AN ASSESSMENT OF PRODUCED WATER IMPACTS TO LOW-ENERGY, BRACKISH WATER SYSTEMS IN SOUTHEAST LOUISIANA

Submitted by the

Louisiana Department of Environmental Quality
Water Pollution Control Division

in Cooperation with

Louisiana Department of Environmental Quality
Technical Services Division

Louisiana Department of Environmental Quality
Nuclear Energy Division

Louisiana State University
Institute for Environmental Studies

Edited by

Kerry M. St. Pé

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Abstract

Produced water is a by-product of the oil production process and is brought to the surface along with petroleum from subsurface formations. Also known as formation water or oil field brine, produced waters associated with Louisiana oil reserves have a much higher salinity than ocean water. Current research interest in the environmental effects of produced water discharges is due to a need by various federal, state, and local agencies to obtain the data necessary for reassessing and updating the existing regulations.

The objectives of this study were to further evaluate past observations made by the LDEQ staff and other investigators and to add to the available data base with respect to produced water discharges to low-flow type systems.

The hydraulic behavior of produced water, when discharged to poorly flushed brackish or saline systems, was evaluated at four study sites in southeast Louisiana. Results indicated that produced water influences on chloride concentrations of the receiving water body were much more apparent in bottom sediments than in the water column. Additionally, conventional CTD instruments may not be capable of consistently detecting produced water chloride impacts because much of the effect, at least in poorly flushed systems, may be below the position of the conductivity sensor.

Toxicity testing of the effluents demonstrated acute toxicity to mysids and sheepshead minnows. The 96 hour acute toxicity to mysids was attributed to components other than salinity. Sheepshead minnows were shown to be less sensitive to produced water effluents. Acute toxicity to a borrowing amphipod using contaminated sediments was attributed to components other than salinity through use of a solid phase testing procedure. Sediment elutriate tests did not indicate significant acute toxicity.

High levels of metals and organics were found. These levels represent a significant negative impact upon receiving waters of natural bayous because of the high volumes of produced waters discharged annually into confined waterways which are often poorly flushed by freshwater flow or tidal exchange. The produced waters were characterized by high concentrations of volatiles, including benzene and toluene, and semivolatile hydrocarbons such as aliphatic hydrocarbons (primarily naphthalenes and phenanthrenes). The discharges also contained high concentrations of aromatic acids and aliphatic fatty acids. Metals content included barium, vanadium, arsenic, and copper.

High radium 226 levels (ranging from 355 pCi/1 to 567 pCi/1) were detected in all study site effluents. High radium 226 levels were also detected in sediments nearest to the outfalls. Radium 226 analysis of tissue from caged oysters indicated that oysters growing near produced water effluents may accumulate petrogenic radionuclides.

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Finally, the editor wishes to acknowledge Messrs. Bruce H. Baird and Duane N. Chisholm, both former DEQ Bayou Region staff members, for their assistance in formulating many of the techniques used in this study.

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EXECUTIVE SUMMARY

Introduction

Produced water is a by-product of the oil production process and is brought to the surface along with petroleum from subsurface formations. Also known as formation water or oil field brine, produced waters associated with Louisiana oil reserves are usually highly saline with ranges reported by Hanor *et al.* (1986) from 50 ppt to 150 ppt. In comparison, the average open-ocean salinity is 35 ppt (Reid, 1961). Louisiana inland water salinities vary considerably with distance from the Gulf of Mexico, but are almost always much less than those found in the open sea.

Produced waters can also contain various radionuclide and volatile and semivolatile organic hydrocarbon contaminants. Boesch *et al.* (1989a and 1989b) demonstrated that produced waters discharged into Louisiana waters contained high concentrations of petrogenic hydrocarbons. Sediments near these effluents were also highly contaminated with semivolatile organic hydrocarbons. Reid (1984) surveyed several Louisiana produced water effluents and found radium 226 levels ranging from 131 ± 3 pCi/l to 393 ± 7 pCi/l.

The recently escalated research interest in the environmental effects of produced water discharges is largely based on increased regulatory concerns by various federal, state, and local agencies. These agencies have directed research efforts towards obtaining the data necessary for reassessing and updating current regulations dealing with produced water discharges.

Louisiana Regulatory History

Within the State of Louisiana, the Louisiana Department of Environmental Quality (LDEQ), Water Pollution Control Division, governs all discharges to surface waters. The current Louisiana regulations which specifically apply to produced waters date back to 1953. The 1953 rule basically allowed produced water effluents into any stream not used for drinking water purposes. In 1968 an additional rule was promulgated which prohibited the discharge of oil field brines into freshwater areas, but allowed for their release into "...normally saline waters, tidally affected waters, brackish waters, or other waters unsuitable for human consumption or agricultural purposes" (Louisiana Administrative Code, 1988).

On November 20, 1985, LDEQ adopted a water discharge permitting system which required all effluents, including those from the oil and gas industry, to be permitted. An agreement was made to allow the petroleum industry until May 20, 1986, to submit applications.

Data from the applications submitted by the petroleum industry were summarized in a study by Boesch and Rabalais (1989a). The total volume of produced water discharged to Louisiana waters at the time of the study was almost 2,000,000 barrels per day.

Study Objectives

Generally, the objectives of this study were derived to further evaluate past observations made by the LDEQ staff and other investigators or to add to the available data base regarding produced water discharges to low-flow type systems. The specific study objectives are presented below along with the report chapters in which they are addressed.

1. To evaluate the hydraulic behavior of produced water effluents to poorly flushed brackish or saline systems, Chapter III.
2. To quantify the organic, inorganic, and radiological pollutants in selected produced water discharges and in proximate sediments and to evaluate the spatial extent of effects, Chapter III, IV, and VI.
3. To evaluate the potential for bio-concentration of polynuclear aromatic hydrocarbons (PAH) from contaminated sediments by benthic biota, Chapter VI.
4. To evaluate the biotoxicity of produced water effluents and proximate sediments, Chapter V.
5. To assess the potential for the accumulation of radionuclides and organic pollutants by caged oysters placed in proximity to produced water discharges, Chapter VII.

Study Design

Four study sites in southeast Louisiana were selected for study. Study sites consisted of a single discharge and were located in the Lirette (LRT), Delta Farms (DF), Bully Camp (BC) and Lake Washington (LW) Oil Fields. Three transects, labeled "A", "B", and "C", radiated from each produced water site outfall. Eight sample points were distributed at varying distances from the outfall along the transects. An unaffected reference sample point was selected for each study site for comparison.

The types of samples collected were either sediments, effluents, biota, or water column. Sediments and water column samples were collected from each transect sample point. Biota were collected from caged oysters placed along a site transect.

This study was meant to be a general assessment of the extent and nature of produced water impacts and therefore did not include the replications necessary for extensive statistical analyses.

Study Sites

Discharge volumes varied from 462 barrels per day (bpd) at the LRT site to 13,458 bpd at the DF site. Effluent salinities were considerably higher than receiving stream concentrations and ranged from 139 ppt at the LRT site to 193 ppt at the LW site. Receiving stream salinities ranged from about 4.0 ppt at the DF site to an average of 23 ppt at the LW site.

Hydraulic Behavior of Produced Water Effluents

Due to their high salinities, Gulf Coast produced waters are generally much denser than Louisiana inland waters. Harper (1986) reviewed literature which reported a bottom layer of higher salinities near produced water effluents into poorly flushed canals. Boesch and Rabalais (1989a) concluded that produced water effluents can act as dense plumes after discharge to estuarine waters. Studies have also shown high concentrations of hydrocarbons in sediments near produced water outfalls (Boesch and Rabalais, 1989a and 1989b; Armstrong *et al.*, 1979). These observations, along with those made by Baird *et al.* (1987) provided the impetus for this further investigation into the hydraulics of produced water effluents.

A slotted core tube was used to collect sediment and overlying water samples from each transect point for chlorides analyses. Overlying water was collected from the core tube at the sediment/water interface (0 level) and at the 10 cm (+10) and 20 cm (+20) levels. Interstitial water was also collected from 10 cm core sections (-10, -20, and -30 levels). Water column measurements were also taken with a commonly-used CTD (conductivity, temperature, depth) instrument.

Results from all 4 study sites indicated that produced water influences on chloride concentrations of the receiving water body were considerably more apparent in bottom sediments in comparison to those effects measured in the water column. At some stations highly elevated sediment chloride concentrations were measured, while no measurable impact in the water column of the same station was detected. This suggests that almost no apparent mixing of these discharges is occurring or that any dilution which might occur is insufficient to completely reduce the density differences between the produced water effluent and the receiving water column.

Produced water was shown to penetrate to a depth of at least 30 cm at some stations and there was a strong positive correlation between depth increases and interstitial chloride increases at the most impacted transect points. The trend of steadily increasing sediment chlorinities suggests that a produced water penetration to levels deeper than 30 cm is likely.

The highest interstitial chlorinities were measured at the stations nearest to the outfall with progressively lessening effects noted at more distant transect points. The most heavily impacted sediments were visibly contaminated with high concentrations of hydrocarbons. Trend analysis of selected study site stations indicated an exponential rate of increase in sediment chloride concentrations as the origin is approached.

Study results also show that conventional CTD instruments may not be capable of consistently detecting produced water chloride impacts since much of the effect, at least in poorly flushed systems, may be below the position of the conductivity sensor. A strict reliance on water column salinity readings near produced water effluents might result in the erroneous conclusion that produced waters are completely mixed and quickly dispersed after discharge.

Radium 226 Activities in Produced Water

Produced waters from Louisiana and locations throughout the world have been shown to contain environmentally high concentrations of radium (Reid, 1984). The regulatory control of naturally occurring radioactive materials (NORM) has not received sufficient attention in the past by federal and state agencies because of limited jurisdictions and staff (LDEQ, 1989).

Current Nuclear Regulatory Commission regulations set a maximum radioactivity level of 30 pCi/l in liquid discharges from nuclear power plants to unrestricted access areas. Standards for drinking water are set not to exceed 5 pCi/l. EPA regulations proposed in response to the Resource Conservation and Recovery Act of 1976 (RCRA) would classify radioactivity levels of greater than 50 pCi/l as a hazardous waste (LDEQ, 1989). The natural radium 226 activity of Louisiana surface waters is usually below 1.0 pCi/l (LDEQ, 1989).

The USEPA and the Conference of Radiation Control Program Directors have recommended remediation of radium-contaminated soils to 5 pCi/g above background. The natural Ra 226 activity of Louisiana surface soils ranges from <1 pCi/g to about 7.0 pCi/g (LDEQ, 1989).

High radium 226 levels were detected in all study site effluents and ranged from a low of 355 pCi/l at the Delta Farms site to 567 pCi/l at the Bully Camp site. The variation between site effluent activities is probably due to differences in the mineral composition of the geologic formations from which petroleum is extracted (Kramer and Reid, 1983).

The top 10 cm of sediment from each transect sample point were analyzed for radium 226. The sediments from the station nearest to the outfalls at the Lirette, Bully Camp, and Lake Washington study sites contained very high concentrations of radium 226 ranging from 182 pCi/g at the Bully Camp transect origin to 533 pCi/g at the Lirette site transect origin.

Radium 226 levels in LRT, BC, and LW sediments located away from the outfalls were lower than transect origin sediments but were still elevated above background levels at most of the transect sample points. Stations indicating radium activities which were greater than 5 pCi/g above the site background (reference) were up to 500 meters from the outfall (Lirette site).

Sediment accumulation of radium 226 at the Delta Farms site did not follow the observed pattern of the other sites. No accumulation of radium was noted in Delta Farms sediments. This was attributed to the predominantly organic nature of the sediments at this site. Radium 226 has been shown to be more effectively adsorbed by the fine-grained, clay type soils which were noted at the Lirette, Bully Camp, and Lake Washington sites (Hanan, 1981; Landa and Reid, 1983).

Although only the top 10 cm of sediments were considered in this study component, there was evidence which suggested that radium 226 contamination in sediments near the produced water outfalls investigated may increase with depth as did the interstitial chloride concentrations. Excavated 50 meter stations at the Lake Washington site showed higher radium 226 activities than another LW station located a similar distance from the outfall. It also appeared that the excavation may have allowed for the transport of radium contaminated sediment to more distant transect stations.

Biotoxicity

Samples of each study site effluent were tested for acute toxicity to mysids and sheepshead minnows. Sediments from a station near each site effluent and a reference from each study site were also tested for acute toxicity using an elutriate and a solid phase procedure.

Each effluent exhibited 96 hour acute toxicities to mysids which was attributed to components other than salinity. The Lirette effluent was the least toxic to mysids with an LC_{50} value of 5.8% effluent. The highest mysid effluent toxicity was measured at 2.6% effluent in the Bully Camp discharge sample. The mean LC_{50} for all effluents was 4.3%.

Effluent toxicity patterns using sheepshead minnows differed from mysid test patterns and sheepshead minnows were shown to be less sensitive to produced water effluents. The 96 hour LC_{50} values for sheepshead minnows ranged from 33.8% effluent (least toxic) at the Bully Camp site to 7.2% effluent (most toxic) at the Delta Farms site. The mean 96 hour LC_{50} value for all effluents used in sheepshead minnow tests was 20.1%.

Two methods were used to measure sediment toxicity. The first method used tested the toxicity of a sediment elutriate to mysids. The elutriate tests failed to show any significant acute toxicity.

The second sediment toxicity method used was a solid phase procedure which measured the toxicity of sediment samples to the burrowing amphipod, *Hyalella azteca*. Significant levels of acute toxicity to *Hyalella*, due to a component other than salinity, were measured using this solid phase procedure. The mean mortality rate for all treatment sediments was 73.3% mortality. One study reference sediment sample, BC-R, demonstrated a significant mortality rate (28.9%). The remaining reference sites showed no significant mortality.

Chemical Characterization of Produced Water Impacts

The chemical composition of four produced water discharges were characterized using gas chromatography/mass spectrometry for the identification and quantification of the organics and inductively coupled plasma/mass spectrometry for the quantification of the trace metals. The produced waters were characterized by high concentrations of volatile, including benzene and toluene, and semivolatile hydrocarbons such as aliphatic hydrocarbons and a series of alkylated polycyclic aromatic hydrocarbons (primarily naphthalenes and phenanthrenes). The discharges also contained high concentrations of aromatic acids and aliphatic fatty acids. The trace metal content of the four discharges was very variable, however, each was characterized by high levels of barium, ranging from 1,521 ppb in the Delta Farms produced water discharge to a maximum of 4,644 ppb in the Lirette field discharge. Vanadium, a trace metal often associated with oil, was also found in each of the four discharges at variable levels. Some discharges contained significant levels of arsenic and copper. These levels of toxic metals and organics represent a significant negative impact upon receiving waters of natural bayous because of the high volumes of formation waters discharged annually into confined waterways which are often poorly flushed by freshwater flow or tidal exchange. Because of the hydrology of these systems and the particle reactive nature of both the metals and organics being discharged, we would anticipate that these substances would accumulate within the sediments in the region of the discharges to high levels.

Assessment of Produced Water Chemical Impacts to Receiving Streams

The impacts of produced water discharges on sediment quality varied in each of the areas studied. Major factors determining the degree of impact were: 1) discharge rate; 2) quantity and quality of the hydrocarbons and trace metals present in a particular discharge; 3) local hydrology; 4) sediment disturbances (i.e., dredging and boat traffic); and 5) sediment types (organic carbon content and texture). Analyses of sediments collected at the four sites revealed that all four receiving water systems were measurably impacted by the discharges in the region. Concentrations of both aliphatic and alkylated aromatic hydrocarbons characteristic of the discharges, as well as barium, were found at elevated levels above background in the sediments surrounding the discharges. The areal extent of this contamination expressed in terms of a Fossil Fuel Pollution Index or Ba concentration was found to extend to the farthest points sampled at each discharge site (~300m). The continuation of these discharges into these receiving waters will likely result in an increase in both the level and extent of contamination at these sites.

Investigations of the genotoxic potential of the produced water carried out in other studies indicated that chemicals in produced waters represent a significant genetic risk to embryo and larval stages of fish. In this study a bioaccumulation model applied to the levels of contamination found in the sediments yielded extremely high potential tissue burdens for benthic invertebrates, including edible species. Thus, these chemicals represent both a potential ecological and human health risk.

Accumulation of Organics and Radium 226 by Oysters

The use of bivalves in bioaccumulation studies has been advocated by researchers from several scientific disciplines (Mix, 1982). Oysters have been shown to accumulate hydrocarbons from produced water effluents (Somerville *et al.*, 1987; Neff, 1988; Boesch *et al.*, 1989). Jeffree and Simpson (1986) demonstrated that freshwater mussels can accumulate radium 226 from uranium mill effluents. There have been no known investigations into radium 226 accumulation potentials by the oyster, *Crassostrea virginica*.

In this study component, caged oysters were used to assess the potential for the uptake of organic contaminants and radium 226. Oyster cages containing 75 individuals each were placed at the Lirette, Bully Camp, and Lake Washington sites. Lirette cages were 110 meters from the outfall and Bully Camp and Lake Washington cages were placed 85 and 70 meters, respectively, from produced water outfalls. A control was deployed at an unaffected location in Caillou Lake. All oysters remained in place for 30 or 33 days.

All of the oysters exposed to produced water impacts in this study component accumulated volatile and semivolatile organic compounds. The control site oysters accumulated no volatile organics and only trace quantities of pyrogenic semivolatiles. Total tissue volatiles among treatment site oysters ranged from 3 ppb at the Lake Washington site to 372 ppb in tissues from the Lirette site. Of all volatiles measured, toluene was detected in the greatest quantity. Petrogenic polynuclear aromatic hydrocarbons were detected ranging from 41 ppb at the Lirette site to 319 ppb at the Lake Washington site.

Radium 226 analysis of caged oyster tissues indicated that oysters growing near produced water effluents may accumulate petrogenic radionuclides. Tissue samples from oysters placed near the Lirette effluent accumulated 3.1 ± 0.3 pCi/g of radium 226. Oysters placed at the Caillou Lake reference and Bully Camp and Lake Washington study sites accumulated no measurable radium activities.

Several studies have shown that oysters can release accumulated hydrocarbons after exposure in contaminant-free water (Somerville *et al.*, 1987; Neff, 1988.) Oysters are usually harvested directly, however, and are not depurated before being consumed. This must be considered when assessing the potential for human health risks associated with chemically contaminated shellfish.

Studies by Jeffree and Simpson (1986) related to uptake of radium 226 by freshwater bivalves show that these organisms can readily accumulate these pollutants in a linear manner from water containing radium at levels which were much less than those measured in the four outfalls studied. A complete in-depth study would be needed to assess the full radiological impact of produced waters on oysters. Such a study is recommended since many of these discharges currently exist near commercial oyster harvesting areas.

Chapter I

INTRODUCTION

by

Kerry M. St. Pé

Produced water is a by-product of the oil production process. Also known as formation water or oil field brine, produced water and petroleum (and/or gas) are brought to the surface by wells drilled into oil-bearing geologic formations. At the surface, produced water is removed from the petroleum primarily by gravity separation techniques. The produced water is then either injected into a well or discharged to surface waters. Produced waters associated with Louisiana oil reserves are usually highly saline due to influences from subsurface salt deposits along the Gulf Coast geosyncline.

As petroleum is initially extracted from a formation the amount of water produced is small. However, as the petroleum reserve is depleted, the amount of produced water usually increases. Characteristically, older wells can produce several barrels of water to every barrel of oil extracted.

Interest in the effects of produced water discharges in general and, in particular, those within Louisiana Waters has intensified in recent years. Various agencies in the local, state, and federal sectors have expressed concerns regarding the impacts of these effluents and have directed research efforts towards obtaining the data necessary for updating current regulations.

State regulatory concerns regarding produced water impacts are largely based on cumulative observations by the Louisiana Department of Environmental Quality field staff made during investigations and inspections of coastal oil fields. Several departmental reports detailing those observations were summarized in the U.S. Environmental Protection Agency's (1987) Report to Congress on the management of oil field and geothermal energy wastes. The EPA report was prepared as a result of a congressional directive under Section 8002(M) of the Resource Conservation and Recovery Act (RCRA).

I.A State Regulatory History

Within the State of Louisiana, the Department of Environmental Quality, Water Pollution Control Division, governs all discharges to surface waters. The current Louisiana regulations which specifically apply to produced waters date back to 1953 (Louisiana Administrative Code, 1988). The 1953 rule allowed the discharge of produced waters into streams not used for drinking water purposes and set an oil and grease effluent limit of 30 parts per million.

In 1968, the Louisiana Stream Control Commission promulgated rules which prohibited the discharge of produced water into freshwater areas. The rule allowed discharges to "... normally saline waters, tidally affected waters, brackish waters or other waters unsuitable for human consumption or agricultural purposes" (Louisiana Administrative Code, 1988). The regulating agency, presently the Louisiana Department of Environmental Quality, was given the authority to provide judgements on a case-by-case basis of what constitutes brackish, saline, or tidally affected waters.

On November 20, 1985, the Louisiana Department of Environmental Quality adopted a discharge permitting system which required all effluents, including those from oil and gas operations, to be permitted. An agreement was made to allow the petroleum industry until May 20, 1986, to submit applications. The Water Pollution Control Division of the Department of Environmental Quality is currently issuing permits for produced water discharges to brackish and saline coastal systems.

The permit applications provided a rather large data base which was summarized and assessed in a study for the Minerals Management Service by Boesch and Rabalais (1989a). The total volume of produced water discharged at the time of the study into Louisiana waters was almost 2,000,000 barrels per day. In regard to regions, the largest number of produced water discharges were reported as being located in the Terrebonne and Barataria estuarine systems. In another study for the Louisiana Division of the Mid-Continent Oil and Gas Association, Boesch and Rabalais (1989b) reported that 23, 22, and 17 percent of the total volume of produced waters discharged into Louisiana waters on a daily basis was directed to fresh, brackish, and saline ecosystems, respectively.

Past studies of produced water impacts have been reviewed and summarized by several authors. Some of the more recent summaries are provided in reports by Neff (1988) and Knecht (1988).

Until recently most of the research efforts dealt primarily with produced water effluents directed into waters of the outer continental shelf (OCS) or other types of open water bodies located within Louisiana waters. The Boesch and Rabalais (1989) report to the Louisiana Mid-Continent Oil and Gas Association is probably the most recent effort directed towards investigating the environmental impacts of produced water discharges in low-energy coastal systems. These types of systems, i.e. poorly flushed, brackish, or saline water bodies, were the targeted areas for this study.

I.B Study Objectives

Generally, the objectives of this study were to further evaluate past observations made by the Department of Environmental Quality staff and other investigators and to add to the available data base regarding produced water discharges to low-flow type systems. The study objectives are presented as follows:

1. To identify and quantify the organic, inorganic, and radiological pollutants within selected produced water discharges.

2. To identify and quantify petrogenic pollutants in sediments in proximity to selected produced water discharges.

3. To evaluate the spatial extent of produced water effects upon the sediments and water column of brackish and/or saline receiving water bodies.

4. To evaluate the hydraulic behavior of produced waters following release to low-flow, brackish, or saline receiving water bodies.

5. To investigate and evaluate the concentrations of radionuclides and organic pollutants in caged oysters, *Crassostrea virginica*, placed in proximity to selected produced water discharges.

6. To evaluate the bio-toxicity of produced water effluents to selected test organisms.

7. To evaluate the bio-toxicity of sediments collected from points near produced water discharges to selected biota.

8. To evaluate the potential for benthic organism bio-concentration of polycyclic aromatic hydrocarbons from sediments near produced water discharges.

I.C Project Participants

Several agencies and agency subdivisions participated in various aspects of this study. The Louisiana Department of Environmental Quality's participation involved primarily the Water Pollution Control Division. Additional Department of

Environmental Quality divisions providing major contributions include the Nuclear Energy Division, the Central Laboratory, and the Bio-toxicity Laboratory.

Other agencies providing major contributions were Louisiana State University, Institute for Environmental Studies, and the U.S. Environmental Protection Agency, Region VI. The U.S. Environmental Protection Agency provided partial funding for this study.

I.D Project Responsibilities

The overall study design and coordination was the responsibility of Kerry M. St. Pé, Department of Environmental Quality, Water Pollution Control Division. He was provided field sample collection and technical assistance by Richard Guidry, Pat Breaux, and Earl Eues, Jr. of the Department of Environmental Quality, Bayou Regional Office in Lockport, Louisiana.

Co-principal investigators were Matt Schlenker of the Department of Environmental Quality, Nuclear Energy Division, Sheri Courtney of the Department of Environmental Quality Bio-toxicity Laboratory, and Jay C. Means of the LSU Institute for Environmental Studies (IES). Jay Means was assisted by Charles S. Milan (IES). Matt Schlenker provided radiological analyses of all sediment, effluent, and oyster tissue samples. Sheri Courtney was responsible for performing the bioassay tests of effluents and sediments. Jay Means and Charles Milan assisted with the collection of sediments and effluents for organics and metals analyses and also performed the analytical procedures. Jay Means also was responsible for evaluating the potential for benthic bio-concentration of polycyclic aromatic hydrocarbons from sediments collected during this study. All of the above participated in data synthesis and report preparation.

Elaine Sorbet, Department of Environmental Quality Central Laboratory, coordinated the analysis of all samples analyzed by the Department of Environmental Quality laboratory.

Emelise Cormier, Water Pollution Control Division, Planning and Assessment Section, coordinated all contractual agreements associated with this study.

Helen Bostock, USL Civil Engineering Department, Center for Louisiana Inland Water Studies, is under contract to the Department of Environmental Quality, Water Pollution Control Division, and provided guidance for the analysis of the chlorides data in Chapter III.

Chapter II

STUDY DESIGN AND SITE DESCRIPTIONS

by

Kerry M. St. Pé and Earl J. Eues, Jr.

II.A Study Design

Four study sites located in southeast Louisiana were selected for examination. The criteria for selecting a site were simply that a produced water discharge exist and that it be directed into a brackish water system of relatively limited flow.

In addition to the collection of effluent samples, the study was designed to allow for a collection of samples and water quality data along three transects radiating from a point selected as near as possible to a produced water outfall. Transects were designated as "A", "B", or "C" according to their position relative to the outfall. The transect line radiating to the left of an observer facing the produced water outfall from the receiving stream was labeled as the "A" transect. The line radiating to the right of the same observer was designated as the "C" transect. The middle transect was represented with the letter "B". This transect labeling format remained consistent for each study site.

Along each transect, sample points were selected at measured distances from the point of origin. Distances, in meters, were obtained in the field with a fiberglass tape measure. Measurements were taken prior to the sample dates and each sample location was marked with a cane pole or surveyor's flagging tape tied to a fixed structure or marker on each bank when possible. Additionally, compass bearings relative to a fixed point were taken and recorded for each sample location. Latitude and longitude readings were also recorded for each sample point using a Si-Tex model 760 Loran C receiver. The Loran readings were recorded primarily for informational purposes only. The bank flagging, cane poles, tape measurements, and compass bearing readings were relied upon for relocating sample points.

At each of the four study sites, eight transect sample points were selected. Also, a reference was collected at each site for data comparison purposes. Reference sample locations were established in dead-end canals at distances which afforded a reasonable degree of certainty of being outside of the influence of the produced water discharge.

In some cases, a transect ran into a canal intersection.

When this occurred, the transect was subdivided into branches extending into both directions of the intersecting canal. For example, a site transect "B" might be subdivided into a B_1 and a B_2 branch.

Each sample point was assigned a unique identification number according to a predetermined format. This format was designed to provide one with a sense of where a sample point was located in terms of which oil field and relative distance from the point of origin.

Each sample point designation begins with a two or three letter abbreviation of the oil field in which the discharge was located. The study site I.D. was followed by a transect designation letter (A, B, or C) and then a number indicating the distance of the sample point from the point of origin. Thus, a sample point identified as XYZ-B200 would have been collected in the "XYZ" oil field, along the "B" transect, 200 meters from the point of origin.

Reference sample points were identified with the field abbreviation followed by the letter "R". The identification of effluent samples followed a similar format with the letter "E" following the field abbreviation.

The common point of all transect origins was labeled with the field abbreviation followed by the letter "O". The points of origin were not immediately under the outfall. Rather, they were placed as close to the outfall as possible. Actual distances of the points of origin from the respective site outfall ranged from 10 to 20 meters.

The types of samples collected for this study were either sediments, effluents, biota, or water column. The sediments and water column samples were obtained from each of the eight transect sample points and from the reference. Effluent samples were obtained from the end of each outfall pipe. Biota samples were from oyster tissues obtained from the *in situ* placement of caged organisms at selected transect sample points near three of the four study sites and a reference location. A summary of all analytical tests performed on the various sample types collected during this study is presented in Table II.1. A list of containers and preservatives used for samples collected is presented in Table II.2 and a list of laboratory analytical methods for each parameter and sample type is shown in Table II.3.

Table II.1 Summary of Field and Laboratory Analyses

Field Measurements

A. Ambient Water Measurements (9 per study site)
  1. Dissolved Oxygen (mg/1)
  2. Specific Conductance (micromhos/cm^2)
  3. Secchi Disc Visibility (depth, in inches)
  4. Temperature (degrees Centigrade)
  5. pH (standard units)
  6. Salinity (ppt)
  7. Total Depth (meters)

B. Effluent Measurements (1 per study site)
  1. Temperature (degrees centigrade)
  2. Refractive Salinity (ppt)
  3. pH (s.u.)

Conventional Water Quality Laboratory Parameters

A. Ambient Water Samples (9 per study site)
  1. Total Suspended Solids (mg/1)
  2. Total Dissolved Solids (mg/1)
  3. Chlorides (mg/1)
  4. Turbidity (Nephelometric units)
  5. TOC (mg/1)

B. Effluent Samples (1 per study site)
  1. Total Suspended Solids (mg/1)
  2. Total Dissolved Solids (mg/1)
  3. Chlorides (mg/1)
  4. Oil and Grease (mg/1)
  5. Turbidity

C. Sediments & Bottom Waters (9 per study site)
  1. Sediment Interstitial Water Salinity (ppt)
  2. Depth Integrated Bottom Water Salinities (ppt)

Heavy Metals (mg/1, total recoverable)

A. Sediments (9 per study site)
  1. Barium
  2. Cadmium
  3. Chromium
  4. Copper
  5. Lead
  6. Mercury
  7. Zinc
  8. Aluminum
  9. Nickel
  10. Vanadium
  11. Arsenic

B. Effluent (1 per study site)
  Metals listed above

Volatile and Semi-volatile Priority Pollutant Organics

A. Effluent Samples (1 per study site)

B. Sediment Samples (9 per study site)

C. Biota (from *in situ* caged oysters)

Biotoxicity (96 hr., LC50, Acute Test)

A. Effluent (1 per study site)
  1. *Cyprinodon variegatus*
  2. *Mysidopis bahia*

B. Sediment (1 treatment and 1 reference from each study site)
  1. *Cyprinodon variegatus*
  2. *Mysidopis bahia*
  3. *Hyalella azteca*

Radium 226 (pico curies) (pCi/1)

A. Effluent (1 per study site)

B. Sediments (9 per study site)

C. Biota (from *in situ* caged oysters)

Table II.2 Container Types and Preservatives Used for Water Column and Effluent Samples*

PARAMETER	VOLUME	CONTAINER TYPE	PRESERVATIVE
Semivolatile Organics (Acid & Base/Neutral)	1.0 gallon	Glass w/teflon lined cap	Cool on wet ice in field
Volatile Organics	40 ml septum vial	Glass w/teflon septum cap	Cool on wet ice in field
Total Metals (Ba, Cd, Cr, Cu, Hg, Pb, Zn, Ni, V, Al)	100 ml	Plastic Nalgene bottle	HNO_3 to pH <2, cool on wet ice in field
Oil & Grease	1 liter	Glass w/teflon lined cap	H_2SO_4 to pH <2, cool on wet ice in field
Chloride, TSS, TDS, Turbidity	1 liter	Plastic cubitainer	Cool on wet ice in field
TOC	100 ml	Plastic Nalgene bottle	HCl to <2, cool on wet ice in field
Biotoxicity	1.0 gallon	Plastic cubitainer	Cool on wet ice in field
Radionuclides	1 liter	Plastic cubitainer	Cool on wet ice in field

* All sediment samples were held on ice until delivery to lab.

Table II.3 Laboratory Analytical Methods

PARAMETER	METHOD CITATION
I. Water Column and/or Effluents:	Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA - 600/4-82-057
Semivolatile Organics (Acid & Base/Neutral priority pollutants)	EPA Method 625
Volatile Organics (priority pollutants)	EPA Method 624
Metals (Total)	Methods for Chemical Analysis of Water and Wastes (Revised March 1983) EPA - 600/4-79-020
Aluminum	EPA Method 202.1
Arsenic	EPA Method 206.2
Barium	EPA Method 208.2
Cadmium	EPA Method 213.2
Chromium	EPA Method 218.2
Copper	EPA Method 220.2
Lead	EPA Method 239.2
Mercury	EPA Method 245.1
Nickel	EPA Method 249.2
Vanadium	EPA Method 286.2
Zinc	EPA Method 289.2
Chloride	EPA Method 325.3
Turbidity	EPA Method 180.1
Total Suspended Solids	EPA Method 160.2
Total Dissolved Solids	EPA Method 160.1
Total Organic Carbon	EPA Method 415.1
Oil & Grease	Standard Methods for the Examination of Water and Wastewater, 16th Edition; APHA; Page 497
Gamma Spectrum Analysis	Methods approved by the U.S. Nuclear Regulatory Commission
Acute Biotoxicity (96 hr, LC$_{50}$)	Method for Measuring the Acute Toxicity of Effluents to Freshwater Marine Organisms EPA/600/4-85/013.
II. Sediments:	
Semivolatile Organics (Acid & Base/Neutral priority pollutants)	EPA Methods 8250 or 8270 with appropriate extraction and cleanup methods - Test Methods for Evaluating Solid Waste.
Total Recoverable Metals	EPA Method 7000 series for Atomic Absorption Spectroscopy with Acid Digestion Method 3050. Test Methods for Evaluating Solid Waste.
Gamma Spectrum Analysis	Procedures approved by the U.S. Nuclear Energy Commission.
Acute Biotoxicity (96 hr LC$_{50}$)	Elutriate and Fractionation Methods Published in Puget Sound Estuary Program Recommended Protocol Manual, 1986. Biological Methods for Determining Toxicity of Contaminated Freshwater Sediments to Invertebrates. (Nebeker, et al., 1984)
III. Biota:	
Gamma Spectrum Analysis	Procedures approved by the U.S. Nuclear Energy Commission
Semivolatile Organics (Acid & Base/Neutral priority pollutants)	Sample preparation according to Fish Extraction and Cleanup Procedures in Pesticide Analytical Manual (DHEW, 1973). Sample analysis - EPA Method 625.
Volatile Organics (priority pollutants)	Sample preparation according to Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue. (U.S. EPA, 1981). Sample analysis - EPA Method 624 (U.S. EPA, 1984)

II.B Site Descriptions

Four study sites (Fig. II.1), each with a produced water discharge to a hydrologically low energy, brackish water system, were chosen for this study. The first site sampled was located in the Lirette Oil and Gas Field in Terrebonne Parish, Louisiana, and was designated as site "LRT". The second and third study sites were both located within Lafourche Parish, Louisiana, in the Delta Farms and Bully Camp oil fields, respectively. The Delta Farms field was designated as site "DF" and the Bully Camp field was designated as site "BC". The fourth production site examined was identified as site "LW" and was located within the Lake Washington Oil and Gas Field in lower Plaquemines Parish, Louisiana. Each site abbreviation, as explained earlier, was an integral part of all sample identifications used during this study.

II.B.1 Lirette Site (LRT)

The LRT study site was located in the Lirette Oil & Gas Field in Terrebonne Parish (Fig. II.2). The facility was located on Humble Canal approximately 1 mile southeast of the Bayou Terrebonne/Humble Canal intersection. The study site is a tidally influenced, brackish marsh environment. The salinity of the area was measured at an average of 3.1 ppt from a depth range of 0.5 meters to 3.0 meters during the initial sampling visit to the site on July 20, 1989.

The facility consisted of a tank battery, separation equipment, compressors, and a production pit. A small field office was also noted at the facility. The earthen production pit levee is covered with clam shells and has 2 compartments. The primary compartment has a surface area of approximately 5,100 square feet and is 3 feet deep. The secondary compartment is approximately 9,830 square feet in surface area and is also 3 feet deep. The total pit surface area is 14,930 square feet. The eastern side of the pit is adjacent to a location canal which contained several transect sampling points.

Five active wells are currently directing produced water to the pit. The monthly average rate of discharge since January, 1988, through January, 1990, was 13,850 barrels per month, or an average of 462 barrels per day according to company representatives. The monthly average oil and grease level for the same period of time was reported as 10.8 mg/L. No historical data was available on the chloride concentration of the effluent. An analysis of the effluent by the Louisiana Department of Environmental Quality on July 27, 1989, showed a chloride concentration of 76,850 ppm.

The tidal flow around the site was most apparent in the.

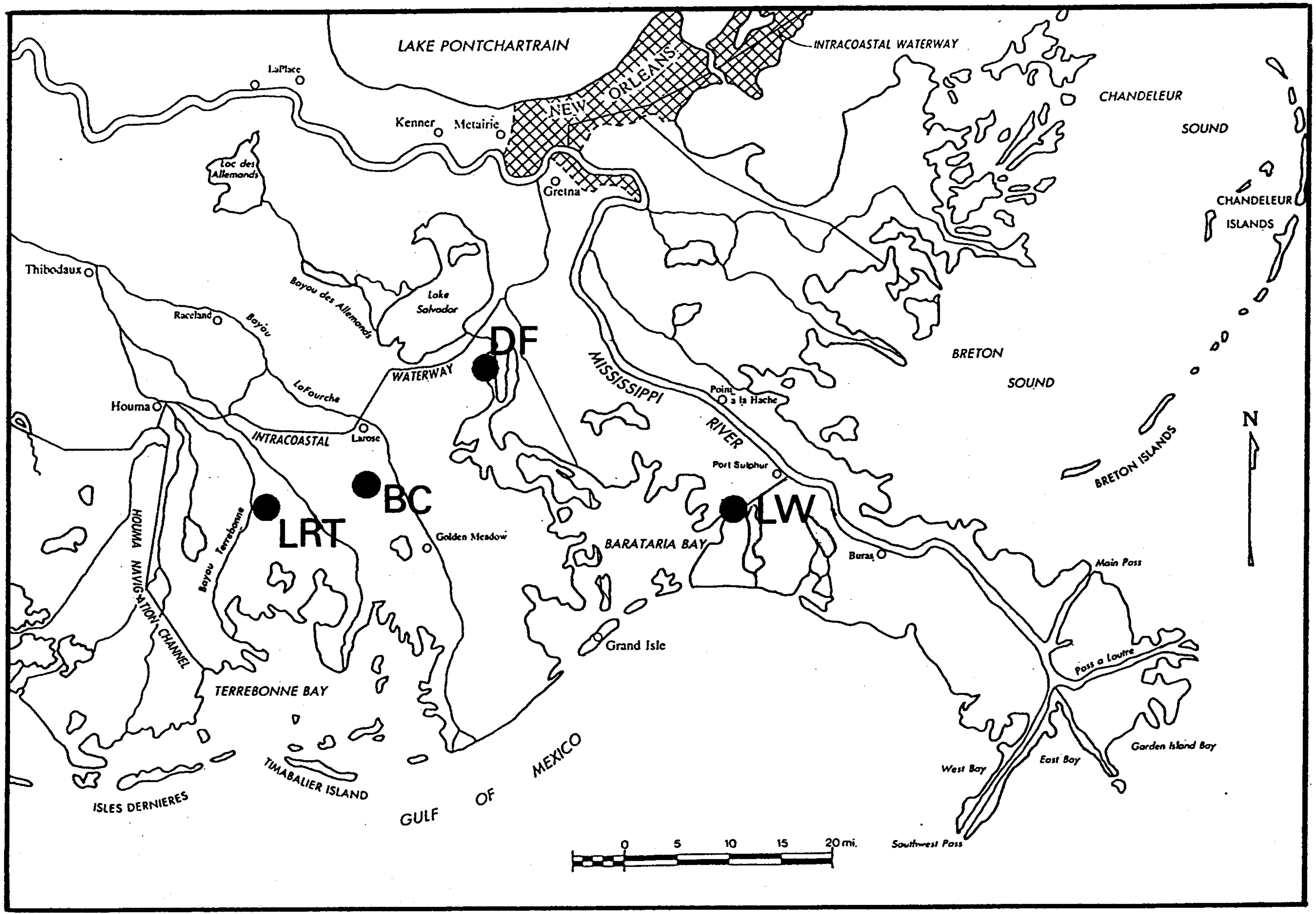

Figure II.1. Locations of the Lirette (LRT), Bully Camp (BC), Delta Farms (DF), and Lake Washington (LW) study sites in southeast Louisiana.

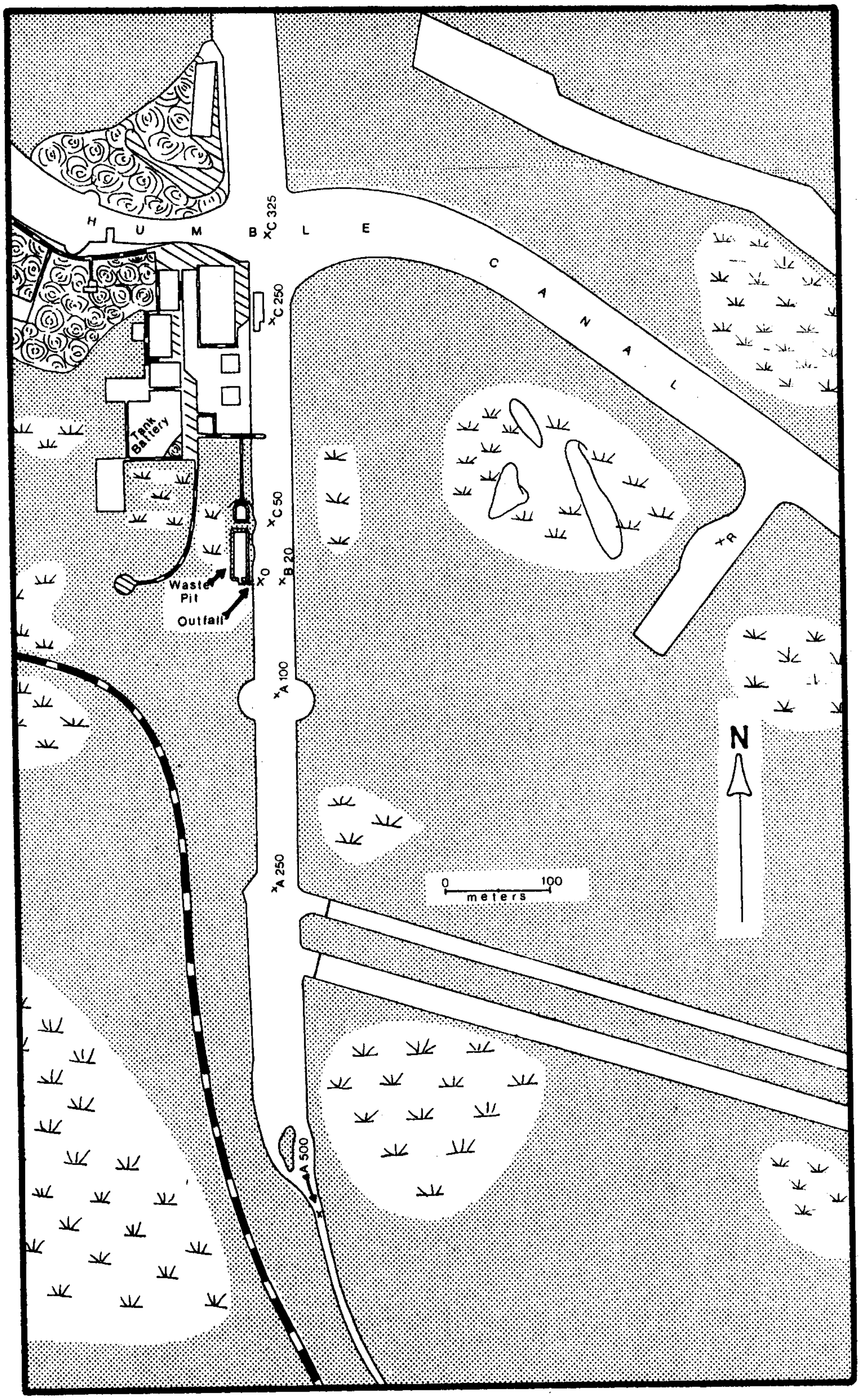

Figure II.2. Locations of Lirette (LRT) site sample points.

Humble Canal. The water movement within the canal was either to the north or to the south at moderate velocities during visits to the LRT site.

The produced water effluent pipe at the LRT site was located on the southern side of the pit. The effluent pipe discharged the produced water from the secondary compartment. The effluent was directed to a small ditch which drained into the adjacent location canal. This location canal was a dead end at the southern most extremity.

The point of origin, LRT-0, for the Lirette Field was 10 meters east of the outfall. The "A" transect extended south of the outfall and contained sample points LRT-A100, LRT-A250, and LRT-A500. The "B" transect traveled to the east of the outfall and contained one sample point, LRT-B20. The "C" transect traveled north from the outfall towards the dead end of the location canal receiving the effluent. The sample points along the "C" transect were LRT-C50, LRT-C250, and LRT-C325. The reference sample point, LRT-R, was east of the outfall in a dead-end location canal approximately one-third of a mile from the facility.

II.B.2 Delta Farms Site (DF)

The DF study site was located in the Delta Farms Oil & Gas Field in Lafourche Parish (Fig. II.3). The facility was located in an oil field location canal west of Bayou Perot and north of Little Lake. Produced water has been discharged from here since the late 1930's or early 1940's. The predominant marsh type of the area is brackish, but an intermediate marsh type is in close proximity (Chabreck and Linscombe, 1978). This site had the lowest salinities of all sites studied. The salinity at the reference point was measured at 0.4 ppt during the initial sample collection on October 5, 1989. The salinity at DF-A300, which is the sample point closest to Bayou Perot, was measured at 1.0 ppt near the bottom on the same date. During a previous visit, on August 24, 1989, ambient salinities at the surface were measured at 4.0 ppt. These latter readings are probably most representative of the average salinities at this site.

The facility consisted of a tank battery with separation equipment, compressors, living quarters, and a production pit. The earthen production pit levees are covered with clam shells. The pit is divided into two compartments. The primary compartment is 8,800 square feet in surface area and approximately 5.5 feet deep. The secondary pit compartment is 7,700 square feet in surface area and approximately 6 feet deep. The total pit surface area is 16,500 square feet and is situated in the marsh with location canals adjacent to two sides of the pit.

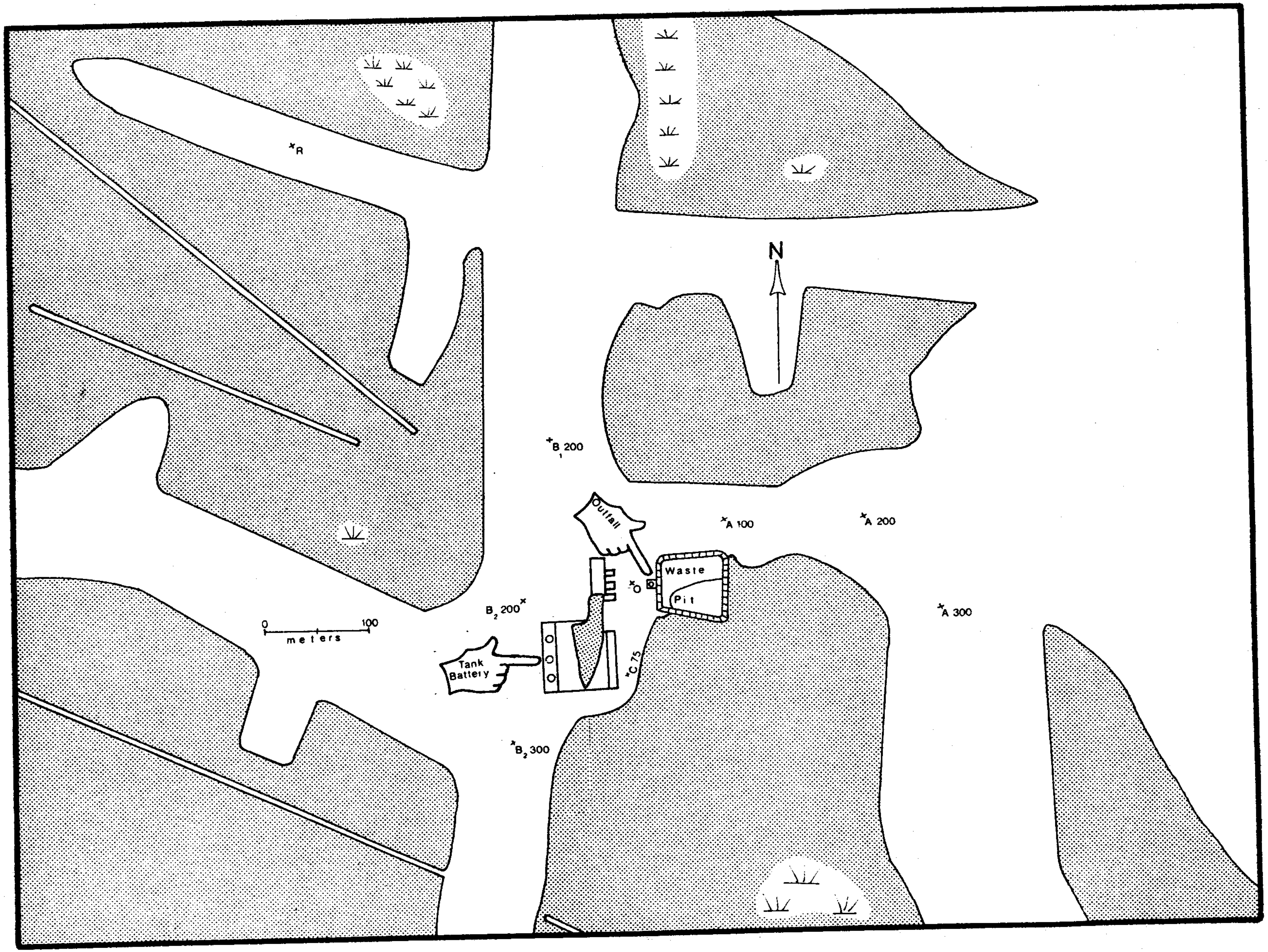

Figure II.3. Locations of Delta Farms (DF) site sample points.

Twenty-four active wells are currently directing produced water to the pit. The monthly average rate of discharge since January, 1988, through January, 1990, was 323,000 barrels per month, or an average of 13,458 barrels per day according to company representatives. The monthly average effluent oil and grease (trichlorotrifluoroethane extractables) level for the same period of time was reported as 13.5 mg/L. No historical data was available on the chloride concentration of the effluent. An analysis of the effluent by the Louisiana Department of Environmental Quality on October 5, 1989, resulted in a chloride concentration of 77,700 ppm.

The tidal flow at the site was most apparent in the canal north and adjacent to the production pit. During sampling visits to the site it was noted that the bottom of this canal was covered with a thick layer of detritus. The water movements within this canal were either to the east or to the west at moderate velocities. The U.S. Geological Survey, 1973 Barataria quad map, shows that the canal is separated from Bayou Perot by a small strip of land. This small strip of land has eroded since 1973 and is now open to Bayou Perot.

The produced water effluent pipe at the DF site was located on the western side of the second compartment of the waste pit. The effluent was directed to an adjacent man-made oil field location canal. This canal is open at both ends, but the flow is restricted at the southern end because of the shallowness at its intersection with another location canal.

The point of origin, DF-0, for the Delta Farms site was 20 meters west of the outfall. The "A" transect ran to the north of the outfall, then turned east towards Bayou Perot. Three sample points were located on this transect: DF-A100, DF-A200, and DF-A300.

The "B" transect traveled north of the outfall then turned west towards another location canal where the transect was then separated into a B_1 and B_2 branch. The B_1 branch traveled to the north and contained one sample point, DF-$B_1$200. The B_2 branch traveled south and contained two sample points, DF-$B_2$200 and DF-$B_2$300.

The "C" transect ran directly south of the outfall and contained one sample point, DF-C75. The reference sample point, DF-R, was northwest of the outfall in a dead-end location canal.

II.B.3 Bully Camp Site (BC)

The BC study site was located in the Bully Camp Oil & Gas Field in Lafourche Parish (Fig. II.4). The facility is located on the state-operated Point au Chien Wildlife Management Area in

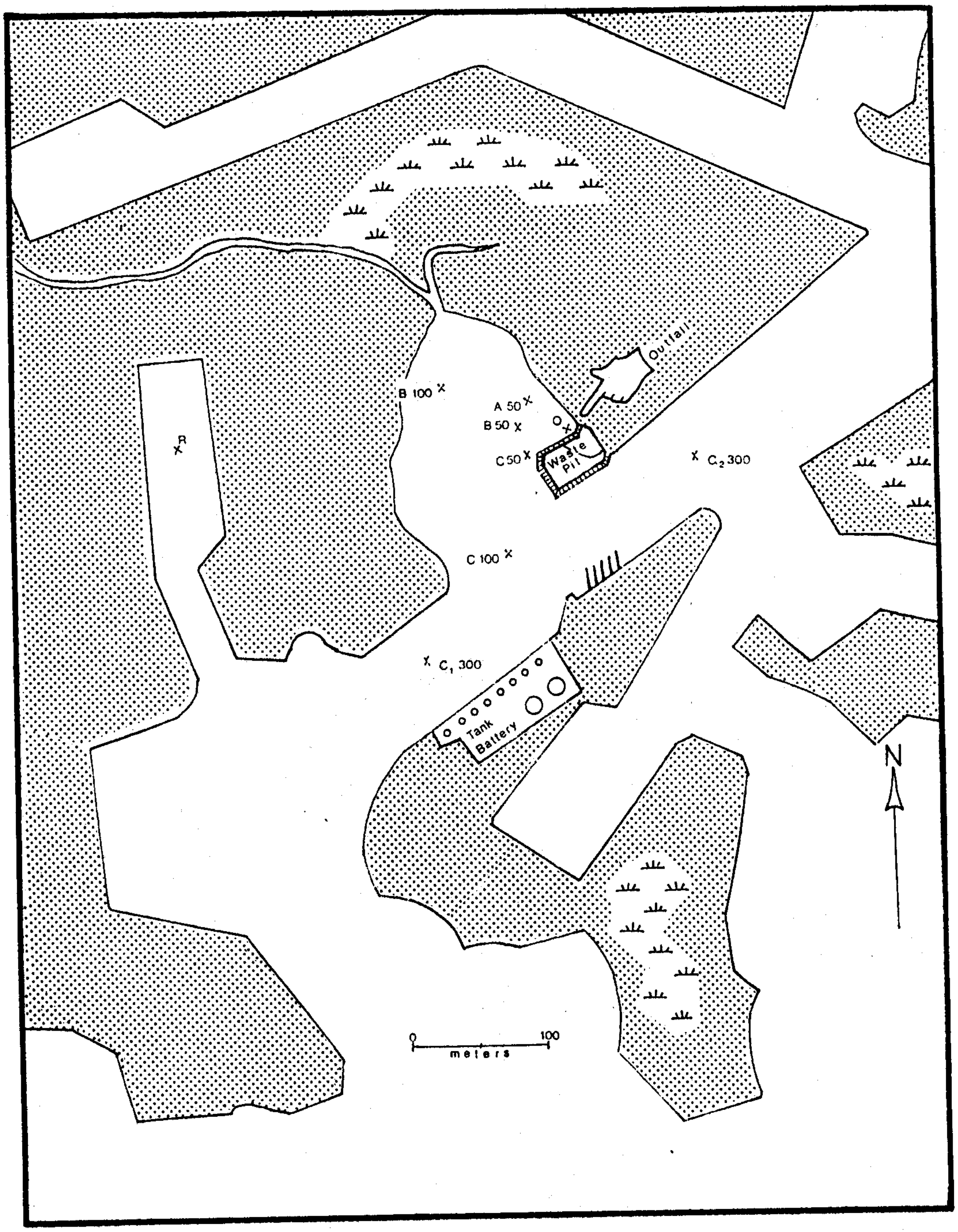

Figure II.4. Locations of Bully Camp (BC) site sample points.

an oil field location canal approximately 3.75 miles west of Grand Bayou and approximately 1 mile north of the abandoned Texas Gulf Sulphur Mine. The facility has been discharging produced water since the late 1930's or early 1940's. The study site area is a tidally influenced, brackish marsh environment. The mid-depth salinity at the reference point was measured at 7.8 ppt during the initial sample collections on December 7, 1989. This measurement would represent the salinity of the general study site.

The facility consisted of a tank battery, separation equipment, living quarters, and a production pit. The tank battery, separation equipment and living quarters are located on an island, across from the production pit. The earthen production pit levees are covered with clam shells. The pit contained two sections. The surface area of the primary compartment is approximately 20,000 square feet. The secondary compartment had a surface area of approximately 4,000 square feet. The primary compartment was 14 feet deep while the secondary compartment was 10 feet deep. The total pit surface area is 24,000 square feet.

Eleven active wells are currently directing produced water to the pit. The monthly average rate of discharge between January, 1988, through January, 1990, was 143,000 barrels per month, or an average of 4,767 barrels per day according to company representatives. The monthly average oil and grease level (trichlorotrifluoroethane extractables) for the same period of time was reported as 13.5 mg/L. No historical data was available on the chloride concentration of the effluent. An analyses of the effluent by the Louisiana Department of Environmental Quality during the initial sampling visit on December 7, 1989, revealed a chloride concentration of 92,625 ppm.

The tidal flow at the site was most apparent in the canal adjacent to the southern side of the production pit and the north side of the production facility island. The water movement within this canal was either to the northeast or to the southwest at moderate velocities.

The produced water effluent pipe at the BC site was located on the northeast side of the pit. The effluent pipe discharged the produced water from within the secondary compartment. The effluent was directed into a small, open bay or cove which had a single opening at the southwest corner. The effluent pipe, located on the northeast corner of the pit, passed horizontally through the pit levee. The end of the outfall pipe was usually about 1.0 foot above the receiving streams surface.

The point of origin, BC-0, for the Bully Camp Field was 10 meters northwest of the outfall. The "A" transect extended northeast of the outfall and contained one sample point, BC-A50. The "B" transect traveled northwest of the outfall and contained sample points BC-B50 and BC-B100.

The "C" transect ran east of the outfall and then turned south through the opening of the cove. At the opening of the cove, the "C" transect split into a C_1 and C_2 branch. The C_1 branch traveled to the west and the C_2 branch traveled to the east. The "C" transect sample points were BC-C50, BC-C100, BC-$C_1$300, and BC-$C_2$300. The reference sample point, BC-R, was southwest of the outfall in a dead-end location canal.

II.B.4 Lake Washington Site (LW)

The LW study site was located in the Lake Washington Oil & Gas Field in Plaquemines Parish (Fig. II.5). The facility was located in an oil field location canal west of the Freeport Sulphur Co. Canal and north of the Rattlesnake Bayou and Freeport Sulphur Canal intersection. This facility has been discharging produced water since approximately 1958 with no cessation of operation. The study site area is a tidally influenced, saline marsh environment (Chabreck and Linscombe, 1978). The salinity of the area was measured at 23.0 ±0.2 ppt. during the initial visit to the site.

The facility consisted of a tank battery with separation equipment and a production pit. The earthen production pit is approximately 2800 square feet in surface area. The pit is approximately three feet deep with location canals adjacent to two sides of the pit. Sixteen active wells are currently directing produced water to the pit. The monthly average rate of discharge since January, 1988, through January, 1990, was 48,000 barrels per month, or an average of 1600 barrels per day, according to the company officials. The chloride concentration of the effluent on January 18, 1990, was measured at 107,000 ppm.

For the period of March, 1989, through January, 1990, the monthly average chloride level was 68,000 ppm and the monthly average effluent oil and grease level was 28 mg/L according to a company official.

The tidal flow at the site was most apparent in the canal adjacent to the tank battery. During sampling visits to the site, water movement in this canal was either to the north or to the south at moderate velocities.

