THE DISTRIBUTION OF COPPER, LEAD AND ZINC IN THE RIBBON-MARSH SEDIMENTS OF THE NORTH ARM OF THE FRASER RIVER, VANCOUVER, B.C.

by

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The Distribution Of Copper, Lead And Zinc In The Ribbon-Marsh Sediments Of The North Arm Of The Fraser River, Vancouver, B.C.

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ABSTRACT

A study of the distribution of copper, zinc and lead in ribbon marsh sediments focussed on the North Arm of the Fraser River delta at Vancouver B.C., Canada. Nine cores were taken from the North Arm. Three others, for comparison purposes, were taken; one from a nearby delta-front tidal marsh and two from Upper Fraser Valley sloughs.

The study shows great variation in metal concentrations within and between cores, and a weak tendency towards increasing concentrations in the downstream direction. The full within-core variation proved so large that statistically significant differences in metal concentrations between cores could not, with a few exceptions, be demonstrated. Within the top 12 cm of each core, however, real differences in metal concentrations between cores were apparent.

The concentrations in the top 12 cm of core were normalized to rubidium (a proxy for grain size) and then compared to similarly normalized baseline values of sediments *ca.* 6800 yr BP. These two steps adjusted for the influence of sediment texture (grain size) upon the heavy metal concentrations and related them to a common reference datum that one can be reasonably confident is free of human contamination.

The results show no significant enrichment of copper in any river core. Zinc is highly enriched at one site and less but sigificantly enriched at three others, all on the North Arm. Lead is significantly enriched at only one river site, also on the North Arm. The levels of copper, zinc and lead in the delta-front core are extremely high. The enrichment of lead is more than an order of magnitude greater in this core than in the one river core in which it is significantly enriched.

Of three cores dated by Cesium^{137}, two yielded usable results, and thus estimates of sedimentation rates.

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Last, and not least, I wish to thank my loving wife Sheila and my family for their support and (mostly) patient forbearance throughout this effort.

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CHAPTER 1

INTRODUCTION

GENERAL INTRODUCTION

Sediments deposited in rivers, along whose banks industrial activity occurs, have been found to contain elevated levels of heavy metals. Industrial activity and the heavy fossil fuel consumption associated with large populations tend to raise the levels of these metals (Bubb and Lester, 1991). For example, for many decades lead was used in gasoline resulting in its widespread emission as part of automobile exhaust. Natural diagenetic processes also have an effect either of enrichment or depletion of heavy metals in sediments (Elderfield and Hepworth, 1975). Diagenetic processes are those changes that take place at relatively low temperature and pressure and which ultimately change an unconsolidated sediment into sedimentary rock.

The term "heavy metal" is often used without a rigid definition and frequently as a synonym for trace metals. Trace metals are a metallic subset of the trace elements. These are elements which are present in minerals and rocks in trace amounts (usually much less than 1%) and are normally measured in parts per million (ppm). In the biological context, the term "trace element" is used to refer to any element which occurs in minute amounts in an organism and is necessary for its growth (Rainbow and Furness, 1990). The term "heavy metal" is generally understood to refer to metallic trace elements with high atomic mass, meaning those with atomic number greater than 20 and particularly the transition metals such as copper and zinc. Heavy metals usually occur in trace amounts except where locally concentrated by pollution or naturally by ores.

OBJECTIVES

The objectives of this thesis are to investigate the heavy metal content of the most recent fluvial sediments in the ribbon marshes of the Fraser River delta and to establish an age control in these sediments by the use of radioisotope emission counting (^{137}C s dating). Ribbon marshes are elongate marshes, parallel to the river, formed by tidal, overbank flooding.

More specifically the objectives are:

a). To investigate the variation of heavy metal levels within each core and to relate such variation to observable sediment characteristics in order to determine if any enrichment of metal(s) results primarily from anthropogenic, rather than natural input. Anthropogenic enrichment should appear in the topmost part of the core(s).

b). To investigate the variation of heavy metal levels between cores which might reflect localized sources of heavy metal(s) contamination or a tendency for heavy metal levels to vary either up- or downstream.

c). To develop a time scale for metal enrichment and for estimating fluvial sedimentation rates by using both ^{137}Cs dating of selected cores and historic evidence of changes which effect such rates.

THE STUDY AREA

The Fraser River, with a total length of 1370 km drains a basin of 231 300 km^2 in B.C. The river rises in an area of the Main (Park) Ranges of the Rocky Mountains. Flowing northwestwards from Moose Lake it enters the Rocky Mountain Trench near Tête Jaune Cache and continues in a northwesterly direction until it reaches Sinclair Mills (Figure 1.1). It then swings around the north end of

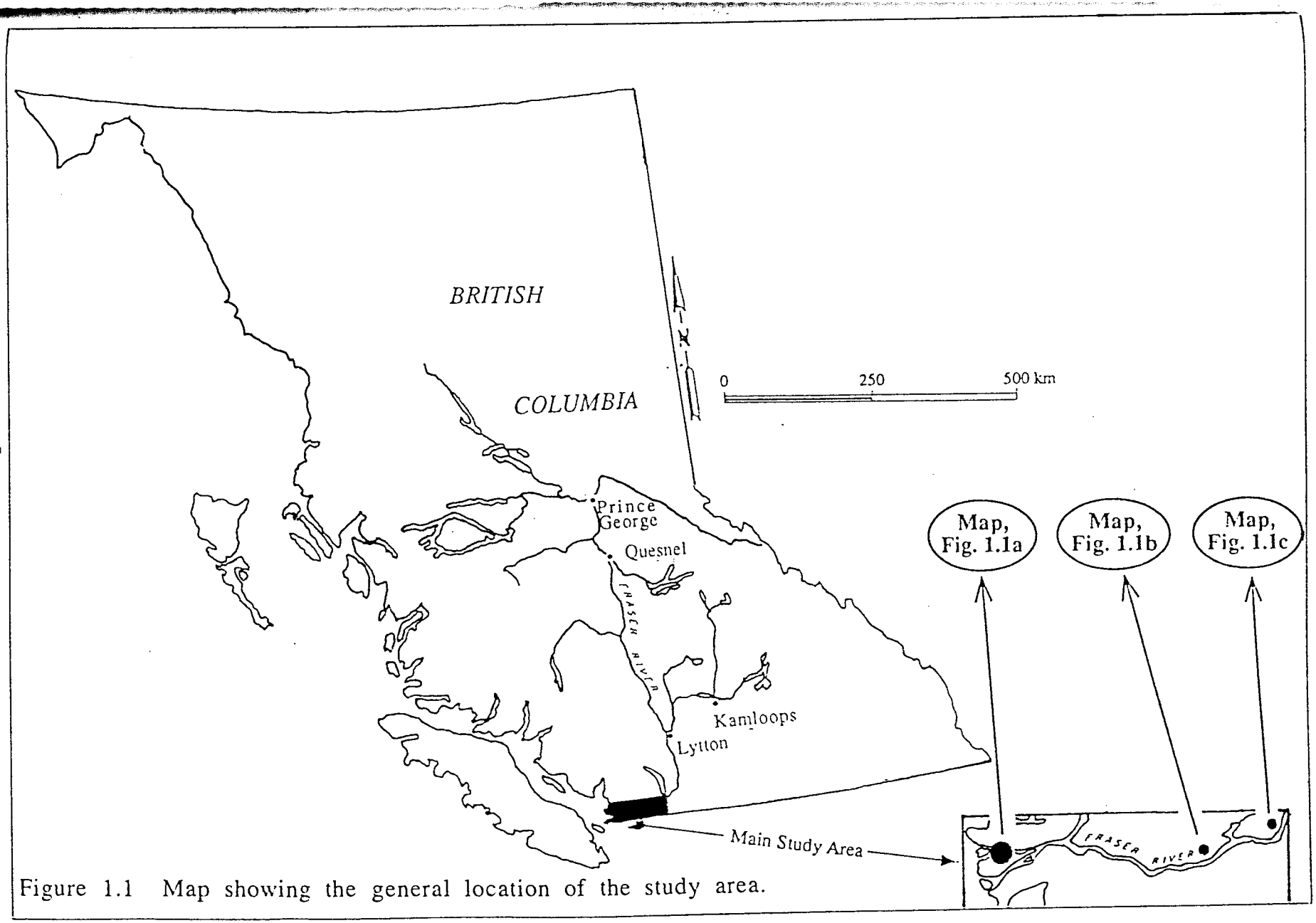


Figure 1.1 Map showing the general location of the study area.

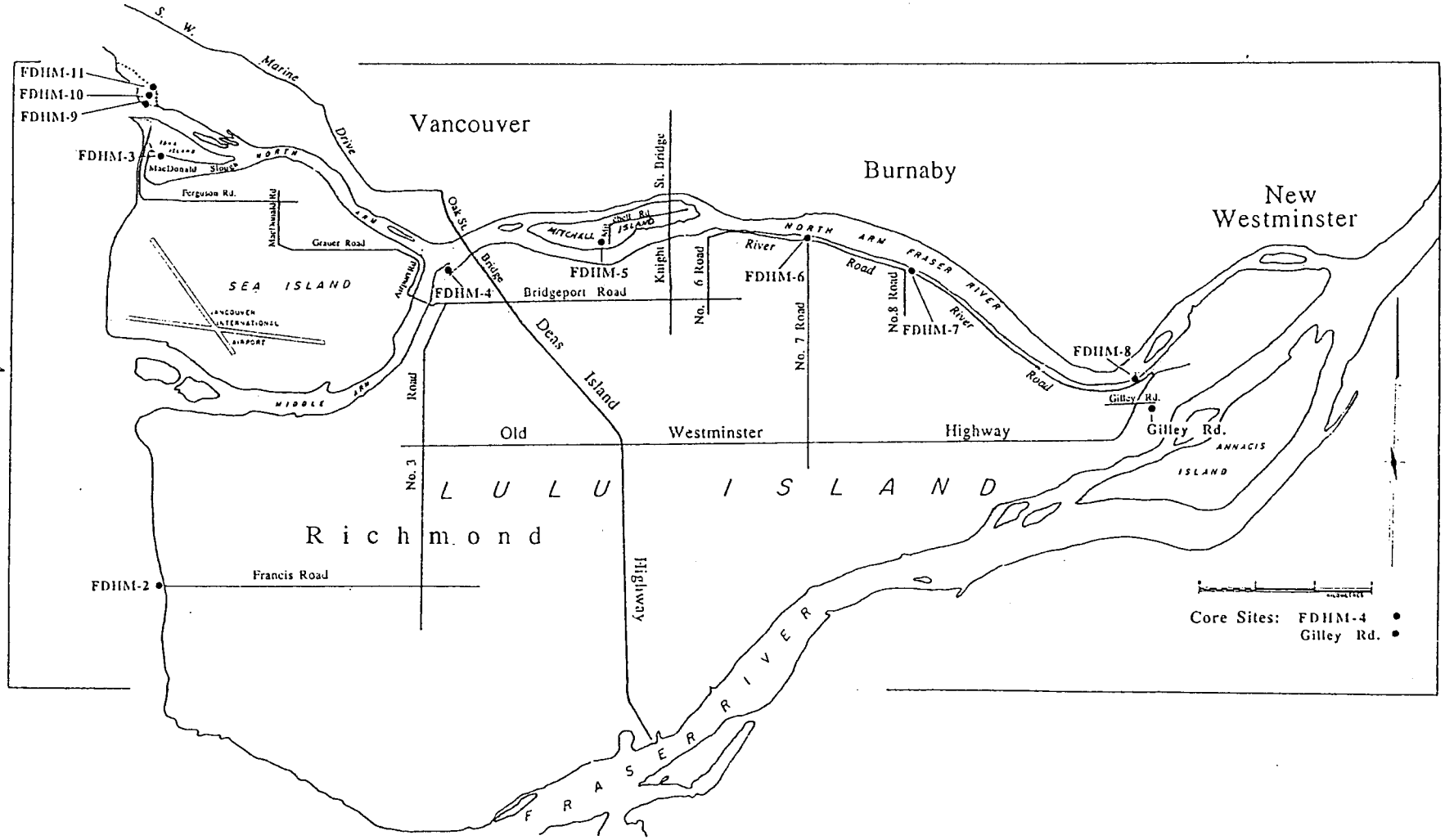


Figure 1.1a Map showing the locations of FDHM-2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and the Gilley Road Core.

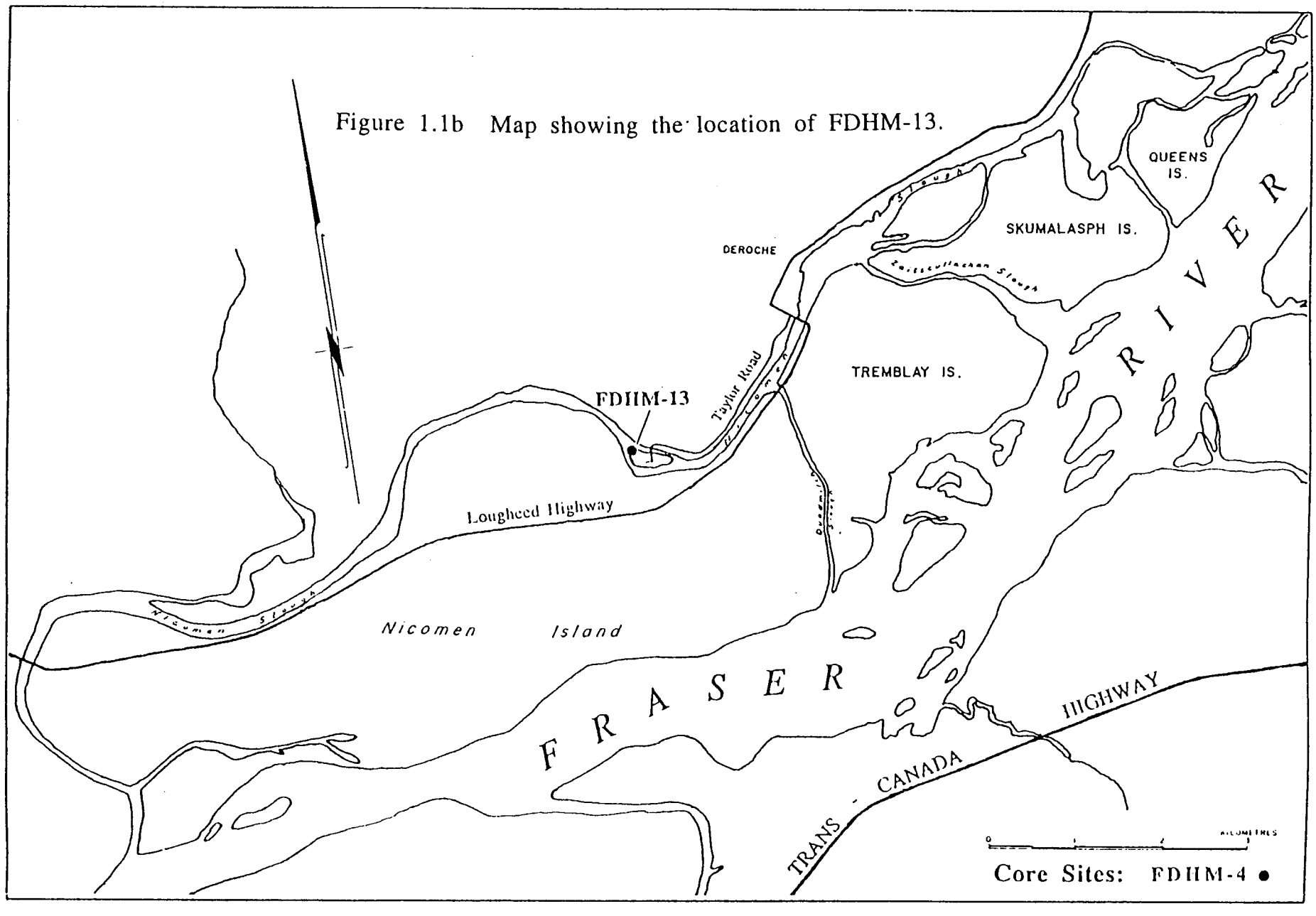
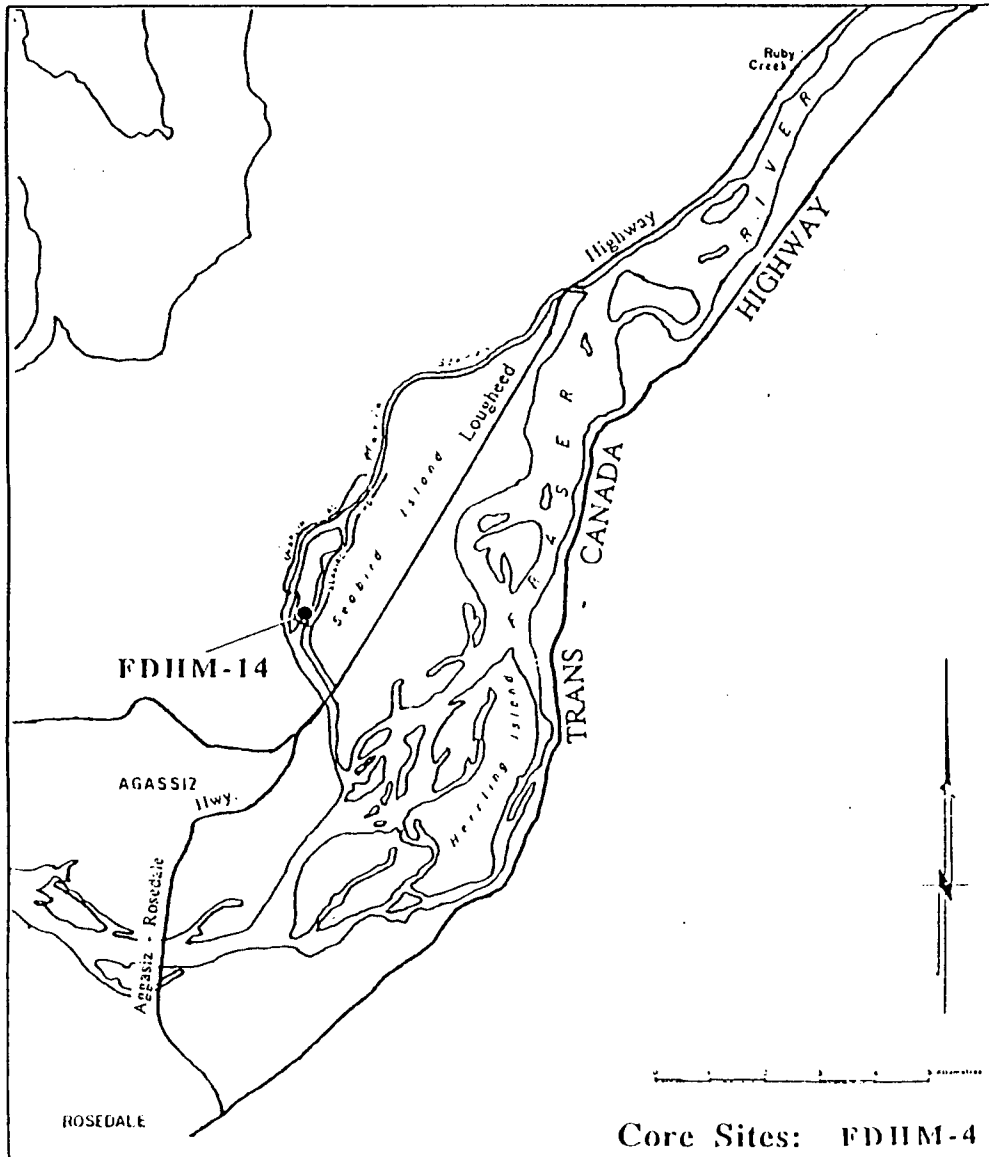


Figure 1.1b Map showing the location of FDHM-13.



Additional maps of the core sites are found in Chapter 4, including one showing more detail of the site of Cores 9, 10 and 11 (Musqueam Marsh).

Figure 1.1c Map showing the location of FDHM-14.

the Cariboo Mountains and flows southwards through the Fraser Basin and Fraser Plateau. South of Quesnel the river becomes increasingly restricted and more incised into the Plateau.

Downstream of Big Bar the river enters increasingly mountainous country and from here to Hope it flows through the Fraser Canyon. Flowing through Hope, 160 km above its mouth, it emerges from the mountains into the Fraser Valley. The valley becomes broader as the river nears tidewater (Holland, 1976). Finally, the river divides into two distributary channels at New Westminster, 20 km above its outlet into the Gulf of Georgia. It is this area of the Fraser delta, which is the geographic focus of my thesis (Figures 1.1 and 1.1a). The Fraser River delta is formed of fine sediments, more than half of which are sand; the annual sediment load of the river amounts to nearly 20 million tonnes of sand, silt and clay (Milliman, 1980). Overbank deposition is now restricted to the immediate margin of the river owing to the construction of dykes over the past century.

The first scientific examination of the delta was made by Johnston (1921). In the past three decades the delta has been extensively and intensively studied (see for example, Mathews and Shepard, 1962; Milliman, 1980; Clague *et al.*, 1983; Williams, 1986 and Williams and Roberts, 1989 among others.). Research has been stimulated by concern about its stability (both subaerial and subaqueous) in the event of an earthquake and by the possibility of finding exploitable quantities of natural gas. As well, increasing environmental awareness has raised concerns about metallic and organic pollution of both water and sediments about the delta. As a result of these investigations we now have a fairly comprehensive picture of the delta in terms of its history and structure. In addition, much knowledge has been gained concerning present sedimentation patterns and rates and water salinity variation.

Most studies of the delta have focussed on its sedimentary structure, history of growth, rates and pattern of sedimentation and so forth, together with complications and modifications to these that arise from tidal effects, distributary channel shift, sea level change and earthquakes. These studies are usually framed within the classically defined Gilbertian structures of topset, foreset and

bottomset beds. Studies which have examined the chemical content of the Fraser delta sediments are rarer (for example Grieve and Fletcher, 1975). In this thesis, I shall examine vertical as well as lateral variations in the heavy-metal content of recent fluvial sediments and attempt to set these variations in a chronostratigraphic framework.

The Fraser River drains a watershed that shows great variation in both soil type and bedrock, including extensive sedimentary, plutonic and metamorphic terranes which are overlaid in some places by great thicknesses of Recent glacial or glacigenic sediments (Holland, 1976). Since it is likely that the sediment contributed by each individual part of the watershed, on average, over time, is a stable proportion of the total sediment load, and since the river has a large drainage area, one might expect that the mineralogical composition of its sediments, though spatially varied, should be relatively constant over time. Consequently, any local input of heavy metals should be detected against such a stable background.

A BRIEF HISTORY

The Fraser River delta has long had at least scattered human occupation. The river which forms the delta yields a bountiful supply of fish, a staple in the diet of the aboriginal people of this region. As well, the channel network of the delta eased travel in this once heavily forested area. Charcoal samples found at the sites of ancient native settlements in the present Musqueam Indian Reserve and the Marpole district of Vancouver have been dated at 3100 years BP (Hutchinson, 1992).

The first Europeans arrived at the mouth of the river in 1791. These were the officers and men of the *Santa Saturnina*, a small Spanish naval vessel commanded by Jose Maria Narvaez, exploring the Gulf of Georgia. The next significant exploration of the Fraser River did not occur until 1808 the year Simon Fraser descended the river. Permanent European settlement did not take place anywhere in the Lower Fraser Valley until 1825, the year that Fort Langley

was established. With Simon Fraser's disclosure that the Fraser River offered access to the Interior, the governor of the the Hudson Bay Company, George Simpson, eventually decided that the Fraser River would replace the Columbia River as the most significant communication route with the company's forts on the west side of the Continental Divide. Hence Fort Langley was to be the port for the transshipment of incoming trade goods and supplies and outgoing furs.

Although a limited amount of farming and commercial fishing had taken place at Fort Langley, it was not until after the Fraser River Gold Rush of 1858 that the delta itself attracted the attention of farming settlers. This was prompted by an increase in demand for agricultural products by the mining camps of the Interior followed in the 1860's by the creation of another market in the small but growing lumber industry on the nearby Burrard Inlet. Settlement began in the 1860's and soon farming was followed by commercial fishing which grew in response to the demands for fish of the growing cannery trade (Ross, 1979). Growth quickened with the arrival of the transcontinental railway at nearby Vancouver in 1887.

Parallel with the growth of Vancouver, there occurred a gradual process of industrialization and urbanization in surrounding municipalities. Among these, probably the most intense activity occurred at Marpole, on the north bank of the North Arm, until then an agricultural area. This occurred in the years leading up to the First World War. Marpole (Eburne as it was then called), was first included in a separate municipality called South Vancouver, then later in another called Point Grey, before these were both eventually incorporated into the City of Vancouver. The industrialization included lumber milling, meat packing, flour milling, distilling, fishing and fish canning and the necessary support services (McNamara, 1976). This development was facilitated by the access to water transport and the construction, about the turn of the century, of branch rail lines into the area. Urbanization intensified with the extension of the Vancouver street car system to Marpole in 1913 making it possible to live here and work in Vancouver. At the same time Richmond, on the the south bank of the North Arm,

remained primarily rural and agricultural in character, (with the exception of the fish canning centre of Steveston) but intense urbanization and industrialization took place here as well following the Second World War (Ross, 1979).

Concurrent with agricultural, urban and industrial development, the river channels were, and continue to be, modified by dyking, dredging and jetty contruction (Clague *et al.*, 1983). Dyking ended vertical accretion on the floodplain. The dredging has, to some degree, altered the flow regime of the river at its mouth so that much of the sediment load is now carried further out into the Gulf of Georgia while the jetties have reduced deposition on the tidal flats by blocking longshore drift of sediments (Milliman, 1980).

THE GEOMORPHOLOGICAL SETTING

The Fraser River delta is located wholly within and on the western edge of the Fraser Lowland. This lowland occupies the southwest corner of the British Columbia mainland and the adjoining northwest corner of Washington State, U.S.A. (Figure 1.1). The Fraser Lowland is flanked on the the north by the Coast Plutonic Complex and on the east and southeast by the Cascade Mountains. The Fraser Lowland has an undulating topography with a few flat-topped uplands, broad shallow valleys and some isolated mountains. The delta is flanked on the south by uplands of Quaternary age and on the north by uplands consisting of Late Cretaceous and Tertiary sedimentary rocks which have been intruded by volcanic dykes, sills and plugs and are overlain by a thin covering of Quaternary sediments (Armstrong, 1984; Holland, 1976; Roddick, 1965). The delta, which once built south as well as west, is now active on its western front alone (Mathews and Shepard, 1962). It is approximately 30 km in length including the subaqueous delta-front portion and 20 km in width at its widest point. Since its formation commenced in the early Holocene, 9 000 to 10 000 years BP, the delta has grown until it now has a terrestrial area (including river channel and tidal flats) of approximately 600 km^2 and a submerged

marine area of approximately 410 km^2. The depth of sediments in some places may be in excess of 200 m but 100 m is more typical (Johnston, 1921; Mathews and Shepard, 1962). The delta assumes the classical, triangular delta-shape and falls between 49° 05.3' N and 49° 13.3' N latitude and between 122° 55' W and 123° 16.5' W longitude. The main study area, from which nine cores were taken, lies along a distributary channel known as the North Arm. In addition, four other cores were taken; one from the nearby delta front, one from beside Gilley Road, and one each from two upriver sites, Nicomen Slough and Maria Slough (Figures 1.1a, 1.1b and 1.1c).

CHAPTER 2

PREVIOUS RESEARCH

INTRODUCTION

The first part of this chapter reviews the literature related to the geology of the Fraser delta and examine some characteristics of its sediments and their mode of deposition. Sediment characteristics have a direct bearing upon the concentrations of heavy metals within these deltaic deposits.

The second part reviews literature concerned with heavy metal accumulation in the sediments of estuarine and other related environments. As well, qualitative and quantitative methods for analysing heavy metals in sediments are examined.

The third part concludes the chapter with a review of literature concerning the application of cesium isotope (^{137}Cs) dating to recent sediments.

SEDIMENTS OF THE FRASER RIVER DELTA, B.C.

The Holocene Record

Formal investigation of the Holocene sediments of the Fraser River delta began in 1921 with the study of Fraser River sedimentation by Johnston (1921). This was part of his general investigation of the Fraser Lowland. It is a wide-ranging study which deals not only with sedimentation, but with the sediment and dissolved load of the Fraser River. In addition, it documents the deltas discharge and tidal regimes. In a work a year later, Johnston (1922) focussed on the stratification of the sediments in the delta. A

number of core samples were taken during his research in order to examine the stratigraphy of the delta front.

Two of the subsequent studies of the delta have more or less followed the pattern set by Johnston in his 1921 paper and have concerned themselves with an overall examination of both the river and its delta. Mathews and Shepard (1962), resurveyed the delta to assess changes since Johnston's time, while Milliman (1980) focussed his study on sediment composition and sediment flux of the river. Some investigations have focussed on sedimentation patterns on the subaqueous delta front and tidal flats (Luternauer and Murray, 1973; Moslow *et al.*, 1991.). This research arises partly in response to the danger posed by submarine slope failures.

Other studies have examined how the growth history of the delta is revealed by its stratigraphy. Clague *et al.* (1983) provided an overview of the sedimentary environments of the delta including bogs. A 367 m drillhole by Luternauer et al, 1991 on the southwestern Fraser delta penetrated the Quarternary deposits underlying the delta. How facies have migrated vertically as well as laterally in response to sea level changes is examined by Williams (1986) and Williams and Roberts (1989). A seismic analysis of the delta stratigraphy was carried out by Jol (1988).

Little attention seems to have been paid to the overbank sediments *per se* which form the ribbon marshes lying along the distributary channels of the Fraser delta. The general characteristics of overbank stratigraphy have been reviewed by Elliot (1986). On the Fraser delta, overbank sediments are deposited either during inundations caused by high spring tides or during the seasonal, mid to late summer floods on the river. Dyking over the past hundred years has now largely confined this overbank deposition to the immediate bank of the river.

The Stratigraphic Record

Johnston (1921) made the first estimate of the rate of delta sedimentation and hence, by projection, of its age. He estimated the average annual linear rate of advance along the delta front to be 3.0 m a^{-1}, which over a distance of 24.4 km from New Westminster to

the present delta front which gives an age for the initiation of the delta of about 8 000 years. Later studies (Clague *et al.* 1983; Mathews and Shepard; 1962, Williams and Roberts, 1989.) have shown the prescience of Johnston's estimate.

Johnston (1922) divided the sediments into two main classes: alluvial flood-plain and deltaic sediments. Using Gilbertian terminology, the latter were further subdivided into topset, foreset and bottomset. Johnston also uses the term "tidal flood-plain sediments", although it is not clear as to whether this refers to sediments deposited in the tidal flat area of the topset beds only, or to overbank sediments along the lowermost reaches of the river that result from tidal back-up of the river as well. He noted that the tidal flood-plain sediments contain very fine laminations which are tidal in origin. Interspersed among these are thicker, seasonal layers, consisting in some places of vegetable matter and in others of alternating silt and sand layers which themselves contain tidal laminations. However, in the alluvial flood-plain sediments he noted that the only laminations found there resulted from seasonal layers of silt and organic matter. Neither type of deposit showed very much fining upwards of grain size.

The study by Mathews and Shepard (1962) deals largely with volume, rate and lithology of the sediment flux. The deposits are discussed in engineering rather than stratigraphic terms. The paper also gives estimates of the growth rate of the Delta which accord closely with those of Johnston. The writers estimate the average thickness of delta sediments to be 116 m and an age of not less than 7 300 years and not more than 11 000 years.

The paper by Moslow *et al.* (1991) is among those that examine sedimentation on the delta front. These studies examine sediment size, distribution and structure of the delta front including both the delta slope and the tidal flats. The primary concerns of these studies are slope stability and the effect of currents upon sedimentation rates and patterns.

Milliman (1980) studied the very different flow regimes of the river during the seasons of the year. From mid-summer through to spring the river flow is very low (an average of less than 3 000 m^3

sec^{-1}); the load is dominated throughout this time by silt and clay sized sediments. The other regime is the freshet flow from spring to mid-summer. Eighty percent of the yearly sediment load is transported at this time with about one-half of it consisting of sand. He also reminds us that only a few rivers carry such a high percentage of sand and attributes this to factors such as the lack of dams upon the Fraser, the nearness of mountains, and the coarse nature of the Pleistocene glacial deposits.

An investigation by Clague *et al.* (1983) examines sedimentary environments of the delta and lower Fraser Valley in a context of postglacial changes in sea level. The authors state that the delta (termed a proto-delta) first began to form about 10 000 years BP after deglaciation had taken place, growing southwards and westwards. In the period from about 7.0 - 7.5 to 5.0 - 5.5 Ka years ago they speculate that a marine transgression inundated parts of this proto-delta and temporarily checked its further seaward growth. Following this, they believe the sea stabilized about 1 to 2 m below its present level, leaving large areas of the delta exposed and allowing the delta to resume its westward but not southward growth. The study distinguishes between the various types of sedimentary deposits and points out the gradational nature of the change from clastic floodplain sediments to tidal-flat deposits. They add that, although these deposits are alike in sedimentological properties, they differ in structure; cross-bedding and bioturbation structures being common in tidal-flat sediments but not in overbank deposits.

A paper by Williams (1986) provides support for the contention of Clague *et al.* (1983) that a proto-delta exists beneath the present-day eastern part of the delta. In contrast to the earlier study however, it suggests that the vertical accretion on the delta kept pace with the sea level rise and that, as a consequence, the delta was not inundated during the 12 m rise in sea level. Further work (Williams and Roberts, 1990) in which a model of delta growth was developed, suggested that an upward as well as lateral displacement of the topset facies occurred as a response to sea level rise.

The role of tides and vegetation in the accretion of sediments in salt-marsh environments like those found on the Fraser delta has been studied and modeled by Randerson (1979).

Dating control has been established throughout the delta by Williams and D'Auria (1991) through the detection of a widespread tephra bed resulting from the violent eruption of Mt. Mazama (*ca.* 6800 BP). Both this marker bed and another, a peat with an age of 6000 ^{14}C BP, are described in Williams and Roberts (1990).

HEAVY METALS IN SEDIMENTS

There is a substantial body of work on the distribution and detection of heavy metals in sediments deposited in freshwater, brackish and marine environments (see, for example, the many references in Burton and Liss, 1976, Rainbow and Furness 1990 and Förstner and Wittmann 1981).

Floodplain and overbank sediments

Heavy metals in floodplain and overbank sediments are discussed by Lewin and Macklin (1987) and Macklin and Dowsett (1989). Both papers examine the effects of past metal mining wastes upon fluvial sytems. The 1987 paper deals with historic mining sites throughout Scotland, England and Wales and distinguishes between different scales of waste dispersal - those which disrupt fluvial systems and those which do not. The 1989 paper focuses upon the flood sediments of the Tyne basin and examines the distribution of the heavy metals within these sediments as a function of their chemical form, i.e whether the metal is particulate or ionized.

Estuarine and Nearshore Sediments

Estuaries are often regarded as critical environments because of their biological productivity and sensitivity. The estuarine environment is one in which natural chemical changes occur because of the transition from fresh through brackish to saline waters. Unfortunately, as a result of their value as harbours and seaports and concomitant centres of population and industrialization, they are often contaminatied by heavy metals and other pollutants (Prohic and Kniewald, 1987). Trace metal pollution in the lower Fraser River and its estuary were examined by Hall and Fletcher (1974) who found the highest concetrations of these metals in waters affected by the Greater Vancouver area. Factors influencing heavy metal concentrations are mostly a function of conditions that prevail in the ambient waters. In addition to the most obvious one —concentration

of the heavy metals in the ambient water (Thomas and Grill, 1976), other influences include; turbulence and currents that redistribute sediments (Grieve and Fletcher, 1976), salinity (Fletcher *et al.*, 1983) grain size or texture (Krumgalz, 1989; Thorne and Nickless, 1981), temperature, pH, oxidizing potential (Gorham and Swaine, 1965), biota and the presence of organic matter (Hamilton-Taylor, 1979; Jones, 1984) and the mineralogy of the sediment (Dossis and Warren, 1980). Because so many factors affect the presence of heavy metals within estuarine sediments, many of the investigations have focused on one aspect of the general problem. By using core rather than grab samples, this study examines historical as well as spatial variation in metal content, both before and after adjustment for sediment texture.

Obviously, each of the above influences can occur at very different scales of time and space. For example, in an estuary, salinity might fluctuate temporally and spatially on a daily or even hourly basis with tidal action; Fletcher *et al.*, (1983) examined this phenomenon and its effect on metal concentration in the Fraser River. While Chapman (1989) examined the vertical and seasonal changes of salinity within interstitial sediments in the same estuary.

Closely connected with salinity is desorption, which is the removal into solution of metal borne on suspended particles in river water when it mixes with saline waters. An investigation by Grieve and Fletcher (1977) showed that *both* adsorption and desorption of zinc occurred in the mixing zone between fresh and brackish waters of the Fraser Estuary. This seeming conflict appears to be the result of Fe coagulation. Estuarine mixing experiments on Mississippi and Hudson River waters have shown that some metals are desorbed while other previously "dissolved" metals will be coagulated (Li *et al.*, 1984). Investigations of the behaviour of dissolved and particulate Mn, Pb, Cu and Zn in Puget Sound, Washington State, by Paulson *et al.* (1988) demonstrate that dissolved Pb is scavenged from the dissolved phase by particulate hydrous manganese oxides. This was not true of Cu and Zn. In a study of waters from Georgia Strait, Thomas and Grill (1976) noted large increases in the amount of dissolved Cu and Zn in spring and early summer. They attribute

this to a freshet-increased particulate load of Cu and Zn which is desorbed when river water mixes with seawater, rather than an increase in the dissolved load of the river itself; in other words, a volume rather than a concentration effect.

Another complication is the relationship between heavy metal concentration and grain size distribution (texture) within a sediment (Cauwent, 1987; Thorne and Nickless, 1981). In general, the finer the texture, the greater the metal concentration. This is because if two sediments of differing texture are exposed to the same concentration of a heavy metal, the finer will retain more metal than the coarser. It is shown by Grant (1990) and Rule (1986) that this grain size effect must be given due allowance if meaningful statistical comparisons are to be made between heavy metal levels of different sediments.

Sediment texture may influence heavy metal content indirectly as well. This occurs when (typically) coarse sediment allows the circulation of oxygen rich waters. This causes the formation of Fe and Mn hydrous oxides which in turn act as scavengers of other metals such as Pb, Zn and Cu. This type of physico-chemical barrier, termed "oxygenating", is extensively discussed, along with other types, by Perel'man (1967). He contrasts this environment to the oxygen deficient "gley" or reducing environment in which reduced, soluble hydroxides of Fe and Mn do not scavenge other metals. That the concentration of metals formed at physico-chemical barriers might persist in the geological record is shown in a study by Schmitz (1985). In this paper he examines the enrichment of heavy metals at the boundary between the oxic Cretaceous chalk and the overlying anoxic Fish Clay of Stevns Klint, Denmark. In this case an oxygenating barrier was augmented by sulfide enrichment of the Fish Clay resulting in the formation of insoluble metal sulfides.

Corrections for grain size effect are essentially of two types. The first consists of separating the finer sediment fraction from the coarser and only analysing the former, although there is some contention arising as to which size fraction is the best to use (Ackermann, *et al.*, 1983). The second requires one to choose some element characteristic of the fine fraction, determine its

concentration as well as those of the metals of interest and then normalize the latter to the former (Ackermann, 1980, Grant and Middleton, 1990, Loring, 1990). Krumgalz (1989) cautions that the grain size effect might be disguised by the formation of larger particles from smaller ones during drying of the sediments. This formation results from cementation by organic matter or sea salt present in the sediment.

The relationship between biota and heavy metals has also been explored. Barnett *et al.* (1989) analysed the heavy metal content of *Fucus vesiculosus* rather than that of the sediments from the Humber Estuary (U.K.). Sinex and Wright (1988) examined both sediment and organisms in their study of heavy metals in Chesapeake Bay. A study on the Fraser River, (Chapman *et al.*, 1980) also examined both sediments and organisms (tubificids) and concluded that there was no seasonal variation of metal levels in the tissues of the organisms.

Sometimes heavy metals form such distinctive and persistent beds that suggestions have been made for the use of them as stratigraphic units on the same order as those defined for fossils (biostratigraphic) or lithology (lithostratigraphic). Such a stratigraphy, as "chemostratigraphy" defines zones of similar chemical content as "chemozones", (Allen and Rae, 1986). The authors first examined the time sequence of metal pollution in late Flandrian intertidal sediments of the Severn Estuary (U.K.) and were able to define three distinct zones that differed from one another in heavy metal content. These zones succeeded one another and could be related to historic human activity. In order to be fully quantitative, such a chemostratigraphy requires a completely mixed system. In a subsequent study, Allen (1987) noted a small but significant statistical anomaly in the distribution of lead and concluded therefrom that the Severn Estuary was not a such a system. He believes though, that even without a fully mixed system, metal pollutants might still be used as a stratigraphic tool.

Chemical Analysis

There is a range of methods available for analysing sediments containing heavy metals. These methods fall into two general

categories. Firstly, there are those which employ leaching of the metals from the sediment followed by quantitative and qualitative analysis of the product solutions, by, for example, Atomic Absorption Spectrometry. When this method is used only the so-called "extractable" metals are analysed. The non-extractable fraction which is part of the sediment substrate is not analyzed. Secondly, there are those methods which utilize some form of X-ray spectroscopy that permits quantitative and qualitative analysis of the whole sediment, for example, X-ray fluorescence (XRF).

Chemical extraction methods are dependent upon sample pretreatment which, if not carefully carried out, can lead to spurious results (Kersten and Förstner, 1987; Martin *et al.* 1987; Rapin *et al.* 1986). In studies which seek to determine the bioavailability of metals however, HCl extraction might be the preferred method. It has been shown that the bioavailability of metals is similar to their HCl extractability (Luoma, 1983).

XRF on the other hand, eliminates pretreatment and is economical and quick. As well, it is non-destructive of sample material, and because it analyses for total metal content (including metals which are part of the composition of the sediment itself), makes normalization to a chosen metal possible (Grant and Middleton 1990).

A practical outline of XRF methods is given by Calvert *et al.* (1984).

THE USE OF RADIOACTIVE CESIUM (^{137}Cs) FOR DATING RECENT SEDIMENTS

Long time-scale dating by the use of radioactive isotopes has been used for some time, but recently, methods have been developed which use short-lived isotopes to date recent sediments (Wise, 1980). The two isotopes best suited for this purpose are ^{137}Cs and ^{210}Pb (a lead isotope) with half-lives of 30 and 22 years respectively. ^{137}Cs, an isotope of cesium, not found naturally, is a product of nuclear arms detonations.

A datum for ^{137}Cs dating has been established by Koide *et al.* (1979). They examined the record of ^{137}Cs in ice of the Ross Ice Shelf, Antarctica, and found a series of peaks which corresponded to the years of maximum "fallout" from nuclear arms test. These reference peaks in recent sediments allows their isotopic dating. This has been done by Ritchie *et al.* (1973) who dated lake and reservoir sediments and by Delaune *et al.* (1983) who estimated vertical accretion, coastal submergence and erosion in a marsh in the Louisiana Gulf Coast, U.S.A., among others. In Saskatchewan, the use of ^{137}Cs dating to estimate erosion rather then accretion rates is investigated by DeJong *et al.*, 1982. Locally, a core extracted from an urban lake in British Columbia, was dated by Mathewes and D'Auria (1982) who related ^{137}Cs peaks to pollen and geochemical changes in the lake sediments.

CHAPTER 3

METHODOLOGY

INTRODUCTION

The objectives of this study, to review briefly, are to investigate the variation of heavy metal content both within and between floodplain sediments cores, in order to ascertain whether enrichment of heavy metals has occurred and to explain such variations. Another objective is to establish a time horizon in order to place any such enrichment in a chronostratigraphic setting.

Heavy metals are most closely associated with the clay/silt fraction of sediments, typically deposited in quiet water environments. Ribbon marshes, found along the distributary channels of the Fraser delta, are such environments. The first step in the investigation was to examine maps and aerial photographs and to carry out a brief field reconnaissance in order to identify and locate these marshes.

SITE SELECTION

Ribbon marshes were selected along the North Arm of the Fraser River (Figure 3.1) because it is along this stretch of the river that the most intensive and extensive industrial activity has taken place. Furthermore, the dense population living here has long generated a significant inflow of potentially heavy metal-bearing run-off water into the North Arm.

