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EXAMINATION OF SEDIMENT IN THE DERWENT RIVER BY SELECTIVE EXTRACTION

by

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To IKA, MAMO and SITI

CONTENTS

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree, or diploma in any university, and to the best of may knowledge contains no copy or paraphrase of material previously published or written by another person, except when due reference is made in the text.

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ABSTRACT

The distribution and bioavailability of zinc, lead, copper and cadmium in sediment samples from the Derwent River has been examined by means of sequential selective extraction. Two types of sediments ; core sediment and suface sediments, were used in the examination. They were taken from two sampling sites, one near the Derwent Sailing Squadron and the other in Prince of Wales Bay.

The majority of the metals in the core sediment were in residual form and appeared to be accumulated in the top part. By contrast, the metals in the surface sediment were found mainly in the bioavailable (non-residual) forms. The core and surface sediments had a different physical appearance and a different pH which may account for in part the apparently anomalous results. The other explanation is that sediments are parts of a dynamic system , and their ecotoxicological impact will be different in different pH environments.

Compared to the total metals concentration measured in the previous studies from similar sites, the results in this study indicated a decrease in the level of the metals concentrations, except for mercury which showed a slight increase in its level.

CHAPTER ONE

INTRODUCTION

1.1. Objective of The Study.

Aquatic systems are chemically dynamic. Identifying and quantifying metal associations in sediments and the reactions that can occur between sediments, water and biota may explain metal transport and its environmental availability. Sediments can also reflect the condition of a water body over longer periods of time.

Sediments are important carriers of trace metals in hydrological cycles, and can accordingly act as a reservoir, sink or source of trace metals in the overlying water. For instance, benthic organisms have direct contact with the sediment, so the contaminant level in the sediment may have greater impact on their survival. The establishment of trace metal levels in sediments can therefore play a key role in detecting the source of pollution in aquatic systems. Remobilization of trace metals from sediments is particularly hazardous not only for the aquatic ecosystem, but also for drinking water supplies.

It is known that the measurement of total metal concentrations may include forms which are chemically inert or unable to be assimilated by biota, and this makes it difficult to identify the mobility and bioavailability of the metal. Analysis of sediments for trace metals would have more significance if it

were possible to quantify the fraction of total metal concentration associated with specific mineral phases, termed as speciation of trace metals. Speciation of trace metals is defined as the determination of the individual physico-chemical forms of the metal which together make up its total concentration (Florence,1982) by applying a selective extraction procedure.

The objective of this study was to examine the level, distribution and speciation of trace metals in the Derwent river sediments by means of selective extraction procedures and to develop the techniques which can be applied to assess metal levels in Derwent River sediments.

1.2. Content of the Study.

This study comprises of five chapters.

The objective, content, and limitations in scope of this study are discussed in chapter one.

Chapter two gives an overview of the examination of sediments . Firstly, the processes which may occur in sediments are studied. The past studies of sediments in The Derwent River are reviewed. This is followed by a description of different methods of speciation of trace metals in sediments. Finally, the method applied in this study was chosen on the basis of the review which considers the magnitude of trace metal levels in Derwent River sediments. The reason for the choice of the method is also discussed.

Chapter three describes the experimental techniques chosen for the study. This includes the sampling method and analysis procedures.

The experimental results of this study are reported and discussed in chapter four.

The final chapter presents conclusions arrived at as a result of this study with suggestion for future work.

1.3. Limitations In Scope.

This study is purely concerned with the objectives discussed in section 1.1. The study does have limitations which can be described as follows;

a. The trace metals to be examined were limited to cadmium, copper, lead, zinc and mercury.

b. The sediments were analysed after applying a selective extraction procedure (for cadmium, copper, lead and zinc).

c. Total mercury was analysed using cold vapour spectroscopy (Flameless AA).

d. The evaluation used core sediments from the Derwent Sailing Squadron site, surface sediments from the Derwent Sailing Squadron site and from Prince of Wales Bay ; and also reference sediment (US NBS Sediment Reference Material No.1645).

e. No attempt was made to determine waterflow rate at the time of sampling.

g. No attempt was made to centrifuge the sediment.

h. No attempt was made to look at the mineral composition of the sediment.

CHAPTER TWO

OVERVIEW

2.1. Evaluation Of the Processes Which May Occur In Sediments.

2.1.1. Composition Of Sediment.

Based on their mineralogical, physico-chemical and mechanical properties, sediments can be divided into two groups (Raudkivi,1976);

a.   Fine sediment with particles smaller than about 50 μm, subdivided into silts and clays. These mainly consists of clay minerals, organic matter and fine grained quartz, carbonate and feldspar particles.

b.   Coarse sediments with grain sizes exceeding 0.05 mm and subdivided into sands and gravels. The mineralogy of coarse sediment in general is less diverse. It consists mainly of quartz with an admixture of feldspar.

Generally, the shape and size of fine sediment is diverse, while the coarse sediment consists of more or less rounded particles (Lambert et al.,1981). The fine particles may be charged, depending on the ionic strength of the surrounding solution and the surface coatings. The surface charge is also responsible for the

cohesion characteristics of the fine grained sediments.

In deposited coarse sediments, the particles are simply stacked upon each other ,while in fine sediments the deposition of flocs formed by inter particle forces, leads to a more open structure with cohesion.

2.1.2. Types Of Metal Association In Sediments.

Allan (1974) reported that the fate of metal ions in sediments which were originally derived from the chemical weathering and mechanical disintegration of host rock, was controlled by many factors. These include atmospheric precipitation, water movement, soil movement, changes in redox and pH conditions, adsorption-desorption processes, chemical complexation, precipitation and hydrolysis, uptake by and decay of vegetation and biochemical-bacterial interactions. Metal enrichment in aquatic system may be understood by means of identifying the different types of metal association in the sediment. Natural metal enrichments in solid substances can originate from the following five sources (Golberg,1954);

a. Lithogenous formation: Weathering products from the source areas or rock debris from the river bed. This material undergoes only slight change regardless of the length of residence time.

b. Hydrogenous formation: Particles, precipitation products and adsorbed substances formed due to physico-chemical changes in water.

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c. Biogenous formation: Biological remains, decomposition products of organics as well as inorganic siliceous or calcareous shells.

d. Atmogenous formation: Metal enrichment resulting from atmospheric fallout and volcanic emissions.

e. Cosmogenous formation: Extra-terresterial particles.

The metal enrichment due to man's activities could be included among the first four processes. Bi-products from the erosion of refuse dumps and mine waste are an important source of lithogenous solids as well as of soil particles, which can be carried into the aquatic system via surface runoff. Hydrogenous metal enrichment may occur during the total course of a primary dissolved contaminant, starting in the waste effluent, moving through the sewage treatment plant , and ending up in the river, lake, or sea. The same processes apply to biogenous formations. Atmogenous metal enrichment can enter water by dissolved or solid form (particularly on large water surfaces), or by way of enrichment processes in the soils .

2.1.3. Sediment as Trace Metal Collectors.

The ability of a sediment to collect and concentrate trace metals is affected by a number of physical and chemical factors. The ability may be examined by means of physical partitioning and chemical partitioning. Physical partitioning is the separation of a sediment sample into various physical categories (including by grain size, surface area, magnetic properties). Chemical partitioning is

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separation of various trace metals with respect to their association with other materials within the sediment (organic matter, carbonates, manganese oxides, iron oxides, silicates, or sulphides) and to the type of association that exists (includes adsorption, complexation, and substitution within mineral lattices).

Grain size is one of the most significant factors controlling sediment capacity for retaining trace metals (Jenne and others, 1980). There is correlation between decreasing grain size with increasing trace metal concentrations. High concentrations are more commonly associated with fine grained material. Cu, Cd, Ni, Co, Zn, and Pb are mostly found in high concentration in fine grained sediment. Surface area is almost indistinguishable from grain size; as grain size decreases, surface area increases sharply. Jackson (1979) has calculated the surface area of simple spheres of differing diameter (grain size). Sand-sized particles have surface areas in the order of 10^{-1} to 10^{-2} cm^2/g, silt-sized particles in the order of 10^{-2} to 10^{-3} cm^2/g, and clay-sized particles have surface areas in the order of 10^{-1} cm^2/g.

The major mechanism for the collection of trace metals on surface is adsorption, which entails the condensation of atoms, ions, or molecules on the surface of another substance. Adsorption can occur with or without cation exchange. Materials with a large surface area are good adsorbers. Jenne (1980) indicates that materials with a large surface are can be viewed simply as mechanical substrates upon which inorganic constituents can concentrate without any chemical interaction between the material and the constituent. Deposited materials which are chemically active sediment components, such as clay minerals, organic matter, hydrous iron and manganese oxide may thus act as metal collectors. They are capable of sorbing cations from solution and releasing equivalent amount of other cations back into solutions. This is called

the cation exchange process.

The capacity of sediments to concentrate trace metals which varies with the type of clay minerals present, concentration of organic matter, pH and Eh of the environment and trace metals involved, has been the subject of several studies. Forstner (1982) in his study of marine material based on sequential extraction, proposed that the relative capacity of the metal collectors is in the order of

manganese oxides > organic matter > iron oxides > clay minerals

Furthermore,based on a hierarchical ranking of correlation coefficients between geochemical substrates and trace metals of freshwater material, Horowitz and Elrick (1987) concluded the order :

amorphous iron oxides> total extractable iron> total organic carbon > reactive iron > clay minerals > total extractable manganese > manganese oxides

These two examples show that the capacity is different between marine material and freshwater material due to the differences either in composition, pH, Eh of the water or the trace metals contents.

The iron and manganese oxides have characteristics of being fine grained, of large surface area, amorphous or poorly crystallized with a high cation exchange capacity. These substances have long been known as excellent scavengers of trace metals from solutions. In soils, suspended and bottom sediments, hydrous iron and manganese oxide commonly occur as coatings on various minerals and dispersed particles (Forstner and Wittmann, 1981), and

the coatings are very capable of concentrating metal . The hydrous oxides are redox sensitive. Under oxidizing conditions they constitute significant sinks of heavy metals in aquatic systems. They readily sorb and coprecipitate cations and anions; even in low concentrations they have a controlling influence on the heavy metal distribution in aquatic systems. Under reducing conditions the sorbed heavy metal, are dissolved / mobilized, so that accumulation of hydrous iron and manganese oxides can therefore act as a major source of dissolved metals in natural water. The accumulation is more effective in the presence of dissolved organic material (Forstner and Wittmann, 1981).

Aquatic and soil organic matter has characteristics such as a large surface area , high cation exchange capacity, high negative surface charge, and is capable of physical trapping. The aquatic organic matter is generally termed humic substance, and subdivided into humins, humic acids, fulvic acids and yellow organic acids (Jonasson, 1977). Humic acids are the most important products formed during decomposition of organic substances. The humic acids are extremely heterogeneous polymers, and contain or readily give rise to a complex aromatic core to which polysaccharides, protein, simple phenols and metals are attached chemically or physically (Haworth, 1971).

Singer (1977) summarized the influence of dissolved organics on the distribution of metals as follows. Dissolved organic substances are capable of

1. Complexing metals and increasing metal solubility.

2. Altering the distribution between the oxidized and reduced forms of metals.

3. Alleviating metal toxicity and altering metal availability to aquatic life.

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4. Influencing the extent to which metals are adsorbed on suspended matter.

5. Affecting the stability of metal containing colloids.

Soxby (1969) has shown that the relative attraction between metals and organic matter associated with colloidal, suspended and bottom sediments can range from weak and readily replaceable (adsorption) to strong (chemically bonded). The ability of organic matter to concentrate metals varies with the constituent and the type of organic matter, and is related to a number of factors including large surface area, high cation exchange capacity, high negative surface charge and physical trapping. In addition, the ability is also related to the stability of the organic-metal constituent complex. The organic metal can concentrate between 1-10% dry weight of Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, V and Zn. It accordingly can be concluded that the enrichment of metals in sediment may be largely attributable to humates having acted as scavengers or complexing agents (Swanson et al., 1970). The stability of the organic-metal constituent complex in soil can be explained by the Irving-William series, with the sequence in descending order as follow: Pb, Cu, Ni, Co, Zn, Cd, Fe, Mn, Mg.   Rashid (1974) found the same phenomena applies to aquatic organic matter. Slowey et al. (1967) found that the major portion of copper in tropical seawater is associated with organic matter; other transition metals were suspected to be similarly bounded and transported.

The characteristics of clay minerals are that they are fine grained, with a large surface area, moderate to high cation exchange capacity, and high negative surface charge. In Jenne's (1976) view the major role of clay minerals as a concentrator is to act as mechanical substrate for the precipitation and flocculation

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of organic matter and secondary minerals (e.g. hydrous iron and manganese oxides).

Various sedimentary geochemical factors can be identified and quantified by means of physical partitioning or chemical partitioning.

In the case of chemical partitioning, an attempt to separate, identify and quantify a sediment sample into various geochemical substrates is known as a phase approach. This has been attempted because individual constituents like Fe, Mn, Cd, Pb, Zn, Ni, Co and Cu may be and usually are associated with several phases.

The approach to separate, identify and quantify a sediment sample into the types of trace metals association with the geochemical substrates is called mechanistic approach. According to Gibbs (1977) there are four mechanisms for inorganic accumulation in or on a sediment;

1. Adsorption and precipitation of metals on fine grained material.

2. Co-precipitation with hydrous iron and manganese oxides and carbonates.

3. Association either by adsorption or organometallic bounding with organic matter.

4. Incorporation in crystalline minerals.

In fact, most attempt are to chemically partition a sediment sample in combination of both aspects; chemically and physically.

One of the methods for determining chemical partitioning is sequential partial chemical extractions . This method attempts to partition trace metals by several sequential extraction steps on increasing strength of the extractant used. The sequential extraction is based on the idea that a particular reagent is either phase-specific or mechanistic-specific; for example ammonium acetate at pH 7 will only remove adsorbates (particular reagent will attack a particular phase).

2.1.4. Chemical Phases in Sediment.

Trace metals are known to concentrate in sediments, and the accumulation is postulated to be caused by adsorption processes with various geochemical phases such as organic matter, hydrous metal oxides and sulphides.

As Gibbs (1977) suggests trace metal association in aquatic solid. substances can be characterized as adsorption and precipitation of metals on fine-grained material, coprecipitation by hydrous iron and manganese oxides and carbonates, complexation by organic molecules, and incorporation in crystalline minerals.

Chemical adsorption is characterized by the formation of chemical associations between ions or molecules from the solution and surface particles. Many active components of sediment with large surface areas such as clay minerals, hydrous iron and manganese oxides , and organic matter are capable of sorbing cations from solution and releasing equivalent amounts of other cations

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into the solution by cation exchange. The mechanism which results in cation exchange is based on the sorptive properties of negatively charged anionic sites -SiOH, $AlOH_2-$, and AlOH-groups in clay minerals; FeOH-groups in iron hydroxides; carbonyl and phenolic OH-groups in organic substances, towards positively charged cations. Furthermore, all fine-grained materials with a large surface areas are also capable of accumulating heavy metal ions at the solid-liquid interface as a result of intermolecular forces, termed as adsorption (Forstner and Wittmann, 1981).

