

Mortalities of \underline{N} . \underline{virens} and \underline{C} . $\underline{capitata}$ reached 100% in all test sediments including the reference sediment after two and three months respectively. Mortalities of \underline{M} . $\underline{balthica}$ were greatest in False Creek and Vancouver Harbor sediments after six months. Sediment toxicity may have been responsible for



the mortalities observed, but other factors could not be ruled out. Research needs identified included determination of the sources and chemical speciation of cadmium and lead as they relate to metal bioavailability in contaminated marine sediments.



ACKNOWLEDGEMENTS

E.V.S. Consultants would like to acknowledge H. Nelson and D. Brothers of the Environmental Protection Service for their assistance in the collection of sediments from Powell River and Vancouver Harbor and their continued support and advice throughout the study. We also acknowledge Arctic Laboratories Ltd. for performing the trace metal analyses, CanTest Ltd. for physical sediment analyses, and Quantum Research Ltd. for statistical treatment of the data.

E.V.S. Consultants acknowledges the principal investigators for this study, E.R. McGreer and B.J. Reid; A. Laing and K. Peters provided technical assistance. Drafting was completed by R. Fink; the manuscript was word processed by S. Irwin. Dr. P. Chapman managed this project to completion and provided in-house editorial review.

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1.0 INTRODUCTION

Several recent laboratory studies have determined the bioaccumufrom polluted sediments of contaminants marine lation invertebrates (e.g. McGreer et al., 1981; Ray et al., 1981; Reid et published studies reported in the al., 1981). However, very few literature have used exposure times greater than 30 days. Concern has been expressed about the potential build up of contaminants in aquatic food chains over extended periods of time (Waldichuk and Buchanan, 1980; Swiss et al., 1980). Much of this concern is related exposure of benthic species to contaminated solid waste materials. A recent review of the ecological consequences of dredging and ocean dispersal in Canada found a paucity of data on the bioaccumulation of contaminants in marine species, or its ecological consequences (Levings, 1982).

The present study was designed to determine the bioaccumulation of cadmium, lead and mercury during a 6 month laboratory exposure to three contaminated marine sediments each representing a different a drydock/ship repair facility (Vancouver industrialized area: Harbor), a heavily industrialized embayment (False Creek), and a pulp effluent discharge (Powell River). mill non-industrialized site in Burrard Inlet (Bedwell Bay) was used for collection of a reference sediment. Two species of marine worms (Nereis virens, Capitella capitata), and a clam (Macoma balthica) were used as test animals. Metal levels in tissues were determined after I and 2 months in N. virens, after I, 2 and 3 months in C. capitata and after 6 months in M. balthica to assess whether a "steady-state" condition was achieved with respect to bioaccum-This study is one of the first from the Pacific Region of ulation. bioaccumulation Canada the term uptake and long contaminants under controlled laboratory conditions.



I.I Objectives

The objectives of the present study were:

- 1. To determine the rate of bioaccumulation of cadmium, mercury and lead from three contaminated marine sediments with different metals content in three marine invertebrates.
- 2. To conduct these uptake studies for up to 6 months to assess achievement of a "steady-state" condition with respect to bioaccumulation of heavy metals.

2.0 METHODS

2.1 Field Methods

2.1.1 Sediment Collection

Sediments from False Creek and Bedwell Bay were collected by Ponar grab by E.V.S. Consultants Ltd. and placed in 5-gallon polyethylene buckets which had been pre-cleaned with dilute HNO3 and rinsed with distilled water. Sediments from Powell River and Vancouver Harbor were supplied by the Environmental Protection Service. Sediments were stored at 4°C in the laboratory until required for testing.

Subsamples of each sediment were frozen for later analysis of physical and chemical characteristics.

2.1.2 Clam Collection

Clams (<u>Macoma balthica</u>) were collected from Roberts Bank in the Fraser River estuary. Sediments containing <u>M. balthica</u> were sieved through a 5 mm screen, and clams greater than 5 mm in length were retained for testing. Clams were transported to the laboratory in polypropylene containers which were pre-treated with dilute nitric



acid, and rinsed with distilled water. Containers were rinsed several times with seawater from the collection site. Clams were maintained in the laboratory in the containers with sediment and sand-filtered seawater (25 ppt) from Burrard Inlet at 10 ± 0.5 °C under a 12 h light/dark photoperiod. Seawater was replaced every 48 h during the two week holding period. Aeration was supplied by a single airstone placed in each container.

2.1.3 Worm Collections

Two polychaete worm species were tested during this study: Nereis virens and Capitella capitata. Nereis virens (approx. 10 mm in length) were obtained from a commercial supplier (Sea Plantation Inc., Salem, Mass.). Worms were obtained from field stocks collected from an uncontaminated beach in Salem Harbor, and were air-shipped in sediment to the E.V.S. Consultants laboratory in North Vancouver, B.C. Upon receipt, worms were placed in sediment from Roberts Bank and covered with seawater to a depth of 1 cm. Seawater was replaced every 48 h as with M. balthica.

<u>Capitella capitata</u> were collected from the outdoor fish holding tanks at the Department of Fisheries and Oceans West Vancouver Laboratory. Detritus at the bottom of the tanks was sieved and worms 5-7 cm in length) sorted out and placed in pre-cleaned polypropylene containers with Burrard Inlet seawater. <u>C. capitata</u> were held in the laboratory in sand-filtered seawater for 2-3 days prior to testing.

2.2 Laboratory Methods

Bioassays were conducted in the marine laboratory facilities of E.V.S. Consultants Ltd., North Vancouver, B.C. Seawater for these facilities is drawn from Burrard Inlet at a depth of approximately -1.0 ft. below MLLW.



2.2.1 Bioaccumulation Studies - Experimental Setup

Six month continuous flow bioassays were conducted in 65 L polypropylene trays (dimensions 90 x 60 x 12 cm). Tests were conducted at 10 ± 3 oC under a 12 h light/dark photoperiod. The laboratory test area was sealed with plastic and equipped with an air filtration unit to minimize particulate contamination. Prior to test initiation all trays, lids and plasticware were pre-soaked in 5% nitric acid for 48 h, then rinsed twice with distilled water and seawater.

The bioaccumulation experiment was initiated by placing 40 L of one type of well-mixed test sediment in each tray. A polypropylene divider was placed across the middle of the tray to separate the two types of test organisms. Seawater was then introduced into each tray at a rate of 30 mL/min so that total volume of sediment and seawater was 60 L (i.e. a ratio of sediment:water volume of 2:1). Turnover time for seawater in the containers was approximately once every 11 h. The level of dissolved oxygen was maintained at air saturation by aeration through two airstones in each tray. Each tray was covered with a glass plate.

2.2.2 Experimental Sampling

Care was taken during all stages of the experimental sampling to ensure that samples were not contaminated. This was especially important for lead in seawater for which order of magnitude errors can be introduced during sampling and handling procedures (Patterson et al., 1976).

