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#### AN INVESTIGATION INTO TOXIC CHEMICAL ACCUMULATION IN ESTUARINE VASCULAR PLANTS

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Prepared by

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#### SUMMARY

AIM Ecological Consultants Ltd. initiated a study in the fall of 1987 to examine the levels of specific contaminants in the Fraser estuary; in the water column, in the sediments, and in various plant species. The objectives of the study were to establish the range of contaminant accumulation in the vascular plants and to determine the suitability of using these plants as indicators of general environmental conditions. Hydroponically grown plants were also analysed to determine background contaminant levels and the rate of contaminant uptake. The research was funded by Supply and Services Canada and Environment Canada.

In September 1987, February 1988 and July 1988 water, sediment and plant samples were collected at 4 sites across the Fraser estuary, selected to reflect a variety of environmental conditions. In the fall and summer aboveground and below ground plant components were collected and analysed. In February, only belowground components were available. The chemical analyses were carried out by Analytical Service Laboratories Ltd. (ASL) of Vancouver.

## **SEDIMENTS**

Results of the sediment sampling revealed consistent patterns across the estuary. The highest levels of cadmium sampled were from Musqueam marsh in September. However, on average, Woodward Island had the highest cadmium levels of the stations sampled. The opposite was true for mercury, copper, lead and zinc. Results were variable between sampling dates, but for any given sampling date, Woodward Island had the lowest levels of mercury and lead in the sediment. The levels of lead sampled at Musqueam Marsh were almost two times that of the other sampling locations. The highest levels of organic contaminants were also detected in Musqueam marsh with one notable exception, that of high TCP levels detected on the Richmond foreshore. In contrast, the Richmond foreshore produced the lowest levels of PCB's detected.

#### WATER

Contaminant levels in the water sampled were well within acceptable concentrations, and in some cases were below detection limits. No relationship was determined between the contaminant concentrations in plants or sediments and the water samples collected.

#### **VEGETATION**

#### Interspecific variability

Vegetation analysis showed that there were significant differences in chemical accumulation between species. Of the 4 species sampled, *Carex lyngbyei*, *Scirpus validus*, *Scirpus americanus* and *Scirpus maritimus*, the latter two showed very similar patterns of chemical accumulation which was also similar to, but less than the *Scirpus validus*. The sedge [*Carex lyngbyei*] showed significantly greater accumulation of metals and organic contaminants, than did the rushes [*Scirpus* spp].

#### Intraspecific variability

There were highly significant differences detected between the plant components within species. The concentration of chemical was consistently greater in the belowground components than in the shoots. There was much greater variability within the rhizomes than the shoots, possibly due to adhering sediment particles, and possibly due to variations in chemical concentrations with depth. The sediment was sampled from a relatively small area compared to that which the root systems extend over. It is also possible that there is selectivity in pumping the chemicals to the shoots. Only PCBs were found to be concentrated in plant shoots at levels exceeding that of the substrates.

#### Intersite variability

Although sediment contaminant levels varied according to site, this was not reflected in the plants to any significant degree.

#### Seasonal variability

Seasonal variability in the concentration of chemicals within the plants to a large extent reflects their annual cycles. High levels of cadmium, mercury and PCB detected in the belowground systems in the fall may indicate the culmination of a season's growth and collection of contaminants within the plant. Changes in the concentration of some chemicals over the winter may reflect leaching. Hydroponic studies and transplant experiments indicated that there may be a more rapid response to changing environmental conditions than initially expected.

#### Concentration of chemicals within plants

Those contaminants which were being accumulated in the vegetation to levels above that found in the sediments included: cadmium, mercury and PCB. PCBs were the only contaminants to be concentrated in the aboveground plant components to levels above [up to 6 times] that found in the sediment. PCB levels in the rhizomes were up to 14 times that of the sediment. Mercury was found in the rhizomes at or slightly above the levels found in the sediments. Cadmium levels in the plants were up to 4 times that found in the sediments. The hydroponic results were consistent with the field results with the exception of lower concentration levels found in the shoots. It is likely that PCBs are absorbed directly by the plants from the water column as well as the sediments. The greenhouse experiment did not flood the plant shoots therefore uptake was restricted to the root systems and shoot levels reflected translocation from belowground components.

The other chemicals were found in the plant shoots at up to 20% of sediment concentrations for Cu and Zn, and 8% for lead. In plant roots the concentrations were, Cu- up to 100 %, Zn up to 40 % and Pb up to 22%. For PCP and TCP, the balance between roots and shoots was more even than for metals and the average concentrations ranged between 40 and 80% of sediment levels.

Different plant species concentrate environmental contaminants to different degrees. Although there is considerable variation, the various species and components of these species follow discernible patterns of concentration for specific chemicals. Intersite variability did not prove to be sufficiently great to merit a broad sampling program. However the concentration of mercury, cadmium and PCB's by the plants merits further investigation.

#### 1. INTRODUCTION

Coastal submergent and emergent vegetation has long been identified as irreplaceable fish and wildlife habitat along all of Canada's coastlines. In British Columbia, most intertidal vascular plants are restricted to estuaries. Estuaries also provide the locale for most of the industrial activity in coastal B.C. but little attention has been focussed on the effects of chemical accumulation in the biota. Although monitoring of water quality does take place in the vicinity of industrial sites, this sampling reflects the environmental condition for only that instant in time during which the sample was collected. Winds, wave action, currents, and river flow all influence the dispersion of contaminants. The fauna exposed to these contaminants are also mobile and the results of any tissue analyses are therefore difficult to interpret.

Algae have been used to show, by their presence or absence, the level of contaminants in their immediate environment. In some cases the algae have also been analysed to determine concentrations of metals and other contaminants in their tissues. Vascular plants on the other hand, have received little attention in terms of their role as accumulators of environmental contaminants and as integrators of the average conditions at any site. Vascular plants not only reflect conditions in the water column but they also draw up nutrients and other chemicals from the substrates.

The high annual productivity of intertidal marshes makes them a vital component of many food webs. All parts of the living plants may be consumed by small mammals and waterfowl. As the plants decay during the fall and winter, the resulting detritus is consumed by bacteria, invertebrates and fish. Heavy metals such as mercury have an affinity for organic particulates, so in many instances the organic detritus becomes enriched with metals as it is washed around in the estuary or when it lies on contaminated substrates.

Terrestrial plants have been found to selectively accumulate heavy metals from the substrate. On the Atlantic coast, salt marsh species have been shown capable of concentrating mercury within the plant roots to levels higher than those found in the sediments. An examination of mercury accumulation within the vascular plant components and associated sediments on the Squamish river estuary [Moody and Moody 1985] showed that although mercury levels were not being concentrated to levels greater than those found in the sediments, mercury was accumulated to different degrees in the various plant organs. There was also an indication that the plants might be pumping mercury from deeper layers in the substrate to the marsh surface. This process would occur when mercury was absorbed at the root and rhizome depth, translocated to the aboveground components and finally deposited on the marsh surface as the aboveground tissues were broken down. Studies of *Sparting alterniflorg* on the Atlantic seaboard have revealed that this species is capable of removing heavy metals from sediments and also of moving those metals into the coastal waters through export of the dead grass.

In 1987 AIM Ecological Consultants Ltd. undertook an investigation of toxic chemical accumulation within the vascular plants of the Fraser River Estuary. The study was funded by Supply and Services Canada in conjunction with Environment Canada, Conservation and Protection. The objectives of the study were to determine which chemicals were being accumulated by the vegetation and to what degree. We also sought to determine differences in accumulation between plant species and between various locations in the estuary. The study also considered the possibility of using vascular plants as indicators of environmental quality.

## 2. **BACKGROUND**

Metal concentrations in estuarine waters are usually derived from riverine sources. The Fraser River estuary is surrounded by highly urbanized and industrialized areas, which discharge effluent into the river and estuary. Industrial sources of contaminants are: pulp, paper and lumber mills, wood treatment plants, cement plants, metal finishing and fabricating plants, landfill leachates, sewage treatment plants and stormwater discharges.

Elevated levels of metals have been found in the vicinity of the Iona Island sewage treatment plant. Lead and zinc levels are high in the North Arm due to industrial input and stormwater discharges. Crabs collected in the Fraser River estuary have been found to have elevated levels of mercury and copper and fish occasionally exceed the Health and Welfare Canada guidelines for mercury. PCBs have been detected at low levels throughout the sediments of the Fraser River estuary and chlorinated phenols have been associated with the sediments and biota adjacent to wood treatment plants.

#### **CHLORINATED PHENOLS**

Pentachlorophenol [PCP] and tetrachlorophenol [TCP] are used for wood treatment. The Fraser estuary area contains some 20 wood treatment plants in addition to 13 pulp, paper and lumber mills. PCP is the most environmentally persistent form and may cause both acute and chronic effects. Acutely toxic levels of sodium pentachlorophenate in fish, especially salmon have ranged from 0.03-0.3 mg/l [96 hr LC50]. Chronic effects have been detected at 1/20 the concentration of the LC 50 values. PCP has been shown to affect growth and food conversion efficiency in salmon at concentration as low as 0.00174 mg/l [Garrett 1982].

#### **POLYCHLORINATED BIPHENYLS** [PCBs]

PCBs are toxic to almost all organisms and accumulate in aquatic organisms at high concentrations. Invertebrates are particularly sensitive during their molting period. Bioassay results have produced LC50 tests as low as 3 mg/l for grass shrimp. Exposure to 1.0 µg/l or greater has been shown to decrease the population of arthropods, amphipods, bryozoans, crabs and molluscs. PCBs have been shown to inhibit growth in phytoplankton and aquatic plants [Garrett 1982].

## **METALS**

Cadmium is used in electroplating and the coating of metal products and parts, for pigments in paints, and as a contaminant in phosphate fertilizer. It is considered one of most toxic metals to aquatic organisms; salmon are particularly sensitive. Sublethal effects are decreased fecundity, reproductive impairment and reduced survival of young. Larval and juvenile stages of aquatic invertebrates are more susceptible to toxic effects of cadmium than adults.

Copper is used for pesticides, pigments, catalysts, paint additives and in the electrical industry. It is an essential element for plants and animals but high levels can be toxic. In plants, copper deficiency is identified at 3-5 ppm, normal range is 5-15 ppm. Although levels above 20 ppm are considered excess [depending on the Fe-Cu ratio], high levels of copper are well tolerated by many terrestrial plants [Hausenbuiller 1972].

Lead is used for electric storage batteries, paint additives, gasoline additive, lead shot, metal plating etc. Its toxicity somewhat lower than zinc. Various invertebrate species are sensitive to lead, and chronic exposure to levels as low as 0.0076 mg/l caused spinal curvature and tail blackening in rainbow trout [Garrett 1982].

A major producer of mercury is the chlor-alkali industry. Mercury is also contained in electrical equipment, pesticides, paints, dental amalgams etc. Mercury can be biomagnified through the food chain and converted to a highly toxic methylated form. Juvenile stages of aquatic invertebrates are generally more susceptible than adults. Mercury is characterized by a long retention time in tissues.

Zinc is used in galvanizing, paints, plastics, rubber etc. It is an essential micronutrient for plants and a lack of zinc in the soil causes interveinal chlorosis and stunting of growth. The normal range of zinc in soils is considered to be 200-500 ppm. Levels of 15 ppm are considered deficient for plant growth and 200-500 ppm is considered excess. The effects of excess zinc are considered rare in terrestrial plants [Hausenbuiller 1972]. Zinc is considered essential in animals for the synthesis of protein and carbohydrate metabolism. High levels are toxic and have been related to problems such as the destruction of fish gills.

#### ECOSYSTEM INTERACTIONS

The primary pathway for exposure of animals to high levels of trace elements is often by ingestion of plant material. Bioassays of invertebrates and fish to determine lethal doses of trace metals or other contaminants are conducted by using known quantities of contaminant in the water column. However, many of the organisms rely on the breakdown of marsh vegetation, detritus, for their food. Although the levels of contaminants in the water column may be very low, in some cases these contaminants are concentrated to high levels by the plants. These high levels of contaminants are then passed on through the food chain. To date we have had a poor understanding of which species of plants are capable of biomagnification, which elements are concentrated and to what degree. Even though high levels of a metal may be tolerated or absorbed by a plant, the consumers of the vegetation may be placed at risk through ingestion of high metal levels contained in the plant.

The plants may also have a useful purpose as indicators of environmental quality. "An indicator organism should fulfil the following requirements, among others: be of reasonable size, be sedentary, be easily collectable and be abundant in the study area [Phillips 1980]."

Plants have been referred to as "living filters of trace elements flowing through the estuary" [Ragsdale and Thorhaug 1980]. The large expanse of marshes in the intertidal area, and the density of plants in them provides a large surface area for chemical element cycling. Plant cell walls and membranes allow a flux of trace elements in and out of plant tissues. The physiology of individual species may lead to active uptake and accumulation of trace elements.

#### **TRACE METAL ACCUMULATION BY PLANTS**

Trace metal uptake by a plant is influenced: externally by pH, redox potential and the organic content of the sediment; and internally by stage of growth, nutrient availability and oxygen supply to belowground organs [Drifmeyer and Redd 1981]. In general, a lower pH, oxidizing conditions, lower organic matter and clay content make metals increasingly available for uptake by plants. Macronutrient and metal interactions have been identified as important in some cases [Beeftink et. al. 1982]. Under the strong reducing conditions normally present in a marsh, large portions of metals may be retained in the sediment in the form of insoluble metal sulfides [Giblin et. al. 1980]. Large amounts of metals may be retained in high marsh areas due to strong reducing conditions. Low marsh areas may lose metals due to the greater frequency and duration of innundation compared to the high marsh.

The capacity of each plant species to accumulate metals in its tissues is determined genetically and varies for different metals. Substantial amounts of Cd, and Zn may be mobilized from the sediment and taken up by biota, whereas Fe and Pb are often retained in forms unavailable to plants or animals [Giblin et. al. 1980]. Lead is not easily translocatable and is therefore not accumulated in aboveground tissues. A lack of correlation between levels of Pb, Fe and Mn in sediment and the grasses has been reported by various investigators [Dunstan and Windom 1975, Lee et al. 1976, Giblin et. al. 1980]. It has been reported that 98% of the lead entering the marsh remained in situ, whereas 33% of the cadmium was taken up by the vegetation [Lee et al. 1976]. Annual species and short lived perennials have been reported to accumulate more cadmium than long-lived grasses [Beeftink et. al. 1982]. Seasonal changes appeared to be stronger with cadmium than with the other metals. Cadmium showed reduced levels in living plants and was rapidly lost from plant litter late in the year through leaching by sea water [Giblin et al 1980, Beeftink et. al. 1982]

Metal uptake by plants varies highly in magnitude between species and generally increases with increasing metal content of the soil [Drifmeyer and Odum 1975]. Generally, the roots and rhizomes reflect much higher levels of trace metals than do the above ground organs [Ragsdale and Thorhaug 1980]. Some metals [Cr,Pb, Hg] are much more concentrated in the roots than in leaves or stems while others [As, Cd, Cu, Ni] can be readily transported from the roots to the tops of plants [Ernst 1974, Peterson 1975, Pilegaard 1978, Ragsdale and Thorhaug 1980, Breteler et al. 1981]. Although all plant parts of *Spartina* have been found to increase in Hg as the sediment levels rise, the differential concentration between roots and other parts suggests presence of blocking mechanism [Breteler et al 1981]. Heavy metals may be taken up along with nutrients, inactivated by the plants, absorbed and finally accumulated in plant tissue [Mhatre et. al. 1980]. Species which are able to accumulate metals without internal damage will tolerate higher levels of environmental contamination and may therefore have a competitive edge in contaminated habitats.

In general it has been found that metals are associated with organic materials in marsh sediments [Lindberg et al. 1975]. However, Beeftink et al. [1982] found that all metals with the exception of cadmium showed better correlations with clay than with POC content. Clay-metal correlations were highly significant for Ni, Cu, and Pb [Beeftink et al. 1982]. Significant correlations for Cd corresponded to its low clay-matrix bonding and high exchangeability [Duursma et al. 1975, Beeftink et al. 1982]. The highest levels of mercury have been found to accumulate in light textured soils with low organic content; however, mercury in sediments has also been strongly associated with POM, and the decomposition of vegetation produces detrital material richer in Hg than the original live plants [Breteler et al. 1981]. The accumulation of Hg in sediments may result from adsorption and sedimentation of suspended matter and the precipitates may carry Hg to the sediments after co-precipitation or adsorption by hydroxides. Adsorption can be influenced by ionic strength thus causing the adsorption process to change throughout an estuary system as the salt water influence changes [Reimers & Krenkel 1974]. Cranston [1976] found that mercury levels were higher in portions of the estuary which were significantly influenced by salt water and where the sediments contained higher levels of organic carbon.

Marsh grasses [Spartina spp.] which occur widely on the eastern coasts of the United States and Canada are noted for selective ion uptake, high internal osmotic pressure, and ion-specific removal mechanisms [Epstein 1969, Waisel, 1972, Smart and Barko 1978]. Studies undertaken with Spartina spp. have shown varying results. No correlation was found to exist between between heavy metal concentrations in Spartina tissues and concentrations in sediment or waters from 6 different estuaries in the eastern U.S. The metal concentrations in plant tissues were low compared to those of sediments and water. However, the early life stages of the plants were most significantly affected by metal levels. Germination of Spartina was found to be inhibited by methyl mercury [but not by other metals], whereas seedling toxicities were attributed to copper, lead and methyl mercury concentrations [Dunstan and Windom 1975].

In a study in Europe, Beeftink et al. [1982] found that Spartina was able to tolerate concentrations of heavy metals several times the average background concentration. The range of metals found in Spartina was quite narrow in comparison to the range for each metal in the water and marsh sediment. It was concluded that either Spartina was "saturated" in its tissue concentration of heavy metals or that by some mechanism it was able to control metal levels in its tissues. The ratio of metal in plant to metal in sediment was close to 1 for most metals, with the exception of mercury which was up to 4 times that found in sediments. 8

Various hypotheses have been suggested for the variability in metal accumulation.

- i] Organic and/or inorganic chelating complexes in the substrate may influence the ion concentration available to the plants [Jensen et. al. 1974].
- Differences in metal tolerance between species may influence their ability to store metals [Karataglis 1980].
- iii] Antagonistic effects [eg. between Cd and Zn] in the uptake and internal transport of metals may influence metal concentration in the plant [Beeftink et al. 1982].
- iv] Specific element tolerance in plants may confirm or refute common physiological mechanisms of tolerance for these metals [Cox and Hutchinson 1979, Ernst 1974].
- v] The concentration of metals within a plant is genetically determined according to species [Mhatre et. al. 1980, Aulio and Salin 1982].