Stumm et al.(1980) summarized two chemical approach theories to interpret the mechanism of adsorption of the metal ions on a solid surface mechanism through interactions with hydrous oxides, these are;

1. The ion exchange model according to which cations (M^{x+}), upon adsorption on the hydrous oxide surface groups (=M-OH), replace protons.

2. The surface complex formation model in which hydrous oxide surface groups (=M-OH or =M-OH-HO) are treated similarly to the amphoteric functional groups in polyelectrolytes as complex forming species.

In general, heavy metals in aquatic environments may be classified into two different categories ;

1. In true solution as free or complexed ions.

2. In particulates by adsorption into the biomass of living organisms from inorganic precipitates such as hydroxides, carbonates, sulphides and sulphates.

$$M^{x+}, L^{y-}, OH^-, e^-, M(OH)_B^{x-B}, ML_A^{x-Ay}$$

WATER

$$M^{x+} + \begin{bmatrix} A\ L^{y-} \\ B\ OH^- \\ C\ e^- \end{bmatrix} \overset{cpx}{\underset{cpx}{\leftrightarrow}} \overset{rox}{\leftrightarrow} \begin{bmatrix} ML^{x-Ay} \\ M(OH)^{x-B} \\ M^{x-C} \end{bmatrix} + \begin{bmatrix} L^{y-} \\ OH^- \\ e^- \end{bmatrix} \overset{pcx}{\underset{pcx}{\leftrightarrow}} \overset{pcx}{\leftrightarrow} \begin{bmatrix} ML^{x-(A+1)y}\ (S) \\ M(OH)^{x-(B+1)}\ (S) \\ M(S) \end{bmatrix}$$

Ads | Des   Ads | Des

SOLID
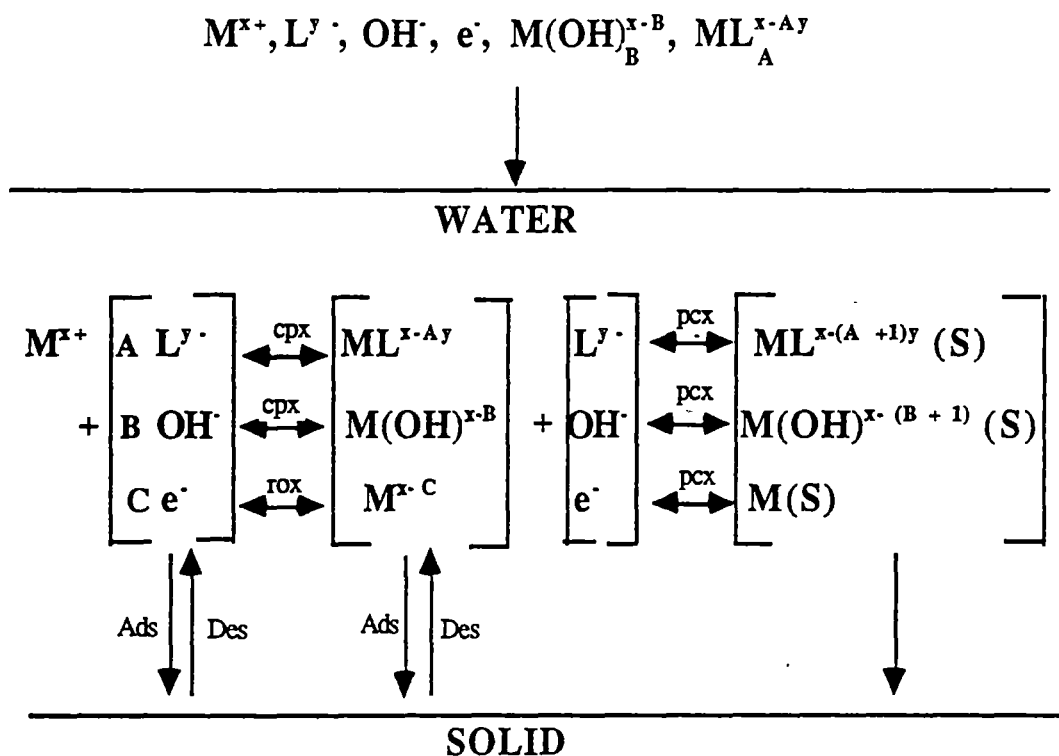
Note : cpx = complex formation, pcx = precipitation, rox = reduction-oxidation, Ads = adsorption and Des = desorption.

Figure 2.1. Schematic model of metal tranformation in soil-water system (From Huang et. al, 1977)

The free and complexed metal ions may be removed from solution by adsorption and precipitation mechanisms, while the particulate heavy metals may

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be transformed by their own dissolution and filtration mechanism of soils. The processes are schematically represented in Figure 2.1. The free metal ion M^{x+} forms the complexed metal ions ($M(OH)^{x-B}$, ML^{x-Ay} and M^{x-C}) through complex formation or reduction-oxidation reactions. These ions may be adsorbed by the sediment. Further reaction of the complexed metal ions with anions in solution form a more complex metal ions ($M(OH)^{x-(B+1)}$, $ML^{x-(A+1)y}$ and M) which are directly precipitated onto the sediment.

In the case of the adsorption of free metal ion M^{x-C}, McNaughton (1974) proposed that the ions are removed from aqueous solution by three mechanism ;

1. Ion exchange reactions,

$$m(\equiv S\text{-OH}) + M^{x+} == (\equiv S\text{-O})_m M^{(x-m)+} + mH^+ \qquad (1)$$

2. Adsorption and hydrolysis at the surface,

$$\equiv S\text{-OH} + mH_2O + M^{x+} == \equiv S\text{-}M(OH)_{m+1}^{(x-m)+} + mH^+ \qquad (2)$$
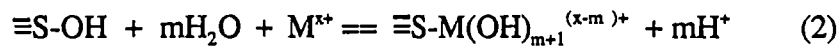
3. Hydrolysis followed by an adsorption reaction,

$$M^{x+} + m\,H_2O == M(OH)_m^{(x-m)+} + mH^+ \qquad (3)$$

$$M(OH)_m^{(x-m)+} + \equiv S\text{-OH} == \equiv S\text{-}M(OH)_{m+1}^{(x-m)+} \qquad (4)$$
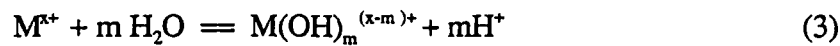
where $\equiv S\text{-OH}$ is hydrated soil surface; M^{x+} is free metal ion.

From reactions (1), (2), and (3), the effects on adsorption by changing pH or adsorbent concentration can be predicted. Increasing the pH will cause the equilibrium to shift to the right and hence increase the adsorption of the cation.

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Variation in solution ionic strength, pH, and ligand and metal concentration can also affect the adsorption of the metal.

According to Benjamin et al.(1982), the adsorption of metals increases from 0 to 100% as the pH increases by 1-2 units. This means that a small shift in pH in surface water causes a sharp increase or decrease in dissolved metal levels. Leckie et al (1980) in his experiment on the adsorption of Cd, Zn, Cu, Pb, and Ag onto amorphous iron oxyhydroxide, γ-alumina, and α-SiO_2 found that the pH of adsorption increases in the order of Pb<Cu< Zn<Cd<Ag. Therefore, it can be concluded that under normal conditions in surface water, Pb and Cu are more weakly bound to the solid than the other metals (or may be they form strongly complexes with water than the other metals).

The adsorption of Cd, Cu, Pb, and Zn onto amorphous Fe_2O_3. H_2O and other hydrous oxides has been studied over a wide range of adsorbate to metal concentrations as a function of pH (Benjamin and Leckie, 1981). They found that surface adsorbate is composed of many groups of binding sites, and the strength of binding between a given metal and the surface is varies from one site to another.

Lion et al. (1982) summarized the results for cation adsorption by hydrous oxides as follows:

i. Fractional trace metal adsorption as a function of pH typically increases sharply over a narrow range of 1-2 pH units.

ii. The fraction of metal adsorbed increases with increasing solid

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concentration at a fixed total metal concentration and constant pH.

iii. At a fixed solid concentration and very low adsorption site occupancies (e.g. less than 1%), fractional metal adsorption increases as the total metal concentration decreases at constant pH. This behaviour is attributed to variations in site-metal binding energies due to differences in the nature of surface sites present.

iv. For the same adsorbent and pH the fraction of metal adsorbed varies with differing metal cations. This is attributed to differences in the site binding energies for different trace metals (different metal cations have different binding intensities).

The variability in metal-binding intensity is likely to be due to the presence of different component of functional groups on solid surface.

Ligands which form dissolved complexes with metal ions can either increase or decrease metal adsorption. Benjamin and Leckie (1981) hypothesised that a complexed metal adsorbs less strongly than the uncomplexed metal. Furthermore the hydrous oxides of iron and manganese and organic coatings substantially control the sorptive behaviour of estuarine particulate matter. Their experiments found that chloride and sulphate (and ammonia) generally decrease fractional adsorption of cadmium at a given pH.

The various ways in which adsorption of metals is affected when metal ions bind to dissolved ligands to form soluble complexes has been represented schematically by Benjamin et.al (1982) as shown in Figure 2.2. This Figure shows that in the presence of a complexing ligand LM (aq) the adsorption of

a metal at low pH is enhanced. This explanation is applicable if the ligand L is

an anion which adsorb strongly at low pH, as shown in the following reaction

(Benjamin et al, 1982) :

$$\overline{SOH} + L^{n-} + mH^+ = \overline{SOH_{m+1}L^{m-n}}$$

where $\overline{SOH}$ represent s a singly protonated surface oxide site and L is an anionic

ligand (adsorbate). In addition, at low pH the ligand may bind to the surface and

take the metal along with it.

Low pH metal-ligand-surface interactions

High pH metal-ligand-surface interactions
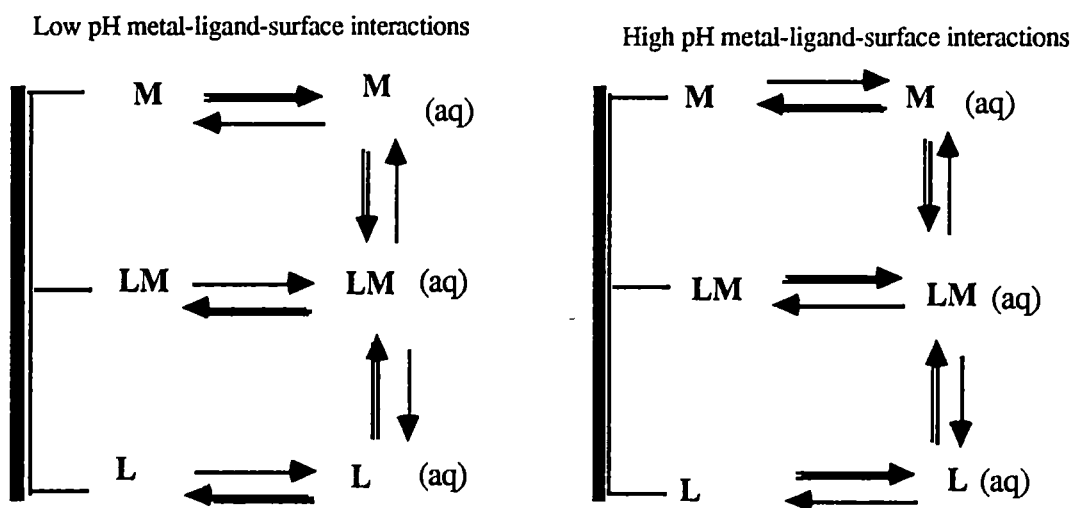
Note : M = metal   L = ligand

Figure 2.2.   Schematic representation of adsorption reaction at low and high pH (From Benjamin et. al 1982)

Furthermore Benjamin and Leckie (1981) defined   a species whose tendency to

adsorb increases as pH increases as a 'metallike complex', while those for which

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the tendency to adsorb decreases with increasing pH is defined as a 'ligand like complex'.

The ionic strength of a solution, for example in the estuarine mixing zone also can affect metal adsorption at changing salinities. Studies by Gupta and Harrison (1981) suggest that major cations, calcium and magnesium are co-adsorbed with trace metals and compete for adsorption sites increasingly with increasing salinity. At high salinity formation of chlorocomplexes compete with adsorption, which tends to reduce the trace metal adsorption. A significant decrease in cadmium adsorption was indicated by Salomons (1980) in his experiments. Data from Bourg (1983) shows that the effect of the chloro complexation, and the competition by magnesium and calcium ions occurs more strongly with zinc than copper. The reason is that the surface constant (the ability to adsorb or surface site) of copper is greater than that of zinc, and the chloro complex constant (the ability to form a complex) of copper is smaller than that of zinc.

Solid phases interact with dissolved constituents in natural waters. The solid phases consist of a variety of components including clay minerals, carbonates, quartz, feldspar and organic solids. These components are usually coated with hydrous oxides and by organic substances. From various investigations Salomon and Forstner (1984) have summarized that the speciation of solid phases, particularly with respect to the nature of their surfaces, determines the extent of the adsorption. Mineral particles in the solid phases are often covered with hydrous iron and manganese oxides and/or organic films which have great ability to remove trace metals from solutions. Data from Lion et al. (1982) shows that substantial fractions of total extractable cadmium and copper (50% and 65%, respectively) were found to be associated with organic phases.

Furthermore they observed that approximately 70% of total extractable lead was removed during the extraction of iron and manganese oxides. This data indicated that iron and manganese oxide coatings may play a relatively greater role in adsorbing lead while adsorption of cadmium and copper may be controlled by organic coatings.

Park (1967) noted that metal oxides exhibit ion exchange properties. The ion exchange capacity of the simple oxide arises from the existence of a pH dependent surface charge. In acid solutions, the surface charge is positive and therefore the hydrous metal oxide acts as anion exchangers. In basic solutions, the surface charge is negative and hence they are cation exchange particles. In neutral solutions, the surface charge is mixed both positive and negative and shows a limited capacity for the exchange of both cation and anion. Trace metals in this phase are readily available for biological uptake.

Iron and manganese oxyhydroxides can be present in X-ray amorphous and microcrystalline forms and in more aged crystalline forms, either as coatings or as discrete phases. They are present in all parts of the hydrocycles, and can exist as nodules, concretions, cement between particles, or simply as coatings on particles. These oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions, that is at low Eh. Morgan and Stumm (1964) found that precipitated manganese oxide has a very significant sorption capacity for trace metals.

It has been found that significant trace metal concentrations can be associated with sediment carbonates. The possibility of coprecipitation trace elements in carbonate phases was explained by Forstner and Wittmann (1981) as a result of mixing different water bodies. When alkaline water become mixed

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in river water with normal Ca^{2+} and HCO_3^- levels under normal pH conditions, the pH will increase. Consequently the solubility product of calcium carbonate is drastically reduced and $CaCO_3$ is precipitated in the mixing zone, carrying trace metals from solution with it. Data from Papova (1961) show that trace metal carbonates of low solubility such as $CoCO_3$ and $PbCO_3$ are completely eliminated from solution as a result of $CaCO_3$ precipitation. Carbonate and hydroxy complexes may control the solubility of lead and zinc in some surface waters relatively high in bicarbonates and /or pH. This is true whether they are of inorganic or biogenitic origin (Hem and Durum, 1973). Trace metals may coprecipitate with carbonates both inorganically and biogenetically. They may undergo anisomorphic exchange with calcium or magnesium, or may be sorbed by iron and manganese oxides which have precipitated onto the carbonates.