Seawater was withdrawn after 24 h, 1, 2, 4, and 6 months from each tray for analysis of dissolved cadmium, lead and mercury. Seawater samples were withdrawn approximately I cm above the sediment interface using pre-cleaned polyethylene tubing fixed to a "T" bar which rested on the sides of the tray. This technique minimized sediment disturbance while sampling, and ensured that samples were collected at the same distance above the sediment on each occasion.



Separate lengths of tubing pre-rinsed with dilute nitric acid and distilled water were used for each tray to prevent cross-contamination. An initial 200 mL sample was withdrawn and discarded on each occasion to further cleanse the tubing. A I L sample was then withdrawn from 5 different locations in the tray into a I L hot acid-cleaned polyethylene bottle. Cleaning procedures followed those outlined by Patterson et al. (1976). An additional 500 mL sample was withdrawn into a Pyrex glass bottle pre-cleaned with potasium dichromate for mercury analysis.

Filtering was conducted in the bioassay laboratory using a Millipore borosilicate glass apparatus with polypropylene receiving flask and polycarbonate filter paper (Nuclepore 0.40 µm). A separate filter paper was used for each sample. Filter papers and the filtering apparatus and flask were pre-cleaned in dilute nitric acid, then rinsed twice with purified Milli-Q water between samples. pre-soaked filter paper was placed in the apparatus and the whole apparatus was rinsed once with dilute nitric acid, twice with purified distilled water and once with 100 mL of sample, with the filtrate The remaining sample was filtered discarded between each rinse. and placed back in the sample bottle. Each sample was subsequently preserved with I mL of distilled high purity nitric acid provided by Arctic Laboratories Ltd. Bottles were sealed within two plastic bags and stored at 4°C.

After initial water samples were collected, dissolved oxygen (YSI Model 57), pH (CORNING Model 610A), salinity and temperature (YSI Model 33) were recorded. Subsequently, these parameters were measured weekly for the test duration. Reduction/oxidation potential (Eh) of sediments to a depth of 5 cm was measured monthly in each tray using an Orion portable meter (Model 407A) equipped with a combination reference/platinum electrode. This electrode is factory-sealed and calibration was carried out according to a three step instrument checkout procedure (zero, slope, maximum output).



After initial physical and chemical measurements were recorded, approximately one hundred and fifty clams (M. balthica) and seventy worms (N. virens) were placed in each tray. Thirty clams and fifteen worms were retained for analysis of background contaminant levels. A total of thirty clams were sieved from each sediment after 1, 2, 4 and 6 months exposure. A minimum of 10 clams were used for each replicate analysis. Prior to being preserved by freezing, clams were placed in pre-cleaned polypropylene tubs for a 48 h depuration period.

Sampling for N. virens was similar with 5 individuals taken for each replicate analysis. As high mortalities were encountered in sampling N. virens after 2 months, the experiment was repeated with a second worm species, C. capitella. In the experiments with C. capitata, 900 mL polyethylene trays were used as test containers. A total of 400 mL of sediment was added to each container. Four small trays were placed in each larger tray containing M. balthica. Initial background tissue samples consisting of three replicates of 5 worms each were sampled and treated as previously described. C. capitata were sieved from trays after 4 and 10 weeks. All animals were depurated for 48 h in clean seawater. Adhering debris was removed from depurated worms and replicate samples were frozen in Whirlpak bags.

2.3 Analytical Methods

The following methodology for trace metal analyses was followed by Arctic Laboratories Ltd. who performed the trace metal analyses for this study. Can Test Ltd. performed analysis of sediment particle size and total organic carbon.



2.3.1 Seawater

2.3.1.1 Cadmium and Lead

Cadmium and lead were pre-concentrated by extraction from seawater using mixed dithiocarbamates into Freon. The pH of a 200 g aliquot of acidified sample was adjusted to pH 5+0.5 with the addition of 0.5 mL of 2M ammonium acetate and ultrapure ammonia water. The metals were sequestered by the addition of 1.0 mL of a 1% ammonium pyrrolidine dithiocarbamate (APDC)/diethylammonium diethyldithiocarbamate (DDDC) solution. The carbamate-metal complexes were extracted twice with 20 and 10 mL aliquots of Extractions were carried out in I L Freon 113 respectively. capacity Teflon separatory funnels with Teflon stopcocks and polypropylene screw-top caps. The Freon extracts were combined in a 125 mL Teflon separatory funnel and were washed gently with 2 x 5 mL aliquots of pH 8 Milli-Q water to remove any carried over salt. The metal-carbamate complexes were broken down in the combined Freon extract by the addition of 200 µL of ultrapure nitric acid and then back-extracted into 10 mL of Milli-Q water. metal content of the aqueous back-extracts was determined by flameless atomic absorption spectrometry. A Perkin-Elmer Model 703 atomic absorption spectrometer coupled to a Model HGA 500 graphite furnace was used for all measurements. Simultaneous background corrections were made using a deuterium source. Volumes of 10 or 20 µL of sample were injected into the furnace with a Perkin-Elmer AS-1 autosampler. Pyrolytic graphite-coated furnace tubes were used.

2.3.1.2 Mercury

Mercury was determined by a cold vapour flameless atomic absorption method.



For samples received in the laboratory, 10 mL of a 2% sodium dichromate solution in concentrated nitric acid were added and samples were left for a minimum of 12 hours. Analysis was initiated by adding 3 mL each of 4% (w/v) potassium permanganate and 4% (w/v) potassium persulphate solutions to the sample bottle. The samples were then heated in a water bath at 80°C for 2 h. After cooling, approximately 1 mL of a 12% (w/v) hydroxylamine hydrochloride solution was added and the solution swirled to reduce excess permanganate. The samples were then divided into two equal aliquots and the air space above the sample was purged for 30 seconds to remove traces of chlorine. The mercury was reduced to elemental mercury by adding 3 mL of a 20% (w/v) stannous chloride solution and swirling for 30 seconds. The mercury was driven off in a stream of dry nitrogen gas into a 30 cm path length cell of a Laboratory Data Control U.V. monitor. Reagents used were all Baker-Analyzed, 'suitable for mercury analysis' grade. Sodium dichromate was Baker-Analyzed Primary Standard grade.

2.3.1.3 Precision and Accuracy

Table A-I in the Appendix summarizes blanks, detection limits, precision and accuracy of the methods for seawater analysis. The accuracy assessment was based on analyses of a certified reference seawater sample (NASS-I) distributed by the National Research Council (Ottawa).

2.3.2 Sediment

2.3.2.1 Total Cadmium and Lead

All analyses were carried out on bulk sediment samples. Sediment samples were thawed, then homogenized by kneading the contents of the Whirlpak bag for several minutes. An approximate 50 g subsample was oven-dried at 70°C for 48 h, then crushed to a fine powder in an agate mortar. An approximate 0.5 g subsample was transferred to an acid-cleaned Teflon bomb and wetted with 2 mL of



aqua regia and 12 mL of HF. The bomb was sealed and heated at 100oC for 1 h. After cooling to room temperature the contents of each bomb were transferred to a tared 30 mL polyethylene bottle containing 2.0 g of boric acid. The bomb was rinsed with Milli-Q water, the rinse water added to the polybottle and the total weight brought to 30.0 g. The cadmium and lead content of the digests was determined by flameless atomic absorption using a Perkin-Elmer Model 703 atomic absorption spectrometer coupled to a HGA-500 graphite furnace.