The produced water effluent pipe at the LW site is located on the northern corner of the waste pit. The effluent is directed to a man-made oil field location canal adjacent to the pit. According to the U.S. Geological Survey, 1973 Bay Baptiste quad map, this location canal was separated from the Freeport

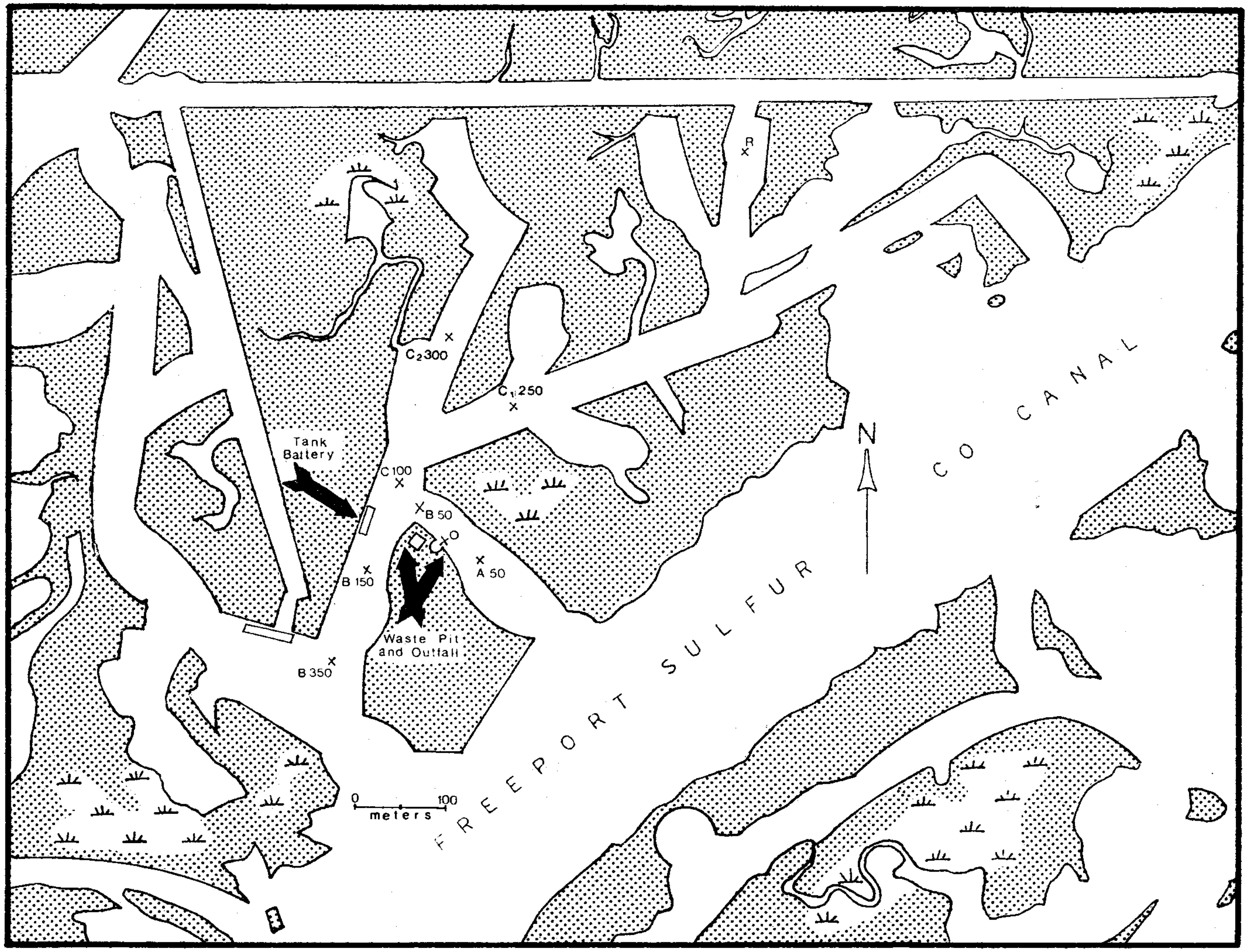

Figure II.5. Locations of Lake Washington (LW) site sample points.

Sulphur Company Canal by a narrow strip of land at the end. The dead end, however, has eroded since 1973 and is now open to the Freeport Sulphur Company Canal. Flow in the location canal is still limited because of the shallowness at its intersection with the Freeport Sulphur Canal.

Two weeks before the sampling effort conducted on January 18, 1990, the location canal receiving the effluent was dredged with the use of a drag line and bucket. According to company representatives, approximately two feet of sediment was removed from the location canal and placed on top of the existing pit levees. During this same period of time, the effluent pipe from the pit to the canal was shortened.

The point of origin, LW-0, for the Lake Washington Field was 20 meters north of the outfall. The "A" transect ran to the east of the outfall and contained one sample point, LW-A50. The "B" transect traveled west of the outfall then turned south into the tank battery canal. Three sample points were located on this transect: LW-B50, LW-B150, and LW-B350. The "C" transect ran west of the outfall and then turned north into the tank battery canal. Three sample points were also located on this transect: LW-C100, LW-C$_1$250, and LW-C$_2$300. The reference sample point, LW-R, was in a location canal northeast of the outfall.

Chapter III

OBSERVATIONS ON THE HYDRAULIC BEHAVIOR OF PRODUCED WATER EFFLUENTS

by

Kerry M. St. Pé, Richard Guidry,
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III.A Introduction

Gulf Coast oil field brines or produced waters generally contain much higher levels of dissolved salts per unit volume than natural sea water. Collins (1967) reported that the major ions in Gulf Coast produced water are sodium, calcium, magnesium, chlorides, bromides, sulfates, and bicarbonates, with sodium being the predominant cation and chloride the most abundant anion. Sea water also contains these salts but may differ from produced water in ionic ratios of calcium and magnesium (Reid, 1961). Sodium chloride accounts for 86% of all dissolved salts in sea water and 73% of dissolved salts in produced water (calculated from Reid, 1961 and Collins, 1967).

The term salinity is frequently used to describe the concentration of dissolved salts in produced water. In the classic sense of the definition, salinity refers to the weight of dissolved salts in one kilogram of sea water. Since the salts in sea water occur in uniform proportions, it is possible to calculate salinity from a known chloride concentration using the formula (Reid, 1961):

$$\text{Salinity (ppt)} = 0.03 + 1.805 \times \text{chlorinity (ppt)}$$

The above empirical formula is based on the fixed relationship of total dissolved solids (TDS) in sea water, particularly the ratio of total dissolved solids to chloride (=1.805).

Salinities of produced waters are generally calculated from this same formula, using chloride concentrations. Although the salts contained in produced waters differ in proportion to those in sea water, the difference between the TDS/chloride ratio in sea water and the TDS/chloride ratio in produced water is slight. A calculated oil field brine salinity can provide an accurate assessment of impacts on biotic osmoregulatory responses in the natural environment.

Hanor *et al.* (1986) evaluated regional variations in physical and chemical properties of south Louisiana oil field brines. Salinities varied with formation depth and ranged from

50 ppt to 150 ppt. Open sea salinities average 35 ppt (Reid, 1961). Louisiana inland water salinities vary considerably with distance from the Gulf of Mexico, but are almost always much less than those found in the open sea. Inland intrusions of waters from the gulf can form persistent stratified conditions in Louisiana estuarine lakes due to density differences attributed to salinity (Schurtz and St. Pé, 1984).

The high salinities of Gulf Coast produced water effluents in relation to inland receiving water bodies results in a substantial density difference. Gulf Coast produced waters are generally much heavier than Louisiana inland waters. Harper (1986), in a review of unpublished literature involving the effects of produced water, reported a bottom layer of higher salinities near effluents discharged into poorly flushed canals. The stratified conditions were apparent also in areas receiving increased tidal influence, but to a lesser degree.

Boesch and Rabalais (1989a) concluded that produced water effluents act as a dense plume after release to estuarine waters. They observed evidence of a limited initial dilution of produced water effluent to a dead-end canal at Pass Fourchon in southeast Louisiana. Because the dilution was not complete, the plume did not readily disperse throughout the water column and retained its identity until the canal intersected a more tidally affected water body. In Bayou Rigaud, where bottom currents were swifter, Boesch and Rabalais (1989a) observed elevated salinities only in the immediate vicinity of the produced water discharge.

Many past studies of produced water impacts have documented high concentrations of petroleum hydrocarbons in sediments near produced water effluents. The sediment concentrations of these pollutants usually decreases with distance from the outfall structure. Armstrong *et al.* (1979) observed heaviest concentrations of naphthalenes in sediments nearest to a produced water effluent structure in Trinity Bay, Texas. Bottom waters near this platform contained four orders of magnitude less naphthalenes than the underlying sediments. Sediment naphthalene levels decreased markedly as distance from the discharge increased.

The impetus for this study component (Chapter III) was largely a function of past observations by DEQ field investigators. These observations were summarized in an unpublished DEQ report (Baird, St. Pé, and Chisholm, 1987) detailing an investigation of a produced water discharge to a freshwater marsh system. One of the outfalls investigated at that time possessed a salinity of 148 ppt and was discharged to an oil field canal with ambient salinities less than 1.0 ppt. The flow rate of the effluent was 3,000 barrels/day. Field water quality measurements were made with a Hydrolab Surveyor II in areas surrounding the outfall at various depths in the water column. Since no salinity readings above the ambient level of 1.0 ppt were detected around the highly saline effluent, it was concluded that a complete mixing of the produced water effluent was not occurring. The investigators speculated that the reason for the absence of effluent detection might be because the denser produced water formed a layer over the bottom sediments which was too thin to be measured with the equipment used. The distance from the bottom of a Hydrolab Surveyor II probe to the conductivity/salinity sensor is 25.5 cm. Thus a thin, bottom-hugging plume of produced water may remain unnoticed if the layer was less than the 25.5 cm interval between the conductivity detector and the bottom of the probe.

Due to repeated observations of the above phenomenon at various produced water discharge sites, a closer examination of the hydraulic behavior of produced water effluents to poorly flushed systems seemed in order. This study component was designed primarily to examine chloride concentrations in that portion of the water column which is immediately above the sediment/water interface (up to +20 cm) and also to examine interstitial chloride levels in bottom sediments (down to -30 cm).

III.B Materials and Methods

Four study sites were selected for examination, each with a produced water discharge to a brackish water system. Study site LRT was located in the Lirette Oil and Gas Field in Terrebonne Parish near Montegut, Louisiana. Sites DF and BC were located in Lafourche Parish in the Delta Farms and Bully Camp Oil Fields, respectively. Study site LW was located in lower Plaquemines Parish, Louisiana, in the Lake Washington Oil Field. Each site is described in greater detail in Chapter II of this report.

Nine sample stations were established at selected distances along transects at each of the 4 study sites. One of the 9 sample points at each site was selected as a reference station for data comparison purposes. Effluent samples were also collected from each site at the outfall structure. Each sample point was identified according to the format described in Chapter II.

III.B.1 Field Water Quality Measurements

At each of the transect sample points *in situ* water quality measurements were obtained with a Hydrolab Surveyor II, Model 9000. Measurements were taken from the vertical water column at 0.5 m below surface and at 1.0 m intervals below surface down to 0.3 m above the bottom. The parameters recorded were sample depth (m), pH (s.u.), salinity (ppt), dissolved oxygen (ppm), temperature (°C), and corrected conductivity (µmhos/cm^2). Additionally, total station depth (m) and secchi disc readings were also recorded for each transect station.

III.B.2 Water Column and Effluent Laboratory Samples

In addition to field readings, water samples were collected from the mid-depth level at each transect sample point at all four study sites. Effluent samples were also collected from each site. Water column samples were collected with a stainless steel wastewater sampling device.

The mid-depth water column samples were analyzed for chlorides, total suspended solids, total dissolved solids, total organic carbon, and turbidity by the Department of Environmental Quality central laboratory in Baton Rouge. Effluent samples were analyzed for the same parameters and additionally for oil and grease. All samples were stored and preserved in the field according to EPA approved protocol as summarized in Table II.2. The analytical methods used are cited in Table II.3. A chain of custody was maintained for all samples collected.

III.B.3 Interstitial and Near-Bottom Water Strata Collections

Sediment core samples along with the overlying bottom water strata were collected in .065 m x .75 m transparent, butyrate tubes. The core tubes were slotted along the vertical axis with a table saw fitted with a fine-toothed blade. A plunge cut was used to form the slot which extended to 6 cm from each end of the tube. Marks were made along the slot at 1.0 cm intervals. The slot was then sealed with silicon adhesive. The core tubes were fitted onto a check valve type coring head constructed according to a description presented in Barrett *et al.* (1971). The above described core tubes were designed for this study to provide a means for extracting sub-samples of the water strata lying immediately over the sediment/water interface with minimal disturbance.

Bottom cores along with overlying water were collected from each transect sample point with the coring device fitted onto a 10 foot rigid plastic pole. At each collection point, the core tubes were carefully inserted into the bottom to a depth which would provide at least 35 cm of collected sediment. The core sampler was maintained in a vertical position at all times to avoid any mixing of the overlying water strata with the surface of the core.

Before removing the coring apparatus from the water a perforated end cap was placed on the still-submerged end of the core tube to guard against any downward shifting of the contents.

The end cap was perforated to avoid a pressure-induced upward shifting of the core sample. The perforations allowed trapped surface water to escape from the cap while it was being placed onto the tube's end.

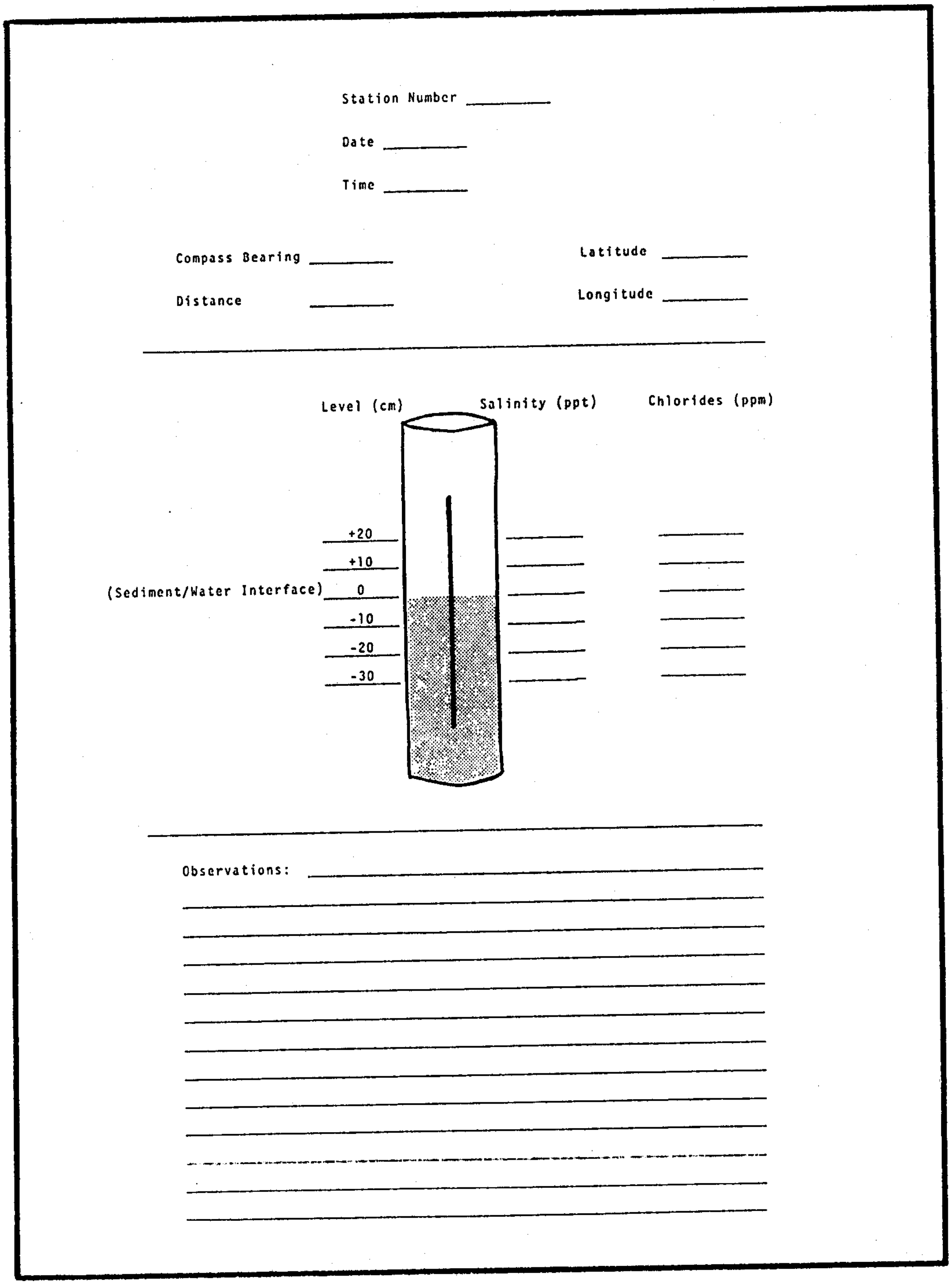
Once the core was brought on board, it was carefully inspected for any signs of mixing with the sediment surface. The overlying water within the core tubes was very clear at all sample points, allowing for a thorough inspection of the core surface. If the core water appeared even slightly turbid at the sediment/water interface, the entire sample was discarded and another was taken. Apparent mixing was rare and occurred only as a result of an inadvertent jarring of the core sampler after collection. Pictures of each sample were taken and observations were recorded on data sheets such as that shown in Figure III.1.

Following visual inspection, 50 ml sub-samples of water overlying the sediment core were removed from pre-selected levels with a 60 c.c. plastic syringe fitted with a 1.2 mm x 40 mm hypodermic needle. The sub-samples were obtained by inserting the hypodermic needle through the silicone-sealed slot of the core tube. The silicone plug allowed no leakage and was resilient enough to re-seal itself once the hypodermic needle was removed.

The overlying core water sub-samples were collected from 3 levels. The first sub-sample extracted was from 20 cm above the sediment/water interface, designated as the +20 level. A refractive salinity was then obtained from a small quantity of the sub-sample with a pre-calibrated Reichert Model 10419 automatic temperature compensated hand-held refractometer. This reading was obtained for use by the Department of Environmental Quality laboratory to determine dilutions necessary for chloride titrations performed later. The +20 cm sub-sample was then placed in a 60 ml clean, Nalgene container labeled with the transect sample point, the sample level, and the date and time collected.

Overlying core water was also collected from 10 cm above the sediment/water interface, designated as the +10 level, and from the sediment/water interface, designated as the 0 level. The above procedure was repeated for each of these levels. All overlying water sub-samples were stored on ice and transported to the Department of Environmental Quality central laboratory for chloride analysis.

After the +20, +10, and 0 water samples were collected, all of the remaining water above the surface of the core was siphoned off and discarded. The core was then extruded in 10 cm sections down to 30 cm below the sediment/water interface. Each sediment core section was stored in sealable, 1 gallon sized plastic bags labeled with the transect sample point, the sample level (-10,



Station Number ________

Date ________

Time ________

Compass Bearing ________ Latitude ________

Distance ________ Longitude ________

Level (cm)	Salinity (ppt)	Chlorides (ppm)
+20	________	________
+10	________	________
(Sediment/Water Interface) 0	________	________
-10	________	________
-20	________	________
-30	________	________

Observations: ________

Figure III.1. Interstitial and Near-Bottom Water Data Sheet

-20, and -30), and the date and time collected. All sediments were immediately stored on ice waiting further processing.

All sediment samples were transported to the laboratory for centrifugation. Each sample was mixed within the plastic sample storage bag. The sub-samples were then centrifuged in a Sorvall Superspeed RC2-B refrigerated centrifuge at 4500 rpm's for 10 minutes. Supernatant liquids were decanted into 60 ml Nalgene bottles, labeled and preserved on wet ice. The samples were transported to the Department of Environmental Quality central laboratory for chloride analysis. Refractive salinity readings of each supernatant were provided to the lab to aid in determining the size of samples used in chloride titrations.

III.C Results and Conclusions

III.C.1 Lirette Study Site (LRT)

The results of all conventional laboratory analyses of LRT water samples collected are shown in Table III.1. The effluent from the facility at this site had a chloride concentration of

Table III.1. Laboratory results of July 27, 1989, sample collections from site LRT.

STATION NUMBER	SAMPLE DEPTH(m)	CHLORIDES (mg/l)	TSS (mg/l)	TDS (mg/l)	TOC (mg/l)	TURBIDITY (NTU)	OIL & GREASE (mg/l)
Lrt-0	0.2	460	21	972	10.3	17	NR
Lrt-A100	0.9	866	17	1686	10.0	13	NR
Lrt-A250	0.9	744	14	1480	10.0	14	NR
Lrt-A500	0.6	557	16	1190	10.3	15	NR
Lrt-B20	0.9	1560	16	2984	10.5	13	NR
Lrt-C50	0.6	1260	15	2390	10.9	12	NR
Lrt-C250	1.1	2280	16	4288	11.0	12	NR
Lrt-C325	1.6	2575	16	4914	10.2	13	NR
Lrt-E	NA	76850	52	134500	97.6	80	<5
Lrt-R	0.9	2545	20	4852	11.6	12	NR

NR = Not Run

76,850 mg/l, and a total dissolved solids content of 134,500 mg/l. The calculated salinity was 138 parts per thousand (g/l). The effluent oil and grease level was reported as less than 5 mg/l. The effluent discharge rate from the production facility at this site averaged 462 barrels/day between January 1988 and January 1990. This represented the lowest rate of discharge of the facilities studied.

The oil and grease parameter is frequently used by regulatory agencies as a measure of trichlortriflouroethane extractable materials. Petroleum hydrocarbons would make up most, but not all, of the extracted components. Typical oil and grease limits in Louisiana Department of Environmental Quality permits for produced water effluents are 48 mg/l (monthly average) and 72 mg/l (daily maximum). The <5 mg/l of oil and grease detected in the LRT effluent is well within permitted limits for that parameter.

The chloride concentrations of interstitial water removed from each core section collected from the 9 Lirette transect points are shown in Table III.2. The top 10 cm section of the sediment core is labeled as the -10 level. The core section beginning at 10 cm below the sediment/water interface and ending at 20 cm below the interface is core level -20. The last 10 cm section examined was labeled as -30 and extended 30 cm below the sediment/water interface.

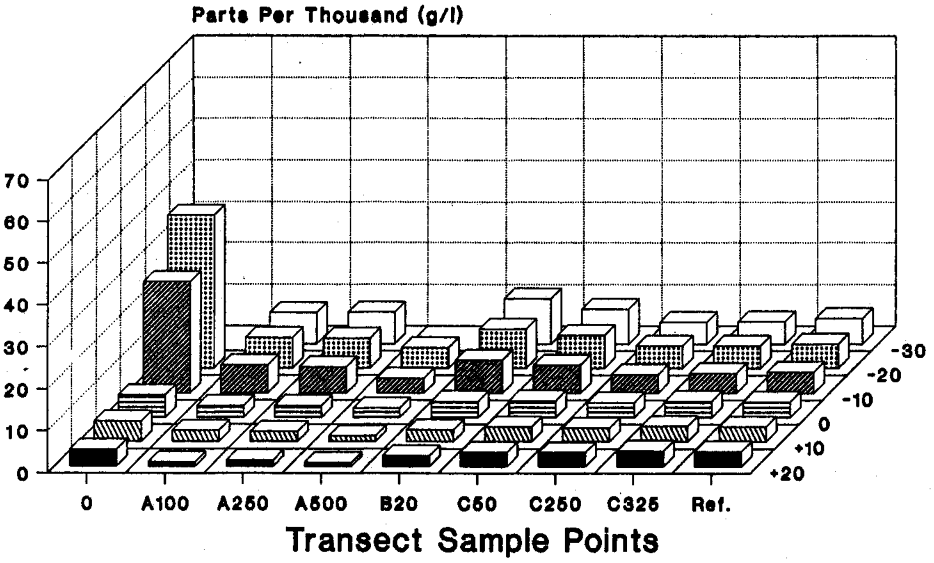
Table III.2 also contains the chloride concentrations of the water column overlying the bottom sediments at the LRT site. The 0 level was located at the sediment/water interface and the +10 and +20 levels were from 10 and 20 cm, respectively, above the sediment/water interface within the core tube.

A graphic representation of the data in Table III.2 is presented in Figure III.2 Generally, the pattern at each LRT transect sample point was one of lower chloride concentrations in the water column than in the sediments. At every LRT station the lowest chloride concentrations were at the uppermost water column level of +20. The highest concentrations were from the deepest core section at each station with the exception of LRT-C250 and LRT-C325. At these latter two stations the highest chloride concentrations were in the -20 core section rather than the -30 level. At stations LRT-0 and LRT-A500, the -30 core section was not collected because the sampler would not penetrate deep enough into the hard clay layer at about the -25 cm level at those stations.

The maximum chloride concentrations detected in the sediments at this site was 36,750 mg/l. These sediments were collected from the -20 cm core level at LRT-0. LRT-0 was the transect common point of origin and was located 10 meters from the end of the produced water effluent pipe. The highest

FIGURE III.2

Chloride Results of Interstitial Water From Sectioned Cores and Overlying Water Strata at all LRT Site Stations



Sample depths (cm) are expressed as above (+) or below (-) the sed/water interface (0).

Table III.2. Chloride results (mg/l) of interstitial water from sectioned cores and overlying water strata collected from site LRT on August 2, 1989.

Core Level (cm)	Transect Sample Point								
	0	A100	A250	A500	B20	C50	C250	C325	Ref.
+20	4000	976	1495	845	2475	3390	3310	3660	3525
+10	4885	2700	2390	1425	2920	3600	3375	3720	3590
0	5275	2800	2875	2290	3835	4000	3500	3785	3735
-10	26350	6630	6210	3475	7800	6620	4360	4670	4915
-20	36750	7220	7140	4870	9400	7800	5390	5420	5800
-30	NR	7300	7500	NR	10775	8270	5070	5300	6060

NR = Not Run

chloride concentration found in LRT overlying water was 5275 mg/l measured at the sediment/water interface of station LRT-0.

The mean chloride concentrations of interstitial water from all core levels at each station was calculated and is presented in Table III.3 in order of highest to lowest. The lowest sediment chloride level, 4172 mg/l, was at LRT-A500, the farthest station from the origin on transect "A". The highest mean sediment chloride concentration, 31,550 mg/l, was at the station closest to the produced water effluent, LRT-0.

Table III.3. **Sediment mean chloride concentrations for each LRT station. Ranked from highest to lowest concentration.**

Station #	Sediment Core Mean Chloride Concentrations (mg/l)
LRT-0	31550
LRT-B20	9325
LRT-C50	7563
LRT-A100	7050
LRT-A250	6950
LRT-R	5592
LRT-C325	5130
LRT-C250	4940
LRT-A500	4172

The sediments from stations LRT-C325, LRT-C250 and LRT-A500 had mean chloride concentrations less than the reference, LRT-R. Reference stations were selected at all sites for comparison purposes in areas which would be least likely to be influenced by produced water discharges. Dead-end location canals were deemed least likely to be influenced by petrogenic pollutants since water flow into these dead-end areas during incoming tides is restricted.

The restricted water movement into the area of the reference stations would also affect the natural chloride levels expected from sea water influences during incoming tides. Therefore, the chloride levels in sediments and overlying water at the reference stations could be expected to be somewhat less than the more distal stations along a transect, especially if the transect station is in a canal or water body which serves as a main tidal transport route.

For these reasons, a simple comparison between chloride levels at a reference station and a particular treatment station can not be used alone to determine which station is affected by a produced water effluent. Rather, all of the chloride data must be considered as a whole along with the observed hydrology of a site.

The observed tidal flow patterns at the Lirette site indicate that the primary water movement in this area is through the Humble Canal. Water velocities in the Humble Canal were moderate during peak rising or falling tidal periods. Water movements within the other canals at this site were too slight to be visually observed. Station LRT-C325 was in the Humble Canal at its intersection with the canal receiving produced water effluent from the facility studied (see Figure II.2).

Station LRT-C250 was located within the canal receiving produced water effluent, at a point 250 meters north of the origin and 75 meters south of the middle of the intersection with the Humble Canal. The interstitial chloride concentrations at LRT-C250 was the second to lowest of all those at the Lirette site. The distal station on the "A" transect, LRT-A500, was the farthest station from any expected natural chloride influence and had the lowest sediment chloride concentrations. The data presented in Tables III.2, III.3 and in Figure III.2 indicates a grouping of stations LRT-A250, LRT-A100, LRT-C50, LRT-B20, and LRT-0 in terms of those station sediments which were most likely impacted by the high chloride levels in the LRT effluent. Produced water influences on interstitial chlorinities were most evident at LRT-0. The impacts to sediment chlorinities at stations LRT-B20, LRT-C50, LRT-A100, and LRT-A250 were less in magnitude. The interstitial chlorinity of the -10 cm section at LRT-0 was 34% of the effluent concentration. The chloride concentration of interstitial water from the -20 cm core section at the same station was 48% of the LRT effluent concentration.

The mean chloride concentrations in the water overlying the Lirette station sediments is shown in Table III.4. The data is presented in order of highest to lowest mean chloride concentrations. Station LRT-A500 had the lowest station water column mean of 1520 mg/l. Station LRT-0 had the highest mean chloride concentration (5275 mg/l) of the overlying water levels analyzed at each station. These two stations, i.e. LRT-A500 and LRT-0, also were, respectively, the least saline and most saline of the LRT sediments (see Table III.3).

Other trends or patterns of water column chloride levels in relation to the location of the outfall were not readily apparent at the Lirette site. For example, while the station closest to the effluent (LRT-0) had the highest water column chlorinities, station LRT-B20 located 20 meters from the origin and 30 meters from the outfall was ranked fourth in order of lowest to highest concentrations. LRT-B20 water column salinities were also lower than those measured at the reference, LRT-R. The sediment chlorinities at LRT-B20, however, were among the highest measured at the Lirette site.

Table III.4. Overlying water mean chloride concentrations (mg/l) at each LRT station. Ranked from highest to lowest concentration.

Station #	Overlying Water Mean Chloride Concentrations (mg/l)
LRT-0	5275
LRT-C325	3722
LRT-C50	3663
LRT-R	3617
LRT-C250	3395
LRT-B20	3077
LRT-A250	2253
LRT-A100	2159
LRT-A500	1520

The chloride concentrations measured in overlying waters and in sediments at the Lirette site treatment stations were standardized to those chloride concentrations measured at the Lirette reference station. That is, the Lirette reference values were subtracted from the Lirette treatment values. The results are presented in Table III.5. Negative values are chloride values which are less than those of the corresponding level at the reference station LRT-R.

Table III.5. Lirette treatment station chloride concentrations minus Lirette reference station chloride concentrations (mg/l).

Core Level (cm)	Transect Sample Point							
	0	A100	A250	A500	B20	C50	C250	C325
20	475	-2549	-2030	-2680	-1050	-135	-215	135
10	1295	-890	-1200	-2165	-670	10	-215	130
0	1540	-935	-860	-1445	100	265	-235	50
-10	21435	1715	1295	-1440	2885	1705	-555	-245
-20	30950	1420	1340	-930	3600	2000	-410	-380
-30	NR	1240	1440	NR	4715	2210	-990	-760

The chloride concentrations in each of the water and sediment levels at stations LRT-C250 and LRT-A500 were less than the corresponding level at the reference station. All of the water column chloride concentrations at stations LRT-A100 and LRT-A250 were less than the corresponding levels at LRT-R. All sediment levels at the latter two stations, however, had greater chlorinities than the reference as did the sediments at LRT-0, LRT-B20, and LRT-C50. Each of the sediment strata at LRT-C325 were less saline than the corresponding reference station sections.

Stations LRT-0, LRT-B20, and LRT-C50 were the only three stations with chlorinities at the sediment/water interface greater than the reference interface concentrations. The standardized concentrations in the -10 and -20 sediment levels increase with depth at all three of these stations. LRT-B20 and LRT-C50 standardized concentrations increased from the 0 through the -30 core depth. The -30 core section was not collected at LRT-0.

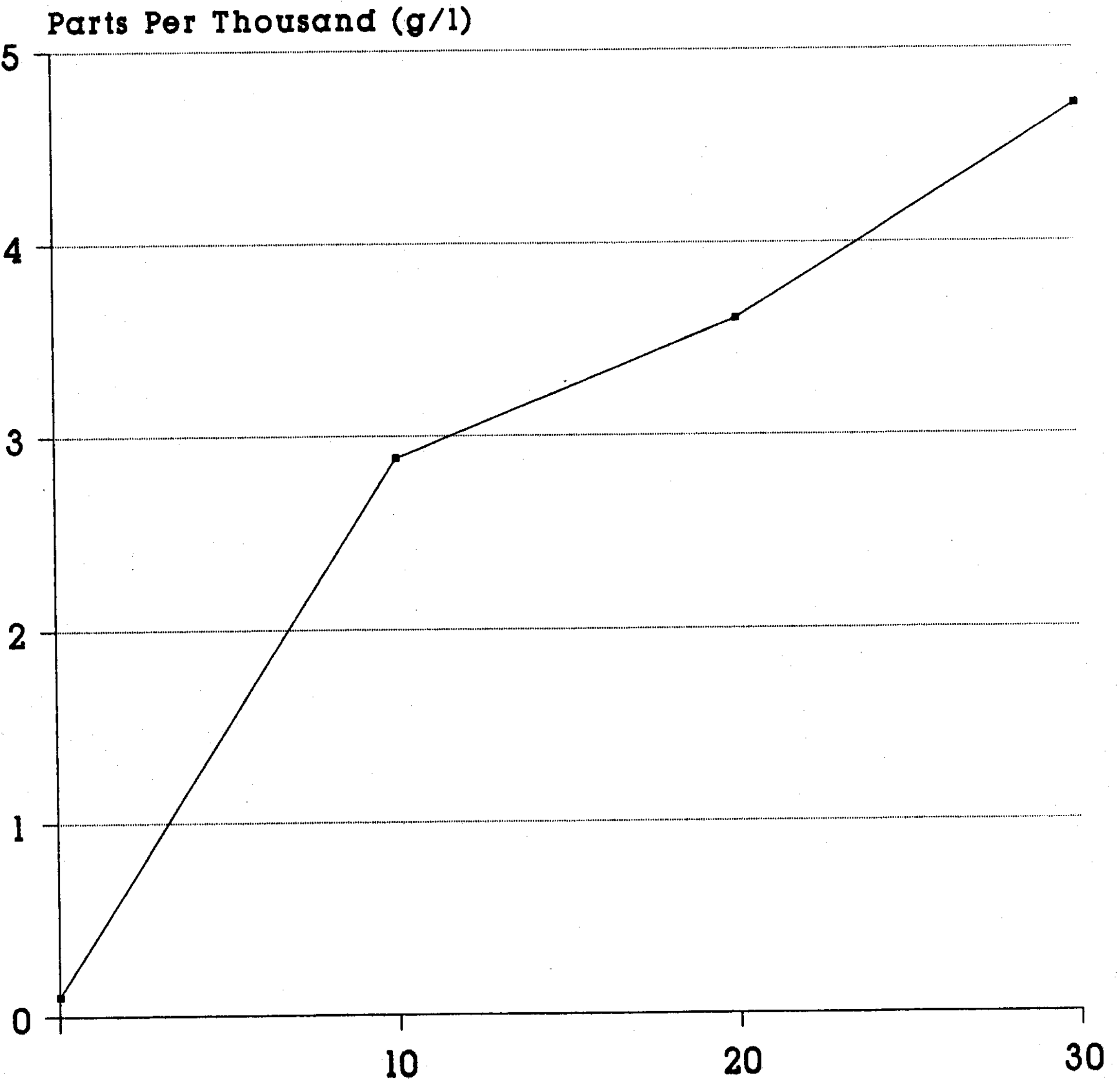
Trends were further examined using the data in Table III.5 for the 0, -10, -20, and -30 depths at stations LRT-B20 and LRT-C50. Slope calculations using chloride concentration as the dependant value (Y) and depth as the X value indicate a positive relationship between depth and chlorinity at station LRT-B20 (slope = +145.6) and LRT-C50 (slope = +61.3).

Linear regression analyses indicated that there was a good correlation between increases in depth and increases in chloride concentration at station LRT-B20 (r = +0.96) and LRT-C50 (r = +0.90). The relationship between depth and standardized chloride concentrations at the 0, -10, -20, and -30 core levels for station LRT-B20 is shown in Figure III.3.

The field water quality data collected from each LRT station on the July 27, 1989, sample date is listed in Table III.6. The data was collected using a calibrated Hydrolab model 9000 Surveyor II at 0.5 meters from the surface and at 1.0 meter intervals from the surface where the total station depth allowed. The deepest reading obtained from each station was 0.3 meters from the bottom. With the bottom of the Hydrolab probe resting on the bottom the conductivity/salinity sensor is about 25.5 cm above the bottom sediments. The depth sensor is near and just above the conductivity sensor.

FIGURE III.3

Relationship between Depth and Standardized Chloride Concentrations at LRT-B20



Plotted values are treatment station concentrations minus reference station concentrations.

Table III.6. Results of July 27, 1989, field water quality measurements at the LRT site.

STATION NUMBER	STATION DEPTH (M)	SAMPLE DEPTH (M)	pH (S.U.)	SALINITY (ppt)	D.O. (mg/l)	CONDUCTIVITY (umhos Corrected)	TEMP. (°C)	SECCHI (inches)
LRT-0	0.6	0.1	8.2	0.7	NR	1620	31.0	16
		0.3	7.7	1.3	NR	3820	31.7	
LRT-A100	1.8	0.5	7.8	0.5	5.4	2050	28.6	15
		1.0	7.6	2.3	4.5	4950	28.9	
		1.5	7.3	4.8	1.3	9200	28.6	
LRT-A250	1.8	0.5	7.7	0.4	5.7	1780	28.6	17
		1.0	7.5	4.3	5.1	8340	29.0	
		1.5	7.3	4.8	4.3	9190	29.0	
LRT-A500	1.3	0.5	7.4	0.7	4.9	2250	29.2	16
		1.0	7.1	2.6	2.5	5330	28.8	
LRT-B20	1.8	0.5	7.4	1.1	NR	2650	29.8	14
		1.0	7.5	3.5	NR	8560	29.8	
		1.5	7.5	5.0	NR	11330	29.7	
LRT-C50	1.3	0.5	7.3	1.1	NR	2907	30.2	15
		1.0	7.7	4.2	NR	9920	30.2	
LRT-C250	2.2	0.5	7.4	3.0	NR	14870	30.1	14
		1.0	7.8	3.7	NR	8960	31.2	
		1.9	7.4	5.0	NR	11410	30.0	
LRT-C325	3.3	0.5	7.6	2.7	NR	6180	31.6	10
		1.0	7.9	3.0	NR	7140	31.3	
		2.0	7.7	4.9	NR	11290	30.2	
		3.0	7.5	5.2	NR	12090	29.8	
LRT-R	1.8	0.5	8.0	2.3	NR	5580	33.4	24
		1.0	7.8	4.7	NR	10890	30.3	
		1.5	7.5	4.8	NR	11300	29.8	

NR = Not Run

The lowest bottom salinity measured at any LRT station with the Hydrolab was 1.3 ppt. This reading was taken at a depth of 0.3 m at the LRT-0 station located 10 meters from the produced water outfall. The highest salinity reading (5.2 ppt) was at LRT-C325, at 1.9 m from the surface or 0.3 m above the bottom.

III.C.2 Delta Farms Study Site (DF)

The results of all laboratory analyses for conventional water quality parameters collected from Delta Farms stations are shown in Table III.7. The effluent from the Delta Farms production facility had a chloride concentration of 77,700 mg/l or a calculated salinity of 140 ppt. The effluent oil and grease content was 7.0 mg/l. The daily average discharge rate of produced water between January 1988 and January 1990 was 13,458 barrels/day.

Table III.7. Laboratory results of October 5, 1989, sample collections from site DF.

STATION NUMBER	SAMPLE DEPTH(m)	CHLORIDES (mg/l)	TSS (mg/l)	TDS (mg/l)	TOC (mg/l)	TURBIDITY (NTU)	OIL & GREASE (mg/l)
DF-0	0.9	850	22	1350	11.7	11.0	NR
DF-A100	1.0	1450	38	2472	13.6	15.5	NR
DF-A200	0.6	800	22	1380	11.8	6.9	NR
DF-A300	0.5	800	12	1352	11.9	6.6	NR
DF-$B_1$200	1.2	775	12	1262	11.3	7.0	NR
DF-$B_2$200	1.0	750	18	1296	11.4	6.9	NR
DF-$B_2$300	0.9	700	20	1282	11.4	8.0	NR
DF-C75	0.8	778	34	1318	11.9	14.0	NR
DF-E	NA	77700	63	130787	27.1	16.0	7.0
DF-R	0.4	540	34	984	12.4	13.0	NR

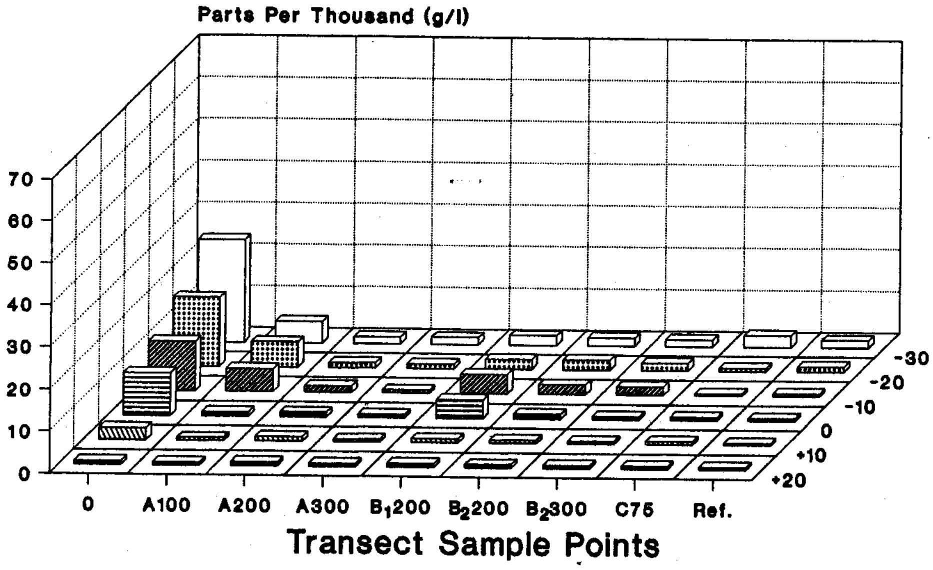
NR = Not Run

The chloride concentrations of interstitial water from each core section level (-10, -20, and -30) and each overlying water level (0, +10, and +20) is shown in Table III.8. This data is also presented in Figure III.4. At this study site, most of the overlying water chloride concentrations were less than the chloride concentrations from the sediment cores. The one exception was at DF-C75 where the 0 level had a higher chloride content than the -10 core section.

The maximum sediment chloride concentration detected at the Delta Farms site was at station DF-0. The -30 strata at this station had a 24,500 mg/l chloride content. Station DF-0 was located 20 meters from the facility's outfall pipe. The chloride concentration in the -30 core section at DF-0 is 32% of the effluent concentration.

FIGURE III.4

Chloride Results of Interstitial Water From Sectioned Cores and Overlying Water Strata at all DF Site Stations



Sample depths (cm) are expressed as above (+) or below (-) the sed/water interface (0).

Table III.8. Chloride results (mg/l) of interstitial water from sectioned cores and overlying water strata collected from site DF on October 5, 1989.

Core Level (cm)	Transect Sample Point								
	0	A100	A200	A300	B_1200	B_2200	B_2300	C75	Ref.
+20	900	725	875	700	840	790	700	775	575
+10	2900	725	1075	700	925	750	675	775	550
0	10000	1025	1125	700	4450	1225	700	775	550
-10	11750	5400	1575	750	4675	2375	2000	510	700
-20	16500	6000	1200	1075	2350	2425	1825	775	1200
-30	24500	5100	1550	1650	2250	1925	1625	2800	1650

The highest chloride concentration measured in DF overlying water was 10,000 mg/l. That sample was collected from the sediment/water interface at DF-0.

The mean chloride concentrations of interstitial water from all core levels at each Delta Farms station is presented in Table III.9 in order of highest to lowest values.

Table III.9. **Sediment mean chloride concentrations for each DF station. Stations are ranked in order of highest to lowest concentration.**

Station #	Sediment Core Mean Chloride Concentrations (mg/l)
DF-0	17583
DF-A100	5500
DF-$B_1$200	3092
DF-$B_2$200	2242
DF-$B_2$300	1817
DF-A200	1442
DF-C75	1362
DF-R	1183
DF-A300	1158

The lowest mean interstitial concentration occurred at DF-A300. Station DF-A300 was located near an opening to Bayou Perot which serves as the major tidal influence to the Delta Farms Oil and Gas field system. The highest mean chloride concentration in DF sediments was detected at DF-0, the transect origin. The mean concentration at DF-0 was 3.1 times greater than the second to highest mean which occurred at DF-A100.

The mean chloride concentrations in the water overlying Delta Farms station sediments is shown in Table III.10. The data is presented in order of highest to lowest values. Station DF-R had the lowest water column mean of 558 mg/l. Station DF-0 had the highest mean chloride concentration (13,800 mg/l). The minimum and maximum water column mean chloride concentrations closely compare to the minimum and maximum interstitial chloride means in that station DF-R was fresher than most of the other stations and DF-0 was the most saline.

Table III.10. Overlying water mean chloride concentrations for each DF station. Stations are ranked in order of highest to lowest concentration.

Station #	Overlying Water Mean Chloride Concentrations (mg/l)
DF-0	13800
DF-$B_1$200	2072
DF-A200	1025
DF-$B_2$200	922
DF-A100	825
DF-C75	775
DF-A300	700
DF-$B_2$300	692
DF-R	558

The chloride concentrations measured in overlying waters and in sediment interstitial water at the Delta Farms site treatment stations were standardized to those chloride concentrations measured at the Delta Farms reference station in a manner similar to that done for the Lirette site. The results are presented in Table III.11. Negative values are chloride values which are less than those of the corresponding level at the reference station LRT-R.

Table III.11. Delta Farms treatment station chloride concentrations minus Delta Farms reference station chloride concentrations (mg/l).

Core Level (cm)	Transect Sample Point							
	0	A100	A200	A300	$B_1$200	$B_2$200	$B_2$300	C75
20	325	150	300	125	265	215	125	200
10	2350	175	525	150	375	200	125	225
0	9450	475	575	150	3900	675	150	225
-10	11050	4700	875	50	3975	1675	1300	-190
-20	15300	4800	0	-125	1150	1225	625	-425
-30	22850	3450	-100	0	600	275	-25	1150

All of the chloride concentrations in each of the Delta Farms overlying water strata were greater than the corresponding strata at the reference station. Four of the Delta Farms stations had interstitial chloride concentrations which were less than or equal to the corresponding strata at DF-R. Standardized chlorinities at station DF-0 indicate the greatest rate of change with depth of all Delta Farms stations.

Station DF-A100 was located at the mouth of the canal which received produced water effluent. The standardized chloride concentrations in the overlying water strata increased gradually from the +20 to the 0 level. The interstitial concentrations showed a marked increase from the 0 to the -10 level, another increase from the -10 to the -20 level, and a decrease in the -30 level.

The data in Tables III.8, III.9, III.11, and in Figure III.4 indicates a grouping of stations DF-0, DF-A100, DF-$B_1$200, DF-$B_2$200, DF-$B_2$300, and DF-C75 in terms of those station sediment chlorinities which were most impacted by the produced water effluent from this facility. The degree of impact to these sediments varied considerably in the various strata. That is, the chloride concentrations in sediments at some stations were highest in the -10 cm strata, while in other stations the highest chloride concentration was in the -30 cm strata. Station DF-C75 was particularly interesting in that the chloride concentration was highest in the -30 cm strata, while the -10 and -20 cm strata had chloride concentrations which were, respectively, 190 and 425 mg/l less than the corresponding strata at the reference station.

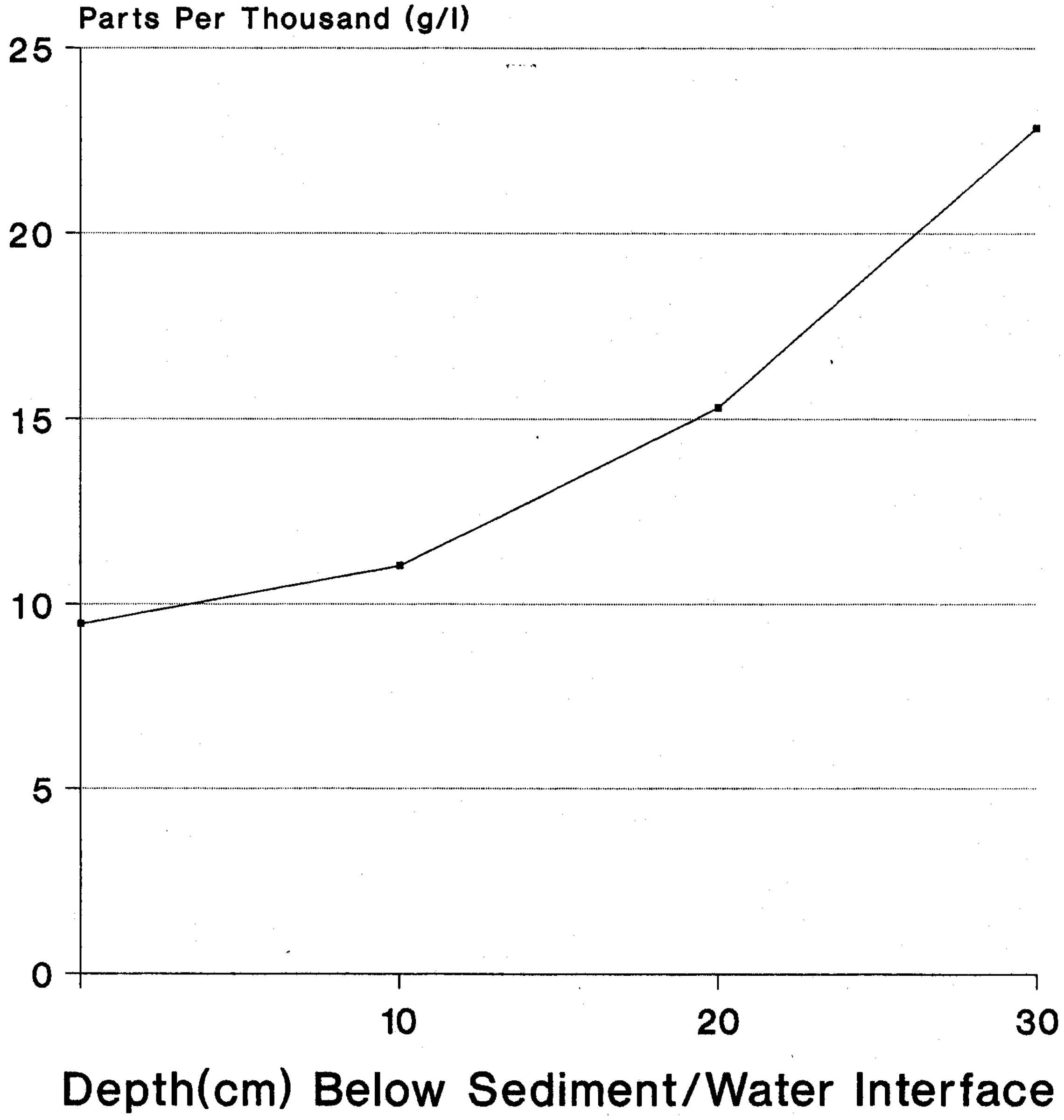
Station DF-0, and DF-$B_1$200 had overlying water chloride concentrations which were most likely affected by the produced water effluent. At DF-$B_1$200 the impact was at the sediment/water interface, while at DF-0 the impact was most evident at the 0 and +10 levels.

A trend of increasing sediment chloride concentrations with depth into the bottom was apparent at station DF-0. This did not occur at any of the other Delta Farms stations. Trend calculations using the data in Table III.11 for station DF-0 resulted in a slope value of +444.5 indicating a positive relationship between sediment strata depth and standardized chloride concentrations. The correlation (r) between sediment depth and chloride concentration at station DF-0 was 0.96. The relationship of standardized sediment chloride concentrations and depth at station DF-0 is shown in Figure III.5.

The field water quality data collected from each Delta Farms station on October 5, 1989 is shown in Table III.12. The data was collected in a manner identical to that collected at the LRT site. The lowest bottom salinity measured at the DF site was 0.4 ppt, at DF-R. The highest bottom salinity was 6.4 ppt, measured at the DF-0 station. DF-$B_1$200 had a bottom salinity of 6.3 ppt, almost equal to that of DF-0. The bottom salinity at DF-A100 (5.0 ppt) was also among the highest measured with the Hydrolab model 9000.

FIGURE III.5

Relationship between Depth and Standardized Chloride Concentrations at DF-0



Plotted values are treatment station concentrations minus reference station concentrations.

Table III.12. Results of October 5, 1989, field water quality measurements at DF site.

STATION NUMBER	STATION DEPTH (M)	SAMPLE DEPTH (M)	pH (S.U.)	SALINITY (ppt)	D.O. (mg/l)	CONDUCTIVITY (umhos Corrected)	TEMP. (°C)	SECCHI (inches)
DF-0	1.9	0.5	7.9	0.9	8.2	2620	25.6	22
		1.6	7.6	6.4	4.7	11980	25.6	
DF-A100	2.0	0.5	7.9	0.7	9.4	2280	26.9	17
		1.7	7.4	5.0	6.5	9690	25.6	
DF-A200	2.2	0.5	8.0	0.7	8.4	2280	26.8	24
		0.9	8.0	0.9	7.8	2640	25.7	
DF-A300	1.0	0.5	8.0	0.7	10.0	2310	26.7	23
		0.7	8.0	1.0	8.2	2920	26.3	
DF-B$_1$200	2.4	0.5	8.1	0.7	10.4	2270	27.3	22
		1.0	7.9	0.8	NR	2440	25.5	
		2.1	7.4	6.3	8.1	11680	26.0	
DF-B$_2$200	2.1	0.5	7.9	0.7	8.5	2240	27.5	18
		1.8	7.8	0.8	7.6	2460	25.3	
DF-B$_2$300	1.8	0.5	7.8	0.7	8.8	2290	25.8	21
		1.5	7.8	0.8	NR	2370	25.4	
DF-C75	1.6	0.5	7.0	0.8	NR	2360	24.8	18
		1.3	7.1	0.8	5.9	2400	24.8	
DF-R	0.8	0.5	7.9	0.4	7.5	1770	25.9	17

NR = Not Run

The bottom salinities measured with the Hydrolab at stations DF-0, DF-A100, and DF-B$_1$200 were noticeably higher than the bottom salinities at other DF stations. Salinities calculated from the +20 cm strata for these same stations are much lower than those measured with the Hydrolab. Since the Hydrolab bottom readings are from 25.5 cm above the bottom, as explained earlier, the salinities calculated from the +20 cm chloride concentrations in Table III.8 were expected to be higher than those obtained with the Hydrolab probe. The reason for this difference between calculated salinities and measured salinities at stations DF-0, DF-A100, and DF-B$_1$200 is unexplained.

III.C.3 Bully Camp Site (BC)

Samples were collected from each BC station for conventional water quality parameter analysis. The results are shown in Table III.13. The effluent from the Bully Camp production facility had a chloride content of 92,625 mg/l and a total dissolved solids content of 152,034 mg/l. The calculated salinity was 167 ppt. The oil and grease concentration of an effluent sample collected on December 7, 1989 was 25 mg/l. The discharge rate between January 1988 and January 1990 averaged 4767 barrels per day according to company officials.

Table III.13. Laboratory results of December 7, 1989, sample collections from site BC.

STATION NUMBER	SAMPLE DEPTH(m)	CHLORIDES (mg/l)	TSS (mg/l)	TDS (mg/l)	TOC (mg/l)	TURBIDITY (NTU)	OIL & GREASE (mg/l)
BC-0	0.7	4600	6	8392	15.0	7.5	NR
BC-A50	0.8	4625	4	8322	13.7	5.9	NR
BC-B50	0.9	4550	4	8406	14.2	6.5	NR
BC-B100	0.9	4825	10	8954	13.6	6.4	NR
BC-C50	0.9	4800	8	8502	13.8	6.1	NR
BC-C100	1.3	5050	6	9230	14.1	5.2	NR
BC-$C_1$300	1.3	4675	12	8750	14.1	5.7	NR
BC-$C_2$300	1.2	4675	10	8572	13.7	4.5	NR
BC-E	NA	92625	64	152034	32.2	4.7	25
BC-R	1.1	4850	12	8980	14.6	5.6	NR

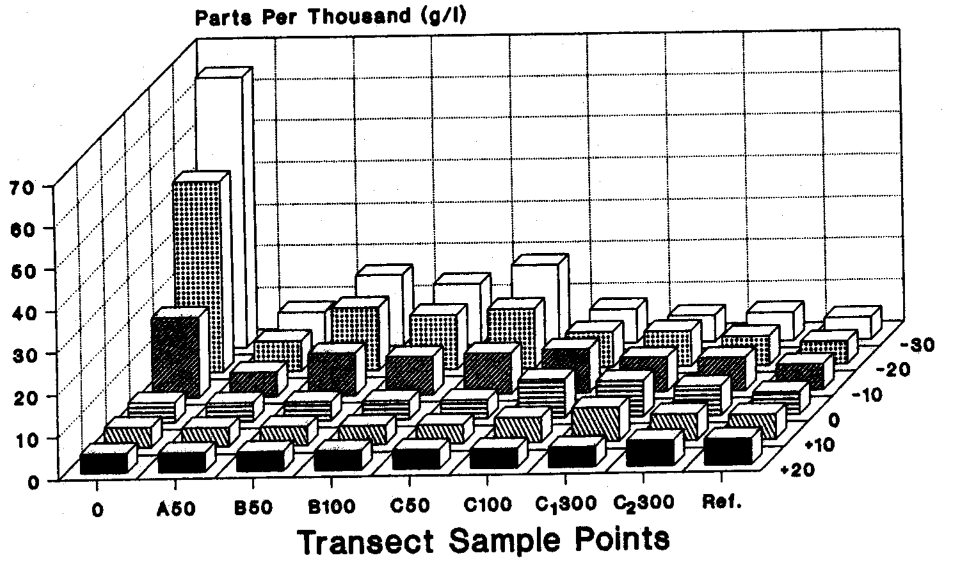
NR = Not Run

The chloride concentration of interstitial water from each station's core section (-10, -20, and -30) and each overlying water strata (0, +10, and +20) is shown in Table III.14 and in Figure III.6. Most of the overlying water chloride concentration were less than the chloride concentration in the sediment cores collected at the same station.

The maximum chloride concentration detected at the Bully Camp site was at station BC-0. The -30 level at this station had a 64,750 mg/l chloride content or 43% of the concentration of the effluent. Station BC-0 was located 10 meters from the end of the effluent pipe. The lowest chloride concentration at the BC site was 4500 mg/l and occurred in the water column at several stations at this site.

FIGURE III.6

Chloride Results of Interstitial Water From Sectioned Cores and Overlying Water Strata at all BC Site Stations



Sample depths (cm) are expressed as above (+) or below (-) the sed/water interface (0).

Table III.14. Chloride results (mg/l) of interstitial water from sectioned cores and overlying water strata collected from site BC on December 7, 1989.

Core Level (cm)	Transect Sample Point								
	0	A50	B50	B100	C50	C100	C_1300	C_2300	Ref.
+20	4500	4500	4500	4500	4500	4500	4750	6000	6250
+10	4750	4500	4500	4500	4500	6000	8000	6250	6000
0	4750	4500	4500	4500	4500	9000	8500	7000	5280
-10	19000	5750	10000	9000	9500	10250	8000	7750	6000
-20	45500	7250	15000	13000	14250	8500	8500	7000	5500
-30	64750	8250	16750	14500	18750	8000	6250	6750	5250

Mean chloride concentrations of interstitial water from all core levels at each Bully Camp station are presented in Table III.15 in order of highest to lowest value. The lowest mean interstitial concentration occurred at BC-$C_1$300. Station BC-$C_1$300 is located within a canal which was observed to be most influenced by natural tidal movements at this study site. The highest mean chloride concentration was measured at BC-0. The mean concentration at this station (43,083 mg/l) was 3.0 times greater than the second to highest mean which occurred at BC-C50 (14,167 mg/l).

Table III.15. Sediment mean chloride concentrations for each BC station. Stations are ranked in order of highest to lowest concentration.

Station #	Sediment Core Mean Chloride Concentrations (Mg/l)
BC-0	43083
BC-C50	14167
BC-B50	13917
BC-B100	12167
BC-C100	8917
BC-$C_2$300	7167
BC-A50	7083
BC-R	5583
BC-$C_1$300	4917

The mean chloride concentrations in the water overlying the sediments at this site are shown in Table III.16 in order of highest to lowest concentrations. Stations BC-A50, BC-B50, BC-B100, and BC-C50 all had mean values of 4500 mg/l, representing the lowest chloride concentrations measured at this site. Station BC-$C_1$300 had the highest mean chloride concentrations in the overlying water column.

The data in Table III.15 indicates a pattern of highest sediment mean chloride concentrations nearest to the outfall. Decreasing concentrations were observed at progressively increasing distances away from the outfall. The rate of decrease is much greater between BC-0 and BC-C50 than between any other two paired stations. This pattern was noted in all of the study site sediments.

Table III.16. Overlying water mean chloride concentrations for each BC station. Stations are ranked in order of highest to lowest concentration.

Station #	Overlying Water Mean Chloride Concentrations (mg/l)
BC-$C_1$300	7083
BC-C100	6500
BC-$C_2$300	6417
BC-R	5843
BC-0	4667
BC-A50, B50, B100 and C50	4500

The ranking in Table III.15 shows that the sediments at BC-A50 are less impacted than the other two stations located 50 meters from the origin, BC-C50 and BC-B50. This was probably due to the location and hydrology of the site. Although station BC-A50 was located 50 meters from the origin, as were BC-B50 and BC-C50, it was not in a position which would place it in the path of effluent flowing from the cove into which it was discharged. Stations BC-B50 and BC-C50 are located at points which would place them in positions which are more likely to be influenced by effluent flowing from the cove.

The effect of the produced water discharge on the Bully Camp water column is not apparent in Table III.16. Stations closest to the outfall had the lowest water column chloride means. Station BC-0, located 10 meters from the outfall was second in the ranking from lowest to highest mean concentrations.

The chloride concentrations measured in overlying waters and in sediment interstitial water at the Bully Camp site treatment stations were standardized to those chloride concentrations measured at the Bully Camp reference station. The results are presented in Table III.17. As in similarly presented tables, all negative values indicate chloride concentrations which are less than those of the corresponding level or strata at the reference station, BC-R.

In most cases the chloride concentrations in each of the Bully Camp overlying water strata were less than the corresponding strata at the reference station. The exceptions to this were in the +10 and 0 strata at stations BC-C100, BC-$C_1$300 and BC-$C_2$300. All of the interstitial chloride concentrations were higher than the corresponding sediment strata at BC-R. The one exception was in the -10 strata at station BC-A50 which was 250 mg/l less than the -10 strata at BC-R. The highest standardized chloride concentrations of all stations were at BC

Table III.17. **Bully Camp treatment station chloride concentration minus Bully Camp reference station chloride concentrations (mg/l).**

Core Level (cm)	Transect Sample Point							
	0	A50	B50	B100	C50	C100	$C_1$300	$C_2$300
20	-1750	-1750	-1750	-1750	-1750	-1750	-1500	-250
10	-1250	-1500	-1500	-1500	-1500	0	2000	250
0	-530	-780	-780	-780	-780	3720	3220	1720
-10	13000	-250	4000	3000	3500	4250	2000	1750
-20	40000	1750	9500	7500	8750	3000	3000	1500
-30	59500	3000	11500	9250	13500	2750	1000	1500

-0 in the sediment strata. The -30 strata at BC-0 had the highest concentration of all stations. Stations BC-A50, BC-B50, BC-B100, and BC-C50 all had respective maximum standardized concentrations in the -30 strata for BC-B50, BC-B100, and BC-C50, however, were noticeably higher in magnitude than the -30 strata concentrations at BC-A50. Four of the Bully Camp stations had standardized chloride values which increased with each depth level beginning with the 0 strata. Those stations were BC-0, BC-B50, BC-B100, and BC-C50.