An attempt was made to select marshes in which no obvious disturbances such as trenching for pipelines or dredging and filling had occurred. Two additional sites were chosen in the upper Fraser Valley (east of Chilliwack) in order to compare results from the North

Arm with those from areas with little or no industrial activity and a limited population. A third site was chosen upon the tidal delta front in order to assess metal levels in sediments from different depositional settings, but having the same source as those of the North Arm.

Figure 3.1 Site FDHM-8 on the ribbon marsh along River Road.

The numbering system of the cores, except for those along the North Arm of the river, does not follow an upstream sequence; the "stream" order and locations follow (see Figures 1.1a, b, and c):

FDHM-2, Fraser River Delta front (Francis Road);
FDHM-9, 10 and 11, Musqueam Marsh;
FDHM-3, MacDonald Slough;
FDHM-4, Brighouse; FDHM-5, Mitchell Island;
FDHM-6, No. Seven Road;
FDHM-7, No. Eight Road;
FDHM-8, River Road;
FDHM-13, Nicomen Slough (Brockman Island)
FDHM-14, Maria Slough (Seabird Island).

Although it was intended to extract cores only at undisturbed sites, subsequent examination of the cores during logging suggested that the intention had been thwarted at several locales. In all the instances in which natural sedimentation appeared to be altered by human activity, the effect was not manifest at the surface. These examples illustrate the difficulty of finding undisturbed core extraction sites in a heavily developed urban area. At two sites, FDHM-3 and 5, the fact that dredging had occurred at the first and filling at the second was only discovered by personal communication with a supervisor of The North Fraser Harbour Commission (N.F.H.C.). Even disturbed sites however, yielded information pertinent to the objectives of the study.

CORE COLLECTION

Once suitable sites had been chosen, coring followed. The vibracorer is the best equipment to employ when collecting shallow cores from fine, wet, unconsolidated sediments. This equipment is simple, reliable, portable, and inexpensive: it can be easily handled by one operator using the smaller machine, or two using the larger. The larger version uses a wheelbarrow-mounted gasoline engine to drive a power transmission cable (Figure 3.2). It is more robust than the smaller version and is generally used for somewhat deeper cores and for cores of broad girth (7.6 cm). The smaller version, which has the advantage of being driven by a back-pack mounted gasoline engine, is best used for shallower cores, cores of narrow girth (5.1 cm) and cores in terrain not easily accessible by the larger version (Figure 3.3).

Under suitable conditions cores as long as 12 m have been obtained using the large machine. More details concerning the construction and use of the large vibracorer may be found in Smith (1984) while those relating to the smaller version may be found in Smith (1987).

Both vibracorers are made mostly of standardized, easily obtained equipment; a small gasoline engine driving, by way of a

Figure 3.2 The large vibracorer with ladder and block-and tackle. The core pipe is resting upon the custom-made coupling sleeve.

Figure 3.3 The small, more portable vibracorer, showing one of the coupling sleeves clamping the vibrating head to the core pipe.

cable, a standard, construction-industry vibrating head as used for concrete emplacement. The only special modification necessary is the coupling device which attaches the vibrating head to the standard aluminum irrigation pipe in which the core is collected. This device, like the core-catchers discussed below, must be custom made by a machine shop.

The vibracorer exploits the property that vibration of fine-textured wet sediments causes liquefaction of those sediments. The intense vibration of the aluminum irrigation pipe induced by the vibrating head results in liquefaction of the sediments in a very localized area about the rim of the pipe. Hence the pipe, when vibrated with some downward pressure applied by the operator, will efficiently and quickly penetrate the sediment. When the pipe has reached the desired depth it is twisted in order to cleanly sever the core from the underlying sediment and then, while vibrating at low speed, is withdrawn from the the ground .

When using the larger vibracorer and sometimes the smaller one as well, it is necessary to use a small portable derrick from which a block and tackle is suspended in order to remove the pipe from the ground (Figure 3.4). A stout ladder may often be substituted for the derrick, especially when using the smaller vibracorer. The best ladder commercially available for this purpose is the TLC Jaws®. In some cases, as when using the small vibracorer for shallow cores, it can simply be pulled out of the drillhole by hand. Saturated sediments often require that a core-catcher be fitted to the end of the collection pipe so that the core is not lost. It is probably best to fit it in any case, because the sediments often become progressively wetter as one goes deeper.

After the pipe was withdrawn, the core was carefully vibrated out upon a length of standard PVC pipe (Figure 3.5) which was halved lengthwise and is of the same, or slightly larger diameter than the vibracorer pipe. Following this, the core was wrapped in heavy, meat-wrapping (butcher's) paper for removal to the laboratory. If not immediately logged and sampled, it was placed in cold storage until these could be done.

Figure 3.4 The large vibracorer in use, showing the derrick.

Figure 3.5 The core being vibrated out upon a halved section of PVC pipe.

LOGGING OF CORES

The core was carefully logged with respect to texture, structure and organic content. Texture refers to sediment particle size as defined by the Udden-Wentworth scale. Structure refers to any recognizable features which result from the deformation of soft-sediments or from the original depositional setting. These structures might include convolutions, slumps and load structures, as well as bedding structures. Organic material is often an indicator of past environments and was recorded and its position in the core carefully noted. All the above information was recorded in a log book and then used in order to draw the individual diagram of each core (see Chapter 4).

Samples for analysis were taken while the core was being logged. This was done by dividing the core into 2 cm sections, crosswise to the length of the core. Each of these sections constitutes an individual sample. If there was ample material, which was usual, especially with the larger diameter cores, then half the sample was retained intact, and the other half was prepared for XRF analysis. Sometimes, when the sample was scant, owing to a large volume of roots or wood for example, it was necessary to keep the entire 2 cm section for analysis.

HEAVY METAL ANALYSIS

In order to determine the variety and quantity of heavy metals present in the sediment samples, a choice had to be made from among several available analytical methods.

Various analytical techniques have been used in the past (e.g. Dossis and Warren, 1989; Prohic and Kniewald, 1987) in order to analyse sediments but, as discussed in Chapter 3, many of them suffer from pretreatment effects on the samples (Kirsten and Forstner, 1987; Martin *et al.* 1987; Rapin *et al.* 1986) or have some

other drawback, such as a failure to analyze all of any given element present in a sediment. The best method of sediment analyses currently available with respect to sensitivity, versatility and cost is X-Ray Fluorescence (XRF); this technique was used in this study.

XRF analysis has many advantages over other currently available methods. It is non-destructive, both qualitative and quantitative analyses are possible for elements with atomic number greater than 12 and complex mixtures can usually be analyzed without prior separation of the components thus greatly reducing time, labour and cost.

This method involves irradiating a sample with X-rays of appropriate wavelength, resulting in X-rays of different wavelengths, characteristic of the elements present, being emitted (fluoresced). In practice, the X-rays produced by the X-ray tube are not allowed to impinge directly on the sample, but rather are directed upon a piece of metal known as the target. The secondary X-rays fluoresced by the target are then directed at the sample. These in turn cause elements in the sample to fluoresce. The detection of these fluoresced X-rays provides both a qualitative and quantitative analyses of the elements present (Calvert *et al.* 1985). A given target can only analyze a certain range of elements, thus if one were to do a complete analysis for all heavy metals it would be necessary to rerun the samples using several different targets. In this study, because of time and money constraints, only a limited number of metals were analyzed. Copper, lead and zinc were chosen because they are most likely to be anthropogenically enriched in the geographic area of this study. For example, the levels of these three metals are found to be elevated in sewage sludge (Förstner and Wittmann, 1981) Furthermore, lead, until recently an additive of gasoline, became widely distributed in the environment by automotive emission. Zinc finds widespread use as a galvanizing metal so it is not surprising that, together with copper and lead, it is found in high concentrations in storm runoff water (Förstner and Wittmann, 1981).

In order to test the XRF analysis of a given element, it is necessary to analyse a standard reference material (SRM) from an

equivalent or similar environment. The SRM used for this purpose was Standard Reference Material 1645, a river sediment.

For each element to be analyzed, a calibration curve is constructed by preparing duplicate sets of six one-gram samples. The first pair of samples consist of 1000 mg of SRM, the second 800 mg of SRM plus 200 mg of somar, an inert organic powder, the third 600 mg of SRM plus 400 mg of somar and so forth, decreasing the SRM by an increment of 200 mg each time while increasing that of the somar by 200 mg. A sixth pair of samples consisting of pure somar provides a zero point. Each sample is formed into a pellet by placing the sample in a die and applying 3.5×10^5 kPa pressure. The two sets of standard samples are of course analyzed in the same way as the sediments undergoing research are analyzed. X-rays produced by 5 mA of current at 40 kV for one-half hour of real time using a molybdenum (Mo) secondary target were used in this study.

The results of the analysis of the duplicate standards were then plotted on a graph of corrected counts versus concentration. The regression line formula for each element obtained from the plot is used to calculate the amount (in ppm) of that element in the research samples. If a satisfactory calibration curve cannot be obtained for a given element then that element is not analyzed. The analyses of standards and the derivation of regression equations from the calibration curves was done by Lowell Wade M.Sc., (technician, Department of Geography, SFU).

Thirteen core samples were obtained in 1991 and 1992, eleven of these were logged in detail and then divided into 2 cm segments down the core (some cores were 5.1 cm, others were 7.6 cm in diametre). Each segment was dried for one week in an oven at 100 ^{o}C. After drying, each segment was milled in a hammer mill for three minutes in order to reduce the sediment to a uniform size (Maximum diametre, 74 μ). The powdered samples thus produced were stored in airtight plastic vials. One core, FDHM-1 (Gilley Road), was used to obtain a standard sample from which 12 duplicate samples were obtained in order to test the reliability of the analyses and to provide a control (or baseline) with which to compare the ribbon marsh sediments. This core reached a depth of 6.47 m and

contained a layer of 6800 year old Mt. Mazama ash at a depth of 6.35 m. The sampling and logging of this core was done by Lowell Wade M.Sc., (technician, Department of Geography, SFU). The standard sample was extracted from the core at a depth extending from 6.23 to 6.35 m. At this depth range, it is reasonable to assume that no anthropogenic enrichment of heavy metal has occurred. In the study by Middleton and Grant (1990), consolidated intertidal muds, approximately 5000 years old, were used as a control.

Pellets of sediment for analysis were prepared using 1 g of powdered sample and formed under the same pressure as those analyzed for the calibration curves. The resulting pellets are circular in cross-section with a diametre of 12.7 mm (0.50 in) and a thickness of *ca.* 4 mm. The thickness could vary slightly with the texture of the sediment. These pellets were then analysed by XRF as outlined on P. 31. The analysis of the 786 samples was performed at the XRF laboratory, Department of Chemistry, SFU under the supervision of Lowell Wade M.Sc., (technician, Department of Geography, SFU), who also analysed FDHM-1 (Gilley Road) and its standard samples and FDHM-2 at U.B.C., using pellets pressed on boracic acid powder. Both cores were analysed at the usual 2 cm interval to a depth of 1 m. Below that depth, every second 2 cm interval was sampled to the lowermost part of the core with the exception of the aforementioned standard sample from FDHM-1 (Gilley Road). This amounts to 172 through-the-core samples plus 24 standard samples for a total of 196 samples analysed. Of the other 11 cores, each 2 cm interval was sampled for a total of 790 samples. Two samples were lost in the oven and two were too scant to test, leaving a grand total of 786 samples analysed.

XRF DATA

The raw data obtained from the analysis are derived from the area under the energy peak for a given metal. This energy peak area is transformed into a number by the computer using the GXL (a personal computer version of the Gamanal©) program. These data

are then entered into a Lotus 1-2-3© program and changed into percentage or parts per million (ppm) numbers for each of the metals analyzed, using the regression equation for the calibration curve. Major elements such as iron and aluminum are usually expressed as weight percentages while trace metals such as copper and zinc are expressed as parts per million.

Grain Size Normalization

Since heavy metal concentration increases as grain size decreases resulting in the preferential adsorption of anthropogenic metals, heavy metals are usually most abundant in the clay fraction (Cauwent, 1987; Thorne & Nickless, 1981). Clay also contains non-anthropogenic metallic ions in its crystal lattices. As a result, metal concentrations in clay are deceptively high. Thus it is necessary to normalize (or standardize) the metal concentrations in some way to compensate for this effect.

The best way to render metal concentrations in sediments comparable is by normalization to a compositional characteristic of the sediments. This normalization becomes a substitute for grain size. By choosing a conservative element, (one which does not itself react with other species) within the clay and analyzing its concentration as well as that of the metal which is being investigated, one is able to establish a ratio between the two concentrations. This is also done for the background or baseline sediment. In turn, the ratio of these two ratios then becomes the enrichment factor for the particular heavy metal being investigated. This was the method employed in this study.

$$\text{Enrichment Factor} = \frac{[X]}{[Rb]}\ \text{sample} / \frac{[X]}{[Rb]}\ \text{baseline.}$$

In the above case, X represents the metal of interest while rubidium (Rb) is the grain size normalizing metal. A factor greater than 1.1 (the extra 0.1 is to allow for maxiumum diagenetic enrichment of metal within the sediments) indicates enrichment of the metal in question (Elderfield & Hepworth, 1975; Grant & Middleton, 1990).

The most suitable metal for use as the grain size control is found by plotting scatter diagrams of the heavy metal versus the constituent of the sediments used as the grain size proxy. Aluminum and iron have been used but they are often anthropogenically enriched. The use of lithium (Loring, 1989) and cesium (Ackermann, 1980) has also been recommended. However, cesium is usually found at low concentrations, while lithium is difficult to measure using XRF because of its low atomic number. Rubidium seems the best choice because it shows good correlation with levels of most metals, can be measured accurately on the pressed powder pellets used with XRF methods and shows no evidence of anthropogenic enrichment (Grant & Middleton, 1990).

Some studies of sediment heavy-metal content separate the sediment into various grain-size fractions and then analyze one particular fraction. Questions arise as to which size fraction is the the best to use. Some choose <60 μ as this covers the non-sand or "mud" fractions. It is argued by Ackermann *et al.* (1983), that the <20 μ fraction is best, while deGroot & Allersma (1975) choose the <16 μ one. An investigation of heavy metals in sediments from Spencer Gulf, Australia by Dossis and Warren (1980) not only separated the fractions by size but also by density through the use of high specific gravity liquids such as bromoform. This was done in order to determine the contribution of trace metals by the metal-rich, so-called "heavy minerals" such as zircon, ilmenite etc.

Physical separation of grain size fractions was applied to only one core in this study, FDHM-9. Two fractions were chosen, <63 μ or "mud" and >63 μ i.e. sand. It was found (see Chapter 4) that there was a good positive correlation between the <63 μ fraction and rubidium and between each of these and the target heavy metals.

^{137}Cs DATING

In order to establish dating control for estimating sediment ages and sedimentation rates, it was decided to attempt ^{137}Cs dating.

^{137}Cs is a synthetic radioisotope of cesium and was produced and released in relatively large quantities during the 1950's and 1960's by large scale atmospheric testing of thermonuclear weapons. The ^{137}Cs was spread non-uniformly about the earth by stratospheric winds. Geographically, concentrations have been found to be highest in the Northern Hemisphere, particularly at higher latitudes (De Jong *et al.* 1982). ^{137}Cs concentrations in soil appear to be enhanced by precipitation (De Jong *et al.* 1982). Since this study covers a relatively small geographic area having a regular, flat topography and uniform climate it is assumed that an even distribution of ^{137}Cs has occurred.

^{137}Cs has a half-life of 30 years. The gamma radiation (the energy of which is unique to a given isotope) resulting from its decay can be detected and counted and used as a good approximate measure of the amount of ^{137}Cs present in a given sample. Because it is man-made (cesium has only one naturally occurring isotope and this a non-radioactive one) and the periods of its peak levels of output are well known within close limits, it becomes potentially valuable as a marker for recent geomorphologic and geologic events. For example, the highest levels occurred in the early 1960's particularly in 1963 (Koide *et al.* 1979). If we were to find a peak within a core at, for example, 20 cm depth then we could reasonably assume that 20 cm of sediment had accumulated since 1963 giving an average sedimentation rate of approximately 0.7 cm a^{-1}. In this study, ^{137}Cs was counted in samples taken at successive 2 cm intervals down the core, which were the same invervals used for the XRF heavy metal analysis. Samples were drawn from the same stock as had been used for the XRF analysis, therefore, sample preparation was necessarily the same as that for XRF analysis. Unlike the pellets for XRF analysis however, larger, 5 g pellets of 19 mm (0.75 in) were used in order to reduce the counting time and they were formed by 9.4×10^4 kPa pressure. These pellets were then each subjected to a gamma radiation count using a germanium-lithium (Ge-Li) detector. The apparatus consists of a lead "castle" which prevents any background radiation from being counted, and a detector within the castle upon which is set the a lucite pellet-holder containing sample

pellet. The Ge-Li detector is immersed in liquid nitrogen in order to enhance its conductivity. The counts are recorded by a computer which uses the Nucleus PCA-II© program to change the counts into radiation peaks. Counting in most cases was carried out for 300,000 sec, (about 3.5 days.). Exceptions were made in cases where a sample could not be counted owing to a dearth of material. In such cases, the samples in the column adjacent to those with insufficent material were counted for a longer time, usually about 600,000 secs. While the counting is taking place, the emissions of an electronic pulser are also being counted. Thus, we can normalize the radiation count of ^{137}Cs emissions either to the number of seconds counted or to the number of pulses emitted by the electronic pulser.

Analysis of Age Data

The radiation data are counted and stored by the Nucleus PCA-II© program. Time also is kept and counted by the computer, both as regular time and by pulses produced by an electronic pulser. The counts acquired must be normalized to the length of time during which counting has taken place. This is done by dividing the radiation counts by either the clock time or the number of pulses. In this study clock time was used in order to express the results as counts per unit time. Two other calculations are also performed: The ratio of ^{137}Cs to ^{40}K (potassium-40) is calculated because of their similar chemical and physical behaviour (Davis, 1963) and a correction is made for the radioactive decay of ^{137}Cs (half-life 30 yrs). In order to accomplish these calculations, the raw count data are copied into a Lotus 1-2-3® spreadsheet for processing. As well as performing these calculations, this program can also plot the data as graphs.

CHAPTER 4

DATA AND RESULTS

INTRODUCTION

Recall that a total of twelve cores were extracted. Nine of these are from the area which is the focus of this thesis, the North Arm of the Fraser River. Two are from Fraser River sloughs at the eastern end of the Fraser Valley and an additional one was obtained from Fraser Delta delta-front sediments (Figures 1.1, 1.1a, b and c). These last are for comparison with those extracted along the North Arm.

In the following descriptions the cores from Musqueam Marsh and the others from the North Arm of the Fraser will be dealt with first, followed by the two from the Upper Fraser Valley and concluding with the one taken on the delta front. In addition to tables and figures each core is discussed under at least two subheadings; "Lithology" and "Heavy Metals" and where applicable, a third, "Cesium-137".

When discussing mean differences in heavy metals concentrations among the cores under "Heavy Metals" it should be noted that these differences might be more real than apparent and this question is addressed at the end of the chapter.

For an explanation of symbols used in the core drawings refer to the symbol key (Figure 4.1). Cores are referred to in the text by their full code designation e.g., "FDHM-14".

N.B.: It is important to remember, when examining the various graphs of heavy metals, that because the graphs are all of equal width and length, the differences in the relative amounts of metals (zinc, for example, is typically about an order of magnitude greater than lead) and in core depth effectively change the scales of the graph from metal to metal and core to core. This means that the graphs give better resolution for lead than for zinc and for shorter

rather than longer cores. Also note that heavy metal concentrations shown on the graph are the absolute concentrations, the normalization to rubidium and baseline values is examined near the end of the chapter.

Rubidium has been included because its ubiquity in clay minerals permits it, as outlined earlier, to be used to normalize the heavy metal concentrations which are likely to be anthropogenically enriched.

Iron is also included because iron and manganese oxides, as also noted earlier, often form a physico-chemical barrier to other trace metals by adsorbing them.

Key

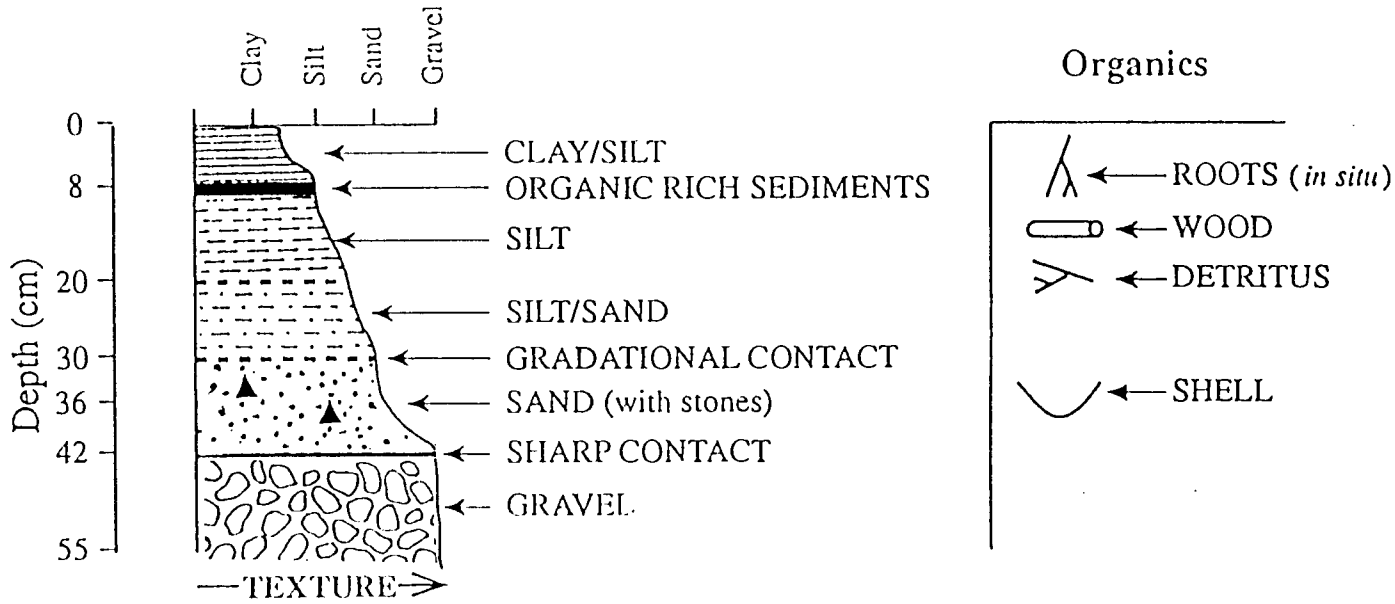


Figure 4.1 Key to symbols used in core drawings.

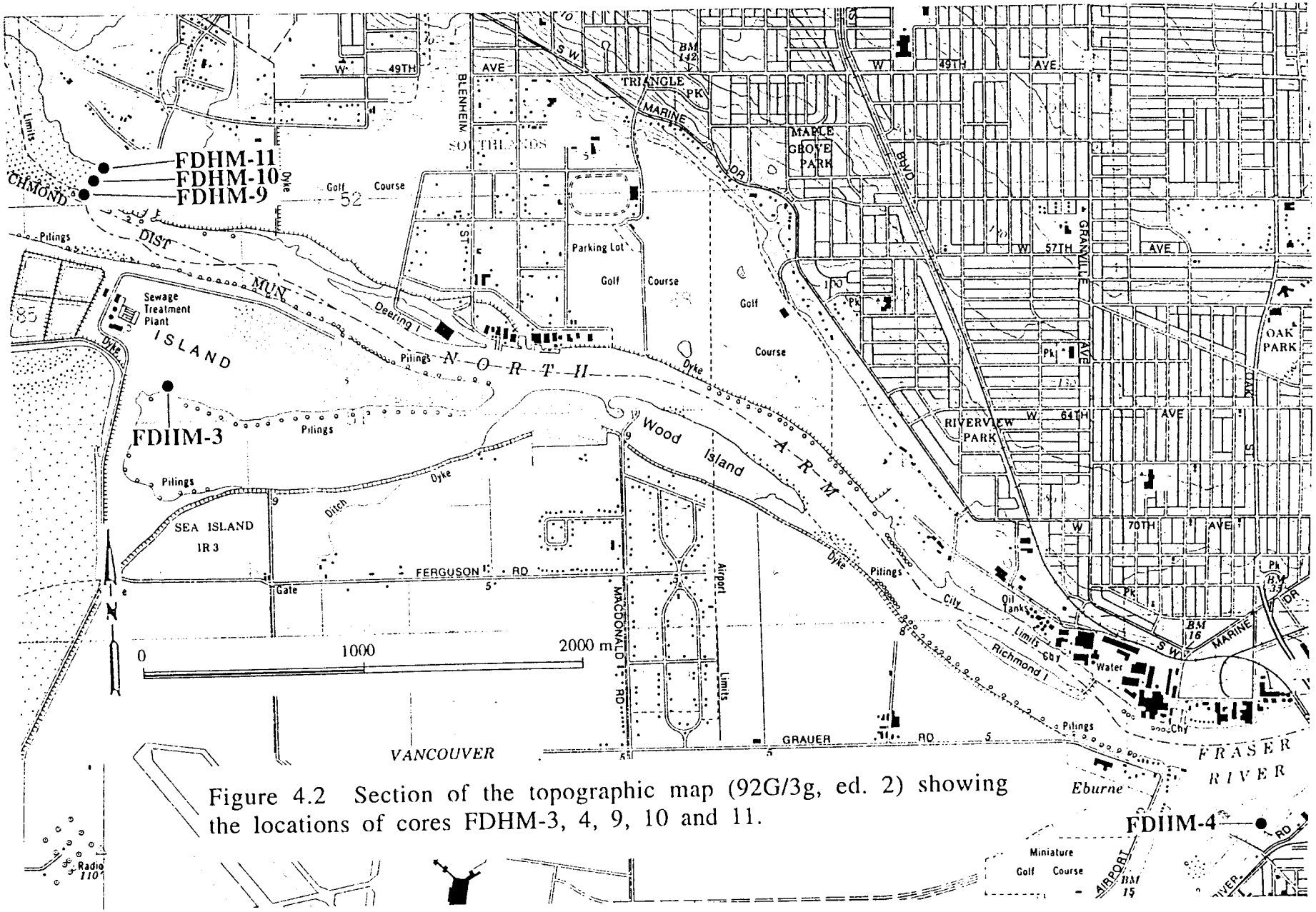


Figure 4.2 Section of the topographic map (92G/3g, ed. 2) showing the locations of cores FDHM-3, 4, 9, 10 and 11.

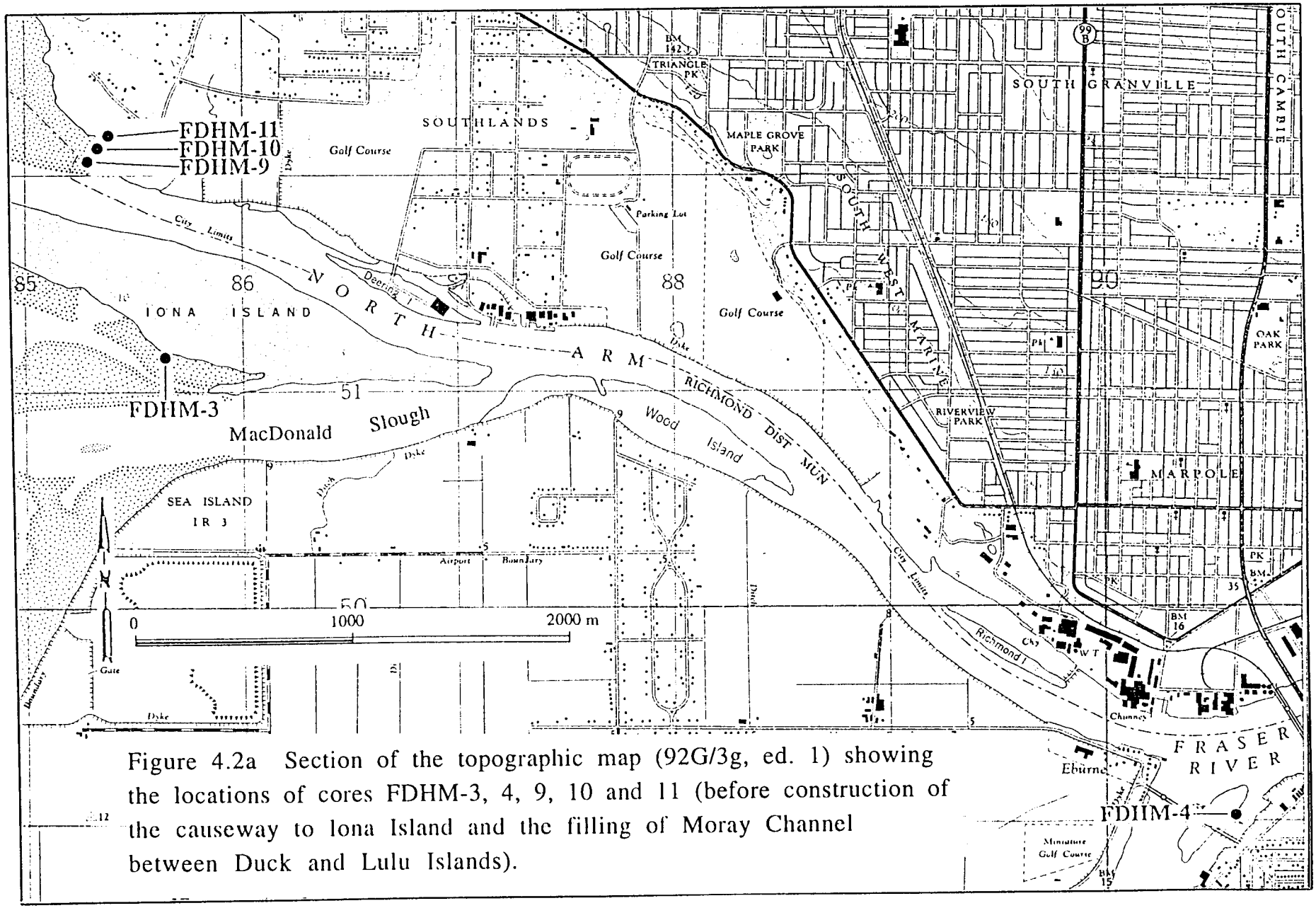


Figure 4.2a Section of the topographic map (92G/3g, ed. 1) showing the locations of cores FDHM-3, 4, 9, 10 and 11 (before construction of the causeway to Iona Island and the filling of Moray Channel between Duck and Lulu Islands).

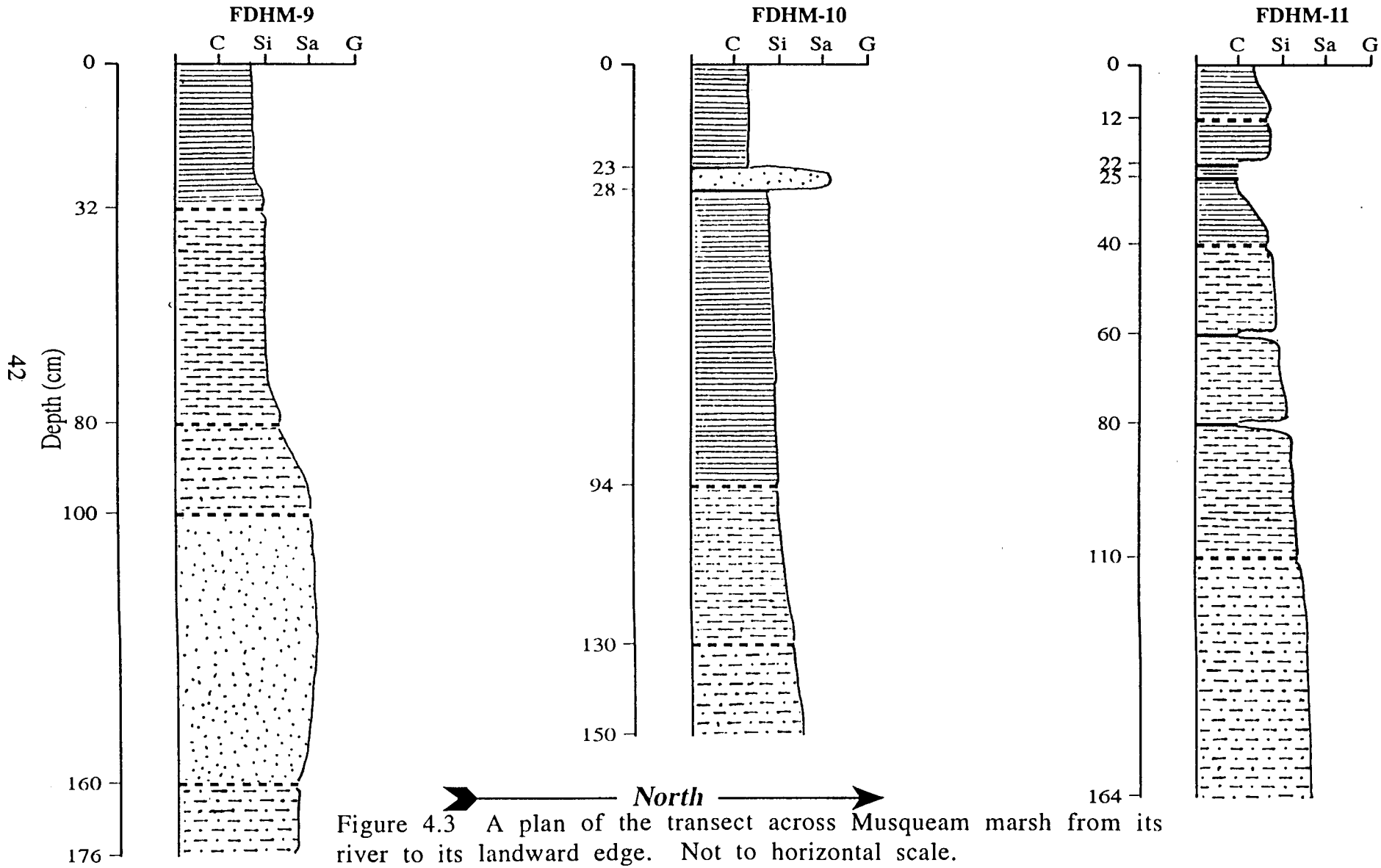


Figure 4.3 A plan of the transect across Musqueam marsh from its river to its landward edge. Not to horizontal scale.

Figure 4.4 Musqueam Marsh from its landward edge.

CORE DESCRIPTIONS

Musqueam Marsh Cores: FDHM-9, 10 and 11

These cores were extracted in a transverse line across the marsh (Figures 4.2 or 4.2a). A cross section of this transect appears in Figure 4.3. Musqueam Marsh was chosen as a site to extract these cores because it is an apparently undisturbed ribbon marsh (Figure 4.4), on the lowermost reach of the river, 4.7 km upstream from its mouth on the Gulf of Georgia and has no obvious point sources of heavy metal contamination.

Core: FDHM-9

Lithology: Core FDHM-9 was extracted immediately adjacent to the river on the south edge of the marsh (Figures 4.5 and 4.6 and Figures. 4.7 to 4.10). It reveals the sort of fining upwards sequence expected in fluvial overbank sediments. The lower part of the core from the bottom upwards to a depth of 100 cm is dominated by sand, which contains, in its lower reaches, considerable shell hash indicating that the overbank facies has succeeded a tidal flat environment. From 100 cm to the surface the core is dominated by increasingly fine silt and clay. From a depth of 55 cm to the surface, the core contains considerable organic debris. This debris is capped by *in situ* roots at and near the surface. The core pictured in Figures 4.7 to 4.10 is a duplicate core obtained at a later date because the original had been partially destroyed by the sampling process. Table 4.1 shows the weight proportions of sand and fines in the core sediments from top to bottom.

Heavy Metals: Figure 4.5 shows the level of heavy metals found in FDHM-9: The highest concentrations of metals are present in the top sediments and are associated with the finer fraction of the sediment. The most variation in the levels of any of the heavy metals is shown by those of lead with a Coefficient of Variation (C.V.) of 46% followed closely by that of copper, with 44% (Table 4.1).

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	2.72	4.74	3.50	0.51	14.48	84	1
Cu (ppm)	3.78	48.22	27.36	12.07	44.11	71	14
Zn (ppm)	50.66	146.34	91.11	27.29	29.95	83	2
Pb (ppm)	2.98	22.29	11.16	5.09	45.64	84	1
Rb (ppm)	41.18	91.59	66.01	16.16	24.49	80	15

Table 4.1 Descriptive statistics of heavy metals in FDHM-9.

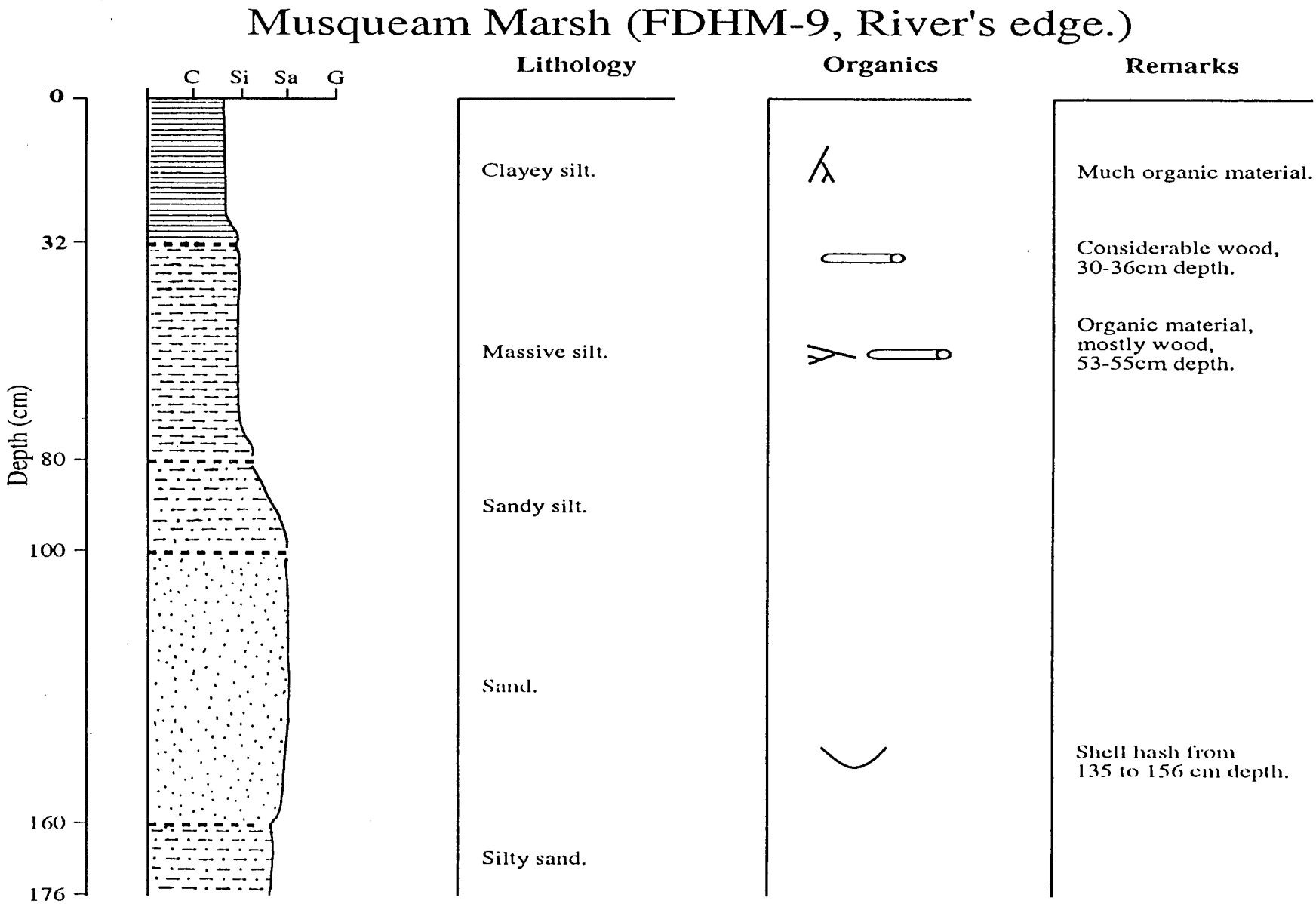


Figure 4.5 Log of the core extracted from Musqueam Marsh immediately adjacent to the bank of the river..

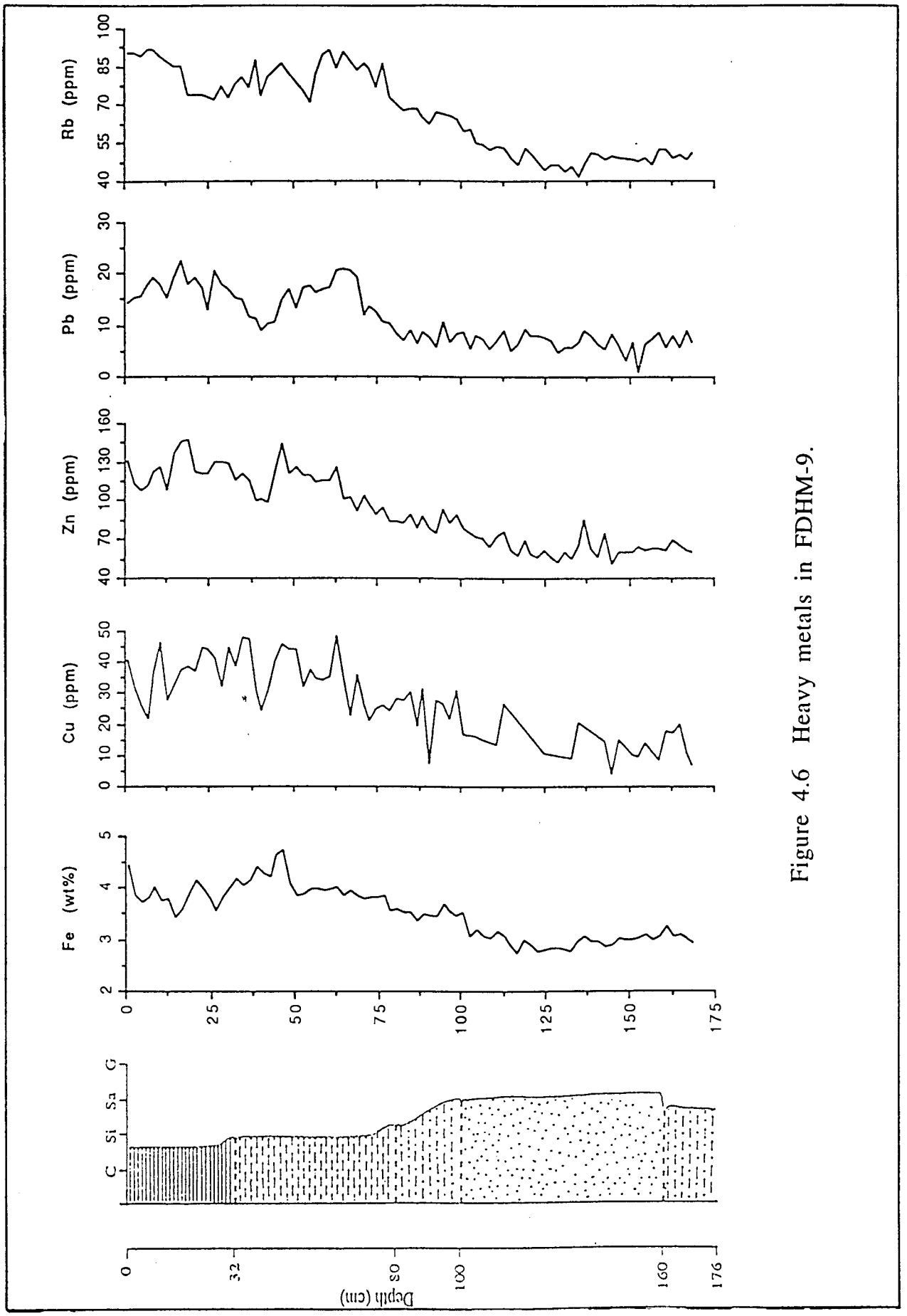


Figure 4.6 Heavy metals in FDHM-9.

