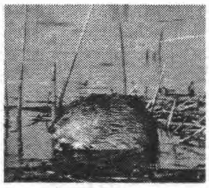
Canada Alberta Northwest Territories

Northern River Basins Study





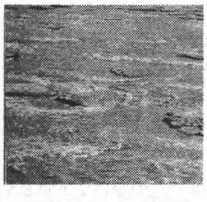





NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 72

DEPOSITIONAL HISTORY OF SEDIMENTS IN LAKE ATHABASCA:

GEOCHRONOLOGY, BULK PARAMETERS, CONTAMINANTS AND BIOGEOCHEMICAL MARKERS





Prepared for the
Northern River Basins Study
under Projects 2332-A1, 2332-B1 and 2332-C1

by

Richard A. Bourbonniere and Sherry L. Telford
National Water Research Institute

and

J. Bryan Kemper
Alberta Environmental Protection

Community Contributors:

Scott Flett, Fort Chipewyan
Gord Antoniuk, Fort Chipewyan

NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 72

DEPOSITIONAL HISTORY OF SEDIMENTS IN LAKE ATHABASCA: GEOCHRONOLOGY, BULK PARAMETERS, CONTAMINANTS AND BIOGEOCHEMICAL MARKERS

Published by the
Northern River Basins Study
Edmonton, Alberta
January, 1996

CANADIAN CATALOGUING IN PUBLICATION DATA

Bourbonniere, Richard A.

Depositional history of sediments in lake Athabasca :
geochronology, bulk parameters, contaminants and
biogeochemical markers

(Northern River Basins Study project report,
ISSN 1192-3571 ; no. 72)
Includes bibliographical references.
ISBN 0-662-24143-6
Cat. no. R71-49/3-72E

1. Marine sediments -- Athabasca, Lake (Sask. and Alta.)
2. Water quality -- Athabasca, Lake (Sask. and Alta.)
I. Kemper, J. B.
II. Telford, Sherry L.
III. Northern River Basins Study (Canada)
IV. Title.
V. Series.

TD387.A83B67 1996 553.7'8'0971241 C96-980032-0

PREFACE:

The Northern River Basins Study was initiated through the "Canada-Alberta-Northwest Territories Agreement Respecting the Peace-Athabasca-Slave River Basin Study, Phase II - Technical Studies" which was signed September 27, 1991. The purpose of the Study is to understand and characterize the cumulative effects of development on the water and aquatic environment of the Study Area by coordinating with existing programs and undertaking appropriate new technical studies.

This publication reports the method and findings of particular work conducted as part of the Northern River Basins Study. As such, the work was governed by a specific terms of reference and is expected to contribute information about the Study Area within the context of the overall study as described by the Study Final Report. This report has been reviewed by the Study Science Advisory Committee in regards to scientific content and has been approved by the Study Board of Directors for public release.

It is explicit in the objectives of the Study to report the results of technical work regularly to the public. This objective is served by distributing project reports to an extensive network of libraries, agencies, organizations and interested individuals and by granting universal permission to reproduce the material.

NORTHERN RIVER BASINS STUDY
PROJECT REPORT RELEASE FORM

This publication may be cited as:

Bourbonniere, Richard A., Telford, Sherry L. and Kemper, J. Bryan. 1996. ***Northern River Basins Study Project Report No. 72, Depositional History of Sediments in Lake Athabasca: Geochronology, Bulk Parameters, Contaminants and Biogeochemical Markers,*** **Northern River Basins Study, Edmonton, Alberta.**

Whereas the above publication is the result of a project conducted under the Northern River Basins Study and the terms of reference for that project are deemed to be fulfilled,
IT IS THEREFORE REQUESTED BY THE STUDY OFFICE THAT;
this publication be subjected to proper and responsible review and be considered for release to the public.

F. Wrona
(Dr. Fred J. Wrona, Science Director)

10 Jan 96
(Date)

Whereas it is an explicit term of reference of the Science Advisory Committee "to review, for scientific content, material for publication by the Board",
IT IS HERE ADVISED BY THE SCIENCE ADVISORY COMMITTEE THAT;
this publication has been reviewed for scientific content and that the scientific practices represented in the report are acceptable given the specific purposes of the project and subject to the field conditions encountered.
SUPPLEMENTAL COMMENTARY HAS BEEN ADDED TO THIS PUBLICATION: [ ] Yes [✓] No

(Dr. P. A. Larkin, Ph.D., Chair)

Jan 9/96
(Date)

Whereas the Study Board is satisfied that this publication has been reviewed for scientific content and for immediate health implications,
IT IS HERE APPROVED BY THE BOARD OF DIRECTORS THAT;
this publication be released to the public, and that this publication be designated for: **[✓] STANDARD AVAILABILITY [ ] EXPANDED AVAILABILITY**

Lucille Partington
(Lucille Partington, Co-chair)

Jan. 11/96
(Date)

Robert McLeod.
(Robert McLeod, Co-chair)

11/01/96
(Date)

DEPOSITIONAL HISTORY OF SEDIMENTS IN LAKE ATHABASCA: GEOCHRONOLOGY, BULK PARAMETERS, CONTAMINANTS AND BIOGEOCHEMICAL MARKERS

STUDY PERSPECTIVE

Depositional sediments can be useful to chronicle natural changes and contamination events in a drainage basin. Studying sediment cores in Lake Athabasca offers the opportunity to (1) understand recent trends in industrial and atmospheric contamination, (2) compare modern contaminant deposition with the magnitude of past events, and (3) compare the relative magnitude of natural versus man-made changes in the basin. Almost all of the studies under the NRBS program have been conducted on mainstem rivers and tributaries which receive some level of contaminant input from industrial, municipal and agricultural sources. Trends revealed by these studies will provide a basis from which to judge the degree of impact on Lake Athabasca, the downstream end of a large watershed altered extensively by human activities.

The primary objective of this study was to collect and analyze high quality, well-described sediment cores for use in defining the depositional history of sediment-bound contaminants in Lake Athabasca, including those which have atmospheric or upstream sources. Dating of the cores was accomplished by using the lead (Pb^{210}) and cesium (Cs^{137}) methods. These geochronological results were used to determine sedimentation rates and time scales, and the suitability of the cores for subsequent contaminant analyses. Selected cores were to be analyzed for (1) particle size distribution, (2) bulk carbon and nitrogen species, (3) radionuclides, (4) total polychlorinated dioxins and furans, (5) heavy metals, (6) polynuclear aromatic hydrocarbons (PAHs), (7) fatty acids and (8) biogeochemical marker parameters derived from alkanes and fatty acids.

Related Study Questions

4a) *What are the contents and nature of the contaminants entering the system and what is their distribution and toxicity in the aquatic ecosystem with particular reference to water, sediments and biota?*

4b) *Are toxins such as dioxins, furans, mercury, etc. increasing or decreasing and what is their rate of change?*

13b) *What are the cumulative effects of man-made discharges on the water and aquatic environment?*

14) *What long term monitoring programs and predictive models are required to provide an ongoing assessment of the state of the aquatic ecosystems? These programs must ensure that all stakeholders have the opportunity for input.*

Results on bulk parameters showed that the depositional environment in Lake Athabasca has been stable for the last 100 years. Radionuclides associated with mining activities have entered the lake; the levels in the sediments have decreased since the 1970s. Since the 1960s, polychlorinated dioxins and furans showed increased concentrations of up to four times their previous levels. Arsenic was the only heavy metal showing an increasing trend, with a five-fold increase over background levels since the 1970s. No clear trends were evident for petroleum and combustion sources of PAHs, except that the downcore distribution of combustion related PAHs correlates with a recent fire frequency curve for Wood Buffalo National Park. Resin acid results from the surficial samples indicate that these pulp mill related contaminants have been transported to Lake Athabasca by riverine processes.

This study offers a better understanding of recent trends for contaminant deposition in sediments, and addresses concerns over ecosystem integrity in the Lake Athabasca basin. Results suggest that contaminant transport to Lake Athabasca has been minimal, and concentrations are much lower than those found in lakes from areas subjected to more significant industrialization and urban growth. This study provides the basis for further analyses of the sediment cores for chlorinated contaminants, hydrocarbons and biogeochemical markers, and for making a comparison between the depositional history of Lake Athabasca and suitable reference lakes in the area.

REPORT SUMMARY

This is the first of two reports expected which attempts to interpret sediment core data with the goal of identifying significant historical trends in the input of contaminants to Lake Athabasca. Trends in overall watershed effects can also be identified using biogeochemical markers, and these may help to separate contamination related changes from broader ecosystem effects. This report covers research conducted for NRBS Study Nos. 2332-B1 and 2332-C1, including that undertaken by the Organic Geochemistry laboratory at NWRI and a number of contract laboratories.

Lake Athabasca is a large depositional basin with probable influence from both the Peace and Athabasca rivers. Sediment cores were collected in March, 1992 and March, 1993 from the main body of the lake, along with fine grained surficial sediments from the shallow western part near the mouth of the Athabasca River. Surficial sediments are used to provide initial estimates of the types and amounts of contaminants which are present, and assist in focusing the analysis of cores. The depositional history of sediment bound contaminants can be inferred from the cores collected after the application of a carefully designed, and iteratively implemented analysis scheme.

Cores were dated by the ^{210}Pb method and Site 1 was chosen as the most promising site for extensive analysis based on its continuous depositional history over more than 100 years and the superior time resolution afforded -- each cm sampled represents a five year interval of integration. Cores collected from Site 1 (the nearest of the deep core sites to the Peace-Athabasca Delta) in 1992 and 1993 were analyzed for (1) particle size distribution, (2) bulk C and N species, (3) radionuclides, (4) total polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs - tetra- to octa- chloro- substituted) and their individual 2,3,7,8chloro- substituted congeners, (5) heavy metals and mercury, (6) polynuclear aromatic hydrocarbons (PAHs), (7) aliphatic hydrocarbons and total hydrocarbons, including petroleum hydrocarbons, (8) fatty acids and (9) biogeochemical marker parameters derived from alkanes and fatty acids.

Results on bulk parameters (particle size and C&N) show that the depositional environment has been stable for at least the last 100 years, the period of interest. Results on all contaminants suggest that their transport to Lake Athabasca has been minimal. Concentrations are much lower than those found in lakes from areas which have undergone more significant industrialization and urbanization.

Radionuclides associated with mining activities, have entered the lake. Surficial and core results suggest that although they have been transported away from the point of release, the levels in the sediment have decreased since the '70s and now approach background levels. PCDD/Fs, represented by the sums of congener classes, show increased concentrations since the '60s of 2-4 times their previous levels, with the possibility that they are on a decreasing trend since the '80s. None of the heavy metals tested show trends except for arsenic which has increased five times over background since the '70s.

PAHs have been found which can be attributed to petroleum and combustion related sources. No clear trends are evident in either of these sources except that the downcore distribution of combustion related PAHs correlates with a recent fire frequency curve (since 1932) for Wood Buffalo National Park. Spatially, the distribution of PAHs over the western part of the lake suggests that atmospheric transport is the main control.

Trends for biogeochemical markers from the hydrocarbon class suggest that hydrocarbon input to the sediments has not varied much over the past 100 years. Periods of higher hydrocarbon inputs have occurred at irregular intervals. One indicator of petroleum contribution to the hydrocarbons, the unresolved complex mixture, has decreased since 1900, and exhibited a major increase at the end of the previous century. Another petroleum pollution indicator, the carbon preference index, shows consistently lower values (suggesting oil contribution to the natural alkane assemblage) since 1960.

Fatty acid biomarkers indicate a consistent downward trend since 1920 in the proportion of terrestrially sourced to aquatic sourced components, which can mean that nutrient enrichment has increased productivity in the lake. However, alkane biomarkers which can indicate the same environmental changes failed to show the same trend, and other fatty acid markers suggest that post-depositional alterations may have affected the ratios.

Resin acid and chlorinated resin acid results from the surficial samples indicate that these pulp mill related contaminants have been transported to Lake Athabasca by riverine processes -- these should also be determined on cores. Di- and tri-chloro dibenzodioxins and dibenzofurans should be determined if they can be considered as markers for pulp mill effluent. As well, non detection of organochlorines (pesticides, polychlorinated biphenyls and Toxaphenes) on surficial samples and cores, suggests that these should be re-analyzed with lower detection limits. Many of these compounds are known to be transported atmospherically as well as by river processes, and may give useful information about the relative importance of these two means of contaminant transport. Analysis of other biogeochemical markers, fatty alcohols and sterols, including coprostanol, should be completed to assist in corroborating the trends indicated by alkane and fatty acid biogeochemical markers.

ACKNOWLEDGEMENTS

The authors appreciate the assistance in field collections from E. Walker and K. Hill in March, 1992 and from D. Allen, B. Jackson and J. Kraft in March, 1993. J. Lee, B. Hilson and S. Smith assisted with the laboratory work-up and chromatography at NWRI. Scott Flett from Fort Chipeweyan provided transportation on the frozen lake to collect the surficial samples. The Parks Canada office in Fort Chipeweyan allowed use of their facilities for core extruding and general logistical support, thanks especially to G. Antoniuk. Several experts who have worked on radionuclide issues in western Canada have provided some review and interpretation of these data in their preliminary form. Some of the comments which were provided by G. Groskopf, S. Joshi and D. Lawson have been incorporated into this section, and their help is greatly appreciated. The current version of this report benefitted from the comments of T.M. Dick, M. Evans, J. Lawrence, J. Marsalek and D. Muir who gave comprehensive reviews of the draft version.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

1.0 INTRODUCTION

The history of natural changes and contamination events which occur in a drainage basin are recorded in the sediments of depositional zones. Studying these sediments, particularly cores collected from them, can lead to an understanding of recent trends in industrial and atmospheric contamination, a comparison of modern contaminant deposition with the magnitude of past events, a comparison of the relative magnitude of natural vs. anthropogenic changes in the basin, and provide an indication of how changes in the hydraulic regime can influence the distribution of sediment-bound contaminants.

Lake Athabasca is a large depositional basin with significant influence from the Athabasca River and probable influence from the Peace River. Sediment cores were collected in March, 1992 and March, 1993 from Lake Athabasca along with fine grained surficial sediments from the shallow western part of the lake. Depositional history of sediment-bound contaminants can be inferred from these cores using a carefully designed analytical program. The requirement for analyses is varied and involved a number of experts and specialized laboratories. The work progressed in an iterative manner to insure that interpretation was be based on the highest quality information and that only necessary chemical determinations were undertaken.

1.1 QUESTIONS POSED

The following questions guided this study throughout. They represent questions which have direct and indirect bearing on certain NRBS guiding questions as well as some which are necessary for a scientifically valid study.

1. Is there evidence of recent sediment-bound contamination on the fine-grained surficial samples collected under ice from the shallow western part of the lake?
2. Which of the sites in the depositional basins where core samples were collected represents the best opportunity to answer the concerns which appear above?
3. On cores selected above, which physical, chemical, and sedimentological parameters best describe overall trends? Have any major changes occurred which may be correlated to settlement and development in the basin?
4. Which analyses for sediment-bound contaminants should proceed? Are trends in industry specific contamination evident in the cores? Is it possible to distinguish between atmospheric and upstream sources of these contaminants?
5. Analyses of selected cores for natural components (biogeochemical markers) can indicate changes in the basin. Is there evidence of land use changes and nutrient status recorded in the cores? How does the magnitude of these changes compare with those brought about by contamination? Are there combined effects of contamination and natural changes which are of special concern?

1.2 FRAMEWORK FOR INVESTIGATION OF LAKE ATHABASCA SEDIMENTS

The most important first step is the formulation of a credible sampling plan and the mounting of a sampling expedition. Little information was available in the published literature about the sediments of Lake Athabasca. Coring sites were chosen using general knowledge of depositional environments and the experience from previous studies on large lakes (Bourbonniere et al., 1986). More details on the sampling methods and implementation are given in section 2.2.

Once cores were successfully collected and judged to be of good quality, the next step was to establish a geochronology (time reference) for each site. To do this successfully requires high quality undisturbed cores, which we were able to collect at all three sites. Since nothing was known about sedimentation rates in Lake Athabasca, all three sampling sites were dated by the ^{210}Pb and ^{137}Cs methods. Results of these geochronologies and their use in interpretation of other results are explained in section 5.1.

Since the primary concern of NRBS with respect to Lake Athabasca sediments is to determine whether they record evidence of past and current anthropogenic activity, the primary period of interest is the past 100 years. This period is within the range where reliable dates can be assigned using the ^{210}Pb method (Anderson et al., 1987). Use of the 100 year interval limits the number of samples that are analyzed. Reliable geochronology which demonstrates whether or not modern deposition was continuous is a necessary step.

Once the geochronology was established, and the primary site for detailed investigation was chosen, analysis strategies were formulated to make best use of the sediment available, insure the tightest time resolution possible, and determine appropriate chemical species. Since Lake Athabasca sediments are potentially a repository for sediment-bound contaminants from many local and remote sources, a large list of target compounds was selected. In addition a number of bulk physical and chemical properties of the sediments were studied. These components are conveniently classed throughout this report as (1) bulk parameters (2) radionuclides, (3) organic contaminants, (4) inorganic contaminants and (5) biogeochemical markers.

1.2.1 Strategy for Bulk Properties Determinations

The bulk character of lake sediments can be used to indicate major changes in depositional environment. Sediment particle size is related to the energy of the environment of deposition, and since Site 1 is on the margin of acceptable depth, this was a good parameter to use in judging core quality. Sediments with fine grain sizes accumulate in low energy environments which are less prone to disturbances, and also tend to contain higher organic matter contents. Contaminants are usually associated with fine grain sediments containing organic matter. The bulk character of the organic matter can indicate changes in the sources of sediment to the lake. Total organic carbon and nitrogen and total inorganic carbon concentrations can be influenced by source and depositional changes. The character of organic matter is further indicated by the atomic C/N ratio.

1.2.2 Strategy for Radionuclide Determinations

Our initial coring strategy was described previously and cores were obtained at three sites. Since no information was available on sedimentation rates, it was decided to use ^{210}Pb geochronology as the first screen to assist in deciding which core(s) to analyze further. All three sites were sufficiently unknown, and all had potential problems associated with them so that their geochronology was unpredictable. During geochronological studies a core from Site 3 exhibited a pronounced subsurface maximum in ^{210}Po activity (cf. sections 5.1 and 5.3) which made it undatable by the ^{210}Pb method.

Turner (1993a) pointed out that such a distribution could have been caused by slumping or turbidity currents, or may be related to the discharge of uranium mine tailings in nearby Langley Bay, as reported by Waite et al. (1988, 1989) and Joshi et al. (1989). This latter possibility led to the determination of other radionuclides, which have been associated with the Langley Bay mine tailings, in the sediments which were collected from surficial and coring sites in March 1992. Details are found in sections 4.1 and 5.3.

1.2.3 Strategy for Organic Contaminant Determinations

The selection of organic contaminants to analyze was made on the basis of which contaminants would be expected in the Lake Athabasca watershed. Specifically, we have concentrated on contaminants which can be transported by river and/or air have, since these are the two main pathways for contaminants entering the lake.

Several of these organic contaminants share similar sources. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs) are produced as by-products from a number of industrial, agricultural and commercial processes (Bjorseth and Ramdahl, 1985; McElroy et al., 1989; Safe and Hutzinger, 1990). The combustion of municipal and hazardous waste, sewage sludge, fossil fuels, wood, and accidental fires involving the burning of PVC or polychlorinated biphenlys (PCBs) are industrial sources which may be relevant to contaminants found in Lake Athabasca. Bactericides, slimicides, fungicides, herbicides, pesticides and wood preservatives are possible agricultural and commercial sources. Organochlorines including pesticides, PCBs and toxaphenes are specifically analyzed here as they are distinctive in themselves and are known to be related to the presence of PCDD/Fs. In addition to PCDD/Fs, other chlorinated contaminants such as chlorinated resin acids, can be derived from the process of chlorine bleaching in the pulp and paper industry (Hutzinger and Blumich, 1985; Mahood and Rogers, 1975; Safe and Hutzinger, 1990). The influence of pulp and paper mill activities on Lake Athabasca can also be measured by analyzing samples for resin and fatty acids as the pulping of coniferous trees is known to be a major source of these acids (Mahood and Rogers, 1975). For petroleum hydrocarbons, the industrial extraction of the naturally occurring tar sands near Fort McMurray is expected to be one anthropogenic source of such organic contaminants. With both the resin acids and petroleum hydrocarbons, it is necessary to distinguish between those which derive from anthropogenic sources and those which are naturally produced.

Many hydrocarbon contaminants are also produced by such individual and commercial activities such as automotive transportation (fuel combustion), disposal/spillage of petroleum products and the burning of wood or fossil fuels for space heating (Bjorseth and Ramdahl, 1985; McElroy et al., 1989). Concern about elevated concentrations of these contaminants is due to the mutagenic, carcinogenic and/or toxic nature of several of these compounds to living organisms (Bjorseth and Ramdahl, 1985; Fiedler and Hutzinger, 1990; Mahood and Rogers, 1975; Morales et al., 1992; Walden and Howard, 1981).

1.2.4 Strategy for Inorganic Contaminant Determinations

Certain metals can be toxic to biota in the right form, and some of them are attributable to anthropogenic sources. Other metals are transformed in the environment to more toxic forms by geochemical processes which themselves can be influenced by anthropogenic perturbations. For instance, mercury can be converted to methyl mercury, a toxic and assimilable form, by the action of bacteria in reducing microenvironments. Excess deposition of organic matter at the sediment surface, or in quiescent zones in rivers can create a demand for oxygen and can result in a reducing microenvironment. The interest in metal contaminants in sediments is not primarily for any in situ toxicity, since burial in sediments is a process for removal of the potential threat, but rather as a record of metal inputs to the lake in the same way as organic contaminants are recorded. However, the reducing environments that occur at depth in the sediment can reduce certain metals to forms that are more mobile and could be diffused upwards.

1.2.5 Strategy for Biogeochemical Marker Determinations

Biogeochemical markers are compounds which are ultimately from biological or polluting origins and which can be used to indicate their source(s) and to reveal something of the environment from which they came and in which they settled. The biogeochemical markers determined here are called "geolipids" and include alkanes and fatty acids. These tracers are prevalent in both terrestrial and aquatic environments. Generally, such markers are transported to sediments either by land erosion and runoff, water processes, or by the atmosphere. By examining the relative concentrations of specific compounds, it is possible to distinguish between terrestrial sourced biomarkers and those produced in aquatic environments. This information can then be used to determine how the two environments interact and, in particular, from where sediments and particulates entering Lake Athabasca came.

Biogeochemical markers are also subject to post depositional processes (diagenesis), and changes in distributions of markers can indicate the degree of microbial or chemical degradation which occurs. Some contaminants can also be degraded by the same processes, so the changes in biogeochemical markers which occur may indicate the potential for microbial degradation of contaminants which occurs naturally in a given sediment. In practice it is often difficult to unambiguously separate changes in marker distribution which are caused by source changes from those which are diagenetic in origin. One way to improve the chances of interpreting trends is to determine all of the geolipid classes so that corroborating, or indeed contradicting data are available.

Watershed scale changes in environmental conditions can also be reflected in the distributions of biogeochemical markers. Some of these changes could result from human activities. For instance, deforestation, which results in increased soil erosion, contributes a greater proportion of terrestrially derived organic matter to the lake. Nutrient enrichment, resulting in increased productivity, contributes greater proportions of algal sourced organic matter. By identifying these trends using biogeochemical markers, the relative magnitude of natural and anthropogenic changes may be determined.

2.0 STUDY AREA

2.1 GEOLOGICAL SETTING OF LAKE ATHABASCA

Straddling the Alberta-Saskatchewan border, Lake Athabasca is Canada's eighth largest lake by area with approximately 30% of the lake occurring within Alberta. An estimated 52% of Lake Athabasca's water comes from the Athabasca River, 21% from the Fond du Lac River in Saskatchewan and the remainder from various other sources (Neill et al., 1981). Neill et al. (1981) have determined that the inflowing Athabasca River water generally extends to about 10 km offshore of the delta under normal conditions. The average depth of this area is approximately 2 m. During periods of high inflow and strong westerly winds, Athabasca River water may advance up to 13 km into the lake and it has even been recorded as extending beyond the Alberta-Saskatchewan border (Rawson, 1947).

The most recent bathymetric charts show relatively few soundings along several well travelled routes, with no contouring except in the shallow western end of the lake. It is expected that the Athabasca River Delta at the western end of the lake acts as a filter for water entering Lake Athabasca. Hence, much of the sediments and thereby, contaminants, will be deposited, at least temporarily, in this shallow region rather than continuing on down the Slave River or far into the lake's deeper eastern basin.

Various ecosystems contribute to the Lake Athabasca drainage basin in Alberta. The Athabasca River runs from the Rocky Mountains through the alpine, subalpine and montane ecoregions. Parts of the Athabasca River also erode and drain large regions which are underlain by petroleum rich geological structures. The Athabasca-McMurray Formation is the most significant of these structures consisting of extensive oil sands. North of the lake are the boreal northlands; to the south is the subregion of boreal mixedwood. The Peace-Athabasca Delta located on the lake's southwestern shore is one of the most biologically productive areas in the world and is considered to be a major North American wetland. Overall, the terrain surrounding the lake is generally flat to gently rolling. Large areas are poorly drained peatland mire complexes although sand dunes and clay-rich till and/or lacustrine or alluvial deposits do exist (Mitchell and Prepas, 1990; La Roi, 1992). Lake Athabasca straddles the Canadian Shield which outcrops primarily to the north.

2.2 SAMPLING STRATEGY AND IMPLEMENTATION

Our initial coring strategy was based on the desire to obtain cores which would lead to information regarding potential dispersion, deposition and burial of contaminants originating in the Athabasca and Peace rivers. Since there was little information available on the sediments of Lake Athabasca, even bathymetry was sparse, we selected the three coring locations on the basis of proximity to the western end and our perceptions of bathymetric depressions discernable from the sparse data (Figure 1). Site 1 (water depth 12 m) is most likely to be influenced by the rivers entering on the west, but such a depth is borderline for influence by wave action. If waves impacted on the bottom, even only occasionally, they could cause discontinuities in sediment deposition which might make cores collected there unsuitable for our purposes. Site 2 is deep enough (water depth 54 m) to avoid

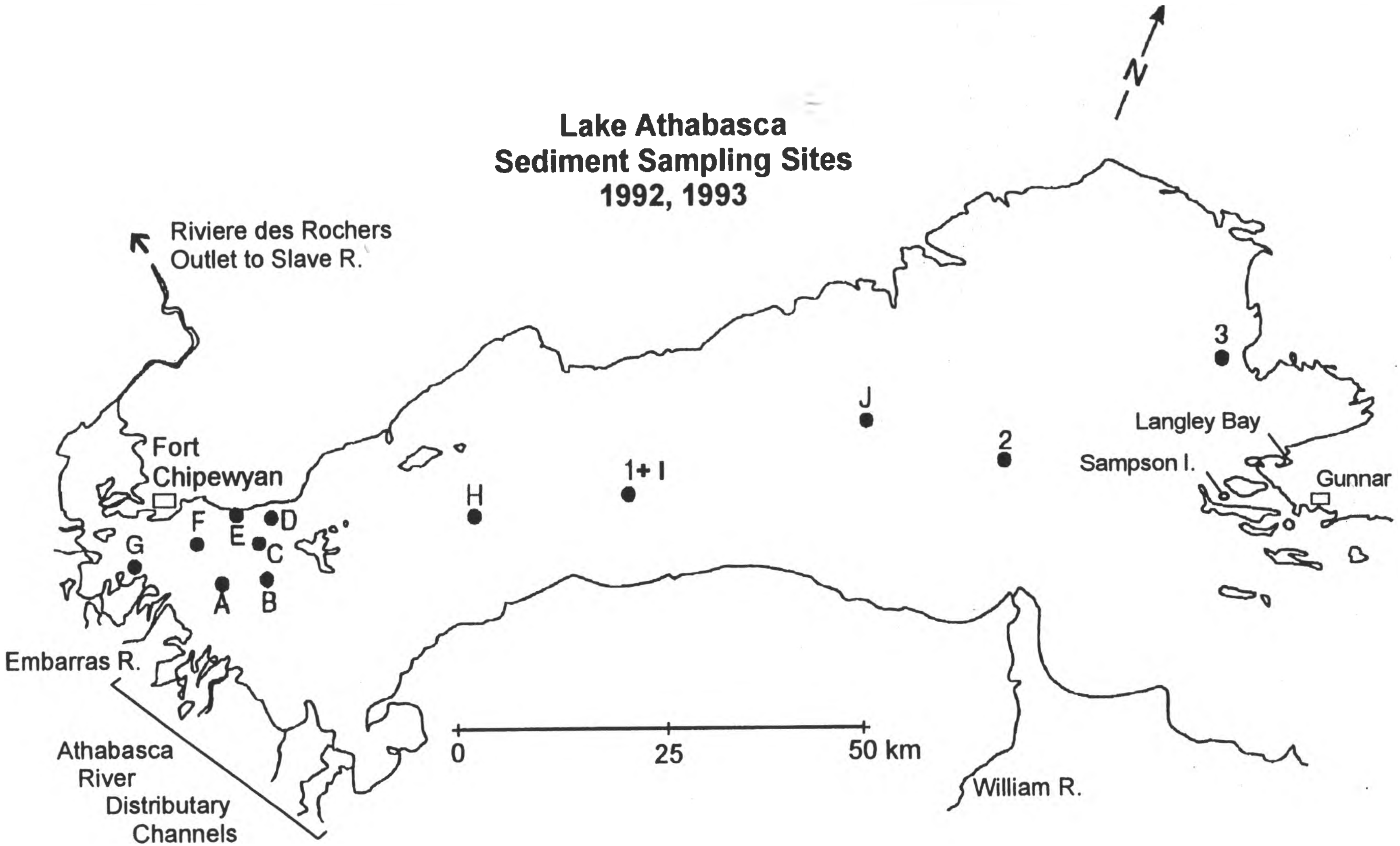


Figure 1: Lake Athabasca Sampling Sites 1992-93.

disturbance by wave action, but is more distant from the rivers of interest and contaminants from those sources may not be detectable there. Site 3 (water depth 110 m) on the northeast arm of the lake is the coring site most distant from the western river inputs. Distance from the contaminant sources of interest make this site least desirable, but it is the deepest part of the lake, and sediment from all over the lake may be focused there. As well, Site 3 proved interesting because of its proximity to former uranium operations.

A sampling expedition was mounted by helicopter in March, 1992 from a base at Wood Buffalo National Park (WBNP) in Fort Chipewyan. There was interest in obtaining samples as near to the mouth of the Athabasca River as possible, so a number of surficial samples were collected from sites at the west end of Lake Athabasca; cores were collected from Sites 1, 2 and 3 (Figure 1) which are in deeper parts of the lake. The choice of March for coring was intentional since the stable ice platform provides ideal conditions to obtain high quality cores. Cores were extruded vertically either on site or back at the Fort Chipewyan base. Although sectioning on site is the most ideal for preservation of sample integrity, the short daylight hours available and deteriorating weather conditions made this impractical. Transport of the cores by helicopter was smooth and disturbance of the cores was minimal.

2.2.1 Summary of Samples Collected

Surficial samples were collected from nine sites mostly in the western part of Lake Athabasca off the Peace-Athabasca Delta (Figure 1). Many of the samples consisted of fine-grained sediments which may have been laid down under quiescent ice-covered conditions. It is possible that the fine sediment sampled from the western end in March, 1992 represents recent deposition laid down in the fall and winter of 1991-92. A complete listing of the surficial samples collected, their locations and descriptions appears in Appendix B.

Three cores were collected and sectioned from Site 1, six from Site 2 and two from Site 3. Descriptions of the core sections were recorded as they were sectioned and summaries of these descriptions are given in Appendix B. All cores had a surficial brown oxidised layer varying from 4 to 13 cm in depth below which the fine grained sediment was grey in colour with occasional black banding. All cores from Site 2 exhibited a pronounced 1-2 cm rust coloured band beginning at about 2 cm. This layer appeared to be slightly coarser than the sediment above or below.

After geochronological results on the 1992 cores became available, it was decided that Site 1 cores had the potential to yield the best data set. This was based on evidence of continuous sediment accumulation for at least the past 100 years and a sedimentation rate which corresponded to a time resolution of approximately five years per cm (see section 5.1). As well Site 1 is closest to the river sources of interest on the western end of the lake. Since only three cores were collected from Site 1 in March, 1992; a resampling occurred at that site in March, 1993 collecting five cores on the second trip. All positioning for both trips was provided by GPS, so confirmation of position for revisiting Site 1 was facilitated. A discussion of the comparability of the Site 1 cores collected from both expeditions, based on geochronology results, appears in section 5.1, and is evident from the descriptions in Appendix B.

3.0 MATERIAL AND METHODS

It is beyond the scope of this report to describe in detail the numerous analytical methodologies used by all of the laboratories that have analyzed sediment samples for this study. Brief descriptions of the methodologies are given here referenced to literature, standard methods and reports from contract laboratories. The methodology for NWRI organic contaminant and biogeochemical analyses is given in greater detail as NRBS does not yet have a printed reference for this. For more details about the methodologies employed reference should be made to the appropriate reports listed in Section 8.

3.1 SEDIMENT SAMPLING

Surficial samples were collected using an Ekman sampler, saving approximately the top 5 cm of sediment (integrating approximately 25 years or less of sediment accumulation) as a pooled sample. Cores were collected from depositional zones using a 10.1 cm ID gravity corer provided by the Technical Operations Division (Mawhinney and Bisutti, 1987) of NWRI. Cores were extruded vertically using an hydraulic device commonly used by NWRI scientists. They were sectioned in 1 cm intervals from the top down to 24 cm, sampling the entire diameter of the 10.1 cm ID butyrate core tube. Below 24 cm the sectioning interval was increased to 2 cm, still retaining the entire core diameter. All sediment samples were stored in wide mouth screw-capped glass jars with Teflon® cap liners. Jars were pre-cleaned and quality-assured by the manufacturer (I-Chem® or Eagle-Picher®). Samples were frozen (-20° C.) immediately after sectioning and stored frozen until thawed just prior to analysis, or where appropriate, freeze dried.

3.2 ANALYSES FOR BULK PARAMETERS

3.2.1 Particle Size Analysis

Particle sizes were determined by the Sedimentology Laboratory at NWRI using the Sieve and Sedigraph Method (Duncan and LaHaie, 1979). The freeze-dried samples were quantitatively split, dispersed in sodium metaphosphate and wet sieved at 4.0 phi (0.063 mm). The sand and gravel percentages were determined gravimetrically on the dried contents of the sieve. The remaining suspension is applied to the Sedigraph Analyzer to obtain the distribution of silt and clay sized particles. Results are reported as percentages of various size fractions and several statistical measures (Duncan, 1994).

3.2.2 Bulk Carbon and Nitrogen Species

Bulk determinations C and N species were made at the National Laboratory for Environmental Testing (NLET) at NWRI using a CHN analyzer at 950° C. An aliquot of the freeze-dried total sediment sample was combusted in the presence of CoO catalyst, measuring the resulting combustion gases (CO_2 and NO_x, which is reduced to N_2) chromatographically. The results are "total carbon" and "total nitrogen". Another aliquot was treated with hydrochloric acid to remove inorganic carbon, dried and combusted as before. The results of the second run were total organic carbon (TOC) and "total organic nitrogen" (TON). Total inorganic carbon (TIC) is determined by difference (total carbon - TOC). There was a potential interference in the TON determination due to hydrolysis effects on certain organic components of the sediments. The atomic C/N ratio of the organic matter is calculated by dividing the TOC and TON results expressed as mg-atoms.

3.3 ANALYSES FOR RADIONUCLIDES

3.3.1 Po-210 for Pb-210 Geochronology

Determinations for ^{210}Pb geochronology were made under contract at NWRI using the method described by Turner (1990). Po-210, a granddaughter nuclide of ^{210}Pb, was determined as a surrogate after careful preparation, spiking with a known quantity of ^{209}Po, plating on a silver disk, and counting with an alpha spectrometer. Po-209 was identified by its 4.88 MeV alpha particle and ^{210}Po by its 5.305 MeV alpha particle. In addition to Po determinations, the geochronology required porosity and dry bulk density determinations which were provided by the laboratory (Turner, 1993a, b).

3.3.2 Cs-137 for Geochronology

Cs-137 was determined non-destructively directly on the dried sediment samples by gamma counting with a NaI(Tl) detector on a Canberra 8180 MCA spectrometer. Cs-137 activity was quantified against National Bureau of Standards (NBS) spiked sediment samples using the 661 KeV gamma ray. Determinations were provided by Flett Research Ltd. (1993) under contract to NRBS (2334-B4)

3.3.3 Thorium and Uranium Series Radionuclides and Total Uranium

Three radionuclides from the thorium series (^{232}Th, ^{228}Th, ^{224}Ra), three from the uranium series (^{230}Th, ^{226}Ra, ^{210}Pb) and total uranium were determined on the same samples as all of the other radionuclides by ARCT Chemtech (1993). Decay charts for these series can be found in Robbins (1978). The thorium and uranium series nuclides were determined by gamma counting against well known traceable standards. Total uranium was determined by fluorometry using a calibration curve made from U standards.

3.4 ANALYSES OF ORGANIC CONTAMINANTS

3.4.1 Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

PCDD/Fs were measured in Lake Athabasca surficial sediments from six different sites and in ten one-centimetre sections from 1992 Site 1, Core B. Analyses were carried out by Axys Analytical Services Ltd. Details of Axys' analytical procedure can be found in their final report to NRBS (Axys, 1993a). The samples were analyzed for total tetra- (T_4CDD/F), penta- (P_5CDD/F), hexa- (H_6CDD/F), hepta- (H_7CDD/F), and octa- (O_8CDD/F) congener classes and for individual 2,3,7,8-substituted PCDD/F congeners. The wet samples were spiked with ^{13}C-labelled surrogates, Soxhlet extracted with toluene:acetone (4:1), the organic layer was concentrated, washed and dried. Cleanup included four chromatographic steps (1) silica gel, (2) alumina, (3) carbon/celite and (4) alumina. Before analysis by high resolution GCMS, ^{13}C-labelled recovery spikes were added.

3.4.2 Resin Acids

Resin acid analyses were completed on the surficial sediments by Axys Analytical Services Ltd.. A detailed account of all samples analyzed for resin acids, methodology and results is given in Axys' final report (Axys, 1993b) to NRBS. In total, samples were analyzed for the presence of ten resin acids. Two of these resin acids are chlorinated and therefore derived from anthropogenic sources. These are 12/14-chlorodehydroabietic acid (i.e., 12- and 14-monochlorodehydroabietic acid) and 12,14-dichlorodehydroabietic acid. The remaining eight resin acids analyzed for are all naturally occurring acids and include: dehydroabietic acid (DHA), pimaric acid, sandaracopimaric acid, isopimaric acid, dehydroisopimaric acid, abietic acid, palustric acid and neoabietic acid. Concentrations of these acids can be augmented by pulp and paper mill processes.

A surrogate (O-methylpodocarpic acid) is added to all samples prior to extraction. Samples are hydrolysed with sonication in methanol:KOH, filtered, acidified, extracted with ether:hexane (1:4), dried and concentrated. The concentrate is methylated, and applied to a Biosil A column (in base form), washed with hexane and eluted with ether:hexane (5:95). The eluent is concentrated, and after the addition of a recovery spike, analyzed by GCMS.

3.4.3 Polynuclear Aromatic Hydrocarbons

PAHs are one of a number of compound groups extracted by methanol:toluene soxhlet extraction. A summary of the methodology used in given in section 3.6. The identification and quantitation methods used at NWRI include detection by GLC with flame ionization detector (FID), HPLC with fluorescence (FL) detector, HPLC with photodiode-array UV (PDA) detector, which affords multiple wavelength monitoring, "maxplot" (total absorbance), and spectral match monitoring. Twenty-five PAHs are scanned for by HPLC and 28 by GLC including all 16 parent PAHs from the EPA list, other parent PAHs, and a number of methyl- and dimethyl- naphthalenes, anthracenes and phenanthrenes. Quantitation is done using the internal standard method (deuterated surrogate) with instrument response factor corrections applied for each component and each detector.

In addition to the analyses done at NWRI for PAHs, separate samples from another Site 1 core were determined by Chemex Labs Alberta Inc. by GCMS using Method 8270 (selected ion monitoring - SIM) and focusing on the EPA list of 16 parent PAHs (Chemex Labs Alberta Inc., 1993, 1994).

3.4.4 Organochlorine Pesticides, Polychlorinated Biphenyls and Toxaphenes

Chemex Labs Alberta Inc. was contracted to determine a suite of organochlorine compounds including 17 pesticides, 50 PCB congeners and toxaphenes. For all samples the results for all 17 pesticides were below the method detection limits (MDL) which ranged from 1.5-2.5 µg/kg. As well toxaphenes were not detected at MDL's ranging from 4.5 to 6.0 µg/kg. Only on a few samples were PCB congeners found in amounts over the MDL. "Trace" quantities were determined in a few samples, but overall little was detected. It should be noted that for PCB congener analysis surrogates were recovered at 85-103%. For pesticides (and toxaphenes) no surrogate was analyzed, so there was no determination of recovery. For further details refer to Chemex Labs Alberta Inc. (1993, 1994). No further discussion of these non-detected components will be made in this report.

3.4.5 Petroleum Hydrocarbons

The samples and procedure for petroleum hydrocarbon analysis were the same as for PAHs and biogeochemical markers (see section 3.6). Petroleum hydrocarbons are a subset of the alkanes, alkenes, isoprenoid and aromatic hydrocarbons which may be found in oil as well as in nature. Petroleum and petroleum products are very complex mixtures of hydrocarbons and behave chromatographically such that baseline resolution is almost never achieved. The resulting chromatographic traces contain an area where the bottoms of many peaks converge in an "unresolved complex mixture" (UCM). The UCM can be quantitated planimetrically or by modern integrators, providing an estimate of petroleum influence.

3.5 ANALYSES FOR INORGANIC CONTAMINANTS

3.5.1 Heavy Metals

Dry sediment samples were sent to Chemex Labs Alberta Inc. (1993, 1994) for determination of arsenic, lead, cadmium, chromium, copper, vanadium and zinc. Arsenic was determined by atomic absorption (AA), lead by graphite furnace atomic absorption (GFAA) and the remainder by inductively coupled plasma spectroscopy (ICP).

3.5.2 Total Mercury and Total Methyl Mercury

The same samples analyzed for heavy metals were also tested for total mercury by cold vapour atomic absorption (CVAA). Analyses were performed under contract to Chemex Labs Alberta Inc. (1993, 1994).

3.6 ANALYSES FOR BIOGEOCHEMICAL MARKERS

Biogeochemical marker analyses which include n-alkanes and n-fatty acids were completed by NWRI. As mentioned in sections 3.4.3 and 3.4.5, the methanol:toluene Soxhlet extraction used by NWRI also extracts PAHs and petroleum hydrocarbons. This extraction procedure which was adapted from that used by Leenheer et al. (1984) follows.

3.6.1 Sample Preparation, Fractionation and Analysis

Prior to extraction and analyses the wet sediments were defrosted and excess water was poured into a centrifuge tube, centrifuged until clear and discarded. The sediment plug was returned to the sample. The thicker wet sediment was then manually homogenized, subsampled and refrozen until extraction. At least 24 hours before extraction, 1 ml of internal standard mixture (1.0 µg/ml phenanthrene-d_{10}; 4.0 µg/ml n-C36-alkane; 40.5 µg/ml n-C17 fatty acid; and 40.0 µg/ml n-C17 alcohol) was added to each sample along with 10.0 g of precleaned `Baker' sand and re-homogenized and stored at 4°C overnight to promote adsorption of the standards onto the sediment particles.