Data collected at the Bully Camp site indicate that sediment chlorinites at stations BC-0, BC-B50, BC-B100, and BC-C50 were impacted by the produced water effluent from the facility at this site. These stations were among those closest to the effluent. Some lesser produced water influences to sediment chlorinities may be evident at BC-C100 in the -10 strata. Station BC-C100 was located in the mouth of the effluent-receiving cove near the canal into which most of the natural tidal movement at this site was noted. Stations BC-$C_1$300 and BC-$C_2$300 were located within that canal and would represent probable natural sediment chlorinities even though they were greater than the reference. Since the chloride concentrations in the -10 strata at BC-C100 were markedly greater than the corresponding strata at BC-$C_1$300 and BC-$C_2$300, it is likely that the upper sediment section at BC-C100 was influenced by the produced water effluent.

Produced water effects on chloride concentrations in the overlying water strata at the BC site were not conclusively evident at any of the site stations. The 0 strata at BC-C100 had the highest of the water column chloride concentrations. However, the measured concentration at that level was only 500 mg/l greater than the next to highest concentration measured in the 0 strata at station BC-$C_1$300. Also, BC-C100 is near the natural tidal chloride influence discussed earlier.

The data in Table III.18 are the results of field measurements taken on December 7, 1989, at the Bully Camp site. Water column salinities measured with the Hydrolab indicated homogeneous conditions throughout the water column at stations BC-0, BC-A50, BC-B50, BC-B100, and BC-C50. The measurements indicated a degree of salinity stratification at BC-C100, BC-$C_1$300, BC-$C_2$300, and, to a lesser degree at BC-R. Because of the location of these stations, the higher bottom salinities are probably due to natural, tidal influences. A possible exception to exclusively natural impacts may be at BC-C100. The Hydrolab

Table III.18. Results of December 7, 1989, field water quality measurements at BC site.

STATION NUMBER	STATION DEPTH (M)	SAMPLE DEPTH (M)	pH (S.U.)	SALINITY (ppt)	D.O. (mg/l)	CONDUCTIVITY (umhos Corrected)	TEMP. (°C)	SECCHI (inches)
BC-0	1.4	0.5	7.6	7.7	NR	13830	16.8	28
		1.0	7.7	7.7	NR	13820	17.2	
		1.1	7.6	7.7	NR	13880	16.9	
BC-A50	1.6	0.5	7.7	7.7	10.8	13770	17.3	24
		1.0	7.6	7.7	NR	13760	17.2	
		1.3	7.6	7.7	10.6	13770	17.2	
BC-B50	1.9	0.5	7.6	7.6	NR	13710	16.9	28
		1.0	7.6	7.6	10.5	13720	16.8	
		1.6	7.6	7.7	NR	13760	16.8	
BC-B100	1.8	0.5	7.6	7.6	9.5	13740	16.7	35
		1.0	7.6	7.6	NR	13720	16.8	
		1.5	7.6	7.6	10.0	13730	16.8	
BC-C50	1.8	0.5	7.6	7.6	NR	13660	16.9	29
		1.0	7.6	7.6	NR	13720	16.8	
		1.5	7.6	7.7	NR	13840	16.7	
BC-C100	2.6	0.5	7.6	7.7	10.5	13880	17.0	30
		1.0	7.6	7.8	NR	14040	16.9	
		2.0	7.3	10.8	NR	18500	15.9	
		2.3	7.1	16.1	5.9	26500	17.3	
BC-$C_1$300	2.6	0.5	7.6	8.0	NR	14090	16.7	27
		1.0	7.5	8.0	NR	14170	16.6	
		2.0	7.3	10.6	NR	18400	15.7	
		2.3	7.2	14.2	7.4	23700	16.0	
BC-$C_2$300	2.4	0.5	7.6	7.5	10.8	13540	16.9	29
		1.0	7.6	7.5	NR	13590	16.8	
		2.0	7.3	9.2	NR	16300	15.5	
		2.1	7.2	10.6	4.1	18400	15.3	
BC-R	2.3	0.5	7.5	7.6	6.6	13690	16.6	29
		1.0	7.7	7.8	NR	13910	16.8	
		2.0	7.3	8.1	8.0	14500	12.7	

NR = Not Run

measured a bottom salinity here of 16.1 ppt. This was 1.9 ppt higher than the bottom salinity measured at BC-$C_1$300.

III.C.4 Lake Washington Site (LW)

The results of all laboratory analyses for conventional water quality parameters collected from the Lake Washington site stations are shown in Table III.19. The effluent, LW-E, from the Lake Washington production facility had a chloride concentration of 107,000 mg/l and a total dissolved solids content of 160,415 mg/l representing a calculated salinity of 192 ppt. The effluent oil and grease content in a sample collected on January 18, 1990 was <5.0 mg/l. The daily average discharge rate of produced water between January 1988 and January 1990 was 1600 barrels/day.

Table III.19. Laboratory results of January 18, 1990, sample collections from site LW.

STATION NUMBER	SAMPLE DEPTH(m)	CHLORIDES (mg/l)	TSS (mg/l)	TDS (mg/l)	TOC (mg/l)	TURBIDITY (NTU)	OIL & GREASE (mg/l)
LW-0	0.3	13550	29	24877	7.4	4.3	NR
LW-A50	0.3	14500	27	25641	8.8	4.7	NR
LW-B50	0.2	13775	16	24766	7.5	4.1	NR
LW-B150	0.8	13900	15	24747	7.6	3.3	NR
LW-B350	0.8	13750	14	24962	7.5	3.3	NR
LW-C100	0.8	13875	15	24956	8.0	3.7	NR
LW-$C_1$250	0.7	13750	14	24922	7.2	3.7	NR
LW-$C_2$300	0.4	13750	12	24398	7.2	3.3	NR
LW-E	NA	107000	76	160415	2.5	4.0	<5
LW-R	0.3	13500	17	24199	10.2	4.3	NR

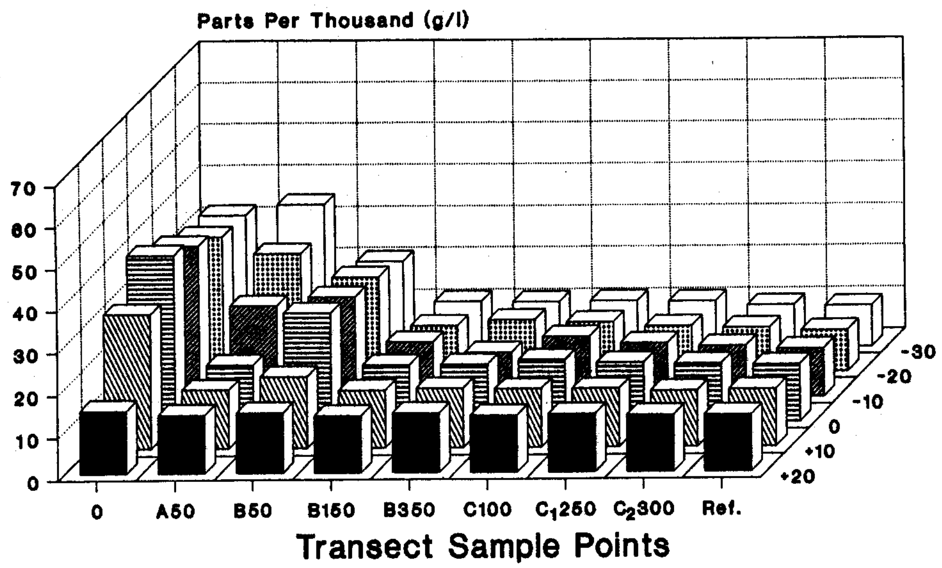
NR = Not Run

The salinity of this effluent was the highest measured of all the study sites. The 192 ppt effluent salinity is 5.5 times more saline than the average open ocean salinity (35 ppt).

The chloride concentrations of interstitial water from each core section strata and each overlying water strata is shown in Table III.20. This data is also presented in graphic form in Figure III.7. Generally, the pattern at each of the 9 Lake

FIGURE III.7

Chloride Results of Interstitial Water From Sectioned Cores and Overlying Water Strata at all LW Site Stations



Sample depths (cm) are expressed as above (+) or below (-) the sed/water interface (0).

Table III.20. Chloride results (mg/l) of interstitial water from sectioned cores and overlying water strata collected from site LW on January 18, 1990.

Core Level (cm)	Transect Sample Point								
	0	A50	B50	B150	B350	C100	$C_1$250	$C_2$300	Ref.
+20	14750	13750	14250	13500	14000	13500	13750	13500	13500
+10	31750	13750	16750	13500	14000	13750	13750	13250	13600
0	40000	13750	26000	13600	13750	14750	14000	13750	13500
-10	36250	22000	24000	13250	10950	14500	12750	12000	11350
-20	32750	28625	23000	11250	12600	12000	11000	10500	9750
-30	32100	34500	20750	11250	11000	11250	11000	10000	9750

Washington transect sample points was one of lower chloride concentrations in the water strata than in the sediments at the same station. The lowest overlying water chloride concentration occurred at LW-$C_2$300 in the +10 level and the highest value was at LW-0 at the sediment/water interface.

The lowest interstitial chlorinity at the LW site occurred at station LW-B350 in the -10 cm core section. The single highest interstitial value was in the -30 cm core section at LW-A50. At all of the other sites studied, i.e. Lirette, Delta Farms, and Bully Camp, the highest interstitial chloride concentration was in the -30 cm core section also, but was at the transect origin stations. The reason for the deviation from this pattern at the Lake Washington site is probably due to the fact that the company operating the Lake Washington production facility removed approximately 2 feet of sediment from the vicinity of stations LW-0 and LW-B50 shortly before the sampling began at this site. The sediment was excavated with a clam-shell type bucket and placed on the production pit levees. The estimate of 2 feet of water bottoms removed was provided by company officials. Also at the time of the removal, the effluent pipe from the production pit was shortened. The mechanical disturbance of the excavation activities resulted in the noted deviation from the patterns observed at the other sites.

The mean chloride concentrations of interstitial water from all core levels at each Lake Washington station is presented in Table III.21 in order of highest to lowest value. The lowest mean sediment core chloride concentration occurred at LW-R. The highest mean value in the LW core sections was at LW-0, one of the two stations mechanically disturbed during the excavation of this area. Station LW-0 was located 20 meters from the opening of the outfall pipe. The mean chloride concentrations at LW-0 equate to a calculated salinity of about 61 ppt.

The mean chloride concentrations in the water overlying the sediments at the Lake Washington site is shown in Table III.22 in order of highest to lowest values. Station LW-$C_2$300 had the lowest mean chloride concentration of all the Lake Washington stations. The LW-R and LW-B150 both had the second to highest mean chloride values.

The highest mean chloride concentration in the overlying water was at LW-0, with a mean value of 28,833 mg/l or a salinity of 52 ppt. The second highest mean was at LW-B50 with a value of 19,000 mg/l. Both of these stations were mechanically disturbed as described above. Station LW-A50, a station located 50 meters from the origin which was not disturbed, was among the three lowest mean chloride values in the overlying water.

Table III.21. Sediment mean chloride concentration for each LW station. Stations are ranked in order of highest to lowest concentration.

Station #	Sediment Core Mean Chloride Concentration (mg/l)
LW-0	33,700
LW-A50	28,375
LW-B50	22,583
LW-C100	12,568
LW-B150	11,901
LW-$C_1$250	11,583
LW-B350	11,517
LW-$C_2$300	10,833
LW-R	10,283

Table III.22. Overlying water mean chloride concentrations for each LW station. Stations are ranked in order of highest to lowest concentration.

Station #	Overlying Water Mean Chloride Concentrations (mg/l)
LW-0	28,833
LW-B50	19,000
LW-C100	14,000
LW-B350	13,917
LW-$C_1$250	13,833
LW-A50	13,750
LW-R and LW-B150	13,533
LW-$C_2$300	13,500

As for the Lirette, Delta Farms, and Bully Camp study sites, the chloride concentrations measured in overlying waters and in sediment interstitial waters at the Lake Washington site were standardized to those chloride concentrations measured at the LW-R (reference) point. This was done by subtracting reference concentrations from the corresponding strata concentrations at the treatment stations. The results are presented in Table III.23. Negative values indicate chloride concentrations which are less than those of the corresponding strata at the reference station.

In most cases the chloride concentrations in the Lake Washington overlying water strata and in the sediment strata were greater than the corresponding strata at the reference station. There were 3 exceptions to this observation. The +10 strata at LW-B150, the -10 strata at LW-B350, and the +10 strata at LW-$C_2$300 each had standardized chloride concentrations which were less than the corresponding reference strata. The highest standardized chloride concentrations in the LW site sediments were at LW-0, LW-A50, and LW-B50.

Table III.23. **Lake Washington treatment station chloride concentrations minus Lake Washington reference station chloride concentrations.**

Core Level (cm)	Transect Sample Point							
	0	A50	B50	B150	B350	C100	$C_1$250	$C_2$300
20	1250	250	750	0	500	0	250	0
10	18150	150	3150	-100	400	150	150	-350
0	26500	250	12500	100	250	1250	500	250
-10	24900	10650	12650	1900	-400	3150	1400	650
-20	23000	18875	13250	1500	2850	2250	1250	750
-30	22350	24750	11000	1500	1250	1500	1250	250

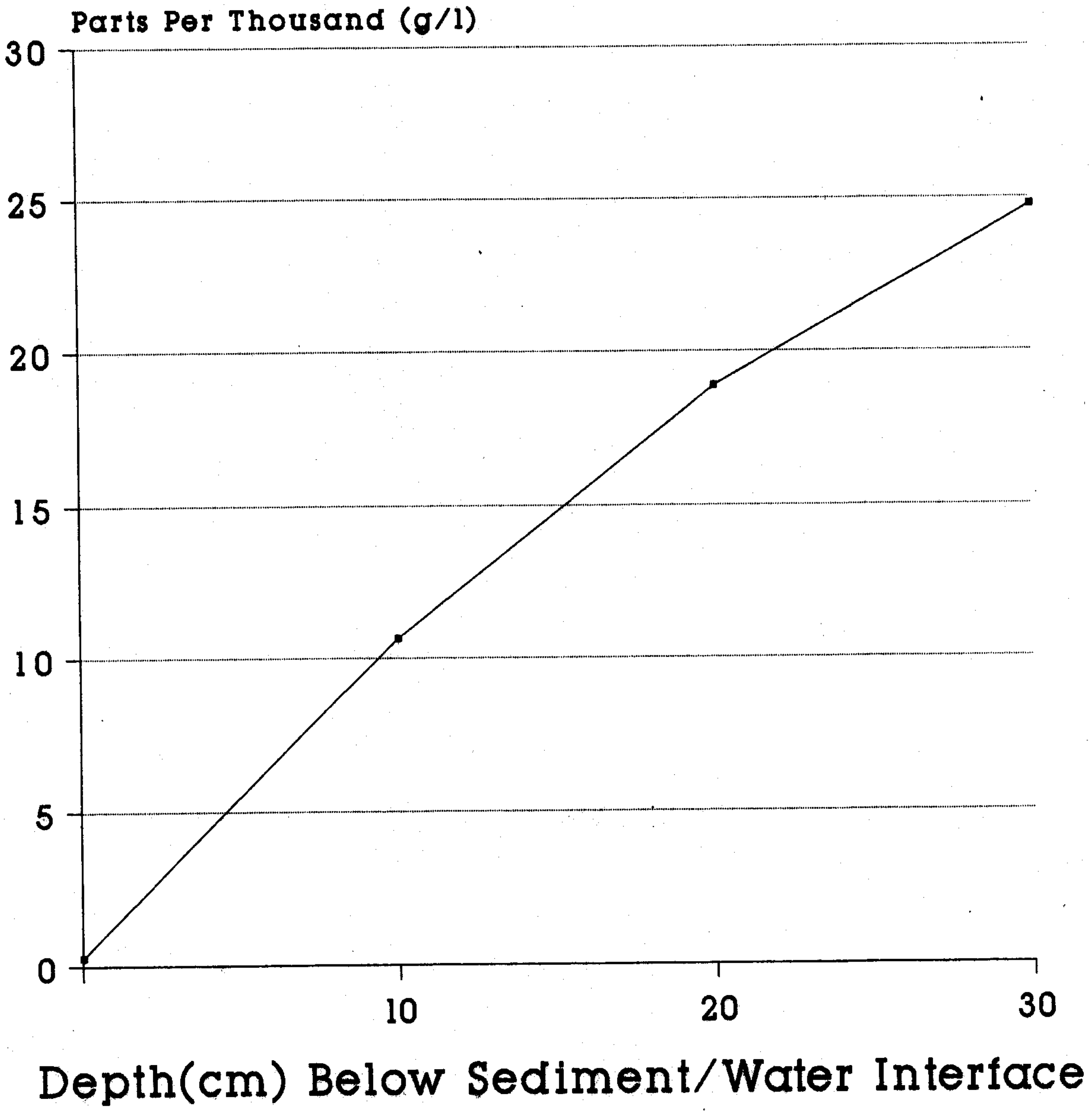
There was a pattern of decreasing standardized sediment chlorinities at LW-0 in the -10, -20, and -30 strata. This was different than the origins at all of the other study sites. The patterns indicated at LW-0 and LW-B50 can not be considered representative of other impacted stations since they were excavated prior to sampling. The interstitial chloride levels at these two stations were definitely impacted, however by the produced water effluent.

Sample point LW-A50, which was not excavated, demonstrated a pattern of increasing standardized chloride concentrations with depth into the sediments. Trend calculations using the standardized data in Table III.23 for station LW-A50 resulted in a slope value of +817.2 indicating a positive relationship and a good correlation (r = 0.99) between sediment depth and chloride concentration. This relationship is shown in Figure III.8.

A consideration of all the data collected at the Lake Washington site indicates that sediment chlorinities at LW-0, LW-A50, and LW-B50 in the -10, -20, and -30 strata were impacted by the produced water outfall from the facility at this site. LW-0 was 20 meters from the actual outfall structure, and LW-A50 and LW-B50 were both 70 meters from the outfall.

FIGURE III.8

Relationship between Depth and Standardized Chloride Concentrations at LW-A50



Plotted values are treatment station concentrations minus reference station concentrations.

Produced water effects to overlying water at the Lake Washington site were evident only at the excavated stations. The overlying water at station LW-A50 and at the stations farther away from the outfall does not indicate influence to the water column from the produced water effluent at this site.

The data in Table III.24 are the result of field measurements taken on January 18, 1990 at the Lake Washington site. The salinity data shows that this site was the most saline of all sites studied. The highest salinity measured with the Hydrolab Surveyor II was 25.1 ppt at 0.3 m above the bottom of LW-0. The lowest reading was 22.8 ppt at 0.3 m above the bottom of LW-R and LW-$C_2$300.

Table III.24. Results of January 18, 1990, field water quality measurements at LW site.

STATION NUMBER	STATION DEPTH (M)	SAMPLE DEPTH (M)	pH (S.U.)	SALINITY (ppt)	D.O. (mg/l)	CONDUCTIVITY (umhos Corrected)	TEMP. (°C)	SECCHI (inches)
LW-0	0.6	0.3	8.3	25.1	7.9	40200	20.2	28
LW-A50	0.6	0.3	8.3	23.1	8.4	36500	20.4	30
LW-B50	0.5	0.2	8.3	23.1	8.0	36600	20.2	18
LW-B150	1.7	0.5	8.1	23.1	7.2	36700	18.7	42
		1.0	8.1	23.2	7.2	36600	18.6	
		1.4	8.1	23.2	7.3	36800	18.5	
LW-B350	1.6	0.5	8.1	22.9	7.0	36400	18.7	42
		1.0	8.1	23.0	7.0	36400	18.7	
		1.3	8.1	23.1	7.3	36700	18.5	
LW-C100	1.6	0.5	8.2	23.0	7.4	36500	18.8	42
		1.0	8.1	23.0	7.2	36600	18.6	
		1.3	8.1	23.1	7.2	36600	18.5	
LW-$C_1$250	1.5	0.5	8.2	23.1	7.4	36600	18.9	30
		1.0	8.2	23.2	7.4	36700	18.6	
		1.2	8.2	23.2	7.4	36800	18.6	
LW-$C_2$300	0.8	0.5	8.2	22.8	7.5	36200	19.0	36
LW-R	0.6	0.3	8.2	22.8	7.5	36100	19.5	36

The data in Table III.20 for the LW-0 station at the +20 cm strata shows a chloride concentration of 14,750 mg/l. This represents a calculated salinity of 26.5 ppt. The calculated salinities at LW-0 for the +10 and 0 strata are 57.3 ppt and 72.2 ppt, respectively. The Hydrolab measurements at this station did not detect the produced water influences to the water column because the effect occurred at a depth below the position of the conductivity/salinity sensor.

III.D. **Summary**

The measured impacts of produced water discharges to overlying water and sediment chlorinities varied with distance from the outfall. The impacts were greatest at the stations nearest to the discharge.

The slotted core tube developed for this study allowed for a depth-integrated examination of overlying water and sediment chlorinities at each station. It is possible that some mixing between adjacent strata within the tube may have occurred, but this was evidently minimal since differences in chloride concentrations in adjacent strata within the tube were frequently quite distinct.

A comparison of chloride levels in overlying water and in sediments at the impacted stations demonstrates that the effects of produced water effluents to poorly flushed systems is considerably more apparent in the bottom sediments than in the water column. This was most apparent at, but not limited to, the origins (those stations which were closest to the outfall). The graph in Figure III.9 demonstrates the degree of chloride stratification at the origin stations for each site and the distinct concentration differences between the water and sediment fractions, especially at LRT-0 and BC-0. The Lake Washington origin, LW-0, was physically disturbed and does not follow the pattern observed at the other site origins.

Produced water was shown to penetrate at least 30 cm into the sediments at several of the study site stations. The full extent of the vertical penetration was not determined. This study only examined sediment chloride impacts down to the 30 cm depth. The trend of steadily increasing concentrations with depth at several of the stations suggests that a deeper penetration is likely.

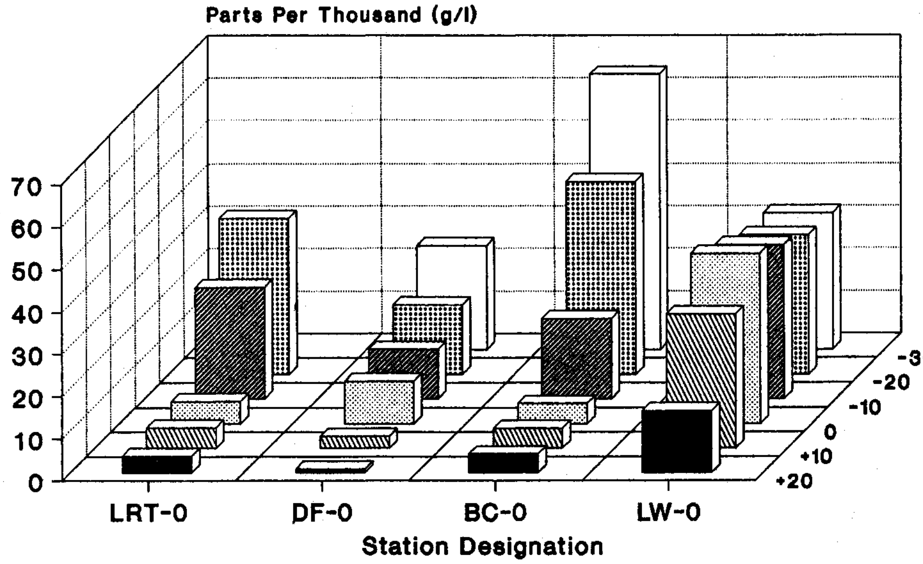
Qualitative observations of sediment samples were made at all transect stations. Sediment samples from the stations nearest to the outfall were visibly contaminated with petroleum hydrocarbons. Disturbances of bottoms at these stations often resulted in the appearance of an oil sheen on the surface of the water. Also, when sample residues from cores collected at affected stations were rinsed, sheens were noted.

Sediments at the origin stations at each site were grossly contaminated with petroleum hydrocarbons. Sediments at those stations were semi-fluid in consistency and dark black in color.

The results of this study also show evidence that conventional CTD instruments used to measure field water quality may not be capable of always detecting produced water chloride impacts to receiving water bodies. Bottom salinity measurements with conventional instrumentation at LRT-0 and BC-0 would not have detected elevated readings at those stations. A strict reliance on water column salinity readings might result in the erroneous conclusion that produced waters are quickly dispersed after discharge.

FIGURE III.9

Chloride Results of Interstitial Water From Sectioned Cores and Overlying Water Strata at all Site Transect Origins



Sample depths (cm) are expressed as above (+) or below (-) the sed/water interface (0).

In terms of area affected by the effluents, the observed effects within the sediments extended farther from the outfall than did the effects in the overlying waters. The stations with noted chloride increases in the water column tended to be those which were closest to the outfall. The outfall from the Lirette facility had the greatest spatial impact with sediment chlorinities showing effects at a station 250 meters from the origin. Since the Lirette production facility had the lowest effluent flow rate of all study sites, the spatial extent of the impacts seems to be more dependant on factors less related to discharge volume. The Lirette outfall was located farther away from significant tidal currents than the other site discharges. It is probable that receiving stream hydrology is the dominant factor related to the spatial extent of interstitial salinity impacts from produced waters.

The relationships of interstitial chloride concentrations and depth of penetration were cumulatively examined at all study site stations. Slopes were calculated for each site at stations representing similar distances from the origin. The slopes calculated for each site at a particular distance from the origin were then averaged and are presented in Table III.25.

The first and second columns in Table III.25 indicate the transect designation and distance from the origin, respectively. The next four columns contain the slope relationships calculated for a particular site station. At station LRT-A250, for example, the calculated slope was +69.4. The figures in the last column were obtained by averaging the study site rates of change at the origin, then at 50, 100, 250, and 300 meters from the origin.

The data in Table III.25 is from selected site stations. There were three criteria used for selection. The first criteria was that more than one station from a particular distance be represented by the data. If only one station at a particular distance from the origin was examined in the study, that data was not utilized since an average across all sites could not be obtained. For example, only one station located 20 meters from an origin was examined (LRT-B20), therefore an average for stations 20 meters from an origin would not be valid. Other stations with only one distance represented were LRT-C75, LW-B150, LRT-C325, and LW-B350.

A second criteria for selection was that more than one site have stations represented at a particular distance. Only Delta Farms had stations 200 meters from the origin (DF-A200, DF-$B_1$200, and DF-$B_2$200), therefore slopes for 200 meter stations were not used.

The third criteria was that station sediments be subject to no more disturbances than would be expected at the other stations. Since stations LW-0 and LW-B50 were excavated shortly before collection, the data from those locations were not utilized.

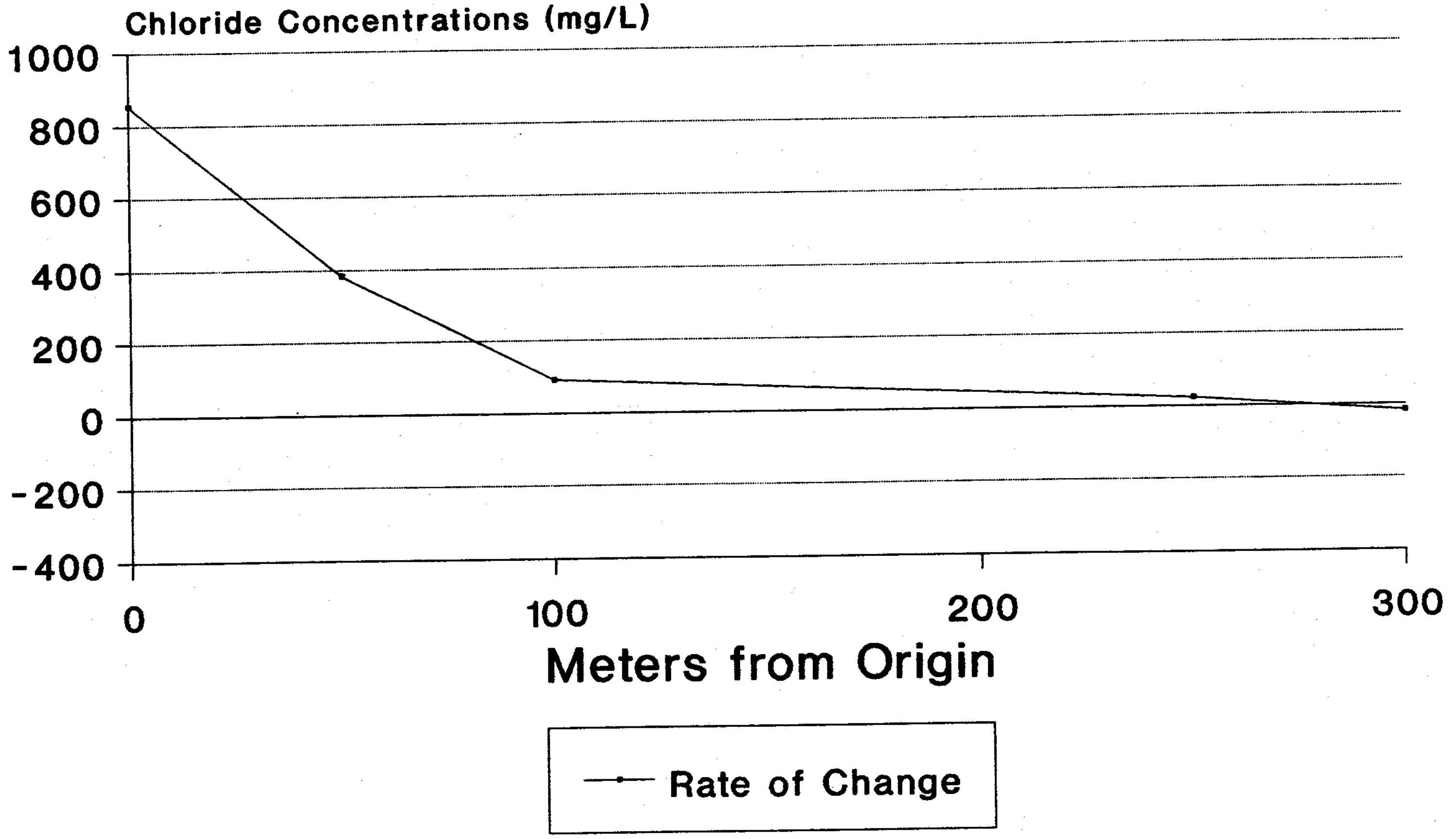
Table III.25. Summary rates of change in sediment chloride concentrations vs. distance from origin at selected study site stations.

Transect	Distance From Origin (m)	Study Site Rates of Change				Average Slope By Distance From Origin
		LRT	DF	BC	LW	
	0	+48.9	+444.5	+2070.9	NA	854.5
A	50	NA	NA	+133.4	+817.2	383.2
B	50	NA	NA	+423.4	NA	
C	50	+61.3	NA	+480.9	NA	
A	100	+62.3	+90.2	NA	NA	91.1
B	100	NA	NA	+345.9	NA	
C	100	NA	NA	-41.6	-1.5	
A	250	+69.4	NA	NA	NA	
B	250	NA	NA	NA	NA	23.1
C	250	-21.2	NA	NA	NA	
C_1	250	NA	NA	NA	+21.0	
A	300	NA	-6.2	NA	NA	
B	300	NA	NA	NA	NA	
B_1	300	NA	NA	NA	NA	-16.6
B_2	300	NA	-12.0	NA	NA	
C_1	300	NA	NA	-56.6	NA	
C_2	300	NA	NA	-9.1	+1.0	

The rate and trend of changes in sediment chloride concentrations at the selected study site stations is shown in Figure III.10. The trend represented in the graph indicates an exponential rate of increase in sediment chloride concentrations as the origin is approached. The greatest rate of change was at the origin stations and the least amount of change was at the stations located 300 meters from the origin. The trend at the 300 meter stations was one of decreasing concentrations with depth (slope = -16.6).

FIGURE III.10

Rate of Changes in Sediment Chloride Concentrations vs. Distance from Origin at Selected Site Stations



Plotted values are average of slopes
calculated from standardized chloride
data from all study sites.

Chapter IV

RADIUM 226 ACTIVITIES IN PRODUCED WATER EFFLUENTS AND PROXIMATE SEDIMENTS

by

Matt Schlenker and Kerry St. Pé

IV.A Introduction

Radium 226 is an intermediate member of the Uranium 238 decay series and the immediate daughter of Thorium 230. The half-life of Ra 226 is 1,622 years. Figure IV.1 shows the principle decay scheme of the uranium series in which radium occurs as an intermediate member. Ra 226 decays to Radon 222 by alpha particle emission. Because Rn 222 is a non-reactive gas, it is the most mobile radioisotope of the U 238 series. Radon is commonly present in natural gas from oil fields. The enrichment of Ra 226 relative to its uranium parent in oil field brines may be the result of the different chemical behaviors of radium and uranium in certain environments according to Hanan (1981). Radium 226 may also be more concentrated in the brine as a result of alpha particle recoil of radium into formation waters when Th 230 decays (Kronfeld *et al.*, 1975).

Formation waters, produced waters, and oil field brines are some of the names used to designate the saline waters brought to the surface during the production of petroleum in oil fields. Produced waters from locations throughout the world have been shown to contain environmentally high radium concentrations (Hanan, 1981). Oil field brines from Louisiana Gulf Coast oil fields have also been shown to contain high levels of radium 226 activity. Table IV.1 and Figure IV.2 present Ra 226 data reported by Reid, 1984.

The variability of Ra 226 ranged from a low of 131 picocuries/liter pCi/l in the Houma District sample to a high of 393 pCi/l at Garden Island Bay, Louisiana.

By definition, a Curie (Ci) is a unit of radioactivity equal to 3.7×10^{10} disintegrations per second or 2.22×10^{12} disintegrations per minute. A pico-Ci is equal to 1×10^{-12} Ci, or 2.22 disintegrations per minute.

The investigation and regulatory control of the impacts of naturally-occurring radioactive materials (NORM) have been overlooked by federal and state agencies in the past, while stringent controls were placed on X-ray and other man-made

Figure IV.1

Principle Decay Scheme of the Uranium Series

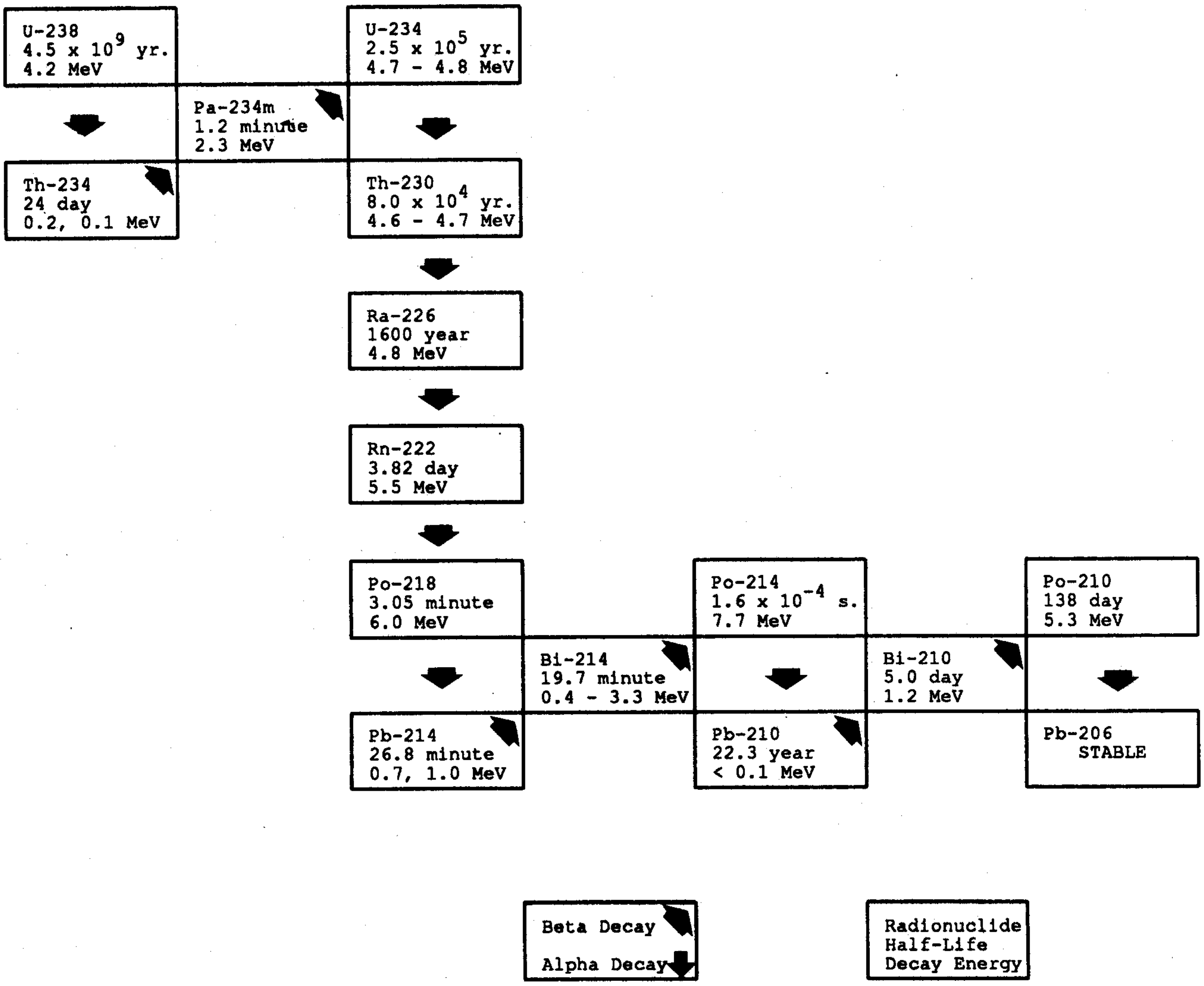


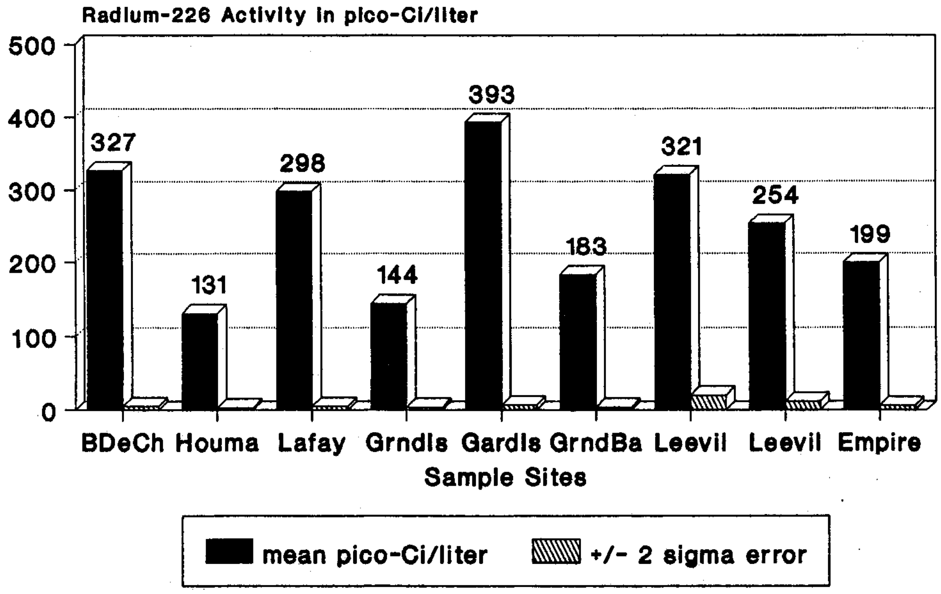
Figure 1 reproduced from Figure F-01-02, EML manual, 1983

Table IV.1. Radium 226 content of some Gulf Coast oil field production brines.

Identification	Radium 226 (pico-Ci/1)
Bay De Chene, Louisiana	327 ± 5
Houma District, Louisiana	131 ± 3
Lafayette District, Louisiana	298 ± 5
Grand Island, Louisiana	144 ± 4
Garden Island Bay, Louisiana	393 ± 7
Grand Bay, Louisiana	183 ± 4
Leeville, Louisiana	321 ± 20
Leeville, Louisiana	254 ± 12
Empire, Louisiana	199 ± 6

(Data provided by Dr. David F. Reid, Naval Ocean Research & Development Activity, National Space Technology Laboratory, Bay St. Louis, MS)

Figure IV.2
Radium-226 Activity in Louisiana Produced Water Effluent



Data Provided by Dr. David F. Reid, NSTL, Bay St. Louis, Mississippi sources of radiation. The lack of regulatory controls for NORM has been due, in part, to the fact that the federal government has limited jurisdiction over NORM, and control was previously left up to the states, which typically did not have adequate programs or staff to deal with the problem (Louisiana Department of Environmental Quality, 1989).

Proposed EPA regulations promulgated in response to the Resource Conservation and Recovery Act of 1976 would classify radioactivity levels greater than 50 pCi/l as a hazardous waste (La. Department of Environmental Quality, 1989). Based on this proposed definition of wastes, hazardous by virtue of radioactivity, oil field production brines could become classified as hazardous. Current Nuclear Regulatory Commission regulations governing the operations of licensees permit no more than 30 pCi/l in liquid discharges to unrestricted access areas, and standards for drinking water are set not to exceed 5 pCi/l (Code of Federal Regulations, 40CFR:141.15, 1986)

Both the U.S. Environmental Protection Agency and the Conference of Radiation Control Program Directors have recommended remediation of radium-contaminated soils to 5 pCi/g above background. The Louisiana Radiation Regulations prohibit the discharge of Ra 226 contaminated liquids with greater than 30 pCi/l activity from licensed facilities to unrestricted areas. The natural Ra 226 activity of surface waters is usually below 1 pCi/l.

The natural Ra 226 activity of surface soils in Louisiana ranges from less than one to around 7 pCi/g, according to the La. Department of Environmental Quality, Nuclear Energy Division (1989). In another baseline study of naturally occurring radium 226 activities, DeLaune *et al.* (1986) examined 37 samples of Louisiana soils and sediments. Their sample locations included saline, brackish, and fresh marshes as well as upland sites. radium 226 activities ranged from 0.8 to 2.8 pCi/g with a mean of 1.65 pCi/g.

On February 20, 1989, the Louisiana Department of Environmental Quality (LDEQ) issued an emergency rule, which amended the Louisiana Radiation Regulations by adding a chapter entitled, "Regulation and Licensing of Naturally-Occurring Radioactive Materials (NORM)". Following several months of review by technical committees, two rounds of public hearings and comments, and a favorable vote by the House and Senate Committees on Natural Resources, the permanent rule was adopted, and Louisiana became the first state to promulgate NORM regulations. Exemptions to this Rule include produced waters, since they are being regulated by the Water Pollution Control Division of LDEQ under the Louisiana water discharge permit system (Bohlinger, 1989).

The radium levels observed in most saline produced waters from the Gulf Coast Region exceed proposed and existing radium discharge limits applied to other sectors (U.S. E.P.A., 1978). Millions of gallons of produced water carrying NORM contamination are being released annually to the environment in coastal Louisiana. We have very little information on the fate and effects of the materials in the coastal environments (LDEQ, 1989).

Produced water samples from Louisiana platforms exhibited total radium activities of 605-1215 pCi/l in a recent study by Neff *et al.* (1987). It has been estimated that production water from the Leeville Oil Field (coastal Louisiana) contributed up to 1.76 Curies of radium to the marsh around the field in a 5-year period (U.S. E.P.A., 1978). Some fields have been in production for 40 years or more which means that the total radium released to the environment at these old fields could be in excess of 10 Curies over the lifetime of the fields.

Hindrichs and Chisholm (1990) analyzed radiological data from produced water discharges to Louisiana surface waters. The data was submitted to LDEQ by the oil production industry as a result of an amendment to LAC 33:IX. Specifically, new language under Section 708 of LAC 33:IX required a one-time analysis for soluble radium 226 and radium 228 of all existing produced water discharges. The submission of the data was required by August 20, 1989.

Three test procedures from Standard Methods, 16th Edition (Greenberg *et at.*, 1985) were allowed for radium 226 analysis: method 706, radium 226 by radon in water; method 707, radium 226 alpha count; and method 707, radium 226 radon emanation procedure. Statistical analysis by Hindrichs and Chisholm (1990) of the submitted data showed a significant variation in results obtained with the various methods. Because of this variation and apparent discrepancies in data from the radon in water and alpha counting methods, Hindrichs and Chisholm (1990) limited their analysis to data obtained with the radon emanation procedure. The latter method accounted for 87% of the data received (n=403) by the Department of Environmental Quality from the produced water dischargers complying with the radiological reporting regulation. Mean radium 226 activity was 175± pCi/l with a reported range of 0-930 pCi/l. Mean discharge loading was 91 µCi/day based on the mean produced water discharge volume and mean activities. The highest total loading by parish was 23,186 µCi/day, occurring in Plaquemines Parish (Hindrichs and Chisholm, 1990).

IV.B Materials and Methods

A total of four study sites with produced water discharges to brackish water systems were selected for examination. The study sites were located in the Lirette (LRT), Bully Camp (BC), Delta Farms (DF) and Lake Washington (LW) Oil Fields (see Chapter II). Nine sample stations were established at selected distances along transects at each of the four study sites. One of the nine sample points at each site was selected as a reference station for data comparison purposes. Each sample point was identified according to the format described in Section II.A of this report.

IV.B.1 Sediment Sample Collection and Preparation

Sediment core samples were collected from each transect sample point at each of the four study sites. Sediment samples from the Lirette site were collected on January 23, 1990; from the Delta Farms site on October 5, 1990; from the Bully Camp site on December 7 and 8, 1990; and from the Lake Washington site on January 18, 1990. Some of the stations at Delta Farms were re-sampled on March 6, 1990, to confirm the results of the initial sampling. The coring device consisted of a 0.065 m X 0.75 m colorless butyrate tube and a check valve type core head fitted onto a 10 ft. rigid plastic pole. At each collection point, the core tube was carefully inserted into the bottom to a depth which would provide at least 15 cm of collected sediment. The core sample was maintained in a vertical position at all times.

Once the core was brought on board the sampling vessel, the overlying water was carefully decanted out of the core tube. The top 10 cm of the core immediately below the sediment/water interface was then extruded into a 500 ml Nalgene wide-mouth jar using a teflon-lined plunger. The jar was sealed and labeled with date, time, and sample location. The sample was then preserved on wet ice and transferred to the laboratory for drying.

Each sediment sample was dried in aluminum trays constructed out of heavy duty aluminum foil. The dimensions of these trays were approximately 7" x 10" x 1". Approximately four layers of foil were needed to construct the trays in order to support the weight of the sediment sample.

The sediment samples were transferred from the 500 ml collection container into the aluminum foil trays. A clean spatula was used to transfer and evenly distribute the sample within the tray. The tray was then labeled, placed in a vented oven, and dried overnight at 75°C.

After drying was complete, the dried sediment was then removed from the oven and transferred to a Waring blender where it was broken into smaller pieces. The sample was further pulverized using a mortar and pestle until a fine powder was obtained.

The powdered sample was transferred to a pre-weighed plastic sample container. The sample and container were then weighed in order to determine the sample weight. The sample container was labeled with the sample number and weight and delivered to the Department of Environmental Quality Nuclear Laboratory for gamma spectrum analysis.

IV.B.2 Sample Analysis

Sediment and effluent samples analyzed for radium 226 by the Louisiana Nuclear Energy Division's Environmental Radiological Surveillance Laboratory were performed by gamma-spectroscopy utilizing the Canberra Series 90 Gemini System. The Gemini System consists of a Canberra Series 90 Multichannel Analyzer computer linked with a Digital Equipment Corporation PDP-11/23 Plus computer. The Series 90 is connected to four Canberra Germanium detectors for high-resolution gamma-ray spectroscopy.

Sediment samples were counted on the Germanium detectors using a 6,000 second live-time count after achieving a standard geometry, which in this case was a four ounce poly-jar container. Effluent samples were counted using a one liter Marinelli Beaker geometry and were counted for 60,000 seconds live-time. Oysters were analyzed using a 500 milli-liter Marinelli Beaker geometry and were also counted for 60,000 seconds live-time.

Analytical results are reported in pico-Ci/gram ± 2 sigma error for both the sediment samples and the oysters. Analysis results for the effluent samples are reported in pico-Ci/liter ± 2 sigma error.

Standards used for the calibration of the Gemini System were acquired from Analytics, Inc. in Atlanta, Georgia, and are traceable to the National Institute of Standards Technology, formerly the National Bureau of Standards.

Quality Control is maintained by counting the standard geometry used for the sediment samples on a daily basis, recording the decay-corrected activity for the isotopes in the standard, as well as the full-width half-maximum value for three isotopes in the standard.

IV.C Results

IV.C.1. Effluents

Table IV.2 and Figure IV.3 presents the results of radium 226 analyses from the four site effluent samples collected. radium 226 activities ranged from 355 ± 246 pCi/l at DF-E (Delta

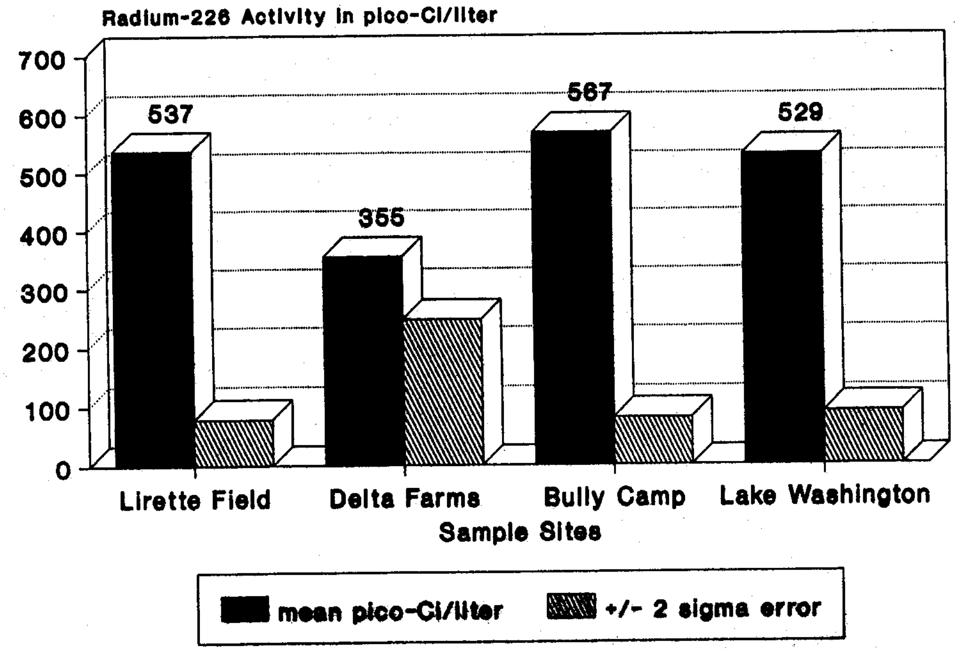
Farms effluent) to 567 ± 79.9 pCi/l in the Bully Camp effluent (BC-E). The high ± 2 sigma error at the Delta Farms site is probably due to the fact that this sample was counted for 6,000 seconds rather than the 60,000 second counting duration used for the other effluent samples.

Table IV.2. Effluent sample analysis results.

Sample Location	Radium 226 Activity pCi/l ± 2 sigma error
Lirette Field	537 ± 77.6
Delta Farms	355 ± 246.0
Bully Camp	567 ± 79.9
Lake Washington	529 ± 89.2

Figure IV.3

Effluent Sample Radium-226 Activity



The results from the four effluent samples analyzed in this study are within the ranges reported in other investigations. Holt *et al.* (1982) reported that oil field brines range from 40-1,000 pCi/l. Processes that are believed to be responsible for radium levels in produced water include chemical leaching from the surrounding formation (Kramer and Reid, 1983). Each of these effluents would be classified as hazardous under proposed EPA guidelines (LDEQ, 1989).

IV.C.2. Sediments

IV.C.2.a. Lirette Study Site (LRT)

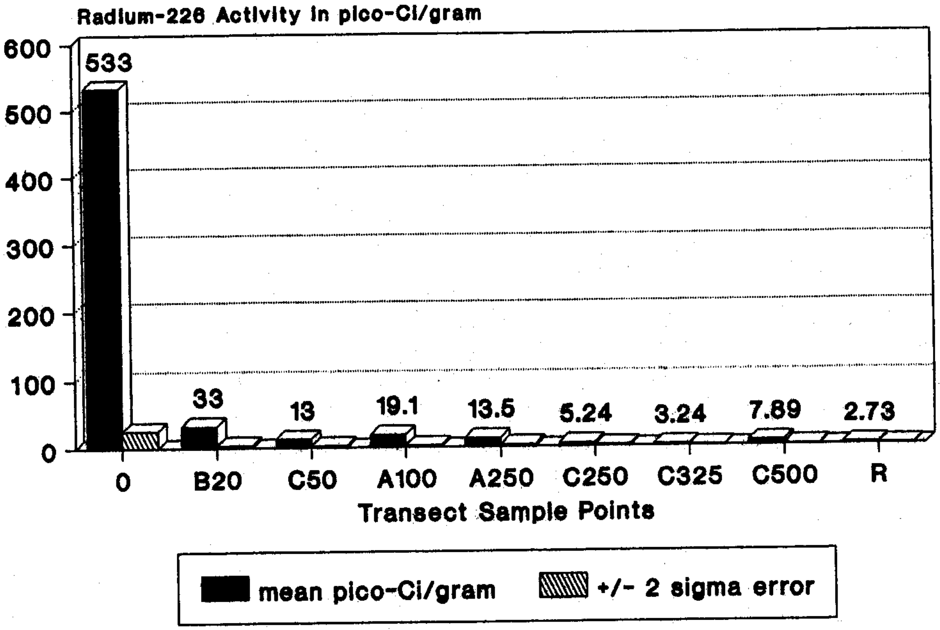
The results of Ra 226 analyses of sediments collected at the 9 Lirette site stations are presented in Table IV.3. The radium 226 activity is shown graphically in Figure IV.4. The sediment data for this and all of the remaining sites are listed according to distance from the origin in order of nearest to farthest.

Table IV.3. Lirette sediment sample activities.

Sample Location	Radium 226 Activity in pCi/g dry weight ± 2 sigma error
LRT-0	533.0 ± 25.9
LRT-B20	33.0 ± 4.0
LRT-C50	13.0 ± 2.8
LRT-A100	19.1 ± 2.8
LRT-A250	13.5 ± 3.4
LRT-C250	5.2 ± 2.0
LRT-C325	3.2 ± 1.4
LRT-A500	7.9 ± 1.6
LRT-R	2.7 ± 1.3

Activities ranged from 2.7 ± 1.3 pCi/g at LRT-R (reference) to a high of 533.0 ± 25.9 pCi/g at LRT-0. LRT-0 was located 10 meters from the outfall at this site. The level of Ra 226 activity in the sediments at LRT-0 was the highest of any site considered in this study and was over an order of magnitude higher than the next highest activity of 33.0 ± 4.0 at LRT-B20. Because of the position relative to the outfall and Ra 226 levels elevated above background, Lirette stations 0, B20, C50, A100, and A250 appear to have been impacted by the effluent from this site.

Figure IV.4
Lirette Sediment Radium-226 Activities



Sample points arranged by distance from origin.

IV.C.2.b. Delta Farms Site (DF)

The Delta Farms sediment results from Ra 226 analyses of samples collected on October 5, 1990, are listed in Table IV.4 for each station and shown graphically in Figure IV.5. The radium activities in the sediments at this site were the lowest of the four examined.

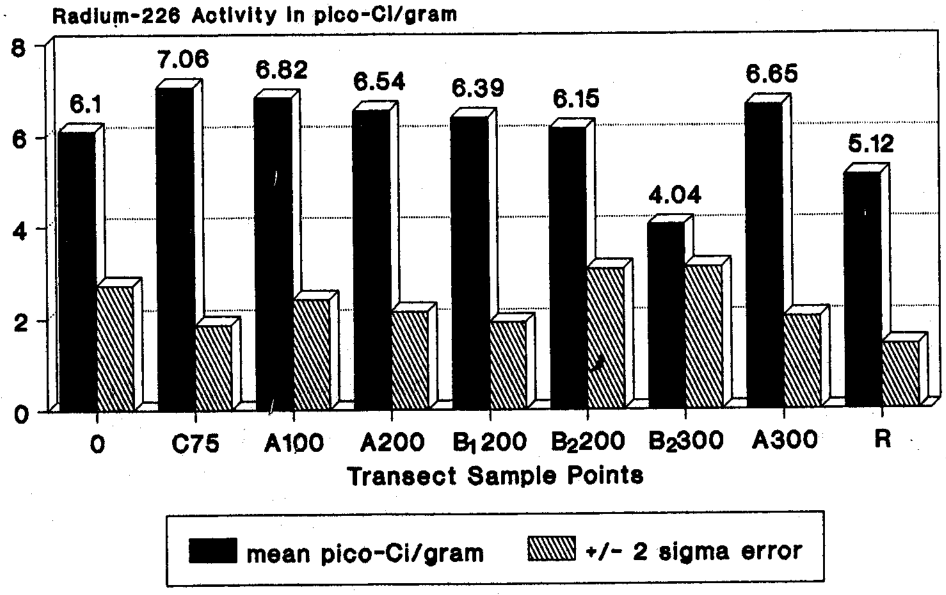
The difference between radium 226 levels in the Delta Farms origin and the origins of the other sites was considerable. Six of the DF stations were re-sampled on March 6, 1990. The results, listed in Table IV.5, were not appreciably different from the results obtained from the initial sampling.

Table IV.4. Delta Farms sediment activities (collected October 5, 1990).

Sample Location	Radium 226 Activity in pCi/g dry weight ± 2 sigma error
DF-0	6.1 ± 2.7
DF-C75	7.1 ± 1.9
DF-A100	6.8 ± 2.4
DF-A200	6.5 ± 2.2
DF-$B_1$200	6.4 ± 1.9
DF-$B_2$200	6.2 ± 3.1
DF-$B_2$300	4.0 ± 3.1
DF-A300	6.6 ± 2.0
DF-R	5.1 ± 1.4

Figure IV.5

Delta Farms Sediment
Radium-226 Activities



Sample points arranged by distance from origin.

Table IV.5. **Delta Farms sediment activities (collected March 6, 1990).**

Sample Location	Radium 226 Activity in pCi/g dry weight ± 2 sigma error
DF-0	4.3 ± 2.5
DF-C75	7.4 ± 1.9
DF-A100	5.0 ± 3.3
DF-A200	9.2 ± 2.1
DF-$B_1$200	6.7 ± 1.8
DF-$B_2$200	6.9 ± 2.4

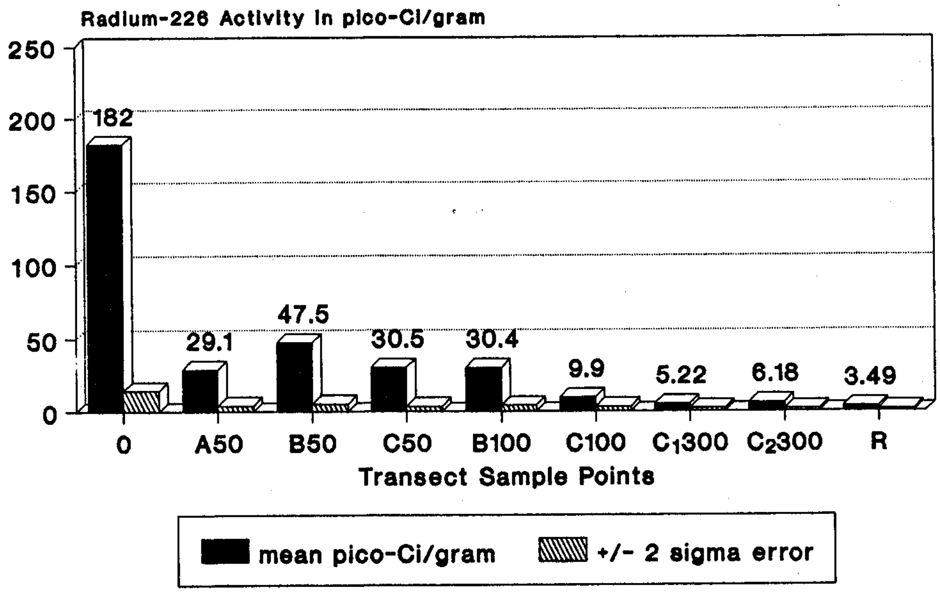
IV.C.2.c. Bully Camp Site (BC)

Radium 226 results of sediments collected at the Bully Camp stations are listed in Table IV.6 and are presented graphically in Figure IV.6. Radium 226 activities ranged from a low of 3.5 ± 1.5 pCi/g at BC-R to a high of 182.0 ± 14.5 pCi/g in the sediments at BC-0. The Ra 226 activities at BC-0 were almost 4 times higher than the next highest level detected at BC-B50 (47.5 ± 5.4 pCi/l). Bully Camp stations 0, A50, B50, C50, and B100 were shown to be impacted by the effluent from this site.

Table IV.6. **Bully Camp sediment activities**

Sample Location	Radium 226 Activity in pCi/g dry weight ± 2 sigma error
BC-0	182.0 ± 14.5
BC-A50	29.1 ± 4.1
BC-B50	47.5 ± 5.4
BC-C50	30.5 ± 3.6
BC-B100	30.4 ± 4.2
BC-C100	9.9 ± 3.3
BC-$C_1$300	5.2 ± 2.2
BC-$C_2$300	6.2 ± 1.8
BC-R	3.5 ± 1.5

Figure IV.6
Bully Camp Sediment
Radium-226 Activities



Sample points arranged by distance from origin.