2.3.2.2 Total Mercury

Between 0.05 and 0.3 g of dry, ground sediment was added to a 500 mL Pyrex glass-stoppered flask and washed down to the bottom of the flask with mercury-free tap water. The flask was then placed into a cold water bath and 15 mL of sulphuric acid-nitric acid (2:1) slowly added followed by shaking. The flask was allowed to stand for about five minutes, and then was placed in a water bath at a temperature of 50-60°C and digested for 2 h. minute cooling period, 10 mL of 6% (w/v) potassium permanganate solution were added while cooling the flask in a cold water bath. After an additional 30 minute period, 5 mL of a 5% (w/v) potassium persulphate solution were added, the solution swirled and allowed to stand overnight. The following day, 10 mL of a 6% (w/v) solution of hydroxylammonium hydrochloride solution were added and the solution stirred until clear. Five mL of mercury-free nitric acid were then added and the sample diluted to 500 mL with tap water. The sample was divided into two 250 mL portions and mercury determined by the cold vapour flameless atomic absorption (at 254 nm) according to the following procedure. The air space above the sample solution was purged with N2 gas for one minute to remove traces of chlorine gas. Just before analysis, 10 mL of a 20% (w/v) stannous chloride solution was added; the diffuser was inserted, the sample shaken for 30 seconds, let stand for 30 seconds and purged with N2 gas at a flow rate of 0.4 L/min for approximately one minute through a 30 cm path length cell of a Laboratory Data



Control U.V. monitor. The peak absorbance of mercury at 253.7 nm is proportional to its concentration. All reagents were Baker reagent 'suitable for mercury determination' grade.

2.3.2.3 Precision and Accuracy

Precision and accuracy were determined by replicate analysis of two marine sediment reference materials supplied by the National Research Council, MESS-I and BCSS-I. The results are presented in Table A-2 in the Appendix.

2.3.2.4 Particle Size and Total Organic Carbon

Sediment particle sizing was carried out by wet sieving sediments through a nest of two sieves with screen sizes of 2.0 and 0.625 mm. Particles passing through the 0.625 mm screen were further classified into silt and clay by the pipette method for sediment analysis.

Sediments for total organic carbon (TOC) analysis were air dried and pulverized prior to digestion. The dried samples were digested in HCI to remove carbonates and the digest filtered through LECO crucibles and re-dried. The residues were then analyzed for organic carbon by LECO Induction Furnace.

2.3.3 Tissues

Tissue samples were thawed, then oven-dried at 100°C to a constant weight. Dried samples were ground to a fine powder in an agate mortar. In some instances, only a small amount of tissue remained after drying (10 mg or less). It was not possible to determine metal levels for these samples. In other cases, there was insufficient material for both Cd/Pb measurements, and Hg determinations. In these instances, Hg analyses were omitted.



2.3.3.1 Cadmium and Lead

When sufficient tissue was available, up to 100 mg was digested. In general, 50 mg or less was used. The dry powdered tissue was placed in a Teflon decomposition bomb together with 10 mL concentrated nitric acid (Aristar), and heated at 100°C for 2 h. After cooling, samples were evaporated to dryness then diluted with 20 mL of Milli-Q water. Lead and cadmium contents of the digest were determined using flameless atomic absorption.

2.3.2 Mercury

Digests for total mercury were carried out as for analysis of sediments. Approximately 20-70 mg of tissue was digested.

2.3.3.3 Precision and Accuracy

Table A-3 of the Appendix summarizes blanks, precision and accuracy. The accuracy assessment was based on analysis of NBS Oyster Tissue (Standard Reference Material 1566).

2.4 Statistical Analysis

Statistical analysis of the data was carried out by Quantum Research Ltd. One-way analysis of variance (ANOVA) was used to test statistically significant differences in the tissue accumulation data for M. <u>balthica</u> by site and by month for each month sampled. Where significant (p less than 0.05) differences were found, distinct subsets were identified by applying the Studentized Neuman-Keuls test. All programs were run on the "BMD 10V - General Linear Hypothesis (No. 2) Revised November 3, 1975" computer program of the Health Sciences Computing Facility, UCLA.



3.0 RESULTS AND DISCUSSION

Data on the physical and chemical characteristics of the test sediments are presented in Tables I and 2. Experimental data on the concentration of cadmium, lead and mercury in seawater and animal tissues are presented in Tables 3 to 5, and summarized in Figures I to 3. Statistical results for the M. balthica tissue data are given in Tables 6 and 7. Insufficient data from the two worm species were obtained for adequate statistical analysis due to the high mortalities experienced in all test sediments, and the resulting lack of sufficient quantities of tissue for some chemical analysis.

3.1 Water Quality and Sediment Monitoring During Bioassays

Weekly monitoring for temperature, dissolved oxygen (DO), pH and salinity showed little variation between test trays during this study. Water temperature ranged from 9.8 to 13.0°C over the study period. DO was generally greater than 90% air saturation values, although on one occasion DO dipped to 6.8 ppm in the Reference tray when the air stone became clogged with sediment. The situation was quickly remedied, and a DO value of 6.8 ppm (approx. 70% air saturation) is within the tolerances of the test species used in this study. A range of pH between 6.7 and 8.2 was recorded over the study period. Values for pH generally decreased over time in the test trays with the lowest values being recorded during the last four weeks of the study in all trays. Salinity ranged between 13.5 and 26.5 ppt over the study period. Lowest salinity values were recorded during the spring freshet period for the Fraser River due to reduced salinity in the surface waters of Burrard Inlet. The salinities experienced were within the tolerance range for the test species, which are euryhaline and under natural conditions are exposed to similar estuarine conditions.

Weekly monitoring of sediment oxidation-reduction potential (Eh) generally indicated positive (50 to 255 mV) (oxygenated) conditions at the surface of all test sediments with reducing conditions (-150 to



-380 mV) at 5 cm depth. This pattern of a shallow surface oxic layer and a deeper anoxic layer is typical of natural marine sediments in depositional areas.

3.2 Precision and Accuracy of Trace Metal Analyses

Accuracy of trace metal analysis for seawater and tissues as determined by comparison with reference standards was in the range of 10-15%. Precision was also in an acceptable range of less than 15%. Trace metal analysis for sediments were similarly acceptable for cadmium and mercury, but recovery of lead compared to certified concentrations was low, averaging only 55% of certified values. The precision of lead results was high, averaging less than 6% for four replicate analyses. Reasons for low lead recovery are unknown, however low recoveries are common with the total digest method used, and incomplete digestion of the sediment particulates or loss during digestion may account for the low recoveries (F. Erickson, Arctic Laboratories Ltd., pers. comm.). No correction factor was applied to sediment lead values reported in this study.