The wet sediment samples were extracted using methanol:toluene (9:8) for a period of 24 hours, followed by a second 24 hour extraction using fresh solvent (1:1). The extracts were then partitioned into hexane using 1/2 saturated NaCl (pH=1) and backwashing. The resulting organic phase was evaporated to `just' dryness and transferred to a centrifuge tube using methanol:toluene (1:1). One ml of a recovery spike (n-C38 alkane and n-C19 fatty acid) was added to the sample along with 5 ml of methanolic KOH and the samples were saponified in a boiling water bath for 20 minutes. Fatty acids were methylated using 5 ml of BF_3 (14%) in methanol in a boiling water bath. The samples are then re-extracted using 15 ml Milli-Q water and 3 X 5 ml hexane rinses. Prior to alumina/silica column chromatography, the samples are adsorbed to one gram of aluminum oxide powder and then column fractionated using the following eluents for each compound group listed:

hydrocarbons (n-alkanes and PAHs) - hexane:toluene (85:15)
fatty acid methyl esters - toluene

For gas chromatography the hydrocarbon and fatty acid fractions were maintained in 1.0 ml heptane. For liquid chromatography analysis, the hydrocarbon samples were exchanged into dimethyl sulfoxide:acetonitrile, (1:1).

3.7 DETECTION LIMITS AND QA/QC

3.7.1 Method Detection Limits

There are a myriad of detection limits possible for all of the parameters determined for this study. We have depended on the laboratories to report data with their appropriate detection limits. The terminology used by different laboratories for similar parameters can be confusing. The Practical

Quantification Limit (PQL) of Chemex Labs Alberta Inc., is the concentration representing a peak with height three times the peak height of the maximum noise in a baseline run (the MDL), and is scaled to the dry sample weight. Chemex identifies any peak found between the MDL and PQL as "trace." Axys Analytical Services Ltd. reports the Sample Detection Limit (SDL), also an MDL which is scaled to the dry weight of the sample. In addition Axys reports "NDR" values. These are given for sample peaks which respond above the SDL but failed to meet one or more of the quanitification criteria. In addition to the "three times peak height of noise" rule, Axys requires that a detected sample peak must have a retention time within three seconds of the retention time of the corresponding compound in the calibration standard. Furthermore, the peak maxima for both characteristic ions must coincide within two seconds and the ratio of areas must be within ±20% of the value in the calibration standard.

As a rule data reported here are above detection limits. However, in some cases a data set contains several values that are at or below detection limits and reported as not detected (ND). Whenever such a situation arises, we have chosen to plot ND values as equal to the MDL or SDL rather than as zero. Each of the different categories of values are plotted on all graphs. Whenever a data set contains "ND", "NDR" or "trace" values in high enough frequency, then a data table is included in the text so that the reader can be sure. Figure captions or legends contain notations whenever "ND", "trace" or "NDR" values are plotted.

3.7.2 QA/QC

Contract laboratories which performed the analyses reported here have passed a certification exercise prescribed by the NRBS. Certification was under the control of the Quality Assurance Working Group, and labs were certified only for specific parameters on specified media (sediments in this case). As well many of the labs used hold accreditation from other private sector organizations.

Each laboratory has its own internal, or commonly used certified standard references. Good laboratory practice requires that every batch of samples be accompanied by runs of certified references, spiked matrices and procedural blank test runs. Periodically standard reference materials obtained from Radian Corporation, USA were submitted by NRBS for PCDD/F analyses. In most cases laboratories report these results along with the contracted analyses so that the client can have confidence in their work. Depending upon the parameter and the method chosen, surrogate or internal standards, recovery spikes and blank determinations are commonly used. Wherever sample size allowed it, we included blind replicates in batches of samples so that we could get our own assessment of quality control. Whenever this was done, average values appear in this report. Blank subtraction is commonly used in some determinations as a routine part of a particular instrumental technique. Here we presume that laboratories have applied appropriate instrumental corrections to the data before they are reported, since this is normal good laboratory practice and some labs specifically state so in their documentation. However, this does not extend to "blank samples" or "method blanks". Such determinations are frequently reported as separate determinations, and are also frequently nil or small. If a significant blank value is routinely encountered, then either the sample data are discarded, or if a correction can be (or has been) made, then such is reported.

4.0 RESULTS AND DISCUSSION - SURFICIAL SEDIMENTS

4.1 RADIONUCLIDES

The uranium series radionuclides (total U, ^{226}Ra, ^{230}Th, and ^{210}Pb) which were reported by Waite, Joshi and co-workers, as well as some thorium series radionuclides (^{232}Th, ^{228}Th and ^{224}Ra) which are often associated with uranium ores (Joshi et al., 1989) were determined on six of the surficial samples. Results of these determinations appear in Table 1 along with comparative data from the upper five cm of each of the cores. The Lake Athabasca sites listed in Table 1 are ordered from west to east and the "uncontaminated" control site and Langley Bay site from Waite et al. (1988) are shown for comparison.

The thorium series isotopes are plotted in Figure 2a and only ^{232}Th shows a slight west to east increasing trend. Th-228 and ^{224}Ra show no trend at all with the activity of the former at about the same level as the control site and about half that of the Langley Bay site. Th-230 and ^{210}Pb show increasing trends from west to east (Figure 2b). These uranium series isotopes are common in uranium mine tailings -- note the high ^{210}Pb activity in Langley Bay sediments (Table 1). The ^{226}Ra activity shows a slight decreasing trend from west to east even though the Langley Bay sediments are high in this isotope.

Total uranium concentration exhibits a marked and fairly steady increasing trend (Figure 3) with values at core sites 2 and 3 about twice that of the background (western) sites and attaining approximately one third of the activity found in Langley Bay sediments. The control site shows the lowest concentration of all sites suggesting that there are sources of background U content throughout the lake basin. Nevertheless the increasing trends evident for total U, ^{230}Th and ^{210}Pb are consistent with a greater source of these isotopes from the east.

If radionuclides from the Langley Bay contamination were to be moving westward, then the west to east increasing trends shown by some of the isotopes would be expected. There could be a number of other sources around the lake from mining activity, this could explain the occasional higher levels found in the westernmost sites (e.g. Site F) and the reason that most of the sampling sites are higher than the control site. Any movement westward seems to be limited in extent to sediments nearest to Langley Bay, namely coring Site 3, which is the deepest part of the lake and would serve as a deposition basin for sediment which is focussed from shallow zones in the eastern part of the lake.

Table 1: Radionuclides in 1992 Surficial Sediments and Comparison Samples.

Sampling Sites	Th-232 (Bq/g)	Th-228 (Bq/g)	Ra-224 (Bq/g)	U (mg/kg)	Th-230 (Bq/g)	Ra-226 (Bq/g)	Pb-210 (Bq/g)	Cs-137 (Bq/g)
Site G	0.043	0.036	0.024	1.6	0.055	0.058	0.06	--
Site F	0.059	0.054	0.048	2.6	0.077	0.079	0.06	--
Site B	0.046	0.040	0.033	2.1	0.046	0.063	0.07	--
Site D	0.057	0.044	0.046	2.4	0.079	0.068	0.09	--
Site H	0.045	0.043	0.036	2.7	0.104	0.075	0.11	--
Site I	0.049	0.049	0.034	3.5	0.089	0.063	0.14	--
S1(0-5)	0.043	0.046	0.052	3.7	0.068	0.057	0.17	0.103
S2(0-5)	0.068	0.037	0.055	6.3	0.123	0.066	0.19	0.135
S3(0-5)	0.092	0.054	0.056	6.4	0.329	0.062	0.28	0.156
[a]Control	--	0.044	--	1.1	--	0.044	0.13	--
[b]Langley	--	0.122	--	16.9	--	28.0	33.6	--

[a] Control Site is from Sampson Island, (Waite et al., 1988)

[b] Langley Bay Surficial Sediment (Waite et al., 1988)

Figure 2: Thorium and Uranium Series Radionuclides - Surficial Sediments 1992.

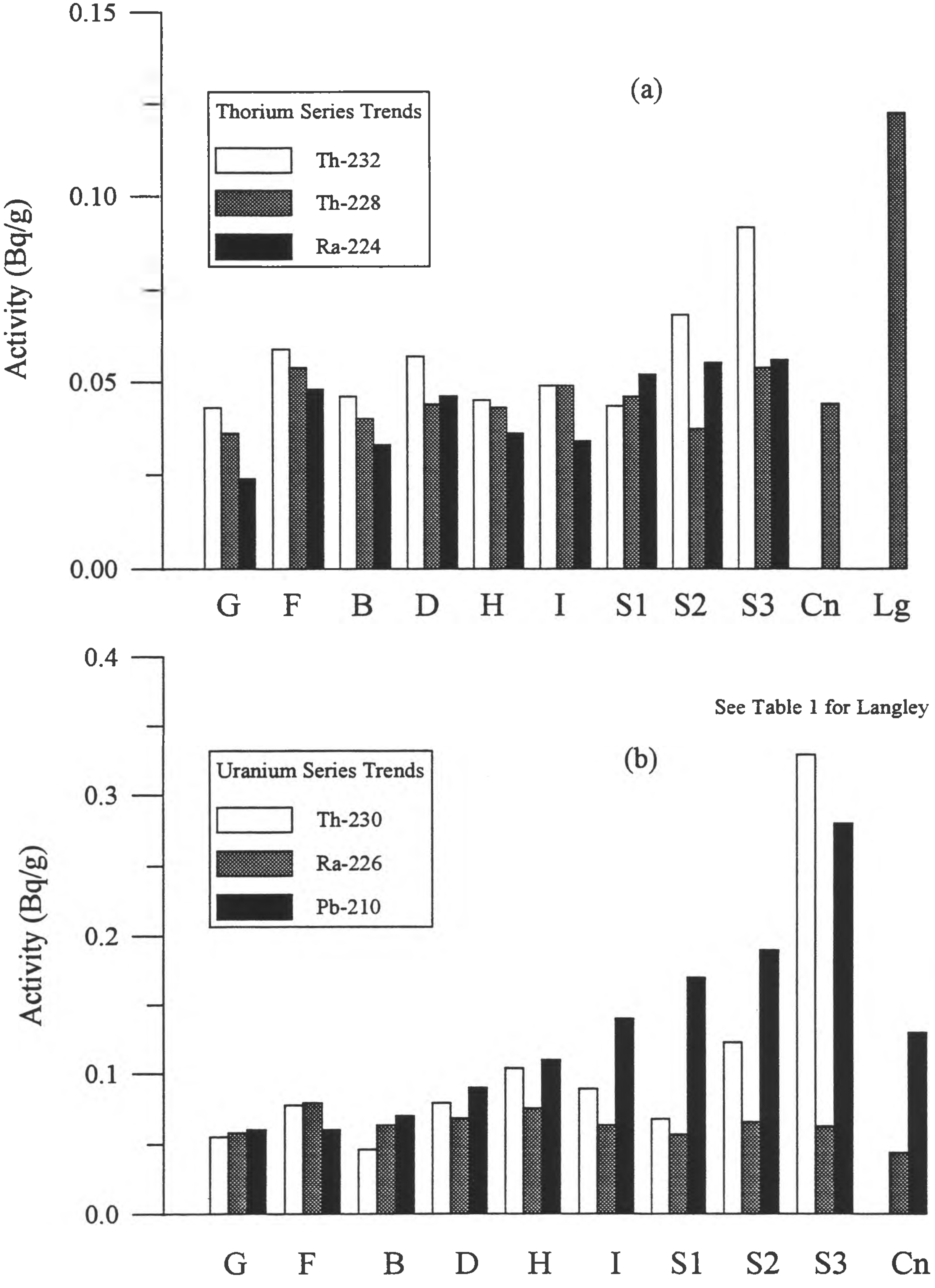
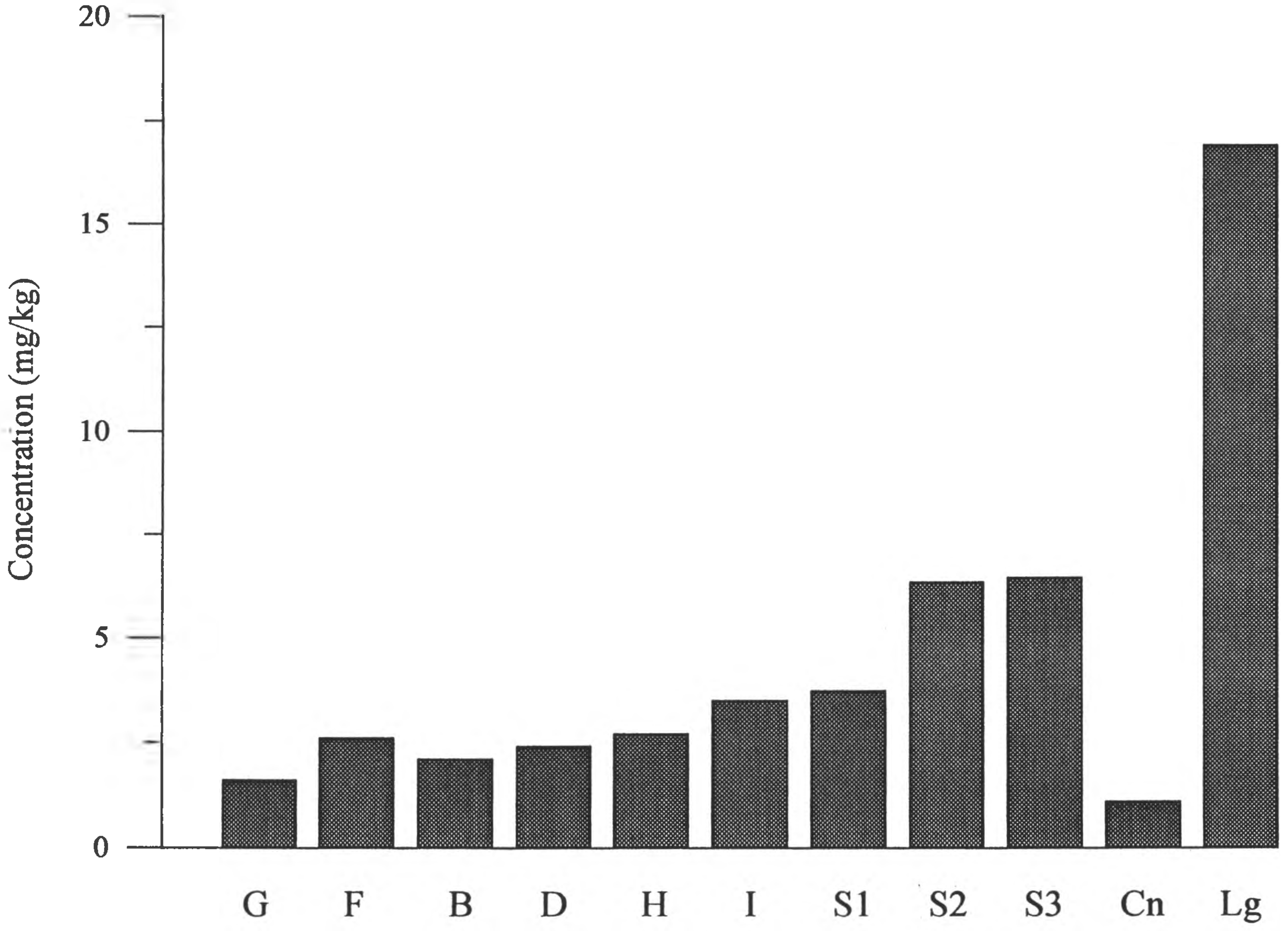


Figure 3: Total Uranium Concentrations, Surficial Sediments - 1992.



4.2 ORGANIC CONTAMINANTS

4.2.1 Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

The total concentrations for each of the five main PCDD and PCDF congener groups (tetra- to octa-) are presented in Table 2. With the exception of P_5CDDs at Site G, the presence of all five PCDD congener groups is detected at each of the sites. This indicates that PCDDs are relatively ubiquitous in this environment -- a sign that the effects of industrialization are reaching this area. As Figure 4 illustrates, differences are not great among the sites. O_8CDD, which is present in the highest concentrations relative to the other congener totals, ranges from 7.2 to 23 ng/kg. T_4CDD is the second most highly concentrated congener group with totals ranging from 2.9 to 11 ng/kg. Of the various congener classes, T_4CDDs, P_5CDDs and H_6CDDs are considered to be more toxic than H_7CDDs and O_8CDD, and particularly the 2,3,7,8-substituted congeners.

Total concentrations for the PCDF congener groups are presented in Figure 5. From Table 2, we can see that many of the values plotted are actually detection limits. Only T_4CDFs were found at each of the sites with values from 0.6 to 2.1 ng/kg. O_8CDF is the second most prevalent of the PCDF groups. Again, there is little spatial difference in PCDF distribution in Lake Athabasca. 2,3,7,8-T_4CDF results are shown in Figure 6. Concentrations range from 0.2 to 0.6 (NDR). At these low concentrations, differences in values between sites can be said to be minimal.

Although we can say that PCDD/Fs are present, identifying their source is somewhat complicated. As mentioned in section 1.3.3, PCDD/Fs have multiple sources, many of which can be expected to play some role in northern Alberta. In a national study of PCDD/Fs concentrations in bottom sediments near pulp and paper mills "slight" levels of PCDD/Fs contamination were reported downstream of the Weldwood of Canada pulp mill in Hinton (Trudel, 1991). This is one possible source for PCDD/Fs found in Lake Athabasca. In the referenced study, the highest concentrations were found for O_8CDD with an average value of 103 ng/kg. Other PCDD/Fs detected include: H_7CDDs (9-15 ng/kg), 2,3,7,8-T_4CDF (2 to 7 ng/kg), H_6CDFs (ND to 2 ng/kg), H_7CDFs (ND to 5 ng/kg) and O_8CDF (4 to 7 ng/kg). As Trudel (1991) reports that no PCDD/Fs were detected upstream of the mill, we can, with some confidence, attribute the presence of PCDD/Fs to the activities at the mill. As one would expect, the PCDD/F concentrations near the pulp mill are generally much higher than what we have found in Lake Athabasca. Sediments from the west end of Lake Athabasca were also analyzed in the national PCDD/Fs study. However, the detection limits given ranged from 5 to 118 ng/kg and hence, no PCDD/Fs were detected. The lower detection limits of our NRBS study has allowed us to determine that PCDD/Fs are indeed present in Lake Athabasca bed sediment.

4.2.2 Resin Acids

The results from the resin acids analyses are presented in Table 3. As with the PCDD/Fs, where ND values were reported, the value of the SDL was used with the actual sample concentration of the given resin acid being less than this limit. Where duplicate analysis was carried out (for samples from sites D, F, G, and H), an average of the two results was taken and is presented here

Table 2: Total PCDD and PCDF Results for 1992 Surficial Sediments.

Site Location	Total T_4CDD (ng/kg)	Total P_5CDD (ng/kg)	Total H_6CDD (ng/kg)	Total H_7CDD (ng/kg)	Total O_8CDD (ng/kg)	Total T_4CDF (ng/kg)	Total P_5CDF (ng/kg)	Total H_6CDF (ng/kg)	Total H_7CDF (ng/kg)	Total O_8CDF (ng/kg)
Site G	2.9	[a]ND(0.5)	2.4	5.6	16	0.9	ND(0.3)	ND(0.6)	ND(0.5)	ND(0.7)
Site F	11	5.9	5.3	2.7	7.2	0.6	ND(0.1)	ND(0.2)	ND(0.3)	0.7
Site B	8.4	6.0	4.8	5.4	17	0.6	ND(0.2)	ND(0.3)	ND(0.3)	ND(0.3)
Site D	8.5	3.7	5.0	2.9	14	1.0	ND(0.1)	1.1	0.6	0.4
Site H	11	3.4	4.4	4.1	10	1.6	ND(0.2)	ND(0.2)	0.8	0.9
Site I	6.4	4.4	5.9	8.8	23	2.1	ND(0.7)	ND(1.1)	ND(1.5)	ND(1.9)
[b]Site 1	8.8	5.6	4.3	4.4	12.9	1.5	ND(0.2)	0.6	0.7	0.9

[a] ND = Not Detected. The value in brackets is the Sample Detection Limit which equals 3x the maximum peak detected on baseline runs. In all related graphs, the SDL value is plotted for ND values.

[b] Site 1 values are the average of section 0 to 1, 2 to 3 and 4 to 5 cm. For P_5CDF 2/3 of the values were ND, for H_6CDF, H_7CDF and O_8CDF 1/3 of the values were ND.

Figure 4: Totals of PCDD classes for 1992 Surficial Sediments.

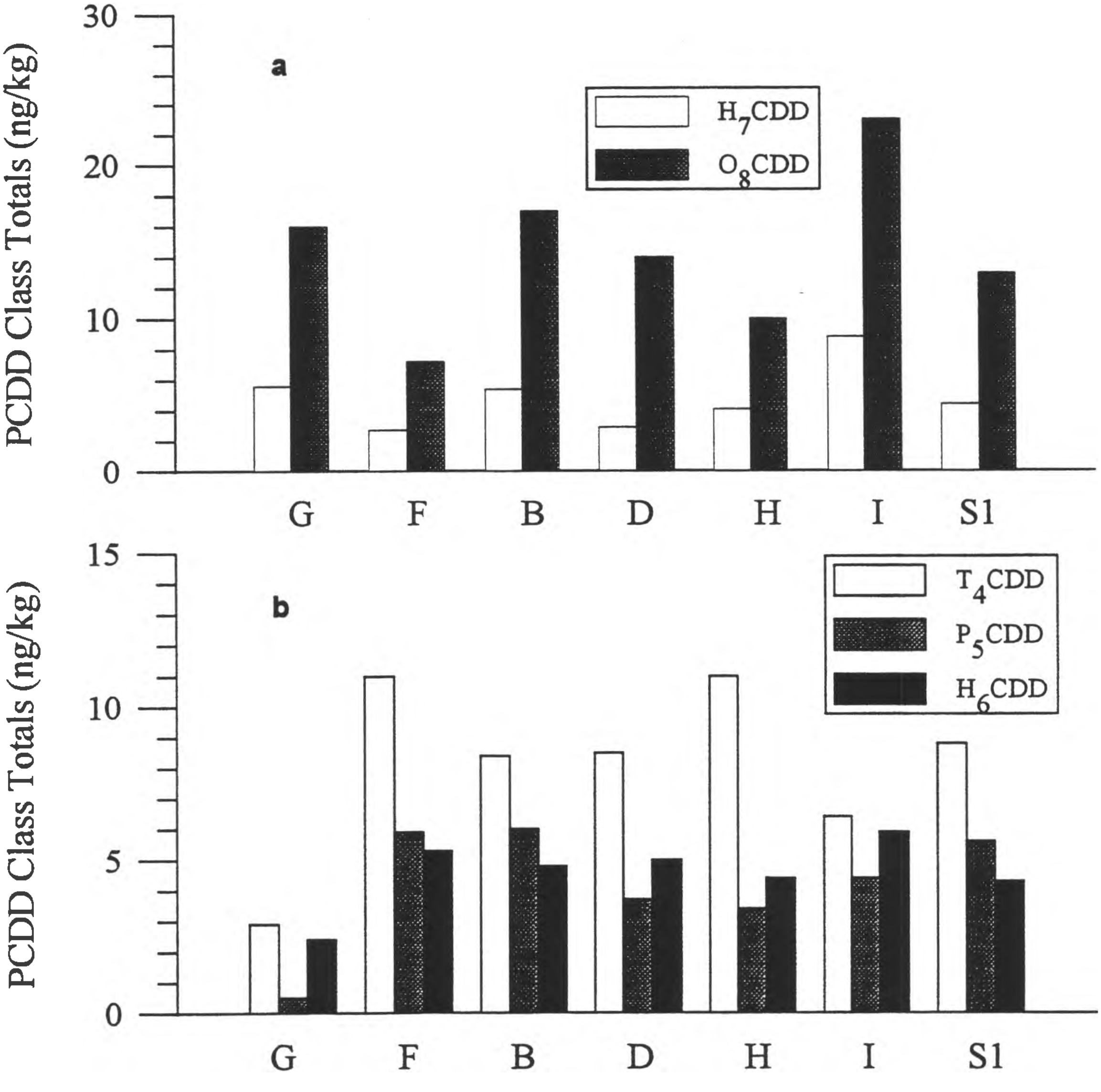


Figure 5: Totals of PCDF Classes for 1992 Surficial Sediments.

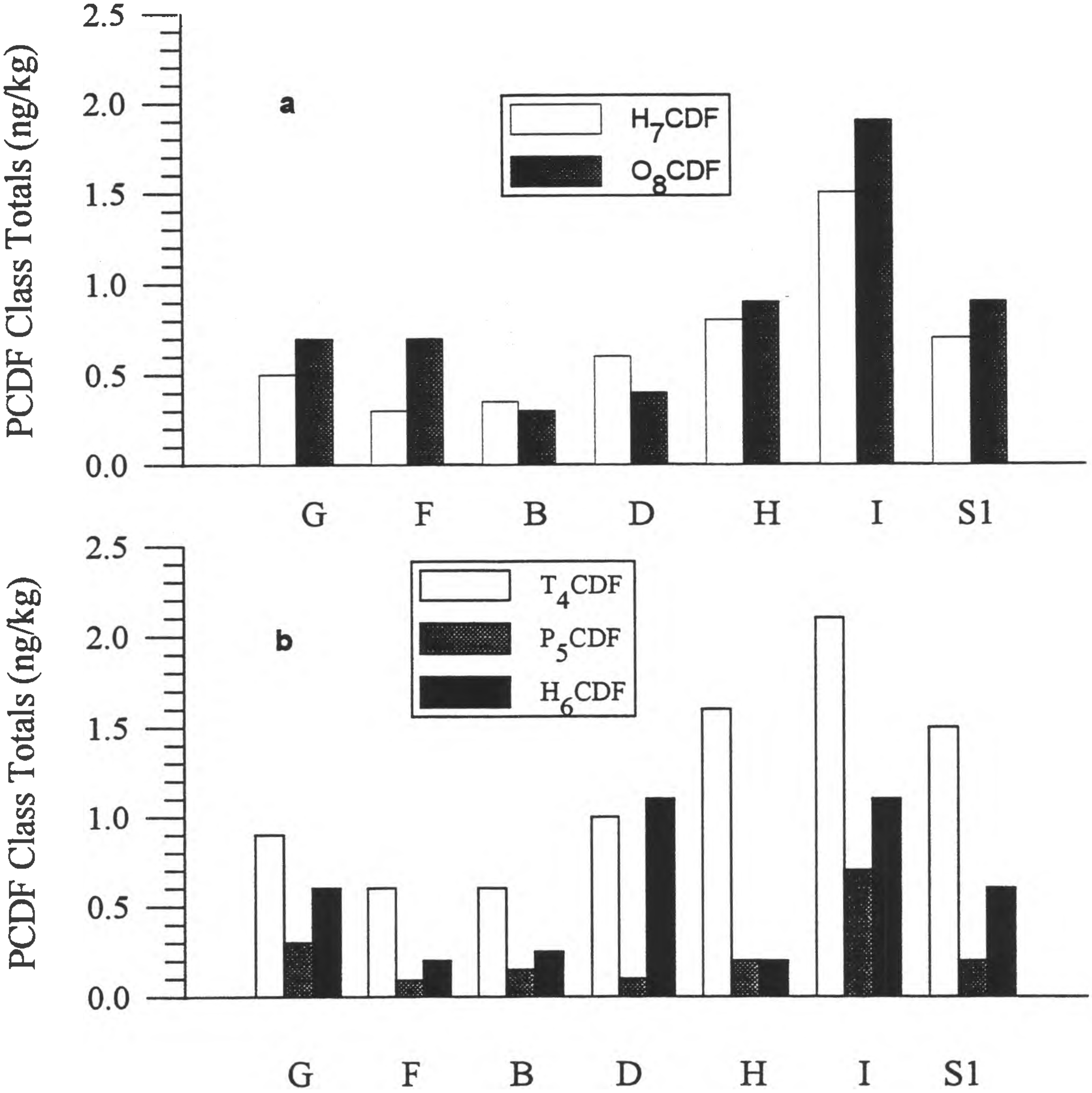


Figure 6: 2378-T_4CDF Concentrations in 1992 Surficial Sediments

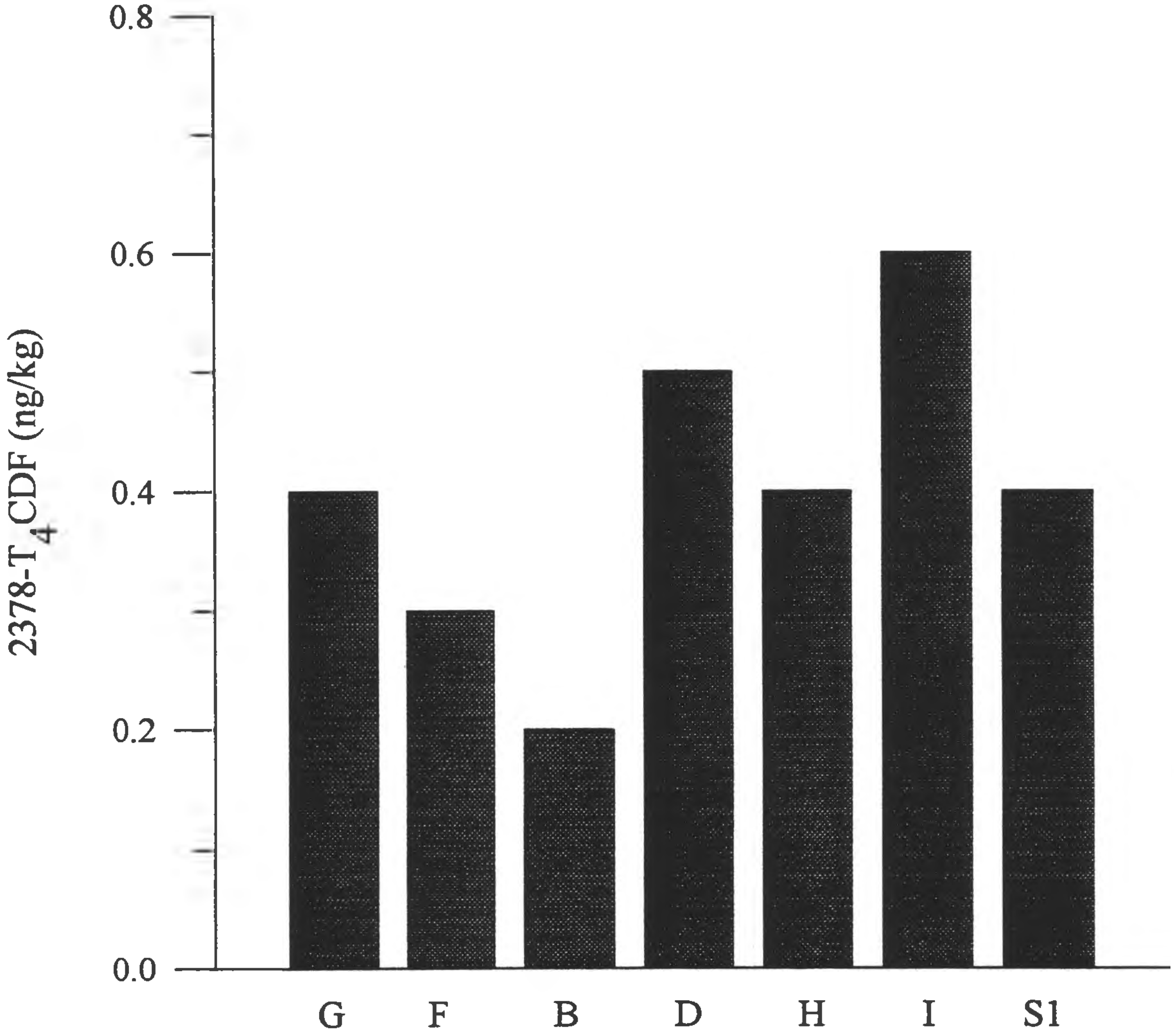


Table 3: Resin Acid Concentrations in 1992 Surficial Sediments[a].

Site Location	Pimaric Acid (ng/g)	Sandara-co-pimaric Acid (ng/g)	Iso-pimaric Acid (ng/g)	Palustric Acid (ng/g)	Dehydro-iso-pimaric Acid (ng/g)	Dehydro-abietic Acid (ng/g)	Abietic Acid (ng/g)	Neo-abietic Acid (ng/g)	12/14 Chloro-dehydro abietic Acid (ng/g)	12, 14 Dichloro-dehydro-abietic Acid (ng/g)
Site G	15.00	7.45	31.00	16.50	2.60	210.00	29.50	1.15	3.75	2.80
Site F	1.45	0.50	1.50	1.40	0.55	13.00	2.00	0.30	0.30	0.20
Site B	1.90	0.50	2.30	11.00	0.30	12.00	2.60	0.20	0.40	0.60
Site D	0.75	0.50	0.68	5.45	0.45	4.45	1.00	0.20	0.15	0.15
Site H	0.40	4.00	0.80	8.60	0.35	10.75	0.75	0.18	0.20	0.10
Site I	5.80	1.20	4.80	17.00	1.20	22.00	5.30	0.10	2.00	2.20

[a] Averages include SDL values rather than zero for ND results or NDR values where appropriate (see text and footnote for Table 2).

in Table 3. In some instances, the original and duplicate results differed in the category of result determined (i.e., "true," ND and NDR). These results were likewise averaged and the results for which this occurred are noted in Table 3.

In Figures 7 to 10 the sites are presented in geographic order from west to east. With respect to spatial distribution of the resin acids, the most obvious observation to be made is that the two sites with the highest concentrations and greatest number of resin acids are sites G and I. This is interesting because these two sites are quite distant from one another and the intermediate sites (all of the other four sites are located between sites G and I -- Figure 1) exhibit little resin acid presence. Site G is the only site which has each of the resin acids present. Furthermore, the concentrations of the resin acids at site G are significantly greater than the concentrations at the other five sites. The presence of chlorinated resin acids, namely 12/14- chlorodehydroabietic acid and 12,14-dichlorodehydroabietic acid, at sites G and I (Figure 7), is important as these can derive only from anthropogenic activity. Their presence at Site I confirms that industrial by-products are settling in the deeper parts of Lake Athabasca.

The notable presence of resin acids at site G but not sites F, B, D and H, suggests two possible interpretations. First, it may be that site G is located in a more sheltered environment than the other four sites. Sediment transport out of the site G area may be somewhat limited whereas sediment reaching those sites east of site G is not hindered in its pathway and continues on to the lake's deeper sites. A second explanation is that winter freezing prevented resin acid laden sediment from travelling beyond site G. This could result in significantly greater resin acids concentrations at site G than at all of the other sites.

Since it is located at its mouth, the most likely source of resin acids for site G is the Embarras River, though some sediment could reach the site from the Peace River during backflows and some are likely produced locally by natural processes (with the exception of the chlorinated resin acids). The Embarras River contains a portion of the Athabasca River flow and thus could carry chlorinated resin acids from pulp mill activities. Resin acid sources for Site I can not be known for certain without further analyses. As mentioned previously in section 2.1, Athabasca River water has been observed to reach far into Lake Athabasca under extreme conditions (Rawson, 1947). This may account for the elevated resin acid concentrations at Site I relative to Sites F, B, D and H.

The actual concentrations of resin acids entering the system from pulp mills will depend upon a number of factors. These include: the type of wood furnished in the mill; the age of the wood chips used; the milling process and; the extent of biological treatment before discharge (Sentar Consultants, 1993). From a structural point a view however, certain observations can be anticipated regardless of source details. First, it is expected that dehydroabietic acid would be the most prevalent and concentrated of the resin acids due to its aromatic nature. This is indeed, the case (Figure 8). As an aromatic acid, dehydroabietic acid is quite resistant to biodegradation. Pimaric, sandaracopimaric, isopimaric and dehydroisopimaric acids with their double bonds, are also fairly stable. These resin acids are present at most of the sites (Figure 9). On the other hand, palustric, abietic and neoabietic acids have conjugated diene structures and can undergo isomerization under certain conditions such as the acid phase of resin acid extraction. The production of such artifacts could result in misleading results and incorrect interpretations. Since abietic acid is the most stable of the trio, followed by palustric acid and then neoabietic acids, the observed concentrations of abietic acid may actually

Figure 7: Chlorinated Resin Acids Concentrations in 1992 Surficial Sediment. Bars below the highest SDL are generated from SDLs. Actual concentrations are therefore less than the value indicated, possibly zero.

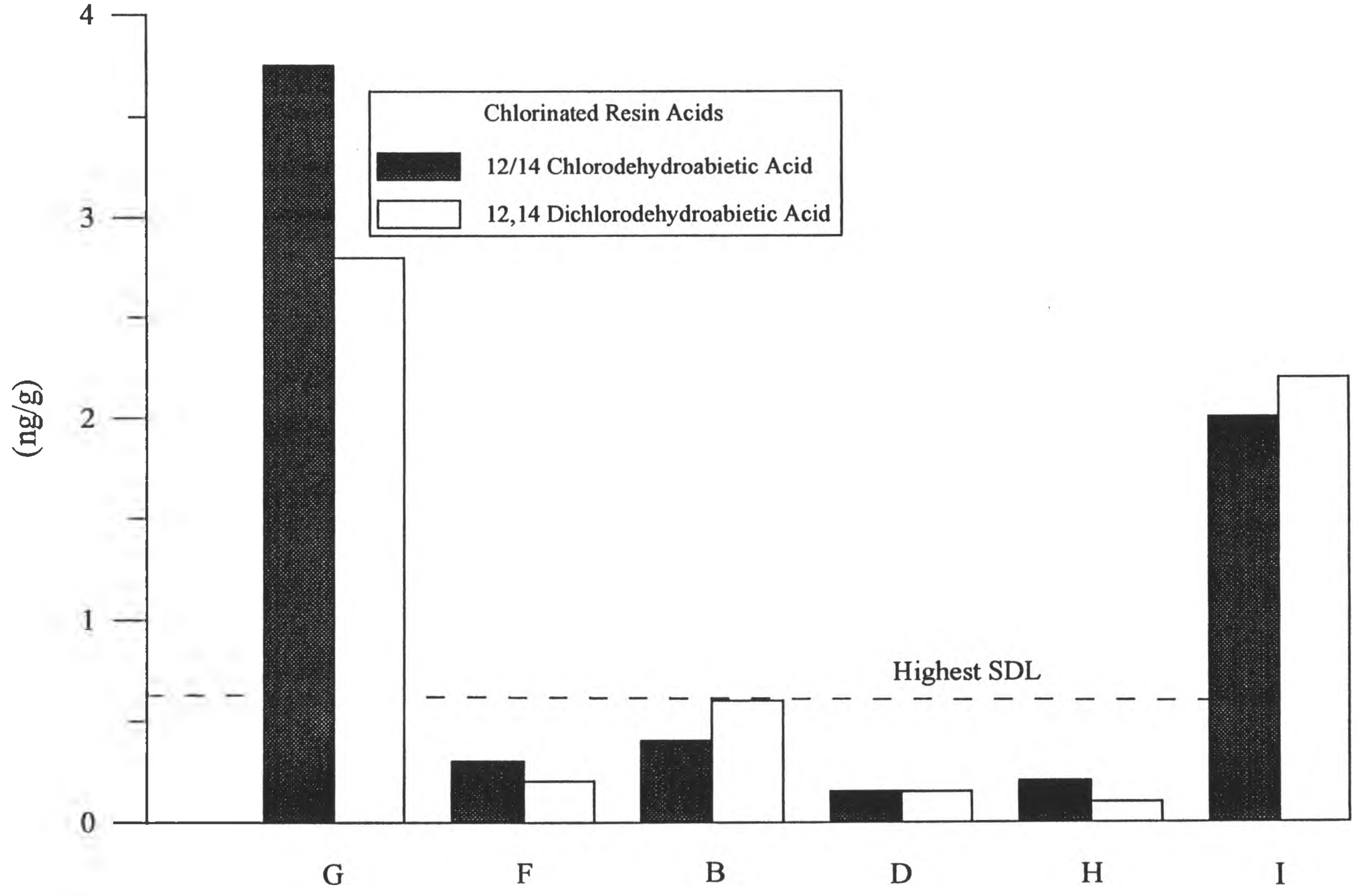


Figure 8: Dehydroabietic Acid (DHA) Concentrations in 1992 Surficial Sediment.

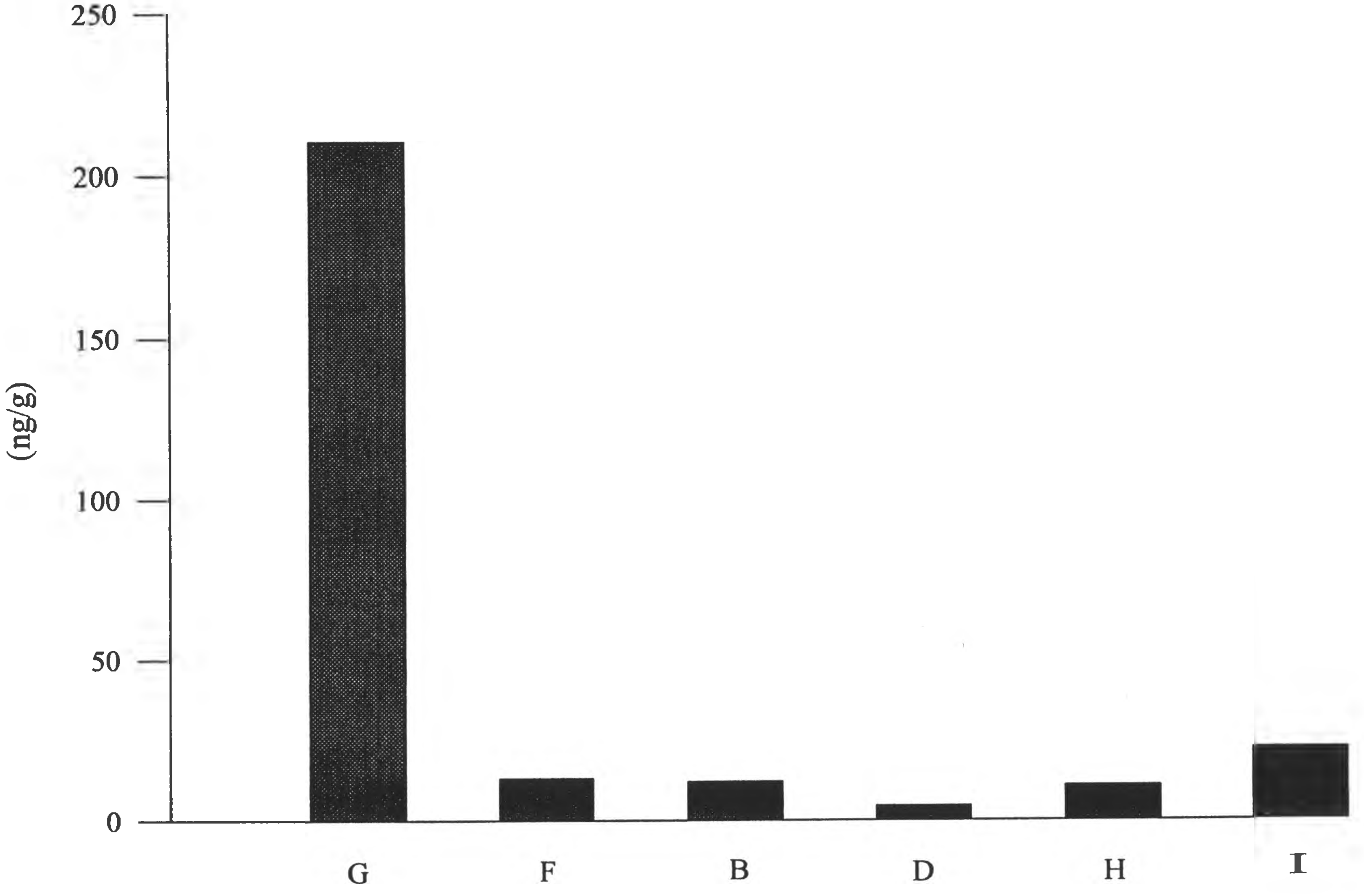
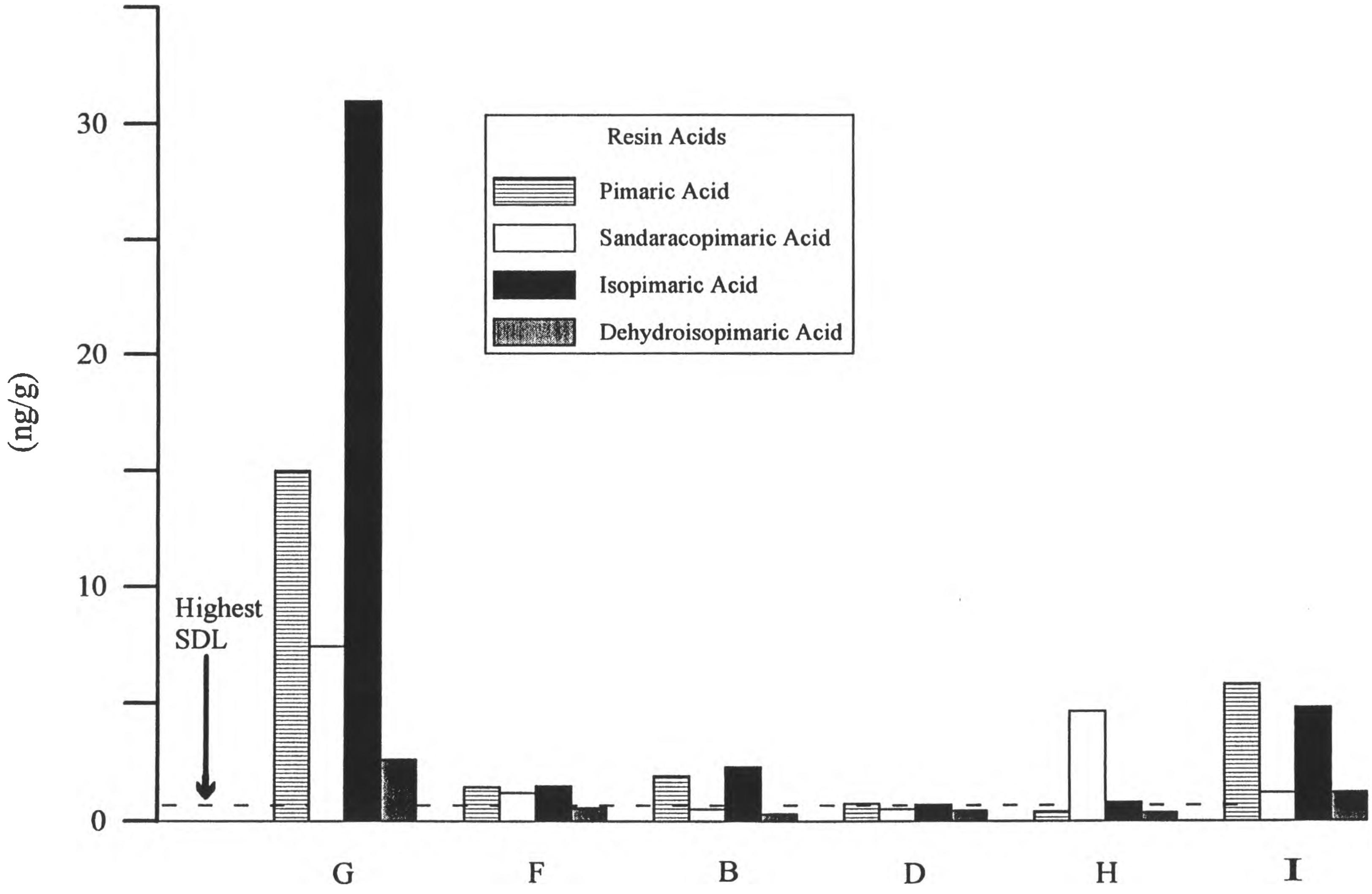


Figure 9: Concentrations of the "Pimaric" Family of Resin Acids in 1992 Surficial Sediment. Bars below the highest SDL are generated from SDLs. Actual concentrations are therefore less than the value indicated, possibly zero.



be greater than its true concentration in nature (Mahood and Rogers, 1975; Morales et al., 1992). The low values for neoabietic acid (Table 3 and Figure 10) seem to support this contention.