In the case of sulphide phases, Jenne (1976) in his work found that the introduction of H_2S caused a marked coagulation of copper-fulvic complexes. This may be one of the processes responsible for the inclusion of trace metals in sediments in anaerobic waters. Jenne suggests that trace metals may be expected to coprecipitate with iron sulphides rather than as discrete sulphide crystals. This is because most of the trace metals generally occur in substantially lower concentration compared to ferrous iron in interstitial and other anoxic water.

Trace metals which co-precipitate with amorphous hydrous oxide, in the carbonates and sulphides phases are available to organism by digestion or can be released into the environment under reducing conditions.

Trace metals may be bound to various forms of organic matter, living

organism, detritus, and coatings on mineral particles. Complexation and peptization properties of natural organic matter are well recognized as is the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters, organic matter can be degraded, releasing soluble trace metals. Trace metals in this forms are available to organism by digestion or by simple oxidation in water. Organic matter and iron/manganese oxides are major components which might affect the rate of mobilization of metals, because they are available for redox processes.

Gibbs (1977) in his experiment of sediment in the Amazon and the Yukon rivers found that the crystalline phase is a major carrier of trace metals. According to him the majority of the world's large rivers will maintain these high percentages of trace metals in crystalline particles. In general, the distribution of metals present in the crystalline silica fraction is determined by the medium as well as chemical factors such as the ionic radius, valence, and electronic configuration. He found that zinc preferentially incorporates in a different structural position from silicates or oxides where it replaces iron and manganese. Lead in silicate structures replaces the position of mono and divalent metals particularly potassium. The residual solid contains mainly primary and secondary minerals, which may hold trace metals within their crystal structure. Metal in the crystalline phases can be taken as a guide to show a degree of contamination: the greater the percentage of metal present in the category, the smaller the pollution of the area , because the metal cannot be remobilized and it is not expected to be released in solution over a reasonable time.

2.2. Previous analysis of Sediments in The Derwent River.

Bloom and Ayling (1977) have shown that Derwent Estuary is one of the most polluted areas of the world . The river is severely affected by metallurgical waste, raw, and partly treated sewage and effluent from the processing of milk, vegetables and meat. The physical, chemical and biological composition of the Derwent River sludge has been determined by Aquahealth TASUNI (1989) who showed that the materials which settle forming part of the sediment between New Norfolk and the Tasman Bridge are as follows :

i.   Natural sources : e.g. silt, sand and decaying plant and animal matter from the upper Derwent and Jordan Rivers; particulate matter and dissolved salts present in seawater and carried into the Derwent River by tidal movement.

ii. Municipal council sources : e.g. several sewage outfalls and numerous stormwater drains and rivulets on the eastern and western shore, which can be diverse in composition.

iii. Recreational and light industrial sources : e.g. refuse made of paper and plastic ; petroleum hydrocarbons from motor vessel ballast waters; abattoir effluents; sawmill effluents.

iv. Heavy industrial sources : e.g. organic effluents from Cadbury food plant; wood fibre, coke/coal and fly ash from the ANM mill at Boyer; material with a high trace element content including arsenic, cadmium,

copper, lead, zinc, and mercury discharged from the EZ Pasminco company at Risdon.

Mercury in the river may also be contributed from a paper-making plant and a chlor-alkali plant. Apparently most of the trace metals contamination originates from the operation of the zinc refining plant.

In Bloom and Ayling's (1977) study of the Derwent Estuary, they carried out analysis for the total concentration of heavy metals in sediment, suspended particulate, filtered water, shellfish, fish, airborne particulate and sewage. The heavy metals analysed were cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel and zinc. In the case of their river bottom-sediment study, they analysed the sediment with a leaching method by boiling the finely ground sample which had been dried 16 hours at 105 °C, in concentrated nitric acid. In their study of different digestion techniques used (i.e. HNO_3, aqua regia, HCl/HNO_3, $HNO_3/HCLO_4$), they obtained similar results. Mercury, the volatile metal, was analysed by cold-vapour atomic absorption spectrophotometry, as this method was shown to be suitable for analysing mercury in The Derwent River sediment.

In September 1981, The Department of The Environment conducted a survey to examine the effects of a dredging operation in the Derwent River on heavy metals concentrations. The sediment was digested with concentrated nitric acid and analysed for non-volatile heavy metals by atomic absorption spectrophotometry. Mercury was extracted by cold-digestion method and the mercury formed from the reduction of the digest was analysed by cold-vapour atomic absorption spectrophotometry. The study found that the operation had not caused any problem in the area of investigation. The study indicated a lower

concentration of the metals than those detected by Bloom and Ayling (1977) who used the same method.

Wood (1988) in his Masters Thesis, examined the sediment of Lindisfarne Bay with leaching method using 1 mol/L hydrochloric acid. The extract was analysed for copper, cadmium , lead and zinc in flame atomic absorption using a Varian Spectic AA-40P instrument. By comparison with Bloom's study (which used concentrated nitric acid leaching method), Wood showed that the concentrations were diluted by a factor between 13 and 21 for the four metals. The results might not be comparable because 1 mol/L hydrochloric acid could not leach the total metal concentration selectively, the most likely explanation being that it leached the non-residual fraction of the metals. It has been noted by Billings and Ragland (1968) that 1 mol/L hydrochloric acid did not leach significant amounts of metals from well crystallised common clays.

Aquahealth TASUNI (1989) conducted a research of sediments (surface sediment and core sediment) of Derwent River between New Norfolk and the Tasman Bridge. They measured total metals (chromium, nickel, lead, copper, cadmium and zinc) concentration by extracting dry sediment in boiling concentrated nitic acid, and total mercury concentration by the cold digestion method. They also analysed the relative availability of the trace metals of the sediments by means of single extraction method. Ion exchangeable metals were determined by extracting wet sediment with 1 mol/L ammonium acetate pH 7; surface adsorbed metals were extracted with 0.1 mol/L hydroxylamine hydrochloride /0.1 mol/L nitric acid pH 2; and organically bound metals were determined by extracting wet sediment with hydrogen peroxide at pH 2. The Elutriate test was conducted by extracting the sediment with water and aerating with filtered air for 1 hour. They found that major portion of the metals are

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chemically bound to organic constituents. They also observed that the metals in the core sediments could only be selectively extracted with hot aqua regia, which indicated that the metals are present in solid solution within the major minerals.

2.3. Literature Review of Sediment Examination By Selective Extraction.

Based on a concept that metal-sediment associations can be extracted selectively by applying an appropriate reagent, several experimental procedures have been proposed for determining the speciation of trace metals in sediment. The methods may be designed to effect separation between residual and non-residual metals only, as examined by Malo (1977), Agemian and Chau (1978). The methods normally involve a single extraction and give a significant differentiation between anomalous and background samples compared to the determination of total metal concentration. The advantages of the methods are that they are rapid and simple. However, it is difficult to find a single reagent which is effective in dissolving quantitatively the non residual forms of metal without attacking the detrital forms.

Agemian and Chau (1978) studied the extractability of metals from sediments by means of total, acid-extractable, and cold-extractable metal extraction methods. Their study proposed a simple, rapid technique for measuring non-residual metal (which includes the exchangeable metal phase, carbonates phase, organic and sulphides phases, as well as oxides and hydroxides of iron and manganese).

The total metal extraction reflect the rock types as well as mineralization. For total metal content, the samples were analysed by hot digestion with $HF + HNO_3 + HClO_4$ reagent mixture.

The cold extractable methods are designed to indicate the non-residual metal phases of the sediment. These methods have used 0.05 mol/L EDTA, 1 mol/L hydroxylamine hydrochloride + 25% v/v acetic acid, or 0.5 mol/L hydrochloric acid.

The acid-leaching technique was performed using boiling nitric acid, boiling aqua-regia , and boiling HNO_3 + $HClO_4$; and shows varying degrees of attack on the crystal lattice .

It was found that 0.5 mol/L hydrochloric acid is the best among them, because it is suitable for simultaneous extraction from the adsorbed, organic and precipitated phases of aquatic sediment ,which provides a contrast between anomolous and background samples.

Malo (1977) proposed that trace metals associated with degradable organics and with the surface coatings of mineral particles would be more available than those incorporated in primary minerals or occluded by secondary structures. He evaluated procedures which can provide an acceptable analytical tool for monitoring trace metals in the surface coatings of mineral sediment particles, using 0.3 mol/L hydrochloric acid, pH 3 buffered citrate-dithionate, and 1 mol/L hydroxylamine hydrochloride + 25% v/v acetic acid solutions as extractants.

Malo found that the solution of trace metals more closely follows the solution of iron and manganese than the structural components silicate and alumina in a serial extraction with 0.3 mol/L hydrochloric acid This lead him to suggest that 0.3mol/L hydrochloric acid extraction procedure was preferable for

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routine use in monitoring the readily acid-soluble trace elements in aquatic sediments.

Furthermore, more elaborate methods have been proposed, making use of sequential extractions. Notably, Tessier et al. (1979) examined the merits of a method of sequential extractions, using sediment samples from Saint-Marcel and Pierreville (Canada). They selected five geochemical fractions for partitioning trace metals; the exchangeable metals fraction was determined using magnesium chloride pH 7 extractant, metals bound to carbonates fraction was determined by extraction with sodium acetate pH 5, the metals bound to iron and manganese oxides fraction was determined with hydroxylamine hydrochloride in 25% acetic acid pH 2, the metals bound to organic matter was extracted with peroxide/nitric acid pH 2 , and the residual form was determined by digestion with a mixture of hydrofluoric and perchloric acids. All extractions were done sequentially . In this study he examined the selectivity of the extraction reagents toward the specific geochemical phases. He found that magnesium chloride treatment does not affect silicates, sulphides, or organic matter; the sodium acetate completely dissolved the carbonates fraction of the sediment; the hydroxylamine hydrochloride in 25% acetic acid pH 2 extracted the reducible iron oxide phases completely. He found that peroxide not only oxidized the organic matter but also extracted sulphide minerals to a large extent; and the residual fraction was dissolved completely by treatment with mixture of hydrofluoric and perchloric acids.

However, it has been recognized that there are experimental problems with sequential procedures; especially nonselectivity of extractants and trace metals redistribution among phases during extraction. Readsorption reactions of metals are influenced by duration of the experiment, temperature and the ratio

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of solid matter to volume of extractant (Tessier et al., 1979). In considering the problems encountered, Salomons and Forstner (1980) proposed a standard extraction method which attempted to minimize the problems. They suggested the following method :

i. An extraction with acidified hydroxylamine hydrochloride, this will extract the exchangeable cations and carbonate-bound metals.

ii. An extraction with acidified hydrogen peroxide (30%), followed by an extraction with ammonium acetate to remove any readsorbed metal ions.

iii. A total digestion with hydrofluoric and perchloric acids of the residue remaining after the first two extractions.

The distribution and bioavailability of copper, cadmium, lead and zinc in sediments from Lake Macquarie (N.S.W.) were examined by Batley (1987). He examined surface adsorbed metals , organically bound metals and residual fraction by sequentially extracting the sediment with 0.1 mol/L hydroxylamine hydrochloride/0.01 mol/L nitric acid pH 2, 30 % hydrogen peroxide at pH 2 and a mixture of concentrated nitric and hydrofluoric acids . The ion-exchangeable metals were determined by extracting the sediment with 1 mol/L ammonium acetate pH 7.

The mobility of trace metals were examined by conducting the Elutriate test. The test has been developed to assess the potential for trace metals release following the dumping. It involves the mixing of a sediment sample to be dredged with the disposal site water.

Batley (1987) found that the majority of the metals are in bioavailable

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forms, and the Elutriate test showed no significant mobilization of metals.

Overall these studies attempted to differentiate between residual and non-residual forms of trace metals, and to estimate bioavailability, by using various reagents to selectively solubilize the metals in a geochemical phase they defined. For example hydroxylamine hydrochloride in 25 % acetic acid was used by Malo (1977) for monitoring trace metals in surface coatings of mineral sediment particles, and Tessier et. al (1979) used the same reagent to determine metals bound to iron and manganese oxide fraction. Therefore, it can be said that geochemical phases have to be defined operationally prior to decide what reagent to be used to extract metals in that phase.

2.4. The Selective Extraction chosen for the study

There are four operational definitions of the geochemical fraction examined in the sediments studied :

2.4.1. Exchangeable cations.

The exchangeable cations are metals loosely bound to the outside of particles. The extractant used to release the exchangeable metal ions should contain cations more strongly bound to the exchange positions compared with the metals. Common extractants in use are barium chloride/triethanolamine , magnesium chloride and ammonium acetate. Salomons and Forstner (1980) indicated that 1 mol/L ammonium acetate pH 7 offers an acceptable compromise for the estimation of ion-exchangeable trace metal contents, compared with barium chloride/triethanolamine (Jackson,1958) or magnesium chloride (Gibbs,1973)

due to the chelating effects of the organic agent and the formation of soluble metal-chloro-complexes.

2.4.2. Surface adsorbed metals.

The surface adsorbed metals are co-precipitated with amorphous hydrous oxide, carbonates and some sulphides.

Amorphous inorganic phases can be leached by reducing the iron and manganese to lower valency states. Combined acid-reducing (e.g. acidified hydroxylamine hydrochloride) solution will selectively dissolve ferro-manganese nodules (and associated iron oxides) and major carbonates phase of sediments while leaving other mineral components intact.

2.4.3. Organically bound metals including some sulphides.

The metal fraction associated with organic matter is extracted through oxidation of this component . Hydrogen peroxide in an acidic medium is generally used to oxidize organic matter in soil and sediment analysis (Gupta and Chen, 1975).

2.4.4. Residual fraction.

The residual fraction metals present in detrital silicates and crystalline iron oxide. They can be dissolved using strong acid such as nitric or perchloric

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acids, or a mixture of hydrofluoric acid and some other strong acid.

Data from Jenne and Luoma (1977) indicated that under mildly acidic conditions, hydrogen peroxide effectively solubilizes manganese oxides and their occluded elements. In this case, it is essential to perform the peroxide extraction after acidified hydroxylamine hydrochloride extractions, to avoid overestimation of metals organically-bound fraction . Accordingly, as shown in Bloom's study (1975), leaching in boiling concentrated nitric acid gave similar result with other digestion methods, therefore the residual fraction will be extracted with concentrated nitric acid as used by Forstner et. al (1981).

Based on the above discussion, in this study, the exchangeable cations were quantified by extracting the sediment with 1 mol/L ammonium acetate pH 7 solution. The surface adsorbed metals were attacked using acidified hydroxylamine hydrochloride at pH 2. Hydrogen peroxide was used to quantify the organically bound metals which include some sulphides. Finally, the residual fraction metals were extracted using concentrated nitric acid . The surface-adsorbed, organically bound, and residual fraction metals were extracted sequentially. Furthermore, since extraction with acidified hydroxylamine hydrochloride at pH 2 will include the extraction of exchangeable cations (Salomons, 1984); the sum of the three sequential extractions will provide the total concentration of the sediment.