IV.C.2.d. Lake Washington Site (LW)

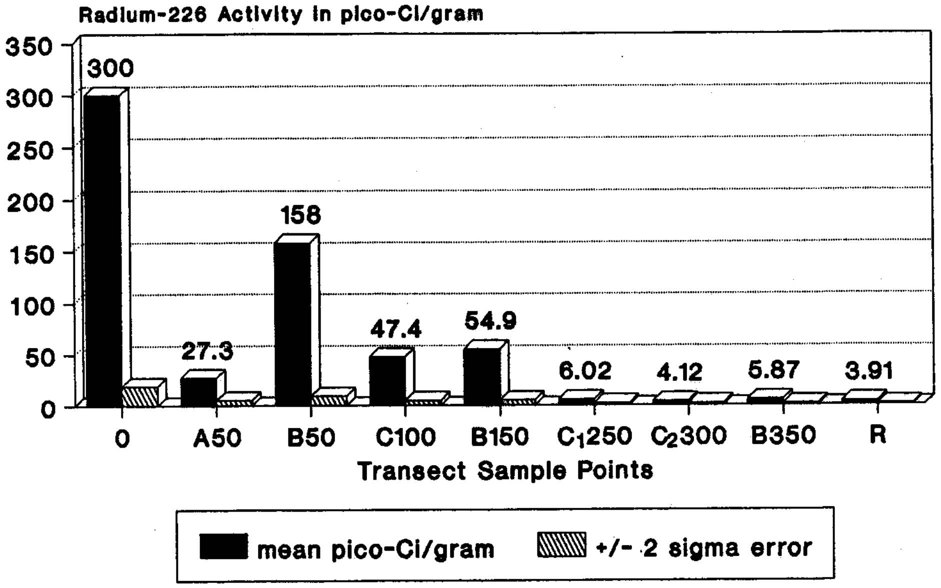
The results of Ra 226 analyses of sediments collected at the Lake Washington site stations are listed in Table IV.7 and presented graphically in Figure IV.7. Sediment radium activities ranged from 3.9 ± 1.5 pCi/g at the reference station, LW-R, to 300 ± 19.1 pCi/g at the origin, LW-0. The Lake Washington origin was 20 meters from the outfall point.

The distribution patterns of radium activities in Lake Washington sediments differed from the patterns observed at the other sites. The second highest sediment activity at the Lake Washington site was 158.0 ± 9.4 pCi/g, at station LW-B50. This was slightly over half of the activity level in the origin. Most of the other sites indicated a much greater difference between the origin and next highest activities. Stations LW-0 and LW-B50 were excavated by the company operating the production facility located at the Lake Washington site. Company employees estimated that 2 feet of sediment were removed from the areas of LW-0 and LW-B50 approximately 2 weeks before the Lake Washington site samples were collected. Station LW-A50, which was not excavated, had radium 226 activities which were comparable to 50 meter

Table IV.7. Lake Washington sediment activities

Sample Location	Radium 226 Activity in pCi/g dry weight ± 2 sigma error
LW-0	300.0 ± 19.1
LW-A50	27.3 ± 5.5
LW-B50	158.0 ± 9.4
LW-C100	47.4 ± 5.1
LW-B150	54.9 ± 5.4
LW-$C_1$250	6.0 ± 2.1
LW-$C_2$300	4.1 ± 2.1
LW-B350	5.9 ± 1.8
LW-R	3.9 ± 1.5

Figure IV.7
Lake Washington Sediment
Radium-226 Activities



Sample points arranged by distance from origin.

stations at other study sites (LRT and BC).

The mechanical disturbance of sediments at the Lake Washington site may explain the high levels of radium 226 activity in the top 10 cm of sediment at LW-B150, located 150 meters from the origin and 170 meters from the outfall. LW-B150 and LW-C100 were located in a canal in which the greatest tidal current velocities were observed. Re-suspended sediments in the vicinity of LW-0 and LW-B50 would be transported across LW-B150 and LW-C100. LW-C100 also had high Ra 226 activities (47.4 ± 5.1 pCi/g). Lake Washington sediments which were impacted by effluent radium 226 activities were at LW stations 0, A50, B50, C100, and B150.

IV.D Summary

Average effluent discharge rates for a 2-year period before this study were obtained from the companies operating the production facility at each site. The Lirette facility discharged produced water effluent of 138 ppt salinity at the average rate of 462 barrels/day. This was the lowest rate of all those studied. The flow rate of the Lake Washington effluent averaged 1600 barrels/day and had a salinity of 192 ppt. Bully Camp effluent had a salinity of 167 ppt and was discharged at the average rate of 4767 barrels/day. The highest rate of discharge was from the Delta Farms facility with an average flow of 13,458 barrels/day with a salinity of 140 ppt.

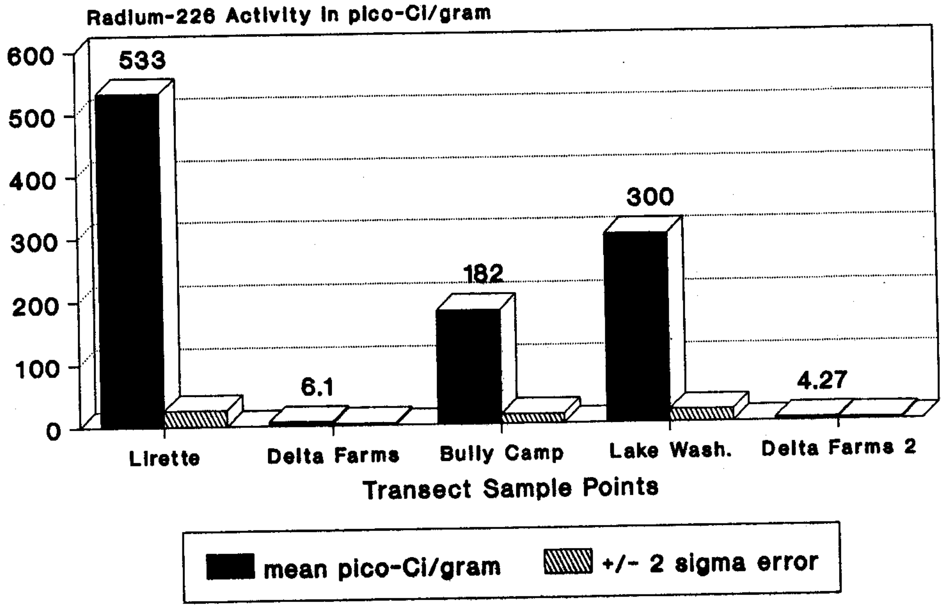
Radium 226 levels detected in all of the effluents studied are considered very high in comparison to the 0.05 pCi/l level of activity found in the open ocean (Holt *et al.*, 1982). The lowest activity of the effluents studied was 355 pCi/l (at DF-E). This represents a level 7100 times greater than the activities found in the open ocean.

Table IV.1 and Figure IV.3 demonstrate that radium 226 activity in produced water effluents can vary from site to site. The variation is probably due to differences in the mineral composition of the geologic formations from which the petroleum is being extracted. Kramer and Reid (1983) suggested that radium 226 was leached from the surrounding subsurface formation.

The sediments analyzed in this study at the Lirette, Bully Camp, and Lake Washington sites indicated a pattern of highest radium 226 activity at the stations (origins) nearest to the outfall. A graph of all sediment origin activities is presented in Figure IV.8. The origin stations were also shown in Chapter III to have the greatest impact in terms of elevated chlorinities.

The Delta Farms sediment activities were the exception to the above observations. The radium levels in the DF-0 sediments were much less than the other site origins. The remaining DF transect stations indicated no discernable trends in radium 226 activity in relation to distance from the outfall. Most of the transect stations at this site showed, in fact, less activity than the origin.

Figure IV.8
Origin Sediment Radium-226 Activities



Since the Delta Farms sediment data differed considerably from the data collected at the LRT, BC, and LW sites, several of the DF stations were re-sampled on March 6, 1990. (The initial samples were collected on October 5, 1989.) The results of the second set of analyses were similar to the first.

The reason for the low levels of Ra 226 activity in the Delta Farms sediments may be related to the observed difference in sediment type at this location. Although sediment composition or grain size analyses were not part of this study, it was noted that Delta Farms bottoms were much more organic in nature than the other site sediments. The LRT, BC, and LW sediments were composed of finer grained, silty-clay types. Hanan (1981) reported that fine grained sediments are more effective at adsorbing radionuclides than coarser sediments because fine sediments have more total surface area and a larger percentage of clay minerals. Correlations by Landa and Reid (1983) indicated that retention of Ra 226 may involve precipitation and ion exchange reactions with the mineral fractions of surficial earth materials.

Radium 226 activities found at all study reference sites were compared to data collected from sites near the Louisiana Universities Marine Consortium (Lumcon) facility in Cocodrie, Louisiana in a baseline study of environmental radioactivity by Beck *et al.* (1986). Figure IV.9 and Table IV.8 demonstrate the variability of background levels of naturally occurring radioactive materials in soils from brackish water areas. A comparison of this figure with Figures IV.4, IV.6, and IV.7, indicates a high degree of radiological impact to sediments near three of the four produced water discharges studied.

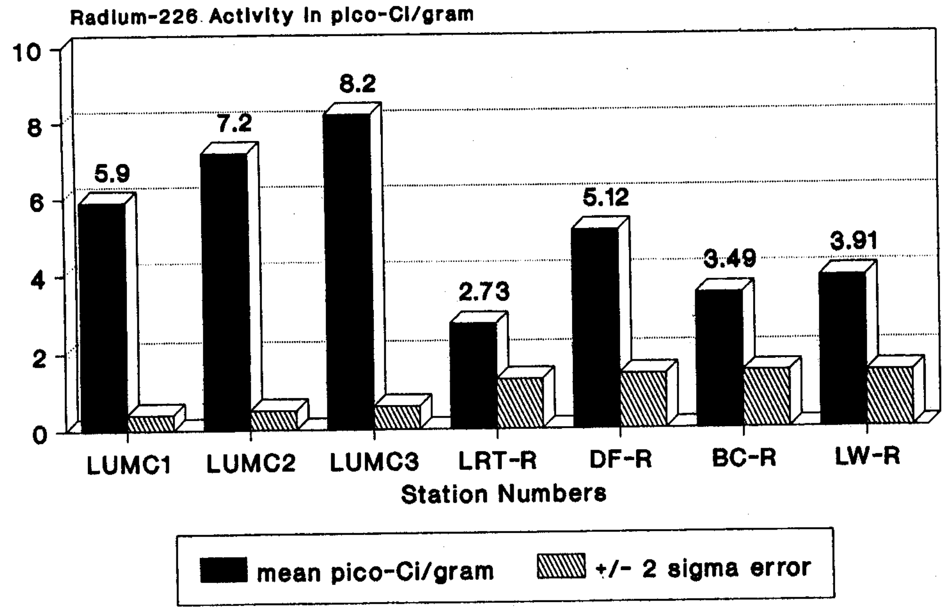
It should be noted that only the top 10 cm of station sediments were analyzed for Ra 226 activities. Chapter III of this report demonstrated that produced water impacts to interstitial sediment chlorinities affect core sections to a depth of at least 30 cm at the stations closest to the outfall. A depth-integrated analysis of Ra 226 activities at these stations would be needed to determine the full extent of radiological impacts to receiving stream sediments. Observations made of the sediment radium levels at the Lake Washington site in relation to the excavation activities suggests that radium activities may increase with depth at some stations as did interstitial chloride concentrations.

Table IV.8. Lumcon surface soil vs. reference sediment.

Sample Location		**Radium 226 Activity pCi/g ± sigma error**	
LUMC1	12/07/84	5.9	± 0.4
LUMC2	03/20/85	7.2	± 0.5
LUMC3	06/04/85	8.2	± 0.6
LRT-R	01/23/90	2.7	± 1.3
DF-R	10/05/89	5.1	± 1.4
BC-R	12/07/89	3.5	± 1.5
LW-R	01/18/90	3.9	± 1.5

NOTE: LUMCON is the Louisiana Universities Marine Consortium, located at Cocodrie, Louisiana.

Figure IV.9
Comparison of Radium-226 Activities in LUMCON Surface Soils and Study Reference



LUMCON Soil Data from Beck *et al.*(1986).

Chapter V

BIOTOXICITY OF PRODUCED WATER EFFLUENTS AND OF SEDIMENTS COLLECTED PROXIMATE TO PRODUCED WATER DISCHARGES

by

Sheri Courtney and Kerry St. Pé

V.A. Introduction

Acute toxicity tests are useful tools for evaluating the potential toxicological responses of test organisms to various pollutants. Biotoxicity testing has been used to assess the possible impacts of produced water effluents to aquatic organisms. Produced water test procedures usually use mortality as the measured response with results of acute tests expressed as an effluent median lethal concentration for an exposure duration of 96 hrs. (96 hr. LC_{50}) or the effluent concentration which results in the mortality of 50% of the test organisms in a 96 hr. exposure period.

V.B Materials and Methods

The Louisiana Department of Environmental Quality Biomonitoring Laboratory analyzed selected effluent and sediment samples from the produced water study area. One effluent and one sediment were analyzed from each of the four study sites. The acute toxicity of the samples was analyzed using mortality as the measured effect. Effluent samples and sediment elutriate samples were analyzed following procedures outlined in EPA's Method for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms (Third Edition) EPA/600/4-85/013. Sediment samples were analyzed following Elutriate and Fractionation Methods published in the Puget Sound Estuary Program Recommended Protocol Manual, 1986 (Prepared for EPA by Tetra Technology, Inc., Bellevue, Wash.). Sediments were also analyzed following the solid phase sediment and water beaker test outlined in Biological Methods for Determining Toxicity of Contaminated Freshwater Sediments to Invertebrates (Nebeker *et al.*, 1984).

V.B.1 Culture Methods for Test Species

Effluent samples were analyzed utilizing *Cyprinodon variegatus*, the sheepshead minnow, and *Mysidopsis bahia*, the opossum shrimp. Sediments were analyzed utilizing *Cyprinodon variegatus*, *Mysidopsis bahia*, and *Hyalella azteca*, an amphipod. The following briefly describes the culturing methods for each species.

Cyprinodon variegatus are cultured in 20 gallon aquaria equipped with an outside filter system. Adult *C. variegatus* are collected locally from the marshes of the Lake Pontchartrain-Maurepas Basin. Cultures are maintained in synthetic sea water at ambient temperatures; the salinity is maintained at 25 ppt ± 2 ppt. Lighting is provided by fluorescent lights on a 16 hour light/ 8 hour dark cycle. Cultures are checked daily for mortality, injury, and sickness. This data, along with action taken, is recorded in the daily log and then transferred to the culture management log book.

Spawning chambers are placed in the aquaria as needed for testing. Aquaria are checked for eggs 24 hours after the placement of the spawning chambers. The eggs are collected by rinsing into a clean 2000 ml beaker. The approximate number of eggs from each tank is recorded in the daily log and the culture management log book. The beaker (hatching chamber) is supplied with aeration. The eggs are checked daily; non-viable eggs are disposed of and newly hatched larvae are transferred to holding chambers. Each holding chamber is dated enabling laboratory personnel to know the age (within 24 hours) of the larvae. The larvae are fed less than 24 hour old *Artemia* sp. (brine shrimp) nauplii twice a day. The larvae are held for testing until they are three to four weeks old. At this time, the remaining larvae are disposed of or transferred to rearing tanks.

Mysidopsis bahia are cultured in 20 gallon and 50 gallon glass aquaria equipped with under-gravel filters. Mysids are maintained in synthetic sea water at ambient temperatures. The salinity is maintained at 25 ppt ± 2 ppt. Lighting is provided by fluorescent lights on a 16 hour light/ 8 hour dark cycle. The initial population was obtained from the United States Environmental Protection Agency. Cultures are checked daily for overall health, reproduction, and condition of the tank. This data, along with action taken, is recorded in the daily log and the culture management log book. Gravid females are removed from the cultures when young are needed for testing. The gravid females are transferred to a dated five gallon holding tank where the young can easily be collected. Mysids are fed less than 24 hour old *Artemia* sp. nauplii three times a day or as needed.

Hyalella Azteca are cultured in 10 gallon glass aquaria supplied with gentle aeration. The primary substrate and food for *H. azteca* is dried maple (*Acer* sp.) and poplar (*Poplus* sp.) leaves. The dried leaves are soaked for several days in dechlorinated tap water, and rinsed with deionized water prior to adding to or establishing a culture. *H. azteca* are cultured in reconstituted very hard water. Approximately 15-30% of the water in each culture is replaced weekly (Ingersoll and Nelson, In Press). *H. azteca* are cultured in a variety of salinities ranging from 0 ppt to 15 ppt. Lighting is provided by fluorescent lights on a 16 hour light/ 8 hour dark cycle. The initial population was obtained from the U.S. Fish and Wildlife Service, Columbia, Mo. Juveniles (less than one week old) are removed from the cultures and separated from the leaf material by removing a portion of the leaf material, placing the leaves on a sieve stack consisting of a #30 (600um) sieve and a #40 (425um) sieve, and sprinkling the leaves with culture water as the leaves are turned. The amphipods are washed from the leaves onto or through the sieves. The upper sieve (#30) retains the adults and allows the juveniles to pass through to the #40 sieve where they are retained (Ingersoll and Nelson, In Press). The adults are rinsed back into the culture tank and the juveniles are rinsed into 2 liter culture dishes. The juveniles are placed in the dark at a temperature of 20±1°C. Gentle aeration is applied to the culture dishes. The juvenile amphipods can be held for 24 hours prior to the start of the sediment toxicity test.

V.B.2 Effluent Toxicity Test Procedures

Definitive, acute toxicity tests were performed on four effluent samples, one from each of the four study sites. The acute toxicity procedures utilized by the Louisiana Department of Environmental Quality's biomonitoring laboratory follow EPA's Method for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms (Third Edition) EPA/600/4-85/013. *Cyprinodon variegatus* and *Mysidopis bahia* were the preferred test species.

The following outlines the procedures followed in the definitive acute toxicity test for *Cyprinodon variegatus* and *Mysidopis bahia*

1. The tests were initiated within 48 hours of sampling, where possible.

2. An appropriate amount of sample for testing and chemical analysis was removed and warmed to 25±1°C. The remaining sample was stored at 4±1°C.

3. An adequate amount of test solution (warmed to 25±1°C) was prepared for each dilution in the test series. The dilution series utilized in the *C. variegatus* tests were 100%, 50%, 25%, 12.5%, 6.25%, and a control. The dilution series used in the mysid tests with unadjusted effluent was 10%, 5%, 2.5%, 1.25%, 0.625%, and a control. The dilution series used in the mysid tests with salinity adjusted effluent was 100%, 50%, 25%, 12.5%, 6.25%, and a control.

4. In the *C. variegatus* tests, two test chambers (A and B) were used for each dilution with a total volume of 500 mls test solution in each chamber. In the mysid test,

four test chambers (A, B, C, and D) were used for each dilution with a total volume of 200 ml test solution in each chamber.

5. A total of 20 organisms was randomly distributed among the test chambers at each dilution (10 per test chamber in the *C. variegatus* tests and 5 per test chamber in the mysid tests).

6. The test chambers were placed in a incubator with a controlled temperature of 25±1°C.

7. The test chambers were checked at the end of 24, 48, 72, and 96 hours with the number of living organisms recorded. Any dead organisms observed throughout the test period were removed from the test chamber.

8. All organisms were discarded after the conclusion of the test. No organisms were reused for subsequent testing.

9. LC_{50} (24 hour, 48 hour, and 96 hour) values with 95% confidence levels were calculated using Toxdat Multi-Method Computer Program (Binomial, Moving Average, and Probit Methods). The reported LC_{50} values are the values determined by Binomial Method. The Binomial Method was able to generate LC_{50} values in all the samples tested, where the other methods were not as reliable. Also, the confidence levels associated with this method were consistently 98% or greater.

V.B.3 Sediment Test Procedures-Elutriate

In the initial Produced Water Study Work Plan, only elutriate tests were to be performed on sediment samples. At that time, the laboratory did not culture any sediment dwelling organisms. The elutriate test proved to be ineffective in determining the acute toxicity of the produced water sediments. The elutriate test allows for the analysis of only dissolved materials from the sediment. An alternate test was researched and adopted. The elutriate test was, however, performed on all sediments for comparison and to establish a database.

The elutriate test was performed on sediments, enabling the sediments to be tested as a liquid. The liquid was then analyzed by performing the definitive, acute toxicity test procedures outline in EPA's Method for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms (Third Edition) EPA/600/4-85/013. The elutriate test was performed on four test sediments and four reference sediments, one test sediment and one reference sediment from each of the four study sites. The elutriate test procedures utilized basically follow the Elutriate and Fractionation Methods published in the Puget Sound Estuary Program Recommended Protocol Manual, 1986 (Prepared for EPA by Tetra Technology, Inc., Bellevue, Wash.).

The following outlines the procedures followed in the elutriate tests:

1. The tests were initiated within 1 week of sampling, where possible.

2. One liter of sediment was mixed with four liters of synthetic sea water at a salinity of 25 ppt. The sediment-to-water ratio was 1:4.

3. The sediment and water mixture was placed in a closed container, and mixed for thirty minutes.

4. The sample was allowed to settle.

5. The supernatant was decanted into a four liter glass container.

6. The supernatant was vacuum filtered through a 0.45um membrane filter.

7. The filtered supernatant was then analyzed using the same methods and organisms (*Cyprinodon variegatus* and *Mysidopsis bahia*) as the effluent samples. (See the procedures followed under Effluent Toxicity Test Procedures)

V.B.4. Sediment Test Procedures-Solid Phase

Solid phase sediment testing was chosen as the alternate test method for the elutriate test. In solid phase testing, any toxicants bound to the particulates may be available to the animals when they feed on or come in contact with the sediment (Nebeker *et al.*, 1984). The amphipod, *Hyalella azteca* (an epibenthic detritivore) was chosen as the test organism for solid phase sediment testing. The following lists some of the major factors involved in choosing *Hyalella azteca* as the test species:

- Time limitations on the completion of testing
- Concerns over the collection of endemic amphipods from "clean' sediment (organisms used in testing must not have come in contact with toxicants or contaminated sediments prior to testing)
- Large volume of data concerning the culturing and testing techniques of *Hyalella* sp.
- Availability of organisms from an in-house culture

- *Hyalella*'s ability to grow and reproduce under saline conditions
- *Hyalella*'s classification as a detritivore
- *Hyalella*'s interaction with sediment by burrowing in the upper surface of the sediment, especially when disturbed, and its digesting bacteria and algae from ingested sediment particles (Hargrave, 1970)

The solid phase sediment and water beaker test was performed on four test sediments, one from each of the study sites. For each test sediment, a reference from the same study site was tested. Also tested was a control sediment. The test procedures utilized by Louisiana Department of Environmental Quality's bioassay laboratory followed Biological Methods for Determining Toxicity of Contaminated Freshwater Sediments to Invertebrates (Nebeker *et al*, 1984).

The following outlines the procedures followed in the solid phase sediment and water beaker test:

1. The tests were initiated within 1 week of sampling, where possible.

2. The sediments were screened to remove large particles and endemic animals.

3. Three test chambers (A, B, and C) were used for each sediment tested with 200 mls of screened sediment placed in each chamber.

4. 800 mls of dilution water (very hard reconstituted water at a salinity of 13ppt) was added to each test chamber.

5. The test chambers were placed in an incubator at 20±1°C. Aeration was supplied to the test chambers and the sediments were allowed to settle overnight.

6. Juvenile amphipods were removed from the cultures, placed in 2000 ml culture dishes, and placed in an incubator at 20±1°C overnight.

7. Fifteen animals were randomly placed in each of the test chambers. Test chambers were returned to the incubator and supplied with aeration.

8. Daily observations were made, if possible. Any dead organisms were recorded and removed.

9. The test was terminated at the end of 10 days.

10. Survivors were screened from the water and sediment by utilizing a #40 sieve.

11. The measured effect was mortality.

V.C Results and Conclusions

V.C.1 Effluent Toxicity

Acute, Definitive Toxicity Tests were performed on the following effluent samples from the produced water study area:

Sample #	Study Site
LRT-E	Lirette Oil and Gas Field
DF-E	Delta Farms Oil and Gas Field
BC-E	Bully Camp Oil and Gas Field
LW-E	Lake Washington Oil and Gas Field

Sample # LRT-E was analyzed using only unadjusted effluent. Samples DF-E, BC-E, and LW-E were analyzed using unadjusted effluent and salinity adjusted effluent (the effluent was diluted to 25 ppt salinity with deionized water prior to testing). The acute, definitive toxicity procedures follow EPA's Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms (Third Edition) EPA/600/4-85/013. The length of the tests was 96 hours. The measured effect was mortality with the mean lethal concentration (LC_{50}) values calculated at 24, 48, and 96 hours. The LC_{50} values for the unadjusted and salinity adjusted effluents are recorded in Tables V.1 and V.2. The initial salinity reading of the sample is also recorded in Tables V.1 and V.2.

Table V.1 contains the mysid results. In the mysid tests, the 96 hour LC_{50} values of the salinity adjusted effluents compared favorably with the 96 hour LC_{50} values of the unadjusted effluents. The unadjusted LC_{50} values are used in further discussion and comparisons. Table V.2 contains the *C. variegatus* results. In these tests, the 96 hour LC_{50} values of the adjusted effluent could not be compared to the unadjusted effluent in samples BC-E and LW-E. In these samples, the initial dilution of the sample (to a salinity reading of 25 ppt) was lower than the toxicity levels. For instance, in sample BC-E the initial dilution was one part sample to five parts deionized water. This lowered the "100%" concentration level to 20%, a level below the toxicity of the sample. The unadjusted data is used in further discussion and comparisons for both the mysids and sheepshead minnows.

Table V.1. *Mysidopsis bahia* LC$_{50}$ values for the produced water effluents

Sample #	Sample Salinity (ppt)	LC$_{50}$ 24 HR	LC$_{50}$ 48 HR	LC$_{50}$ 96 HR	Sal. Adjusted LC$_{50}$ 96 HR
LRT-E	118.0	7.74%	6.37%	5.77%	NA
DF-E	115.2	3.81%	3.64%	3.54%	4.61%
BC-E	126.8	7.07%	4.55%	2.64%	3.10%
LW-E	148.4	7.07%	6.02%	5.23%	5.02%

Table V.2. *Cyprinodon variegatus* LC$_{50}$ values for the produced water effluents

Sample #	Sample Salinity (ppt)	LC$_{50}$ 24 HR	LC$_{50}$ 48 HR	LC$_{50}$ 96 HR	Sal. Adjusted LC$_{50}$ 96 HR
LRT-E	118.0	26.17%	18.80%	17.14%	NA
DF-E	115.2	13.62%	7.16%	7.16%	10.0%
BC-E	126.8	35.36%	35.36%	33.78%	NA-"100%"=20%
LW-E	148.4	23.58%	23.58%	22.44%	NA-"100%"=16.67%

M. bahia exhibited acute toxicity to all samples tested. The samples ranked from highest toxicity level (lowest LC$_{50}$ value) to the lowest toxicity level (highest LC$_{50}$ value) are BC-E, DF-E, LW-E, and LRT-E. The LC$_{50}$ values ranged from 2.64% in BC-E to 5.77% in LRT-E. The mean LC$_{50}$ for the produced water sites was 4.30%. The salinity readings ranked from the highest level to lowest are LW-E, BC-E, LRT-E, and DF-E. The salinity readings ranged from 115.2 in DF-E to 148.4 in LW-E. The salinity readings and the toxicity levels do not follow a pattern in these samples; LW-E had the highest salinity reading (148.4) and the second highest LC$_{50}$ value (5.23%), DF-E had the lowest salinity reading (115.2) and the second lowest LC$_{50}$ value (3.54%).

Although high salinity can result in toxicity to mysids, it does not appear to be the major cause of toxicity in the samples tested. *M. bahia* have been cultured successfully in Louisiana

Department of Environmental Quality's biomonitoring laboratory in salinities as high as 35 ppt. Lussier *et al.* (1985) suggest a salinity of 30 ppt for culturing and testing mysids. In their testing of heavy metals and cyanide on mysids, the seawater controls averaged 30 ppt salinity with a range of 28 ppt to 32 ppt. Table V.3 contains the sample number; the 24, 48, and 96 HR LC_{50} values for each sample; the sample's initial salinity reading; and the calculated salinity value for the 96 HR LC_{50} concentration. The salinity range of the 96 HR LC_{50} values was 23.37 ppt to 31.45 ppt salinity. These values are in the range at which mysids are successfully cultured. The toxicity of the effluents appear to be due to a component of the effluent other than salinity.

Table V.3. LC_{50} and salinity values - *Mysidopsis bahia*

Sample #	Sample Salinity (ppt)	LC_{50} 24 HR	LC_{50} 48 HR	LC_{50} 96 HR	Dilution Water Salinity	Salinity At LC_{50} 96 HR
LRT-E	118.0	7.74%	6.37%	5.77%	23.0	28.48
DF-E	115.2	3.81%	3.64%	3.54%	20.0	23.37
BC-E	126.8	7.07%	4.55%	2.64%	23.0	25.74
LW-E	148.4	7.07%	6.02%	5.23%	25.0	31.45

Sheepshead minnows exhibited acute toxicity to all the samples tested. The samples ranked from the highest toxicity values to the lowest toxicity values are DF-E, LRT-E, LW-E, and BC-E. The 96 hr. LC_{50} values ranged from 7.16% in DF-E to 33.78% in BC-E. The mean 96 hr. LC_{50} value for the produced sites was 20.13%. Again, the salinity readings and the toxicity levels do not follow similar patterns in the samples: DF-E had the lowest salinity reading at 115.2 ppt and the highest toxicity with a LC_{50} value of 7.16%. Although high salinity can result in toxicity to *C. variegatus*, it does not appear to be the major cause of toxicity in the samples tested. Sheepshead minnows have been cultured successfully in Louisiana Department of Environmental Quality's laboratory at salinities as high as 40 ppt. Andreasen and Spears (1983) determined that the salinity 96 hour LC_{50} value for brine diluted with seawater was 52 ppt with some sheepshead minnows surviving at salinities of 80 ppt. Table V.4 contains the sample number; the 24, 48, and 96 hour LC_{50} values; the sample's initial salinity; and the calculated salinity of the 96 hour LC_{50} concentration. The salinity range of the 96 hour LC_{50} values was 26.82 ppt to 58.06 ppt. The data indicates that produced water effluent toxicity to *C. variegatus* is due to a sample component other than salinity.

Table V.4. LC_{50} and salinity values - *Cyprinodon variegatus*

Sample #	Sample Salinity (ppt)	LC_{50} 24 HR	LC_{50} 48 HR	LC_{50} 96 HR	Dilution Water Salinity	Salinity At LC_{50} 96 HR
LRT-E	118.0	26.17%	18.80%	17.14%	23.0	39.28
DF-E	115.2	13.62%	7.16%	7.16%	20.0	26.82
BC-E	126.8	35.36%	35.36%	33.78%	23.0	58.06
LW-E	148.4	23.58%	23.58%	22.44%	24.0	51.92

In general, mysids are more sensitive to various toxicants than sheepshead minnows. The difference in sensitivity is evident in the acute toxicity test results. The results of the mysid test and *C. variegatus* tests can be compared with toxicity levels shown in Figure V.1. LRT-E and LW-E were similar in their toxicity to both the mysid and sheepshead minnows. Mysids were most sensitive to BC-E (LC_{50}=2.64%), while the sheepshead minnows were least sensitive to this sample. DF-E was the most toxic sample to both the mysid and the sheepshead minnow.

V.C.2 Sediment Toxicity-Elutriate

Elutriate tests were performed on the following sediment samples from the produced water study area:

Sample #	Study Site
LRT-B20	Lirette Oil and Gas Field
LRT-R	Lirette Oil and Gas Field
DF-C75	Delta Farms Oil and Gas Field
DF-R	Delta Farms Oil and Gas Field
BC-C50	Bully Camp Oil and Gas Field
BC-R	Bully Camp Oil and Gas Field
LW-B50	Lake Washington Oil and Gas Field
LW-R	Lake Washington Oil and Gas Field

The elutriate tests enabled the sediments to be tested as a liquid. The water recovered from elutriate tests was analyzed by performing an acute toxicity test. The acute toxicity tests followed EPA's Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms (Third Edition)

EPA/600/4-85/013. The length of the tests was 96 hours. The measured effect was mortality with the mean lethal concentration (LC_{50}) values calculated (where possible) at 24, 48, and 96 hours. Test organisms utilized were *Mysidopsis bahia* and *Cyprinodon variegatus*.

The elutriate tests, along with the acute toxicity tests on the recovered water, failed to show significant toxicity in the sediments tested. *C. variegatus* showed no toxicity to any of the eight samples tested (Table V.5). Although the mysids showed some acute toxicity in the 100% concentrations, LC_{50} values could not be calculated on any of the eight samples (Table V.6).

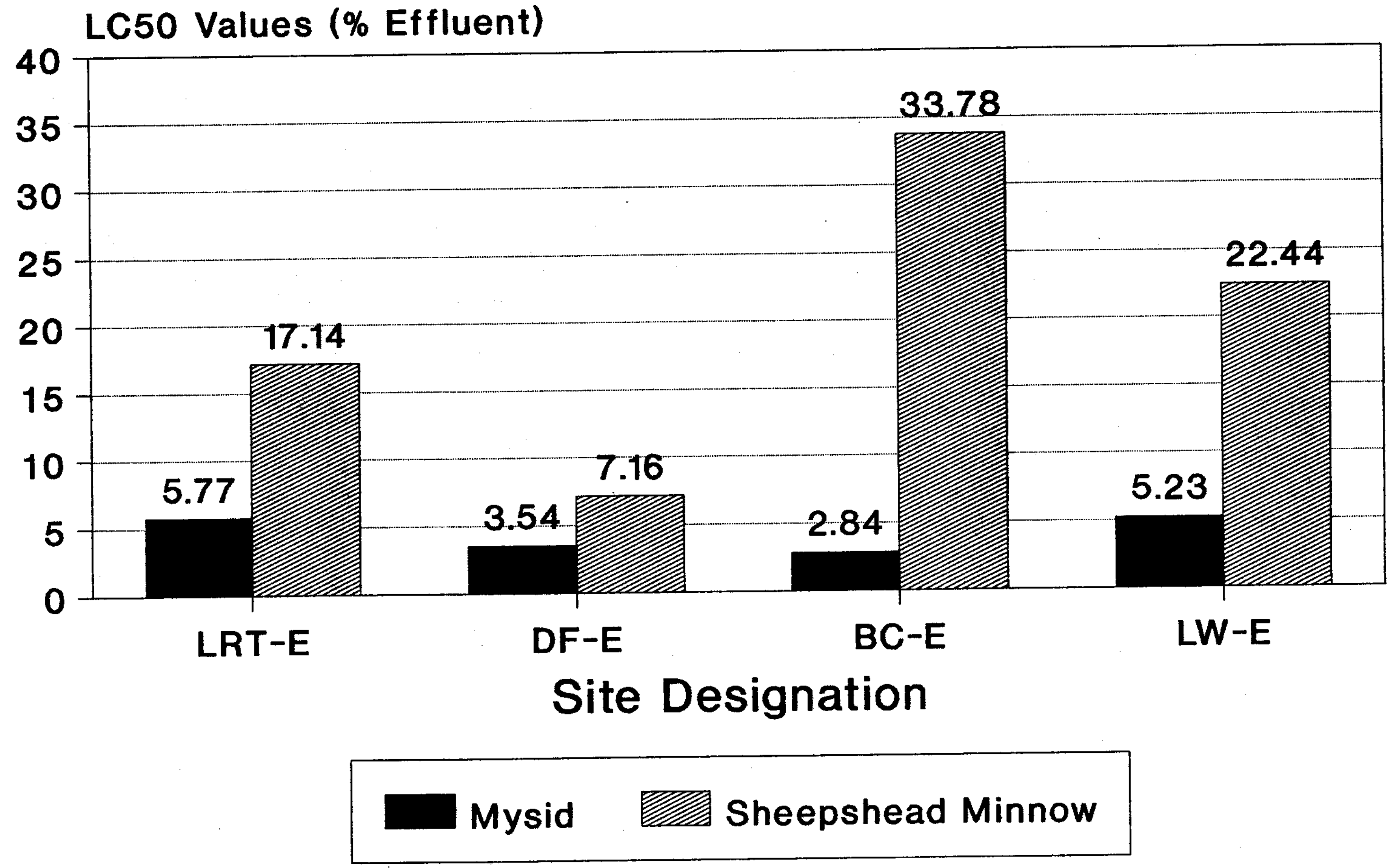
Table V.5. ***Cyprinodon*** **mortality rates in 100% concentrations of sediment elutriate.**

Sample #	Mortality Rate- 100% Elutriate	LC_{50} Value
LRT-B20	0%	NA
LRT-R	5%	NA
DF-C75	0%	NA
DF-R	0%	NA
BC-C50	0%	NA
BC-R	0%	NA
LW-B50	0%	NA
LW-R	0%	NA

Table V.6. ***Mysidopsis*** **mortality rates in 100% concentrations of sediment elutriate.**

Sample #	Mortality Rate- 100% Elutriate	LC_{50} Value
LRT-B20	55%	NA
LRT-R	10%	NA
DF-C75	25%	NA
DF-R	25%	NA
BC-C50	35%	NA
BC-R	20%	NA
LW-B50	30%	NA
LW-R	10%	NA

Figure V.1
Sensitivity of Mysids and Sheepshead
Minnows to Produced Water Effluents



The lack of significant acute toxicity of sediment elutriate to sheepshead minnows and mysids may indicate that the majority of the toxicants found in the sediments are bound to the particulates of the sediment and are not water soluble, or that the toxic fractions were lost during the manipulation of the sediments. The elutriate tests only for those toxicants that are dissolved from the sediment into the recovered water. The elutriate test may not be effective in testing sediments impacted by produced water contaminants or other non-water soluble fractions.

V.C.3 Sediment Toxicity to *Hyalella azteca* Solid Phase and Water Beaker Test

The solid phase and water beaker test was performed on the following sediment samples from the produced water study area:

Sample #	Study Site
LRT-B20	Lirette Oil and Gas Field
LRT-R	Lirette Oil and Gas Field
DF-C75	Delta Farms Oil and Gas Field
DF-R	Delta Farms Oil and Gas Field
BC-C50	Bully Camp Oil and Gas Field
BC-R	Bully Camp Oil and Gas Field
LW-B50	Lake Washington Oil and Gas Field
LW-R	Lake Washington Oil and Gas Field

Sediments were analyzed following the Solid Phase and Water Beaker Test described in Biological Methods for Determining Toxicity of Contaminated Freshwater Sediments to Invertebrates (Nebeker *et al.*, 1984). The length of the tests was 10 days. The measured effect was mortality. Along with the test sediments, a control sediment (Sample Number MB-1 and MB-2) was analyzed. The control sediment was similar to the sediments tested with a high detritus content. The sediments were tested utilizing culture water (salinity of 13 ppt) as the overlying water.

Table V.7 contains the sample number and the per cent mortality in each sample. All the test sediments exhibited significant toxicity to *Hyalella azteca*. One of the four reference sediments (BC-R) showed acute toxicity at a significant level when compared to the control sediments. The maximum mortality rate acceptable in a control sediment is 15% (EPA/SCD# 5, 1986). The control sediments validate the other data generated with an average mortality of 8.5%. Control sediment MB1 had a mortality rate of 5%; control sediment MB2 had a mortality rate of 11.12%.

Table V.7. Mortality rates in produced water sediments to *Hyalella azteca*.

Sample Number	Mortality Rates 100% Sediment
LRT-B20	77.78%
LRT-R	13.33%
DF-C75	57.58%
DF-R	17.78%
BC-C50	91.11%
BC-R	28.89%
LW-B50	66.67%
LW-R	17.78%
MB-1	5.00%
MB-2	11.11%

Table V.8 contains, the sample number, the % mortality to *Hyalella*, and the salinity readings at 0 (water/sediment interface), -10 cm, -20 cm, and -30 cm for each sediment sample used in the tests. *Hyalella* burrow in only the top 1 cm of the sediment surface. LW-B50 had very high salinity and chloride levels. In this sample, the toxicity to *Hyalella* may be a result of the high salinity level. This sample should not be considered as valid data.

Table V.8. Salinity levels of produced water sediments used in solid phase bioassays tests with *Hyalella azteca*.

		Salinity ppt			
Sample #	% Mortality	0 cm	-10 cm	-20 cm	-30 cm
LRT-B20	77.78	7	14	16	18
LRT-R	13.33	6	8	11	12
DF-C75	58.58	2	1	2	6
DF-R	17.78	2	2	3	4
BC-C50	91.11	8	16	25	32
BC-R	28.89	6	10	10	10
LW-B50	66.67	44	44	41	38
LW-R	17.78	26	22	20	20

The test sediments (excluding LW-B50) ranked from highest toxicity to lowest are BC-C50, LRT-B20, and DF-C75. It should be noted that both BC-C50 and LRT-B20 had higher mortality rates than LW-B50. A significant increase in the salinity of the overlying water in the test chambers was not apparent in any of the samples tested. This may explain why the mortality of LW-B50 was lower than some of the other sediments. In LW-B50, the *H. azteca* were observed on the surface of the sediment. By not burrowing in the sediment, they may not have exposed themselves to the toxicants in the sediment. In all other samples, the *H. azteca* appeared to burrow readily.

BC-R showed significant toxicity compared to the control sediments with a mortality rate of 28.89%. DF-R and LW-R had some toxicity with a mortality rate of 17.78% in each sediment (greater than 15% mortality indicates possible acute toxicity). Their mortality rate, however, is not significantly different from the control sediments. LRT-R showed no apparent acute toxicity with a mortality rate of 13.33%.

Hyalella azteca can be utilized successfully to analyze many produced water sediments. The limiting factor in the use of *Hyalella* as a test organism is salinity.

The overall results of the bioassays indicate significant toxicity in the produced water effluents to the mysid shrimp, *Mysidopsis bahia*, and the sheepshead minnow, *Cyprinodon variegatus*. The elutriate test, along with the acute toxicity effluent test, should not be used in analyzing sediments impacted by produced water. The elutriate test does not allow the organisms to come in contact with the toxicants bound to the sediment. Finally, sediments in the study sites appear to be contaminated with significant toxicity apparent to *Hyalella azteca*.

Chapter VI

Hydrocarbon and Trace Metal Concentrations in Produced Water Effluents and Proximate Sediments

by

Jay C. Means, Charles S. Milan and Debra J. McMillin

VI.A Introduction

The major discharges associated with offshore and onshore oil and gas production are drilling fluids, drill cuttings, and produced water. During the production of oil and gas, water that is trapped within permeable petroleum-bearing sedimentary rocks is brought to the surface, carrying with it traces of crude oil, drilling fluids, and other geological materials (Boesch and Rabalais, 1985). This water, called produced water or formation water, may contain elevated levels of various inorganic (trace metals) and organic (petroleum hydrocarbons) substances of a potentially toxic nature.

Prior studies of the effects of oil field discharges on aquatic organisms have concentrated upon the effects of petroleum hydrocarbons on marine species residing offshore in the vicinity of a drilling platform or at the site of an oil spill (Neff, 1979). While these studies have suggested there is reason for great concern over the effects of these contaminants upon marine organisms, little, if any, research has been directed toward ascertaining the impacts which may occur in near-shore or on-shore environments as the result of the release of constituents of drilling and production operations, i.e. formation water. This is especially true for studies of discharges into the relatively confined waterways and coastal marshes along the Gulf Coast. Boesch and Rabalais (1985) estimate that as much as 3.4 million barrels per day (bbls/day) of formation water are generated and discharged into estuarine, coastal, and continental shelf environments as the result of offshore operations in the Gulf of Mexico. While some of this water may be re-injected into the well, a large percentage of the produced water is piped to treatment and separation facilities on shore, after which the formation water is discharged into fresh and estuarine environments.

Approximately 95% of the oil and gas produced from federally-controlled outer-continental shelf (OCS) sites comes from the central and western regions of the Gulf of Mexico (Boesch and Rabalais, 1985). Roughly 23% of the produced waters generated in OCS waters (192,386 bbl/day) is discharged into near-shore and estuarine waters of the Louisiana coast. It has been suggested that the contaminants present in these produced waters may pose a threat to estuarine organisms far in excess of that posed to marine species due to differences in dilution volume, advection, the rates of dilution of hydrocarbons and the rates of sedimentation. The impact of production water in shallow semi-enclosed canals and natural bayous may be heightened because of depressed flushing rates, high particulate retention (turbidity), and the relatively high organic matter content of the particles; all conditions that might well facilitate the persistence of hydrocarbons and other organic compounds in the water column. Other potential ecological risk factors include: the very large volumes of produced water discharged on a routine basis, the low dissolved oxygen content of the water as the result of organic carbon decomposition and the alteration of ion ratios, as well as the high levels of metals and brine associated with these waters (Neff *et al.*, 1988).

Due to the widespread discharge of produced waters into the brackish and marine waters of the northwestern region of the Gulf of Mexico and because these estuaries represent some of the most productive spawning grounds for many commercially important species of fish, shellfish, and crustaceans, it is critical that any potential impacts that these complex mixtures may have upon aquatic life be accurately assessed. In the present study, we report the results of investigations which characterize the chemical contaminants present in produced water collected at four discharge sites: Lirette (LRT), Delta Farms (DF), Bully Camp (BC) and Lake Washington (LW) in south Louisiana. The impact on sediments spatially (top 5 cm) is presented for sites LRT, BC, and LW. The sediments from the Delta Farm site were examined both spatially and vertically for 10 cm sections.

VI.B Materials and Methods

VI.B.1 Sample Collection

Sediment samples were collected in coordination with DEQ Water Pollution Control Division personnel at their sample stations using a coring device similar to that described in Barrett *et al.* (1971). A 0.065 m x 0.46 m transparent, butyrate tube was attached onto the coring device and inserted into the sediment. The core was brought to the surface, but before removal from the water, a plastic cap was fitted to the bottom of the core tube. Once onboard, the coring device was removed and a plastic cap was fitted onto the top of the core tube; any overlying water was allowed to remain. The core tube was dried, the caps sealed with electrical tape, and the tube marked on the top and side with the station name, date, and time. Duplicate cores were taken at each station and designated "#1" and "#2". Cores were kept on ice in the field until transported the same day to the laboratory, where they were maintained at 5°C until sectioning. The longer of the duplicate cores was archived in a freezer at -20°C, after removal of any overlying water and length measurement. Overlying water was removed by suction, being careful not to disturb the surface of the core. The top 5 cm (0-5 cm) of the non-archived cores from sites LRT, BC, and LW were sectioned, after removal of any overlying water, into solvent-rinsed glass jars with Teflon-lined screw caps, after which the remaining sediment was discarded. The archived cores from site DF were divided into 10 cm sections for depth profile analysis. The frozen cores had desiccated and contracted, therefore cores were divided into 9 cm sections representing the original 10 cm. All samples were thoroughly mixed in the jar and stored at 5°C until analysis.

Effluent samples were collected for volatile organics (VOA), semivolatile organics, and trace metals. Glass sample bottles for organics, 40-ml (VOA) and 1-liter (semivolatiles), were solvent rinsed and heated at 160°C overnight. Trace metal plastic bottles were cleaned in 20% nitric acid overnight, then rinsed with deionized water.

VI.B.2 Organic Sample Analysis

VI.B.2.a Sediment Extractions

The sediment extraction method was a modification of that described by MacLeod *et al.* (1985). After thorough mixing, 10-15 g of wet sediment were weighed to 0.01 g into an amber bottle fitted with a Teflon-lined cap. The bottles were centrifuged at 2,000 rpm for 10 min, and excess moisture decanted. Seventy-five milliliters of dichloromethane (DCM), 50 g sodium sulfate, and 4 µg each of a mixture of the deuterated standards (surrogate spike) were added to the bottle. Contents of the jar were mixed using a spatula, then tightly capped and shaken, making sure contents were loose and did not stick to the sides of the jar. Twelve samples and a reagent blank were prepared at one time. The jars were placed on a modified rock tumbler and tumbled overnight. The DCM from each jar was decanted into a 240-ml amber jar and refrigerated. Another 75 ml aliquot of DCM was added, and the jars were tumbled for 6 hr, followed by decanting. A third aliquot of DCM was added, and tumbled overnight. The decanted DCM was filtered through funnels packed with sodium sulfate into 300-ml round bottom flasks, and rotary evaporated to approximately 2 ml. The concentrated extract was transferred to a 4-ml vial and further concentrated with solvent exchange to hexane to a final volume of 500 µl. Fine granular copper was added to reduce sulphur interferences. Extracts from the tumbling procedure were not subjected to further cleanup or fractionation. Analysis of the "whole" extract allowed for simultaneous estimation of aromatic and aliphatic hydrocarbon concentrations.

A 3-5 g subsample of wet sediment was taken for dry weight determination. The wet sediment was dried in an oven at 90°C until a constant dry weight was obtained from which the percent moisture value was calculated. Sample weights for hydrocarbon determinations were corrected for moisture content, and analyte concentrations are reported on a dry weight basis.

VI.B.2.b Volatile Organic Analysis of Water

Water samples for volatile organic analysis (VOA) were stored at 5°C until analysis. All samples were analyzed within 5 days of receipt by a purge and trap/gas chromatography (GC) technique similar to EPA Method 624. The instrumentation used was a Tekmar LS-2 purge and trap interfaced to a Hewlett Packard 5890 GC equipped with a 30 meter J&W 624 megabore capillary column and a flame ionization detector (FID). Quantitative results were based on an external standard method using authentic standards and a 3-point standard curve.

VI.B.2.c Extraction of Water for Semivolatile Organics

Samples were extracted by a liquid-liquid extraction method similar to EPA Method 625. Surrogate standards of d5-phenol, 2-fluorophenol, d5-nitrobenzene, d4-1,4-dichlorobenzene, d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene, and d12-perylene were added to each sample prior to extraction. One liter of effluent sample was first adjusted to pH >11 with 10N NaOH and extracted three times with 60 ml of dichloromethane (DCM) for the base/neutral fraction (BN). Extracts were filtered through funnels packed with sodium sulfate into 500-ml round bottom flasks. The sample was then adjusted to pH<2 with sulfuric acid (1:1) and extracted three times with 60 ml of DCM to obtain the acid fraction. Extracts were treated as above and combined with the BN extract. Sample extracts were first reduced in volume to 2 ml using a rotary evaporator and then brought to a final volume of 1 ml under a stream of purified nitrogen. Extraction blanks were analyzed to verify adequate glassware cleanliness and solvent purity. Duplicate and spiked samples were extracted to verify analytical recoveries and ensure reproducibility.

A 200 µl aliquot of the extracts was separated into three fractions by silica gel chromatography. The F1 fraction, containing the aliphatic hydrocarbons, was eluted with hexane, the F2 fraction, containing the polynuclear aromatic hydrocarbons (PAHs), was eluted with DCM/hexane (1:1), and the F3 fraction, containing polar compounds, was eluted with methanol. The fractions were reduced under a stream of purified nitrogen to a final volume of 200 µl.

After GC/MS analysis of the F3 fraction for phenols, these fractions were derivatized with boron trifluoride/methanol (BF_3/MeOH) to obtain fatty acid methyl esters (FAME). This derivatization was necessary to enhance chromatographic separation and quantification of aliphatic and aromatic fatty acids. Samples were added to a 13-ml culture tube with 1.5 ml of BF_3/MeOH (14% w/v). The mixture was heated in a water bath at 65-70°C for 15 min, then cooled and extracted with 6 ml of water and 4 ml hexane by shaking for 2 min. The hexane extract was removed and dried by passing through sodium sulfate into a 4-ml vial. The volume was reduced under a stream of purified nitrogen to a final volume of 200 µl and the extracts analyzed by GC/MS.

VI.B.2.d Semivolatile Instrumental Analysis

F-1 fractions for water samples were analyzed using a Hewlett Packard 5890 GC equipped with a J&W 30 meter DB-5 capillary column, 0.25 mm ID and 0.25 micron film thickness, and a flame ionization detector (FID). An estimation of the total saturated hydrocarbons (aliphatics), total resolved saturated hydrocarbons, and total unresolved saturated hydrocarbons was determined using a response factor based upon a standard containing nC-15 to nC-30 alkanes, pristane, phytane, and squalane. Total resolved hydrocarbons were determined by a valley-to-valley integration technique, total saturated hydrocarbons by integrating the entire chromatogram, including the unresolved complex (UCM), as a single peak. The total unresolved saturated hydrocarbons were determined by subtracting the resolved saturated hydrocarbons from the total.

Sediment sample extracts and the F2, F3, and derivatized F3 fractions of the effluent samples were analyzed using a Hewlett Packard 5890 GC equipped with a J&W 30 meter DB-5 capillary column, 0.25 mm ID and 0.25 micron film thickness, directly interfaced to a Hewlett Packard 5970B Mass Spectrometer. Quantifications were based on an internal standard technique compared to authentic standards where available and corrected for recoveries of the surrogate standards. To ensure reproducible instrument performance, the MS was tuned daily using the autotune program. Column performance was verified by the use of a Grob standard (Grob *et al.*, 1975), internal standards, and standards of the analytes of interest.

Quantitative determination of the semivolatile target compounds listed in Table VI.1 utilized an extracted ion/internal standard method similar to methods described in EPA Method 625. The primary ion in Table VI.1 was used for quantitation, while the secondary ion was used to confirm identification. The target

Table VI.1. Primary and secondary ions of semivolatile target compounds.

	Primary ion (m/z)	Secondary ion (m/z)
Acid Extractables		
Phenol	94	66
Cresols (C1-Phenols)	108	107
C2-Phenols	122	107
Benzoic Acid (Methyl ester)	105	77
C1-Benzoic Acids (Methyl esters)	119	91
C2-Benzoic Acids (Methyl esters)	133	164
Aliphatic Fatty Acids (Methyl esters)	74	87
PAHs		
Naphthalene	128	129
C1-Naphthalenes	142	141
C2-Naphthalenes	156	141
C3-Naphthalenes	170	155
Acenaphthylene	152	153
Acenaphthene	153	152
Fluorene	166	165
Dibenzothiophene	184	185
C1-Dibenzothiophenes	198	197
C2-Dibenzothiophenes	212	211
C3-Dibenzothiophenes	226	225
Phenanthrene	178	179
C1-Phenanthrenes	192	191
C2-Phenanthrenes	206	191
C3-Phenanthrenes	220	205
Anthracene	178	179
Fluoranthene	202	101
Pyrene	202	101
Benz(a)anthracene	228	226
Chrysene	228	226
Benzo(b&k)fluoranthene	252	253
Benzo(a)pyrene	252	253
Indeno(1,2,3-cd)pyrene	276	278
Dibenzo(a,h)anthracene	278	276
Benzo(g,h,i)perylene	276	278

compounds were chosen because of: 1) their relative abundance in petroleum sources such as crude oil and production water; 2) their potential to rapidly partition into the sediment and accumulate due to their low water solubilities; and 3) their relative persistence in the environment. In addition to the petrogenic compounds, common pyrogenic compounds (i.e. fluoranthene, pyrene, and higher molecular weight PAHs) were qualitatively and quantitatively identified to aid in differentiating the contaminant source. The surrogate deuterated standard was used to correct for recovery. The homologous series components, C1- and C2-naphthalenes, C1-dibenzothiophenes, and C1- and C2-phenanthrenes, were quantified with a standard mix of these alkylated homologs. The C3-naphthalenes, C2- and C3-dibenzothiophenes, and C3-phenanthrenes were estimated by extracted ions using the response factor of representative compounds. The minimum detection limit (MDL) was calculated for each sample, based upon the minimum detectable amount of phenanthrene, as determined from a standard curve, corrected for recovery of d10-phenanthrene and the dry weight of the sample.

Saturated hydrocarbons in sediment samples were determined by an extracted ion/internal standard method using mass 57, d10-phenanthrene as a surrogate standard and a response factor based on the saturate standard described previously. Integration was performed as outlined for the F1 fraction analyzed by GC/FID. Acid-extractable compounds were not determined in sediment samples.

VI.B.3 Trace Metal Sample Analysis

A 3 g subsample of sediment was transferred to an acid washed plastic bottle and then frozen. The frozen sediment samples and produced water samples were shipped to the Molecular Ecology Institute (MEI) at California State University, Long Beach. After receipt, sediment and water samples were stored at -80°C until processing. Each sediment sample was thawed to room temperature for approximately 15 min and entire samples individually homogenized using a Teflon spatula. A 1 g aliquot was removed and transferred to an individual polypropylene 20-ml digestion container. The samples were oven dried for 24 hrs at 60°C from which water contents and dry weights were calculated. The dry sediment samples were digested using a CEM Microwave Digestion system by addition of 2.5 ml concentrated HNO_3, and digesting for 3 hrs at a mean power setting of 300 watts. A 4 ml aliquot of each produced water sample was removed and transferred to a culture tube for direct metal analysis.

A procedural blank and a sample of Standard Reference Material marine sediment (NRC MESS-1) were processed with each batch of ten samples. Resulting digestants were quantitatively transferred, brought to a final volume of 50 ml and a 4 ml aliquot analyzed for: Al, V, Cr, Ni, Cu, Zn, As, Cd, Ba, Hg, and Pb. Sample digestants were spiked with 100 ppb Yttrium as an internal standard.

Samples were analyzed using a VG PlasmaQuad Inductively Coupled Plasma Mass Spectrometer (ICP/MS). In addition to the standard ICP/MS configuration, the instrument was equipped with a water-cooled spray chamber and ETP dynode detector to optimize sensitivity and stability and minimize background noise. Samples were calibrated using regression statistics based on the analysis of five aqueous metal standards including 0.1, 1.0, 10.0, 100.0, and 1000.0 ppb (ng/ml) of the eleven metals.

Standard laboratory protocols for sample analysis using ICP/MS techniques include 2 reagent blanks and one aqueous metal sensitivity standard (100 ppb) per approximately 10 environmental samples. Additionally, three samples of SRM trace metals in freshwater are analyzed for each analytical run. All environmental samples, standard reference materials, procedural, and reagent blanks were analyzed at the same time on the ICP/MS for an identical suite of metal isotopes. The data are reported as µg metal/g dry weight (ppm) for sediments and ng metal/ml water (ppb) for water samples. These values are corrected for any artifacts indicated by procedural and reagent blanks.

VI.B.4 Data Presentation

Figures for effluent samples consist of bar graphs displaying the relative amounts of hydrocarbon constituents from different effluents. Figures for sediment samples consist of distribution bar graphs and depth profiles (site DF) of: 1) the total parent PAHs and total homologs, 2) FFPI and resolved saturates/total saturates, and 3) selected trace metals. The sample points in the sediment bar graphs are arranged by distance from the origin of the transect.

Tables for water samples contain concentrations of: 1) target PAHs, 2) identified volatile aromatic hydrocarbons, 3) acid extractable compounds, and 4) saturated hydrocarbons. Sediment tables list: 1) total concentrations of parent PAHs, 2) total concentrations of PAH (polynuclear aromatic hydrocarbon) homologs, 3) FFPI, 4) the ratio of resolved saturates/total saturates, and 5) total saturates.

The "fossil fuel pollution index" (FFPI) (Boehm and Farrington, 1984) indicates the relative percentage of petroleum-derived hydrocarbons in the measured total PAHs. This index is based on the distribution of PAHs in petroleum, which contains a relative abundance of alkylated homologs of naphthalene, phenanthrene, and dibenzothiophene compared to their unalkylated parent compounds. Crude oil would have an FFPI of about one (1). The FFPI is a continuum, which decreases with a decrease in petroleum-derived hydrocarbons and/or an increase in pyrogenic hydrocarbons. The index is a useful tool in studies monitoring the impact of petroleum-derived PAHs. The FFPI is determined by the following formula modified from Boehm and Farrington (1984):

$$\text{FFPI} = [\Sigma\text{naphthalenes } (C_0\text{-}C_3) + \Sigma\text{dibenzothiophenes } (C_0\text{-}C_3) + 1/2\ \Sigma\text{phenanthrenes } (C_0\text{-}C_1) + \Sigma\text{phenanthrenes } (C_2\text{-}C_3)] \,/\, \Sigma \text{ PAHs},$$

C_n = number of alkyl carbons substituted.

The ratio of resolved saturates/total saturates (RS/TS) can be used as an indicator of degradation. The higher the ratio, the more recent the contamination. If sediments receive a continuous input of 'fresh' hydrocarbons, the ratio will reflect that of the source. As distance from the source increases, the ratio will decrease due to degradation of resolved hydrocarbons.

The appendices contain tables which list: 1) sample dry weights; 2) minimum detection limit (MDL); 3) concentrations of target PAHs; 4) concentrations of saturated hydrocarbons; and 5) ratios and indices. The ratios of nC-17/Pristane and nC-18/Phytane are used as indicators of oil degradation. The normal alkanes (such as nC-17 and nC-18) are usually the first of the saturated hydrocarbons to undergo degradation, while the branched-chained, isoprenoid, hydrocarbons (pristane and phytane) are more resistant. These ratios will decrease with increasing degradation. The ratio of pristane/phytane can aid in determining the source of contamination because of the relative stability of these compounds in the environment.

VI.B.5 Quality Control/Quality Assurance

VI.B.5.a Methods

One produced water sample (LW-E) and 6 (six) sediment samples were analyzed in duplicate and matrix spiked with known amounts of analytes. The water volatiles sample was spiked with 10 ng of an aromatic hydrocarbon volatiles standard (Ultra Scientific # DWM-550). The water sample analyzed for semivolatiles was spiked with: 1) 40 ng of a deuterated standard containing: d4-1,4-dichlorobenzene, d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene, and d12-perylene (Ultra Scientific # US-108); 2) 35 ng of another deuterated standard containing: d5-phenol, 2-fluorophenol, d5-nitrobenzene; 3) 12 ng of a base/neutral standard (Ultra Scientific # 625-MA); and 4) 15 ng of an acid standard (Ultra Scientific # PHM-804). Only the deuterated standards were added before extraction to the duplicate samples.

