

LOOP MARINE AND ESTUARINE MONITORING PROGRAM, 1978-95

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VOLUME 6: SEDIMENT QUALITY

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ABBREVIATIONS USED

Abbreviation	Meaning
AET	Apparent Effect Treshold
GC	Gas Chromatography
FID	Flame Ionized Detection
MS	Mass Spectroscopy
PAH	Polynuclear Aromatic Hydrocarbon
μg	Microgram
kg	Kilogram

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EXECUTIVE SUMMARY

Introduction

This report on Sediment Quality is the fifth component in a series of five reports that analyze the impacts of LOOP construction, operation, and maintenance on the estuarine/marine environment. Sediment samples were collected quarterly from 1979 through 1995 at designated stations near the LOOP offshore tanker unloading facility, the Clovelly salt dome storage facility, and along the pipeline route between these areas. Also, samples were collected at some support facilities such as the small boat facility (LOOP Diesel Dock) used in association with LOOP operations, other selected activity areas, canals and bayous in the area around the Clovelly storage facility and control areas.

For the greater LOOP monitoring effort, sediment, water, nekton, zooplankton, benthos, and climatological data were collected for numerous physical, chemical, and biological analyses for the following objectives: 1) establishing baseline conditions at the sampling stations, 2) determining what changes may occur seasonally and over longer time periods, and 3) having reference information to which future physical, chemical, and biological data collected in association with a spill could be compared for purposes of determining whether or not the coastal system was impacted and the degree of impact. The extended monitoring period from 1978 through 1995 should be sufficient to meet these objectives.

Each of the data sets have to be evaluated somewhat differently because of the nature of the systems being sampled. For example, fish populations may change seasonally, and there may be other factors contributing to long-term fluctuations in populations of some fish species attributable to natural causes or anthropogenic activities other than LOOP. The sediment data is somewhat simpler to evaluate from the perspective of seasonal effects. Seasonal changes are expected to be minimal for most parameters collected compared to biological measurements. Other factors, however, may make sediment sampling somewhat more complex. For example, storm currents may transport sediments and contaminants to or away from particular sampling stations; some small spills and contamination events can be so small that samples collected relatively short distances apart around a designated sampling station could be expected to show

very different levels of measured components contributing to considerable variability in the data. Degradation and burial by natural sedimentation are two processes that can also contribute to variability over time. Also, most contaminants are more strongly associated with or retained to fine-textured sediments (high clay content) than coarse textured sediments (sands). Thus, should major textural differences occur over short distances near sampling stations as a result of natural variability or storm events changing sediment textural conditions at a station over time, the retention and recovery of contaminants such as petroleum hydrocarbons would be affected and should be considered in evaluating the data.

Also, for the sediment quality data set, only spill events could affect or contribute to some of the parameters measured. For some of the other systems being monitored, both spills and other activities associated with LOOP might possibly cause measurable effects. Thus for the sediment quality evaluation, particular emphasis was placed on evaluating changes in sediment levels of petroleum hydrocarbons at stations in the vicinity of reported spills.

Methods

Methods for measuring petroleum hydrocarbons changed during the course of the LOOP monitoring effort. The early measurements of light oil, heavy oil, and condensate were reasonably state-of-the-art methods at the time this monitoring effort was being planned and implemented. However, as improved analytical methods became more available in later years, and because of increasing interest in the polynuclear aromatic hydrocarbons (PAHs) in petroleum, the decision was made to switch to more modern methods that were less susceptible to interferences, much more sensitive (greatly improved detection limits), and enabled the analysis of many individual PAHs with a high level of confidence in the analytical results. High resolution gas chromatography with flame ionization detection (GC/FID) was the primary analytical tool utilized from 1985 on where mass spectroscopy (GC/MS) was used for detection on selected samples for confirmation of the FID results.

Results

The light oil and heavy oil analyses used in the early years resulted in the reporting of much higher levels of petroleum hydrocarbons than the compound-specific analyses used in later years; thus these two data sets (early years and later years) are not compatible. This is likely due to the simultaneous extraction of non-petroleum organic humic materials from sediments. These humic materials generally contribute the high percentage of organic matter in typical fine textured sediments. Also, the primary reason for the incompatibility is that the light oil/heavy oil measurement is fundamentally different from the PAH analysis. Crude oil contains hundreds of individual petroleum compounds, and many are far more abundant than the PAH's. The light oil/heavy oil analysis is intended to extract all of these, including PAHs, which might make up a small part of the total. On the other hand, the PAH analysis focuses on relatively few of the persistent compounds commonly found in petroleum hydrocarbons that tend to be more toxic and more of an environmental problem in other ways than other classes of petroleum hydrocarbons.

The light oil and heavy oil data from the early years cannot be combined with the analytical data on individual PAH compounds collected in later years as these data sets are not compatible. Thus these data sets were analyzed separately to answer the pertinent questions on both an "early years" and "later years" basis. The light oil and heavy oil analyses were only available at most for the five years from 1979 through 1984, but for many stations, less than the full five years data were collected. The individual PAH compounds were measured more consistently for a ten-year period. Thus in the statistical evaluations of the Sediment Quality Data, both the light/heavy oil data and the "total" PAH data are presented and discussed, but it should be noted that they are respectively measuring very different components in petroleum hydrocarbons.

LOOP spill reports indicate most spills occurred in the Clovelly Storage Dome Facility and the Offshore Pumping Station. Two approaches were used to test for LOOP activity effects on petroleum hydrocarbon content in sediments. One was to look for differences in petroleum hydrocarbon levels in designated impact stations versus control stations where the test included looking for the effect of reported spills occurring during the months (two quarters) prior to the sampling quarter. This was done with the realization that due to degradation and other factors

(such as possible transport or burial processes), the effects of a spill are usually not permanent. Thus we looked for effects of reported spills close to the time when the spills occurred. The other approach was a simple comparison of petroleum hydrocarbon levels in sediments of potential impact stations versus controls. This was done because repeated spills or releases may contribute to some long-term elevation of petroleum hydrocarbons in sediments. Thus depending on the area possibly impacted by a spill and whether or not the nearest potential impact stations were truly affected, this presented another reasonable way of looking for impacts that the spill-association approach might miss.

Clovelly Dome Storage Facility

The data indicate that reported spills were significantly related to elevated sediment light oil concentrations within months of the spill during the early years and that considered over the entire early period when light oil was measured, the sediments at Clovelly contained significantly more light oil than control sediments. However, heavy oil at these potential impact stations was not significantly different at the five or one percent levels of significance, either in association with spills or when potentially impacted stations were compared to control sites over all the years these fractions were measured. For the period 1985-1995 when individual PAH compounds were measured, no significant spill effect was detected and the potentially impacted stations were not significantly different from the control stations. For these later years, the average and maximum levels of PAH compounds measured at the impact sites appear reasonably similar to the control sites.

Clovelly Area (canals and bayous leading away from the storage facility)

In the early years (1980-1984) when light oil and heavy oil were measured, and during the period 1985-1995 when individual PAH compounds were measured, there was no significant effect of reported spills in elevating petroleum hydrocarbons at potential impact sites versus control sites. However, long-term differences in levels at control and potential Clovelly area impact sites were shown to be significant for both heavy oil (early years) and total PAH compounds for the later years. It appears two of the eight Clovelly Area stations likely

contributed to the significant differences for PAHs.

Even though the impact sites are statistically elevated in PAHs, the data suggest the contamination is not substantial. Also, it should be noted that impacts in canals and bayous around Clovelly may or may not be due to LOOP activities as these are generally public waterways and contamination could have occurred from non-LOOP sources. Station 625 is an example where sediment contamination has apparently occurred due to non-LOOP boating activity.

Offshore Pumping Station

At the Offshore Pumping station where tankers transfer their load to the pipeline, there was a significant relationship between reported spills and sediment light oil content during the early years. A total of nine spills exceeding 500 gallons were reported for the period March 1982 through May of 1994. Heavy oil in the early years and total PAHs for the period 1985-1995 did not show a significant effect. When the potentially impacted station (station 481) was compared with the offshore controls over the entire early years (1980-1984) and later years (1985-1995), heavy oil at the impact site was significantly different from the control stations, but light oil for the early years and total PAHs for the last years were not significant. Thus the data for the Offshore station suggests that though some significant increases in petroleum hydrocarbons may have occurred, impacts are not long-lasting since no significant difference was noted for the period 1985-1995.

Brine Diffuser Outlet

The statistical results show no differences in oil associated with the sediments at the brine diffuser outlet during and after the major pumping for the excavation of the dome. Also, there was no significant difference in light and heavy oil between the diffuser stations and the control over the early years, nor between these stations from 1985 to 1995 when PAH compounds were measured. Thus there was no significant impact of the brine discharge on the petroleum hydrocarbon content of the sediments at the Brine Diffuser Outlet.

LOOP Diesel Dock

Stations near the LOOP Diesel Dock showed the highest amount of total PAH compounds of any stations associated with LOOP activities. The PAH levels were elevated not on just a few, but on very many of the sampling dates. Considering that the largest spills (a sum of over 100 gallons) occurred only in 1981, 1982, and 1992, and considering the fact that there is a lot of other boating activity (docks and other services for commercial and private vessels) in the immediate area, the significantly elevated levels of PAHs in the area of the LOOP Diesel Dock cannot be attributed to any one source. For example, the most contaminated station in the LOOP monitoring study in terms of average concentration of total PAHs was station 625 where heavy vessel traffic from non-LOOP activities apparently resulted in a unusually high PAH concentrations on several of the sampling dates.

Pore Water Salinity at the Brine Diffuser Facility

No statistical effect was seen of brine discharge on pore water salinity. A visual examination of the pore water salinity data indicate that fairly narrow ranges of salinity occurs at all offshore stations and the average of all the stations were near the same. The variability of the salinity data was much less than found for the petroleum hydrocarbon data.

Conclusions

Only the Offshore Pumping Station, the Clovelly Dome Storage facility, and, should a rupture occur, the area around the pipeline are likely to be impacted by LOOP activities. No leak from the pipeline has yet occurred. For both the Offshore Pumping Station and the Clovelly Dome Storage facility, a statistically significant increase in petroleum hydrocarbons in sediments was noted for the early years. No difference between potential impact sites and control sites were noted for the last ten years of monitoring. If impacts occurred, they are not long-lasting.

The sediments in canals around the Clovelly facility and the LOOP Diesel Dock area showed statistically significant increases in petroleum hydrocarbons. For these sampling stations in the area around Clovelly, the data suggest increased levels (which were modest) could have been due to non-LOOP activities since only a few stations, mostly public waterways some

distance away from Clovelly, showed these increases. The sediments near the LOOP Diesel Dock showed substantial, consistent elevations in PAH compounds relative to control sites. Again, however, extensive boating activities other than for LOOP are associated with this area, so it is not possible to identify the source.

No effect of brine discharge was seen on pore water salinity.

In conclusion, the data indicate that some modest, relatively short-term impacts have occurred in terms of petroleum hydrocarbon levels in sediments of sampling stations associated with the Offshore Pumping Station and the Clovelly Dome Storage facility. But it should be emphasized that the increases were modest and are not long-term. Where highest levels of petroleum hydrocarbons were found, boating and possibly other petroleum activities other than those associated with LOOP are likely contributing sources. The relative contribution from the various possible sources at these sites cannot be determined.

**DATA ANALYSIS OF THE
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INTRODUCTION

Louisiana Offshore Oil Port

The Louisiana Offshore Oil Port (LOOP) facilities in coastal Louisiana provide the United States with the country's only superport for off-loading deep draft tankers. The facilities are located in Lafourche Parish in southeast Louisiana, south of New Orleans and adjacent offshore waters west of the Mississippi River Delta. The development is operated by LOOP LLC., a private corporation owned by Shell Oil Company, Texaco Inc., Ashland Inc., Murphy Oil Corporation, and Marathon Pipeline Company.

LOOP INC., (later restructured as LOOP LLC.) was organized in 1972 as a consortium of companies to design, construct and operate a deepwater port on the Louisiana coast. Pre-permit baseline studies related to the proposed development were conducted from 1972 to 1975. Major documents related to these studies are listed in Table 1. State and federal licenses to own and operate a deepwater port were issued in January 1977, and accepted on August 1, 1977. The state license was issued to LOOP pursuant to the Louisiana Offshore Terminal Act (LA R.S. 34:3101 et seq.). A federal *License to Own, Construct and Operate a Deepwater Port* was issued to LOOP by the U.S. Department of Transportation (USDOT) pursuant to the federal Deepwater Ports Act (33 U.S.C. 1501, et seq.). The first oil tanker was offloaded on May 5, 1981.

Facility Description

The superport complex consists of an offshore marine terminal located about 30 kilometers (km) from the mainland in the Gulf of Mexico, an onshore storage facility at the Clovelly Storage Dome near Galliano about 50 km inland from the coast, and a large diameter pipeline system including the Fourchon Booster Station pumping facility near Fourchon to deliver oil to the storage facility. The pipeline system also connects the Clovelly Storage Dome oil storage facility to transportation facilities on the Mississippi River. A large brine storage reservoir (101 hectares) is positioned near the Clovelly Storage Dome. A small-boat harbor and logistics facility is located at Port Fourchon, on Bayou Lafourche.

The Offshore Terminal consists of three Single Point Mooring (SPM) structures connected by pipelines to a platform-mounted pumping station in the Gulf of Mexico, 30 km southeast of Belle Pass, Louisiana. Water depth at the platform is 36 meters. From the Offshore Terminal facility, crude oil is pumped northward through a large diameter (48 inch) buried pipeline, through the Fourchon Booster Station to the Clovelly Storage Dome complex near Galliano. The crude oil is stored in caverns constructed in subterranean salt domes. These storage chambers were formed by solution mining utilizing local surface water in the area. A second pipeline extends southward parallel to the oil pipeline and carries brine leached from the Clovelly Storage Dome to the Brine Diffuser brine disposal site located in open Gulf of Mexico waters approximately 4.8 km (3 mi.) offshore and adjacent to the LOOP oil pipeline. Additional distributary pipelines move oil from the Clovelly complex to outlying pipelines and refining centers.

Table 1. List of reports produced for superport planning (after Sasser et al. 1982).

Year	Title	Comment
1972	LOOP feasibility study	LOOP's Engineering Feasibility Study
1972	A Superport for Louisiana	Superport Task Force Report
1972	LSU Superport Study #1	Requested by Superport Task Force
1972	LSU Superport Study #2	Requested by National Sea Grant Program
1973	LSU Superport Study #3	Requested by LOTA to formulate EPP
1973	LSU Superport Study #4	Requested by LOTA to formulate EPP
1974	Alternate Site Location Evaluation	Prepared by Dames and Moore for LOOP, Inc.
1976	Environmental Baseline Studies Vols. 1B4	Prepared by LSU for LOOP, Inc.
1976	Environmental Impact Study	US Department of Transportation

Project Area

The Barataria estuary and the offshore area in which LOOP is located is an extremely diverse and complex natural system. It is located in the Mississippi River Deltaic Plain region. This region was formed and is continually influenced by processes associated with the deposition of massive amounts of sediments carried by the Mississippi River. The LOOP pipeline traverses the major wetland habitats in the Louisiana coastal area. The 159 km pipeline crosses the near-

offshore Gulf of Mexico, beach/barrier headland, and estuary. Within the estuary, four salinity zones--saline, brackish, intermediate and fresh--are traversed, each providing a unique habitat supporting a variety of species.

The coastal marshes of Louisiana are one of the most productive ecosystems in the world, supporting a wide variety of estuarine-dependent organisms. Louisiana leads fishery production within the northern Gulf of Mexico and is second only to Alaska among all states (NMFS 1997). Louisiana is the leader in the United States for the production of shrimp, blue crab, oyster, crawfish, tuna, red snapper, wild catfish, black drum, sea trout, and mullet (McKenzie et al. 1995). Ninety-five percent of the Louisiana fish and shellfish landings are estuarine-dependent species (McKenzie et al. 1995). The fish community of Barataria estuary is the most diverse of any estuary in Louisiana with 191 species from 68 families (Condrey et al. 1995).

Monitoring Program

In recognition of the potential for significant environmental impacts much attention was given to environmental safeguards by state and federal agencies and by the superport developers (see review by Sasser et al. 1982). Because of the potential risks associated with the construction and operation of the superport (e.g. bringing the world's largest oil tankers to one of the most productive fisheries resources in the world), both state and federal licenses required environmental monitoring of LOOP construction and operational activities. The environmental monitoring program (EMP) was developed under mandate of the Superport Environmental Protection Plan (revised, 1977), a regulation of the State of Louisiana implementing the Offshore Terminal Act. Components of the estuarine/marine monitoring program include: water chemistry, physical hydrography, brine discharge, zooplankton/ichthyoplankton, demersal nekton, benthos, and sediment quality. The Louisiana Department of Wildlife and Fisheries collected the data related to these components from 1978 to 1995. Vegetation and wildlife components were monitored by LSU (see Visser et al. 1996 and references therein). This report is the sediment quality component in a series of five reports that analyze the impacts of LOOP construction, operation, and maintenance on the estuarine/marine environment. These five

reports analyzed the following components: 1) Water Chemistry, 2) Physical Hydrography, 3) Zooplankton / Ichthyoplankton, 4) Demersal Nekton, and 5) Sediment Quality.

OBJECTIVES

The EMP (section 3.1, page 8, March 1986) lists the objectives of the monitoring program as:

- (1) to obtain seasonal environmental and ecological data so that conditions existing during operation can be related to historical baseline conditions;
- (2) to detect during the operation of the project any adverse alterations or damages to the environment so that corrective action can be taken as soon as possible;
- (3) to obtain sufficient data to determine the cause or causes of environmental damages or alterations so that responsibility can be properly placed; and
- (4) to provide information in order to evaluate long- and short-term impacts of the project.

The general goal of our data analysis program was to analyze and report on the LOOP Marine/Estuarine environmental monitoring data collected from 1978-1995, with respect to the EMP objectives.

LITERATURE REVIEW

General Information

The term petroleum hydrocarbons includes oil and grease, polynuclear aromatic hydrocarbons (PAHs), and aliphatic (non aromatic) hydrocarbons. The aliphatic hydrocarbons have not received as much environmental attention as they tend to be less toxic and less persistent than the aromatic hydrocarbon compounds. The major distinction between oil and grease and PAHs is the analytical methods used for analysis. An oil and grease analysis includes a solvent extraction but not a compound-specific analysis. The solvent is effective in extracting petroleum hydrocarbons, but other materials may be extracted as well such as sulfur and some of the naturally occurring sediment humic material. Often a gravimetric analysis of the extracted sample after evaporation of the solvent is the method of analysis. An infrared analysis to quantify functional groups associated with oil is another method of analysis. Both detection methods are not compound specific and are subject to interferences, but this approach was commonly used, especially the 1980s, because of a lack of widespread availability of better methods. An analysis for many of the particular polynuclear aromatic hydrocarbons and other hydrocarbons in environmental samples is the preferred approach in recent years as there is less chance of interference by non-petroleum hydrocarbon substances.

PAHs are part of the petroleum hydrocarbon group, and their environmental chemistry differs substantially from polychlorinated biphenyls (PCBs) and most pesticides (Tatem 1990). Tatem cites their presence in various environmental components at low levels due to natural deposits, normal oil drilling operations, and as a result of dispersion in the atmosphere from fires and fossil fuel combustion. Unlike PCBs and other non-polar chlorinated hydrocarbon compounds which exhibit similar solubilities and lipid partitioning properties within a fairly narrow range, the approximately 40 or so PAH compounds found in sediments have a wide range of toxicity, solubility, and potential for bioaccumulation.

Clark and Gibson (1987) reported discussions in a three-day workshop on the identification of petroleum hydrocarbons in sediments and dredged material. The list of compounds selected for consideration were 15 priority pollutant PAHs that included:

acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, phenanthrene, and pyrene. This list is very similar to the suite of compounds used for monitoring of LOOP environmental impacts since 1985.

Levels of Petroleum Hydrocarbons Reported in Sediments

Boehm and Fiest (1983) identified about 15 individual PAH compounds associated with dredged material in the New York Bight at levels from less than one to about seven parts per million (micrograms per gram).

Creosote is a mixture of primarily PAH compounds derived from coal tar. In a field study of a waterway in Louisiana more than a decade after a major creosote spill occurred in which sediments became highly contaminated, light oily sheens on water were still observed in the area under normal conditions, and minor disturbance of the sediment such as pushing a boat paddle into the mud released creosote from the sediment that floated to the surface giving a strong oily sheen on the water (Catallo and Gambrell 1987). In the immediate vicinity of the spill, concentrations of naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(j)fluoranthene/benzo(k)fluoranthene, and benzo(a)pyrene ranged from 600 to 29,000 ug/g (parts per million).

Short and Heintz (1997) working with the identification of Exxon Valdez oil in sediments and tissues from Prince William Sound reported that natural seeps contribute to total PAH concentrations that rarely exceed 100 ng/g (parts per billion) in intertidal sediments and 200 ng/g (parts per billion) in subtidal sediments in the spill area.

Biological Availability

Petroleum hydrocarbons include a wide range of compounds with differing toxicities, and, pertaining to mobility, they exhibit a wide range of solubilities. Thus it is not possible to generalize as a class concerning their mobility and bioaccumulation potential. Considering this and the interaction of their range of properties with the range of properties of sediments, dredged

material, marsh soils, and particular biological populations, it is expected that some studies will show release and toxicity of these compounds associated with sediments (Pequegnat et al. 1978) and other studies will not (Hirsch et al. 1978; DiSalvo et al. 1977).

In a study of laboratory tests for predicting field bioaccumulation of contaminants, PCBs were reported to give the best results, but the PAH results were less consistent, possibly due to more rapid degradation of many of the PAHs and a wider range of degradation rates for this class of compounds compared to the PCBs (Lake et al. 1987).

Gentile et al. (1988) showed the higher molecular weight PAHs were not taken up as well by mussels as the lower molecular weight compounds. They also reported that worms (*N. virens*) exposed to Black Rock Harbor sediment accumulated PAHs orders of magnitude higher than control worms, but, unlike what was observed for PCBs, the levels of PAHs fell rapidly during depuration. PAHs were said to have a greater range of physical and chemical properties than PCBs and to be metabolized more rapidly, thus PAH accumulation can be more difficult to predict. Nelson et al. (1987) supports this by noting tissue concentration and exposure levels for PCBs in blue mussel agree well, but this is not the case for the lower molecular weight PAHs. They mention excretion and metabolism as possible factors in the difference in tissue levels of the two materials, but differences in solubility may be a factor as well.

Clarke and McFarland (1991) point out that fish tend to have a higher capacity for breaking down PAH compounds than do some invertebrates and amphipods, thus this needs to be considered in selecting appropriate organisms for bioassays.

In general, it has been reported that binding and bioconcentration increase as solubility decreases (hydrophobicity increases), and that dissolved compounds are more available than PAHs bound to the sediment solid phase (Clark and Gibson 1987).

The above discussion focuses on aromatic hydrocarbons. There are other classes of hydrocarbons that may contaminate sediments, but, except in cases of major spills, these are not as much concern as the aromatics (Landrum's comments in workshop, Clark and Gibson 1987). Phenols are a class of hydrocarbons that may contaminate sediments, but their relatively high solubility and degradation rate compared to PAHs contribute to their rarely being a problem in sediments and dredged materials. Similarly, aliphatic hydrocarbons associated with oil spills

may be toxic at sufficiently high concentrations (approaching saturation in water for the higher molecular weight compounds), but, at moderate levels, they are not expected to be toxic in sediments and dredged materials. Many monoaromatics (eg., benzene and toluene) are very toxic, but they are somewhat volatile and soluble compared to the PAHs and are rarely a problem except for major spills (comments of Landrum in Clark and Gibson 1987).

Creosote is derived from coal tar and has a very high concentration of PAHs which make it effective as a biocide for preserving wood where it is commonly used for treating utility poles, railroad crossties, and marine pilings. As reported elsewhere in this review, Catallo and Gambrell (1987) found levels of individual PAH compounds ranging from 600 to 29,000 ug/g (parts per million) in sediments more than a decade after a major creosote spill. Microbial and benthic animal populations were greatly reduced at this site.

In an interim report on the Times Beach confined disposal area which included aquatic, wetland, and upland placement of contaminated dredged material and contaminant measurements in all of these zones, PAHs were below detection limits in vertebrate top predators, but fish were believed to have accumulated some in the aquatic portion of the disposal site (Stafford et al. 1991).

Simmers et al. (1989), reviewing the work of other investigators, indicated some PAH compounds may be taken up by plant roots, but most of what researchers label as uptake is probably atmospheric deposition. Working with *Spartina alterniflora* and sediments and dredged materials in particular, Folsom (1982) and Folsom and Preston (1986) saw no evidence of PAH uptake.