In addition, extraction with 0.05 mol/L EDTA was also chosen in order to examine the bioavailable metals fraction as originally employed to extract the non-residual fraction of metals (Agemian and Chau, 1978).

The mobility of the sediment was examined by means of the Standard Elutriate test, using seawater extractant (Engler et al., 1974).

EXPERIMENTAL TECHNIQUES

3.1. Sampling.

The sediment samples used in this study were :

i.   Core sediments which were collected from the north side of Wrest Point Hotel (Derwent Sailing Squadron) on Tuesday 9/4/91. The sediment samples were collected using a gravity corer. The core sediment samples (average length about 12 cm), were sectioned into three equal parts; top, middle, and bottom and kept in a freezer at - 4°C until frozen. The respective sections then were kept under nitrogen to prevent oxidation and after thawing they were combined according to each part : top, middle and bottom. The appearance of the sediments was chocolate brown and they contained a lot of coarse material particularly in the bottom part.

ii. Core sediments which were collected from the same site as (i), on Monday 20/5/91. Temperature, pH and Eh measurements were done in site on surface water, at half depth, and in water sediment interface; while Eh of the sediments approximating to top, middle, and bottom parts were measured in the boat. The measurement were taken using the Eh/pH meter called a Reduction-oxidation meter. The pH of the three sections of the sediment were measured in the laboratory at room temperature on a slurry made from 0.5 g of the sediment with 5 ml of deionized water. The pH meter used was calibrated using buffer solutions pH 4.0 and 6.88.

The samples were kept under nitrogen to prevent oxidation. The appearance of the samples was chocolate brown and they contained a lot of coarse material.

iii. Surface sediment which was collected from The Derwent Sailing Squadron site on Monday 4/11/91, (sampled by Department of Environment and Planning personnel). The samples were kept under nitrogen to prevent oxidation. The pH of the sediment was measured using a calibrated pH meter at room temperature. The appearance of the sediment was chocolate brown-grey, fine but still containing coarse material.

iv. Surface sediment which was collected from the Prince of Wales Bay site on Monday 4/11/91; which also sampled by the Department of Environment and Planning personnel. The samples were kept under nitrogen to prevent oxidation. The pH of the sediments measured using a calibrated pH meter at room temperature. The appearance of the sediment was chololate brown-grey, smelly ,possibly due to a lot of sulphur content, composed of fine mud with high homogeneity.

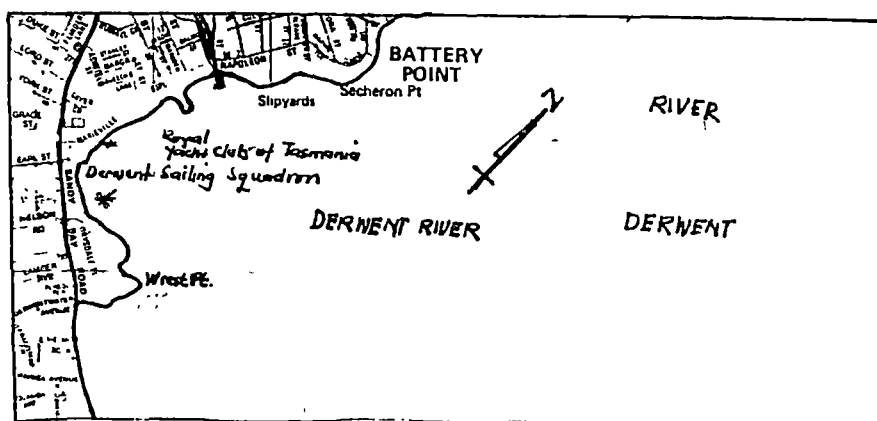The sites sampling were represented in following Figure 3.1.1 and 3.1.2.:

Figure 3.1.1. Sampling location, the Derwent Sailing Squadron site.
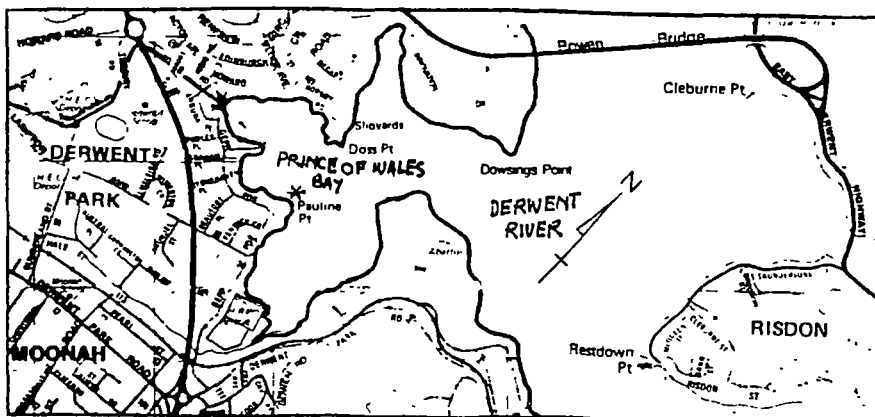
Figure 3.1.2.   Sampling location, Prince of Wales Bay.

The moisture content of the all sediments was determined by heating 15 g of the sediment in an evaporating dish in an oven at 100° C overnight.

3.2. Analysis Procedures.

The sediments were analysed for copper, cadmium, lead, zinc and mercury. The extraction procedures described in Batley (1987) was used prior to analysis for copper, cadmium, lead and zinc. The total amount of mercury in the sample was determined separately by the cold digestion procedures described in Bloom (1975).

3.2.1.   Reagents.

Reagents used in this study were prepared from analytical grade reagents in deionized water.

- Hydrochloric acid 31.5 % w/w.

- Nitric acid 70.5 % .

- Hydrogen peroxide 30 % w/v.

- Acetic acid glacial 99.8% .

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- Ammonium acetate 96 %.

- Hydroxylamine hydrochloride 98 %.

- EDTA 99.5 - 100 %.

3.2.2. pH measurement.

The pH of solutions used were measured using a calibrated pH meter (LC80 pH - mv meter) at room temperature. The pH meter was calibrated using phthalate buffer pH 4.0 and phosphate buffer pH 6.88.

3.2.3. Analytical Standards.

1000 μg/ml standard atomic absorption solutions were prepared as follows Varian Techtron,1986) :

- 1000 μg/mL zinc standard solution

1 g of granulated zinc in 40 mL 1:1 hydrochloric acid diluted to 1000 mL.

- 1000 μg/mL lead standard solution

1 g of lead foil in 1:1 nitric acid diluted to 1000 mL.

-1000 μg/mL copper standard solution

1 g of copper clipping in 1:1 nitric acid diluted to 1000 mL.

-1000 μg/mL cadmium standard solution

1 g of cadmium foil in 1:1 nitric acid diluted to 1000 mL.

-1000 µg/mL mercury standard solution

1 g of mercury metal   in 10% nitric acid diluted to 1000 mL.

The procedures for the extraction   of copper, cadmium , lead and zinc prior to analysis were as follows :

i.   Hydroxylamine hydrochloride Extraction.

The slurry equivalent of 0.4 g dry sediment was extracted with   40 mL of 0.1 mol/L hydroxylamine hydrochloride /0.01 mol/L nitric acid pH 2 . Nitrogen gas was passed through solution and the bottle capped. It was stirred overnight, and filtered through a 0.45 µm membrane filter. The filtrate was acidified with 1 mL concentrated nitric acid.

ii.   Hydrogen peroxide extraction.

The residue from the hydroxilamine extraction was furthermore extracted with 40 mL of 30% peroxide plus nitric acid at pH 2 ,heated to 85°C for 1 hour. The solution was passed through to a 0.45 µm membrane filter, and   acidified with 1 mL concentrated nitric acid.

iii.   Acid Extraction.

The residue from peroxide   extraction was digested with 5 mL of concentrated nitric acid and evaporated to dryness. A second evaporation to reduce   the volume with another 5 mL concentrated nitric acid was carried out

and the solution was filtered using Whatman no. 42 paper filter and diluted to 10 mL.

iv. **Ammonium acetate extraction.**

An equivalent of approximately 2.0 g of dry sediment was extracted with 40 mL of 1 mol/L solution ammonium acetate pH 7 . Nitrogen gas was passed through the solution and the bottle capped. It was agitated in a wrist-action shaker for 2 hours, and the solution was passed through a 0.45 μm membrane filter and acidified with 1 mL concentrated nitric acid.

-v. **Elutriate Test.**

To the slurry equivalent of approximately 2 g of dry sediment , 40 mL of seawater was added , the mixture was agitated for 1 hour, allowed to settle for 30 minutes, and filtered through a 0.45 μm membrane filter and acidified with
1 mL concentrated nitric acid.
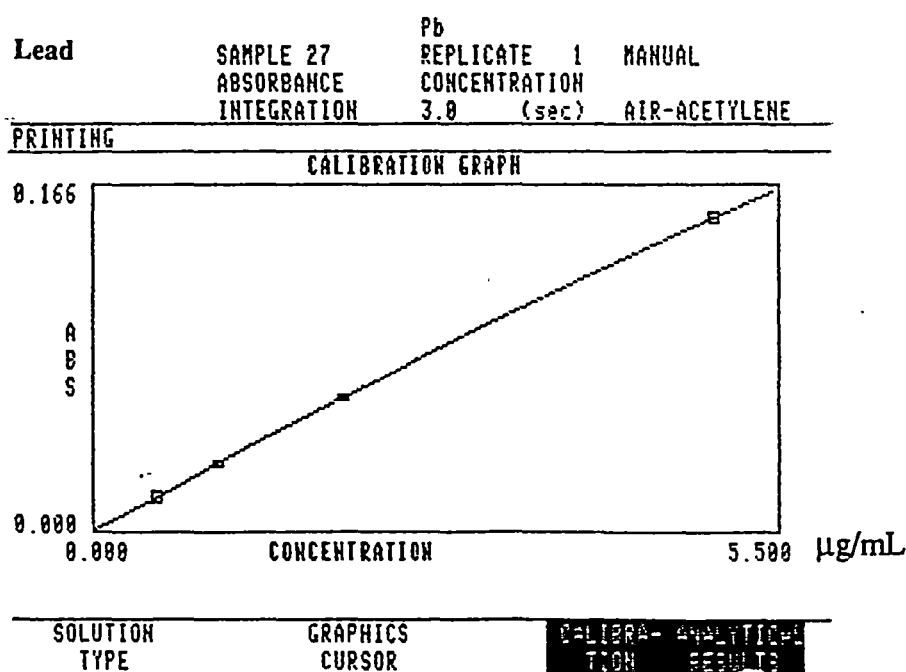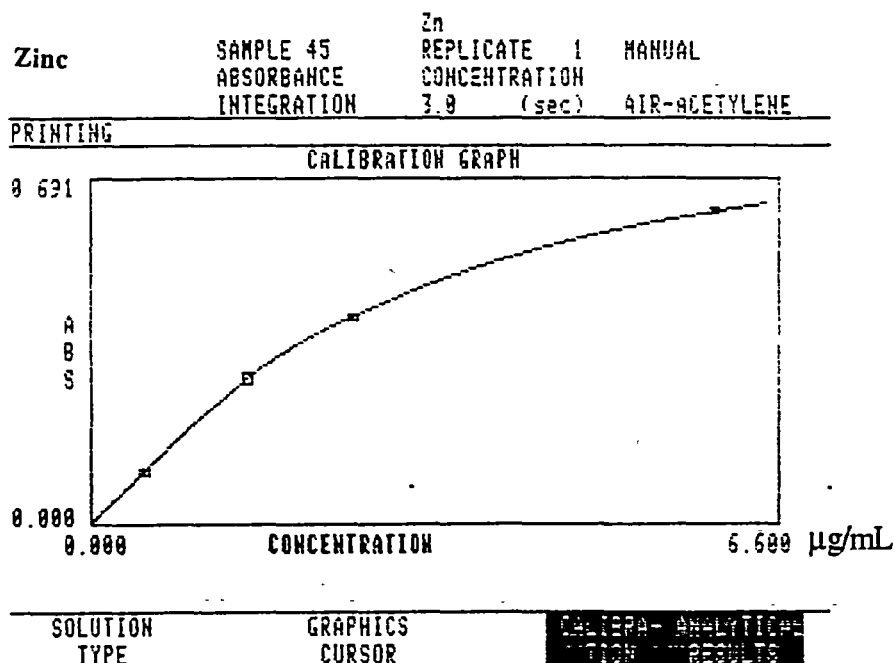

vi. **EDTA Extraction.**

An equivalent of approximately 0.4 g of dry sediment was extracted with 40 mL of 0.05 mol/L EDTA and shaken overnight. The solution was filtered through 0.45 μm membrane filter.
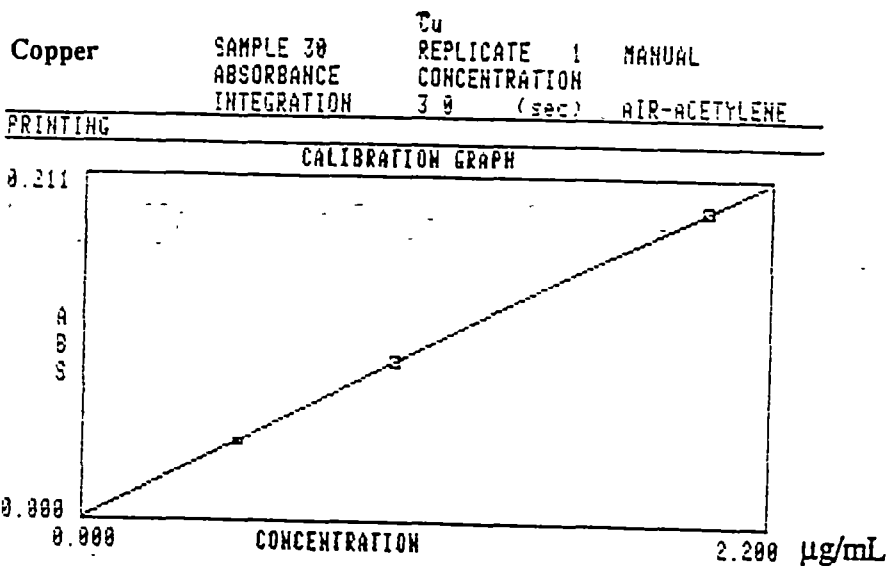

All extracts were analysed for copper, cadmium, lead, and zinc by

atomic absorption spectrometry (Spectrometer AA 10- Varian Techron) using air- acetylene flame. To avoid matrix problems created by pH, salt composition, and concentration, a standard solution for each procedure was prepared in the respective extraction solution; and the blank used was the extractant solution. The technique used in analysis was a calibration curve. Calibration curves were prepared for the respective cations in the ranges 0.05 - 0.50 µg/mL for cadmium; 0.10 -2.0 µg/mL for copper; 0.50 - 5.0 µg/mL for lead and 0.50 - 6.0 µg/mL for zinc. The example of characteristic calibration curves of the metals are shown in Figure 3.2.1. These curves were automatically prepared by the instrument and the concentration of unknown calculated. The instrumental conditions for the analysis was showed in Table 3.1.

The method for zinc, lead, copper and cadmium was checked by analysing a standard reference material "NBS No.1645, Reference Sediment" for total metal concentration. Approximately 0.5 g of reference sediment was digested with 5 ml concentrated nitric acid for 30 minutes filtered through a No.42 Whatman filter paper which was previously acid washed with 4 mol/L nitric acid and made up to a volume of 50 mL.