Sediment samples were spiked with: 1) 4 ng of a deuterated standard containing: d4-1,4-dichlorobenzene, d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene, and d12-perylene (Ultra Scientific # US-108); and 2) 2 ng of a PAH standard (Ultra Scientific # US-106). Again, only the deuterated standards were added to duplicate sediment samples.

VI.B.5.b Water Results

Tables VI.2a and VI.2b show results of duplicate analyses and recoveries of spiked compounds for sample LW-E. The reproducibility in analyses for acid-extractable compounds, saturated hydrocarbons, and PAHs is <10%, while volatiles analyses of separate samples varied 7-50%. This is probably the result of differences in sample collection, as the reanalysis of the same sample had repeatability of 15%. Recoveries of spiked compounds in volatile samples was >100%, probably resulting from inaccuracies in measurement of final volume of the sample extracts. The average recoveries of spiked compounds were 80% for acid-extractables and 87% (65-123%) for PAHs.

VI.B.5.c Sediment Results

Tables VI.3a - VI.3c lists the results of duplicate analysis of sediment samples. The relative percent difference (RPD) was calculated for each analyte spiked. The values from the two duplicates, for a particular analyte, are subtracted and then divided by the average of the duplicates to yield the RPD. The range of the (RPD) for "Total PAHs + Homologs" was 6-34% and for "Total Saturated Hydrocarbons" was 7-29%.

The recoveries of spiked compounds are presented in Table VI.4. Average recoveries for spiked PAHs ranged from 45% (chrysene) to 96% (indeno(1,2,3-cd)pyrene), while for the deuterated standards the range was 72% (d8-naphthalene) to 97% (d10-phenanthrene). Some of the factors affecting recoveries of spiked PAHs are: 1) variability in the amount of a certain PAH already in the sample, 2) the sample matrix, 3) extraction efficiency, 4) laboratory technique, and 5) lack of sample homogenicity. The recoveries of spiked individual PAHs varied widely, but recoveries of deuterated standards, which are not present in sample, covered a narrower range and may be a better indicator of extraction and sample handling techniques.

Table VI.2a. Volatiles, acid-extractable compounds, and saturated hydrocarbons detected in duplicate produced water samples and % recoveries of spikes.

	LW-E R1	LW-E R2		LW-E Spk
Volatiles				
Benzene	880	820	Benzene	98%
Toluene	380	230	Toluene	112%
Ethylbenzene	17	12	Ethylbenzene	111%
Xylenes	180	110	Xylenes	109%
Isopropylbenzene	6.2	2.9	Isopropylbenzene	110%
n-Propylbenzene	8.5	4.2	n-Propylbenzene	113%
1,3,5-Trimethylbenzene	9.7	5.2	1,3,5-Trimethylbenzene	113%
1,2,4-Trimethylbenzene	19	11	1,2,4-Trimethylbenzene	112%
Naphthalene	22	10	Naphthalene	112%
Total Volatiles	1,500	1,200	Avg	110%
Acid-Extractable Compounds				
Phenol	710	720	d5-Phenol	24%
Cresols (C1-Phenols)	690	720	Phenol	127%
C2-Phenols	330	330	Cresols (C1-Phenols)	86%
Benzoic Acid	1,600	1,500	C2-Phenols	83%
C1-Benzoic Acids	1,400	1,200		
C2-Benzoic Acids	410	340	Avg	80%
Aliphatic Fatty Acids	19,000	17,000		
Total Acid Compounds	24,000	22,000		
Saturated Hydrocarbons				
Resolved	5,200	5,200		
Unresolved	20,000	20,000		
Total	26,000	25,000		
Resolved/Total	0.20	0.21		
nC-17/Pristane	0.94	0.93		
nC-18/Phytane	1.83	1.76		
Pristane/Phytane	1.80	1.71		

Table VI.2b. Polynuclear aromatic hydrocarbon (PAH) concentrations detected in duplicate produced water samples and recoveries of spiked PAH and deuterated standards and co-injected hexamethylbenzene (HMB).

	LW-E R1	LW-E R2		LW-E Spk
PAHs				
Naphthalene	23	24	d8-Naphthalene	70%
C1-Naphthalenes	64	66	Naphthalene	105%
C2-Naphthalenes	140	140	Acenaphthylene	79%
C3-Naphthalenes	370	420	HMB	84%
Acenaphthylene	nd	nd	d10-Acenaphthene	88%
Acenaphthene	0.56	0.58	Acenaphthene	102%
Fluorene	2.7	2.9	Fluorene	108%
Dibenzothiophene	2.3	2.2	d10-Phenanthrene	82%
C1-Dibenzothiophenes	8.9	9.9	Phenanthrene	115%
C2-Dibenzothiophenes	18	18	Anthracene	90%
C3-Dibenzothiophenes	11	12	Fluoranthene	67%
Phenanthrene	9.1	9.3	Pyrene	71%
C1-Phenanthrenes	46	49	Benz(a)anthracene	74%
C2-Phenanthrenes	56	57	d12-Chrysene	65%
C3-Phenanthrenes	27	23	Chrysene	80%
Anthracene	0.62	0.50	Benzo(b&k)fluoranthene	74%
Fluoranthene	0.56	0.56	Benzo(a)pyrene	82%
Pyrene	0.71	0.63	d12-Perylene	98%
Benz(a)anthracene	0.80	1.0	Indeno(1,2,3-cd)pyrene	84%
Chrysene	1.9	2.0	Dibenzo(a,h)anthracene	123%
Benzo(b)fluoranthene	nd	nd	Benzo(g,h,i)perylene	90%
Benzo(k)fluoranthene	nd	nd		
Benzo(a)pyrene	nd	nd	Avg	87%
Indeno(1,2,3-cd)pyrene	nd	nd		
Dibenzo(a,h)anthracene	nd	nd		
Benzo(g,h,i)perylene	nd	nd		
Total Parent PAH	43	44		
Total Homologs	740	800		
Total PAH + Homologs	780	840		
FFPI	0.95	0.96		

nd: not detected

Table VI.3a. Hydrocarbon concentrations (ppb, dry wt.) in duplicate sediment samples.

	BC-R (0-5cm) R1	BC-R (0-5cm) R2	LRT-C250 (0-5cm) R1	LRT-C250 (0-5cm) R2
Dry Weight (g)	3.4	3.5	5.9	4.5
MDL (ppb)	69	78	33	33
Naphthalene	nd	nd	tr	nd
C1-Naphthalenes	nd	nd	nd	nd
C2-Naphthalenes	nd	nd	nd	nd
C3-Naphthalenes	nd	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd
Fluorene	nd	nd	nd	nd
Dibenzothiophene	nd	nd	nd	nd
C1-Dibenzothiophenes	nd	nd	nd	nd
C2-Dibenzothiophenes	nd	nd	nd	nd
C3-Dibenzothiophenes	nd	nd	nd	trc
Phenanthrene	nd	nd	61	55
C1-Phenanthrenes	nd	nd	nd	nd
C2-Phenanthrenes	nd	nd	69	50
C3-Phenanthrenes	nd	nd	nd	nd
Anthracene	nd	nd	tr	35
Fluoranthene	trc	trc	160	200
Pyrene	tr	tr	140	220
Benz(a)anthracene	nd	nd	59	95
Chrysene	nd	nd	330	250
Benzo(b&k)fluoranthene	nd	nd	200	210
Benzo(a)pyrene	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parent PAHs	tr	tr	960	1,100
Total Homologs	nd	nd	69	50
Total PAHs + Homologs	tr	tr	1,000	1,100
FFPI	n/a	n/a	0.10	0.07
Saturated Hydrocarbons				
Resolved	3,000	4,900	4,600	3,300
Unresolved	66,000	59,000	52,000	44,000
Total	69,000	63,000	57,000	47,000
Resolved/Total	0.04	0.08	0.08	0.07
nC-17/Pristane	3.17	3.05	0.95	0.90
nC-18/Phytane	n/a	n/a	0.28	0.32
Pristane/Phytane	0.49	0.51	1.49	1.45

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table VI.3b. Hydrocarbon concentrations (ppb, dry wt.) in duplicate sediment samples.

	LW-B350 (0-5cm) R1	LW-B350 (0-5cm) R2	DF-B$_1$200 (0-9cm) R1	DF-B$_1$200 (0-9cm) R2
Dry Weight (g)	4.4	4.2	3.7	3.4
MDL (ppb)	40	76	52	54
Naphthalene	nd	nd	130	120
C1-Naphthalenes	nd	nd	650	820
C2-Naphthalenes	nd	nd	2,600	3,000
C3-Naphthalenes	nd	nd	11,000	13,000
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	nd	nd	tr	55
Fluorene	nd	nd	130	190
Dibenzothiophene	nd	nd	72	77
C1-Dibenzothiophenes	nd	nd	390	480
C2-Dibenzothiophenes	nd	nd	760	830
C3-Dibenzothiophenes	tr	nd	430	590
Phenanthrene	130	98	390	500
C1-Phenanthrenes	nd	nd	1,300	1,600
C2-Phenanthrenes	40	tr	1,600	2,100
C3-Phenanthrenes	130	nd	730	1,200
Anthracene	43	150	tr	76
Fluoranthene	340	260	150	220
Pyrene	300	240	170	210
Benz(a)anthracene	130	91	120	72
Chrysene	200	180	170	200
Benzo(b&k)fluoranthene	240	160	190	150
Benzo(a)pyrene	99	tr	nd	tr
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parent PAHs	1,500	1,200	1,600	1,900
Total Homologs	170	tr	19,000	24,000
Total PAHs + Homologs	1,700	1,200	21,000	26,000
FFPI	0.14	0.04	0.91	0.91
Saturated Hydrocarbons				
Resolved	1,200	940	440,000	430,000
Unresolved	46,000	63,000	700,000	830,000
Total	48,000	64,000	1,100,000	1,300,000
Resolved/Total	0.03	0.01	0.40	0.33
nC-17/Pristane	2.03	1.74	0.59	0.68
nC-18/Phytane	0.41	0.52	0.73	0.76
Pristane/Phytane	0.91	1.76	1.83	1.40

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table VI.3c. Hydrocarbon concentrations (ppb, dry wt.) in duplicate sediment samples.

	DF-$B_2$200 (18-25cm) R1	DF-$B_2$200 (18-25cm) R2	DF-$B_2$300 (27-30cm) R1	DF-$B_2$300 (27-30cm) R2
Dry Weight (g)	4.2	4.2	4.3	4.1
MDL (ppb)	44	40	52	62
Naphthalene	tr	tr	62	tr
C1-Naphthalenes	72	69	51	65
C2-Naphthalenes	1,400	1,400	1,400	1,600
C3-Naphthalenes	6,900	7,500	7,400	7,600
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	190	160	82	100
Fluorene	250	230	150	170
Dibenzothiophene	65	63	64	tr
C1-Dibenzothiophenes	330	390	400	400
C2-Dibenzothiophenes	600	660	490	580
C3-Dibenzothiophenes	460	560	370	330
Phenanthrene	440	500	320	310
C1-Phenanthrenes	1,000	1,100	930	1,000
C2-Phenanthrenes	1,400	1,600	1,200	1,400
C3-Phenanthrenes	730	730	540	610
Anthracene	74	70	82	71
Fluoranthene	300	360	220	220
Pyrene	310	280	230	230
Benz(a)anthracene	170	130	190	170
Chrysene	270	250	310	230
Benzo(b&k)fluoranthene	180	100	200	240
Benzo(a)pyrene	100	63	140	110
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parent PAHs	2,300	2,200	2,100	1,900
Total Homologs	13,000	14,000	13,000	14,000
Total PAHs + Homologs	15,000	16,000	15,000	16,000
FFPI	0.83	0.85	0.85	0.86
Saturated Hydrocarbons				
Resolved	140,000	140,000	140,000	170,000
Unresolved	400,000	440,000	460,000	520,000
Total	540,000	580,000	590,000	690,000
Resolved/Total	0.26	0.24	0.24	0.25
nC-17/Pristane	0.08	0.06	0.05	0.08
nC-18/Phytane	n/a	n/a	0.01	0.04
Pristane/Phytane	1.72	1.76	1.58	1.73

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table VI.4. Recoveries of spiked PAH and deuterated internal standards and co-injected hexamethylbenzene (HMB) in sediment samples.

	BC-R (0-5cm) % Recovery	LRT-C250 (0-5cm) % Recovery	LW-350 (0-5cm) % Recovery	DF-B$_1$200 (0-9cm) % Recovery	DF-B$_2$200 (18-25cm) % Recovery	DF-B$_2$300 (27-30cm) % Recovery	Avgerage % Recovery
d8-Naphthalene	83%	61%	89%	75%	67%	54%	72%
Naphthalene	50%	42%	52%	61%	63%	39%	51%
Acenaphthylene	64%	69%	70%	72%	69%	79%	71%
HMB	112%	97%	108%	126%	92%	119%	109%
d10-Acenaphthene	104%	81%	110%	79%	76%	86%	89%
Acenaphthene	84%	71%	75%	83%	63%	75%	75%
Fluorene	97%	92%	93%	69%	78%	83%	85%
d10-Phenanthrene	137%	112%	130%	60%	76%	68%	97%
Phenanthrene	113%	107%	104%	34%	83%	60%	84%
Anthracene	87%	116%	80%	49%	80%	61%	79%
Fluoranthene	136%	155%	118%	25%	47%	27%	85%
Pyrene	126%	157%	102%	26%	33%	32%	80%
Benz(a)anthracene	83%	115%	36%	72%	5%	56%	61%
d12-Chrysene	98%	103%	61%	72%	28%	84%	74%
Chrysene	65%	65%	21%	73%	-10%	53%	45%
Benzo(b&k)fluoranthene	70%	88%	27%	70%	19%	77%	58%
Benzo(a)pyrene	50%	67%	44%	87%	38%	70%	59%
d12-Perylene	100%	103%	74%	78%	52%	92%	83%
Indeno(1,2,3-cd)pyrene	98%	153%	115%	40%	73%	99%	96%
Dibenzo(a,h)anthracene	72%	151%	108%	59%	70%	67%	88%
Benzo(g,h,i)perylene	54%	115%	108%	50%	80%	74%	80%
Avgerage	90%	101%	82%	65%	56%	69%	77%

VI.C Results

VI.C.1 Characterization of Produced Water

VI.C.1.a Volatile Organics

All produced water samples were found to contain high concentrations of the volatile aromatic hydrocarbons benzene, toluene, and xylenes (Table VI.5 and Figure VI.1). Benzene showed the highest concentration of all volatile organics, comprising 50-70% of the total. DF-E contained the greatest abundance of volatile hydrocarbons (1,800 µg/l), while BC-E contained the least (760 µg/l). Other volatile organic compounds, such as short-chain normal alkanes (i.e. hexane), ketones, alcohols, and cyclic alkanes, were probably present at low levels in these effluents. These other compounds were not characterized, as the volatiles that were identified comprised 70-95% of the total volatiles.

VI.C.1.b Acid-Extractable Compounds

The acid-extractable compounds comprised a large part of the total organics identified in all effluents, with the exception of BC-E (Table VI.5 and Figure VI.2). These compounds are a small portion of crude oil, but because of their high water solubility they comprise a large portion of the organic load in produced water. The highest concentration of acid compounds was found in station DF-E, with the majority derived from aliphatic fatty acids. Normal fatty acids from pentanoic acid thru dodecanoic acid, branched aliphatic acids, cyclic carboxylic acids, and unknown acid compounds make up this group.

VI.C.1.c Saturated Hydrocarbons

The saturated hydrocarbons were found to be the highest organic component for all effluents except DF-E (Table VI.5 and Figure VI.3). This fraction is composed of normal straight-chain hydrocarbons (alkanes), isoprenoid hydrocarbons, branched-chain hydrocarbons, and naphthenes (cycloalkanes). Saturated hydrocarbons are classified as resolved or unresolved components. The unresolved class represents petroleum oil components that cannot be fully separated by gas chromatographic methods.

VI.C.1.d Aromatic Hydrocarbons

The major polynuclear aromatic hydrocarbons (PAHs) identified in the produced water samples were naphthalene and its

Table VI.5. Volatiles, acid-extractable compounds, and saturated hydrocarbons detected in produced water samples.

	LRT-E	DF-E	BC-E	LW-E
Volatiles (MDL µg/l)	1.0	1.0	1.0	1.0
Benzene	800	1,200	500	840
Toluene	580	440	150	280
Ethylbenzene	29	16	9.4	14
Xylenes	210	120	58	130
Isopropylbenzene	5.9	nd	2.4	4.0
n-Propylbenzene	2.8	1.4	3.8	5.6
1,3,5-Trimethylbenzene	14	5.1	6.2	6.7
1,2,4-Trimethylbenzene	29	11	12	14
Naphthalene	6.4	16	18	14
Total Volatiles	1,700	1,800	760	1,300
Acid-Extractable Compounds (MDL µg/l)	1.6	1.4	1.6	1.8
Phenol	400	890	240	720
Cresols (C1-Phenols)	380	850	370	710
C2-Phenols	180	420	240	330
Benzoic Acid	1,600	3,600	150	1,500
C1-Benzoic Acids	1,600	2,700	320	1,300
C2-Benzoic Acids	590	880	190	380
Aliphatic Fatty Acids	7,500	28,000	1,000	18,000
Total Acid Compounds	12,000	37,000	2,500	23,000
Saturated Hydrocarbons (MDL µg/l)	1.4	1.0	1.0	1.4
Resolved	10,000	2,500	2,600	5,200
Unresolved	12,000	4,800	7,900	20,000
Total	22,000	7,300	10,000	25,000
Resolved/Total	0.45	0.34	0.26	0.21
nC-17/Pristane	1.12	1.29	0.86	0.93
nC-18/Phytane	2.06	2.37	1.77	1.79
Pristane/Phytane	2.41	1.79	1.95	1.76

MDL: Minimum Detection Limit
nd: not detected

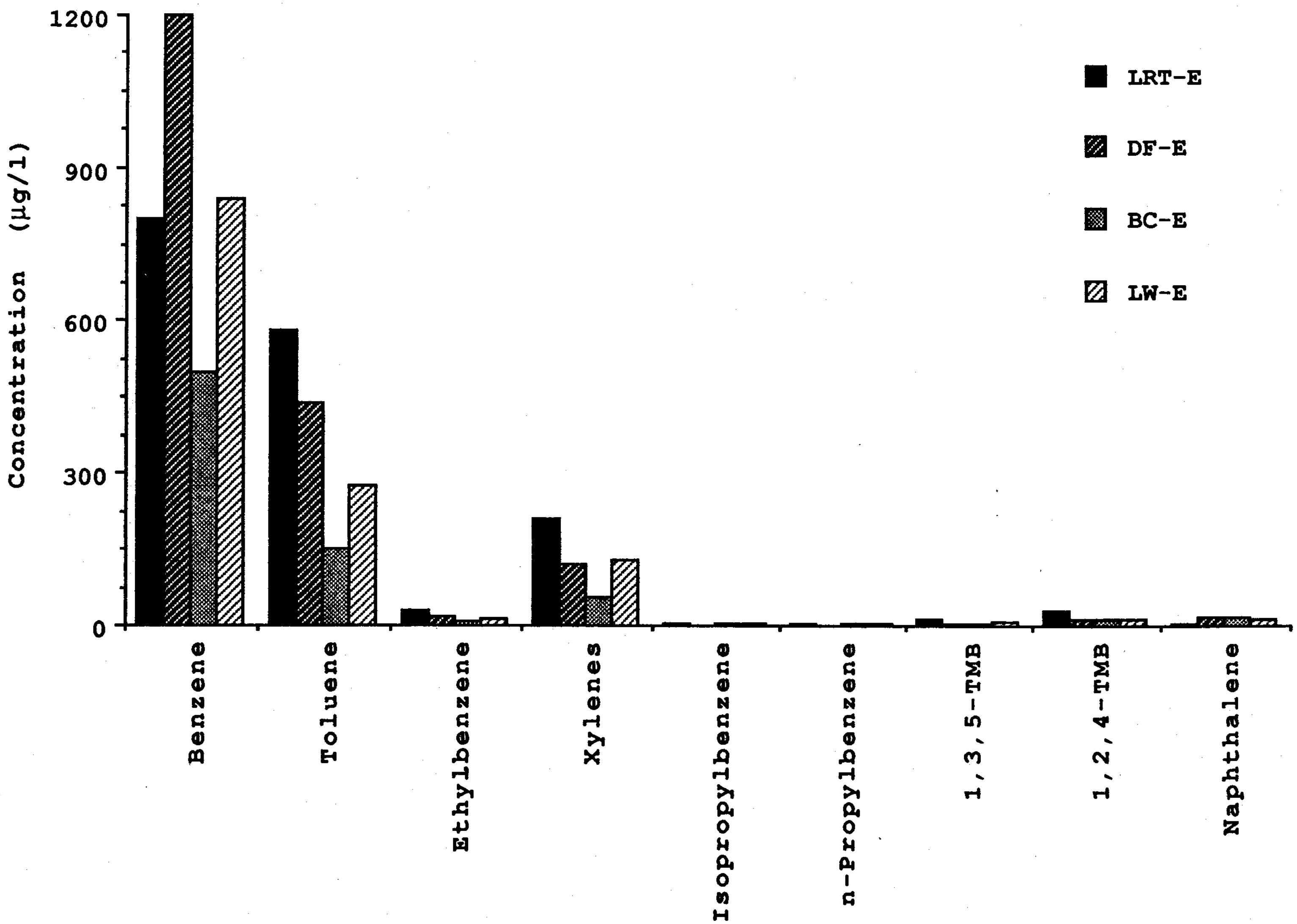


Figure VI.1. Volatile organics detected in produced water samples.

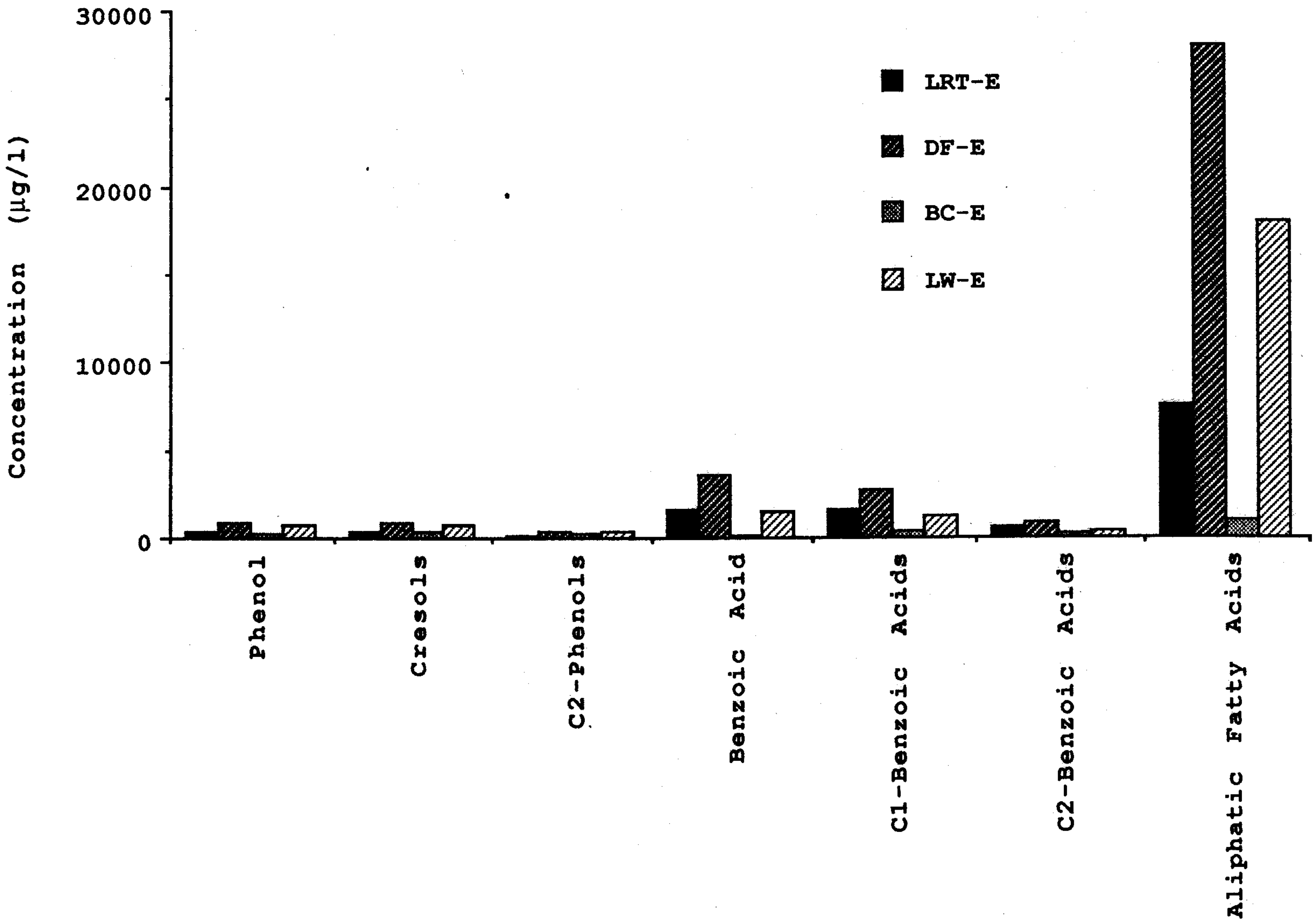


Figure VI.2. Acid-extractable compounds detected in produced water samples.

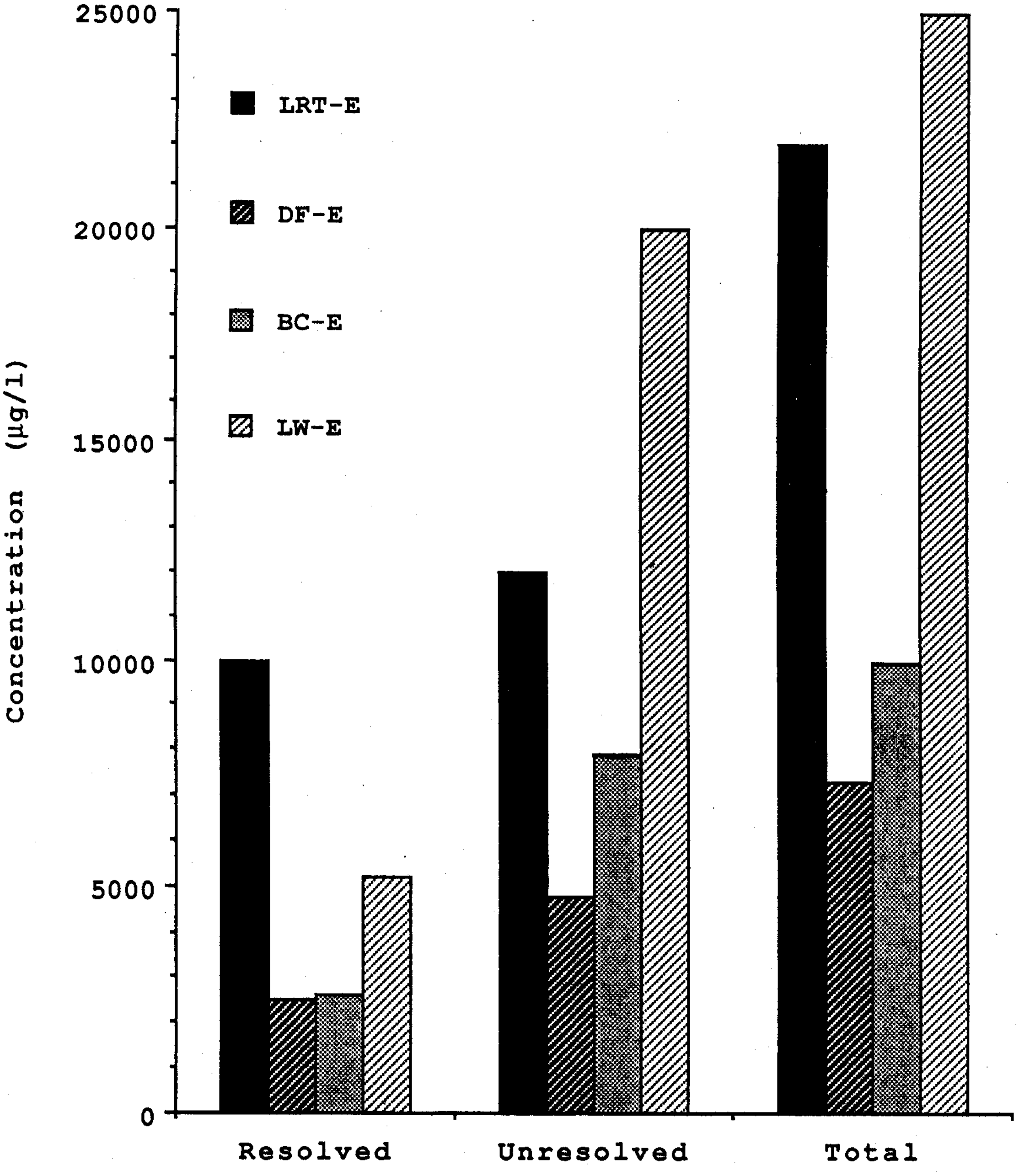


Figure VI.3. Saturated hydrocarbon concentrations in produced water samples.

alkylated analogs, ranging in concentration from 18 (LRT-E) to 41 µg/l (BC-E) for naphthalene and 100 (LRT-E) to 600 µg/l (LW-E) for all naphthalene homologs (Table VI.6 and Figure VI.4). The next highest in concentration were phenanthrenes, with the parent compound phenanthrene ranging from 0.49 (LRT-E) to 9.2 µg/l (LW-E) and 1.3 (LRT-E) to 129 µg/l (LW-E) for the homologs. The effluent at station LW-E contained the highest concentration of total PAHs and homologs, stations DF-E and BC-E had about equal amounts, and station LRT-E contained the lowest levels of of total PAHs and homologs. Only trace amounts of pyrogenic hydrocarbons, containing four rings or more, were detected in these effluents. The main sources of pyrogenic hydrocarbons are from combustion sources such as automobile exhausts, factory exhausts, and fires.

Base-extractable compounds, such as pyridines and quinolines, were not detected in any of these effluents. Other heterocyclic compounds, such as carbazole, indole, fluorenone, and dibenzofuran, were also not detected. These compounds make up a very small portion of the total hydrocarbons in South Louisiana crude oil.

VI.C.1.e Trace Metals

The trace metal content of the four produced water samples collected as part of this study was highly variable (Table VI.7). Several metals were not detected at all. These were aluminum, nickel, cadmium, mercury, and lead. Barium was the metal detected at the highest levels in all four produced waters, ranging from 1,521 ppb in the Delta Farms produced water discharge to a maximum of 4,644 ppb in the Lirette field discharge (Figure VI.5). Vanadium, a trace metal often associated with oil, was also found in each of the four discharges but at varying levels (Figure VI.5) In the Delta Farms and Lake Washington sites the levels of vanadium were very low (<3 ppb), while at the Bully Camp site an intermediate level of 15 ppb was detected. In the Lirette discharge the levels were much higher (60 ppb). This suggests that the oil reservoirs being treated at these four facilities have very different levels of this element. Zinc was also found in all four discharges at concentrations of from 7.3 ppb in the Delta Farms discharge to a maximum of 25 ppb in the Bully Camp discharge (Figure VI.5).

The remaining three metals detected, arsenic, chromium, and copper, were not detected in all four discharges. Arsenic was detected only in the Lirette discharge at 87 ppb and in the Bully Camp discharge at 30 ppb. Copper, in contrast, was only detected in the Delta Farms discharge at 32 ppb and the Lake Washington discharge at 58 ppb. Chromium was detected at concentrations less than 1 ppb in only the Lirette and Delta Farms discharges.

Table VI.6. Polynuclear aromatic hydrocarbon (PAH) concentrations in produced water samples.

	LRT-E	DF-E	BC-E	LW-E
PAHs (MDL µg/l)	0.18	0.17	0.22	0.34
Naphthalene	18	36	41	24
C1-Naphthalenes	28	57	66	65
C2-Naphthalenes	34	64	66	140
C3-Naphthalenes	42	100	99	400
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	0.29	0.42	0.50	0.57
Fluorene	0.33	2.0	1.9	2.8
Dibenzothiophene	tr	0.64	0.52	2.3
C1-Dibenzothiophenes	trc	2.4	1.6	9.4
C2-Dibenzothiophenes	trc	3.2	2.4	18
C3-Dibenzothiophenes	tr	2.4	2.0	12
Phenanthrene	0.49	4.0	2.9	9.2
C1-Phenanthrenes	0.68	9.9	7.8	47
C2-Phenanthrenes	0.55	9.8	10	57
C3-Phenanthrenes	trc	5.1	4.5	25
Anthracene	nd	nd	tr	0.56
Fluoranthene	tr	trc	0.23	0.56
Pyrene	tr	tr	tr	0.67
Benz(a)anthracene	tr	0.28	tr	0.91
Chrysene	tr	0.32	tr	1.9
Benzo(b)fluoranthene	nd	nd	nd	nd
Benzo(k)fluoranthene	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parent PAHs	19	43	47	43
Total Homologs	110	250	260	770
Total PAHs + Homologs	120	300	310	810
FFPI	0.99	0.97	0.97	0.96

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits

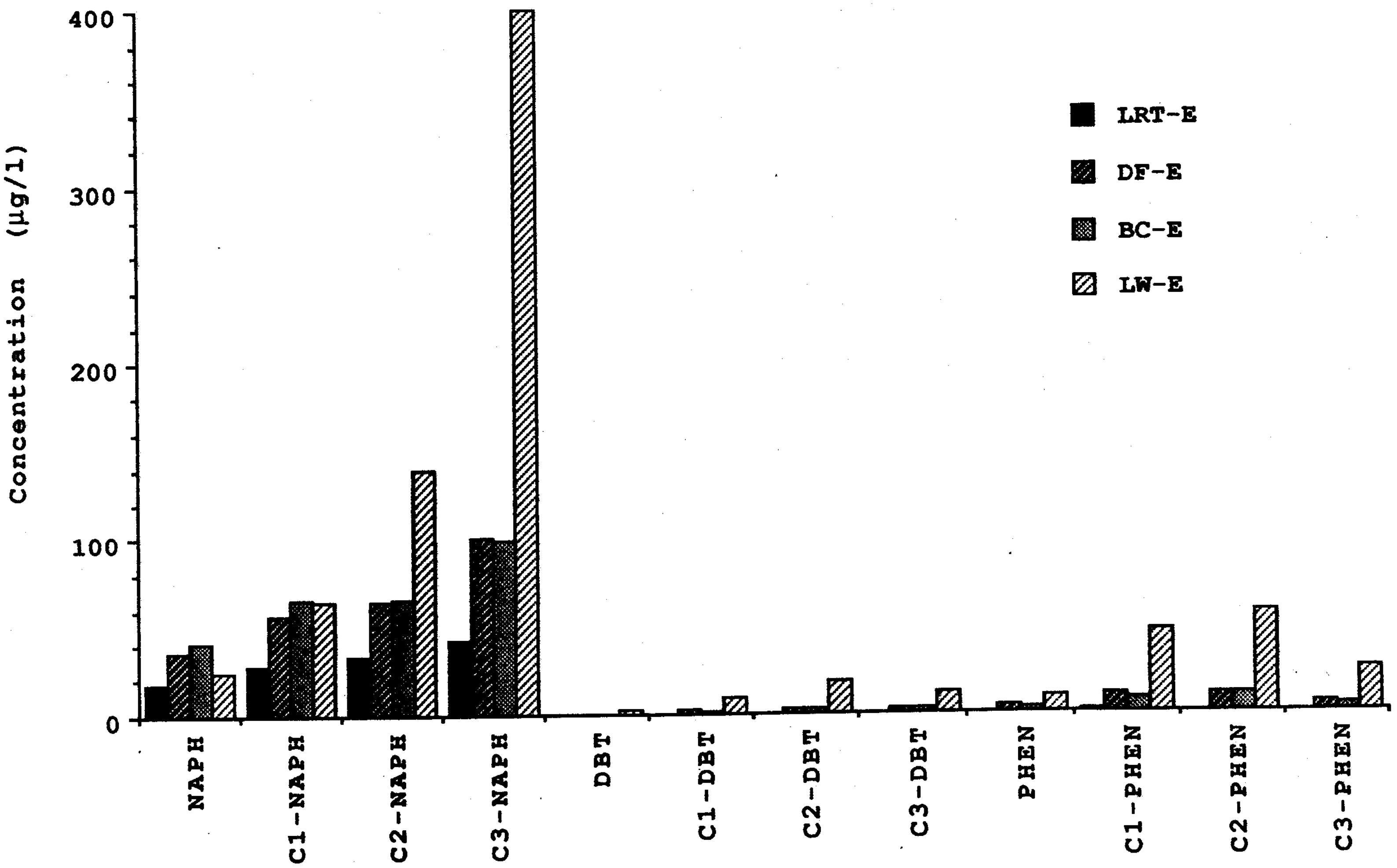


Figure VI.4. Major semivolatile hydrocarbons detected in produced water samples.

Table VI.7. Concentrations of selected trace metals in produced water discharges.

Metal (µg/l)	MDL (µg/l)	LRT-E	BC-E	DF-E	LW-E
Al	0.44	nd	nd	nd	nd
Cr	0.01	0.41	nd	0.17	nd
V	0.01	60	15	2.9	1.2
Ni	0.22	nd	nd	nd	nd
Cu	0.05	nd	nd	32	58
Zn	0.08	23	25	7.3	13
As	0.11	87	30	nd	nd
Cd	0.06	nd	nd	nd	nd
Ba	0.14	4,644	3,153	1,521	2,885
Hg	1.7	nd	nd	nd	nd
Pb	0.08	nd	nd	nd	nd

MDL: Minimum Detection Limit
nd: not detected

VI.C.1.f Summary

The four produced water discharges in this study varied greatly in the type and amount of organic compounds identified. The composition of effluents is effected by the type of formation from which the oil/brine is extracted, the age of the field, and the methods used at the surface to separate the oil and water before discharge. The composition of a particular discharge should remain relatively constant over the short term, but may change as the field is depleted or if separation techniques are altered.

The largest component of these effluents was found to be saturated hydrocarbons. However, saturated hydrocarbons are the least dense, least soluble, and least toxic fraction of petroleum. The acid-extractable compounds, which were found to be as high in concentration as the saturates in some effluents, are very water soluble and reactive, therefore their residence time in the environment is probably short. The volatile fraction, the next highest in concentration, contains compounds which are highly water soluble and are acutely toxic to organisms exposed to high concentrations. The high water solubility of these compounds means they are less likely to be sorbed onto particulate matter and be deposited in the sediments. Their fate consists of becoming diluted in the water column and eventually being dispersed far from the discharge point. The PAHs are the smallest component in these effluents, however this fraction is the heaviest, most toxic, and most environmentally stable fraction of crude oil. The toxicity of crude oil is a reflection

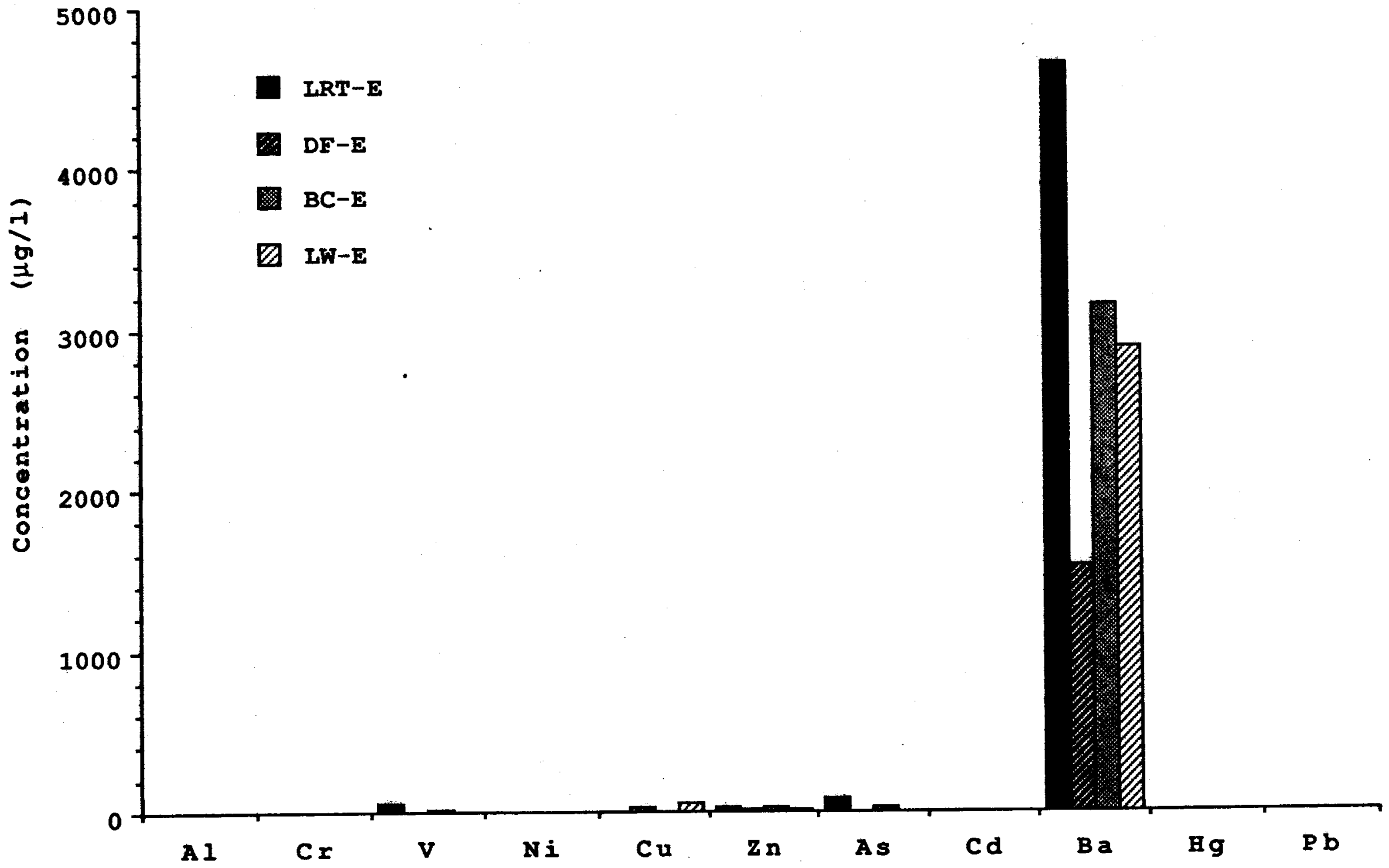


Figure VI.5. Concentrations of selected trace metals detected in produced water samples.

of its aromatic content, primarily the alkyl-substituted naphthalenes (di-ringed) and phenanthrenes (tri-ringed). PAHs are more likely to be incorporated into the sediments because of lower water solubilities and higher sorption coefficients than the volatile compounds. However, because the di and tri-ringed PAHs are somewhat water soluble, they will exist in the environment both as dissolved and adsorbed chemical species.

Based on the discharge rates at the different sites, the amounts of total PAHs + homologs entering the environment daily are: LRT = 8.9 g, DF = 650 g, BC = 240 g, and LW = 210 g. This suggests that the sediments in the Delta Farms area have received the greatest input of toxic aromatic hydrocarbons of any of the sites studied.

The trace metal concentrations observed in the four produced water discharge samples were highly variable. However, from the trace metal data, it appears that barium is the primary pollutant metal found in all discharges, with vanadium and zinc being of secondary concern. Other metals, such as arsenic and copper, may be important in some discharges, but not in others, depending upon the specific characteristics of the oil reservoirs undergoing production. In terms of total loadings of metals to individual regions, it is clear that the Lirette and Bully Camp sites are receiving the greatest overall metal discharges.

VI.C.2 Lirette Site (LRT)

Produced water from the Lirette discharge enters into a canal that it is not well flushed. This discharge has low concentrations of PAHs and a slow rate of flow. Figure II.2 shows the locations of the sediment sampling points, which generally form a straight line in the canal. The reference sampling point is situated about 1 km south of the discharge in a dead-end canal.

VI.C.2.a Semivolatile Hydrocarbons

The surficial sediment hydrocarbon data for site LRT are presented in Table VI.8 and Figure VI.6. There is a large decrease in PAH concentrations from the origin out to station B20, which is only 30 m from the outfall. The concentration of PAH homologs decreases by a factor of 20 at B20 and by 100 at C50 and A100. This type of decrease is also evidenced in the concentrations of total saturated hydrocarbons. It appears from this data that the majority of the contamination is concentrated in the immediate vicinity of the discharge. The low effluent flow and PAH concentrations in the effluent could account for this "pooling" of contamination. The PAHs in highest concentrations were the C2- and C3-naphthalenes (Tables A.1a and

A.1b), which reflects their relative concentrations in the effluent. There is still evidence of contamination out to stations A250 and C325, even though the majority of the hydrocarbons present are of pyrogenic origin. This evidence is represented by the presence of low levels of PAH homologs, especially C2- and C3-dibenzothiophenes and C2- and C3-phenanthrenes (Tables A.1a and A.1b). Petrogenic hydrocarbons detected at station C325 could be from sources other than the Lirette discharge, as this station is at the intersection of two canals and there are other discharges in the immediate area. Station A500 displays no evidence of contamination, the result of the low discharge flow and the hydrology of the area.

The FFPI and RS/TS ratios also show the same extent of contamination, with stations LRT-0, B20, C50, and A100 having very petrogenic FFPI's and RS/TS ratios decreasing away from the discharge, indicating decreasing influence from the produced water. The FFPI for C50 is lower than the other stations that exhibit contamination. The concentration of PAH homologs at C50 is similar to A100, but this station has high concentrations of pyrogenic hydrocarbons which lower the FFPI and are probably not related to the discharge.

The reference station contained low levels of mostly pyrogenic PAHs and no alkylated PAH, which yielded FFPI=0 (Table VI.8). The RS/TS ratio is similar to the contaminated stations, but there are only low levels of total saturates. This is the result of the presence of resolved odd-numbered high molecular weight alkanes, which are unrelated to petroleum and are probably plant waxes.

Table VI.8. Hydrocarbon concentrations (ppb, dry wt.) in sediments at the Lirette (LRT) site.

Station	Depth (cm)	Parent PAHs	PAH Homologs	FFPI	RS/TS	Total Saturates
LRT-0	0-5	12,000	200,000	0.93	0.28	40,000,000
LRT-A100	0-5	390	2,400	0.86	0.18	800,000
LRT-A250	0-5	190	tr	0.00	0.06	190,000
LRT-A500	0-5	35	nd	0.00	0.05	18,000
LRT-B20	0-5	430	9,300	0.94	0.24	1,700,000
LRT-C50	0-5	1,600	1,900	0.56	0.13	550,000
LRT-C250	0-5	1,000	60	0.08	0.08	52,000
LRT-C325	0-5	1,100	260	0.19	0.05	47,000
LRT-R	0-5	180	nd	0.00	0.25	14,000

nd: not detected
tr: trace; one ion present, but below detection limits
RS/TS: Resolved/Total Saturates

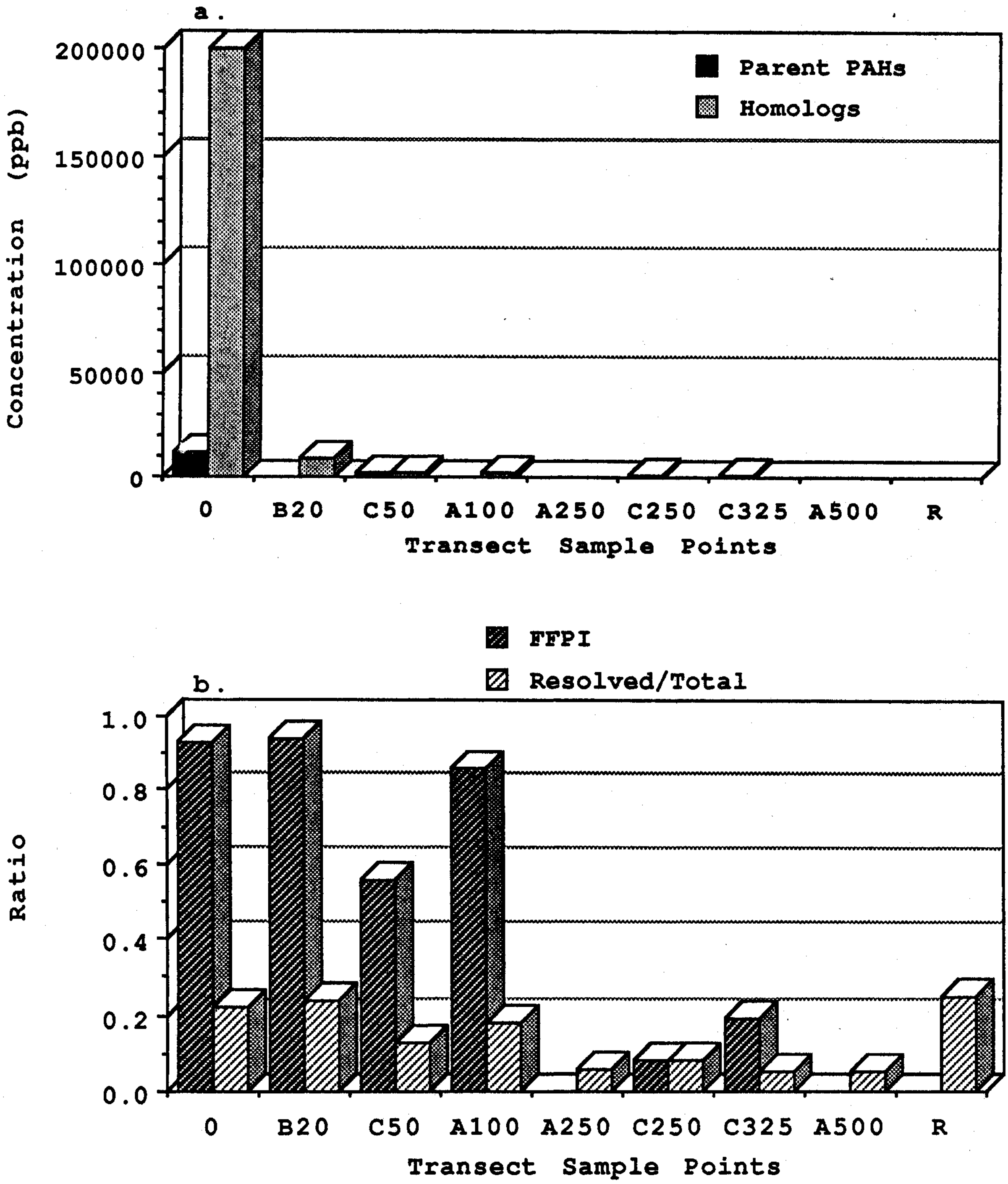


Figure VI.6. Distribution of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons, in surface sediments at the LRT site.

VI.C.2.b Trace Metals

The concentrations of trace metals in the surficial sediments in the region of the Lirette field discharge show that certain metals appear to have their source at the discharge (Table VI.9). These include: barium, mercury, arsenic, nickel, and cadmium. Some other metals, including aluminum, chromium, copper, zinc, and lead, show no source-associated spatial trends or elevated levels relative to the reference site. Figure VI.7 shows the distribution of the discharge associated metals as a function of distance away from the discharge point. Arsenic shows a maximum at the discharge point and concentrations decline rapidly to fairly constant levels at the surrounding stations. Nickel shows a maximum at the origin and much lower concentrations along the "A", "B" and "C" transects, however a second maximum is observed at the A250 station suggesting either enhanced deposition at this site or perhaps a secondary source of the metal. Cadmium and mercury show similar distributions around the discharge site with one maximum at the origin and a secondary maximum at A100. A high level of mercury was also observed at station C325. The origin of this metal at the latter site is unknown. It should be noted that the Lirette site was the only site where detectable quantities of mercury were found at all stations. Barium shows a clear source at the discharge with levels declining along all transects with distance.

Table VI.9. Concentrations of trace metals (ppm, dry wt.) in surface sediments at site Lirette (LRT), Bully Camp (BC), and Lake Washington (LW).

Sample ID	Depth (cm)	Dry Wt. (g)	Al	Cr	V	Ni	Cu	Zn	As	Cd	Ba	Hg	Pb
MDL (ppm)			0.082	0.002	0.002	0.041	0.010	0.015	0.021	0.011	0.026	0.312	0.014
LRT-0	0-5	0.33	18	12	21	5.2	20	108	16	0.86	249	1.1	11
LRT-A100	0-5	0.34	1.1	18	15	2.4	22	121	5.9	1.1	313	1.1	30
LRT-A250	0-5	0.33	1.8	21	17	7.9	28	130	6.2	0.87	275	0.51	36
LRT-A500	0-5	0.33	18	15	17	2.0	27	72	5.4	0.59	159	0.63	32
LRT-B20	0-5	0.37	20	19	15	4.3	23	127	6.3	0.71	308	0.47	30
LRT-C50	0-5	0.32	9.6	17	14	0.14	21	129	6.2	0.67	331	0.53	39
LRT-C250	0-5	0.38	2.0	14	12	0.41	20	102	6.1	0.49	220	nd	30
LRT-C325	0-5	0.54	7.8	9.1	7.7	0.22	12	60	4.1	0.39	113	1.5	19
LRT-R	0-5	0.30	14	18	15	nd	23	95	6.4	0.61	179	nd	36
BC-0	0-5	0.24	21	13	20	12	28	170	7.7	0.68	623	0.31	27
BC-A50	0-5	0.38	6.0	15	10	7.2	19	98	4.7	0.53	507	nd	34
BC-B50	0-5	0.29	8.9	13	12	9.2	18	108	7.2	0.40	719	nd	28
BC-B100	0-5	0.25	8.4	15	13	19	18	136	8.0	0.43	973	nd	149
BC-C50	0-5	0.29	8.9	14	11	19	17	120	6.8	0.61	827	nd	34
BC-C100	0-5	0.27	10	17	13	22	20	122	9.0	0.79	786	nd	37
BC-C$_1$300	0-5	0.22	10	14	14	28	19	101	8.5	0.60	312	nd	39
BC-C$_2$300	0-5	0.25	12	15	13	28	20	105	8.0	0.57	304	nd	39
BC-R	0-5	0.22	17	16	15	28	20	85	6.7	0.59	213	nd	37
LW-0	0-5	0.24	18	11	14	37	14	178	11	0.55	971	nd	11
LW-A50	0-5	0.17	0.60	13	19	28	21	274	14	0.31	1683	nd	26
LW-B50	0-5	0.29	18	13	14	20	17	237	8.3	0.33	1483	nd	18
LW-B150	0-5	0.27	18	14	16	21	17	125	10	0.45	419	nd	25
LW-B350	0-5	0.26	17	11	15	20	15	80	9.3	0.25	248	nd	24
LW-C100	0-5	0.23	19	12	14	20	16	265	9.7	1.0	959	nd	26
LW-C$_1$250	0-5	0.23	15	12	16	19	16	111	11	1.1	339	nd	24
LW-C$_2$300	0-5	0.33	12	12	14	9.2	13	70	7.7	0.39	211	nd	22
LW-R	0-5	0.18	22	13	19	13	18	80	13	0.34	245	nd	27

MDL: Minimum Detection Limit
nd: not detected

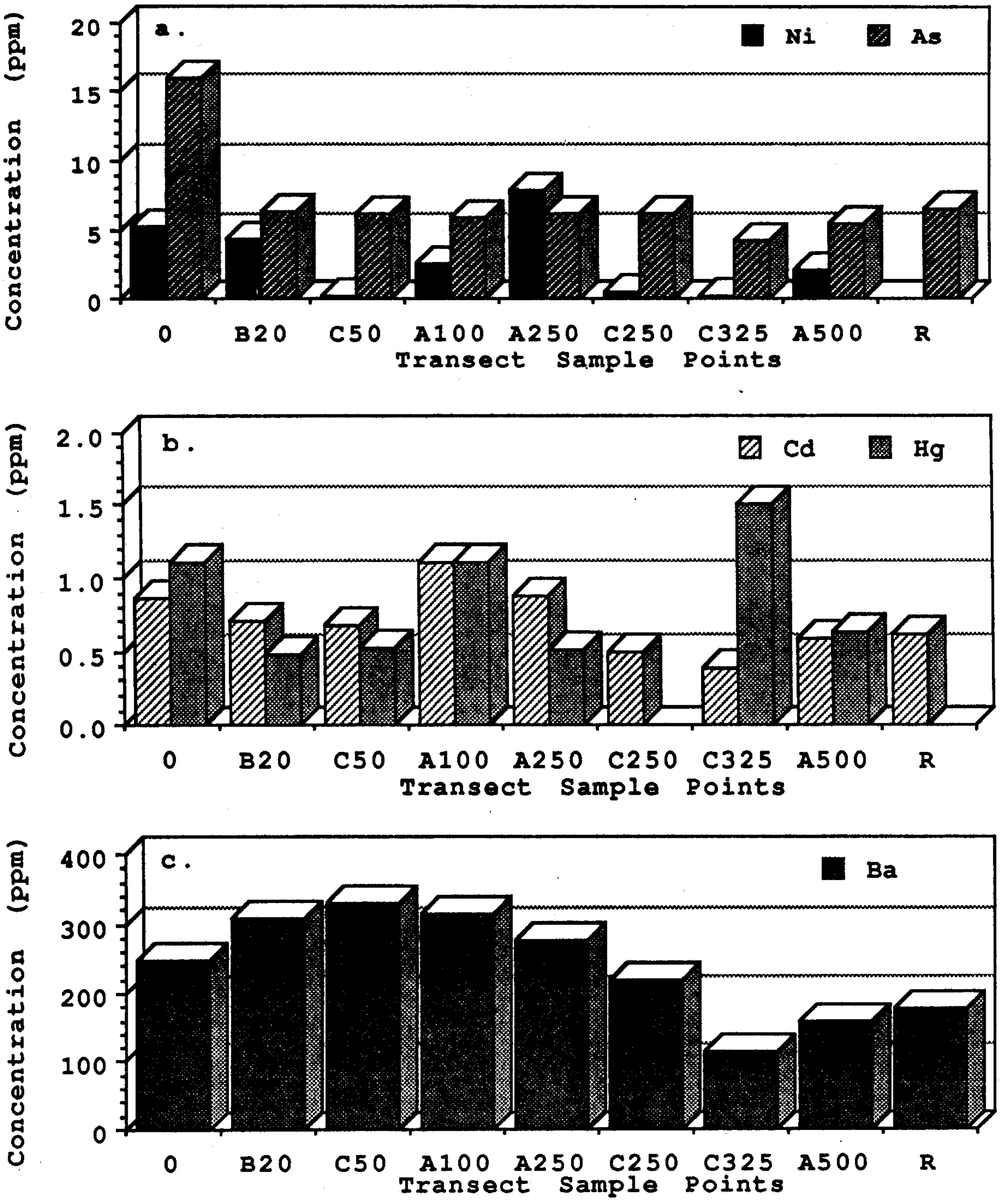


Figure VI.7. Distribution of a) Ni & As, b) Cd & Hg, and c) Ba, in surface sediments at the LRT site.

VI.C.3 Delta Farms Site (DF)

The separation facility at Delta Farms is located on the banks of a small island located within a natural tidal fresh water bayou channel which has been modified by dredging operations. The discharge enters the bayou opposite the island at the margin of a waste pond and spills directly into the bayou along the shore. Figure II.3 shows a map of the site indicating the sampling points where water and sediment samples were collected as well as the reference station within the Delta Farms study site.

VI.C.3.a Spatial Distributions of Semivolatile Hydrocarbons

Table VI.10 presents a summary of the semivolatile hydrocarbon data for sediments in the vicinity of the Delta Farms discharge station and the reference station. Figure VI.8a shows the distribution of normal aromatic and alkylated homolog PAHs in surficial sediments at various distances away from the Delta Farms discharge point. The concentrations of alkylated homologs of PAHs (dominated by C2- and C3-naphthalenes and C2- and C3-phenanthrenes with lesser amounts of C1-, C2- and C3-dibenzothiophenes) exhibit maximal concentrations (140,000 ppb) at station DF-0 and decline to lower values in all directions along all of the transects, thus indicating a clear source pattern (Tables A.2a - A.2h). In contrast, total normal PAHs (dominated by a number of pyrogenic PAHs) are found maximally (34,000 ppb) in the area 200 meters from the discharge along the B_2 transect and decline rapidly to 1,700 ppb or less within 100 m of the discharge. Among the normal PAHs, phenanthrene, naphthalene, fluorene, fluoranthene, pyrene, and chrysene were found most frequently in the sediments of this region. The total normal PAHs in the reference sediment was 490 ppb. The distribution of normal PAHs and their alkylated and heterocyclic analogs at the reference station are not shown graphically. However, the value of the total homolog PAHs at this station was 320 ppb, the lowest value obtained at the Delta Farms study site.

Figure VI.8b shows the distribution of FFPI values and resolved saturates to total saturates ratios. The FFPI values (a measure of the relative contribution of petrogenic vs. pyrogenic PAHs) are consistently high (>0.78) along the "A", "C", and "B_1" transects but decline to <0.50 along the "B_2" transect. This is due to the very high pyrogenic PAH concentrations observed at the $B_2$200 and $B_2$300 stations. The FFPI at the reference station was 0.43, the lowest value obtained in this region.

Table VI.10. Hydrocarbon concentrations (ppb, dry wt.) in sediments at the Delta Farms (DF) site.