Pyrene and benzo(a)pyrene (PAH compounds) were found to be more bioavailable to worms under open marsh conditions relative to wooded uplands at the Times Beach experimental dredged material disposal site (Cromartie and Simmers 1985). The authors did not offer an explanation, but as suggested for PCBs, differences in degradation rates may have played a role in how much was present in the dredged material at the time of the uptake studies.

In a study of hydrocarbon degradation and changes in toxicity in a silty loamy soil under presumably aerobic conditions, 50-75 percent of the hydrocarbons degraded from the low organic matter (0.3%) soils and 10-90 percent of the hydrocarbons degraded from the high organic matter

(4.7%) soil in about three to four months. Artificial weathering of the petroleum hydrocarbon amended soils showed that after a period of bioremediation (normal microbial activity), the toxicity and leachability of aromatic hydrocarbons were greatly reduced even though 1,000 to 8,600 ug/g (parts per million) of residual petroleum hydrocarbons remained in the soil (Salanitro et al. 1997).

Chemistry

In contaminated sediments, the concentrations of oil and grease would be expected to often greatly exceed the levels of toxic synthetic organics and toxic metals. There were early concerns about oil and grease causing sediments to accumulate more of the toxic metals and synthetic organic materials than would accumulate in sediments uncontaminated with oil and grease, and, subsequently facilitating their biological exposure and uptake. Some of the work done in the 1970s indicated this is not a problem because sediment-bound petroleum hydrocarbons may act as a solvent more effectively immobilizing chlorinated hydrocarbons with the solid phase (Brannon 1978). Other early studies indicated that petroleum hydrocarbons, if released, do not mobilize trace metals or synthetic organics (Lu et al. 1978; Blum et al. 1976).

Clarke and McFarland (1991) pointed out that sediments usually do not have very high oil and grease levels. But, where they do, they cited the work of Boyd and Sun where discrete droplets or tar balls may form which act like humic materials in partitioning toxic synthetic organics and may do so more effectively than typical humic material. This was said to reduce bioavailability of other organic chemicals, but again, it may be that especially high levels of oil and grease contamination are necessary to result in this effect.

Except for a very thin surface layer (3 mm to 2 cm), flooded soils and sediments are predominately anaerobic where the chemistry and microbial processes affecting contaminants such as petroleum hydrocarbons are very different from what occurs in upland soils or surface sediments. Gambrell et al. (1978) cited a few studies indicating little effect of redox conditions on degradation or greater degradation under reducing conditions. However, at the time of that report, and more recently, the majority of data indicate petroleum hydrocarbons and PAHs degrade more quickly under aerobic rather than anaerobic conditions (Gunnison et al. 1989;

DeLaune et al. 1981; DeLaune et al, 1990; Hambrick et al. 1980).

Though it is established that PAHs degrade much slower in anaerobic sediment, it is important to note that upon initial association with sediments, PAHs are going to be associated with the thin surface oxidized sediment layer. Thus initial degradation of many compounds may be more rapid than will occur later as the sedimentation process continues and surface sediments eventually become buried and anaerobic.

At the Times Beach experimental dredged material disposal site where equivalent concentrations of petroleum hydrocarbon-contaminated sediment were placed in different redox environments, higher levels of PAHs were found in the marsh environment compared to the upland placement site (Cromartie and Simmers 1985). Within the upland site, more was found in shaded areas. This probably reflects the influence of dredged material physicochemical conditions under different drainage conditions on degradation and shade effects on volatilization.

PAHs have been reported to cross the air-water interface in both directions, depending on water and air temperature, rainfall events, and periods of dry weather (Gustafson and Dickhut 1997).

Pyrene, a PAH compound, has been shown to be strongly bound to aquatic (soluble) humic substances where increasing aromatic content and molecular weight of the humic substances are associated with increased binding strength (Chin et al. 1997). This tends to enhance soluble levels of normally hydrophobic PAH compounds. As is the case with most contaminants, PAHs in the environment tend to be retained more strongly by soils and sediments with higher organic matter content and higher clay content (Wilcke et al. 1996)

There is much evidence that aged PAH-sediment associations result in strong binding of the PAHs to the point that degradation is limited by the slow desorption process. This would predominate where fine textured sediments contain substantial natural organic matter levels (Carmichael et al. 1997).

Mobilization of Petroleum Hydrocarbons from Bottom Sediments

Where toxicity of petroleum hydrocarbons does occur, its association with sediments tends to reduce the toxicity relative to that released into the water column (DiSalvo et al. 1977). The

work cited above shows that the degradation rate is slower in anaerobic sediments. Thus in undisturbed anaerobic sediment, petroleum hydrocarbons may persist for extended periods, but they tend to be effectively immobilized and should not be a problem except for the possibility of burrowing benthic organisms. As an example of the stronger association of hydrophobic organics to fine-textured materials over coarse materials, Brannon et al. (1985) noted that a five-cm fine-textured New Haven Harbor sediment and a Vicksburg (MS) silt were more effective in immobilizing PAHs than a five-cm sand cap.

In a field study of a waterway in Louisiana more than a decade after a major creosote spill occurred and the sediments became highly contaminated, oily sheens on water were still observed in the area under normal conditions and minor disturbance of the sediment released materials that floated to the surface giving a strong oily sheen (Catallo and Gambrell 1987). However, as reported elsewhere in this review, concentrations of PAHs were excessively high. At background levels or moderate contamination levels, significant release to soluble forms by disturbance of the sediment should not occur (see next section).

Contaminated Sediments and Surface Water Quality

In an earlier review on this topic, Gambrell et al. (1978) reported that monitoring of subaqueous dredged material disposal sites has shown that petroleum hydrocarbons sometimes are found to exceed water quality criteria, but this occurs on a short-term basis and the released compounds are mostly associated with suspended particulates. Petroleum hydrocarbons do not pose a long-term threat to surface waters because of several processes at work. These include primarily the strong association of these compounds with the solid phase (Van Vleet and Quinn 1977; DiSalvo et al 1977) and subsequent settling of suspended particulates over the short-term. Volatilization, photo degradation, and greater microbial degradation in surface waters than sediments also contributes to reduced water column impacts.

In early work, Lee et al. (1977) and DiSalvo et al. (1977) found releases in sediment elutriate tests to be very low, something noted even with very oily sediments (Engineering Science 1977), and, again, where some release was noted, it was associated with suspended particulates. Boehm and Fiest (1983) reported hydrocarbons associated with dredged materials

are altered rapidly in the water column by dissolution and microbial degradation and that monitoring PAH levels was a sensitive indicator for following dredged material plumes. Thus except during periods when contaminated sediments are disturbed, release of PAHs to the overlying water column should not be a major problem in open water systems.

In a previous report on disposal alternatives for contaminated dredged materials, Gambrell et al. (1978) pointed out that total petroleum hydrocarbons in effluents from confined disposal facilities often exceeded criteria, but that soluble levels were below criteria.

Fate of PAHs Under Upland Conditions - Degradation, Atmospheric Deposition, and Mobilization by Leaching

Though atmospheric deposition from off-site sources may account for PAHs found associated with plant materials, the amount deposited to land and water surfaces by atmospheric deposition is believed to be insignificant (Brannon et al. 1990).

In a study that included leachate prediction as part of an evaluation of contaminated sediment disposal alternatives, Palermo et al. (1989) examined 33 organic contaminants and only 8 were released in measurable amounts with all of these being near detection limits. Except for PCBs, no other organics were consistently found in column or batch leach tests. In permeameter leaching tests of this material, leachate concentrations of PAHs were below detection limits for both aerobic and anaerobic columns.

Under upland conditions where drainage and soil oxidation occur, and, where pH is not strongly acid or is managed to prevent development of strongly acid conditions, degradation of petroleum hydrocarbons should occur at a more rapid rate than in the original contaminated sediment material or under conditions of subaqueous disposal.

At the Times Beach contaminated dredged material disposal site, it was observed that PAHs are gradually disappearing from the upland disposal site. This has important management implications. Mechanisms believed to be contributing to this loss were volatilization and degradation (Stafford et al. 1991).

Mobilization by Surface Runoff

Though most of the discussion focused on metals released by surface runoff tests, Palermo et al. (1989) mentioned that in simulating placement in an upland confined disposal facility for contaminated dredged material, the primary initial problem is a high concentration of suspended, anaerobic sediment particles present in the early runoff events. Apparently, this decreases with time, but the higher the humic material content, the more likely it was for the surface to remain fluffy longer; and the loss of suspended solids remains high for a longer period of time. Obviously, these processes would contribute to enhanced loss of petroleum hydrocarbons associated with suspended particulates. Thus it would be anticipated that early runoff events may show elevated total loss of petroleum hydrocarbons and PAHs, but as drainage and oxidation occur and particulate runoff decreases, surface runoff losses should substantially decrease as a result of microbial degradation, photo degradation, and volatilization.

It should be noted that Palermo et al. (1989) were referring to a confined contaminated dredged material disposal facility filled by pumping the dredged material into the containment facility as a slurry. This will usually not apply to an upland spill associated with LOOP activities where the spill would likely be on consolidated, vegetated soil. This information from Palermo et al.'s experience with confined disposal facilities would only apply to a scenario where a LOOP spill contaminated a sediment and might be dredged and placed in an upland confinement facility as part of a cleanup effort. Where LOOP spills might occur in an upland environment, the runoff will predominantly be oil subject to gravity flow since upland soils and marsh soils would be stable. Once gravity flow ends, the long-term situation should be the same as Palermo et al. (1989) reported for effluents from confined dredged material disposal sites. That is, that in situ microbial degradation, photo degradation, and volatilization should maintain predominancy in the long term over continued loss by surface runoff.

Sediment Quality Criteria for Petroleum Hydrocarbons for Determining the Degree of Contamination or Environmental Risk

For at least a couple of decades, scientists and regulatory agencies have wanted precise sediment contamination guidelines to assist in identifying contaminated sites and the risks associated with

contamination. Over the years, such guidelines have been proposed and published for metals, synthetic organics, and petroleum hydrocarbons, including PAHs. For the LOOP monitoring effort, such a criteria, if it were valid, would obviously be useful in identifying the extent of impacts associated with spills, the effectiveness of cleanup efforts, and the time it takes for contamination levels to return to background levels by natural processes.

Proposed criteria has been presented, but it is arguably not exact. The purpose in presenting these early criterion is just to show some general, non-quantitative comparison of PAH levels found in the LOOP monitoring effort with levels some have perceived to be a problem.

In a review of the literature on the biological consequences of bioaccumulation of toxic materials, Dillon (1984) concluded that aquatic animals were more sensitive to chlorinated organic compounds than to petroleum hydrocarbons and that metals generally were intermediate. Again, however, this must be considered in terms of the relative concentrations of contaminants in different classes.

As stated elsewhere in this document, a broadly applicable national sediment criteria for identifying contaminated sediments does not exist. However, to get a qualitative feel for relative toxicities, it might be instructive to examine reports on relative toxicities of contaminants based on a specific study site and on a report that makes an attempt to define what the authors consider to be high levels of contamination. With this qualifier, it may be useful to compare the "apparent effects threshold" for toxicity and benthic effects reported by Krull et al. ([1988) for contaminated sediments in Commencement Bay, Washington. Table 2 below is adapted from their Table 2. A similar data set has been reported by Long and Morgan (1990) in association with the NOAA National Status and Trends Program (Table 3).

In Tables 2 and 3, it is seen that for "Low Molecular Weight" and "High Molecular Weight" aromatics, "Oil and Grease," and "Total PAHs," those developing these data at that time thought that: 1) the petroleum hydrocarbon compounds were substantially less toxic at equivalent concentrations than most other contaminants and 2) petroleum hydrocarbons in sediments do not contribute to adverse biological effects at below part per million (ug/g or mg/kg) levels.

Table 2. Apparent effect threshold (AET) for selected contaminants and sediment properties reported on a dry weight basis (adapted from Krull et al. (1988)).

Contaminant	Units	Toxicity AET	Benthic Effects AET
Antimony	mg/kg	5.3	3.1
Arsenic	mg/kg	93	85
Cadmium	mg/kg	5.8	5.8
Copper	mg/kg	310	310
Lead	mg/kg	660	660
Mercury	mg/kg	0.59	0.52
Nickel	mg/kg	39	39
Zinc	mg/kg	490	260
Phenol	µg/kg	420	1,200
2-methylphenol	µg/kg	63	72
4-methylphenol	µg/kg	670	670
LMW aromatics	µg/kg	5,200	5,200
HMW aromatics	µg/kg	12,000	17,000
Chlorinated benzenes	µg/kg	270	400
Chlorinated butadienes	µg/kg	>47,000	>47,000
Total phthalates	µg/kg	3,400	5,200
Total PCBs	µg/kg	420	1,100
Benzyl alcohol	µg/kg	130	130
Dibenzofuran	µg/kg	540	540
n-Nitrosodiphenylamine	µg/kg	28	28
Tetrachloroethene	µg/kg	140	140
Ethylbenzene	µg/kg	37	37
Total xylenes	µg/kg	120	120
Oil and grease	mg/kg	2,200	4,300
Total volatile solids	%	22.2	22.2
Total organic carbon	%	15.1	15.1
Nitrogen	%	0.28	0.28

Table 3. Dry weight concentrations of selected sediment-sorbed metals and organic compounds that may possibly have a biological effect (adapted from Long and Morgan 1990).

Substance	Units	Concentration Possibly Contributing to Biological Effects
Cadmium	mg/kg	9
Chromium	mg/kg	145
Copper	mg/kg	390
Lead	mg/kg	110
Mercury	mg/kg	1.3
Silver	mg/kg	2.2
Zinc	mg/kg	270
total DDTs	µg/kg	350
total PAHs	µg/kg	35,000
total PCBs	µg/kg	400

However, information such as this should be used with much caution as there are a number of factors affecting the mobility and biological availability of contaminants and the subject of sediment criteria is far from being developed as a reliable and meaningful tool to be universally applied. It has been reported many times that, with the possible exception of some neutral chlorinated hydrocarbon compounds, bulk sediment concentrations appear to have little relationship to biological effects in site to site comparisons (Gambrell and Patrick 1978; Gambrell and Patrick 1991 ([unpublished report])).

While the data for toxic organic's apparent effects thresholds is an interesting comparison, the differential degradation and transport properties of these compounds and classes of compounds in different soil and sediment environments makes it difficult to use data like these for evaluating disposal options for contaminated sediment or risk of particular levels of contamination in different settings. These data may be an indication of relative toxicities for a number of compounds or classes of contaminants compared in a study conducted the same way. Data such as these do reinforce the point that measurable levels of some contaminants, and even

what is considered relatively high concentrations of some contaminants, do not necessarily mean sediments will cause adverse environmental problems.

Quality Criteria for sediments for most contaminants are not as well developed as water quality criteria (drinking water and aquatic life water quality criteria). However, for comparison purposes, published or recommended criteria will be used for comparing the LOOP sediment levels of petroleum hydrocarbons. One such source is from Sauer and Boehm (1991) where it is stated that "The desired detection limits in sediment and tissue samples are ten ng/g for individual VAH (sediment only) and PAH compounds, 0.1 µg/g for individual saturated hydrocarbons, and ten µg/g for total hydrocarbons." This report goes on to say that the method detection limits of EPA Method 8270 (approximately 100 ng/g) for individual PAHs in sediments is about an order of magnitude greater than desirable for scientifically defensible studies.

Nearly 20 years ago, Gambrell et al. (1978) stated that concentrations of various classes of contaminants does not always directly relate to toxicity or ecological problems. Contamination needs to be considered with the properties of the soil or sediment-water system in question because many contaminants can be effectively immobilized and made non-toxic by some sediments. Alternatively, the same concentration in other soils and sediments could be mobile and toxic. The degree of problem is determined by a combination of factors that includes:

- a. the particular contaminants present and their chemical form,
- b. the amounts of contaminants present,
- c. possible interactions between contaminants (mixture effects),
- d. the physical and chemical properties of the original sediment and dredged material if contaminated sediment is removed and placed in a different environment, subsequent to disposal,
- e. the biological populations exposed, and
- f. the fate (environmental chemistry and transport processes) of contaminants under different sediment or dredged material disposal environments.

Charles Henry of the Institute for Environmental Studies at Louisiana State University is recognized as an international expert on petroleum hydrocarbons. He believes that no simple numeric quality criteria would be valid for evaluating the risks associated with contamination by oil and that spills and contamination levels must be evaluated on a case-by-case basis (C. Henry, personal communication, December, 1997).

Renner (1997) reported early this year that within a month the EPA's Science Advisory Board would begin review of a proposal for assessing sediment contamination from chemical mixtures in fresh and estuarine water and the marine environment. The importance of sediment quality criteria for PAHs was acknowledged to affect a wide range of regulatory decisions including permits for industrial discharges, dredging permits, and Superfund cleanups. It was pointed out that currently there are no national guidelines relating particular concentrations of contaminants to adverse effects. Renner reports that a few states and federal programs have adopted their own guidelines using a variety of empirical and theoretical approaches, but if the EPA should adopt guidelines these states and agencies would have to use the EPA's criteria as a minimum.

It is believed the new proposed criteria may be a substantial improvement over earlier versions. The new proposal is based on equilibrium partitioning theory (as were previously proposed sediment quality criteria), but, in addition, it utilizes recent research and considers mixtures of contaminants (especially PAHs) present which recent theoretical and experimental data support. However much improved over previously proposed guidelines, there is still widespread concern that this approach to establishing criteria or guidelines may be used too strictly as a pass-fail criteria for different purposes (dredging and disposal of contaminated sediments, for example), when perhaps all contaminated sediment problems should still have some site-specific evaluation.

Thus the above brief discussion of the history of sediment quality criteria and the most recent version and its current evaluation by the EPA explains why we are reluctant to set or accept a PAH contamination level, or different levels, and categorize the relative degree of risks associated with sediment concentration levels at this time. Perhaps in the not to distant future this will be possible.

Petroleum Hydrocarbons, Oil and Grease, PAHs: Summary

Chlorinated hydrocarbons and PAHs are usually the major concern of the organic compounds contaminating sediments. Unlike PCBs and most of the problem chlorinated hydrocarbon pesticides found in sediments, different petroleum hydrocarbon compounds (including PAHs) exhibit a wide range of toxicity, solubility, and potential for bioaccumulation. Thus in evaluating the potential problems of contaminated sediment, it may be important to consider the particular PAH compounds present and their relative levels. Modern analysis methods for individual PAH compounds make this possible for most environmental analyses done during the last ten years or so. PAHs tend to be more persistent under anaerobic sediment or dredged material conditions and degrade reasonably fast under upland conditions (except for the very slow degradation of PAHs with five or more rings). The compounds in this class that most frequently are found in dredged material that do not degrade readily under reducing sediment conditions, tend to be effectively immobilized in reducing sediments and dredged materials. Under conditions where these compounds may be released into water during sediment disturbance, volatilization, photo degradation, and increased microbial degradation tends to reduce water column impacts.

Regarding leaching of this class of compounds in upland environments, the soluble members tend not to be a problem, and reports indicate leaching under upland conditions is very minimal (usually found to be near or below detection limits). Surface runoff would not be a long-term problem after contamination of an upland site. Soon after upland application of dredged material while it is unconsolidated, losses may be expected which are associated with runoff of contaminated, suspended particulates. After a short period of time, photo degradation, volatilization, and low loss of particulates should result in very low losses of this class of compounds by surface runoff. Except for major spills, the compounds in this group that represent potential problems tend to be persistent but immobile in reducing sediments and dredged materials. PAH compounds dissolved in water (very low solubility for most) or associated with suspended particulates, and those associated with the surface oxidized sediment layer should degrade more quickly than PAH compounds that persist in sediment until they are buried in anaerobic sediment depths. Some benthic animals in direct contact with the material

can accumulate these compounds. Leaching and plant uptake are not problems.

While development of good sediment quality criteria may not be too far off in the future, at this time, broadly applicable criteria for identifying levels of PAHs in sediments that represent a threshold above which adverse environmental impacts may occur are not available.

METHODS

Field Sampling and Lab Analyses

Sample Collection

For all LOOP inshore sediment quality stations, samples were collected with a hand-held plastic core barrel (Barrett type) attached to a PVC coring head equipped with a one-way ball valve. An approximately 30 to 45 cm core section was collected by direct insertion of the coring device. For water depths of less than three meters, galvanized pipe was used to guide the core barrel. For deeper, offshore stations a box core was taken with a Smith-McIntire sampler where the top 15 cm of the core was recovered and processed for selected chemical and physical constituents. Each core was transported and stored upright to prevent mixing the profile of soft sediments. As described elsewhere, one core was used for petroleum hydrocarbons, and the other was used for all other sediment parameters measured.

From 1978-1984, there was a random sample design for core collection. Three cores were taken at each station, then at every fifth station, five cores were collected. Sediment pH was measured in the field using the slurry method on cores to be analyzed for grain size and salinity.

Sample Processing

From 1985-1995, two cores were taken at each sediment station. Upon return to the laboratory, the top ten cm of each core was extruded onto a clean Formica tray. One core (A) was processed for hydrocarbon analysis, and the other (B) for all other sediment measurements. The A core was either processed immediately for hydrocarbon analysis or stored at 4 °C in a plastic bag until extracted. Core B was split vertically with one portion dried overnight (or until all moisture was removed) at 105 °C, then ground with a mortar and pestle and sieved to pass a 100 mesh screen. All bulk sediment analyses were performed on this dried portion. The other part of the split core B was pressed to remove interstitial water for analysis of chloride content and other constituents.

Laboratory Analysis

Figure 1 is a time line for the laboratory methods used for sediment quality monitoring for the LOOP study from 1978 through 1995.

Total Organic Carbon

From 1978 through 1987, total organic carbon was measured by acidifying wet sediment samples by placing the samples in 50 percent HCl for 12-18 hours to remove inorganic carbon (carbonates). The acidified samples were filtered through a glass fiber filter and rinsed with distilled water until all HCl was removed. The residue was dried at 70°C overnight. Then, a sample of approximately 0.25 grams was weighted out for analysis on a LECO radiofrequency inductively coupled furnace which oxidized the carbon to carbon dioxide, which was then routed to a gasometric analyzer where the results reported as percent C. The method is described in a letter dated 18 November 1982 from Woodward-Clyde Consultants to Mr. Tim Morrison of Louisiana Wildlife and Fisheries.

Light Oil and Heavy Oil

The method for light oil and heavy oil was adopted from Whelan (1977) and is described in a letter dated 18 November 1982 from Woodward-Clyde Consultants to Mr. Tim Morrison of Louisiana Wildlife and Fisheries. A 100 ml volume of wet sediment was mixed with 150 ml of water and 350 ml of spectroquality hexane. The mixture was homogenized on a wrist-action shaker, the solvent and water phases separated, and an aliquot of the hexane extract analyzed with a Perkin-Elmer 204A Fluorescence Spectrophotometer. The samples were excited at 265 nm and the emission wavelength scanned from 250 to 450 nm. Light Oil was quantified at 310 nm and Heavy Oil quantified at 365 nm using a sample of South Louisiana Crude Oil provided by the US EPA as a standard. Results were reported in parts per million on a wet weight basis.

Salinity

From 1978 to 1987, the method used for salinity was described in a letter dated 18 November 1982 from Woodward-Clyde Consultants to Mr. Tim Morrison of Louisiana Wildlife

Grain Size Analysis	PAH Analysis
1978 - 1995: Folk sieve method(sand) and Folk pipette method(silt and clay) (Folk, 1974)	1978 - Fall, 1984 : Oil and Grease
	Fall, 1984 - Fall, 1986: HPLC
	Fall, 1986 - Summer, 1987: GC/MS ¹
	Summer, 1987 - Spring, 1995: GC/FID ²
	Spring, 1990 - 1995: GC/MS ²

¹ For some samples, but levels were below detectable limits.

² Most samples analyzed by GC/FID, with two/quarter and any unusual samples being run also on GC/MS for comparison, or identification of unknown FID peaks.