Figure 3.2.1. Characteristic of calibration curves of the metals observed.

Copper

SAMPLE 30   Cu
ABSORBANCE   REPLICATE 1   MANUAL
INTEGRATION   CONCENTRATION
3 0   (sec)   AIR-ACETYLENE

PRINTING

CALIBRATION GRAPH

0.211

A
B
S

0.000

0.000   CONCENTRATION   2.200 µg/mL

SOLUTION TYPE	GRAPHICS CURSOR	

Cadmium

SAMPLE 1   Cd
ABSORBANCE   REPLICATE 1   MANUAL
INTEGRATION   CONCENTRATION
3.0   (sec)   AIR-ACETYLENE

PRINTING

CALIBRATION GRAPH

0.122

A
B
S

0.000

0.000   CONCENTRATION   0.550 µg/mL

SOLUTION TYPE	GRAPHICS CURSOR	CALIBRA-TION	ANALYTICAL RESULTS

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Table 3.1. Instrumental analysis condition of determination zinc, lead, copper and cadmium in Spectrometer AA - 10 Varian

	Zinc	Lead	Copper	Cadmium
Wavelength, nm	213.9	217.0	324.8	228.8
Slitwidth,nm	1.0	1.0	0.5	0.5
Flame	Air-acetylene	Air-acetylene	Air-acetylene	Air-acetylene
Acetylene flow	1.5	1.5	1.5	1.5

Because mercury is volatile, it was analysed by a cold-digestion procedure (Bloom, 1975). The sediment sample was oven dried at 100°C overnight and ground and mixed thoroughly to render the sample homogeneous. A flask with 2 g of dry sample was cooled in an ice-bath and 10 ml of a 3:2 concentrated nitric and sulphuric acids mixture was added. This was left to digest for 3 days at room temperature; and shaken every twelve hours for about 5 minutes. It was then cooled in an ice-bath while 40 ml of saturated potassium permanganate solution was added dropwise from a burette, and left for a further 48 hours in room temperature to digest completely. Then 15 ml of hydroxylamine hydrochloride solution was added to decolorize the permanganate. This was allowed to stand at room temperature until the digest was completely free from coloration (about 5 hours). The extract then reduced with stannous- chloride. The absorption of the generated Hg vapour in the extract was measured by cold-vapour atomic absorption spectrophotometry (Hg - 3, manufactured by Precision Devices, Hobart, Tas.). A calibration curve was constructed using standard mercury solution. The example of a calibration curve obtained is shown in Figure 3.2.2 This procedure was also checked by analysing reference sample (NBS no.1645) with the same treatment.

Figure 3.2.2. Calibration curve for the analysis of mercury in core sediment (ii)
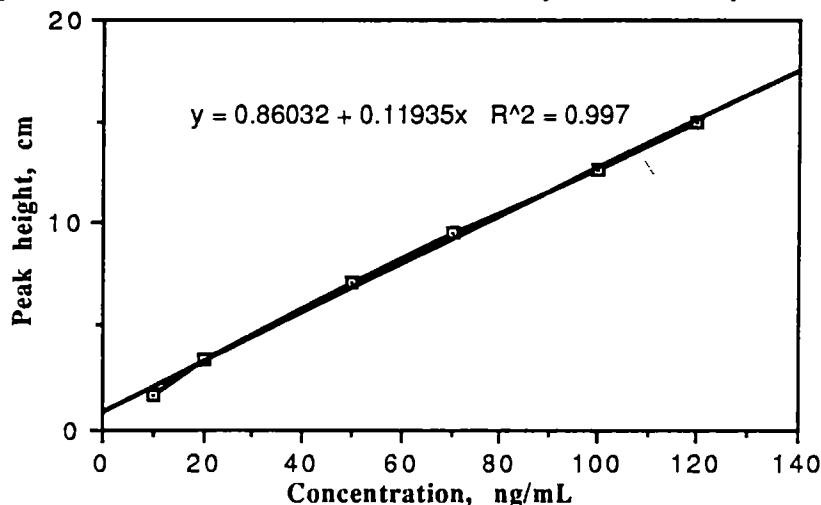
The total concentration of copper, cadmium, lead and zinc of reference sediment, surface sediment samples from Derwent Sailing Squadron and Prince of Wales Bay was also analyzed using differential pulsed anodic stripping voltammetry (DPASV). The instrument used was combination of a polarographic analyzer PAR Model 174 A and Static Mercury Drop Electrode Model 303 A, with a dropping mercury electrode as working electrode, Ag/AgCl reference electrode and platinum wire as a counter electrode. Two methods of digestion of samples which have been used are as follows :

A. About 0.5 g sample was digested with 5 mL concentrated nitric acid to dryness and diluted to 50 mL with distilled water.

B. About 0.5 g sample was digested with 5 mL concentrated nitric acid to dryness and diluted and adjusted to pH ~ 4.6 using 4 mol/L sodium acetate.

Standard solutions used were made by diluting AAS stock standard solution with acetate buffer pH 4.6. The samples were analysed in DPASV using Acetate Buffer pH 4.6 as the supporting electrolyte, by the standard addition method. The peak height of certain volume of sample was measured, then followed by

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the measurement of the peak height of a series solutions which made of the sample (contains the same volume with the previous one) plus an incremental amount of the standard solution. The graph of peak height reading against the concentration of added standard were plotted. and the concentration of the sample was calculated from the graph. This is shown in Figure 3.2.3

The Model 174A Polarographic was set as follows:

Scan rate : 5 mV/s

Deposition time : 3 Mins.

Modulation amplitude : 50 mV

Low pass filter : 0.3 s

Clock switch : 0.5 s.

Initial potential (which represent the deposition potential) is characteristic for each metal, and current range (which represents sensitivity)were varied according to its concentration in the sample.

Figure 3.2.3. Calibration curve of total zinc determination of DSS sample by DPASV.

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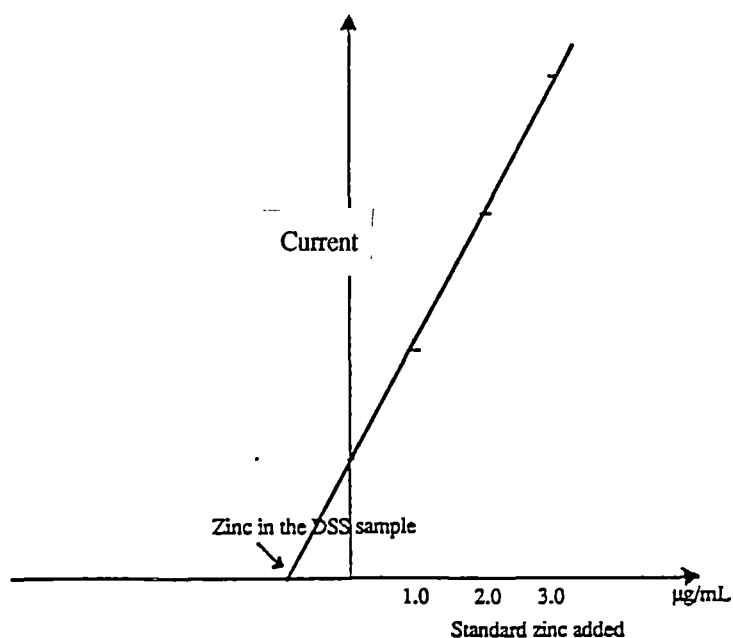
The concentrations were measured in a wet preparation of the samples and converted to dry matter basis (DMB) according to it's % moisture content.

Thermal Gravimetric Analysis was also carried out on the core sediment (ii) in order to determine the organic matter content. The sediments were ground and sieved to 180 μm and analysed in SETARAM TG-DTA92. About 28 mg sample was heated to 900°C at a sampling rate of 0.8 second for about 3000 seconds. From the loss in weight, the organic matter content was calculated. An example of the run performed is shown in Figure 3.2.4.

Figure 3.2.4. Example of a run performed using the middle part of core sediment (ii) by SETARAM TG-DTA92
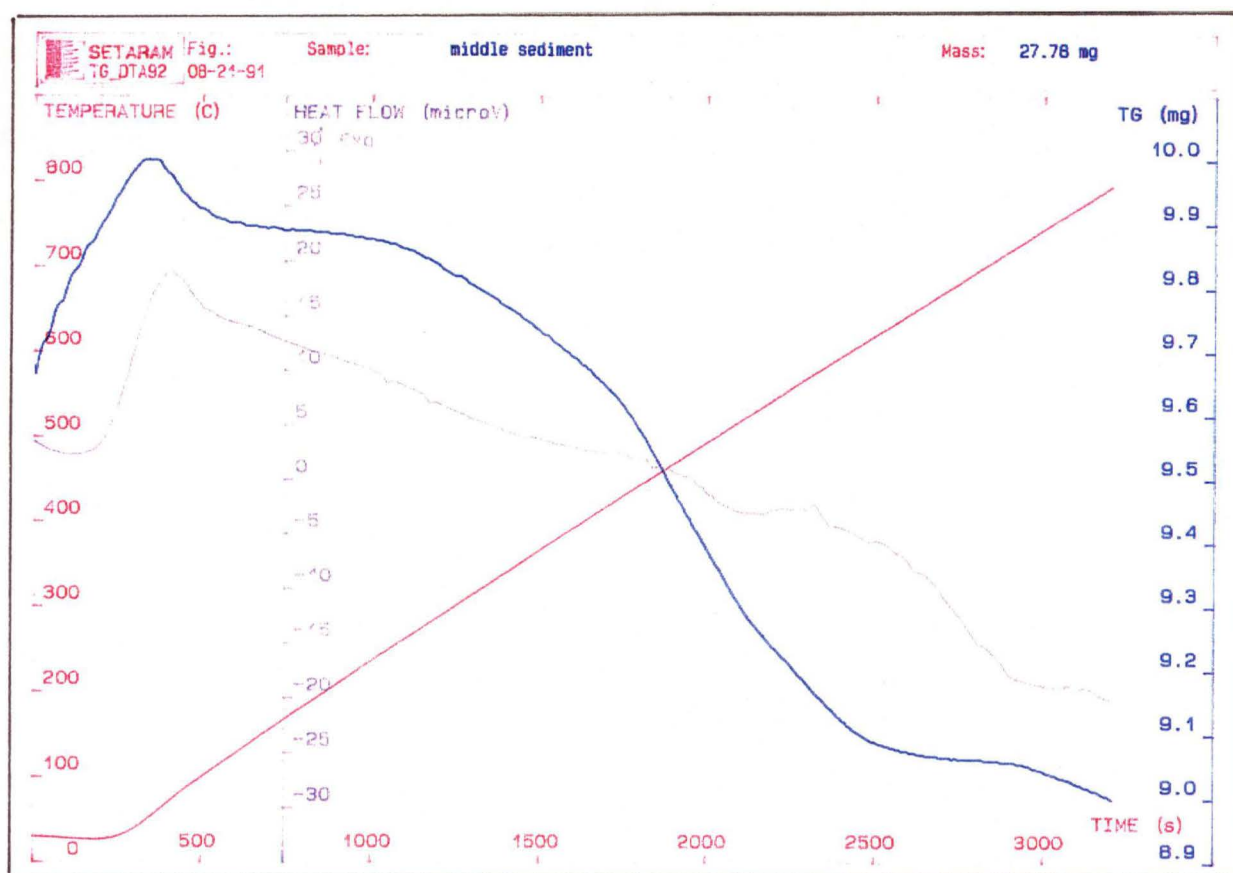
CHAPTER FOUR
RESULTS AND DISCUSSION

In the following discussion, core sediment (i) refers to core sediments which were collected on Tuesday 9/4/91, and core sediment (ii) was that collected on Monday 20/5/91.

Core sediment (i) was used in a preliminary experiment in order to establish the analysis method used in the study. The calibration of the atomic absorption was performed using standard solutions in 10 % nitric acid. No mercury analysis was performed for this sediment sample. Vertical distribution of the metals occurring in the sediment are summarized in Appendix A.

The results obtained for the concentrations of zinc, lead, copper and cadmium of the core sediment (i) are found to be lower than those of core sediment (ii) which used standard solutions made up in each extractant for its calibration. This is possibly the implication of the negative absorbance which was observed for acid extract of lead, peroxide extract for cadmium and hydroxylamine hydrochloride extract for copper. Regardless to the difference in sampling date, this figure indicates that the matrix effect significantly affects the result.

Hereafter, the core sediment (i) will not be taken into consideration. The results obtained were summarized in Table 4.1., 4.2., 4.3. and 4.4. for core sediment (ii), surface sediment from the Derwent Sailing Squadron site, surface sediment from Prince of Wales Bay and reference sediment sample no.1645.

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Table 4.1. Analytical results for core sediment (ii)

	TOP	MIDDLE	BOTTOM
Moisture content, %	40.5	31.2	25.1
pH at room temperature	7.7	7.5	7.3
Eh, mV	-16	-17	-20

CONCENTRATION MEASURED BY AAS

	TOP, ug/g		MIDDLE,ug/g		BOTTOM,ug/g	
	Conc.	S.D	Conc.	S.D	Conc.	S.D
ZINC						
Hydr.HCl	75	2.9	15.7	1.2	20.8	0.7
Peroxide	275.6	5.5	52.7	2.6	21.7	1.8
Acid	378.4	7.2	135.7	3.7	70.4	0.4
EDTA	149.3	7.3	42.4	2.6	11.5	0.4
Amm.Acetate	13.7	0.6	5.7	0.3	3.3	0.2
Seawater	0.44	0.02	1.00	0.01	0.90	0.05
LEAD						
Hydr.HCl	6.7	0.2	4.2	0.4	5.6	0.4
Peroxide	135.7	3.2	27.4	0.9	24.0	0.5
Acid	193.2	3.9	31.6	0.6	24.2	0.6
EDTA	108.9	1.9	24.5	1.0	8.1	0.3
Amm.Acetate	2.9	0.05	1.95	0.09	2.07	0.08
Seawater	0	-	0	-	0	-
COPPER						
Hydr.HCl	2.7	0.1	2.8	0.1	2.90	0.06
Peroxide	49.2	1.0	20.7	0.8	11.9	0.2
Acid	74.7	1.3	60.0	3.9	35.4	0.4
EDTA	1.20	0	1.21	0.06	0.72	0.06
Amm.Acetate	0.06	0	0.09	0.01	0.09	0.01
Seawater	0.70	0	0.66	0.05	1.21	0.03
CADMIUM						
Hydr.HCl	1.20	0	1.31	0.06	2.67	0.20
Peroxide	2.24	0.15	1.4	0.1	1.29	0
Acid	1.8	0.2	1.6	0.1	1.61	0.06
EDTA	0.83	0.06	0.29	0	0	-
Amm.Acetate	0.28	0.01	0.21	0.03	0.26	0.02
Seawater	0	-	0	-	0	-
TOTAL MERCURY	2.80	0.16	0.40	0.01	0.30	0.11

Note : Conc. is mean concentration and S.D is standard deviation of triplicate analysis.

Table 4.2. Analytical results for surface sediment from the Derwent Sailing Squadron site.