Ragsdale and Thorhaug [1980], in their synthesis of trace metal cycling concluded that Mn and Fe are generally present in the highest quantities within the plants [for sedge - 341 and 2,400 ppm respectively]. Present in moderate amounts are Copper [10 ppm], Pb [97] ppm], and Zn [45 ppm]. Cadmium and mercury were determined to be present in the lowest quantities. However, all of these concentrations reflected the availability of the metals within the sediments. The only metals to be bioamplified were Cd and Hg [Ragsdale and Thorhaug 1980, Beeftink et. al. 1982]. In contrast, Gallagher and Kibby investigating Carex hyngbyei concluded that plants grown in substrates contaminated with Cd did not have significantly higher levels of Cd than in normal soils. They stated that either the plants did not have the ability to absorb Cd or it was not in an available form. Gallagher and Kibby do not provide any growth results in their paper but it is interesting to note that all of the sedges grown in dredge materials [which contained high levels of contaminants] had lower levels of contaminants than those grown in the uncontaminated soils. It may be possible that the interactions with other contaminants in the dredge material reduced the availability of Cd to the plant. The bioavailability of dissolved Cd was found to be suppressed when levels of Zn and Mn were high [Bruan 1985]. In Spartina alterniflora Cd uptake was reduced at elevated Cd concentrations in dredged material and zinc was identified as a complicating factor [Lee et al. 1978].

Results of growth experiments with various concentrations of Cd on bush beans revealed a significant decrease in yield at higher concentrations of Cd but a dramatic increase in the plant concentration of Cd as the concentration in the culture solution was increased. Despite washings of the roots with 0.1 N HCl to remove Cd adsorbed onto roots, most of the Cd was associated with the roots rather than stems and leaves [Wallace and Romney 1977]. It has also been shown that uptake of Cd by rice was increased as the redox

potential increased to moderately oxidized conditions. This uptake was enhanced by acidic soils [Reddy and Patrick 1977]. Even under aerobic soil conditions and alkaline pH values Cd mobility could be unexpectedly high as Mn oxides become mobilized [Esser and El Bassan, 1981].

A lack of correlation between levels of Pb, Fe and Mn in sediment and the grasses has been reported by various investigators [Dunstan and Windom 1975]. Iron can become unavailable when there is an excess of copper or manganese (or very low level of Mn]. Fe, Mn, Zn and Cu are rapidly immobilized by the soil, in particular Fe is noted for rapid conversion to compounds of low availability [Hausenbuiller 1972]. "Interactions of Fe with Cu and Mn, and sometimes with Zn, appear to be physiological in nature. They reflect the joint participation of these nutrients in some of the same biochemical systems, the proper functioning of which depends on the relative proportions of each of the nutrients present" [Hausenbuiller 1972]. If the soils are Mn deficient, Fe converts to its oxidized form thus reducing mobility in plant. However, if the soils are Mn abundant, Mn occupies Fe position in plant system without taking over its normal physiological function. Zn and Fe deficiencies have been associated with heavy application of P fertilizers, and Fe deficiencies have been associated with excess Cu in soil [Hausenbuiller 1972]. Excess iron has been implicated as a factor in preventing nutrient transport into plants in waterlogged soils. The roots may become coated with an iron oxide layer which may have caused phosphorous, potassium, calcium and magnesium deficiencies [Howeler 1973]. However, the iron layer may also be beneficial in protecting roots from sulfide toxicities [Armstrong and Boatman 1967].

Lead has been found to accumulate in large quantities in roots of bush beans with very little translocation to shoots whereas iron, copper and cadmium, although concentrated in the roots, is also transported to the shoots [Wallace and Romney 1977]. Zinc appears to be evenly distributed throughout the plant. The studies with bush beans identified Cd in association with roots, with little translocation to shoots, but other studies have shown that the transfer of Cd from roots to shoots in other species may be considerably greater [John 1972 and Pettersson 1975 cited in Wallace and Romney 1977]. One of the factors affecting correlations between metal levels in sediment and plants is the large specific difference in metal uptake and transport towards the shoots of the plants. A lack of correlation was found between metal levels in sediments and plants, with the exception of Cd which showed increased accumulation in many plant species sampled from higher contaminated marshes [Beeftink et. al. 1982]. The Cd accumulation was partially attributed to the fact that Cd is adsorbed mainly in exchangeable positions in marine sediments. They also found that annuals and short-lived perennials accumulated higher levels of Cd than the long-lived species. The study concluded that the major plant groups displayed three main pathways of translocation:

Artemesia-Aster group - high Cd, Cu Festuca/Triglochin -- high Hg, Ni and Pb, Atriplex/Spartina -- relatively low concentration of all metals.

### MECHANISM OF ACCUMULATION IN THE PLANT

Plants may absorb metals directly from the air, from flooding water, or from sediments deposited directly on leaves and stems of the plant. Most studies of emergent plants have suggested that the primary source of metals is from the substrate, with the exception of lead which may be absorbed in significant amounts through the stomata.

Algae appear to absorb mercury directly from the water column [Elliott and Griffiths 1986]. Mangrove studies showed that trace elements were accumulated quickly in submerged leaves and more gradually through the roots [Ragsdale and Thorhaug 1980]. Water hyacinth, a free floating aquatic, essentially grows hydroponically, taking up metals from the solution. Increasing the root mass of the plant increases copper uptake. As the amount of free copper in solution decreases, the amount of copper removed from solution by the plant decreases [Lee and Hardy 1987].

Zinc content in eelgrass is derived from the ambient water for the aboveground parts and interstitial water in belowground parts, but translocation is insignificant [Lyngbyei et al. 1982]. In the tropical seagrass, *Thalassia*, the concentration of zinc was determined to be at the leaf tip rather than at the base [Rand 1980]. Concentrations of lead, zinc and copper, in eelgrass reflected sediment levels whereas cadmium concentrations reflected water levels [Lyngbyei and Brix 1982]. Cadmium appears to be translocated from the leaves to the root-rhizomes of eelgrass, but not in the opposite direction [Brix et. al. 1983]. Therefore, the concentrations in the aboveground parts and the belowground parts of eelgrass may provide a guide for the bioavailability of certain trace metals in the ambient and interstitial water, but for other metals, translocation in the plant may be more important. As eelgrass above and belowground parts have short lifespans [55-83 days and 193 days respectively, Jacobs 1979, Sand-Jensen 1975], the trace metal concentration in the plants represents bioavailability in a relatively short period.

Sediments overlain by shallow water are characterized by a thin [a few mm to a few cm in depth], surface-oxidized horizon overlying a thick, reduced horizon. The nutrient and trace metal exchange which takes place in this zone is similar to that of oxidized soils. The surface-oxidized horizon may serve as a barrier to phosphorous movement from sediments

to the water column and may also reduce levels of pesticides and trace metals in the water [Gambrell and Patrick 19]. Pellenbarg [1984] concluded that there was a metal-rich microlayer on the marsh surface which was distributed with tidal water movements into litter covered areas, thus enriching the litter with metals.

Trace element ions may be adsorbed onto the plant surfaces or onto particulate material in the water or sediment surface. Those ions which do not fix or chemically precipitate may remain in the water column and be lost from the estuary with outgoing tides. Elements attached to particulates may be deposited on the sediment or the plant surfaces or may remain suspended in the water column where, again, they may be lost from the estuary. The plant community may filter elements surficially or internally [cellular absorption]. Surface adsorbed elements may reenter the water over a realtively short time span due to the changing chemical gradients of estuarine water. These elements may alternatively be moved across the cell wall and membranes into the plant tissue. Although the absorbed elements may be leached from the plant, it is more likely that they reenter the estuarine system as the plant tissue decays at the end of the growing season. Plants exchange trace elements both with sediment and water and may act as a pump or diffusion straw when high concentration gradients occur. The plant roots absorb elements from interstitial water which may be stored in the root, translocated to the aboveground organs or to the rhizomes. While subject to tidal flooding the stems and leaves may absorb trace elements directly from the water and epiphytic biota may increase the plant surface area significantly [Rand 1980]. The plants which inhabit litter-enriched high marsh areas may translocate a greater amount of metals than those growing where plant debris are removed by tidal action [Beeftink et al. 1982].

Generally, trace element concentration is increased in standing biomass of dead plants and also in plant detritus. The decay of intact plant membranes apparently increases the chargeunsaturated organic surfaces, allowing an increase in trace element concentration on and in plant tissue. Adsorption of metal-enriched organic substances occurs during tidal flooding of the marsh surface [Breteler and Teal 1981]. Active metabolism of microorganisms may also increase trace element concentration in dead plant tissue. Concentrations of Hg, Zn, Cu and Fe in litter of *Spartina* increase proportionately with the length of time the litter is exposed to the marsh surface. Trace metal enrichment in ageing *Spartina* depends on the extent to which the sorbed metal complexes are held by the litter [Breteler et al. 1981b].

Concentrations of Cd, Cr and Mn in live plants have been found to change throughout the growing season. However, concentrations of Pb, Zn, Cu, and Fe remain relatively constant [Rand 1980]. On the other hand, Kavetskiy et al. [1984] found that during the vegetative period, levels of Hg and Pb decreased in water but increased in plants, they

concluded all of the heavy metals [Hg, Pb, Zn, and Cu] were accumulated in aquatic plants. A concentration of most trace metals was found to occur at the end of the growing season when the plants became senescent [Drifmeyer and Redd 1981]. Fe, and Cu were in greatest concentration at the end of the growing season. Cd concentration increased through part of the growing period and then declined continually through the standing dead litter stage [Rand 1980] probably as a result of leaching by sea water [Giblin et al 1980]. The loss of metals is promoted by dissolved complexants, to which Cd and Zn become easily bound [Long and Angino 1977]. Elevated levels of Cu and Pb have been found in Spartina litter [Giblin et al. 1980] which may indicate an ability by Spartina to accumulate large amounts of metals, at least temporarily [Beeftink et al. 1982]. Consistently higher concentrations of metals found in dead plant material than live have been attributed to the fact that the dead tissues may be more porous and interstitial spaces may be contaminated with sediment [Gallagher and Kibby 1980]. The porous structure may provide surfaces for adsorption of ions while decomposition may be removing other components. In addition the microbial population of detritus may contribute to the precipitation of metals [Rand 1980]. The lowest metal values were found in summer. The dilution associated with rapid spring and summer growth was considered a possible explanation for this phenomenon [Gallagher and Kibby 1980].

## EFFECTS OF CONTAMINANTS ON THE PLANT

Long-term pollution by heavy metals can be toxic to a variety of species. The toxicity can result in: population changes [favouring tolerant species]; evolution of metal-tolerances; or, sublethal effects manifesting themselves by lower growth rates, lower reproductive capacity or other characteristic toxic symptoms [Beeftink et al. 1982]. The addition of heavy metals to a hydroponic growth solution in some species suppressed the yield of plant tops, roots and rhizomes; reduced the number of live stems, and number of new stems; and suppressed the height of plant tops for various marsh species [Lee et al. 1976]. In other cases, plants did not show any uptake of heavy metals [Lee et al. 1976]. The results of this study should be interpreted with caution as the plants were transplanted from field conditions into the lab and the researchers admit there may have been problems with transplant shock. In a different study, yields of most vegetables except tomatoes and squash were unaffected by applied digested sewage sludge [Giordano and Mays 1977].

#### **BETWEEN SPECIES VARIABILITY**

The accumulation of metals within plants appears to be specific to the metal and to the species of plant. Even within a genus there are dramatic differences in the selective uptake of contaminants. Five species of pondweeds [*Potamogeton* spp.] tested from a uniform environment, showed that the amount of uptake was species specific and no relationship was found among lifeforms. The high concentrations found in the plants reflected the highly contaminated environment [Aulio and Salin 1982]. In contrast Dunstan and Windom [1975] found no correlation between heavy metal concentration in *Spartina* tissue and in the concentration of sediment or waters from 6 different estuaries. The concentration of metals was low compared to that of the sediment and water. They concluded that the metal concentration in the plants was either saturated or controlled by the plant.

#### **NUTRIENT FACTORS**

Mendelssohn [1979] indicated that nitrogen fertilization of Spartina may overcome the effects of stress. Nitrate concentrations in the tall zone of Spartina were significantly greater than those of the shorter forms. Root and leaf nitrate concentrations in general showed higher concentrations in the tall form. Seasonal changes in leaf tissue concentrations were similar between forms with late winter concentrations high, decreasing in March after spring growth began and decreasing gradually to a minimum in the fall. The field concentrations were very small compared to that which the plants were shown to be capable of absorbing in the lab. Absolute concentrations available to the plants were relatively low therefore it was assumed that nitrate played a minor role in the nitrogen nutrition of Spartina. However, if nitrate is made available the plant species may use it. The major source of interstitial water ammonium is the organic detritus of the marsh compounded by the poor drainage in this zone. Ammonium appears to be the dominant inorganic nitrogen source used by Spartina.

#### **ORGANIC CONTAMINANTS**

PCBs have been shown to accumulate in aquatic biota [Woodwell et al. 1967]. However, very few studies have been conducted to identify the role of plants in the movement of organic contaminants through the aquatic ecosystem. Spartina alterniflora has been found to have the the capacity for uptake, translocation and accumulation of PCB's from contaminated sediments. This process appears to be modulated by the plant [Mrozek et al. 1982]. Selectivity by the plant appears to be for the lesser chlorinated components of the

[Mrozek and Leidy 1981, Mrozek et al. 1982]. Belowground plant component concentrations of PCB were found to be an order of magnitude greater than soil samples [Mrozek and Leidy 1981]. The rate of PCB uptake was reduced by organic soil which also probably affects the potential total uptake [Mrozek et al. 1982]. Accumulation of PCBs by *S. alterniflora* represents a potential pathway for the mobilization of sediment bound chlorinated hydrocarbons from sediments into the estuarine food chain [Mrozek and Leidy 1981, Mrozek et al. 1982].

#### FOOD CHAIN EFFECTS

Decomposing plant litter is in general considered highly enriched with heavy metals. This has been explained by a lower turnover rate of metals as opposed to carbon [Tyler 1971]. Metal-enriched substances may also be adsorbed to the senescent vegetation during tidal flooding of the marsh surface [Breteler and Teal 1981] or through the aqueous surface microlayer [Pallenbarg 1978]. Therefore, detritus retains metals which have been largely extracted from marsh sediments. Following a pattern set by Windom [1975] the average annual uptake of metals through major marsh species can be calculated using average concentrations of leaves and stalks and the average rate of production and assuming it to be constant over the marsh environment. Windom's calculations showed that if all the metals taken up by S. *alterniflora* were released to the water column, there would probably be no significant increase in metal levels with the exception of mercury.

In a heavily Cd contaminated marsh, uptake occurred in marsh and aquatic plants and all species of animals tested [Kneip and Hazen 1979]. The distributions found in the tissues of plants and animals showed significant availability of cadmium to the biota despite its relative stability in sediments. Cd uptake by two filter-feeding mussles depended primarily on percent total sedimentary organic matter and the amounts of metal desorbed. Mercury uptake was dependent on amounts of acid leachable metal and amounts of metal desorbed from the sediment [Breteler and Saksa 1985]. Although biomagnification of mercury from lower to higher trophic levels, appeared not to be taking place overall, increases were occurring along several direct consumer routes Elliott and Griffiths [1986]. Biomagnification from seaweed to grazers represented a two fold increase [Bryan et al. 1983].

## 3. <u>METHODOLOGY</u>

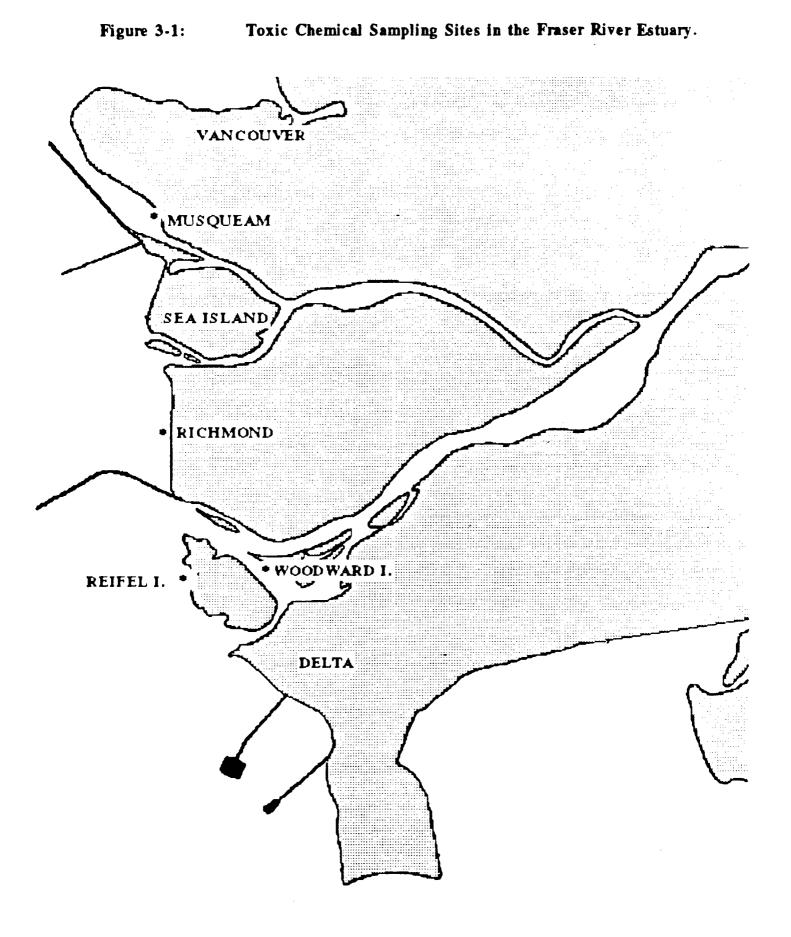
The objectives of this study were to determine levels of specific contaminants in the environment, both in the water column and in the substrate, and to relate these to the level of contaminants in various plant species. In order to meet these objectives four sampling stations were established across the Fraser estuary [Figure 3-1]. The northernmost station was at Musquearn marsh, adjacent to the North Arm of the Fraser River. Two stations were established on the foreshore marshes, one at Richmond and the other at Reifel Island. The fourth station was in the mainstern of the Fraser River at Woodward Island.