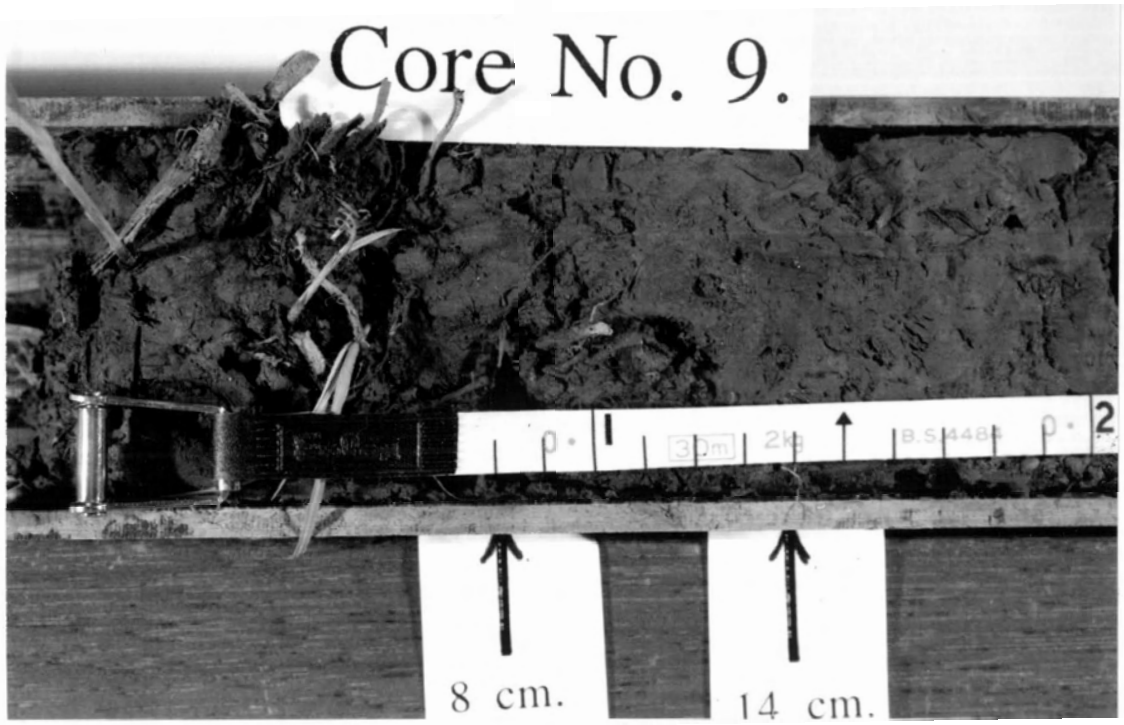
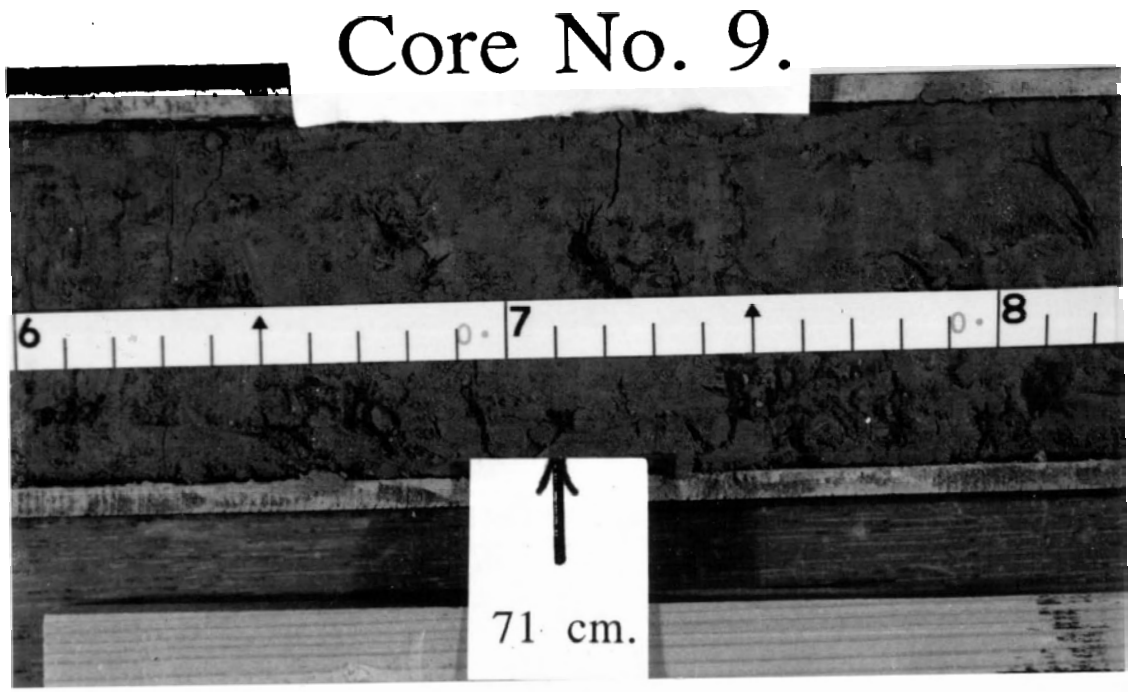


Figure 4.7 The uppermost 8 cm of the core consists mostly of undecayed plant matter, while from 8 to 14 cm depth it is formed of an organic rich silty clay.

Figure 4.8 From 14 to 71 cm the core consists of silt with a fine network of partially decayed plant matter.



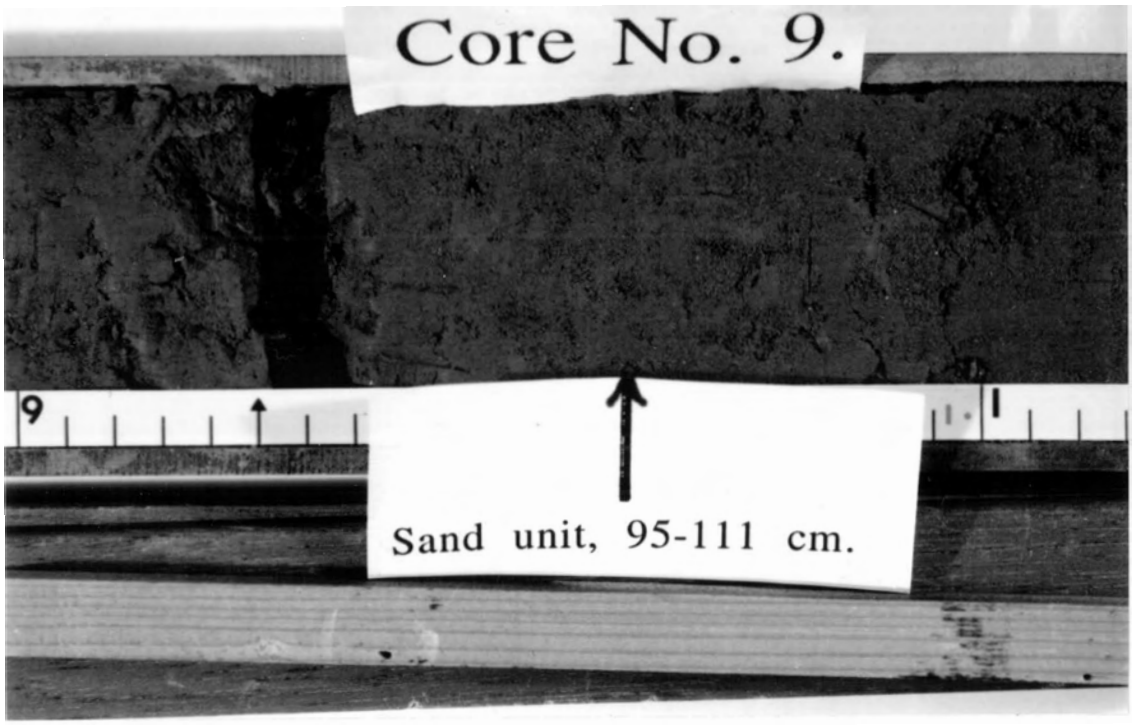
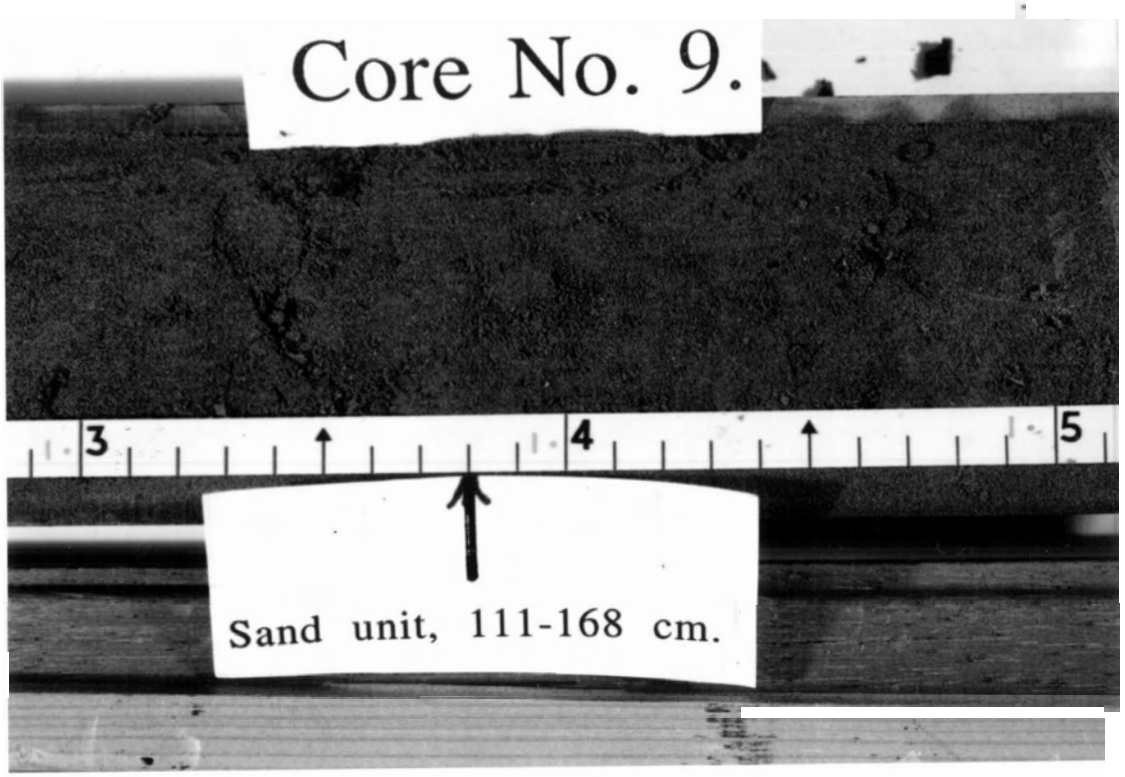


Figure 4.9 From a depth of 71 to 95 cm the core is made up of clayey silt with sand and partially decayed plant matter. From 95 to 111 cm depth there is a unit of silty sand including scattered, partially decayed plant matter.

Figure 4.10 The lowermost part of the core grades to silty and finally to medium sand.



Core: FDHM-10

Lithology: This core was extracted from Musqueam Marsh about half-way between the river bank and a low scarp-like embankment which marks the begining of the upland area on the landward side of the marsh (Figures 4.2 and 4.3). It is lithologically similar to FDHM-9 in that it represents the same sort of fining upwards sequence (Figure 4.11), with the noteworthy exception of a sand bed between 23 and 28 cm depth. In the case of FDHM-10 however, the silt/clay layer is 94 cm in thickness compared to 32 cm for that of FDHM-9. The core has a very uniform gradation from sandy silt upwards to silty clay. This no doubt reflects two factors linked to its distance from the river: less agitated tidal inundations and a thicker ground vegetation which both traps the finer sediments and reduces erosion (Randerson, 1979).

Heavy Metals: Metal levels are highest in the top 23 cm of the core (Figure 4.12), although copper shows a secondary concentration from 40 to 50 cm depth. Copper, with a CV of 48.86% (Table 4.2), shows the greatest variability of all the metals, a pattern that is repeated in most cores. There is a pronounced drop in the concentration of four of the five metals coincident with the 5 cm layer of sand beds. This well illustrates the lower affinity of the metals with the coarser fraction of the sediments.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	2.45	4.01	3.30	0.34	10.37	75	0
Cu (ppm)	3.52	47.31	22.04	10.77	48.86	73	2
Zn (ppm)	54.00	260.56	83.85	28.78	34.49	75	0
Pb (ppm)	3.49	22.31	10.68	4.18	39.10	75	0
Rb (ppm)	43.36	113.19	65.91	16.83	25.54	71	4

Table 4.2 Descriptive statistics of heavy metals in FDHM-10.

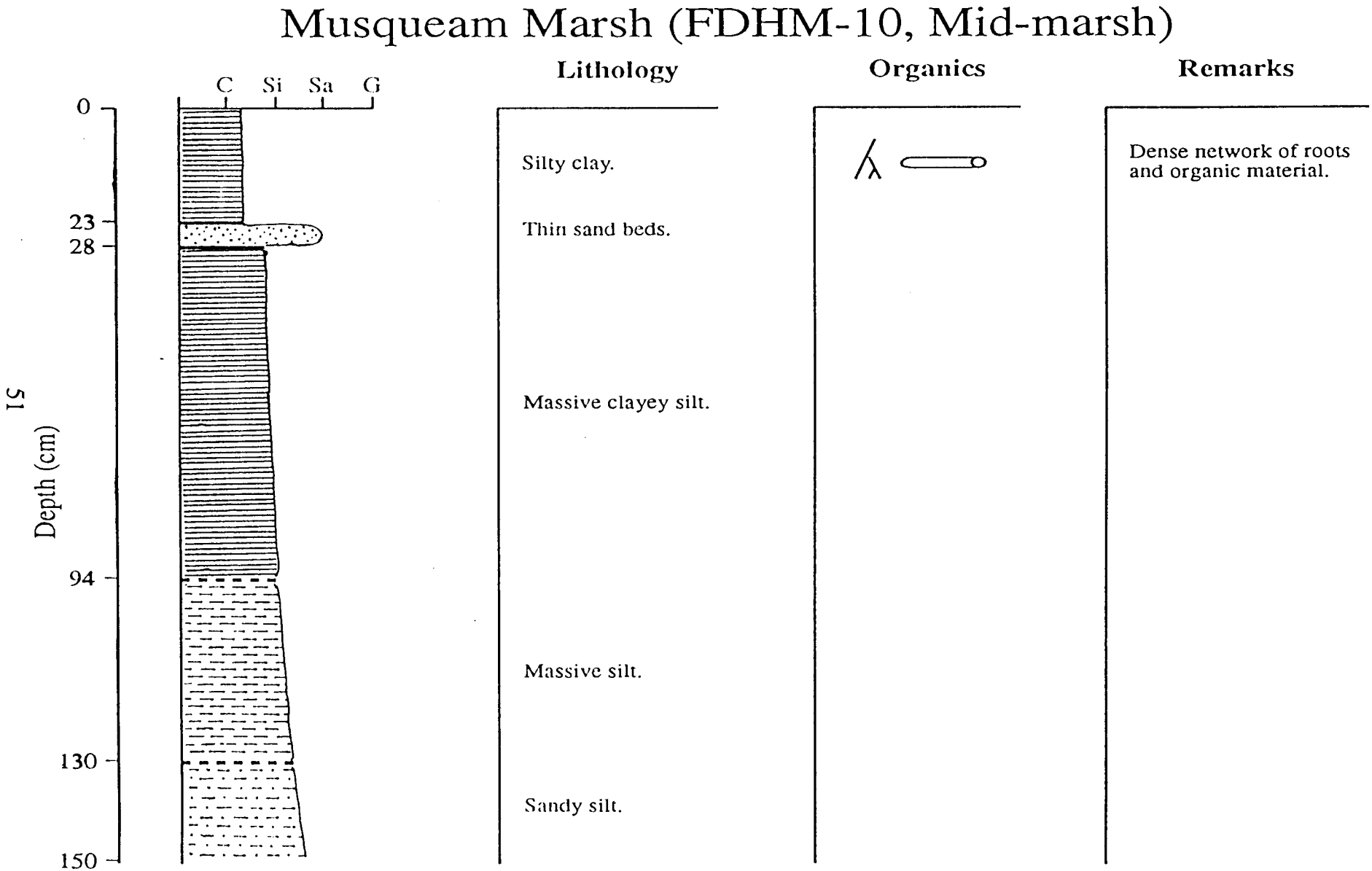


Figure 4.11 Log of the core extracted from Musqueam Marsh, 100 m from the river bank.

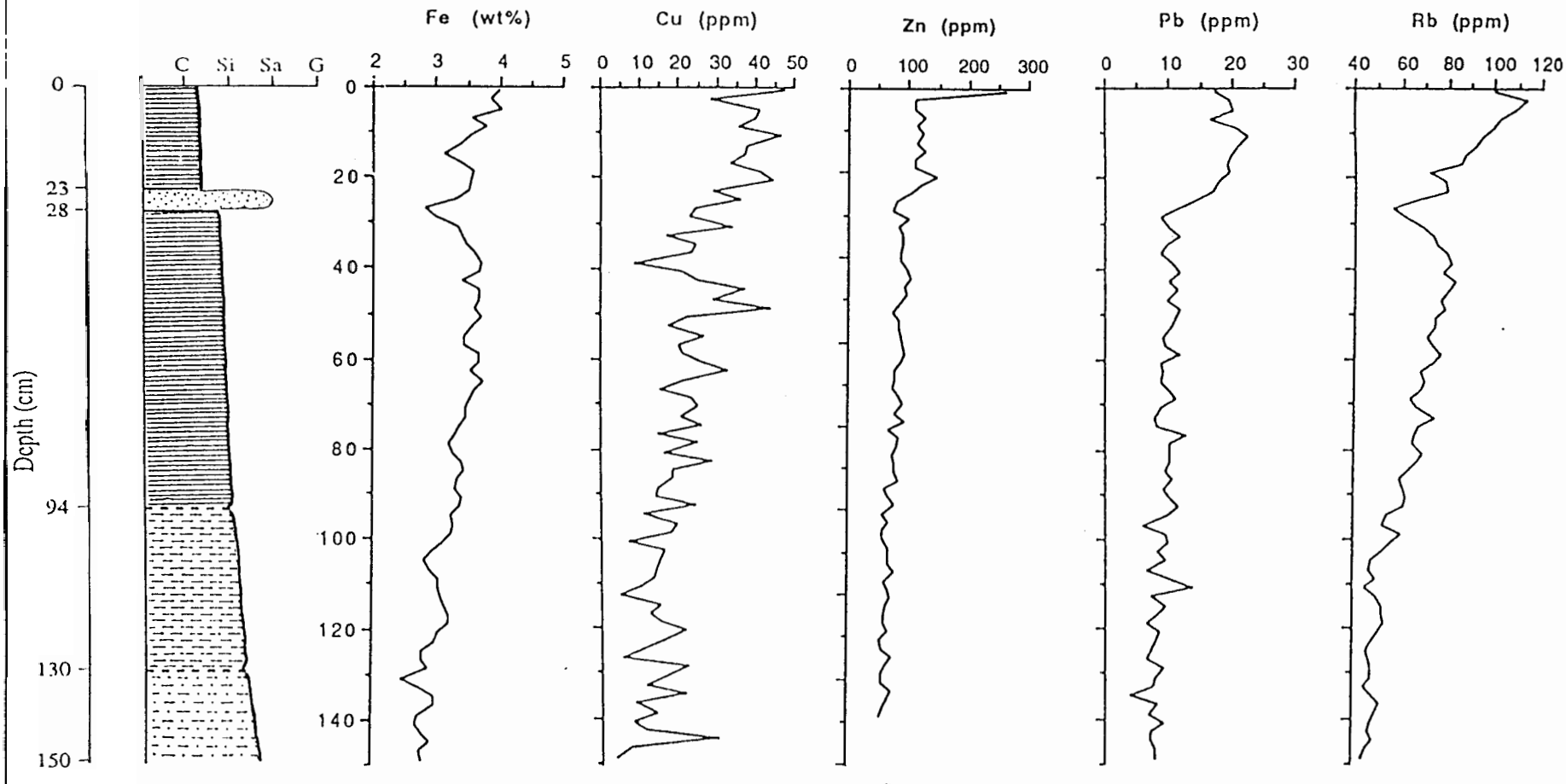


Figure 4.12 Heavy metals in FDHM-10.

Cesium-137: FDHM-10 is one of three cores from which sediment samples were used in order to determine variations in radiation of the energy level associated with ^{137}Cs decay and if and how these variations relate to depth (Figure 4.13). In order to establish a base line of radiation counts, a sample taken from a core extracted beside Gilley Road, located on the east side of the Delta (Figures. 2.1a, 4.47), was counted. Since the sample was taken from a part of the core directly above a layer of Mt. Mazama ash, which has been dated at 6800 yr BP, we can be confident of having a sediment sample virtually that old and free of ^{137}Cs which has only appeared in the last five decades.

There is a very definite peak in the counts at about 23 cm depth, with a another, lesser one directly above it at 12 cm, and one, possibly two, lesser peaks below it, at 30 and 34 cm depth. The highest peak appears to coincide with the top of the sand bed. The summary statistics for ^{137}Cs counts for FDHM-10 are shown in Table 4.3.

Min	Max	Mean	St D	C V (%)	Count	Miss
66	785	292.00	188.89	64.69	23	2

Table 4.3 Descriptive statistics of ^{137}Cs in FDHM-10

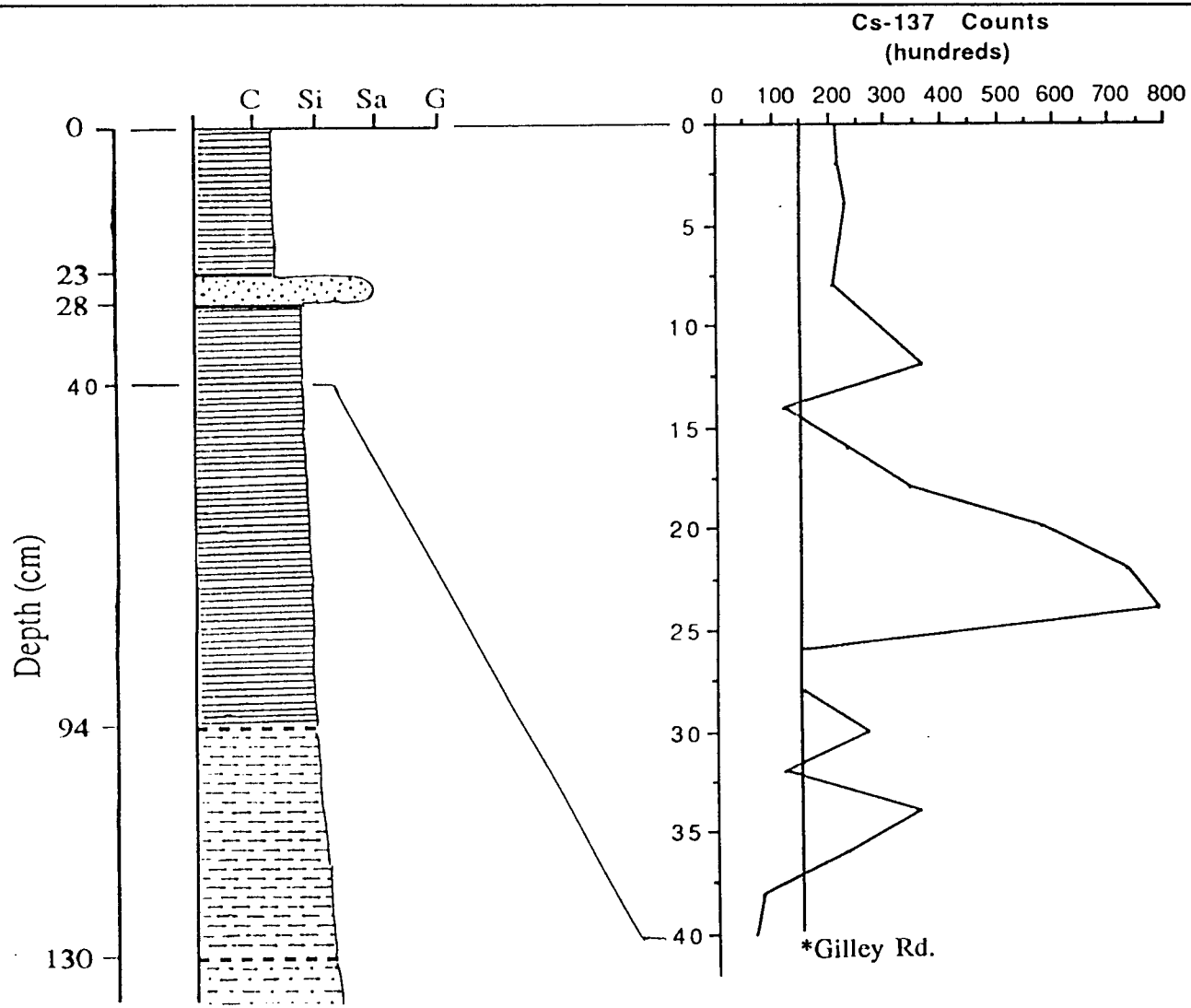


Figure 4.13 Cesium-137 counts from a part of FDHM-10.
*The line marked "Gilley Rd." represents the count of a sediment sample from among those of the Gilley Road core. This sample was extracted from that part of the core immediately above the Mt. Mazama ash layer.

FDHM-11

Lithology: This core is the most landward of the three cores taken (FDHM-9, 10 and 11) from Musqueam Marsh (Fig 4.3). Its log (Figure 4.14) is similar to both FDHM-9 and 10 in having a fairly uniform upward fining sequence. However, it differs slightly from the pattern of the other two, in that the overall sequence is interrupted at three different depths in the silt by thin clay beds. One might expect that being the most landward it, rather than FDHM-9 or 10, would have the thickest stratum of silt/clay, but this is not the case. The site of FDHM-11 is more densely vegetated than those of either FDHM-9 or 10, but no doubt this greater capacity to trap sediment is offset by reduced tidal inundation (Randerson, 1979).

Heavy Metals: Metal levels are highest in the top 40 or so centimeters of the core (Figure 4.15), with a distinct rise between 25 and 40 cm depth. A distinct dip in iron, copper and zinc values is apparent between approximately 40 and 60 cm depth. There are three spikes in rubidium values at depths of approximately 60, 140 and 155 cm. Recalling the association between rubidium and clay, the spike at about 60 cm depth is likely attributable to the the clay bed at this same depth, while the two at 140 and 155 cm are most likely a result of the clay balls found throughout the core from a depth of 110 to 164 cm.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	2.93	4.08	3.39	0.26	7.63	82	0
Cu (ppm)	4.31	45.41	21.95	9.43	42.95	78	4
Zn (ppm)	55.95	131.25	80.51	16.91	21.00	82	0
Pb (ppm)	4.26	38.17	11.05	4.85	43.89	80	2
Rb (ppm)	48.31	257.07	71.24	32.24	45.26	82	0

Table 4.4 Descriptive statistics of heavy metals in FDHM-11.

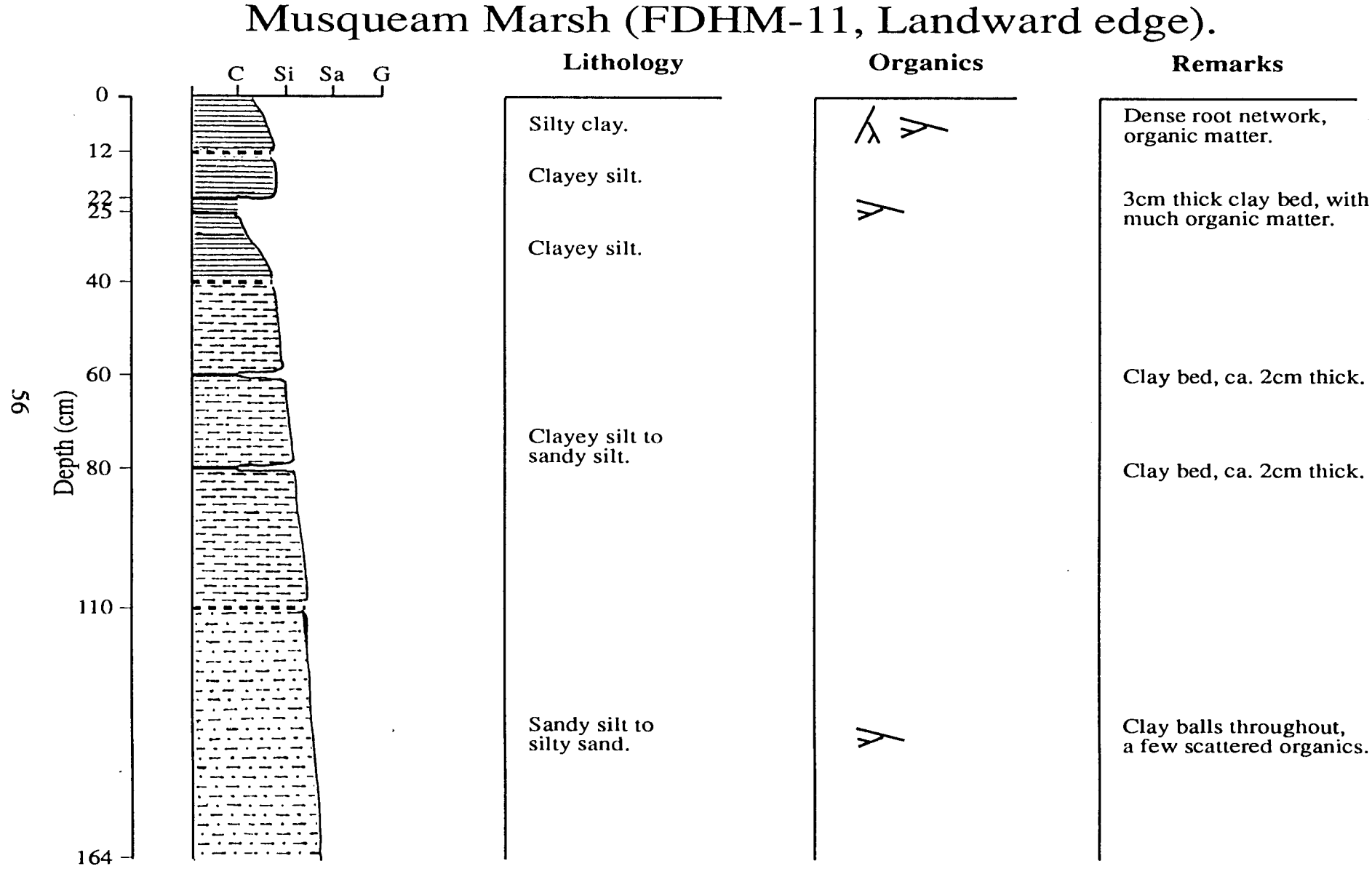


Figure 4.14 Log of the core extracted from the landward edge of Musqueam Marsh.

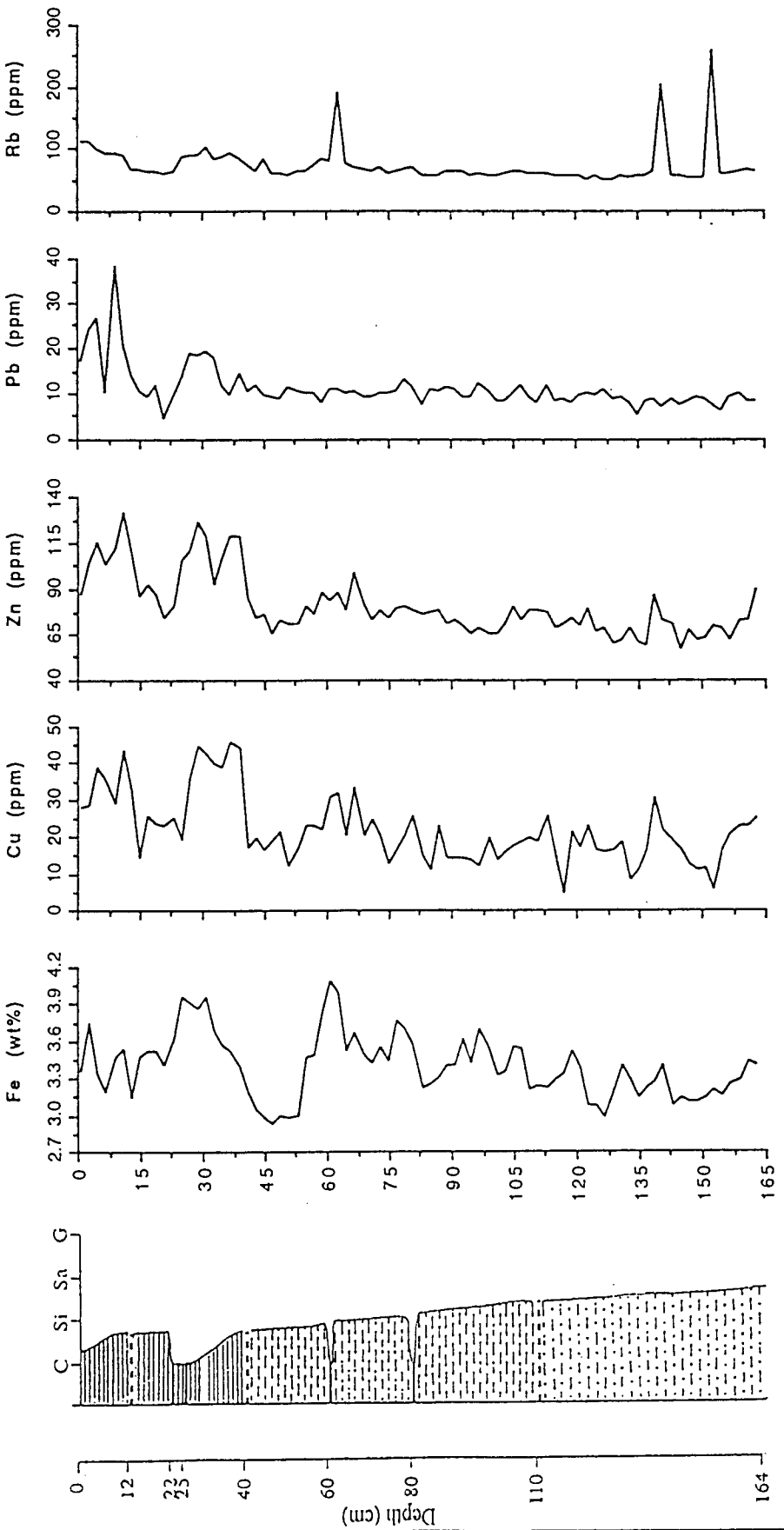


Figure 4.15 Heavy metals in FDHM-11.

North Arm Cores: FDHM-3, 4, 5, 6, 7 and 8

Core: FDHM-3

This core was obtained from from a branch of the North Arm called McDonald Slough which lies between Iona Island and Lulu Island (Figure 4.2). This slough once connected directly with the Gulf of Georgia but was cut-off from it by construction of the causeway to service the Iona Island Sewage Treatment Plant *ca.* 1961 (Compare the map in Figure 4.2 with an earlier edition of the same map shown in Figure 4.2a).

The core site was a marsh located on the the north bank of the slough, about 75 m east of the Iona Causeway road. This core was the longest one obtained in this study. The fining upward sequence was interrupted on two occasions by periods of deposition of coarser material.

Lithology: From the bottom of the core upwards, (Figure 4.16) this is a typical fining upwards sequence like that found in each of the cores from Musqueam Marsh. From 90 up to 70 cm depth the sediment suddenly coarsens upward somewhat. Then above 70 cm it resumes fining upward, until 35 cm depth, where it once again begins to coarsen upwards.

The core, shown in Figures 4.18 to 4.23, is a duplicate like the ones photographed for FDHM-9, 6, and 7. However, this duplicate core taken from the edge of McDonald Slough is generally similar to the first one (Figures. 4.16 and 4.18 to 4.23), with the exception of the layer of coarse material found at the top of the original core. Common to both are the laminae found in the lower one-third or so of the cores. These start out as sand laminae within finer sediment and end as laminae of fine sediment within sand just before the sediment changes completely to sand (Figures. 4.19 to 4.24). These fine laminae are associated by Johnston (1922) with tidal flood-plain sediments. These are not found to any extent in the other cores. This suggests that this lower part of the core represents a tidal-front environment which laterally migrated over a beach and was itself subsequently buried by overbank sediments.

Heavy Metals: A distinct dip in metal concentrations, associated with the 30 cm thick layer of silty sand, dominates the upper part of the core (Figure 4.17). The spike-shaped peaks in the levels of zinc and lead in the lowermost parts of the core (at a depth of 185 and 230 cm for zinc, 200 cm for lead) do not seem to represent a trend, but rather appear to be episodic in nature, being formed in every case by the result from one sample only.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	2.41	4.89	3.79	0.47	12.50	118	0
Cu (ppm)	6.91	56.25	29.41	9.51	32.32	108	10
Zn (ppm)	45.57	188.75	97.65	22.15	22.68	118	0
Pb (ppm)	5.52	42.07	12.10	4.85	40.12	115	3
Rb (ppm)	42.95	117.10	75.48	12.21	16.18	118	0

Table 4.5 Descriptive statistics of heavy metals in FDHM-3.

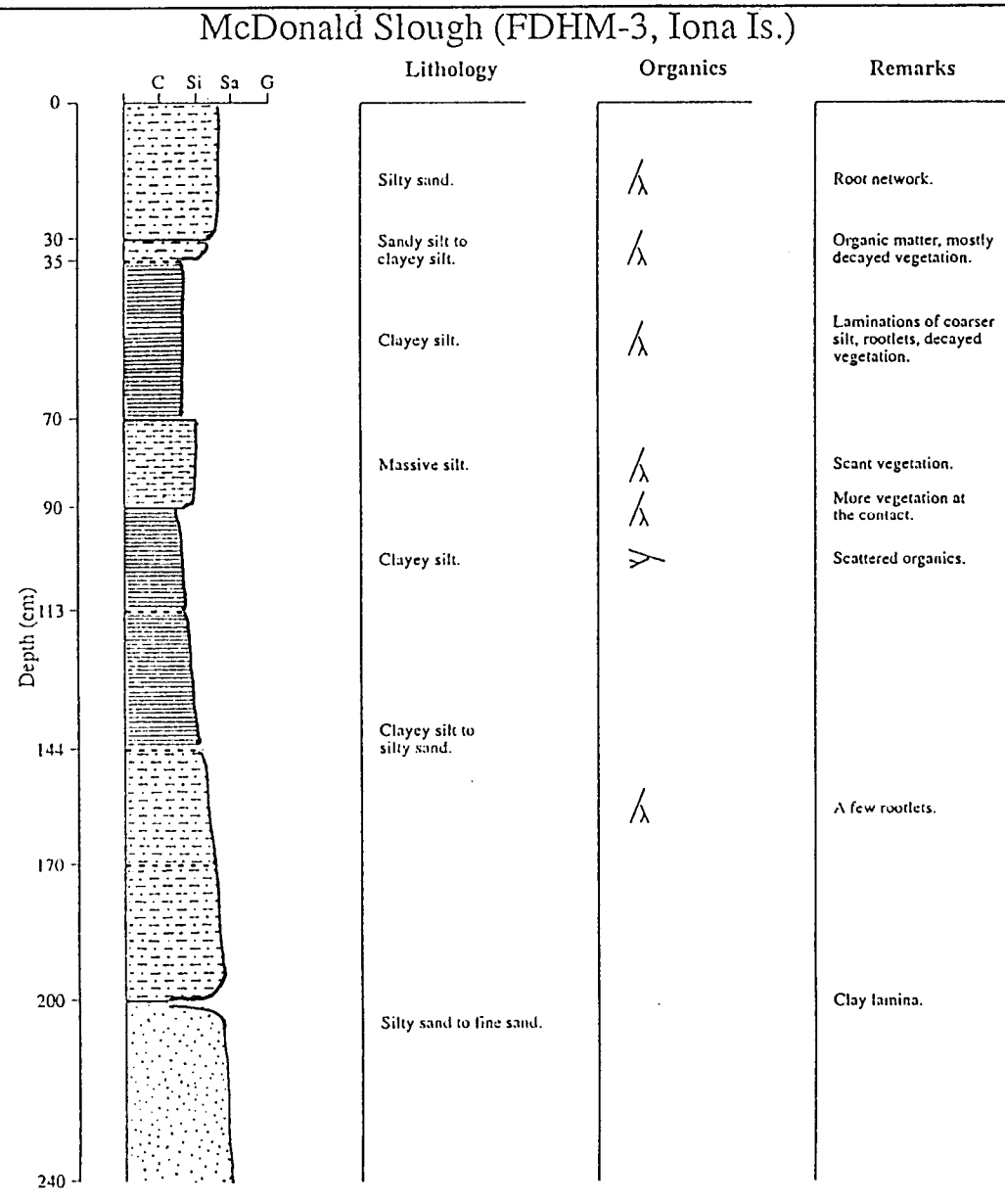


Figure 4.16 Log of the core extracted from McDonald Slough, on the Iona Island bank.

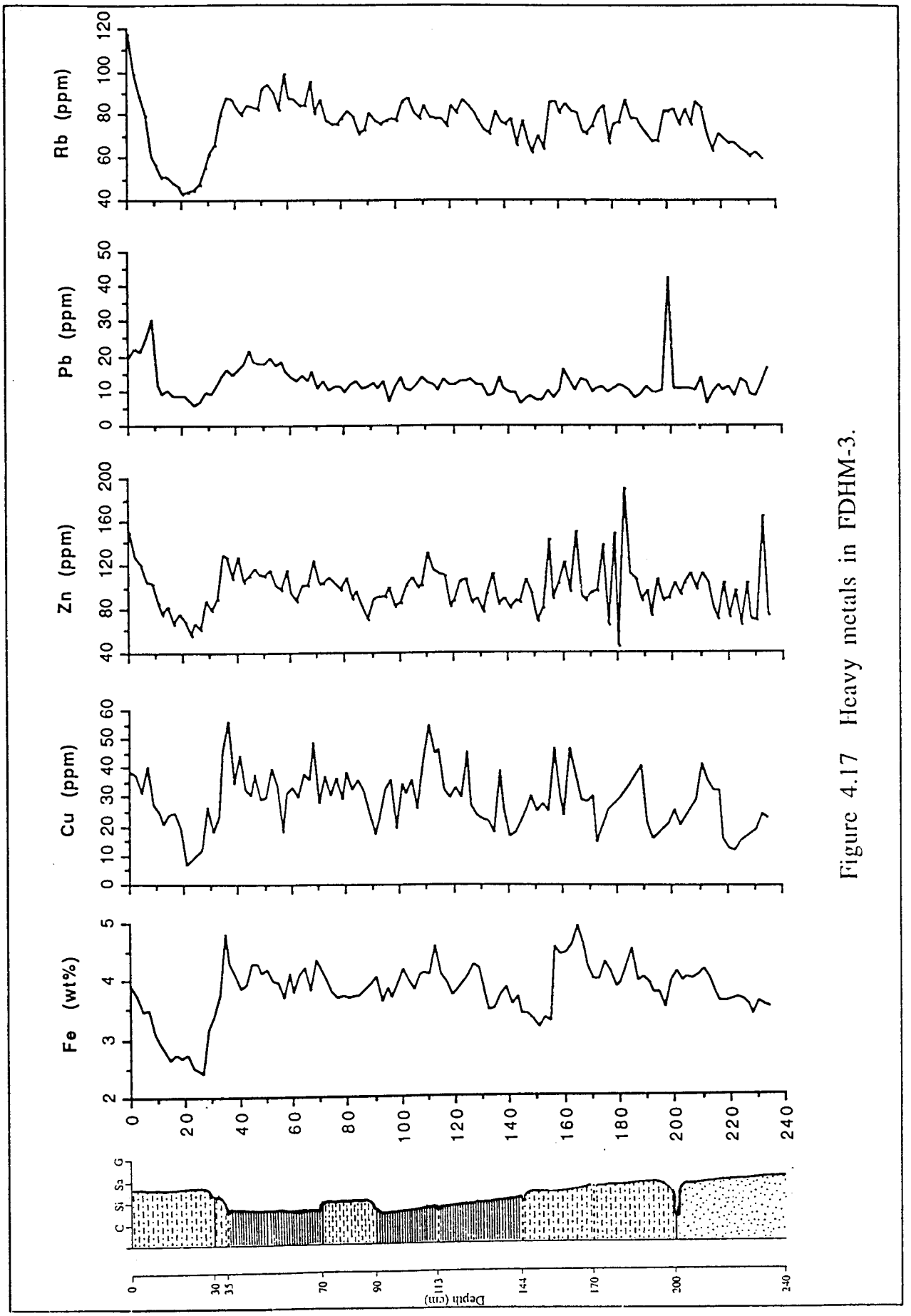


Figure 4.17 Heavy metals in FDHM-3.