MOISTURE CONTENT : 48.6 %
pH AT ROOM TEMPERATURE : 7.2
CONCENTRATION MEASURED BY AAS

	Zinc ug/g		Lead ug/g		Copper ug/g		Cadmium ug/g		Mercury ug/g
	Conc.	S.D	Conc.	S.D	Conc.	S.D	Conc.	S.D	
TOTAL	653.9	0.4	224.5	4.6	26.3	0.8	3.7	0.1	2.1
SPECIATION									
Hydr. HCL extract.	58.2	0.99	16.7	0.7	0	-	2.4	0.2	
Peroxide extract.	438.3	0.65	151.5	0.3	16.8	0.9	0.70	0.05	
Acid extract.	182.9	0.14	84.0	0.5	7.90	0.01	1.30	0.05	
EDTA extract	338.6	0.12	170.3	1.2	7.00	0.05	3.70	0.25	
Amm. Acetate extract.	10.9	0.01	3.70	0.05	0.70	0.01	0.40	0.05	
Seawater extract.	8.2	0.01	1.80	0.05	0.60	0.05	0.04	0.00	

Note : Conc. is mean concentrations and SD is standard deviation of triplicate analysis

CONCENTRATION MEASURED BY DPASV

	TOTAL EXTRACTION,ug/g	PEROXIDE EXT.,ug/g
Zinc	643.5	493.9
Lead	222.3	141.9
Copper	28.1	13.9
Cadmium	4.0	0.9

Table 4.3. Analytical results for the surface sediment from Prince of Wales Bay

MOISTURE CONTENT : 80.5 %
pH AT ROOM TEMPERATURE : 7.1

CONCENTRATION MEASURED BY AAS

	Zinc ug/g		Lead ug/g		Copper ug/g		Cadmium ug/g		Mercury ug/g
	Conc.	S.D	Conc.	S.D	Conc.	S.D	Conc.	S.D	
TOTAL	8099.9	81	2195.1	7.5	643.1	2.0	71.7	0.5	28.2
SPECIATION									
Hydr. HCL extract.	469.2	0.6	15.8	0.08	5.1	0.05	1.6	0.17	
Peroxide extract.	5623.30	0.05	961.1	15.1	584.1	2.0	71.4	0.69	
Acid extract.	1442.1	10.9	1176.7	7.4	53.7	2.4	13.4	0.05	
EDTA extract	1840.0	129	1291.1	13.6	6.1	0.05	22.9	0.05	
Amm. Acetate extract.	11.41	0.05	3.4	0.05	2.2	0.05	0.4	0.05	
Seawater extract.	0.9	0.05	0.6	0.08	0.3	0.05	0.007	0.0009	

Note : Conc. is mean concentrations and SD is standard deviation of triplicate analysis

CONCENTRATION MEASURED BY DPASV

	TOTAL EXTRACTION,ug/g	PEROXIDE EXT.,ug/g
Zinc	8906.9	5678.7
Lead	2294.2	884.4
Copper	647.8	554.6
Cadmium	81.8	69.4

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Table 4.4. Analytical results for Reference sediment no.1645

CONCENTRATION MEASURED BY AAS

	Zinc ug/g		Lead ug/g		Copper ug/g		Cadmium ug/g		Mercury ug/g
	Conc.	S.D	Conc.	S.D	Conc.	S.D	Conc.	S.D	
TOTAL	1873.6	2.0	741.7	5.8	113.8	0.4	9.4	0.2	1.3
SPECIATION									
Hydr. HCL extract.	392.2	0.3	22.8	0.4	0	0	2.0	0.2	
Peroxide extract.	1263.6	9.7	392.8	1.7	81.7	3.2	6.2	0.2	
Acid extract.	204.8	0.2	267.0	0.2	18.8	0.1	2.10	0.05	
EDTA extract	398.2	0.4	236.8	0.3	4.90.	0.08	2.70	0.08	

Note : Conc. is mean concentrations and SD is standard deviation of triplicate analysis.

CONCENTRATION MEASURED BY DPASV

.	Total Extract ,ug.g	Peroxide Extract ,ug.g
Zinc	1840	1253.2
Lead	720	407.3
Copper	112	90.5
Cadmium	10.7	7.0

Recommended Concentration of Reference Sediment No.1645

Zinc, ug/g	Lead, ug/g	Copper,ug/g	Cadmium,ug/g	Mercury,ug/g
1720 +/- 169	714 +/- 28	109 +/- 19	10.2 +/- 1.5	1.1 +/- 0.5

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4.1. Distribution of metals in the sediment samples.

The distribution of metals among geochemical fractions in the sediment depends upon many factors, including the type of sediment/source of material. From the environmental pollution view of point ,Wood (1974) classifies metals into non-critical, toxic but very rare and very toxic and relatively accessible. From which zinc, lead, copper, cadmium and mercury are classified as very toxic and relatively accessible. Furthermore, the metals are also known to be toxic to plants and especially to animals. According to Chaney (1983) the toxicity occurs in the following dry matter basis in most animals : zinc ~ 1000 μg/g, lead ~ 30 μg/g, copper ~ 25-300 μg/g and cadmium ~0.5 μg/g.

The distribution of the metals in each sediment sample studied will be discussed as follows :
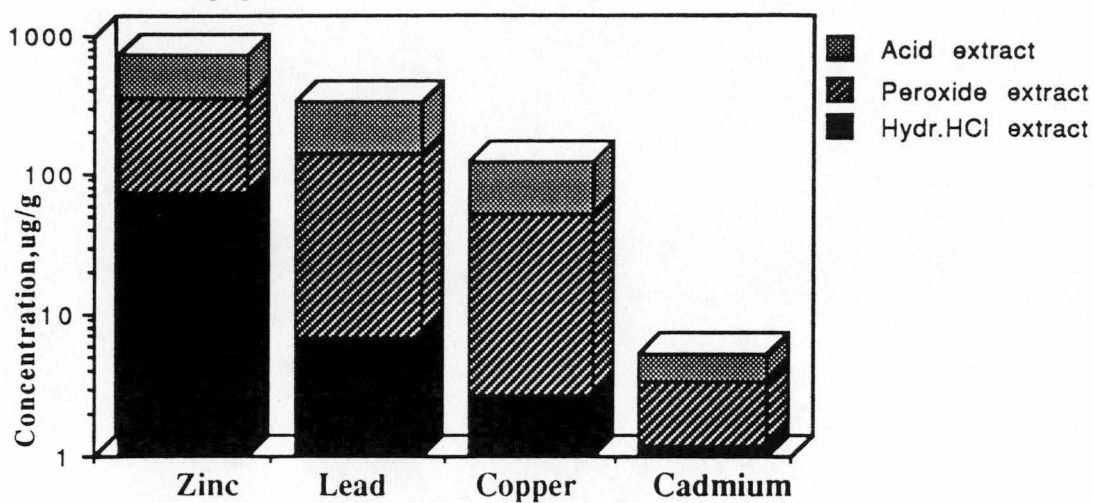
4.1.1. Core sediment (ii).

The total concentration of zinc, lead, copper and cadmium {Figure 4.1.1 a), b) and c) } showed a similar vertical distribution in core sediment (ii). A decrease of their total concentration with the sediment depth were observed. An abrupt decrease in total concentration of zinc, lead and copper with the sediment depth was observed between the top part and the middle part. In addition for zinc, copper and cadmium , a clear decrease in the residual form (acid extract) with depth was shown. These data suggested that the surplus of metal contaminants introduced into the aquatic system from man's activities exists in relatively unstable chemical forms.

Data obtained from thermal gravimetric analysis indicated that organic matter content of the sediment also decreased with depth. There was 21%, 6% and 4 % for the top, middle and bottom parts of the sediment. This data parallels the concentration of zinc, copper and cadmium in the peroxide extract (that is bound to organic and sulphides), which also showed a decrease with depth. Therefore, there was a correlation between the organic content of the sediment and zinc, copper and cadmium concentration in the organic and sulphides fraction. From which it was also indicated that the interaction between the organic matter and the metals was an important process for the removal and fixation of the metals.

In general, the majority (accounting more than 50% of total concentration) of zinc, lead and copper in the sediment appeared in the residual fraction. Therefore less than 50% of total concentration of the three metals were in bioavailable forms. With regard to Chaney data, this site might be expected to be free from toxic level of zinc contamination. Cadmium on the other hand was mainly found in the non-residual fraction ,and hence was more bioavailable, It was mainly present in surface adsorbed and bound to organic matter and sulphides.
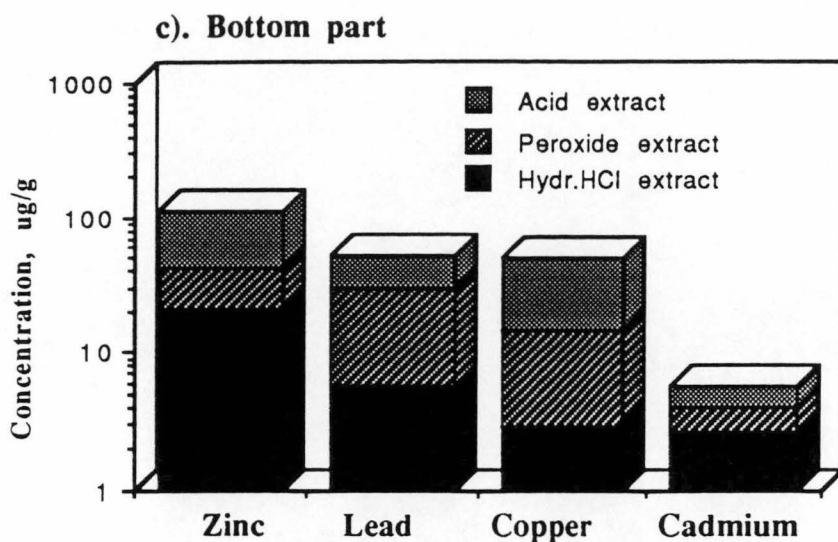
Figure 4.1.1.   Metals distribution in core sediment (ii)
a). Top part

b). Middle part

c). Bottom part
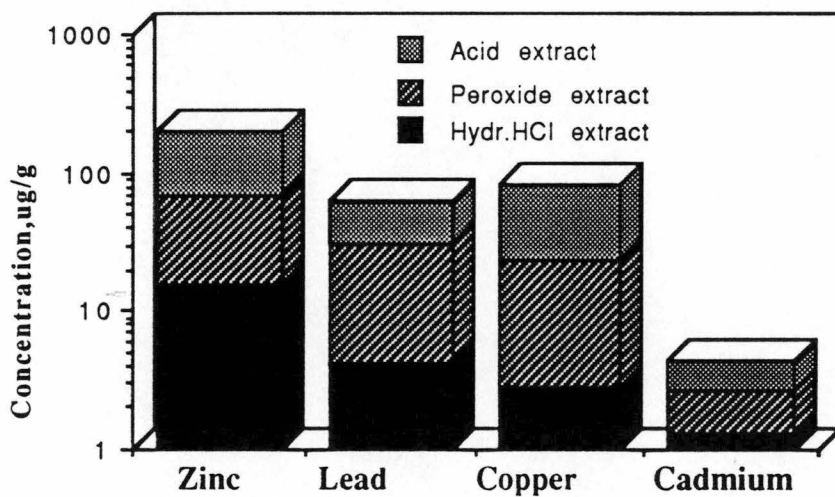
4.1.2. Surface sediment from the Derwent Sailing Squadron site.

The appearance of this type of sediment was finer compared to the core sediment (ii). Although it still contains some coarse material there is not as much as in the core sediment (ii). Distribution of the metals in the sediments showed a similar trend to the core sediment (ii), zinc was the highest, followed by lead, copper, cadmium and mercury. However, the distribution of the metals in the geochemical phases indicated a significant differences to core sediment (ii). Most of zinc, lead and copper were extracted by peroxide extraction, indicating that the majority of the metals were associated with " the organically bound and sulphides" fraction, which accounted about 65%, 60% and 68% for zinc, lead and copper respectively. In addition, about 27%,33% and 32% of zinc, lead and cadmium were present in residual form. These data suggested that different types of sediment showed a different speciation pattern and behaviour of the metals in it. With regard to the data of Chaney (1983), this sediment can

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be expected to be free from zinc and copper at toxic levels. However, lead and cadmium are potential toxic in the sediment contaminates in the environment because their concentration exceeds the values given by Chaney. From their speciation behaviour, it can be said that lead and cadmium were very mobile and provided a significant percentage concentrations of the surface adsorbed fraction. The high lead concentration might be attributed to the high auto traffic around and boating density.

Figure 4.1.2.Metals distribution of DSS sediment sample
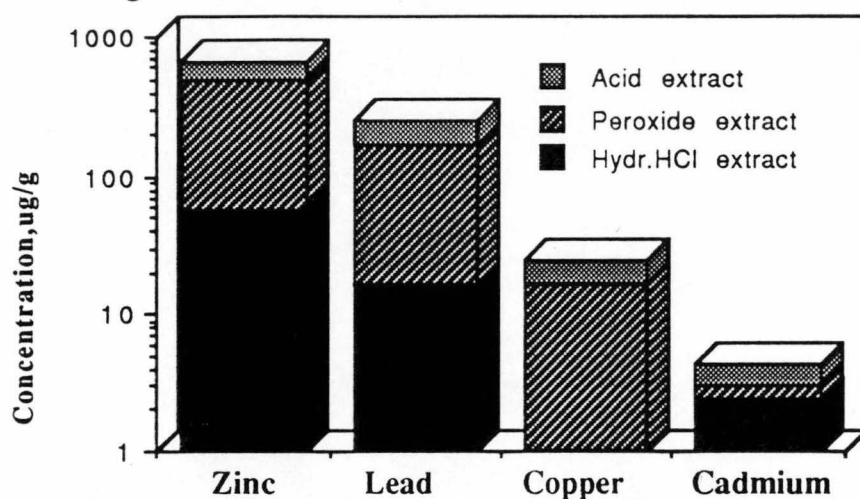
The analytical results of core sediment (ii) and surface sediment from the Derwent Sailing Squadron site were compared to the analytical results obtained by Bloom (1975) and Department of Environment (1981) and this is represented in Table 4.1.1. In general, the metals studied showed a decrease in concentration. However, copper in the top part core sediment (ii) showed an elevated level compared to the results of Department of Environment. It should be noted the different results between the core sediment (ii) and surface sediment from the Derwent Sailing Squadron site. It was noticed that the sediments were quite

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different in appearance which suggest that the sampling sites may have been

different. It may also reflect the time of the year that the samples were taken.

They were might be responsible for the results.

Table 4.1.1. Comparison to the literature data of DSS sediment sample

	Zn ug/g	Pb ug/g	Cu ug/g	Cd ug/g	Hg ug/g
BLOOM'S STUDY 1975	3180	999	214	18	21
DEPT. OF THE ENVIRON. 1981	1140	420	71	6.8	9.8
THIS STUDY 1991	* 729.1	335.5	126.6	5.2	2.8
	** 679.4	252.2	24.7	4.4	2.1

Note :   *Top part of Core sediment   (ii) from the Derwent Sailing Squadron site
         ** Surface sediment sample   from the Derwent Sailing Squadron site

4.1.3. Surface sediment from Prince of Wales Bay.

The appearance of this sediment was very fine and has a sulphur odour.