#### 3.1 Field Methods

The field studies consisted of collection of water samples, sediment samples and plant components. The biomass as well as the phenological state of the plant were evaluated at each of three sampling dates [September 1987, February 1988 and July 1988]. Four species of plants [Carex lyngbyei, Scirpus validus, Scirpus maritimus, Scirpus americanus] were chosen for evaluation because they were among the most common species in the estuary and represented major contributions to the estuarine food web.

Water samples were collected from water flooding the marsh [whenever possible]. In some cases pond water adjacent to the sample sites was used. Replicate samples of aboveground vegetation were clipped at each site. Replicate cores of belowground vegetation and sediments were collected within the same plots as the aboveground components. The plant samples were packed in food storage bags and refrigerated until processed. Sample processing consisted of washing all adhering sediment from plant components and in isolating the rhizomes from the remainder of the belowground components. Processed samples were refrigerated and transferred to the laboratory for analyses. Sediment samples were collected from the centre of the cores and stored in glass jars for laboratory analysis.

Two species of plants, Carex lyngbyei and Scirpus validus were germinated from seed collected at the sampling sites and cultured hydroponically in a peat and vermicullite substrate for 4 months. As the cultured plants reached maturity, contaminants were introduced into the nutrient solution. Samples of nutrient solution and both above and belowground plant components were sampled periodically to determine uptake of contaminants. Specimens of greenhouse grown plants were transferred to each of the sampling sites in May 1988 and collected in July 1988 to determine uptake.



The laboratory analyses undertaken included the following:

Trace metals	- mercury, zinc, cadmium, lead and copper
Nutrients	- Total phosphorous, dissolved ortho P, Kjeldahl N, nitrite, nitrate, ammonia, sulphate, sulfide
Other	- salinity, pH

## 3.2 Laboratory Methods

## Water

**Conventional Parameters and Metals** 

Analyzed in accordance with "Standard Methods for the Examination of Water and wastewater" published by the American Public Health Association, 1985.

## **Polychlorinated Biphenyls**

The samples were analysed in accordance with U.S. EPA Method 608. This procedure involves the extraction of the sample with dichloromethane [DCM] followed by column chromatography cleanup. The concentrated extract is then analysed using a gas chromatograph equipped with an electron capture detector [ECD].

## **Chlorinated Phenols**

The samples were analysed using the procedure outline in U.S. EPA Method 604 [40 CFR Part 136, 1984] with additional clean-up of the sample by ion-exchange chromatography. The resulting extract was analysed by gas chromatography with electron capture detection.

## Sediment

Samples were analysed using procedures acceptable to regulatory agencies including appropriate quality control measures. After homogenizing the sediment, representative aliquots were removed for analysis as follows:

## Moisture

Determined gravimetrically after drying the sample for 12 hours at 103° C.

## Metals

Subsamples were digested using a combination of nitric and hydrochloric acids then bulked to volume with deionized-distilled water. Copper, cadmium, lead and zinc were determined in the extract by direct flame atomic absorption spectrophotometry [AAS]. Mercury was determined in the extract by cold vapour AAS.

## **Chlorinated Phenols**

A representative portion of each sample was extracted using a modification of the procedure given in the Puget Sound Protocols. This procedure involves the soxhlet extraction of the sample with acidified hexane/acetone followed by solvent partitioning. The crude extract is then cleaned-up using Sephadex QAE-A25 ion exchange resin. The resulting extracts are derivatized using acetic anhydride and analysed by gas chromatography with electron capture detection.

## Polychlorinated Biphenyls

The samples were extracted using acetonitrile. The extract was transferred to a separatory funnel and back extracted into hexane. After florisil column chromatography cleanup and sulfur removal the samples were analysed by gas chromatography with an electron capture detector.

## Plants

Samples were analysed using procedures acceptable to regulatory agencies including appropriate quality control measures. Plant tissue samples were homogenized using a blender and a Tissuemizer. Representative aliquots were removed for analysis as follows:

## Biomass

Determined gravimetrically after drying the sample for 12 hours at 103°C.

## Metals

Representative aliquots of tissue were homogenized and digested using a combination of nitric and perchloric acids. Copper, cadmium, lead and zinc were analysed by graphite furnace atomic absorption equipped with automatic background correction. Mercury was determined in the extract by cold vapour atomic absorption spectrophotometry [AAS].

#### **Chlorinated Phenols**

A representative portion of each sample was extracted using a modification of the procedure given in the Puget Sound Protocols. This procedure involves the soxhlet extraction of the sample with acidified hexane/acetone followed by solvent partitioning. The crude extract is then cleaned-up using Sephadex QAE-A25 ion exchange resin. The resulting extracts are derivatized using acetic anhydride and analysed by gas chromatography with electron capture detection.

## **Polychlorinated Biphenyls**

The samples were extracted using acetonitrile. The extract was transferred to a separatory funnel, back extracted into hexane, and further partitioned to remove lipids. After florisil column chromatography cleanup and sulfur removal the samples were analysed by gas chromatography with an electron capture detector.

#### Total Kjeldahl Nitrogen

The samples were analysed in accordance with Method 2.055 of the Association of Official Analytical Chemists, 1984.

### 4. **RESULTS AND DISCUSSION**

## 4.1 SEDIMENTS

# 4.1.1 Mean Levels of Contaminants

Zinc was found at the highest concentration of all the elements sampled. Copper and lead showed the next highest concentrations [Table 4.1.1-1]. The average levels are provided above in order to place the Fraser River estuary in perspective with other estuaries.

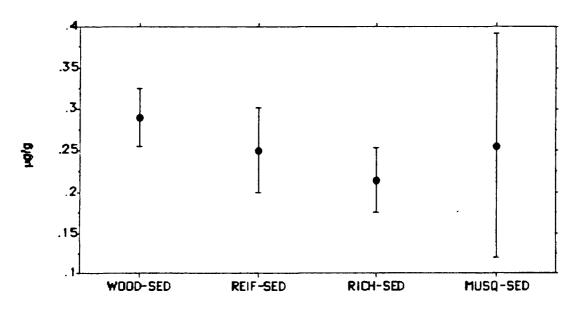
Table 4.1.1-1:	Average Sediment Contaminant Levels [µg/g]							
	Cd	Hg	Cu	РЪ	Zn	РСВ	РСР	ТСР
Musqueam	0.26	0.074	50.41	29.36	113.3	0.013	0.004	<b>0.0</b> 07
Reifel	0.26	0.064	49.53	13.48	103.0	0.007	0.002	0.004
Richmond	0.23	0.073	48.63	18.12	112.3	0.004	0.004	0.017
Woodward	0.31	0.057	44.73	11.07	97.4	0.007	0.002	0.004
AVERAGE	0.26	0.067	48.33	18.00	106.5	0.008	0.003	0.008

20

## Cadmium

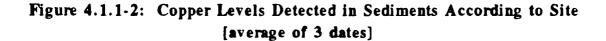
The highest levels of cadmium sampled were from a *Scirpus validus* stand in the Musqueam marsh in September [0.5 ppm] However, on average, Woodward Island had the highest Cadmium levels of the stations sampled. Average values of cadmium ranged from a low of 0.22 at Richmond to a high of 0.31 at Woodward Island.

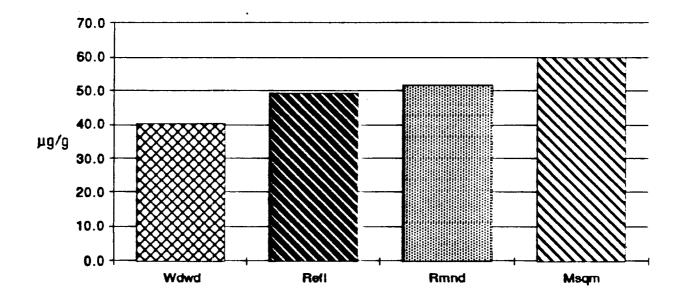
Figure 4.1.1-1: Variation in Cadmium Concentration According to Site Averaged Over Three Dates [±s.d]



Copper

Average copper levels increased from south to north. The lowest levels were detected at Woodward Island and the highest levels at Musqueam Marsh. Copper values declined slightly from north to south with Musqueam having the highest values and Woodward Island the lowest. The range of copper in the sediments would be considered excessive for plant growth in terrestrial plants (>20ppm).



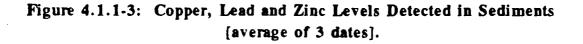


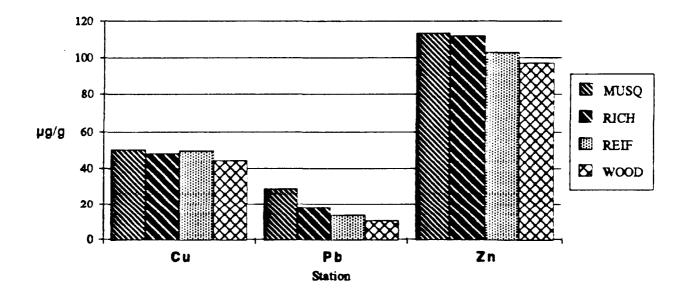
#### Lead

Average lead values declined from north to south. The levels of lead sampled at Musqueam Marsh were almost two times that of the other sampling locations. Woodward Island had the lowest levels sampled.

## Zinc

Zinc levels were the highest of all the metals sampled with a distribution pattern similar to that of lead.

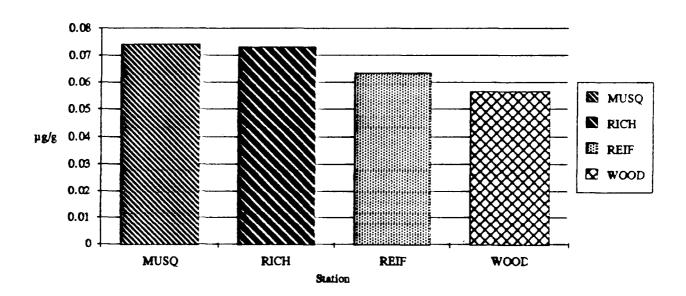




# Mercury

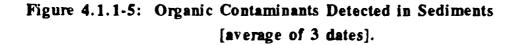
Mercury levels followed the same pattern as lead and zinc with the highest levels being found at Musquearn marsh and the lowest levels at Woodward Island.

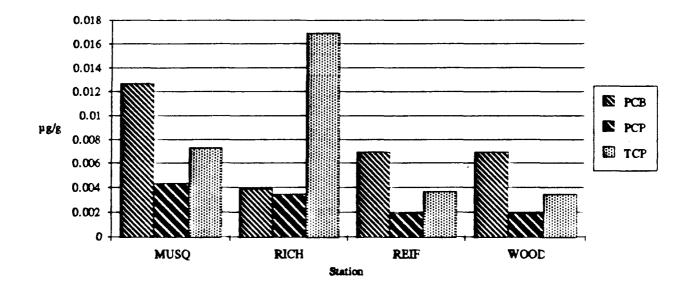




### ORGANICS

The highest levels of organic contaminants were detected in Musquearn marsh probably as a result of the wood products industries related to the North arm. There was one notable exception, that of high TCP levels detected on the Richmond foreshore. In contrast, the lowest levels of PCB's detected were from the Richmond foreshore which probably has the least riverine influence.





#### 4.1.2 Seasonal Variability

Results of the field sampling have revealed considerable variation across the estuary. For cadmium, the greatest seasonal extremes were seen at Musqueam marsh and the greatest uniformity at Woodward Island. Mercury results were highly variable between sampling dates, but for any given sampling date, Woodward Island had the lowest levels of Mercury in the sediment. Because of the high degree of variability, no trend was apparent in the mercury levels. In general terms lead levels reflected the same seasonal patterns at each site as did the mercury levels, possibly indicating sampling variability. When averaged over time, the pattern followed that of Cu, Pb and Zn, with lowest levels found at Woodward Island.

Figure 4.1.2-1: Variation in Sediment Cadmium Levels Over Time

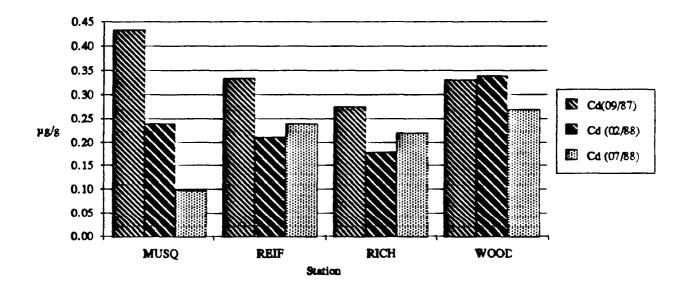
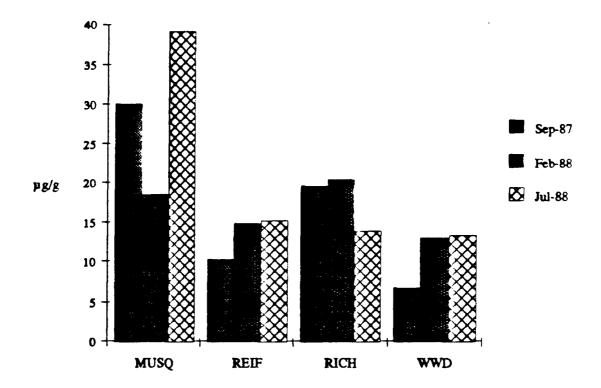


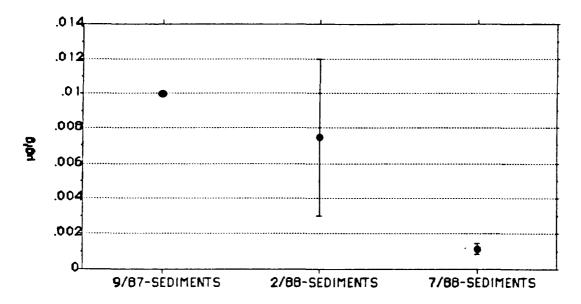
Figure 4.1.2-2: Variation in Sediment Lead Levels Over Time.



## Organics

Seasonal changes were observed in PCB levels in the sediment. Although there were significant differences between the September and July sediment PCB levels, there was virtually no variability between sites at those dates. The February sampling on the other hand showed a high degree of variability between sites.

Figure 4.1.2-3: Seasonal Change in Sediment PCB Levels.



## 4.2 WATER

Contaminant levels in the water sampled were well within acceptable concentrations, and in some cases were below detection limits. No relationship was determined between the contaminant concentrations in plants or sediments and the water samples collected.

The most consistent pH levels were at the Woodward Island station. The general pattern appeared to be a lower pH in the summer and higher in the winter.

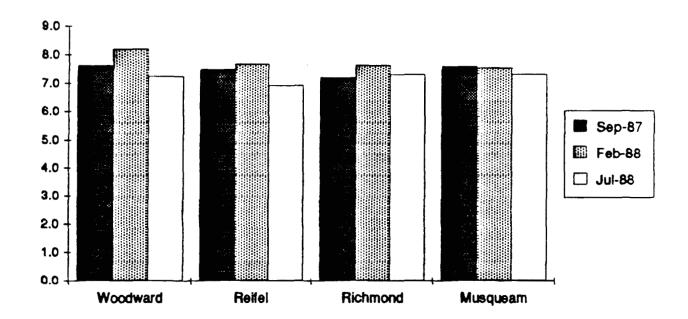
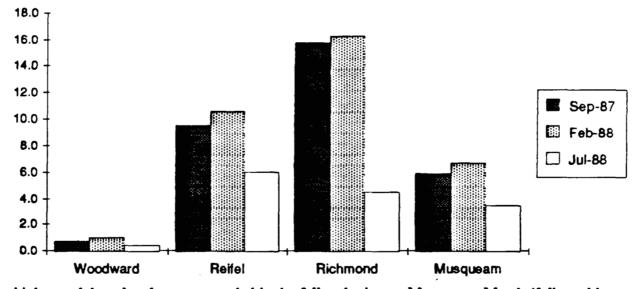


Figure 4.2-1: Seasonal pH Changes in Marsh Water.

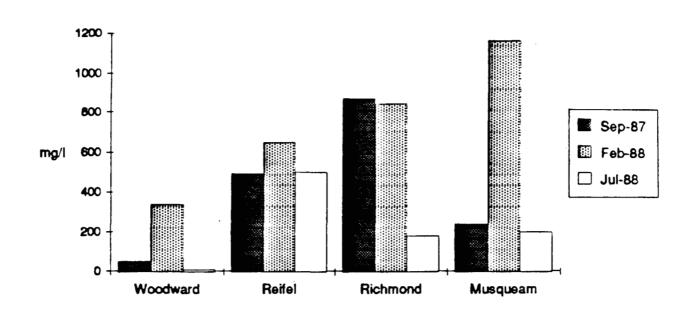
The highest salinities were measured at Richmond, followed by Reifel and Musqueam. The seasonal effects reflected the low river flows in the fall and winter with high salinities. The lowest salinities were recorded during July.





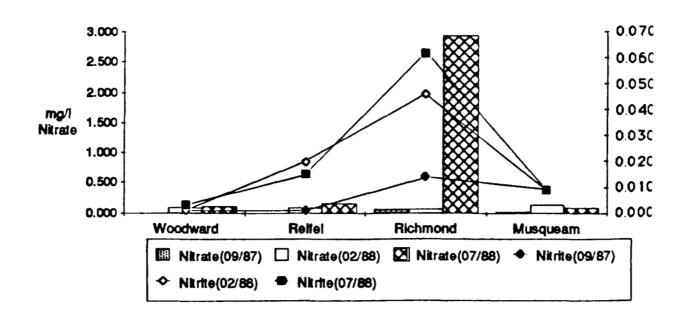
The highest sulphate levels were recorded in the fall and winter. Musqueam Marsh (followed by Richmond) yielded the highest sulphate levels in February. Reifel Island showed the most consistent sulphate levels.

Figure 4.2-3: Seasonal Variation in Sulphate Concentrations.



Nitrates were found at very low levels with the exception of a high reading at Richmond in July. Nitrite levels similarly, were highest in Richmond in July.

Figure 4.2-4: Seasonal Concentrations of Nitrate and Nitrite in Marsh Water.