4.2.3 Polynuclear Aromatic Hydrocarbons

PAH results presented here are those whose presence has been detected by NWRI, some of which were confirmed by Chemex on separate samples. While other PAHs were detected, confirmation by GC-FID, HPLC-FL and HPLC-UV analyses as well GC-MS gives a high degree of confidence in the PAH results. Eleven PAHs were consistently detected in the surficial sediments by HPLC-FL. For convenience, their names have been abbreviated as indicated in Table 4. The two sets of results (HPLC-FL and GCMS) are presented along side one another in Table 5.

Table 4: PAH Nomenclature Abbreviations.

PAH	Abbreviation
Naphthalene	Npth
1-Methylnaphthalene	1-MeNpth
2-Methylnaphthalene	2-MeNpth
Fluorene	Fl
Phenanthrene	Ph
Fluoranthene	Fth
Pyrene	Py
Benzo (b) fluoranthene	B(b)Fth
Benzo (k) fluoranthene	B(k)Fth
Benzo (a) pyrene	B(a)Py
Benzo (ghi) perylene	B(ghi)Per

Figures 11, 12, 13 and 14 depict the distribution of the eleven PAHs across the western end of Lake Athabasca from west to east determined by HPLC-FL. Only moderately defined trends are apparent: 1-MeNpth and 2-MeNpth (Figure 11b) and Ph (Figure14b) show slight west to east increasing trends. The remainder show no trend, each component shows nearly the same concentration at all sites. This distribution can be expected of contaminants for which the main pathway for dispersal is atmospheric. The former three components can have a petroleum related source (petrogenic - see discussion in Section 5.4) and the remainder might be combustion related (pyrogenic). The hint of west to east increasing trend may be related to particle size distribution.

Figure 10: Palustric, Abietic and Neoabietic Resin Acids in 1992 Surficial Sediment. Bars below the highest SDL are generated from SDLs. Actual concentrations are therefore less than the value indicated, possibly zero.

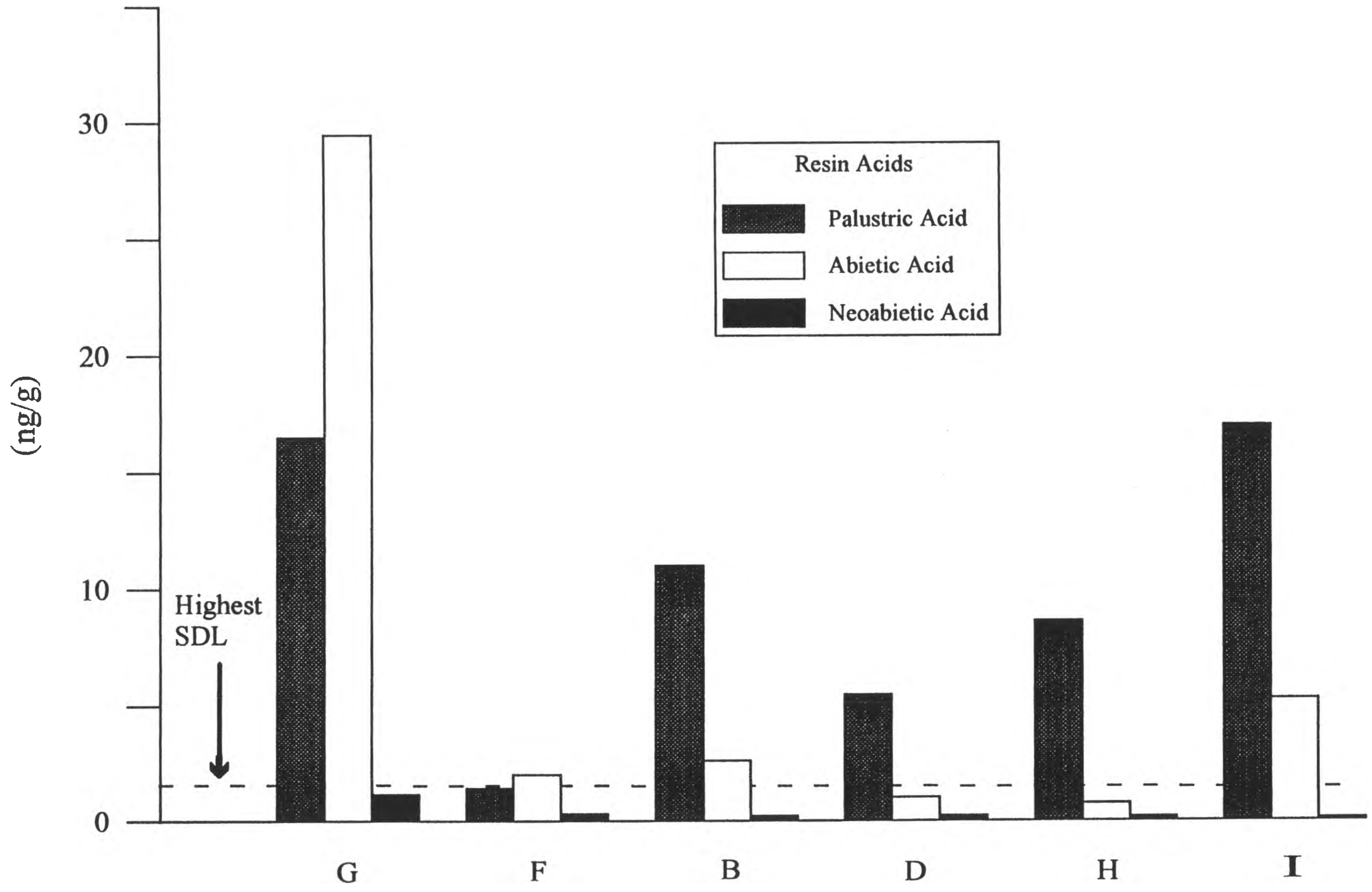


Table 5: Concentrations of Eleven PAHs from 1992 Surficial Sediments[a].

Site	Npth (ng/g)		1-MeNpth (ng/g)		2-MeMpth (ng/g)		Fl (ng/g)		Ph (ng/g)		Fth (ng/g)	
	[b]FL	[c]MS	FL	MS	FL	MS	FL	MS	FL	MS	FL	MS
G	11.3	4.8	13.7	[f]NA	24.7	NA	3.1	[e]ND(0.5)	93.8	22.0	11.0	11.0
B	2.4	[d]tr(2.7)	19.8	NA	26.0	NA	7.0	ND(0.5)	170.5	26.0	15.2	11.0
D	1.5	8.0	17.8	NA	20.5	NA	5.6	ND(0.4)	179.0	42.0	18.9	12.0
H	6.1	tr(2.0)	18.8	NA	27.4	NA	4.2	ND(0.6)	138.3	25.0	11.1	11.0
I	2.4	tr(1.7)	26.0	NA	32.3	NA	5.9	ND(1.0)	201.8	29.5	17.3	15.0

Site	Py(ng/g)		B(b)Fth(ng/g)		B(k)Fth(ng/g)		B(a)Py(ng/g)		B(ghi)Per(ng/g)	
	FL	MS	FL	MS	FL	MS	FL	MS	FL	MS
G	18.3	18.0	37.2	24.0	4.5	ND(0.5)	26.1	ND(0.5)	13.9	ND(0.5)
B	19.7	18.0	32.4	29.0	4.9	ND(0.5)	23.7	8.9	10.8	22.0
D	23.3	21.0	34.9	35.0	5.9	ND(0.4)	26.2	15.0	16.7	30.0
H	12.1	13.0	34.4	36.0	5.5	ND(0.6)	28.3	ND(0.6)	16.5	29.0
I	19.2	13.5	39.1	40.5	5.3	ND(1.0)	25.0	17.5	16.2	35.0

[a] See Table 4 for abbreviations used for PAHs
[b] HPLC Fluorescence detection, NWRI
[c] GCMS with selective ion monitoring, Chemex Labs Alberta, Inc.
[d] "trace" value are greater than the method detection but less than the quantitation limit (i.e. NDR)
[e] ND values are less than the method detection limit (given in brackets)
[f] NA - Component not analyzed

Figure 11: Naph, 1-MeNpth and 2-MeNpth in 1992 Surficial Samples.

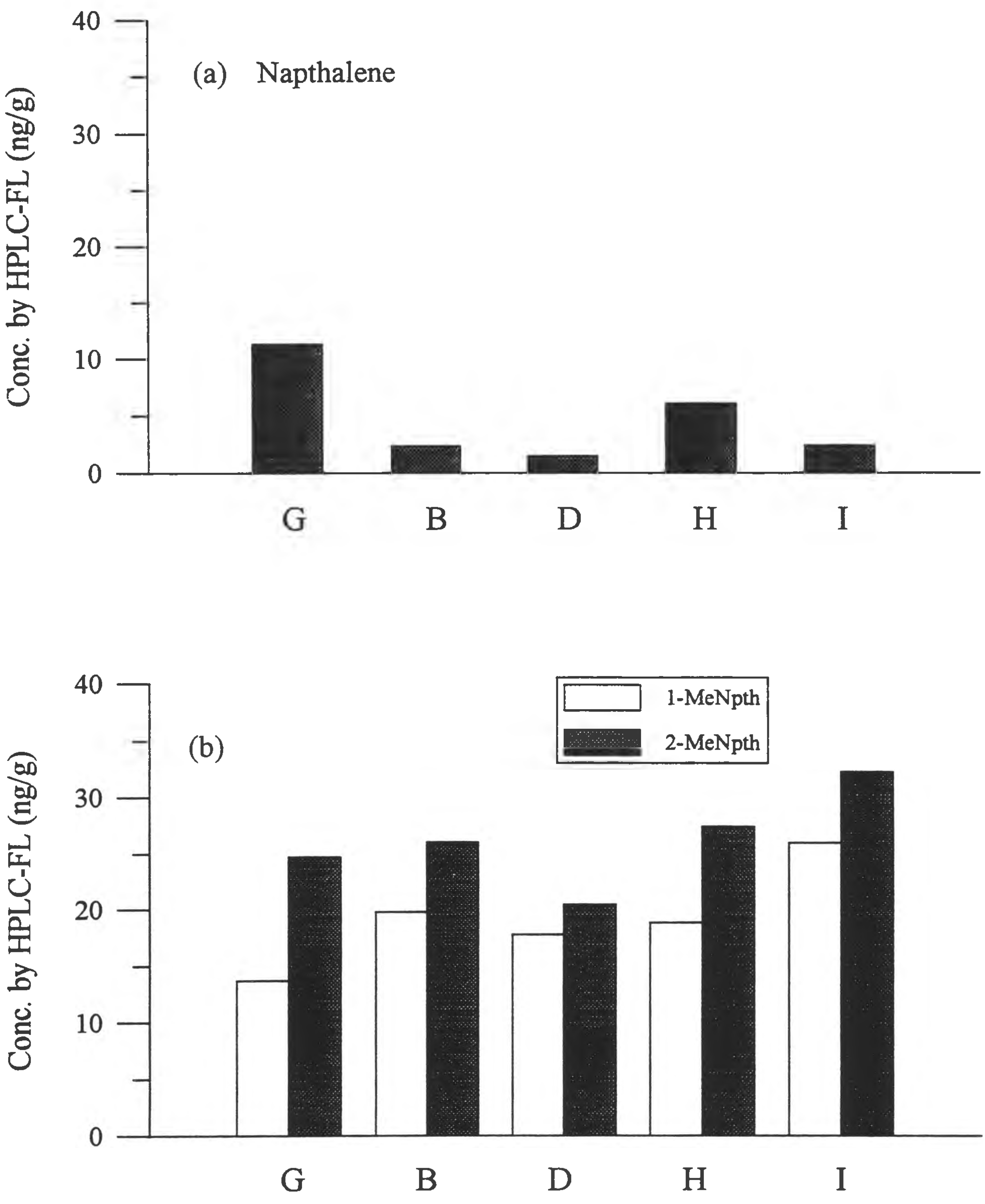


Figure 12: Py, B(b)Fth and B(a)Py in 1992 Surficial Samples.

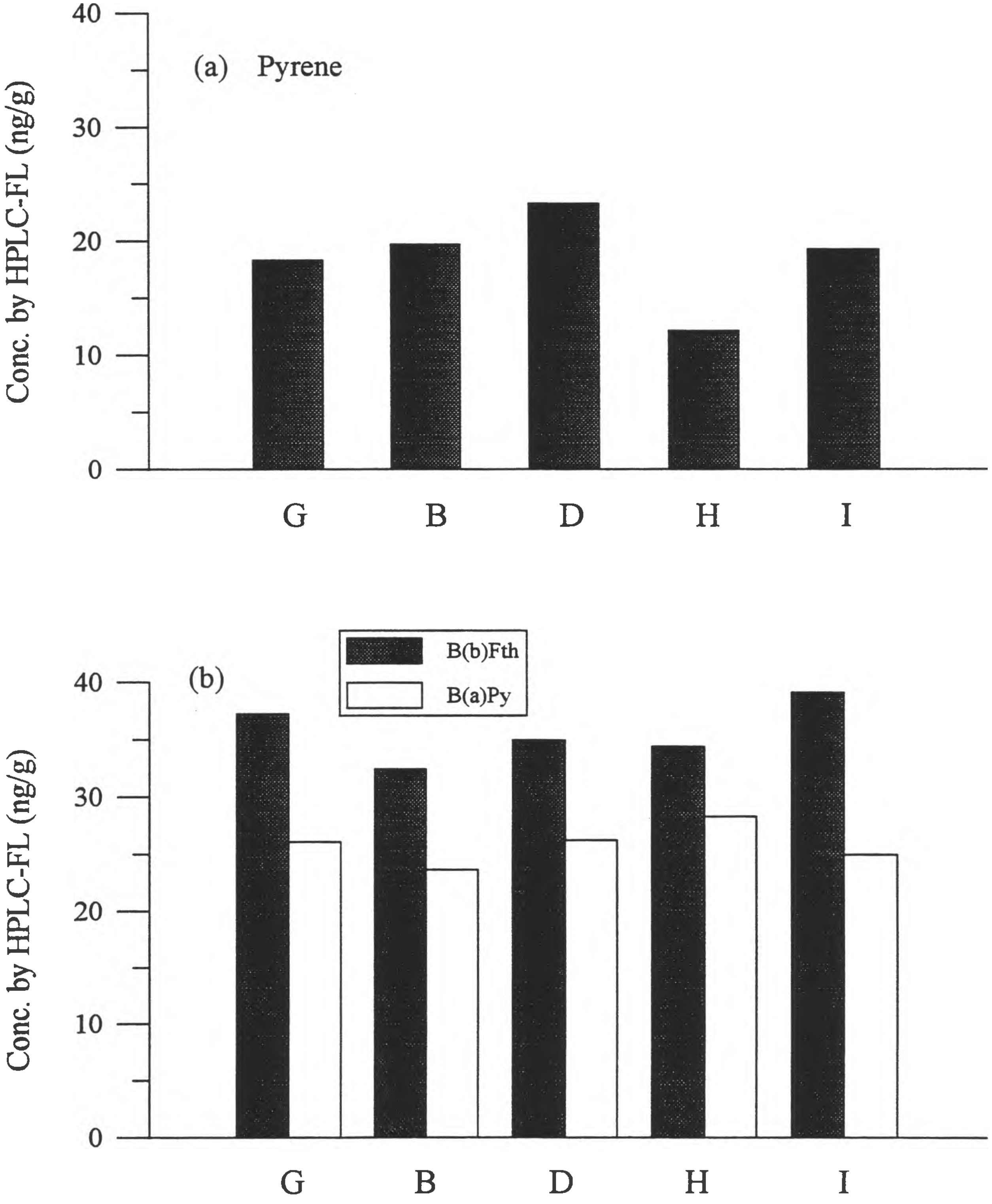


Figure 13: Fl, Fth and B(ghi)Per in 1992 Surficial Samples.

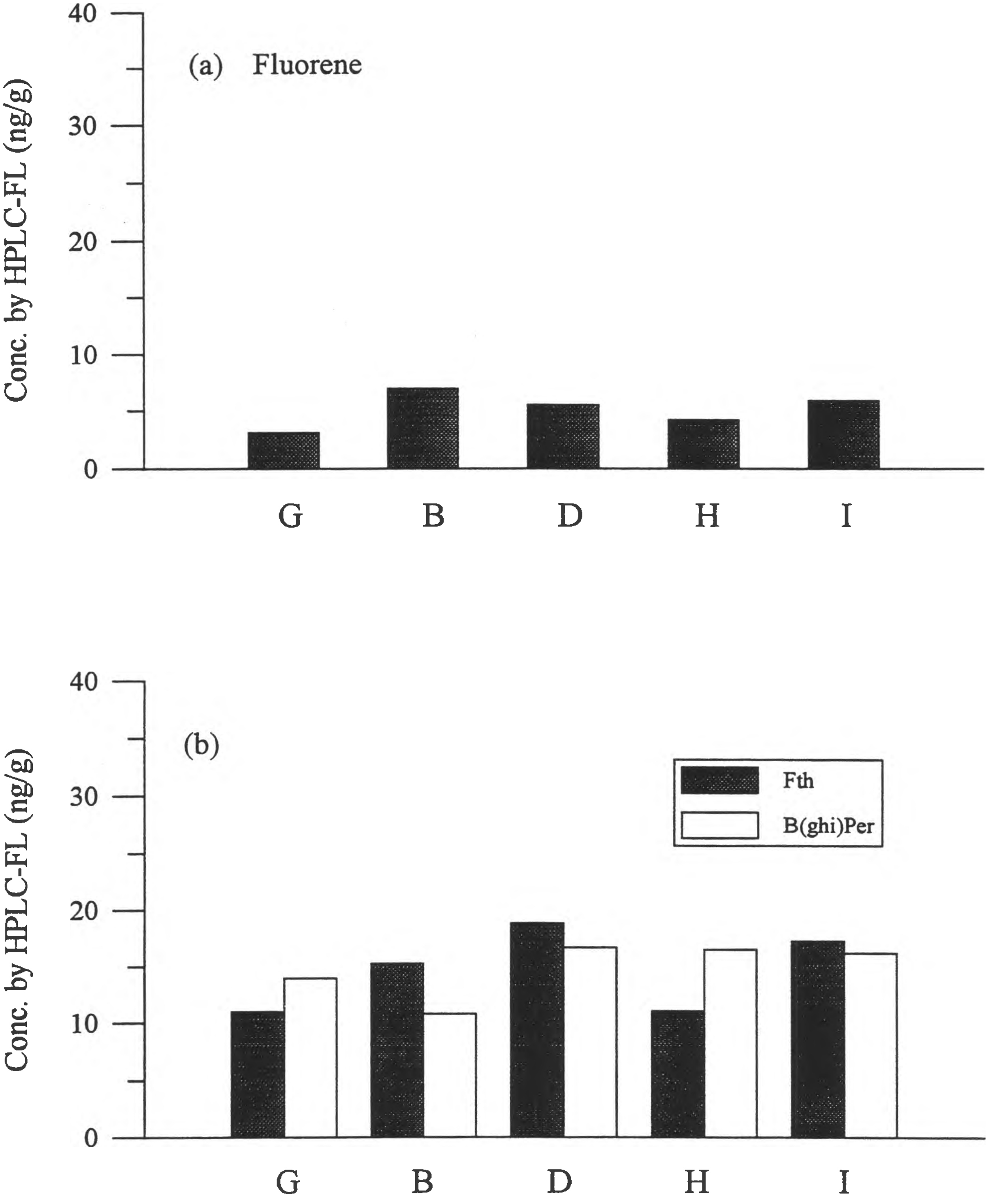
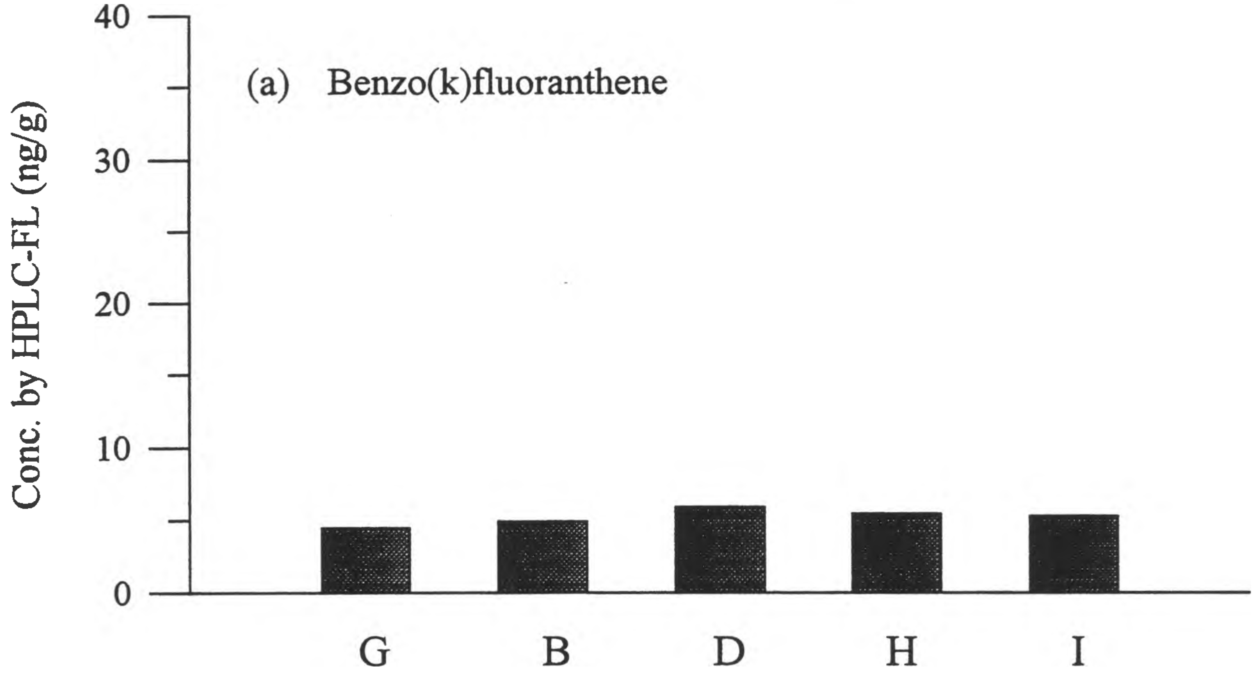
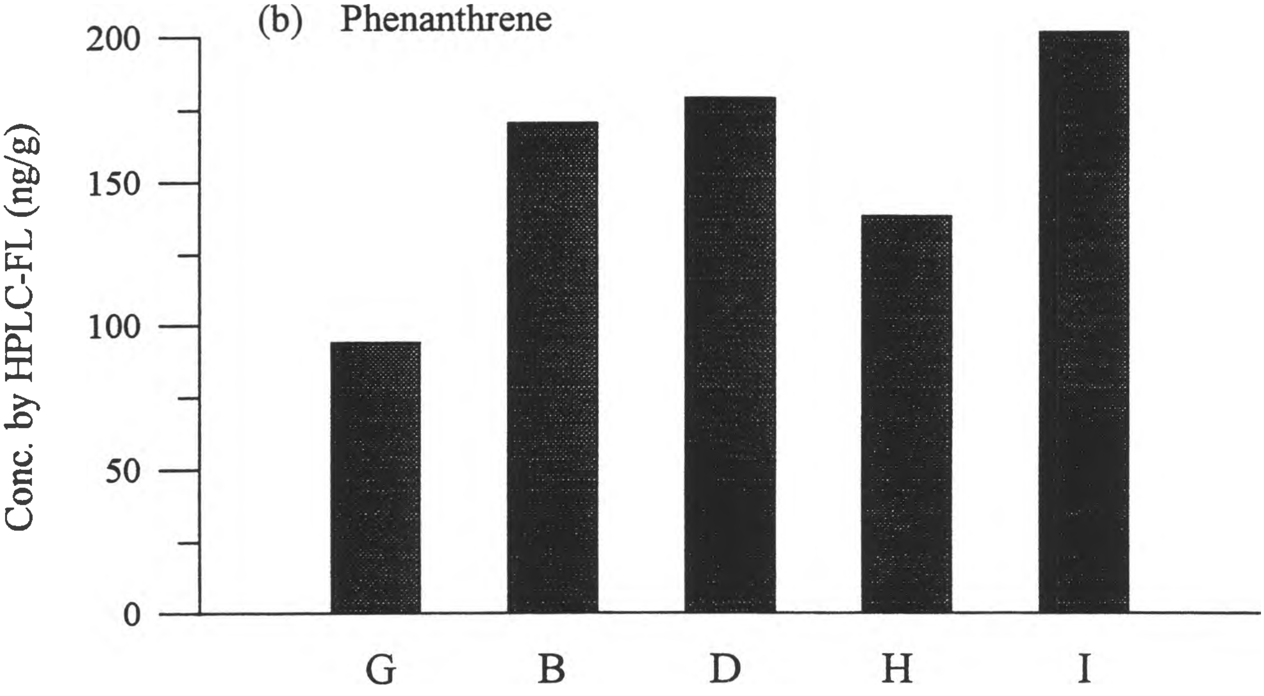


Figure 14: **B(k)Fth and Ph in 1992 Surficial Samples.**





4.3 INORGANIC CONTAMINANTS

4.3.1 Heavy Metals and Mercury

The following heavy metals were determined in surficial sediments: arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), vanadium (V), zinc (Zn) and mercury (Hg). Discussion of Hg is separate from the other metals because its methylated form (MeHg) was also determined. Results for four sites in the west end of the lake, Site I and averaged upper layers from cores at Sites 1, 2 and 3 (cf. Figure 1) are shown in Table 6.

Table 6: Heavy Metal Results - Surficial Sediments - 1992.

Sample Site	As (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	V (mg/kg)	Zn (mg/kg)
Site G	8.5	8.8	1.8	26.5	23.1	36.2	98.2
Site F	8.5	8.2	2.1	27.8	26.6	36.5	102.0
Site B	3.1	7.4	2.2	28.8	24.3	32.6	98.5
Site D	5.0	8.5	2.1	27.8	25.3	36.4	106.0
Site I	22.9	10.9	2.5	30.6	23.2	40.4	100.0
S1CB(0-6)	5.5	9.1	ND(0.3)	31.7	25.6	46	110
S2CA(0-6)	9.5	7.2	ND(0.3)	35.5	22.7	46.4	87.1
S3CB(0-6)	9.1	5.9	ND(0.3)	24.4	14.7	30.3	54.2

Chromium, V and Pb show no trend from west to east up to Site 1 or Site 2 and decrease somewhat in the eastern part of the lake - Sites 2 and 3 (Figure 15a,b). Zinc is relatively high over the entire western part and also decreases to the east. The same can be said for Cu, but at about one third the value. Arsenic is the most variable of the metals discussed here with a value at Site I more than twice as high as for any of the other surficial sediments. Both total Hg and total methyl Hg are about equal for the samples in the west end of the lake with a slight decreasing trend from west to east (Figure 16). The highest value for total Hg occurs at Site 1 and decreases substantially from there. Methyl Hg is absent (ND or just over) in the tops of the cores from Sites 1, 2 and 3.

These data can be compared with those from Allan and Jackson (1978). Cu, Zn, As and total Hg from the present study compare well with their results from Lake Athabasca. They report values of V which are about twice those determined here. It appears that many of these metals have sources in the western part of the lake and probably move offshore according to grain size. An

Figure 15: Heavy Metal Concentrations for Surficial Samples. See Table 6 and text for descriptions of sampling sites.

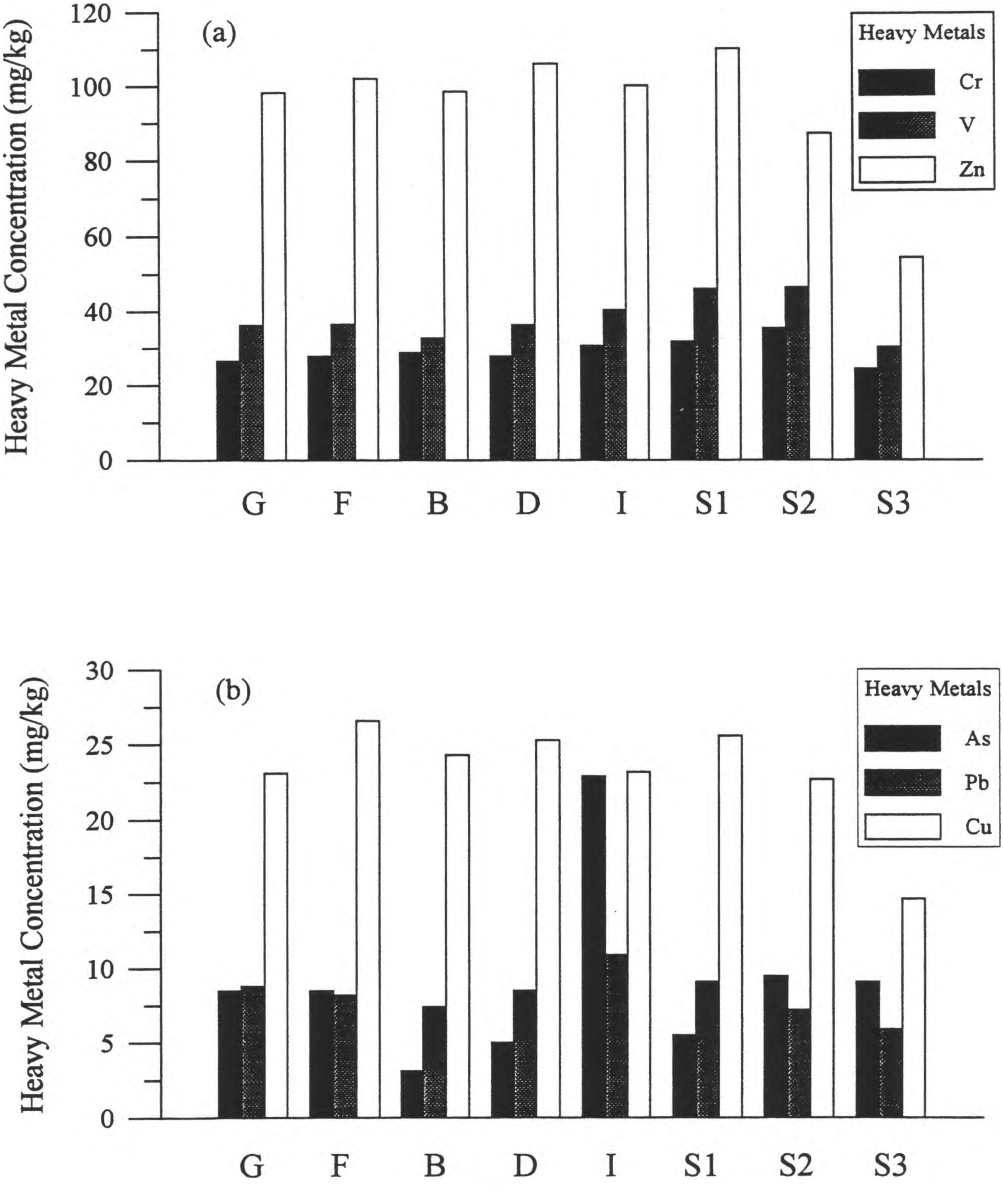
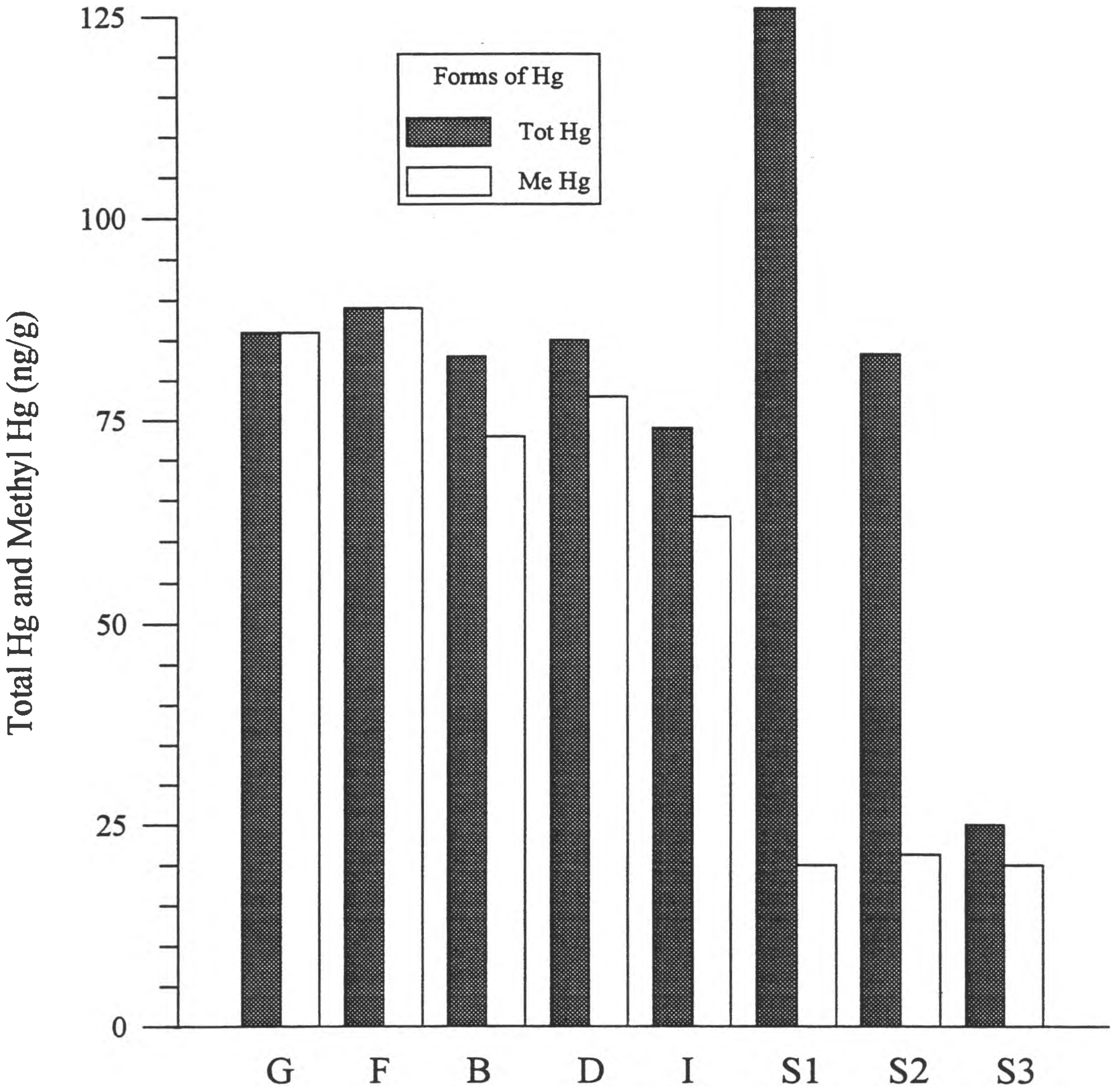


Figure 16: Total Hg and Methyl Hg Concentrations for Surficial Samples. See Table 6 and text for site descriptions. Values for MeHg at S1 and S3 were ND. The SDL of 20 ng/g was plotted.



increasing trend from river to delta to lake for many of the same metals studied was reported by Allan and Jackson (1978), and bears out this assertion.

Table 7: Total Hg and Total Methyl Hg in 1992 Surficial Sediments.

Sample Site	Tot Hg (ng/g)	Me Hg (ng/g)
Site G	86.0	86.0
Site F	89.0	89.0
Site B	83.0	73.0
Site D	85.0	78.0
Site I	74.0	63.0
S1CB(0-6)	126	ND(20)
S2CA(0-6)	83.3	21.3
S3CB(0-6)	25	ND(20)

4.4 BIOGEOCHEMICAL MARKERS

4.4.1 Alkane Terrestrial and Aquatic Source Indicators.

Chain length distributions of n-alkanes are often used to infer the source of the organic matter to a lake system and its sediments (Cranwell, 1973; Meyers and Ishiwatari, 1993). The alkanes from the leaf waxes of higher plants that live on land usually are dominated by longer chain homologs from C23 to C35 with a pronounced predominance of odd carbon components. Shorter chain alkanes in the range of C15 to C21 are more common in aquatic algae (Meyers and Ishiwatari, 1993) and also exhibit a pronounced predominance of odd carbon homologs over even carbon ones. Many authors use a ratio derived from the n-alkane distribution of a sample to classify the sediment according to the relative proportions of terrestrial and aquatic sourced components. Thus the n-alkane ratio:

$$\text{T/A ratio (alkanes)} = (\text{n-C27} + \text{n-C29} + \text{n-C31}) / (\text{n-C15} + \text{n-C17} + \text{n-C19})$$

was defined as the T/A ratio (Terrestrial/Aquatic Ratio) by Bourbonniere et al (1991) and applied to sediments from the Great Lakes. Other authors use similar ratios where higher values indicate greater relative contributions from terrestrial sources of organic matter, e.g. the "long/short ratio" of Meyers and Ishiwatari (1993).

Five surficial sediment samples were analyzed at NWRI for hydrocarbon biogeochemical markers. Figure 17 shows the results for total n-alkanes (Σ C15... C35) and T/A ratio among other derived parameters. Sites G, B and D are all in the shallow west end of the lake (Figure 1) and G is the closest to the Embarras River mouth. Sites H and I are more offshore and deeper. Total n-alkanes decrease progressively from west to east (G > H) suggesting that coarser higher plant fragments are preferentially deposited en route. This is borne out by the decrease in T/A ratio which occurs also from west to east. At site I (identical to coring Site 1) the increase in total n-alkanes may be attributed to a possible smaller grain size (but there are no particle size data to prove this) at the deeper site. Smaller grain size is usually associated with higher TOC (also not done for these sites) and therefore higher concentrations of all classes of organics present. The T/A ratio is concentration independent and the slightly lower values found at Sites D and I might be caused by a small increase in the proportion of aquatic sourced components.

4.4.2 Alkane Indicators of Petroleum Contamination

In contrast to natural assemblages of n-alkanes, the distribution of chain lengths in petroleum is characterized by equal predominance of odd and even numbered components. This lack of predominance can be used as an indication of the contribution of petroleum to sediments. Bray and Evans (1961) studied ratios of odd to even n-alkanes in crude oils, source rocks and recent sediments. Their work leads to a parameter they called the "carbon preference index" (CPI) which is of the general form:

$$\mathrm{CPI}(n \ldots m) = 0.5 \times [\Sigma\, C_a\mathrm{Odds}(n \ldots m-2) + \Sigma\, C_a\mathrm{Odds}(n+2 \ldots m)] \,/\, [\Sigma\, C_a\mathrm{Evens}(n+1 \ldots m-1)]$$

where: n and m are alkanes with an odd number of C atoms
C_a represents the concentrations of n-alkanes

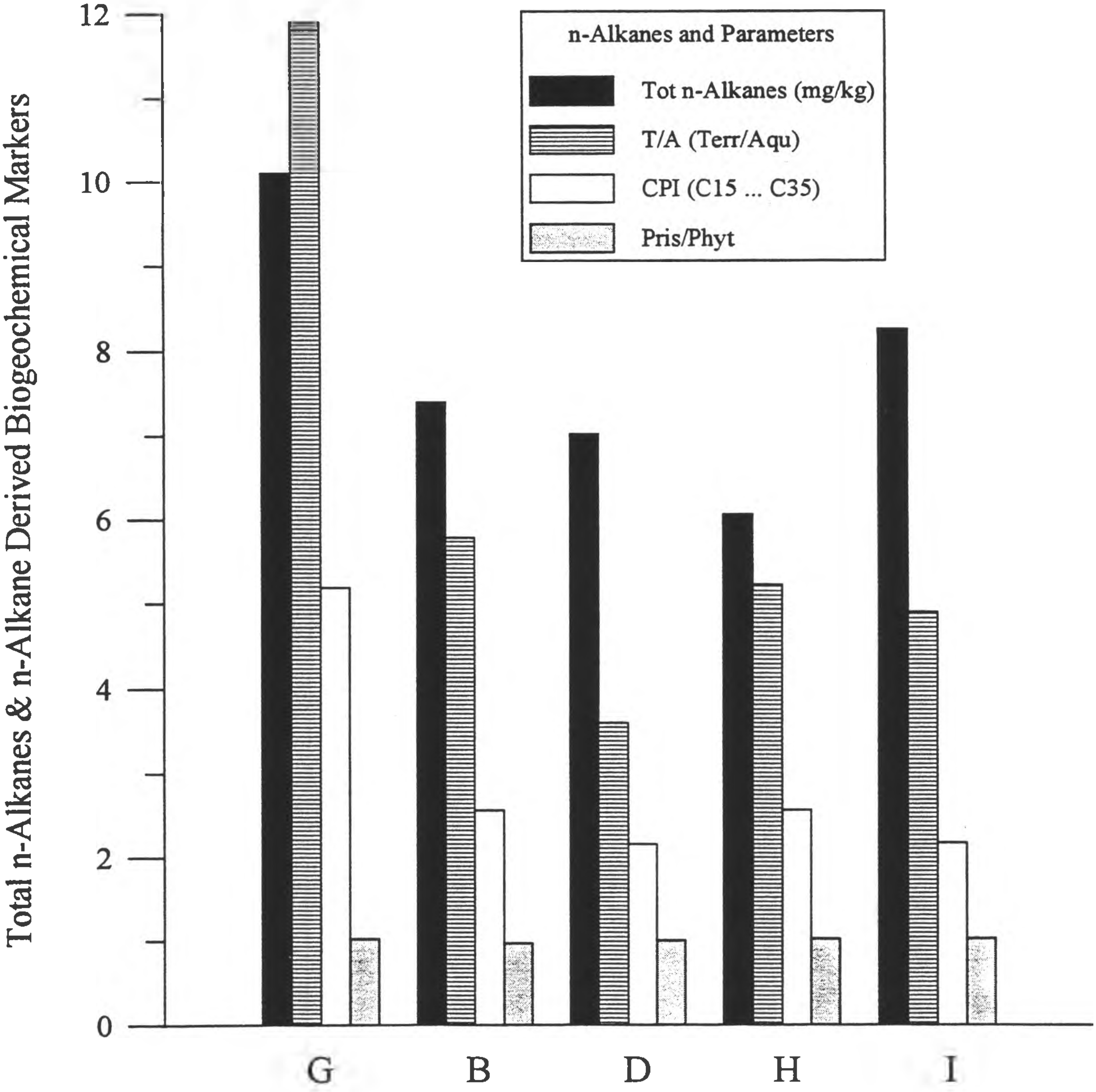
The mean value of two summations for the odd chain n-alkanes is used in the numerator to minimize bias from either end of a sample's alkane distribution. Such a bias might be caused by enhanced concentrations at one end or the other summation range because of a higher proportion of terrestrial or aquatic sourced components. Crude oils show no predominance and thus give CPIs near unity, recent sediments fall in the range of 1.5-5 and terrestrial plants from 4-7 (Bray and Evans, 1961; Hunt, 1979).