Compared to the surface sediment from the Derwent Sailing Squadron site, the

physical appearance of this sediment seems to indicate that it contains more

organic matter . The majority of the zinc, copper and cadmium appeared in "

the organically bound and some sulphide" fraction, which accounted for about

75%, 91% and 83% of zinc, copper and cadmium respectively. Accordingly,

only about 19%, 8% and 16 % of the zinc, copper and lead were present in

residual form. These data indicated that most of the metals were bioavailable.

In the case of copper in this sediment, this was consistent with the asumption

that copper is predominantly associated with organic colloidal matter. Lead

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behaved differently from the other metals with about 55% of the lead existing in the residual form. It showed the similar distribution between non-residual and residual fractions.

In general, the experimental data obtained showed that the metal levels exceed the values according to Chaney(1983) indicating that the sediment is very polluted.

The comparison with the results of previous studies presented in Table 4.1.2 showed a decrease in their concentration. This indicated a progress in the effluent and waste processing. However mercury showed slightly increase when compared to earlier studies .

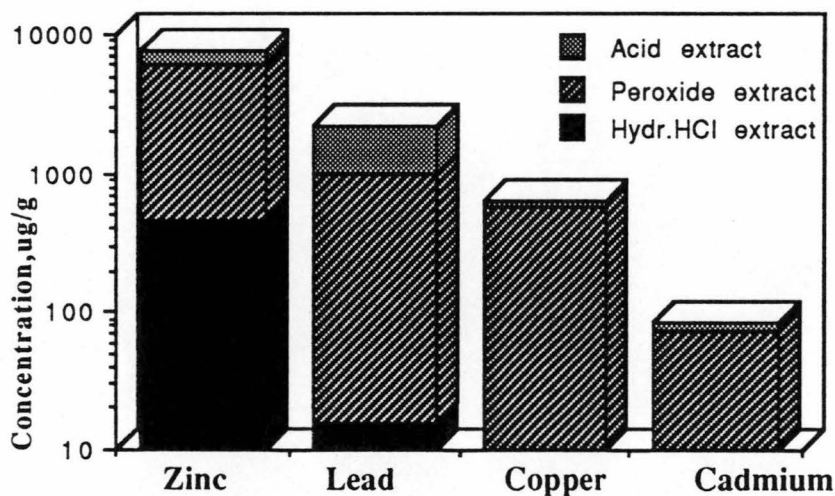**Figure 4.1.3. Metals distribution of PWB sediment sample.**

Table 4.1.2. Comparison to the literatures data of PWB sediment sample

	Zn ug/g	Pb ug/g	Cu ug/g	Cd ug/g	Hg ug/g
BLOOM'S STUDY 1975	* 15,100	4240	1220	171	21.5
	** 21,200	4880	1520	303	50.0
	***14,100	3500	1100	154	27
AQUAHEALTH DATA 1989	* 11,400	2310	550	88	28
	** 52,100	4530	1110	238	134
THIS STUDY 1991	8099.9	2195.1	643.1	71.7	28.2

Note : * Site no.38 in Bloom's study = north side in Aquahealth study.
** Site no.35 in Bloom's study = south side in Aquahealth
*** Site 37 in Bloom's study which was the nearest with the location in this study

d. Reference sediment No.1645.

The distribution of metals in the reference sediment no.1645 showed a similar trend to the other sediments. The distribution of the metals in speciation was similar to the surface sediments. With no exception, the majority of all metals studied were associated with "organically bound and some sulphides". This accounted about 68%, 58%, 82% and 60% of zinc, lead, copper and cadmium respectively. The percentage of zinc present in the surface adsorbed fraction was higher than in residual fraction. Cadmium appeared in similar percentages for the two fractions. However, as with the surface sediment from the Derwent Sailing Squadron: no copper was observed in the surface adsorbed fraction.

Figure 4.1.4. Metals distribution of Reference sediment sample
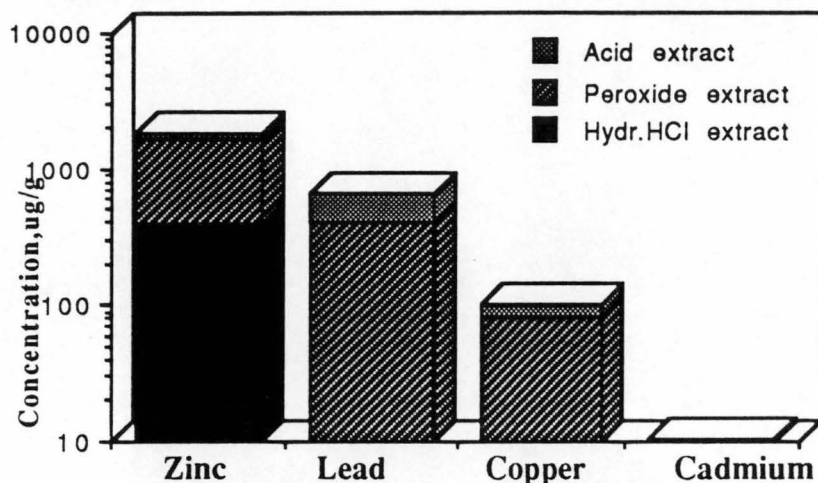
4.2. Speciation of the metals.

Surface adsorbed metals which co-precipitate with amorphous hydrous oxides, carbonates and some sulphides were extracted with acidified hydroxylamine hydrochloride. The acidified hydroxylamine hydrochloride may be an advantage for the investigation of processes involved in diagenitic remobilization and enrichment of metals in iron/manganese concretions as it indicates the relative availability of the metals in the easily reducible fractions of micronodules and sediments (Callender and Bowser, 1980). Hydroxylamine hydrochloride extracted about 8.6%, 6.2%, 10.3% of total concentration of zinc of surface sediment samples from the Derwent Sailing Squadron site, Prince of Wales Bay and from the top part of core sediment (ii) ,respectively. About 6.6%. 0.7%, 1.9% of the total concentration of lead was leached from

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surface sediment sample from the Derwent Sailing Squadron site, Prince of Wales Bay and from the top part of core sediment (ii), respectively. Moreover, about 56%, 1.9% and 19.4% of total concentration of cadmium was extracted from the surface sediment sample from the Derwent Sailing Squadron site, Prince of Wales Bay and from top part of core sediment (ii), respectively. However, no copper was leached from the surface sediment sample of the Derwent Sailing Squadron site, about 0.9% copper was extracted from the surface sediment sample of Prince of Wales Bay, and 2.1% of the top part of core sediment (ii). In the case of core sediment (ii), the extractable lead, copper and cadmium showed an increase with depth, except for zinc which displays variability. Overall the acidified hydroxylamine hydrochloride extracted more cadmium in all samples, which indicated that the majority of cadmium is bound in inorganic form. On the other hand, very little copper was leached in this extraction which showed that copper was strongly bound in an organic complex.

Peroxide extraction was expected to leach the organically bound metals including some sulphides. Heavy metals become associated with organic matter through biological uptake, and adsorption with the subsequent incorporation into resistant organic degradation products, such as humic substances. Metal sulphides can be either detrital or formed as a result of diagenitic processes in reducing layers of sediments. Organics are the major source of zinc, lead and copper of surface sediment from the Derwent Sailing Squadron site; the major source of zinc, copper and cadmium of the surface sediment from Prince of Wales Bay, and the major source of zinc, lead, copper and cadmium of the reference sediment sample no.1645 in this extraction. This was indicated by the high concentrations in which they appear in this fraction.

The residual fraction of the metals present in detrital silicates and crystalline iron-oxide in the sediment samples were extracted with concentrated nitric acid. Concentrated nitric acid extraction represent a major proportion (more than 50% of the total concentration) of the copper, lead and zinc of core sediment (ii). It shows that the highest proportion of the metals in the sediment were in the crystalline fraction (residual fraction). The vertical distribution of the metals was observed to show different behaviour. Zinc and copper show an increase in their residual fractions with depth. On the other hand, the residual fraction of lead decreased with depth. In the case of cadmium, its residual fraction was less than 50% of total concentration. However, its vertical distribution shows an increase in the residual fraction with depth. Metals associated with this fraction of other sediments studied were varied, particularly copper which was 19%, 8%, and 32% of total of reference , surface sediments from the Derwent Sailing Squadron site and Prince of Wales Bay respectively. About 55% of the lead of surface sediment from Prince of Wales Bay was associated with the residual fraction.

Ammonium acetate extraction was performed in order to leach metals loosely bound to the outside particles (exchangeable metals) in sediment. With the exception of cadmium, the amount of heavy metals studied in exchangeable fraction are generally found to represent a minor fraction of the total metal concentration. The relatively high concentration of exchangeable cadmium (between 0.5% - 9% of total) suggested that cadmium exist in the reduced form.

Chemical extraction with EDTA has previously been used (Goldberg and Arrhenius, 1958; Agemian and Chau, 1978) to determine the distribution of metals in detrital igneous minerals and authigenic phases (mainly the oxide

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minerals and microcrystalline apatite) in pelagic sediment . Agemian and Chau (1978) observed that 0.5 mol/L hydrochloric acid and 0.05 mol/L EDTA are suitable for simultaneous extraction of ten elements from the adsorbed ,organic and precipitated phases of aquatic sediments. However, in some sediments the adsorbed metals are bound strongly in which case the 0.05 mol/L EDTA is incapable of extracting them. Of the sediment samples studied, in the reference sediment sample, about 22%, 35%, 5% and 26% of total zinc, lead, copper and cadmium were removed by EDTA extraction respectively. EDTA extracted about 50% zinc, 67.5% lead ,28 % copper and 86 % cadmium in the surface sediment from the Derwent Sailing Squadron site. Furthermore , from the Prince of Wales Bay sediment, about 24%, 60%, 1%, and 26% of total of zinc, lead, copper and cadmium, respectively were extracted. This closely paralled the behaviour the top part of core sediment sample (ii), (20.5%, 32.5%, 0.9% and 16 % of total of zinc, lead, copper and cadmium, respectively). In the vertical distribution of the core sediment (ii), the EDTA extractable copper increased with depth, while cadmium showed a decrease in concentration with depth. The other metals, zinc and lead showed variability in its concentration with depth in EDTA extraction. Overall, EDTA extraction removed consistently more lead, which is probably related to the greater stability of lead-EDTA complex. On the other hand, copper was leached with difficulty by the EDTA extraction which was might be because of strongly bounded of copper.

The Standard Elutriate test (Engler et. al, 1974) is designed to detect any significant release of chemical contaminants in dredged material. Insignificant amounts of the metals studied were released by the test (less than 1% of total concentration), except for copper and zinc in surface sediment sample of the Derwent Sailing Squadron site, which released ~ 2.4% and ~ 1.2 % of total concentration, respectively. Cadmium analysis of the seawater extract of surface

sediment samples by atomic absorption spectrometry gave negative results. However, when the extract was analysed in a graphite furnace it was observed in ppb level, and the concentration cadmium in the blank seawater was higher than in the samples. It was also found as expected the cadmium concentration in surface sediment sample from the Derwent Sailing Squadron site was higher than that from Prince of Wales Bay. The likely explanation is because the surface sediment sample from Prince of Wales Bay contains higher organic matter than that from the Derwent Sailing Squadron site, in which the higher organic matter might adsorb more cadmium by forming cadmium-organic matter complexes . According to Windom (1976) , in the elutriate test extraction procedure even if some metals did become more soluble under aerobic conditions, reoxidation would lead to their reprecipitation as soon as the sediments are dispersed.

4.3. The behaviour of each metal studied.

With regard to its percentage distribution, the behaviour of each metal of the sediments studied in the speciation extraction can also be pointed out. In the following figures, CS refer to the core sediment (ii) with T, M and B standing for top, middle and bottom part of the sediment. REF., PWB and DSS stands for reference sediment, surface sediment from Prince of Wales Bay and from the Derwent Sailing Squadron site.

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**Figure 4.3.1. Zinc behaviour in the sediments**
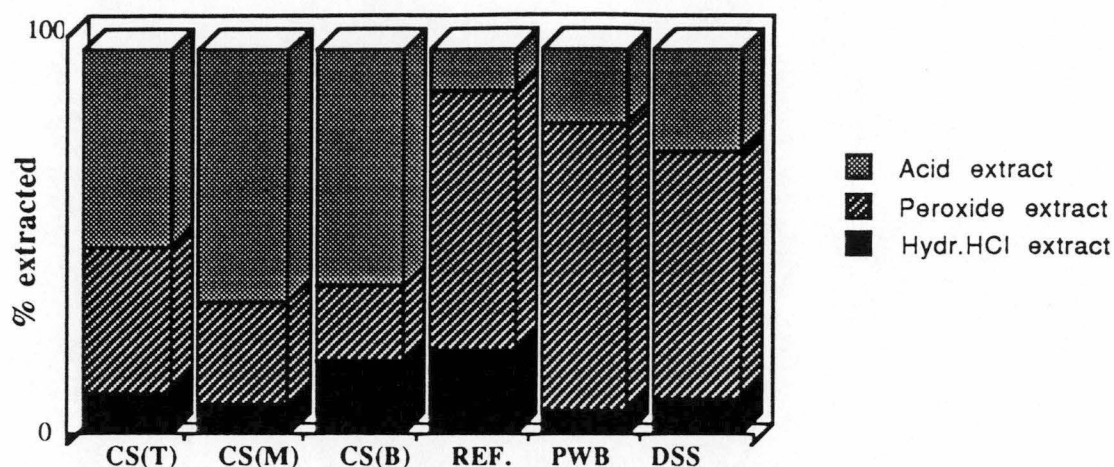
Zinc. This metal is mainly present in the " organic matter and sulphides" and "residual " fractions. In all sediments studied (with exception of the bottom part of core sediment (ii) and reference sample) the surface adsorbed fraction , that is metal co-precipitated with amorphous hydrous oxides, carbonates and some sulphides, accounts only for a small percentage of the total zinc concentration. In general, the majority of zinc exists in the " organic matter and sulphides" fraction of the reference sediment no 1645, and both the surface sediments from the Derwent Sailing Squadron site and Prince Of Wales Bay. However, in core sediment (ii) , the majority of zinc observed exists in residual fraction, while the second category was the organic matter and sulphides fraction, the percentage of which shows a decrease with depth. This shows a significant difference in behaviour of zinc between the core sediment (ii) and both the surface sediments.