Total Phosphate and Ortho-Phosphate concentrations were higher at the Reifel and Richmond locations than in the riverine locations. The highest Ortho-Phosphate concentrations were found in Richmond in July, whereas the highest Total Phosphate concentrations occurred at Reifel Island in July.

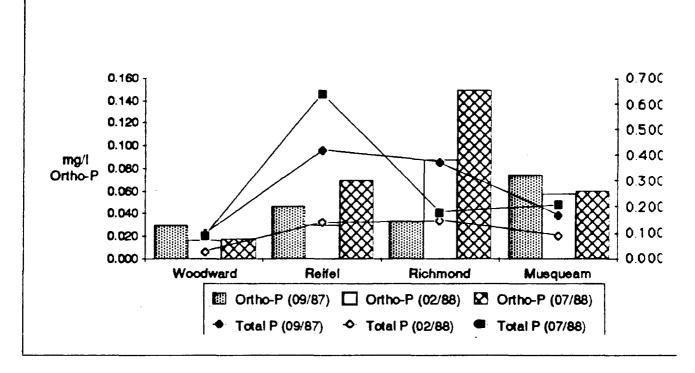
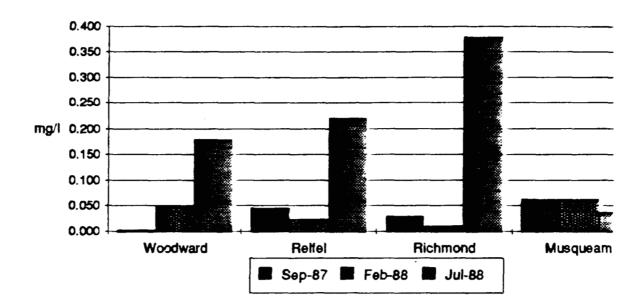


Figure 4.2-5: Seasonal Phosphate Concentations in Marsh Water.

Ammonia followed the same pattern as the other nutrients with the highest concentrations occuring in the summer, and at Richmond. In contrast to the other sites, Musquearn showed a decline in ammonia in July.

Figure 4.2-6: Seasonal Ammonia Concentrations in Marsh Water.

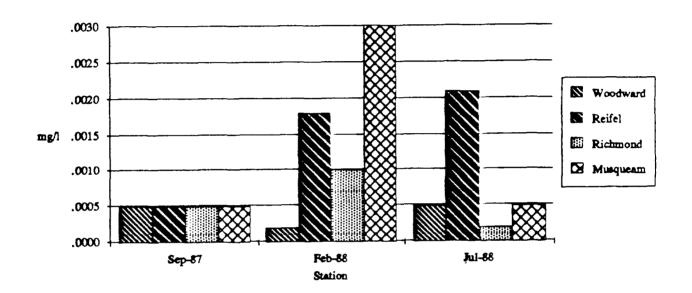


# Table 4.2-1: SUMMARY OF WATER SAMPLE RESULTS [pH, Salinity, Nutrients]

	Woodward	Reifel	Richmond	Musquean
pH[09/87]	7.67	7.51	7.23	7.61
pH[02/88]	8.24	7.57	7.69	7.67
pH[07/88]	7.27	6.94	7.31	7.31
Salinity[09/87]	0.8	9.6	15.8	5.9
Salinity[02/88]	1.1	6.7	10.7	16.3
Salinity[07/88]	0.5	6.0	4.5	3.5
Sulfate[09/87]	55	495	873	243
Sulfate[02/88]	339	1162	651	<b>84</b> 6
Sulfate[07/88]	10	<b>5</b> 05	181	201
Ortho-P [09/87]	0.03	0.047	0.034	0.074
Ortho-P [02/88]	0.017	0.058	0.03	0.088
Ortho-P [07/88]	0.018	0.07	0.15	0.06
Total P [09/87]	0.1	0.42	0.37	0.17
Total P [02/88]	0.028	0.089	0.14	0.15
Total P [07/88]	0.089	0.64	0.18	0.21
Nitrate[09/87]	0.01	0.01	0.07	0.02
Nitrate[02/88]	0.09	0.14	0.10	0.08
Nitrate[07/88]	0.12	0.17	2.94	0.08
Nitrite[09/87]	0.001	0.001	0.014	0.009
Nitrite[02/88]	0.001	0.009	0.020	0.046
Nitrite[07/88]	0.003	0.015	0.062	0.0
Ammonia[09/87]	0.005	0.046	0.03	0.063
Ammonia[02/88]	0.051	0.64	0.026	0.012
Ammonia[07/88]	0.18	0.22	0.38	0.037
Sulphide[09/87]	0.01	0.01	0.01	0.01
Sulphide[02/88]	0.01	0.01	0.01	0.01
Sulphide[07/88]	0.02	0.02	0.02	0.02

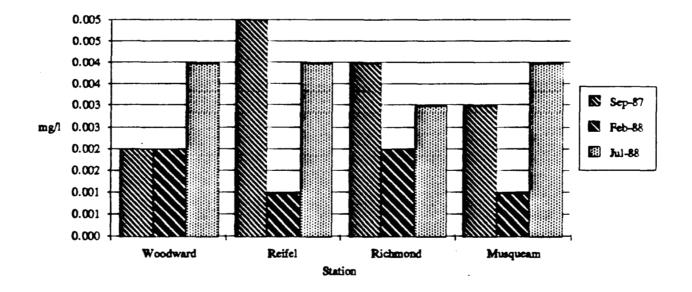
Cadmium levels in the water, unlike the sediment, tended to be lower than or equal to other locations at Woodward Island. The highest single result for Cd was at Musqueam marsh [0.003mg/l]. However, the highest average water level Cd was at Reifel Island [0.0015mg/l].

Figure 4.2-7: Cadmium Levels Detected in Marsh Water.



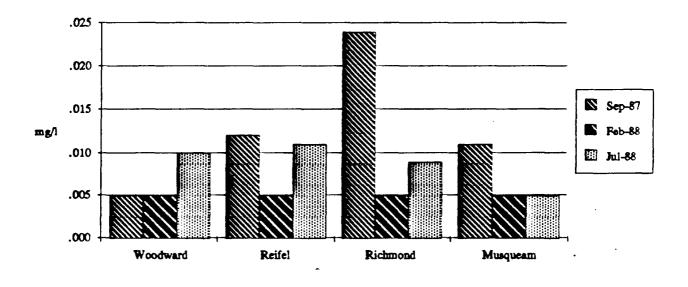
Copper levels in the water appeared to show a seasonal distribution with the lowest levels detected in February at all stations. The highest copper levels were found at Reifel Island [0.005 mg/l] in September.





Zinc levels were similar to copper in that the lowest levels in the water were found during the winter. The highest zinc level [twice that of the closest at Reifel and Musqueam] was found at Richmond marsh in September.





Mercury, lead and the organic contaminants were found at extremely low levels in the water. Mercury levels in the water at all sites and dates were less than 0.00005 mg/l. The highest lead levels were detected in the water at all stations in September [0.002mg/l], with the exception of Woodward Island where the highest lead level was detected in February.

		or		-	NANDON NATED
Table 4.2-2:	SUMMAKI	Ur .	METAL LEVELS	IN	MARSH WATER

		Cđ		<u> </u>	Cı		[	Pb			Za			Hg	
	<b>S-8</b> 7	<b>F-8</b> 8	<b>J-8</b> 8	<b>S-8</b> 7	F-88	<b>J-8</b> 8	<b>S-8</b> 7	<b>F-8</b> 8	<b>J-8</b> 8	S-87	F-88	J-88	<b>S-8</b> 7	F-88	<b>J-8</b> 8
W	.0005	.0002	.0005	.002	.002	.004	.001	.002	. <b>0</b> 01	.005	.005	<b>.0</b> 10	<.00005	<.00005	<.00005
Re	.0005	. <b>0</b> 018	. <b>0</b> 021	.005	.001	.004	.002	<.001	. <b>0</b> 01	.012	.005	.011	k.00005	<.00005	<.00005
Ri	.0005	. <b>0</b> 01	.0002	.004	.002	.003	.002	<b>&lt;.0</b> 01	.001	.024	.005	.009	<b>&lt;.000</b> 05	<.00005	<.00005
м	.0005	.003	.0005	.003	. <b>0</b> 01	.004	.002	<.001	. <b>0</b> 01	.011	.005	.005	<.00005	<.00005	<.00005

Water levels of organic contaminants were consistently below detection limits at all sites and dates.

	Table 4.2-3: 5	SUMMARY OF	<b>ORGANIC</b>	CONTAMINANTS	IN MARSH WATER
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		PCB	······		PCP	<u></u>		TCP	
·	Sep-87	Feb-88	Jul-88	Sep-87	Feb-88	Jul-88	<b>Sep-8</b> 7	Feb-88	Jui-88
Woodward	<.001	<b>&lt;.0</b> 01	<b>&lt;.00</b> 1	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
Reifel	<.001	<b>&lt;.001</b>	<b>&lt;.00</b> 1	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
Richmond	<b>&lt;.00</b> 1	<.001	<.001	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
Musqueam	<.001	<.001	<.001	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002

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## 4.3 VEGETATION -- FIELD RESULTS

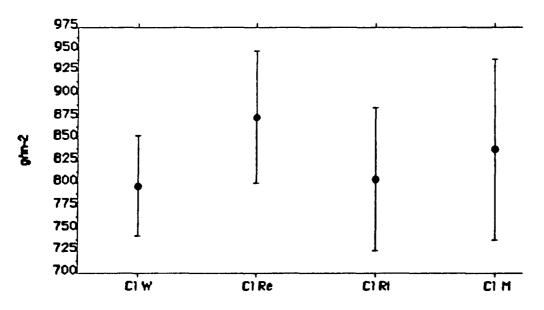
## 4.3.1 Biomass

Biomass determinations were only made during the peak growth period in July. The highest biomass occurred on Reifel Island, followed closely by Musqueam marsh, Richmond, and Woodward Island. No significant difference between sites was detected at a 95% significance level.

Table 4.3-1: Aboveground Biomass of Marsh Vegetation

Location	Mean Biomass [g/m <sup>2</sup> ]	Std. Dev.	Range [n=5]
Woodward	798	56.2	725-857
Reifel	875	73.1	<b>798-96</b> 0
Richmond	805	79.8	719-898
Musqueam	838	100.0	705-978

Figure 4.3-1: Aboveground Biomass [± s.d.] of Carex lyngbyei.



Biomass determinations are difficult to relate to reduced growth as a consequence of metal or organic contaminants due to the high degree of natural variability across the estuary. This type of determination would best be carried out under laboratory conditions in which the variables can be closely monitored. 40

## 4.3.2 CONCENTRATION OF CHEMICALS WITHIN PLANTS

The metal levels examined could be segregated into two basic groups:

- i] Those which were accumulated within the plants at levels close to or above those of sediment levels, i.e. cadmium and mercury; and
- ii] those in which plant levels were significantly lower than sediment levels, i.e. copper, lead and zinc.

Carex lyngbyei rhizomes showed the greatest concentration of all metals with the exception of mercury for which Scirpus maritimus rhizomes showed the greatest concentration.

# Table 4.3.2-1: Average Contaminant Concentration of Plant Components in the Fraser River Estuary.

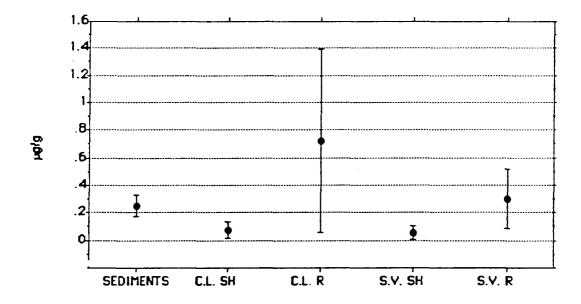
	Cu	Pb	Zn	Cd	Hg	РСВ	PCP	ТСР
		ppm	······································			<b>p</b> pb		
SEDIMENT	48.33	18.00	106.52	260.0	67.0	8.0	3.0	8.0
CL RHIZ	26.87	3.39	36.25	750.0	57.0	14.0	2.0	2.0
SARHIZ	10.98	0.50	18.75	100.0	13.0	14.0	5.0	7.0
SM RHIZ	10.36	1.78	22.60	120.0	48.2	8.0	1.0	2.0
SVRHIZ	13.13	1.97	25.39	320.0	<b>6</b> 0.0	18.0	1.0	2.0
CLSHOOT	8.82	1.38	23.54	80.0	30.0	8.0	2.0	3.0
SASHOOT	6.00	0.65	14.00	<b>8</b> 0.0	18.0	20.0	2.0	9.0
SMISHOOT	4.40	0.61	11.46	<b>3</b> 0.0	32.0	11.0	1.0	1.0
SVSHOOT	3.85	0.06	10.69	60.0	29.0	7.0	1.0	3.0
WATER	0.0029	0.0013	0.0089	0.9	0.1	1.0	0.8	0.8

CL-Carex Tyngtyel; SA-Scirpus americanus; SM-Scirpus maritimus; SV-Scirpus validus

## Cadmium

For cadmium, rhizome concentrations were 28 to 288% and shoot concentrations were approximately 11-31% of sediment concentrations. *Carex lyngbyei* and *Scirpus validus* both showed cadmium concentrations in excess of sediment levels in belowground components.





Despite the apparent concentration of cadmium by the plants, the regression of plant cadmium levels on sediment cadmium levels showed very weak relationships as shown in the following figures. The lack of correlation between sediment levels and plant levels is probably related to two major factors. The plant components analysed are once removed from the site of uptake, i.e. the roots would probably reflect sediment levels more closely than do the shoots and the rhizomes to which the ions are translocated. Secondly, although the concentration of metals was assessed at the rhizome level in the sediments, the root system can take up the metals over a much broader area. Therefore the sediment values identified may or may not reflect the concentration of metal available to the plant, and high levels of zinc may interfere with Cd uptake by the plants.

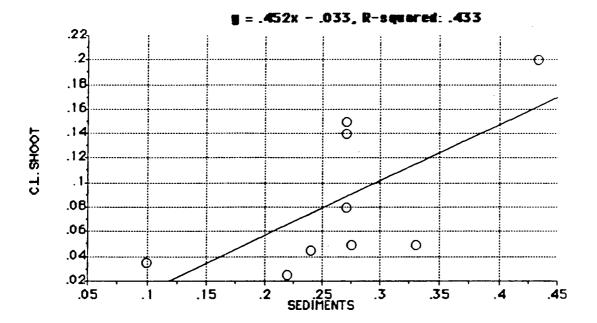
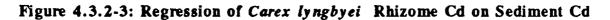
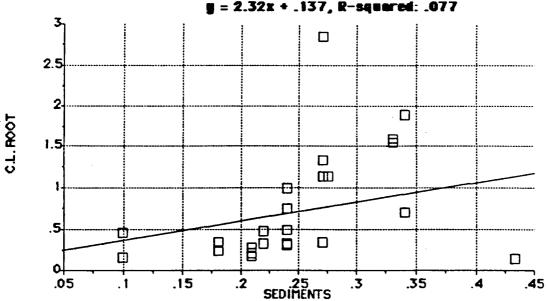


Figure 4.3.2-2: Regression of Carex lyngbyei Shoot Cd on Sediment Cd





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= 2.32x + .137, R-squared: .077

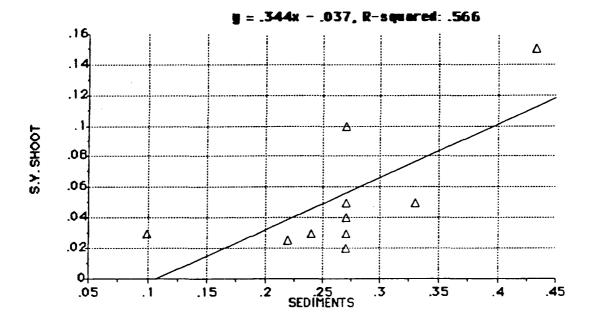
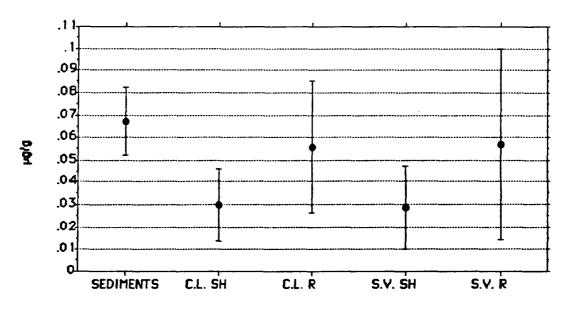


Figure 4.3.2-4: Regression of Scirpus validus Shoot Cd on Sediment Cd

## Mercury

For mercury, average rhizome concentrations were 19 to 90% and shoot concentrations were approximately 27-48% of sediment concentrations. Carex lyngbyei, Scirpus validus and Scirpus maritimus all showed levels approximating those of sediment levels in the belowground organs. Carex lyngbyei, Scirpus validus and S. maritimus all showed approximately the same concentration of mercury in the aboveground components. Although the average figures do not show it, during peak biomass, Carex lyngbyei rhizome mercury values on both Woodward Island and Reifel island exceeded the sediment values almost two fold. At other sites the concentration was less. At Richmond in July the mercury concentration in the rhizomes was more than 82% of sediment levels while at Musqueam it was approximately 72%. The concentration of mercury in the rhizomes was actually relatively uniform across the estuary, whereas the sediment levels at Richmond and Musqueam were distinctly higher than at Woodward and Reifel Islands.

# Figure 4.3.2-6: Mercury Levels in Vegetation and Sediments Averaged Over All Dates and Sites [±s.d.]



Despite the apparent concentration of mercury by the plants, the regression of plant mercury levels on sediment mercury levels showed very weak relationships as shown in the following figures.