Station	Depth (cm)	Parent PAHs	PAH Homologs	FFPI	RS/TS	Total Saturates
DF-0	0-9	9,300	140,000	0.92	0.36	6,400,000
DF-0	9-18	8,300	140,000	0.93	0.22	8,200,000
DF-0	18-27	13,000	300,000	0.94	0.18	12,000,000
DF-0	27-30	13,000	140,000	0.89	0.17	2,700,000
DF-C75	0-9	4,900	62,000	0.90	0.26	3,200,000
DF-C75	9-18	23,000	63,000	0.73	0.25	2,100,000
DF-C75	18-25	30,000	66,000	0.69	0.26	2,200,000
DF-C75	25-28	7,100	51,000	0.86	0.26	2,400,000
DF-A100	0-9	2,500	25,000	0.89	0.28	960,000
DF-A100	9-18	2,500	25,000	0.90	0.28	1,000,000
DF-A100	18-27	2,700	36,000	0.91	0.27	1,100,000
DF-A100	27-36	3,300	44,000	0.91	0.24	1,200,000
DF-A200	0-9	2,800	21,000	0.87	0.23	700,000
DF-A300	0-9	1,700	6,500	0.78	0.15	360,000
DF-A300	9-18	3,200	17,000	0.83	0.19	640,000
DF-A300	18-27	1,800	13,000	0.86	0.23	810,000
DF-A300	27-30	2,200	19,000	0.87	0.25	920,000
DF-B$_1$200	0-9	1,700	35,000	0.91	0.36	1,200,000
DF-B$_1$200	9-18	1,500	14,000	0.88	0.18	550,000
DF-B$_1$200	18-25	1,400	7,300	0.81	0.18	430,000
DF-B$_1$200	25-28	890	6,000	0.84	0.16	410,000
DF-B$_2$200	0-9	34,000	21,000	0.43	0.34	880,000
DF-B$_2$200	9-18	3,600	16,000	0.81	0.27	740,000
DF-B$_2$200	18-25	2,300	14,000	0.84	0.25	560,000
DF-B$_2$200	25-27	9,100	22,000	0.74	0.26	650,000
DF-B$_2$300	0-9	9,500	7,700	0.45	0.18	420,000
DF-B$_2$300	9-18	1,900	6,400	0.75	0.18	350,000
DF-B$_2$300	18-25	1,800	6,300	0.77	0.13	400,000
DF-B$_2$300	25-27	2,000	13,000	0.85	0.25	640,000
DF-R	0-9	490	320	0.43	0.13	110,000
DF-R	9-18	350	300	0.50	0.11	86,000
DF-R	18-27	530	370	0.41	0.06	160,000
DF-R	27-30	540	1,100	0.68	0.07	200,000

RS/TS: Resolved/Total Saturates

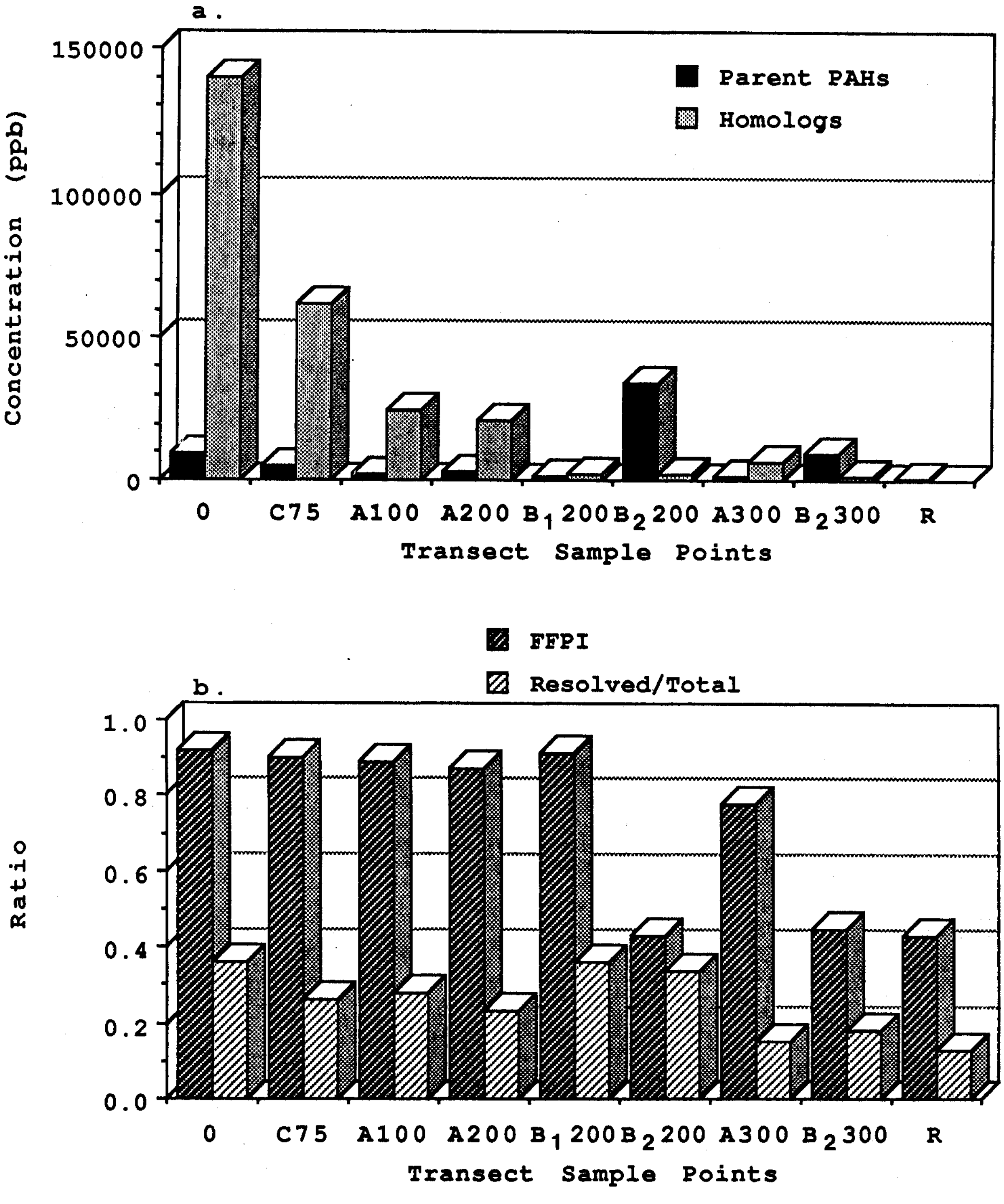


Figure VI.8. Distribution of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons, in surface sediments at the DF site.

Aliphatic hydrocarbons were distributed in a similar pattern to the aromatics in the vicinity of the Delta Farms discharge (Table VI.10). Figure VI.8b shows the distribution of aliphatic hydrocarbons around the discharge expressed in terms of the ratio of chromatographically resolved saturated hydrocarbons to total saturated hydrocarbons (RS/TS). This ratio is an indicator of the amount of weathering or microbial degradation which has occurred in the sample, with lower ratios indicating more degradation. The pattern of hydrocarbon concentrations in sediments around the discharge is very similar to that for the more soluble aromatic compounds. The RS/TS ratio tends to decrease with increasing distance from the discharge (DF-0 = 0.36 and DF-$B_2$300 = 0.18) showing weathering of hydrocarbons with distance.

VI.C.3.b Spatial Distributions of Trace Metals

The spatial distribution of trace metals in the surface sediments in the region of the Delta Farms produced water discharge indicate that several metals are concentrated in the sediments nearest the discharge point (Table VI.11). These include: vanadium, zinc, arsenic, cadmium, barium, and lead. Several other metals showed no enrichments either regionally or in comparison with the reference site. These included: aluminum, chromium, nickel, copper, and mercury. Figure VI.9 shows the distribution of cadmium, arsenic, nickel, barium and zinc. In each case the maximum concentrations were observed at the DF-A100 site rather than at the discharge point itself.

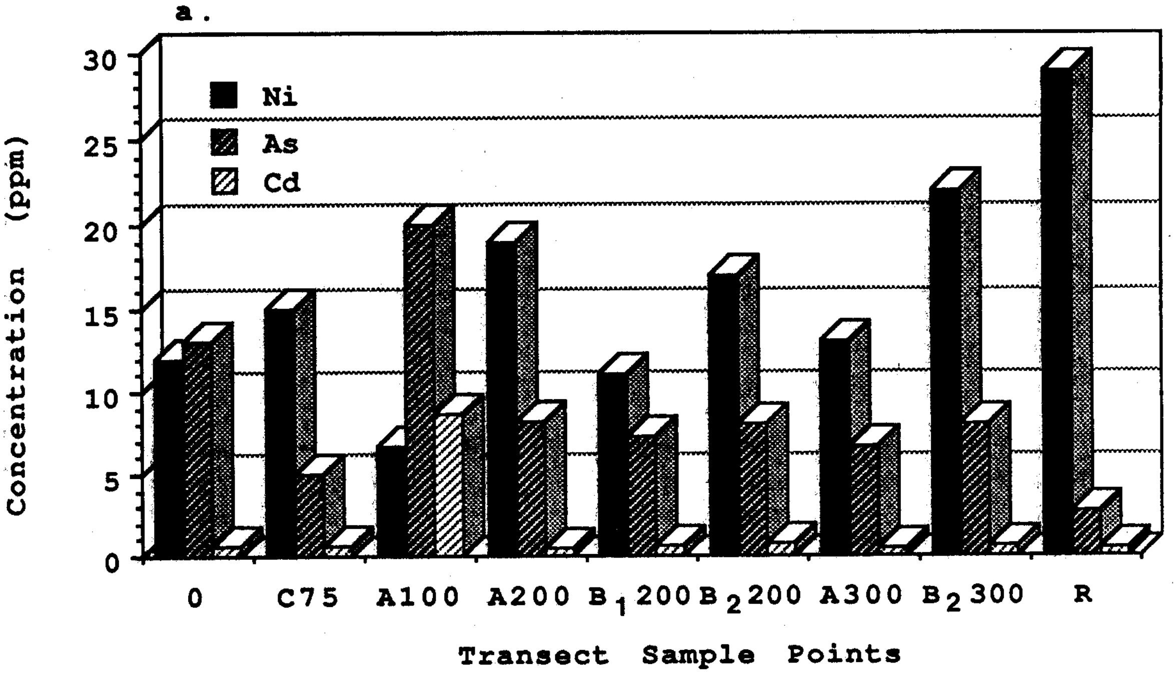
Barium concentrations as high as 480 ppm were observed at the A100 site. They decrease steadily with distance away from the discharge in all directions (Figure VI.9b). Levels of barium in the sediments were approaching reference levels beyond 300 meters from the discharge. The reference station had similar levels of Ba as the C75 sediment indicating that little deposition is occurring in this dead-end canal. Vanadium (not shown) was found at maximum levels at the A100 station but levels declined rapidly, to levels similar to the reference station, in all directions at further distances, suggesting that this metal is rapidly removed from the water column and deposited in the sediments. A similar pattern was observed for cadmium, which, although it was not detectable in the produced water itself on the day of sampling, is clearly detected in sediments at the A100 site at elevated levels. However, concentrations decline by an order of magnitude in all directions away from this point (Figure VI.10a).

Arsenic, lead, and zinc were observed at maximum values at station A100, and sediment concentrations decline in all directions away from this point, but arsenic levels do not reach reference levels (2.8 ppm) within the 300 meter range of the discharge (Figure VI.9a). It is interesting to note that neither

Table VI.11. Concentrations of trace metals (ppm, dry wt.) in sediments at the Delta Farms (DF) site.

Sample ID	Depth (cm)	Dry Wt. (g)	Al	Cr	V	Ni	Cu	Zn	As	Cd	Ba	Hg	Pb
MDL (ppm)			0.082	0.002	0.002	0.041	0.010	0.015	0.021	0.011	0.026	0.312	0.014
DF-0	0-9	0.24	21	18	18	12	22	112	13	0.60	280	nd	38
DF-0	9-18	0.27	14	14	16	8.1	23	89	9.6	0.63	182	nd	34
DF-0	18-27	0.24	171	10	15	7.5	22	90	8.6	0.52	216	nd	30
DF-0	27-36	0.20	238	7.8	14	22	15	75	12	0.71	232	nd	26
DF-C75	0-9	0.29	150	11	14	15	23	90	5.0	0.61	189	nd	40
DF-C75	9-18	0.26	64	9.1	13	19	18	87	6.0	0.40	189	0.04	42
DF-C75	18-25	0.35	34	13	9	9.3	65	56	6.7	0.33	134	nd	27
DF-C75	25-28	0.29	28	13	15	9.5	27	92	6.7	0.74	167	nd	40
DF-A100	0-9	0.08	42	16	24	6.6	37	147	20	8.7	480	nd	50
DF-A100	9-18	0.19	nd	12	15	11	23	91	12	0.51	273	nd	44
DF-A100	18-27	0.40	32	9.3	13	6.6	18	60	8.7	0.37	130	nd	29
DF-A100	27-36	0.16	95	11	15	16	22	83	16	0.49	241	nd	42
DF-A200	0-9	0.19	326	12	17	19	24	86	8.2	0.53	235	nd	42
DF-A300	0-9	0.24	17	13	13	13	21	80	6.7	0.45	198	nd	36
DF-A300	9-18	0.15	103	12	16	16	25	88	7.9	1.5	254	nd	44
DF-A300	18-27	0.18	229	11	13	13	22	84	6.4	1.0	176	nd	35
DF-A300	27-30	0.15	285	15	15	14	26	94	9.4	0.60	231	nd	40
DF-B$_1$200	0-9	0.24	6.5	12	15	11	25	87	7.2	0.63	246	nd	39
DF-B$_1$200	9-18	0.25	nd	11	15	8.9	23	72	7.4	0.61	190	nd	33
DF-B$_1$200	18-25	0.28	13	11	16	5.7	24	73	6.9	0.57	179	nd	38
DF-B$_1$200	25-28	0.29	8.6	12	17	5.7	26	72	8.1	1.3	174	nd	42
DF-B$_2$200	0-9	0.26	nd	10	14	17	21	77	8.1	0.82	206	0.28	35
DF-B$_2$200	9-18	0.25	nd	10	15	21	23	79	8.5	1.3	228	nd	34
DF-B$_2$200	18-25	0.29	nd	13	16	19	24	75	8.6	0.72	214	nd	30
DF-B$_2$200	25-27	0.28	nd	10	17	21	24	71	9.8	0.57	178	nd	37
DF-B$_2$300	0-9	0.26	nd	11	16	22	23	77	8.0	0.65	207	nd	41
DF-B$_2$300	9-18	0.28	nd	10	15	20	22	70	6.5	0.66	173	nd	38
DF-B$_2$300	18-27	0.27	nd	9.5	15	26	23	66	6.3	0.82	176	nd	33
DF-B$_2$300	27-30	0.28	nd	9.2	15	27	21	65	7.2	0.58	176	nd	41
DF-R	0-9	0.30	nd	16	17	29	37	77	2.8	0.43	189	nd	38
DF-R	9-18	0.38	nd	16	16	26	33	69	2.6	0.96	136	nd	35
DF-R	18-27	0.34	nd	16	17	28	32	65	2.9	0.41	117	nd	34
DF-R	27-30	0.36	nd	13	15	24	27	53	2.9	0.33	113	nd	32

MDL: Minimum Detection Limit
nd: not detected



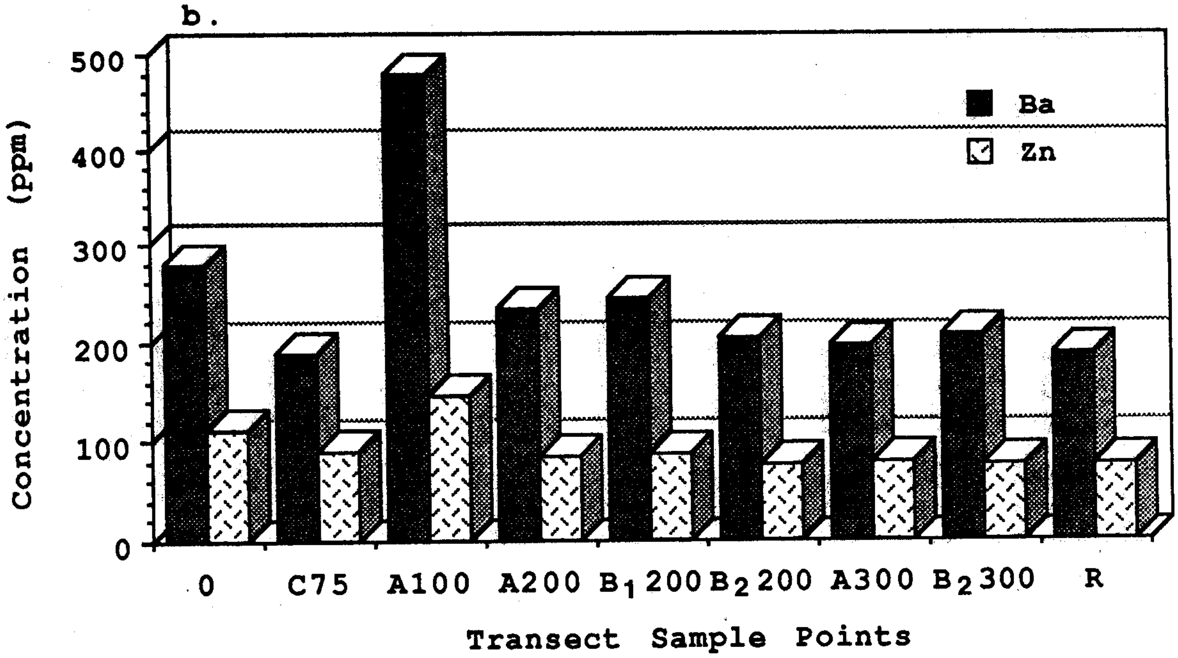


Figure VI.9. Distribution of a) Ni, As, & Cd and b) Ba & Zn, in surface sediments at the DF site.

lead nor arsenic were found in the produced water on the day of sampling but are clearly present in the sediment record at this site indicating that some source oils contain these metals.

The fact that maximum levels of most discharge-associated metals were observed at the A100 station rather than the DF-0 station may be a result of several factors. First, acids are typically added to the discharges to facilitate solubilization of metals, thus some dilution within the bayou must occur before some metals will become insoluble. Second, particle concentrations in the receiving bayou are high and time is required for sorption reactions and for sedimentation to occur. Third, although iron determinations were not performed on these samples, produced waters typically contain high concentrations of reduced iron. When the iron is discharged into oxygenated waters it rapidly forms insoluble precipitates which may carry other metals along toward deposition in the sediments. Again some time is required for these processes to occur. Finally, the sediments at A100 were very fine-grained, which tends to maximize metal sorption. This characteristic may have contributed to the high metal concentrations observed at this station.

VI.C.3.c Vertical Distributions of Semivolatile Hydrocarbons

The data for the vertical distribution of organic compounds in Delta Farms sediment samples and the reference station are presented in Table VI.10. Figures VI.10 thru VI.17 show the vertical distribution of normal PAHs and alkylated homolog PAHs and the vertical distribution of FFPI values and RS/TS ratios for aliphatic hydrocarbons. All of these parameters are plotted versus depth in centimeters. It should be noted that the sections of these cores are the same as those already discussed earlier in this report, however, the values plotted are at the midpoint of that particular section (i.e., 0-9 cm plotted at 4.5 cm).

Figure VI.10 shows the distributions of the various parameters at station DF-0. Total normal (parent) aromatic hydrocarbons exhibit relatively constant concentrations with depth at this station while, in contrast, the alkylated homolog PAHs show a very marked increase in concentrations to 300,000 ppb at -23 cm in the core. This suggests the possibility that in the past, much higher concentrations of these petrogenic PAHs were being discharged to this station. The values of the FFPI parameter in this core show a consistent high value between (0.83 and 0.94) at all depths. An interesting pattern is observed in the RS/TS ratio at the DF-0 station. Values of this parameter decline with depth from 0.36 at the surface to 0.17 at -28 cm, suggesting that microbial degradation of the aliphatic hydrocarbons is active in these sediments.

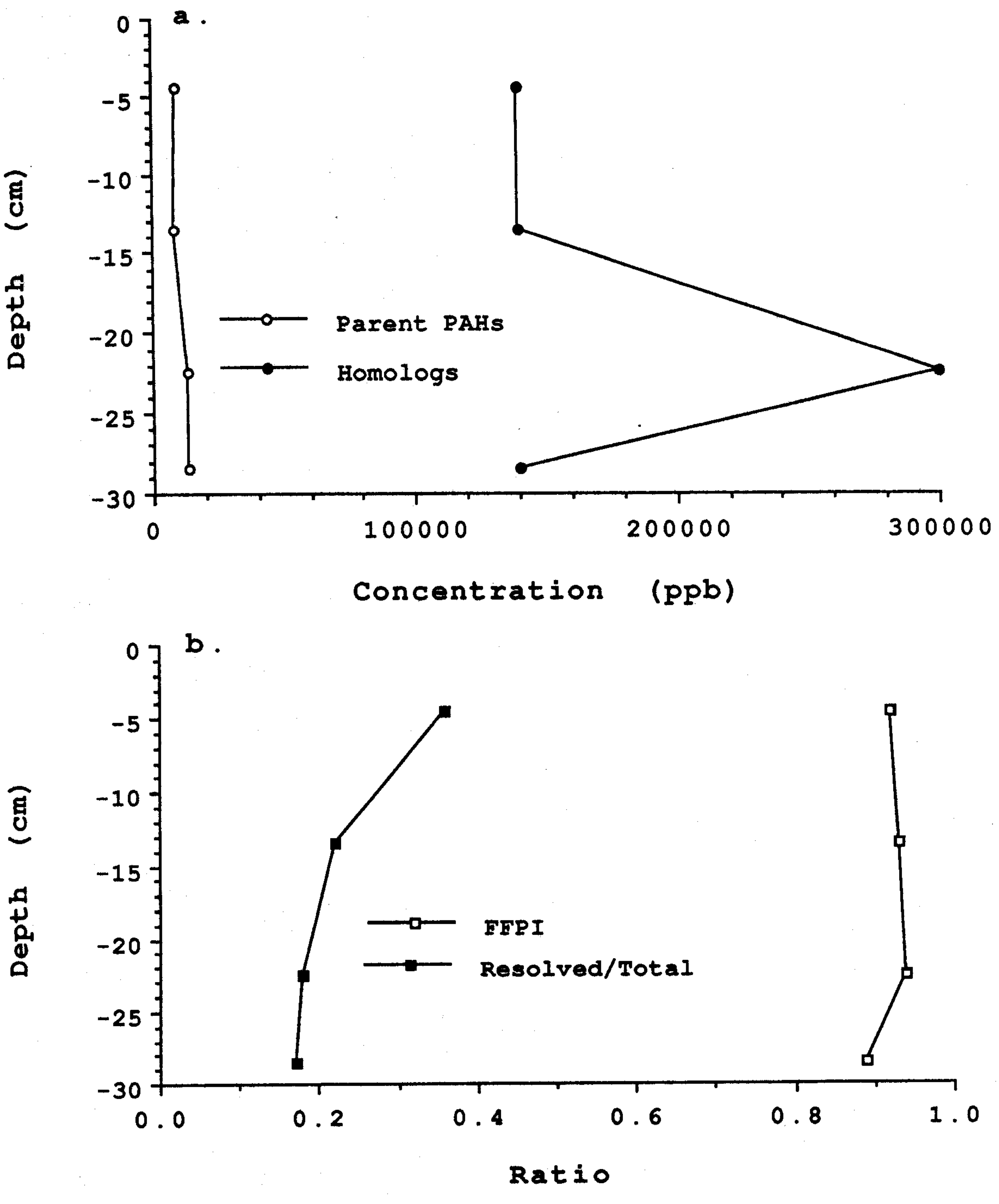


Figure VI.10. Depth profiles at station DF-0 of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons.

The depth distributions of hydrocarbons at the other points in the Delta Farms area show some contrasting patterns depending upon the direction away from the discharge point. At station C75 (Figure VI.11), just to the south of the discharge, there is a subsurface maximum in pyrogenic normal PAHs followed by a decline, while petrogenic PAHs are relatively constant with depth, except for the bottom section of the core where they decrease. The levels of alkylated PAHs in this core were approximately half of those at the discharge. The result of this pattern is that the FFPI values appear to decline with depth and then increase at the bottom of the core. RS/TS ratios for aliphatic hydrocarbons were consistently in the range of 0.25, suggesting the presence of a partially degraded oil throughout the core.

Cores taken along the "A" transect to the east of the discharge at distances of 100 and 300 m both show a large subsurface increase (>2x) in petrogenic PAHs, while pyrogenic PAHs are relatively constant throughout the core (Figures VI.12 and VI.13). This suggests either that there has been a decline in the amounts of petrogenic PAHs put into the system, or that uncontaminated sediments have entered this portion of the waterway and been deposited over the contaminated sediments. Since the patterns of PAHs concentrations in this transect differ from those of the "B" transect stations, the latter case is probably the more likely one. A storm event may have flushed clean sediments into the region, which were deposited in the region over contaminated sediments. The FFPI values observed in these cores confirm the fact that surficial sediments along this transect are lower in petrogenic PAHs, since a steady increase is observed with depth. The RS/TS ratios do not vary much with depth at the A100 station but exhibit a slight increase with depth at the A300 station, again suggesting the import and deposition of relatively uncontaminated sediments in this portion of the system.

At the $B_1$200 station (Figure VI.14), a definite decline in alkylated homolog PAHs was observed with depth while parent normal PAHs were relatively constant. In contrast, at both the $B_2$200 and $B_2$300 stations (Figures VI.15 and VI.16) there was a subsurface maximum, at 25-27 cm, of alkylated PAHs while pyrogenic PAHs declined dramatically below the surface and then remained relatively constant. Also, while the FFPI values at the $B_1$200 station were relatively constant, there was a marked increase in FFPI with depth at both of the "B_2" stations to the levels observed at $B_1$200. This undoubtedly related to the sharp decline in pyrogenic normal PAH concentrations, but also appears to be related to increases in various pyrogenic PAH concentrations with depth as well.

Figure VI.17 shows the depth profiles of the various parameters in the Delta Farms reference station sediment. This

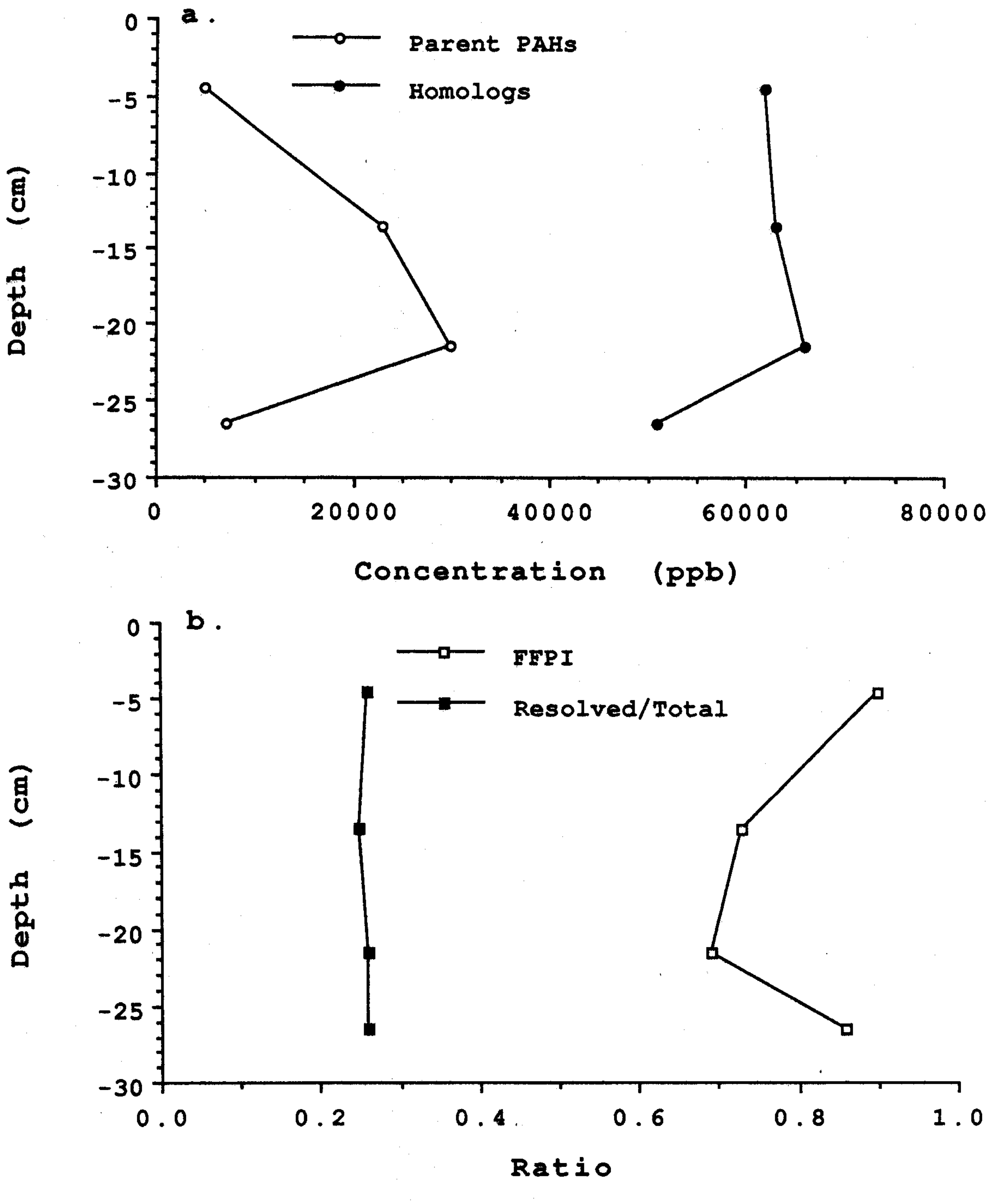


Figure VI.11. Depth profiles at station DF-C75 of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons.

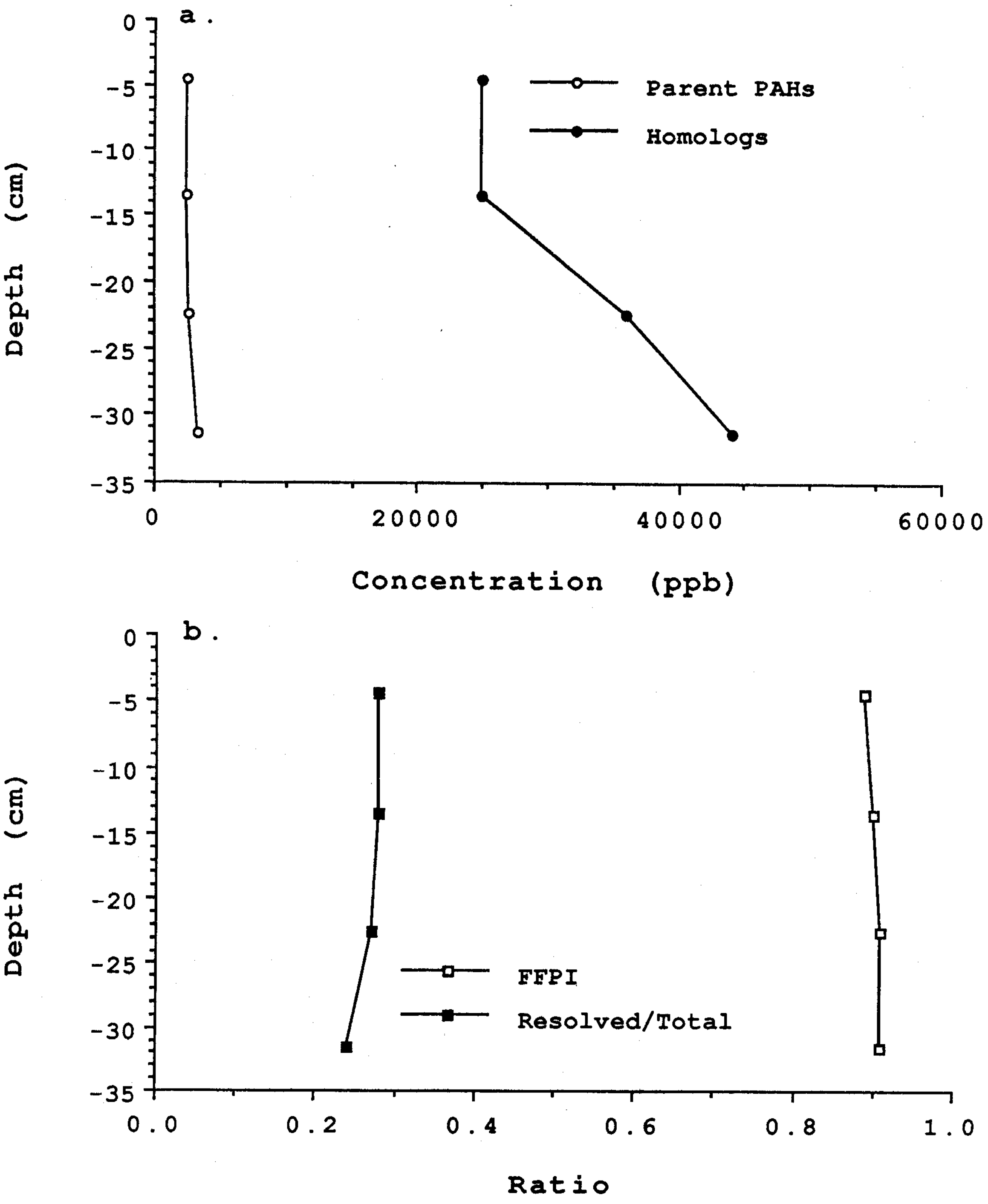


Figure VI.12. Depth profiles at station DF-A100 of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons.

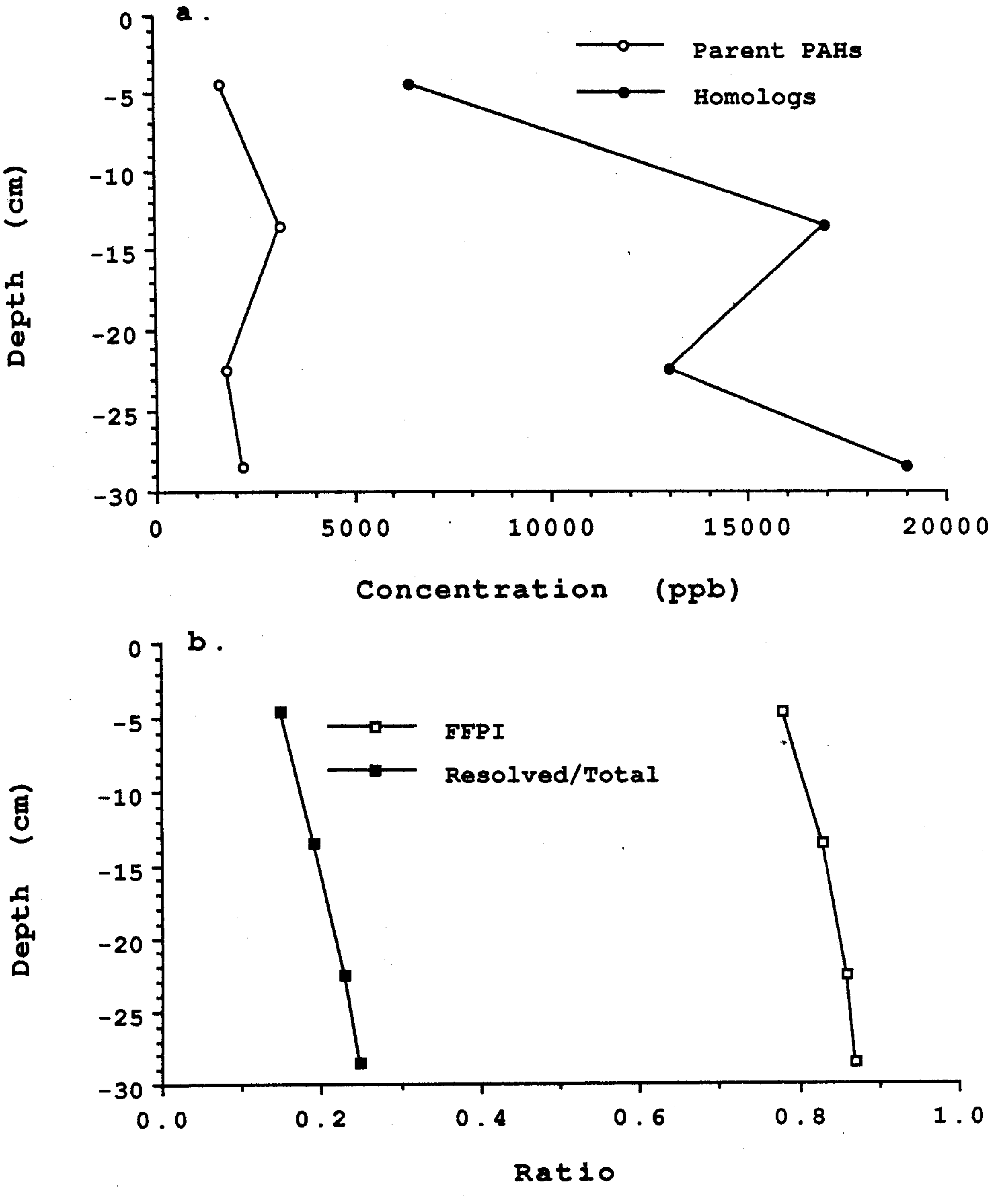


Figure VI.13. Depth profiles at station DF-A300 of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons.

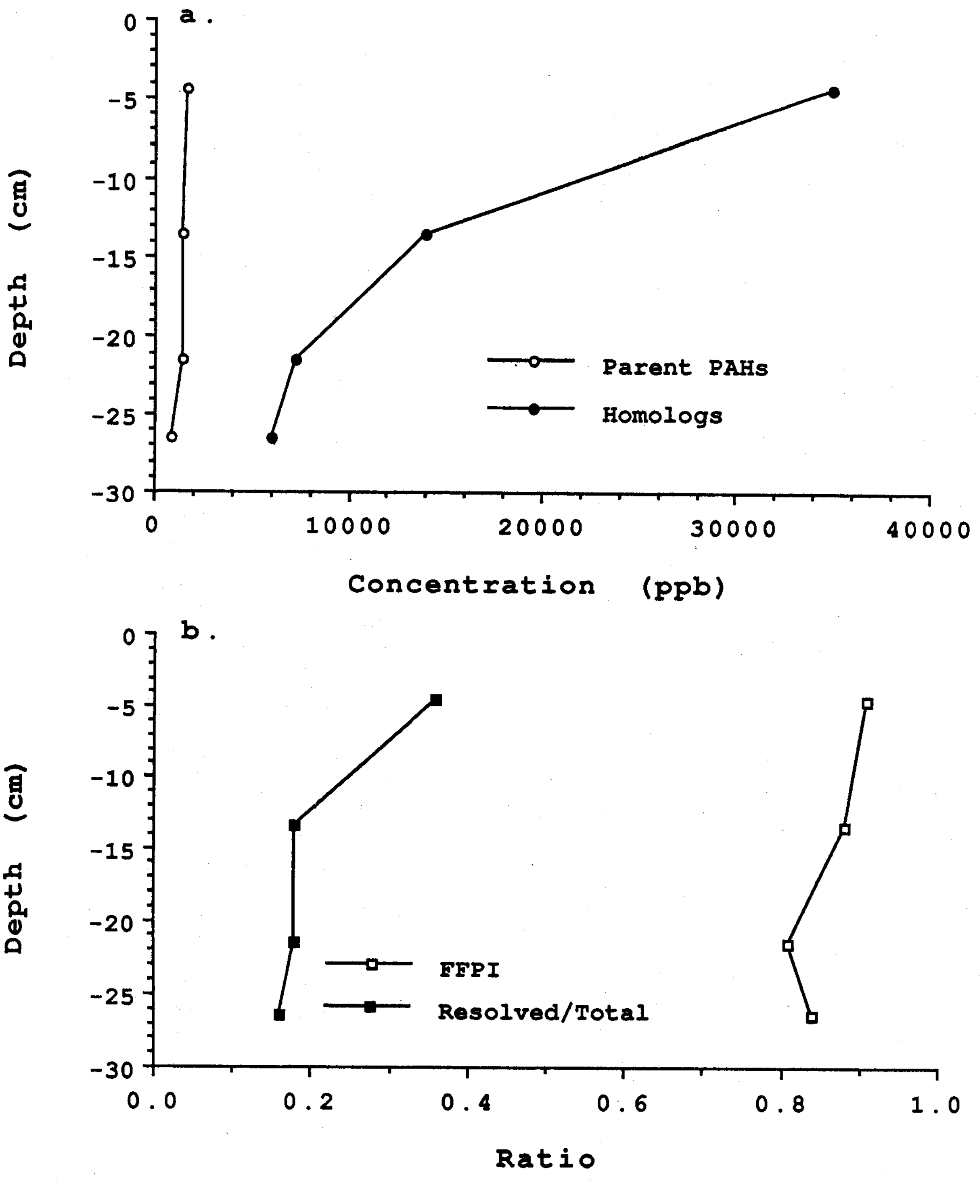


Figure VI.14. Depth profiles at station DF-$B_1$200 of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons.

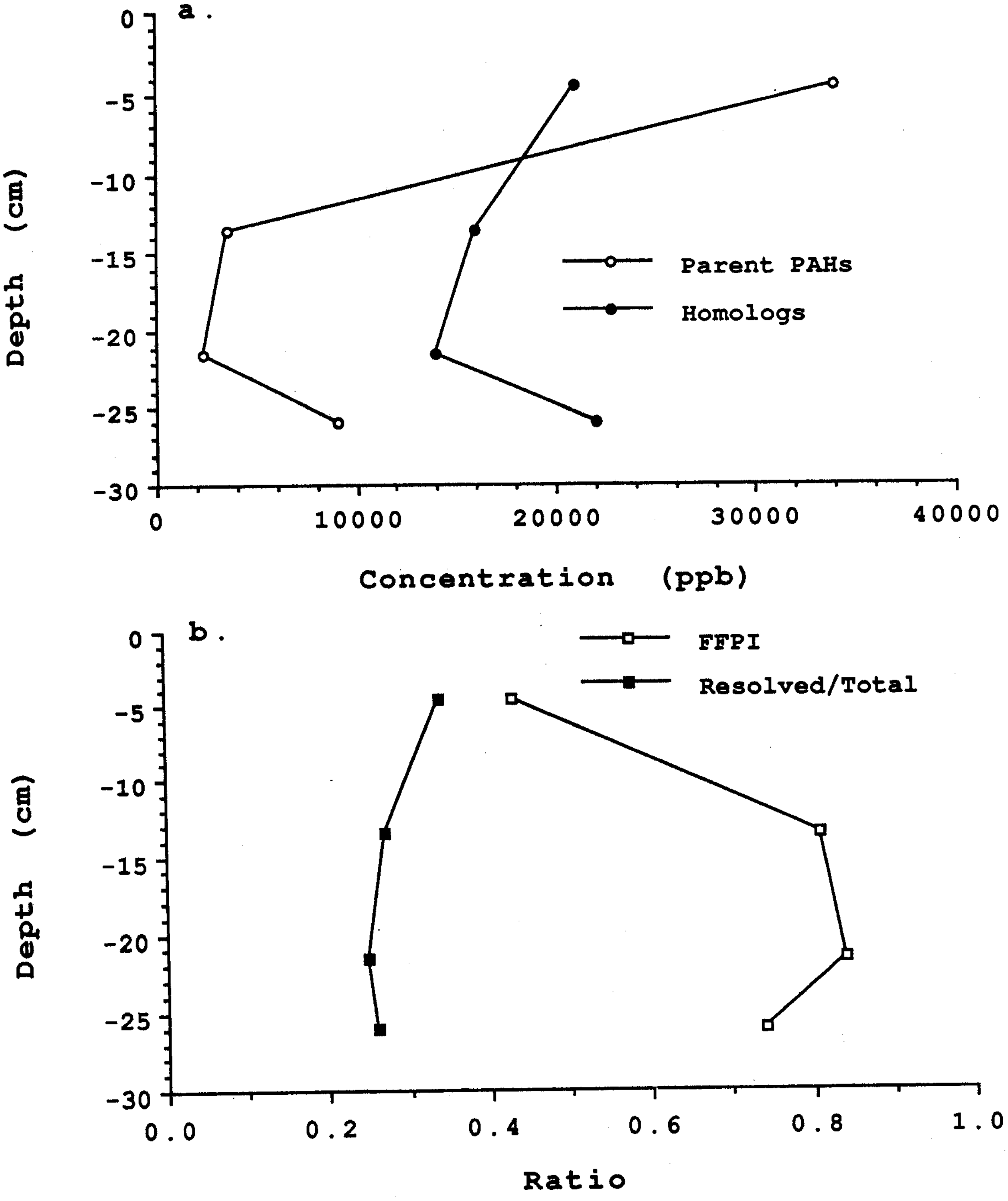


Figure VI.15. Depth profiles at station DF-B$_2$200 of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons.

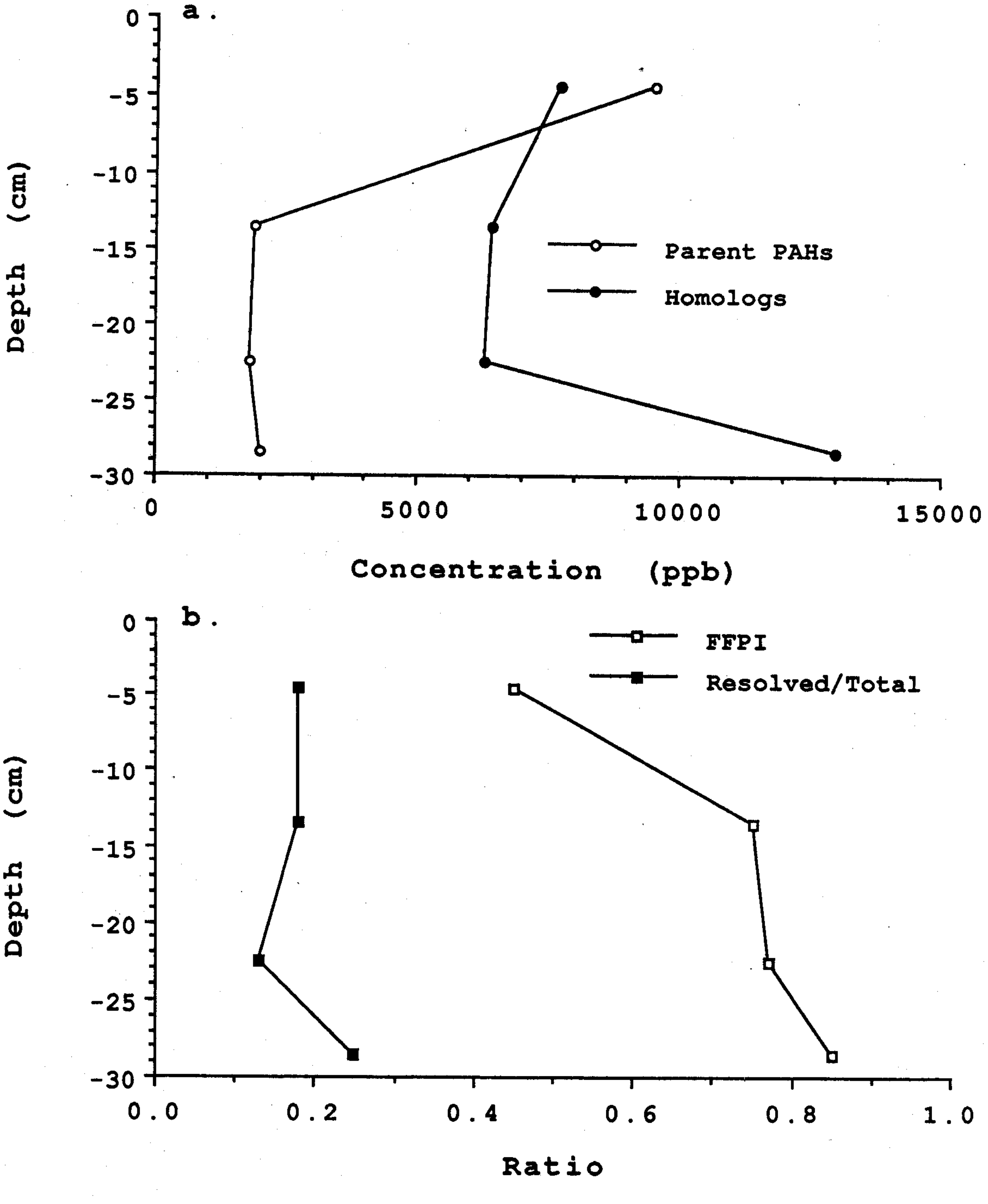


Figure VI.16. Depth profiles at station DF-$B_2$300 of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons.

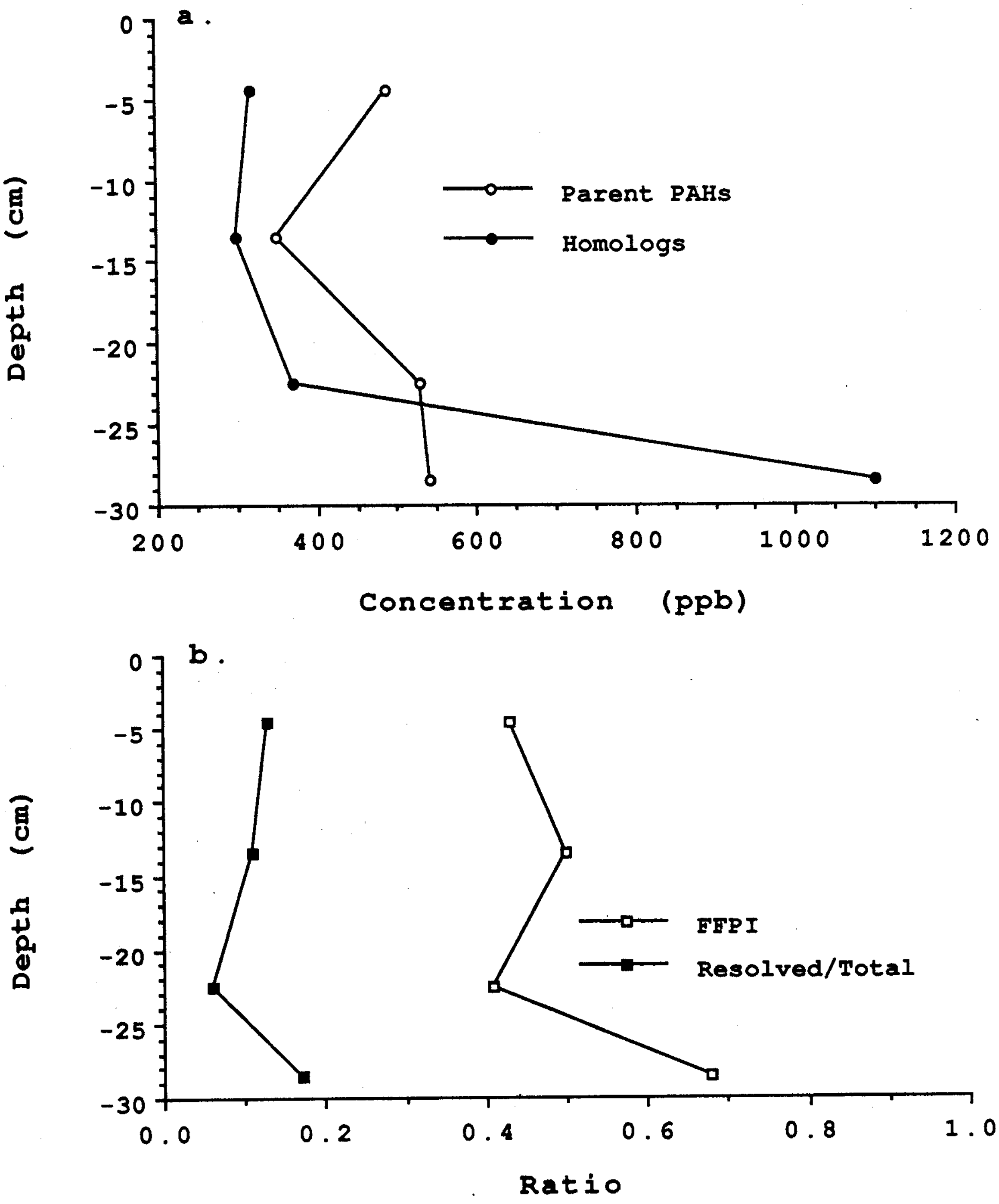


Figure VI.17. Depth profiles at station DF-R of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons.

core shows several interesting patterns which differ markedly from the other stations in the system. First, there is a decline in normal PAH concentrations at 9-18 cm, but the concentrations increase at the bottom of the core to values slightly higher than at the surface. In contrast, the alkylated homolog PAH concentrations are relatively constant at the top of the core but increase by approximately a factor of three at the bottom of the core. This suggests that at some time in the past this station was impacted by petrogenic PAHs either through a spill or perhaps a storm event that transported contaminated sediments to the reference station.

The FFPI values observed at the reference station tend to confirm the conclusions just discussed since a very marked increase in the FFPI value from 0.41 to 0.68 is observed in the bottom of this core. The low values of RS/TS ratios observed in this core at all depths indicate substantial degradation of saturated hydrocarbons, even though there was a large input of aliphatic hydrocarbons (200,000 ppb) to this station at some time in the past.

The relatively constant levels of pyrogenic PAHs observed in all of the cores with depth, except at the $B_2$200 and $B_2$300 stations, suggest that an input of pyrogenic PAHs has occurred along that transect from an unknown source (possibly marsh burning). The very high levels of 4 and 5-ring PAHs seen in the surface sections of these two cores may yield some information which may be used to identify the source.

VI.C.3.d Vertical Distributions of Trace Metals

The vertical distributions of trace metals in the sediments in the region of the Delta Farms produced water discharge are presented in Table VI.11 and Figures VI.18 to VI.25. Figure VI.18 shows the vertical trends of Ni, As, Cd, Ba and Zn at the DF-0 station. Each of the elements shows a general decline in concentrations with depth, however, there is a clear subsurface increase in Ni, As, and Cd at the bottom of the core, and also for Ba in the bottom two segments of the core. This suggests that at some point in the past discharges of these metals were greater than at intermediate times. Alternatively, import of clean sediments by storm evens could result in the lower concentrations observed at intermediate depths. At the C75 station (Figure VI.19) in a dead-end canal, the highest concentrations of the five metals, with the exception of As, were observed at the surface, with concentrations declining with depth but increasing again in the bottom segment of the core. Arsenic showed a slight trend of increasing concentration with depth.

At the A100 station (Figure VI.20), clear surface maxima for Ba, Zn, Cd, and As were observed, while little or no trend was

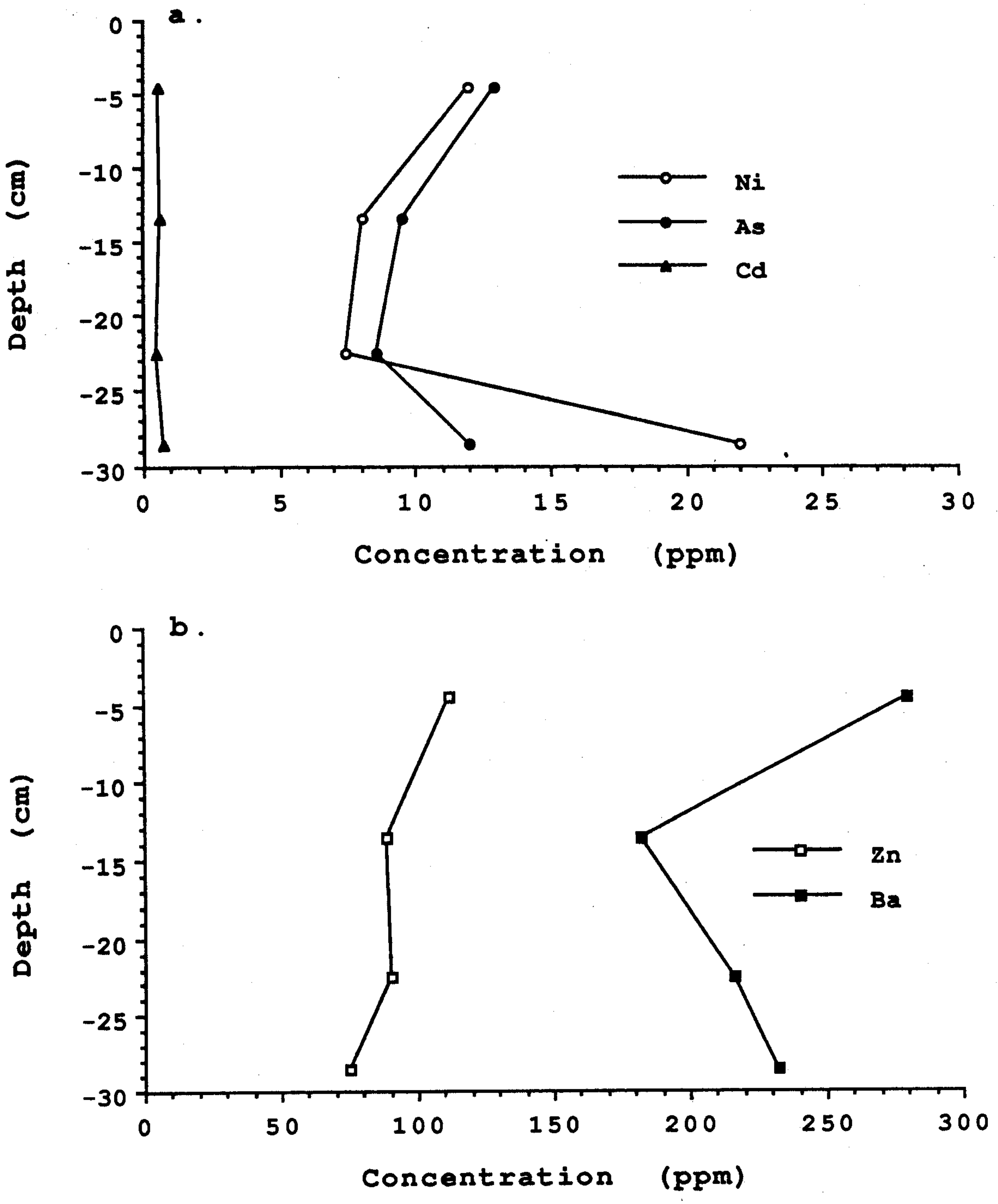
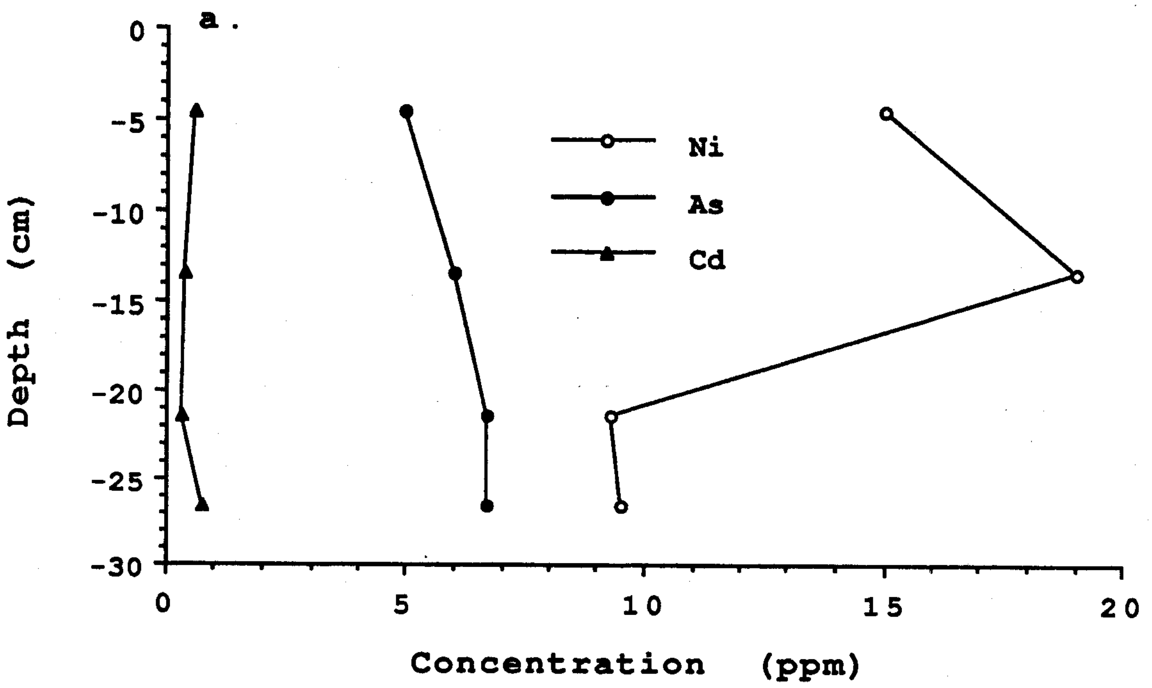


Figure VI.18. Depth profiles at station DF-0 of a) Ni, As, & Cd and b) Zn & Ba.