Figure 4.3.2. **Lead behaviour in the sediments**
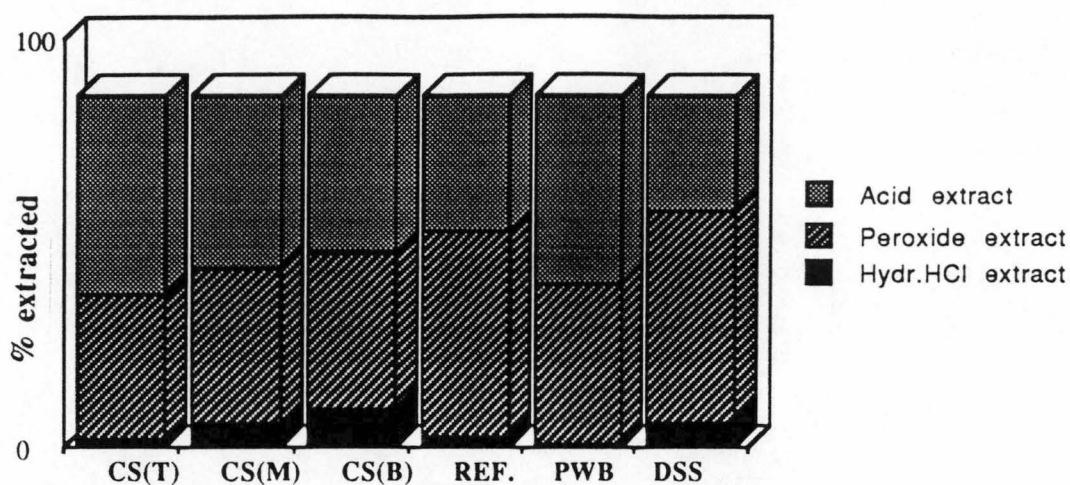
Lead. The majority of this metal appeared in the same fraction as zinc. Mostly "bound to organic matter and sulphides" and "residual" fractions. Almost the same percentage of distribution between "organic matter and sulphides" and "residual" fractions was observed for the core sediment (ii), particularly in the bottom part ; and also for surface sediment from Prince of Wales Bay. The majority of lead was associated with "organic matter and sulphides" in the reference and surface sediment from the Derwent Sailing Squadron site. Relatively high lead concentration (33-68%) was removed by EDTA extraction in this study.

Figure 4.3.3. Copper behaviour in the sediments

Figure 4.3.3. Copper behaviour in the sediments
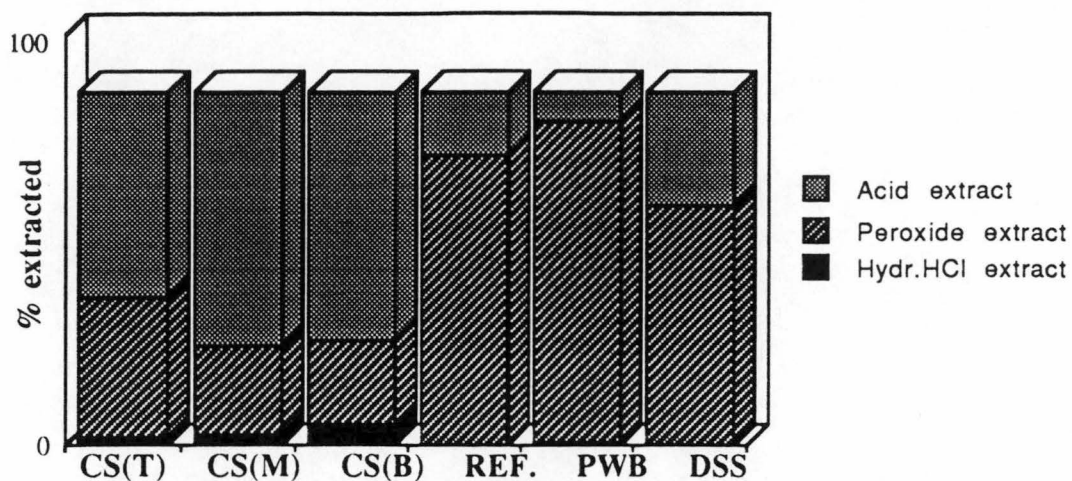
Copper. With the exception of core sediment (ii), copper showed a strong association with "bound to organic matter and sulphides" fraction. According to Salomons and Forstner (1980) and Smies (1983), this trend is typical for copper in sediments and waters. The similar behaviour of copper to zinc in the two types of sediments, core sediment (ii) and both the surface sediments was also observed. The association of copper with the adsorbed surface fraction of all sediments studied was very low. In the reference sediment and the surface sediment from the Derwent Sailing Squadron site, no copper associated with surface adsorbed fraction was observed. Unlike lead, a relatively small concentration of copper was extracted by EDTA, that is less than 5% of total concentration, except in the surface sediment from the Derwent Sailing Squadron site from which about 28% of copper was removed.

Figure 4.3.4. Cadmium behaviour in the sediments
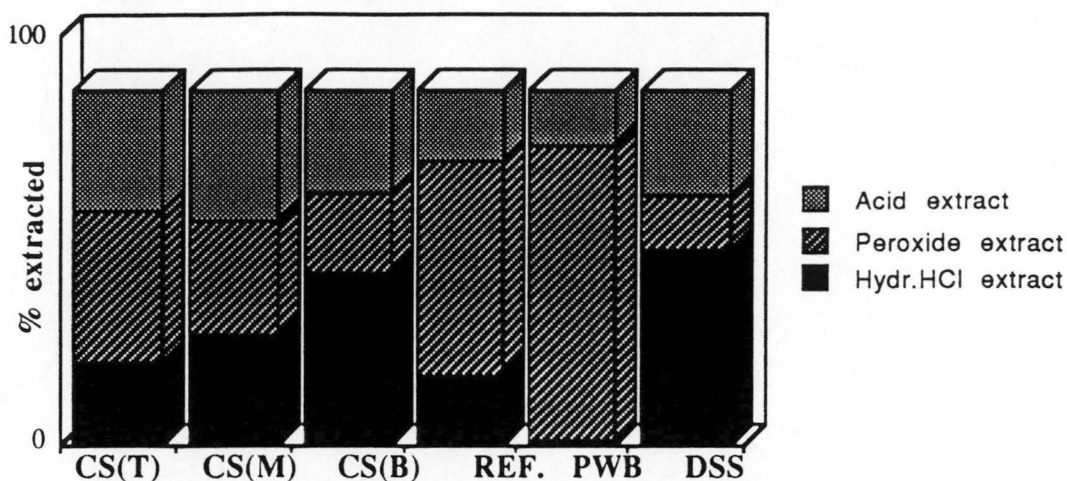
Cadmium. The behaviour of this metal varied among the sediments studied. In the core sediment (ii), its fraction in the surface adsorbed phase increases with depth, while the fraction in association with bound to organic matter and sulphides decreases with depth.   The majority of cadmium in the reference sediment no 1645 and surface sediment from Prince of Wales Bay was associated with " bound to   organic matter and sulphides" fraction. Unlike the other sediments   studied, most cadmium in the surface sediment from the Derwent Sailing   Squadron site is present in the surface adsorbed fraction.

Overall the four metals studied by means of speciation have different polluting potentials : zinc, copper and to a lesser extend lead in the core sediment (ii) were present in the residual fraction. This indicates that a large fraction of the metals exists in a form which is unavailable to organisms. However, in the two surface sediment samples and in the reference sediment no.1645, zinc and copper and also to a lesser extend lead showed the opposite behaviour.   They were   mainly present in   the non-residual form, in which is available to

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organisms and can be remobilized by changing environmental condition. In general in all the sediment studied, cadmium showed a mobile behaviour,because it mainly appeared in the non-residual form. Cadmium also appeared in a higher percentage concentration in its exchangeable fraction than other metals in the same sediment. In the case of copper in the core sediment (ii), it can be seen that as the organic content decreased with depth, its concentration in the surface adsorbed fraction was increased. This showed that copper was strongly bound in its organic complexes.

Mercury. An analysis of total concentration of mercury shows that its concentration was significantly dependent on the homogeneity of the sample and the size of the sediment particle. Poorest reproducibility (standard deviation about 37%) was observed in the analysis of total mercury in the bottom part of core sediment (ii). It was believed that sediment heterogeneity and particle size are responsible for the result.

4.4. Analytical performance.

The analytical accuracy for each extraction step and for the overall procedure was tested by subjecting a reference sediment sample No.1645 to the selective extraction used in this study. The results obtained along with the certified or recommended values for total metal concentrations are represented in Table 4.4.. The results obtained for this reference sample are within the range of the certified values.

In addition, the analytical precision of each extraction and of overall procedures was examined by conducting three replicate analyses to the samples. The reproducibility of the results was generally good, and was less than 10% of mean concentration. Low reproducibility of the results were observed for cadmium in the ammonium acetate extract of the middle part of core sediment (ii), and the surface sediment samples from the Derwent Sailing Squadron site and Prince of Wales Bay. Leaching is probably responsible for this result, in which a low absorbances were observed. Low reproducibility was also observed in the mercury analysis result of the bottom part of core sediment (ii). In this case, the results was attributed to the heterogeneity of the bottom part of the sediment .

Total extraction of the reference sediment no 1645 and the surface sediment samples was also performed, by boiling about equivalent of 0.5 g of dry weight of sample in 5 ml concentrated nitric acid for 30 minutes. Results of the total extraction are compared to the sum of the sequential extraction. A discrepancy of about 0.6%, 4 % and 7% for zinc; 9%, 7% and 2% for lead and 7 %, 7% and 0.03% for copper was observed for the reference, the sediments from the Derwent Sailing Squadron site and Prince of Wales Bay respectively. The total concentration of cadmium observed was about 9%,16% and 21% lower than the sum of the sequential extraction for reference, the sediments from the Derwent Sailing Squadron site and Prince of Wales Bay respectively. It was suspected that boiling the sample in concentrated nitric acid for 30 minutes was not strong enough to extract all cadmium in the sample. In order to prove this assumption , a total extraction was also done by heating gently about equivalent of 0.5 g of dry weight of sample in 5 mL concentrated nitric acid to dryness. Results obtained in this extraction procedure were 10.4 µg/g, 4.8 µg/g and 88.5 µg/g for the reference sediment no 1645, the sediments from Derwent Sailing

Squadron and Prince of Wales Bay respectively. These results were about 0.9%, 9% and 2.4% higher than the sum of its sequential extraction.

The bottom part of core sediment (ii) and the reference sediment no.1645 were subjected to preliminary analysis in order to establish the total digestion method, analysis method and the instrument setting. An attempt to analyse the speciation extracts by means of differential pulsed anodic stripping voltammetry (DPASV) was also carried out on the reference sediment no 1645, both surface sediments from Derwent Sailing Squadron and Prince of Wales Bay. Peroxide was the only extract which was analyzed successfully with this technique. Zinc cannot be determined at a pH below 4.5, because at pH lower than 4.5 hydrogen ion reduction occur, which interferes with zinc determination (Piotrowicz et.al, 1983). Zinc and cadmium generally produced clear, well defined peaks. The results obtained were included in results data of each sediment in Table 4.2. - 4.4. Generally, the comparison of the results to the results obtained in AAS indicated good agreement that gave a discrepancy of less than 10% for zinc, lead and copper in both total and peroxide extracts . However, cadmium in both extract appeared higher than the AAS results, and was about 14% and 13 % in the total and peroxide extracts respectively for reference sediment no.1645. It was about 29% higher in the peroxide extract for surface sediment from the Derwent Sailing Squadron site, and about 14 % higher in total extracts of surface sediment from the Prince of Wales Bay. It was consistent with the result observed from AAS that, among the metals, cadmium showed a high percentage in its exchangeable and surface adsorbed forms and that these data supported assumption that cadmium is mostly present as a free ion in inorganic form.

CHAPTER FIVE
CONCLUSION

Information on total metal concentrations can only be used for monitoring, but cannot be used to assess the bioavailability and ecotoxicological of the metals to environment. Speciation of trace metals in sediments can give information both bioavailability and ecotoxicological impact on the environment.

Selective chemical extractions of the sediments studied indicated that zinc, lead,copper and cadmium in surface sediments from the Derwent Sailing Squadron site and Prince of Wales Bay were enriched in " some sulphide and organically bound" and surface adsorbed forms. A different behaviour was showed by the core sediment (ii) which was enriched in residual form.

Generally, in all cases higher percentages of copper were associated with "organically bound and sulphides" fraction, especially in surface sediment of Prince of Wales Bay. This showed copper strongly associated to organic matter. Allen et.al (1980) noted the strong affinity of humic acid to copper.

Comparison of the sum of the metal concentrations in the individual fractions with the total metal concentration shows good agreement for zinc, lead and copper. Note that the significantly lower total cadmium concentration than the sum of its concentrations in the individual fractions was found because of boiling the sample in concentrated nitric acid for 30 minutes was not strong enough to extract all the cadmium in the sample. It was shown that instead of

boiling the sample, heating gently to dryness gave results which provided a better agreement between its total concentration and the sum of its concentration in individual fractions.

Comparison of the results obtained in this study to literature data found in the same or the nearest location site showed the Table 4.1.1 and 4.1.2. Speciation results of the metals in the top part of core sediment (ii) and of surface sediment from the Derwent Sailing Squadron site were compared to the results data from Bloom's study (1975) and data from Department of Environment (1981). In general, all of the metals studied showed a decrease in concentration, except copper, in the top part of core sediment (ii) which indicated an increasein concentration. However it should be noted that the speciation results of the metals in surface sediment from Prince of Wales Bay were compared to the results of the nearest location site from Bloom's study (site 37). Overall, the results observed in this study indicated a decrease in the concentration, except mercury which showed a slight increase. It suggested that progress has been made in the effluent and waste processing, particularly from the electrolytic zinc company.

Short- term elutriate testing suggested that no significant releases of the trace metals would occur during the mixing of dredged sediments with seawater.

The results obtained from thermal gravimetric analysis which examine the organic content of the sediment was consistent with the concentrations of the metals extracted in peroxide extraction.

Since different types of sediment exhibited a different speciation behaviour, it is important to have a knowledge of the principal characteristics of

the samples studied.

Based on the above discussion, it is suggested that further studies to examine the selectivity of each extraction reagents toward specific geochemical phases. That is by applying for example X-ray diffraction to evaluate the degree of geochemical phases associated in a sediment sample. Furthermore, the results found of a selective extraction is compared to the X-ray diffraction result; from which the degree of selectivity of extraction reagents can be determined.

APPENDIX.

APPENDIX A. RESULTS DATA OF CORE SEDIMENT (i)

	Top	Middle	Bottom
Moisture content, %	33.73	32.42	31.06
pH at room temperature	8.3	8.4	8.5

CONCENTRATION MEASURED

	TOP, ug/g	MIDDLE,ug/g	BOTTOM,ug/g
ZINC			
Hydr.HCl	69.50	43.70	46.10
Peroxide	165.10	150.30	52.00
Acid	58.55	61.90	38.78
EDTA	185.10	137.90	68.60
Amm.Acetate	47.20	42.44	23.00
Seawater	2.18	2.66	1.14
LEAD			
Hydr.HCl	93.40	56.40	13.10
Peroxide	147.30	122.2	66.90
Acid	27.93	NEGATIVE	NEGATIVE
EDTA	112.50	80.80	58.30
Amm.Acetate	11.36	8.12	6.00
Seawater	1.14	2.06	0.98
COPPER			
Hydr.HCl	11.80	15.00	NEGATIVE
Peroxide	48.20	51.20	12.50
Acid	12.43	4.10	7.33
EDTA	34.50	27.90	12.50
Amm.Acetate	3.62	2.10	2.14
Seawater	1.80	0	0
CADMIUM			
Hydr.HCl	2.80	3.30	1.60
Peroxide	3.00	0	NEGATIVE
Acid	0.40	0.38	0.28
EDTA	1.04	0.54	0.83
Amm.Acetate	0.26	0.21	0.24
Seawater	0.10	0.10	0

Note : Only one analysis was done and mercury was not analysed.

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