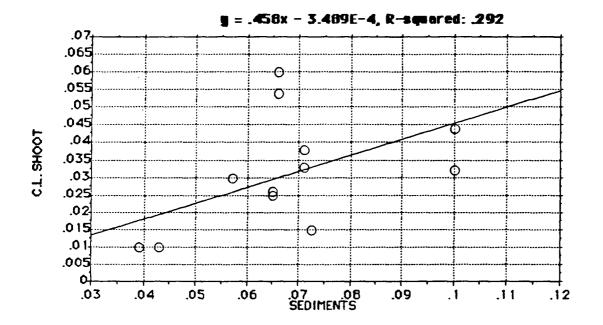
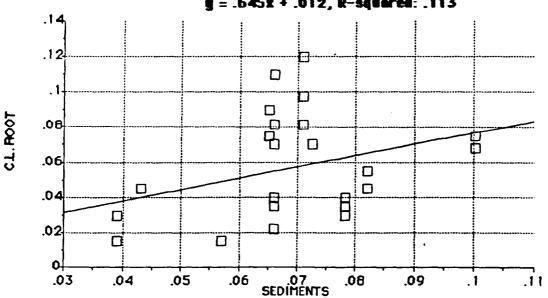


Figure 4.3.2.7: Regression of Carex lyngbyei Shoot Hg on Sediment Hg





y = .645x + .012, R-squared: .113

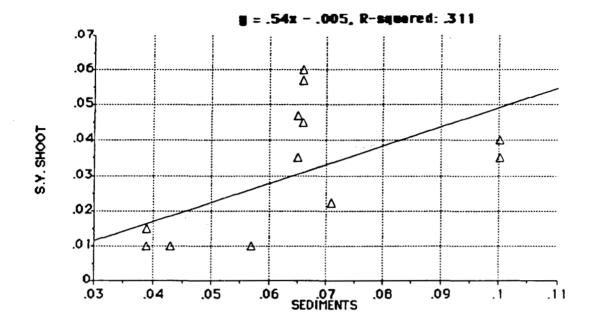
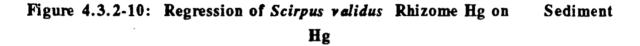
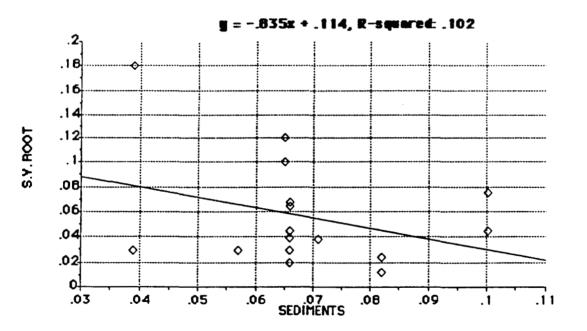


Figure 4.3.2-9: Regression of Scirpus validus Shoot Hg on Sediment Hg





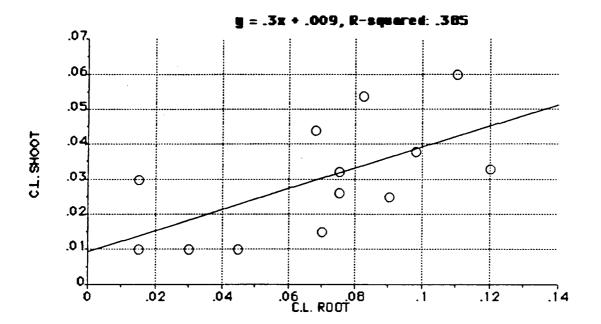
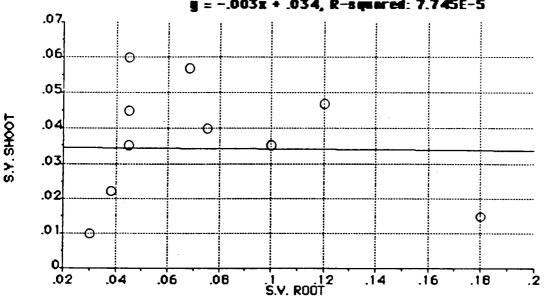


Figure 4.3.2-11: Regression of Carex lyngbyei Shoot Hg on Rhizome Hg



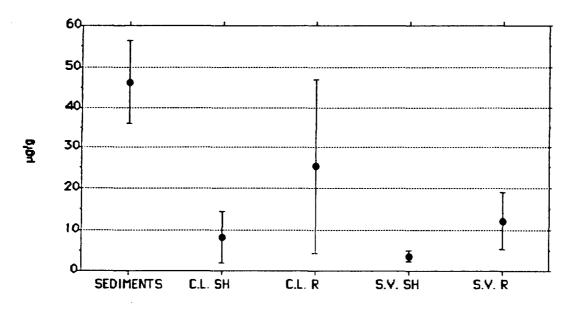


## g = -.003x + .034, R-squared: 7.745E-5

## Copper

For copper, rhizome concentrations were roughly 23 to 50% and shoot concentrations were approximately 8-18% of sediment concentrations. *Carex lyngbyei* was the species showing the greatest copper concentrations in either aboveground or belowground components.

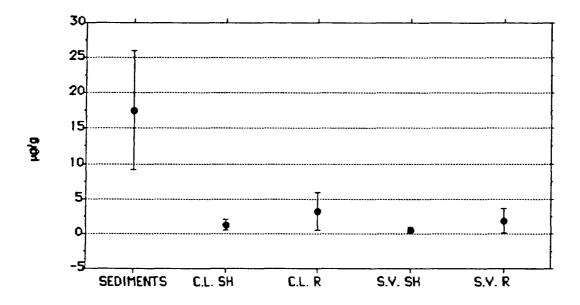
# Figure 4.3.2-13: Copper Levels in Vegetation and Sediments Averaged Over All Dates and All Stations [±s.d.].



Lead

For lead, rhizome concentrations were roughly 3 to 19% and shoot concentrations were from less than 1 to 8% of sediment concentrations. *Carex lyngbyei* was the species showing the greatest lead concentrations in either aboveground or belowground components.

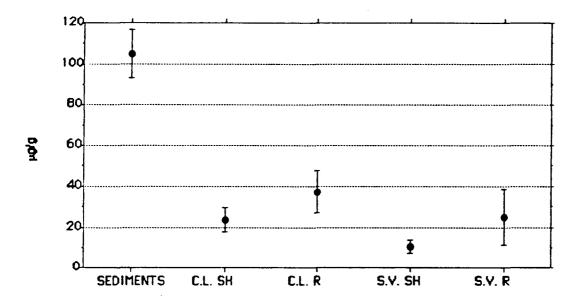
# Figure 4.3.2-14: Lead Levels in Vegetation and Sediments Averaged Over All Dates and All Stations [±s.d.].



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For zinc, rhizome concentrations were roughly 18 to 34% and shoot concentrations were approximately 10-22% of sediment concentrations. *Carex lyngbyei* was the species showing the greatest zinc concentrations in either aboveground or belowground components.

# Figure 4.3.2-15: Zinc Levels in Vegetation and Sediments Averaged Over All Dates and All Stations [±s.d.].



## ORGANICS

Zinc

All of the organic contaminants were accumulated in the plants at levels close to those found in the sediment.

# PCB

Sediment levels of PCB's were met or exceeded by all of the aboveground and belowground plant components with the exception of S. validus shoots which were slightly less than sediment levels. Scirpus americanus rhizomes showed higher than sediment levels of PCP and shoots showed higher than sediment levels of TCP.

### **4.3.3.BETWEEN SPECIES VARIABILITY**

Vegetation analysis showed that there were significant differences in the chemical accumulation between species. Of the 4 species sampled, Carex lyngbyei, Scirpus validus, Scirpus americanus and Scirpus maritimus, the latter two showed very similar patterns of chemical accumulation which was also similar to, but less than Scirpus validus. The sedge [Carex lyngbyei] showed significantly greater accumulation of all metals and organic contaminants, than did the rushes [Scirpus spp].

The capacity of each species to accumulate or magnify metals within their tissues is determined by the genetic make-up of that particular species. The tolerance of plants for heavy metals is genetically controlled, varying for different metals. Heavy metals taken up by plants along with nutrients, may be inactivated by some mechanism in the plants, absorbed, and finally accumulated in plant tissue [Mhatre et al. 1980]. Species which are able to accumulate metals, tolerate higher levels of environmental contamination and may therefore out compete other species.

 Table 4.3.3-1: Typical Metal Concentrations Found in Marshes of the Northeast

 and Northwest Coasts of North America

		Sedime	nts		
	Cd	Pb	Cu	Zn	Hg
NE marshes					0.03-0.11 <sup>2</sup>
	8	78-146	46-63	<b>78-146<sup>1</sup></b>	0.27-1.7 <sup>3</sup>
NW marshes	0.3	18	48	106	0.075
Carex lyngbyei	0.2	8	94	1011	0.026-15.74
Salicornia sp.	0.5	13	87	<b>86</b> <sup>1</sup>	

		Vegetati	on		
	Cd .	Pb	Cu	Zn	Hg
NE marshes		<u> </u>			0.17-0.5 <sup>2</sup>
	0.12-0.15	<b>2</b> 6.0	3.0	311	0.07-1.47rt <sup>4</sup>
NW marshes				<u></u> ** * * <u>**</u> *	
Carex lyngbyei	0.08	1.4	8.8	23.5	0.035
Carex lyngbyei	<20.0	<b>9</b> 7.0	10.0	45 <sup>1</sup>	0.04-7.9 rt <sup>4</sup>
Salicornia	ځ.0	2.8	13.0	<b>6</b> 0 <sup>1</sup>	
tagsdale and Thorhaug 1980 foody and Moody 1985	<sup>2</sup> Dunst <sup>5</sup> this st	an and Wind tudy	iom 1975	<sup>3</sup> Windom	et. al. 1976

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From the above table it is apparent that Carex lyngbyei, the species sampled in the Northwest marshes, effected a much greater concentration of Cd and Pb than Spartina in the Northeast marshes despite the lower concentration of metals in the sediment. Carex lyngbyei had the highest concentration ratio tissue/substrate of all the species sampled.

The highest cadmium levels were detected at Woodward Island in the rhizomes of sedge [2.85  $\mu g/g$ ]. In September, at all locations with the exception of Musqueam marsh *Carex lyngbyei*, rhizome concentrations of cadmium far exceeded the sediment concentrations at rhizome depth. Because the Musqueam rhizome result was so low [0.15  $\mu g.g$  - comparable to shoot levels] it may mean that the sedge is not concentrating cadmium to above sediment levels, rather that it is drawing on higher concentrations in deeper sediment levels. This may be confirmed by looking at the root mass of *Carex lyngbyei*, compared to the *Scirpus* species. The rooting system of the sedge is many-fold larger than that of the rushes, which would indicate that it has a much larger metal pool to draw on from all the sediments the roots come into contact with. The fact that *C. lyngbyei* is the species which concentrates the metal to the greatest extent would confirm that there must be some relationship between the surface area of roots and the concentration within the plant. It could also reflect young rhizomes which have not had a chance to accumulate as much as older rhizomes or it could reflect sampling or analytical error.

#### **4.3.4 PLANT COMPONENT VARIABILITY**

In virtually all cases, belowground organs contained higher levels of contaminants than did the aboveground components. This implicates the sediment as the source of the contaminant. Previous studies have indicated an ability on the part of the plant to selectively take up ions from the sediment. Although aquatic plants are able to take up contaminants from both the soil and water column, for submergents the major uptake is through the leaves, and for emergents it is through the root systems [Ragsdale and Thorhaug 1980]. Various studies have shown that for terrestrial plants, the level of concentration is much greater in the roots than in the rhizomes and that the rhizome level is often more similar to the shoot level than to the root concentrations. In this study, roots were not analysed for several reasons:

- it is very difficult to separate the live from dead roots in a plug of marsh fibre,

- it is also very difficult to remove all traces of sediment adhering to the fine roots
- analysis was focussed on those parts of the plants which could be passed on in the food chain [primarily the aboveground components in detritus, and the rhizomes as consumed by waterfowl].

In comparisons with a previous study from the Squamish estuary [Moody and Moody 1985], it is apparent that even relatively uncontaminated sites in the Squamish estuary produced substantially higher mercury values than found in the Fraser estuary. However, the pattern for shoot and rhizome concentration [Figure 4.3.3-1] in the Squamish estuary appears similar to that found in the Fraser. The example is used here to compare root and rhizome concentrations. Although the concentrations in roots are slightly higher than in the rhizomes, the difference is not substantial.

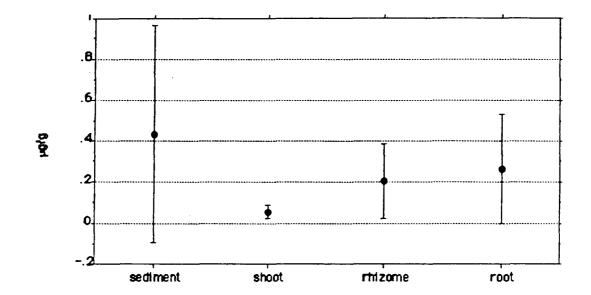
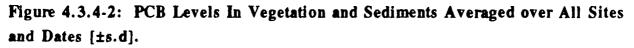
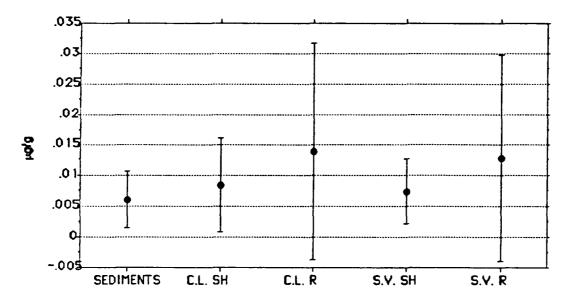


Figure 4.3.4-1: Mean Mercury Concentrations in Sediments and Carex lyngbyei from the Squamish estuary [based on Moody and Moody 1985].

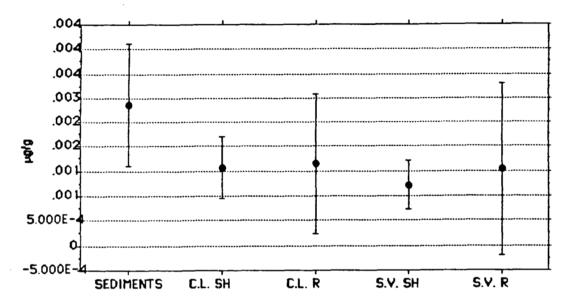
There were highly significant differences detected between the plant components within species. The concentration of chemical was consistently greater in the rhizomes than in the shoots. There was also much greater variability within the rhizomes than the shoots, possibly due to adhering sediment particles, and possibly due to variations in chemical concentrations with depth. The sediment was sampled from a relatively small area compared to that which the root systems extend over. The root system of a sedge plant may extend over 1 meter in depth and over a similarly broad area, depending on the extent of its rhizome network. Although the sediments were sampled at rhizome depth, it would probably have been more effective to sample the sediments over the rooting depth, to give an indication of the range of contaminants the root system is exposed to. It is also possible that there is selectivity in pumping the chemicals to the shoots. The only contaminant identified which consistently showed elevated levels in both shoots and rhizomes was PCB.





In comparison to the PCB levels, PCP concentrations in the plant parts were all significantly lower than the sediment levels.

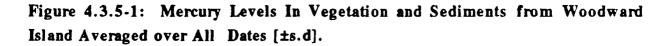
Figure 4.3.4-3: PCP Levels In Vegetation and Sediments Averaged over All Sites and Dates [±s.d].

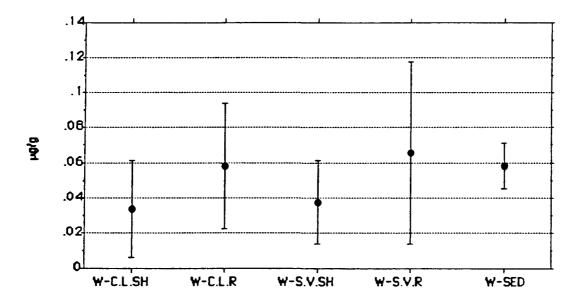


## **4.3.5 INTERSITE VARIABILITY**

As indicated previously, there were some changes in sediment contaminant levels over the various sites sampled in the estuary. However, this variability did not appear in the plants to any significant degree.

Even though the mercury levels changed from site to site the pattern of mercury uptake was similar between the species and plant components at each site.





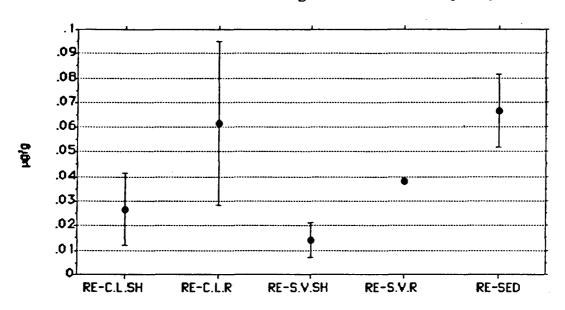
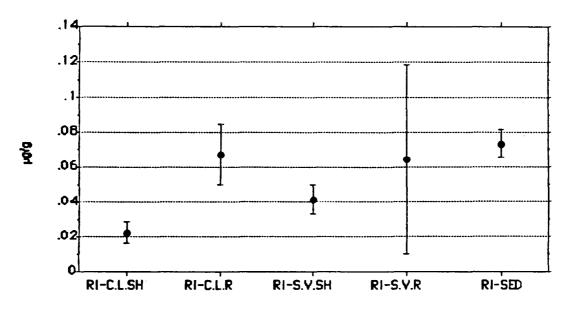


Figure 4.3.5-2: Mercury Levels In Vegetation and Sediments from Reifel Island Averaged over All Dates [±s.d].

Figure 4.3.5-3: Mercury Levels In Vegetation and Sediments from Richmond Averaged over All Dates [±s.d].



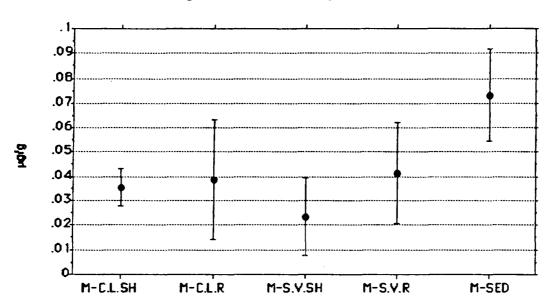
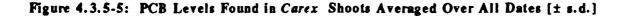


Figure 4.3.5-4: Mercury Levels In Vegetation and Sediments from Musqueam Marsh Averaged over All Dates [±s.d].

The highest levels of PCBs found in aboveground plant parts occurred in sedge shoots at Reifel Island and Richmond. No significant difference was found between these two sites even though there was substantial variability between dates. The lowest levels of PCBs were found at Woodward Island. In contrast the sediments at Woodward Island, Reifel and Musqueam marshes had similar levels of PCBs. Richmond was the only site which had significantly lower levels of PCBs in the sediment.