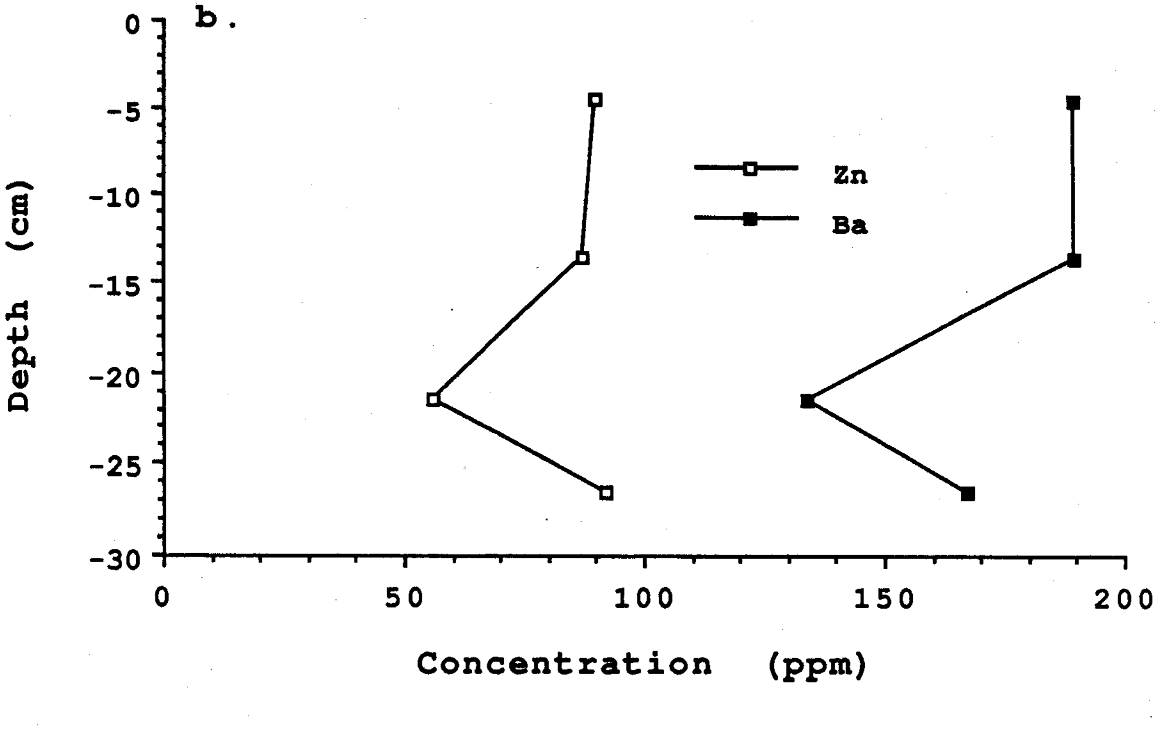
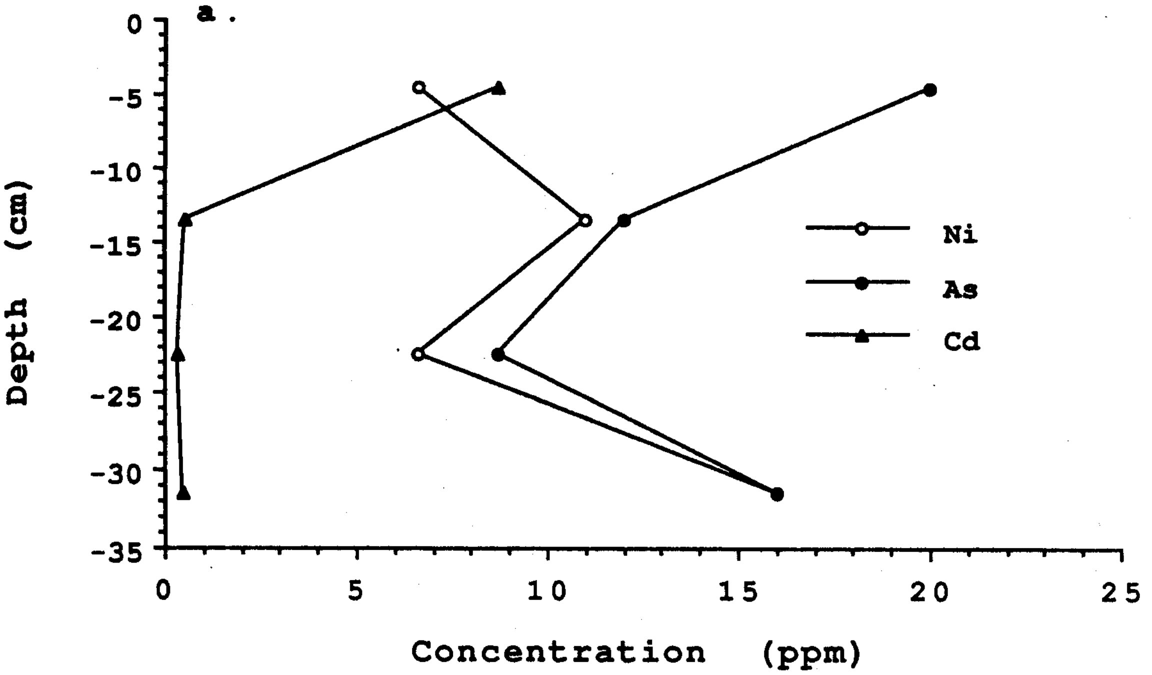


Figure VI.19. Depth profiles at station DF-C75 of a) Ni, As, & Cd and b) Zn & Ba.



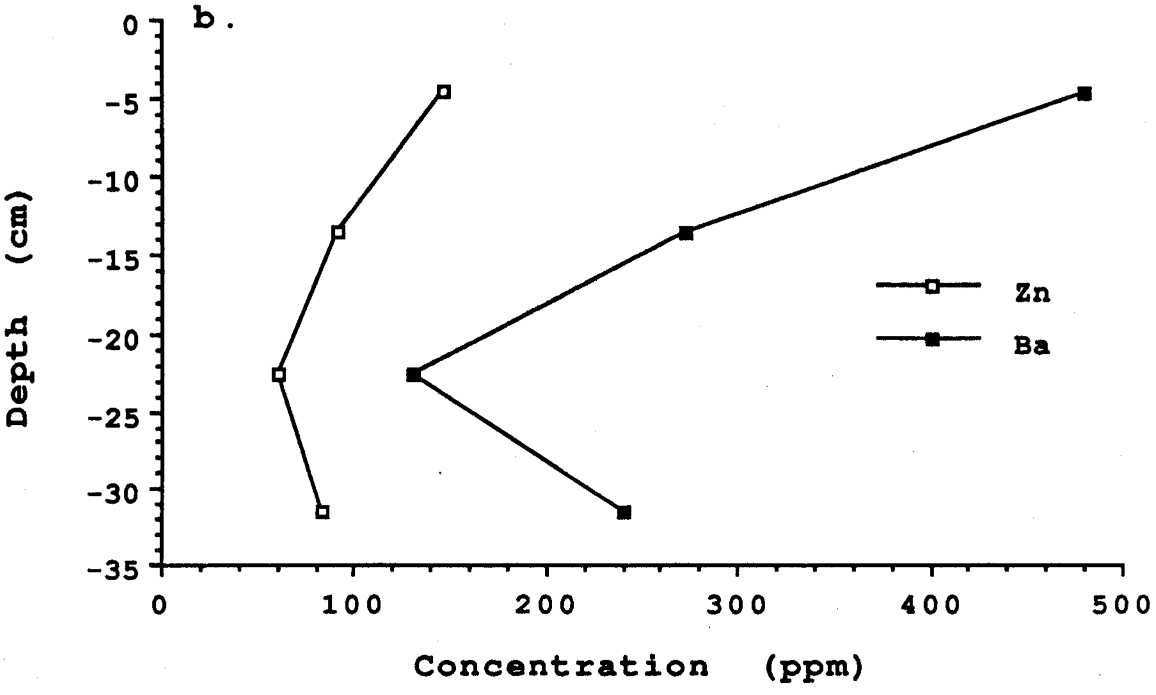


Figure VI.20. Depth profiles at station DF-A100 of a) Ni, As, & Cd and b) Zn & Ba.

seen for nickel. Similar to the DF-0 station, a general decline in concentrations was seen with a subsurface increase in metal concentrations in the bottom of the core. At the A300 station (Figure VI.21), the concentrations of metals were variable with depth and showed no clear trends.

At station $B_1$200 (Figure VI.22), Ba, Zn, and Ni showed a clear decreasing trend in concentrations with depth. However, Cd showed an initial decline in concentrations but then a very strong subsurface maximum at the bottom of the core. Arsenic concentrations showed a weak increasing trend with depth at this station. At the $B_2$200 station (Figure VI.23) concentrations of As and Ni tended to increase with depth, while Zn concentrations showed no depth-related trends. Cd and Ba concentrations showed a maximum at 9-18 cm, but then declined with depth. The reasons for these trends are not clearly understood but may be the result of differences in the hydrology around the discharge site or storm events.

At the $B_2$300 station (Figure VI.24) As, Cd, and Zn showed no clear trends with depth. Ba concentrations showed a surface maximum but then remained relatively constant below the surface. Ni concentrations showed first a decrease but then an increase to a maximum at the bottom of the core.

The reference station was located more than 1000 meters away from the discharge at Delta Farms. However, the concentrations of some of the metals in this core show that this area has been impacted to some degree (Figure VI.25). Ba, Zn, and Ni all show a surface maximum in concentrations and a decline with depth. Arsenic concentrations show no depth related trends, while Cd had a maximum below the surface of the core.

VI.C.4 Bully Camp Site (BC)

The Bully Camp effluent is discharged into a shallow embayment, which is connected to a canal. Figure II.4 shows the sediment sampling points, with half located in the embayment and the rest in the canal. The reference sampling point is located about 600 m west of the discharge in a dead-end canal.

VI.C.4.a Semivolatile Hydrocarbons

Table VI.12 and Figure VI.26 presents the semivolatile hydrocarbon data for Bully Camp surface sediments. The highest concentration of PAH homologs was at sampling point B50 (87,000 ppb), and not at the origin of the transects (BC-0). This is probably the result of environmental variability, whereby duplicate cores at the same sampling point could yield varying PAH concentrations. The main reason for this is that the

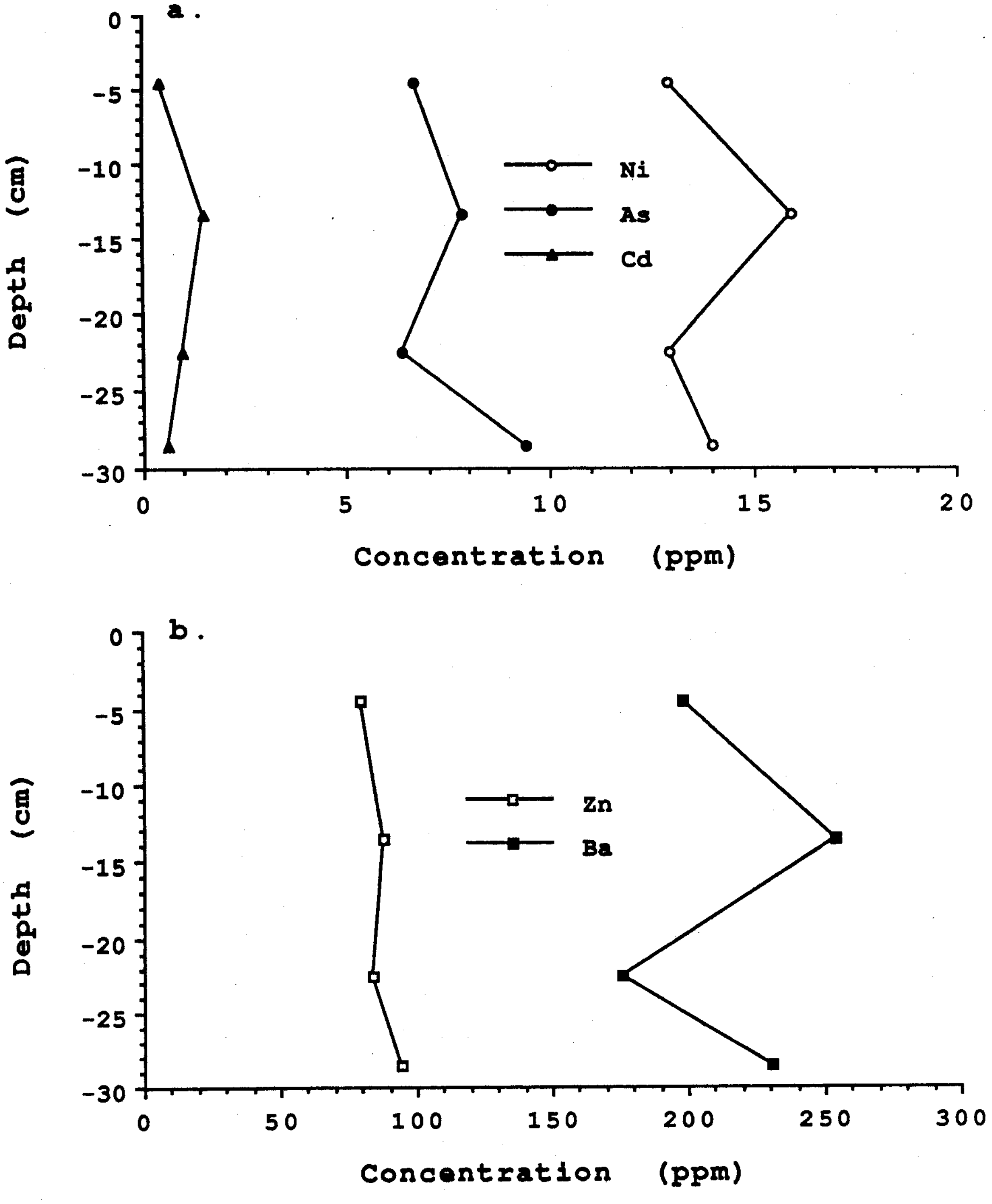
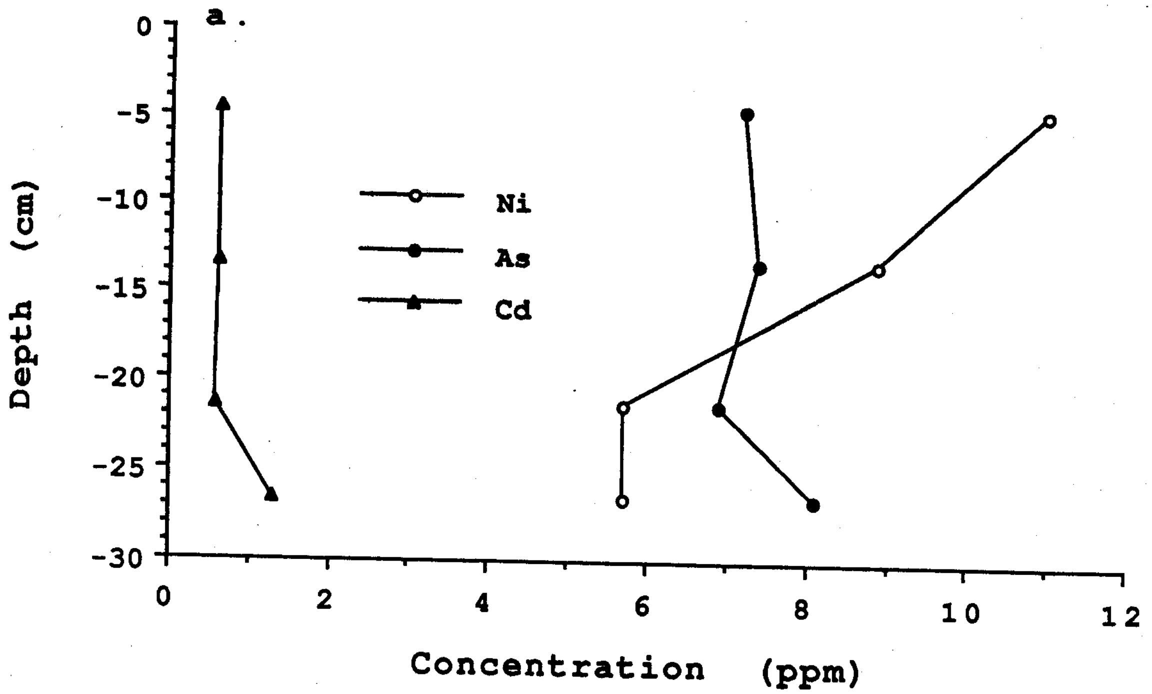


Figure VI.21. Depth profiles at station DF-A300 of a) Ni, As, & Cd and b) Zn & Ba.



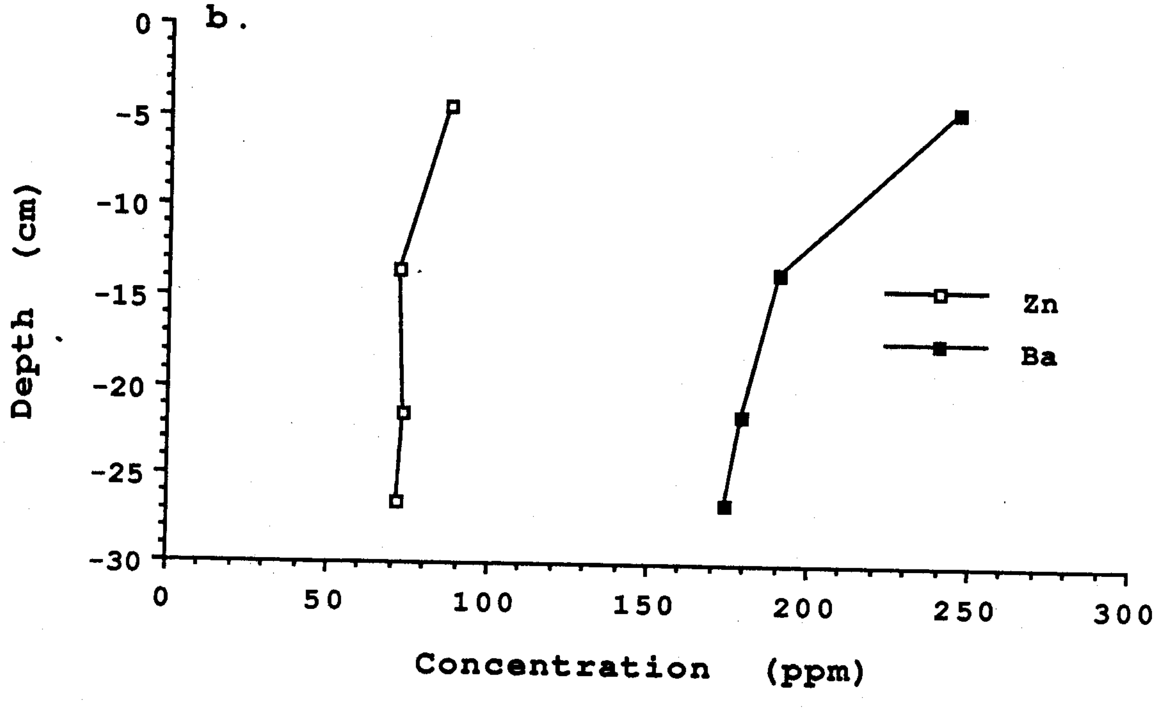


Figure VI.22. Depth profiles at station DF-$B_1$200 of a) Ni, As, & Cd and b) Zn & Ba.

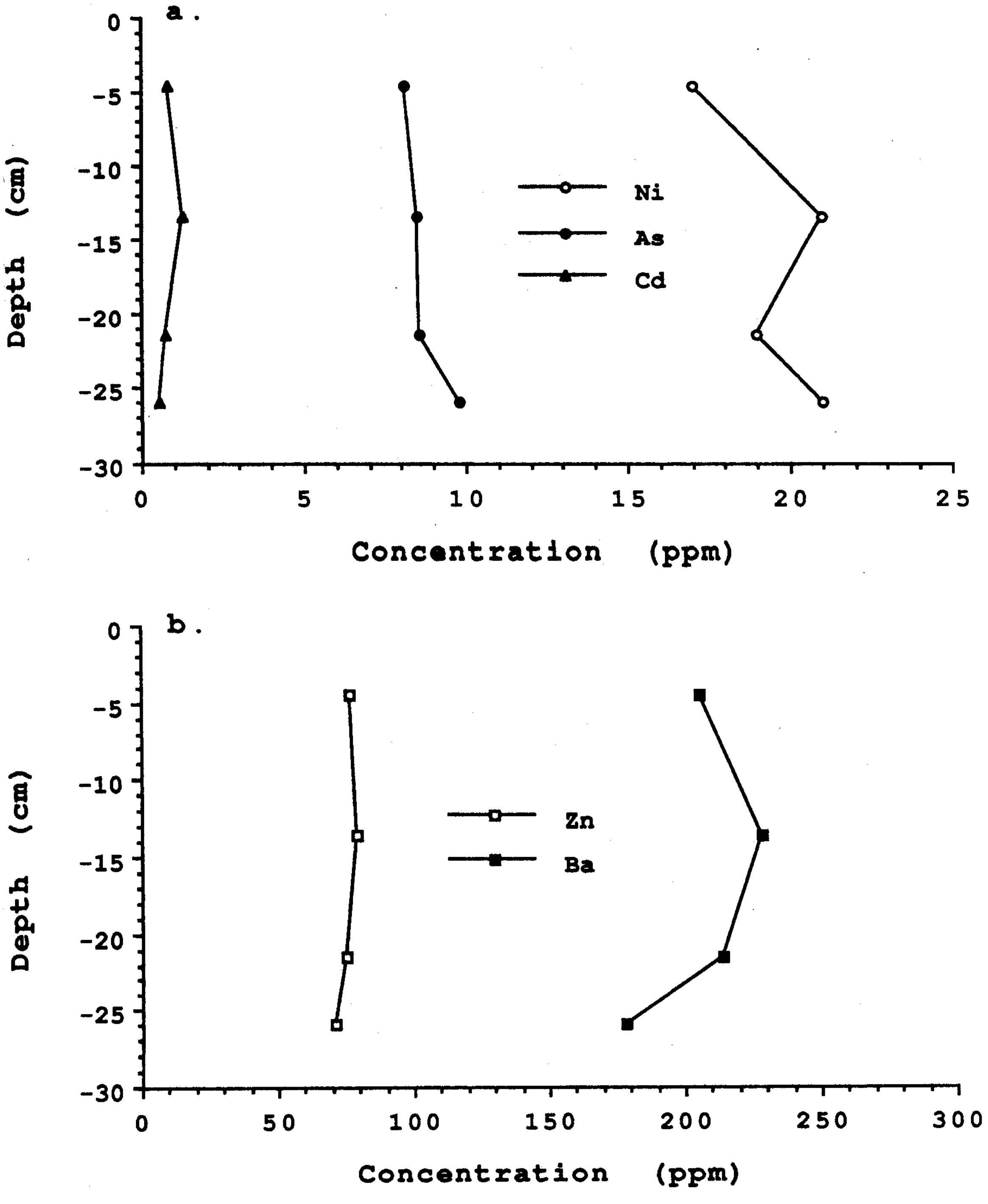


Figure VI.23. Depth profiles at station DF-$B_2$200 of a) Ni, As, & Cd and b) Zn & Ba.

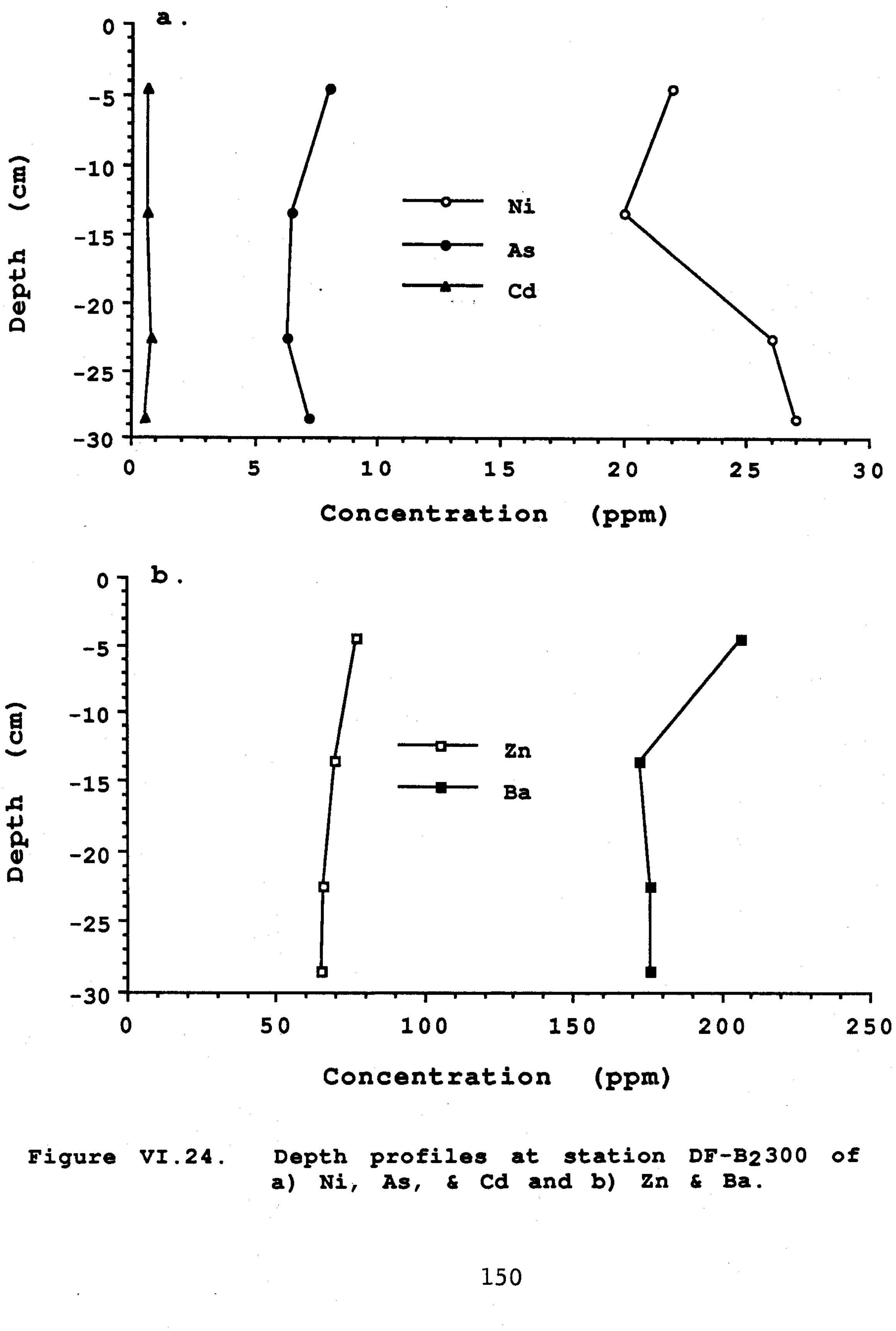
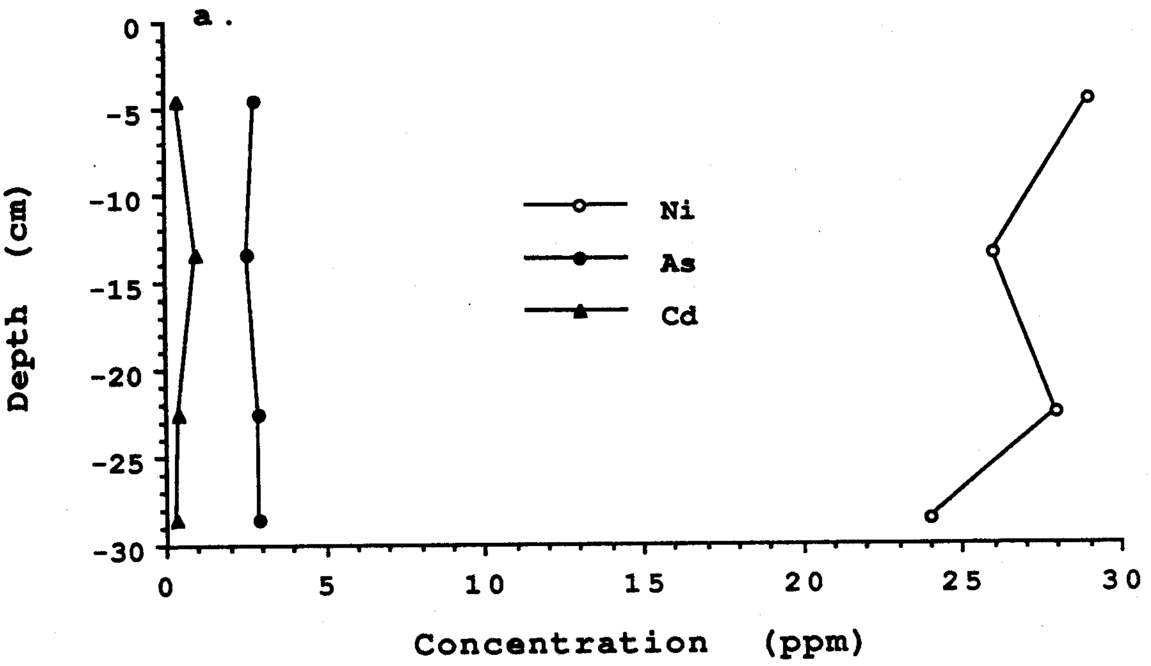


Figure VI.24. Depth profiles at station DF-$B_2$300 of a) Ni, As, & Cd and b) Zn & Ba.



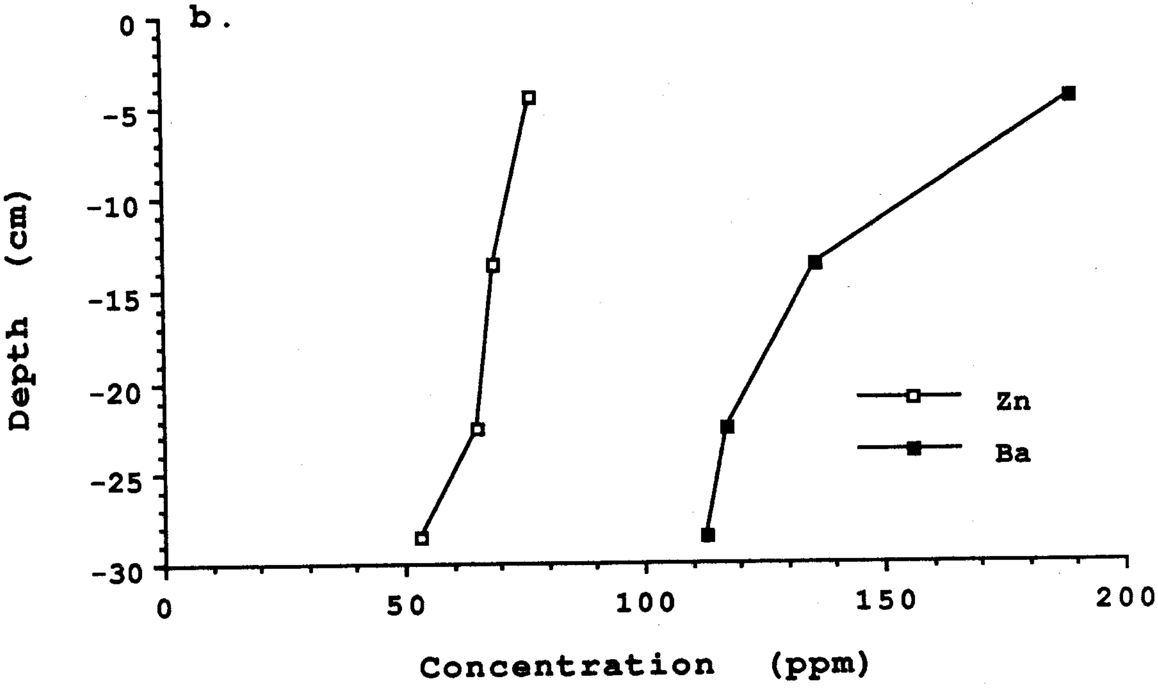


Figure VI.25. Depth profiles at station DF-R of a) Ni, As, & Cd and b) Zn & Ba.

contamination is not distributed evenly over the bottom because of topography, currents, boat traffic, and dredging activities. Although B50 is the most contaminated station, all the stations situated in the embayment (BC-0, A50, B50, B100, and C50) are very contaminated with petrogenic hydrocarbons. There is probably no significant difference between the homolog concentrations at BC-0, B50, and C50 (Table VI.12). All stations in the embayment contain a similar suite of PAHs as the effluent (BC-E), with alkylated naphthalenes, phenanthrenes, and dibenzothiophenes the dominant PAHs (Tables A.3a and A.3b). Station C100, which is in the canal, also contains high levels of alkylated PAHs (40,000 ppb). The remaining two stations in the canal, $C_1$300 and $C_2$300, show lower levels of PAH homologs compared to stations closer to the discharge, but display a similar array of hydrocarbons, confirming contamination from the discharge. The reference station contained no detectable concentrations of PAHs.

The FFPI (Table VI.12 and Figure VI.26) confirms that all stations sampled at the Bully Camp site are contaminated with petrogenic hydrocarbons. The FFPI's range from a very petrogenic 0.96 to 0.51 at station $C_1$300. The high concentration of pyrogenic hydrocarbons at $C_1$300 lowered the FFPI even though this station contained higher amounts of alkylated PAH than station $B_2$300, which had a FFPI of 0.87. The RS/TS ratio illustrates the decreasing influence of the discharge with an increase in distance. Station BC-0 has a RS/TS of 0.22, very similar to that of the discharge (0.26). The RS/TS ratio decreases away from the discharge, indicating that the produced water plume is undergoing degradation as it moves out into the canal.

Table VI.12. Hydrocarbon concentrations (ppb, dry wt.) in sediments at the Bully Camp (BC) site.

Station	Depth (cm)	Parent PAHs	PAH Homologs	FFPI	RS/TS	Total Saturates
BC-0	0-5	1,600	66,000	0.96	0.22	6,400,000
BC-A50	0-5	930	33,000	0.96	0.13	3,000,000
BC-B50	0-5	1,800	87,000	0.96	0.17	6,300,000
BC-B100	0-5	1,300	41,000	0.96	0.14	3,700,000
BC-C50	0-5	1,400	56,000	0.96	0.15	4,400,000
BC-C100	0-5	1,100	39,000	0.95	0.15	2,900,000
BC-$C_1$300	0-5	3,400	3,300	0.51	0.05	240,000
BC-$C_2$300	0-5	320	2,200	0.87	0.08	300,000
BC-R	0-5	tr	nd	n/a	0.06	66,000

nd: not detected
tr: trace; one ion present, but below detection limits
n/a: not applicable
RS/TS: Resolved/Total Saturates

VI.C.4.b Trace Metals

Trace metals in the surficial sediments at the Bully Camp site showed elevated levels as compared to the other sites (Table VI.9). Figure VI.27 shows the trends along the transects surrounding the discharge. Ba was high near the origin and tended to decrease in concentrations along the "A" and "C" transects, but tended to increase along the "B" transect. The reasons for this trend are not clear. Ni, As, and Cd also showed some confusing patterns at this site. While concentrations of these metals tended to decrease or remain relatively constant along the "A", "B" and "C" transects, the concentrations of Ni were observed to increase along the "B" and "C" transects. Concentrations of Al, Cr, Cu, V, and Pb showed no enrichment in sediments related to the discharge.

VI.C.5 Lake Washington Site (LW)

The Lake Washington (LW) effluent is discharged into a shallow dead-end canal that had recently been dredged. This effluent had the highest concentration of PAHs, but the second lowest discharge rate of the produced water discharges studied here. Figure II.5 shows that about half the sampling points are located in a canal perpendicular to the discharge canal, which drains into the Freeport Sulfur Co. Canal. The reference station is located 700 m northeast of the discharge.

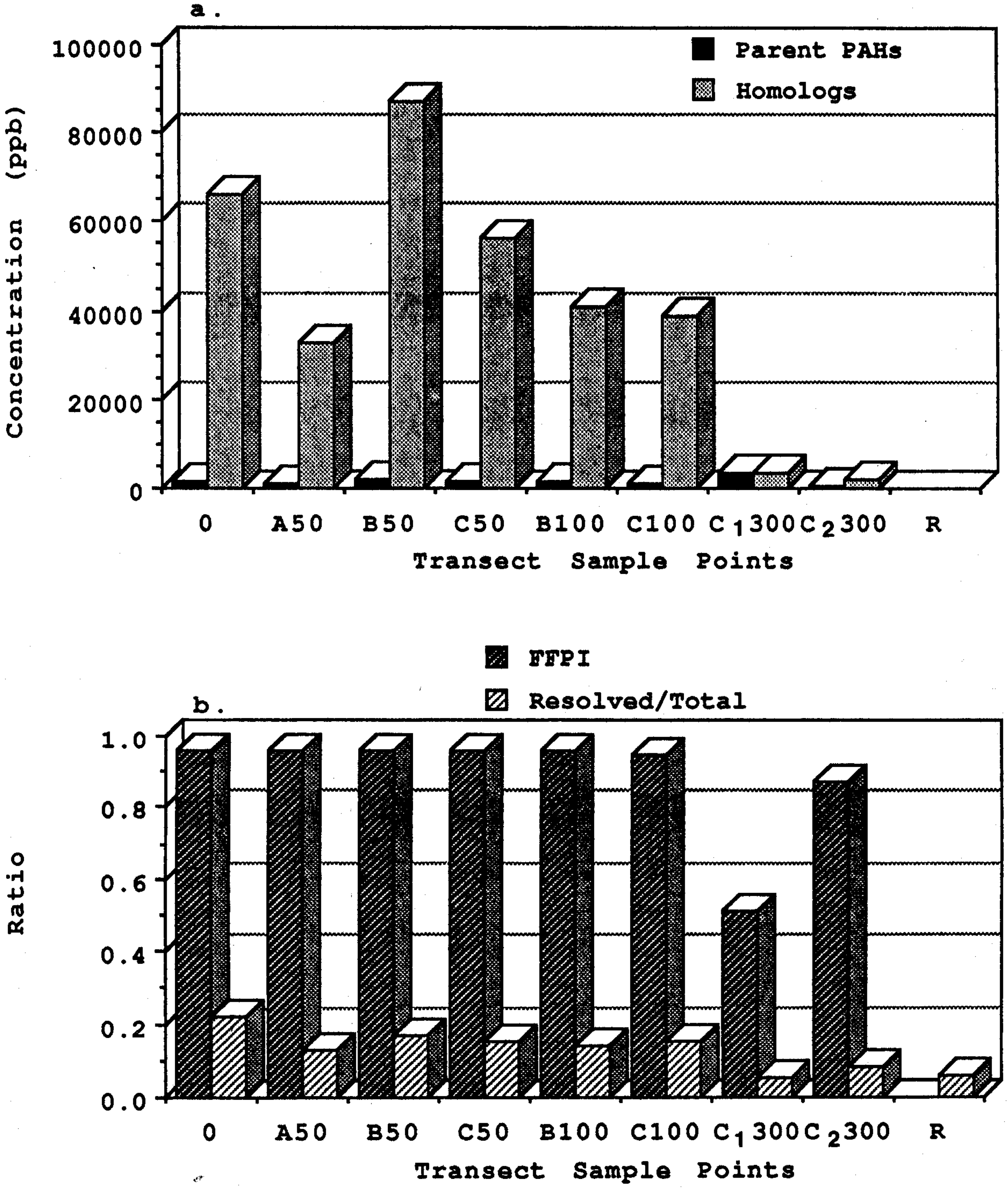
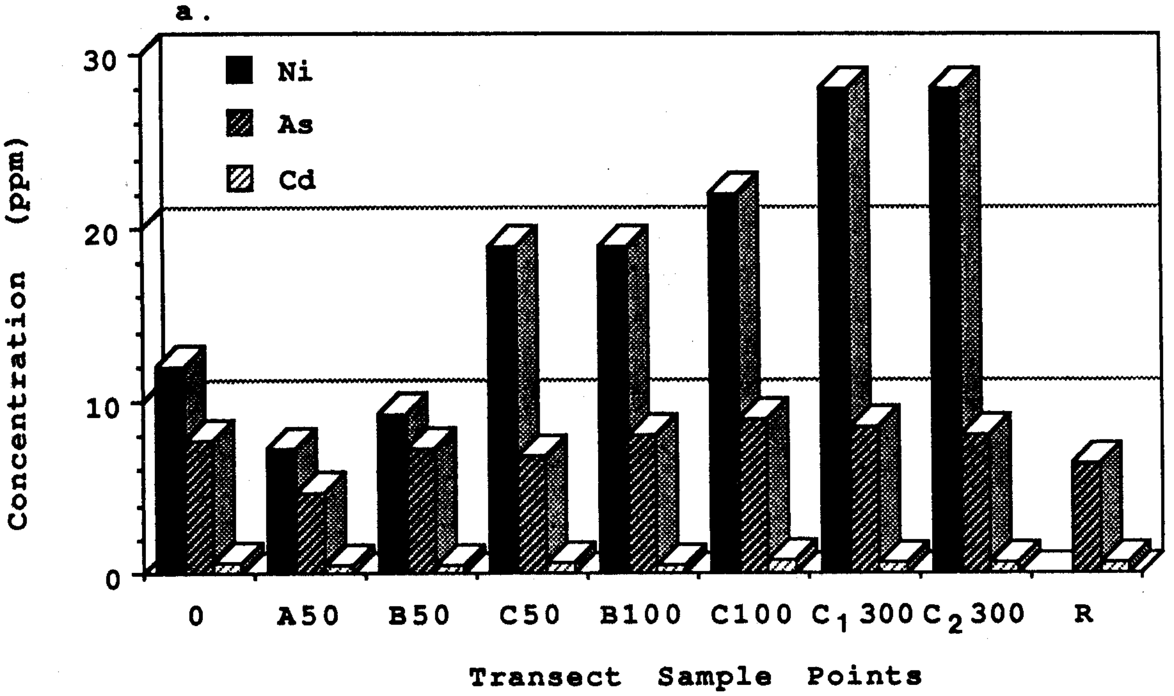


Figure VI.26. Distribution of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons, in surface sediments at the BC site.



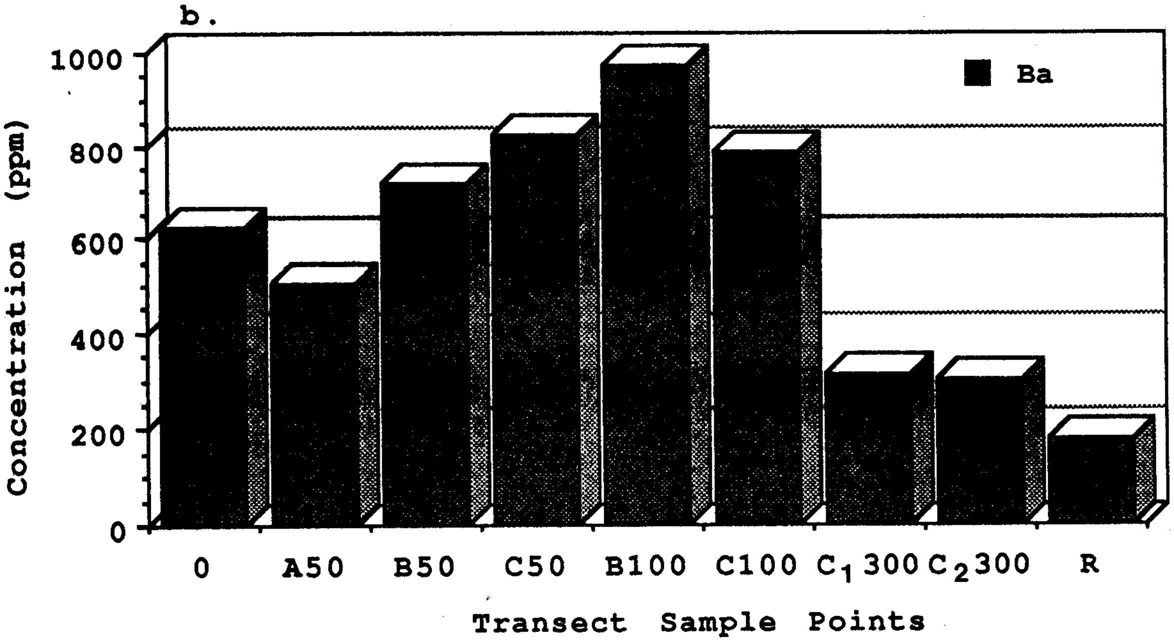


Figure VI.27. Distribution of a) Ni, As, & Cd and b) Ba, in surface sediments at the BC site.

VI.C.5.a Semivolatile Hydrocarbons

Table VI.13 lists the summary hydrocarbon data for Lake Washington surface sediments, while Figure VI.28 shows the distribution of these data. The concentrations of both PAHs and saturated hydrocarbons, drop off substantially, decreasing by 8-10 times, with increasing distance out from the origin. This is similar to the pattern observed at the LRT site which also has a low discharge flow. Sediments at stations A50, B50, and C100 are very contaminated with petroleum hydrocarbons containing high concentrations of alkyl-substituted naphthalenes, phenanthrenes, and dibenzothiophenes (Tables A.4a and A.4b). Contamination from the discharge extends out to stations $C_1$250 and $C_2$300, where there are low to trace levels of substituted phenanthrenes and dibenzothiophenes. Station B350 may have received some contamination from the discharge, however the majority of PAHs are pyrogenic in origin. This is based on the presence of trace levels of C2-phenanthrenes and low levels of C3-phenanthrenes. The reference station contained only trace levels of pyrogenic PAHs; however because of high water content in the sediment (probably plant material), the detection limit was 120 ppb, which may account for the number of undetected compounds.

The FFPI (Table VI.13 and Figure VI.28b) illustrates that significant petroleum hydrocarbon contamination exits at stations LW-0, A50, B50, B150, and C100. Station $C_1$250, with an FFPI of 0.49, shows less influence from the discharge than these stations, while stations $C_2$300 (0.19) and B350 (0.09) contain mostly pyrogenic PAHs. The RS/TS ratio decreases with increasing distance from the discharge. This indicates that the contamination reaching these distant stations has undergone some degradation.

Table VI.13. Hydrocarbon concentrations (ppb, dry wt.) in sediments at the Lake Washington (LW) site.

Station	Depth (cm)	Parent PAHs	PAH Homologs	FFPI	RS/TS	Total Saturates
LW-0	0-5	14,000	400,000	0.94	0.24	7,200,000
LW-A50	0-5	1,600	43,000	0.94	0.23	660,000
LW-B50	0-5	1,800	56,000	0.94	0.16	950,000
LW-B150	0-5	610	8,300	0.90	0.09	200,000
LW-B350	0-5	1,300	65	0.09	0.02	56,000
LW-C100	0-5	1,100	40,000	0.96	0.10	690,000
LW-C$_1$250	0-5	630	600	0.49	0.07	63,000
LW-C$_2$300	0-5	810	190	0.19	0.04	75,000
LW-R	0-5	tr	nd	n/a	0.10	26,000

nd: not detected
tr: trace; one ion present, but below detection limits
n/a: not applicable
RS/TS: Resolved/Total Saturates

VI.C.5.b Trace Metals

Figure VI.29 shows the trends in concentrations of selected metals around the Lake Washington discharge site. Ni showed a maximum at the origin and decreasing concentrations along all transects. Arsenic and Cd concentrations were elevated in the sediments at the origin but remained at these relatively high levels throughout the region. Ba and Zn concentrations were highest at the origin and stations near the discharge (A50, B50, C100), but then declined with increasing distance. None of the other metals detected showed any trends in concentrations around this site.

VI.D Synthesis and Conclusions

The impacts of produced water discharges on sediment quality varied in each of the areas studied. Major factors determining the degree of impact were: 1) discharge rate, 2) quantity and quality of the hydrocarbons present in a particular discharge, 3) water movement, 4) sediment disturbances (i.e. dredging and boat traffic) and 5) sediment types. Figure VI.30 is a bar graph showing the concentrations of PAH homologs in surface sediments at all the stations analyzed except the reference stations. The sites are listed on the graph in order of total overall contamination. The DF site has the greatest areal extent of contamination. Even 300 meters away from the discharge, sediments at station A300 contained 6,500 ppb of PAH homologs and a FFPI = 0.78. The BC site is also heavily contaminated, with

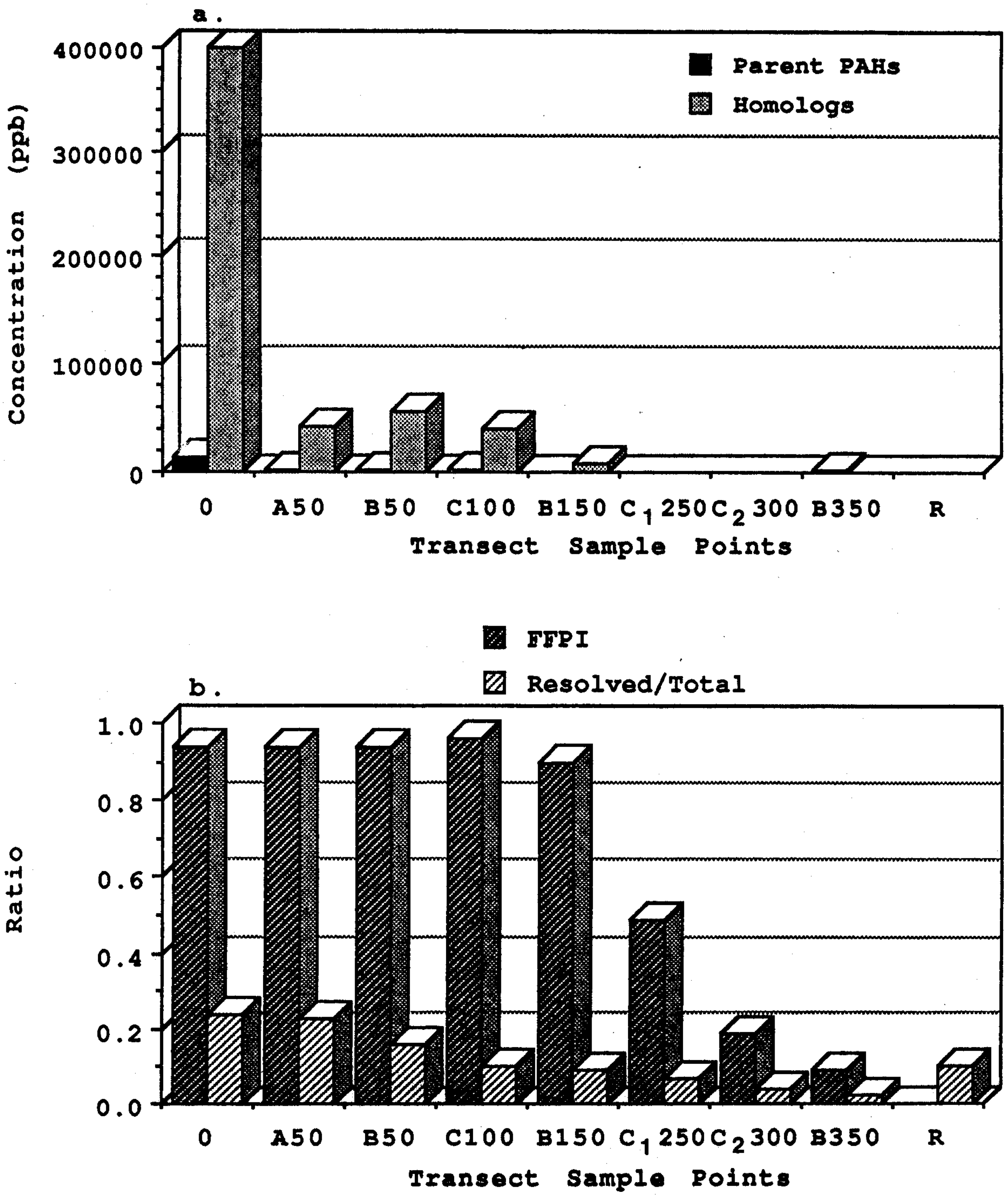


Figure VI.28. Distribution of a) parent PAHs & homologs and b) FFPI & resolved/total saturated hydrocarbons, in surface sediments at the LW site.

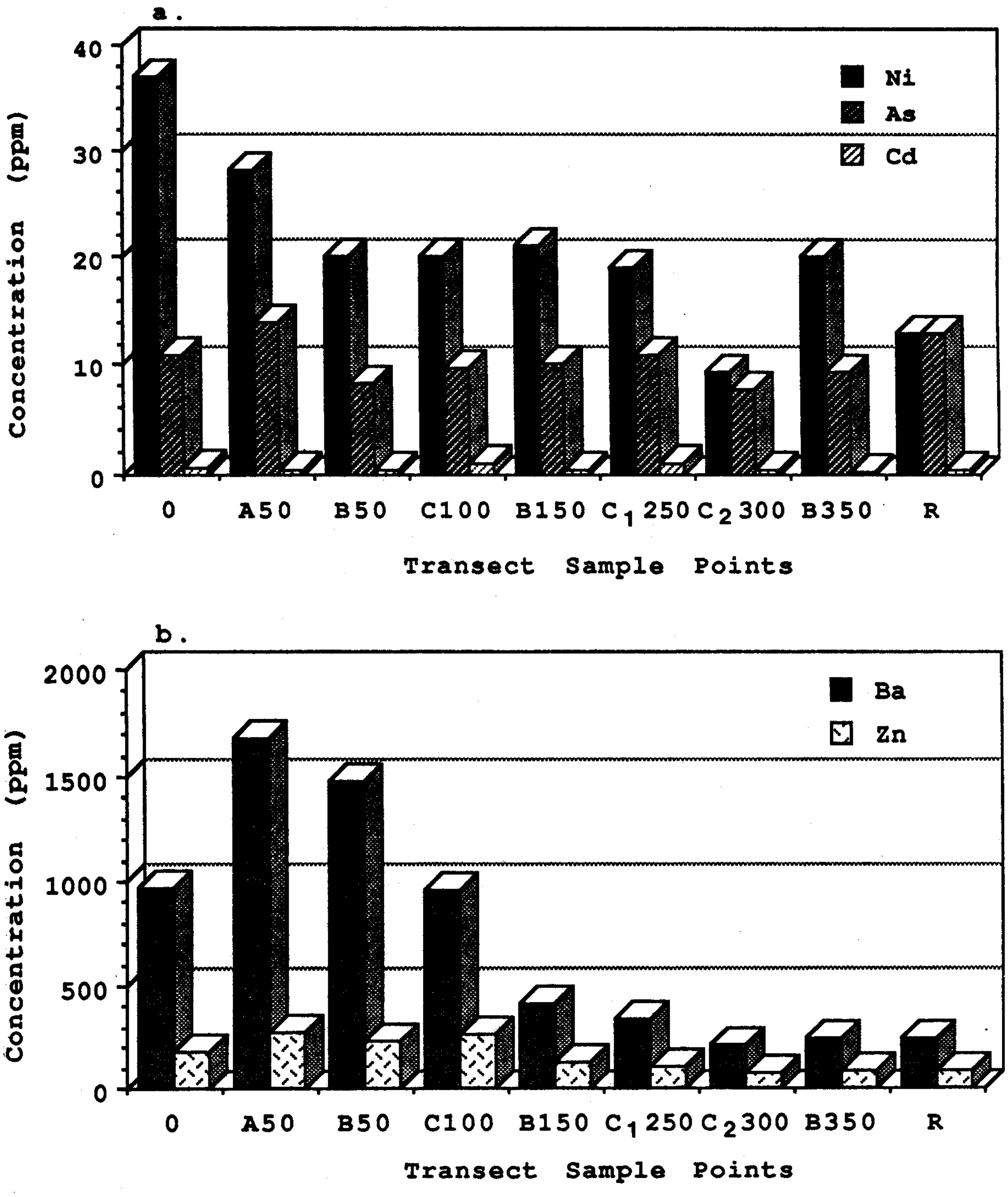


Figure VI.29. Distribution of a) Ni, As, & Cd and b) Ba & Zn, in surface sediments at the LW site.

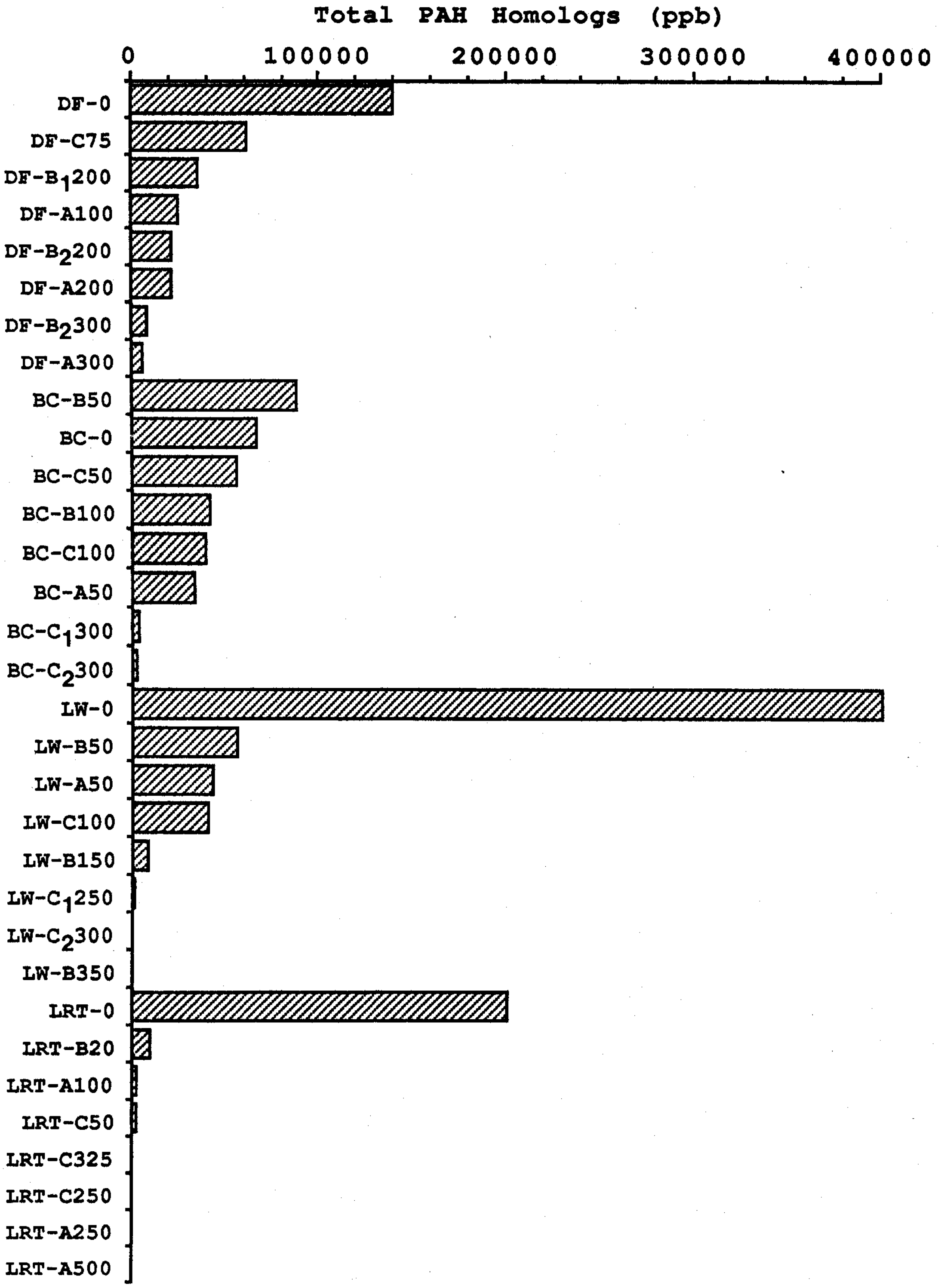


Figure VI.30. Total PAH homologs detected in sediments in the vicinity of four produced water discharges.

sediments at station C_2300 containing 2,200 ppb of homologs and a FFPI = 0.87. It is impossible to speculate from these data exactly how far away hydrocarbons from these discharges have contaminated the sediments at these sites as no samples were taken beyond 300 meters. The sediment from the LW site nearest the discharge was the most heavily contaminated with petrogenic PAH. However, the areal extent of contamination was less than at sites DF and BC, because there is only slight contamination at 350 meters away. The LRT site is the least impacted of all the sites studied here, with contamination at lower levels than the other sites and extending about 250 meters. Similar patterns and extents of barium and other trace metal contamination were observed at these sites.

The ranking of these sites closely follows the quantity of hydrocarbons and metals in the discharge and its flow rate. The LRT discharge contained the lowest concentration of hydrocarbons and metals and had the lowest flow rate, while the LW discharge which contained the highest amounts of hydrocarbons and metals had the second lowest flow rate. These low flow rates along with high particulate loading in the region may have caused most of the hydrocarbons and metals to concentrate in the near-field vicinity of the discharge. The discharges from BC and DF contained approximately the same amount of PAH homologs, but the flow rate of the DF effluent was almost 3 times greater. Discharge flow rate and hydrocarbon or metal concentrations may not be the only factors causing the amounts of contamination measured at these sites; they appear to be major factors, however.

In order to fully understand the movement of the produced water and the contaminants it contains, hydrocarbon data in surface sediments was compared to some of the other parameters measured and discussed in previous chapters. At sites LRT and LW, hydrocarbon data correlated well with both interstitial chloride and Ra 226 data ($r^2 > 0.82$), however, the areal extent of hydrocarbon contamination was less at these sites than the other two. This suggests that the manner in which these components of produced water are transported is similar at those sites close to the discharge. There was no correlation between hydrocarbon data and Ra 226 activities at site DF, but a slight correlation ($r^2 = 0.65$) with chloride concentration. Removing the data for station DF-C75, a dead-end canal, increases r^2 value to 0.90. Possible explanations are: 1) that the hydrocarbons present at this station might not be the result of the discharge alone, but may be from other activities at the site, 2) lateral movement of contamination below the surface, whereby the particle reactive hydrocarbons migrate and contaminate surface sediments, while the soluble chlorides concentrate at a lower depth (note high chlorides at -30 cm), and 3) the highly saline produced water is contaminating this area, but because of the loose detrital material at the surface the chlorides migrate down due to high density, while the hydrocarbons are adsorbed at the surface. The BC site displayed poor correlation ($r^2 < 0.30$) between hydrocarbons, chlorides, and Ra 226, however, correlation between chlorides and Ra 226 activities for both soluble chemical species was good ($r^2 = 0.84$). Two possible reasons for this difference are that the mechanisms for transporting hydrocarbons are different from those for the more water soluble chlorides and radium at this site, or that an oil spill that occurred sometime before sampling is an additional source of PAHs. Since there were no depth integrated analysis at this site it is impossible to tell if this hydrocarbon pattern is just a surface phenomenon. It would appear from these correlations that the contamination at these sites with hydrocarbons, chlorides, and radium is a result of produced water discharges. This is shown by the decrease in these contaminants with increasing distance away from the discharge.