3.3 Characteristics of Test Sediments

Results of the particle size analysis are presented in Table I. Test sediment from False Creek was a fine mud. Other test sediments were mainly sand. The False Creek sediment had the highest level of TOC (11.0%). Other sediments had TOC levels between 0.4 and 1.3%. Sediments from Vancouver Harbor had concentrations of cadmium and lead 10 to 30 times higher than other sediments tested (Table 2). False Creek sediments had the second highest levels of cadmium and lead, and the highest levels of mercury. An unexpected result was that the non-industrialized reference sediment from Bedwell Bay showed elevated concentrations of cadmium (2.67 µg/dry g). Previous information on the levels of trace metals at this site obtained by the Environmental Protection Service had shown concentrations at acceptable background levels (H. Nelson, pers. comm.). The elevated levels of cadmium recorded in the samples



collected in the present study indicate considerable variation in the concentration of cadmium at this site and suggest a possibly unidentified source of contamination in this area.

3.4 Release of Metals from Test Sediments

Following from the different methods used for analysing metals in seawater results for cadmium and lead are reported by weight as $\mu g/Kg$, and mercury by volume as $\mu g/L$.

3.4.1 Cadmium

A rapid release of cadmium was observed from all test sediments after 24 h with highest levels recorded from the Powell River and Bedwell Bay sediments (Fig. 1). Levels of dissolved cadmium were lower for all sediments after 1, 4 and 6 mo. A "pulse" of dissolved cadmium was recorded after two months.

Cadmium has been shown to be less tightly bound to particulates than other metals (Konasewich et al., 1982). A significant fraction of cadmium in organically rich sediments can also be available for release (Stukas, 1983). In the present study, maximum release was observed in the sediment with the lowest organic content (Table 2).

A consistent feature common to long-term release studies and observed for all sediments in the present study was a "peak" release of cadmium from sediments after 60 days (Lu and Chen, 1977; Reid et al., 1981). There appears to be a time dependent reaction associated with this peak release of cadmium.

3.4.2 Lead

After 24 h, the sediment from Vancouver Harbor showed considerably greater release of dissolved lead than the other test sediments (10 µg/Kg compared to less than 2 µg/Kg)(Fig. 1). The concentration of dissolved lead in seawater overlying the Vancouver Harbor sediment



dropped sharply (1.57 μ g/Kg) by the 1 mo. sampling, and levels were near background for the remainder of the study. Sediments from False Creek showed their greatest release (5.39 μ g/Kg) after 30 days.

Studies on the release of dissolved lead from contaminated marine sediments are rare, however gradual increase in concentration has been shown to occur over time (Stukas, 1983) even after five months Concentrations of soluble lead exposure (Lu and Chen, 1977). measured in the two studies cited above were in the range of 0.2 One reason this gradual release ug/Kg to 0.8 ug/Kg in seawater. was not apparent in the present study was the higher background concentration of lead in the seawater (0.8 µg/Kg) which precluded measurement of release at lower concentrations. (1977) reported background concentrations of lead of 0.1 µg/Kg in seawater collected outside Los Angeles Harbor. Stukas (1983) collected seawater from a relatively pristine site in Saanich Inlet, B.C. for which previous studies had determined background levels of lead to be 0.005 µg/Kq. Sampling and analytical techniques employed in the present study permitted detection limits of lead in seawater of 0.001 µg/Kg.

Of particular interest in the present study is the immediate release of dissolved lead observed from the Vancouver Harbor sediments (Fig. 1). A previous study conducted over a 30 day period on the release and bioavailability of lead in sediments collected at this site also reported the release of extremely high levels of dissolved lead (McGreer et al., 1981). The site is located immediately adjacent to a major ship repair/dry dock facility in Vancouver Harbor. The concentration of lead measured in these sediments (660 µg/dry g) are in the same range as the highest levels found in Puget Sound by Malins et al. (1980) - also in a heavily industrialized waterway. However, such comparisons must be made with care, as the lead determinations reported in the present study were not corrected for the low degree of recovery (50-60%) during analysis compared to certified reference sediments (Appendix A-2).



The existence of several different contributing sources for lead to the Vancouver Harbor site was previously suggested by McGreer et al. (1981) as a possible explanation for the high degree of bioavailability of lead in these sediments. Vessel protective measures (e.g. anti-fouling paint) and fuel consumption have been shown to contribute 9-12 metric tons/y of lead to Puget Sound, compared to 350 metric tons/y for urban runoff from Seattle (Schell and Nevissi, 1977 cited in Konasewich et al., 1982). In a 12,000 km area of the Southern California Bight, 55% of the lead was estimated to come from wastewater, storm runoff or river input (Patterson et al., 1976).

3.4.3 Mercury

Mercury was not released to an appreciable degree in the present study from any of the test sediments (Fig. 1). Elevated concentrations were measured in seawater after 6 months for all test sediments. However, even the highest value recorded (0.12 µg/L) is within the range for baseline values for total mercury in seawater reported from around the world (EPA, 1978).

Previous laboratory release studies with contaminated marine sediments have reported relatively little change in the concentration of mercury in interfacial seawater after 5-6 months (Lu and Chen, 1977; Macdonald and Morse, 1981). Given the relatively high organic content of the mercury-contaminated sediments in the present study, it is likely that the mercury is bound in organic complexes or is present as a metal sulfide and thus not readily soluble.



3.5 Bioaccumulation

3.5.1 Cadmium

A monthly comparison of the accumulation of cadmium by the clam M. balthica (Fig. 2) shows higher uptake from False Creek sediments compared to the other test sediments after I month, and from These results were statistically Bedwell Bay after 6 months. significant at p less than 0.05 (Table 6). Accumulation from Bedwell Bay sediments increased steadily over the exposure period while accumulation from False Creek sediments reached a maximum after I month then declined to a relatively steady state after 2 months. Cadmium uptake from Vancouver Harbor sediments appeared to reach a steady state between months I and 4, but then declined after 6 months. Bioaccumulation of cadmium from sediments was greatest after I and 4 months exposure. The monthly trends described above for the bioaccumulation of cadmium for each test sediment were shown to be statistically significant (p less than 0.05) when compared to initial tissue levels (Table 7).

Cadmium did not accumulate over time in the worm N. virens but was taken up by C. capitata from all sediments except Vancouver Harbor (Fig. 3). The highest concentration of cadmium (16 µg/dry g) in tissues of C. capitata was recorded from Bedwell Bay sediment. The high degree of cadmium bioavailability observed from the Bedwell Bay (reference) sediment was an unexpected result in this study. There are no known or obvious sources of pollution or freshwater runoff to this non-industrialized embayment which can account for the elevated levels of cadmium found.

The marked differences in accumulation of cadmium by the three test species emphasize the importance of inter-species differences with respect to bioavailability of contaminants (Livingston, 1979). Cadmium accumulation in \underline{N} . \underline{virens} has been shown to be highly variable depending on the test sediment. Ray et al (1981) reported significant (p less than 0.05) differences in the bioaccumulation of



cadmium from polluted harbor sediments collected only 200 m apart after 30 days exposure. In contrast, Rubinstein et al. (1983) found cadmium did not bioaccumulate above background levels in \underline{N} , virens after a three month exposure to sediments from New York Harbor.