PAH Extraction	PAH Extraction Laboratories
1978 - Winter, 1987: Tumbled	Fall, 1981 - Spring, 1982: Carbon Systems, Inc.
Winter, 1987 - 1990: Sonicated	Spring, 1982 - Winter, 1982: Woodward-Clyde Consultants
1990 - 1995: Tumbled	Winter, 1982 - Winter, 1987: LSU Coastal Ecology Institute
	Winter, 1987 - Winter, 1991: LSU Institute for Environmental Studies
	Winter, 1991 - 1995: LSU Veterinary Medicine (same personnel as for 1987 - 1995)

Figure 1. Sediment Laboratory Methods Time Line (courtesy LDWF)

and Fisheries. Using the method reported by Kalil and Goldbaker (1973), sediment samples were pressed to squeeze out interstitial water. An aliquot of the interstitial water was analyzed for chloride using a modified argentometric method found in Standard Methods (Method #408A, 1975). The modifications reported were: using one ml of sample, a final volume of 30 ml, preparing a solution of 3.5 g K_2CrO_4 /liter of water, and preparing a 0.0675 N $AgNO_3$ solution. From chloride, porewater salinity in parts per thousand was calculated from the following equation:

$$\text{Salinity}_{ppt} = 0.03 + 1.80655 (\text{Cl}_{ppt})$$

Because it was discovered in January of 1984 that the bottom water salinity was different from pore water salinity, the bottom water overlying the sediment cores was decanted or siphoned off in the field before transported back to the laboratory. From 1987 to 1995, the sample was centrifuged to remove pore water which was then analyzed by a chloridometer.

Clay

The Folk pipette method (Folk 1968) was used for measuring clay content of the sediment samples for the period 1978 through 1995. There are many different methods for measuring clay content, and, different disciplines define the clay-sized fraction of soils and sediments separately. But, because of the importance of the clay-size fraction in retaining contaminants of all types, it was good that one method was used for the duration of the monitoring effort.

Individual PAH Compound Extraction and Analysis

The samples were solvent extracted by mechanical mixing or “tumbling” the sediment while in solvent until the winter of 1987, and then extracted by “tumbling” again from 1990 to 1995. Sonication was used to extract the PAH compounds into the organic solvent instead of tumbling from the winter of 1987 through 1989. This is where an ultrasonic probe is placed in a

vessel containing sediment and the extraction solvent, and sonification results in the efficient release of the PAHs from the solid phase to the solvent phase.

The Sediment Laboratory Methods Time Line (Figure 1) indicates from late 1984 to late 1986, HPLC (high performance liquid chromatography) was the analytical tool for individual PAH compounds. Very little measurable PAH data was reported during this period. The time line indicates that gas chromatography with flame ionization detection (GC/FID) was the primary analytical instrumentation used from the summer of 1987 through 1995. Gas chromatography with mass spectrometry (GC/MS) for detection and identification was used on selected samples as a primary analytical tool for PAH analysis from the fall of 1986 through the summer of 1987, then used as the confirmation analysis method from the summer of 1987 through the end of the monitoring in 1995.

Quality Assurance and Quality Control

Sediment data were provided to LSU by LDWF and consisted of several data sets that are described in the data assessment report (Sasser and Visser 1997). Two substantially different methods for measuring petroleum hydrocarbons were used during the 17-year period (see Figure 1). The change to more modern analytical methods as they become available justifies this major change.

A number of different labs, personnel, and instrumentation were used for analyzing a suite of specific PAH compounds associated with oil activities during the last 13 years of data collection. The personnel involved and methods used indicate reliable data were collected. An examination of the data over time for specific sampling locations indicates that the data do display some variability. This variability, however, seems reasonable for the type of data that was generated.

All data obtained from LDWF was transformed so that variables were reported in a consistent manner (all PAH compounds were transformed to a dry weight basis) after which they were combined into one SAS dataset.

Statistical Analysis

Due to the late starting date for the sediment monitoring component, insufficient data were available to evaluate construction impacts. Brine impacts could only be evaluated with a “during and after” comparison, because insufficient data from before the start of the brine discharge were available. Impact analyses were focused on the most sensitive parameters in the dataset. These variables are the following:

1. Interstitial salinity

This variable was measured consistently throughout the period of study.

Analyses using this variable therefore, were performed on the whole data record.

2. Light oil and heavy oil

These variables were measured from 1978 to 1984.

3. PAH

To improve consistency among the different laboratory analyses, this variable was modified to include the sum of the compounds given below. This modification was made because, although most of the individual PAH compounds analyzed in the 1985 - 1989 period were the same as those measured during the 1990 - 1995 period, there were some differences. Therefore, we selected 10 of the compounds common to both periods that appeared most often and summed the concentrations of these in both datasets to give a modified total PAH variable that improved the consistency over the 1985 to 1995 period. The 10 compounds included were:

fluorene, phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene, indenopyrene, dibenz(a,h)anthracene, and benzo(g,h)perylene.

4. Percentage clay in the sediment sample was used as a co-variable in all impact analyses on oil variables.

For each test, different parts of the dataset were analyzed. A summary of stations used for each impact evaluated is provided in Table 4.

Table 4. Summary of statistical techniques used to investigate possible impacts of LOOP. Listed for each potential impact type, is the variable evaluated, the time period over which the analysis was performed, the LDWF station used in the analysis, and the type of analysis. The stations are classified either as control, low impact, or high impact stations.

Impact	Variable	Time Period	Control	Low Impact	High Impact	Statistical Tests
Brine Discharge	Salinity	79-95	435		473 474	BACI Model
	Light Oil	79-84	435		475	
	Heavy Oil					
Oil Spills						
Clovelly Dome	Light Oil	79-84	610	461	463	ANOVA
	Heavy Oil	79-84	612	464	605	
	PAH	85-95	613	601	606	
			623	602		
			624	604	607	
				608 609		
Fourchon Diesel Dock	Light Oil	79-84	619		617	ANOVA
	Heavy Oil	79-84	620		618	
	PAH	85-95	621 622			
Offshore Terminal	Light Oil	79-84	482		481	ANOVA
	Heavy Oil	79-84	484			
	PAH	85-95				

Selection of Sampling Stations to Include in the Evaluation

Generally, sampling stations numbered below 400 were sampled for such a short period (many for only one date) that they were not included in the data set. Samples in the 400 series (numbered between 400 and 500) were part of the benthic sampling program, but for some of these stations, data were also collected for the sediment quality monitoring as well. It is reported

that sediment quality data were collected as well. Samples in the 600 series were taken specifically for sediment quality monitoring.

From the various data sets described elsewhere, we consolidated all the field variables of interest into one data set for the data evaluation process. This was done for all of the samples in the 400 and 600 series of samples.

Spill reports showed that most of the oil spills occurred at the Clovelly Storage Dome site and the Offshore Terminal. Far fewer spills (for example, less than ten spills of 25 gallons or more) were reported for the Small Boat Harbor and only a few spills at other sites.

No oil should have been associated with the brine pumped out as the dome was being formed by leaching of salt with nearby surface waters prior to oil being stored. Once the oil storage cavern in the salt dome was formed and made operational, water from a pond at the facility was pumped into the storage dome as the oil was pumped out. Similarly, this water would be removed and stored in ponds as more oil was put back into the dome. There is no reason to believe substantial oil amounts would be in the brine discharge associated with normal oil pumping into and out of the salt dome cavern. Some oil could, however, get mixed with water during the routine operation of the storage dome, and as a result, this effect was analyzed.

The stations were grouped into the following categories:

Clovelly: High Potential for Impact

These stations were very near the Clovelly Storage Dome activities and were within the containment area.

Clovelly Area: Low Potential for Impact

These stations were located on canals and bayous outside of the containment area where distance from the Clovelly Storage Dome ranged from perhaps a few hundred meters to several kilometers. The intent was to have a group of stations where a major spill at the Clovelly facility might impact sediments in waterways for some distance away from the spill site.

Onshore Control Stations

In order not to bias the statistical analysis, inland sites that were remote from specific LOOP activities were grouped and designated as controls, rather than examining the analytical data for each and then deciding if it should be a control. Seven stations seemed to fit this designation. However, there is an inherent risk in this approach. A major or even small spill, or chronic small releases associated from non-LOOP petroleum activities could easily contribute to substantial elevation of petroleum hydrocarbons in sediments at what would otherwise appear to be a good control station. Thus it seemed reasonable after the initial statistical evaluation of the data to carefully look at the petroleum levels in the controls with the plan to discard perhaps one, but no more than two of the originally designated inshore control stations if Light Oil, Heavy Oil, or modified total PAH levels in one or two were excessively high.

An evaluation of the control sites originally selected by the LSU author showed several had one or two substantially elevated petroleum hydrocarbon levels with clearly the majority of the values being relatively low (Table 5). After consulting with Louisiana Wildlife and Fisheries (LWF) personnel, the LSU author learned that station 625 should never have been considered a control station because it was known to be in a heavy boat traffic area. Also, stations 630 and 631 were removed from the inland control group by LWF personnel most knowledgeable about these stations. Table 5 gives general information about the PAH concentrations in the control groups. Though removed from the statistical evaluation, stations 625, 630, and 631 remain in this table for visual comparison purposes and to illustrate that control stations cannot simply be selected from maps, but that first-hand, site-specific information must be considered as well.

Brine Diffuser

Three stations near the Brine Diffuser were clearly intended to measure potential impacts associated with brine release. Oil spills should not occur at this facility since only brine was being released as the dome was being constructed.

Because there may be some possibility, however, for some of the water used to pump or “lift” oil out of the storage dome that has been in contact with oil to be released into the brine

Table 5. Average and maximum PAH values (from modified totals) in first round of selecting designated inshore control stations, brine diffuser control stations, and offshore control stations ($\mu\text{g}/\text{kg}$).

Station	Overall Mean PAH value & (# of values in mean)	Mean PAH excluding highest two values	Highest value	Second highest value
<i>Inshore Controls</i>				
610	81 (32)	69	274	251
612	887 (27)	202	11,493	7,125
613	572(9)	213	3,511	147
623	264 (28)	215	1,020	790
624	108 (17)	46	785	360
625	5,214 (18)	378	61,950	25,845
630	65 (25)	46	342	230
631	68 (13)	47	250	108
<i>Offshore Control</i>				
482	132 (29)	58	2,090	162
484	29 (24)	20	145	97
<i>Brine Diffuser Control</i>				
435	40 (27)	102	458	310

pipeline, it was decided to include the brine diffuser outlet in the statistical analysis for oil impacts even though no impact was expected.

Brine Diffuser Control

This station was clearly intended for a control station for the Brine Diffuser. It was several kilometers away from the brine outlet and approximately the same distance from shore.

Offshore Terminal

There was only one sediment station in the area of the offshore terminal.

Offshore Control

Two stations were identified as intended offshore control stations.

LOOP Diesel Dock

Two sediment stations were located very close to the LOOP Diesel Dock. However, the LOOP Diesel Dock was not the only activity in this area that may have contributed to petroleum hydrocarbons being released to accumulate in sediments. In the surrounding area were mooring docks, docks for loading or off loading cargo, and fueling facilities for other boating activities.

Selection of Spill Events to Include in Evaluation

Just over 320 spill events were reported related to LOOP covering the period from the fall of 1980 to late 1995. The reported volume of these spills ranged from less than one gallon to a maximum of 21,000 gallons.

The impact of an oil spill would depend on several factors. One factor would be whether the spill occurred inland versus offshore. A moderate spill on land, or in an inland waterway, would likely have more of an impact where the spill is more confined and surrounded by land than the same spill if it occurred offshore where more rapid dispersion would occur. The U.S. Coast Guard/USEPA categorizes spill sizes in terms of potential impact as shown in Table 6.

Initially, a spill level of 500 or more gallons was arbitrarily selected as the criteria for looking for elevated petroleum hydrocarbons levels in sediments. Out of the just over 320 reported spills, there were 19 spills reported to exceed 500 gallons (Table 7). The 500 gallon threshold was considered in discussing the data where the possible impact of spill events on sediment hydrocarbon levels was examined. However, in the statistical analysis testing for spill effects on hydrocarbon levels in sediments, all reported spills for the two quarters preceding a sampling event were included in the model.

Table 6. US Coast Guard / USEPA Oil Spill Designations.

Spill Category	Range of spill barrels (gallons)		Location
Minor	< 24	(1,008)	Inland
Minor	< 240	(10,080)	Offshore
Moderate	24 - 240	(1,008 - 10,080)	Inland
Moderate	240 - 2,400	(10,080 - 100,800)	Offshore
Major	> 240	(10,080)	Inland
Major	> 2,400	(100,800)	Offshore

Table 7. Reported Spill Events Exceeding 500 Gallons.

Date	Amount (gallons)	General Location	Nearest Sampling Station
2 June 1982	515	Inshore, Clovelly	463, 605, 606
9 June 1983	630	Inshore, Clovelly	463, 605, 606
30 June 1983	1,400	Inshore, Clovelly	463, 605, 606
17 February 1985	500	Inshore, Clovelly	463, 605, 606
2 July 1987	672	Inshore, Clovelly	463, 605, 606
6 February 1994	1,470	Inshore, Clovelly	463, 605, 606
5 May 1992	630	LOOP Diesel Dock	617, 618
26 March 1982	1,600	Offshore Pumping Facility	481
28 March 1982	1,260	Offshore Pumping Facility	481
20 June 1982	630	Offshore Pump. Fac. (SPM 102)	481
1 September 1982	1,260	Offshore Pumping Facility	481
1 February 1983	504	Offshore Pump. Fac. (SPM 103)	481
2 April 1983	16,758	Offshore Pump. Fac. (SPM 104)	481
10 December 1983	1,470	Offshore Pumping Facility	481
22 May 1984	7,350	Offshore Pumping Facility	481
24 May 1984	7,350	Offshore Pumping Facility	481
21 October 1985	21,000	Offshore Pumping Facility	481
26 July 1989	2,940	Offshore Pump. Fac. (SPM104)	481
31 March 1990	2,940	Offshore Pump. Fac. (SPM 103)	481

RESULTS AND DISCUSSION

Approach for Evaluating Sediment Data

Emphasis was given to levels of selected PAH compounds at stations designated as either impact or control stations and whether or not statistically significant differences in sediment levels of these compounds existed. As described in the methods section, we developed a modified total PAH concentration value for the statistical comparisons for the 1985-1989 and the 1990-1995 data sets where individual PAH compounds were reported. Both of these data sets included their own total concentrations which consist of the sum of the individually measured PAH compounds. However, since there were some differences in the individual compounds measured in the different data sets, a modified total was developed that was the sum of selected compounds reported in both data sets (the sum of the concentration of ten PAH compounds common to both data sets).

Prior to evaluating the data, the stations were grouped as described under "METHODS" based on location (near a LOOP activity, or far away and presumed intended for a control station). The questions asked for a statistical analysis included:

1. Is there a difference in petroleum hydrocarbon contamination between the designated potential impact sites and control sites?
2. Have reported spills contributed to an increase in petroleum hydrocarbons in the designated potential impact sites?
3. Have the LOOP Diesel Dock area sediments been contaminated with petroleum hydrocarbons?
4. Is there an effect of sediment clay content on the amount of petroleum hydrocarbons measured in control sites?
5. Did extended discharge of a large volume of brine at the Brine Diffuser Outlet increase pore water salinity in this area?

Data Evaluation

Table 8 presents a statistical evaluation of whether or not sediment impacts occurred at the major LOOP activity areas in terms of accumulation of petroleum hydrocarbons.

Methods for measuring petroleum hydrocarbons changed during the course of the LOOP monitoring effort. The early measurements of light oil, heavy oil, and condensate were reasonably state-of-the-art methods at the time this monitoring effort was being planned and implemented. However, as better methods became more available in later years, the decision was made to switch to a more modern method that was less susceptible to interferences, much more sensitive (greatly improved detection limits), and enabled the analysis of many individual polynuclear aromatic hydrocarbons (PAHs) with a greater level of confidence in the analytical results.

The light oil and heavy oil analyses used in the early years apparently resulted in reporting of much higher levels of petroleum hydrocarbons than the compound-specific analyses used in later years. This is likely due to some extraction of non-petroleum organic humic materials from sediments that typically have several percent organic matter.

The light oil and heavy oil data from the early years cannot be combined with the analytical data on individual PAH compounds collected in later years as these data sets are not compatible. Thus statistical analyses for petroleum hydrocarbons was done by keeping these data sets separate and using the statistical models to answer the pertinent questions on both an “early years” and “later years” basis. The PAH data sets are definitely more accurate, but we feel that the light oil and heavy oil data, while likely reporting concentrations that may be higher than actual, may provide useful information on relative hydrocarbon levels in the different station groupings used in this evaluation. The light oil and heavy oil analyses were only available for the at most for the five years from 1979 to 1984, but for many stations, less than five full years of data were collected. The individual PAH compounds were measured more consistently for a ten-year period. Thus in the statistical evaluations of the Sediment Quality Data, both the light/heavy oil data and the “total” PAH data are presented and discussed, but perhaps more emphasis should be given to the PAH data set.

Table 8. Probability of significant differences in petroleum hydrocarbon content of sediments in potential impact versus control areas: a) within 6 months of reported spills, or, b) over all years.

Location	Period	Impact Potential	Impact after Spill, or, Pot. Impact vs. Control over all years	Light or Heavy Oil, or PAH	Pr>F
Clovelly	80-84	High	6 months after spill	Light Oil	0.03
Clovelly	80-84	High	6 months after spill	Heavy Oil	0.08
Clovelly	85-95	High	6 months after spill	Total PAHs	0.42
Clovelly	80-84	High	Pot. Impact vs. Control	Light Oil	0.01
Clovelly	80-84	High	Pot. Impact vs. Control	Heavy Oil	0.50
Clovelly	85-95	High	Pot. Impact vs. Control	Total PAHs	0.20
Clovelly area	80-84	Low	6 months after spill	Light Oil	0.94
Clovelly area	80-84	Low	6 months after spill	Heavy Oil	0.67
Clovelly area	85-95	Low	6 months after spill	Total PAHs	0.57
Clovelly area	80-84	Low	Pot. Impact vs. Control	Light Oil	0.99
Clovelly area	80-84	Low	Pot. Impact vs. Control	Heavy Oil	0.002
Clovelly area	85-95	Low	Pot. Impact vs. Control	Total PAHs	0.047
Offshore	80-84	High	6 months after spill	Light Oil	0.03
Offshore	80-84	High	6 months after spill	Heavy Oil	0.61
Offshore	85-95	High	6 months after spill	Total PAHs	0.31
Offshore	80-84	High	Pot. Impact vs. Control	Light Oil	0.23
Offshore	80-84	High	Pot. Impact vs. Control	Heavy Oil	0.01
Offshore	85-95	High	Pot. Impact vs. Control	Total PAHs	0.20
Brine Outlet	80-84	Low	Pot. Impact vs. Control	Light Oil	0.06
Brine Outlet	80-84	Low	Pot. Impact vs. Control	Heavy Oil	0.08
Brine Outlet	85-95	Low	Pot. Impact vs. Control	Total PAHs	0.21
Brine Outlet	80-84	Low	During / After Discharge	Light Oil	0.76
Brine Outlet	80-84	Low	During / After Discharge	Heavy Oil	0.06
Diesel Dock	80-84	High	Pot. Impact vs. Control	Light Oil	0.89
Diesel Dock	80-84	High	Pot. Impact vs. Control	Heavy Oil	0.38
Diesel Dock	85-95	High	Pot. Impact vs. Control	Total PAHs	0.02

LOOP spill reports indicate most spills occurred in the Clovelly Storage Dome Facility and the Offshore Terminal. Two approaches were used for testing for LOOP activity effects on petroleum hydrocarbon content in sediments. One was to look for differences in petroleum hydrocarbon levels in designated impact stations versus control stations where the test included looking for the effect of reported spills occurring during the six months (two quarters) prior to the sampling quarter. This was done with the realization that due to degradation and other factors (such as possible transport or burial processes), the effects of a spill are usually not permanent. Thus we looked for effects of reported spills close to when the spills occurred. The other approach was a simple comparison of petroleum hydrocarbon levels in sediments of potential impact stations versus controls. This was done because repeated spills or releases may contribute to some long-term elevation of petroleum hydrocarbons in sediments. Thus depending on the area possibly impacted by a spill and whether or not the nearest potential impact stations were truly affected, this presented another reasonable way of looking for impacts that the spill-association approach might miss.

Table 9 is a simple presentation of the mean modified total PAH compound concentrations for each station showing the maximum value measured for the station. This simple presentation is given here to assist in the discussion of the statistical findings.

Clovelly Dome Storage Facility

Table 8 indicates that reported spills were significantly ($P > F$ of 0.03) related to elevated sediment light oil concentrations within six months of the spill during the early years and that considered over the entire early period when light oil was measured, the sediments at Clovelly contained significantly more light oil than control sediments. However, heavy oil at these potential impact stations was not significantly different at the five or one percent levels of significance, either in association with spills nor when potentially impacted stations were compared to control sites over all the years these fractions were measured. From 1985-1995 when individual PAH compounds were measured, no significant spill effect was detected and the potentially impacted stations were not significantly different from the control stations.

Table 9. Mean modified total and maximum PAH concentrations (1985-1995) for sediment sampling stations.

Station Grouping and Number	Mean μg/kg	Maximum Value μg/kg
Clovelly Dome Sites:		
-- 463	557	2,188
-- 605	507	3,354
--606	33	68
Clovelly Dome Area, connecting canals:		
--461	197	863
--464	106	577
--601	813	3,904
--602	224	3,421
--604	158	852
--607	259	2,102
--608	1,176	22,420
--609	289	1,320
Offshore Pumping Station:		
--481	71	683
Brine Diffuser Outlet:		
--473	95	838
--474	471	9,600
--475	269	4,858
LOOP Diesel Dock:		
--617	3,790	49,520
--618	3,858	40,831
LOOP Diesel Dock Controls:		
--619	309	5,385
--620	63	390
--621	164	417
--622	232	1,250
Inland Control Sites:		
--610	81	274
--612	377	11,493
--613	572	3,511
--623	264	1,020
--624	108	785
Offshore Control:		
--482	132	2,090
--483		

(Table 9 continued:)

Station Grouping and Number	Mean µg/kg	Maximum Value µg/kg
Brine Diffuser Control:		
--435	40	458
Near LOOP Pipeline/Booster Stations:		
--616	119	628
Bayou Moreau:		
--614	314	3,060
--615	163	1,667
--630	65	342
--631	68	250
King's Ridge Canal:		
--625	5,21	61,950

Looking at Table 9, it is seen that for the later years, the average and maximum levels of PAH compounds measured at the impact sites appear reasonably similar to the control sites.

The literature review section presented a case for not comparing PAH levels with threshold effect levels proposed in the past. However, as a general comparison, the average levels at the Clovelly Storage Dome facility is well below problem levels indicated in Tables 2 and 3.

Clovelly Area (canals and bayous leading away from the storage facility)

From 1980 to 1984 when light oil and heavy oil were measured, and during the following period (1985-1995) when individual PAH compounds were measured, there was no significant effect of reported spills in elevating petroleum hydrocarbons at potential impact sites versus control sites. However, long-term differences in levels at control and potential Clovelly area impact sites were shown to be significant for both heavy oil (1980-1984) and total PAH compounds for the following years. The effect was highly significant ($P < 0.002$) for heavy oil, but barely significant at the five percent level for total PAH compounds ($P > 0.047$). Though the data in Table 9 represents a very simplified way of looking at PAH concentrations, two of the

eight Clovelly Area stations appear to have likely contributed to the significant differences for PAHs. These were stations 601 and 608.

As discussed before, comparisons of these concentrations to proposed threshold values is not believed to be a valid exercise as yet. However, even the highest mean concentrations reported in the LOOP monitoring studies are less than levels reported to be problems according to published material regarding extensive work in 1989 and 1990. Thus even though the impact sites are statistically elevated in PAHs, the data suggest the contamination is not substantial.

Also, it should be noted that impacts in canals and bayous around Clovelly may or may not be due to LOOP activities as these are generally public waterways and contamination could have occurred from non-LOOP sources. Station 625 is an example where sediment contamination has apparently occurred due to non-LOOP boating activity.

Offshore Terminal and Pumping Station

At the Offshore Terminal station where tankers transfer their load to the pipeline, there was a significant relationship between reported spills and light oil content from 1980-1984. A total of 12 spills exceeding 500 gallons were reported from March 1982 to May of 1994. Heavy oil did not show a significant effect from 1980-1984, nor did total PAHs for the following period. When the potentially impacted station (station 481) was compared with the offshore controls for 1980-1984 and 1985-1995, heavy oil at the impact site was significantly different from the control stations, but light oil for the early years and total PAHs for the last ten years were not significant. Thus the data for the Offshore Terminal station suggests that though some significant increases in petroleum hydrocarbons may have occurred, impacts are not long-lasting since no significant difference was noted from 1985-1995.

Brine Diffuser Outlet

The statistical results (Table 8) show no differences in oil associated with the sediments at the brine diffuser outlet during and after the major pumping for the excavation of the dome. Also, there was no significant difference in light and heavy oil between the diffuser stations and the control over the early years, nor between these stations between 1985 and 1995 when PAH

compounds were measured. As a result, there is no impact of the brine discharge on the petroleum hydrocarbon content of the sediments at the Brine Diffuser Outlet.