Core No. 3.

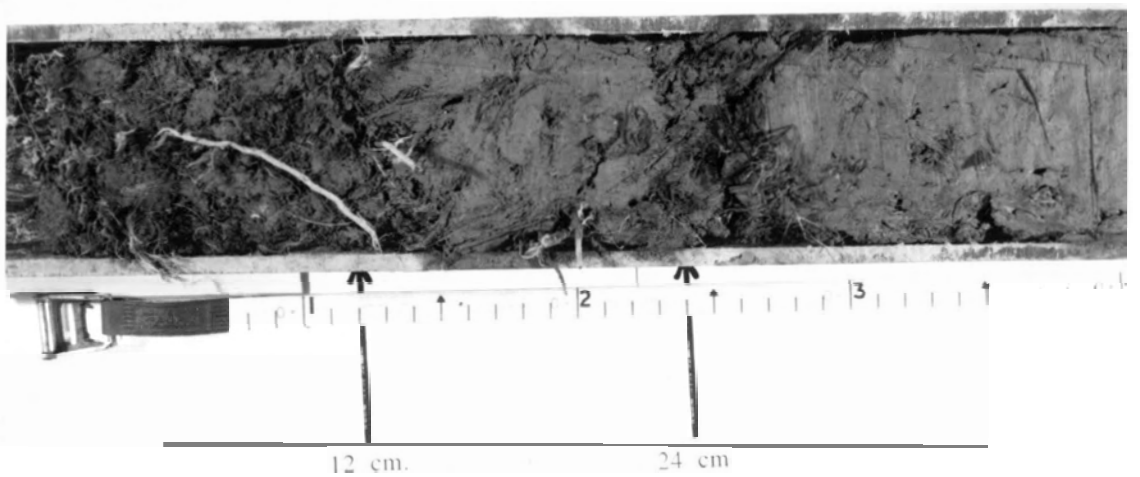
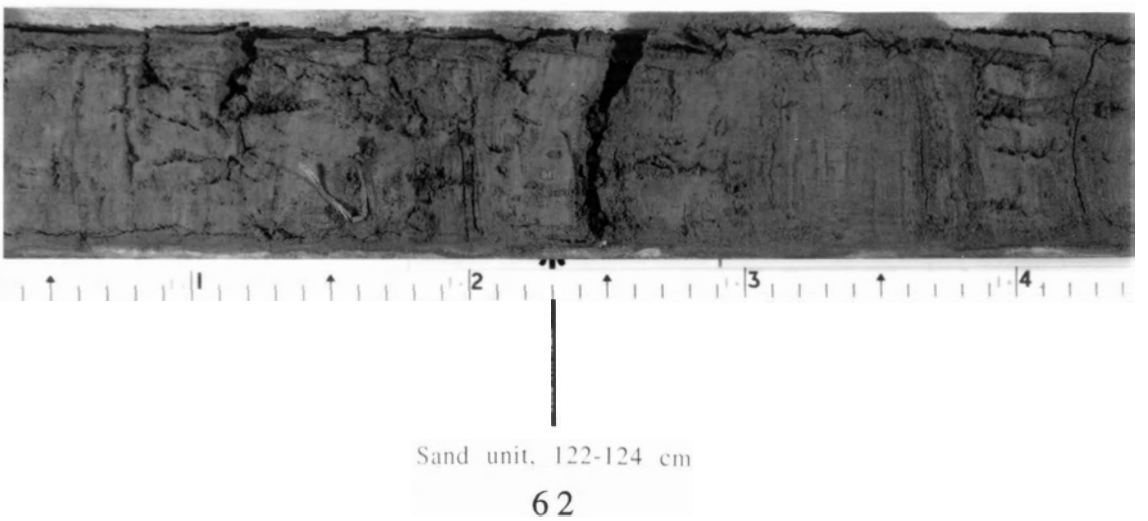


Figure 4.18 The top 12 cm of the core consists of clayey silt with a dense root network.

Figure 4.19 The silt coarsens downwards and contains fine sand laminae.

Core No. 3.



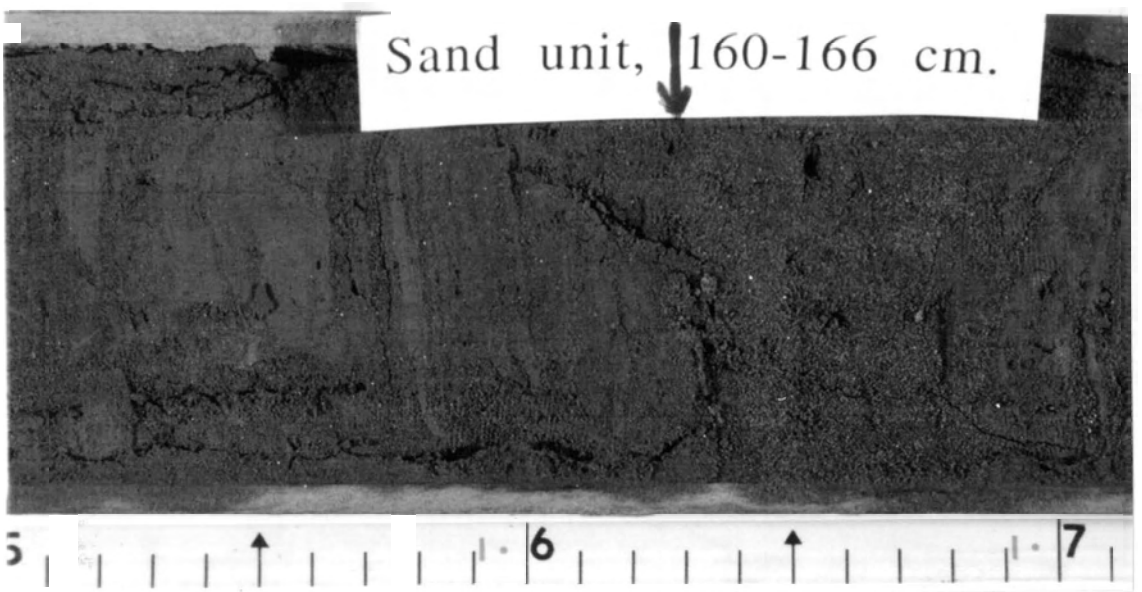
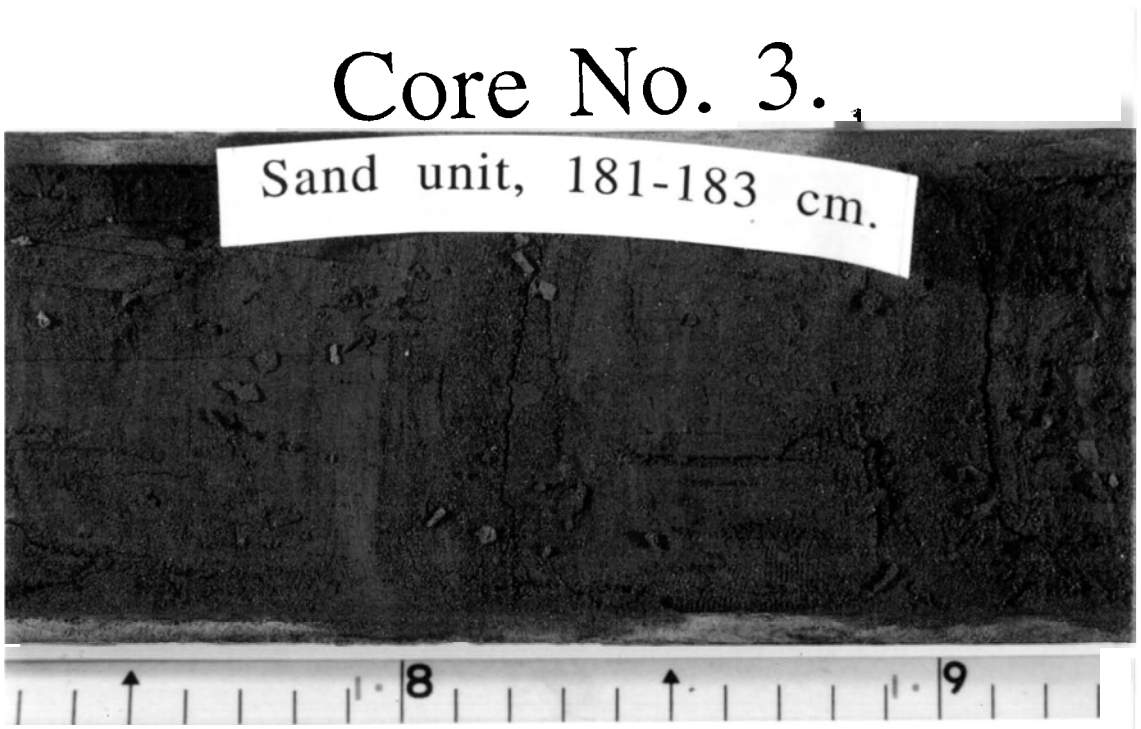


Figure 4.20 A sand bed extends from a depth of 160 to 166 cm.

Figure 4.21 Another sand bed extends from a depth of 181 to 183 cm.



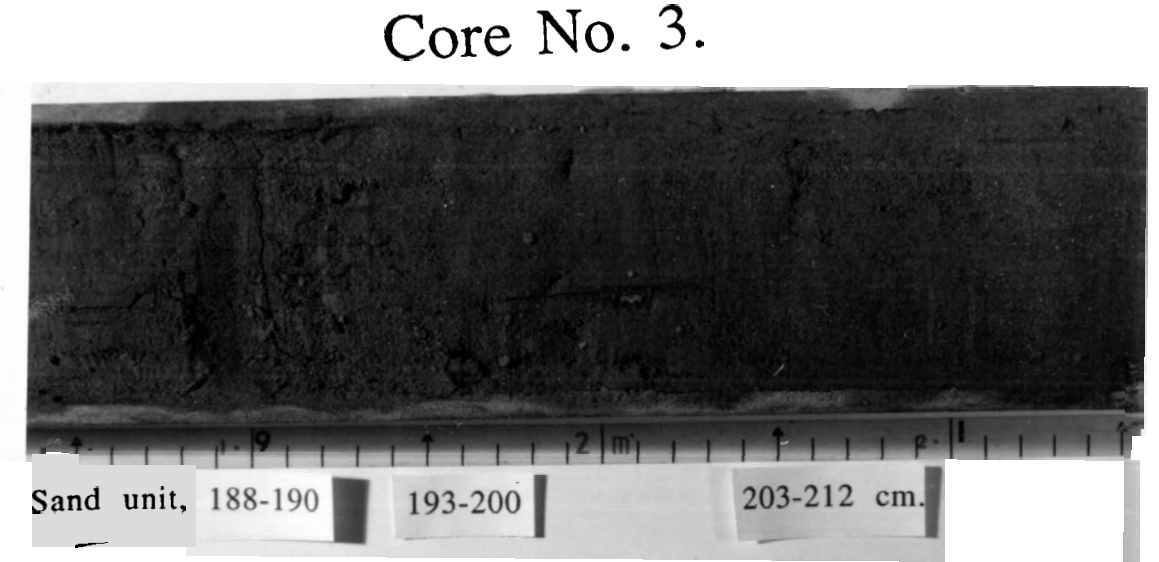
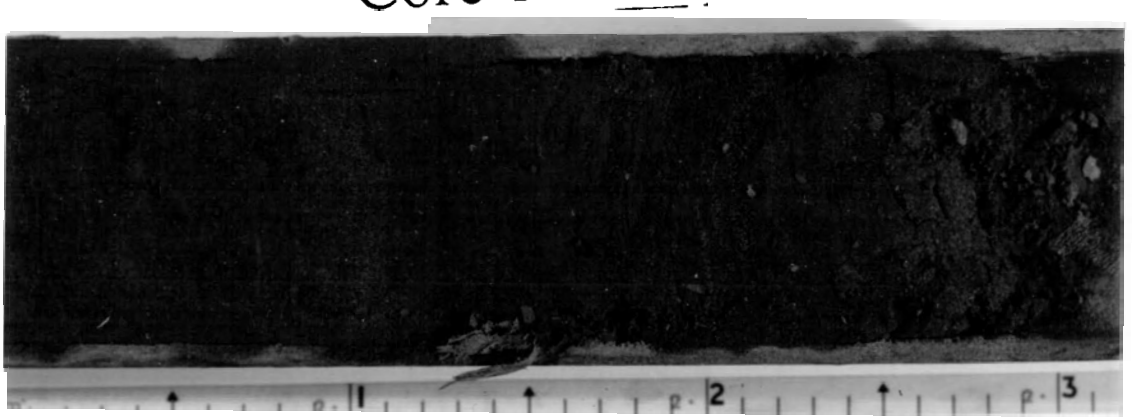


Figure 4.22 Sand beds and sand laminae become more frequent.

Figure 4.23 The core becomes predominantly sand with silt laminae finally grading entirely to sand.



Cesium-137: FDHM-3 was also investigated using ^{137}Cs counting (Figure 4.24). There is not nearly so definite a peak in these counts as there was in FDHM-10, with perhaps the exception of the one at 65 cm depth. The peaks at 78 and 87 cm depth are formed by individual sample counts in both cases and cannot be relied upon to represent an upward trend in ^{137}Cs at these depths. Counting was started much lower in the core with the idea of comparing two independent estimates of time, assuming that the change in sedimentation at 70 cm depth was attributable to the blocking off of McDonald Slough by the causeway. The maximum reading for this core, 584, is lower than both FDHM-10 at 785 and FDHM-8 at 1243. The two negative values can only be explained as a result of the computer processing of extremely low raw counts.

Min	Max	Mean	St D	C V (%)	Count	Miss
-85	584	243.96	163.14	66.87	24	0

Table 4.6 Descriptive statistics of ^{137}Cs in FDHM-3.

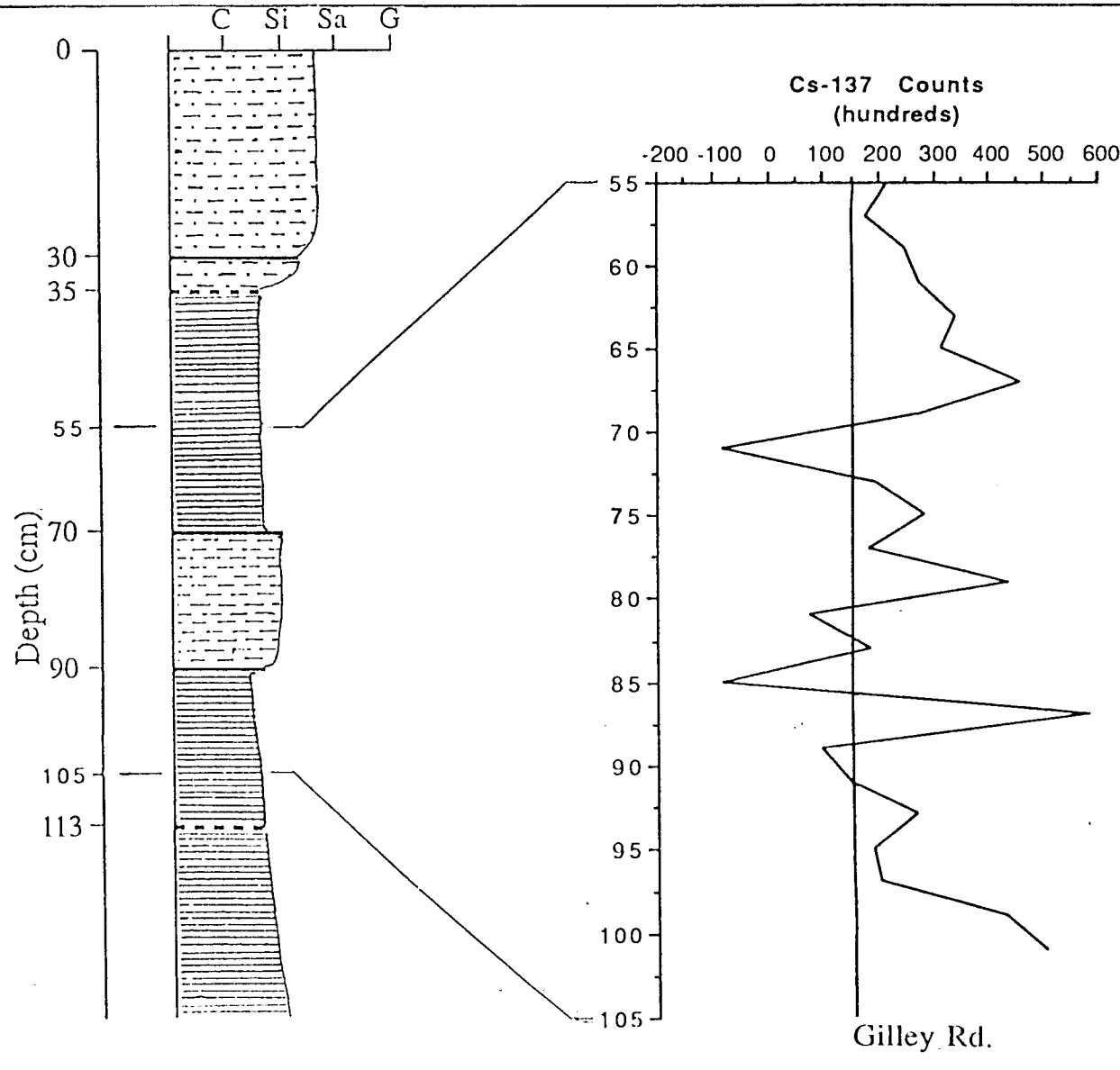


Figure 4.24 Cesium-137 counts from a part of FDHM-3.

Core: FDHM-4

This core (Figure 4.2) was extracted from the southwest side of Bridgeport Marsh which is wider than a typical ribbon marsh. It is not a ribbon marsh but one which formed when the channel separating Lulu Island and Duck Island silted-in because of blockage by fill.

Lithology: Although overall there is fining upward sequence (Figure 4.25), it is not a gradual one like that of Musqueam Marsh or that part of the core from McDonald Slough from a depth of 240 cm up to 90 cm, but rather one which changes abruptly, often into an entirely different type of sediment. There is a great deal of organic material, some of it concentrated in two distinct horizons from 59 to 63 cm depth and 71 to 74 cm depth as well as two thinner units at 41 and 46 cm depth.

Undecayed bark and woodchips are found in the lowermost part of the core, in coarse and medium sand, suggesting that rapid deposition occurred here. These sands fine upwards from the bottom of the core at a depth of 116 cm to 63 cm.

The side of the marsh from which this core was taken borders a gravel washing operation, situated on (former) Duck Island, so sand may have been flushed into the marsh from this establishment in the past. However, there is evidence which points to another origin for the coarse material. This is found in the two editions of the same topographic map which are shown by Figures 4.2 and 4.2a, as was done for FDHM-3. The later edition shows that Duck Island is no longer an island, but has been joined to the larger Lulu Island by extensive fill. The significance of this change with respect to sedimentation will be discussed in Chapter 5.

Heavy Metals: Two of this core's samples, covering the interval 78 to 82 cm depth, were destroyed in the drying oven. The graphs (Figure 4.26) show that metal levels are highest in the top 40 cm of the core which consists of clayey silt and that there is a pronounced drop in concentrations associated with the sand bed at 30 cm depth.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	0.88	4.87	3.05	0.98	32.17	56	0
Cu (ppm)	1.37	54.61	26.32	15.99	60.74	47	9
Zn (ppm)	13.00	198.12	91.41	44.47	48.65	56	0
Pb (ppm)	3.88	29.11	14.56	6.60	45.36	56	0
Rb (ppm)	26.29	371.88	55.33	47.74	86.29	54	2

Table 4.7 Descriptive statistics of heavy metals in FDHM-4.

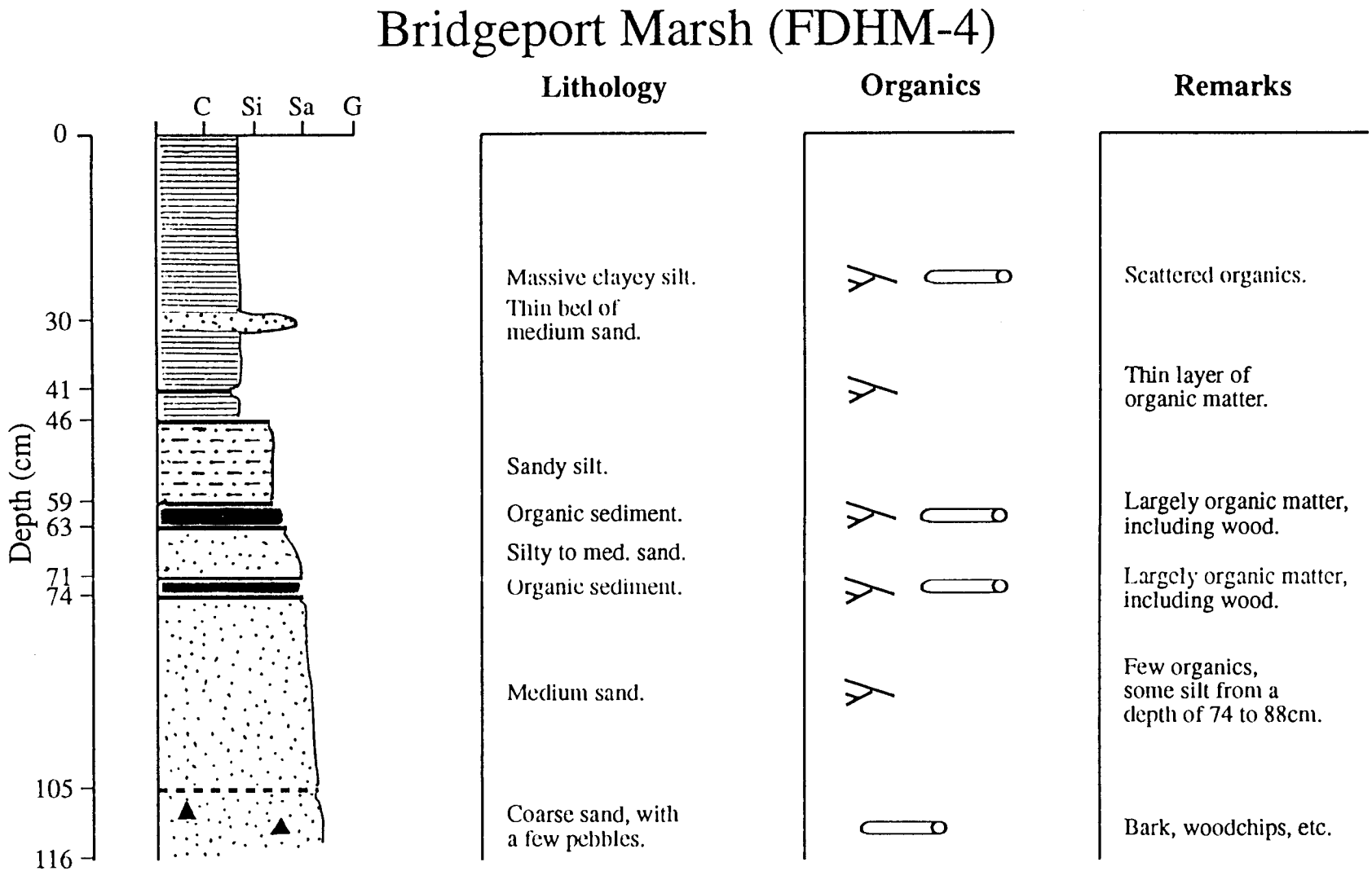


Figure 4.25 Log of the core extracted from Bridgeport Marsh.

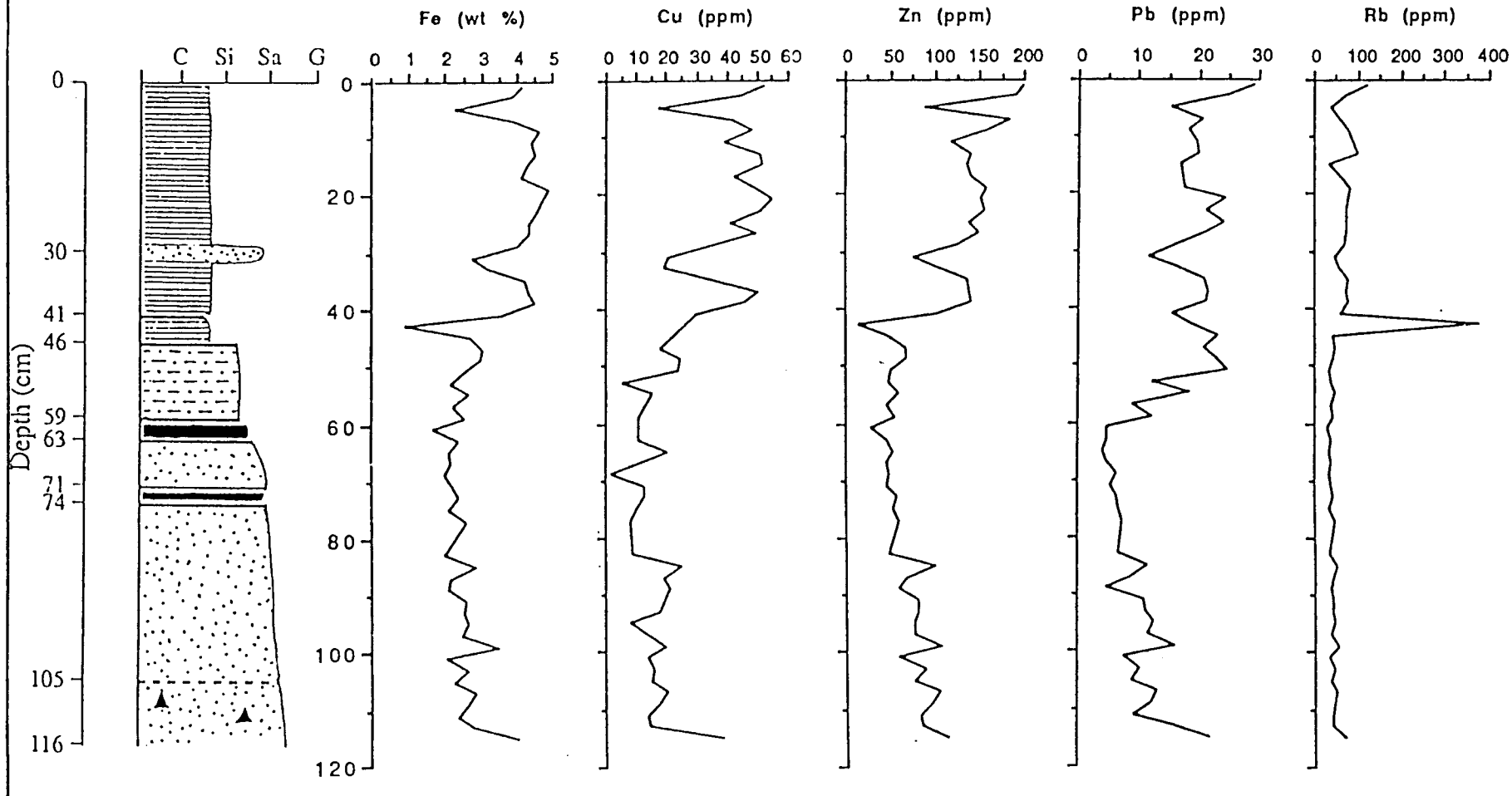


Figure 4.26 Heavy metals in FDHM-4.

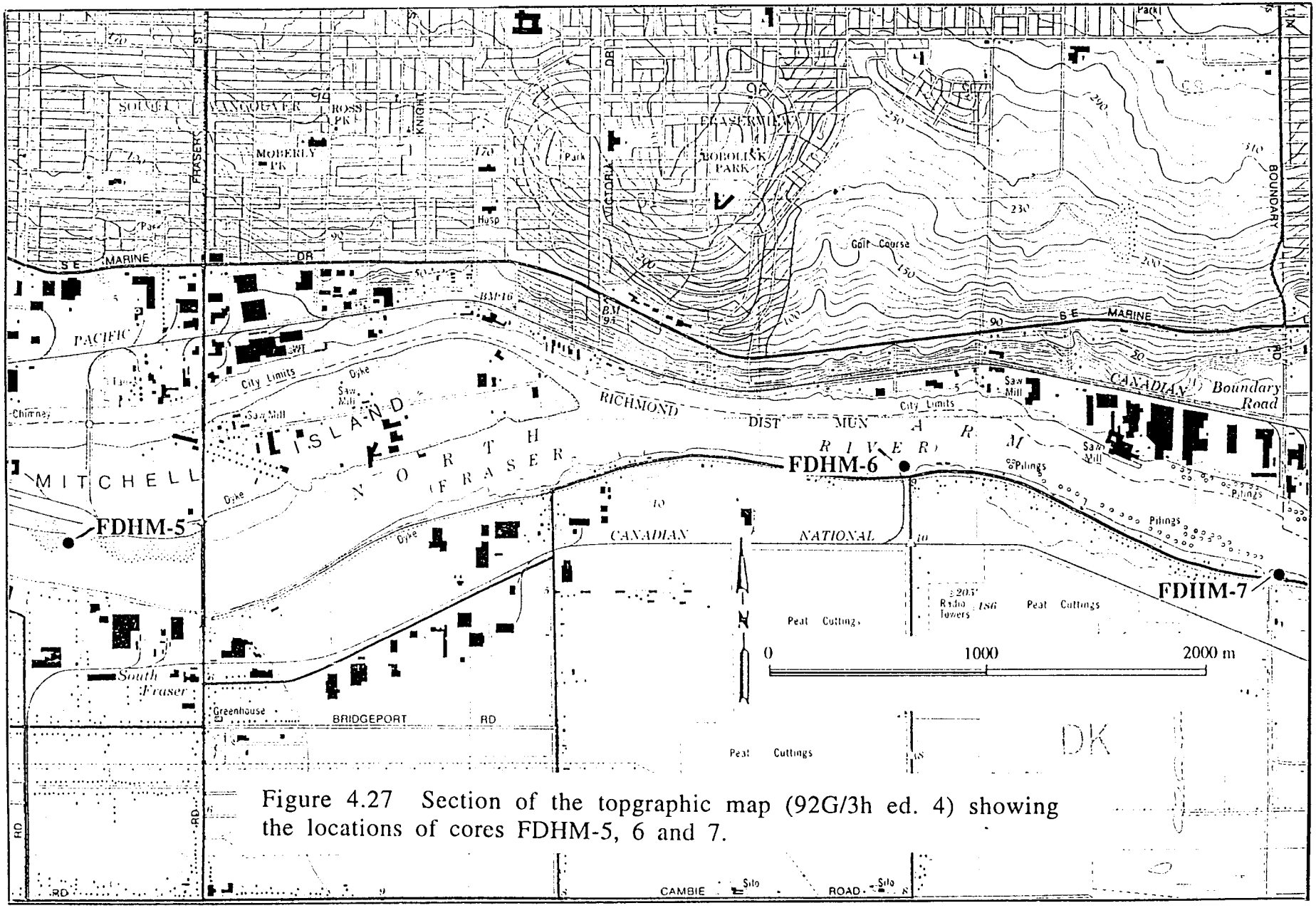


Figure 4.27 Section of the topgraphic map (92G/3h ed. 4) showing the locations of cores FDHM-5, 6 and 7.

Core: FDHM-5

This core was extracted from a marsh on the southern edge of Mitchell Island (Figure 4.27), an intensely industrialized site, in the North Arm of the Fraser.

Lithology: FDHM-5 has a most unusual stratigraphy. The core, (Figure 4.28) begins at a depth of 90 cm as a unit of clayey silt and changes abruptly at 60 cm depth into a sandy silt unit that coarsens upwards to silty sand. This sequence is finally capped by a 5 cm thick layer of sandy silt.

Heavy Metals: An interesting pattern of heavy metal enrichment is shown in the graphs (Figure 4.29). Higher concentrations occur in the lowermost 30 cm or fine sediments, sharply diminishing into the coarser material above 60 cm depth. The metal concentrations then rise again in the finer sediments which form the topmost 5 cm of the core.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	2.58	3.86	3.07	0.38	12.47	45	0
Cu (ppm)	7.94	56.48	24.41	10.75	44.04	45	0
Zn (ppm)	57.73	416.64	135.58	96.83	71.42	45	0
Pb (ppm)	6.66	25.54	13.35	5.07	37.95	45	0
Rb (ppm)	39.34	106.90	52.11	12.90	24.76	45	0

Table 4.8 Descriptive statistics of heavy metals in FDHM-5.

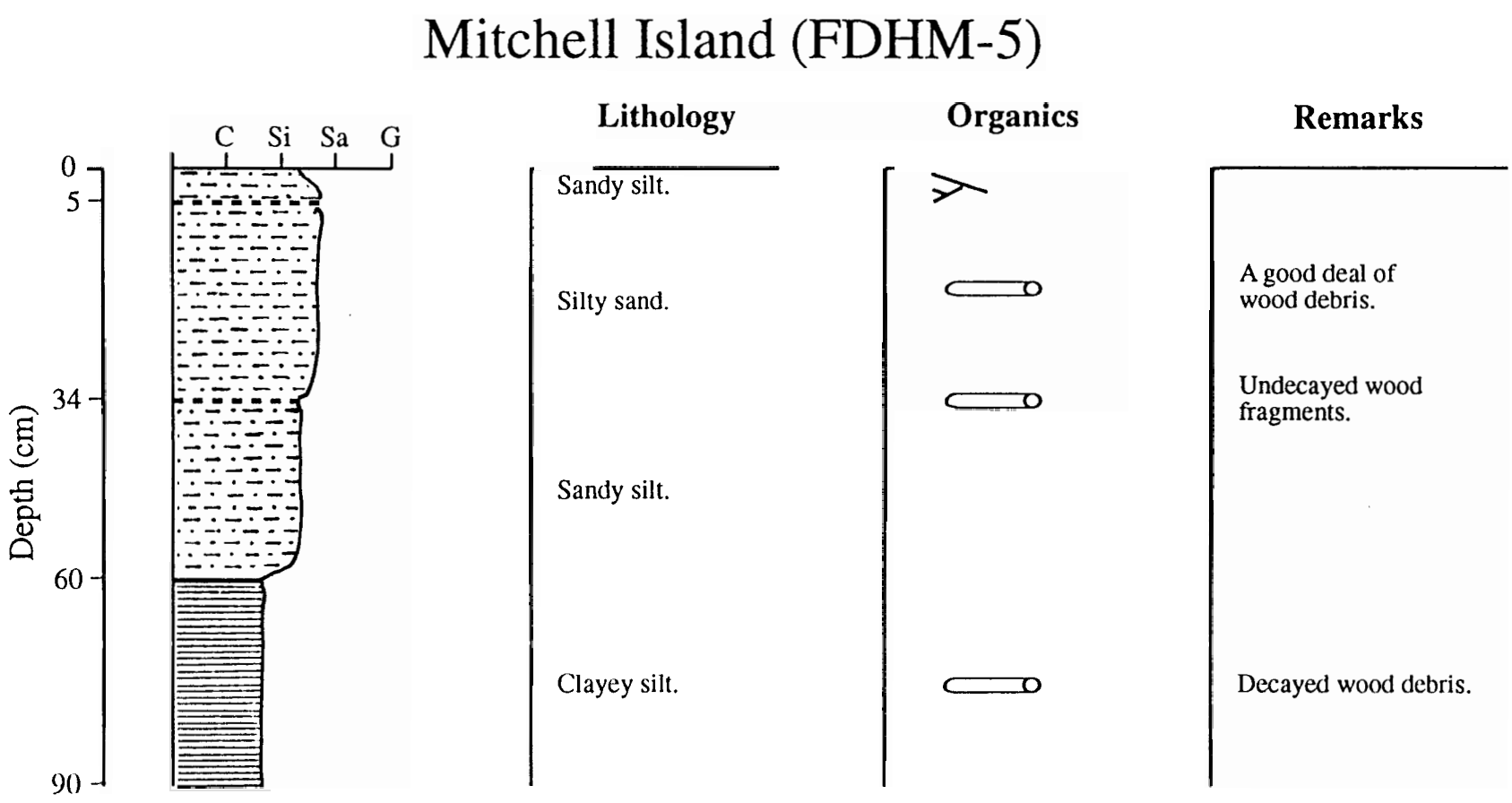


Figure 4.28 Log of the core extracted from a ribbon marsh on the South side of Mitchell Island.

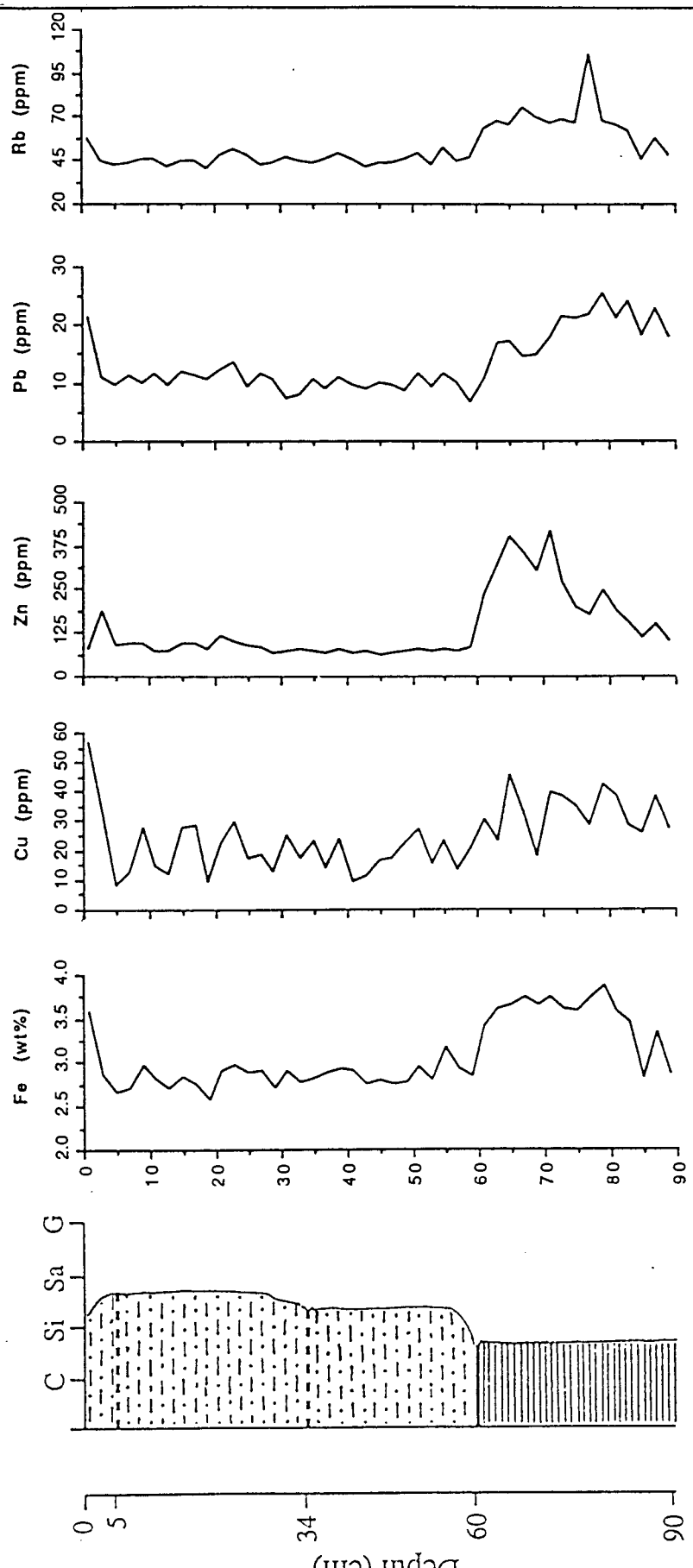


Figure 4.29 Heavy metals in FDHM-5.

Core: FDHM-6

This core was extracted from a small marsh at the north end of No. 7 Road. The marsh is adjacent to a CN Rail carslip and a drainage pumping station discharge channel. The core illustrated in the photographs (Figures 4.32 to 4.36) was obtained only a few meters from the original core.

Lithology: Whereas the original core (Figure 4.30) had a veneer of silt capping a much finer silt, the duplicate core (Figures. 4.32 to 4.36) has a thin covering of fine silt resting upon a 36 cm thick unit of coarse sand. This coarse sand in turn overlies a silt unit, almost the reverse of the sequence in the sampled core. This suggests that the sediments at this site are not original material. The silt unit contains a detrital layer and sand/detrital layer. The sampled core was characterized by very sharp contacts at the interfaces between predominantly silt and predominantly sand units in the lowermost 65 cm or so of the core. The sharp contacts may also be seen in the photographed core (Figures 4.32 to 4.36).

Heavy Metals: The graphs showing the heavy metals concentrations of FDHM-6 are given in (Figure 4.31). Overall, the highest concentrations of metals are found in the top 85 cm of the core particularly in the 30 to 40 cm depth range. There appears to be some diminution in concentrations in approximately the top 25 cm. Note the overall drop in concentrations in the lowermost 40 cm or so of the core. This seems at least partly attributable to the coarser sediment forming this part of the core.

Table 4.9 Descriptive statistics of heavy metals in FDHM-6.

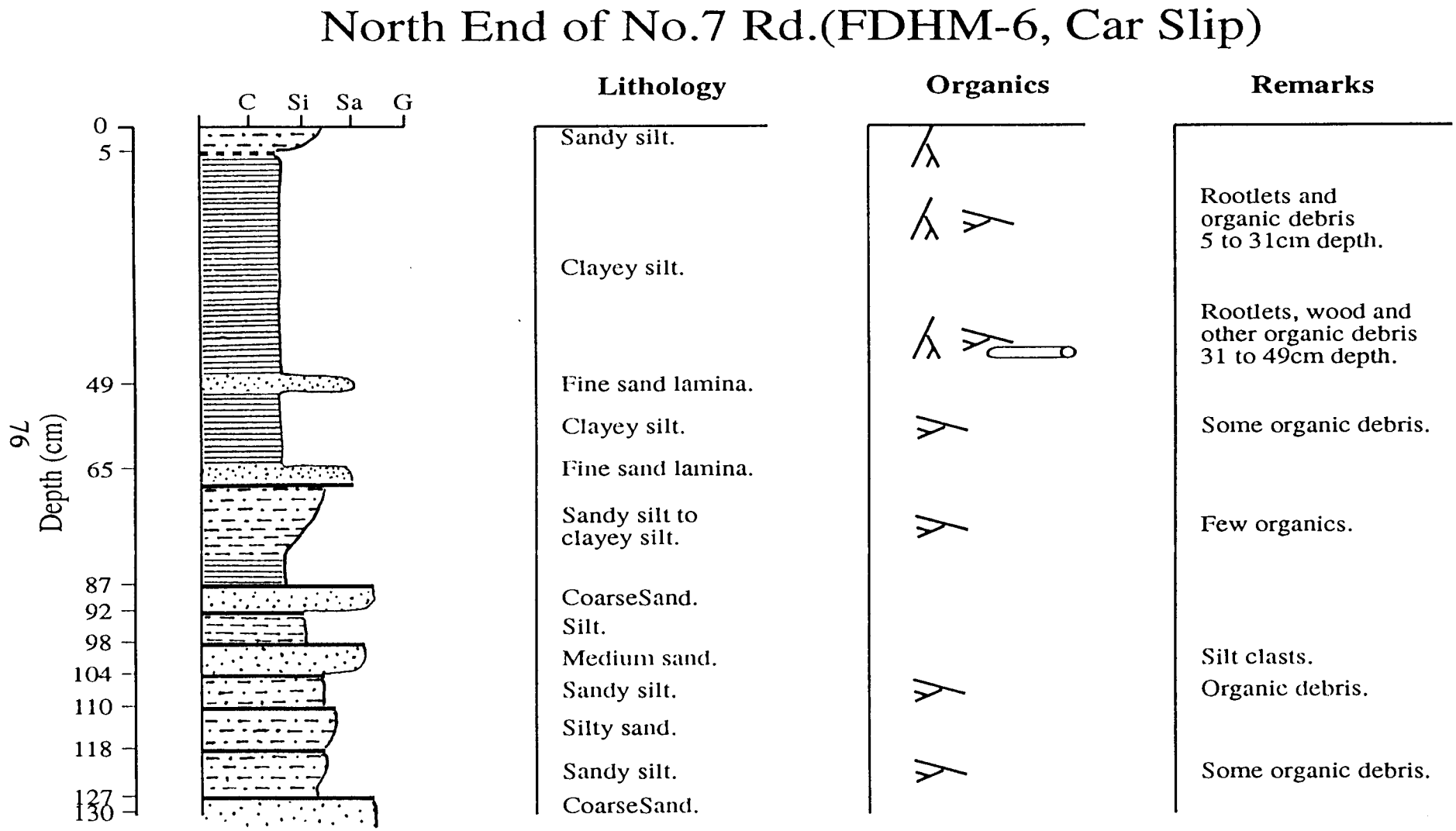


Figure 4.30 Log of the core extracted approximately 70 m east of the CN car slip at the North end of No. 7 Road.