The wide disparity in bioaccumulation observed for each test sediment for any one species suggests a different chemical speciation of cadmium in each sediment. The chemical species of a metal, and partitioning between different sediment constituents have been shown to be major factors controlling bioavailability of many metals including cadmium (Luoma and Bryan, 1982; Livingston, 1979; McGreer and Reid, 1980; Engel and Fowler, 1979). Elevated levels of cadmium have been found in clams (Protothaca staminea) and mussels (Mytilus edulis) from False Creek at levels similar to those observed for M. balthica in the present study (Reid et al., 1981). Considerable spatial variability in relation to the amount of accumulation of cadmium was observed at different sites sampled within False Creek (Reid et al., 1981). No data on cadmium in resident biota for the Bedwell Bay or Powell River sites was found.

Results presented in the present study suggest a need to further investigate the sources, chemical speciation, and bioavailability of cadmium in sediments from False Creek (an active dredge site), and Bedwell Bay. Although not reflected in the Powell River sediments collected in the present study, recent sampling surveys near other coastal pulp mills have reported sediment cadmium levels up to 60 ppm (H. Nelson, pers. comm.). Additional study of the sources and bioavailability of cadmium associated with marine pulp mill discharges is required to identify the significance of the levels reported.

3.5.2 Lead

Accumulation of lead in $\underline{\mathsf{M}}.$ <u>balthica</u> was significantly greater in Vancouver Harbor sediment than other sediments after 2 and 6 months exposure (Table 6). Results for other sediments varied from



one month to another with no clear pattern evident (Table 6). One surprising result was that no significant differences in bioaccumulation of lead between the Vancouver Harbor, False Creek and reference sediments were observed after I month despite the high values for dissolved lead in the seawater in these two test This suggests that lead is containers, and in the sediments. accumulated relatively slowly by M. balthica. Bioaccumulation of lead increased steadily over time for all sediments between month I and 4 (Fig. 2). Values for lead then declined after 6 months in \underline{M} . balthica exposed to False Creek and Powell River sediments, and Vancouver Harbor increased dramatically in the sediment. Statistically, only Vancouver Harbor and False Creek showed significant differences (p less than 0.05) in the bioaccumulation of lead compared to time 0 (Table 7). These results suggest that long-term (4-6 month) laboratory exposures are required to detect bioaccumulation of lead from polluted marine sediments. of M. balthica tissues indicated that there was a greater standard error for lead than for cadmium or mercury (Fig. 2). This difference was also observed in clams analyzed for "background" lead levels. These results suggest a high degree of variability in the uptake of lead by M. balthica.

Lead was accumulated by N. virens from False Creek sediments after I month but levels then declined. C. capitata also showed elevated concentrations of lead from Power River (I month) and Bedwell Bay (3 months) but there were too few analyses with which to establish any definite trends.

The present study confirmed previous predictions of the potential for lead to bioaccumulate from Vancouver Harbor sediments (McGreer et al., 1981). The concentrations of lead which accumulated in clams from the present study were similar to concentrations detected in resident mussels (M. edulis) at this site (McGreer et al., 1981). M. balthica was also shown to accumulate lead in a study with sediments from Dalhousie Harbor (Ray et al., 1981). It appears that harbors are a major source of bioavailable lead. Insufficient data on



the toxicity of different species of lead to marine organisms, particularly under different seawater-freshwater mixtures, exist to assess the implications of the levels recorded (Konasewich et al., 1981). It would also be desirable to use chemical analytical methods which could be used to relate the concentrations of lead in sediments to their biological availability. For example, the bioavailability of lead in one species of bivalve (Scrobicularia plana), and a polychaete worm (Nereis diversicolor) can be predicted when surface sediments are extracted with 1 N hydrochloric acid (Luoma and Bryan; 1982).

3.5.3 Mercury

Mercury did not bioaccumulate appreciably in any of the sediments tested (Tables 4 and 5). The highest value recorded was 1.394 μ g/dry g in \underline{M} . $\underline{balthica}$ after 6 months in Powell River sediment. Of the three sites for which data was available, none showed a statistically significant uptake in \underline{M} . $\underline{balthica}$ over time (Table 7).

The Canadian Ocean Dumping Control Act Regulations prohibit dumping of solid wastes containing a concentration of mercury in excess of 0.75 µg/dry g. Of the sediments tested in the present study, only sediment from False Creek exceeded the guideline for mercury. However, the False Creek sediment also had the highest organic content (11%). Sedimentation is an important process affecting the eventual distribution of mercury in the marine environment, particularly where the sediments have a high organic content (Konasewich et al., 1982). The major concern with respect to bioaccumulation of mercury is for the organo-mercury compounds. Methylation of inorganic mercury from sediments by bacteria can be an important process in the uptake of mercury (Wood, 1974). Results of the present study indicate that the mercury contained in the test sediments is not readily bioaccumulated. Similar results have been obtained with respect to the uptake of mercury by N. virens from New York Harbor sediments (Rubinstein et al., 1983).



3.5.4 Rate of Uptake and Achievement of Steady State Condition

Information developed in the present study on the rate of uptake and achievement of a steady state condition are summarized below from data on the clam $\underline{\mathsf{M}}$. $\underline{\mathsf{balthica}}$. As discussed previously, mortalities experienced with the two species of polychaete worms resulted in insufficient numbers of tissue analyses with which to identify definite trends.

Subsequent to an initial, rapid uptake from all test sediments after one month, the rate of cadmium uptake followed three different patterns. Uptake and bioaccumulation appeared to stabilize in $\underline{\mathsf{M}}$. $\underline{\mathsf{balthica}}$ exposed to False Creek and Vancouver Harbor sediments, but continued to accumulate steadily from Bedwell Bay sediments. Bioaccumulation from Powell River followed a third pattern which showed considerable variability.

The uptake of lead also appeared to follow two different patterns. Uptake was observed between one and four months in the Powell then declined sediments, False Creek River and months - never achieving a steady state. Uptake from Bedwell Bay and Vancouver Harbor showed a continued, steady accumulation after two months with no leveling off (i.e. steady state) being reached. The rate of uptake was much greater from the Vancouver Harbor than the Bedwell Bay sediment during this period. The relatively high levels of lead in seawater reported in this study did not appear to affect the relative bioaccumulation of lead from sediments. The highest values of lead in tissues of M. balthica were found in those test sediments with the highest lead levels. This observation suggests that the sediments were the major source of bioavailable lead.