LOOP Diesel Dock

Stations 617 and 618 are near the LOOP Diesel Dock. These stations showed the highest amount of total PAH compounds of any station associated with LOOP activities (average / max values in $\mu\text{g}/\text{kg}$ of 3,790 / 49,520 and 3,858 / 40,831 for stations 617 and 618 respectively). The PAH levels were elevated not on just a few, but on many of the sampling dates. Total gallons of spills reported included: 280 (1981); 180 (1982); <1 (1983); 4 (1988); 630 (1992); and, <1 (1993).

In the spill reports, all of these fell into the minor spills category, but one could argue the LOOP Diesel Dock area is a relatively small, confined area where a small spill is going to have a greater impact than if the same spill occurred in open, deeper water. Considering the largest spills (summing to over 100 gallons) occurred only in 1981, 1982, and 1992, and considering the fact that there is a lot of other boating activity (docks and other services for commercial and private vessels) in the immediate area, the significantly elevated levels of PAHs in the area of the LOOP Diesel Dock cannot be attributed to any one source. For example, the most contaminated station in the LOOP monitoring study in terms of average concentration of total PAHs was station 625 where heavy vessel traffic from non-LOOP activities occur (personal communications, LWF personnel). This non-LOOP boating activity, or possibly other petroleum activity in the area, may have resulted in a few unusually high PAH concentrations on several of the sampling dates.

Relationship between Clay Content and Petroleum Hydrocarbons

Table 10 shows the relationship between clay content and petroleum hydrocarbon levels looking separately at control and impact sites, and examining the relationship if both control and impact sites are included in the model. It is well known that finer textured sediments (higher clay content) are more effective in trapping and retaining most classes of contaminants, including petroleum hydrocarbons as mentioned in the literature review. Most of the station groupings

Table 10. Analysis of relationship between petroleum hydrocarbon levels and clay content.

Stations or Activity Area	Pr>F
CONTROL SITES ONLY ASSOCIATED WITH:	
Clovelly Dome Storage Facility	0.79
Clovelly Connecting Canals	0.49
Offshore Pumping Station	0.03
Brine Discharge Outlet	0.46
IMPACT STATIONS ONLY ASSOCIATED WITH:	
Clovelly Dome Storage Facility	0.63
Clovelly Connecting Canals	0.86
Offshore Pumping Station	0.70
Brine Discharge Outlet	0.45
LOOP Diesel Dock	0.69
CONTROL AND IMPACT STATIONS INCLUDED IN MODEL:	
Clovelly Dome Storage Facility	0.72
Clovelly Connecting Canals	0.86
Offshore Pumping Station	0.02
LOOP Diesel Dock	0.69

here did not show a significant relationship. This may be due in part to a fairly narrow range of sediment clay content at most of the stations (south Louisiana sediments tend to be fine-grained), and possibly more contamination occurring at very few sites that happen to have a slightly lower amount of clay content.

Pore Water Salinity at the Brine Diffuser Facility

Table 11 gives the statistical data for whether the major brine discharge that occurred during the early years of LOOP had an effect on pore water salinity. No effect was seen. A visual examination of the pore water salinity data indicate that fairly narrow ranges of salinity

Table 11. Analysis of brine discharge effects on porewater salinity

Effect Tested	Pr>F
During / After Major Discharge Period, Impact vs. Control	0.31
Year (BA)	0.0001

were observed at all offshore stations and the average of all the stations were near the same. The variability of the salinity data was much less than found for the petroleum hydrocarbon data. The BA(CI) term for years does indicate some trends for changing salinity at either the impact or control site over years, but, again, there was no difference between the impact or control sites.

CONCLUSIONS

Only the Offshore Terminal area, the Clovelly Dome Storage facility, and, should a rupture occur, the area around the pipeline are likely to be impacted by LOOP activities. No leak from the pipeline has occurred. For both the Offshore Terminal and the Clovelly Storage Dome facility, a statistically significant increase in petroleum hydrocarbons in sediments was noted from 1980-1984. No difference between potential impact sites and control sites was noted for the last ten years of monitoring. If impacts occurred, they were not long-lasting.

The sediments in canals around the Clovelly facility and the LOOP Diesel Dock area sediments showed statistically significant increases in petroleum hydrocarbons. For these sampling stations in the area around Clovelly, the data suggest increased levels (which were modest) could have been due to non-LOOP activities since only a few stations, mostly public waterways some distance away from Clovelly, showed these increases. The sediments near the LOOP Diesel Dock showed substantial, consistent elevations in PAH compounds relative to control sites. Again, however, extensive boating activities other than for LOOP are associated with this area, so it is not possible to identify the source. No effect of brine discharge was seen on pore water salinity.

In conclusion, the data indicate that some modest, relatively short-term impacts have occurred in terms of petroleum hydrocarbon levels in sediments of sampling stations associated with the Offshore Terminal and the Clovelly Storage Dome facility. But it should be emphasized that the increases were modest and are not long-term. Where highest levels of petroleum hydrocarbons were found, boating and possibly other petroleum activities other than those associated with LOOP are likely contributing sources. The relative contribution from the various possible sources at these sites cannot be determined. Also, it was concluded there was no effect of brine discharge on pore water salinity at the brine diffuser facility.

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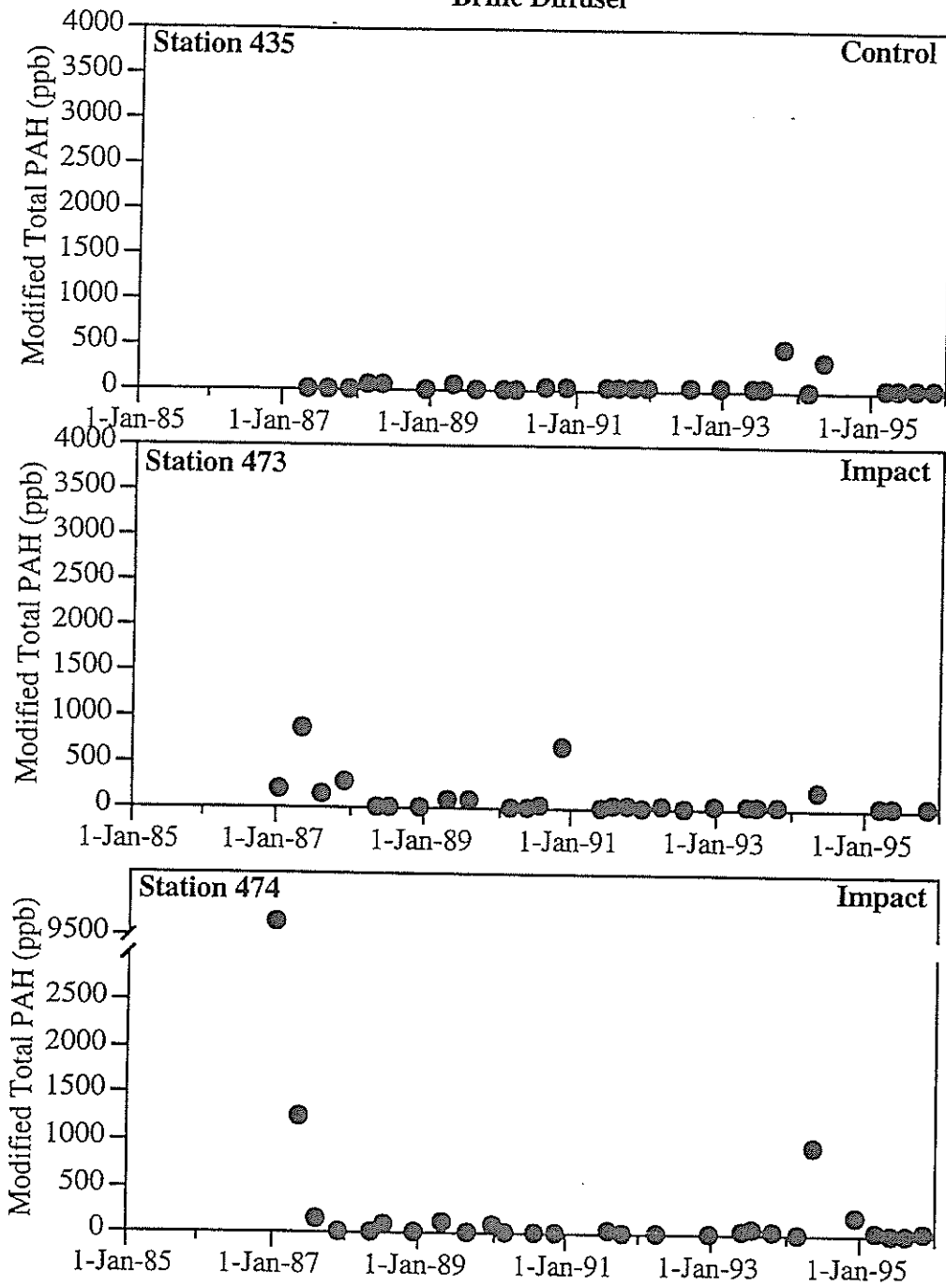
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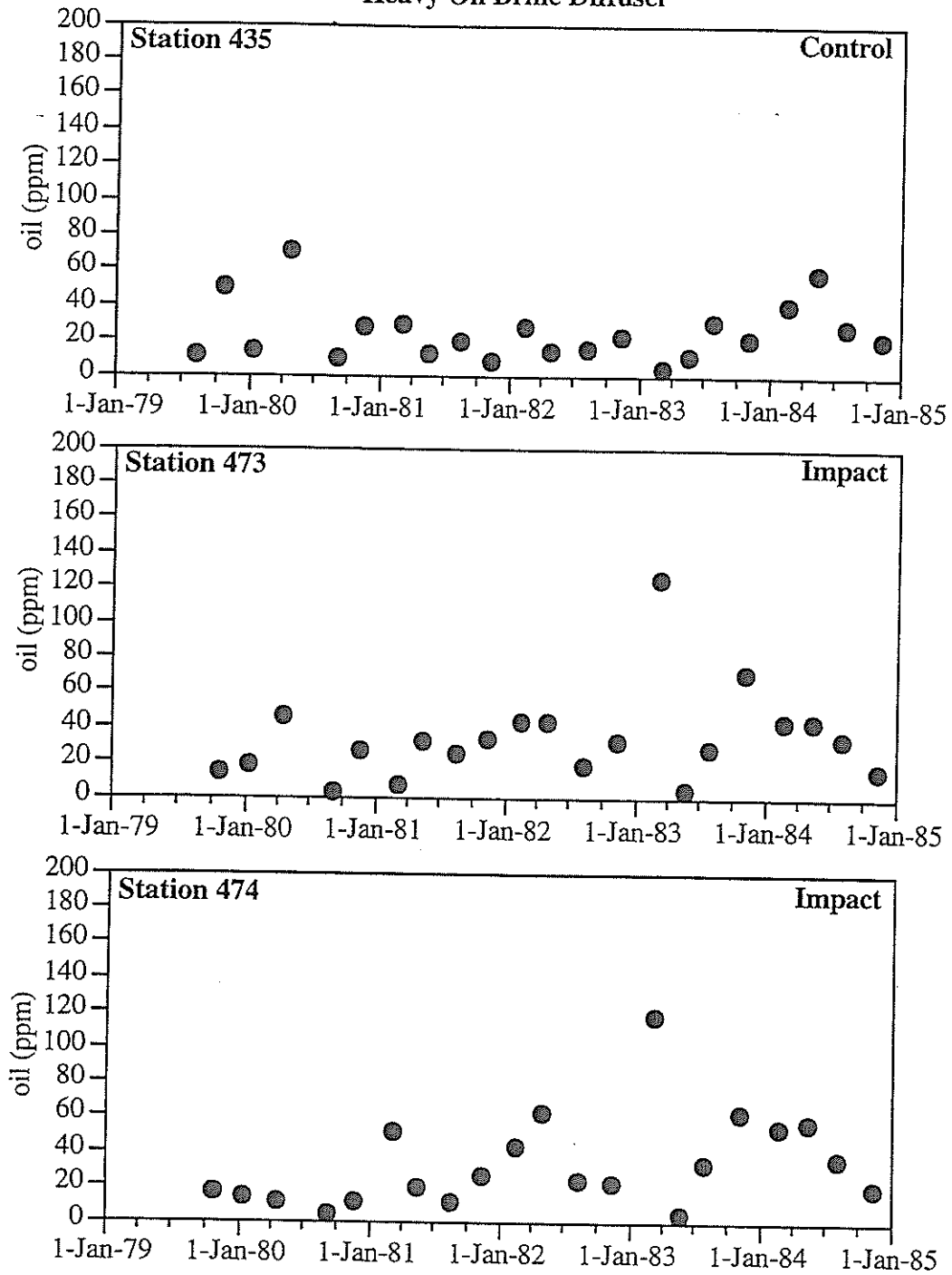
APPENDIX A:
Modified total Polynuclear Aromatic Hydrocarbons
for control and impact stations near the brine diffuser

Brine Diffuser

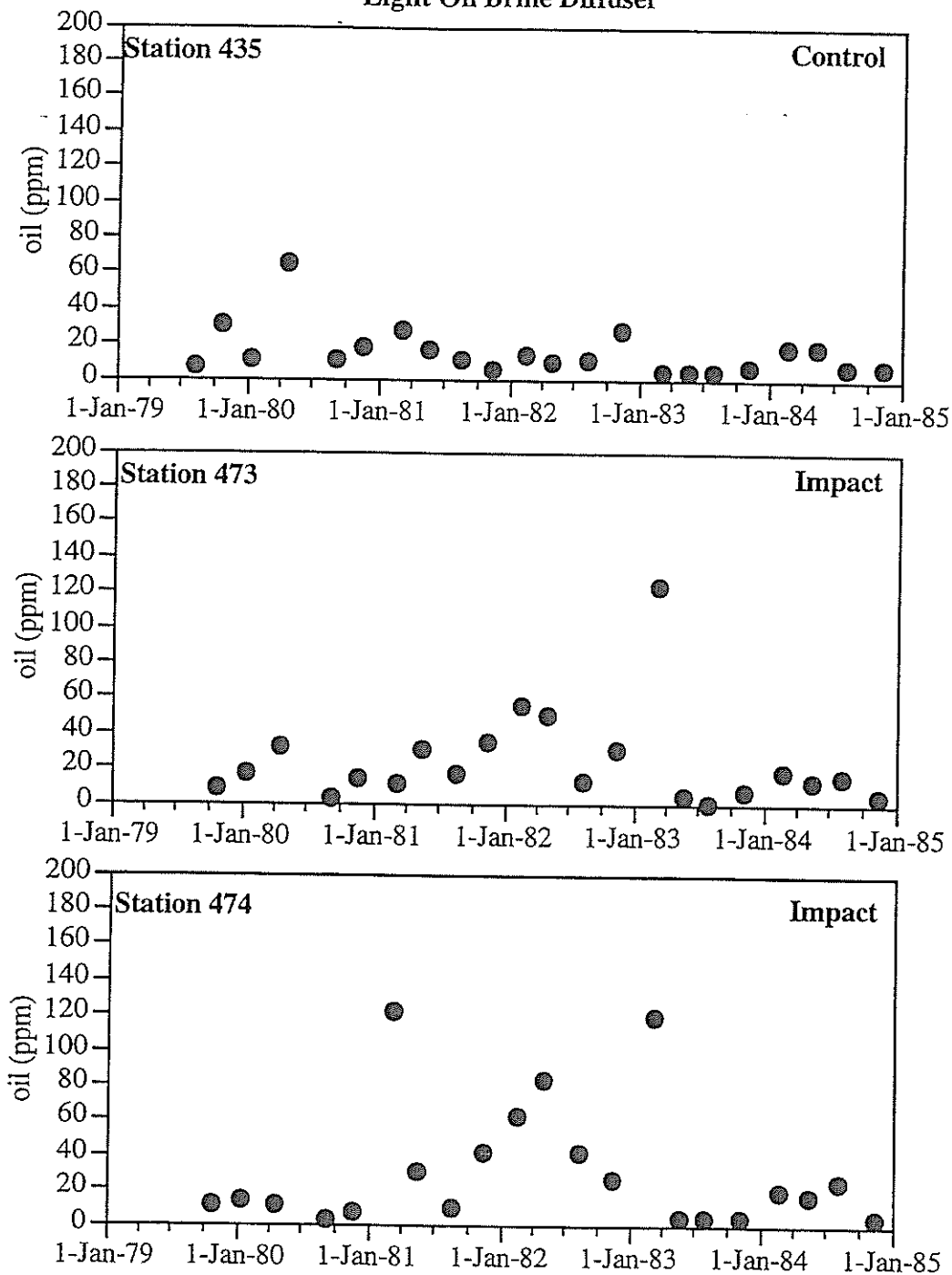


APPENDIX B:
Heavy and light oil concentrations (ppm)
for control and impact stations near the brine diffuser

Heavy Oil Brine Diffuser

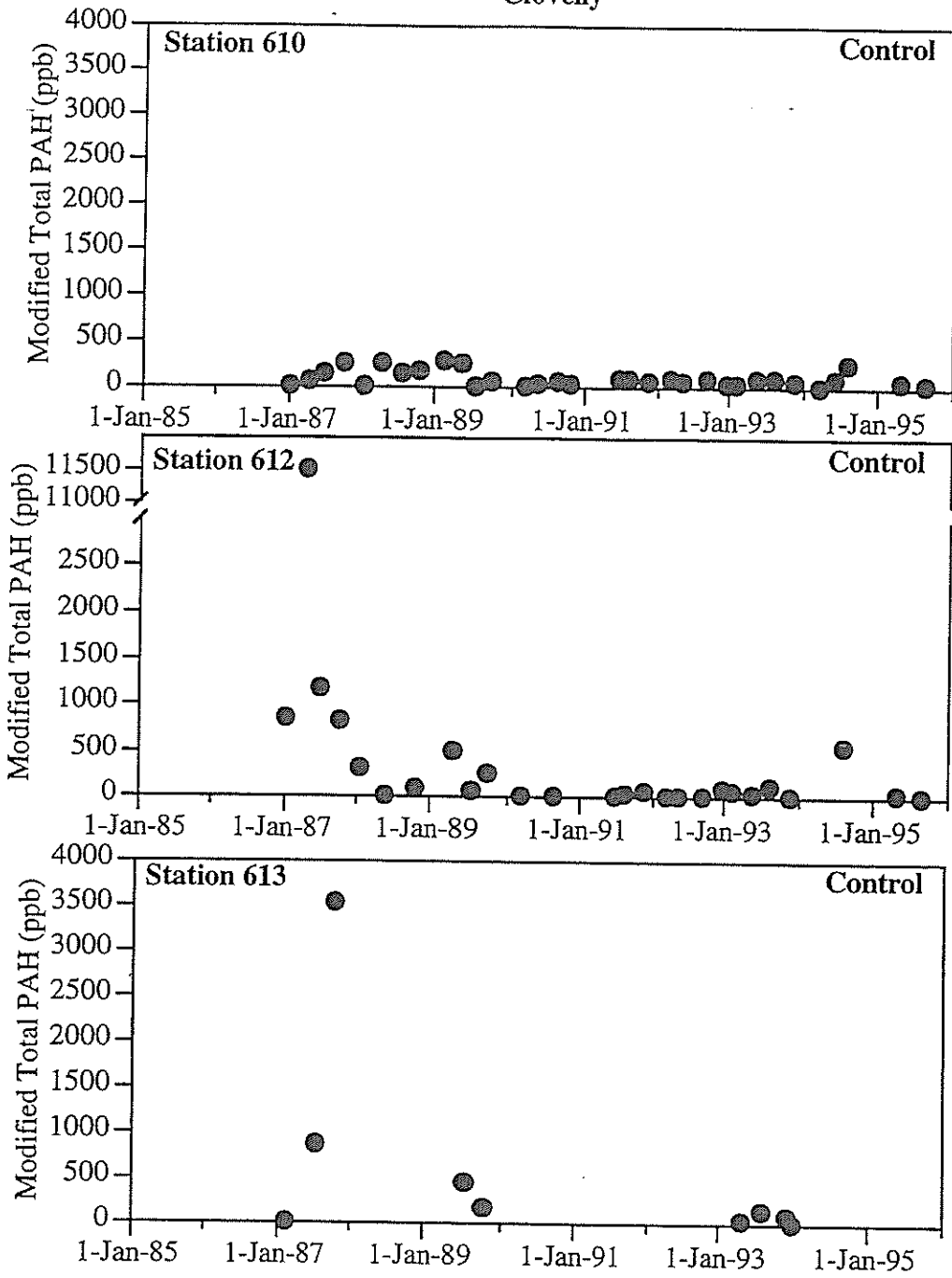


Light Oil Brine Diffuser

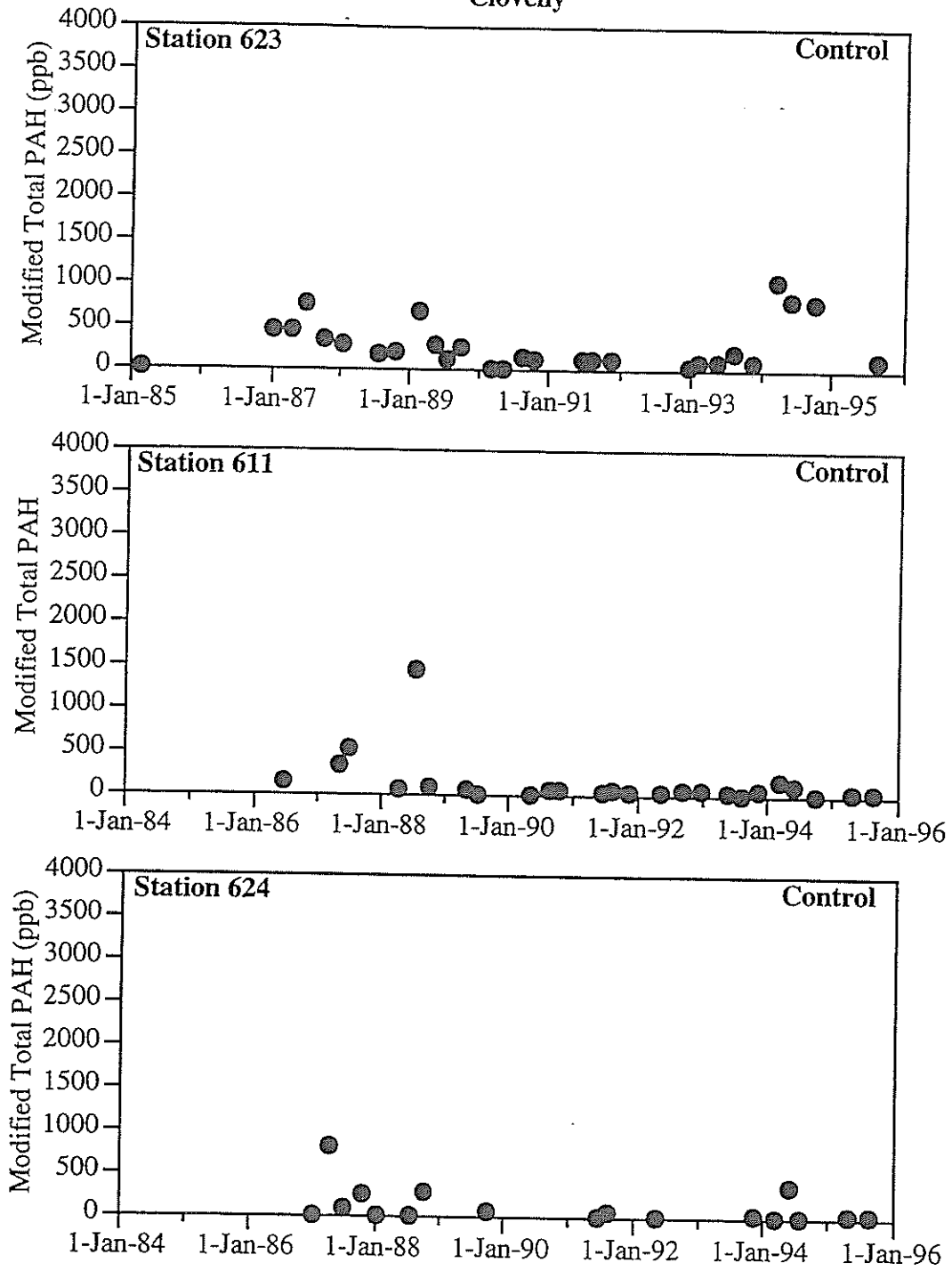


APPENDIX C:
Modified total Polynuclear Aromatic Hydrocarbons
for control and impact stations near the Clovelly Storage Dome