The CPI ratios for surficial sediments tested (Figure 17) are in the range of recent sediments except for the higher value found at Site G. This is consistent with higher amounts of terrestrial plant fragments as a possible source of alkanes to this site, agreeing with the suggestion made above. The values for all sites are not sufficiently close to unity to suggest that petroleum contamination is a major source of n-alkanes, but small amounts of petroleum could be responsible for the decrease compared to that at Site G.

4.4.3 Isoprenoid Indicators of Depositional Environment

The isoprenoid hydrocarbons pristane and phytane are common in petroleum and in recent sediments.

Figure 17: Total n-Alkanes and Derived Biogeochemical Markers. Surficial sediments are arranged from West to East.



The ultimate source of both of these branched hydrocarbons is the release of the phytyl side chain during the degradation of chlorophyll. Under aerobic conditions the phytol which is released by cleavage from the tetrapyrrole structure of chlorophyll is oxidized to intermediates which ultimately produce pristane upon later burial. Under anaerobic conditions, the phytol is reduced at or near the sediment surface, and the resulting intermediates eventually produce phytane (Tissot and Welte, 1978). Higher ratios of pristane to phytane indicate an environment of deposition which is more aerobic (Hunt, 1979).

The pristane/phytane (Pris/Phyt) ratio determined at the surficial sites (Figure 17) show no trend and are about unity. No trend in this ratio suggests no change in depositional environment, which would appear as a lower ratio if the environment was reducing, or as a higher ratio if significant petroleum contamination has occurred.

5.0 RESULTS AND DISCUSSION - CORE SEDIMENTS

5.1 GEOCHRONOLOGY

For the results from core studies of contaminants and biogeochemical markers to be interpretable, the sediment cores must be dated. For this study the "proving" of each site by ^{210}Pb geochronology was the first step taken after collection. The geochronology serves to put a time scale upon the core profile so that each section can be assigned an approximate deposition date. The profiles of ^{210}Pb and other radionuclides used in geochronology (e.g. ^{137}Cs) not only provide data for producing a time scale based on the rate of deposition, but also yield information about the continuity of deposition. Both of these are important considerations if one is to make accurate judgements about temporal trends in contaminant inputs or degradation. The ^{210}Pb method was chosen as the first method to use because it was readily available at NWRI, more straightforward in most cases than ^{137} Cs, gives better accuracy for dates greater than 40 years (up to about 100-150 years) and discontinuities in deposition can be readily identified. Subsequent analyses of the same cores for ^{137}Cs yields profiles which can be used to check on the accuracy of the ^{210}Pb geochronology.

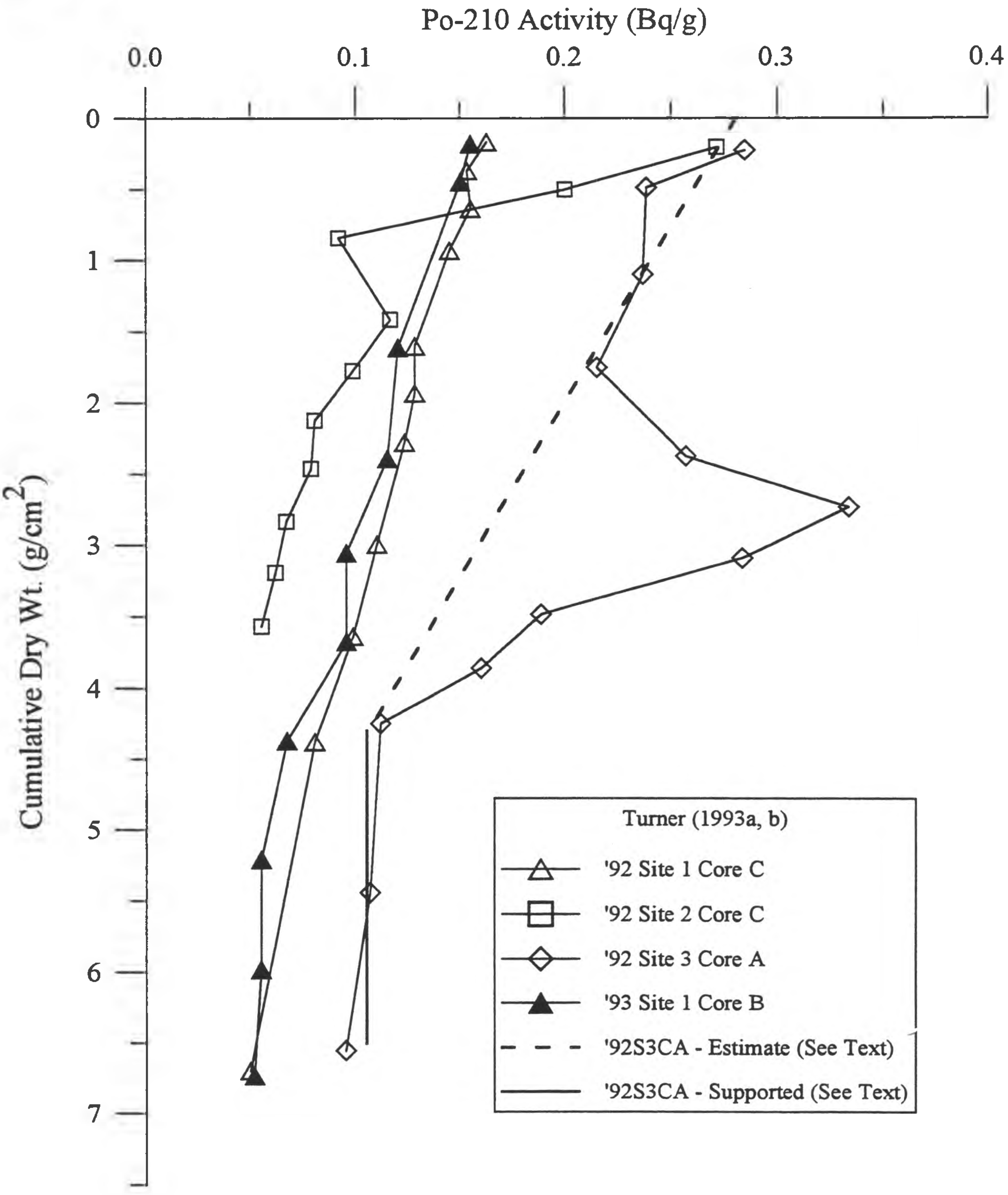
As discussed in a previous section multiple cores were taken from each of the candidate sites. Ideally, it would be best to date every core but that is impractical, expensive and time consuming. As well, some of the processing required for radionuclide determinations could compromise the utility of samples for other parameters. Here we dated a single core from each 1992 coring site, and another core from the 1993 sampling trip to Site 1. For parallelism among the replicate cores we must rely on the core descriptions which appear in Appendix B and some replicate determinations. Based on there observations we can assume that replicate cores are sufficiently parallel so that geochronology developed for one core can be applied to all cores from the same site and sampling time. Visible deviations in strata from core to core have been observed in the range of 1-2 cm.

5.1.1 Pb-210 Geochronology

Four of the cores were processed for determination of ^{210}Po by the geochronology laboratory at NWRI. This isotope is the granddaughter nuclide of ^{210}Pb and is determined by alpha counting. Details of the methodology, including assumptions, quality control, calculations and ancillary measurements are given in Turner (1993a, b). The theory of ^{210}Pb dating has been discussed in many publications (e.g. Robbins and Edgington, 1975; Matsumoto, 1975; Robbins, 1978; Farmer, 1978) and will not be repeated here. The method used by Turner (1993a, b) is patterned closely to that of Matsumoto (1975) and assumes that the concentration of ^{210}Pb on the particles settling to the bottom of the lake remains constant -- the constant initial concentration (CIC) model.

The observed ^{210}Po activities for the four cores analyzed are shown in Figure 18. Plotted here are the samples which represent the last 100 years of deposition at each site. These data are plotted here against cumulative dry weight for comparison. Note that not all cores have reached background or "supported" ^{210}Pb activities at the 100 year level. Note also the good parallelism between the two Site 1 cores taken a year apart. The anomalous nature of the profile for Site 3 Core A is a good example of how this method can indicate discontinuities or other disturbances at a site. The

Figure 18: Po-210 Activities, Turner Data. Activity of Po-210 plotted against cumulative dry weight. All cores determined as part of the Pb-210 dating method. See text for discussion of regression lines.



pronounced maximum which occurs from 2-4 g/cm^2 was likely caused by contamination from the Gunnar Mine near Uranium City (Waite et al., 1988, 1989; Joshi et al., 1989; cf. below in Section 5.3). It is not possible to get accurate dates from such a profile, but an estimate can be made by assuming that the profile would have been continuous had there been no contamination.

For comparison, the samples which were analyzed for ^{210}Po, were sent off to another laboratory several months later for determination of ^{210}Pb by direct gamma counting. The observed data from these analyses on the 1992 cores are shown in Figure 19. Comparison among all three 1992 cores by both methods is quite good (compare Figures 18 and 19).

5.1.2 Estimation method for Site 3 Core A

The upper zone of the core where ^{210}Pb activity occurs in excess of that which is supported by ^{226}Ra in the sediments is estimated by extrapolating across the contaminated zone, and is represented by a dashed regression line in Figures 18 and 19. The lower "supported" zone is estimated by the line of constant activity in the lower part of the profiles (solid vertical lines in Figures 18 and 19). Note that the slopes of the dashed lines are the same for both data sets, but the intercepts are different. The analysis of these data uses the density and porosity data from Turner (1993a) and follows the calculations in that report to produce an estimated geochronology using the average of the results calculated from both the Turner and ARCT Chemtech data sets.

5.1.3 Summary of Pb-210 geochronology results

5.1.3.1 Sedimentation Rate parameters. Table 8 contains parameters which result from the sedimentation rate model calculations, and some derived from the age vs. depth relationships of each core (see below).

Figure 19: Pb-210 Activities, ARCT Chemtech Data. Activity of Pb-210 plotted against cumulative dry weight. All cores determined by direct gamma counting. See text for discussion of regression line.

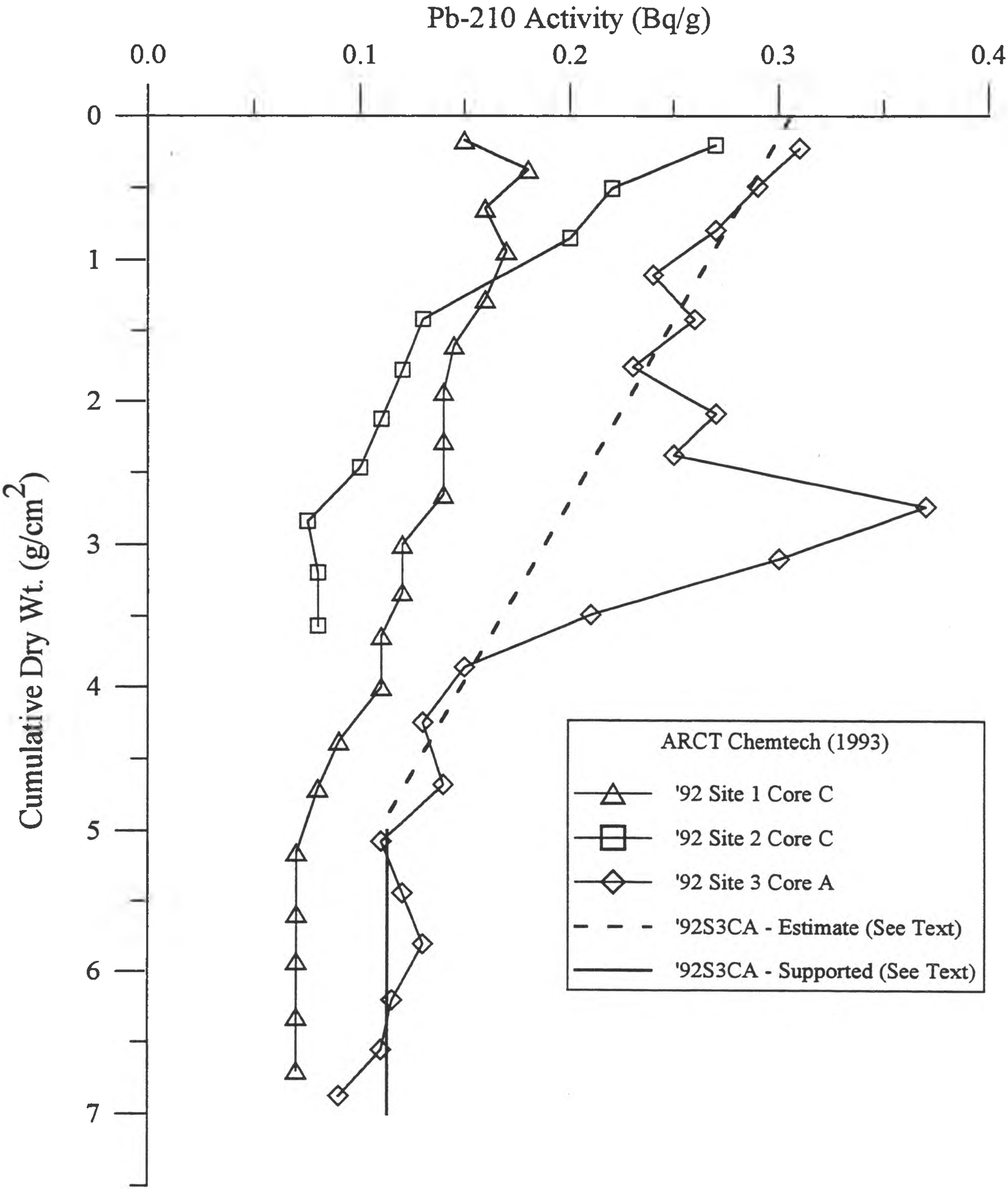


Table 8: Sedimentation Rate Parameters. Measured, calculated and derived parameters for four cores after application of the Pb-210 dating method[a].

Core Date and Location	Initial Porosity %	[b]Specific Gravity g/cm^3	[c]Mass Sed. Rate g/cm^2/yr	[d]Linear Sed. Rate cm/yr	[d]Time Resolution yr/cm	Depth to 100 years cm
'92 Site 1 Core C	91.42	2.626	0.072	0.20	4.9	20.4
'92 Site 2 Core C	91.98	2.676	0.038	0.10	10	10
'92 Site 3 Core A[e]	90.98	2.617	0.051	0.15	6.8	14.7
'93 Site 1 Core B	92.91	2.651	0.069	0.19	5.3	18.9

[a]Source Turner (1993a, b) and this work
[b]Averaged from at least 15 samples representing the entire length of each core
[c]From top of core, assumed constant throughout by CIC model
[d]Averaged over 100 years of sedimentation, uncorrected for compaction
[e]Estimate based on averaged results from regressions in Figures 18 and 19

5.1.3.2 Age - Depth Relationships A time scale was applied to each core by dividing the cumulative dry weight (g/cm^2) for each section downcore by the mass sedimentation rate (g/cm^2/yr) as listed in Table 8. Plots of sample depth against deposition date are presented in Figure 20. The plots extend for the most recent 110 years of depositional record which is within the acceptable range for the ^{210}Pb method (Anderson et al., 1987). These deposition dates constitute the age axes against which all core data are plotted in this report.

The data shown in Figure 20 demonstrate the good agreement obtained between cores collected at Site 1 in 1992 and 1993. The age-depth agreement is good overall and is exact for the upper ten years. At the 30 year level the depth deviation is 1.3 cm and at the 100 year level, 1.8 cm. If agreement between cores taken on two different occasions can be this good, then it builds confidence in the correlation of depths from multiple cores taken from the same location at the same time.

5.1.4 Cs-137 Results

To check on the ^{210}Pb dating results, the same samples from the 1992 cores were sent for ^{137}Cs determination by direct gamma counting (Flett Research Ltd., 1993). The upper 20 cm of Site 1 Core C and Site 3 Core A, and the upper 10 cm of Site 2 Core C were analyzed. The results for all three cores are presented in Figure 21 plotted against the deposition date by ^{210}Pb.

These are unusual results and each core requires a separate interpretation. The profile from Site 1 Core C shows nearly constant activity for the upper five cm, a maximum at about 1972, a broad zone of increased activity between 1945 and 1965, and the onset over background at 1930 (Figure 21a).

Figure 20: Age vs. Depth Plots for All Sites. Depths are plotted against deposition date according to Pb-210 geochronology. See text for explanation, especially for Site 3.

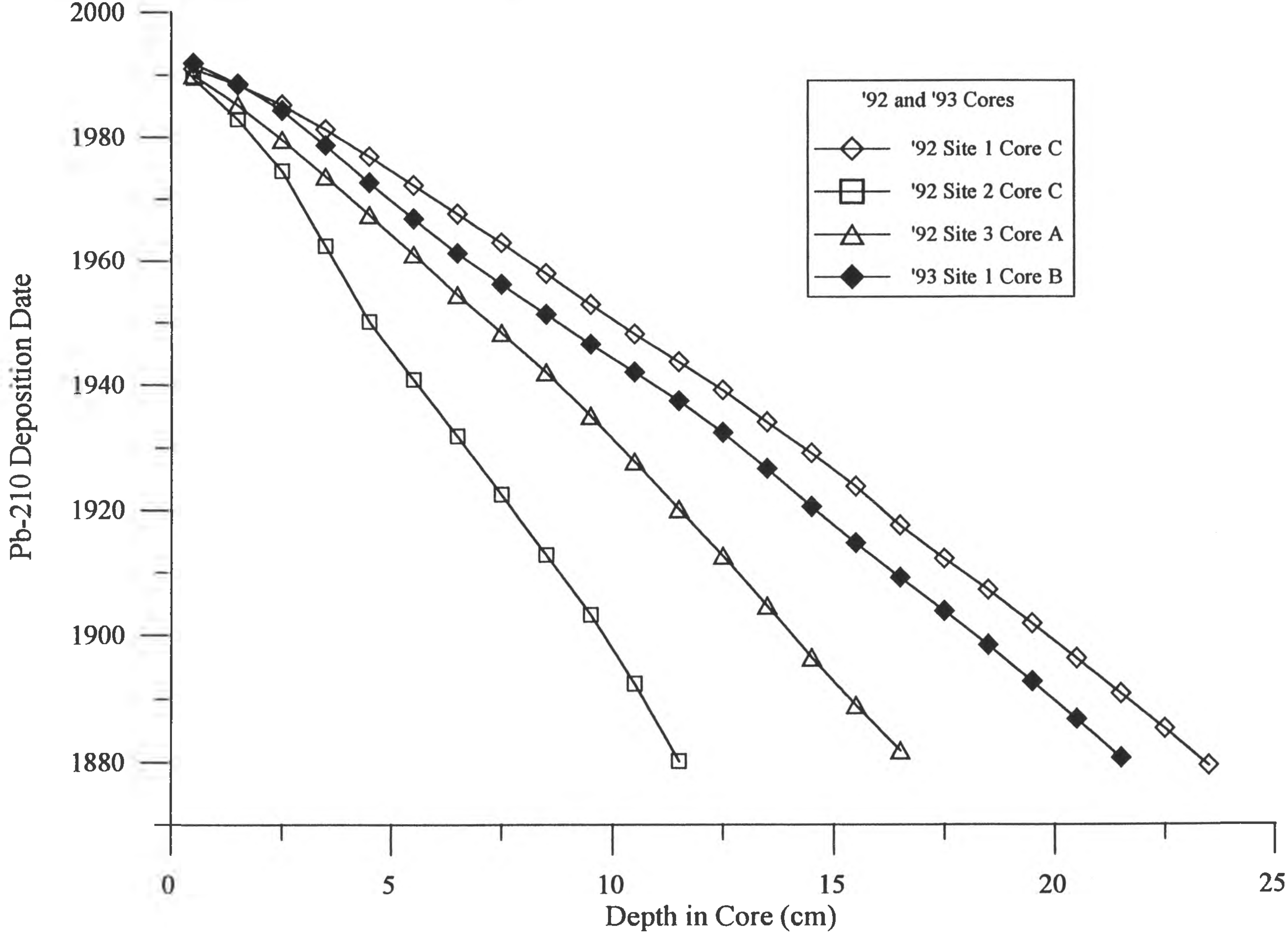
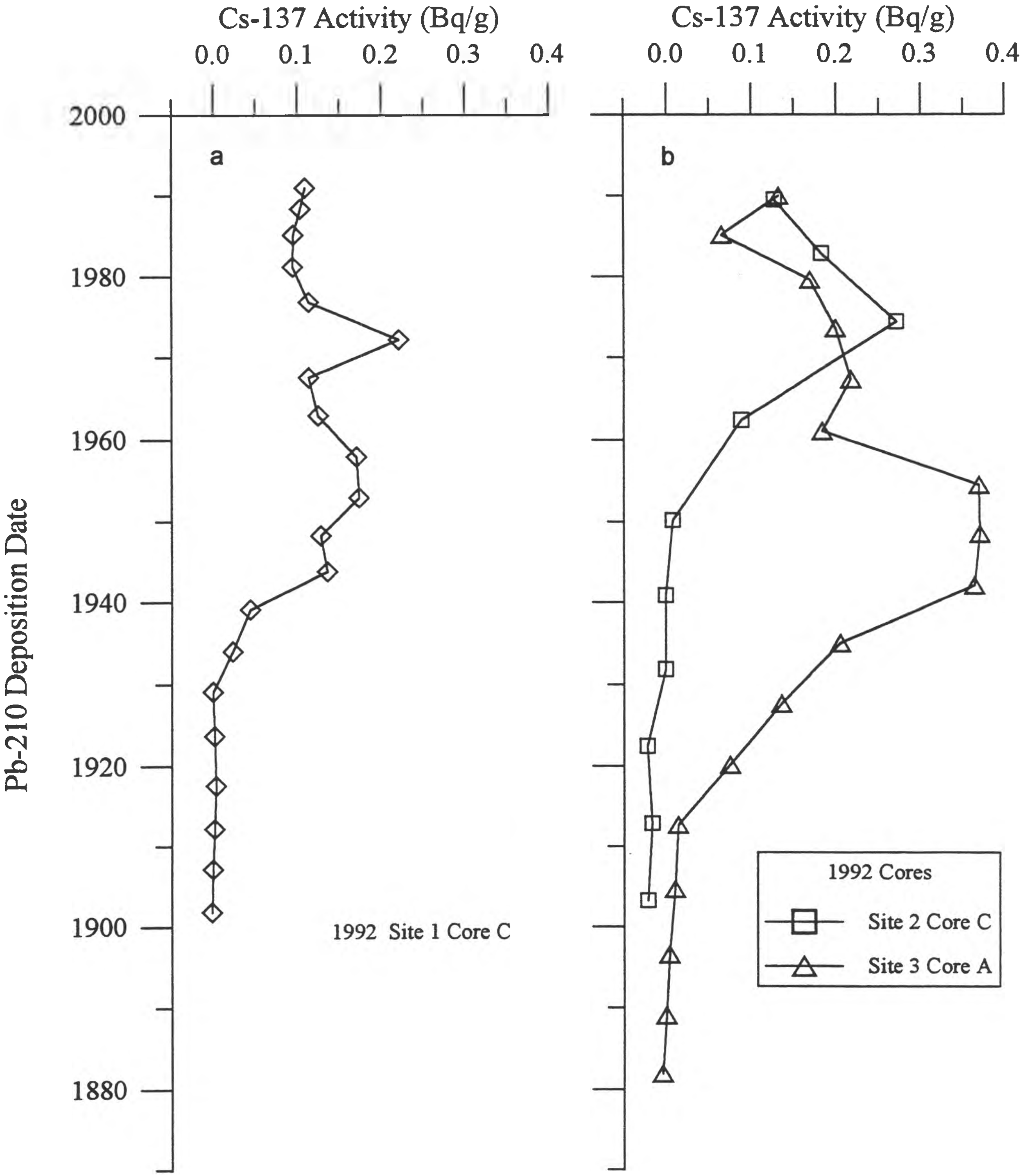


Figure 21: Cs-137 Activity, 1992 Cores.
Cs-137 is plotted against Pb-210 age as a check on the geochronology (See text).



The upper zone may be caused by post-depositional mixing of the sediments, by physical or biological processes (Anderson et al., 1987; Robbins and Edgington, 1975). The maximum which corresponds to the ^{210}Pb date of 1973 may result from the downward mixing of recent inputs from the Chernobyl accident or Chinese bomb tests. The broad bimodal zone resembles the results of Robbins and Edgington (1975) where the 1963 and 1959 atmospheric flux maxima are mixed downward, as well as the 1945 onset of bomb testing. Overall these results tend to confirm the ^{210}Pb results for Site 1. The shape of the ^{137}Cs profile contains interpretable maxima, and their downward shift is consistent with what would be expected from a combination of physical and biological mixing, as well as the possibility that smearing during gravity coring may have occurred. The upper mixed layer of 5 cm is approximately equivalent to the oxidized zone where benthic organisms are active, and its presence supports the downward mixing hypotheses invoked to explain the maxima below.

Site 2 Core C shows a distinct maximum at 1975 and the onset of activities over background at 1950. This profile (Figure 21b) suffers from the low resolution afforded by the lower sedimentation rate, so that little detail is evident. The onset of ^{137}Cs is approximately correct, but the maximum at 1975 is difficult to explain since there is no evidence of a mixed layer in this low resolution profile, so downward mixing of Chernobyl material in more speculative than for Site 1.

Core A from Site 3 exhibits an initial decrease, a broad zone of increased activity between 1980 and 1960, a broad maximum between 1960 and 1930, with the onset of values above background beginning at about 1910 (Figure 21b). It is tempting to argue that the broad high maximum occurring between 1960 and 1940 is caused by local contamination, but ^{137}Cs is a fission product and should not be associated with uranium mining (Joshi, Personal Communication) and indeed was used as a sediment tracer in Langley Bay near the Gunnar Mine tailings (Joshi et al., 1989). We are left with the interpretation that the maximum is a downward shifted 1963 signal, mixed with the 1959 signal (the tail), and recent inputs are also mixed downward. The causes here could be the same as those explained above for Site 1, but also it must be remembered that the ^{210}Pb geochronology for this site contains a number of uncertainties (cf. 5.1.2).

5.1.5 Regarding Core Quality

The best cores for subsequent determinations of contaminants and biogeochemical markers are those collected from Site 1. Indeed this was the main reason for revisiting the site in 1993. Cores from both years agree well as far as age-depth relationship is concerned, the five year per cm time resolution is the best available, and the ^{137}Cs profile is consistent with some of the effects observed by others. Based on the recommendation that most effort be expended on Site 1 cores, the remainder of this report will focus on results from there, except where another site exhibits an important trend as in the radionuclide data from Site 3, (cf. section 5.3). Ongoing and future work will be done for selected parameters which may exhibit post-depositional changes (diagenesis). In these cases it is useful to use two sites with significantly different sedimentation rates, as is found between Sites 1 and 2. Results of such work will be presented in a future report.

5.2 BULK PROPERTIES

Particle size was determined on samples from the 1993 sampling of Site 1 (Core E). Bulk C&N analyses were done on aliquots of the freeze-dried cores that were used for ^{210}Pb dating -- 1992: Site 1 Core C, Site 2 Core C, Site 3 Core A, and 1993: Site 1 Core B.

5.2.1 Particle Size

The sediment at Site 1 can be classified as clay (Duncan, 1994; Folk, 1974). The sand content is < 0.6% throughout (Table 9). Silt content is predominantly in the 11 to 17% range for the entire core (Figure 22a). A minimum of 6.5% occurs at the 25-27 cm interval which was deposited about 120 years ago, and the maximum silt content of 22% shows up in the 45-47 cm interval (> 250 years ago). The mean particle size remained between 1.4 and 2.0 µm for the entire length of the core, except for the layers of minimum and maximum silt content mentioned above. The mean particle size for the 25-27 cm section dipped to 1.2 µm and for the 45-47 cm interval rose to 2.2 µm (Table 9 and Figure 22b). The standard deviation of mean particle sizes are also low and fairly constant throughout the core, even where the minimum and maximum occur (Table 9 and Figure 22b).

For the period of interest (100 years, or the upper 20 cm of this core) it appears that there were no major changes in the depositional environment at Site 1. Indeed the entire length of the core, which likely represents more than 500 years of deposition, shows little indication of change in depositional environment by these criteria. Wave disturbances to the bottom sediment do not show up in these sedimentological data from modern sediments. Given these results for Site 1, Sites 2 and 3 were not analyzed for particle size, reserving sample for contaminant and other analyses.

Figure 22: Site 1 Sediment Particle Size. Relative composition of clay, silt and sand size particles, and mean particle size in sediment from Site 1 Core E sampled in 1993. Composition is plotted against intervals sampled and mean particle size against the mid depth of the intervals.

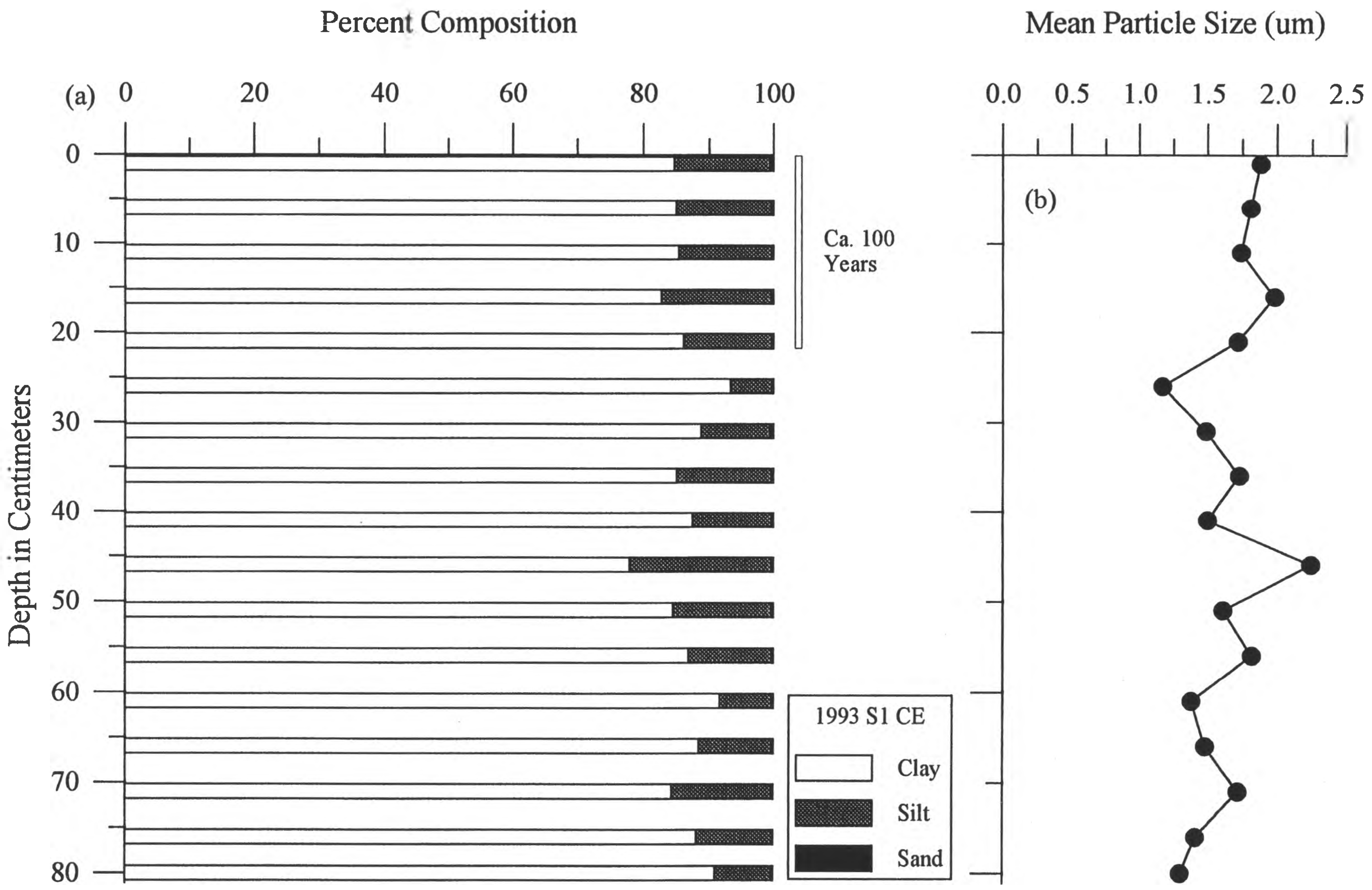


Table 9: Particle Size Results from 1993 Site 1 Core E

Sampling Interval		Particle Size			Clay	Silt	Sand
Upper	Lower	Mean	S.D.	Mean			
(cm)	(cm)	([a]phi)	(phi)	(μm)	(%)	(%)	(%)
0	2	9.05	1.82	1.88	84.68	14.76	0.56
5	7	9.11	1.80	1.71	85.03	14.58	0.38
10	12	9.17	1.73	1.74	85.39	14.41	0.19
15	17	8.98	1.71	1.98	82.74	16.88	0.38
20	22	9.18	1.74	1.72	86.11	13.61	0.28
25	27	9.74	1.38	1.17	93.33	6.51	0.16
30	32	9.39	1.65	1.49	88.80	10.74	0.45
35	37	9.18	1.57	1.73	85.08	14.61	0.31
40	42	9.38	1.60	1.50	87.52	12.34	0.14
45	47	8.80	1.30	2.24	78.00	21.68	0.32
50	52	9.28	1.59	1.61	84.56	15.09	0.35
55	57	9.10	1.48	1.82	86.85	12.95	0.20
60	62	9.51	1.52	1.38	91.70	8.15	0.15
65	67	9.4 0	1.60	1.48	88.49	11.39	0.12
70	72	9.18	1.68	1.72	84.40	15.40	0.20
75	77	9.47	1.43	1.41	88.14	11.75	0.11
79	81	9.59	1.44	1.30	91.02	8.69	0.29

[a] Commonly used grain size parameter: phi = - $\log_2$ (diam in mm). Converted in 5th column.

5.2.2 Bulk Carbon and Nitrogen Species

The organic matter contained in lake sediments is comprised of materials which are transported from all over the watershed by water (i.e. allochthonous origin), by air (i.e. atmospheric origin) or produced in the lake itself (i.e. autochthonous origin). Major temporal changes in the relative proportions of these sources may be reflected in the concentration of bulk components such as total organic carbon (TOC), total inorganic carbon (TIC) and total "organic" nitrogen (TON), and by the atomic C/N ratio which is a rough indicator of organic matter character (Meyers and Ishiwatari, 1993). All of these parameters were determined for one core from each of the sites sampled in 1992 and for Site 1 sampled in 1993. The data reported here are limited to those from sections of the cores which represent the last 100 years of deposition.

5.2.2.1 Total Inorganic Carbon. TIC concentrations are plotted against deposition date for four cores in Figure 23. The values are low and for Site 1 many of the concentrations are at or below the MDL of 0.1 mg/g (Table 10). Both of the Site 1 cores also show a significant maxima, but at different parts of each core. Site 1 Core C from the 1992 sampling shows a prominent maximum at about 1895, and the 1993 Site 1 Core B shows one at about 1985. Both cores agree better in the mid portions corresponding to deposition dates from 1900 to 1980. Inorganic C is normally transported to lakes from the erosion of calcareous soils in the watershed. The Lake Athabasca watershed contains regions to the west and south which have such soils, but much of the watershed adjacent to the lake is on the Canadian Shield and consequently low in carbonates (Mitchell and Prepas, 1990). The mixture of sediments with higher and lower carbonate contents that is contributed to the deeper parts of the lake will vary during the year depending upon the extent to which the western river inputs extend into the lake.

Sites 2 and 3 show overall higher and more variable values for TIC than Site 1 cores, but they are still low relative to those found in the Laurentian Great Lakes (Table 11) where carbonates are common in the watersheds. TIC values from Lake Athabasca are nearer to those found in Lake Superior sediments, and that lake also has a large portion of its watershed on the Shield. The slightly higher values found for Sites 2 and 3 relative to Site 1 may be caused by the winnowing of fine grained sediment from the shallower zones in the western part of the lake, carrying clay sized carbonate rich particles to be deposited downslope along an energy gradient.

Table 10: Total Inorganic Carbon, All Coring Sites.

'92 site 1 Core C		'93 Site 1 Core B		'92 Site 2 Core C		'92 Site 3 Core A	
Pb-210 date	TIC mg/g	Pb-210 date	TIC mg/g	Pb-210 date	TIC mg/g	[b]Pb-210 date	TIC mg/g
1991	0.4	1992	0.8	1990	0.3	1990	0.5
1988	0.4	1989	0.4	1983	1.2	1985	0.7
1985	[a]ND(0.1)	1984	1.9	1974	0.8	1980	0.2
1981	0.3	1979	0.2	1962	1.0	1974	ND(0.1)
1977	ND(0.1)	1973	0.4	1950	0.2	1967	0.4
1972	0.4	1967	0.3	1941	2.0	1961	0.4
1968	0.5	1961	0.3	1932	0.5	1954	0.8
1963	0.6	1956	ND(0.1)	1922	0.8	1948	0.5
1958	0.8	1951	0.4	1913	0.2	1942	0.3
1953	0.5	1947	ND(0.1)	1903	0.5	1935	0.4
1948	ND(0.1)	1942	0.3	1880	1.4	1928	0.6
1944	0.5	1937	ND(0.1)			1920	1.4
1939	ND(0.1)	1932	ND(0.1)			1913	0.5
1934	0.3	1927	0.1			1905	0.7
1929	ND(0.1)	1921	ND(0.1)			1896	0.8
1924	0.2	1915	0.4			1889	1.0
1918	0.2	1909	ND(0.1)			1882	0.6
1912	ND(0.1)	1904	0.1				
1907	ND(0.1)	1898	0.2				
1902	0.6	1893	0.2				
1896	2.2	1887	0.3				
1891	0.4	1881	0.2				
1885	0.3						
1879	0.5						

[a] ND(0.1) - Below the MDL of 0.1 mg/g, but plotted as 0.1 in Figure 23

[b] Estimate based on averaged results from regressions in Figures 18 and 19.

Figure 23: Inorganic Carbon, All Sites. Concentrations of TIC for '92 and '93 cores. Values are plotted against Pb-210 deposition date, see Section 5.1. For non-detectable values, the MDL was plotted (see Table 10).

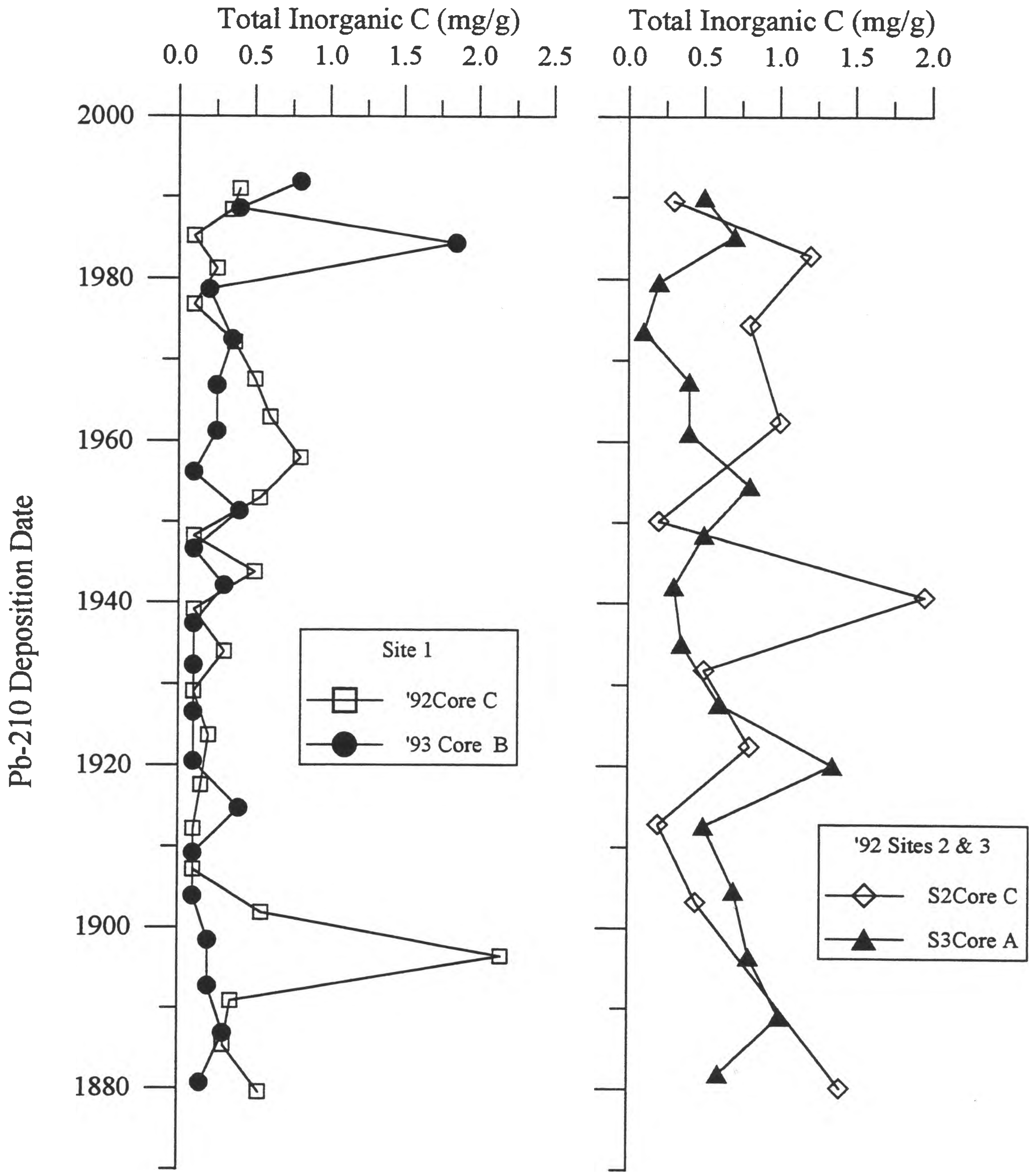


Table 11: Some Typical TIC and TOC Values from Great Lakes' Sediments.