3.6 Sediment Toxicity

Chronic toxicity of test sediments including the Bedwell Bay (reference) sediment may have been responsible for mortalities observed in the test animals used in this study (Table 8). N. virens did not survive beyond two months in any sediment. Mortalities of greater than 80% were recorded for C. capitata in all sediments except Powell River by the end of three months. Mortality in \underline{M} . balthica was greatest in the False Creek (28%) and Vancouver Harbor (24%) sediments after a 6 month exposure (Table 8). The distinctive smell of hydrogen sulfide was not detected in the sediments at any time over the study period. As oxygenated seawater was available to the test animals at all times, a reasonable assumption would be that sediment toxicity was due to contaminants However, as the polychaete worm species showed similar mortalities in both the reference and test sediments, some other factor may have been responsible for the deaths observed. example, laboratory populations of C. capitata have been shown to be susceptible to lethal viral infections (P. Chapman, pers. comm.).

Toxicity observed in the present study resulted from chronic exposure to test sediments for 60 to 180 days. Previous toxicological studies with these sediments showed no elevated mortalities in adult M. balthica after 30 days exposure to Vancouver Harbor sediment (McGreer et al., 1981), or in M. balthica and C. capitata exposed to sediments from False Creek for 60 days (Reid et al., 1981). However, exposure of eggs of the Pacific cod (Gadus macrocephalus) to a 1 mm covering of sediment from False Creek resulted in 99% mortality after 70 h (McGreer and Munday, 1982).

Data on the chronic toxicity of contaminants in sediments or seawater to marine species are rare. Cadmium and lead were shown to be released into interfacial waters from all test sediments in this study. Konasewich et al (1982) concluded that cadmium could have significant sublethal effects at levels of 5 µg/L in seawater. Toxicity data for lead to marine species, particularly under estuarine



conditions, has been identified as a research priority for Puget Sound (Konasewich et al., 1982). No direct relationships can be established between bioaccumulation of various contaminants and biological effects without such basic toxicological data for marine species. In addition the presence of other contaminants in the polluted test sediments may have contributed to the observed toxicity. In the absence of supporting data on the acute and chronic toxicity of contaminants to the marine test species, the mortalities observed can only be considered idiopathic.

Comparison of laboratory data and field observations indicate a strong correspondence between sediment toxicity and the distribution of benthic invertebrates. Previous studies have reported that test sites sampled in Vancouver Harbor and False Creek appear to be devoid of benthic infauna (McGreer and Reid, 1980; Reid et al., 1981). Benthic surveys at Powell River (which had the lowest toxicity to M. balthica) have documented a diverse benthic community (McGreer and Coustalin, 1982). Several recently published studies suggest that a direct relationship exists between sediment toxicity and the distribution of marine invertebrate populations (McGreer, 1982; Swartz et al., 1982). Sediment toxicity may be a major factor in explaining the distribution of benthic animal populations in polluted areas.



4.0 CONCLUSIONS

The following conclusions can be drawn from the experimental data produced in this study:

- I. Cadmium was readily released at variable rates into interfacial seawater from all sediments tested. Cadmium appeared to be loosely bound even in sediments with a high organic content.
- 2. Lead was released most rapidly and to the highest concentration from harbor sediment collected adjacent to a ship dry dock/repair facility. Vessel protection measures and stormwater runoff were considered possible sources of the highly bioavailable form of lead to these sediments.
- 3. Mercury was not readily released into interfacial seawater from test sediments. Mercury present in the sediments was considered to be in a relatively insoluble form bound in organic complexes or as a sulfide.
- 4. Bioaccumulation of cadmium varied widely among the species tested and from the different test sediments. Differences in the sources, and chemical speciation and partitioning of cadmium in the sediments were considered to be the major factors controlling bioavailability.
- 5. Lead bioaccumulated slowly in M. <u>balthica</u> with significant differences in tissue concentrations over background occurring only after 4-6 months exposure. Sediments from harbor areas, especially near ship drydock/repair facilities appear to be a major source of bioavailable lead.
- 6. Mercury did not bioaccumulate to appreciable levels during the course of the study from any of the sediments tested. Mercury in sediments from the industrial areas tested was not readily bioavailable.



- 7. Bioaccumulation results for cadmium and lead indicate that the rate of uptake and ability to achieve a steady state is highly variable, and dependent on the type of contaminated sediment tested.
- 8. Mortalities occurring during exposure of polychaete worms to the test sediments could not be explained. Mortalities in M. balthica may have been the result of sediment toxicity but this hypothesis could not be confirmed in the absence of baseline toxicological data on the chronic toxicity of contaminants to this species.

5.0 RESEARCH NEEDS

The following research needs are identified as the result of this study:

- I. There is a need to determine the sources and chemical speciation of cadmium as it relates to bioavailability from marine sediments. Sediments from False Creek and adjacent to pulp mill discharges appear to be priority sites in this regard.
- There is a need to determine the sources, fate and extent of lead contamination in harbor sediments, particularly near ship repair/drydocking facilities.
- 3. In future studies of this type, there is a need to utilize chemical analytical methods which are suitable for relating the concentrations of metals in sediments to their biological availability. Such methods could include selective extraction procedures.
- 4. There is a need to obtain baseline data on the toxicity of both cadmium and lead in seawater and sediments to determine the significance of mortalities observed in long term bioaccumulation



studies. Tests under a range of salinity conditions are required. Toxic effects observed should be related to levels of tissue bioaccumulation.

5. There is a need for continued research into the possible relationship between sediment toxicity and the distribution of resident invertebrate populations. Such studies should include both field (e.g. recolonization) and laboratory (e.g. toxicity) aspects in order to determine cause and effect relationships.



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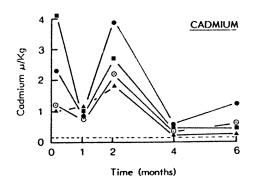


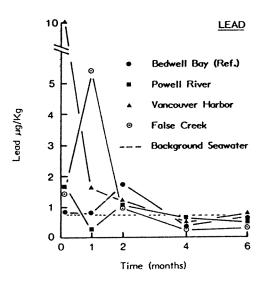
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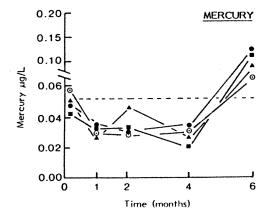


Figure 1. Concentrations of dissolved metals in seawater overlying test sediments.



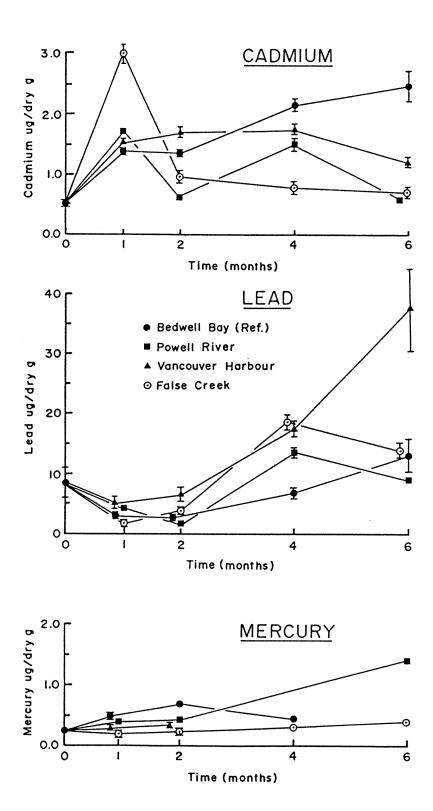


Figure 2. Mean <u>+</u> SE values for tissue metal concentrations in <u>M. balthica</u> exposed to test sediments. No error bar shown for single measurement (background tissue concentration indicated as values at time "0").