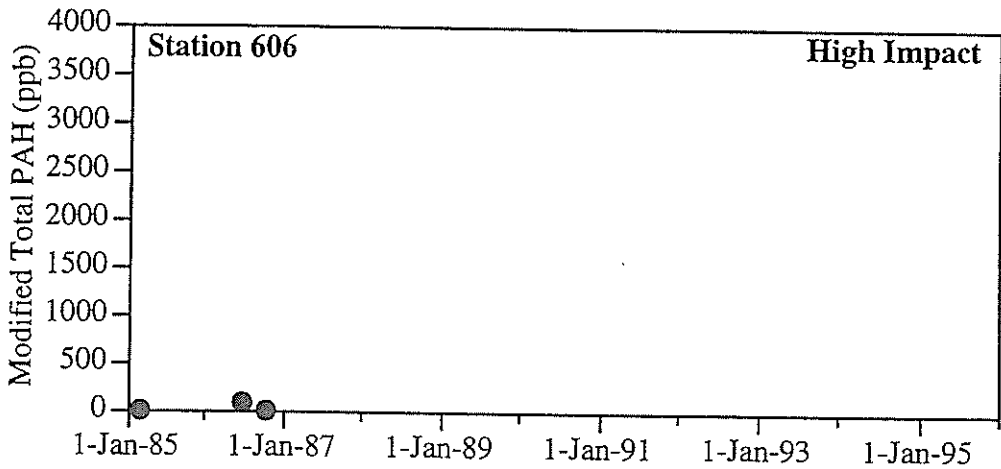
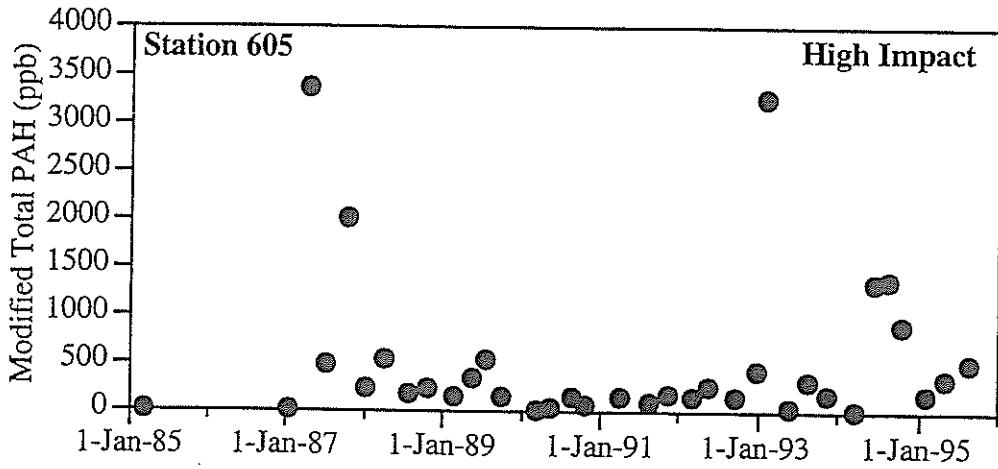
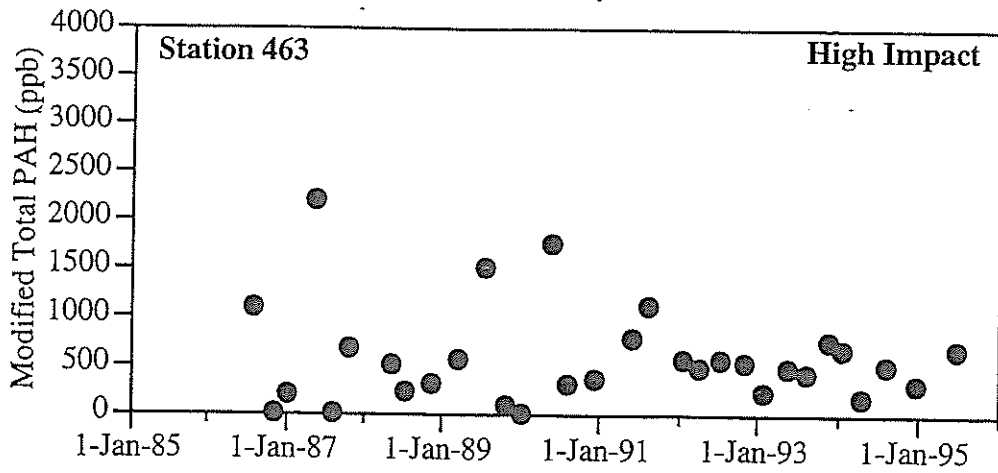
Clovelly



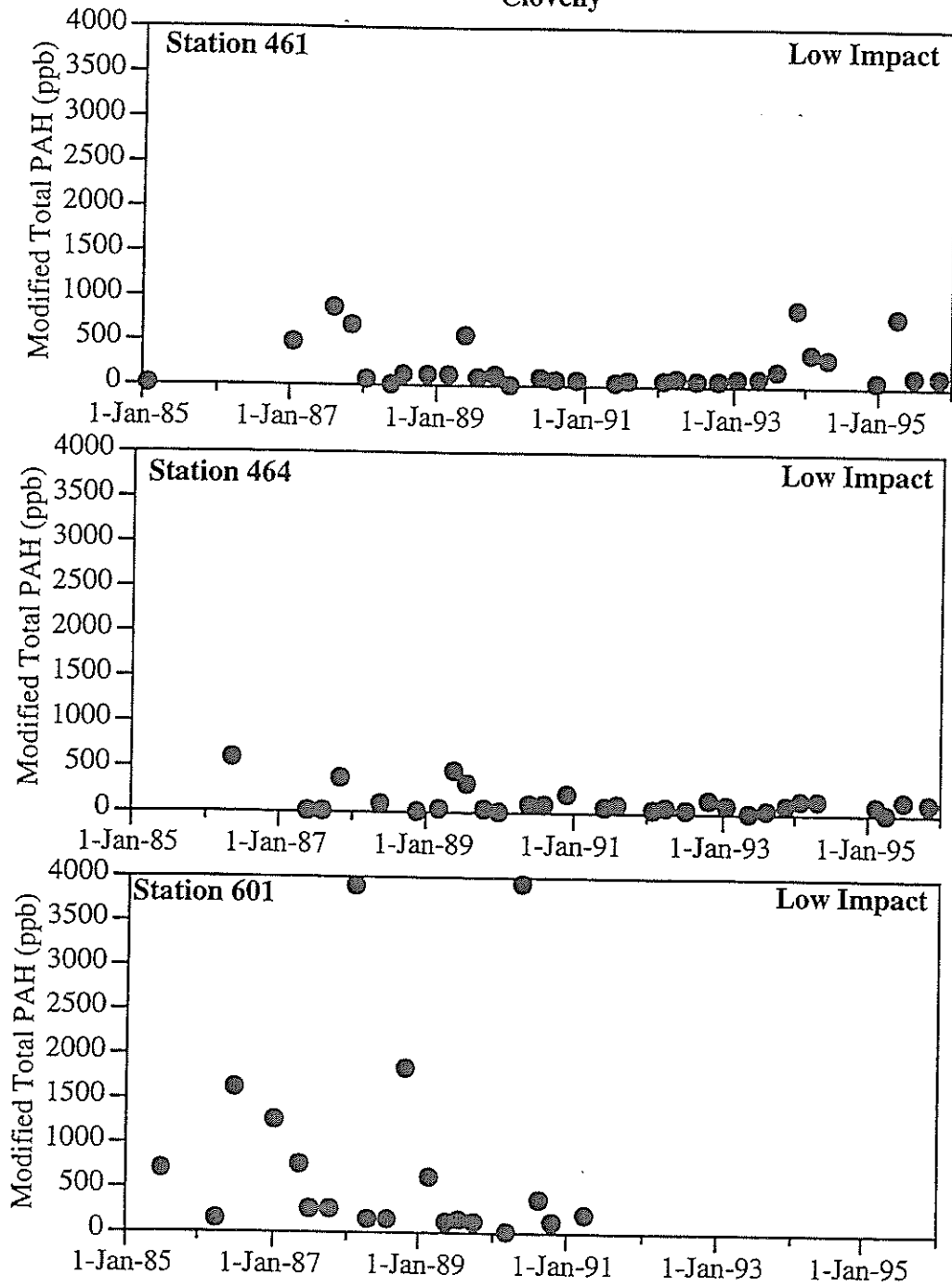
Clovelly



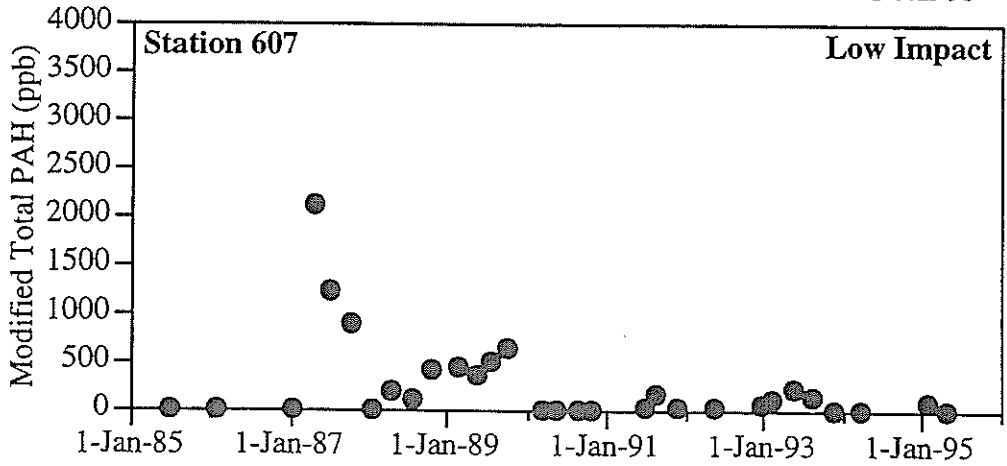
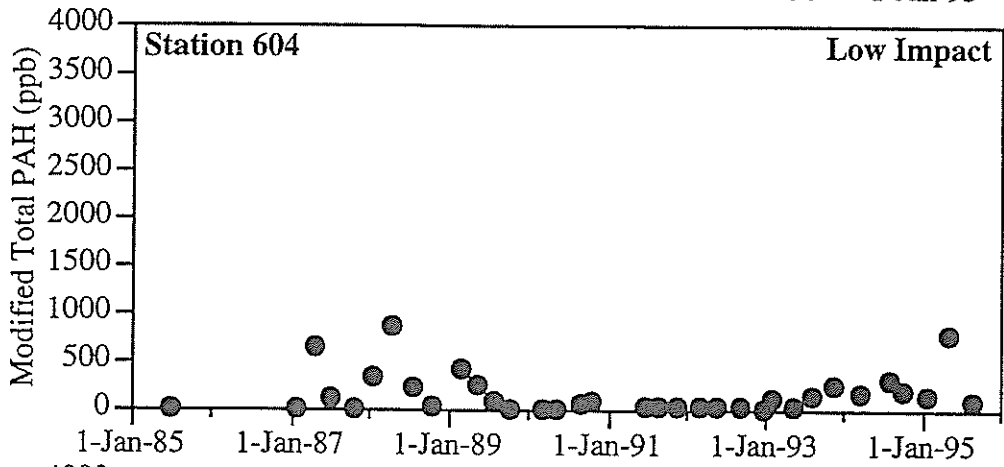
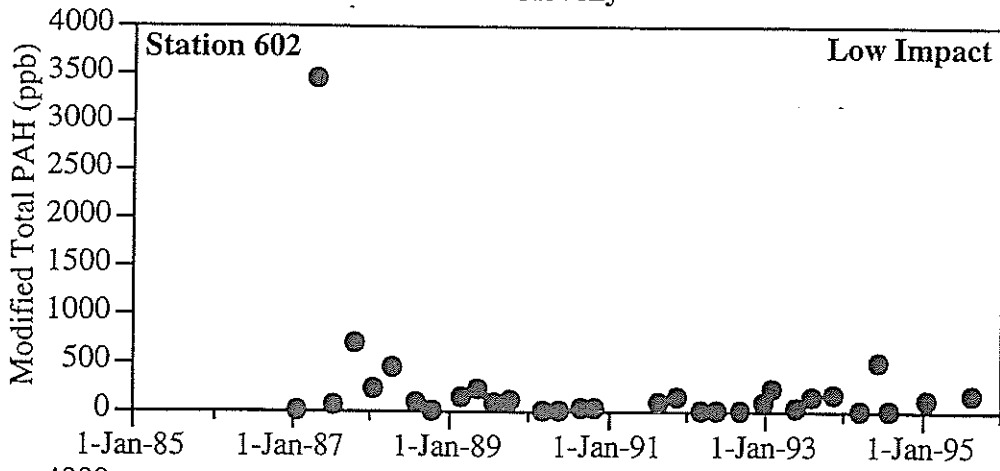
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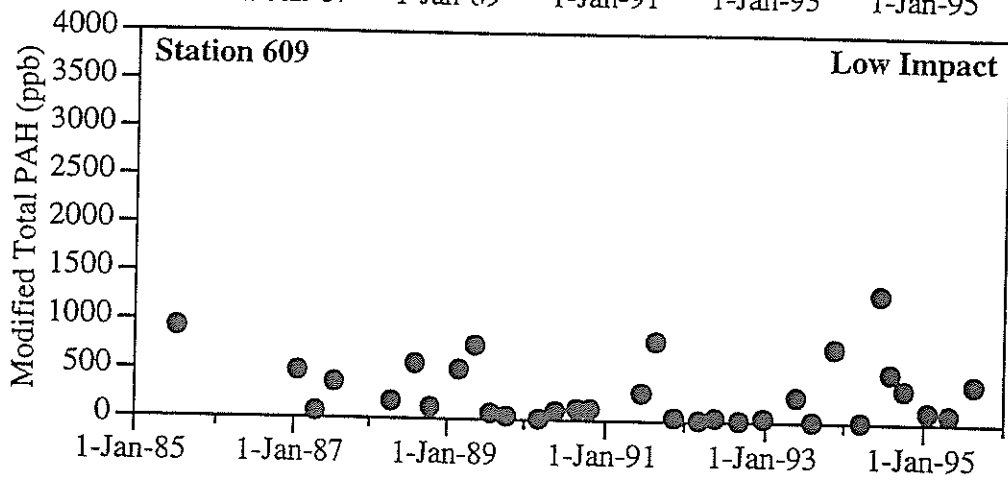
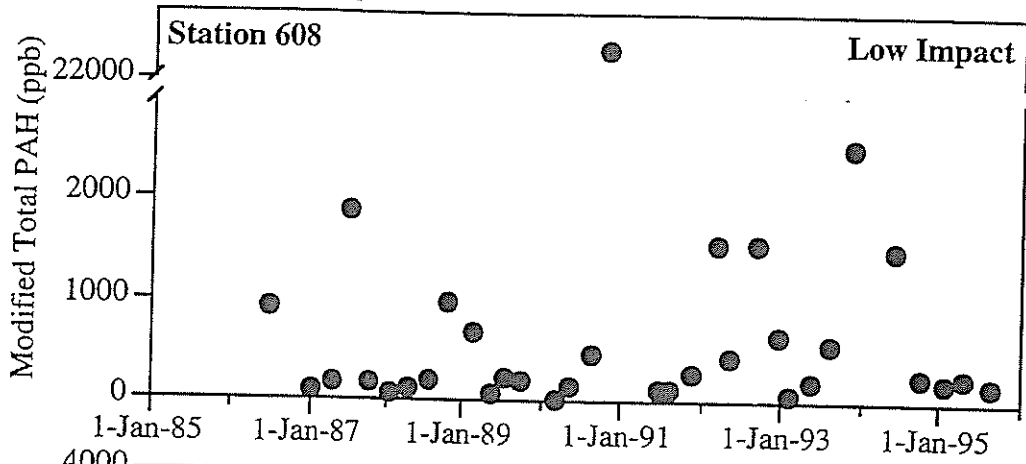
Clovelly



Clovelly

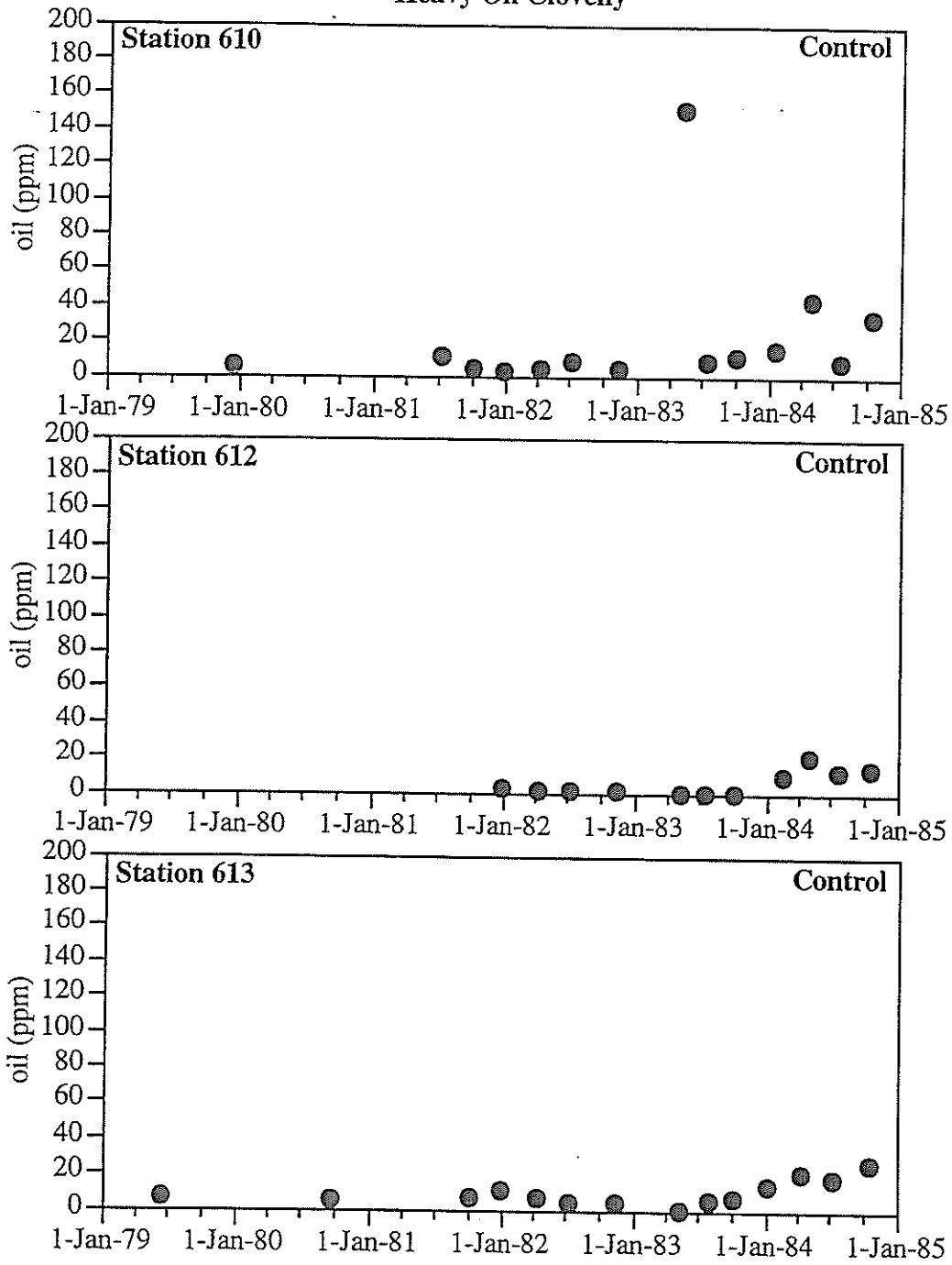


Clovelly

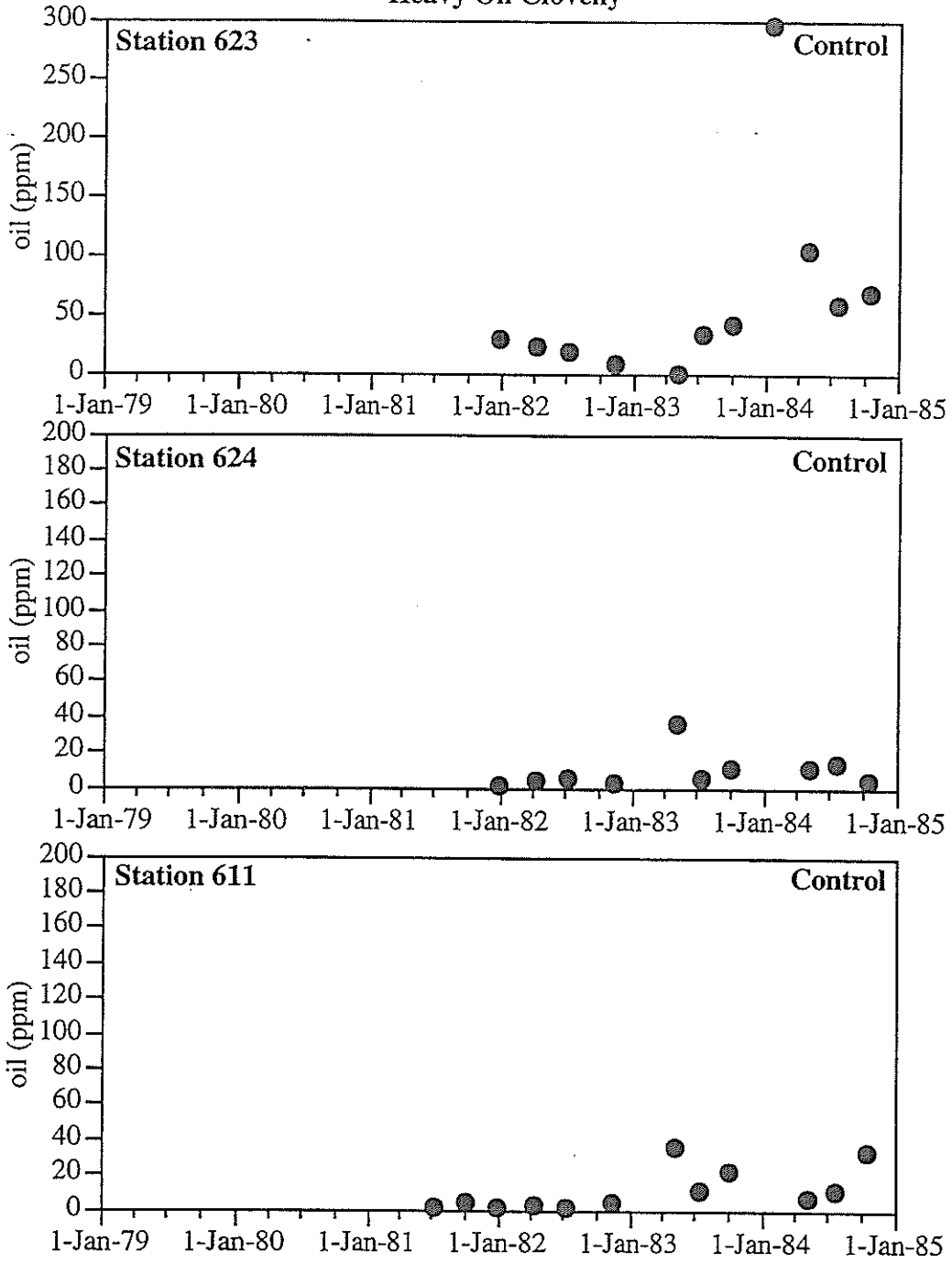


APPENDIX D:
Heavy and light oil concentrations (ppm)
for control and impact stations near the Clovelly Storage Dome