Lake	TIC (mg/g)	TOC (mg/g)	References
Lake Ontario			
Five Sites	11 - 19	32 - 55	Kemp and Mudrochova (1973)
Deposition Zones	10 - 20	35 - 45	Bourbonniere et al. (1986)
Lake Erie			
Deposition Zones	2 - 6	25 - 45	Bourbonniere (unpubl.)
Lake Huron			
Goderich Basin	3 - 28	17 - 40	Thomas et al. (1973)
Depositional Zones	2 - 8	35 - 45	Bourbonniere et al. (1986)
Lake Michigan			
Core	15 - 35	12 - 25	Bourbonniere (1979)
Lake Superior			
Deposition Zones	0 - 3	26 - 37	Bourbonniere (unpubl.)

5.2.2.2 Total Organic Carbon. TOC concentrations are given in Figure 24a for the Site 1 cores. Both cores are similar except that the 1992 Core C is more variable than the 1993 Core B. The highest value for '92 Site 1 Core C occurs at the same deposition date that the maximum TIC occurred - 1895. This coincidence suggests that a deposition event was recorded in this core and that other parameters may also show up with anomalous values here. The most recent parts of both cores, since 1980, show a progressive decrease downcore. This commonly occurs in fine grained sediments (Meyers and Ishiwatari, 1993) and is thought to be related to biodegradation in the uncompacted, oxidized surface layers of the sediments (see core descriptions in Appendix B). Overall the upper sections of the '93 Core B (since 1960) is slightly higher in TOC concentration than the older sediment in the same core. In Lake Ontario, where anthropogenic impacts are important, TOC concentrations increase dramatically beginning at settlement and deforestation and with an increasing rate since 1950 (Schelske et al., 1988). If TOC can be used as a rough indicator of anthropogenic impact, then the Site 1 data show none or relatively small impacts (Figure 24a). The '92 cores from Sites 2 and 3 show similar results (Figure 25a), except that the TOC from Site 3 shows a significant reversal of the decreasing trend in the older parts of the core.

5.2.2.3 Total "Organic" Nitrogen. TON concentrations parallel the TOC values for all four cores (Figures 24b and 25b) and are about an order of magnitude lower throughout. Nitrogenous components of the bulk organic matter (proteins, etc.) degrade microbially in transport and after deposition at faster rates than does the bulk organic matter (Meyers and Ishiwatari, 1993), and consequently the decreasing trend with age is slightly more prominent than that for TOC at Site 1. The Site 2 distribution of TON is more variable than Site 1 and Site 3 shows an initial sharp decrease to nearly constant values at mid core, and higher values in the older parts of the core (Figure 25b). The TON and TOC results from Site 3 suggest that there have been variable sources

Figure 24: Site 1 Organic Carbon & Nitrogen. Concentrations of total organic C, total "organic" N and atomic C/N ratio for cores taken in 1992 and 1993. Values are plotted against deposition date determined for each core by the Pb-210 method.

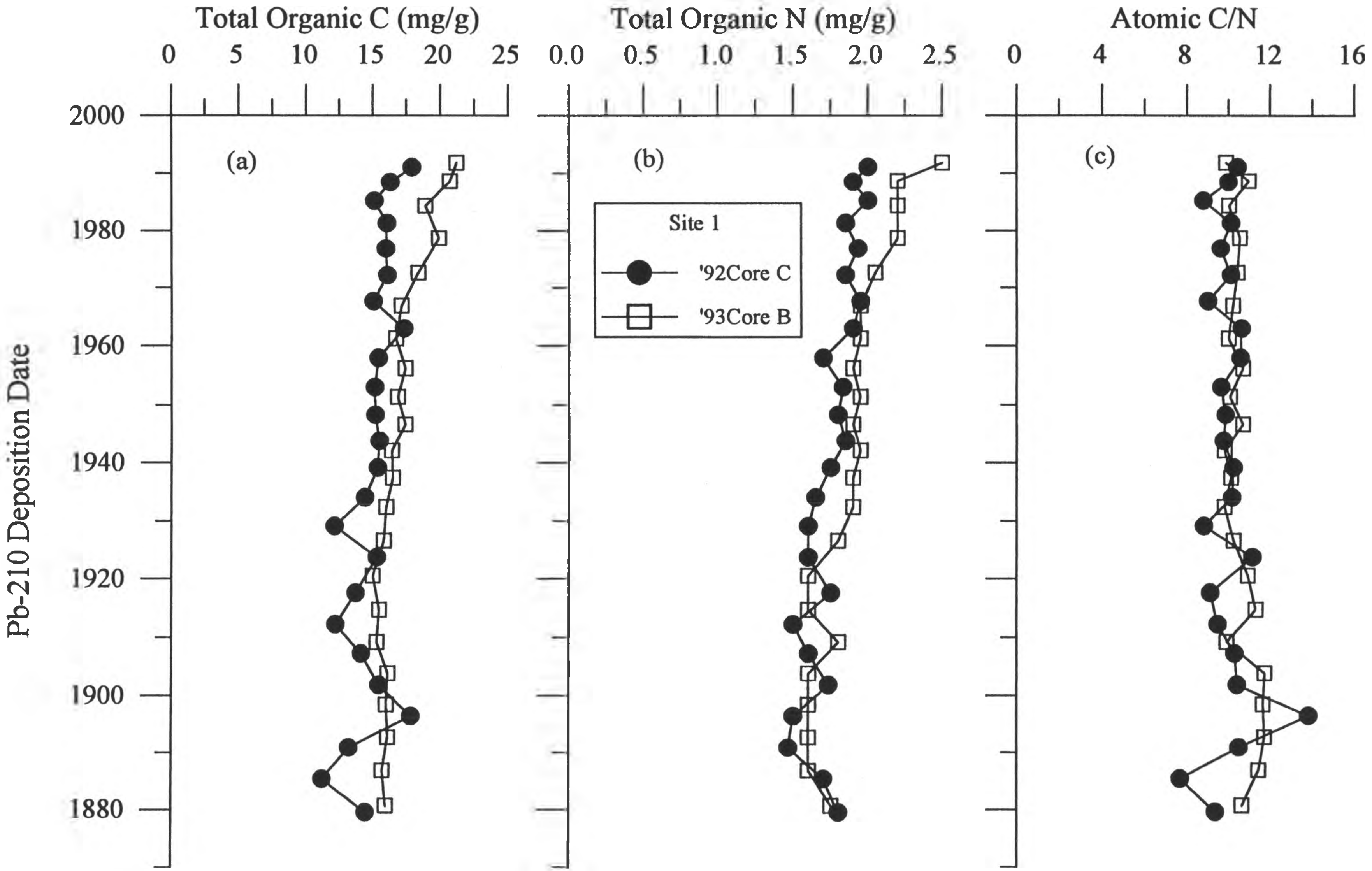
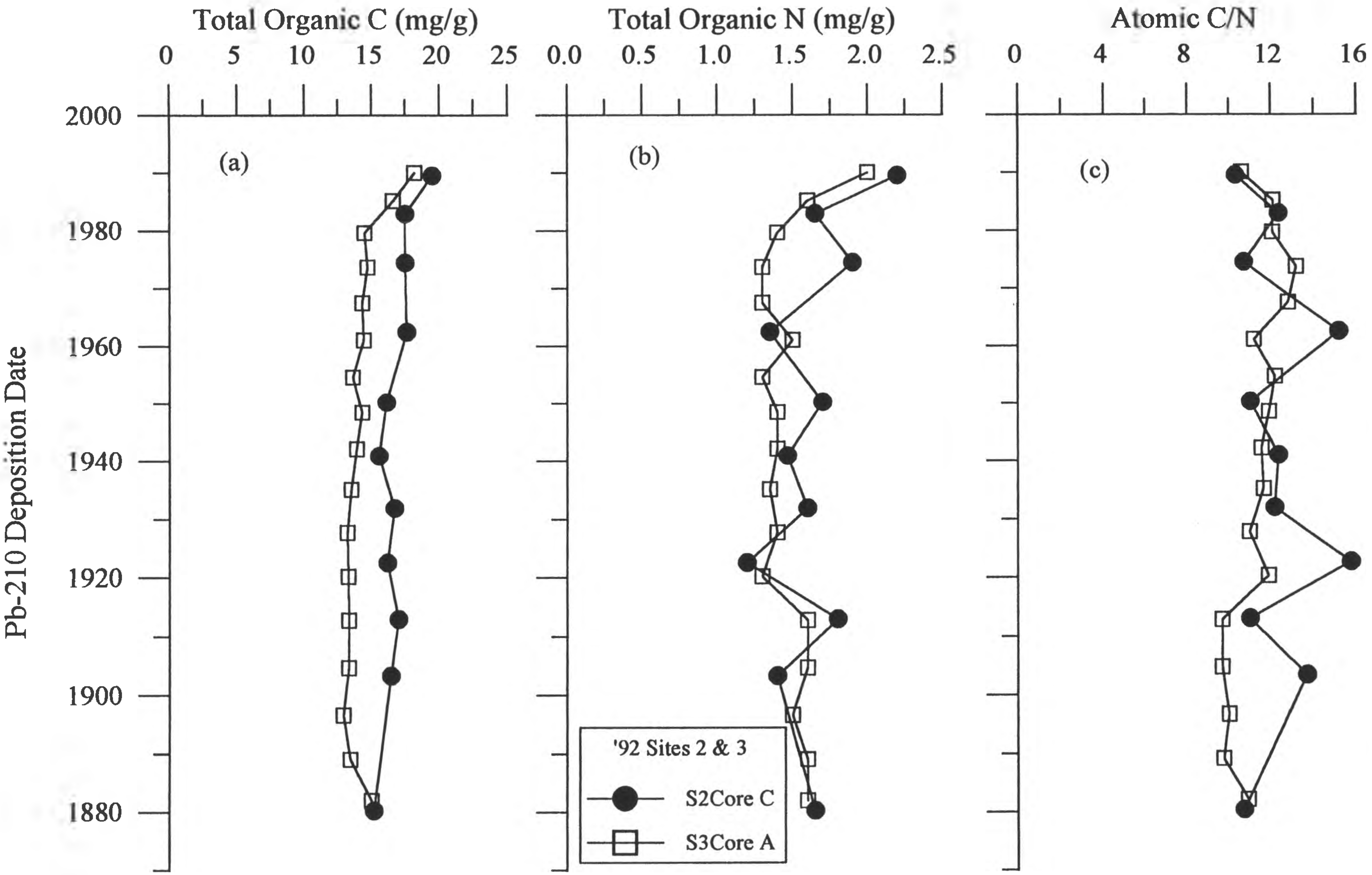


Figure 25: Sites 2 & 3, Organic Carbon & Nitrogen. Concentrations of total organic C, total "organic" N and atomic C/N ratio for cores taken in 1992. Values are plotted against Pb-210 deposition date, see Section 5.1.



of organic matter over the past 50-100 years, i.e. with different bulk character, to this the deepest part of the lake.

5.2.2.4 Atomic C/N Ratio. Terrestrial plants contain much greater proportions of carbohydrates than they do proteins, thus their C/N ratios are very high (>20) depending upon the type of tissue sampled. Aquatic plankton on the other hand contain much lower proportions of carbohydrates and are characterized by C/N ratios in the range of 6-9 (Meyers and Ishiwatari, 1993). Lake sediments are usually a mixture of both terrestrial and aquatic sourced organic matter and consequently are characterized by an intermediate atomic C/N ratio. Lakes with higher autochthonous inputs usually show lower ratios (Meyers and Ishiwatari, 1993). Both cores from Site 1 show essentially the same atomic C/N ratio throughout, at about 10, with the most significant deviations occurring at the older parts of the '92 Core C before 1895 (Figure 24c). This suggests that for the past 100 years, this site has received bulk organic inputs with both terrestrial and aquatic sources in nearly constant relative proportions. Site 2 shows a more variable C/N ratio, and higher than those form Site 1 suggesting a greater proportion of terrestrial sources (Figure 25c). The data from Site 3 show a progressive decrease downcore suggesting that the changes in source indicated above in the TOC and TON data changed from a greater to a lesser planktonic source of the organic matter deposited there over the past 50-100 years.

5.3 RADIONUCLIDES

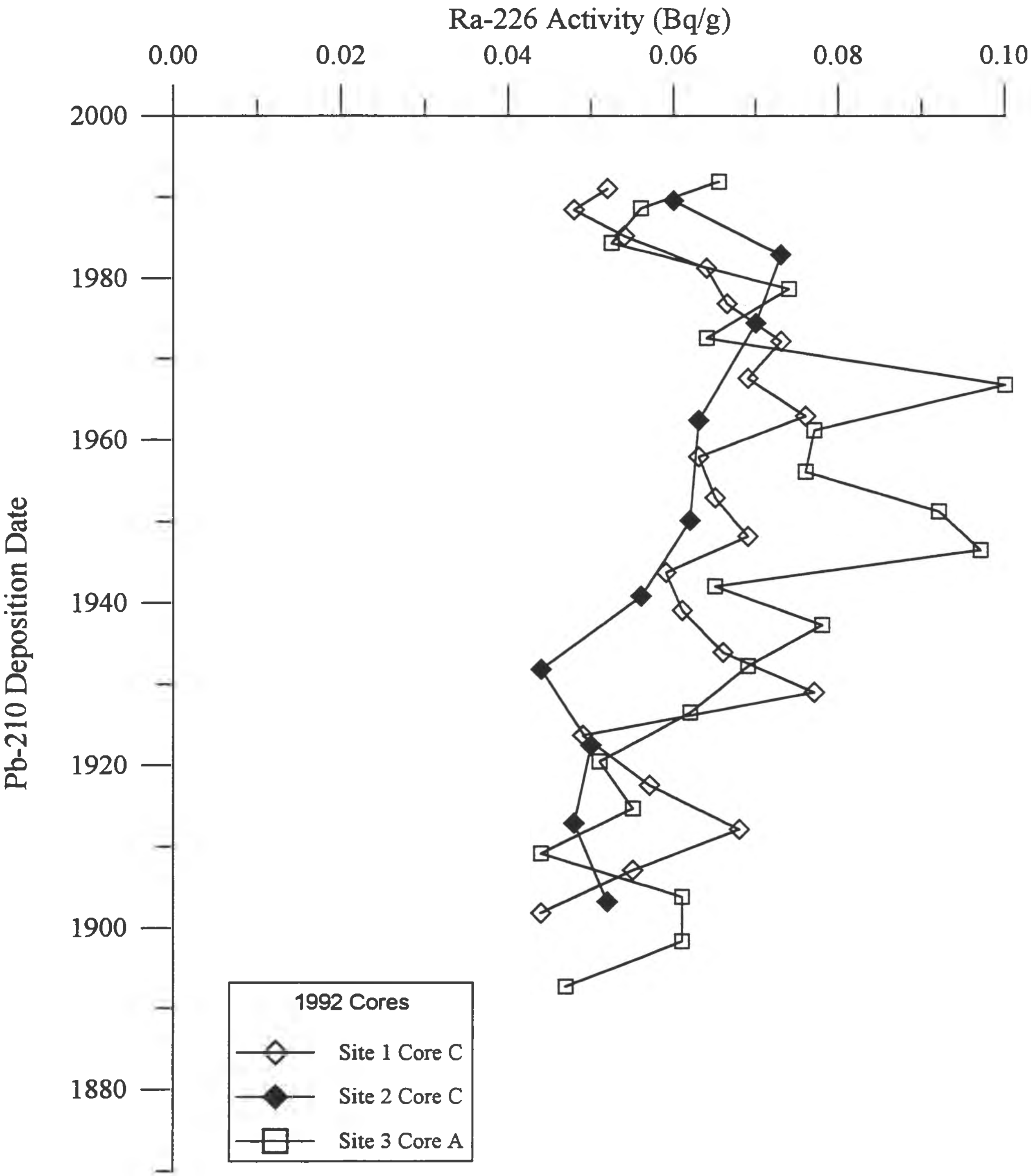
Based upon the geochronology results (section 5.1) the upper 20 cm from Site 1 Core C and Site 3 Core A and similarly the upper 10 cm from Site 2 Core C were sent for further radionuclide analyses. In all three cases the sediments sent represented about the past 100 years of modern sedimentation. Freeze-dried and ground samples were sent first for ^{137}Cs determination, then the same samples were sent on for determinations of total U, ^{210}Pb, ^{226}Ra, ^{224}Ra, ^{232}Th, ^{230}Th and ^{228}Th.

5.3.1 Radium-226

The highest levels of ^{226}Ra found in sections from Site 1 Core C (Figure 26) are of the same magnitude as was found in the surficial sediments from the western part of the lake (Table 1), and higher than the control site near Sampson Island from the work of Waite et al. (1988). Although the profile for Site 1 shows a decreasing trend since 1960, which coincides with the midpoint of the operation of the Gunnar Mine, levels at depths corresponding to deposition earlier in the twentieth century are as high or higher, suggesting that this site is influenced by other background uranium sources. The data for Site 2 Core C (Figure 26) show continuous increases in ^{226}Ra since 1930 and a decrease since 1980. Again maximum levels are similar to those found in the surficial sediments (Table 1).

The ^{226}Ra profile exhibited by the Site 3 Core A results (Figure 26) shows a band of highest activity corresponding to deposition between approximately 1940 and 1970 with maxima appearing at approximately 1947 and 1968. This site is the closest to Langley Bay and being the deepest part of

Figure 26: Radium-226 Distribution in Cores from Three Sites - 1992.



the lake one would expect it to be a focus for the deposition of fine-grained sediments. These dates don't correspond well with the onset and history of mining activity at the Gunnar Mine site (Joshi *et al.*, 1989) and the influence that the mine had on Langley Bay, but this is likely related to uncertainties in the ^{210}Pb geochronology for this site (see Section 5.1).

5.3.2 Thorium-230

Thorium-230 shows a band of increased activity over background for the Site 2 and Site 3 cores (Figure 27) and a very pronounced spike exhibited in the Site 3 data. The highest level of ^{230}Th determined at Site 2 is about two times that of the background level and the increase begins at about 1960 with the maximum appearing at 1970. At Site 3 the highest level is more than 20 times the background level, with the increased band beginning at 1930, peaking at 1948, and beginning to tail off slowly at about 1960. For both of these sites the ^{230}Th profile corresponds well with the total uranium profile (see below). The band of increased activity corresponds for Site 2 at a time consistent with the onset of mining activity. For Site 3 all dates are early and this is likely caused by estimates of geochronology by ^{210}Pb (see Section 5.1). The profile for ^{230}Th shows no significant variation over background levels for Site 1 Core C (Figure 27), providing evidence that no transport of sediment bound ^{230}Th has occurred that far west.

5.3.3 Total Uranium

The profiles of total uranium are shown in Figure 28. As for ^{230}Th above, the Site 1 profile shows no increase over background for the entire upper 20 cm of the core. The values at this site are about five times that which was determined at the control by Waite et al. (1988) but only about one fifth that found in Langley Bay by the same authors. The profile for Site 2 shows a shift to about 1.5 times background (one third of the Langley Bay value) for the upper portion of the core beginning at about 1955.

At Site 3 a well-defined subsurface maxima occurs between 1940 and 1970, with the maximum value at twice the background value, which corresponds to half the value reported for Langley Bay (Waite et al., 1988). Since 1960 the level has been decreasing to 1.5 times background. Thorium-230 is a long-lived member of the ^{238}U series (Robbins, 1978) and the correspondence between both of these is expected. Unfortunately there are no ^{230}Th data from Langley Bay for comparison.

5.3.4 Lead-210 and Cesium-137

Interest in these particular radionuclides is mostly for their value in geochronology as discussed in Section 5.1 but their distributions in these cores provide more evidence of the influence of Langley Bay sediments. Lead-210 profiles are shown in Figure 19. Sites 1 and 2 exhibit profiles with the expected decrease of ^{210}Pb in excess of that which is supported by ^{222}Rn in the sediments. All three cores show about the same supported (background) activity, on the order of 0.08 Bq/g. The profile for Site 3 again shows a marked increase between 2 and 4 g/cm^2. This isotope is also a member of the uranium series and was found enriched in the Langley Bay samples (Table 1).

Figure 27: Thorium-230 Distribution in Cores from Three Sites - 1992.

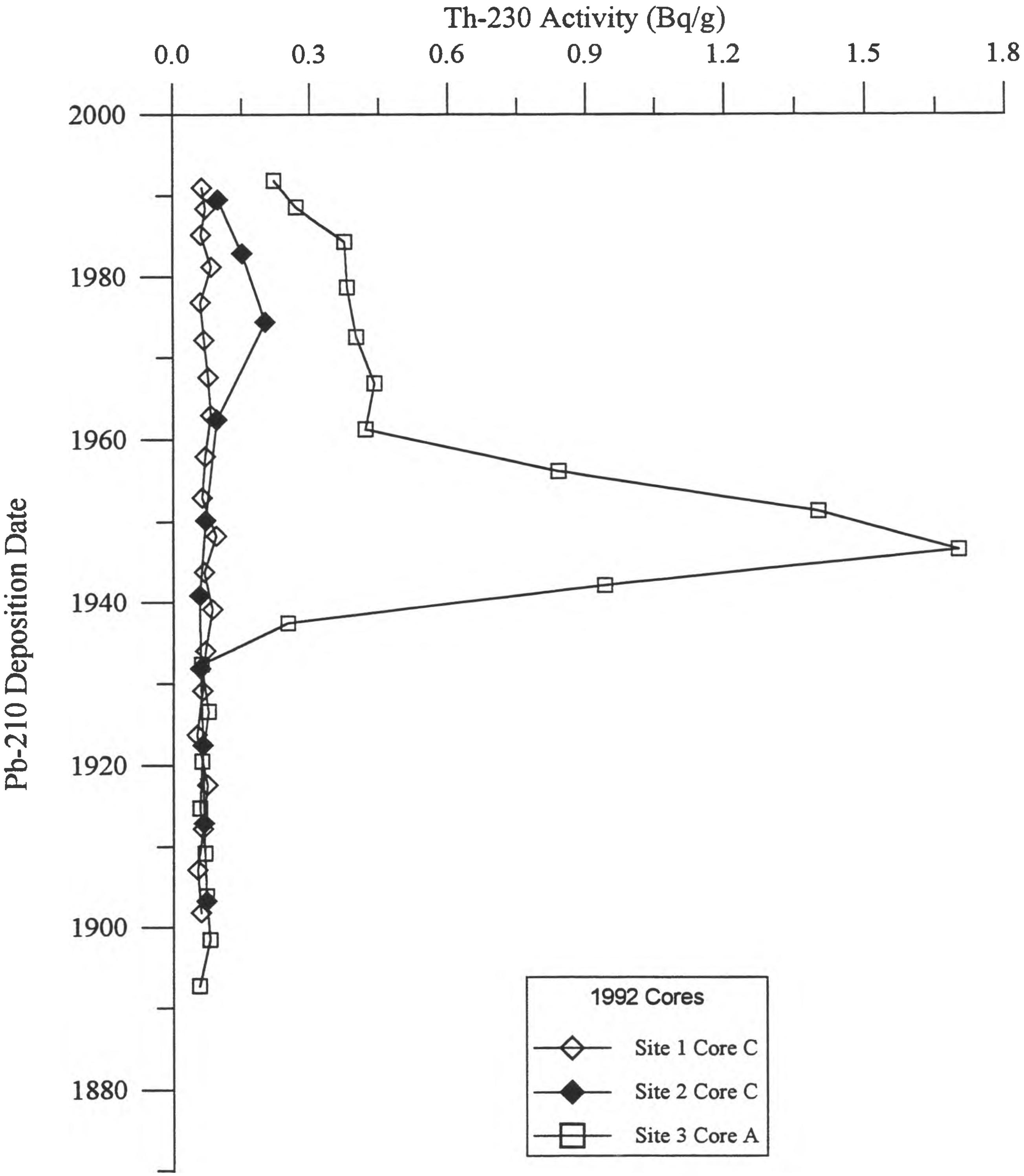
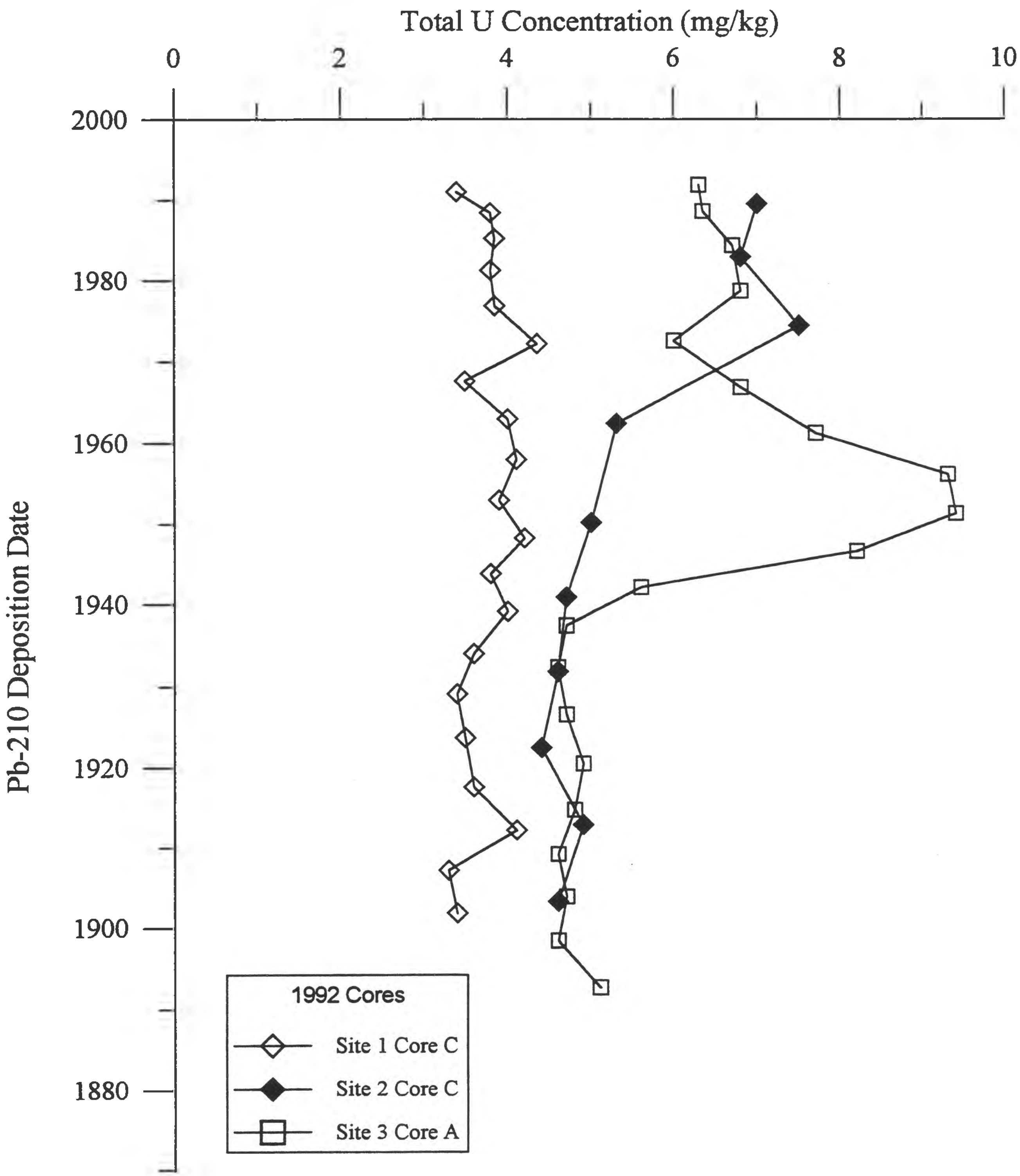


Figure 28: Total Uranium Distribution in Cores from Three Sites - 1992.



Cesium-137 is not related to the mine tailings (Joshi et al., 1989) but comes from fallout due to atmospheric testing of nuclear weapons. Its well-known distribution (Robbins and Edgington, 1975) is the basis of dating methods with the onset of testing beginning in 1958 and peaking in 1963. This peak happens to coincide with the period during which the sediments of Langley Bay were influenced by the Gunnar Mine tailings. The fact that all three cores show increases for the period bracketed by 1940-1980 (Figure 21) suggests that this radionuclide has a bomb source and not a source from Gunnar.

5.4 ORGANIC CONTAMINANTS

5.4.1 Polynuclear Aromatic Hydrocarbons

5.4.1.1 Analytical Considerations As discussed in Section 4.2.3 PAHs have been determined by two laboratories on separate samples with mixed results. The 1992 core from Site 1 (Core D) was analyzed by NWRI using HPLC-FL with confirmation by UV-PDA and GLC-FID. Another core from Site 1, collected in 1993 (Core C) was sent to Chemex for numerous parameters. Ten sections of this core were analyzed for PAHs using GC-MS with SIM. Data presented here were selected first from the HPLC-FL results and wherever possible corroborating results from GC-MS are also included.

It should be noted that the HPLC-FL technique is highly sensitive for many of the PAHs and more selective than HPLC-UV or GLC-FID, and that the GC-MS (selected ion monitoring) technique is more selective and less sensitive. The UV-PDA detector is also more selective and less sensitive. As an example of the relative sensitivities, Table 12 shows some sample size dependent MDLs reported for four PAHs by each method discussed above.

The combination of all these techniques, on the *same* samples could yield very convincing qualitative and quantitative data. Here we report results from a combination of techniques on samples from two different cores.

5.4.1.2 Compounds Found Eleven PAHs were found by HPLC-FL to be present over the MDL in all sections of 1992 Site 1 Core D. Their shortened names are used here, see Table 4 for their complete names:

Npth	1-MeNpth	2-MeNpth	Fl
Ph	Fth	Py	B(b)Fth
B(k)Fth	B(a)Py	B(ghi)Per	

Other PAHs were found in some sections but there were enough ND values that trend analysis would be uncertain. The first three PAHs listed above were also confirmed by spectral matching on the PDA detector. These data will be presented in both tabular and graphical form so that ND and trace values will be discernable. Table 13 contains the HPLC-FL results for all 11 of the components which were found in all sections. Six of the components which were found by HPLC-FL were also found by GCMS analysis of alternate sections of 1993 Site 1 Core A. These results appear in Table

14 and it is clear that the two methods differ significantly in their ability to detect and quantify PAHs.

Table 12: MDLs for Several PAH Detection Techniques.

Method	Py	Ph	B(b)Fth	B(k)Fth
MDLs for the next four methods (ng/g) based on 5 gram dry sample size:				
HPLC-FL[a]	4.0	0.80	0.40	0.04
HPLC-254[b]	28	5.2	8.4	14
HPLC-Maxplot[c]	5.0	5.4	10	17
GLC-FID[d]	9.0	9.0	9.2	9.6
MDLs for the next method (ng/g) based on 20-40 gram dry sample sizes:				
GCMS-SIM[e]	1.0	1.0	1.0	1.0

[a] Fluorescence detection (Waters 470) used in 4 step program mode - NWRI
[b] Monitoring of 254 nm channel from Photodiode Array UV detector (PDA) (Waters 996) - NWRI
[c] Monitoring sum of absorbances from all channels on PDA - NWRI
[d] On-column capillary with Flame Ionization Detector (Hewlett-Packard 5890A) - NWRI
[e] Selected Ion Monitoring GCMS (Method 8270) - Chemex Labs Alberta, Inc.

The fluorescence technique can be sensitive as described above, but in the case where there is a complex mixture of hydrocarbons in the sample, as is often the case in sediments, there can be interferences from co-eluting and nearby components. In the case of Npth, 1-MeNpth and 2-MeNpth the chromatographic peaks were sufficiently pure that they could be confirmed by spectral matching using the PDA. The other components were confirmed only by HPLC-FL and GC-FID. The GC-FID technique gives superior resolution over the HPLC, but is less selective since many aliphatic and cyclic hydrocarbons which occur in these complex mixtures also cause co-elution problems. The GCMS technique with SIM can be very selective for PAHs, but also suffers when complex mixtures contain many co-eluting peaks and there are high noise levels from the multitude of fragments which can occur in such cases. Discussion will centre around the HPLC-FL results with the understanding that they represent the worse-case scenario (greater number of components and higher apparent concentrations).

5.4.1.3 Possible Sources All of the parent PAHs (non methylated) above are known from general combustion sources, such as forest fires, space heating using biomass and other distinctively anthropogenic activities such as coal-fired plants (Bjorseth and Ramdahl, 1985; Ramdahl, 1985). The methylated PAHs can be associated with low temperature combustion sources and petroleum (Blumer, 1976). The lower molecular weight PAHs (2 and 3 ring compounds) have also been attributed to unburned petroleum sources (Eganhouse and Gossett, 1991). The methylated

Table 13: PAH Concentrations (ng/g) by [a]HPLC-FL from 1992 Site 1 Core D.

Date	[b]Npth	1-MeNpth	2-MeNpth	Fl	Ph	Fth	Py	B(b)Fth	B(k)Fth	B(a)Py	B(ghi)Per
1991	14.0	21.0	38.0	5.0	131.0	12.0	11.0	5.0	(0.04)	5.0	(0.7)
1988	13.0	20.0	39.0	6.0	153.0	19.0	17.0	1.0	1.0	4.0	(0.7)
1985	16.0	16.0	33.0	5.0	122.0	18.0	16.0	25.0	5.0	15.0	12.0
1981	11.0	18.0	34.0	5.0	137.0	18.0	15.0	14.0	3.0	18.0	5.0
1977	10.6	16.5	25.0	3.7	153.5	11.3	10.6	23.1	3.7	6.1	4.6
1972	18.0	19.0	36.0	5.0	124.0	19.0	20.0	18.0	3.0	12.0	8.0
1968	22.0	26.0	49.0	5.0	137.0	19.0	17.0	16.0	3.0	14.0	(0.7)
1963	17.0	21.0	38.0	5.0	142.0	25.0	18.0	19.0	3.0	18.0	7.0
1958	10.4	17.9	26.6	4.9	161.5	12.8	11.1	5.7	1.1	4.5	1.1
1953	[c](0.9)	(0.3)	(0.4)	(0.4)	57.0	31.0	23.0	16.0	3.0	16.0	12.0
1948	31.0	23.0	41.0	8.0	132.0	13.0	18.0	13.0	2.0	13.0	5.0
1944	9.0	12.0	24.0	4.0	182.0	16.0	16.0	14.0	2.0	13.0	7.0
1939	24.0	22.0	44.0	6.0	152.0	21.0	19.0	18.0	3.0	27.0	5.0
1934	7.9	16.8	23.9	5.3	163.2	14.0	13.4	9.0	1.1	4.0	2.4
1929	33.0	31.0	51.0	8.0	167.0	27.0	27.0	36.0	6.0	41.0	26.0
1924	14.0	20.0	36.0	7.0	140.0	22.0	22.0	15.0	2.0	21.0	2.0
1918	12.0	21.0	40.0	8.0	162.0	16.0	15.0	9.0	1.3	4.0	(0.7)
1912	7.0	14.0	27.0	6.0	146.0	14.0	14.0	13.0	2.2	5.0	(0.7)
1907	11.0	17.2	24.7	5.7	154.8	12.3	11.5	14.5	1.8	3.8	1.8
1902	13.0	23.0	43.0	9.0	149.0	14.0	19.0	21.0	3.3	8.0	10.0
1896	6.0	16.0	33.0	7.0	174.0	16.0	16.0	15.0	2.3	8.0	4.0
1891	16.0	21.0	38.0	6.0	180.0	16.0	16.0	3.0	(0.04)	3.0	(0.7)
1885	9.8	15.7	21.5	7.4	167.9	19.6	27.5	12.3	2.1	9.6	1.5
1879	13.0	18.0	36.0	6.0	169.0	16.0	14.0	12.0	1.7	4.0	1.0

[a]Fluorescence detection, NWRI [b]See Table 4 for abbreviations [c]Value was < MDL (given in brackets)

Table 14: PAH Concentrations (ng/g) by [a]GCMS from 1993 Site 1 Core A.

Date	[b]Npth	1-MeNpth	2-MeNpth	Fl	Ph	Fth	Py	B(b)Fth	B(k)Fth	B(a)Py	B(ghi)Per
1989	[c]tr(1.7)	[d]NA	NA	[e]ND(1.0)	3.6	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)
1979	3.2	NA	NA	ND(1.0)	9.0	tr(2.0)	3.5	tr(2.8)	ND(1.0)	ND(1.0)	3.7
1967	7.8	NA	NA	ND(1.0)	20.5	5.0	10.2	7.8	ND(1.0)	ND(1.0)	11.6
1956	4.0	NA	NA	ND(1.0)	6.3	tr(1.1)	tr(2.1)	tr(1.4)	ND(1.0)	ND(1.0)	tr(2.2)
1947	3.0	NA	NA	ND(1.0)	3.2	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)
1937	tr(2.3)	NA	NA	ND(1.0)	tr(2.3)	ND(1.0)	ND(1.0)	nd(1.0)	ND(1.0)	ND(1.0)	ND(1.0)
1927	3.4	NA	NA	ND(1.0)	9.7	tr(2.0)	3.2	tr(2.7)	ND(1.0)	ND(1.0)	4.3
1915	tr(1.4)	NA	NA	ND(1.0)	tr(2.6)	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)	tr(1.1)
1904	tr(2.0)	NA	NA	ND(1.0)	tr(2.8)	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)	ND(1.0)
1893	5.0	NA	NA	ND(1.0)	13.8	ND(1.0)	tr(2.9)	tr(2.8)	ND(1.0)	ND(1.0)	3.3

[a] GCMS with selective ion monitoring, Chemex Labs Alberta, Inc.
[b] See Table 4 for abbreviations used for PAHs
[c] "trace" values are greater than the method detection limit but less than the quantitation limit (i.e. NDR)
[d] NA - Component not analyzed
[e] ND values are less than the method detection limit (given in brackets)

naphthalenes (1-MeNpth and 2-MeNpth) and the parent PAHs (Ph and Py) are the major PAH constituents of the wastewater discharge from the Suncor, Inc. oil sands plant in Fort McMurray and are found to a lesser extent in natural discharges from oil sands mines and rivers which drain watersheds in the oil sands region (Bourbonniere and Lee, Unpubl.).

5.4.1.4 Comparisons to Other Lakes Concentrations of four of the PAHs that were determined in Site 1 sediments are many times lower than those found in the sediments of lakes in more heavily industrialized areas. For instance Eadie et al. (1991) reported values for Ph, Fl, Py and B(a)Py from Lake Ontario and Lake Erie sediment cores which are in the 700-1000 ng/g range, 50 times more abundant than those reported here, except five times more for Ph (cf. Table 13). Eganhouse and Gossett (1991) report concentrations in marine sediments offshore from a Los Angeles sewage outfall for the same PAHs to be about half those found in Lake Ontario. Gschwend and Hites (1981) found lower values for lacustrine sites in the northeastern US, but were still 3-10 times higher than those found here. The fate of low molecular weight PAHs deposited in sediments is primarily degradation by microbial means in the oxidized layers, but this is less likely in the reducing zone according to Eganhouse and Gossett (1991). These authors propose that the higher molecular weight PAHs (4 to 6 rings) are resistant to biodegradation in sediments and survive better than the lower molecular weight ones.

5.4.1.5 Depositional History at Site 1 Four types of historical profiles are found among the 11 PAHs determined and shown in the plots which appear in Figures 29, 30 and 31. Concentrations are nearly invariant, at low levels, over the past 100 years for Fl and B(k)Fth (Figure 30). 1-MeNpth and B(ghi)Per (Figure 29) and Fth and Py (Figure 30) exhibit more varied profiles with some indication of cyclic behaviour, but no clear increasing or decreasing trends. The third type of historical profile is one that is considerably more variable but still with no clear increasing or decreasing trend. This is shown by Npth and 2-MeNpth (Figure 29) and B(b)Fth (Figure 30). The two PAHs plotted in Figure 31 are the only ones to show an overall trend. B(a)Py exhibits an erratic decreasing trend since the 1920s, with an almost constant low value prior to then. Ph has undergone an overall decrease, albeit quite erratic, over the last 100 years of about 30% from a value of 175 ng/g around 1890 to a recent concentration of about 125 ng/g. Overprinted on 1-MeNpth, 2-MeNpth and indeed overshadowing all else in the case of Ph, is a significant minimum value occurring at 1953. As well B(ghi)Per, B(k)Fth and B(a)Py exhibit a significant maximum at 1929, a time when many of the other components also show maxima.

It is often instructive to normalize downcore distributions of components which have possible sources in the watershed by the TOC content of the sediments. This normalization converts the concentrations to a mass per mgC basis and has the potential to remove any variations in the data that are associated with "normal" variability in sediment input caused by year-to-year climate variability. The PAH data are good candidates for such normalization because of the variability exhibited in nearly all 11 parameters (Figures 29, 30 and 31). The rationale for normalization is that if such treatment of the data reduced the variability, then it supports the idea that the variability of the selected parameter was associated with the bulk organic matter (and by extension, the bulk sediment). Any variation that remains after normalization to TOC is more likely to have been caused by an unusual occurrence (e.g. a contamination event, major watershed disruption, lake process not related to the watershed).

Figure 29: Site 1 PAH Data - Npth, 1-MeNpth, 2-Npth and B(ghi)Per.
Fluorescence HPLC data shown by solid circles and GCMS data by crosses. SDLs are plotted whenever an ND occurred, as are "tr" values, see Tables 13 and 14.

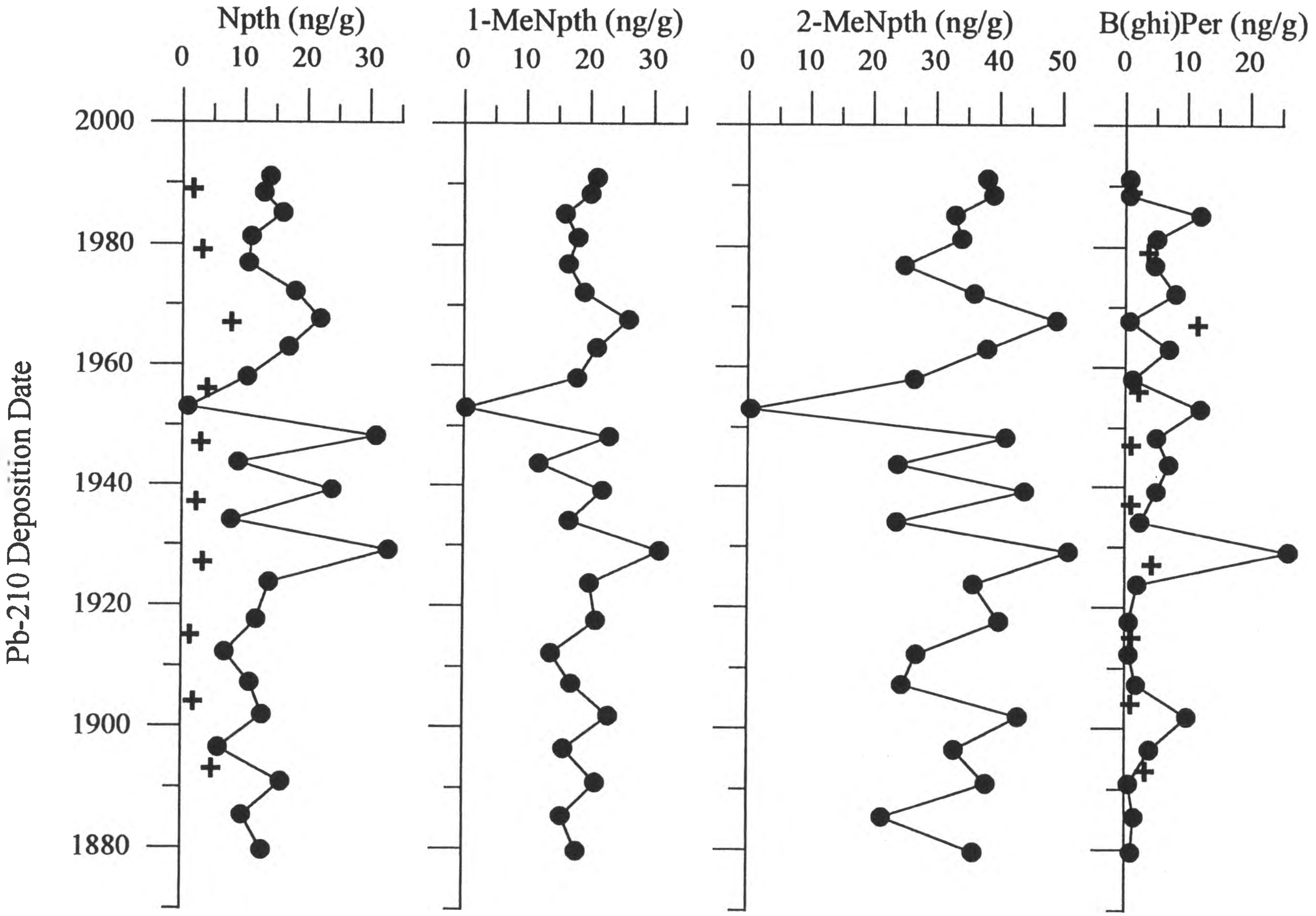


Figure 30: Site 1 PAH Data - Fl, B(k)Fth, Fth, B(b)Fth and Py.
Fluorescence HPLC data shown by solid circles and GCMS data by crosses. SDLs are plotted whenever an ND occurred, as are "tr" values, see Tables 13 and 14.