Table VI.14 compares discharges studied in this report with other produced water discharges in southern Louisiana. The four discharges studied here appear typical of those found in south Louisiana with respect to discharge rate, volatiles, and PAH homologs. These discharges tended to be higher in the less toxic saturated hydrocarbons than the other discharges in Table VI.14, except Conoco at Bayou Rigaud. The Bayou Rigaud and Pass Fourchon discharges have higher flow rates because these facilities process large amounts of oil/brine from numerous OCS sources.

Table VI.15 compares sediment contamination from the discharges described in Table VI.14. The four sites from this study had high hydrocarbon contamination at the point of discharge. This is probably because the effluents from this study flow initially into poorly-flushed systems, while the other discharges were into hydrologically more active canals and bayous. Moving away from the discharges, the sediment contamination decreases, but at differing rates and with no clear trends. Each area has its own unique features that will ultimately determine the extent of contamination.

Table VI.14. Comparison of hydrocarbon concentrations in 11 produced water discharges located in South Louisiana.

Discharge	Rate (bbl/day)	Volatiles (μg/l)	Saturates (μg/l)	PAH Homologs (μg/l)
Lirette	462	1,700	22,000	110
Delta Farms	13,458	1,800	7,300	250
Bully Camp	4,767	760	10,000	260
Lake Washington	1,600	1,300	25,000	770
Bayou Sale*	2,500	2,100	4,800	650
Lafitte*	3,676	2,400	4,900	400
Golden Meadow TB#7*	2,845	3,500	3,700	180
Golden Meadow TB#8*	3,808	4,100	5,800	400
Bayou Rigaud/Conoco**	105,000	4,500	48,000	1,100
Bayou Rigaud/Exxon**	40,000	2,400	6,400	<20
Pass Fourchon**	26,000	2,900	16,000	410

* Boesch and Rabalais, 1989b
** Boesch and Rabalais, 1989a

VI.D.1 Predicted Bioaccumulation from Contaminated Sediments

The bioaccumulation of neutral hydrophobic organic compounds from sediments, such as the PAHs measured as part of this study, has been hypothesized to be controlled in part by the sediment-water partitioning (Foster *et al.*, 1987). Such hydrophobic compounds are strongly sorbed to sediments, exhibiting high sediment-water partition coefficients, which have been shown to be highly correlated to sediment organic carbon contents (Means *et al.*, 1980). The assumption is made that during bioaccumulation the organism responds only to the aqueous phase concentration of the chemical and that the sediment-bound fraction of the contaminant is "unavailable" to the organism except through desorption into the aqueous phase. Currently, the USEPA is developing sediment quality criteria based upon these and other assumptions, therefore, it is important to elucidate the factors which may control the accumulation processes in aquatic benthos. A recent review of the issues and assumptions made in these sediment quality criteria estimations has been published by Chapman (1989).

In a series of research studies conducted using natural sediments and various bivalves, a predictive relationship between sediment concentrations of hydrophobic contaminants and tissue concentrations of those same contaminants bioaccumulated from those sediments has been developed (Means and McElroy, 1988,

Table VI.15. Comparison of hydrocarbon concentrations in surface sediments in the vicinity of 10 produced water discharges.

Location	Station	Distance from nearest discharge (m)	Total Homologs (ppm)	Total Saturates (ppm)
Delta Farms (this study)				
At Discharge	DF-0	20	140	6,400
Moderate Contamination	DF-$B_2$300	320	7.7	420
Background	DF-R	600	0.32	110
Lirette (this study)				
At Discharge	LRT-0	10	200	40,000
Moderate Contamination	LRT-C250	260	0.60	52
Background	LRT-R	1000	<0.03	14
Bully Camp (this study)				
At Discharge	BC-0	10	66	6,400
Moderate Contamination	BC-$C_2$300	320	2.2	300
Background	DF-R	600	<0.07	66
Lake Washington (this study)				
At Discharge	LW-0	20	400	7,200
Moderate Contamination	LW-$C_1$250	270	0.60	63
Background	DF-R	600	<0.12	26
Bayou Sale (Boesch and Rabalais, 1989b)				
At Discharge	BS0	10	50	1,200
Moderate Contamination	BS500E	500	10	260
Background	BS1000E	1,000	0.37	24
Lafitte (Boesch and Rabalais, 1989b)				
At Discharge	L0	10	3.9	350
Moderate Contamination	L250NE	250	1.30	190
Background	L750NE	750	0.13	41
Golden Meadow (Boesch and Rabalais, 1989b)				
At Discharge	GM0	10	0.08	88
Moderate Contamination	GM100S	100	0.17	110
Background	GM1000S	1,000	0.26	14
Bayou Rigaud (Boesch and Rabalais, 1989a)				
At Discharge	BR1, Oct	200	26	1,300
Moderate Contamination	BR5, Oct	400	0.78	145
Background	BR4, Oct	1,300	<0.04	38
Pass Fourchon (Boesch and Rabalais, 1989a)				
At Discharge	PF2, Jan	400	39	650
Moderate Contamination	PF7, Jan	600	0.11	5.2
Background	PF11	2,800	<0.70	43

Foster *et al.*, 1987). The relationship is as follows:

$$AF = \frac{[\text{conc. tissues of } X/ \text{ fraction lipid}]}{[\text{conc. sediment of } X/ \text{ fraction organic carbon}]}$$

where X is some hydrophobic contaminant and AF is a constant accumulation factor having a value of ~0.5.

Thus if the sediment concentrations of various chemicals are known and normalized for organic carbon content, a theoretical maximum tissue burden can be calculated on a lipid weight basis. Table VI.16 shows the predicted tissue concentrations (calculated from sediment concentrations normalized for a 2% organic carbon content) for the Lake Washington LW-0 site on both a lipid dry-weight basis and a wet-weight basis assuming an average tissue lipid content of 5% for oysters. Using this approach, field collected bioaccumulation data can be compared to predicted maximum exposure concentrations. The concentrations of various PAHs presented in Table VI.16 represent the levels of these compounds which might be expected to accumulate in the tissues of oysters which reside in the region of the Lake Washington produced water discharge. The levels of PAHs may represent a significant ecological risk factor for oysters as well as other aquatic organisms in these areas. Recent studies which employed transplantation of oysters from pristine environments to sites adjacent to produced water discharges have resulted in high mortalities near the discharge points (Means and Milan, unpublished data; St. Pé, Chapter VII). The very high predicted tissue concentrations may also represent a human health risk if oysters or other shellfish were taken from these areas for human consumption. Although the toxicological risks associated with consumption of high concentrations of alkylated PAHs in food are poorly understood, the concentrations of some known carcinogens such as benz[a]anthracene are probably high enough to cause concern. Further, the very high total hydrocarbon tissue burdens predicted make organisms thus exposed organoleptically unacceptable for human consumption. In general, when field collected organism data are compared to the model, lower values are found in the real tissue data sets. In the case of PAHs and their alkylated homologs, the low measured values in tissues relative to the predicted values as presented in Table VI.16 may be the result of 1) non-achievement of steady-state tissue concentrations in relation to sediment concentrations and 2) resistance to transport across biological membranes of some of the alkylated PAH homologs.

Aside from the effects to the benthic community, produced water discharges represent a potential threat to endemic finfishes. Daniels and Means (1989) presented data which indicated that produced waters discharged into semi-enclosed areas may pose long-term ecological effects to estuarine finfishes due to induced mutagenic responses.

Table VI.16. Estimated bioaccumulated polynuclear aromatic hydrocarbons.

Analyte	LW-0 (ppb)	Conc. Sed./ frac. OC* (ng/g C)	Conc. tissues (ng/g lipid)	Conc. tissues** (ng/g wet wt.)
Naphthalene	1,500	75,000	38,000	1,900
C1-Naphthalenes	9,800	490,000	250,000	12,000
C2-Naphthalenes	70,000	3,500,000	1,800,000	88,000
C3-Naphthalenes	220,000	11,000,000	5,500,000	280,000
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	110	5,500	2,800	140
Fluorene	960	48,000	24,000	1,200
Dibenzothiophene	1,200	60,000	30,000	1,500
C1-Dibenzothiophenes	6,000	300,000	150,000	7,500
C2-Dibenzothiophenes	11,000	550,000	280,000	14,000
C3-Dibenzothiophenes	6,900	350,000	170,000	8,600
Phenanthrene	6,000	300,000	150,000	7,500
C1-Phenanthrenes	32,000	1,600,000	800,000	40,000
C2-Phenanthrenes	30,000	1,500,000	740,000	37,000
C3-Phenanthrenes	12,000	600,000	300,000	15,000
Anthracene	310	16,000	7,800	390
Fluoranthene	320	16,000	8,000	400
Pyrene	370	19,000	9,300	460
Benz(a)anthracene	590	30,000	15,000	740
Chrysene	2,000	100,000	50,000	2,500
Benzo(b)fluoranthene	280	14,000	7,000	350
Benzo(k)fluoranthene	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parent PAHs	14,000	700,000	350,000	18,000
Total Homologs	400,000	20,000,000	10,000,000	500,000
Total PAHs + Homologs	410,000	21,000,000	10,000,000	510,000

* Fraction of organic carbon = 2%

** Fraction of lipid = 5%

nd: not detected

Chapter VII

ACCUMULATION OF PETROGENIC ORGANICS AND RADIUM 226 BY CAGED OYSTERS, *Crassostrea virginia*, PLACED NEAR PRODUCED WATER DISCHARGES

by

Kerry M. St. Pé, Matt Schlenker, and Richard Guidry

VII.A Introduction

Previous sections in this report have indicated that pollutants including organic chemicals and radium 226 can accumulate into bottom sediments near produced water outfalls to poorly flushed systems. Concerns about potential human health effects resulting from produced water discharges has prompted several investigations into the ability of commercially important fishery organisms to accumulate petrogenic pollutants. Most of this work has been associated with the polynuclear aromatic hydrocarbon (PAH) components within produced water.

As discussed by Mix (1982), the use of bivalve mollusks in bioaccumulation studies has been advocated by researchers from several scientific disciplines. Oysters were preferred for use in this study component over other bivalves because in addition to being nonmotile, benthic inhabitants which have been shown to concentrate water borne contaminants, they are commercially important seafood products and were easily obtainable from an area without direct produced water influence.

Neff (1988) reviewed available literature on the bioaccumulation of chemicals by marine organisms from oil field wastes including produced water. The accumulation of aromatic hydrocarbons by marine animals has been shown to vary with the phylogeny of the organism. This is due primarily to differences in the ability of the various marine animals to metabolize body burdens of hydrocarbons by means of the mixed-function oxygenase (MFO) enzyme system (Neff, 1988). The MFO system of fishes and crustaceans is more highly developed than that of oysters, for example. Consequently aromatic hydrocarbon retention within oysters is of greater duration since the loss of these pollutants by bivalve mollusks is almost exclusively dependant on passive, nonenzymatic processes (Neff, 1988).

Somerville *et al.* (1987) reported data from a long term produced water monitoring program in the North Sea Brent Field. *In situ* cages containing mussels, *Mytilus edulis*, were used to assess the potential for biotic hydrocarbon accumulation. Mussel cages were placed at 0, 6, 10, 25, and 60 km from an open-sea produced water outfall for a 10 to 16 week period. At the platform site, hydrocarbons were accumulated at levels 60 to 100 times greater than in unexposed controls. Hydrocarbon levels accumulated at the 6 km site were 6 to 10 times greater than the control station and levels in mussels at the 10 km station were close to the control site concentrations (Somerville *et al.*, 1987).

Boesch *et al.*, (1989) collected oysters, *Crassostrea virginica*, from indigenous specimens attached to structures located in coastal southeast Louisiana near produced water discharges and from a nearby reference site. The number of samples were limited and the authors were cautious in their interpretation of results, however, analyses of the oyster tissues demonstrated the potential for petrogenic hydrocarbon uptake from produced water effluents.

The accumulation of radionuclides by bivalve mollusks and other estuarine species from produced water discharges has received little attention in comparison to effluent-associated hydrocarbon uptake. Much of the limited work dealing with biotic radionuclide uptake has been associated with investigations into the effects of discharges from uranium ore mining and milling operations. Radium 226 is associated with uranium mill tailings as a water-borne pollutant because it is an intermediate member of the Uranium 238 decay series.

Jeffree and Simpson (1986) exposed tropical freshwater mussels, *Velesunio angasi* (Sowerby), contained in tanks to various radium 226 concentrations which approximated levels found in uranium mill discharges. Mussels held for 56 days in tanks containing water with a mean of 50 pCi/l radium 226 accumulated a mean dry weight tissue concentration of 679 pCi/g radium 226. The accumulation was linear over exposure periods of 28 and 56 days. Further investigation by Jeffree and Simpson (1986) showed that freshwater mussels which had accumulated radium 226 under both field and laboratory conditions lost no significant amounts of radium concentrations when held in radium-free water for a 286 day period.

The objective of this study component was to assess the potential for the accumulation of petrogenic pollutants, including radium 226, by native oysters placed near 3 of the 4 produced water outfalls studied. An unaffected control site was also used. This component was designed and purposely intended to be a general measure of possible influences from existing produced water discharges.

VII.B Materials and Methods

VII.B.1 *In Situ* Oyster Cages

Caged oysters (*Crassostrea virginica*) were used to assess the potential for the uptake of volatile organics, polynuclear aromatic hydrocarbons (PAHs) and radium 226 from produced water discharges by biota. All of the oysters were obtained on January 22, 1990, from the Louisiana state oyster seed ground in Caillou Lake south of Houma, Louisiana. The seed ground is maintained by the Louisiana Department of Wildlife and Fisheries (LDWF). The oysters were obtained with a small version of a commercial rake-type oyster dredge pulled with a 13 foot Boston Whaler.

Following collection, the oysters were divided into 4 groups of 75 individuals. Length measurements were obtained and recorded. The overall mean length of the oysters used was 93.09 mm. The mean weight of each individual was 23.6 grams (soft tissue).

Oysters were placed in cages constructed of 20 gauge, vinyl-coated wire. The mesh configuration was 13/16 inch square with a diagonal measurement of 1.25 inches. This mesh size was chosen to minimize the possibility of predation.

Each cage was 15 inches wide x 20 inches long x 4 inches high and completely enclosed the oysters contained within. Access was provided by a hinged, wire mesh door fitted over a 5 inch x 10 inch opening in the cage top. Three cages were secured together to form one unit. Twenty-five (25) oysters were eventually placed into each of the 3 cage compartments comprising a unit, creating a total of 75 oysters to be used for deployment near a produced water outfall.

Since the sediments at several of the study sites were extremely soft, a sheet of 29 gauge galvanized metal measuring 35 x 70 inches was secured to the bottom of the tray unit to keep the oysters from sinking. Also, six 10-inch lengths of plastic ½ inch pipe were attached to the sides of the cages in a manner which would allow 3 inches to extend below the metal sheeting into the bottom sediments. This was done to minimize lateral movement of the cage unit. Each unit was additionally secured to a wooden stake on the canal banks with a rope and bridle fitted with lead weights. Care was taken to conceal the location of the cages to avoid vandalism or tampering.

The tray units were deployed at three of the four study sites and a control site. The control site was located at the Louisiana Department of Wildlife and Fisheries, Sister Lake camp dock located in the Caillou Lake oyster seed ground. Each tray arrangement was deployed for about a 30 day period and visually checked after about 15 days following the initial placement. Water quality readings were obtained at the time of deployment, at the 15 day inspection, and at the time of retrieval.

The control site (Caillou Lake) oysters were deployed on January 22, 1990. The total depth at the oyster placement site was 1.0 meter. The salinity measured at a depth of 0.7 m was 11.2 ppt. The dissolved oxygen content at the same depth was 11.0 mg/l. The oysters ranged in size from 75 mm to 120 mm in length with an average of 91.09 mm. The control site oyster cages were removed on February 21, 1990, 30 days after the initial placement.

In addition to the control site, oysters were placed at the Lirette, Bully Camp, and Lake Washington sites. The salinities at the Delta Farms study site were judged to be too low to support oyster growth.

The Lirette site (Fig. II.2) oysters ranged in size from 65 mm to 115 mm with an average length of 90.91 mm. These were placed in the canal receiving effluent, 100 meters north of LRT-0 along transect "C". The date of deployment was January 23, 1990. The water depth at this station was 1.1 meters. The salinity measurement at 0.8 meters was 6.5 ppt and the dissolved oxygen content was 5.7 mg/l.

The oysters placed at the Lirette site were examined on February 5, 1990, 13 days after the initial deployment. On that date the water level was noted to be low due to the prior passage of a cold front. A salinity measurement of 3.6 ppt near the bottom was recorded. About ½ inch of sediment covered most of the oysters in the cages and one mortality was noted and removed.

The Lirette oysters remained in place for a total of 30 days and were retrieved on February 22, 1990. The bottom salinity recorded on that date was 5.1 ppt. It was estimated that up to 1.0 inch of fine sediment covered most of the caged individuals. Four additional mortalities were recorded and discarded (total mortalities = 5).

The Bully Camp site (Fig. II.4) oyster cages were deployed on January 23, 1990, at a station located on the "B" transect, 75 meters WNW of the origin. The total depth at this station was 1.0 m. The salinity was 6.4 ppt at a depth of 0.7 meters and the dissolved oxygen content was 11.2 mg/l. The 75 individual oysters within the Bully camp cage ranged in length from 67 mm to 120 mm (average 96.04 mm).

The Bully Camp site was revisited on February 5, 1990, for the purpose of inspecting the cages. The oysters were raised and noted to have approximately ¼ inch of fine silt covering about

20% of the individuals. No mortalities were noted. Water quality measurements on that date indicated a bottom salinity of 4.7 ppt at a depth of 0.8 m.

Oysters were retrieved from the Bully Camp site on February 22, 1990, 30 days after the initial deployment. A light (<¼ inch) silt coating was observed on the upper valves of the test organisms. No mortalities were recorded. At the time of retrieval, the bottom salinity was 8.9 ppt.

The Lake Washington site (Fig. II.5) oyster cages were placed at station LW-A50 on January 24, 1990. This station was extremely shallow (0.8 m). The bottom was composed of soft silty sediments which were observed to be highly contaminated with petroleum hydrocarbons. The bottom salinity at this station was 22.9 ppt. The dissolved oxygen concentration at the same depth (0.5 m) was 8.9 mg/l.

On February 7, 1990, the Lake Washington oysters were raised and examined. The resulting disturbance of the bottom dislodged sediment-bound petroleum contaminates which rose to the surface and resulted in a sheen. Approximately ¼ inch of silt covered 50% of the oysters in the cages. The total depth on the date of this examination was 0.6 m. Readings taken at 0.3 m indicated a salinity of 19.1 ppt. No mortalities were recorded on this date.

The Lake Washington oyster cages were retrieved on February 26, 1990, thirty-three days after the initial placement. A total of 48 mortalities were recorded. Approximately 1/8 inch of silt covered the oysters in the tray. The salinity measured near the bottom was 14.3 ppt.

Following the retrieval of cages from the Lirette, Bully Camp, Lake Washington, and Caillou Lake sites, the surviving oysters were shucked with stainless-steel knives and were divided into the differing tissue quantities needed for volatile organics, PAH, and radium 226 analyses. The amount of tissue used was largely dependant on the number of survivors retrieved from the trays (Table VII.1). Since the percent mortality was greatest in the trays from the Lake Washington site (64%), tissue quantities available from that location were less than the remaining study areas.

Organics analysis was performed by the Louisiana Department of Environmental Quality (LDEQ) Central Laboratory and radium 226 analysis was by the LDEQ Nuclear Energy Division Laboratory. Organics samples for each site were composited and placed in specially cleaned glass jars. Composited radium 226 samples for each site were placed in sealed plastic bags. All oyster tissue samples were frozen and delivered to the respective laboratories.

Table VII.1 Oyster cage survival and numbers of individuals used for analyses.

Study Site	Oysters Deployed	Number Surviving	Percent Mortality	Number Individuals Per Sample Volatiles	PAH	Ra 226
Lirette	75	70	7	5	35	30
Bully Camp	75	75	0	5	40	30
Lake Washington	75	27	64	4	12	11
Caillou Lake	75	75	0	5	40	30

VII.B.2 Analytical Methods

Volatile Organics

There is currently no EPA (U.S. Environmental Protection Agency) accepted method for analyzing volatile organics in marine organisms. EPA has, however, developed an interim method which provides a qualitative and semi-quantitative determination of these compounds in biota (U.S. Environmental Protection Agency, 1981). This analytical approach is currently considered to be the best method available for determining volatile organic concentrations in fish and shellfish tissues (EPA, 1981).

Oyster tissues used for volatile organic analysis were homogenized in a specially cleaned blender. One to 10g of still-frozen, homogenized tissue were sonified at maximum probe power for 30 seconds in organic-free water in duplicate vials. Each vial was sealed immediately. One vial was dosed with standard while the other remained undosed. The sample vials were allowed to equilibrate to room temperature, heated to 80°C for 5 minutes with heating tape, and purged with a Tekmar LS-2 purge and trap interfaced to a Finnigan OWA GC/MS. The identification and quantification procedures followed EPA method 624 (U.S. EPA, 1984).

Semivolatile Organics

Oyster tissues (40g per sample) for semivolatile organics analysis were extracted with hexane according to a procedure outlined by the Food and Drug Administration (U.S. Department of Health and Human Services, 1982). Analysis of the base/neutral fractions was with a Finnigan GC/MS to identify and quantify the polynuclear aromatic hydrocarbons. Quantitative determination of the target compounds followed procedures described in EPA Method 625. The alkylated homologs (C1 through C3) of naphthalene and phenanthrene were quantified by using the response factor of the parent compound. The detection limit for the PAH compounds was 20 ppb (wet wt.) with the exception of chrysene. The detection limit for chrysene was 40 ppb (wet wt.).

Radium 226

Analysis of the oyster tissues for radium 226 was performed by the Louisiana Department of Environmental Quality, Nuclear Energy Division's Environmental Radiological Surveillance Lab. The analysis was by gamma spectroscopy utilizing the Canberra Series 90 Gemini System. The Gemini System consists of a Canberra Series 90 Multichannel Analyzer computer interfaced to a Digital Equipment Corporation PDP-11/23 Plus computer. The Series 90 is connected to four Canberra Germanium detectors for high resolution gamma ray spectroscopy.

Radium 226 activities were determined using a 500 ml Marinelli beaker geometry and were counted for 60,000 seconds live time. Results are reported in pCi/l ±2 sigma error.

Quality control procedures used during the analytical process were maintained in accordance with the Louisiana Department of Environmental Quality, Quality Assurance/Quality Control Program Manual and in accordance with the respective EPA method. Standards used for daily calibration of GC/MS instrumentation are acquired from EPA.

Standards used for the Gemini System are obtained from Analytics, Inc. in Atlanta, Georgia, and are traceable to the National Institute of Standards Technology. The system is calibrated on a daily basis.

VII.C Results

VII.C.1 Organics

Concentrations of targeted volatile organics and polynuclear aromatic hydrocarbons found in oyster tissues placed at the Lirette, Bully Camp, Lake Washington, and Caillou Lake sites are presented on a wet weight basis in Table VII.2. Total tissue concentrations of volatiles ranged from 0.0 ppb at the Caillou Lake Reference site to 372 ppb at the Lirette site. Lake Washington oyster tissues had the lowest volatile concentrations of the 3 produced water discharge sites considered.

Benzene was detected at 2 of the 3 treatment sites while toluene and ethyl benzene were detected in tissues from all 3 treatment sites. Proportionately, toluene comprised the highest percentage of the targeted volatiles at each of the treatment stations.

Polynuclear aromatic hydrocarbons (PAHs) detected in tissues from *in situ* oyster experiments at each site are also presented in Table VII.2. Oyster tissues from the Lake Washington site contained the highest concentration of PAHs (319 ppb). Tissues from the Lirette site contained 41 ppb PAHs, the lowest concentrations detected in treatment site tissues. The Caillou Lake reference tissues contained trace quantities of pyrogenic PAHs. PAH results indicated as trace concentrations were qualitatively identified, but the peaks were quantitatively below detection limits.

Table VII.2. Volatile organics and polynuclear aromatic hydrocarbons in oyster tissues. Results reported in parts per billion (ppb) on a wet weight basis.

Compound	Lirette	Bully Camp	Lake Washington	Caillou Lake (Reference)
Volatile Organics (ppb)				
Benzene	66	7	ND	ND
Toluene	220	9	2	ND
Ethyl benzene	86	1	1	ND
Total Volatiles	372	17	3	ND
Polynuclear Aromatic Hydrocarbons (ppb)				
Naphthalene	ND	ND	ND	ND
C1-Naphthalenes	Trace	Trace	Trace	ND
C2-Naphthalenes	Trace	Trace	Trace	ND
C3-Naphthalenes	Trace	Trace	27	ND
Fluorene	ND	ND	ND	ND
Phenanthrene	Trace	28	66	ND
C1-Phenanthrenes	Trace	Trace	Trace	ND
C2-Phenanthrenes	ND	Trace	32	ND
C3-Phenanthrenes	ND	Trace	Trace	ND
Anthracene	ND	ND	ND	ND
Fluoranthene	Trace	41	37	Trace
Pyrene	22	61	46	Trace
Benzo(a)Anthracene	ND	Trace	ND	ND
Chrysene	ND	Trace	72	ND
Benzo(b)Fluoranthene	ND	ND	ND	ND
Benzo(k)Fluoranthene	ND	ND	ND	ND
Benzo(a)Pyrene	ND	ND	ND	ND
Total PAHs	22	130	280	Trace

ND = Not Detected

VII.C.2 Radium 226

Table VII.3 lists the results of oyster tissue Ra 226 activities. As indicated earlier, the distance at which the oysters were placed from the respective outfall varied from site to site. Caillou Lake was used as a control site.

Table VII.3. Oyster sample activities (wet wt.)

Site Location	Distance from outfall (meters)	Radium 226 Activity pCi/g ± 2 sigma error
Lirette Field	110	3.1 ± 0.3
Bully Camp	85	< LLD
Lake Washington	70	< LLD
Caillou Lake	Control	< LLD

NOTE: LLD denotes Lower Level of Detection.

The oysters placed at the reference site showed no activity above the detection limit of 0.0868 pCi/g. Oysters set at the Bully Camp and Lake Washington sites also did not accumulate any Ra 226 above detection limits (0.170 pCi/g and 0.169 pCi/g, respectively). Oyster samples from the Lirette site, however, indicated a Ra 226 activity of 3.1 ± 0.3 pCi/g.

VII.D Discussion and Conclusions

The radiological and chemical characterizations of effluents and sediments presented in Chapter IV and VI of this report demonstrate a considerable degree of radium 226 and hydrocarbon contamination associated with the produced water discharges investigated. The effects in these poorly flushed systems were most apparent in bottom sediments. The levels of contamination varied between study sites and among transect sample points at the same study site. Variations in contaminant levels among effluents and/or transect sample points is largely dependant on the treatment practices used by the production facility, the discharge volume, and the hydrography of the area.

Because of the chemical and physical variations discussed above it is not possible to fully explain the reasons for the hydrocarbon variations in oyster tissues between study sites. Also, the sample replication necessary for making statistically valid comparisons of tissue contaminants between sites was not part of this study component. However, the radiological and hydrocarbon data from the *in situ* experiments clearly demonstrated that oysters growing near produced water outfalls can accumulate radium 226, volatile aromatics, and polynuclear aromatic hydrocarbons in soft tissues within a relatively short time period (30 days).

Other investigators have demonstrated the potential for hydrocarbon accumulation by oysters from produced waters. Generally, the total PAH concentrations detected in tissues of oysters used in this study were less than the total PAH concentrations reported in tissues collected by Boesch *et al.* (1989). This was expected since the animals used in our study were exposed to produced water influences for only a 30 day period while the oysters analyzed by Boesch *et al.* (1989) were sampled from a natural population. Presumably the latter oysters were exposed to produced water influences for a longer period of time.

Evidence has been shown which indicates that sediment-bound hydrocarbons have an enhanced lethal and sublethal effect on *Crassostrea virginica* when compared to the effects of water soluble hydrocarbon exposure. Mahoney and Noyes (1982), used oil-clay mixtures of fuel oil and Nigerian crude oil of 0.50 ppm and 0.05 ppm in chronic exposure experiments. Significant mortalities occurred at both concentrations and significant decreases in survivor body weight and filtering activity were noted. As discussed by Mahoney and Noyes (1982) other exposure studies using only water soluble oil fractions at low concentrations showed no significant mortalities.

Most of the available literature on radium 226 uptake by bivalve mollusks pertains to effluents associated with uranium mining and milling activities. There is no available literature which focuses on radium 226 accumulation by oysters exposed to produced water discharges. Radium 226 activities were detected in only 1 of the 3 composited tissue samples from oysters deployed in areas receiving produced water discharges. Radium 226 activities, however, were detected at elevated levels in each of the 3 effluents and also within sediments where the oyster cages were placed. It is not completely clear whether radium accumulation by the Lirette oysters was from the sediments or from the water column. The sediments were observed to be quite mobile at the Lirette site, probably due to propeller wash from boats moving through this area or from strong outgoing tidal movements. The oyster trays at the Lirette site were noted to be covered with about 1.5 cm of silt at the time of retrieval. The oysters may have ingested radium contaminated sediment particles which could have accumulated in their digestive tract. The radium 226 accumulation differences between sites can not be conclusively explained. Environmental and physical conditions at each site varied considerably.

Past studies indicate that pumping rates of adult oysters exposed to hydrocarbons can decrease. Varying pumping rates between sites is one factor which may have influenced observed differences in radium 226 accumulation. Oysters at Lake Washington were closest to a produced water outfall and were deployed at a transect station which was among the highest in sediment hydrocarbon content. Oyster trays deployed at the Bully Camp site were slightly farther away, but were also in an area with a hydrocarbon sediment concentration which was much higher than the Lirette oyster station. It may be possible that a reduction in filtering rates in the Bully Camp and Lake Washington oysters may have been sufficient enough to inhibit an accumulation of radium 226 to levels above detection limits.

Several studies have shown that oysters can release accumulated hydrocarbons after exposure in contaminant-free water (Somerville *et al.*, 1987; Neff, 1988). Oysters are usually harvested directly, however, and are not depurated before being consumed. This must be considered when assessing the potential for human health risks associated with chemically contaminated shellfish.

The studies by Jeffree and Simpson (1986) related to the uptake of radium 226 by freshwater bivalves show that these organisms can readily accumulate these pollutants in a linear manner from water containing radium at levels which were much less than those measured in the four outfalls studied. A complete in-depth study would be needed to assess the full radiological impact of produced waters on oysters. Such a study is recommended since many of these discharges currently exist near commercial oyster harvesting areas.

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APPENDIX

Table A.1a. Hydrocarbon concentrations (ppb, dry wt.) in surface sediments from the Lirette (LRT) site.

	LRT-0 (0-5cm)	LRT-A100 (0-5cm)	LRT-A250 (0-5cm)	LRT-A500 (0-5cm)
Dry Weight (g)	4.3	3.4	3.4	4.7
MDL (ppb)	240	62	68	34
Naphthalene	860	nd	nd	nd
C1-Naphthalenes	5,300	nd	nd	nd
C2-Naphthalenes	45,000	90	nd	nd
C3-Naphthalenes	120,000	1,600	nd	nd
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	tr	nd	nd	nd
Fluorene	890	nd	nd	nd
Dibenzothiophene	290	nd	nd	nd
C1-Dibenzothiophenes	1,800	80	nd	nd
C2-Dibenzothiophenes	3,700	170	nd	nd
C3-Dibenzothiophenes	2,100	tr	tr	nd
Phenanthrene	1,700	nd	tr	nd
C1-Phenanthrenes	10,000	trc	nd	nd
C2-Phenanthrenes	9,200	300	tr	nd
C3-Phenanthrenes	3,000	170	tr	nd
Anthracene	tr	nd	nd	nd
Fluoranthene	2,200	200	81	trc
Pyrene	2,300	190	110	35
Benz(a)anthracene	890	nd	nd	nd
Chrysene	1,800	nd	nd	nd
Benzo(b&k)fluoranthene	840	nd	nd	nd
Benzo(a)pyrene	240	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parent PAHs	12,000	390	190	35
Total Homologs	200,000	2,400	tr	nd
Total PAHs + Homologs	210,000	2,800	190	35
FFPI	0.93	0.86	n/a	n/a
Saturated Hydrocarbons				
Resolved	11,000,000	140,000	11,000	840
Unresolved	29,000,000	650,000	180,000	17,000
Total	40,000,000	800,000	190,000	18,000
Resolved/Total	0.28	0.18	0.06	0.05
nC-17/Pristane	1.35	0.14	0.60	2.50
nC-18/Phytane	1.09	n/a	n/a	n/a
Pristane/Phytane	1.72	1.85	1.50	0.85

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.1b. Hydrocarbon concentrations (ppb, dry wt.) in surface sediments from the Lirette (LRT) site.

	LRT-B20 (0-5cm)	LRT-C50 (0-5cm)	LRT-C250 (0-5cm)	LRT-C325 (0-5cm)	LRT-R (0-5cm)
Dry Weight (g)	3.8	4.9	5.21	7.2	3.7
MDL (ppb)	53	33	33	50	40
Naphthalene	tr	nd	tr	nd	nd
C1-Naphthalenes	tr	nd	nd	nd	nd
C2-Naphthalenes	660	52	nd	nd	nd
C3-Naphthalenes	6,700	1,000	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd	nd
Acenaphthene	tr	tr	nd	nd	nd
Fluorene	tr	tr	nd	nd	nd
Dibenzothiophene	tr	36	nd	nd	nd
C1-Dibenzothiophenes	170	78	nd	nd	nd
C2-Dibenzothiophenes	400	240	nd	nd	nd
C3-Dibenzothiophenes	250	110	nd	tr	nd
Phenanthrene	tr	92	58	trc	tr
C1-Phenanthrenes	290	tr	tr	nd	nd
C2-Phenanthrenes	670	270	60	100	nd
C3-Phenanthrenes	180	140	tr	160	nd
Anthracene	tr	tr	tr	tr	nd
Fluoranthene	180	260	180	290	85
Pyrene	160	260	180	320	92
Benz(a)anthracene	nd	170	77	88	nd
Chrysene	87	230	290	170	nd
Benzo(b&k)fluoranthene	nd	400	200	220	nd
Benzo(a)pyrene	nd	160	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd
Total Parent PAHs	430	1,600	1,000	1,100	180
Total Homologs	9,300	1,900	60	260	nd
Total PAHs + Homologs	9,700	3,500	1,100	1,300	180
FFPI	0.94	0.56	0.08	0.19	n/a
Saturated Hydrocarbons					
Resolved	400,000	70,000	4,000	2,500	3,500
Unresolved	1,300,000	480,000	48,000	45,000	11,000
Total	1,700,000	550,000	52,000	47,000	14,000
Resolved/Total	0.24	0.13	0.08	0.05	0.25
nC-17/Pristane	0.03	0.31	0.93	1.24	3.08
nC-18/Phytane	0.04	0.11	0.30	n/a	n/a
Pristane/Phytane	1.71	1.58	1.47	1.12	1.19

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.2a. Hydrocarbon concentrations (ppb, dry wt.) in sediments at station DF-0.

	DF-0 (0-9cm)	DF-0 (9-18cm)	DF-0 (18-27cm)	DF-0 (27-30cm)
Dry Weight (g)	3.4	3.9	4.2	2.5
MDL (ppb)	150	120	98	51
Naphthalene	410	130	168	91
C1-Naphthalenes	5,000	5,200	11,000	2,100
C2-Naphthalenes	24,000	26,000	68,000	23,000
C3-Naphthalenes	79,000	78,000	160,000	79,000
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	220	220	220	870
Fluorene	890	850	1,400	1,600
Dibenzothiophene	390	430	710	210
C1-Dibenzothiophenes	2,500	2,600	4,300	2,800
C2-Dibenzothiophenes	3,300	2,800	6,800	4,100
C3-Dibenzothiophenes	2,100	1,900	4,900	2,800
Phenanthrene	3,300	3,500	7,100	4,900
C1-Phenanthrenes	10,200	9,800	22,000	11,000
C2-Phenanthrenes	12,000	12,000	18,000	9,300
C3-Phenanthrenes	4,800	5,000	7,200	4,200
Anthracene	240	250	230	540
Fluoranthene	850	820	690	1,600
Pyrene	860	840	680	1,200
Benz(a)anthracene	430	290	510	430
Chrysene	800	610	1,000	790
Benzo(b&k)fluoranthene	620	380	300	400
Benzo(a)pyrene	250	tr	nd	220
Indeno(1,2,3-cd)pyrene	nd	nd	nd	150
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	230
Total Parent PAHs	9,300	8,300	13,000	13,000
Total Homologs	140,000	140,000	300,000	140,000
Total PAHs + Homologs	150,000	150,000	320,000	150,000
FFPI	0.92	0.93	0.94	0.89
Saturated Hydrocarbons				
Resolved	2,300,000	1,800,000	2,200,000	470,000
Unresolved	4,100,000	6,500,000	9,700,000	2,200,000
Total	6,400,000	8,200,000	12,000,000	2,700,000
Resolved/Total	0.36	0.22	0.18	0.17
nC-17/Pristane	0.46	n/a	n/a	n/a
nC-18/Phytane	0.78	n/a	n/a	n/a
Pristane/Phytane	1.84	1.33	0.91	1.87

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.2b. Hydrocarbon concentrations (ppb, dry wt.) in sediments at station DF-C75.

	DF-C75 (0-9cm)	DF-C75 (9-18cm)	DF-C75 (18-25cm)	DF-C75 (25-28cm)
Dry Weight (g)	3.4	3.3	4.4	4.3
MDL (ppb)	79	69	75	76
Naphthalene	83	110	240	98
C1-Naphthalenes	410	390	270	210
C2-Naphthalenes	8,100	9,800	10,000	7,700
C3-Naphthalenes	36,000	35,000	37,000	29,000
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	350	1,300	2,100	660
Fluorene	610	1,400	2,000	750
Dibenzothiophene	130	200	200	160
C1-Dibenzothiophenes	1,110	1,200	1,400	1,100
C2-Dibenzothiophenes	2,300	2,100	2,100	1,800
C3-Dibenzothiophenes	1,300	1,400	1,200	1,100
Phenanthrene	1,300	4,600	6,400	1,900
C1-Phenanthrenes	5,100	5,300	6,000	4,100
C2-Phenanthrenes	5,200	5,000	6,100	4,000
C3-Phenanthrenes	2,400	2,400	2,400	2,100
Anthracene	210	680	1,200	240
Fluoranthene	700	2,800	4,000	1,100
Pyrene	550	2,000	2,800	830
Benz(a)anthracene	210	1,700	2,200	300
Chrysene	400	1,900	2,500	440
Benzo(b&k)fluoranthene	360	2,400	2,500	400
Benzo(a)pyrene	nd	1,400	1,300	210
Indeno(1,2,3-cd)pyrene	nd	690	1,200	nd
Dibenzo(a,h)anthracene	nd	250	250	nd
Benzo(g,h,i)perylene	nd	1,200	1,500	nd
Total Parent PAHs	4,900	23,000	30,000	7,100
Total Homologs	62,000	63,000	66,000	51,000
Total PAHs + Homologs	67,000	85,000	97,000	58,000
FFPI	0.90	0.73	0.69	0.86
Saturated Hydrocarbons				
Resolved	820,000	530,000	580,000	630,000
Unresolved	2,400,000	1,600,000	1,600,000	1,800,000
Total	3,200,000	2,100,000	2,200,000	2,400,000
Resolved/Total	0.26	0.25	0.26	0.26
nC-17/Pristane	0.10	0.08	n/a	n/a
nC-18/Phytane	n/a	n/a	n/a	n/a
Pristane/Phytane	1.38	2.06	2.10	1.49

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.2c. Hydrocarbon concentrations (ppb, dry wt.) in sediments at stations DF-A100 and DF-A200.

	DF-A100 (0-9cm)	DF-A100 (9-18cm)	DF-A100 (18-27cm)	DF-A100 (27-36cm)	DF-A200 (0-9cm)
Dry Weight (g)	2.7	3.6	4.5	4.1	3.7
MDL (ppb)	38	45	34	38	40
Naphthalene	110	96	38	tr	54
C1-Naphthalenes	590	670	227	210	150
C2-Naphthalenes	2,700	3,200	4,100	5,500	1,900
C3-Naphthalenes	13,000	13,000	24,000	29,000	13,000
Acenaphthylene	nd	nd	nd	nd	nd
Acenaphthene	48	70	130	180	86
Fluorene	240	210	330	430	240
Dibenzothiophene	68	65	69	59	58
C1-Dibenzothiophenes	540	700	730	710	510
C2-Dibenzothiophenes	1,100	1,100	950	1,100	820
C3-Dibenzothiophenes	990	990	520	670	590
Phenanthrene	490	570	780	1,100	430
C1-Phenanthrenes	1,800	1,800	2,200	2,700	1,300
C2-Phenanthrenes	2,400	2,600	2,600	3,100	2,000
C3-Phenanthrenes	1,400	1,400	1,100	1,300	930
Anthracene	70	61	78	100	89
Fluoranthene	410	370	340	420	390
Pyrene	370	350	290	350	320
Benz(a)anthracene	150	130	110	160	250
Chrysene	320	260	290	320	380
Benzo(b&k)fluoranthene	120	150	200	120	330
Benzo(a)pyrene	110	120	70	61	180
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd
Total Parent PAHs	2,500	2,500	2,700	3,300	2,800
Total Homologs	25,000	25,000	36,000	44,000	21,000
Total PAHs + Homologs	27,000	28,000	39,000	47,000	24,000
FFPI	0.89	0.90	0.91	0.91	0.87
Saturated Hydrocarbons					
Resolved	270,000	280,000	300,000	290,000	160,000
Unresolved	690,000	720,000	820,000	900,000	540,000
Total	960,000	1,000,000	1,100,000	1,200,000	700,000
Resolved/Total	0.28	0.28	0.27	0.24	0.23
nC-17/Pristane	0.44	0.24	n/a	n/a	0.07
nC-18/Phytane	0.56	0.30	n/a	n/a	n/a
Pristane/Phytane	1.27	1.37	1.54	1.71	1.54

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.2d. Hydrocarbon concentrations (ppb, dry wt.) in sediments at station DF-A300.

	DF-A300 (0-9cm)	DF-A300 (9-18cm)	DF-A300 (18-27cm)	DF-A300 (27-30cm)
Dry Weight (g)	4.2	3.8	4.5	4.3
MDL (ppb)	59	40	69	63
Naphthalene	tr	52	trc	tr
C1-Naphthalenes	66	150	78	89
C2-Naphthalenes	620	1,400	1,200	1,500
C3-Naphthalenes	3,100	9,600	6,500	9,300
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	tr	130	tr	tr
Fluorene	130	250	130	190
Dibenzothiophene	69	76	73	tr
C1-Dibenzothiophenes	230	530	480	650
C2-Dibenzothiophenes	290	770	740	960
C3-Dibenzothiophenes	370	570	460	900
Phenanthrene	150	450	270	740
C1-Phenanthrenes	590	1,200	1,000	2,000
C2-Phenanthrenes	730	2,000	2,000	2,600
C3-Phenanthrenes	500	790	870	1,200
Anthracene	tr	96	tr	68
Fluoranthene	240	410	320	400
Pyrene	230	300	290	400
Benz(a)anthracene	160	360	150	170
Chrysene	290	420	280	250
Benzo(b&k)fluoranthene	230	370	210	nd
Benzo(a)pyrene	170	320	73	nd
Indeno(1,2,3-cd)pyrene	nd	tr	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	tr	nd	nd
Total Parent PAHs	1,700	3,200	1,800	2,200
Total Homologs	6,500	17,000	13,000	19,000
Total PAHs + Homologs	8,200	20,000	15,000	21,000
FFPI	0.78	0.83	0.86	0.87
Saturated Hydrocarbons				
Resolved	55,000	120,000	190,000	230,000
Unresolved	300,000	520,000	630,000	680,000
Total	360,000	640,000	810,000	920,000
Resolved/Total	0.15	0.19	0.23	0.25
nC-17/Pristane	0.54	0.03	0.05	n/a
nC-18/Phytane	n/a	n/a	n/a	n/a
Pristane/Phytane	1.29	1.51	1.73	1.56

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.2e. Hydrocarbon concentrations (ppb, dry wt.) in sediments at Station DF-$B_1$200.

	DF-$B_1$200 (0-9cm)	DF-$B_1$200 (9-18cm)	DF-$B_1$200 (18-25cm)	DF-$B_1$200 (25-28cm)
Dry Weight (g)	3.5	3.9	4.5	4.2
MDL (ppb)	53	75	42	52
Naphthalene	120	tr	tr	tr
C1-Naphthalenes	740	86	trc	trc
C2-Naphthalenes	2,800	1,100	570	570
C3-Naphthalenes	12,000	7,000	3,300	3,000
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	40	tr	tr	tr
Fluorene	160	200	86	110
Dibenzothiophene	74	88	tr	tr
C1-Dibenzothiophenes	440	350	230	140
C2-Dibenzothiophenes	800	730	450	430
C3-Dibenzothiophenes	510	720	440	470
Phenanthrene	450	330	190	130
C1-Phenanthrenes	14,500	1,200	720	580
C2-Phenanthrenes	1,900	1,600	940	510
C3-Phenanthrenes	970	1,100	650	340
Anthracene	63	tr	tr	tr
Fluoranthene	190	310	210	200
Pyrene	190	300	260	190
Benz(a)anthracene	94	tr	59	trc
Chrysene	180	130	130	160
Benzo(b&k)fluoranthene	170	120	310	100
Benzo(a)pyrene	nd	nd	140	tr
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parents PAH	1,700	1,500	1,400	890
Total Homologs	35,000	14,000	7,300	6,000
Total PAHs + Homologs	36,000	15,000	8,700	6,900
FFPI	0.91	0.88	0.81	0.84
Saturated Hydrocarbons				
Resolved	430,000	97,000	77,000	67,000
Unresolved	770,000	450,000	360,000	340,000
Total	1,200,000	550,000	430,000	410,000
Resolved/Total	0.36	0.18	0.18	0.16
nC-17/Pristane	0.64	0.23	0.09	0.07
nC-18/Phytane	0.75	n/a	n/a	0.02
Pristane/Phytane	1.62	1.74	1.63	1.45

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.2f. Hydrocarbon concentrations (ppb, dry wt.) in sediments at station DF-$B_2$200.

	DF-$B_2$200 (0-9cm)	DF-$B_2$200 (9-18cm)	DF-$B_2$200 (18-25cm)	DF-$B_2$200 (25-27cm)
Dry Weight (g)	3.8	3.6	4.2	3.5
MDL (ppb)	52	36	42	47
Naphthalene	290	100	tr	54
C1-Naphthalenes	950	390	71	97
C2-Naphthalenes	2,900	1,800	1,400	2,800
C3-Naphthalenes	9,100	7,700	7,200	12,000
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	1,400	270	180	1,600
Fluorene	1,500	360	240	1,600
Dibenzothiophene	350	86	64	150
C1-Dibenzothiophenes	490	480	360	420
C2-Dibenzothiophenes	750	610	630	920
C3-Dibenzothiophenes	560	520	510	700
Phenanthrene	6,500	610	470	3,500
C1-Phenanthrenes	2,900	1,200	1,100	1,800
C2-Phenanthrenes	2,500	2,100	1,500	2,300
C3-Phenanthrenes	1,000	860	730	910
Anthracene	2,000	130	72	610
Fluoranthene	4,300	560	330	600
Pyrene	3,200	440	300	430
Benz(a)anthracene	2,700	190	150	130
Chrysene	2,700	290	260	150
Benzo(b&k)fluoranthene	3,800	250	140	230
Benzo(a)pyrene	2,300	150	81	84
Indeno(1,2,3-cd)pyrene	1,300	120	nd	nd
Dibenzo(a,h)anthracene	200	nd	nd	nd
Benzo(g,h,i)perylene	1,100	tr	nd	nd
Total Parent PAHs	34,000	3,600	2,300	9,100
Total Homologs	21,000	16,000	14,000	22,000
Total PAHs + Homologs	55,000	19,000	16,000	31,000
FFPI	0.43	0.81	0.84	0.74
Saturated Hydrocarbons				
Resolved	300,000	200,000	140,000	170,000
Unresolved	590,000	530,000	420,000	480,000
Total	880,000	740,000	560,000	650,000
Resolved/Total	0.34	0.27	0.25	0.26
nC-17/Pristane	0.62	0.35	0.07	0.05
nC-18/Phytane	0.71	0.32	n/a	n/a
Pristane/Phytane	1.83	1.67	1.74	1.74

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.2g. Hydrocarbon concentrations (ppb, dry wt.) in sediments at station DF-B$_2$300.

	DF-B$_2$300 (0-9cm)	DF-B$_2$300 (9-18cm)	DF-B$_2$300 (18-27cm)	DF-B$_2$300 (27-30cm)
Dry Weight (g)	3.3	3.9	4.0	4.2
MDL (ppb)	90	51	44	57
Naphthalene	tr	tr	tr	tr
C1-Naphthalenes	94	52	45	58
C2-Naphthalenes	510	520	490	1,500
C3-Naphthalenes	2,600	2,800	3,000	7,500
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	190	53	45	93
Fluorene	280	110	140	160
Dibenzothiophene	97	tr	68	59
C1-Dibenzothiophenes	140	200	210	400
C2-Dibenzothiophenes	440	380	380	540
C3-Dibenzothiophenes	350	370	400	350
Phenanthrene	1,100	250	230	320
C1-Phenanthrenes	1,100	650	500	970
C2-Phenanthrenes	1,500	980	800	1,300
C3-Phenanthrenes	1,000	470	510	580
Anthracene	330	58	73	76
Fluoranthene	1,700	280	230	220
Pyrene	1,400	290	210	230
Benz(a)anthracene	780	120	140	180
Chrysene	950	260	340	270
Benzo(b&k)fluoranthene	1,300	270	190	220
Benzo(a)pyrene	630	160	100	130
Indeno(1,2,3-cd)pyrene	370	nd	nd	nd
Dibenzo(a,h)anthracene	tr	nd	nd	nd
Benzo(g,h,i)perylene	410	nd	nd	nd
Total Parent PAHs	9,500	1,900	1,800	2,000
Total Homologs	7,700	6,400	6,300	13,000
Total PAHs + Homologs	17,000	8,300	8,100	15,000
FFPI	0.45	0.75	0.77	0.85
Saturate Hydrocarbons				
Resolved	76,000	64,000	52,000	160,000
Unresolved	350,000	290,000	340,000	490,000
Total	420,000	350,000	400,000	640,000
Resolved/Total	0.18	0.18	0.13	0.25
nC-17/Pristane	0.35	0.30	0.34	0.07
nC-18/Phytane	0.13	n/a	0.09	0.03
Pristane/Phytane	1.59	1.40	1.19	1.66

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.2h. Hydrocarbon concentrations (ppb, dry wt.) in sediments at Station DF-R.

	DF-R (0-9cm)	DF-R (9-18cm)	DF-R (18-27cm)	DF-R (27-30cm)
Dry Weight (g)	3.9	4.6	4.3	4.6
MDL (ppb)	44	43	46	40
Naphthalene	tr	tr	tr	tr
C1-Naphthalenes	tr	nd	tr	tr
C2-Naphthalenes	tr	tr	tr	46
C3-Naphthalenes	nd	nd	nd	390
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	tr	nd	nd	nd
Fluorene	trc	trc	trc	trc
Dibenzothiophene	nd	nd	nd	tr
C1-Dibenzothiophenes	tr	tr	tr	tr
C2-Dibenzothiophenes	tr	tr	tr	tr
C3-Dibenzothiophenes	tr	tr	tr	200
Phenanthrene	57	55	tr	53
C1-Phenanthrenes	tr	tr	tr	trc
C2-Phenanthrenes	220	170	240	220
C3-Phenanthrenes	99	120	130	210
Anthracene	tr	tr	tr	tr
Fluoranthene	110	83	120	110
Pyrene	130	110	120	130
Benz(a)anthracene	50	44	53	47
Chrysene	87	54	120	88
Benzo(b&k)fluoranthene	52	tr	120	56
Benzo(a)pyrene	tr	tr	tr	58
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parent PAHs	490	350	530	540
Total Homologs	320	300	370	1,100
Total PAHs + Homologs	810	640	900	1,600
FFPI	0.43	0.50	0.41	0.68
Saturated Hydrocarbons				
Resolved	14,000	9,300	10,000	14,000
Unresolved	98,000	77,000	150,000	180,000
Total	110,000	86,000	160,000	200,000
Resolved/Total	0.13	0.11	0.06	0.07
nC-17/Pristane	3.79	2.71	0.92	0.34
nC-18/Phytane	0.31	n/a	n/a	n/a
Pristane/Phytane	0.87	0.72	0.70	0.88

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.3a. Hydrocarbon concentrations (ppb, dry wt.) in surface sediments from the Bully Camp (BC) site.

	BC-0 (0-5cm)	BC-A50 (0-5cm)	BC-B50 (0-5cm)	BC-B100 (0-5cm)
Dry Weight (g)	4.1	3.5	3.4	3.4
MDL (ppb)	110	91	110	110
Naphthalene	tr	tr	tr	tr
C1-Naphthalenes	570	tr	480	tr
C2-Naphthalenes	11,000	2,800	12,000	3,700
C3-Naphthalenes	44,000	22,000	57,000	29,000
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	tr	tr	tr	tr
Fluorene	220	91	210	190
Dibenzothiophene	130	110	120	120
C1-Dibenzothiophenes	740	250	1,200	560
C2-Dibenzothiophenes	1,400	890	2,200	1,000
C3-Dibenzothiophenes	1,000	750	1,600	980
Phenanthrene	440	110	750	240
C1-Phenanthrenes	2,500	1,500	4,800	1,600
C2-Phenanthrenes	3,000	3,000	5,500	2,800
C3-Phenanthrenes	1,900	2,100	2,800	1,400
Anthracene	nd	tr	tr	tr
Fluoranthene	120	160	230	250
Pyrene	110	170	150	180
Benz(a)anthracene	210	110	150	160
Chrysene	320	180	220	190
Benzo(b&k)fluoranthene	nd	tr	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parent PAHs	1,600	930	1,800	1,300
Total Homologs	66,000	33,000	87,000	41,000
Total PAHs + Homologs	67,000	34,000	89,000	42,000
FFPI	0.96	0.96	0.96	0.96
Saturated Hydrocarbons				
Resolved	1,400,000	380,000	1,100,000	530,000
Unresolved	4,900,000	2,600,000	5,200,000	3,100,000
Total	6,400,000	3,000,000	6,300,000	3,700,000
Resolved/Total	0.22	0.13	0.17	0.14
nC-17/Pristane	0.22	0.33	0.21	n/a
nC-18/Phytane	0.25	n/a	n/a	n/a
Pristane/Phytane	2.11	1.25	1.55	1.31

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.3b. Hydrocarbon concentrations (ppb, dry wt.) in surface sediments from the Bully Camp (BC) site.

	BC-C50 (0-5cm)	BC-C100 (0-5cm)	BC-C$_1$300 (0-5cm)	BC-C$_2$300 (0-5cm)	BC-R (0-5cm)
Dry Weight (g)	4.3	4.1	3.3	4.0	3.4
MDL (ppb)	68	66	62	52	74
Naphthalene	tr	tr	nd	nd	nd
C1-Naphthalenes	390	trc	nd	nd	nd
C2-Naphthalenes	7,200	3,900	70	tr	nd
C3-Naphthalenes	38,000	26,000	1,300	930	nd
Acenaphthylene	nd	nd	nd	nd	nd
Acenaphthene	tr	tr	tr	nd	nd
Fluorene	160	130	63	tr	nd
Dibenzothiophene	73	tr	tr	nd	nd
C1-Dibenzothiophenes	620	540	77	70	nd
C2-Dibenzothiophenes	1,200	1,100	240	200	nd
C3-Dibenzothiophenes	890	1,000	330	270	nd
Phenanthrene	420	310	400	tr	nd
C1-Phenanthrenes	2,300	1,900	200	tr	nd
C2-Phenanthrenes	3,200	3,000	660	410	nd
C3-Phenanthrenes	1,800	1,700	390	290	nd
Anthracene	tr	tr	120	nd	nd
Fluoranthene	170	180	620	77	trc
Pyrene	160	160	450	73	tr
Benz(a)anthracene	180	100	380	81	nd
Chrysene	230	210	460	84	nd
Benzo(b&k)fluoranthene	nd	nd	580	nd	nd
Benzo(a)pyrene	nd	nd	320	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	tr	nd	nd
Dibenzo(a,h)anthracene	nd	nd	tr	nd	nd
Benzo(g,h,i)perylene	nd	nd	tr	nd	nd
Total Parent PAHs	1,400	1,100	3,400	320	tr
Total Homologs	56,000	39,000	3,300	2,200	nd
Total PAHs + Homologs	57,000	40,000	6,700	2,500	tr
FFPI	0.96	0.95	0.51	0.87	n/a
Saturated Hydrocarbons					
Resolved	670,000	430,000	11,000	23,000	3,900
Unresolved	3,700,000	2,500,000	230,000	280,000	62,000
Total	4,400,000	2,900,000	240,000	300,000	66,000
Resolved/Total	0.15	0.15	0.05	0.080	0.06
nC-17/Pristane	0.31	0.18	0.98	0.8	3.11
nC-18/Phytane	n/a	n/a	n/a	n/a	n/a
Pristane/Phytane	1.35	1.42	1.06	0.98	0.50

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.4a. Hydrocarbon concentrations (ppb, dry wt.) in surface sediments from the Lake Washington (LW) site.

	LW-0 (0-5cm)	LW-A50 (0-5cm)	LW-B50 (0-5cm)	LW-B150 (0-5cm)	LW-B350 (0-5cm)
Dry Weight (g)	4.2	3.3	4.0	4.3	4.3
MDL (ppb)	93	73	61	57	58
Naphthalene	1,500	80	92	nd	nd
C1-Naphthalenes	9,800	920	530	nd	nd
C2-Naphthalenes	70,000	6,300	6,700	470	nd
C3-Naphthalenes	220,000	22,000	32,000	5,100	nd
Acenaphthylene	nd	nd	nd	nd	nd
Acenaphthene	110	tr	tr	tr	nd
Fluorene	960	140	190	78	nd
Dibenzothiophene	1,200	120	180	tr	nd
C1-Dibenzothiophenes	6,000	730	1,100	96	nd
C2-Dibenzothiophenes	11,000	1,800	2,300	330	nd
C3-Dibenzothiophenes	6,900	1,200	1,500	420	nd
Phenanthrene	6,000	510	550	69	110
C1-Phenanthrenes	32,000	3,100	4,500	600	nd
C2-Phenanthrenes	31,000	4,600	5,200	770	tr
C3-Phenanthrenes	12,000	2,300	2,400	500	65
Anthracene	310	tr	tr	tr	97
Fluoranthene	320	200	140	130	300
Pyrene	370	160	110	100	270
Benz(a)anthracene	590	130	120	94	110
Chrysene	2,000	250	300	140	190
Benzo(b&k)fluoranthene	280	nd	130	nd	200
Benzo(a)pyrene	nd	nd	nd	nd	65
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd
Total Parent PAHs	14,000	1,600	1,800	610	1,300
Total Homologs	400,000	43,000	56,000	8,300	65
Total PAHs + Homologs	410,000	45,000	58,000	8,900	1,400
FFPI	0.94	0.94	0.94	0.90	0.09
Saturated Hydrocarbons					
Resolved	1,700,000	150,000	150,000	17,000	1,100
Unresolved	5,500,000	510,000	800,000	190,000	55,000
Total	7,200,000	660,000	950,000	200,000	56,000
Resolved/Total	0.24	0.23	0.16	0.09	0.02
nC-17/Pristane	0.93	0.87	0.27	0.35	1.89
nC-18/Phytane	0.91	0.97	0.34	0.25	0.47
Pristane/Phytane	1.64	1.79	1.59	1.75	1.34

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable

Table A.4b. Hydrocarbon concentrations (ppb, dry wt.) in surface sediments from the Lake Washington (LW) site.

	LW-C100 (0-5cm)	LW-$C_1$250 (0-5cm)	LW-$C_2$300 (0-5cm)	LW-R (0-5cm)
Dry Weight (g)	3.6	3.2	4.7	2.7
MDL (ppb)	83	73	63	120
Naphthalene	tr	nd	nd	nd
C1-Naphthalenes	190	nd	nd	nd
C2-Naphthalenes	2,100	nd	nd	nd
C3-Naphthalenes	25,000	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	tr	nd	nd	nd
Fluorene	tr	nd	nd	nd
Dibenzothiophene	130	nd	nd	nd
C1-Dibenzothiophenes	1,000	nd	nd	nd
C2-Dibenzothiophenes	2,000	nd	74	nd
C3-Dibenzothiophenes	1,100	tr	tr	nd
Phenanthrene	130	98	tr	nd
C1-Phenanthrenes	1,600	94	nd	nd
C2-Phenanthrenes	4,700	260	tr	nd
C3-Phenanthrenes	2,300	250	120	nd
Anthracene	tr	nd	nd	nd
Fluoranthene	170	160	190	trc
Pyrene	210	150	190	tr
Benz(a)anthracene	150	110	87	nd
Chrysene	270	110	150	nd
Benzo(b&k)fluoranthene	nd	nd	190	nd
Benzo(a)pyrene	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
Total Parent PAHs	1,100	630	810	tr
Total Homologs	40,000	600	190	nd
Total PAHs + Homologs	41,000	1,200	1,000	tr
FFPI	0.96	0.49	0.19	n/a
Saturated Hydrocarbons				
Resolved	67,000	4,300	3,000	2,700
Unresolved	620,000	59,000	72,000	24,000
Total	690,000	63,000	75,000	26,000
Resolved/Total	0.10	0.07	0.04	0.10
nC-17/Pristane	0.97	1.30	1.28	6.80
nC-18/Phytane	0.72	0.62	0.29	0.22
Pristane/Phytane	1.15	1.79	1.15	0.62

MDL: Minimum Detection Limit
nd: not detected
tr: trace; one ion present, but below detection limits
trc: trace confirmed; two ions present, but below detection limits
n/a: not applicable