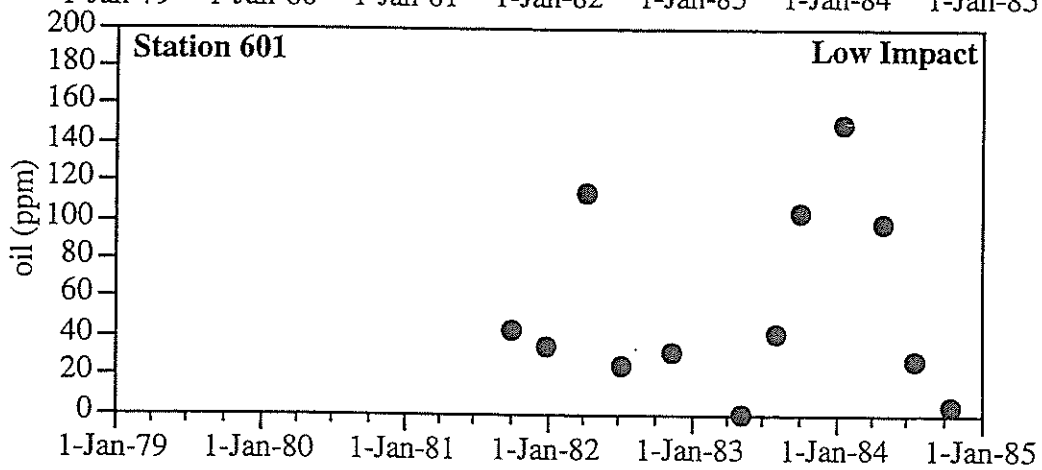
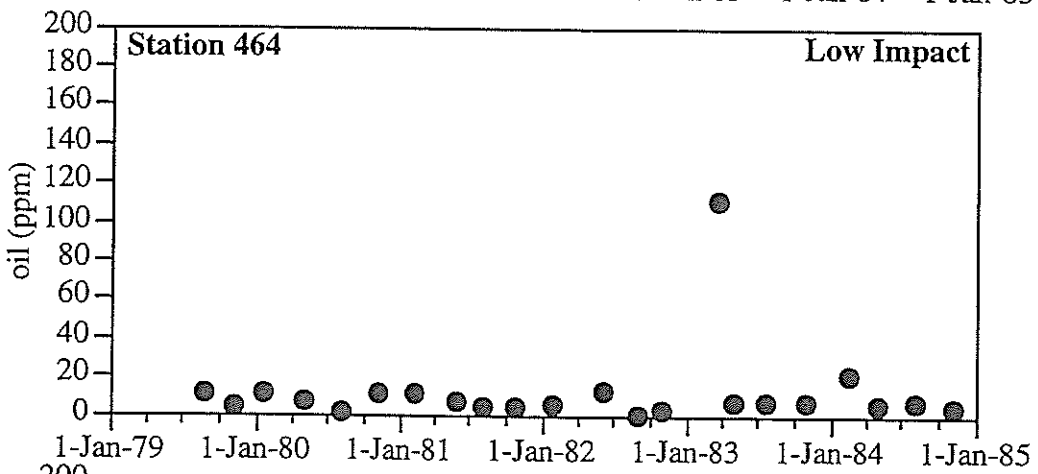
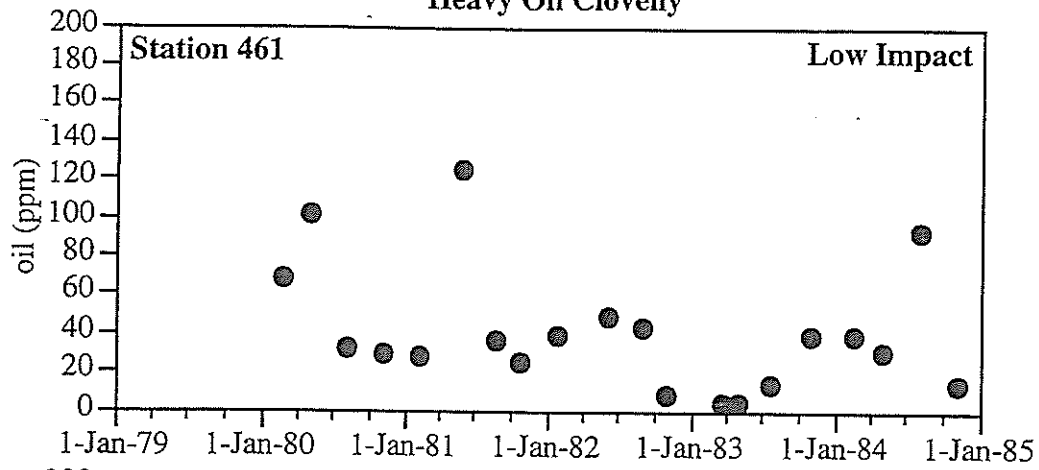
Heavy Oil Clovelly



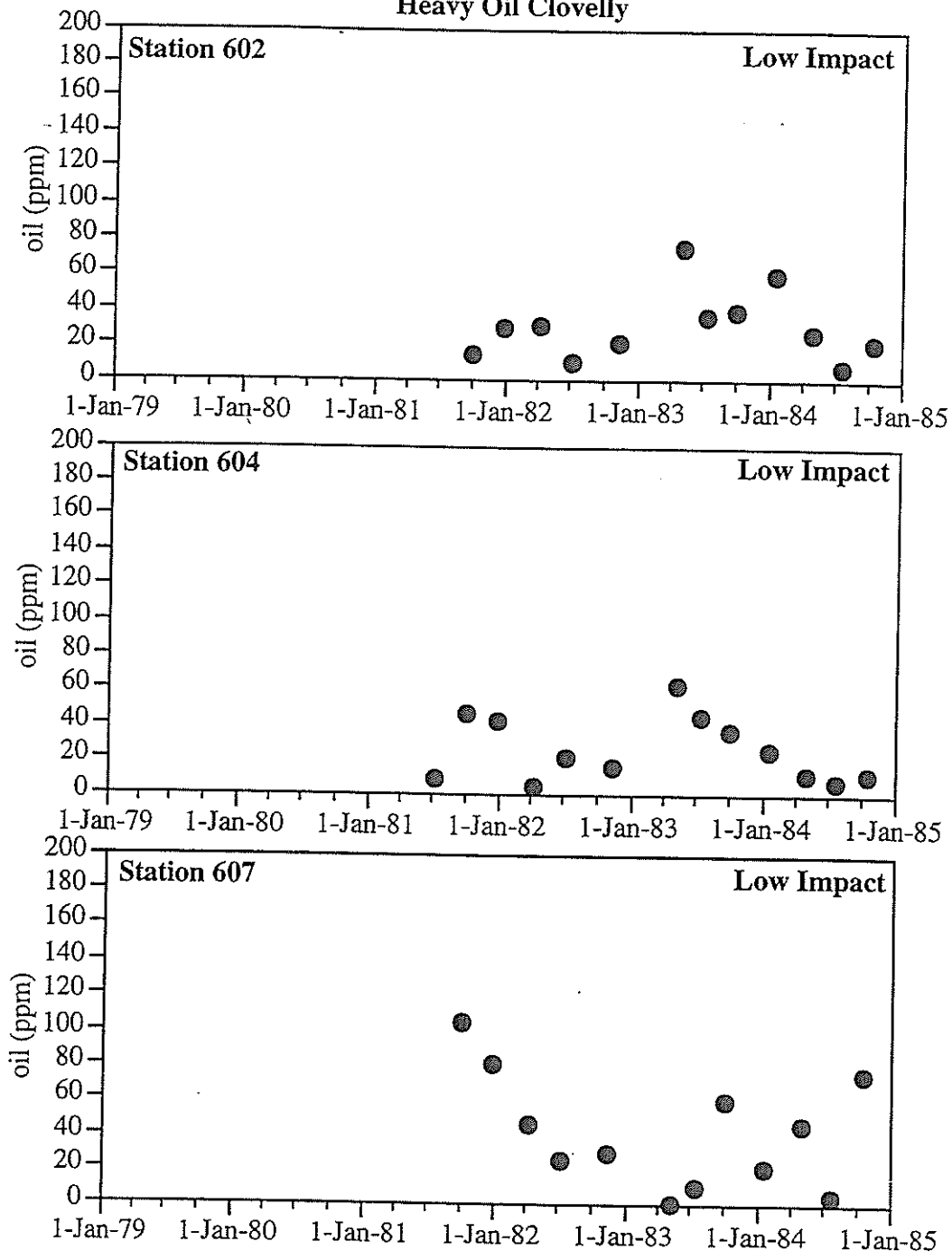
Heavy Oil Clovelly



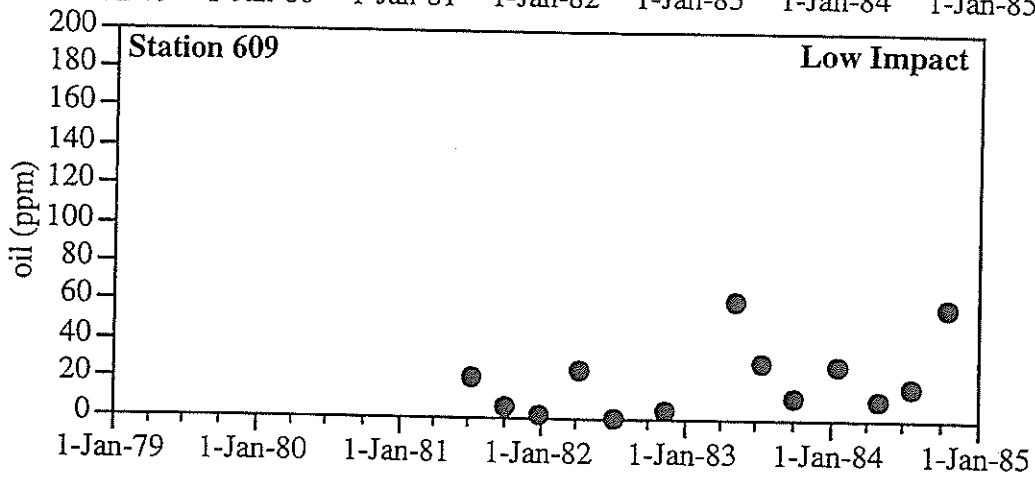
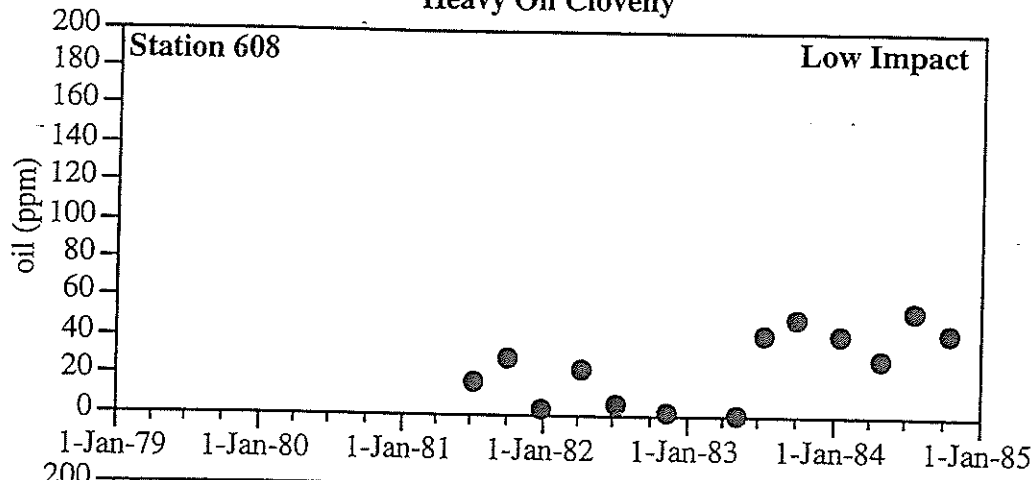
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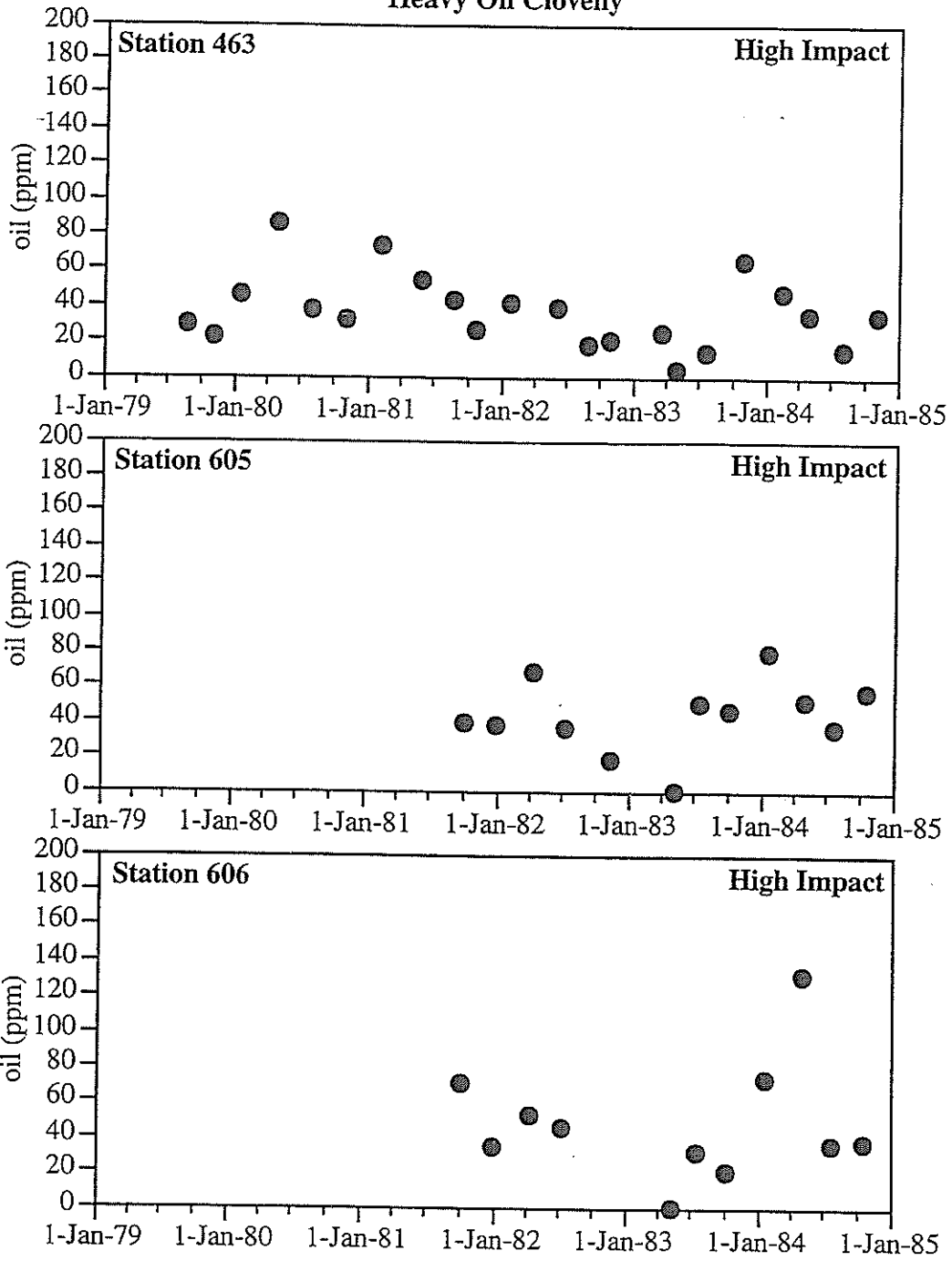
Heavy Oil Clovelly



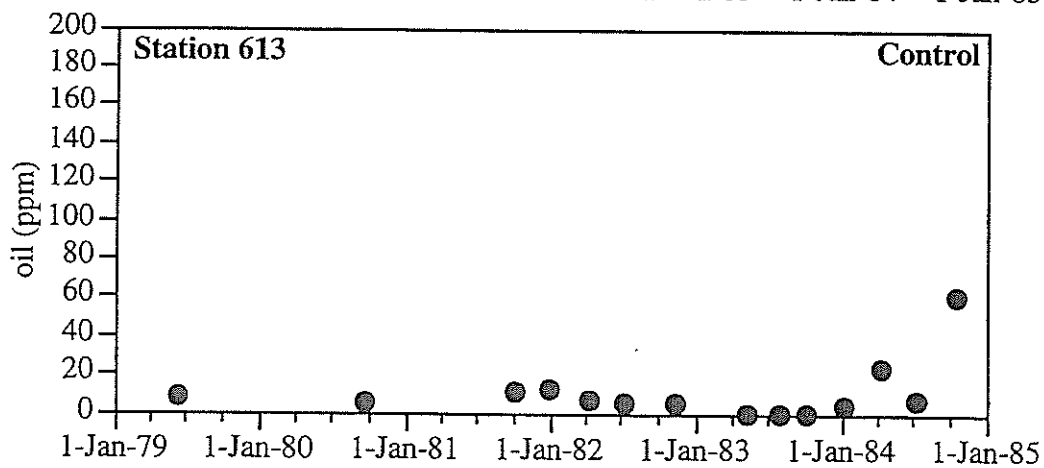
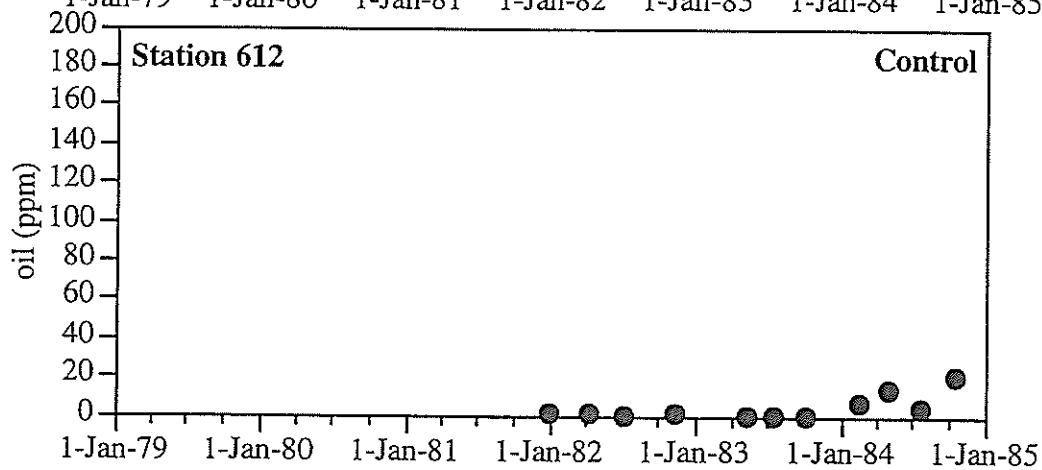
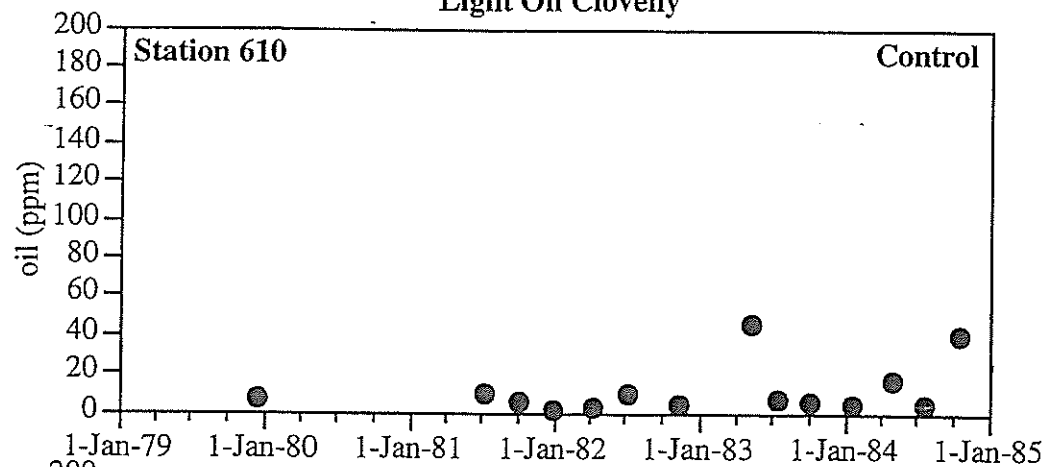
Heavy Oil Clovelly



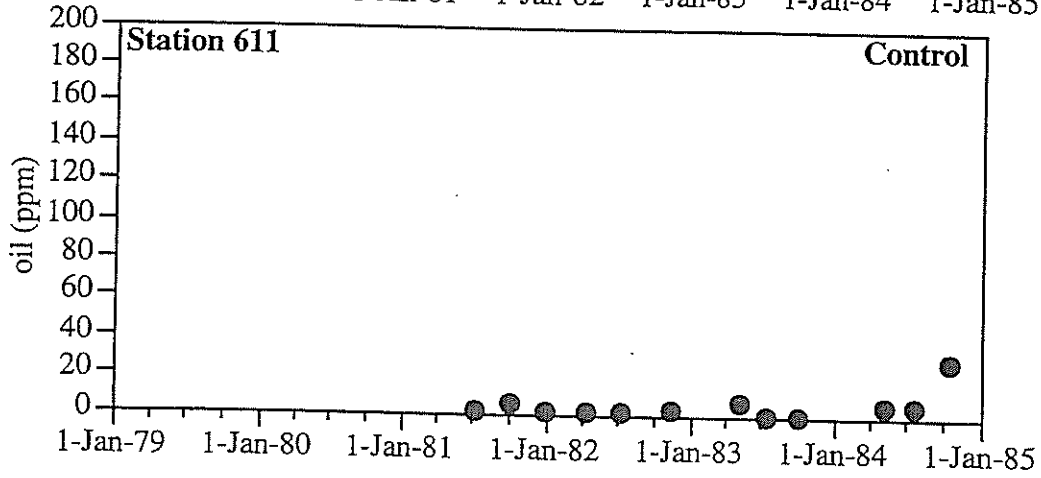
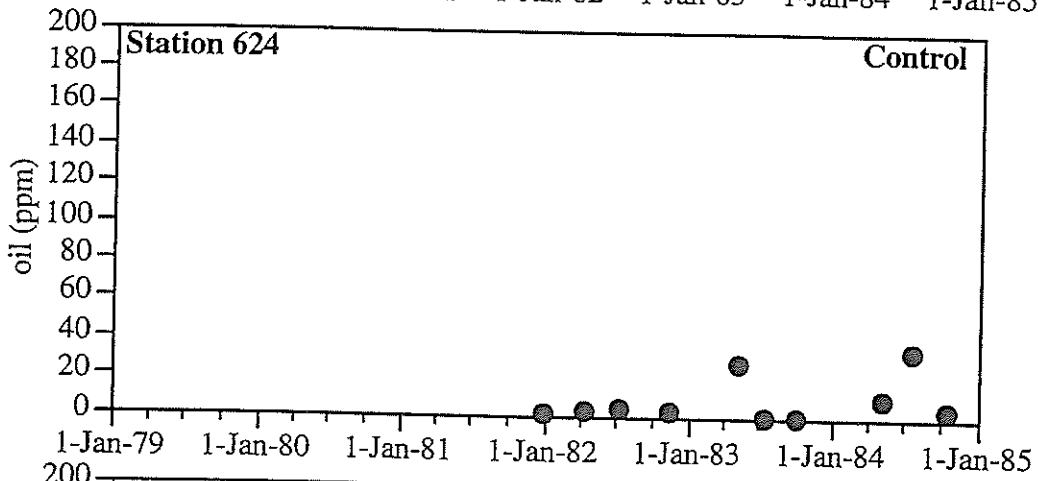
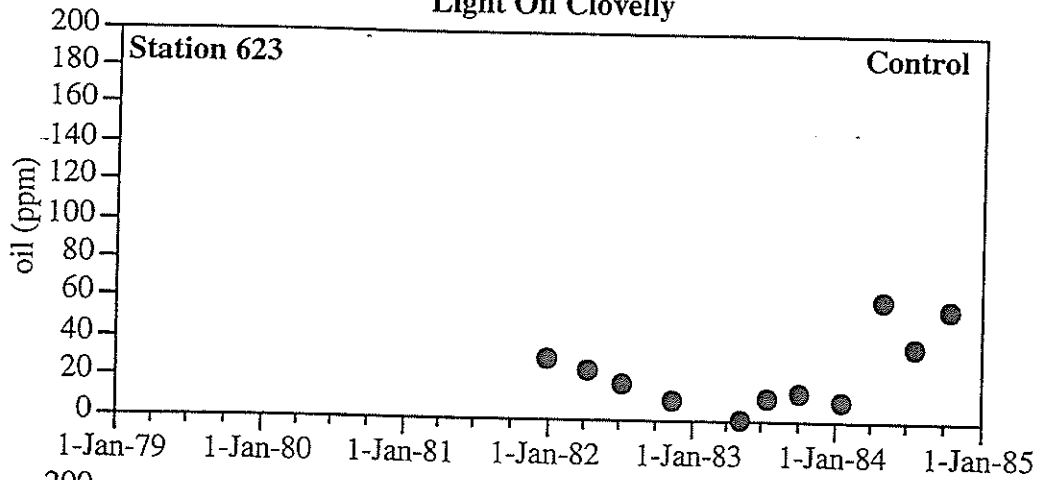
Heavy Oil Clovelly