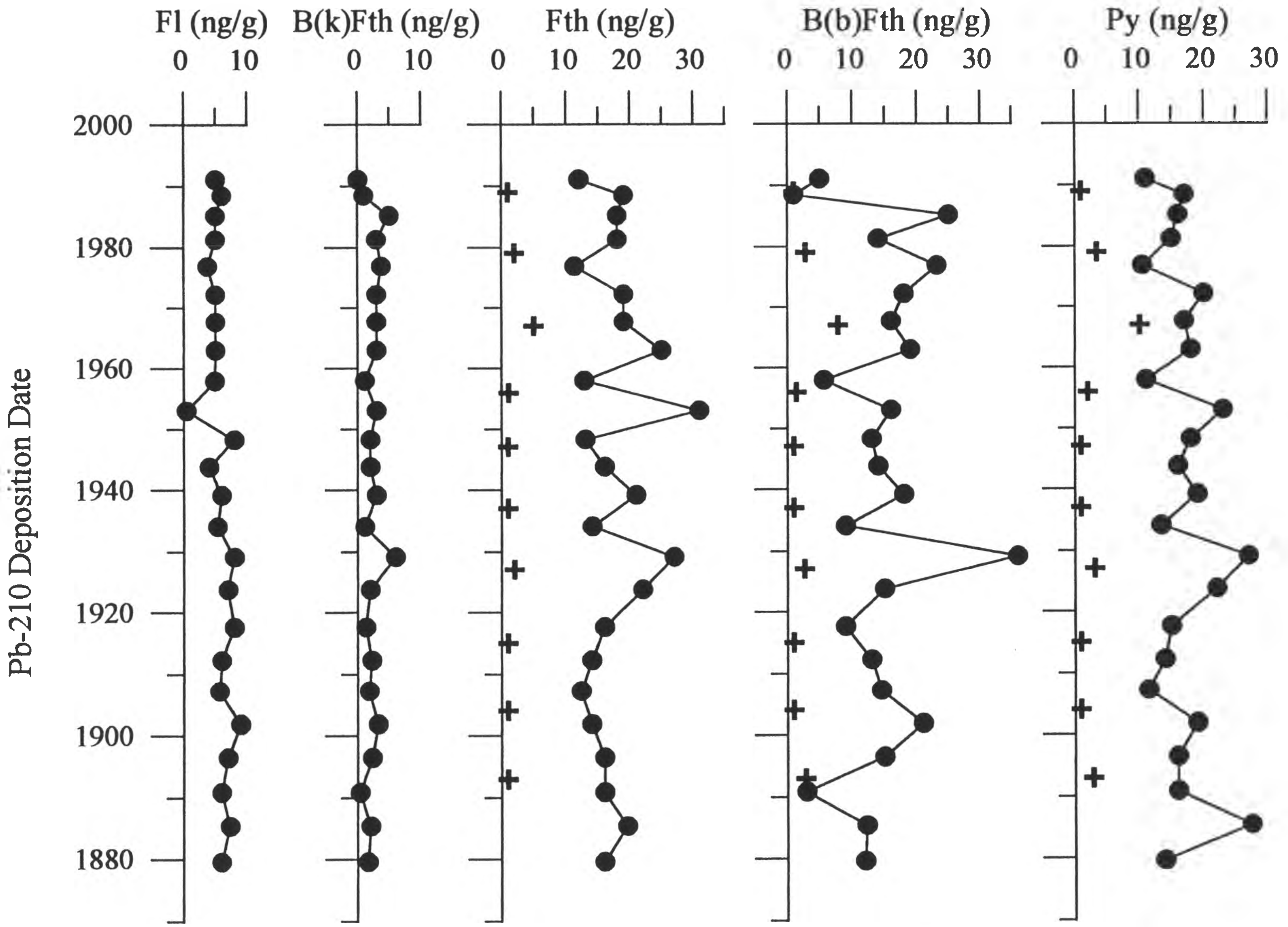


Figure 31: Site 1 PAH Data - B(a)Py and Ph.

Fluorescence HPLC data shown by solid circles and GCMS data by crosses. SDLs are plotted whenever an ND occurred, as are "tr" values, see Tables 13 and 14.

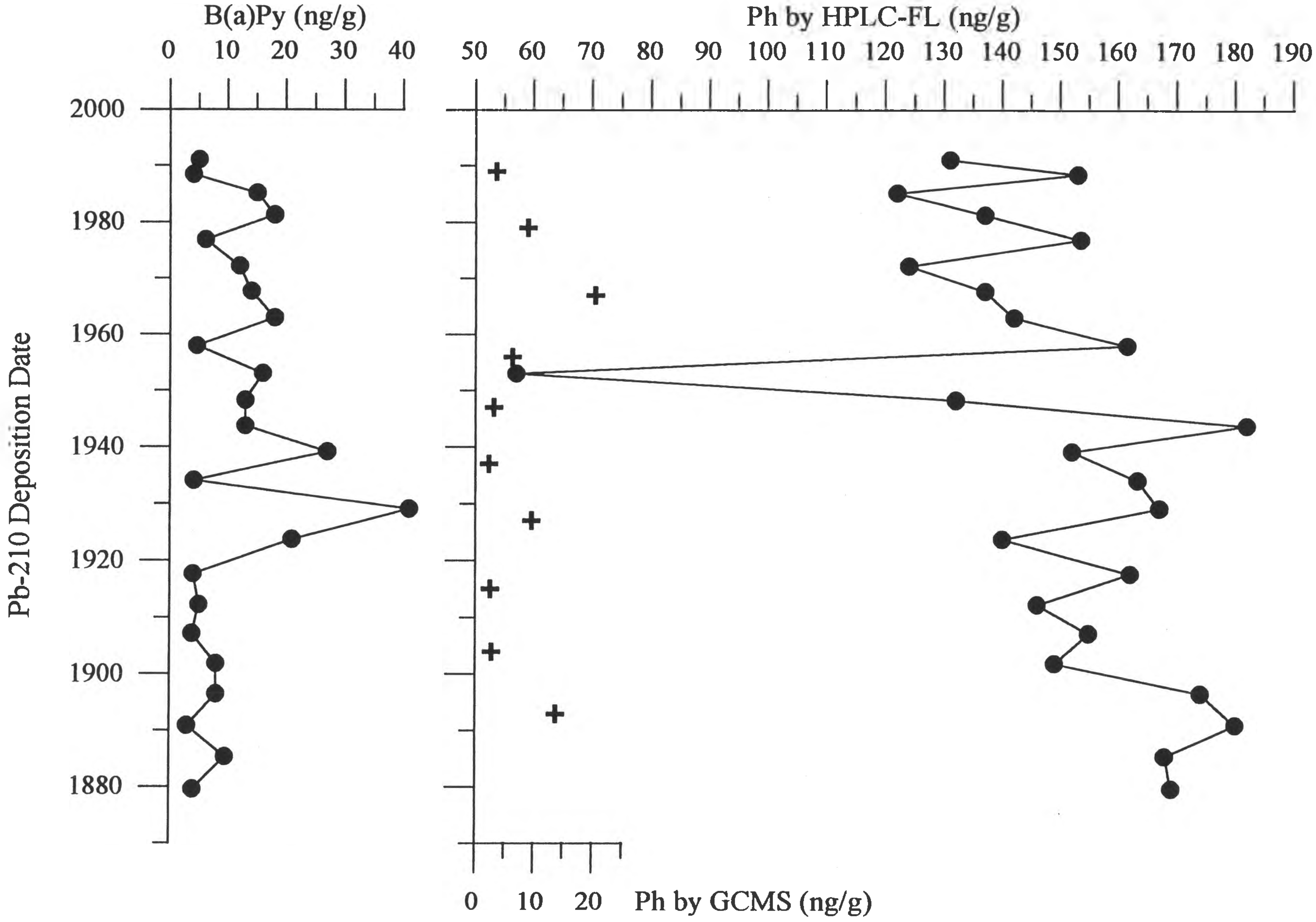


Figure 32: Site 1 TOC Normalized PAH Data - Npth, 1-MeNpth, 2-Npth and B(ghi)Per. Fluorescence HPLC data only are shown. Values from Table 13 are divided by TOC (Section 5.2).

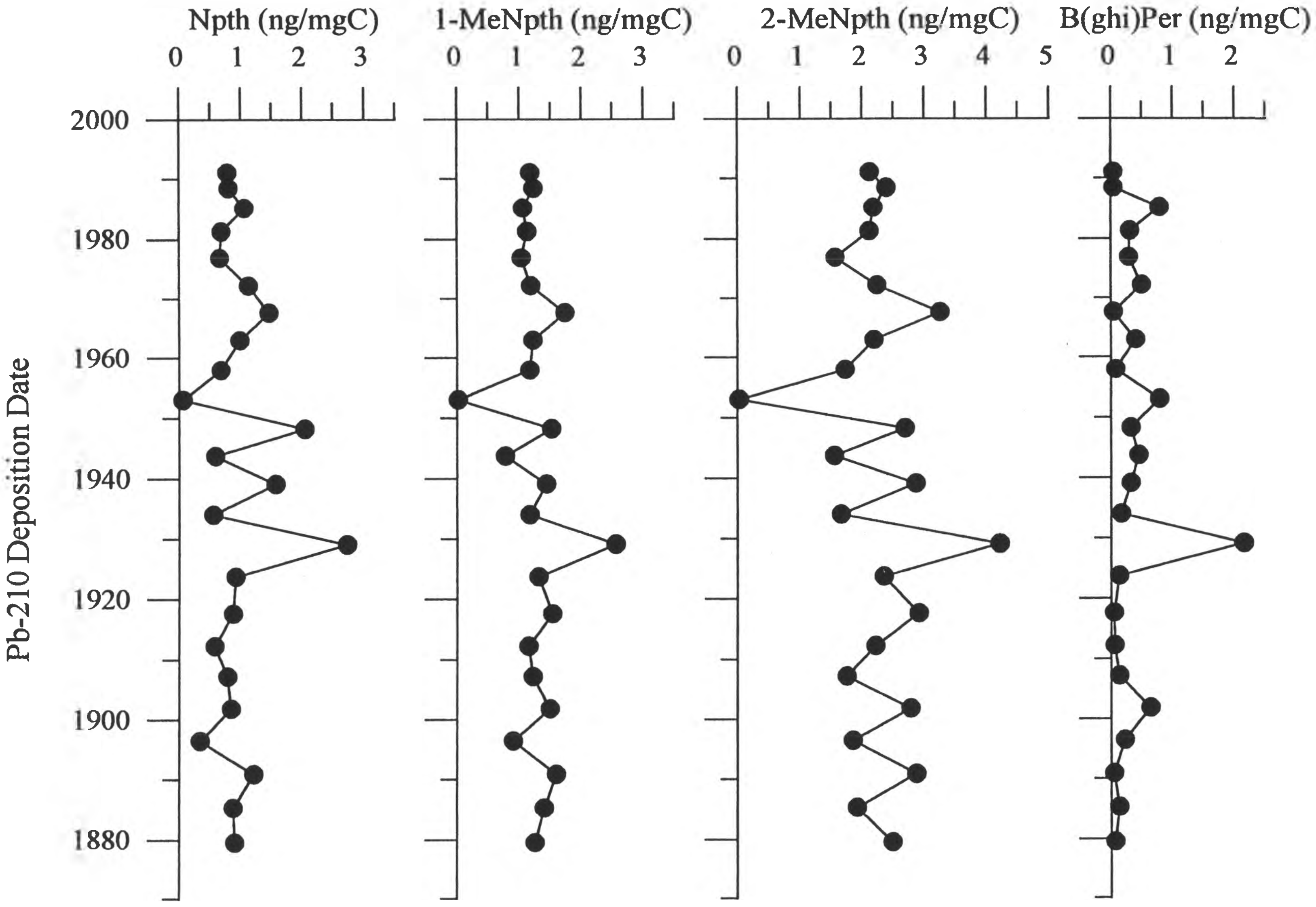


Figure 33: Site 1 TOC Normalized PAH Data - Fl, B(k)Fth, Fth, B(b)Fth and Py.
Fluorescence HPLC data only are shown. Values from Table 13 are divided by TOC (Section 5.2).

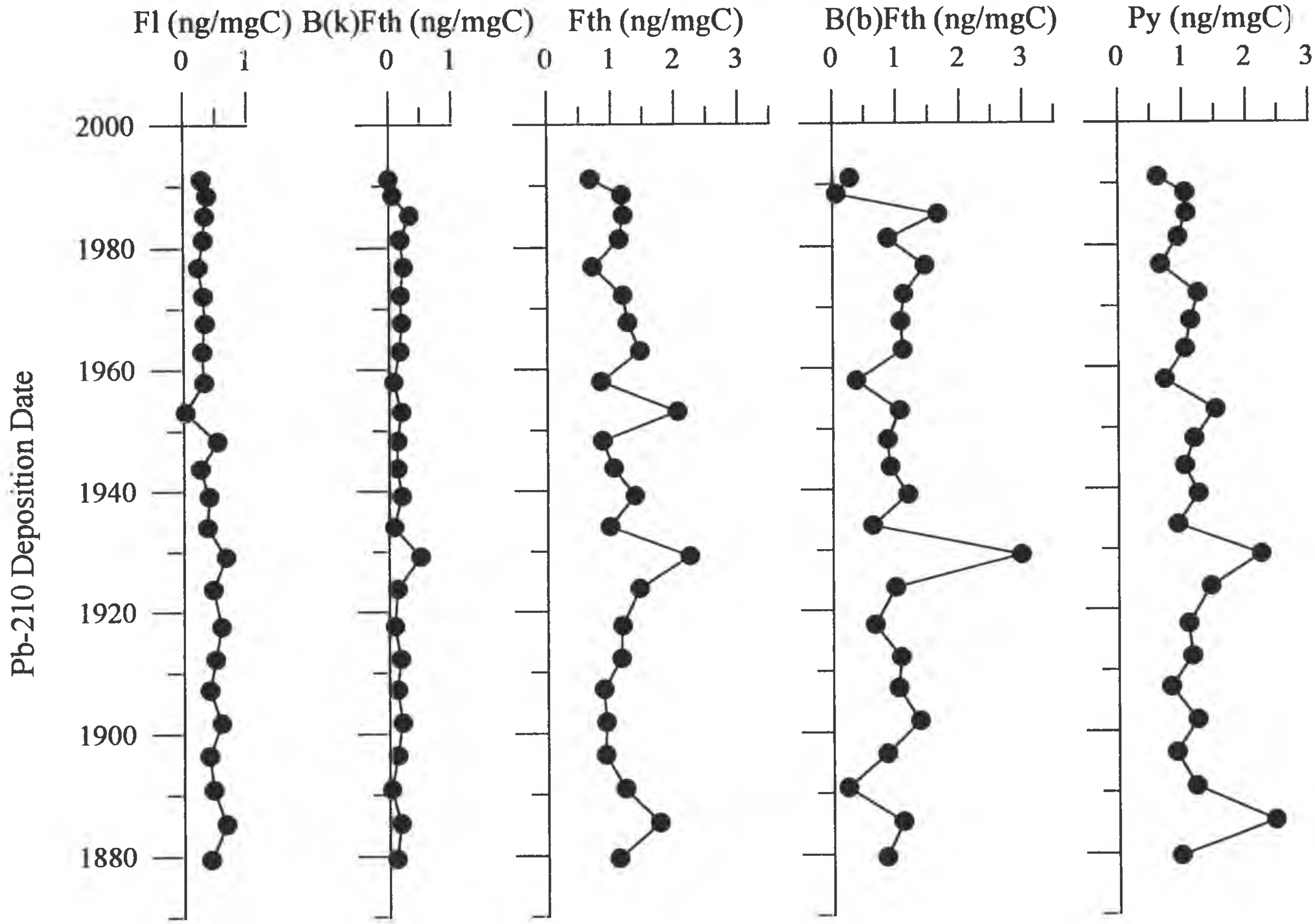
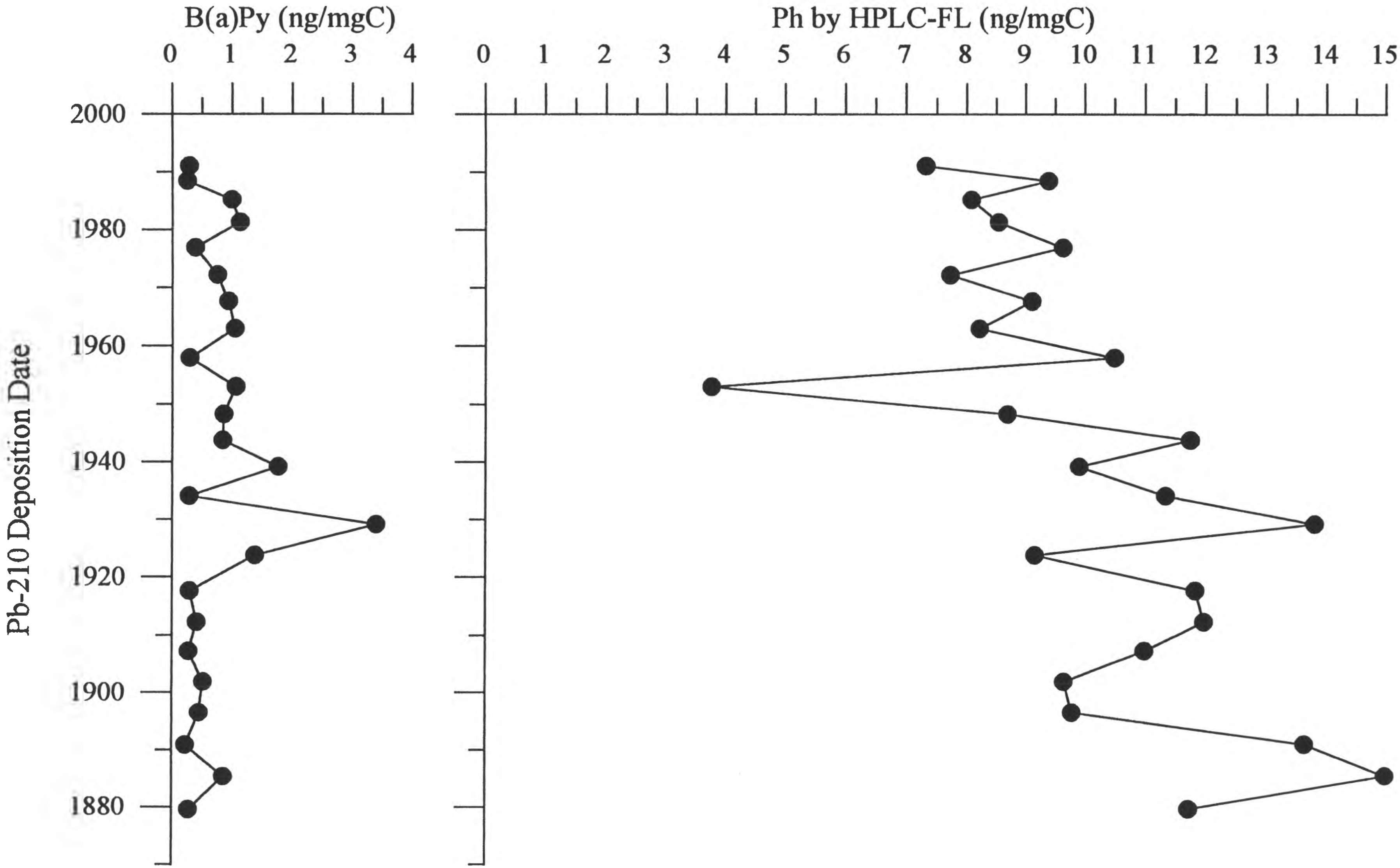


Figure 34: Site 1 TOC Normalized PAH Data - B(a)Py and Ph.
Fluorescence HPLC data only shown. Values from Table 13 are divided by TOC (Section 5.2).



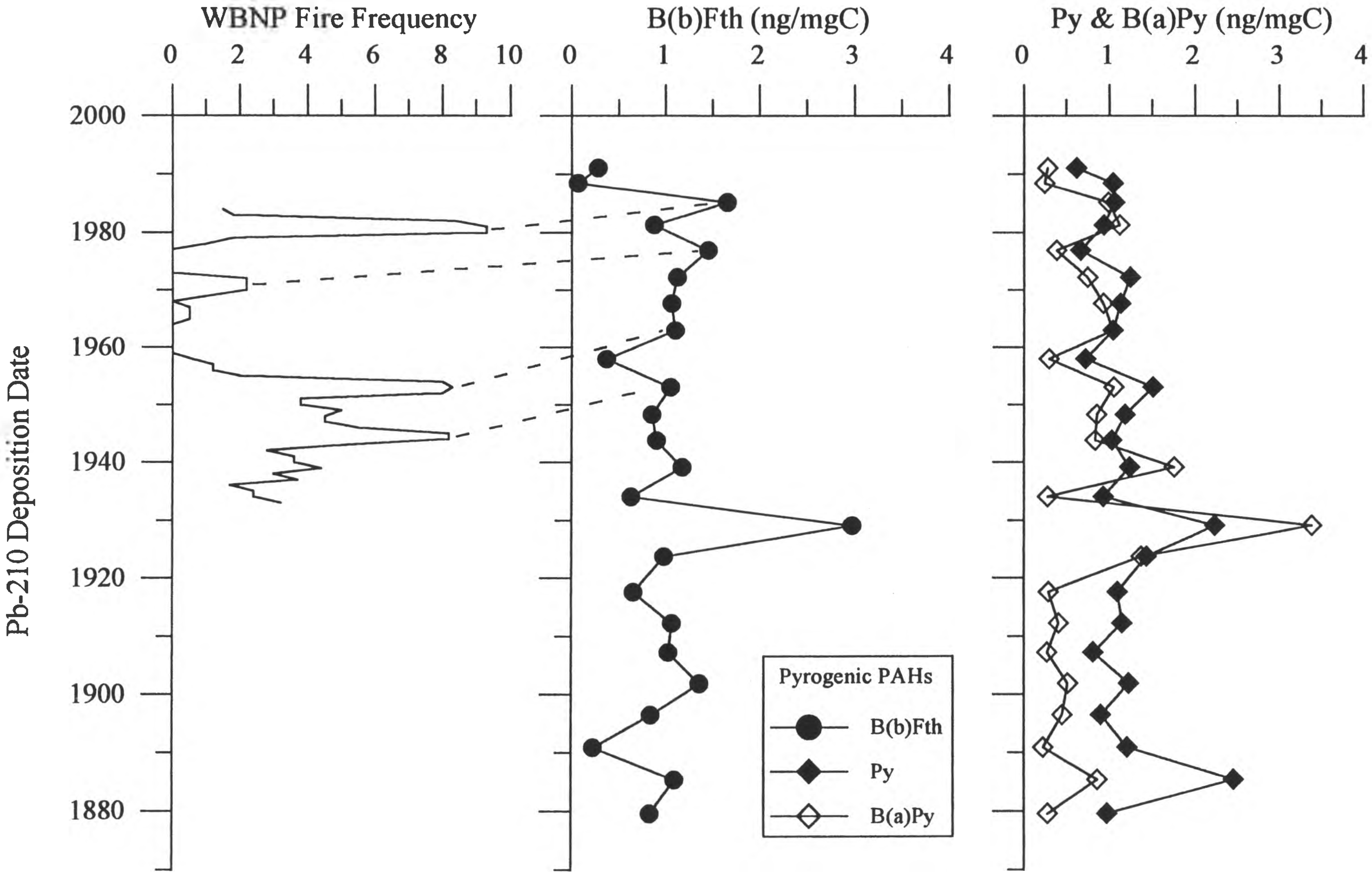
The HPLC-FL data from Site 1 Core D were all normalized to TOC and the results are shown in Figures 32, 33 and 34. Comparing all of the plots in Figures 32-34 with the corresponding ones in figures 29-31, it is evident that overall the variations are dampened. In all cases the peak in normalized concentrations occurs in the section corresponding to 1929. As well the minimum associated with deposition at 1953 remains prominent for 1-MeNpth, 2-MeNpth and Ph. The suggestion is that the increased PAH contents associated with the 1929 deposition interval may be pyrogenic in origin, coming from a higher frequency of forest fires which may have occurred during the drought period of the 1930s. Note that no signal is shown for increases in other parameters that may be deemed associated with "normal" runoff (See below in Section 5.6).

Larsen (1989) has developed a surrogate record of forest fire frequency based on stand ages in Wood Buffalo National Park. Fire frequency is transformed from proxy data related to area burned in a given year. Using three year running averages (compared with the 5 year integration per cm in sediment samples at Site 1) the three periods of highest forest fire frequency which occurred since data are available (i.e. 1932) were centred at 1980, 1953 and 1945. There was a period of generally higher frequency between 1932 and 1956, and another less prominent period centered at 1971.

Three of the PAHs found in the core can be considered as pyrogenic in origin (i.e. 5 or 6 rings) and their TOC normalized concentrations are shown along with the Larsen (1989) fire frequency curve in Figure 35. Assuming a lag period (see below), there is general agreement between the peaks and valleys of the fire frequency curve and those for these three PAHs. What differences that exist in matching the time scales could be explained by (1) the lag between the fire and the arrival of the pyrogenic PAHs to the sediment, (2) different "averaging" between the fire frequency data (3 years) and the core sectioning interval (5 years), (3) inaccuracies in the geochronology and (4) post-depositional mixing of sediments by physical or biological means. The fire frequency curve ran out of data at 1932, but the trend backwards in time is towards higher fire frequency; if so, it would agree well with the trend in the pyrogenic PAH data. One would expect longer range effects on the pyrogenic PAH content of the sediments of Lake Athabasca. Fire was used during periods of settlement and mining, and natural fires occur commonly in the entire Lake Athabasca watershed. Historical dry periods should be evident as horizons of increased pyrogenic PAH content. These data should be compared to more historical data on fire frequency and extent than just the WBNP data.

The minima which occur at 1953 for Npth, 1-MeNpth, 2-MeNpth, Fl and Ph are more difficult to explain. First, note that the first four compounds are all plotted at their MDLs. The early part of the HPLC-FL chromatogram (before the internal standard peak - Ph_{d10}) for this sample was unusually low in response, but the remainder of the chromatogram was "normal" - the Ph value was lower than in the rest of the samples, but the remainder of the PAHs were the same or higher, so there is no good argument in the chromatography data to ignore the entire chromatogram. Other data are not abnormally low for this section, so it must rest for now that a major decrease occurred in these (petroleum related) PAHs in a time period centred around 1953. Indeed the Ph record indicates that major changes occurred many times over the past 100 years (Figure 31) even when the data are normalized with TOC (Figure 34). Most of the variability which occurs in three of the petroleum related PAHs occurs between 1920 and 1970 (Figure 32) - Ph varies throughout the last 100 years (Figure 34). It is only speculation, but significant, and presumably less well controlled, experiments with oil sands mining, extraction and refining occurred along the Athabasca River (Waterways, Abasands, Bitumount, etc.) during the period from 1919-1951 (Ferguson, 1985). Note that little

Figure 35: Pyrogenic PAHs Related to WBNP Fire Frequency.
Normalized to TOC, the peaks in these three PAHs relate well to a reconstructed forest fire frequency curve for WBNP after the data from Larsen (1989). Dashed lines indicate speculative correlations assuming a lag in arrival of PAHs to the sediments.



variability in Npth, 1-MeNpth and 2-MeNpth since 1970, and also before 1920 for Npth and 1-MeNpth (Figure 32).

5.4.2 Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans

Total PCDD/F results are presented numerically in Table 15 and graphically in Figures 36 and 37. Both the PCDD and PCDF graphs demonstrate a marked increase in several of the congener group totals since about the mid-'70s. For PCDDs, the increase is most notable for total H_7CDDs and O_8CDDs. The remaining congener groups, T_4CDDs, P_5CDDs and H_6CDDs also exhibit an increase but it is more gradual and appears to commence around 1940-1950. The PCDF data in Figure 37 likewise show a significant increase in PCDF concentrations since the mid-'70s. Before this time, most PCDF congeners are undetectable with the exception of O_8CDF (Table 15). Accompanying this increase in total PCDF congeners, 2378-T_4CDF has also been detected since 1974 (Table 15, notes). This very obvious increase in PCDDs and PCDFs since around 1974 reflects either new source(s) of PCDD/Fs coming on stream, increased emissions from old source(s), or a lag in transport to the lake. Determining which of these is responsible could be quite difficult given the various potential sources of PCDDs and PCDFs.

The pulp and paper mill at Hinton, which began operations in the 1950s is one possible source for PCDDs and PCDFs, especially in the past. Contaminants from that mill's operation (or any other mill) could be many years in the aquatic system before settling in Lake Athabasca (hence a lag between PCDD and PCDF release and their appearance in core sediments). The likely causes of long lag times are the numerous opportunities for sediment bound contaminants to be temporarily deposited in low energy marginal zones in the Athabasca or Peace Rivers, or indeed very likely in the Peace-Athabasca Delta. Merging of these data with more information about possible sources (new industries, practices, timing etc.) would be useful.

Both Figures 36 and 37 suggest a slight possible decrease in PCDD/F values in the last decade. However, with only one data point to support this observation, we cannot yet be sure if a trend is indicated. As with the surficial sediments, O_8CDD and T_4CDD are the predominant PCDDs present and T_4CDF followed by O_8CDF are the predominant PCDFs. Unfortunately, there is no real discernable trend in PCDD and PCDF distribution across the lake as the core values fall within the range of the different surficial site values. Thus, a comparison between the different sites yields little hard information about the source of PCDDs and PCDFs.

5.5 INORGANIC CONTAMINANTS

5.5.1 Heavy Metals and Mercury

We report here analyses of seven heavy metals including total Hg determined on ten sections from Site 1 Core B taken in 1992. Six of the heavy metals (Pb, Cr, Cu, V, Zn and Hg) exhibit a monotonous nearly constant concentration with depth (Figures 38 and 39). Only As shows any sort of profile and that is one with increasing values beginning in 1970 where As concentration starts at 2 µg/g and increases to 10 µg/g at the 1990 deposition level. Allan (1979) found a similar profile

Table 15. Total PCDD and PCDF Results for 1992 Site 1, Core B.

Date	Total T_4CDD (ng/kg)	Total P_5CDD (ng/kg)	Total H_6CDD (ng/kg)	Total H_7CDD (ng/kg)	Total O_8CDD (ng/kg)	Total T_4CDF (ng/kg)	Total P_5CDF (ng/kg)	Total H_6CDF (ng/kg)	Total H_7CDF (ng/kg)	Total O_8CDF (ng/kg)	2378 T_4CDF (ng/kg)
1990	8.5	5.4	4.5	5.5	17	1.8	ND(0.1)	0.2	1.0	1.5	0.5
1983	8.2	5.7	5.1	7.0	16	2.4	0.4	1.4	1.3	0.9	0.4
1974	9.7	5.4	3.3	0.8	5.6	0.3	ND(0.2)	ND(0.2)	ND(0.3)	ND(0.2)	ND(0.2)
1964	7.3	[a]ND(0.1)	2.3	1.3	4.3	0.3	ND(0.2)	ND(0.1)	ND(0.1)	0.6	ND(.08)
1954	7.4	3.2	1.7	1.4	4.4	0.4	ND(0.2)	ND(0.2)	ND(0.2)	[b]NDR(0.3)	ND(0.1)
1944	7.5	3.1	1.8	0.5	4.2	0.3	ND(0.2)	ND(0.2)	ND(0.2)	NDR(0.3)	ND(0.1)
1935	4.3	2.4	2.4	1.6	5.4	0.4	ND(0.2)	ND(0.1)	ND(0.1)	0.9	ND(0.1)
1925	7	2.55	2.25	1.4	4.3	0.55	ND(0.2)	ND(0.1)	ND(0.2)	NDR(0.2)	ND(0.1)
1914	5.5	2.9	2.3	1.1	4.2	ND(0.2)	ND(0.2)	ND(0.2)	ND(0.1)	NDR(0.3)	ND(0.1)
1904	4.2	3.5	2.0	1.4	4.7	ND(0.2)	ND(0.2)	ND(0.2)	ND(0.2)	ND(0.2)	ND(0.1)

[a] ND = Not Detected. The value in brackets is the SDL which equals 3 X the maximum peak detected on baseline runs.

[b] NDR = Peak detected but does not meet quanification criteria. The value in brackets is the value determined ignoring quantification criteria.

Figure 36: Distribution of PCDD Class Totals - 1992 Site 1 Core B.
ND values are plotted as their respective SDLs (see Table 15).

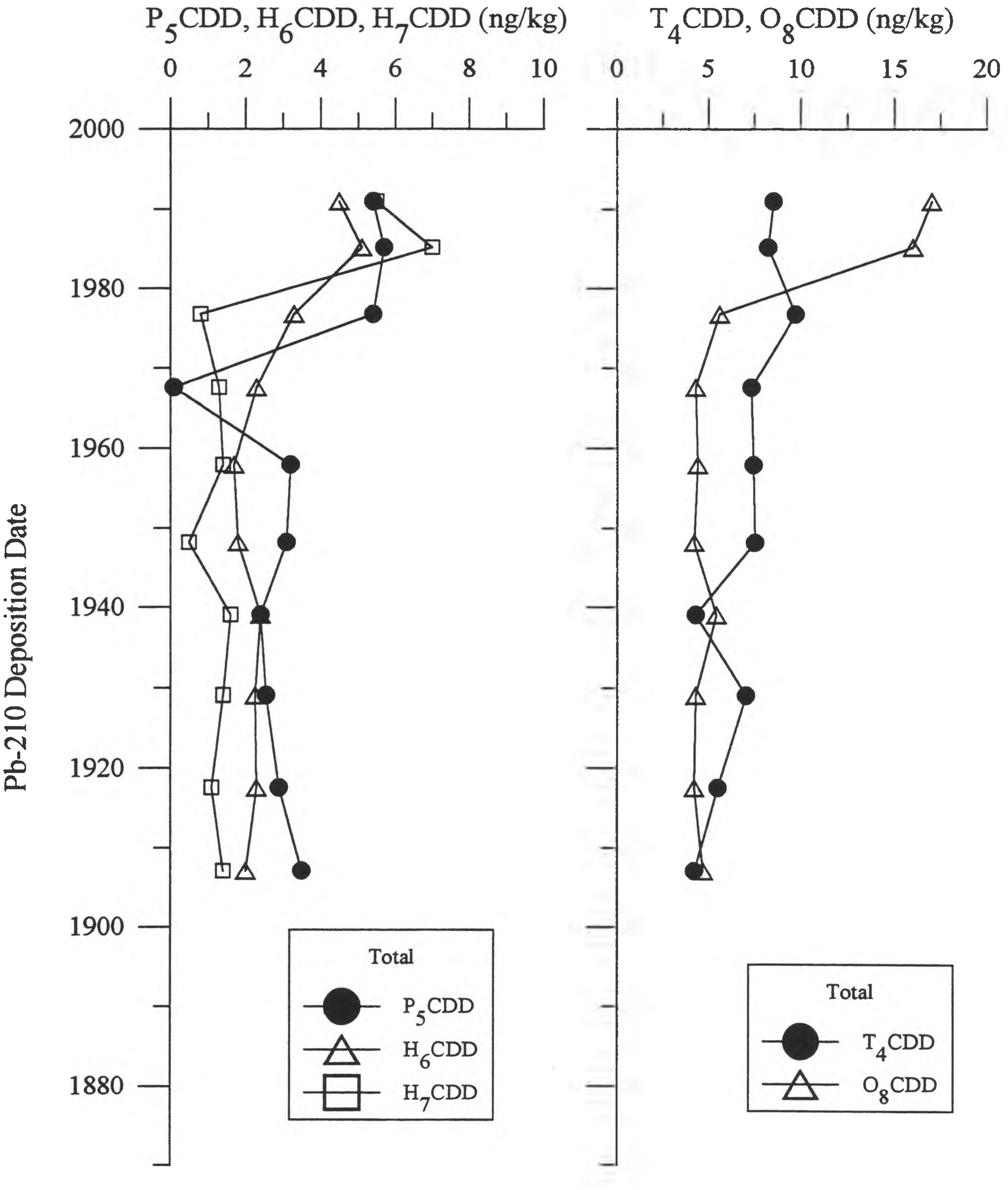
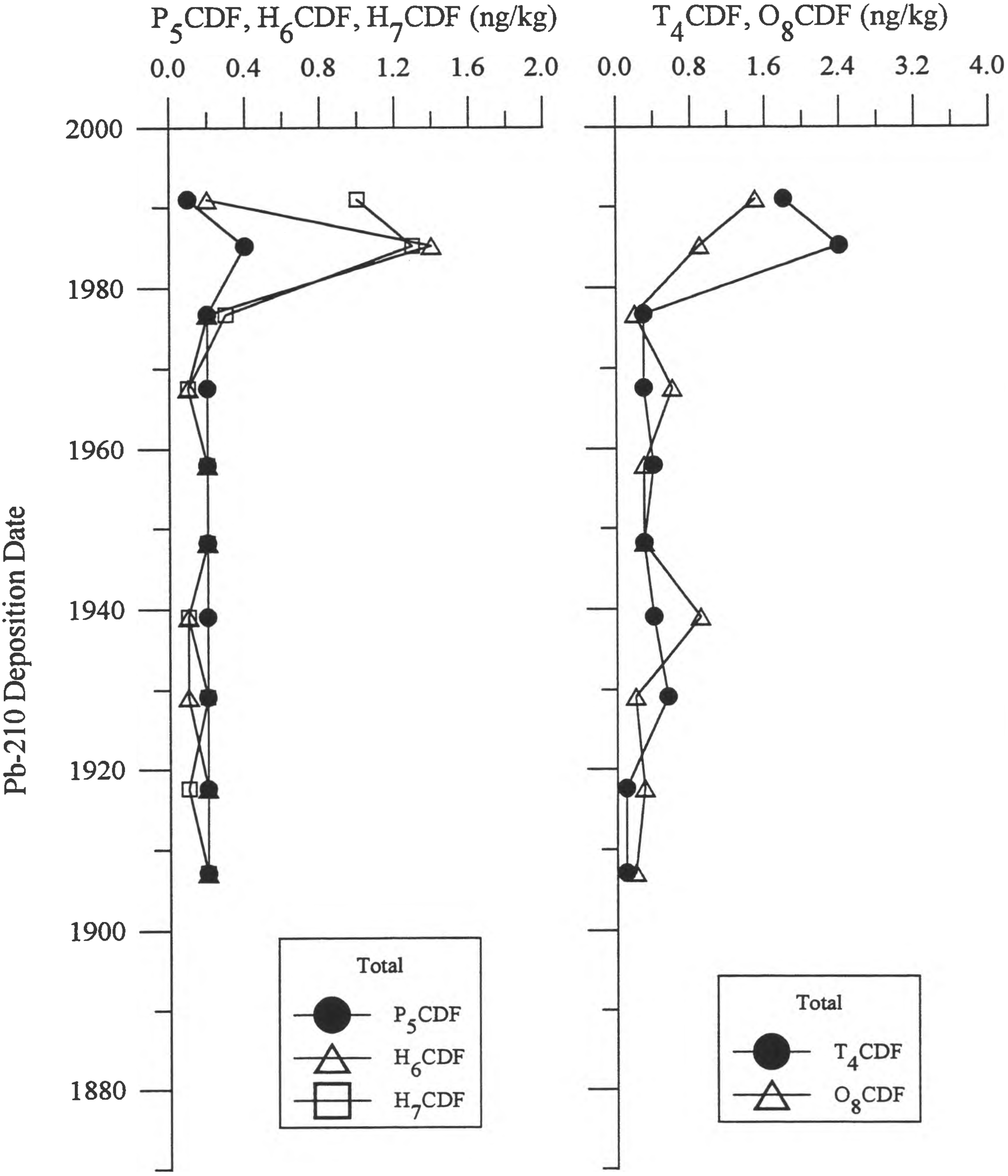


Figure 37: Distribution of PCDF Class Totals - 1992 Site 1 Core B.

ND values are plotted as their respective SDLs (see Table 15).



for As in the central-west basin of Great Slave Lake and suggested that surface enrichment may be related to processing at gold mines on the northern shore. Joshi et al. (1989) found a significant sediment enrichment factor for As at one Langley Bay coring location and they chose As to study as one of four "uranium analogue elements". The surficial data for As (cf Section 4.3) suggests that there may be a source in the eastern part of the lake. A closer look at core data from Site 3 (Figure 38a) reveals that a single high value on top of the core at Site 3 (22 µg/g) is responsible for much of the value presented in Figure 15. The Site 2 core (Figure 38a) exhibits a reverse trend to that of Site 1, namely a progressive increase with depth from 4 to 20 µg/g back to 60 years ago. Therefore an east to west transport is less likely and another source must be invoked to explain higher recent values for As at Site 1 and in the past at Site 2.

5.6 BIOGEOCHEMICAL MARKERS

5.6.1 Hydrocarbons

Every cm of Core D from Site 1 collected in 1992 was analyzed down to 24 cm depth (110 years) for a whole suite of geolipids. This work was part of that performed for the Honours B.A. Thesis of Telford (1993). This high resolution sampling yielded biogeochemical marker and hydrocarbon contaminant data with five year time resolution. In this section the results from total hydrocarbon analyses and alkane derived biogeochemical markers (cf. Section 4.4) are presented.

Figure 40a illustrates the changes in total resolved hydrocarbons and total n-alkanes (n-C15 to n-C35) concentrations over the past 110 years. Also plotted (Figure 40b) is the total unresolved hydrocarbons (termed the "unresolved complex mixture" or UCM by many researchers (cf Meyers and Ishiwatari, 1993; Broman et al., 1987; among others). The UCM is quantified as the area under the resolved peaks and using the internal standard area a concentration is calculated. The components of the UCM are unknown but are likely the "bottoms" of many of the resolved peaks and numerous small peaks which are buried in the "envelope". Crude oils, some oil products, and oil contaminated sediments and other samples frequently contain UCMs. It is so common in contaminated sediments that it has come to be considered an indicator of oil pollution (Volkman et al.., 1992). Note that the UCMs in the present work are likely hydrocarbons, since the more polar classes of lipids have been isolated by the alumina/silica chromatography (see Section 3.6.1).

Generally speaking, n-alkanes account for roughly one half of the total resolved hydrocarbons in the core except during the periods when the total resolved hydrocarbons show increases. In years of peak hydrocarbon values, ca. 1885, 1925, 1935, 1950, 1970 and 1990, the total resolved hydrocarbons increase to a larger extent than the n-alkanes. This suggests that n-alkanes are neither the source of increased total resolved hydrocarbons, nor are they as susceptible to the conditions which are resulting in the increased total resolved hydrocarbons.

Normalizing the total resolved hydrocarbons and total n-alkanes data to TOC is one means of determining the nature of these peaks. Figure 41a shows that both data sets are only slightly dampened by this application, the main peaks are still prominent. If the total resolved hydrocarbons and total n-alkanes had been completely dampened by the normalization to TOC, it would have

Figure 38: Arsenic in 1992 Sites 1, 2 and 3; Pb and Cr in 1992 Site 1 Core B.