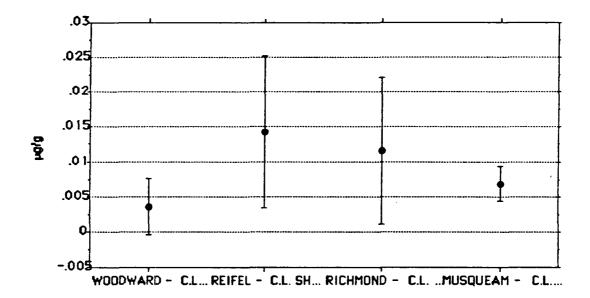
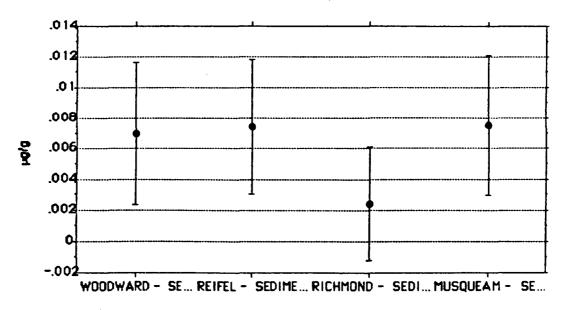


Figure 4.3.5-6: PCB Levels Found in Sediments Averaged Over All Dates [± s.d.]



### 4.3.6 SEASONAL VARIABILITY

Seasonal variability in sediment concentrations may be to a large degree be explained by sampling error as the samples were obtained from below surface layers [a different mix of sediment layers (ic. representing different depositional times) at each sampling], and slight changes in location from one sampling date to the next.

Seasonal variability in the concentration of chemicals within the plants to a large extent reflects their annual cycles. High levels of cadmium, mercury and PCB which were detected in the root systems in the fall may indicate the culmination of a seasons growth and collection of contaminants within the plant. Changes in the concentration of some chemicals over the winter may reflect leaching to the sediments. Hydroponic studies and transplant experiments indicated that there may be a more rapid response to changing environmental conditions than we had expected at first.

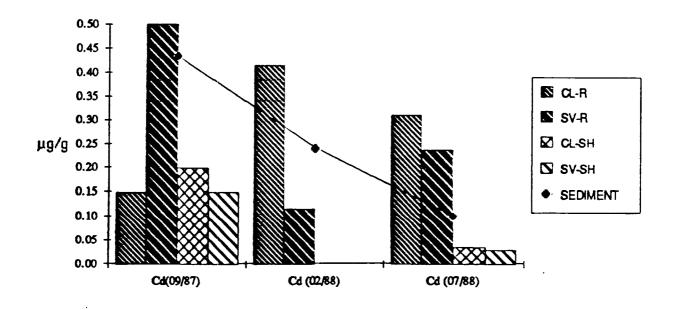
Table 4.3.6-1:	Seasonal Changes in Average Cadmium Concentrations [µg/g]
i	n Plant Components and Sediments from the Fraser River estuary.

	Sep-87	Feb-88	<b>Jul-88</b>
CL SHOOTS	0.1200		0.0538
SA SHOOTS	0.0750		
SM SHOOTS			0.0270
SV SHOOTS	0.1000		0.0288
CL RHIZOMES	1.2571	0.5211	0.0573
SA RHIZOMES	0.1000		
SM RHIZOMES	0.1500	0.1258	0.1075
SV RHIZOMES	0.4833	0.2867	0.2844
SEDIMENT	0.3429	0.2580	0.1860

The highest levels of cadmium in plant components were detected in September. Cadmium levels in the sediments of Woodward, Richmond and Reifel marshes remained relatively uniform over the three sampling periods. The results from Musqueam marsh showed radically different concentrations of Cadmium in the sediment over the seasons probably due to a difference in sampling location [ the marker for the original sample site was lost]. Previous studies have shown that cadmium is rapidly leached form the vegetation once senescence begins. We did not find this to be true, in fact cadmium followed the pattern of the other metals in being most concentrated in the fall. The relationship between the root concentrations and substrate concentrations of Cd in the Musqueam marsh appears to be relatively consistent even though some fluctuations do occur between the two species

The highest cadmium levels were detected at Woodward Island in the rhizomes of sedge [2.85  $\mu g/g$ ]. In September, at all locations with the exception of Musqueam marsh Carex lyngbyei rhizome concentrations of cadmium far exceeded the sediment concentrations at rhizome depth.

# Figure 4.3.6-1: Cadmium Levels Detected in Vegetation and Sediments of Musqueam Marsh, Fraser River Estuary.



Sep-87	Feb-88	Jul-88	
10.310		7.888	
6.000			
		4.400	
3.938		3.806	
49.808	45.060	52.340	
44.714	23.156	16.756	
10.975			
17.000	9.463	9.600	
19.767	13.833	10.444	
	10.310 6.000 3.938 49.808 44.714 10.975 17.000	10.310         6.000         3.938         49.808       45.060         44.714       23.156         10.975         17.000       9.463	10.310       7.888         6.000       4.400         3.938       3.806         49.808       45.060       52.340         44.714       23.156       16.756         10.975       17.000       9.463       9.600

Table 4.3.6-1: Seasonal Changes in Copper Levels

The belowground plant components of *Carex lyngbyei* and *Scirpus validus* contained significantly higher levels of copper during the fall than they did during the summer period. This could indicate a translocation of copper reserves within the plant from aboveground growth at the end of the growing season.

Table 4.3.6-2: Seasonal Changes in Lead Levels

	Sep-87	Feb-88	Jul-88
CL SHOOTS	1.2300	_ <u></u>	1.4813
SA SHOOTS	0.6500		
SM SHOOTS			0.6100
SV SHOOTS	0.5750		0.5393
SEDIMENT	16.7617	17.160	24.1000
CL RHIZOMES	2.5857	2.726	4.1922
SA RHIZOMES	0.5000		
SM RHIZOMES	2.4000	0.870	2.5375
SV RHIZOMES	2.0500	1.417	2.3111

Lead levels did not appear to change dramatically with the seasons with the exception of the higher levels noted in the sedge rhizomes in the summer.

	Sep-87	Feb-88	Jul-88
CL SHOOTS	22.500		24.188
SA SHOOTS	14.000		
SM SHOOTS	14.000		11.460
SV SHOOTS	9.250		11.763
CL RHIZOMES	36.571	41.600	34.744
BA RHIZOMES	18.750		
SM RHIZOMES	25.500	22.300	22.225
SV RHIZOMES	20.933	32.500	22.178
SEDIMENT	115.858	100.300	100.320

#### Table 4.3.6-3: Seasonal Changes in Zinc Levels

Zinc levels in rhizomes were higher during the winter sampling period compared to the fall and summer levels. This may indicate a translocation from the remaining live vegetation in the fall to the underground organs. Shoot levels remained fairly consistent between fall and summer.

Table 4.3.6-2: Seasonal Changes in Average Mercury Concentrations

	Sep-87	Feb-88	Jul-88
CL SHOOTS	0.0150		0.0390
SA SHOOTS	0.1750	_	
SM SHOOTS	0.0200	-	0.0320
SV SHOOTS	0.0108	-	0.0426
CL RHIZOMES	0.0529	0.073	0.0824
SA RHIZOMES	0.0336	0.043	0.0889
SM RHIZOMES	0.0125		
SV RHIZOMES	0.0250	0.025	0.2733
SEDIMENT	0.0800	0.032	0.0718

Mercury levels in the plant components were in all cases highest during the peak of growth in the summer. This would indicate active uptake during the growing period which was reflected both in the shoots and the rhizomes. The somewhat higher levels in winter than fall may reflect translocation which was was occurring in the late fall.

		РСВ				РСР			ТСР	
	Sep-87	Feb-88	Jul-88	S	əp-87	Feb-88	Jul-88	 <b>Se</b> p-87	Feb-88	Jul-88
CL SHOOTS	0.0132		0.0066	0.	0022		0.0012	 0.0070		0.0010
SASHOOTS	0.0200			0.	0019		-	0.0085		_
SM SHOOTS			0.0108	0.	0011		0.0010			0.0010
SVSHOOTS	0.0108		0.0087	0.	0021		0.0010	0.0068		0.0015
CL RHIZ	0.0203	.0053	0.0234	0.	0042	. <b>00</b> 16	0.0011	0.0050	.0014	0.0012
SARHIZ	0.0140			0.	0055		<u> </u>	 0.0068		
SM RHIZ	0.0390	.0016	0.0043	0.	0030	.0012	0.0010	0.0091	. <b>0</b> 018	0.0010
SVRHIZ	0.0627	.0018	0.0166	0.0	0049	.0011	<b>0.0</b> 010	0.0064	.0013	0.0013
SEDIMENT	0.0100	.0084	0.0042	0.0	0027	.0027	0.0035	0.0164	.0028	0.0045

Table 4.3.6-3: Seasonal Changes in Organic Contaminant Concentrations

The highest levels of organics were measured in the plants during the fall period. Because the contaminant levels appeared to decline over winter, we infer that translocation is not occurring to the same degree as with the metals discussed above. The plants may be responding quite quickly to sediment and water column levels.

#### 4.4 VEGETATION -- HYDROPONIC RESULTS

The objective of the hydroponic experiments was to produce plants under controlled conditions so that the concentration of contaminants could be altered in the nutrient medium and the effects on the plants could be monitored. The most unexpected result of the whole study was the finding that both the hydroponic fertilizers used for the nutrient solution and the growth medium [vermicullite and peat] contained contaminants at levels approaching that found in the estuary. This created a number of problems for the hydroponics experiment and for the production of "clean" plant stock for transplantation to the estuary. The greenhouse produced plants were transplanted to the estuary and after a period of growth they were sampled along with the adjacent plant communities. No significant differences could be discerned between the chemical levels in the natural or transplanted species at any site. However, the transplanted stock contained levels of contaminants prior to their move.

Table 4.4-1 Concentration of Contaminants in Hydroponically Grown Marsh Plants [µg/g]

	Cd	Hg	Pb	Cu	Zn	PCB	PCP	ТСР
Cl/sh	0.05	0.043	0.25	3.02	22.6	0.005	0.001	0.001
Cl/rz	0.85	0.038	0.7	13.1	30.8	0.005	0.001	0.001
Sv/sh	0.08	0.038	0.3	3.2	14.1	0.004	0.0015	0.0026
Sv/rz	0.24	0.03	0.5	8.35	25.2	0.003	0.001	0.001

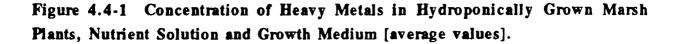
Table 4.4-2 Range of Contaminants in Hydroponic Nutrient Solutionand Growth Medium [µg/g]

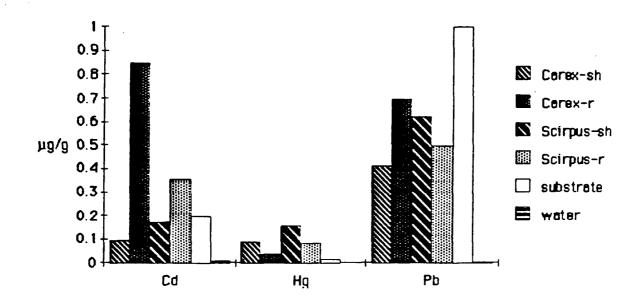
	H <sub>2</sub> 0	Substrate
Cd	0.005-0.012	0.2
Hg	0.0005-0.00005	0.016
Pb	0.0002-0.01	1.0
Cu	0.51-0.07	5.87
Zn	0.96-0.02	34
PCB	0.0001-0.001	0.001
PCP	0.0002-0.002	0.0027
TCP	0.0002-0.002	0.0039

The ratio of plant concentration of elements to substrate concentration displays the same pattern evident in the field sampling. Cadmium, mercury and PCBs were being concentrated by the plants. However, in the case of the greenhouse stock, shoot mercury levels exceeded that of the rhizome concentration. It may be possible that leaching of aboveground material is occurring in the natural state which did not occur in the greenhouse. All of the elements absorbed by the plant in the greenhouse would have been absorbed through the root system from the substrate or the nutrient solution. Airborne lead may have been a contaminant in the greenhouse due to its location near a moderately trafficked road.

	Cd	Hg	Pb	Cu	Zn	PCB	PCP	TCP
Cl/sh	0.3	2.7	0.3	0.5	0.7	5.0	0.4	0.3
Cl/rz	4.3	2.4	0.7	2.2	0.9	5.0	0.4	0.3
Sv/sh	0.4	2.4	0.3	0.5	0.4	4.0	0.6	0.7
Sv/rz	1.2	1.9	0.5	1.4	0.7	3.0	0.4	0.3

Table 4.4-3Ratio of Plant Concentration to Substrate Concentrationin Hydroponically Grown Marsh Plants

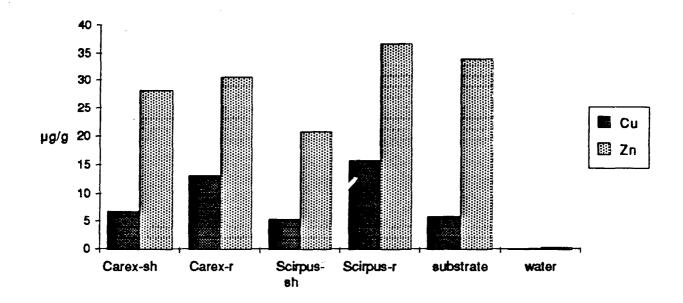




Cadmium and mercury concentrations exceeded substrate and water concentrations in both *Carex* and *Scirpus* rhizomes. The only metal concentration in aboveground plant components was of mercury, for both species.

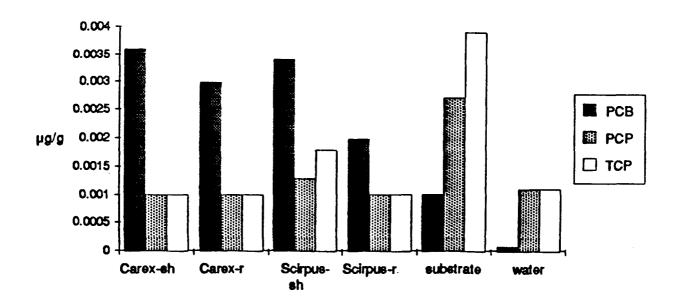
Copper and zinc were found in the hydroponically grown plants at levels approximating the substrate concentrations.

Figure 4.4-2 Concentration of Copper and Zinc in Hydroponically Grown Marsh Plants, Nutrient Solution and Growth Medium [average values].



PCBs were concentrated in both the aboveground and belowground parts of both plant species.

# Figure 4.4-3 Concentration of PCB, PCP and TCP in Hydroponically Grown Marsh Plants, Nutrient Solution and Growth Medium [average values].



The average concentrations of the hydroponically grown plants were as follows.

	Cd	Hg	PCB
SEDGE RHIZOME	4.3X	2.5X	5X
SEDGE SHOOT	0.3X	2.5X	5X
RUSH RHIZOME	1.2X	1.9X	3X
RUSH SHOOT	0.4X	2.4X	4X

### 5. CONCLUSIONS AND RECOMMENDATIONS

This study has shown that marsh vegetation is capable of concentrating mercury, cadmium and PCB's to levels higher than those detected in sediments. The other metals and organics were taken up at levels less than those found in the substrate. The mercury levels detected in the sediments of the Fraser River estuary ranged from a low of 0.035 to a high of 0.11µg/g of sample. These are significantly lower than nearby areas such as the Squamish estuary (0.03 to15.7 µg/g) or Bellingham Bay (0.8 to 10.7 µg/g) which contain chlor-alkali plants as sources of mercury (Moody & Moody 1985). The mercury in the water flooding the marshes was in all cases below detection limits (<0.00005 µg/g). The mercury concentration of the plant components also reflected the relatively low level of mercury in that plant mercury levels approximated that of the sediments, but in general did not exceed sediment levels.

In both field and hydroponics experiments, the *Carex lyngbyei* rhizome concentrations of cadmium were up to 4 times that of the substrate levels whereas *Scirpus validus* rhizomes were a maximum of 1.2 times substrate levels. The levels detected in the plant shoots of the Fraser Estuary were among the lowest reported in the literature. This reflects the levels of cadmium found in the sediments. Of concern is the fact that the plants are capable of concentrating cadmium. Should ambient cadmium levels change, the implications of concentration of cadmium in the food chain are significant.

Unlike mercury and cadmium which appear to be taken up from sediments and are concentrated primarily in the belowground components of the estuarine plants, PCBs were concentrated in the plant shoots as well. The higher concentration of PCBs in the shoots of the field experiments as opposed to the hydroponic trials may indicate that a considerable portion of PCB uptake occurs directly from the water column.

Copper, lead, zinc and mercury levels in the rhizomes from the hydroponic experiments exceeded two-fold those found in the field conditions even though the metal levels in the hydroponic solution and substrate were much lower than found in field conditions. Major differences between the field and laboratory growth conditions were the substrate type and oxygen environment. The natural marsh substrates are made up of a mixture of organic components, clay, silt and sand. The binding of metals to the fines and organic components in these substrates may reduce their availability to the vegetation. The nutrient solution in the greenhouse was constantly circulated and oxygenated whereas in the field, anoxic conditions prevail. Previous studies have indicated that oxidizing conditions make metals more available to the plants.

This study was a relatively broad brush approach to identifying which species and which metals were of concern in the local environment. Cadmium, mercury and PCB have been identified as contaminants which are concentrated by the plants both in the field and laboratory situation. Further studies are required to refine our understanding of uptake by the plants, residency of the metals and organics in the plants and further implications to the food web. The one species which consistently showed metal and organic concentrations greater than other species was *Carex lyngbyei*. This is a useful species for further investigations due to its ubiquitous distribution and its importance in the estuarine food web.

Given the relatively rapid response of the plants to changing contaminant levels in the substrate, and the possibility of significant uptake of PCBs from the water column it does not seem feasible to use the estuarine plants as indicators of average environmental conditions. However, due to their significance in the food web, monitoring of contaminant levels [especially Cd, Hg, and PCB] in the plants may provide an early warning system for potential food web concerns.