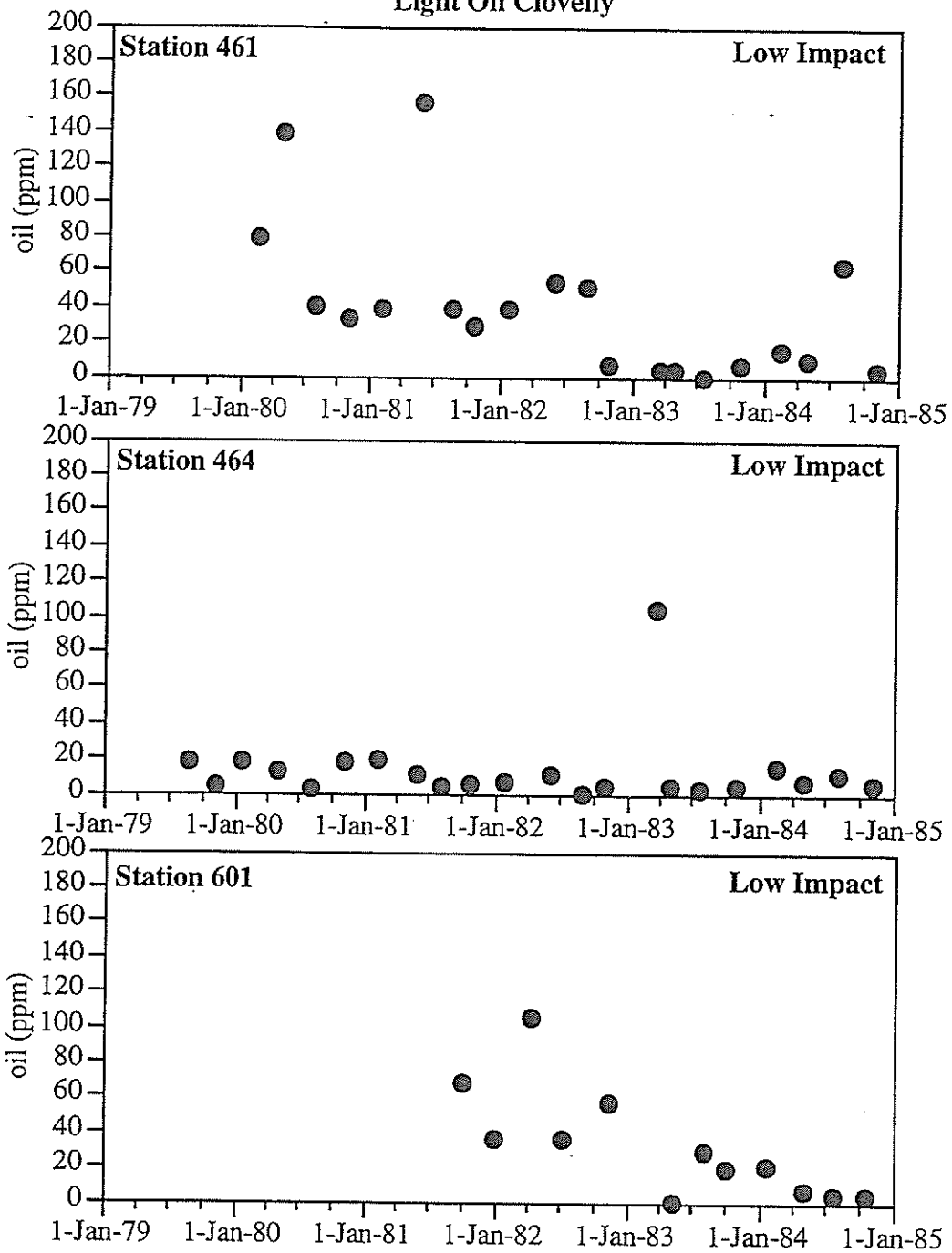
Light Oil Clovelly



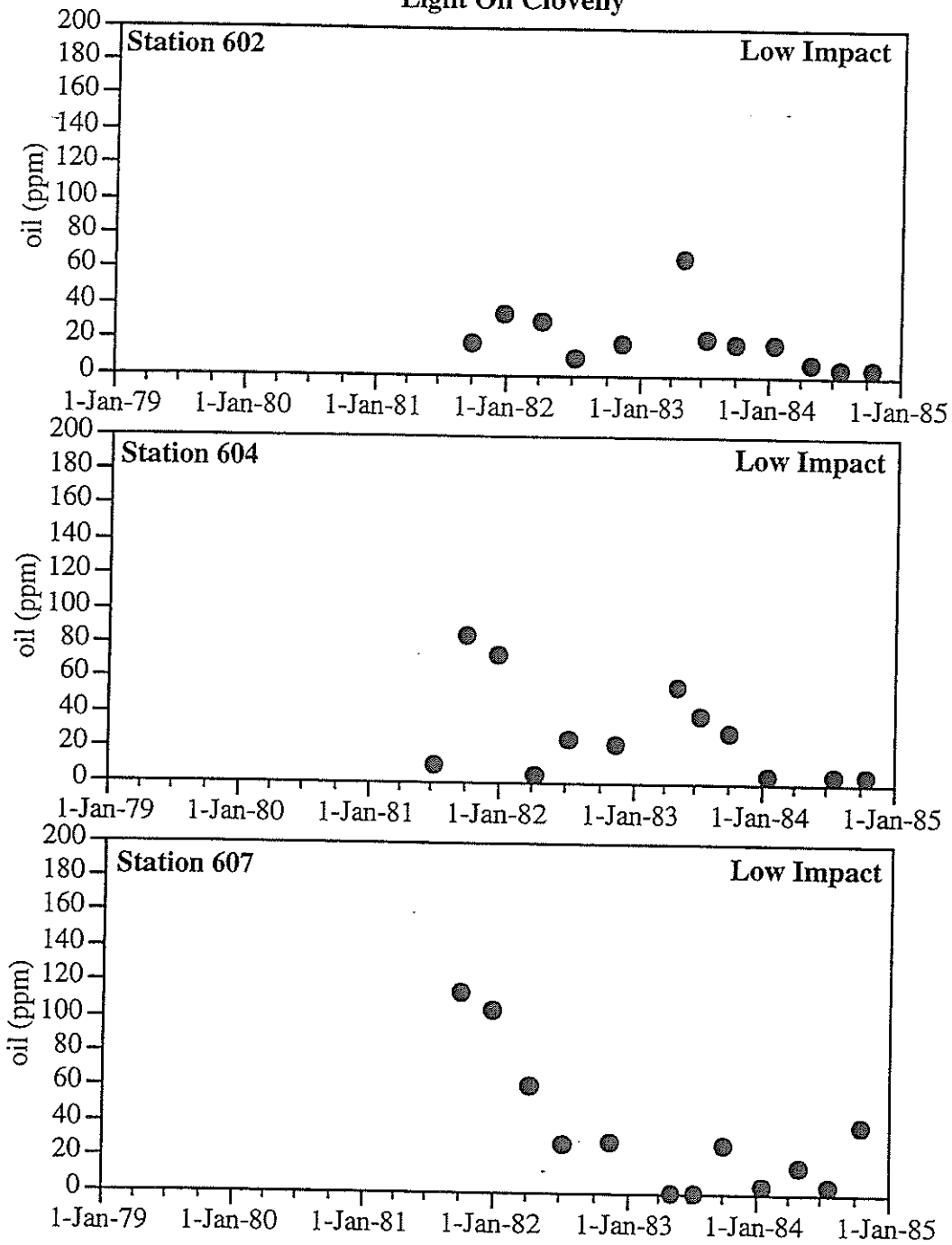
Light Oil Clovelly



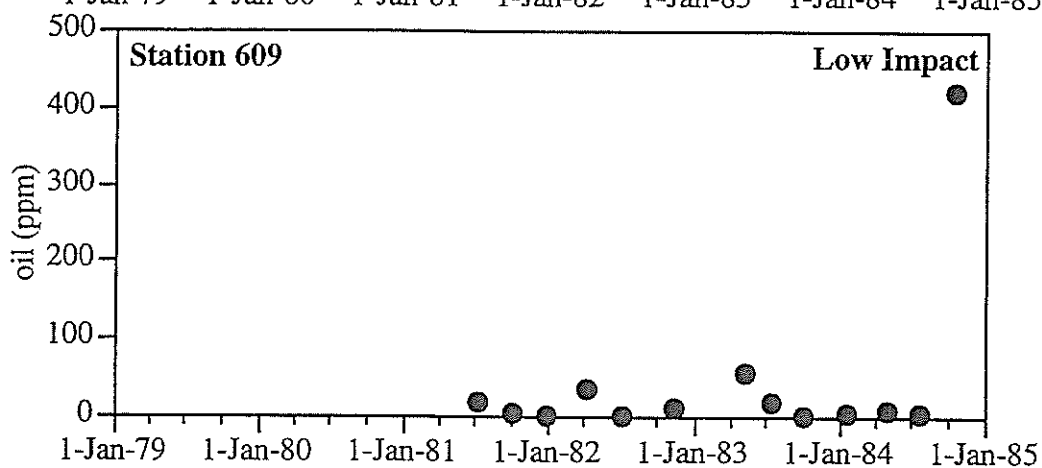
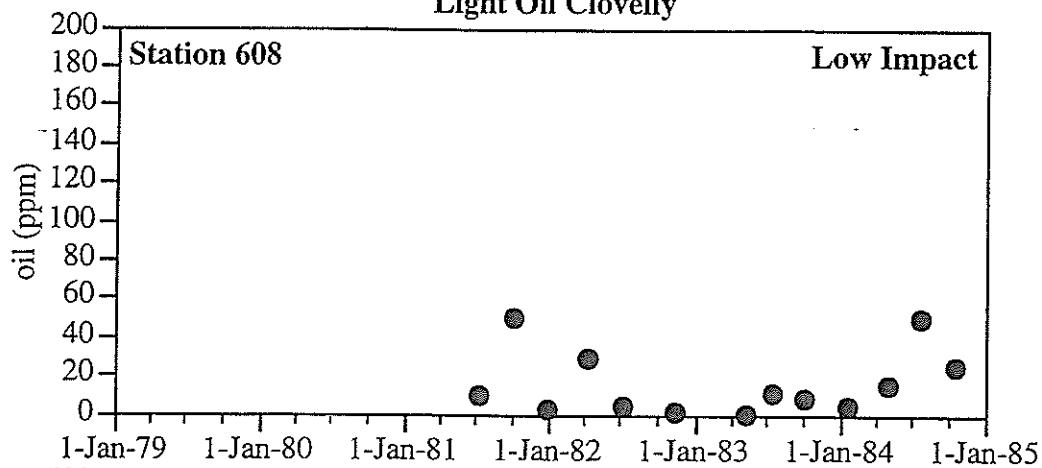
Light Oil Clovelly



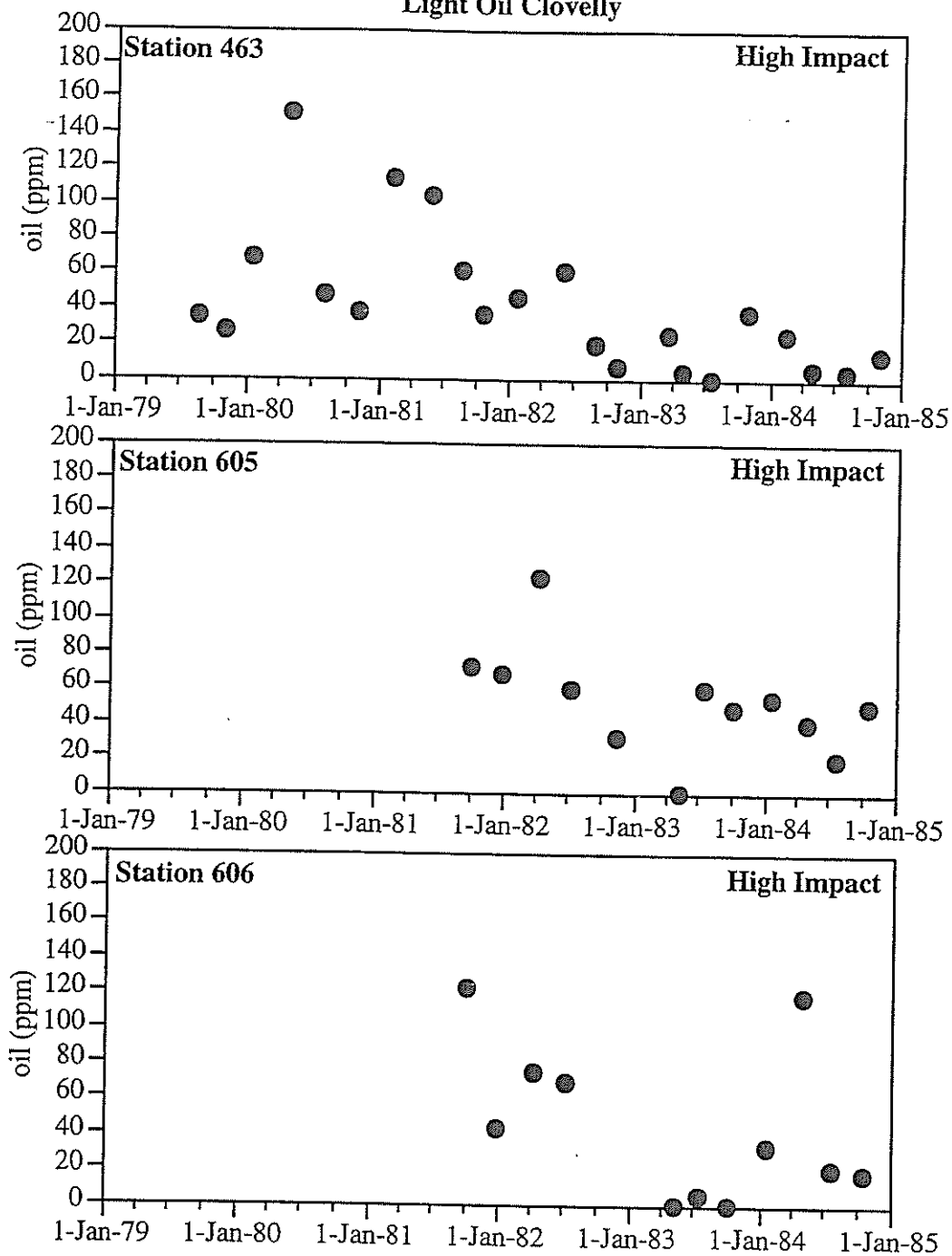
Light Oil Clovelly



Light Oil Clovelly

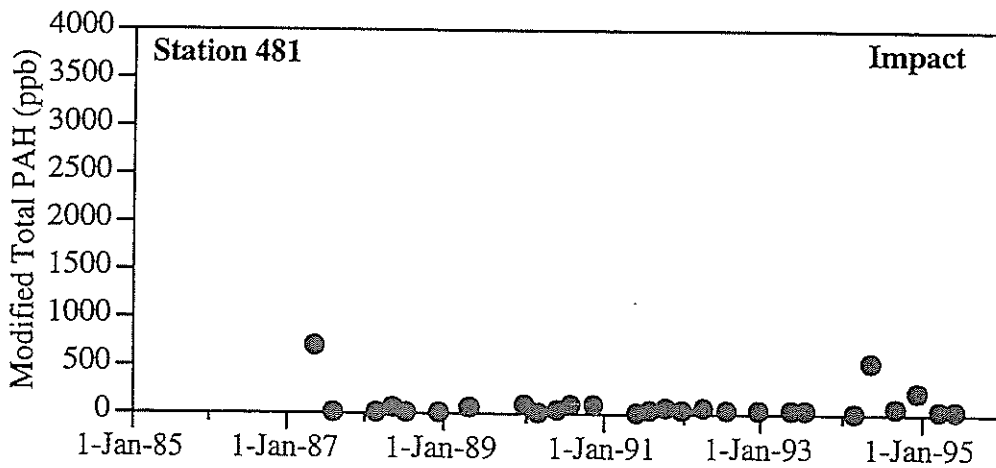
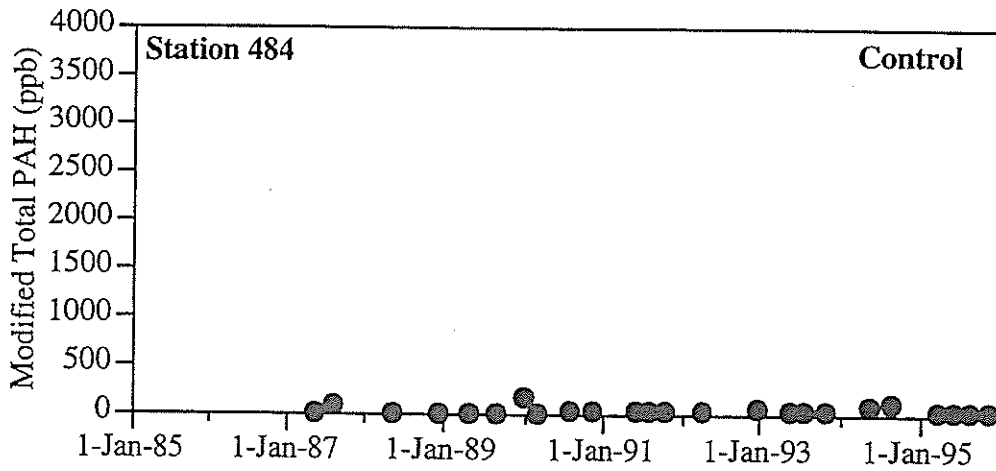
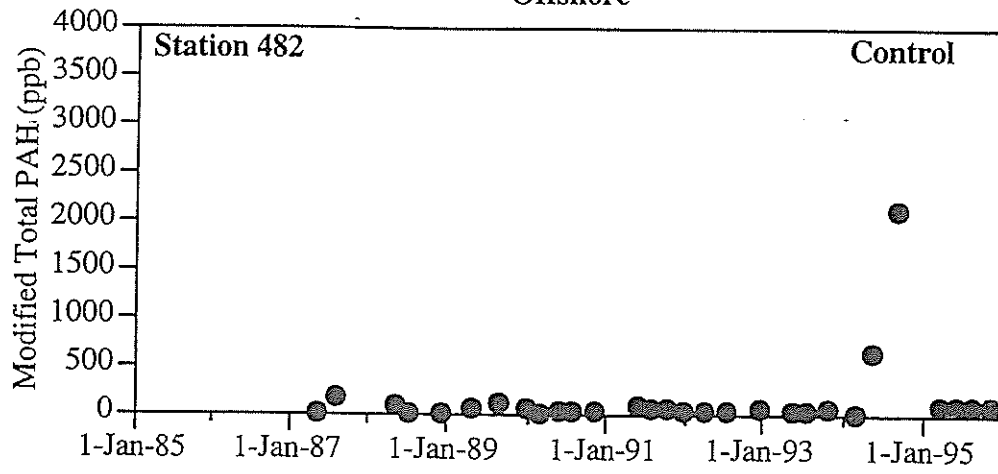


Light Oil Clovelly



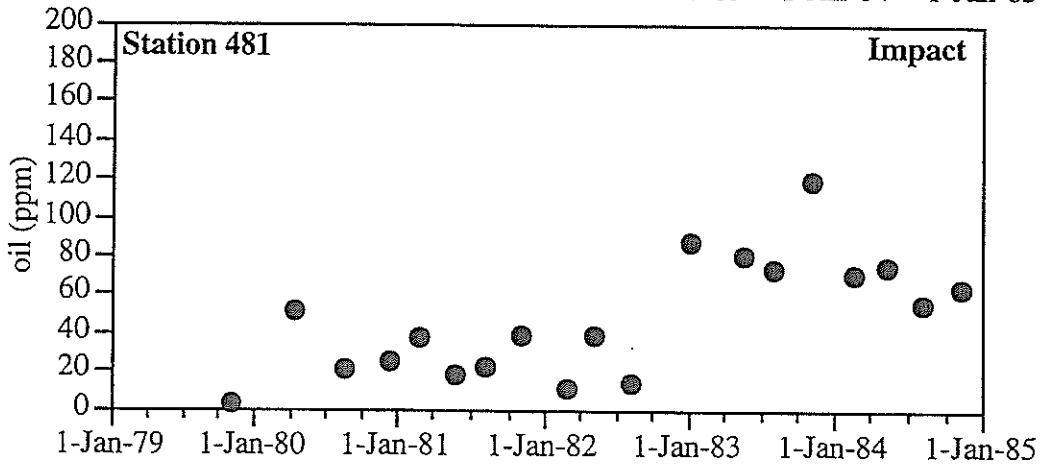
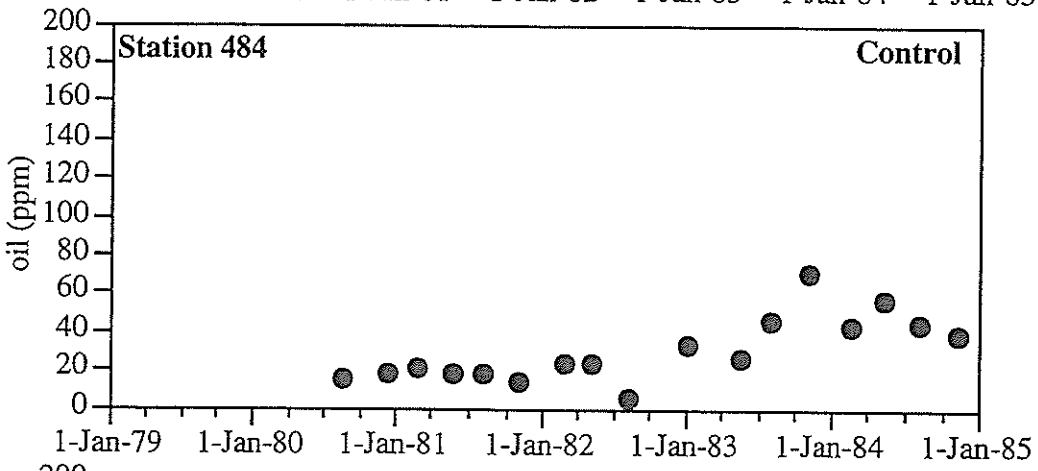
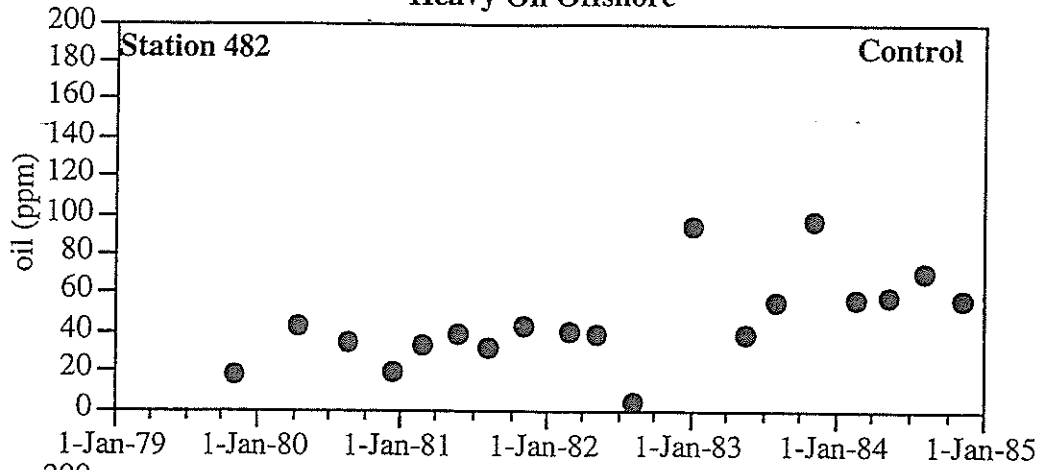
APPENDIX E:
Modified total Polynuclear Aromatic Hydrocarbons
for control and impact stations offshore