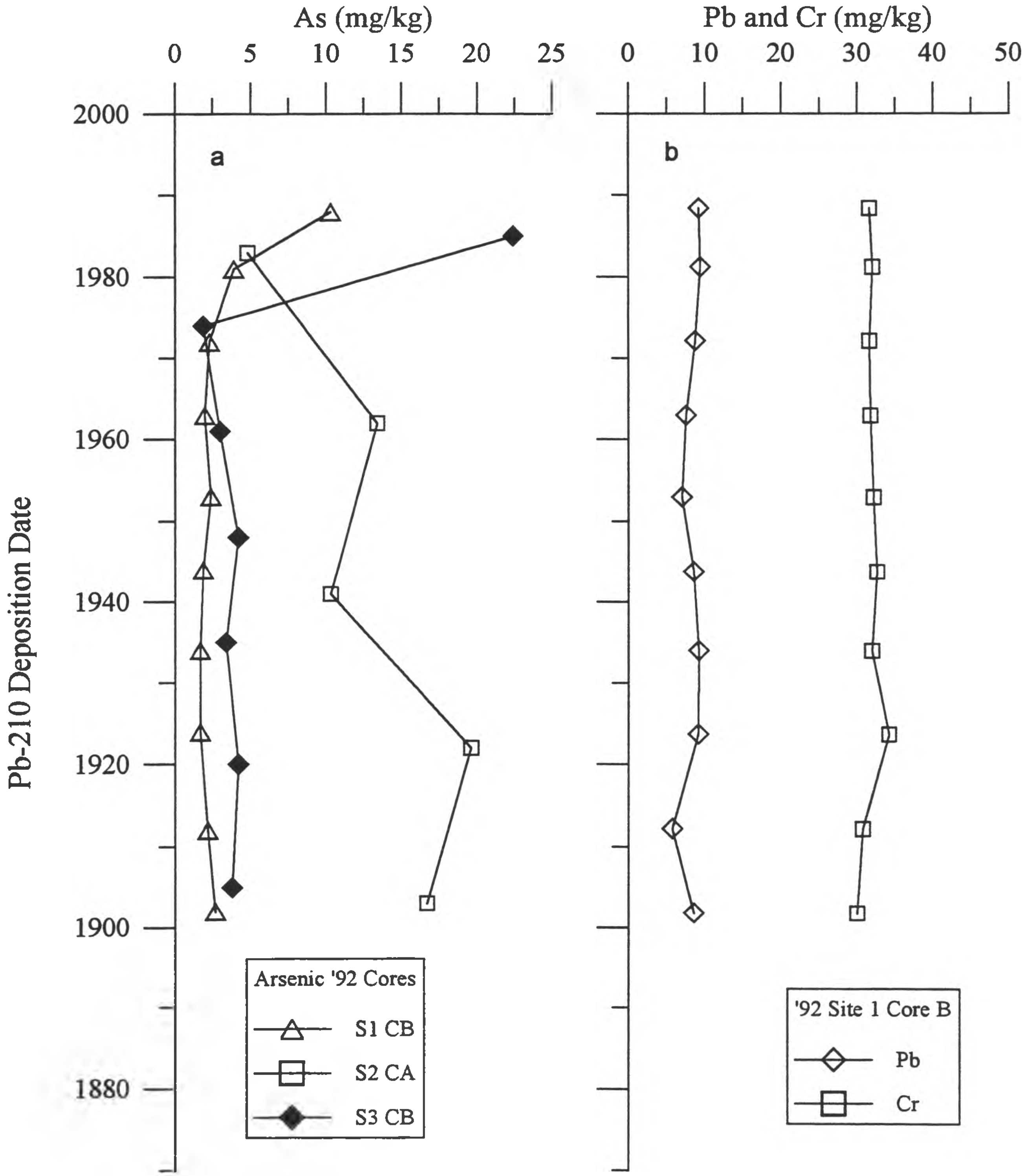


Figure 39: Copper, Vanadium, Zinc and Total Mercury in 1992 Site 1 Core B.

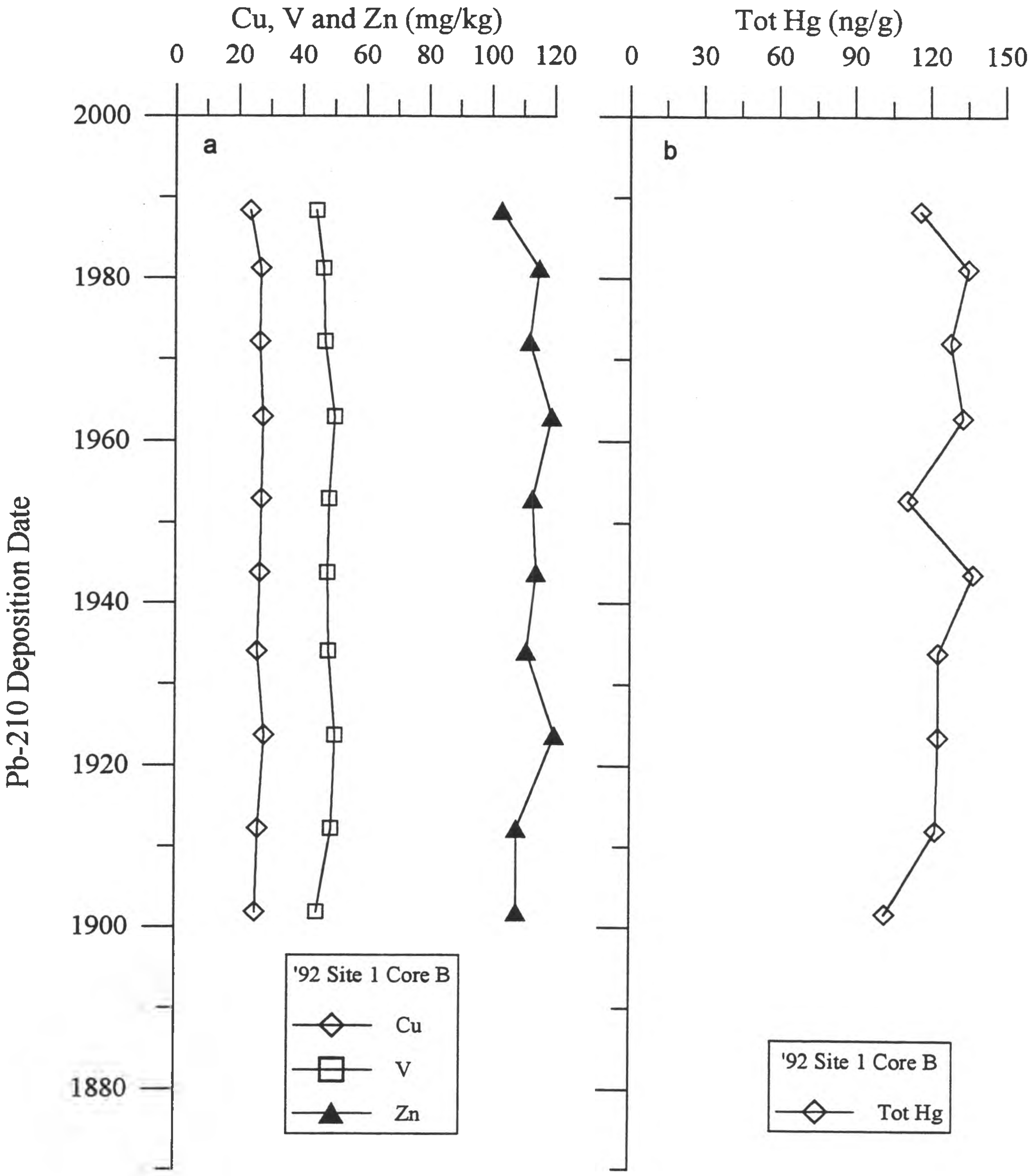


Figure 40: Total Hydrocarbon Fractions for 1992 Site 1 Core D.
Values from GLC-FID, total resolved hydrocarbons and UCM corrected for blank, internal standard and recovery standard; not necessary for sum of individual n-alkanes.

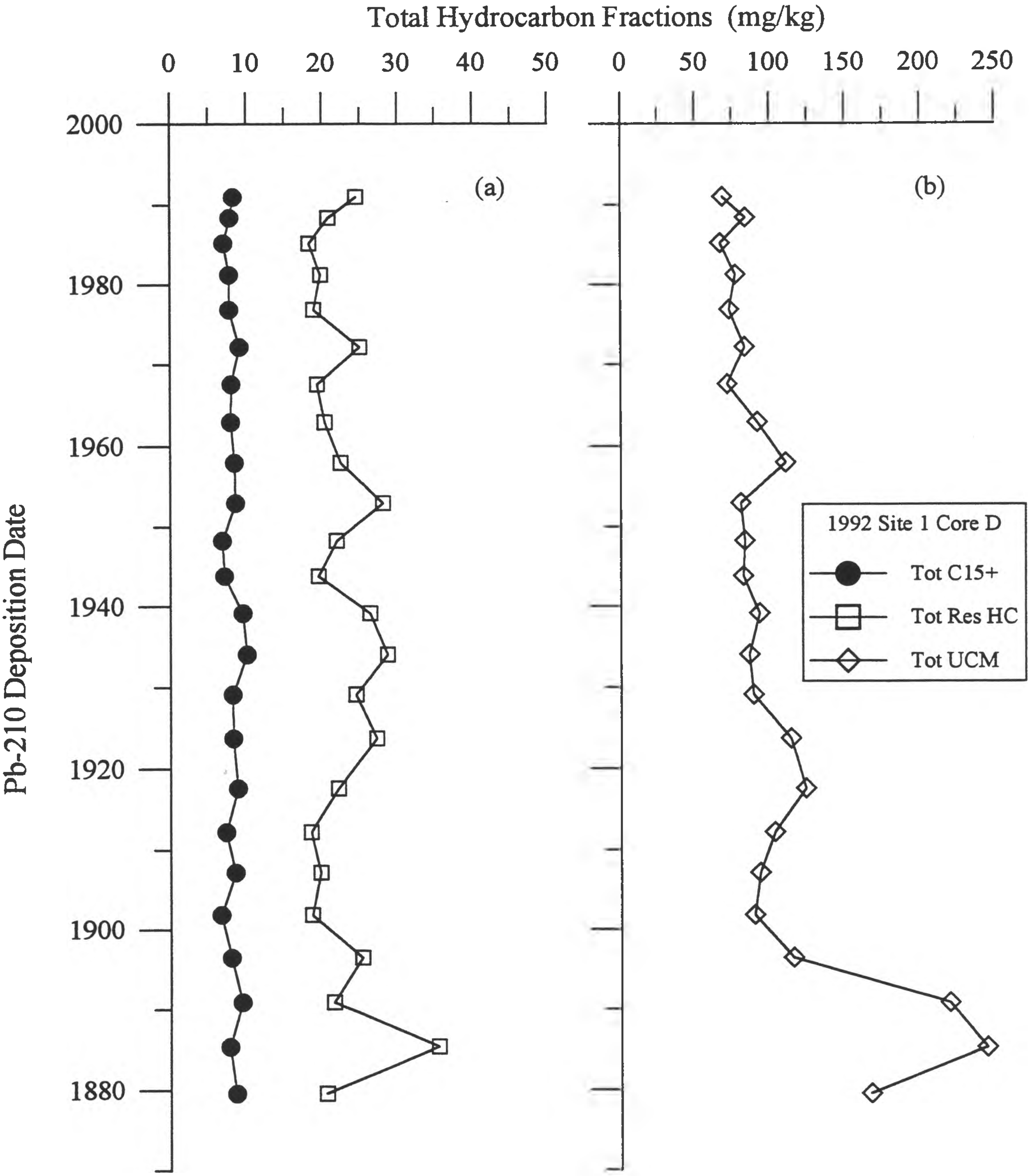
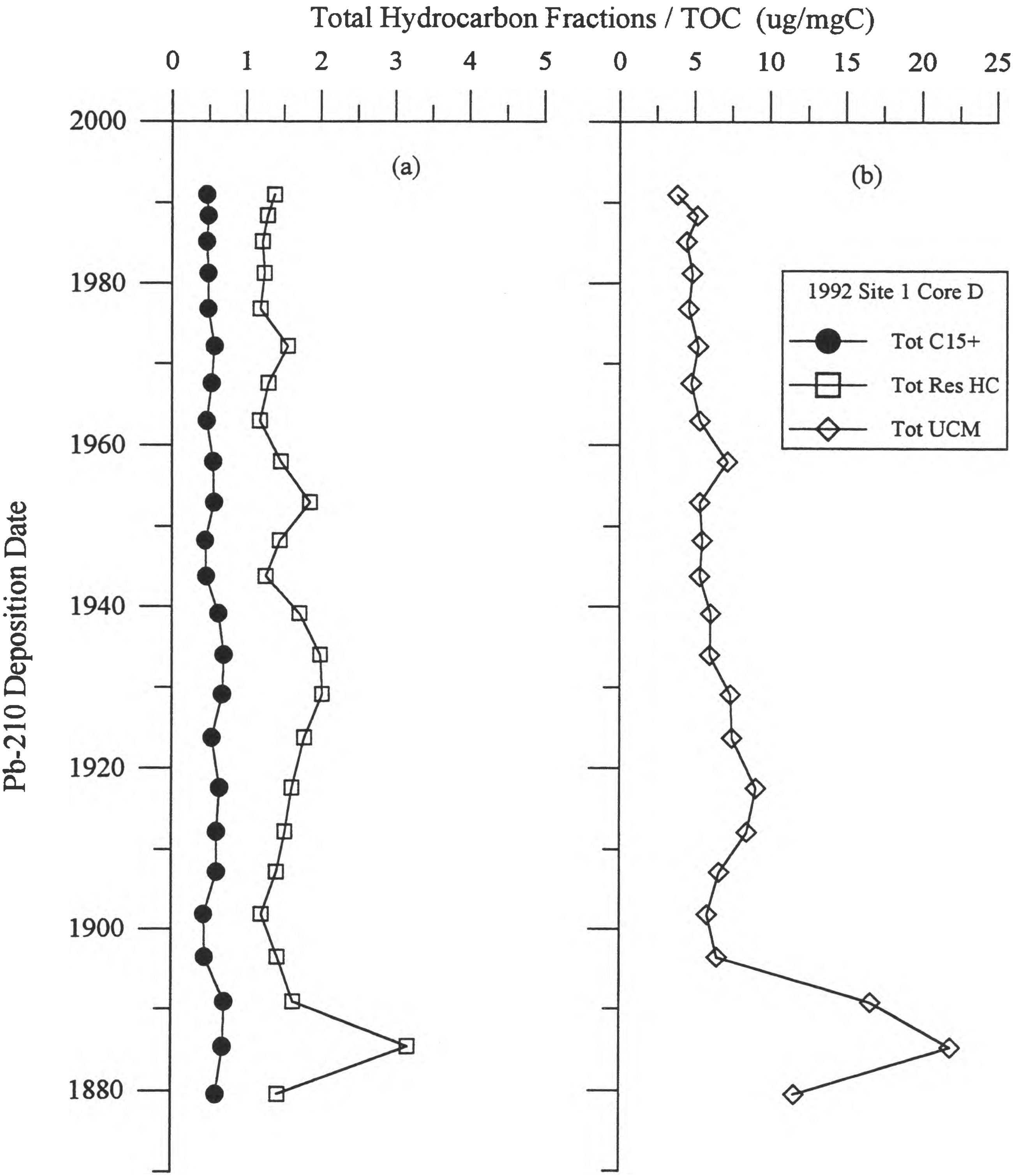


Figure 41: Total Hydrocarbon Fractions Normalized to TOC - 1992 Site 1 Core D. Values from GLC-FID, TOC data reported in Section 5.2 ('92 S1 CC).



meant that the peaks were related to soil action (e.g., increased run-off). However, this did not occurindicating that there is an irregular hydrocarbon cycle operating within Lake Athabasca.

The maximum peak in 1885 is interesting in that it appears in several of the other data results as well. A notable UCM maximum is found in this section (Figure 41b) and for pyrogenic PAHs (Figure 35). A gradual decrease in the amount of UCM is observable in the years following 1885. The source of this possible petroleum contamination/seepage is unclear. With respect to documented anthropogenic activity, there were no major experiments on the Athabasca Oil Sands underway at the time and fuel-powered transportation had yet to be introduced to the area.

The n-alkanes identified ranged from n-C12 to n-C37 with n-C27 and n-C29 dominant. The dominance of n-C27 and n-C29 alkanes indicates that the biomarkers from higher plant matter on land are important to Lake Athabasca's biogeochemical history. Each section also exhibits some degree of odd predominance (CPI > 1.5) indicating that the n-alkanes generally come from natural sources (Figure 42). The increases in CPI observed around 1948 and 1958 indicate a change in n-alkane source or preservation. In general though, the CPI trend is towards decreasing CPI values. This may be the result of the development of industry along the Athabasca River. The CPI has remained at its lowest values since 1960. Work on the oil sands has been underway since the turn of the century especially since the 1920s (Ferguson, 1985) and this may have impacted upon the CPI of the aquatic environment.

The T/A ratio (Figure 42) which is more sensitive to changes in runoff than the other parameters, shows a progressive, although irregular, decrease towards the present. A major increase in terrestrial sources is indicated between 1900 and 1910, which may relate to deforestation and the growth of agriculture. Peaks in the T/A ratio do not correspond to any of the other peaks for total resolved hydrocarbons, UCM or CPI. With respect to the total hydrocarbons and UCM, it may be that an event involving river erosion of the oil sands caused the 1885 peak. Lack of agreement between T/A ratio and CPI is expected and this shows up fairly well in Figure 42. The zone of increased UCM at 1885 is also characterized by an increase in CPI. If this was an oil sands source for the UCM, it's degraded nature prevents it from supplying alkanes.

Pristane and phytane were found in all sections analyzed. As illustrated in Figure 42 the Pris/Phyt ratio has changed very little over the past 100 years. This is as would be expected since depositional environment should not have changed much over that period.

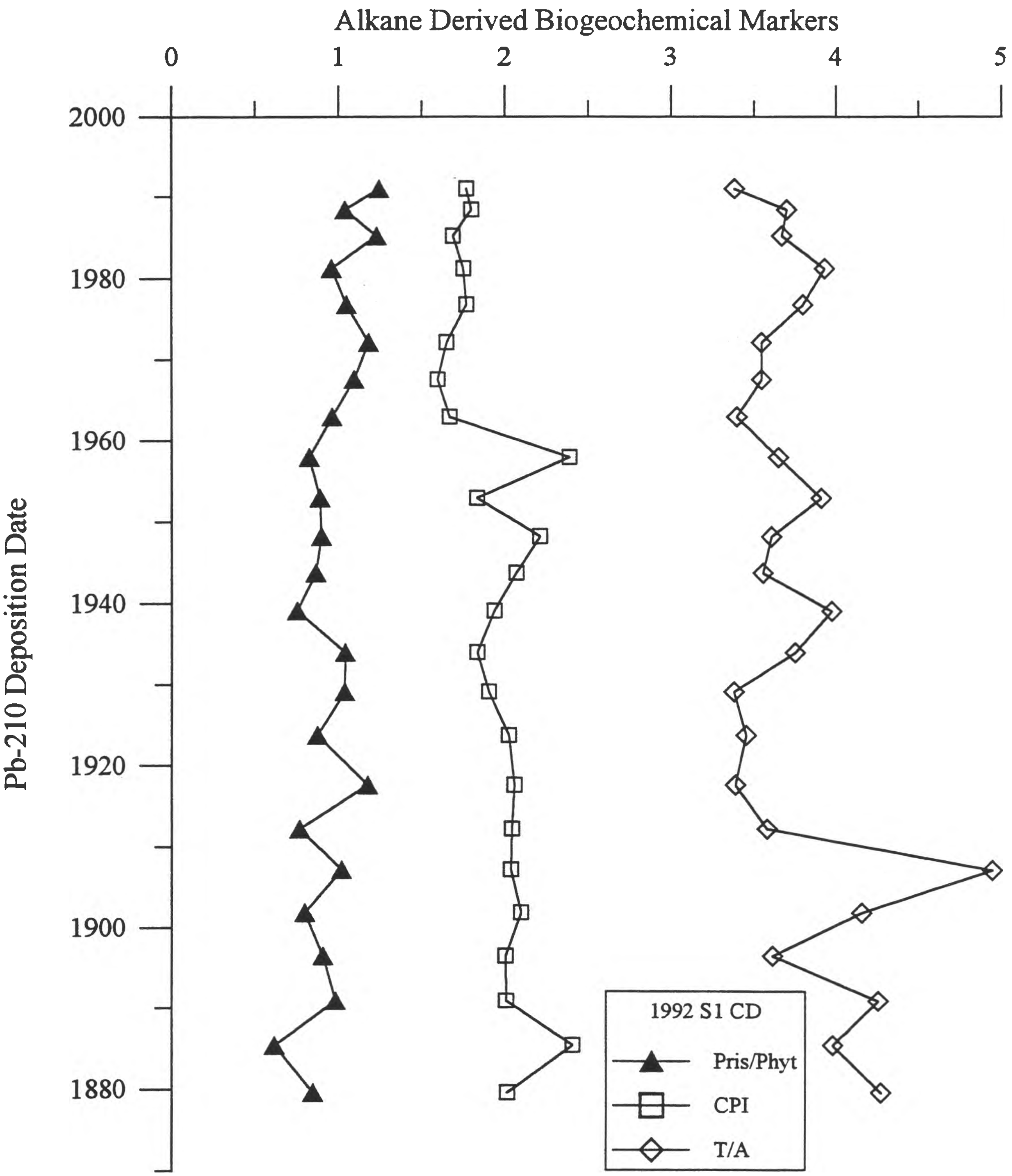
5.6.2 Fatty Acids

5.6.2.1 Terrestrial and Aquatic Source Indicators Like the n-alkane distributions above, the distributions of n-fatty acids with respect to carbon chain length can be used as indicators of original source materials (Meyers and Ishiwatari, 1993). Bourbonniere et al. (1991) defined a T/A ratio for fatty acids similar to that for alkanes:

$$\text{T/A acid ratio} = (\text{n-C24} + \text{n-C26} + \text{n-C28}) / (\text{n-C12} + \text{n-C14} + \text{n-C16})$$

using the fact that fatty acids from terrestrial sources are dominated by longer even chain components

Figure 42: Alkane Derived Biogeochemical Markers for 1992 Site 1 Core D. Ratios derived from individual n-alkane concentrations from GLC-FID runs, no blank corrections necessary.



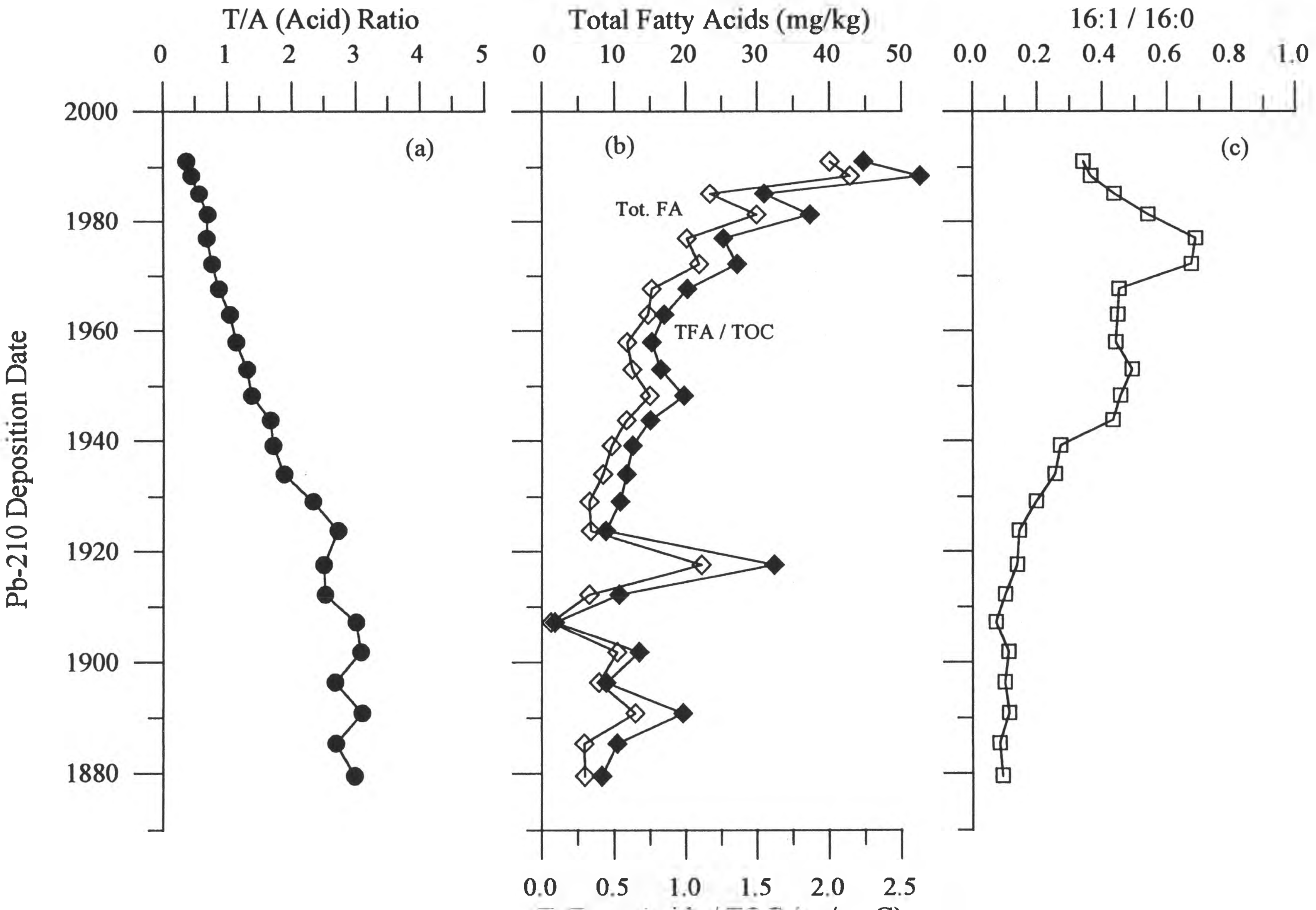
and aquatic sources by shorter even chain components. Data shown in Figure 43a indicate a large decrease in T/A acid ratio since 1920. It is tempting to suggest that increases in productivity have caused these ratios to decrease, but the magnitude of change is about the same as that experienced in Lake Erie since 1930 (Bourbonniere et al., 1991) and Lake Athabasca has not seen the same degree of anthropogenic activity which would supply nutrients to the lake. The progressive decrease downcore for total fatty acids (Figure 43b) is normal for lacustrine sediments and represents the post-depositional biodegradation of these relatively labile compounds. Normalizing to TOC does not dampen the profile at all. The fatty acid source or diagenesis signal is maintained over the relatively constant TOC signal. The large maximum at 1915 and the smaller peaks at 1900 and 1890 are periods when a pulse input of fatty acids came to the lake in a disproportionate amount relative to the bulk organic matter and sediment.

5.6.2.2 Indicators of Postdepositional Microbial Activity Fatty acids are more labile to microbial attack than alkanes and their depth distribution can be an indicator of microbial activity. As well unsaturated fatty acids are more labile than their saturated counterparts. Hexadecanoic acid (n-C16:0) and its monounsaturated analog hexadecenoic acid (n-C16:1) are commonly found in recent sediments in high concentrations. Thus the ratio:

n-C16:1 / n-C16:0

can be also used as an indicator of microbial activity (Bourbonniere et al., 1991; Meyers and Ishiwatari, 1993). In Figure 43c the plot of this ratio for Site 1 Core D shows a slow and somewhat irregular decrease with depth in the anoxic zone of the sediment (below 5 cm). In contrast Lake Erie exhibits a much sharper decrease but it starts from higher values (Bourbonniere et al., 1991). The sharp increasing trend with depth in the oxic zone suggests that C16:1 survives better than C16:0 under oxidizing conditions. Hexadecenoic acid (n-C16:1) has been found to be the most dominant fatty acid in Asterionella formosa, a common diatom species in the Great Lakes (Bourbonniere, 1979). Microbial activity is likely slower on an annual average at this higher latitude, and the lower quantity of labile organic matter to the sediments minimizes the 16:1/16:0 ratio at the outset.

Figure 43: Total Fatty Acids, Normalized and Related Biogeochemical Markers, 1992 Site 1 Core D.
Total resolved fatty acids corrected for blank, normalized to TOC; ratios derived from individual n-fatty acid concentrations by GLC-FID.



6.0 CONCLUSIONS

6.1 SOURCES OF SEDIMENT CONTAMINANTS

The evidence presented in this report demonstrates the complexity of the source mix of organic contaminants to the sediments of Lake Athabasca. Contaminant classes - PCDDs, PCDFs, chlorinated resin acids, and petroleum - which contain components which may have an industrial source are likely contributed mostly from transport down rivers (Peace and Athabasca) from points south and west. PAHs are more likely to come from atmospheric transport since association with fire history is a dominant trend for many of the PAHs identified. The possibility that these pyrogenic PAHs also enter the Lake from terrestrial runoff (after being deposited there from fires) is also likely and cannot be ruled out, nor is it easily separated from direct atmospheric sources. Petroleum related PAHs would likely be borne by the rivers from sources that are industrial or municipal.

The sources of radiation which may pose a threat to health at higher concentrations, with respect to the uranium mining industry, are those isotopes in the uranium series, e.g. ^{238}U, ^{226}Ra, ^{230}Th and ^{210}Pb (Joshi et al., 1989). Even as there is evidence in the core data that several radionuclides have been deposited in increased amounts in the past, the modern trends shown in these cores is a decreasing one. It remains to be seen whether the effect would again be evident if mining and processing activities were to be restarted.

6.2 DEPOSITIONAL HISTORY OF CONTAMINANTS

The downcore distributions of components that are tied to anthropogenic activities, show horizons that begin in the 1960s and 1970s, and give some hint that they are already on the decrease since the 1980s. Such is the case for PCDDs, PCDFs and radionuclides. All three of these classes of contaminants exhibit significant increases over background levels at times which are reasonable considering the multitude of possible sources. Petroleum related contamination, to the extent that it can be inferred by several indirect measures (petroleum related PAHs, CPI, UCM) has occurred over a much more broad time span and its history is characterized by irregular, low amplitude peaks. Such behaviour suggests that petroleum contamination is caused by a multitude of small sources and is overprinted in this area by natural sources of degraded oil leaching from exposed oil sands deposits.

Unfortunately, information about the history of pesticides and other organochlorines is lacking. These contaminants are also indicative of anthropogenic activity, but may have both a runoff source and a large atmospheric source. Chlorinated resin acids should be contributed only from effluents and therefore should be a marker of riverine transport.

6.3 CONTAMINANT LEVELS

Overall the contaminants found in Lake Athabasca sediments were at much lower concentrations than are found in other lakes from more heavily industrialized regions (e.g. the Great Lakes). Sediment contaminant levels give an indication of the amount of impact that has occurred and its temporal characteristics. Its not the concentration found in the sediment that is of concern but what concentration in the water column existed en route to cause the deposition of measurable amounts. To the extent that sediment bound contaminants are available to biological systems, there is potential for food-chain magnification and thus possible threats to human health.

Many parameters measured were low in concentration and near to the detection limits of the methods of analysis used. Such data often show considerable apparent temporal variability usually indicative of the expanded scale used to display them. Often if these parameters are compared to others on comparable scales, then the apparent wide swings dampen somewhat, which can lead to different interpretation of the same results.

The magnitude of modern changes in concentrations of contaminants relative to historical values is sometimes clear, as in the PCDD data, or sometimes diffuse, as in the PAH data. PCDDs exhibit a sharp increase, then a continued source and hints of an apparent decrease. Some PAHs however show profiles which contain many peaks and apparent cyclic behaviour.

6.4 BIOGEOCHEMICAL MARKERS

Biogeochemical marker data and bulk properties yield evidence that there are gradual, and sometimes abrupt changes occurring in the watershed which are indirect results of anthropogenic activity. The magnitude of modern changes is not always greater than some of those in the past. The strong peak in UCM corresponding to 1885, which occurs at the same time as a peak in some pyrogenic PAHs, total resolved hydrocarbons, and a peak in CPI may or may not indicate a petroleum contamination source as is usually the case. In this region however, it may be indicative of a natural phenomenon e.g. increased input of degraded hydrocarbons from oil sands deposits that are eroded along with soil erosion which contains recently biosynthesized hydrocarbons, thus higher CPI. The clear and consistent decreasing trend in T/A acid ratio may be an example of long-term environmental change, in this case likely caused by increased nutrient loadings from multiple sources. These data need to be corroborated so that the effects of post-depositional changes can be either ruled out or corrected.

7.0 RECOMMENDATIONS

7.1 UTILITY OF SEDIMENT DATA

The results described here show that sediments in Lake Athabasca provide a record of some of the changes that have occurred in the Lake Athabasca watershed over the last 100 years. Most of the work has been done on cores from Site 1. From the information we have at hand that site provides the best time resolution, proximity to western sources, etc. and any further work on new contaminant components should be done on the remaining cores from Site 1. However, the experience gained from the radionuclide analyses done here shows that other sites can yield important information. Indeed if determinations of radionuclides had been limited to Site 1, the evidence that radionuclides could have migrated from Langley Bay westward would have been missed altogether. This underscores the necessity to carefully plan sampling strategies with as complete an information base as possible, and where information is lacking, "bracketing" the sampling sites to improve the chances of obtaining the most relevant cores.

7.2 FURTHER WORK ON EXISTING LAKE ATHABASCA CORES

The data collected to date by analysis of sediment cores, provides time series information about some contaminants, but not all of the data are specific to sources of interest to the Northern River Basins Study. Data collected on dioxins and furans, for example, are not specific enough to the pulp and paper industry to be considered complete. The following list explains what further analyses should be done, and why.

- Congener specific analysis of di- and tri- chlorodibenzodioxins and furans should be performed on selected core sections - they have been shown to be more directly relatable to pulp mill effluents.
- Determination of chlorinated resin acids and other resin acids in selected core sections for the same reason as above.
- Determination of alcohol biomarkers to corroborate the fatty acid biomarker work regarding possible nutrient enrichment over the past 70 years.
- Determination of indicators of municipal sewage, like the fecal sterol coprostanol, to track impacts of urban development - (data can be extracted from same results as alcohols).
- Revisit on selected samples with careful control of MDLs, organochlorine analyses for pesticides and PCBs which can yield more information on the extent of contribution of atmospherically transported materials.
- Consider analysis of biomarkers specific for petroleum sources (e.g. hopanes). This may be extractable from existing archived GCMS data, or run on hydrocarbon fractions already used for alkanes. Are there any specific to Athabasca oil sands?
- Consider analyses of biogeochemical markers and PAHs on a Site 2 core, to use the slower sedimentation rate compared to Site 1 for determination of post-depositional degradation rates and downslope transport within Lake Athabasca.

- Look for a more complete record of forest fire history for all of the Athabasca and Peace watersheds to compare with the pyrogenic PAH record. These natural occurrences - or anthropogenic in the case of intentional fires - commonly occur in western Canada. They may be the most important modifier of organic matter in the watersheds and consequently may have a concomitant impact on Lake Athabasca sediments.

7.3 FURTHER ANALYSES ON REFERENCE SITES

Cores were collected from Legend and Weekes Lakes for comparison with Lake Athabasca results. These two remote lakes have no sources of contamination in their watersheds except for those contaminants which are atmospherically transported. Both sites have been successfully dated and bulk parameters determined. Many of the same parameters that were determined on Lake Athabasca cores should also be determined on both of these reference sites cores, such as:

- ^{137}Cs determinations for checking ^{210}Pb geochronology.
- Biogeochemical markers, last 100 years, both lakes.
- PAHs, last 100 years, both lakes.
- Organochlorines - initially three sections bracketing 30 years.
- Resin Acids - initially three sections bracketing 30 years.
- Dioxins/furans di- through octa- chlorinated - initially three sections bracketing 30 years.

Once a complete data set is available for Lake Athabasca and both reference sites, then we should have hard information from which to judge the relative contributions of atmospheric and riverine sources for the appropriate contaminants.

8.0 REFERENCES

Allan, R.J. 1979. Heavy metals in bottom sediments of Great Slave Lake (Canada): A reconnaissance. Environmental Geology 3:49-58.

Allan, R. and T. Jackson. 1978. Heavy metals in bottom sediments of the mainstem Athabasca River system in the AOSERP study area. Alberta Oil Sands Environmental Research Program, Project HY 2.4.

Anderson, R.F., S.L. Schiff and R.H. Hesslein. 1987. Determining sediment accumulation and mixing rates using ^{210}Pb, ^{137}Cs, and other tracers: Problems due to postdepositional mobility or coring artifacts. Canadian Journal of Fisheries and Aquatic Sciences 44(Suppl. 1):231-250.

ARCT Chemtech. 1993. Northern River Basins Study, Radioanalytical Report, Approval Nos. 114 and 115. Calgary, AB. 7pp.

AXYS 1993a. Report to Northern River Basin Study (1992/1993): Analytical Results for the Analysis of Sediment and Water Extract Samples for PCDDs and PCDFs. Sydney, BC.

AXYS 1993b. Report to Northern River Basin Study (1992/1993): Analytical Results for the Analysis of Sediment and Water Extract Samples for Resin Acids. Sydney, BC.

Bjorseth A. and T. Ramdahl. 1985. Sources and Emissions of PAH. Pages 1-20 in A. Bjorseth and T. Ramdahl, eds. Handbook of Polycyclic Aromatic Hydrocarbons, Volume 2, Marcel Dekker, Inc., New York. 411pp.

Blumer, M. 1976. Polycyclic aromatic compounds in nature. Scientific American 234:34- [Information reprinted in Bjorseth and Ramdahl (1985)]

Bourbonniere, R.A. 1979. Geochemistry of humic matter in Holocene great lakes sediments. Ph.D. Thesis. University of Michigan, Ann Arbor, 373pp.

Bourbonniere, R.A., B.L. VanSickle and T. Mayer. 1986. The great lakes sediment bank - I. Lakes Huron and Ontario. NWRI Rpt. No. 86-151. 75pp.

Bourbonniere, R.A., P.A. Meyers, B.J. Eadie and J.A. Robbins. 1991. Environmental and diagenetic effects on geolipid compositions of sediments in Lakes Erie and Ontario. Pages 498-501 in D.A.C. Manning, ed. Organic Geochemistry: Advances and Applications in the Natural Environment. Manchester University Press, Manchester, UK, 662pp.

Bray E.E. and E.D. Evans. 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. Geochimica et Cosmochimica Acta 22: 2-15.

Broman, D., A. Colmsjo, B. Ganning, C. Naf, Y. Zebuhr and C. Ostman. 1987. 'Fingerprinting petroleum hydrocarbons in bottom sediment, plankton and sediment trap collected seston. Marine Pollution Bulletin 18(7):380-388.

Chemex Labs Alberta Inc. 1993, 1994. Data reports to NRBS, LAA # 111, 113 and others, project # 2332-B3 and others. Calgary, AB.

Cranwell, P.A. 1973. Chain-length distribution of n-alkanes from lake sediments in relation to post-glacial environmental change. Freshwater Biology 3:259-265

Duncan, G.A. and G.G. LaHaie. 1979. Size analysis procedures used in the Sedimentology Laboratory. NWRI Hydraulics Div. Manual. September, 1979.

Duncan, G. 1994. Lake Athabasca particle data report. NWRI Rpt. No. RAB-TN-93-51. 64pp.

Eadie, B.J., J.A. Robbins, W.R. Faust and P.F. Landrum. 1991. Polycyclic aromatic hydrocarbons in sediments and pore waters of the lower Great Lakes: Reconstruction of a regional benzo(a)pyrene source function. Pages 171-189 in R.A. Baker, ed. Organic Substances and Sediments in Water. Vol 2. Lewis Publishers, Inc., Chelsea, MI. 535pp.

Eaganhouse, R.P. and R.W. Gossett. 1991. Historical deposition and biogeochemical fate of polycyclic aromatic hydrocarbons in sediments near a major submarine wastewater outfall in southern California. Pages 191-220 in R.A. Baker, ed. Organic Substances and Sediments in Water. Vol 2. Lewis Publishers, Inc., Chelsea, MI. 535pp.

Farmer, J.G. 1978. The determination of sedimentation rates in Lake Ontario using the ^{210}Pb method. Canadian Journal of Earth Sciences 15:431-437.

Ferguson, B.G. 1985. Athabasca Oil Sands - Northern Resource Exploration, 1875-1951. Alberta Culture/Canadian Plains Research Centre. 283pp.

Flett Research Ltd. 1993. Project 2332-B4 - Lake Athabasca Cores - Cs-137 Analysis. Winnipeg, Man. 9pp.

Folk, R.L. 1974. Petrology of Sedimentary Rocks. Hemphill Publ. Co., Austin, TX. 182pp.

Gschwend, P.M. and R.A. Hites. 1981. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. Geochimica et Cosmochimica Acta. 45:2359-2367.

Hunt, J.M. 1979. Petroleum Geochemistry and Geology. W.H. Freeman & Co., San Francisco, CA. 615pp.

Joshi, S.R., D.T. Waite and R.F. Platford. 1989. Vertical distribution of uranium mill tailings contaminants in Langley Bay, Lake Athabasca sediments. Science of the Total Environment 87/88:85-104.

Kemp, A.L.W. and A. Mudrochova. 1973. The distribution and nature of amino acids and other nitrogen-containing compounds in Lake Ontario surface sediments. Geochimica et Cosmochimica Acta 37:2191-2206.

Larsen, C.P.S. 1989. A fire history analysis of Wood Buffalo National Park. Report to Canadian Parks Service, Environment Canada, Winnipeg, Man. 84pp.

Leenheer, M.J, K.D. Flessland and P.A. Meyers. 1984. Comparison of lipid character of sediments from the Great Lakes and the Northern Atlantic. Organic Geochemistry 7:141-150.

Mahood, H. W. and I. H. Rogers. 1975. Separation of resin acids from fatty acids in relation to environmental studies. Journal of Chromatography 109: 281-286.

Matsumoto, E. 1975. ^{210}Pb geochronology of sediments from Lake Shinji. Geochemical Journal 9:167-172.

Mawhinney M.R. and C. Bisutti. 1987. Common corers and grab samplers operating manual available through technical operations. N.W.R.I. Technical Note Rev.3.87. 33pp.

McElroy A.E., J.W. Farrington and J.M. Teal. 1989. Bioavailability of polycyclic aromatic hydrocarbons in the aquatic environment. Pages 1-39 in U. Varanasi, ed. Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. CRC Press Inc., Boca Raton, FL.

Meyers, P.A. and R. Ishiwatari. 1993. Lacustrine organic geochemistry - an overview of indicators of organic matter sources and diagenesis in lake sediments. Organic Geochemistry 20(7):867-900.

Mitchell P. and E. Prepas (Eds.). 1990. Lake Athabasca. Pages 63-72 in Atlas of Alberta Lakes. University of Alberta Press, Edmonton. xxx pp.

Morales, A., D. A. Birkholz, and S. E. Hrudey. 1992. Analysis of pulp mill effluent contaminants in water, sediment, and fish bile - fatty and resin acids. Water Environment Research 64 (5): 660-668.

Ramdahl, T. 1985. PAH emissions from combustion of biomass. Pages 61-85 in A. Bjorseth and T. Ramdahl, eds. Handbook of Polycyclic Aromatic Hydrocarbons. Volume 2, Marcel Dekker, Inc., New York. 411pp.

Rawson D.S. 1947. Lake Athabasca. Bulletin of the Fisheries Research Board of Canada 72:69-85.

Robbins, J.A. 1978. Geochemical and geophysical applications of radioactive lead. Pages 285-393 in J.O. Nriagu, ed. The Biogeochemistry of Lead in the Environment. Elsevier/North Holland, Amsterdam.

Robbins, J.A. and D.N. Edgington. 1975. Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. Geochimica et Cosmochimica Acta 39:285-304.

Safe, S. and O. Hutzinger. 1990. PCDDs and PCDFs: Sources and environmental impact. Pages 1-20 in S. Safe and O. Hutzinger, ed.s Polychlorinated Dibenzo-p-dioxins and -furans (PCDDs/PCDFs): Sources and Environmental Impact, Epidemiology, Mechanisms of Action, Health Risks. Springer-Verlag, Heidelberg, FRG. 145 pp.