## 6. **LITERATURE CITED**

- 1 Aulio, K. and M. Salin. 1982. Enrichment of Copper, Zinc, Manganese, and Iron in Five Species of pondweeds (*Potamogeton spp.*). Bull. Environm. Contam. Toxicol. 29, 320-325 (1982).
- 2 Beeftink, W.G., J. Nieuwenhuize, M. Stoeppler, and C. Mohl. 1982. Heavy-Metal Accumulation in Salt Marshes from the Western and Eastern Scheldt. The Science of the Total Environment, 25 (1982) 199-223. Elsevier Scientific Publishing Company.
- Berry, Wade L. Dose-Response Curves for Lettuce Subjected to Acute Toxic Levels of Copper and Zinc. pp. 365-369 in: Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- 4 Bisogni, J.J. Jr. and A.W. Lawrence 1975. Kinetics of Mercury methylation in aerobic and anaerobic aquatic environments. Journal WPCF Vol 47(1): 135-152.
- 5 Bissonnette, Pam. 1977. Extent of Mercury and Lead Uptake from Lake Sediments by Chironomids. pp609-622. in: Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- 6 Black, S. A. 1983. The use of marshlands in wastewater treatment. Proceedings Technology Transfer Conference No. 4, Ministry of the Environment, Toronto, Ontario, Canada pp. 168-183.
- 7 Breteler, R.J. and F.I. Saksa. 1985. "The Role of Sediment Organic Matter on Sorption-Desorption Reactions and Bioavailability of Mercury and Cadmium in an Intertidal Ecosystem," Aquatic Toxicology and Hazard Assessment: Seventh Symposium. ASTM STP 854, R.D. Cardwell, R Purdy, and R.C. Bahner, Eds. American Society for Testing and Materials, Philadelphia, 1985, pp.454-468.
- 8 Breteler, R.J. and J.M. Teal. 1981. Trace Element Enrichments in Decomposing Litter of Spartina alterniflora. Aquatic Botany, 11 (1981) 111-120.
- 9 Breteler, R.J., I. Valiela and J.M. Teal. 1981. Bioavailability of Mercury in Several Northeastern U.S. Spartina ecosystems. Estuarine, Coastal and Shelf Science (1981) 12 155-166.

- 10 Brix, H., J.E. Lyngby and H.Schierup. 1983. Eelgrass (Zostera marina L.) as an Indicator Organism of Trace Metals in the Limfjord, Denmark. Marine Environmental Research 8 (1983) 165-181.
- 11 Bruan, G.W. 1985. The use of Multi-Estuary comparisons to Elucidate Factors Governing the Bioaccumulation and Effects of Heavy Metals in Benthic Organism. Abstract in Estuaries (1985) 8[2B]:99A.
- 12 Cranston, R.E. 1976. Accumulation and Distribution of Total Mercury in Estuarine Sediments. Estuarine & Coastal Mar Sci. 4:695-700
- 13 Desjardins, R.M., P.L. Seyfried, & G. Palmateer. 1986. Heavy Metal Effects on Marsh Treatment Systems. Water Poll. Res. J. Canada Vol. 21(4) 1986.
- 14 Drifmeyer, J.E. and B. Redd 1981. Geographic Variability in Trace Element Levels in Spartina alterniflora. Estuarine, Coastal and Shelf Science (1981) 13, 709-716.
- 15 Drifmeyer, J.E., G.W. Thayer, F.A. Cross and J.C. Zieman 1980. Cycling of Mn, Fe, Cu and Zn by Eelgrass, Zostera marina L. Amer. J. Bot. 67(7);1089-1096. 1980.
- 16 Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- 17 Dunstan, W.M. and H.L. Windom. 1975 The Influence of Environmental Changes in Heavy Metal Concentrations on Spartina alterniflora. In: E. Cronin (ed) Estuarine Research, Vol. 2, p. 393-404. Academic press, New York.
- 18 Elliott, M. & A.H. Griffiths (1986). Mercury Contamination in Components of an Estuarine Ecosystem. Wat. Sci. Tech. Vol. 18.
- 19 Gallagher, J.L. & H. V. Kibby 1980. Marsh Plants as Vectors in Trace Metal Transport in Oregon Tidal Marshes. Amer. J. Bot. 67(7):1069-1074.
- 20 Gallagher, John, L., Sarah E. Robinson, William J. Pfeiffer & Denise M. Seliskar 1979. Distribution and Movement of Toxaphene in Anaerobic Saline Marsh Soils. Hydrobiologia 63(1):3-9.
- 21 Gambrell, R.P. and W.H. Patrick, Jr. 19 . Chemical and Microbiological Properties of Anacrobic Soils and Sediments pp 375-421 in: Armstrong, W. Plant Life in Anaerobic Environments Processes in Anaerobiosis

- Gardner, W.S., D.R. Kendall, R.R. Odom, H.L. Windom & J.A. Stephens 1978. The Distribution of Methyl Mercury in a Contaminated Salt Marsh Ecosystem. Environ. Pollut. (15) (1978): 243-252.
- 23 Garrett, C.L. 1982. Pacific and Yukon Region Toxic Chemicals Profile. Prepared for the Pacific and Yukon Region Environment Canada Toxic Chemicals Committee.
- Gerhart, Ellen Heath 1975. Pesticides in Fish, Wildlife, and Estuaries. Concentrations of Total Mercury in Several Fishes from Delaware Bay, 1975. Pesticides Monitoring Journal Vol 11(3) Dec. 1977.
- 25 Giblin, A.E., A. Bourg, I. Valiela, and J.M. Teal. 1980. Uptake and Losses of Heavy Metals in Sewage Sludge by a New England Salt Marsh. Amer. J. Bot. 67(7):1059-1068.
- 26 Giordano, Paul M. & David A. Mays. 1977. Yield and Heavy-Metal Content of Several Vegetable Species Grown in Soil Amended with Sewage Sludge. <u>in:</u> Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- 27 Howeler, R.H. 1973. Iron-Induced Oranging Disease of Rice in Relation to Physico-Chemical Changes in a Flooded Oxisol. Soil Sci Soc. Am. Proc. 37:898 cited in Gambrell, R.P. and W.H. Patrick, Jr. 19. Chemical and Microbiological Properties of Anaerobic Soils and Sediments pp 375-421 in: Armstrong, W. Plant Life in Anaerobic Environments Processes in Anaerobiosis
- 28 Jenne, Everett, A. and Samuel N. Luoma 1977. Forms of Trace Elements in Soils, Sediments and Associated Waters: An Overview of Their Determination and Biological Availability. pp 110-143 in: Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- 29 Kavetskiy, V.N, A.I. Karnaukhov, and I.M. Paliyenko. 1984. Content of Heavy Metals in Water and Some Aquatic Plants of the Danube and Dniester Estuaries. Hydrobiol. J. (1984) 20(2):67-70.
- 30 Kneip, T.J. and R.E. Hazen. 1979. Deposit and Mobility of Cadmium in a Marsh-Cove Ecosystem and the Relation to Cadmium concentration in Biota. Environmental Health Perspectives Vol.28 pp 67-73. 1979.

- 31 Lee, C.R., T.C. Sturgis & M.C. Landin. 1976. A Hydroponic Study of Heavy Metal Uptake by Selected Marsh Plant Species. Technical Report D-76-5 Dredged Material Research Program. Waterways Experiment Station, U.S. Army Corps of Engineers, Vicksburg Mississippi.
- 32 Lee, C.R., R.M. Smart, T.C. Sturgis, R.N. Gordon, Sr. and M.C. Landin. 1978. Prediction of Heavy Metal Uptake By Marsh Plants Based on Chemical Extraction of Heavy Metals from Dredged Material. Technical Report D-78-6 Dredged Material Research Program. Waterways Experiment Station, U.S. Army Corps of Engineers, Vicksburg Mississippi.
- 33 Lee, T.A. and J.K. Hardy. 1987. Copper Uptake by the Water Hyacinth. J. Environ. Sci. Health, A22(2), 141-160.
- 34 Luoma, S.N., Bryan, G.W., and W.J. Langston 1982. Scavenging of heavy metals from particulates by brown seaweed. Mar. Poll. Bull., 13, 394-396.
- 35 Mhatre, G.N., S.B. Chaphekar, I.V. R.Rao, M. R. Patil, & B.C. Haldar. 1980. Effect of Industrial Pollution on the Kalu River Ecosystem. Environmental Pollution [Series A] 23: 67-78.
- 36 Mortvedt, J.J and P.M. Giordano 1977. Crop Uptake of Heavy-Metal Contaminants in Fertilizers. in:Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- 37 Mrozek, E. Jr. & R.B. Leidy. 1981. Investigation of Selective Uptake of Polychlorinated Biphenyls by Spartina alterniflora Loisel. Bull. Environm. Contam. Toxicol. 27, 481-488.
- 38 Mrozek, E. Jr., E. D. Seneca & L.L. Hobbs. 1982. Polychlorinated biphenyl uptake and Translation by Spartina alterniflora Loisel. Water, Air and Soil Pollution 17 (1982) 3-15.
- 39 Pellenbarg, R.E. 1984. On Spartina alterniflora Litter and the Trace Metal Biogeochemistry of a Salt Marsh. Estuarine, Coastal and Shelf Science (1984) 18, 331-346.
- 40 Pezeshki, S.R., R.S. DeLaune and W.H. Patrick, Jr. 1987. Response of the freshwater marsh species, *Paniceum hemitomon* Schult., to increased salinity. Freshwater Biology (1987) 17, 195-200.
- 41 Ragsdale, Harvey L. & Anitra Thorhaug. 1980 Trace Metal Cycling in the U.S. Coastal Zone: A Synthesis. Amer. J. Bot. 67(7):1102-1112

- 42 Rahn, W.R., Jr. 1973. The role of *Spartina alterniflora* in the transfer of mercury in a salt marsh environment. M.S Thesis. Georgia Institute of Technology. 61 p.
- 43 Reimers, R.S. and P.A. Krenkel. 1974. Kinetics of mercury adsorption and desorption in sediments. Journal of the Water Pollution Control Federation 46, 352-365.
- 44 Sarsfield, Linda J. and K. H. Mancy. 1977. The Properties of Cadmium Complexes and Their Effect on Toxicity to a Biological System. pp335-345. in: Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- 45 Serne, R.J. 1977. Geochemical Distribution of Selected Trace Metals in San Francisco Bay Sediments. pp280-296. in: Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- 46 Sharma, R.P. and J.L. Shupe. 1977. Trace Metals in Ecosystems: Relationships of the Residues of Copper, Molybdenum, Selenium and Zinc in Animal Tissues to Those in Vegetation and Soil in the Surrounding Environment. pp595-608. in: Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- 47 Tiffin, L. The Form and Distribution of Metals in Plants: An Overview. pp315-335. in: Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975. Technical Information Center, Energy Research and Development Administration.
- Valiela, I., S. Vince and J.M. Teal. 1976. Assimilation of Sewage by Wetlands. In: Wiley, M.
   (ed) 1976. Estuarine Processes I. Academic Press N.Y.
- 49 Wallace, A and E.M. Romney 1977. Roots of Higher Plants as a Barrier to Translocation of Some Metals to Shoots of Plants. pp 370-379. in: Drucker, Harvey, & Raymond E. Wildung 1977. Biological Implications of Metals in the Environment. Proceedings of the Fifteenth Annual Hanford Life Sciences Symposium at Richland, Washington, September 29-October 1, 1975.

50 Windom, H.L., W.S. Gardner, W.M. Dunstan and G.A. Paffenhofer 1976. Cadmium and Mercury Transfer in a Coastal Marine Ecosystem. <u>In:</u> Marine Pollutant Transfer; H. L. Windom, & R.A. Duce (eds.) Lexington Books. Lexington pp.135-157.

	07/88	02/88	09/87	
W-cll-Rhizome	0.350	0.700	1.350	
W-cl2-Rhizome	1.150	1.910	2.850	
W-sv 1-Rhizome	0.160	0.480	0.150	
W-sv1D-Rhizome	0.200			
W-sv2-Rhizome	0.480	0.480	<0.800	
Re-cll-Rhizome	0.500	0.280	1.600	
Re-cl1D-Rhizome	0.750	0.180	1.550	
Re-cl2-Rhizome	1.000	0.210		
Re-m1-Rhizome	0.100	0.073		
Re-sm2-Rhizome	0.090	0.130		
Re-svl-Rhizome	0.210			
Re-sa-Rhizome			<0.050	
Ri-cl1-Rhizome	0.470	0.340	1.150	
Ri-cl2-Rhizome	0.320	0.240		
Ri-sv1-Rhizome	0.200	0.250		
Ri-sv2-Rhizome	0.600	0.280		
Ri-sm1-Rhizome	0.120	0.100	0.150	
Ri-sm2-Rhizome	0.120	0.310		
Ri-sa-Rhizome			0.150	
M-cll-Rhizome	0.160	0.500	0.150	
M-c12-Rhizome	0.460	0.330		
M-sv1-Rhizome	0.100	0.310	0.5000	
M-sv2-Rhizome	0.160	0.100		
M-sv2D-Rhizome	0.450	0.130		
W-c.L1-Shoot	0.140		0.150	
W-c.1.2-Shoot	0.080		0.150	
W-sv 1-Shoot	0.040		0.050	
W-sv1D-Shoot	0.030		0.000	
W-sv2-Shoot	0.020		0.100	
Re-cl1-Shoot	0.045		0.050	
Re-c12-Shoot	0.045			
Re-sm1-Shoot	<0.025			
Re-sm2-Shoot	<0.025			
Re-sv1-Shoot	0.030		0.050	
Re-sa-Shoot		4	0.050	
Ri-cl1-Shoot	<0.025	•	<0.050	
Ri-cl1D-Shoot	<0.025			
Ri-sv1-Shoot	<0.025			
Ri-sv2-Shoot	<0.025			
Ri-sm1-Shoot	0.030			
Ri-sm2-Shoot	0.030			
Ri-sm2D-Shoot	<0.025			
	<0.020		0 100	
Ri-sa-Shoot			0.100	
M-cll-Shoot	0.035		0.200	
A-c12-Shoot	0.035		2	
M-sv1-Shoot M-sv2-Shoot	0.030 0.030		0.150 0.150	

APPENDIX 1: Cadmium Detected in Vegetation Samples (µg/g dry weight)

	07/88	02/88	09/87	
W-w	0.0005	<0.0002	<0.0005	
Re-w	0.0021	0.0018	<0.0005	
Ri-w	0.0002	0.0010	<0.0005	
M-w	0.0005	0.0030	<0.0005	

### Appendix 1a: Cadmium Levels Detected in Water Samples (mg/l)

Appendix 1b: Cadmium Levels Detected in Sediment Samples (µg/g dry weight)

	07/88	02/88	09/87	
W-sed	0.270	0.340	0.330	
Re-sed	0.240	0.210	0.333	
Ri-sed	0.220	0.180	0.275	
Ri-sedD	<0.100			
M-sed	<0.100	0.240	0.433	
M-sedD		0.320		

# Abbreviations Used in Appendices

			W-cl1-R		
	location	Spec	ries & Replicate #	Plant	Component
w	-Woodward L	ત	-Carex lyngbyei	R	-rhizome
Re	-Reifel L	sv	-Scirpus validus	S	-shoot
Ri	-Richmond	*	-Scirpus americanus		
M	-Musqueam	sm	-Scirpus maritimus		

	07/88	02/88	09/87	
W-cl1-R	10.800	14.000	29.500	
W-c12-R	22.400	61.600	47.000	
W-sv 1-R	5.900	18.000	11.000	
W-sv1D-R	6.500			
W-sv2-R	9.650	20.000	19.800	
Re-cl1-R	19.400	14.500	62.000	
Re-cl1D-R	22.800	11.500	58.500	
Re-c12-R	22.800	14.300		
Re-sm1-R	12.100	4.850		
Re-sm2-R	9.250	7.000		
Re-sv1-R	18.200			
Re-sa-R			4.450	
Ri-cl1-R	8.300	27.500	<b>94.00</b> 0	
Ri-c12-R	13.400	28.500		
Ri-sv1-R	7.650	15.700		
Ri-sv2-R	14.600	12.300		
Ri-sm1-R	<b>7.95</b> 0	19.500	17.000	
Ri-m1D-R	9.100	10.500		
Ri-sm2-R		6.500		
Ri-sa-R			17.500	
M-cl1-R	13.700	19.500	11.500	
M-cl2-R	17.200	17.000	10.500	
M-sv1-R	5.400	13.900	28.500	
M-8v2-R	6.300	10.000		
M-sv2D-R	19.800	7.000		
W-c.1.1-S	15.600		9.500	
W-c.12-S	<b>9.75</b> 0		<b>7.0</b> 00	
W-sv 1-S	4.900		3.900	
W-sv1D-S	4.500			
<b>W-sv2-S</b>	4.550		<b>3.70</b> 0	
Re-cl1-S	7.500		<b>6.00</b> 0	
Ro-cl2-S	8.500			
Re-sm1-S	6.000			
Re-em2-S	6.000			
Re-sv1-S	3.950		3.250	
Ro-sa-S			5,500	
Ri-cl1-S	3.650		4.050	
Ri-cl1D-S	3.400			
Ri-sv1-S	3.350			
Ri-sv2-S	2.300			
Ri- <b>a</b> m1-S	3.300			
Ri-m2-S	3.000			
Ri-sm2D-S	3.700			
Ri- <del>m</del> -S			6.500	
M-cii-S	8.200		25.000	
M-c12-S	6.500			
M-sv1-S	3.050		4.900	

APPENDIX 2: Copper Detected in Vegetation Samples (µg/g dry weight)

<b>W-</b> w	0.004	0.002	0.002	
Re-w	0.004	0.001	0.005	
Ri-w	0.003	0.002	0.004	
M-w	0.004	0.001	0.003	

## Appendix 2a: Copper Levels Detected in Water Samples (mg/l)

## Appendix 2b: Copper Levels Detected in Sediment Samples (µg/g dry weight)

W-sed	46.600	47.2000	40.400	
Re-sed	48.600	50.5000	49.500	
Ri-sed	48.500	46.4000	<b>51.00</b> 0	
Ri-sedD	<b>65.70</b> 0			
M-sed	.52.300	40.6000	58.330	