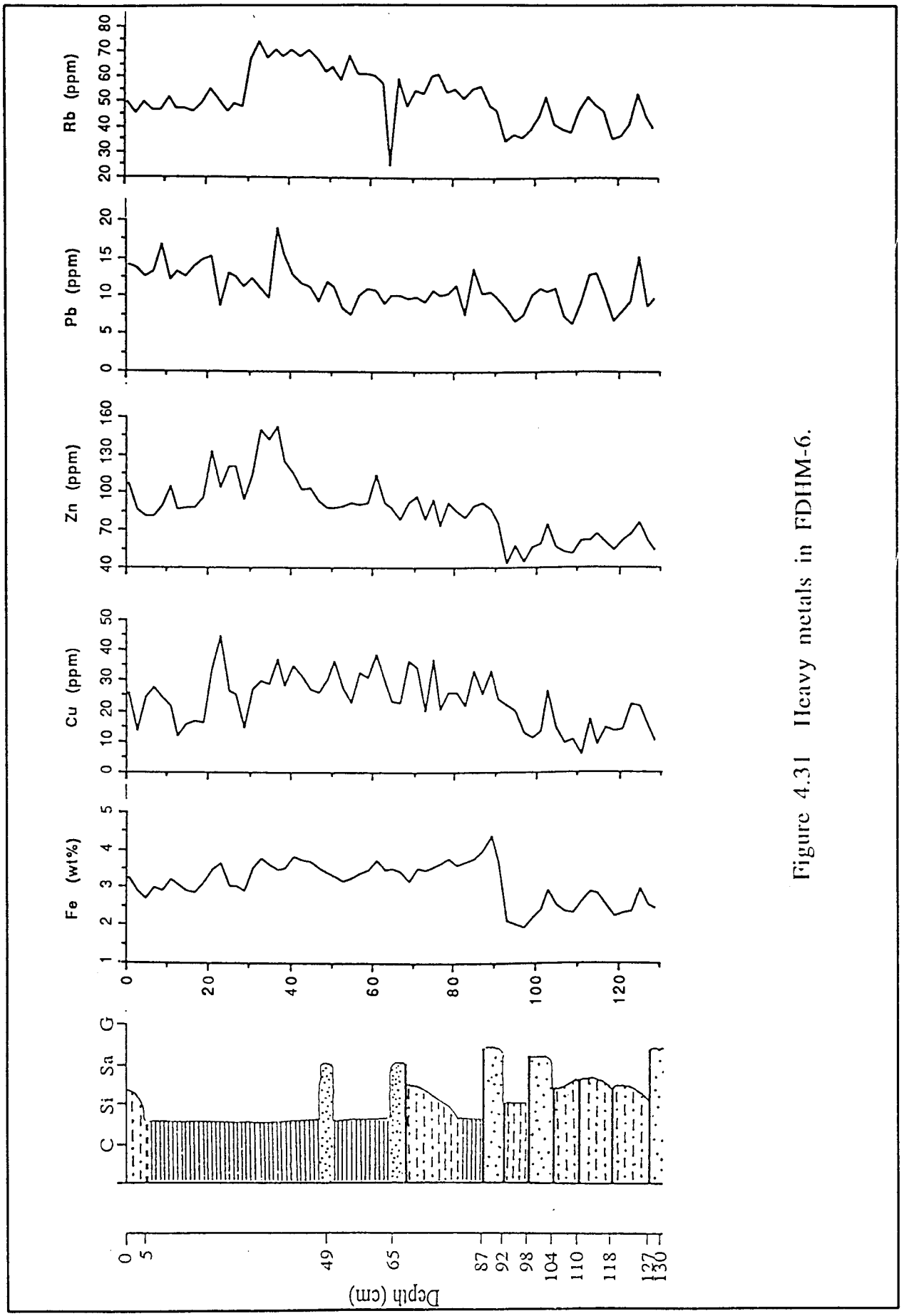


Figure 4.31 Heavy metals in FDHM-6.

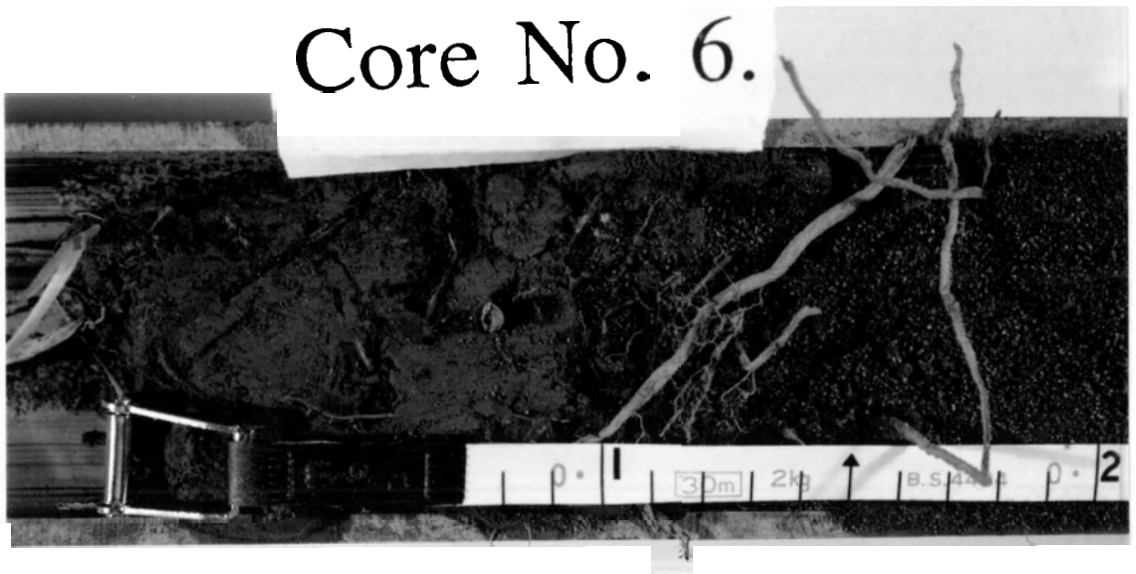
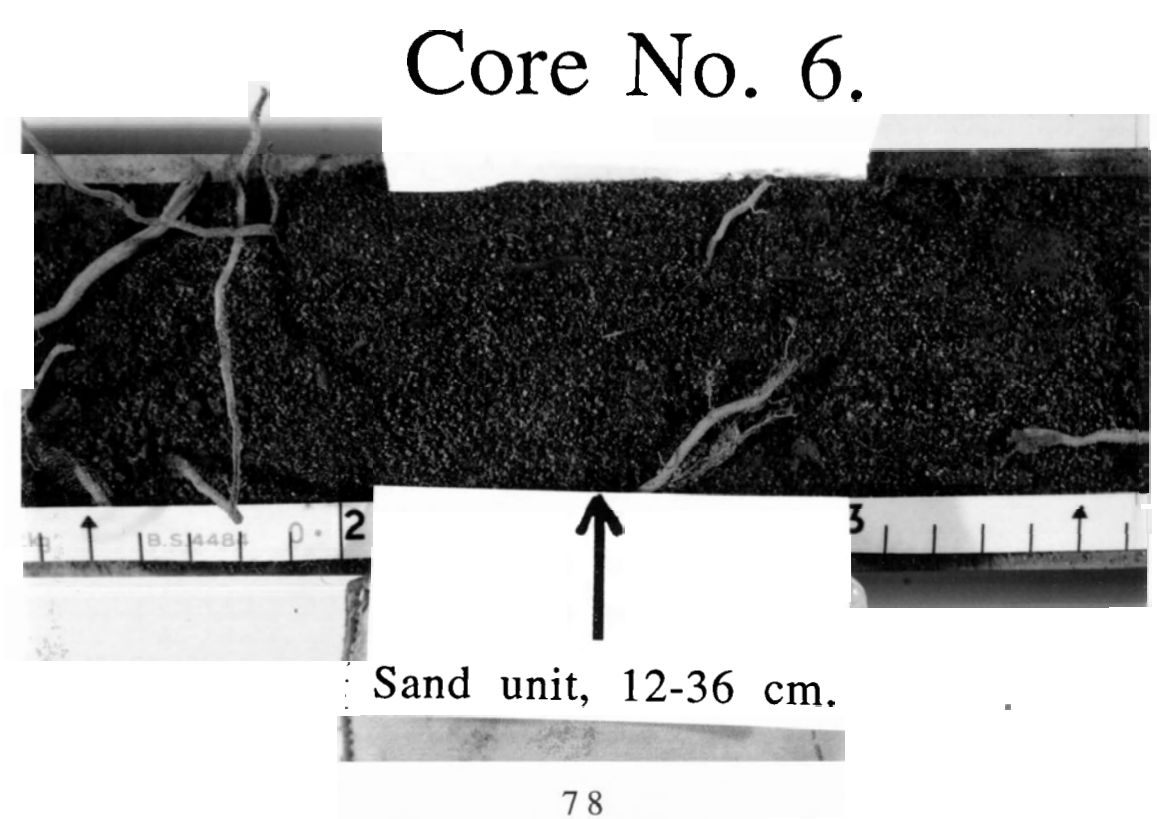


Figure 4.32 The top 10 cm of the core is a fine silt with organics. It changes sharply to coarse sand.

Figure 4.33 The coarse sand unit changes abruptly to silt at 36 cm depth.



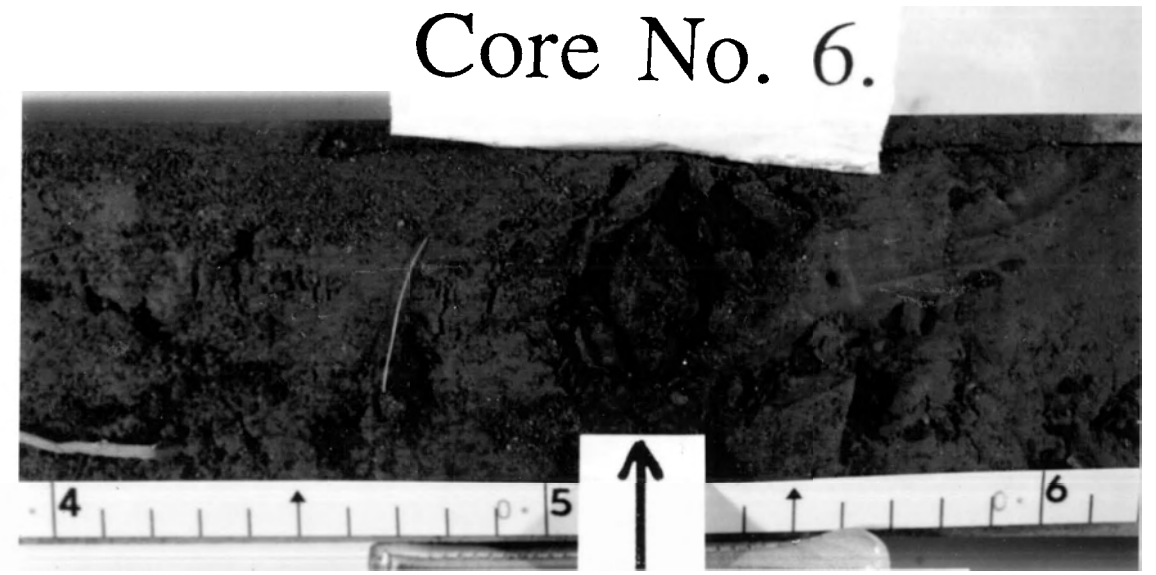
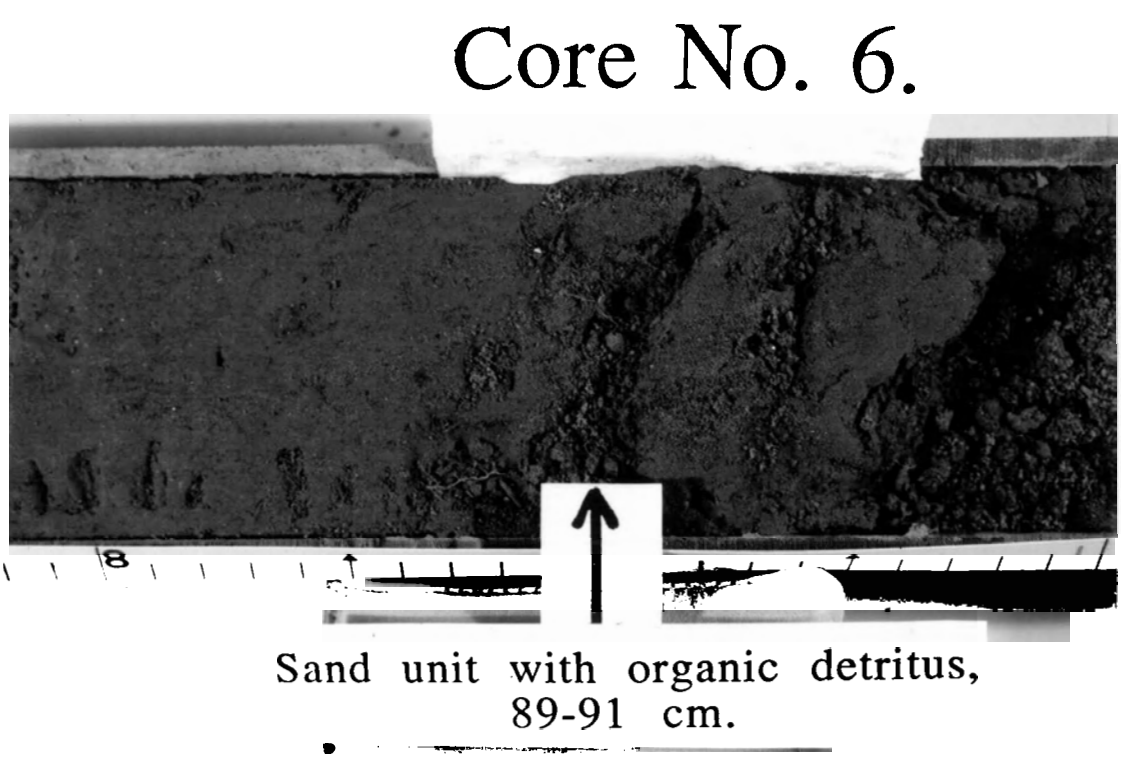


Figure 4.34 A layer of detrital organics.

Figure 4.35 A layer of silty sand containing detrital organics.



Core No. 6. [redacted]

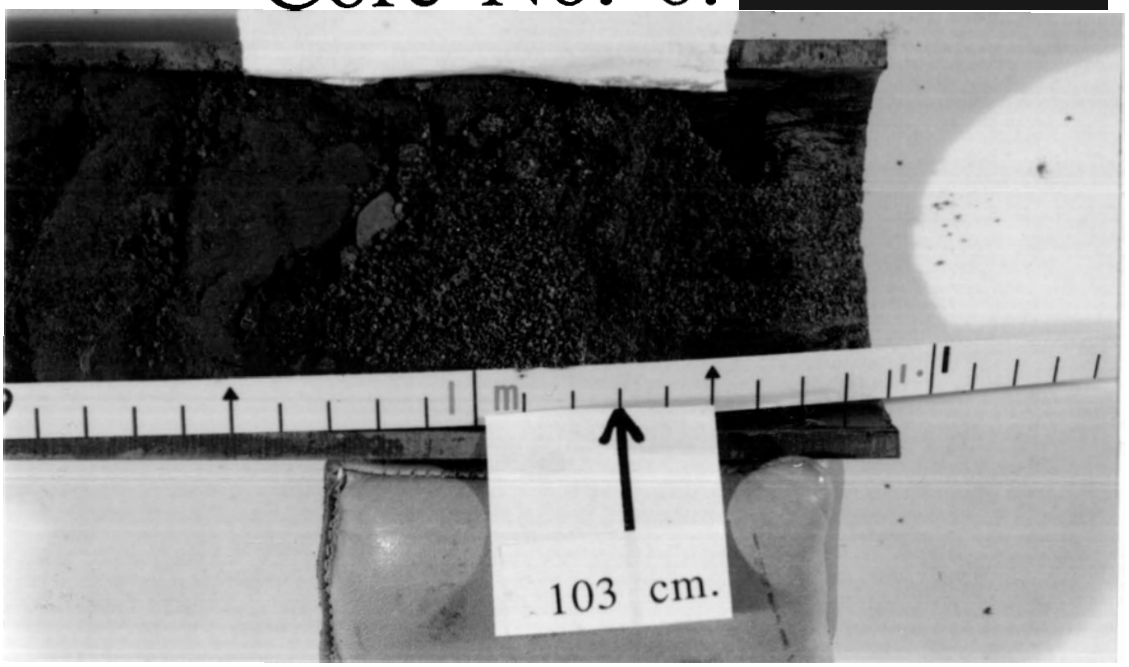


Figure 4.36 The silt changes abruptly at 103 cm depth to coarse sand. The contact is very irregular.

Core: FDHM-7

This core was taken at the north end of No. 8 Road (Figure 4.27) from a small ribbon marsh which lay between the road and what appeared to be a small, partly overgrown and inactive bar. This placed the marsh in a small swale, where, protected from the energetic waters of the channel, sediment could be deposited.

Lithology: It was surprising, because of these conditions, to find the sequence of sediments prevailing there: a sandy silt, overlying a coarse sand which in turn overlies a peaty clay (Fig 4.37). The second core (Figures. 4.39 to 4.45), when examined consisted of essentially the same sequence, but with much more organic matter in the top silt unit. A sand bed which appears at 40 cm depth in the original core appears at 56 cm depth in the second one. However, both the other contacts at 88 cm and 144 cm are sharp, irregular (inclined) and similar to those of the original core.

Heavy Metals: The heavy metals concentrations, shown in the graphs of Figure 4.38, reveal an interesting pattern: higher concentrations near the bottom of the core associated with the finer (and original?) sediments, diminished concentrations in the coarse sand unit, spikes in all metals except zinc at the sand/silt contact around 54 cm depth and from these spikes to the surface, apparent higher concentrations of heavy metals, on average, than those of the coarse sand unit but somewhat lower than those of the 20 cm of peaty clay at the bottom of the core. The spike in iron concentration (Table 4.10), 16.05 wt%, is by far the highest value for iron of any core and, as will be discussed in Chapter 5, is no doubt significantly related to the spikes in copper and lead within the same depth range.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	1.85	16.05	3.20	1.83	57.35	59	0
Cu (ppm)	6.45	105.15	23.59	15.88	67.35	45	14
Zn (ppm)	10.18	179.73	76.05	33.50	44.05	55	4
Pb (ppm)	2.71	22.77	8.85	4.74	53.55	58	1
Rb (ppm)	29.30	130.80	52.36	20.44	39.03	59	0

Table 4.10 Descriptive statistics of heavy metals in FDHM-7.

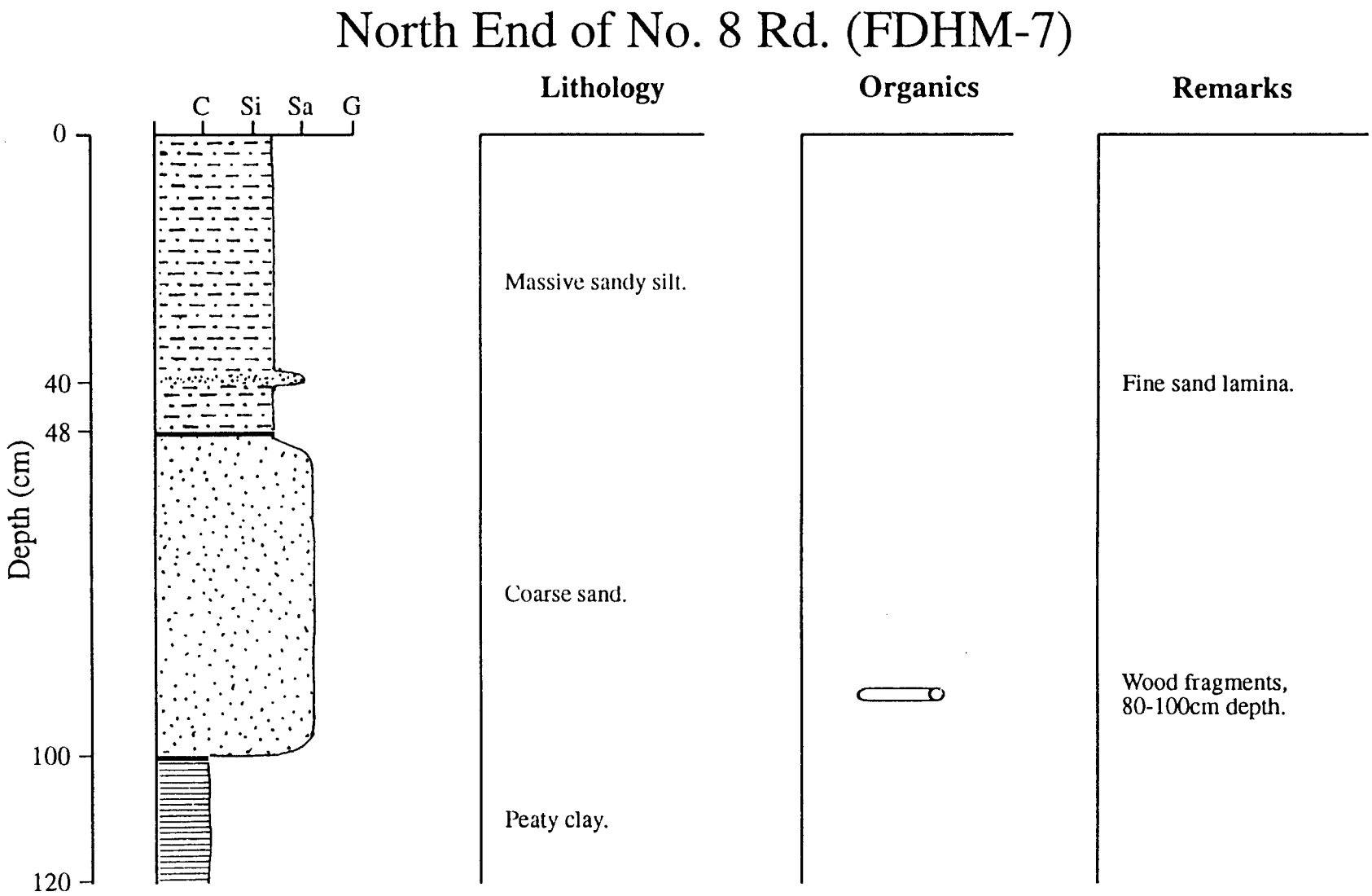


Figure 4.37 Log of the core extracted from the ribbon marsh at the North end of No. 8 Road.

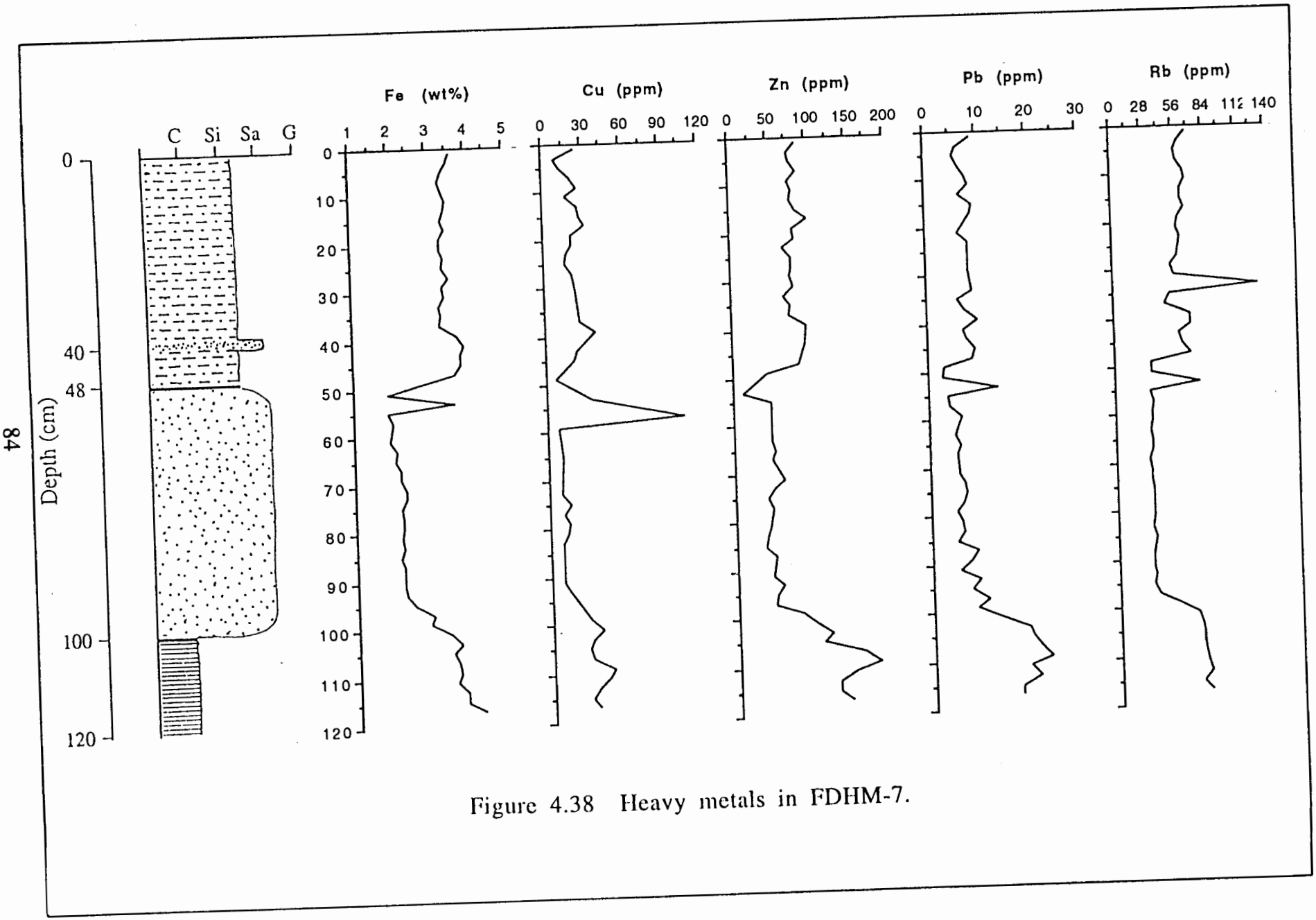


Figure 4.38 Heavy metals in FDHM-7.

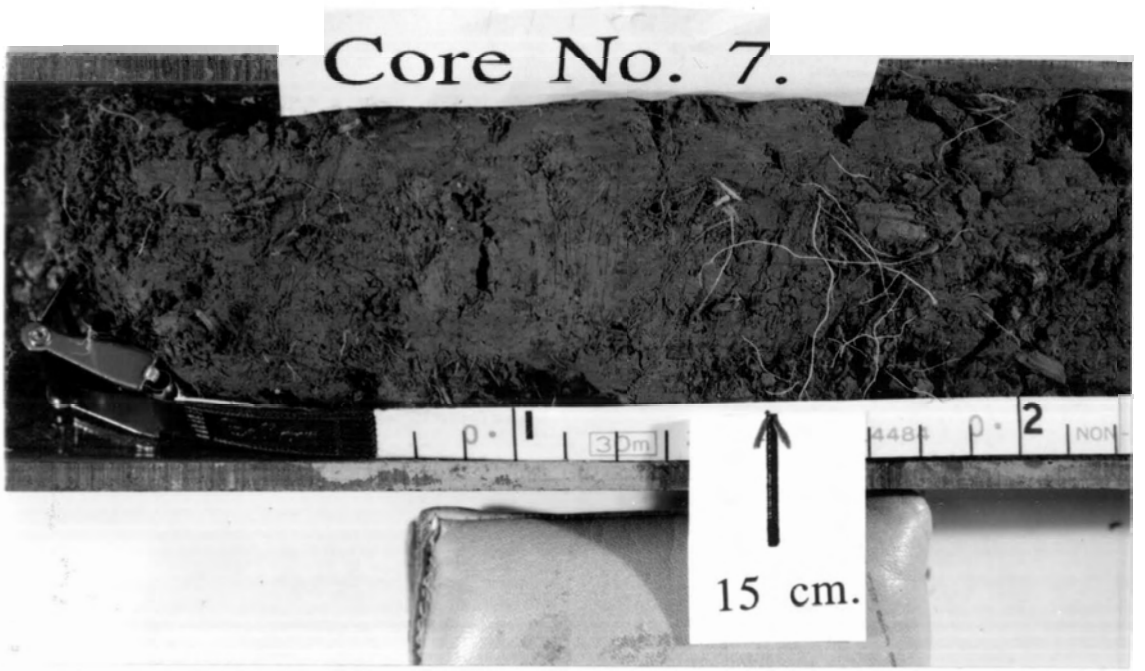
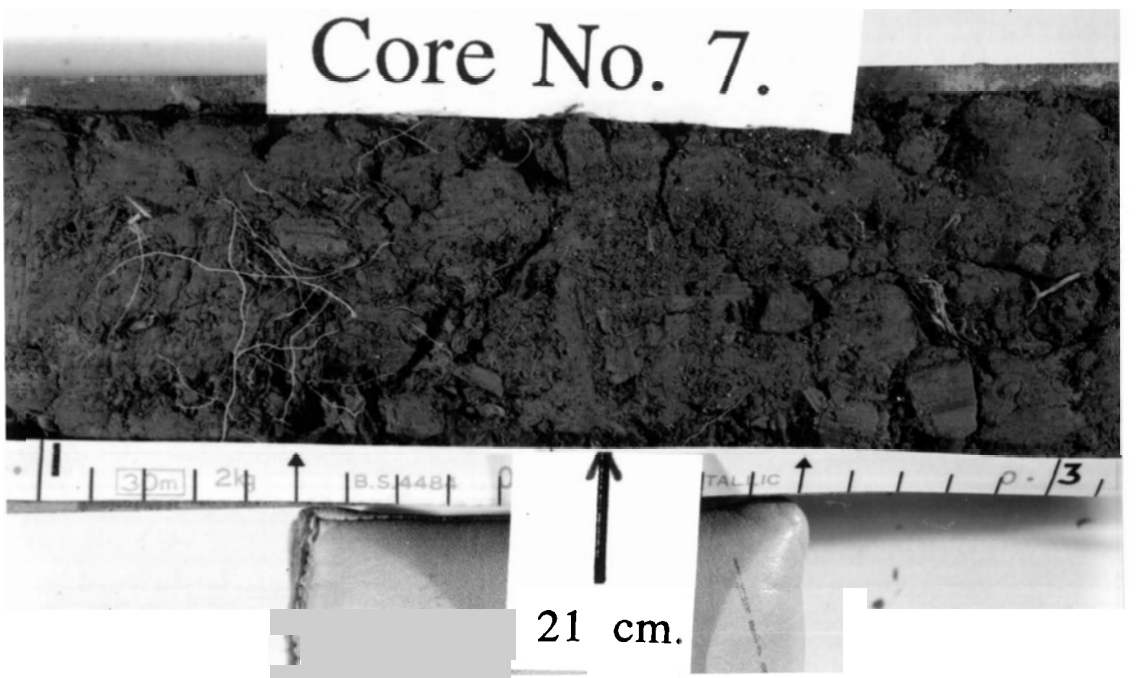


Figure 4.39 The first 15 cm of the core consists of silt containing a dense network of undecayed plant matter

Figure 4.40 From 15 to 21 cm the plant matter diminishes. There are many wood chips.



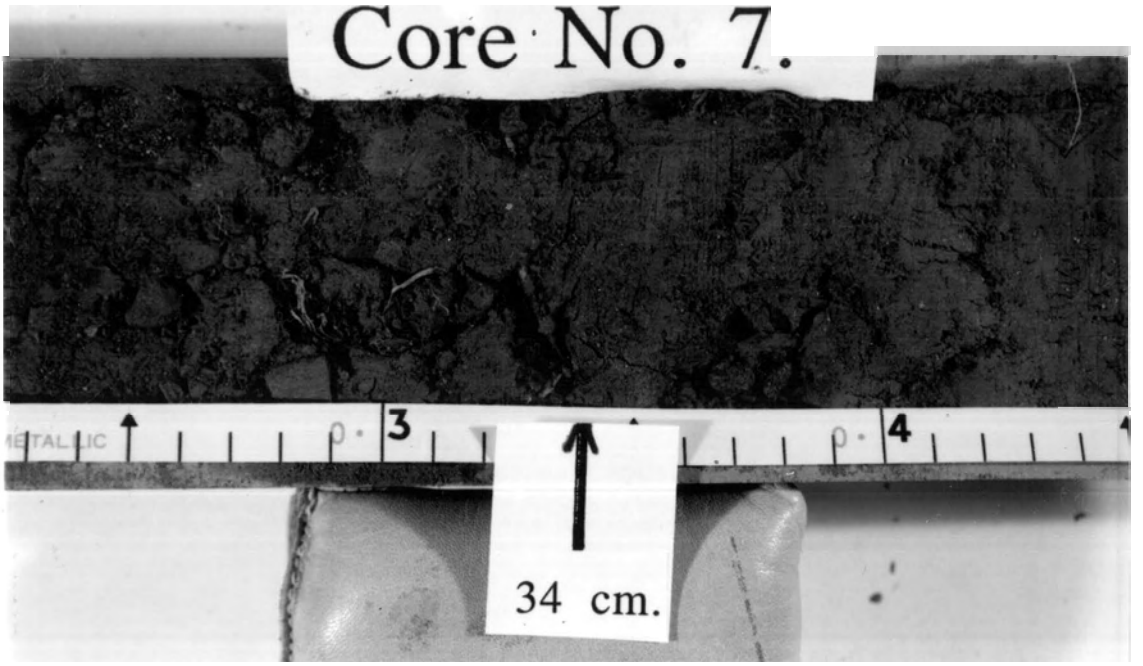
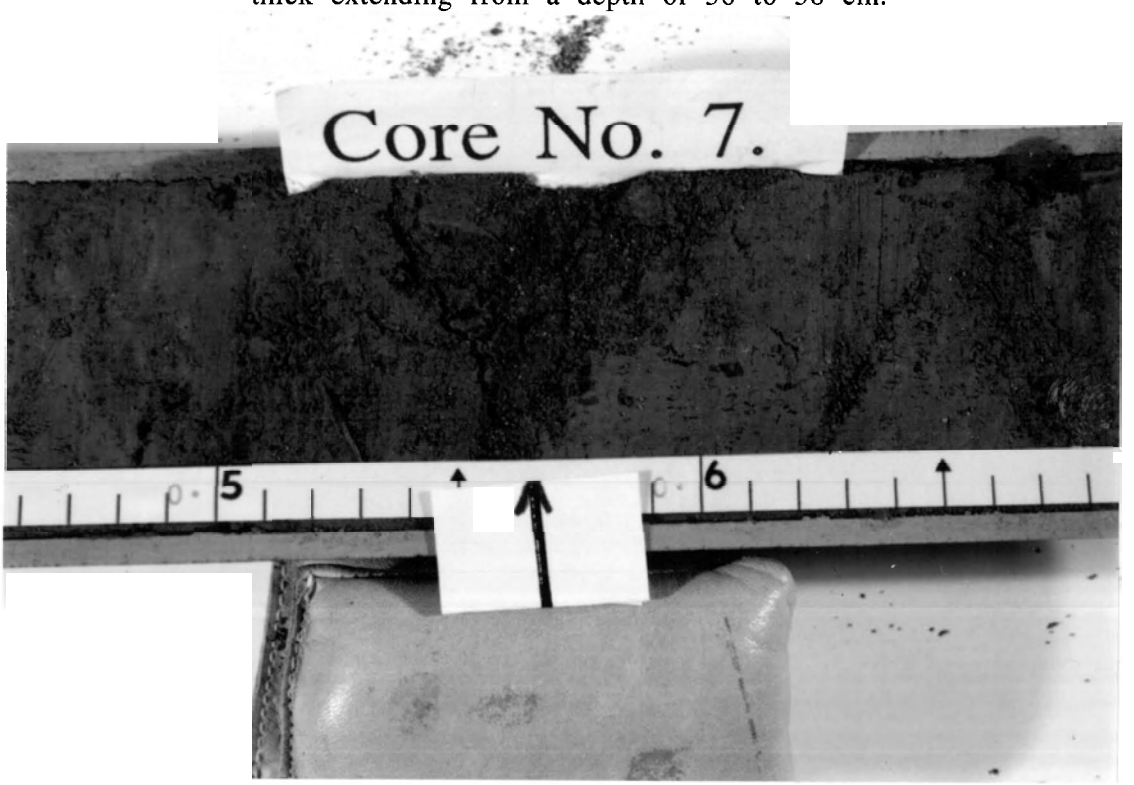


Figure 4.41 From a depth of 21 to 34 cm the silt is clayey with a dense network of finely divided roots. There are also partially decayed wood fragments.

Figure 4.42 From 34 to 88 cm depth the core consists of clayey silt with scattered, decayed wood fragments. There is an inclined sand bed 1 to 2 cm thick extending from a depth of 56 to 58 cm.



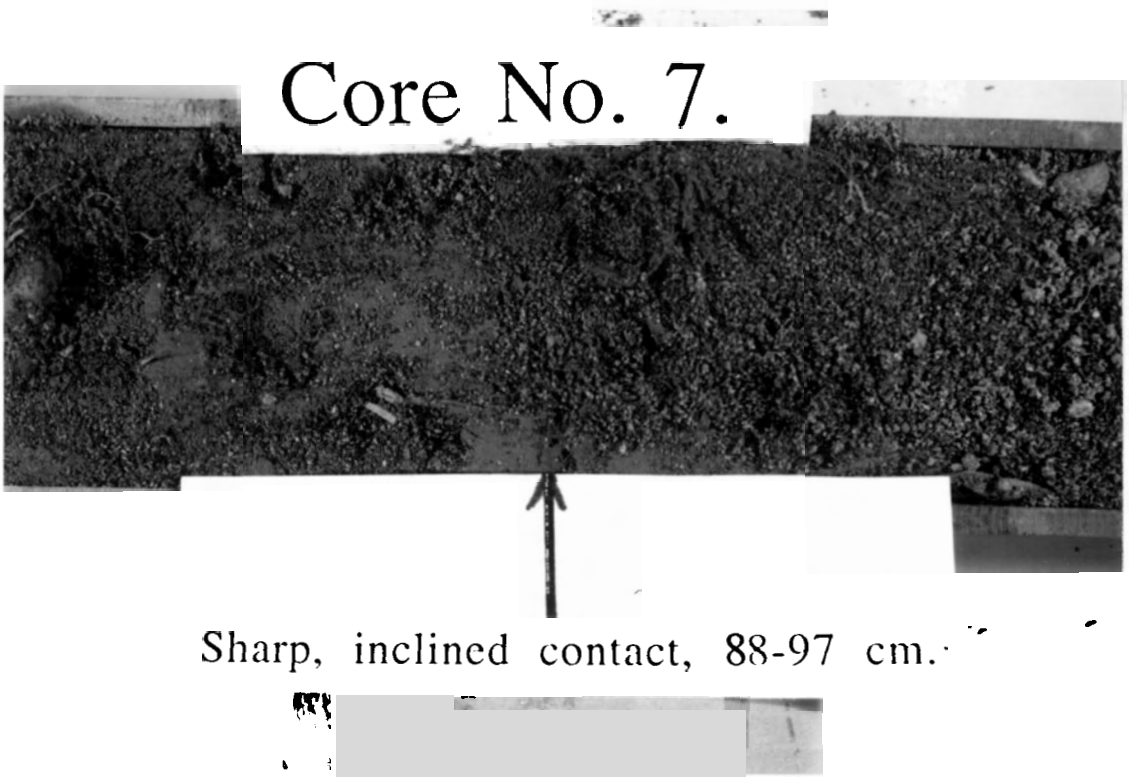
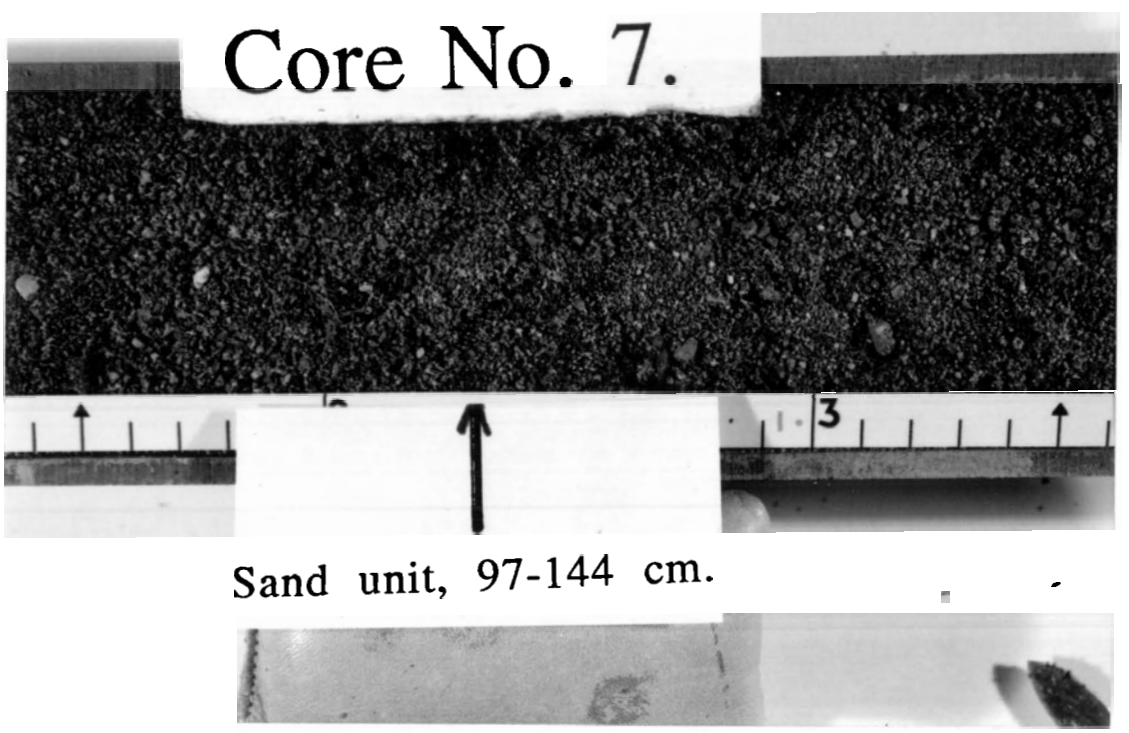


Figure 4.43 A sharp, inclined contact between the clayey silt and an underlying bed of corse sand extends from 88 to 97 cm depth.

Figure 4.44 The coarse sand unit extends from a depth of 97 to 144 cm.