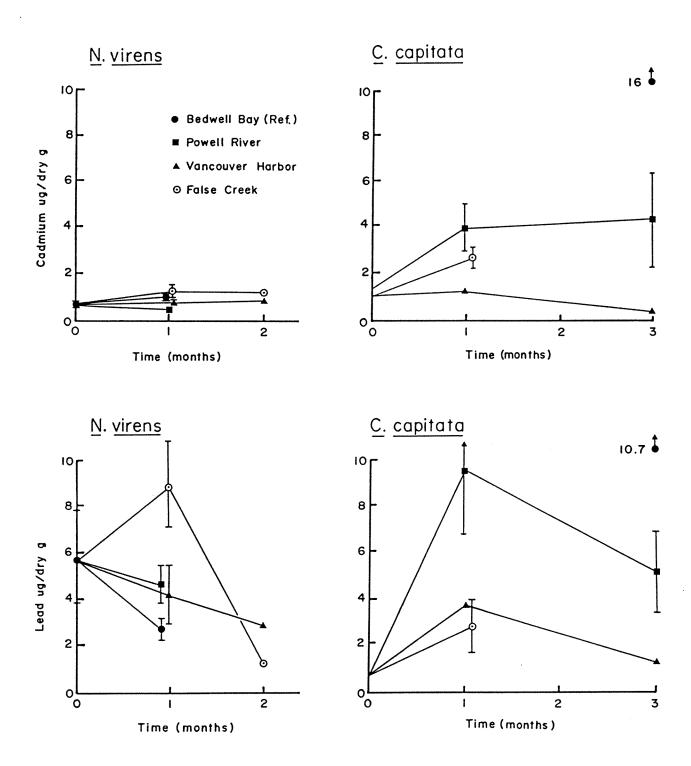


Figure 3. Mean + SE values for tissue metal concentrations in N. virens and C. capitata exposed to test sediments. No error bar shown for single measurement (background tissue concentrations indicated as values at time "0").



TABLE I
PHYSICAL CHARACTERIZATION OF TEST SEDIMENTS

Sediment	نّ	Gravel	Sand	pu pu		Silt	Clay	γc	Moisture	fure
	Initial	Final	Initial	Final	Initial	Final	Initial	Finat	Initial	(%) Initial Final
Bedwell Bay (Ref.)	•	9.0	6.16	91.3	5.3	5.3	2.8	2.8	22	25
Powell River	12.5	7.0	85.8	91.6	0.3	0.5	7.1	6.0	21	61
Vancouver Harbor	2.2*	3.6	80.9	87.8	11.9	10.0	5.0	3.6	33	45
False Creek	*6.4	19.3*	24.4	25.7	38.9	29.4	31.8	25.6	65	11

*indicates samples in which the >2 mm size fraction consisted primarily of wood chips; gravel >2.0 mm; sand 2.0-0.0625 mm; silt 0.0625-0.004 mm; clay <0.004 mm.



TABLE 2
CHEMICAL CHARACTERIZATION OF TEST SEDIMENTS

		5	7 - 7		- -		8) _
	Initial	Final	Wg/ary g/ Initial Final	ry g) Final	Initial	Final	(%) Initial Final	Final
Bedwell Bay (Ref.)	2.61	2.33	15.6	15.9	0.061	0.057	. 86.0	0.27
Powell River	0.25	0.23	26.5	14.0	0.035	0.055	0.51	0.17
Vancouver Harbor	21.2	23.2	099	393	0.630	0.376	1.34	1.68
False Creek	4.72	4.73	364	248	0.908	0.955	0.11	12.8

*lead values uncorrected for low recovery during analysis compared to certified reference sediments



TABLE 3
CADMIUM, LEAD AND MERCURY IN SEAWATER

Sediment	Time	Cd (µg/kg)	Pb (µg/kg)	Hg (ng/L)
Bedwell Bay (Ref.)	24h	2.31	0.84	48
	Imo	0.85	0.78	35
	2mo	3.91	1.72	30
	4mo	0.55	0.28	33
	6mo	1.24	0.62	123
Powell River	24h	4.17	1.56	39
	I mo	0.93	0.14	31
	2mo	2.74	1.01	33
	4mo	0.45	0.62	21
	6mo	0.46	0.58	112
Vancouver Harbor	24h	1.05	10.00	49
	Imo	1.23	1.57	27
	2mo	1.78	1.18	46
	4mo	0.19	0.42	27
	6mo	0.30	0.76	84
False Creek	24h	1.22	1.42	57
	Imo	0.78	5.39	29
	2mo	2.22	1.08	30
	4mo	0.38	0.26	32
	6mo	0.63	0.34	65



TABLE 4

VALUES FOR TISSUE METAL CONCENTRATIONS IN Maccoma balthica

Test Sediment	Time (months)	Codmium	Lead (µg/dry g)	Mercury
Background		0.41	2.30	0.272
•		0.55	8.89	0.352
		0.53	12.30	0.174
Bedwell Bay (Ref.)	1	1.39	3.45	0.486
		1.02	3.07	0.240
		1.72	2.60	0.582
	2	1.31	4.49	0.651
	-	1.37	2.43	-
		1.38	3.06	-
	. 4	2.57	4.80	0.461
	. •	1.91	8.26	0,461
		1.98	8.40	
	6	2.45	10.0	
	•		18.8	-
		3.02	8.85	-
		1.66	11.7	•
Powell River	1	1.70	2.81	0.345
		1.69	3.78	0.328
		1.69	4.61	•
	2	0.67	2.64	0.427
		0.66	2.07	0.378
		0.39	1.83	•
	4	1.35	13.5	
		1.86	14.9	•
		1.40	14.1	•
	6	0.59	8.79	1.394
		0.72	8.81	•
		0.53	10.4	•
Vancouver Harbor	1	1.49	5.70	0.205
Vancouver Harbor	•	1.74	4.08	0,253
		1.19	3.05	0.273
	2	1.85	8.64	0.310
	•	1.52	4.34	-
		1.57	6.23	-
	4	2.19	19.9	-
	~	1.73	16.4	-
		1.33	17.2	-
	6	1.08	48.1	
	•	1.34	27.3	:
		1.34	27.3	:
False Creek	ŧ	3.20	4.32	0.332
ruise Creek	1	3.20 2.36	4.32 2.9 4	0.332
		2.36 3.18	3.33	0.167
	2	1.32	3.28	0.300
		0.66	5.47	0.253
		0.87	4.13	0.205
	4	0.49	20.5	0.300
		0.79	17.5	-
		1.05	16.3	•
	6	1.05	16.3	0.336
		0.53 0.90	14.6	•
			14.0	