Schelske, CV.L., J.A. Robbins, W.D. Gardner, D.J. Conley and R.A. Bourbonniere. 1988. Sediment record of biogeochemical responses to anthropogenic perturbations of nutrient cycles in Lake Ontario. Canadian Journal of Fisheries and Aquatic Sciences 45(7):1291-1303.

Telford, S.L. 1993. The biogeochemical history of a site in Lake Athabasca, northern Alberta. Bachelor Arts and Science Honours Thesis. McMaster University, Hamilton, ON.

Thomas, R.L., A.L.W. Kemp and C.F.M. Lewis. 1973. The surficial sediments of Lake Huron. Canadian Journal of Earth Sciences 10:226-271.

Tissot, B.P. and D.H. Welte. 1978. Petroleum Formation and Occurrence. Springer-Verlag, Berlin. 538pp.

Turner, L.J. 1990. Laboratory determination of ^{210}Pb-^{210}Po using alpha spectrometry. Second Edition. NWRI Tech. Note LRB-90-TN-07. 63pp.

Turner, L.J. 1993a. ^{210}Pb dating of lacustrine sediments from Lake Athabasca (Core 038, Station 1-C; Core 039, Station 2-C; and Core 040, Station 3-A). NWRI Tech. Note RAB-92-12 (Rev. 5/93). 31pp.

Turner, L.J. 19946. ^{210}Pb dating of lacustrine sediments from Lake Athabasca (Core 046, Station 93S1B), Alberta. NWRI Tech. Note RAB-93-21. 17pp.

Volkman, J.K., D.G. Holdsworth, G.P. Neill and H.J. Bavor Jr. 1992. Identification of natural anthropogenic and petroleum hydrocarbons in aquatic sediments. The Science of the Total Environment 112:203-219.

Waite, D.T., S.R. Joshi and H. Sommerstad 1988. The effect of uranium mine tailings on radionuclide concentrations in Langley Bay, Saskatchewan, Canada. Archives of Environmental Contamination and Toxicology 17:373-380.

Waite, D.T., S.R. Joshi and H. Sommerstad 1989. Movement of dissolved radionuclides from submerged uranium mine tailings into the surface water of Langley Bay, Saskatchewan, Canada. Archives of Environmental Contamination and Toxicology 18:881-887.

Walden, C. C., and T. E. Howard. 1981. Toxicity of pulp and paper mill effluents. A review. Pulp and Paper Canada 82:115.

APPENDIX A: TERMS OF REFERENCE

A.1 Project 2332-A1

NORTHERN RIVER BASINS STUDY

SCHEDULE OF TERMS OF REFERENCE

PHYSIO-CHEMICAL ANALYSIS OF LAKE ATHABASCA SEDIMENT

PROJECT 2332-A1

GENERAL OBJECTIVES

From the archive of cores and surficial sediment collected from Lake Athabasca in March, 1992 define the depositional history of sediment-bound contaminants. The history of natural changes and contamination events will be recorded in sediments collected from depositional zones. Their study could lead to an understanding of recent trends in industrial and atmospheric contamination, a comparison of modern contaminant deposition with the magnitude of past events, a comparison of the relative magnitude of natural vs. Anthropogenic changes in the basin, and an indication of how changes in the hydraulic regime can influence the distribution of sediment-bound contaminants.

Some of the questions which require answers in order to fulfil the general objectives:

1. Is there evidence of sediment-bound contamination on the fine-grained surficial samples collected under ice from the shallow western part of the lake? Results of analyses from these samples will assist in setting up future parameter lists for sediment analyses. These results will link to the planning of work in the perched basins.

2. Which of the sites in the depositional basins sampled represents the best opportunity to answer the concerns which appear in the initial paragraph above? Is more, or a different type of sampling required? How much effort should be put into obtaining additional samples fro these sites or other sites? How? When? Where? Is there sufficient reason to continue with analyses of the core samples collected?

3. On cores form site(s) selected above analyse bulk physical and chemical parameters to determine overall sedimentological trends. Have any major changes occurred which may be correlated to settlement and development in the basin? Such results could assist in focusing further work on these cores.

4. Analyses of selected cores for sediment-bound contaminants should proceed after results are known from scans of surficial sediments. Are trends in industry specific contamination evident in the cores? Is it possible to distinguish between atmospheric and upstream sources of these contaminants?

5. Analyses of selected cores for natural components which indicate changes in the basin. Is there evidence of land use changes and nutrient status recorded in the cores? How does the magnitude of these changes compare with those brought about by contamination? Are there combined effects of contamination and natural changes which are of special concern?

To a certain extent this study can be viewed as providing a baseline condition since surficial sediment reflects present conditions. The determinations that will be done on downcore samples can assist in setting realistic goals based on past conditions which represent natural and anthropogenic causes.

REQUIREMENTS

To make best use of resources available the analysis of the sediment collected from Lake Athabasca will be approached in an iterative manner. The furtherance of each step will depend on interpretation of the results of analyses form previous steps. Decisions to proceed are to be based upon sound theory and practices backed up by scientific advice available from experts and the published literature.

1) Statement of tasks

listed below are some suggested tasks which should be undertaken in the order given. This is a logical and cost-effective means of determining the history of contamination of the basin as recorded in Lake Athabasca sediments. Numbers in square brackets indicate which of the sets of questions above is addressed by the particular task. In parentheses is information on the possible provider for the required work. QA/QC is assumed to be part of all tasks.

A) Geochronology - I [2]

Radiodating of one core form each of the three sites by the ^{210}Pb method (up to 144 core sections to analyse).

(NWRI can supply these through a no additional cost amendment to the collection contract by reallocating the unused portion of helicopter support.)

B) Geochronology - II [2]

Radiodating of 1-3 cores from A by the ^{137}Cs method as a check on ^{210}Pb and to better define the most recent deposition (48-144 core sections to analyse).

(Private or university lab.)

C) Contaminant Scan [1]

Broad scans on 5-10 fine-grained surficial sediments collected from the shallow western part of Lake Athabasca off the delta. Parameter list should include organochlorines (pesticides and industrial sources), chlorophenolics, hydrocarbons, selected metals, dioxins and furans (on three samples initially).

(Private lab certified for sediment analyses.)

D) Bulk sediment parameters [2,3]

Determination of bulk physical and chemical parameters on the core chosen as "best" from the results of geochronology as well as on the surficial sediments from C above (up to 48 core sections).

(Total organic carbon, inorganic carbon, and total nitrogen will be done by NWRI on subsamples from the ^{210}Pb core selected as "best" - no charge to study. Grain size and mineralogy through private, government or university lab.)

E) Lake history - I [3,4]

Paleolimnological study of the "best" site using biogeochemical markers (geolipids) to document natural and development related changes in the basin (up to 48 core sections).

(Thesis work by S. Telford to be done at NWRI - no charge to the study.)

F) Lake history - II [3,4]

Other appropriate paleolimnological parameters (e.g., diatoms, pollen) for corroboration of results in E and for discernment of other trends not determined by biogeochemical markers (up to 48 core sections).

(Private, government or university lab.)

G) Contaminant history [4]

Downcore analyses for sediment-bound contaminants selected from results of C and knowledge of industrial development in the basin and parameters normally associated with atmospheric sources. Cores and sections selected from results of A, B, E and F (up to 48 core sections).

(Private lab certified for sediment analyses.)

H) Interpretive report

A comprehensive report which combines and correlates the results of all of the tasks A-G, and makes recommendations of how such results have a bearing on basin management decisions. The report should also recommend if further sampling is required (e.g. Great Slave Lake) and/or further analyses.

(Recognized sediment expert(s).)

2) Variables and parameters to be studied

Generally the parameters required are include in the brief task descriptions above. Contaminants to be analysed are pretty much the same as for other sediment and water studies.

3) Timing

The overall time frame for tasks A-H is approximately one year. Suggested time slots for each task are:

A: Geochronology I - 01/04/92 - 15/05/92
B: Geochronology II - 15/05/92 - 15/06/92
C: Contaminant Scan - 01/04/92 - 15/05/92
D: Bulk sediment parameters - 15/05/92 - 15/07/92
E: Lake history I - 01/07/92 - 15/12/92
F: Lake history II - 01/07/92 - 15/12/92
G: Contaminant history - 01/07/92 - 15/12/92
H: The assignment of the contractor(s) for this task should be done by 01/09/92, and all other task providers should be directed to provide them finalized information in a timely manner. The contractor(s) should be in a position to recommend any additional coring on by 15 Dec 1992, so that there is time to mobilize a crew for March/April 1993 sampling on a stable ice platform. The final report on Lake Athabasca should be finished by 31 Mar 1993.

4) Quality Assurance

All providers of analyses for the Lake Athabasca core samples will be expected to follow the standard QA/QC protocols developed for and approved by the Study Board. In the absence of a standard for the parameter measured all providers will be expected to document their own QA/QC procedures as part of the terms of reference for their contract. Blind replicates and standards should be added to the sample sets submitted for analysis by contractors.

5) Reporting

All of the tasks (A - H) described above require some kind of written report to be submitted. In each case the providers are expected to submit a draft report within two weeks of the deadline stated under “timing”. Comments will be returned to each provider within one week, and the provider must submit a final report within two weeks of the final date under “timing”. Each task requires a report of different calibre:

Data reports only: Tasks C and D
Data reports with minor interpretation: Tasks A, B. And G
Data and significant interpretation: Tasks E and F
Comprehensive interpretive report: Task H

All providers are expected to document all of their procedures and if requested copies of raw data (chromatograms, etc.) May be required.

Prepared by R. A. Bourbonniere
March 19, 1992

A.2 Project 2332-B1

NORTHERN RIVER BASINS STUDY

Project Information Sheet

PROJECT 233	LAKE ATHABASCA SEDIMENT CORES
SUB-PROJECT 2332	PHYSICO-CHEMICAL ANALYSIS.

Purpose

From the archive of cores and surficial sediment collected in March, 1992 define the depositional history of sediment-bound contaminants, including those which have an atmospheric source or an upstream source.

Rationale

The history of natural changes and contamination events will be recorded in sediments collected from depositional zones. Their study could lead to an understanding of recent trends in industrial and atmospheric contamination, a comparison of modern contaminant deposition with the magnitude of past events, a comparison of the relative magnitude of natural vs. anthropogenic changes in the basin, and an indication of how changes in the hydraulic regime can influence the distribution of sediment-bound contaminants.

Technical Background

Sediment cores were collected in March, 1992 from three depositional sites on Lake Athabasca along with fine grained surficial sediments from the shallow western part of the lake. Depositional history of sediment-bound contaminants can be inferred from these cores with a carefully designed analytical program. The requirement for analyses is varied and will involve a number of experts and specialized laboratories over a one year period. The work will progress in an iterative manner to insure that interpretation will be based on the highest quality information and that only necessary determinations are undertaken.

Proposed Work

The year-long work schedule is divided into eight tasks which must be undertaken in the order given.

A: Geochronology I - ^{210}Pb dating of three cores
B: Geochronology II - ^{137}Cs dating of 1-3 cores
C: Contaminant scan - Surficial sediments
D: Bulk sediment parameters - one core
E: Lake history I - Biogeochemical markers on one core
F: Lake history II - Paleolimnological parameters on one core
G: Contaminant history - Result-directed contaminant analyses on one core
H: Interpretive report - Comprehensive synthesis of all results with implications regading basin management decision making and further work required.

Subsequent steps

At this time no subsequent work should be planned until the fall of 1992 when preliminary interpratation of the Lake Athabasca sediment data in available from task H. At that time it may be appropriate to consider additional coring in the basin (e.g. Great Slave Lake, especially on the Slave River delta, additional cores or sites on Lake Athabasca or on the Peace-Athaasca delta, outside "control" lake for atmospheric input).

A.3 Project 2332-C1

NORTHERN RIVER BASINS STUDY

TERMS OF REFERENCE

Project 2332-C1: Lake Athabasca Sediment Cores - Geochronology, Bulk Properties and Biogeochemical Markers

I. Introduction

In March 1992, deep sediment cores were sampled from three sites in Lake Athabasca and surficial sediments were sampled from ten sites at the west end of the Lake. In March 1993, an additional deep sediment core was collected from northeast of Burntwood Island. The purpose of this contract is to complete bulk parameter and biogeochemical marker determinations on the samples collected in 1992, as well as ageing the cores collected in March 1993 can be analyzed for contaminants. The results of this work and that carried out in 1992 must then be synthesized and reported on. In addition data from this work is to be placed into an electronic database and analyzed for trends.

II. Requirements

1) Sediment preparation, geochronology and bulk properties of the Site 1 cores collected in March 1993. Work is to include:
    - Freeze-drying, sediment preparation and density (1 core);
    - Pb^{210} dating (1 core);
    - TOC, TIC and TN (2 cores, '92 & '93)
    - Grain Size (1 core).

2) Compilation of an electronic database (dBase IV and/or Quattro Pro format) and preliminary data analysis (graphing) of the results already received from the various laboratories for the March 1992 surficial and core samples. This is to include data on bulk parameters, radionuclides, organic contaminants, metals and biogeochemical markers. This work is to be coordinated with the overall database construction being carried out by the NRBS Study Office.

3) Carry out additional biogeochemical marker work from Site 1, Core D. This is to include fatty acid, alcohol and sterol biomarkers.

III. Reporting Requirements

1) Prepare a report on the collection and description of the sediment cores collected from Lake Athabasca during 1992 and 1993 by August 1st, 1993.

2) Prepare a report on the geochronology and bulk parameters of the 1992 and 1993 sediment cores by October 15th, 1993.

3) Prepare a report or submit a preliminary draft of a journal article that outlines biogeochemical marker data and incorporates literature on fires and other changes in the basin over the past 100 years. The report is to be submitted to the Component Coordinator by November 15th, 1993.

4) Prepare a summary report that makes recommendations regarding additional contaminant and/or paleoecological work that will enable a better understanding of the depositional history of contaminants in the basin. The report is to be submitted to the Component Coordinator by December 1st, 1993.

5) All existing and new data generated through this contract are to be submitted in a form (dBase IV and/or Quattro Pro) which is similar to compatible databases being developed by the NRBS Study Office. Specifications for such a database are to be provided to the contractor by the Component Coordinator.

IV. Project Administration

The Component Coordinator for this contract will be Greg Wagner, Northern River Basins Study, 690 Standard Life Centre, 10405 Jasper Avenue, Edmonton, Alberta T5J 3N4 (phone: (403) 427-1742, fax: (403) 427-3055).

APPENDIX B: DESCRIPTION OF SEDIMENT SAMPLES

SURFICIAL SEDIMENT DESCRIPTIONS

All surficial samples were taken with Ekman sampler.

Site: A **Date of Collection:** 09-03-92
Location (d-m-s): lat. 58 42 06, long. 110 50 24
Depth: 2.5 m **No. of samples:** 4
Description: very fine sediment/mud, grabbing approximately the top 5 cm of surficial sediments

Site: B **Date of Collection:** 09-03-92
Location (d-m-s): lat. 58 44 12, long. 110 46 00
Depth: 3 m **No. of samples:** 4
Description: very fine sediment/mud, grabbing approximately the top 5 cm of surficial sediments

Site: C **Date of Collection:** 09-03-92
Location (d-m-s): lat. 58 46 48, long. 110 48 45
Depth: 3 m **No. of samples:** 4
Description: very fine sediment/mud, grabbing approximately the top 5 cm of surficial sediments

Site: D **Date of Collection:** 09-03-92
Location (d-m-s): lat. 58 48 30, long. 110 48 36
Depth: 3 m **No. of samples:** 4
Description: very fine sediment/mud, grabbing approximately the top 5 cm of surficial sediments

Site: E **Date of Collection:** 09-03-92
Location (d-m-s): lat. 58 47 00, long. 110 53 30
Depth: 2.5 m **No. of samples:** 4
Description: very fine sediment/mud, grabbing approximately the top 5 cm of surficial sediments

Site: F **Date of Collection:** 09-03-92
Location (d-m-s): lat. 58 44 24, long. 110 56 54
Depth: 2.5 m **No. of samples:** 4
Description: very fine sediment/mud, grabbing approximately the top 5 cm of surficial sediments

Site: G **Date of Collection:** 09-03-92
Location (d-m-s): lat. 58 40 24, long. 111 02 48
Depth: 1.5 m **No. of samples:** 6
Description: very fine sediment/mud, grabbing approximately the top 5 cm of surficial sediments, lots of vegetative material in samples

Site: H **Date of Collection:** 10-03-92
Location (d-m-s): lat. 58 56 24, long. 110 27 48
Depth: 6 m **No. of samples:** 4
Description: very fine sediment/mud, grabbing approximately the top 5 cm of surficial sediments

Site: I **Date of Collection:** 10-03-92
Location (d-m-s): lat. 59 02 43, long. 110 13 23
Depth: 12 m **No. of samples:** 4
Description: very fine sediment/mud, grabbing approximately the top 5 cm of surficial sediments

CORE SEDIMENT DESCRIPTIONS -92 SAMPLES

Site: Site 1, Core B **Date of Collection:** 10-03-92
Location (d-m-s): lat. 59 02 43, long. 110 13 23
ID: 6.5 cm **Total Length:** 42 cm
Extruded and Described by:
Date of Extrusion: 10-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

Notes: The core was divided into 1 cm samples for sections 0-1 cm through 23-24 cm. Subsequent sectioning was completed at 2 cm intervals (hence, 24-26 through 40-42 cm). Recorded descriptions of this core have not been found.

Site: Site 1, Core C **Date of Collection:** 11-03-92
Location (d-m-s): lat. 59 02 43, long. 110 13 23
ID: 10.1 cm **Total Length:** 80
Extruded and Described by: Rick Bourbonniere
Date of Extrusion: 12-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

Notes: Core C was extruded on March 12, 1992 off-site at the garage. It has approximately 4-5 cm of brown fluid sediment in the top layers and then turns to gray.
The length of the core from its top to the bottom of the bung is 85 cm. When the extrusion was completed at 80 cm, less than 1 cm of the core remained above the bung.

UpD	LwD	Colour	Other Comments After Sectioning
0	1	brown with some gray pieces on one side	very wet and fluid; about 20 % of sample was lost during sectioning
1	2	brown with some gray	wet and fluid
2	3	brown	wet and fluid
3	4	brown	wet and fluid
4	5	brown	wet, though somewhat consolidated
5	6	brown with gray in the centre	wet and somewhat consolidated
6	7	mostly gray with some brown	somewhat consolidated
7	8	mostly gray	somewhat consolidated
8	9	gray with a small amount of black lamination	somewhat consolidated
9 thru 20	10 21	gray with considerable black lamination	somewhat consolidated
21	22	gray with considerable black lamination, there is a black chunk 4 to 5 mm in diameter which looks like cinder	somewhat consolidated
22 thru 26	23 28	gray with considerable black lamination	somewhat consolidated

28	30	gray with considerable black lamination	somewhat consolidated; capped off for 2 hours before sectioning continued
30	32	gray with considerable black lamination	somewhat consolidated
32	34	gray with considerable black lamination	somewhat consolidated; top 1 mm oxidized (black streaks faded)
34 thru 64	36 66	gray with considerable black lamination	somewhat consolidated
66 thru 78	68 80	gray with considerable black lamination	somewhat gelatinous

Site: Site 1, Core D **Date of Collection:** 11-03-92
Location (d-m-s): lat. 59 02 43, long. 110 13 23
ID: 10.1 cm **Total Length:**
Extruded and Described by:
Date of Extrusion: 12-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

SITE 1 - CORE D (cm)

GENERAL OBSERVATIONS

Site 1 Core D was extruded on March 12, 1992 in the parks warehouse but a core description cannot be found.

Site: Site 2, Core A **Date of Collection:** 11-03-92
Location (d-m-s): lat. 59 14 09, long. 109 27 56
ID: 10.1 cm **Total Length:** 46 cm
Extruded and Described by: Rick Bourbonniere & Sherry Telford
Date of Extrusion: 11-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

CORE A (46 cm)

GENERAL OBSERVATIONS

Site 2 Core A was extruded March 11, 1992 on site. The samples from top to bottom was actually 53.5 cm long. The top was not all even. Colour progresses from brown (O-4 cm) to light gray to dark gray. At about 4-5 cm and 19-20 cm there were gas pockets with more problems from 32-46 cm. From 4-13 cm the core is 1/2 brown and 1/2 gray - was the core skewed? The core consistency was not recorded.

UpD	LwD	Colour	Other Comments After Sectioning
0 thru 3	1 4	brown	
4 thru 12	5 13	1/2 brown, 1/2 gray	
13 thru 44	14 46	gray	

Site: Site 2, Core B **Date of Collection:** 11-03-92
Location (d-m-s): lat. 59 14 09, long. 109 27 56
ID: 10.1 cm **Total Length:** 72 cm
Extruded and Described by: Rick Bourbonniere
Date of Extrusion: 11-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

SITE 2 - CORE B (72 cm)

GENERAL OBSERVATIONS

Site 2 Core B was extracted March 11, 1992 on site. The original core was about 78 cm long but the last 6 cm were not extracted due to water problems. The core had a stiff brown layer in the 2-4 cm sections. The depth of changes in the consistency are not exactly identified except that there is definitely an increase in the stiffness at about 50 cm. Changes in the amount of black laminations are also not recorded though they range from relatively little to considerable amounts.

UpD	**LwD**	**Colour**	**Other Comments After Sectioning**
0	1	brown	wet and fluid
1	2	brown	wet and fluid
2	3	brown	very dry and stiff (hard)
3	4	brown	very dry and stiff (hard)
4 thru 7	5 8	gray	somewhat consolidated
8 thru 10	9 11	gray with a small amount of black lamination	somewhat consolidated
11 thru 48	12 50	gray with black lamination	somewhat consolidated
50 thru 70	52 72	gray with black lamination	gelatinous and somewhat stiff

Site: Site 2, Core C **Date of Collection:** 11-03-92
Location (d-m-s): lat. 59 14 09, long. 109 27 56
ID: 10.1 **Total Length:** 72 cm
Extruded and Described by: Rick Bourbonniere & Sherry Telford
Date of Extrusion: 11-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

SITE 2 - CORE C (72 cm)

GENERAL OBSERVATIONS

Site 2 Core C was extracted on March 11, 1992 on site. The original core was about 75 cm long though it was only extracted to 72 cm due to water influx problems which caused the sample to subsided/shift. At 3-4 cm there was a brown `hard pan-like layer.

Detailed descriptions are not available therefore only definite changes in colour, laminations and/or consistency are noted. Sections divided as follows: 1 cm sections for 0-24 cm, 2 cm sections for 24+ cm.

UpD	LwD	Colour	Other Comments After Sectioning
0 thru 2	1 3	brown	wet and fluid
3	4	brown	very dry and stiff (hard)
4	5	gray	somewhat consolidated
5	6	gray	somewhat consolidated
6 thru 20	7 21	gray with a small amount of black lamination	somewhat consolidated
21 thru 30	22 32	gray with black lamination	somewhat gelatinous
32 thru 70	34 72	gray with black lamination	gelatinous and somewhat stiff

THE NEXT THREE CORES, SITE 2, CORES D, E AND F WERE ALL DISTURBED AS A RESULT OF FREEZING AND THE SUBSEQUENT DEFROSTING PROCESS. THE SURFICIAL SEDIMENTS TENDED TO RUN DOWN THE SIDE OF THE CORING CASE.

Site: Site 2, Core D **Date of Collection:** 11-03-92
Location (d-m-s): lat. 59 14 09, long. 109 27 56
ID: 10.1 cm **Total Length:** 62 cm
Extruded and Described by: Sherry Telford
Date of Extrusion: 12-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

SITE 2 - CORE D (62 cm)
GENERAL OBSERVATIONS

Core D was extruded off-site on March 12, 1992. It was transported by helicopter and van and stored in an outside garage overnight. Due to both transportation and partial freezing, the sides of the core were slightly disturbed (see slides). The overlying water layer was partially frozen and some of its ice crystals sheared the top 3.5 cm of the core. When the core was defrosted some of the soft, brown surficial sediment fell down the sides of the core. This may affect the results of analytical studies carried out on the sample. To minimize this problem, as the sections were extruded from the coring tube, their edges were not transferred to the jars. Consequently, the volume of the sample is less than its true value for each section.

The length from the top of the core to the bottom of the bung is 73 cm. From 2.3-4.5 cm there is a hard layer which is relatively dry. It changes in colour from dark brown to rusty brown to the "normal" dark gray. Sectioning was discontinued because the sediment below 62 cm was frozen.

At least two pontoporeia Sp. were observed swimming in the water layer or burrowing in the surficial sediments.

UpD	**LwD**	**Colour**	**Other Comments After Sectioning**
0	1	brown	very wet and fluid
1	2	brown	very wet and fluid
2	3	brown to dark brown	very wet and fluid until hits dry, stiff dark brown layer
3	4	dark brown layer with dark gray mud	very dry and stiff layer in dark gray mud

4	5	dark gray with small portion of dark brown layer	mostly soft mud with small portion of dry, stiff brown layer
5	6	dark gray with small portion of dark brown layer	somewhat consolidated
6	7	dark gray with a small amount of black lamination	somewhat gelatinous
7	8	gray with a small amount of black lamination	somewhat gelatinous
8	9+	gray with a small amount of black lamination and brown mud	somewhat gelatinous
9+ thru 12	10 13	gray with some black lamination	gelatinous
13	14	gray with some black lamination	very wet, perhaps due to melting ice
14	15	gray with some black lamination	very wet, perhaps due to melting ice
15 (lost some)	16	gray with some black lamination	somewhat consolidated
16	17	gray with some black lamination	somewhat gelatinous
17	18	gray with some black lamination - bit of brown	gelatinous
18	19	gray with some black lamination	somewhat consolidated
19	20	gray with some black lamination	somewhat gelatinous, changing consistancy may be due to ice melting
20 thru 38	21 40	gray with some black lamination	gelatinous
40 thru 60	42 62	gray with some black lamination	gelatinous and somewhat stiff

Site: Site 2, Core E **Date of Collection:** 11-03-92
Location (d-m-s): lat. 59 14 09, long. 109 27 56
ID: 10.1 cm **Total Length:** 12 cm
Extruded and Described by: Rick Bourbonniere
Date of Extrusion: 12-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

THIS CORE CANNOT BE USED FOR DATING, VOLUME DATA WILL NOT BE REPRESENTATIVE ALTHOUGH CHEMICAL ANALYSIS MAY BE OKAY. ONLY FIRST 10-12 CM RECOMMENDED FOR EXAMINATION.

SITE 2 - CORE E (12 cm)

GENERAL OBSERVATIONS

The extruding conditions for Core E are similar to those of Site 2, Core D. It too was partially frozen after having been stored overnight in the garage (again, it appears that only the outer edge of the core was frozen). It was extruded March 12, 1992. The overall appearance of the core is standard for this site; that is, a domed centre at the top of the core, approximately 3-4 cm of brown sediment (silty) with a hard layer of darker brown sediment at about 4 cm and finally gray clay in the lower layers (this gray may become darker with depth). There appears to be air pockets throughout the core causing separation. Due to ice in the overlying water, some of the surficial sediment was lost (disturbed to roughly 1.5 cm depth).

The length of the core from the top to the bottom of the bung is 87 cm. However, due to extrusion problems, only 12 cm of the core was well extruded and thus only this amount is available for analysis.

UpD	LwD	Colour	Other Comments After Sectioning
0	1	brown with some ice	very wet and fluid, section was domed up a bit
1	2	brown	very wet and fluid
2	3	brown	wet and fluid
3	4	dark brown clay with stiff, brown layer about 2 to 3 mm, then dark brown organic material in dark gray mud	very dry and stiff layer in wet and fluid sediment
4	5	dark gray with small portion of dark brown stiff layer and some brown organic matter	mostly soft mud with small portion of dry, stiff brown layer

5	6	gray clay with some brown "staining" on it	somewhat consolidated
6	7	gray with a small amount of black lamination	somewhat consolidated, section was slightly disturbed due to freezing
7	8	gray with a small amount of black lamination	somewhat consolidated with slight sulphide odour
8	9	gray with some black lamination	somewhat consolidated with sulphide odour
9	10	fine, dark gray clay with some black lamination	somewhat consolidated
10	11	gray with a small amount of black lamination, rust coloured streaks start about 1 cm in from edge and proceed across section	somewhat consolidated
11	12	gray with a small amount of black lamination	somewhat consolidated
12	13	gray with some black lamination	somewhat consolidated but wet due to water from the sides
13	14	gray with some black lamination	somewhat consolidated, the water is leaking past the bung inhibiting extrusion
14	15	gray with some black lamination	somewhat consolidated

Site: Site 2, Core F **Date of Collection:** 11-03-92
Location (d-m-s): lat. 59 14 09, long. 109 27 56
ID: 10.1 cm **Total Length:** 46 cm
Extruded and Described by: Rick Bourbonniere
Date of Extrusion: 12-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

SITE 2 - CORE F (46 cm)

GENERAL OBSERVATIONS

Core F was sampled on March 11, 1992 and extruded March 12, 1992. As in the two previous cores, core F was frozen overnight. After having been stored in the heated garage for a few hours, the core has defrosted and most of the ice-induced cracks have been filled in with mud. The top 3 cm (approximately) consists of brown, fluid material. The surficial dome is skewed to one side and much of the surface sediment has smeared down the edge of the sample, thus these edges will not be saved in the jars with the sediment sample. Site 2's characteristic hard layer is present.

The core length from surface to bung bottom is 51 cm.

There are two+ pontoporeia swimming in the surficial water.

UpD	LwD	Colour	Other Comments After Sectioning
0	1.5	brown and already breaking into some of the dark brown, dry layer	very wet and fluid with some of the stiff, dry layer
1.5	2	dark brown oxidised layer	mostly dry and stiff layer in wet mud
2	3	dark brown, dry and stiff layer in brown mud	dry, stiff layer in wet and fluid sediment
3	4	bit of dark brown, stiff layer in gray sediment which has oxidised slightly, some black lamination	dry, stiff layer in wet and fluid sediment
4	5	gray with some brown clay, some black lamination	wet and fluid
5	6	gray clay with a bit of brown colouring, some black lamination	wet and fluid
6	7	gray clay with a bit of brown clay around edges (oxidation?), considerable black lamination	wet and fluid

7 thru 10	8 11	gray with some black lamination	somewhat consolidated
10 thru 15	11 16	gray with chunks of black matter	somewhat consolidated
16	17	gray with considerable black lamination	somewhat gelatinous, lost about 1/4 of samples
17 thru 23	18 24	gray with considerable black lamination	somewhat gelatinous
24 thru 38	26 40	gray with considerable black lamination	gelatinous and somewhat stiff
40	42	gray with considerable black lamination	gelatinous and stiff
42	44	gray with considerable black lamination	gelatinous and stiff
44	46	gray with considerable black lamination	gelatinous and stiff, pulled up some of next section since sediment is so dry

EXTRUSION DISCONTINUED - THE REMAINING SECTIONS APPEAR TO HAVE CONSIDERABLE CONTAMINATION FROM THE SURFACE; THAT IS, THERE IS A LOT OF BROWN AROUND THE EDGES. CONTAMINATED SAMPLES ARE NOT WORTH SAVING (ONLY DISCARDING ABOUT 2-3 CM)

Site: Site 3, Core A **Date of Collection:** 12-03-92
Location (d-m-s): lat. 59 27 24, long. 109 06 53
ID: 10.1 cm **Total Length:** 84 cm
Extruded and Described by: Sherry Telford
Date of Extrusion: 12-03-94
Transcribed by: Sherry Telford **Date of Transcription:**

SITE 3 -CORE A (84 cm)

GENERAL OBSERVATIONS

This core was extruded on the same day it was extracted but off-site at the garage. There is nothing particularly distinctive about this core. The top layers are the standard brown colour observed in the previous cores. At about 3 cm, the colour changes to the usual gray mud, although a bit of brown remains until the 5-6 cm section.

The core from the top layer to the bottom of the bung is 94 cm long. After extruding as much as possible, the length of sediment remaining and the double bung was approximately 9 cm. There were no pontoporeia visible.

UpD	**LwD**	**Colour**	**Other Comments After Sectioning**
0	1	brown	very wet and fluid, lost some as it ran down the side of the coring tube
1	2	mostly brown with a bit of gray and considerable black lamination	very wet and fluid
2	3	brown and gray with considerable black lamination	very wet and fluid
3	4	dark brown with a bit of gray and considerable black lamination	very wet and fluid
4	5	dark brown with a bit of gray and considerable black lamination	wet and fluid
5	6	dark gray with considerable black lamination	very wet and fluid
6	7	dark gray with a brown rim around 1/4 of perimeter and considerable lamination	very wet and fluid

7	8	dark gray with some brown clay and considerable black lamination	somewhat consolidated
8	9	dark gray with some brown clay around the perimeter and considerable black lamination	somewhat consolidated
9 thru 17	10 18	gray with considerable black lamination	somewhat consolidated
18	19	gray with considerable black lamination	consolidated and somewhat stiff
19	20	gray with considerable black lamination	consolidated and somewhat stiff
20	21	gray with considerable black lamination	wet and fluid
21	22	gray with considerable black lamination	somewhat consolidated
22	23	gray with considerable black lamination and a slight smear of brown	somewhat consolidated
23 thru 46	24 48	gray with considerable black lamination and a slight smear of brown	somewhat consolidated
48 thru 52	50 54	gray with some black lamination	gelatinous and somewhat stiff
54	56	gray with considerable black lamination	gelatinous and stiff
56	58	gray with considerable black lamination	somewhat gelatinous but watery
58	60	gray with considerable black lamination	somewhat gelatinous but watery
60	62	gray with considerable black lamination	gelatinous and somewhat stiff
62	64.1	gray with considerable black lamination	somewhat gelatinous but watery

64.1	66	gray with considerable black lamination	somewhat gelatinous but watery
66 thru 82	68 84	gray with considerable black lamination	gelatinous and somewhat stiff

Site: Site 3, Core B **Date of Collection:** 12-03-92
Location (d-m-s): lat. 59 27 24, long. 109 06 53
ID: 10.1 cm **Total Length:** 52 cm
Extruded and Described by: Sherry Telford
Date of Extrusion: 12-03-92
Transcribed by: Sherry Telford **Date of Transcription:**

SITE 3 - CORE B (52 cm)

GENERAL OBSERVATIONS

This core was extruded on the same day it was extracted but off-site at the garage. There is nothing particularly distinctive about this core. The top layers are the standard brown colour observed in the previous cores. At about 2 cm, the colour changes to the usual gray mud, although a bit of brown remains until the 11-12 cm section.

The core from the top layer to the bottom of the bung is 57 cm long. There were no pontoporeia visible.

UpD	LwD	Colour	Other Comments After Sectioning
0	1	brown with a small amount of black lamination	very wet and fluid, actually lost some sample as it spilled over
1	2	brown with a small amount of black lamination	wet and fluid
2	3	mostly dark gray with some brown clay and black lamination	wet and fluid
3	4	dark gray with a bit of brown clay around the perimeter and considerable black lamination	wet and fluid
4 thru 6	5 7	gray with some brown around the perimeter and considerable black lamination	somewhat consolidated
7 thru 9	8 10	gray with some brown around the perimeter and considerable black lamination	somewhat gelatinous
10	11	gray with trace of brown and considerable black lamination	somewhat gelatinos

11	12	gray with trace of brown and considerable black lamination	somewhat gelatinous
12 thru 14	13 15	gray with considerable black lamination	somewhat gelatinous
15 thru 46	16 48	gray with considerable black lamination	gelatinous and somewhat stiff
48	50	gray with considerable black lamination, underwent some measure of oxidation and thus colours are lighter than usual	gelatinous and somewhat stiff, 2 hour interval between extrusion of this section and preceding sections (final sample jars were in different location)
50	52	gray with considerable black lamination	gelatinous and somewhat stiff

GARAGE BLANKS

Ran blanks to determine the extent of contamination, if any, on the sediments due to extraction in the garage which obviously has several sources of contamination (oil, gas, etc.). One blank each was run for .5, 1.0, 1.5 and 2.0 hours. No sediment section should be exposed to the garage air for more than 2-3 minutes (except perhaps for the surface of cores which required defrosting).

CORE SEDIMENT DESCRIPTIONS - '93 SAMPLES

Site: Site 1, Core A **Date of Collection:** 24-03-93
Location (d-m-s): lat. 59 02 42, long. 110 13 25
ID: 10.1 cm **Total Length:** 80
Extruded and Described by: Brian Jackson
Date of Extrusion: 24-03-93
Transcribed by: Richard Bourbonniere **Date of Transcription:** 05-03-94

Notes: "Light (dirty) brown" on surface, has numerous worm holes on top, small bubbles on side
Total Length (T --> BB) 56.5 cm at start,
distance remaining to bottom of bung = 8.0 cm

1.6 (100% - (48 cm / (56.8 cm - 8.0 cm) *100)) = % compression

UpD	**LwD**	**Colour**	**Other Comments After Sectioning**
0	1		
1	2	light brown	jello-like consistency
2	3	light brown	same consist, but more sticky
3	4	no change	little stickier, v. fine grained
4	5	red brown spots mixed w/ grey, transition zone, v. fine grain	
5	6	pale gray	same consistency, v fine grained
6	7	pale gray	same
7	8	darker gray	some black streaks across & some brown streaks along length
8	9	darker gray almost black streaks across and vertically	
			still little brown but mostly black (streaks?)
9	10	same w/ black streaks	
10	11	same but more streaks, slightly darker gray	
11 thru 13	12 14	same with black streaks	

14	15	same	same, more sticky
15	16	maybe slightly darker harder to see black streaks	
16	17	same	same
17	18		
18	19	same dark grey less streaking, same consistency, dry cottage cheese	
19	20		
20	21	same	More sticky - stiffer - pulling away from tube edge
21	22	same	same
22	23	same	same - less streaking
23	24	same	same - no streaking
24	26	same	black streaks
26	28	sl lighter	black streaks - no sulfide odour
28	30	lighter gray	black streaks - no sulfide odour
30	32	"light gray"	black streaks - no sulfide odour
32	34	dark gray	black streaks - same consistency
34	36	dark gray	same consist - black streaks
36	38	darker gray - less streaking - getting quite stiff - no sulfide odour	
38	40	slightly darker	less streaking
40	42	dark gray w/ streaks	
42	44	gray w/ black streaks - no odour	
44	46	darker gray w/ black streaks - stiff	
46	48	dark gray w/ black streaks	

Site: Site 1, Core B **Date of Collection:** 24-03-93
Location (d-m-s): lat. 59 02 42, long. 110 13 25
ID: 10.1 cm **Total Length:** 84.5
Extruded and Described by: Dave Allen
Date of Extrusion: 24-03-93
Transcribed by: Richard Bourbonniere **Date of Transcription:** 06-03-94

Notes: top surficial sediment is light brown with some holes in the centre, there are small larvae (perhaps mayfly or gamarus though Brian Jackson thinks that it is not mayfly - lost them), Otherwise similar to Core A. Distance remaining to BB: 38.4 cm; The core EXPANDED 4.1 % during extrusion (delay?... (100% - (48 cm / (84.5 cm - 38.4 cm) *100)) = % compression).

UpD	**LwD**	**Colour**	**Other Comments After Sectioning**
0	1	light brown	v. liquidy - consistency like floc
1	2	light brown	like chocolate pudding
Two-hour power failure interrupted extruding - continuing now w/ flashlights?			
2	3	light brown	homogeneous - lights off again
3	4	must be same colour but can't see - no lights	
4	5	light brown	little gray(?) clay showing up
5	6	light brown & gray	
6	7	light gray	brown along edges - stiffer
7	8	light gray	brown along edges - black streaks
Still no power using flashlight			
8	9	light-med gray	black streaks - same consistency
9	10	same colour	same consistency - no odour
10	11	same	getting stickier, black streaks, v.little light brown on edges
11	12	grey w/ blk streaks	
12	13	little darker gray	

13	14	little darker gray	
14	15	same	stiffer
15	16	same	"cottage cheese"
16	17	light gray w/ black streaks	
17	18	same	same
18 thru 23	19 24	same	stiffer a few cracks
24	26	same	little stiffer - almost cake
26	28	same	stiffer as cake on plate
28	30	same	same - no sulfide smell
30 thru 46	32 48	same	same - getting stiffer

Site: Site 1, Core C **Date of Collection:** 24-03-93
Location (d-m-s): lat. 59 02 42, long. 110 13 25
ID: 10.1 cm **Total Length:** 77.5
Extruded and Described by: Bryan Kemper
Date of Extrusion: 24-03-93
Transcribed by: Richard Bourbonniere **Date of Transcription:** 06-03-94

Notes: There is a small hole on top of the core which is uniform brown. The final 29.5 cm were not extruded.

UpD	LwD	Colour	Other Comments After Sectioning
0	1	light brown	"uniform drywall mud texture" - small roundworm
1	2	light brown	Crustacean wiggling
2	3	light brown	loose but not watery
3	4	light brown	streaking due to holes? sl darker colour
4	5	uniform brown	granular texture
5	6	gray	clay - granular interface
6	7	uniform gray	sticky
7 thru 9	8 10	gray with dark streaks	granular texture
10	11	gray with dark streaks	putty like
11	12		
12	13	gray	firm consistency, streaking
13	14	gray with streaks	not quite as smooth
14	15	gray with streaks	
15 thru 17	16 18	gray with dark streaks	uniform texture, firm
18	19	same	same w/ maybe more blk streaks
19	20	(gap in tape)	

20	21		
21	22	same	fewer streaks
22	23	same	core firm, pulling away from tube
23	24	same	streaks maybe darker
24	26		
26 thru 32	28 34	same	maybe slightly darker streaks
34	36	same	maybe fewer streaks
36	38	darker gray	switched to tap water for cleaning utensils (previously used nanopure water)
38	40	same	fainter streaking, tiny bit more odour
40	42	same?	v. little odour
42	44	sl dark gray	little bit more streaking
44	46	same?	more fine streaking, from pinholes, stiff
46	48	same?	

Site: Site 1, Core D **Date of Collection:** 24-03-93
Location (d-m-s): lat. 59 02 42, long. 110 13 25
ID: 10.1 cm **Total Length:** 77.0
Extruded and Described by: Bryan Kemper
Date of Extrusion: 24-03-93
Transcribed by: Richard Bourbonniere **Date of Transcription:** 05-03-94

Notes: The core is very, very slightly skewed. One ponto was seen. Extruding began at 23:30. 28.6 cm of the core remained (not extracted) - 0.8 (100% - (48/(77-28.6)*100) = % compression.

UpD	LwD	Colour	Other Comments After Sectioning
0	1	brown	no signs of life , no odour
1	2	brown	same
2	3	uniform brown	same exactly
3	4	brown granular	little bit of streaking (gray?)
4	5	same	little more gray streaking
5	6	gray interface	pronounced, faint odour
6	7	same	
7 thru 9	8 10	gray	a little coarser with black streaks
10	11	gray	slight black streaks
11 thru 13	12 14	gray	less streaking
14	15	uniform gray	faint streaking
15	16		
16 thru 22	17 23	(purposely limited description because identical to other cores)	
23 thru 46	24 48	uniform gray	not much streaking

Site: Site 1, Core E **Date of Collection:** 24-03-93
Location (d-m-s): lat. 59 02 42, long. 110 13 25
ID: 10.1 cm
Total Length: 81 cm
PHOTO CORE: split and photographed by Rick Bourbonnniere (27 March 93)

UpD	LwD	Colour and Other Comments
0	4	10YR4/4 - fluid brown oxidized layer
4	81	2 5Y3/2 - gray, no noticeable banding (contrast to extruding descriptions) -at 31 to 80 cm, samples for W. Morris' paleomagnetic analysis were taken (Labelled A1 -> 21A & A1 ->21 B)

Sedimentology UpD	Samples LwD	Comments
0	2	Sampled into plastic vials and stored in fridge Shipped at ambient temperature. Some rusting of samples occurred during shipping.
5	7	
10	12	
15	17	
20	22	
25	27	
30	32	
35	37	
40	42	
45	47	
50	52	
55	57	
60	62	
65	67	
70	72	
75	77	
79	81	