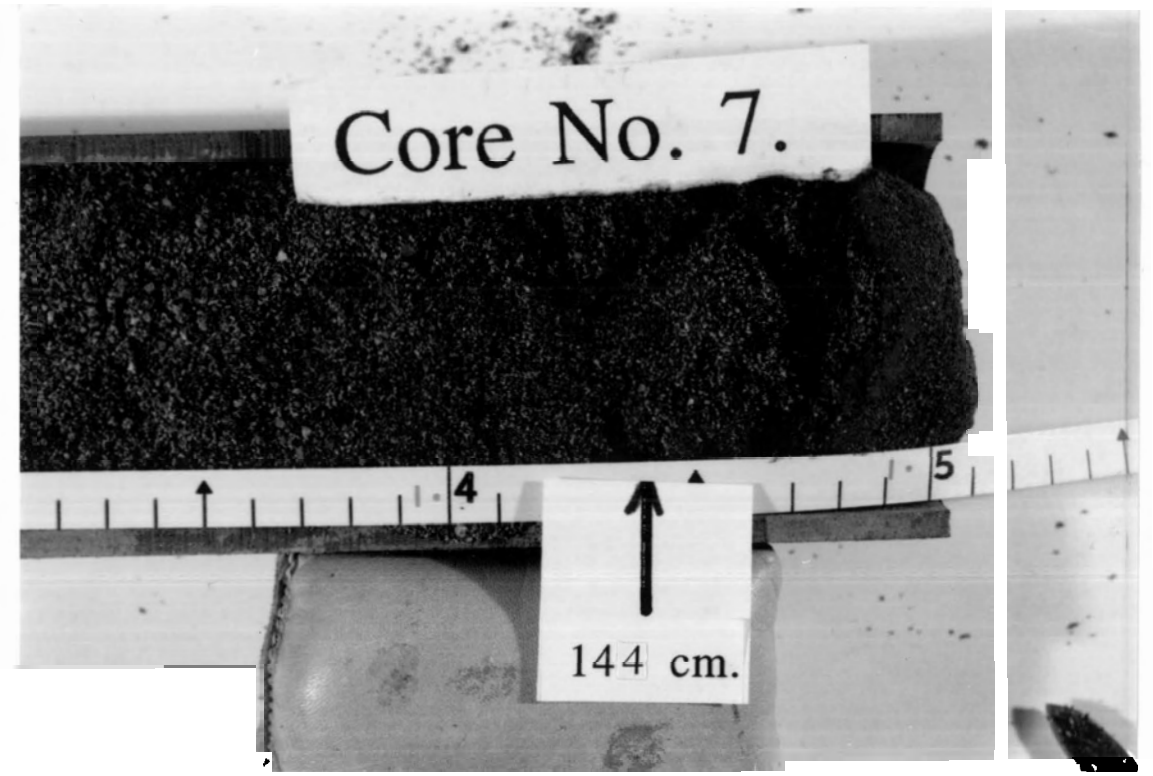


Figure 4.45 At 144 cm depth the coarse sand unit has a sharp contact with clay. Whether this is merely a clay ball or an entire unit, is not certain.

Core: FDHM-8

This core was extracted from a ribbon marsh at the junction of River road and the Old Westminster Highway (Figures 3.1 and 4.48).

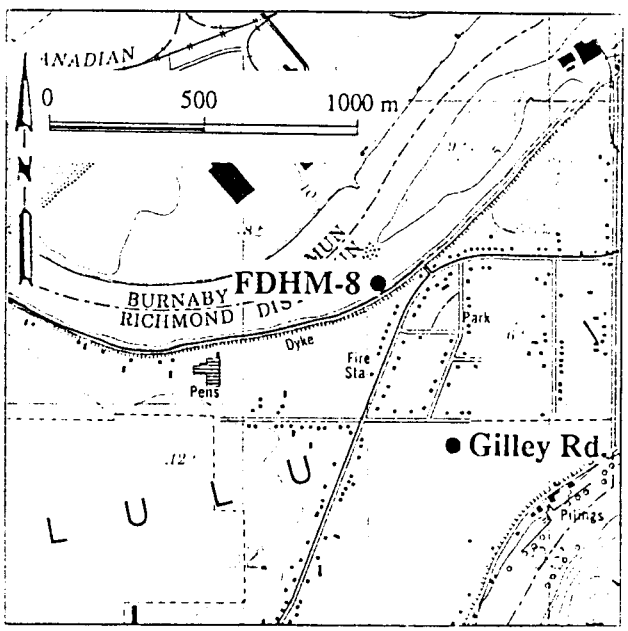


Figure 4.46 Section of the topographic map (92G/2e, ed. 3) showing the locations of FDHM-8 and the Gilley Road core.

Lithology: This core, which had a length of 174 cm, had the most uniform texture of all the cores in the study (Figure 4.47). The sequence fined evenly and gradually upwards without break or interruption. Only in the very topmost and bottomost portions of the core is there more than the most gradual change. Little organic matter and no developed root network was found in the top half of the core, indicating rapid depostion of sediment with vegetation growth just keeping pace with surface accretion.

Heavy Metals: Two of this core's samples, taken from the intervals 2 to 4 cm and 10 to 12 cm depth, were too scant for analysis. The metals, with the exception of zinc and to a lesser degree lead, do not show unusually high concentrations in the uppermost part of the core (Figure 4.48) but their means are generally high. The higher

zinc concentration (Table 4.11) is significant, because there is a galvanizing plant a short way upstream of this marsh.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	3.03	4.17	3.65	0.27	7.39	87	0
Cu (ppm)	8.26	42.82	27.82	7.27	26.11	87	0
Zn (ppm)	58.38	195.74	93.65	21.58	23.04	87	0
Pb (ppm)	6.92	29.55	13.52	3.87	28.64	85	2
Rb (ppm)	44.69	77.79	63.40	6.82	10.76	85	2

Table 4.11 Descriptive statistics of heavy metals in FDHM-8.

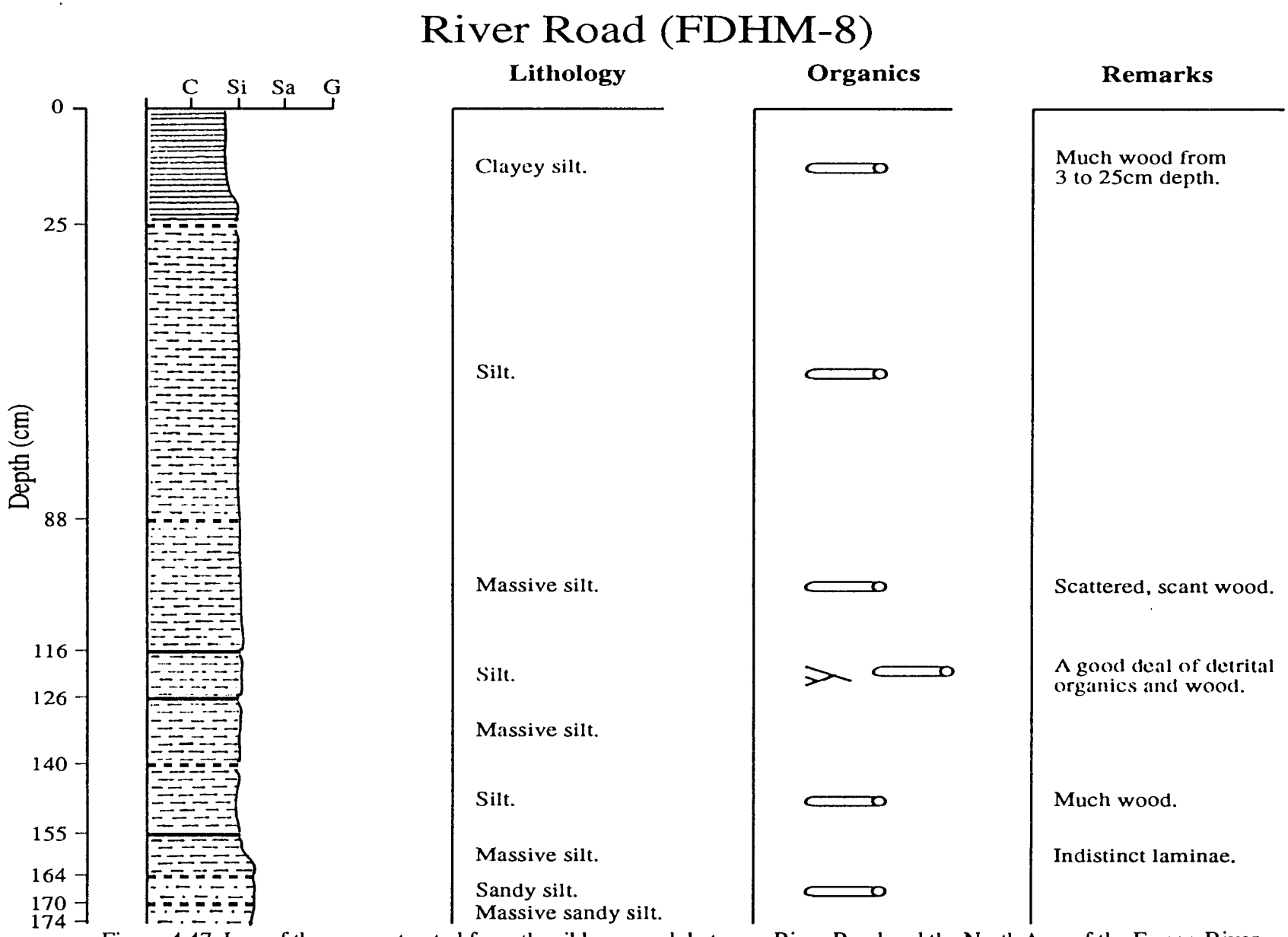


Figure 4.47 Log of the core extracted from the ribbon marsh between River Road and the North Arm of the Fraser River.

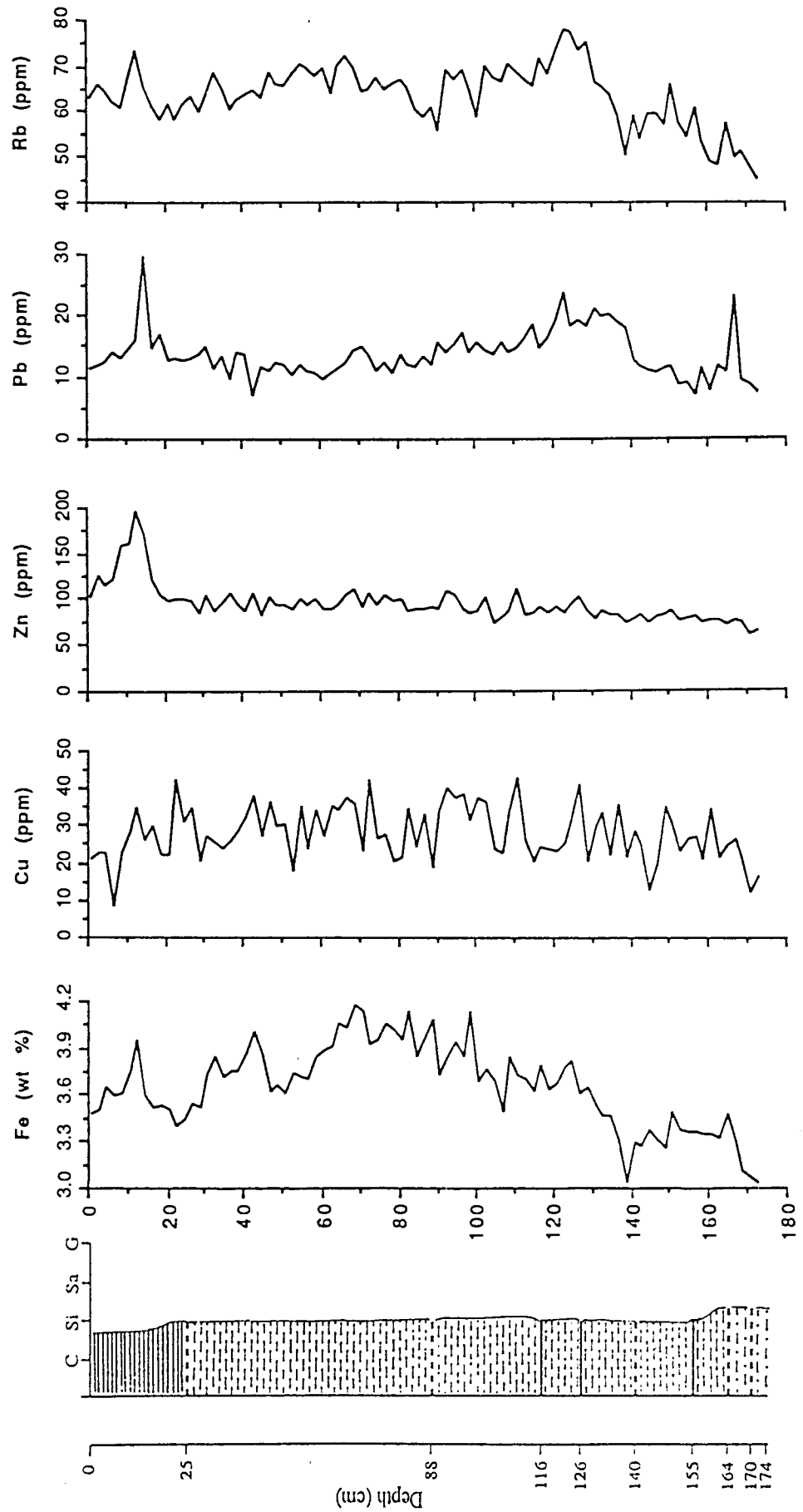


Figure 4.48 Heavy metals in FDHM-8.

Cesium-137: ^{137}Cs was counted for this core (Figure 4.49). Counting started at 20 cm depth because the samples were too scant above this depth to provide the necessary 5 g pellets. The highest counting peak is found at 4 cm depth, a lower one at 90 cm and perhaps another, about the same height as the second, at 57 cm depth. The CV is much lower in this core (Table 4.12) at 47.72 as opposed to 64.69 for FDHM-10 and 66.87 for FDHM-3. The baseline, 150 counts, was obtained by counting a sample from the Gilley Road sediments.

Min	Max	Mean	St D	C V (%)	Count	Miss
153	1243	529.55	252.68	47.72	40	5

Table 4.12 Descriptive statistics of ^{137}Cs in FDHM-8.

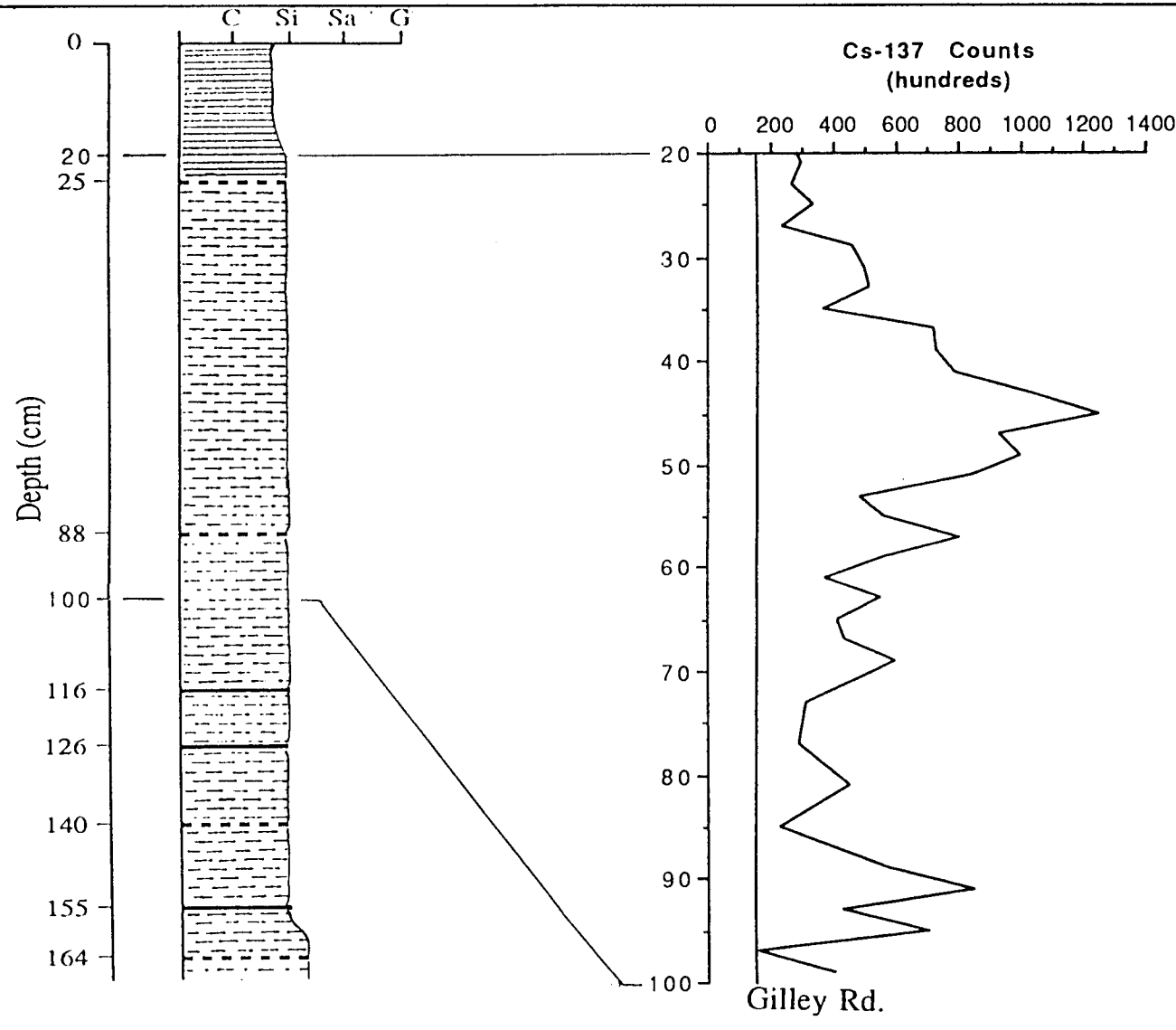


Figure 4.49 Cesium-137 counts from a part of FDHM-8.

Upper Fraser Valley Cores: FDHM-13 and 14

FDHM-13 and 14 were extracted from two sloughs in the Upper Fraser Valley which are nearly abandoned channels of the main river, but which historically were subject to the same mode of deposition as the ribbon marshes of the North Arm. It was thought useful to compare heavy metal levels in sediments from backwaters of the river system, to those from an active channel in a densely populated area subject to heavier inputs of these metals.

Core: FDHM-13

Lithology: This core was extracted from the tip of a small island in Nicomen Slough (Figure 4.50).

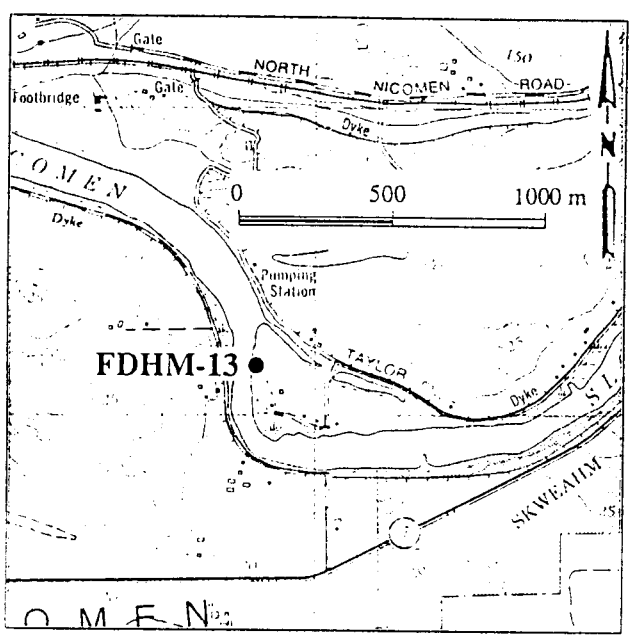


Figure 4.50 Section of the topographic map (92G/1h, ed. 4) showing the location of core FDHM-13.

Little water now passes through this slough. It has been dammed at its eastern extremity at Skumalasph and Queens Islands (Figure 1.1b) since 1951 in order to prevent flooding of Nicomen Island. This has no doubt increased deposition of fine sediments in the slough channel.

Lithology: The log (Figure 4.51) shows a fining upwards sequence overlying a unit of silt. The silt extends from the bottom of the core upwards to 112 cm depth, here a sharp contact separates it from the fining upwards sequence. This sequence consists, from its base at 112 cm depth, of medium sand fining upwards through fine sand to sandy silt which is overlain, at a depth of 22 cm, by an organic layer of coarse wood. Above this organic layer the balance of the core, from 20 cm depth to the surface, is formed of clayey silt.

Heavy metals: Heavy metal levels (Figure 4.52) appear most elevated in those parts of the core with the finest texture.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	1.81	4.29	2.88	0.59	21.09	65	0
Cu (ppm)	2.94	35.63	19.01	6.94	36.51	63	2
Zn (ppm)	43.64	94.43	62.85	13.75	21.87	65	0
Pb (ppm)	2.44	15.42	7.38	2.51	34.02	62	3
Rb (ppm)	34.19	197.70	47.37	20.37	43.00	65	0

Table 4.13 Descriptive statistics of heavy metals in FDHM-13.

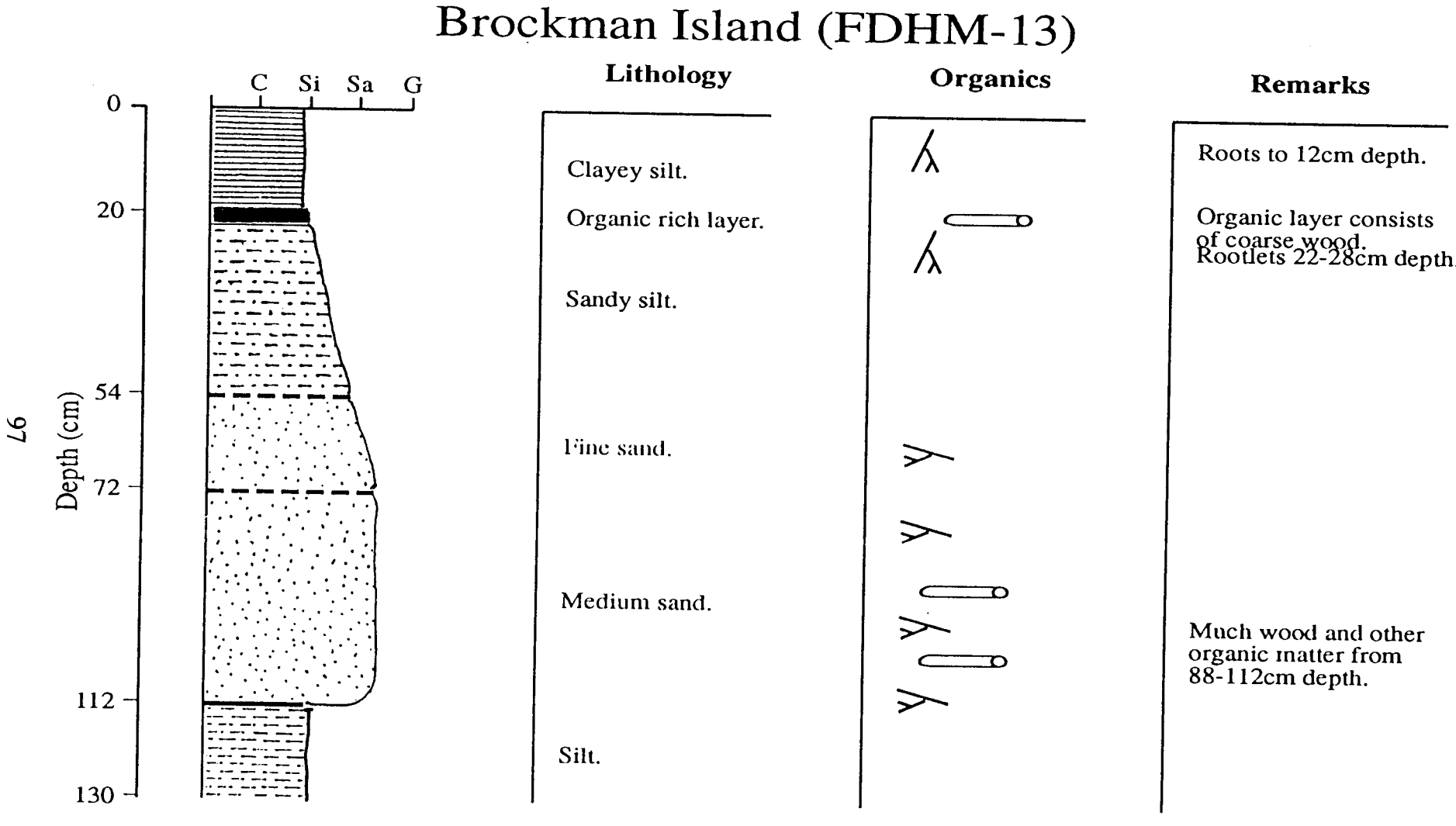


Figure 4.51 Log of the core extracted from Brockman Island in Nicomen Slough.

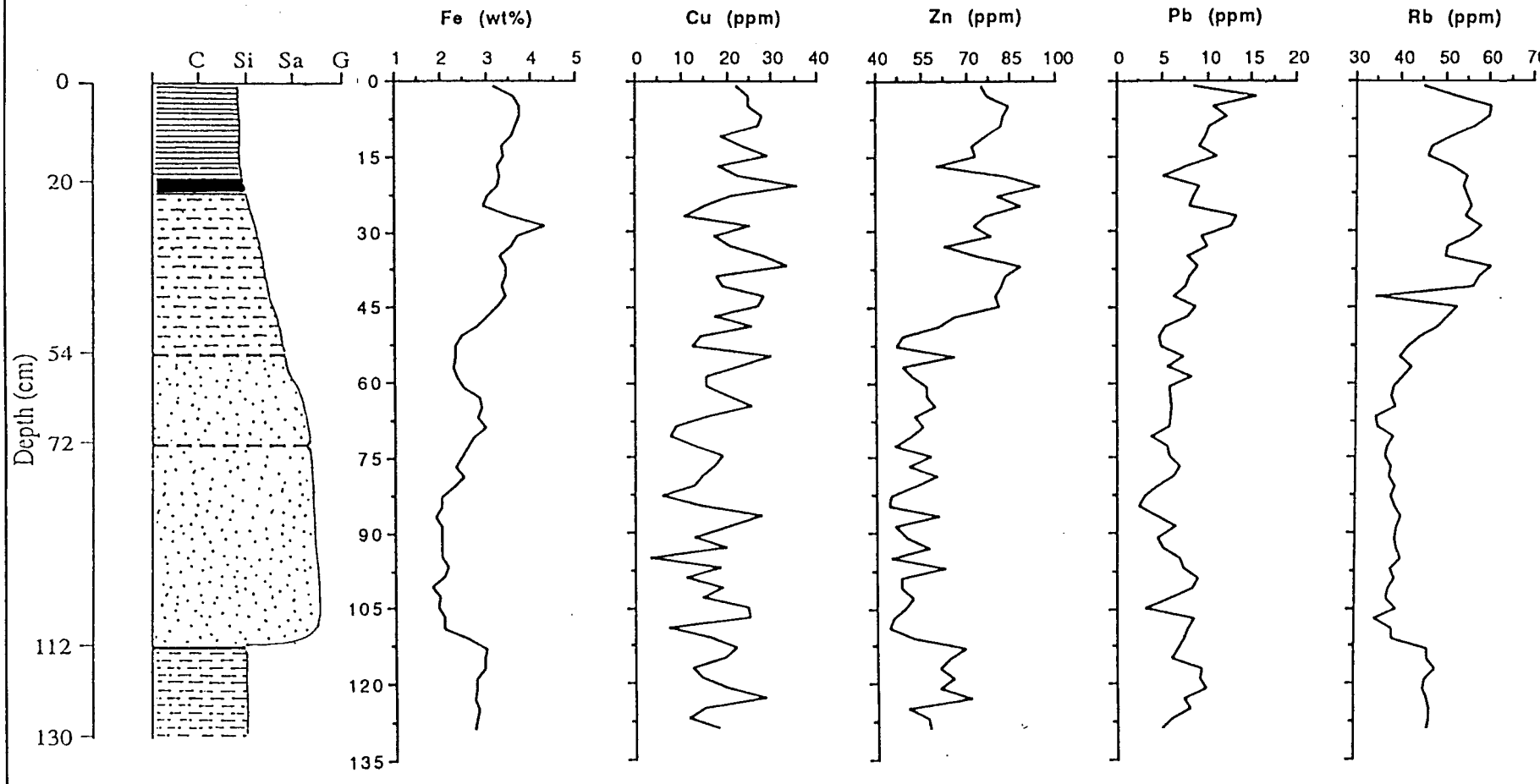


Figure 4.52 Heavy metals in FDHM-13.

Core: FDHM-14

This core was extracted from Maria Slough (Figure 4.53) which is even less active than Nicomen Slough. Its eastern end has silted-in to the extent that trees now grow in the depression formed by the old channel. Thus, there is no through flow of Fraser River waters. The core site was immediately upstream of a short causeway (pierced by a culvert) which bridges the slough at this point (Figure 4.54).

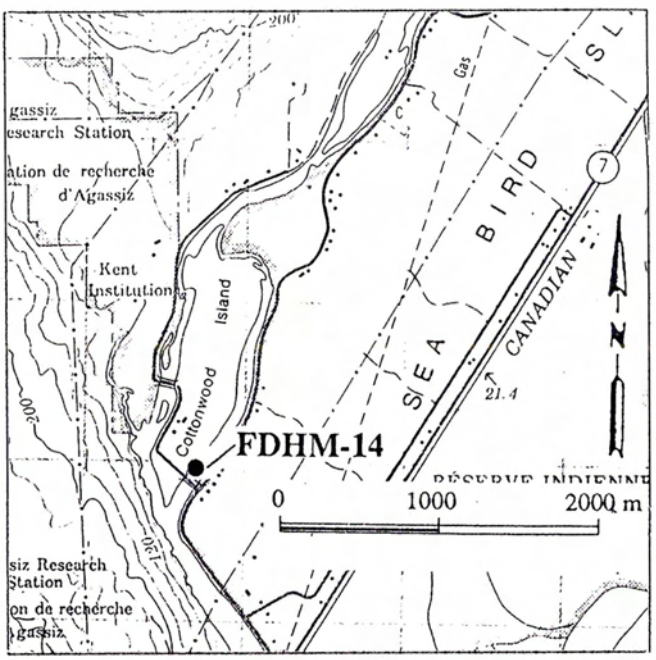


Figure 4.53 Section of the topographic map (92H/5, ed. 4) showing the location of core FDHM-14.

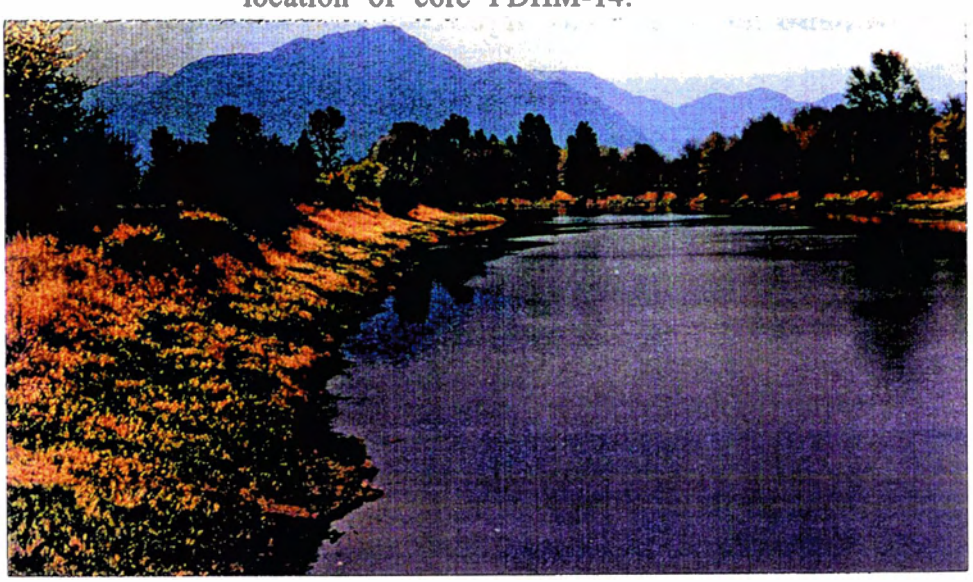


Figure 4.54. The site of FDHM-14 at Maria Slough, Seabird Island.

Lithology: The log (Figure 4.55), resembles that of Nicomen Slough in so far as it consists of a fining upwards sequence overlying a unit of fine silt. It differs, however, in that the fining upwards sequence is punctuated by two periods of deposition of sediment of finer texture than that immediately above and below it. The fine silt unit, which forms the core from a depth of 66 to 95 cm, lies upon pebbly gravel. The sharp contact between silt and gravel indicates that Maria Slough was once a reach of the river and underwent a sudden channel cut-off.

Heavy Metals: Heavy metal levels (Figure 4.56) show an interesting pattern in this core. These levels, like those of FDHM-13, are generally low in comparison with those of cores taken from the delta. However, there are some peaks which stand out in this core. One set of these is at the very bottom of the core from about 90 to 95 cm depth. The other set, which relates to Fe and Pb only, is centred about a depth of about 60 cm. Both sets of peaks are associated with a boundary between fine and coarser textured sediments.

The mean for iron is the highest of any core (Table 4.14). The highest values for iron within the core are associated with the peaks mentioned above and are likely related to the higher levels of zinc and lead found at the same depth. This relationship will be discussed in the Chapter 5. It is also noteworthy that the levels of iron and rubidium are in a sort of rough inverse relationship to one another.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	2.83	10.15	4.23	1.96	46.25	49	0
Cu (ppm)	9.59	36.87	19.71	6.27	31.79	46	3
Zn (ppm)	32.79	101.12	68.69	12.47	18.15	48	1
Pb (ppm)	4.52	18.90	7.78	2.60	33.47	48	1
Rb (ppm)	6.54	58.58	39.42	8.64	21.92	45	4

Table 4.14 Descriptive statistics of heavy metals in FDHM-14.

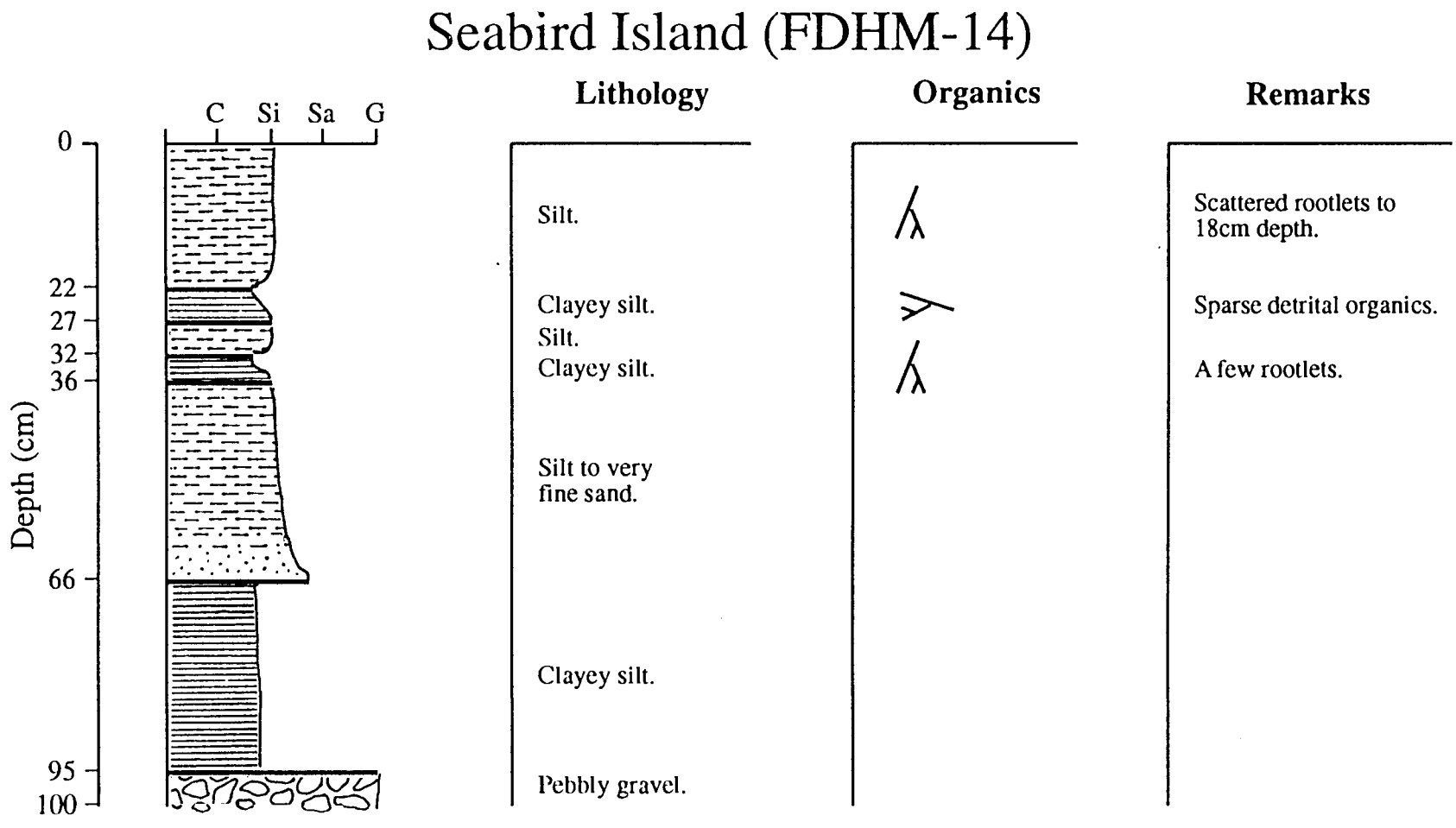


Figure 4.55 Log of the core extracted from Maria Slough on the North side of Seabird Island.

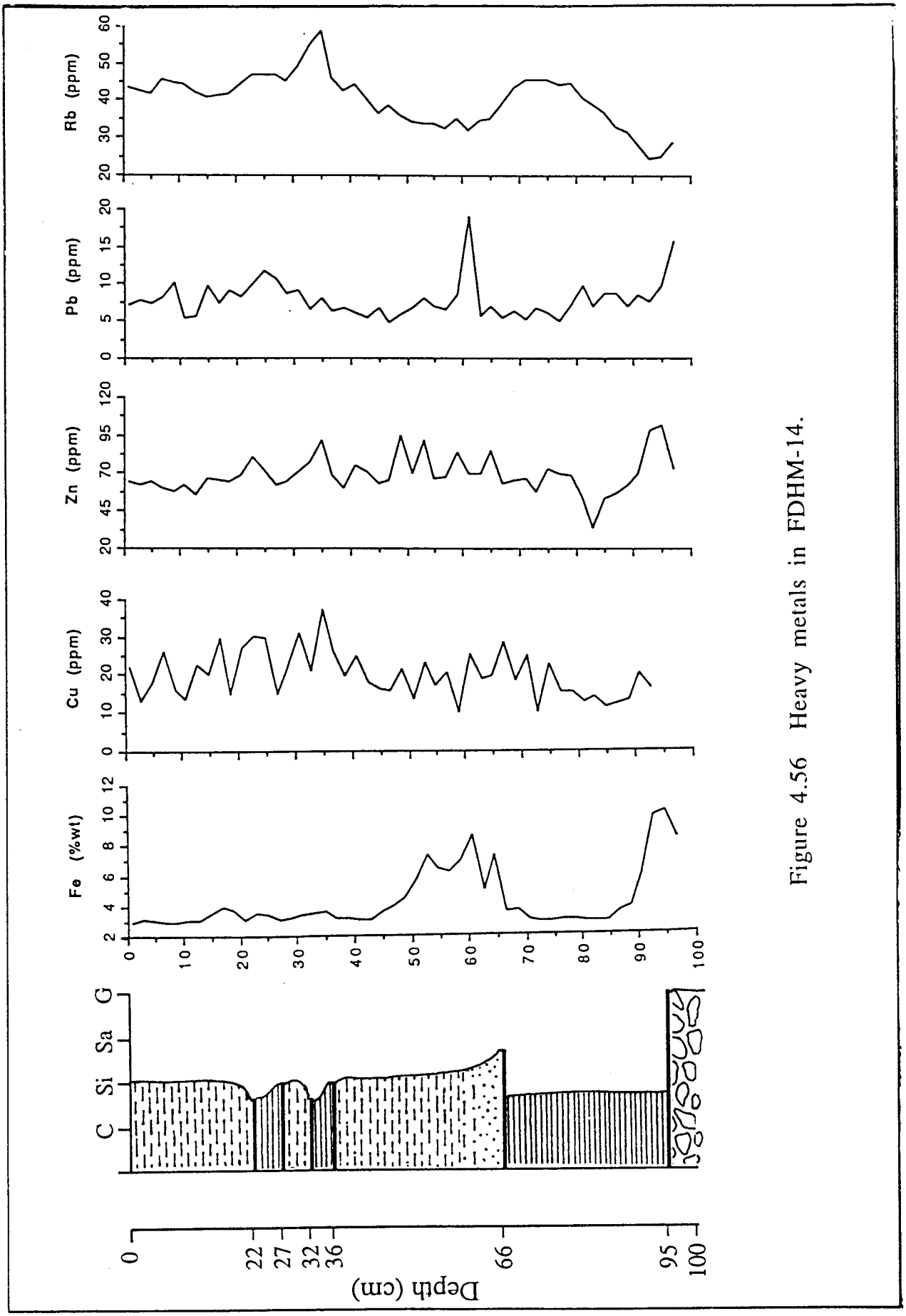


Figure 4.56 Heavy metals in FDHM-14.

Core: FDHM-2

This core was extracted from the high marsh, delta-front sediments of Lulu Island at the foot of Francis Road (Figure 4.59). The site of the core was about 10 m seaward of the dyke.

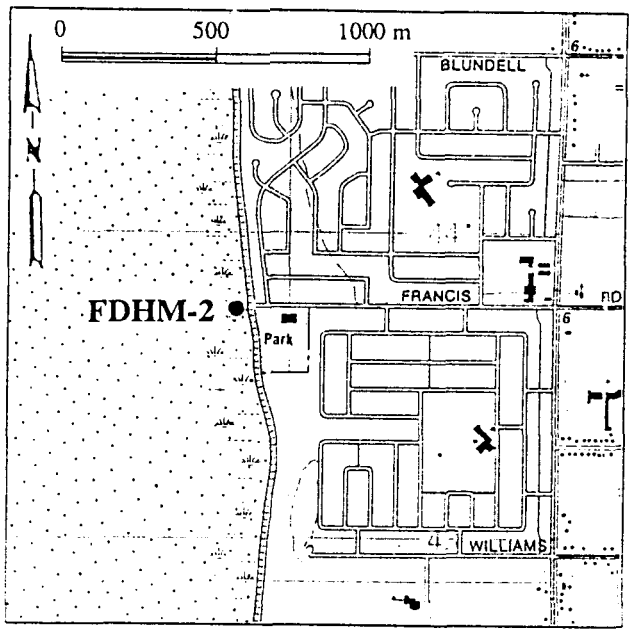


Figure 4.57 Section of the topographic map (92G/3g, ed. 2) showing the location of core FDHM-2.

Lithology: Its log (Figure 4.57) reveals a very uniform sequence which fines gradually upwards, ranging from fine sand to silt in texture and capped by a 10 cm layer of fine, silty peat.

Heavy Metals: The concentrations of copper, zinc and lead (Tables 4.15 and 4.16) are consistently and startlingly higher (an order of magnitude so in the case of lead) than those of any other core. There is also an intriguing peak of both copper and zinc centered about a depth of approximately 52 cm.

Since this core was not taken from a fluvial, overbank environment like the others, it was not included in the overall statistical figures for those cores.

The mean for copper in FDHM-2 at 72.83 ppm is almost three times higher than the overall means of the river cores at 24.56 ppm (Tables 4.15 and 4.16). The highest individual reading is 587.43 ppm, more than five times the river core maximum of 105.15 ppm. Fe was not analysed in this core.

The mean for zinc is 127.85 ppm, well above the river core mean of 87.71 ppm. The highest individual reading for this metal in FDHM-2 is 427.03 ppm, very similar to the 416.64 ppm maximum of the river cores.

The mean lead concentration of 63.74 ppm, is almost six times that of the overall river core mean of 11.17 ppm. The highest individual value for lead is 581.37 ppm, more than ten times the highest individual value found in the river cores.

The rubidium mean of this core, at 60.37 ppm, is the same as the overall mean for the river cores at 60.55 ppm. The highest individual value for rubidium in this core, 84.91 ppm is much lower than that of the river cores, which is 371.88 ppm.

The CV's are high for all metals but most so for copper and lead at 142.31% and 191.65% respectively, reflecting the extreme range of values found in this core.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Cu (ppm)	20.84	587.43	72.83	103.65	142.31	67	0
Zn (ppm)	64.03	427.03	127.85	72.75	56.90	67	0
Pb (ppm)	9.10	581.37	63.74	122.15	191.65	67	0
Rb (ppm)	32.02	84.91	60.37	16.04	26.56	67	0

Table 4.15 Descriptive statistics of heavy metals in FDHM-2.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	0.88	16.05	3.41	0.91	26.74	784	2
Cu (ppm)	1.37	105.15	24.56	10.85	44.17	727	59
Zn (ppm)	10.18	416.64	87.93	37.13	42.23	779	7
Pb (ppm)	2.44	42.07	11.17	4.88	43.67	773	13
Rb (ppm)	4.77	371.88	60.55	22.98	37.95	769	17

Table 4.16 Descriptive statistics of heavy metals in all cores except FDHM-2.