		-		•
	07/88	02/88	09/87	
W-cll-R	0.93	1.25	2.60	
W-c12-R	1.65	1.86	2.05	
W-sv 1-R	0.50	1.50	1.00	
W-sv1D-R	0.15			
W-sv2-R	0.90	0.60	1.80	
Re-cl1-R	1.65	1.30	2.05	
Re-cliD-R	1.65	0.65	1.80	
Re-cl2-R	1.65	1.02		
Re-sm1-R	1.00	0.53		
Re-sm2-R	0.85	0.85		
Re-sv1-R	1.95			
Re-sa-R			0.15	
Ri-cll-R	5.20	6.50	7.50	
Ri-cl2-R	<b>8.0</b> 0	3.80		
Ri-sv1-R	2.90	1.35		
Ri-sv2-R	7.50	2.71		
Ri-sm1-R	1.80	0.80	2.40	
Ri-sm2-R	6.50	1.45		
Ri-sa-R			0.85	
M-cl1-R	11.00	5.50	1.05	
M-cl2-R	6.00	2.65	1.05	
M-sv1-R	0.90	1.54	3.35	
M-sv2-R	1.40	0.80	••••	
M-sv2D-R	4.60			
W-c.11-S	2.15		1.50	
W-c.12-S	1.40		0.95	
W-sv 1-S	0.01		0.65	
W-sv1D-S	0.60		0.70	
W-ev2-S	1.40			
Re-cl1-S	1.20		1.45	
R <del>o-</del> c12-S	1.35			
Re-sm1-S	0.95			
Re-sm2-S	0.60			
Re-sv1-S	0.60		1.10	
Re-sv1D-S			0.35	
Re-sa-S			0.60	
Ri-cl1-S	0.75		0.20	
Ri-cl1D-S	0.50		0,20	
Ri-sv1-S	0.55			
Ri-sv2-S	0.25			
Ri-sm1-S	0.35			
Ri-sm2-S	0.45			
Ri-sm2D-S	0.70			
Ri-m-S			0.70	
M-cll-S	2.50		2.05	
M-c12-S	2.30 2.00		2.VJ	
M-sv1-S	0.45		0.35	
M-5v2-S	0.45		0.30	

APPENDIX 3: Lead Detected in Vegetation Samples (µg/g dry weight)

W-w	<0.0010	0.002	0.001	
Ro-w	0.0010	<0.001	0.002	
Ri-w	<0.0010	<0.001	0.002	
M-w	<0.0010	<0.001	0.002	

## Appendix 3a: Lead Levels Detected in Water Samples (mg/l)

Appendix 3b: Lead Levels Detected in Sediment Samples (µg/g dry w	reight)
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W-sed	13.40	13.00	6.8	
Re-sed	15.20	<b>14.9</b> 0	10.3	
Ri-sed	14.00	20.60	19.8	
Ri-mdD	38.60			
M-sed	39.30	18.60	30.2	
M-sedD		18.70		

	07/88	02/88	09/87	
W-cl1-R	12.70	29.00	31.500	
W-c12-R	23.60	38.90	20.500	
W-sv 1-R	9.20	<b>26.0</b> 0	15.500	
W-sv1D-R	9.10		21.300	
W-sv2-R	12.00	27.50		
Re-cll-R	39.80	46.00	45.000	
Re-cl1D-R	41.50	37.50	44.000	
Re-cl2-R	37.50	50.50		
Re-sm1-R	23.10	<b>17.0</b> 0		
Re-sm2-R	24.00	<b>17.0</b> 0		
Re-sv1-R	19.60			
Re-sa-R			7.000	
Ri-cl1-R	<b>56.3</b> 0	<b>54.0</b> 0	46.500	
Ri-cl2-R	35.20	<b>51.0</b> 0		
Ri-sv1-R	<b>26.0</b> 0	54.10		
Ri-sv2-R	<b>50.6</b> 0	45.70		
Ri-sm1-R	22.00	28.50	25.500	
Ri-sm2-R	<b>19.8</b> 0	26.50		
Ri-sa-R			30.500	
M-cl1-R	<b>27.6</b> 0	36.00	34.500	
M-cl2-R	38.50	31.50	34.000	
M-sv1-R	17.70	32.20	26.000	
M-sv2-R	18.60	25.40		
M-sv2D-R	36.80	16.00	······	
W-c.1.1-S	30.00		19.000	
W-c.12-S	17.30		14.500	
W-sv 1-S	9.25		10.500	
W-ev1D-S	9.40		8.500	
W-sv2-S	9.25			
Re-cl1-S	25.50		23.500	
Re-c12-S	26.50			
Re-sm1-S	13.00			
Re-sm2-S	14.00			
Re-sv1-S	<b>9.3</b> 0		7.500	
Re-sv1D-S			7.500	
Re-sa-S			14.000	
Ri-cl1-S	22.80		19.500	
Ri-cl1D-S	21.70			
Ri-sv1-S	18.80			
Ri-sv2-S	17.15			
Ri-sm1-S	8.45			
Ri-m2-S	8.75		14.000	
Ri-sm2D-S	13.10			
Ri- <b>sa</b> -S				
M-cl1-S	25.60		36.000	
M-c12-S	24.10		~~~~	
M-sv1-S	9.75		11.000	
M-sv2-S	11.20		10.500	

APPENDIX 4: Zinc Detected in Vegetation Samples (µg/g dry weight)

W-w	0.010	< 0.005	<0.005	
Re-w	0.011	<0.005	0.012	
Ri-w	0.009	<0.005	0.024	
M-w	<0.005	<0.005	0.011	

Appendix 4a: Zinc Levels Detected in Water Samples (mg/l)

Appendix b:	Zinc Levels Detected in Sediment Samples (µg/g dry weig	ht)
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W-sed	98.20	<b>97.9</b> 0	96.10	_
Re-sed	102.00	102.00	105.00	
Ri-sed	104.00	110.00	123.00	
Ri-sedD	<b>91.4</b> 0			
M-sed	106.00	<b>94.7</b> 0	139.33	
M-sedD		97.10		

· · · · · · · · · · · · · · · · · · ·	07/88	02/88	09/87
W-cl1-R	0.110	0.040	.01500
W-c12-R	0.082	0.070	.03000
W-sv 1-R	0.045	0.065	.03000
W-sv1D-R	0.045		.18000
₩-sv2-R	0.068	0.030	
Re-cll-R	0.098	0.035	.04500
Re-cl1D-R	0.120	0.030	.04500
Ro-c12-R	0.082	0.040	
Re-sm1-R	0.098	0.019	
Re-sm2-R	0.829	0.040	
Re-sv1-R	0.038	0.055	
Re-sa-R			.01000
Ri-c11-R	0.090	0.055	.07000
Ri-cl2-R	0.075	0.045	
Ri-sv1-R	0.120	0.024	
Ri-sv2-R	0.100	0.012	
Ri-sm1-R	0.068	0.020	.02500
Ri-sm2-R	0.098	0.030	
Ri- <b>58-</b> R			.01500
M-cl1-R	0.068	<b>0.04</b> 0	.01500
M-cl2-R	0.075	0.035	.01500
M-sv1-R	0.045	0.022	.03000
M-sv2-R	0.075	0.039	
M-sv2D-R	0.110	0.020	
W-c.L1-S	0.060		.01000
W-c.1.2-S	0.054		.01000
W-sv 1-S	0.045		.01000
W-sv1D-S	0.060		.01500
W-sv2-S	0.057		
Re-cl1-S	0.038		.01000
Re-c12-S	0.033		
Re-sm1-S	0.030		
Re-sm2-S	0.030		,
Re-sv1-S	0.022		.01000
Re-sv1D-S			.01000
Re-ma-S			.02000
Ri-cl1-S	0.025		.01500
Ri-cl1D-S	0.026		
Ri-sv1-S	0.047		
Ri-sv2-S	0.035		
Ri- <b>am</b> 1-S	0.040		
Ri- <b>m2-S</b>	0.038		.02000
Ri-sm2D-S	0.022		.02000
Ri- <b>sa</b> -S	U.ULL		01600
	0.044		.01500
M-cl1-S			.03000
M-c12-S	0.032		A1000
M-5v1-S M-5v2-S	0.035 0.040		.01000 .01000

APPENDIX 5: Mercury Detected in Vegetation Samples (µg/g dry weight)

Appendix 5a: Mercury Levels Detected in Water Samples (mg/l)

<b>W-</b> w	<0.00005	<0.00005	<0.00005	
Re-w	<0.00005	<0.00005	<0.00005	
Ri-w	<0.00005	<0.00005	<0.00005	
M-w	<0.00005	<0.00005	<0.00005	

Appendix5b: MercuryLevels Detected in Sediment Samples (µg/g dry weight)

W-sed	0.0660	0.0660	0.0390	
Re-sed	0.0710	0.0780	0.0433	
Ri-sed	0.0650	0.0820	0.0725	
Ri-sedD	0.1100			
M-sed	0.1000	0.0660	0.0567	
M-sedD		0.0740		

	07/88	02/88	09/87	
W-cl1-R	0.0630	0.0010	0.0260	
W-c12-R	0.0010	0.0010	0.0230	
W-sv 1-R	0.0600	0.0010	0.0280	
W-sv1D-R		<b>0.0</b> 010		
<b>W-sv2-</b> R	0.0290	<b>0.0</b> 010	0.1300	
Re-cl1-R	0.0190	0.0013	0.0170	
Ro-cl1D-R		0.0012	0.0140	
Re-c12-R	0.0170	<b>0.0</b> 016		
Re-sm1-R	0.0100	0.0015		
Re-m2-R	<b>&lt;0.001</b> 0	0.0012		
Re-sv1-R	<b>&lt;</b> 0.0010	0.0029		
Re-sa-R			0.0150	
Ri-cll-R	0.0030	0.0024	0.0120	
Ri-c12-R	0.0060	0.0030		
Ri-sv1-R	<b>&lt;0.00</b> 10	0.0025		
Ri-sv2-R	<0.0010	0.0018		
Ri-sm1-R	0.0050	0.0013	0.0390	
Ri-sm2-R	<b>&lt;0.00</b> 10	0.0023		
Ri-sa-R			0.0130	
M-cl1-R	0.0120	0.0034	0.0230	
M-cl2-R	0.0660	0.0018	0.0270	
M-sv1-R	0.0230	0.0023	0.0300	
M-sv2-R	0.0090	0.0026		
M-sv2D-R	0.0090	0.0021		
W-c.1.1-S	0.0010		<0.0010	
W-c.12-S	0.0030		0.0094	
W-sv 1-S	0.0060		0.0082	
W-sv1D-S			0.0110	
₩-sv2-S	0.0060		0.0130	
Re-cl1-S	0.0080		0.0270	
Ro-c12-S	0.0080			
Re- <b>sm1-S</b>	0.0270			
Re-sm2-S	0.0050			
Re-sv1-S	<0.0010		0.0110	
Re-sv1D-S				
Re- <del>sa</del> -S			0.019	
Ri-cl1-S	<0.0010		0.0120	
Ri-cl1D-S	0.0220			
Ri-sv1-S	0.0130			
Ri-sv2-S	0.0180			
Ri- <b>am1-S</b>	0.0030			
Ri-m2-S	0.0080			
Ri- <b>sm2D-S</b>				
Ri- <b>sa-S</b>			0.0210	
M-cll-S	0.0060		0.0093	
M-c12-S	0.0040		0.0084	
M-sv1-S	0.0090		<0.0010	
M-5v2-S	0.0080			i

# APPENDIX 6: PCB Detected in Vegetation Samples (µg/g dry weight)

<b>W-w</b>	<0.0010	<0.001	<0.0010	
Rc-w	<0.0010	<0.001	<0.0010	
Ri-w	<0.0010	<0.001	<0.0010	
M-w	<0.0010	<0.001	<0.0010	

Appendix 6a: PCB Levels Detected in Water Samples (mg/l)

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Appendix 6b: PCB	Levels Detected	in Sediment Sam	ples (µg/g dry weight)
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W-eed	<0.0010	<0.0100	<0.01	
Re-sed	< 0.0010	<0.0100	<0.01	
Re-sedD		<0.0100		
Ri-sed	<0.0010	<0.0010	<0.01	
Ri-mdD	< 0.0010			
M-sed	0.0170	0.0110	<0.01	

	07/88	02/88	09/97	
W-cll-R	0.0018	<0.0010	<0.0010	
W-c12-R	<0.0010	0.0014	0.0029	
W-sv 1-R	<0.0010	0.0013	0.0017	
W-sv1D-R		0.0009	0.0081	
W-sv2-R	<0.0010	<b>&lt;</b> 0. <b>0</b> 010		
Re-cll-R	0.0010	0.0015	<0.0010	
Re-cl1D-R		<b>&lt;0.00</b> 10	<0.0010	
Re-c12-R	<0.0010	<b>&lt;0.0</b> 010		
Rc-sm1-R	<0.0010	0.0016		
Re-sm2-R	<0.0010	<b>&lt;0.0</b> 010		
Re-sv1-R	<0.0010	0.0010		
R <del>c-sa</del> -R			0.0050	
Ri-cl1-R	<0.0010	<0.0010	<0.0010	
Ri-c12-R	<0.0010	0.0059		
Ri-sv1-R	<0.0010	0.0015		
Ri-sv2-R	<0.0010	<0.0010		
Ri-sm1-R	<0.0010	<0.0010	0.0030	
Ri-m2-R	<0.0010	0.0013		
Ri-sa-R			0.0059	
M-cl1-R	<0.0010	<0.0010	0.0046	
M-cl2-R	<0.0010	<0.0010	0.0052	
M-sv1-R	<b>&lt;0.00</b> 10	0.0013	<0.0010	
M-sv2-R	<0.0010	<0.0010		
M-sv2D-R	<0.0010	<0,0010		
W-c.11-S	<0.0010		0.0018	
W-c.12-S	<0.0010		0.0027	
W-sv 1-S	<0.0010		0.0013	
W-sv1D-S	<0.0010		0.0027	
W-sv2-S	<0.0010		0.0023	
Re-cl1-S	<0.0010		0.0020	
Re-c12-S	<0.0010			
Re-sm1-S	<0.0010			
Re-m2-S	<0.0010		0.0011	
Re-sv1-S	0.0012			
Re-sv1D-S				
Re-se-S			0.0011	
Ri-cl1-S	0.0012		0.0028	
Ri-cl1D-S	<0.0010	-		
Ri-sv1-S	<0.0010			
Ri-sv2-S	<0.0010			
Ri- <b>am1-S</b>	<0.0010			
Ri-m2-S	<0.0010			
Ri-sm2D-S				
Ri-m-S			0.0026	
M-cl1-S	0.0013		0.0017	
M-c12-S	0.0017		0.0019	
M-sv1-S	<0.0010		<0.0010	
M-5v2-S	<0.0010			

## APPENDIX 7: PCP Detected in Vegetation Samples (µg/g dry weight)

W-w	<0.0020	<0.0020	<0.0002	
Re-w	0.0020	<0.0020	<0.0002	
Ri-w	0.0020	<0.0020	<0.0002	
M-w	0.0020	<0.0020	<0.0002	

Appendix 7b: PCP Levels Detected in Sediment Samples (µg/g dry weight)

W-eed	<0.0020	<0.0020	<0.002	
Re-sed	<0.0020	<0.0020	0.002	
Re-sedD		<0.0020		
Ri-sed	0.0050	<0.0020	0.0037	
Ri-æđD	0.0036			
M-aed	0.0048	0.0055	0.003	

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	07/88	02/88	09/87	
W-cl1-R	0.0012	<0.0010	0.0025	
W-c12-R	<0.0010	0.0026	0.0023	
W-sv 1-R	<0.0010	0.0015	0.0034	
W-sv1D-R		0.0012	0.0130	
W-sv2-R	<0.0010	0.0016		
Re-cl1-R	0.0023	0.0018	0.0044	
Re-cl1D-R		<0.0010	0.0039	
Re-c12-R	<0.0010	<0.0010		
Re-sm1-R	<0.0010	0.0031		
Re-sm2-R	<b>&lt;0.0</b> 010	<0.0010		
Re-sv1-R	0.0032			
Ro-sa-R			0.0065	
Ri-cl1-R	<0.0010	<0.0010	0.0044	
Ri-cl2-R	<0.0010	0.0016		
Ri-sv1-R	<0.0010	<0.0010		
Ri-sv2-R	<0.0010	<0.0010		
Ri-sm1-R	<0.0010	<0.0010	0.0091	
Ri-sm2-R	<b>&lt;0.00</b> 10	0.0021		
Ri-sa-R			0.0070	
M-cl1-R	<0.0010	<0.0010	0.0085	
M-cl2-R	<b>&lt;0.00</b> 10	0.0020	0.0091	
M-sv1-R	<b>&lt;0.0</b> 010	0.0023	0.0028	
M-sv2-R	<0.0010	<0.0010		
M-sv2D-R	< <u>0.0010</u>	<0.0010		
W-c.L1-S	<0.0010		0.0062	
W-c.1.2-S	<b>&lt;0.00</b> 10		0.0082	
<b>W-s</b> v 1-S	<0.0010		0.0094	
W-sv1D-S	<b>&lt;0.001</b> 0		0.0064	
W-sv2-S	<b>&lt;0.00</b> 10		0.0051	
Re-cli-S	<b>&lt;0.00</b> 10		0.0073	
Re-c12-S	<b>&lt;0.001</b> 0			
Re-sm1-S	<b>&lt;0.0</b> 010			
Re-sm2-S	<b>&lt;0.00</b> 10			
Re-sv1-S	0.0039		0.0097	
Re-sv1D-S	0.0041			
Ro-sa-S			0.0110	
Ri-cl1-S	<0.0010		0.0110	
Ri-cl1D-S	<0.0010			
Ri-sv1-S	<0.0010			
Ri-sv2-S	<0.0010			
Ri-sm1-S	⊲0.0010			
Ri-sm2-S	<0.0010			
Ri-sm2D-S				i
Ri- <b>sa</b> -S			0.0060	
M-c11-S	0.0010		0.0041	
M-c12-S	<0.0010		0.0050	
M sv1-S	0.0018		0.0033	
M-5v2-S	<0.0010		~.~~//	

APPENDIX 8: TCP Detected in Vegetation Samples (µg/g dry weight)

₩- <b>₩</b>	<0.0020	<0.0002	<0.0002	
Re-w	<0.0020	<0.0002	<0.0002	
Ri-w	<0.0020	<0.0002	<0.0002	
M-w	<0.0020	<0.0002	<0.0002	

Appendix 8a: TCP Levels Detected in Water Samples (mg/l)

## Appendix8b: TCP Levels Detected in Sediment Samples (µg/g dry weight)

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W-sed	<0.0020	<0.0020	0.0066	
Re-sed	0.0033	<0.0020	0.0061	
Re-sedD		<0.0020		
Ri-sed	0.0067	<0.0020	0.042	
Ri-sedD	0.0053			
M-sed	0.0050	0.0060	0.0108	