⁻ insufficient tissue for analyses; each analysis is based on one "sample" of a minimum of $10\ \text{clams}$



TABLE 5

VALUES FOR TISSUE METAL CONCENTRATIONS IN Nereis virens AND Capitella capitata

Species	Test Sediment	Time (months)	Cadmium	Lead (µg/dry g)	Mercury
N. virens	Background		0.67 0.53 0.67	2.53 5.66 9.22	0.347 0.229 0.290
	Bedwell Bay (Reference)	Î	0.68 0.49 1.11	2.90 3.56 2.06	0.286 0.158 -
	Powell River	ŧ	0.59 0.50 0.61	3.24 5.54 4.73	0.414 - -
	Vancouver Harbor	I	1.56 0.30 0.31	6.60 2.19 3.71	:
	,	2	0.97 - -	3.04 - -	-
	False Creek	1	1.42 0.66 1.17	11.3 4.83 10.6	-
		2	1.24 - -	1.31	-
C. capitata	Background		1.11	0.44	0.160
	Bedwell Bay (Reference)	1 3	16.0	10.7	-
	Powell River	1	2.9 5.1 1.9	7.68 15.6 5.17	- -
		3	6.2 3.3	6.81 2.32	-
	Vancouver Harbor	! 3	1.38 0.21	3.84 1.33	-
	False Creek	1	3.8 2.62 2.35	2.87 4.41 1.09	- - -

⁻ insufficient tissue for analyses; each analysis is based on one "sample" of a minimum of 5 individuals



TABLE 6

SUMMARY OF ONE WAY ANOVA* BY SITE FOR CLAM TISSUE METAL CONCENTRATION FOR EACH MONTH SAMPLED

REF - Bedwell Bay Reference sediment; PR = Power River sediment; VH = Vancouver Harbor sediment; FC = False Creek sediment

Metal	Month	Distinct Homogeneous Subsets (i.e. <u>Sites</u>) Identified by Studentized Newman-Keuls Range Test (p < 0.05)
Cadmium	I	(REF, PR, VH) (FC)
	2	(PR, FC) (REF, VH)
	4	(FC) (REF, PR, VH)
	6	(PR, VH, FC) (REF)
Lead	I	ns
	2	(REF, PR, FC) (VH)
	4	(REF) (PR, VH, FC)
	6	(REF, PR, FC) (VH)
Mercury	I	ns
,	2	(PR, VH, FC) (REF)
	4	-
	6	-
	6	<u>-</u>

^{*}all results were significant at p < 0.05 except where indicated; ns = not significant



⁻ indicates insufficient data for analysis

TABLE 7
SUMMARY OF ONE WAY ANOVA* BY MONTH FOR CLAM TISSUE METAL CONCENTRATION FOR EACH SITE SAMPLED

Sediment	Distinct Homogeneous Subsets (i.e. Months) Identified by Studentized Newman-Keuls Range Test (p < 0.05)
Bedwell Bay (Ref.)	(0) (1, 2, 4) (4, 6)
Powell River	(0, 2, 6) (1, 4)
Vancouver Harbor	(0) (1, 2, 4, 6)
False Creek	(0, 2, 4, 6) (1)
Bedwell Bay (Ref.)	(0, 1, 2, 4) (0, 4, 6)
Powell River	(1, 2) (0, 1) (0, 6) (4)
Vancouver Harbor	(0, 1, 2, 4) (6)
False Creek	(0, 1, 2) (4, 6)
Bedwell Bay (Ref.)	ns
Powell River	ns
Vancouver Harbor	-
False Creek	ns
	Bedwell Bay (Ref.) Powell River Vancouver Harbor False Creek Bedwell Bay (Ref.) Powell River Vancouver Harbor False Creek Bedwell Bay (Ref.) Powell River Vancouver Harbor Powell River Vancouver Harbor

^{*}all results were significant at p < 0.05 except where indicated; ns = not significant



⁻ indicated insufficient data for analysis

TABLE 8

PERCENT MORTALITY OF BIOASSAY SPECIES IN TEST SEDIMENTS DURING BIOACCUMULATION EXPERIMENT

Time (months) 0 1 2 3 4 5 6	100%	88%	13%
		———————————————————————————————————	
Species	Nereis <u>virens</u> Powell Bay (Ref.) Powell River Vancouver Harbor False Creek	Capitella capitata Bedwell Bay (Ref.) Powell River Vancouver Harbor False Creek	Macoma <u>balthica</u> Bedwell Bay (Ref.) Powell River Vancouver Harbor False Creek



APPENDIX TABLES



TABLE A-I

ACCURACY AND PRECISION OF SEAWATER ANALYSES

Element	Blank ng	Detection Limit ^a ng	NASS-I (found) ng/L	NASS-I (certified) ng/L	Precision ^b %
Cd	0.5	0.5	25 <u>+</u> 2	29 <u>+</u> 4	2.5
РЬ	2	I	32 <u>+</u> 4	38 <u>+</u> 6	12
Hg	1.5	1	Not	certified	15

a defined as 2x standard deviation of the blank



 $^{^{\}rm b}$ relative standard deviation at level of 10 ng/L for Hg; 60 ng/L Cd; 30 ng/L Pb

TABLE A-2
ACCURACY AND PRECISION OF SEDIMENT ANALYSES

Element	Blank ng	Detection Limita	MESS-1b Certified µg/g	MESS-Ic Found µg/g	BCSS Certified µg/g	BCSS Found µg/g
P	50	20	0.59 ± 0.10	0.63 ± 0.04	0.25 ± 0.04	0.27 ± 0.02
Pb		25	34.0 ± 6.1	20.3 ± 1.2	22.7 ± 3.4	11.4 ± 2.0
Hg	2	5	0.171 ± 0.014	0.173 ± 0.020	0.129 ± 0.012	0.125 ± 0.015

a 2x standard deviation of the blank

b the uncertainties for the reference values represent 95% tolerance limits

^C The values obtained for the reference materials are the mean of four analyses and the uncertainty expressed as the standard deviation (10).



TABLE A-3

ACCURACY AND PRECISION OF TISSUE SAMPLES

Blank ng	Detection Limit ^a ng	NBS Certified µg g-l	NBS Found µg g-l	Precision ^b %
5	5	3.5 <u>+</u> 0.4	3.3 <u>+</u> 0.05	9
11	15	0.48 <u>+</u> 0.04	0.41 <u>+</u> 0.09	12
5	4	0.057 <u>+</u> 0.015	0.051 <u>+</u> 0.013	8
-	ng 5 11	ng Limit ^a ng 5 5 11 15	ng Limita Certified pg g-1 5 5 3.5 + 0.4 11 15 0.48 + 0.04	ng Limita ng Certified $\mu g g^{-1}$ Found $\mu g g^{-1}$ 5 5 3.5 \pm 0.4 3.3 \pm 0.05 11 15 0.48 \pm 0.04 0.41 \pm 0.09

a 2x standard deviation of blank



b relative standard deviation at level of oyster tissue (NBS) (n=60)