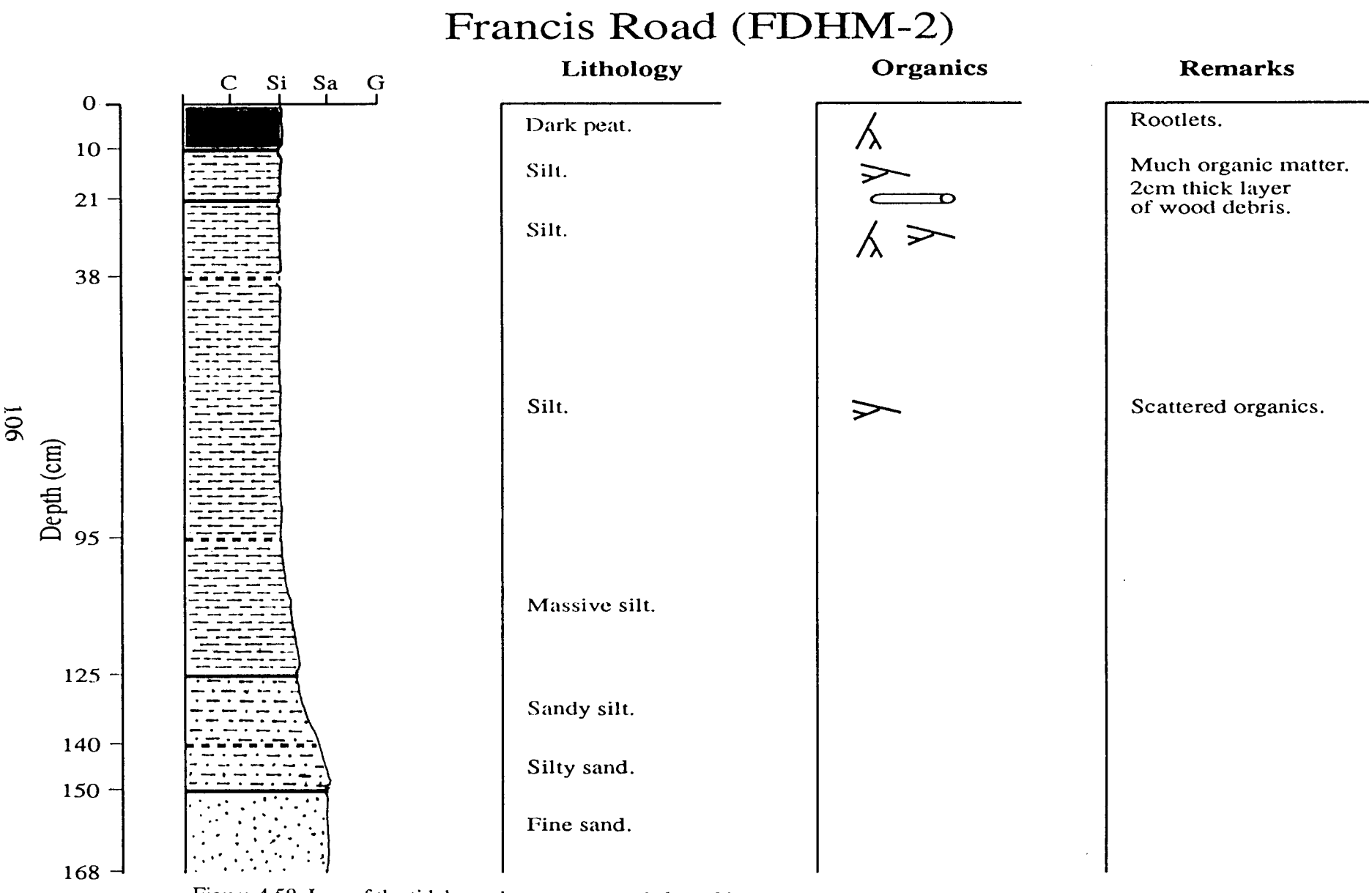


Figure 4.58 Log of the tidal marsh core, extracted about 20 m seaward of the dyke at the foot of Francis Road.

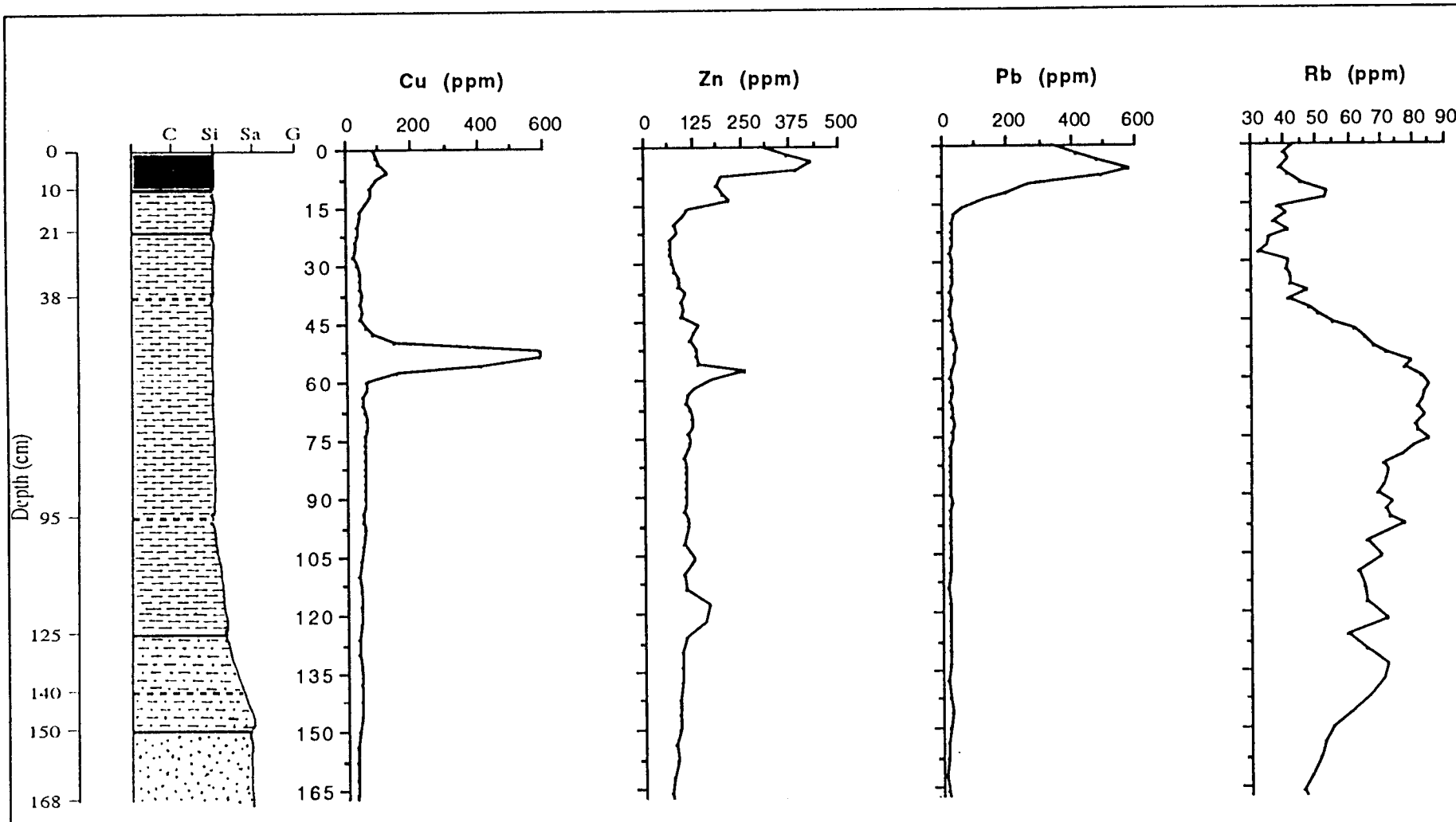


Figure 4.59 Heavy metals in FDHM-2.

SUMMARY OF DATA AND RESULTS

Core Sequences and Metal Concentrations: Examination of the core diagrams indicate that the sediment sequences from which they were extracted might be divided into two classes. The first, and most useful, is the undisturbed sequence.

This type is most useful because in order to place changes in metal concentrations in their correct sedimentological (and chronological) order, it is necessary to relate the heavy metal concentrations to unaltered sediment sequences.

It appears that four of the eight cores extracted from North Arm sediments fall into this class. They are; FDHM-9, 10, 11, 4 and 8. FDHM-3 appears to be somewhat altered but not to the degree that it should be rejected from this group. The sediments from these cores all seem to conform in texture and sequence to the model of overbank deposits. This is also true of those from the Upper Fraser Valley. The delta-front core from the foot of Francis Road appears to be completely unchanged.

The remaining cores, FDHM-5, 6, and 7, appear to be altered. However, important information might still be drawn from them, if the changes are recognized.

The means and standard deviations of Cu, Zn and Pb in every core except FDHM-2 are shown in Figures 4.60, 4.60a and 4.60b. There appears, with some exceptions, to be a slight declining trend in metal concentrations upstream and away from the river (Musqueam Marsh). Copper in FDHM-4 and 8, Zinc in FDHM-5 and Lead at FDHM-4 and 8 appear to be notable exceptions to the trend. However, there is so much variation, particularly with respect to copper, that it is questionable whether there are real differences between concentration means for most cores.

Another, related, problem must also be addressed. The cores vary in depth from 90 cm (FDHM-5) to 240 cm (FDHM-3). The length of the zones of highest metals concentrations also vary. In FDHM-5, for example, the highest metal concentrations are found in 34 cm, or

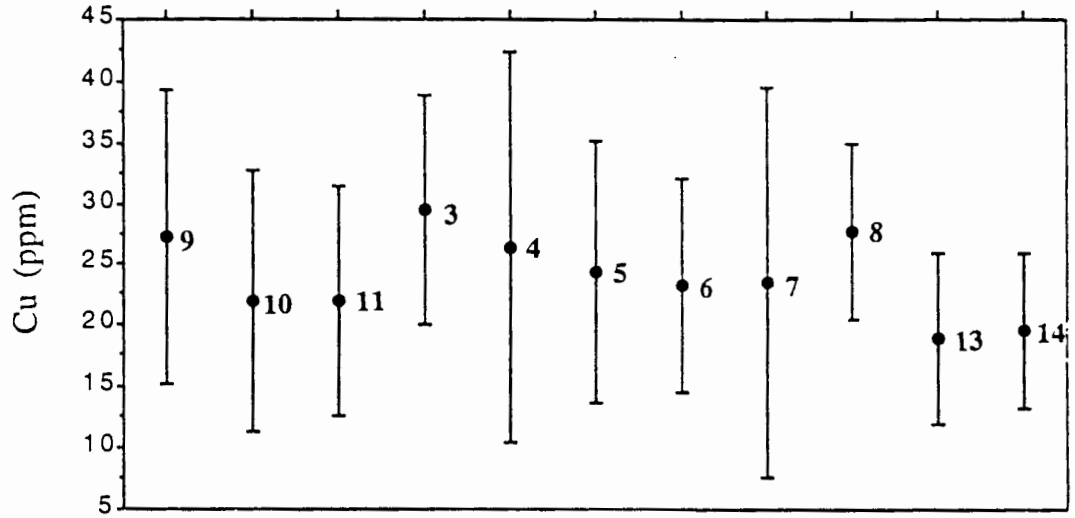


Figure 4.60 Means and S.D.'s of Cu of all cores except FDHM-2.

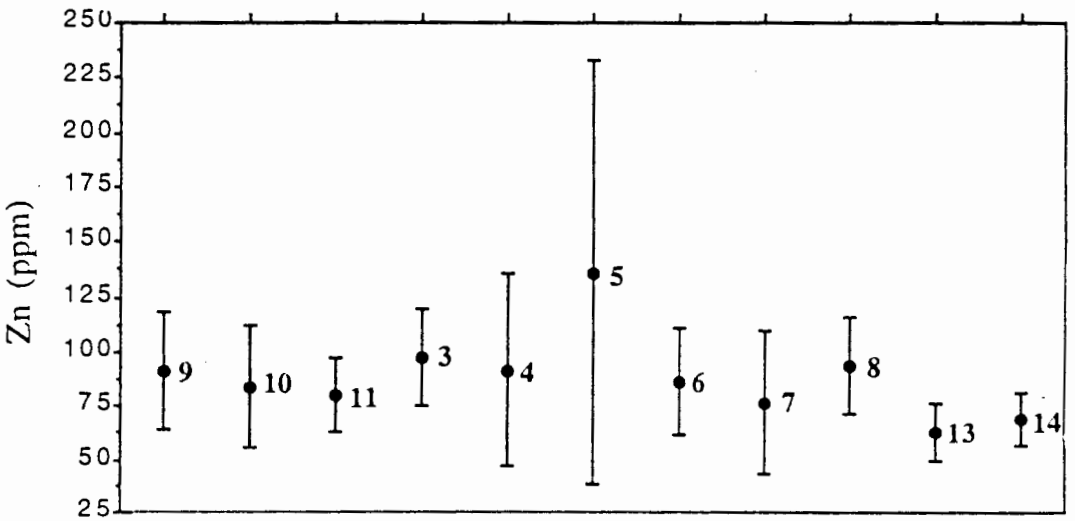


Figure 4.60a Means and S.D.'s of Zn of all cores except FDHM-2.

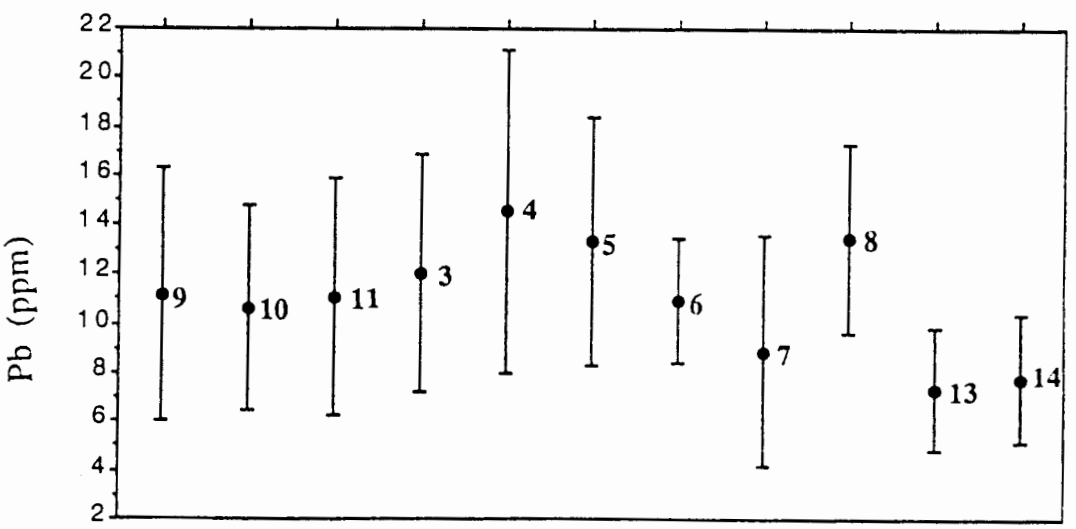


Figure 4.60b Means and S.D.'s of Pb of all cores except FDHM-2.

38% of the core, while in FDHM-11 (164 cm in length) they are found in the top 40 cm, or 24% of the core. Thus, length differences in both core and higher concentration zones act to vary the proportion of the core containing high metal concentrations and will therefore affect within-core mean metal concentrations.

These two circumstances; great within-core variability and varying core and maxiumum concentration zone length, might conceal real differences (or create apparent differences) in metal concentrations between cores.

To overcome these problems, it was decided to select a fixed and equal length from each core and compare the means of each metal through this interval. The choice was necessarily an arbitrary one but after due consideration the interval chosen was 0 to 12 cm depth (6 data points). In two cores, FDHM-3 and 5, the intervals 34 to 44 cm and 60 to 70 cm respectively were chosen because, for reasons explained in Chapter 5, they were regarded as more representative than the current surface. With respect to FDHM-8, in order to obtain six data points for the mean of Pb, it was necessary to use the interval from 0 to 20 cm because two Pb data points had been discarded for the reason outlined in Chapter 3 and because there was insufficient sediment sample from the 2-4 and 10-12 cm depth intervals. For Cu and Zn, the interval 0-16 cm gave the requisite number of points. The reason for selecting the surface 12 cm was that near-surface sediments appear to contain the highest heavy metal concentrations and because it is at and near the surface that anthropogenic input is most likely to occur. As well, sediment texture is similar from core to core in this interval. A review of the graphs indicates that metal concentration variation appears less over this limited interval. Also, 12 cm was near the usable limit in FDHM-8, because two samples in this interval were too scant for analysis and below about 20 cm depth a rapid falloff in zinc and lead concentrations occurs. Thus, the maximum for one becomes the maximum for all. The means and standard deviations of Cu, Zn and Pb for the top 12 cm of every core except FDHM-2 are shown in Figures 4.61, 4.61a and 4.61b. Because these new means were all calculated using the same number of data points, it was possible to

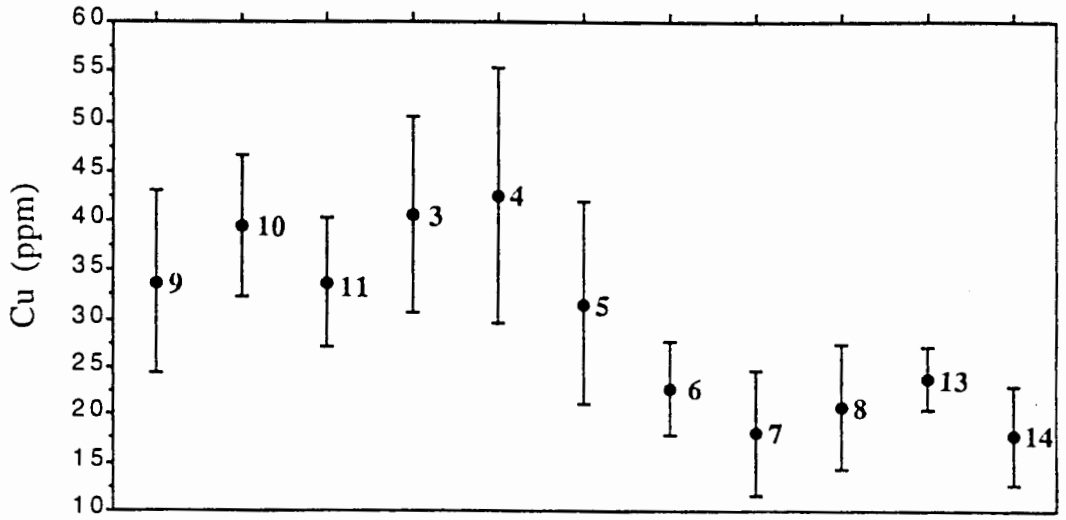


Figure 4.61 Means and S.D.'s of Cu of the top 12 cm of all cores except FDHM-2.

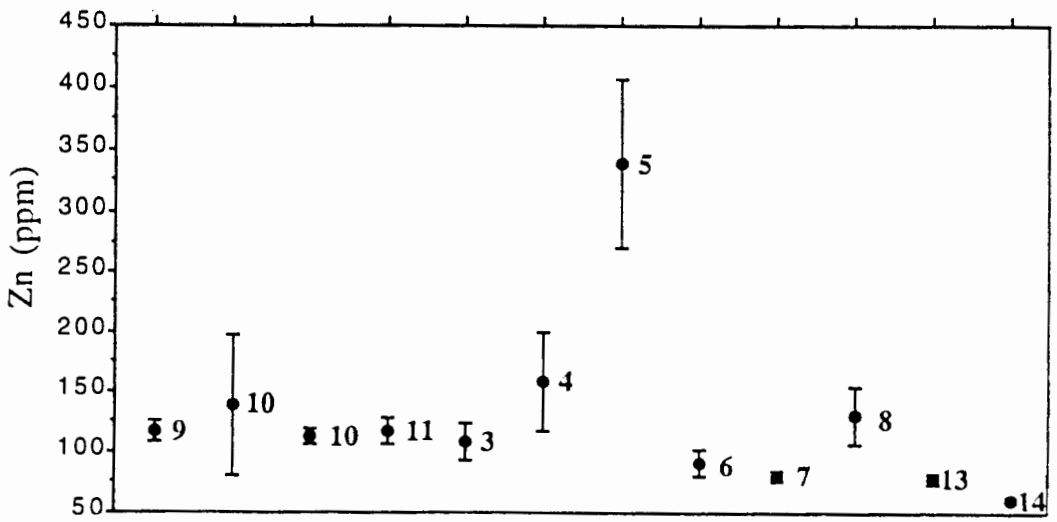


Figure 4.61a Means and S.D.'s of Zn of the top 12 cm of all cores except FDHM-2.

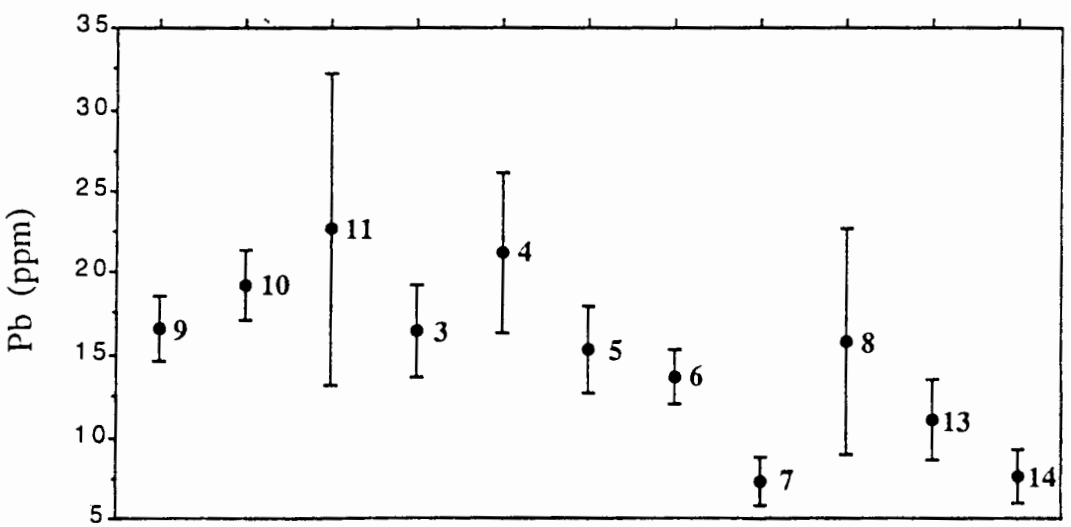


Figure 4.61b Means and S.D.'s of Pb of the top 12 cm of all cores except FDHM-2.

make paired t-tests for statistically significant differences between them. The results of these tests may be found in the Appendix.

Copper still shows the greatest variability, but variation in all three metals is much lessened from that of the complete cores (Table 4.17). FDHM-2 (bold type) from the delta front is included for comparison with the river cores. The only core that now shows greater variation with respect to Cu is FDHM-8 which increases from 26.1% in the complete core to 31.8%. The paired t-tests (Appendix A) show that the means of all cores downstream of, and including FDHM-5 are significantly greater than those upstream of it. Within the downstream group only FDHM-10 and 5 differ significantly (FDHM-10 being greater than FDHM-5). Among the group upstream of FDHM-5, FDHM-6 does not differ significantly from FDHM-8, 13 and 14 but does differ so from FDHM-7. FDHM-7 is significantly less than FDHM-13 but not significantly different from FDHM-8 and 14. FDHM-8, 13 and 14 do not differ significantly. The Cu mean of FDHM-2 is, of course, significantly greater than that of any river core.

Copper	**Complete Core**		**Top 12 cm**	
Core No.	Mean (ppm)	C. V.(%)	Mean (ppm)	C. V.(%)
FDHM-9	27.36	44.11	33.74	27.25
FDHM-10	22.04	48.86	39.51	17.88
FDHM-11	21.95	42.95	33.77	19.11
FDHM-3	29.41	32.32	40.56	24.29
FDHM-4	26.32	60.74	42.41	30.25
FDHM-5	24.41	44.04	31.64	32.47
FDHM-6	23.35	37.52	22.77	21.90
FDHM-7	23.59	67.35	18.22	35.88
FDHM-8	42.82	26.11	20.84	31.98
FDHM-13	19.01	36.51	24.06	13.83
FDHM-14	19.71	31.79	17.91	29.05
FDHM-2	**72.83**	**103.65**	**93.26**	**20.10**

Table 4.17 Means and C.V.'s of Cu of the complete cores and their top 12 cm.

Zinc appears to decline slightly in concentration upstream, with the outstanding exception of FDHM-5 which has the highest Zn concentration of any core (Table 4.17a). FDHM-4, 5 and 10 show a good deal more variation in Zn concentrations than the other cores. The higher Zn variation in FDHM-10 results from its extremely high surface concentration value (260.56 ppm), because of this, the Zn C.V. actually increases from 34.5% in the complete core to 42.9% for the surface values. For this reason two points are shown for FDHM-10: the first employing the usual 0-12 cm interval, the second the interval 2-14 cm, effectively treating the surface value as an outlier. When this is done we see that the variation is greatly reduced and FDHM-10 becomes very similar to the other Musqueam Marsh cores with respect to zinc. Paired t-tests show the North Arm Zn means, with the exception of FDHM-5 which has a significantly greater mean than all other river cores, to be significantly greater than those from the Upper Fraser Valley. The Zn mean of FDHM-2 is significantly greater than that of every river core except FDHM-5.

Zinc	**Complete Core**		**Top 12 cm**	
Core No.	Mean (ppm)	C. V.(%)	Mean (ppm)	C. V.(%)
FDHM-9	91.11	29.95	118.16	8.22
FDHM-10	83.85	34.49	139.40	42.90
FDHM-11	80.51	21.00	108.67	13.63
FDHM-3	97.65	22.68	116.91	9.58
FDHM-4	91.41	48.65	159.16	25.74
FDHM-5	135.58	71.42	339.22	19.77
FDHM-6	86.44	28.23	91.46	12.69
FDHM-7	179.73	44.05	80.81	6.45
FDHM-8	93.65	23.04	130.08	18.42
FDHM-13	62.85	21.87	79.37	4.81
FDHM-14	68.69	18.15	61.26	4.23
FDHM-2	**127.85**	**72.75**	**310.76**	**32.92**

Table 4.17a Means and C.V.'s of Zn of the complete cores and their top 12 cm.

Lead now shows markedly reduced variation in all cores except FDHM-11 where it is only marginally reduced and FDHM-8 in which it increases substantially from the complete core mean of 28.6% to 43.6% (Table 4.17b). Concentrations appear to rise away from the river at Musqueam Marsh and decline from FDHM-4 in the upstream direction with the exception of FDHM-8. All North Arm core Pb means are significantly greater than those from the Upper Fraser Valley. The Pb mean of FDHM-2, not surprisingly, is significantly greater than that of any river core.

Lead	**Complete Core**		**Top 12 cm**	
Core No.	Mean (ppm)	C. V.(%)	Mean (ppm)	C. V.(%)
FDHM-9	11.16	45.64	16.60	11.91
FDHM-10	10.68	39.10	19.34	11.31
FDHM-11	11.05	43.89	22.64	42.12
FDHM-3	12.10	40.12	16.48	17.33
FDHM-4	14.56	45.36	21.26	23.29
FDHM-5	13.35	37.95	15.25	17.49
FDHM-6	18.87	23.05	13.68	12.07
FDHM-7	8.85	53.55	7.30	20.13
FDHM-8	13.52	28.64	15.83	43.58
FDHM-13	7.38	34.02	11.03	22.39
FDHM-14	7.78	33.47	7.58	20.85
FDHM-2	**63.74**	**122.15**	**427.94**	**27.13**

Table 4.17b Means and C.V.'s of Pb of the complete cores and their top 12 cm.

Before making a final comparison of metal content between cores, recall from Chapter 3 the influence that grain size has upon heavy metal concentrations. It is not sufficient to simply make gross comparisons of levels of metals from one core with those of another or even make them of those from one part of a core with another without making due allowance for grain size. This can be done in either of two ways: firstly and directly, by doing an actual physical analysis of the grain sizes by means of standard seives, a Visual

Analysis Tube (VAT) and a Sedigraph or secondly and indirectly, as outlined in Chapt 3, by choosing some metal which is ubiquitous in the fine fraction and using it as a "proxy" for that fraction. For reasons of speed and economy the second method was used in this thesis, although FDHM-9 was analyzed using both methods in order to see how closely the results agreed (Tables 4.18 and 4.18a). The physical analysis of grain size was carried out by Mr. John Martin, graduate student, Geography SFU, with whom this core was shared for theses research. The results of this analysis are shown in Table 4.18 and plots of the target metals against Rb are shown in Figure 4.62. The relationship between the target metals, Zn and Pb on the one hand and Rb on the other does not seem to be quite linear; the concentration of the first two increasing disproportionately when the concentration of Rb exceeds *ca.* 80 ppm.

Depth Range	% Sand	% Clay/silt
0-10	18	82
10-20	14	86
20-30	12	88
30-40	18	82
40-50	17	83
50-60	16	84
60-70	12	88
70-80	25	75
80-90	44	56
90-100	39	61
100-110	68	32
110-120	76	24
120-130	86	14
130-140	88	12
140-150	80	20
150-160	75	25
160-170	68	32
170-175	69	31

Table 4.18 The increasing proportion of sand (by weight) with depth in the core. The coarse and fine fractions were separated using a #230 seive (0.063 mm).

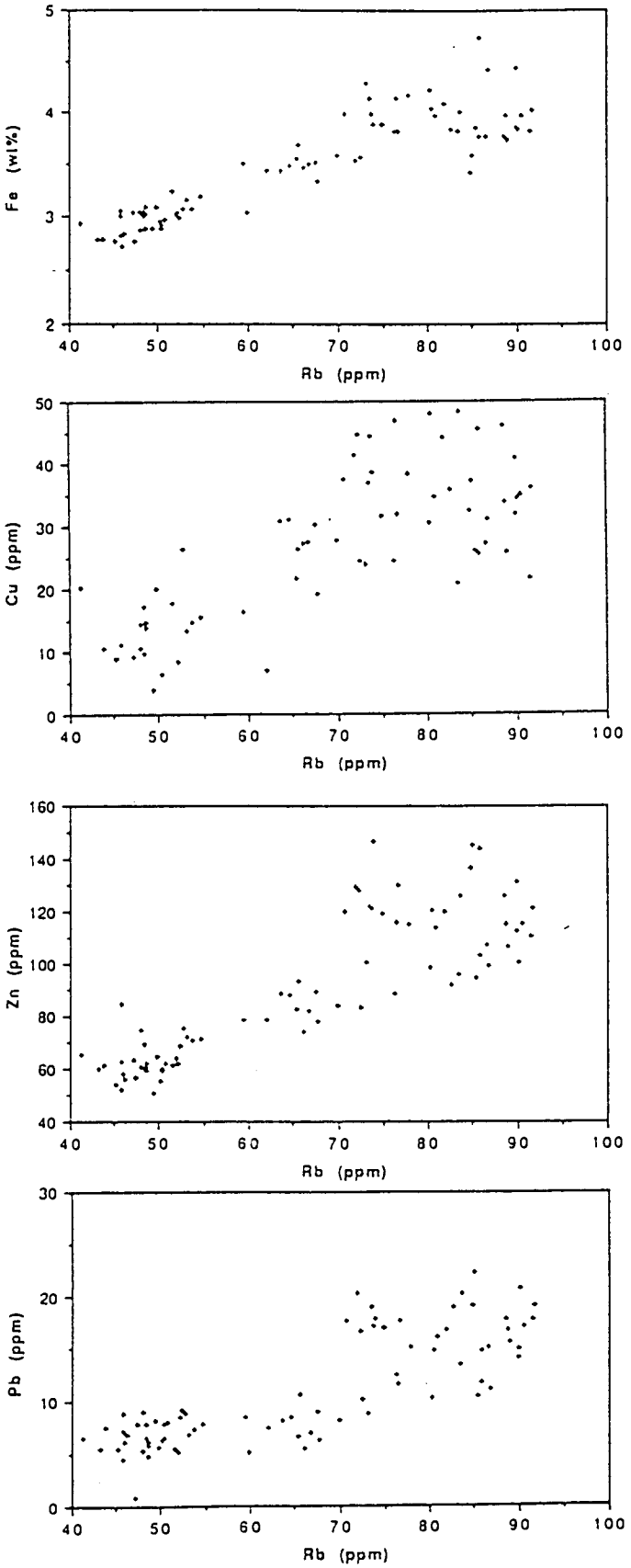


Figure 4.62 Plot of target metals against rubidium in FDHM-9.

Spearman (r_s), non-parametric correlations were used to test the strength of the relationship between the fine fraction and heavy metals on the one hand, and its proxy, Rb and heavy metals on the other, because it was felt that the assumptions necessary for parametric, Pearson-R correlations were not met. The results (Tables 4.19 and 4.19a) show that rubidium is almost as strongly correlated with the metals as the fine fraction and these correlations are strong indeed.

Fe	Cu	Zn	Pb	Rb
0.88	0.89	0.90	0.92	0.86

Table 4.19 Non-parametric (r_s) correlations of Fe, Cu, Zn. Pb and Rb concentrations with weight percentage of the fine fraction in core FDHM-9.

Fe	Cu	Zn	Pb
0.87	0.71	0.84	0.80

Table 4.19a Non-parametric (r_s) correlations of Fe, Cu, Zn and Pb concentrations with Rb in core FDHM-9.

Enrichment: In order to determine if a given core has higher than expected concentrations of a particular metal, the method outlined in Chapter 3 is followed. To review briefly, this consists of dividing the core metal-to-rubidium concentration ratio, by the baseline metal-to-rubidium concentration ratio of the same metal. (The mean concentrations of rubidium and their C.V., used to calculate the target metal-to-rubidium ratio and its error for the top 12 cm of each core, are given in Table 4.20. The Rb mean of the complete FDHM-2 core is similar to those of the complete river cores with the exception of FDHM-13 and 14, but the Rb mean of its top 12 cm appears significantly lower than those all river cores but FDHM-14. Tables 4.21 and 4.22 show respectively the average of the analyses of 10 replicate Laboratory Standard samples from the Gilley Road Core and the baseline factors derived from these averages). If the number resulting from the above calculation, the

Rubidium	Complete Core		Top 12 cm	
Core No.	Mean (ppm)	C. V.(%)	Mean (ppm)	C. V.(%)
FDHM-9	66.01	24.49	90.09	1.39
FDHM-10	65.91	25.54	102.55	6.53
FDHM-11	71.24	45.26	98.21	10.93
FDHM-3	75.48	16.18	83.30	4.05
FDHM-4	55.33	86.29	75.41	38.90
FDHM-5	52.11	24.76	67.55	6.00
FDHM-6	52.07	20.70	48.13	5.18
FDHM-7	52.36	39.03	63.07	7.13
FDHM-8	63.40	10.76	64.11	4.16
FDHM-13	47.37	43.00	53.99	10.69
FDHM-14	39.42	21.92	43.48	3.20
FDHM-2	**60.37**	**26.56**	**41.62**	**6.01**

Table 4.20 Means and C.V. of Rb of the complete cores and their top 12 cm.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	3.64	3.74	3.69	0.03	0.93	10	0
Mn (ppm)	413.47	518.40	466.30	32.60	6.99	10	0
Cu (ppm)	21.08	45.82	35.18	9.09	25.85	10	0
Zn (ppm)	96.67	113.90	102.68	5.00	4.87	10	0
Pb (ppm)	13.59	17.54	15.44	1.55	10.02	10	0
Rb (ppm)	76.83	82.60	80.53	2.13	2.64	10	0

Table 4.21 Heavy metal means of the Gilley Road replicate samples.

Metal	Mean	Factor (Met/Rb)
Cu (ppm)	35.18	0.4369
Zn (ppm)	102.68	1.2751
Pb (ppm)	15.44	0.1917
Rb (ppm)	80.53	Not applicable

Table 4.22 Baseline factors for Cu, Zn and Pb as derived from the Gilley Road samples.

enrichment factor (EF), is greater than 1.1 (the 0.1 part represents a 10% allowance for diagenetic enrichment), it indicates anomalously high levels of the target metal in that core. The results of the enrichment calculations and their calculated errors are given below (Tables 4.21). Error was calculated by taking the square root of the sum of the squares of Standard Deviation-to-Mean ratios for the four numbers used in calculating each EF.

Core No.	Cu EF	Zn EF	Pb EF
FDHM-3	1.11±0.36	1.10±0.12	1.03±0.21
FDHM-9	0.86±0.38	1.03±0.10	0.96±0.16
FDHM-10	0.88±0.32	1.07±0.44	0.98±0.17
FDHM-11	0.79±0.34	0.87±0.18	1.20±0.45
FDHM-4	1.23±0.56	1.62±0.47	1.47±0.47
FDHM-5	1.07±0.42	3.94±0.21	1.18±0.21
FDHM-6	1.08±0.34	1.49±0.15	1.48±0.17
FDHM-7	0.66±0.45	1.00±0.11	0.60±0.24
FDHM-8	0.74±0.41	1.59±0.20	1.27±0.45
FDHM-13	1.02±0.31	1.15±0.13	1.07±0.27
FDHM-14	0.94±0.39	1.11±0.08	0.91±0.23
FDHM-2	**5.13±0.33**	**5.86±0.34**	**53.64±0.30**

Table 4.23 Enrichment of Cu, Zn and Pb in all cores.

It appears that no river core is indisputably enriched in copper, although it is quite possible that FDHM-3, 4, 5 and 6 may be enriched. The delta front core FDHM-2 has no less than a five-fold enrichment of copper. Less certain are FDHM-13 and 14. FDHM-9, 10 and 8, if enriched, would be only slightly so. FDHM-10 and 7 definitely have no enrichment.

With respect to zinc, among river cores FDHM-5 is most certainly highly enriched in this metal, much more so than any other core, while FDHM-4, 6 and 8 although much less so than FDHM-5, are also definitely enriched. FDHM-3, 9, 10, 7, 13 and 14 may be enriched (3, 9, 7 and 14 only slightly at most). It appears unlikely that FDHM-11, 13 and 14 have any enrichment. As with Pb, FDHM-2

has far greater enrichment of Zn than any river core with an almost six-fold enrichment of this metal.

Finally, lead appears to be definitely enriched in FDHM-6 only, but has a strong possibility of enrichment in FDHM-4, 5, 8 and 13 the possibility of, at most, slight enrichment in FDHM-9, 10 and 14 and no enrichment whatsoever in FDHM-7. FDHM-2 has a staggering enrichment factor of over 53, more than an order of magnitude greater than any river core EF.

Cesium-137 Chronology: If the determination of the correct relationship between heavy metal concentrations and depositional sequences depends upon the originality of the deposits, then so too must dating of sequences using some distinctive chemical or radioactive property. Any disturbance at a core site that redistributed or disarranged the sediment following the development of a physically distinctive horizon would, if not destroy the horizon, render its dates suspect.

Therefore, the task of correctly associating these phenomena with one another must await the analysis of Chapter 5.

CHAPTER 5

DISCUSSION AND CONCLUSIONS

INTRODUCTION

An examination of the drawings, graphs and tables of Chapter 4 reveals general trends in the heavy metal concentrations; higher levels of heavy metals in the uppermost parts of the cores and a tendency towards higher levels in the downstream cores compared to those upstream. The latter trend is more pronounced when only the top 12 cm of each core are examined. The highest concentrations of all are found in FDHM-2. This last core of course, was taken, not from the overbank sediments, but from the upper tidal sediments of the delta front. There are some other less obvious differences as well which shall be examined later.

Before considering the heavy metal levels of the cores, the time estimates derived from the Cs-137 data will be examined. This is done in order that such dates might be used to relate any enrichment of heavy metals in sediments to a definite time interval.

CESIUM-137 DATING

^{137}Cs dating methodology is discussed in Chapter 3, pages 36 to 38.

The cesium-137 statistics given in individual tables for each core in Chapt 4. are summarized in Table 5.1.

FDHM-10: There is a very definite peak in the counts at about 23 cm depth in this core, with a another, lesser one directly above it at 12 cm, and one, possibly two, lesser peaks below it, at 30 and 34 cm depth (Figure 4.13).

Core	Min	Max	Mean	St D	C V (%)	Count	Miss
10	66	785	292.00	188.89	64.69	23	2
3	-85	584	243.96	163.14	66.87	24	0
8	153	1243	529.55	252.68	47.72	40	5

Table 5.1. Summary of ^{137}Cs statistics from Chapter 4.

Conclusions: It is concluded that the peak centred about 23 cm depth represents 1964, the year of maximum fallout from atmospheric nuclear arms testing (Koide, *et al.* 1979). This conclusion is reinforced by the fact that there was extremely high water during the spring freshet of that year (Inland Waters Directorate, 1985) which could account for the thin sand bed at the same depth (23 cm). The core was taken in 1991, thus we have an estimate of sedimentation rate of 0.9 cm a^{-1}.

FDHM-3: There is no such definite peak in these counts as there was in FDHM-10 (Figure 4.8), with the exception of the one at 65 cm depth. The maximum values at 78 and 87 cm depth are formed by individual sample counts; neither are parts of an upward trend in ^{137}Cs counts.

Counting began at a depth of 55 cm, much lower in this core than it was in either FDHM-10 or 8. This was done on the assumption that the sudden change in sediment texture at 70 cm depth results from the blocking of McDonald Slough by the causeway in 1961. The change in topography resulting from this is apparent if one compares two editions of the same map (Figs. 4.2 and 4.2a): the earlier map shows the area before, the later one the area following, construction of the causeway and treatment plant. It can be seen that parts formerly occupied by water are now dry land and that the site of FDHM-3 lies at the edge of this filled area. These construction changes ended flow in the slough and it might be expected that the resulting sudden change to a lower energy environment would

produce an abrupt shift to deposition of finer textured sediment. This shift, in turn, could be related to the year of construction. Thus, two independent dates for the sediments might be obtained, the first derived from the ^{137}Cs counting and the second by using the date of the slough's blockage.

However, it is now concluded that the coarser unit from a depth of 70 to 90 cm represents either a period of more energetic flow in the slough or is dredge spoil.

When the summary statistics for ^{137}Cs radiation counts are examined it is seen that the maximum count is 584 for this core, while for FDHM-10 it is 785 and for FDHM-8, 1243 counts.). This maximum is not part of a trend but is an isolated count. The highest reading which could be regarded as a peak is at about 65 cm depth where the maximum count is 450 but with such a high C.V. (66.87%), it impossible to say if this an apparent rather than real peak.

Conclusions: since the maximum readings for this core are so low and the peaks isolated, rather than part of a trend, no dating can be done using the ^{137}Cs data from FDHM-3.

FDHM-8: Counting started at 20 cm depth because the samples were too scant above this depth to allow the necessary 5 g pellets to be made. Between 70 and 92 cm depth only every second sample (i.e., every 4 cm) was counted as the Cs-137 counts began to diminish. However, with the sudden jump in counts at 92 cm depth, counting of every sample was resumed for the balance of the core. Note the peak at a depth of 45 cm, the lesser one at 93 cm and perhaps one at 56 cm.

The maximum count for this core is 1243 compared with 785 and 584 for 10 and 3 respectively. The peak at 45 cm depth is not isolated and is the culmination of a trend while the one at 93 cm depth is not so definite.

Conclusions: The high ^{137}Cs values of the peak centred about 45 cm depth lead to the conclusion that it represents the maximum fallout in 1964. The undisturbed, uniform nature of the sediments at FDHM-8 as shown by the core log and the definite peak at 45 cm lend confidence that a reliable estimate of the sedimentation rate

from 1964 to 1991 might be made at this core site. This yields an estimate of the average rates of sedimentation from from 1964 to 1991 of 1.7 cm a^{-1}. The peak at 93 cm depth is not considered definite enough to yield a reliable date, but it may represent the onset of fallout in 1954.

CORES AND HEAVY METALS

Each core and its peculiarities are discussed separately. Significant features which warranted special treatment are also discussed.

Cores FDHM-9, 10 and 11

FDHM-9, 10 and 11: All three of these cores have well-defined, "classic", overbank fining upwards sequences with thick clay/silt units in the topmost part of the core (Figure 4.3). Because of the clay content, the top 12 cm of all three cores have high Rb means, in fact the highest all cores (Table 4.20). The absolute concentrations of Cu, Zn and Pb are also high compared to other cores. However, these high absolute values do not translate into high EF's. All three cores have Cu EF's apparently less than 1.00. With respect to Zn, FDHM-9 and 10 appear about 1.00 and FDHM-11 appears to be definitely less than 1.00 for this metal. Only in FDHM-11 does it appear possible that Pb might be enriched. The EF of FDHM-10 appears to be about 1.00 for Pb and possibly some enrichment in FDHM-11. A great deal of spent shotgun shells were found in and about Musqueam Marsh which might account for this possible lead enrichment.

Cores FDHM-3 and 4.

FDHM-3: There is a distinct dip in metal values in the top 35 cm of the sediment but the values again increase as one nears the surface (Figure 4.17). (The trough of the dip is centred about 20 cm depth). This dip is attributable to the sand cap which is not riverborn sand but rather windblown sand from the tidal flats to the west of the causeway. Below this trough the concentrations of Cu, Zn and Pb are quite uniform. When the tide is low, the flats dry enough to allow sand to be blown inland. Such sands are more than a meter thick on the leeward side of the North Arm jetty. (Personal communication, J. MacFarlane, North Fraser Harbour Commission, 1994). If one examines the maps (Figures. 4.2 and 4.2a) drawn before and after the blockage of the channel by the causeway, it will be seen that the

tidal flats have become much more extensive than before and now fill the large area formerly occupied by the channel. Hence, an area once a channel is now a potential source of aeolian sand.

Since the core below 35 cm is, by and large, a fining-upwards one, it was concluded that this is the original river-deposited material which was subsequently capped by the aeolian sand and therefore represents, with the exception of the sand cap, an overbank deposit sequence. Except for the above mentioned 35 cm unit, the levels of copper, zinc and lead, are quite uniform.

It is because the top 35 cm is primarily aeolian in origin that the interval from 34 to 46 cm was chosen, as the fluvially-deposited surface, for analysis. Paired t-tests of the two 12 cm intervals showed no significant differences in Zn and Pb means but the Cu mean of the 34 to 46 cm interval was significantly higher than that of the 0 to 12 cm interval.

FDHM-4: This core was extracted from an area once occupied by a channel that separated Duck Island from Lulu Island (Figure 4.2). The channel silted-up after construction of a causeway 35 years ago (City of Richmond Archives, 1960) which replaced a bridge giving access to Duck Island and ultimately Sea Island *via* another bridge on the opposite side of Duck Island (Figure 4.2a). Therefore, the lowermost sands, from the bottom of the core at (Figure 4.25) a depth of 116 cm up to a depth of 74 cm and fining upwards from coarse to medium texture, are no doubt buried channel sands. The high absolute metal concentrations as well as the higher enrichment factors are doubtless mostly a result, like those of FDHM-5, of intensive and extensive industrial activity in this area.

The highest concentration of heavy metals is in fine sediments in the upper part of the of the core from a depth of 46 cm upwards to the surface.

Cores FDHM-5, 6 and 7

These three cores all showed unusual stratigraphy.

FDHM-5: This core does not have particularly high levels of metals in that part of the core between 5 and 60 cm depth (Figure 4.28). Below this depth, however, the levels rise sharply to those which are among the highest of any of the river cores. The reason for this apparent contradiction is twofold: firstly, the original sediment surface was covered in the spring of 1988 in order to create wildlife habitat; secondly, a sewer which drains Mitchell Island has its outfall on the eastern (upstream) edge of the marsh.

When a marina/market complex was built at Bridgeport, beside the same marsh from which FDHM-4 was removed, it entailed the destruction of some wildlife wetland habitat there. In order to compensate for this destruction, habitat had to be enhanced elsewhere, in this case at Mitchell Island. Hence, sediment dredged from the construction site at Bridgeport was dumped upon the marsh at Mitchell Island in order to provide a base for the necessary vegetation (Williams, 1993). This accounts for the sudden change from a finer to a coarser a texture at a depth of 60 cm, this coarser texture is maintained upwards to a depth of 5 cm when the sediment begins to fine upwards. The top 5 cm must constitute newly deposited river sediments which, like those below 60 cm, have levels of metals sharply higher than those of the 5 to 60 cm stratum. If one considers only the naturally deposited sediments (those below 60 cm and above 5 cm depth), then the means for FDHM-5 become much higher (Table 5.2, 5.2a).

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	2.58	3.17	2.83	0.12	4.21	28	0
Cu (ppm)	7.94	29.35	18.52	6.49	35.05	28	0
Zn (ppm)	57.73	117.94	79.00	13.14	16.63	28	0
Pb (ppm)	6.66	13.58	10.13	1.54	15.18	28	0
Rb (ppm)	39.34	51.83	44.75	2.94	6.56	28	0

Table 5.2 Means of metals from 5 to 60 cm depth (filled material) in FDHM-5.

Metal	Min	Max	Mean	St D	C V (%)	Count	Miss
Fe (wt%)	2.82	3.86	3.47	0.33	9.42	17	0
Cu (ppm)	17.52	56.48	34.12	9.26	27.14	17	0
Zn (ppm)	79.41	416.64	228.78	103.26	45.13	17	0
Pb (ppm)	10.51	25.54	18.66	4.29	23.01	17	0
Rb (ppm)	44.15	106.19	64.23	13.86	21.58	17	0

Table 5.2a Means of metals from 0 to 5 cm and 60 to 90 cm depth (river deposited material) in FDHM-5.

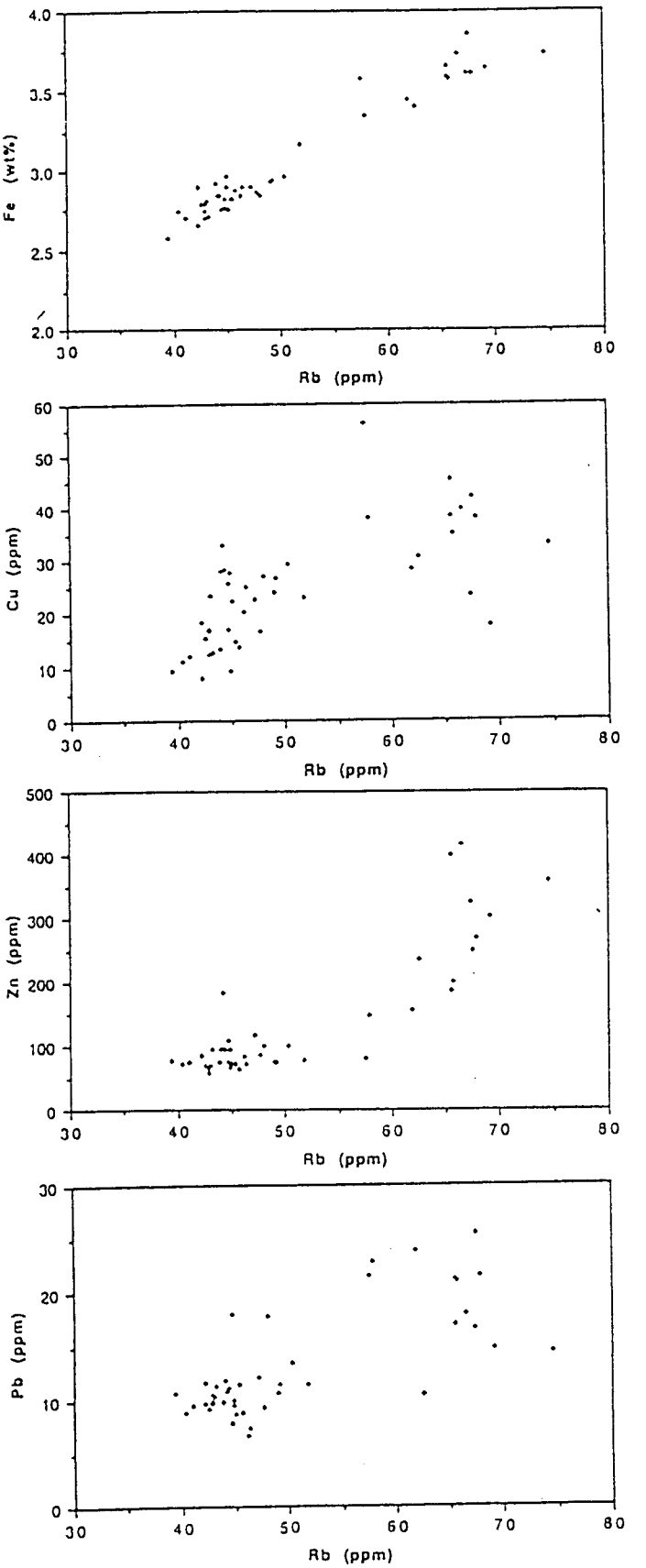


Figure 5.1 Plot of target metals against rubidium in FDHM-5.

Knowing when the material was dumped also allows a good estimate to be made of the sedimentation rate at this marsh. The core was extracted in the summer of 1991; the dredge spoil from Bridgeport was dumped in the spring of 1988; there has been 5 cm of deposition over 3.3 years. Therefore the rate of deposition is approximately 1.5 cm a^{-1}.

Comparing metal levels after partitioning the core samples into two classes, river deposited and dumped, it is noted that the river deposited samples have higher levels of every metal. The means of copper and lead, 34.12 ppm and 18.66 ppm respectively, are almost twice as great in the original sediment as in the dumped material, where they are 18.52 ppm for copper and 10.13 ppm for lead. The mean of zinc at 228.78 ppm is almost three times greater than that of the dumped material which is 79.00 ppm. The scattergrams of target metals against rubidium (Figure 5.1) show the clustering of the metal concentrations into two populations.

Because the burial of the original surface was definitely dated and because of the sharp rise in concentrations below 60 cm depth, the interface at 60 cm was chosen as the true "surface" and the 12 cm interval below this this point examined.

Mitchell Island is the site of many industries which might be expected to release large quantities of heavy metals into the environment, such as a steel plant - now defunct, auto wreckers, metal salvage, metal fabrication and an establishment producing acetylene and other commercial gases. The outfall of a sewer which serves the island is 50 m east (upstream) of the site from which FDHM-5 was taken. These two factors no doubt account for the elevated levels of heavy metals found in that part of the core comprised of river-deposited sediment.

FDHM-6: This core (Figure 4.30), has a silt unit superimposed upon alternating layers of sand and silt, divided from one another by sharp contacts. This sequence is unlike those of the other cores the most of which much more closely resemble the overbank sediments as described in Elliott (1986). The immediate vicinity of the small marsh from which the core was extracted has been built upon both

by a pumphouse which services a City of Richmond drainage ditch and by a CN Railway right-of-way and carslip. In addition, the marsh is exposed to the wash from a great deal of water traffic, this turbulence would be particularly intense when tugs were docking and removing railcar barges at the presently disused car slip. This appears to be reflectd in the alternating layers of sand and silt in the core's lower 65 cm. The overlying 65 cm thick unit of mostly clayey silt suggests that a more stable mode of sedimentation has established itself.

There is no obvious explanation for the relatively high enrichment factors at this core site. One answer may be that the drainage pump station discharge water carries a proportion of heavy metals which settled on fields as atmospheric fallout. These metals could subsequently be transported to the drainage system by precipitation and/or groundwater flow. Urban air in the United States has been found to be enriched relative to the earth's crust by a factor of 83 for copper, 270 for zinc and 2300 for lead (Förstner and Wittmann, 1981) and a significant proportion of the metals in stream runoff of urban areas has been attributed to atmospheric deposition (Bubb and Lester, 1991)

FDHM-7: This core, like FDHM-5 and 6, has an unusual stratigraphy (Figure 4.37), specifically, a coarse sand unit sandwiched between two much finer units. This core was taken from a ribbon marsh located in a shallow swale formed by a low rise at the river's edge on one side and a road embankment on the other, and is *ca.* 8 m wide. One explanation for the sand unit is that it results from a flood event. The sharp boundaries at its upper and lower surfaces would support this. Recall, from Chapter 4, Figure 4.38, the spikes in Fe, Cu, and Pb at the upper boundary of the sand. It was observed while logging the core that the sand had the brownish cast associated with an oxidizing environment, while the overlying silt layer had the grayish cast associated with a reducing one. It is reasonable to conclude that the sand is a conduit for river water, rich in oxygen, which meets the overlying reduced sediments. At such boundaries an "oxygen barrier" develops which results in the formation of insoluble ferric

oxides and manganese oxides (Perel'man, 1967). These oxides in turn become a "sorbent barrier" for metals such as copper, zinc and lead by adsorbing them (Perel'man, 1967). This would account for the elevated levels of these metals at this boundary, especially iron, remembering that there is fully four times the concentration of iron at this point than that found in any other core.

The superposition of anthropogenic upon original material at FDHM-5 suggested that perhaps the same thing had occurred here and that this, rather than a flood event, was responsible for the sand unit. The pattern of heavy metal concentrations; low in the overlying sand unit (48 to 98 cm depth) and increasing sharply in the peaty clay, argued the same conclusion (Figure 4.38). I found no documentary evidence for fill emplacement, but the marsh was beside a road embankment from which material might have been inadvertently dumped. The coarse sand is mostly free of any organic material except some wood fragments in the lower 20 cm of the unit (Figure 4.37). Paired t-tests showed the mean concentrations of Cu, Zn and Pb to be significantly greater in the top 12 cm of the peaty clay unit (98 to 110 cm depth) than in the surface 12 cm of the core (Appendix, Table 5.2). Therefore, the EF's for FDHM-7 were re-calculated using the upper 12 cm of the peaty clay unit. The results are shown in Table 5.3 together with the original calculation.

FDHM-7	Cu EF	Zn EF	Pb EF
SURFACE	0.66±0.45	1.00±0.11	0.60±0.24
CLAY	1.09±0.34	1.41±0.29	1.29±0.28

Table 5.3 Recalculation of enrichment in FDHM-7.

The EF's calculated for the clay unit are much increased over those calculated for the present surface sediments, suggesting that the upper 12 cm of the peaty clay unit represents the original surface, the overlying material having been anthropogenically emplaced.

Core FDHM-8

FDHM-8: This core (Figure 4.47) with its uninterrupted and uniform sedimentation sequence, was taken about 5 m from the river's edge. The high EF of zinc likely relates to a galvanizing plant only 1.0 km upstream of the core site. This was also thought to be the cause of elevated concentrations of zinc found in surface samples taken nearby in 1989 by Swain and Walton (1990).

Cores FDHM-13 and 14.

These cores are also discussed together; both sites are located in almost abandoned channels 80 km (FDHM-13) and 110 km (FDHM-14) upstream (east) of the main study area.

FDHM-13: During the 1948 flood, Nicomen Island was completely covered with water. In order to protect the island, dykes (including dams at Skumalasph and Queens Islands) were constructed in1950/51. The dams greatly reduced the circulation of water through Nicomen and Dewdney Sloughs. Since 1984 Suicide (Norris) Creek has carried an increased amount of debris and bed load, most probably the result of logging in its watershed. The debris has blocked Nicomen Slough about 2 km east of Dewdney and resulted in almost total loss of flow in the slough upstream of the mouth of the creek. This is shown by the gauge at the dam on Skumalasph Island which shows no difference in levels from one side to the other, when the true difference should be about 1.5 m (Personal Communication, Mr Fred Wodtke, Deputy Inspector of Dykes, 1994). The height difference results from the higher elevation of the dammed upstream entrance to Nicomen Slough, as compared to its undammed downstream entrance on Dewdney Slough.

It is necessary that some water flow through the slough in order to flush it out, therefore attempts, without permanent success, have been made to clear the blockage at Suicide Creek.

It seems likely that the sand unit (Figure 4.51) and the capping layer of coarse organics from a depth of 112 cm upwards to 18 cm are a result of the 1948 Fraser River flood and that the clayey silt which forms the top unit represents subsequent deposition in an

environment of diminished energy resulting from restricted flow. If this is so, then only 18 cm of clay/silt sediment have been deposited since the dams were built in 1951.

This core had the lowest mean values for heavy metals of any core with the exception of rubidium which was only higher in FDHM-14. The lower heavy metal values in this core as compared with the delta cores suggests that the input of such metals is lower than that of the delta.

FDHM-14: The set of localized peaks in metal concentrations associated with the coarse/fine contacts in this core (Figure 4.55), is no doubt the result, as in FDHM-7, of the phenomenon of sorption which results when a reducing environment is suddenly succeeded by an oxidizing one. The coarse sediment bears oxygen rich waters while the finer sediment is a gleyed, reducing environment. This has occurred at two different contacts and more extensively in FDHM-14 than in FDHM-7. There is a highly significant relationship between zinc on the one hand and iron and manganese on the other in the two sections of the core (50 to 66 cm and 92 to 98 cm depth) which have elevated levels of iron and manganese; no such relationship exists between zinc and rubidium in these same sections.

Data from 51 to 65 and 93 to 97 cm depth were analysed because of the correlationships between Fe/Mn and Zn and Pb (Figure 4.54 and Table 5.9), which indicates that the oxygen barrier formed against Fe and Mn at these depths has become a sorbent barrier for at least Zn and Pb (Manganese, though analysed, was not presented throughout the data sets because it was only necessary to use it in this one calculation.). Fe and Mn are strongly and positively correlated with one another but Fe and Mn are both *negatively* correlated with Rb. This inverse relationship between Fe and Rb is seen in the top scattergram of Figure 5.2. Both Zn and Pb are strongly correlated with Fe and Mn. Cu is weakly correlated with Fe but not Mn. Cu, Zn and Pb are all negatively correlated with Rb. In the remaining, larger part of the core (Table 5.4a), Cu has a stronger correlation with Rb than with either Fe or Mn; Zn has the same correlation with both Fe and Rb and virtually none with Mn, while Pb

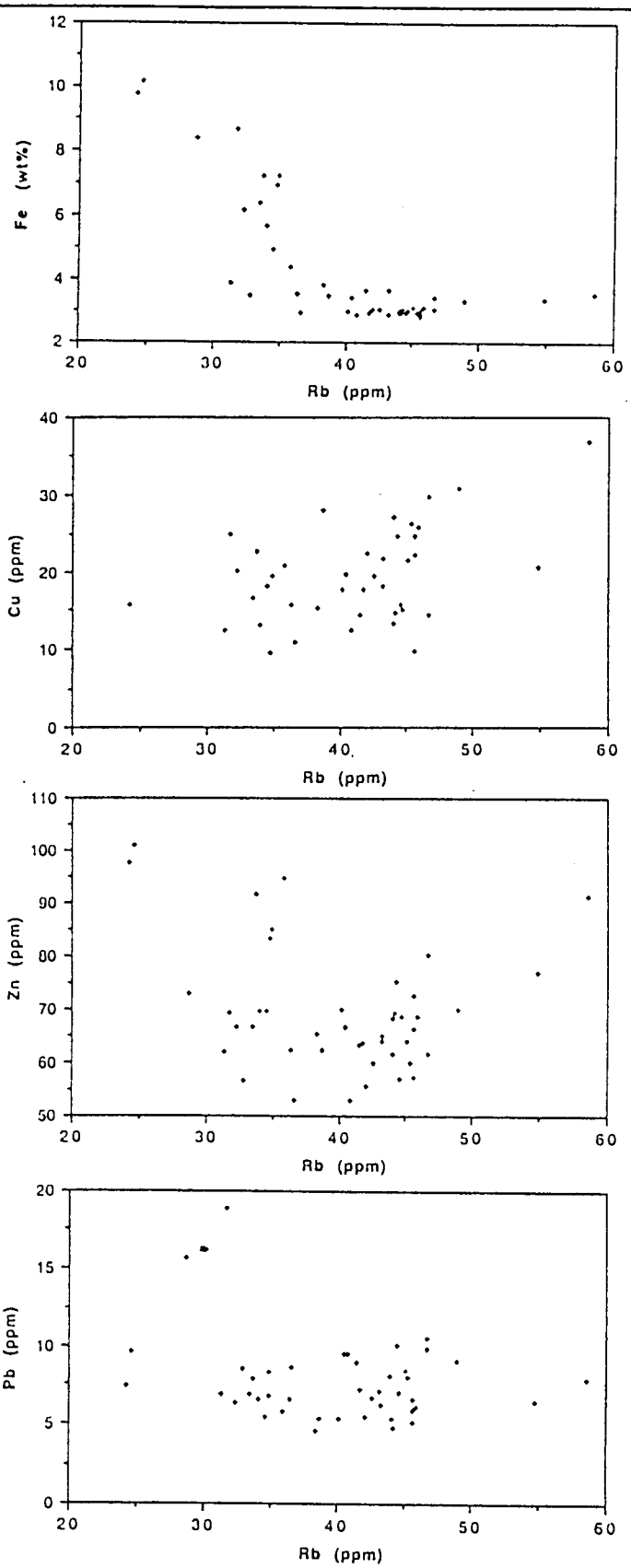


Figure 5.2 Plot of target metals against rubidium in FDHM-14.

is only significantly correlated with Mn. These relationships suggest that Fe/Mn oxides play the main role in retaining metals in these two parts of the core.

	Fe	Mn	Cu	Zn	Pb	Rb
(1) Fe	-	0.91	*0.25	0.62	0.77	-0.65
(2) Mn	-	-	†NS	0.61	0.81	-0.77
(3) Rb	-	-	-0.30	-0.18	-0.47	-

Table 5.4 Non-parametric (r_S) correlations of Fe, Mn, Cu, Zn, and Pb concentrations with Fe, Mn and Rb in two parts of FDHM-14.

	Fe	Mn	Cu	Zn	Pb	Rb
(1) Fe	-	0.58	*0.22	0.31	0.01	-0.29
(2) Mn	-	-	0.16	0.09	0.34	-0.22
(3) Rb	-	-	0.32	0.31	NS	-

Table 5.4a Non-parametric (r_S) correlations of Fe, Mn, Cu, Zn, and Pb concentrations with Fe, Mn and Rb in the balance of core FDHM-14.

*Significant at the 0.05 level. †Not statistically significant.

Delta Front Core

FDHM-2: This core, from a tidal-flat environment, shows the greatest heavy metals concentrations of all. The peat within its top 10 cm (Figures 4.57 and 4.58) might account for the high metals concentrations in that part of the core, (De Groot *et al.* 1976; Perel'man, 1967) but there is no apparent reason for the high copper and zinc concentrations found between 50 and 62 cm depth.

In its top 12 cm it has an EF of more than 5 of Cu, almost 6 times of Zn and more than 50 of Pb (Table 4.23). Rb was used for the enrichment calculations because it is difficult to separate the

adsorptive effects of clay from that of organic carbon (Förstner and Wittmann, 1981).

Even when one considers that the organic carbon found in this core is an effective barrier to heavy metals (Burton, 1976; Pere'lman, 1967 Förstner and Wittmann, 1981;), it must be concluded that the largest share of all three heavy metals is being deposited in the delta front sediments. This accords with the findings of Grieve and Fletcher (1975).

CONCLUSIONS

Allowing for diagenetic enrichment of 10%, there appears to be no significant enrichment of copper in any river core except perhaps in FDHM-3, 4 and 5. Because FDHM-4 shows higher enrichment values for all three metals and because it is located in an intensely industrialized area, I conclude that there is real enrichment here.

Zinc shows extremely high enrichment at FDHM-5, most probably the result of industrial practices. There is also significant enrichment of this metal at FDHM-4, 6 and 8 and, if one accepts that its true surface is the buried one at 100 cm depth, at FDHM-7. At all core this enrichment is explicable, as in FDHM-5, by highly localized indutrial sources.

Lead appears to be enriched at FDHM-6 only.

The enrichment of metals among river cores seems a mostly localized phenomena with some evidence overall of increasing downstream enrichment.

There is too much variation in the delta sedimentation and the heavy metal concentrations to allow any sort of chemostratigraphy to be constructed.

Highly focussed metal concentration in the lower parts of FDHM-7 and 14 are caused by Fe/Mn oxides which are in turn formed by oxidizing-reducing zone interfaces.

A large amount of heavy metal appears to be finding its way onto the delta front as shown by the much greater values —both absolute and normalized— of metals in FDHM-2. Previous studies

have shown that these higher values are most likely the result of a complex process of adsorption/desorption and precipitation by Fe/Mn oxides. In FDHM-2 the main agent of concentration at the surface appears to be organic carbon. The high levels metals in FDHM-2 conforms to the recognition of estuaries in general as sinks for heavy metals and with earlier studies of heavy metals in the Fraser Estuary in particular.

Using a suitably chosen normalizing metal together with a baseline of which one can be certain is not anthropogenically enriched is an effective method of pinpointing anomalously high metal levels in sediments.

Recommendations for further study.

Further studies should focus on those core locations where we are now certain that undisturbed sedimentation has taken place i.e. Musqueam Marsh and FDHM-8. As well, one might do further work at FDHM-5 and FDHM-4 where fill at the first and blockage at the second have produced notable and datable changes in sedimentation style. As well, FDHM-5 has been shown to be a point source of metal contamination. The age datum at both sites would allow changes in heavy metals concentrations subsequent to the dated events to be placed within an accurate age range as well providing a basis for measuring sedimentation rates. Besides Cu, Zn and Pb, further studies should include the following metals in the analysis; chrome (Cr), owing to its use in electroplating, arsenic (As) and cadmium (Cd) —both toxic, mercury (Hg) —a very pernicious metal, and antimony (Sb). The last metal is often alloyed with lead in shotgun pellets, and if detected, its presence might allow us to discriminate between pellet lead and that from other sources. The presence of these pellets in marsh sediments poses a toxic hazard to wildlife. A great deal of discharged shotgun shells were found in a very short time in and by Musqueam Marsh.

APPENDIX

The first three tables show the t-test probabilities for significant differences between the means of metal concentrations in the top 12 cm of each core. The "+ " or "-" sign in front of each probability value indicates whether the core mean listed on the diagonal line is greater or less than the one listed on the vertical line. In Table A1a, for example, the number found by matching 11 on the diagonal with 3 on the vertical is -.2218. This indicates that the mean of Zn in the top 12 cm of FDHM-11 is less, but not significantly so, than that of FDHM-3. Table A.2 shows the t-test probabilities for significant differences between means in the uppermost 12 cm of the peaty clay unit and those of surface 12 cm in FDHM-7. The rejection level (α) is 0.05 for all tables.

9	**9**										
10	-.0869	**10**									
11	-.4975	+.0541	**11**								
3	-.1623	-.4341	-.1541	**3**							
4	-.0389	-.3141	-.1231	-.3877	**4**						
5	+.3697	+.0359	+.2280	+.1227	+.1283	**5**					
6	+.0309	+.0002	+.0076	+.0102	+.0096	+.0415	**6**				
7	+.0062	+.0004	+.0078	+.0048	+.0015	+.0340	+.0295	**7**			
8	+.0017	+.0022	+.0065	+.0085	+.0062	+.0379	+.3295	-.2835	**8**		
13	+.0528	+.0051	+.0191	+.0041	+.0123	+.0931	+2933	-.0433	-.2178	**13**	
14	+.0142	+.0003	+.0033	+.0016	+.0042	+.0131	+.0081	+.4531	+.2798	+.0128	**14**

Table A.1a Paired t-tests (one-tailed) for significant differences between Cu means of the topmost 12 cm of the cores.

9	**9**										
10	-.1878	**10**									
11	+.1375	+.1692	**11**								
3	+.4195	+.1808	-.2218	**3**							
4	-.0229	-.2032	-.0316	-.0128	**4**						
5	-.0003	-.0044	-.0001	-.0003	-.0036	**5**					
6	+.0001	+.0381	+.0391	+.0050	+.0043	+.0002	**6**				
7	+.0001	+.0260	+.0061	+.0001	+.0023	+.0001	+.0320	**7**			
8	-.1389	+.3879	-.0094	-.1827	+.1125	+.0002	-.0067	-.0033	**8**		
13	+.0003	+.0321	+.0021	+.0005	+.0032	+.0001	+.0514	+.3228	+.0019	**13**	
14	+.0001	+.0111	+.0003	+.0001	+.0011	+.0001	+.0005	+.0001	+.0007	+.0002	**14**

Table A.1a Paired t-tests (one-tailed) for significant differences between Zn means of the topmost 12 cm of the cores.

9	9										
10	-.0162	10									
11	-.0814	-.1891	11								
3	+.4506	+.0076	+.0853	3							
4	-.0664	-.2471	+.3986	-.0636	4						
5	+.1404	+.0012	+.0538	+.1496	+.0453	5					
6	+.0093	+.0024	+.0259	+.0509	+.0073	+.1738	6				
7	+.0001	+.0001	+.0057	+.0002	+.0003	+.0015	+.0002	7			
8	+.3873	+.0861	+.1009	+.3663	+.1150	-.4085	-.2612	-.0116	8		
13	+.0048	+.0009	+.0182	+.0099	+.0029	+.0069	+.0459	-.0256	+.1010	13	
14	+.0001	+.0001	+.0042	+.0009	+.0008	+.0014	+.0001	-.3893	+.0254	+.0126	14

Table A.1b Paired t-tests (one-tailed) for significant differences between Pb means of the topmost 12 cm of the cores.

Metal	Cu	Zn	Pb
Probability	+.014	+.0202	+.0041

Table A.2 Paired t-tests (one-tailed) for significant differences between the Cu, Zn and Pb means of the topmost 12 cm of the peaty clay unit and those of the surface 12 cm of FDHM-7. The "+" signifies that the mean of the metal in the peaty clay is greater in every case than that of the surface layer.

BIBLIOGRAPHY

Ackermann, F. 1980. A procedure for correcting the grain size effect in heavy metal analyses of estuarine and coastal sediments. Environmental Technology Letters, 1: 518-527.

Ackermann, F., Bergmann, H. and Schleichert, U. 1983. Monitoring of heavy metals in coastal and estuarine sediments - a question of grain-size: <20 mm versus <60 mm. Environmental Technology Letters, 4: 317-328.

Allen, J.R.L. and Rae, J.E. 1986. Time sequence of metal pollution, Severn Estuary, southwestern U.K. Marine Pollution Bulletin, 17: 427-431.

Allen, J.R.L. 1987. Towards a quantitative chemostratigraphic model for sediments of late Flandrian age in the Severn estuary, U.K. Sedimentary Geology, 53: 73-100.

Armstrong, J.E. 1981. Post-Vashon Wisconsin glaciation, Fraser Lowland, British Columbia, Canada. Geological Survey of Canada, Bulletin 322.

Burton, J.D. and Liss, P.S. 1976. Estuarine Chemistry. Academic Press, London.

Barnett, B.E., Forbes, S. and Ashcroft, C. 1989. Heavy metals on the South Bank of the Humber Estuary. Marine Pollution Bulletin, 20: 17-21.

Bubb, J.M. and Lester, J.N. 1991. The impact of heavy metals on lowland rivers and the implications for man and the environment. The Science of the Total Environment. 100: 207-233.

Calvert, S.E., Cousens, B.L., and Soon, M.Y.S. 1985. An X-ray fluorescence spectrometric method for the determination of major and minor elements in ferromanganese nodules. Chemical Geology, 51: 9-18.

Cauwent, G. 1987. Influence of sedimentological features on the distribution of trace metals in marine sediments. Marine Chemistry, 22: 221-234.

Chapman, P.M. 1989. Seasonal changes in the depth distributions of intersitial salinities in the Fraser River estuary. Estuaries, 4(3): 226-228.

Chapman, .M., Churchland, L.M., Thomson, P.A., and Michnowsky E. 1980. Heavy metal studies with oligochaetes. *In:* Aquatic Oligochaete Biology. *Edited by:* Ralph O. Brinkhurst and David G. Cook. Plenum Publishing, New York.

City of Richmond Archives. 1960. Agreement with North Fraser harbour Commissioners re: Duck Island spoil disposal area and municipal flood box. July 25, 1960. Series: Agreements Location: 5732.

Clague, J.J., Luternauer, J.L., and Hebda, R.J. 1983. Sedimentary environments and postglacial history of the Fraser Delata and lower fraser Valley, British Columbia. Canadian Journal of Earth Sciences, 20: 1314-1326.

Davis, J.J. 1963. Cesium and its relationships to potassium in ecology. *In:* Radioecology: Proceedings of the First National Symposium on radioecology held at Colorado State University, Ft. Collins, Col. Sept 10-15, 1961. *Edited by:* Schultz, V. and Klement, A. W. Reinhold, New York.

de Groot, A.J. and Allersma, E. 1975. Field observations on the transport of heavy metals in sediments. *In:* Heavy Metals in the Aquatic Environment. pp 85-101. *Edited by:* P.A. Krenkel. Pergamon Press. Oxford.

de Groot, A.J., Salomons, W., and Allersma, E. 1976. Processes affecting heavy metals in estuarine sediments. *In:* Estuarine Chemistry. *Edited by:* J.D. Burton and P.S. Liss. Academic Press, London.

De Jong, E., Villar, H. and Bettany, J.R. 1982. Preliminary investigations on the use of ^{137}Cs to estimate erosion in Saskatchewan. Canadian Journal of Soil Science, 62: 673-683.

DeLaune, R.D., Baumann, R.H. and Gosselink J.G. 1983. Relationships among vertical accretion, coastal submergence, and erosion in a Louisiana Gulf coast marsh. Journal of Sedimentary Petrology, 53: 147-157.

Dossis, P. and Warren, L.J. 1980. Distribution of heavy metals between the minerals and organic debris in a contaminated marine sediment. *In:* Contaminants and Sediments, Volume1. *Edited by:* Robert A. Baker. Anne Arbor Science Publishers, Inc, Ann Arbor, MI.

Elderfield, H. and Hepworth, A. 1975. Diagenesis, metals and pollution in estuaries. Marine Pollution Bulletin, 6: 85-87.

Elliott, T. 1986. Deltas. *In:* Sedimetary facies and environments. 2nd Ed. *Edited by:* H.G.Reading. Blackwell Scientific Publications, Oxford.

_____, T. 1986. Siliciclastic shorelines. *In:* Sedimetary facies and environments. 2nd Ed. *Edited by:* H.G.Reading. Blackwell Scientific Publications, Oxford.

Fletcher, W.K., Holmes, G.S. and Lewis, A.G. 1983. Geochemistry and biological availability of iron and trace elements in the Upper Fraser River Estuary. Marine Chemistry, 12: 195-217.

Förstner, U. and Wittmann, G.T.W. 1981. Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin.

Furness, R.K.W.and Rainbow, P.S. Heavy Metals in the Marine Environment.. CRC Press, Inc. Boca Raton, Florida.

Gorham E. and Swaine, D.J. 1965. The influence of oxidizing and reducing conditions upon the distribution of some elements in lake sediments. Limnology and Oceanography, 10: 268-279.

Grant, A., 1990. Multivariate statistical analyses of sediment geochemistry. Marine Pollution Bulletin, 21: 297-299.

Grant, A. and Middleton, R. 1990. An assessment of metal contamination of sediments in the Humber Estuary, U.K. Estuarine, Coastal and Gulf Science, 31: 71-85.

Grieve, D. and Fletcher, K. 1975. Trace Metals in Fraser Delta Sediments. Geological. Survey of Canada, Paper 75-1, Part B. 161-163.

Grieve, D.A. and Fletcher, W.K. 1976. Heavy metals in deltaic sediments of the Fraser River, British Columbia. Canadian Journal of Earth Sciences, 13: 1683-1693.

Grieve, D.A. and Fletcher, W.K. 1977. Interactions between zinc and suspended sediments in the Fraser River Estuary, British Columbia. Estuarine and Coastal Marine Science, 5: 415-419.

Hall, K.J. and Fletcher, W.K. 1974. Trace metal pollution from a metropolitan area: Sources and accumulation in the lower Fraser River and estuary. *In:* Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Ecosystems, Ottawa Ont., May 1974.

Hamilton-Taylor, J. 1979. Enrichments of zinc, lead, and copper in recent sediments of Windermere, England. Environmental Science and Technology, 13: 693-697.

Holland, S.S. 1976. Landforms of British Columbia: A Physiographic Outline. British Columbia Department of Mines and Petroleum Resources, Bulletin 48.

Hutchinson, I. 1992. Holocene sea level change in the Pacific Northwest: A catalogue of radiocarbon dates and an atlas of regional sea level curves. Discussion paper number1. Institute for Quaternary Research, Simon Fraser University.

Inland Waters Directorate, Water Resources Branch, Water Survey of Canada. Historical Streamflow Summary, British Columbia. 1985. Ministry of Supply and Services Canada. Ottawa.

Jol, H.M. and Roberts, M.C. 1988. The seismic facies of a delta onlapping an offshore island: Fraser River Delta, British Columbia. *In:* Sequences, Stratigraphy, Sedimentology: Surface and Subsurface. *Edited by:* D. P. James. and D. A. Leckie. Canadian Society of Petroleum Geologists, Memoir 15: 137-142.

Jones, Roger. 1984. Heavy metals in the sediments of Llangorse Lake, Wales, since Celtic-Roman times. Verh. Internat. Verein. Limnol., 20: 642-648.

Johnston, W.A. 1921. Sedimentation of the Fraser River delta. Geological Survey of Canada, Memoir 125, 46pp.

_____ 1922. The character of stratification of the sediment in the Recent delta of Fraser River, British Columbia, Canada. Journal of Geology, 30: 115-129.

Kersten, M. and Förstner, U. 1987. Effect of sample pretreatment on the reliability of solid speciation data of heavy metals - implications for the study of early diagenetic processes. Marine Chemistry, 22: 299-311.

Koide, M., Michel, R., Goldberg, E.D., Herron, M.M. and Langway, Jr. C. C. 1979. Depositional history of artificial radionuclides in the Ross Ice Shelf, Antarctica. Earth and Planetary Science Letters, 44: 205-223.

Krumgalz, B. 1989. Unusual grain size effect on trace metals and organic matter in contaminated sediments. Marine Pollution Bulletin. 20: 608-611.

Lewin, John and Macklin, Mark.G. 1987. Metal mining and floodplain sedimentation in Britain. *In:* International Geomorphology 1986, Part I. *Edited by:* V. Gardiner. John Wiley & Sons. New York.

Li, Yuan-Hui, Burkhardt, L. and Teraoka, H. 1984. Desorption and coagulation of trace elements during estuarine mixing. Geochimica et Cosmochimica acta, 48: 1879-1884.

Loring, D.H. 1990. Lithium-a new approach for the granulometric normalization of trace metal data. Marine Chemistry, 29: 155-168.

Luoma, S.N. 1983. Bioavailability of trace metals to aquatic organisms - A review. The Science of the Total Environment, 28: 1-22.

Luternauer, J.L., and Murray, J.W. 1973. Sedimentation on the western delta-front of the Fraser river, British Columbia. Canadian Journal of Earth Sciences. 10: 1642-1663.

Luternauer, J.L., Clague, J.J. and Feeney, T.D. 1991. A 367 m core from southwestern fraser river delta, British Columbia. *In:* Current Research, Part E; Geological Survey of Canada, Paper 91-1E, p 127-134.

Macklin, M.G. and Dowsett, R.B. 1989. The chemical and physical speciation of trace metals in fine grained overbank flood sediments in the Tyne basin, North-east England. Catena. 16: 135-151.

McNamara, P. 1975 Marpole— Heritage of 100 Years. Marpole-Oakridge Area Council. Vancouver.

Martin, J. M., Nirel, P. and Thomas, A. J. 1987. Sequential extraction techniques: promises and problems. Marine Chemistry, 22: 313-341.

Mathews, W.H. and Shepard, F.P. 1962. Sedimentation of Fraser River Delta, British Columbia. Bulletin of the American Association of Petroleum Geologists, 46: 1416-1443.

Mathewes, R.W. and D'Auria, J.M. 1982. Historic changes in an urban watershed determined by pollen and geochemical analyses of lake sediment. Canadian Journal of Earth Sciences, 19: 2114-2125.

Milliman, J.D. 1980. Sedimentation in the Fraser River and its estuary, Southwestern British Columbia (Canada). Estuarine and Coastal Marine Science, 10: 609-633.

Moslow, T.F., Luternauer, J.L., and Kostaschuk, R.A.1991. Patterns and rates of sedimentation on the Fraser River delta slope, British Columbia. *In:* Current research part E; Geological Survey of Canada, Paper 91-1E: 141-145.

Paulson, A.J., Feely, R.A., Curl Jr., H.C., Crecelius, E.A. and Geiselman, R. 1988. The impact of scavenging on trace metal budgets in Puget Sound. Geochimica et Cosmochimica Acta, 52: 1765-1779.

Perel'man, Aleksandr I. 1967. Geochemistry of Epigenesis. Translated from the Russian by N. N. Kohanowski. Plenum Press. New York.

Prohic, E. and Kniewald, G. 1987. Heavy metal distribution in recent sediments of the Krka River Estuary - an example of sequential extraction analysis. Marine Chemistry, 22: 279-297.

Rainbow, P.S. and Furness, R.W. 1990. Heavy metals in the marine environment. *In:* Heavy Metals in the Marine Environment. *Edited by:* Robert W. Furness and Philip S. Rainbow. CRC Press, Inc. Boca Raton, Florida.

Randerson, P.F. 1979. A simulation model of salt-marsh development and plant ecology. *In:* Estuarine and Coastal Land Reclamation and Water storage. *Edited by:* B. Knights and A.J Phillips. Saxon House in association with the Estuarine and Brackish-water Sciences Association Westmead, U.K.

Rapin, F., Tessier, A., Campbell, P.G.C., and Carignan, R. 1986. Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure. Environmental Science and Technology, 20: 836-840.

Ritchie, Jerry C., McHenry, J. Roger and Gill, Angela C. 1973. Dating recent reservoir sediments. Limnology and Oceanography, 18: 254-263.

Roddick, J.A. 1979. Vancouver North, Coquitlam, and Pitt Lake map-areas, British Columbia. Geological Survey of Canada, Memoir 335.

Ross, Leslie J. Richmond - Child of the Fraser. 1979. Richmond 1979 Centennial Society. Richmond, B.C.

Rule, J. H. 1986. Assessment of trace element geochemistry of Hampton Roads Harbor and Lower Chesapeake Bay area sediments. Environmental and Geological Water Science, 8: 209-219.

Schmitz, B.. 1985. Metal precipitation in the Cretaceous-Tertiary boundary clay at Stevns Klint, Denmark. Geochemica et Cosmochimica Acta, 49: 2361-2370.

Sinex, S.A. and Wright, D.A. 1988. Distribution of trace metals in the sediments and biota of Chesapeake Bay. Marine Pollution Bulletin, 19: 425-431.

Smith, D.G. 1984. Vibracoring fluvial and deltaic sediments: tips on improving penetration and recovery Journal of Sedimentary Petrology, 54: 660-663.

Smith, D.G. 1987. A mini-vibracoring system. Journal of Sedimentary Petrology, 57: 757-758.

Swain, L.F. and Walton, D.A. 1990. Report on the 1989 Fraser River sediment monitoring program. Province of British Columbia.

Thomas, D.J. and Grill, E.V. 1976. The effect of exchange reactions between Fraser River sediment and seawater on dissolved Cu and Zn concentrations in the Strait of Georgia. Estuarine and Coastal Marine Science, 5: 421-427.

Thorne, L.T. and Nickless, G. 1981. The relation between heavy metals and particle size fractions within the severn estuary (U.K.) inter-tidal sediments. The Science of the Total Environment, 19: 207-213.

Williams, G.L. 1993. Mitchell Island marsh compensation project: monitoring results and implications for estuarine management. Proceedings of the 1993 Canadian Coastal Conference. The Coastal Zone Engineering Program, National Research Council Canada, Ottawa, Ont.

Williams, H.F.L. 1986. Depositional facies and evolution of Lulu Island topset deposits, Fraser River delta, British Columbia. *In:* Current research part A; Geological Survey of Canada, Paper 86-1A: 717-722.

Williams, H.F.L. and D'Auria, J. 1991. A Mazama tephra marker bed in the Fraser Lowland, British Columbia. Canadian Journal of Earth Sciences, 28: 150-153.

Williams, H.F.L. and Roberts, M.C. 1989. Holocene sea-level change and delta growth: Fraser River delta, British Columbia. Canadian Journal of Earth Sciences, 26: 1657-1666.

Williams, H.F.L. and Roberts, M.C. 1990. Two middle holocene marker beds in vertically accreted floodplain deposits, lower Fraser River, British Columbia. Geographie physique et Quarternaire, 44: 27-31.

Wise, S.M. 1980. Caesium-137 and lead-210: A review of the techniques and some applications in geomorphology. *In:* Timescales in Geomorphology. *Edited by:* Cullingford, R. A. *et al.* John Wiley & Sons, Chichester.