Offshore

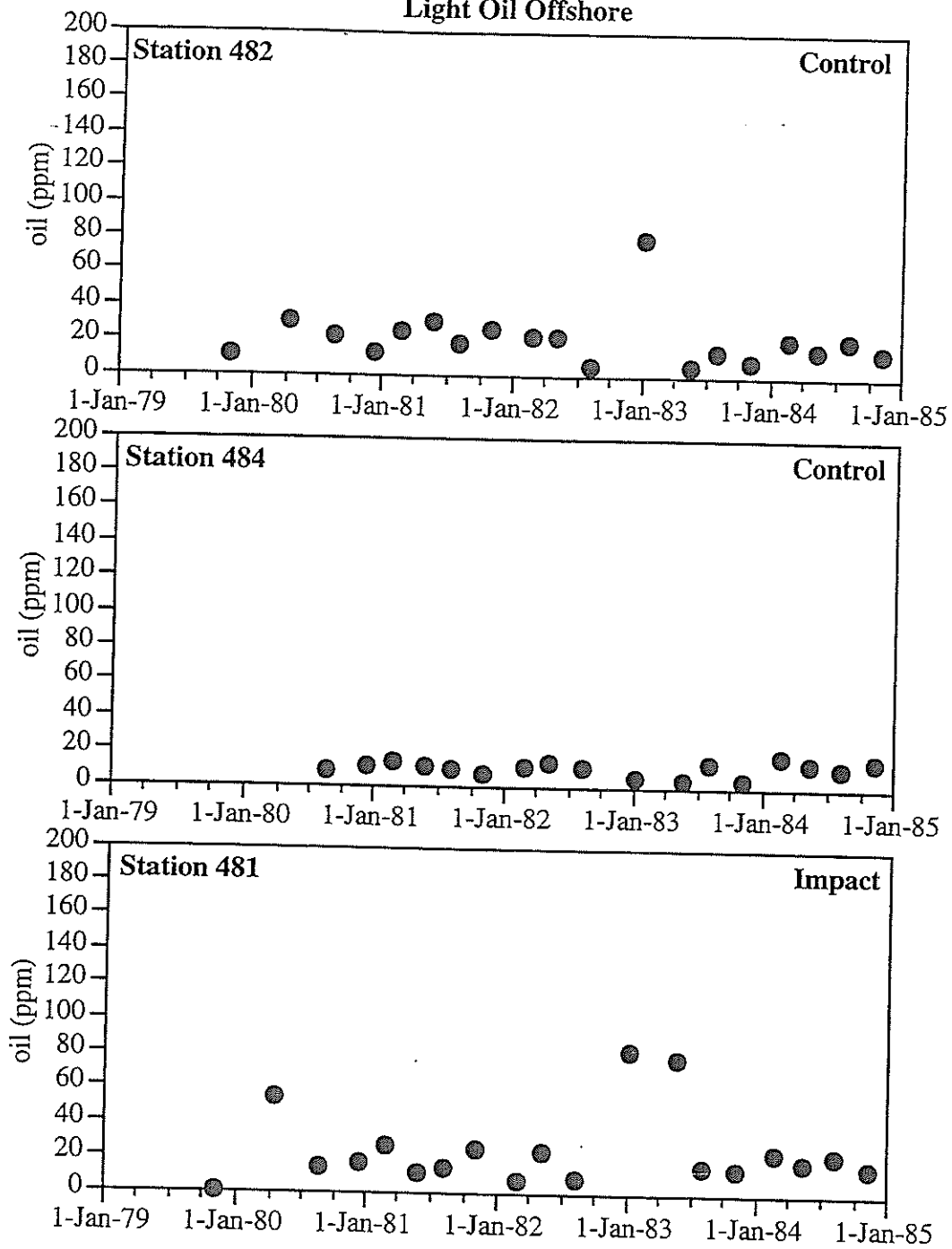


APPENDIX F:
Heavy and light oil concentrations (ppm)
for control and impact stations offshore

Heavy Oil Offshore

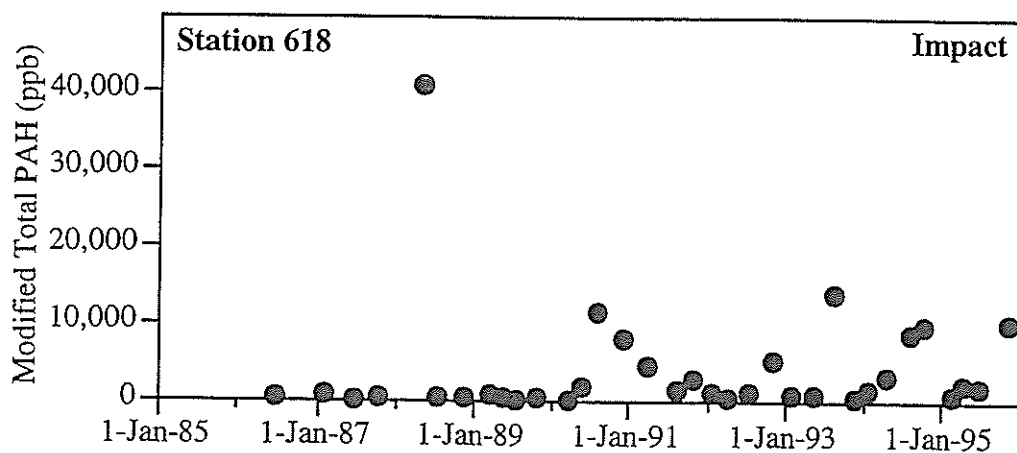
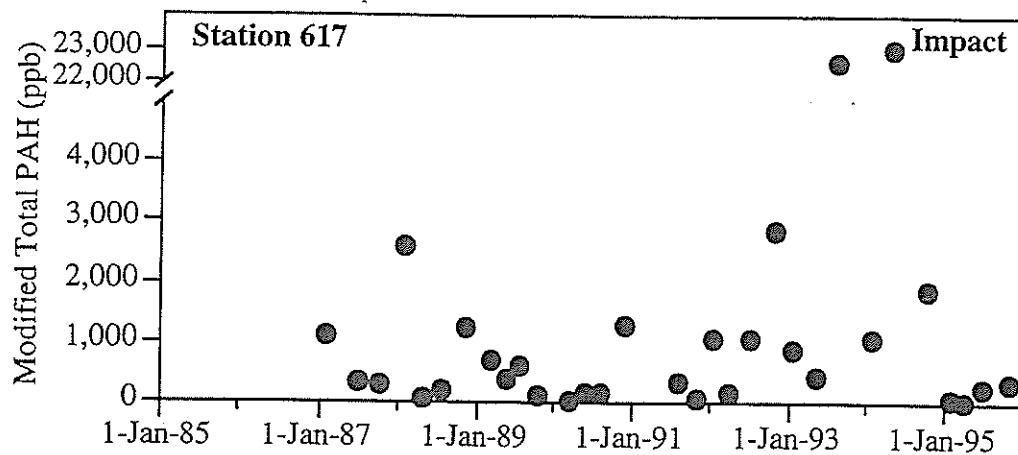


Light Oil Offshore



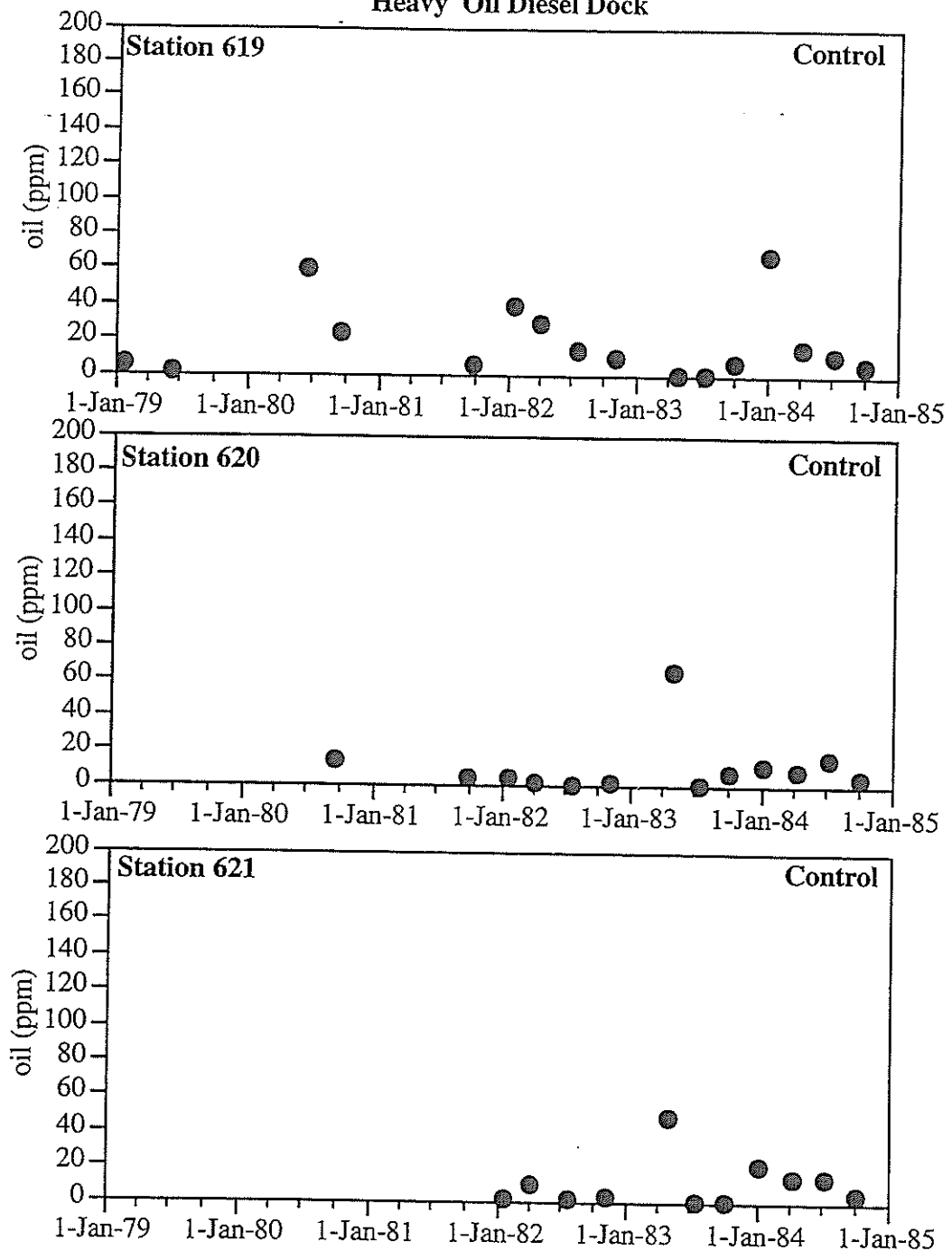
APPENDIX G:
Modified total Polynuclear Aromatic Hydrocarbons
for control and impact stations near the LOOP Diesel Dock

LOOP Diesel Dock

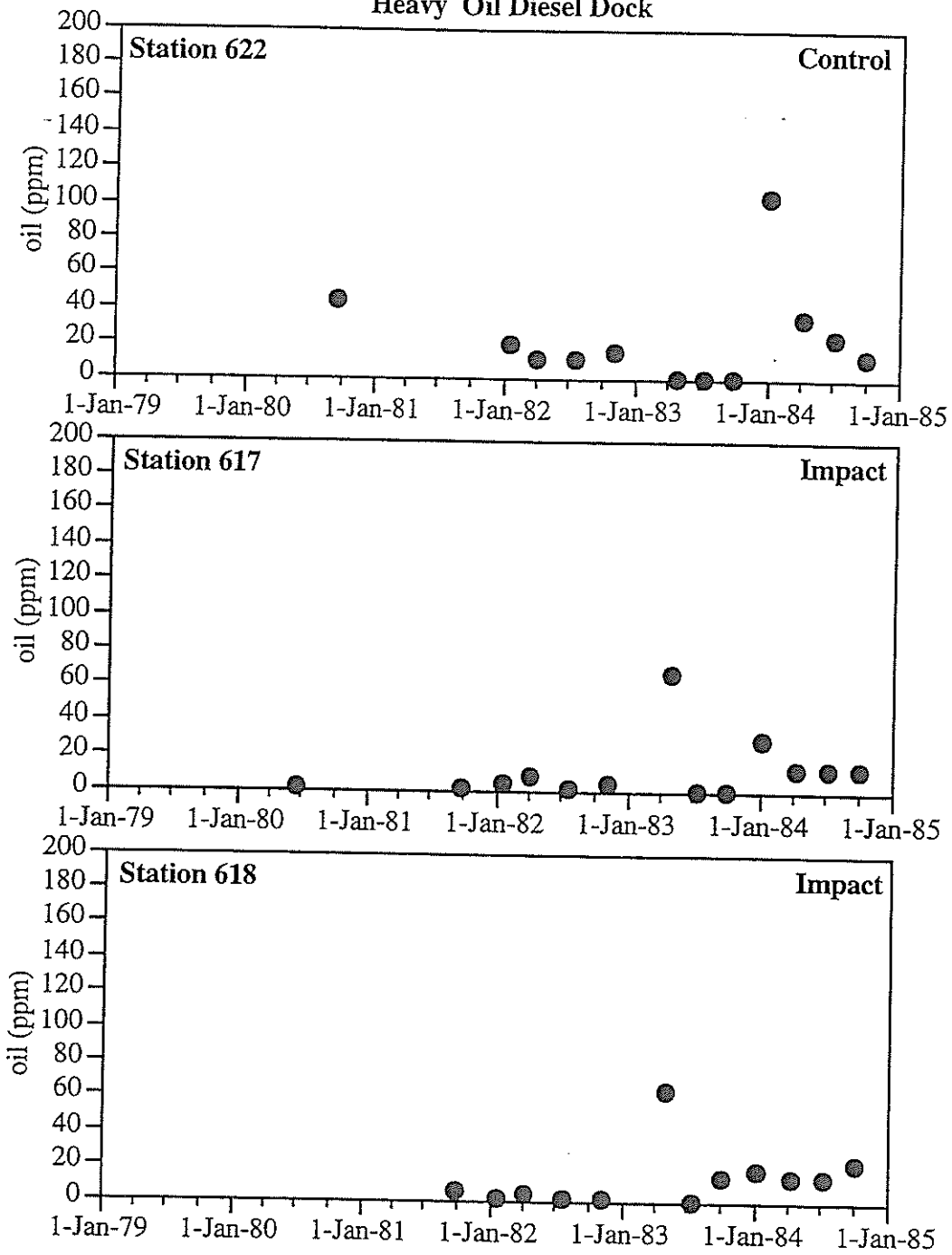


APPENDIX H:
Heavy and light oil concentrations (ppm)
for control and impact stations near the LOOP Diesel Dock

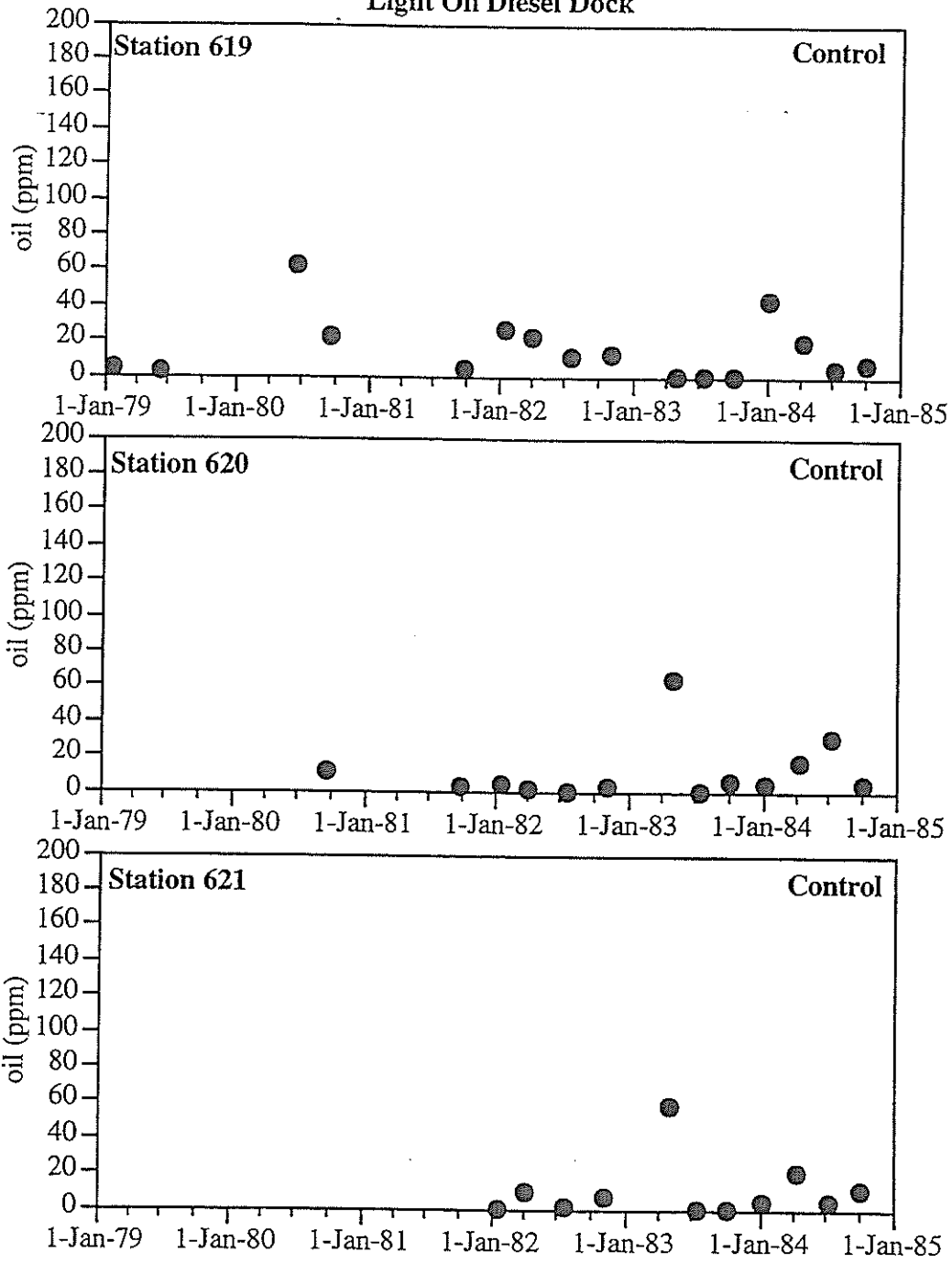
Heavy Oil Diesel Dock



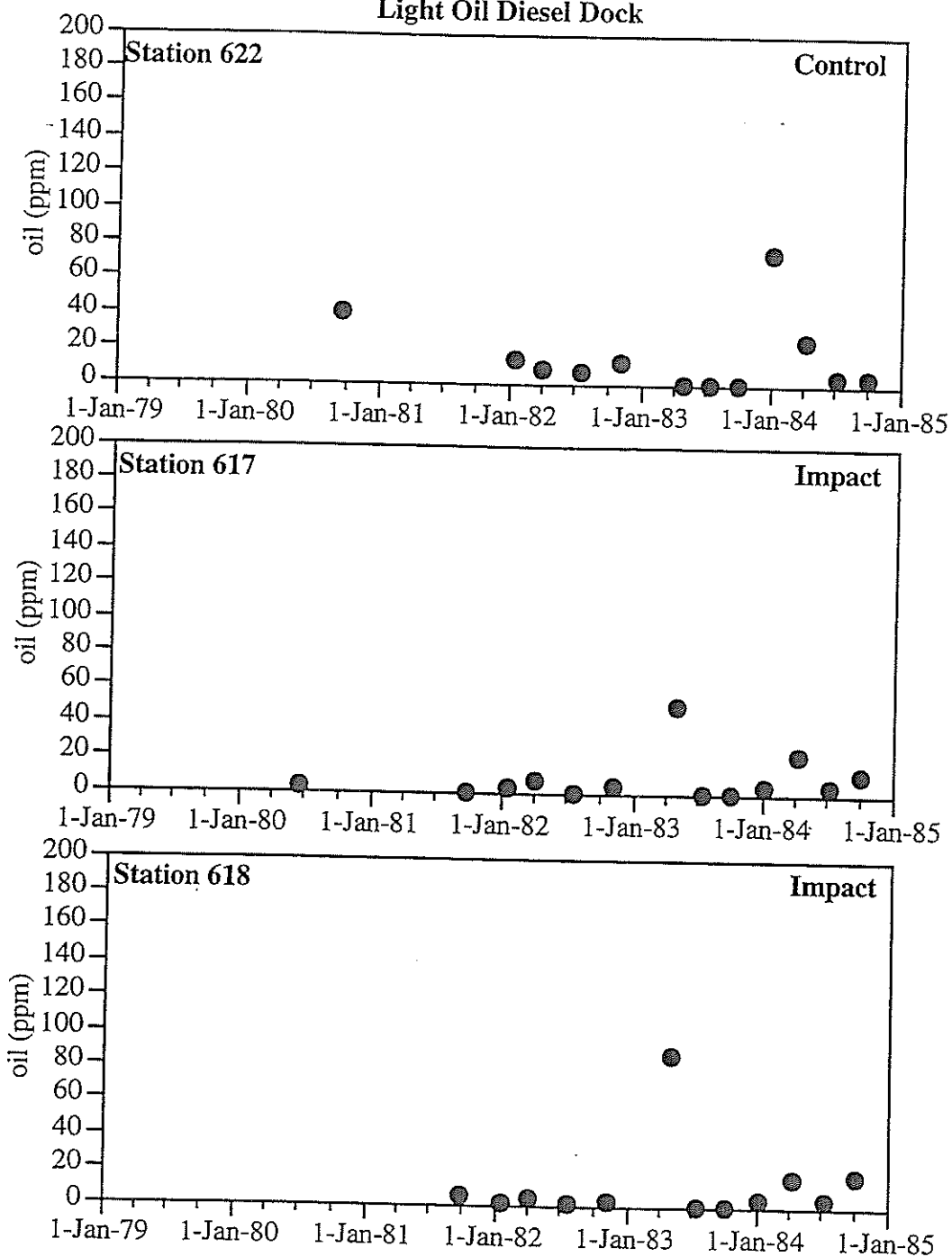
Heavy Oil Diesel Dock



Light Oil Diesel Dock



Light Oil Diesel Dock



**TECHNICAL INFORMATION
FOR THE LOOP MARINE AND ESTUARINE
MONITORING PROGRAM REVISION**

by

Robert P. Gambrell

Wetland Biogeochemistry Institute
Center for Coastal, Energy, and Environmental Resources
Louisiana State University

RESULTS

Significant Results

Table 12. Significant temporal results from Task 2 Data Analyses.

Variable of interest	Temporal trends	Significant Impacts
Light oil, Clovelly storage facility	Increased levels	Possible, but for early years only
Light oil, offshore pumping station	Increased levels	Possible, but for early years only

Table 13. Significant spatial results from Task 2 Data Analyses.

Variable of interest	Spatial trends	Significant Impacts
Total PAHs, LOOP Diesel Dock	Increased levels	Boat servicing activity, but likely non-LOOP activity is contributor
Total PAHs & heavy oil in canals around Clovelly	Increased levels	A few of eight stations may be elevated, again, non-LOOP boating activities may be the significant contributing factor
Light oil, Clovelly storage facility	Increased levels	Possible short-term conditions, not apparent last 10 years
Heavy oil, offshore pumping station	Increased levels	Possible short-term condition, not apparent last 10 years

The above spatial and temporal trends include statistically significant findings with the light oil and heavy oil components for petroleum hydrocarbons measured during the early years (1979 through 1984). For reasons explained in the Phase II report, findings reported for the PAH component of petroleum hydrocarbons measured during the last ten years (1985 through 1995) are believed to be more reliable.

Non-Significant Results

There is only weak evidence that LOOP related spills contributed to increased petroleum hydrocarbons in the stations representing the Clovelly storage facility, sediments in canals connecting with the Clovelly facility, and at the offshore pumping facility. Statistically significant differences seen for these were associated with the data generated during the early years which may be less reliable than the data generated during the later years.

Though statistically significant increases in PAHs were found in the Clovelly area at a few stations in connecting canals, and in the LOOP Diesel Dock area, these findings should be considered “insignificant” or at least not a clear implication of LOOP impacts because of the likely contribution of non-LOOP boating and perhaps non-LOOP petroleum activity in these areas. In the “Clovelly area” grouping, only two or three stations out of about eight likely contributed to the significant increased PAH levels; but these are in public waterways and not necessarily the closest stations to the Clovelly storage facility. Similarly, a small proportion to a large proportion of the source of significantly elevated PAH levels at the LOOP Diesel Dock area could have been due to other boating activity in the immediate area. It is not possible to attribute the findings at this site entirely to LOOP.

The reasons for the non-significant finding of brine water release on pore water salinity at the Brine Diffuser Outlet stations is due entirely to a very small, non-significant change in pore water salinity at this site relative to the control station. The salinity values for both sets of stations were very consistent over time (not nearly as variable as petroleum hydrocarbon content) and essentially the same level. Thus there was no salinity impact at these outlet stations.

RECOMMENDATIONS

The recommendations below are primarily designed to reduce the cost of monitoring while retaining the ability to assess the degree and areal extent of contamination should a major spill associated with LOOP activities occur.

- **Reduce sampling frequency for sediment quality monitoring to once a year**

PAHs degrade slowly in sediments, but they are relatively persistent and significant impacts due to a spill should be evident for many months to many years, depending on the magnitude of contamination. If a spill results in a measurable impact in terms of PAH levels that can be detected for only less than a year, it is likely not an ecologically significant impact. Of course, if a major spill occurs, then sampling should be done soon and more frequently than annually. But, for baseline monitoring where spills are not known to have occurred, annual measurements of sediment PAH levels should be sufficient.

- **Eliminate all on-shore stations intended to be controls if the Louisiana Oil Spill Coordinator's office completes an on-going three-year baseline monitoring study**

This study is measuring more than 65 different petroleum hydrocarbon compounds in marsh soils and sediments at approximately 1,000 coastal sites, and LOOP areas are well represented. The analytical protocol and quality control procedures are very exacting and the data being generated are supposed to be reviewed by an expert before they are accepted. If a LOOP related spill should occur, then at the same time impacted areas are being sampled, LOOP control sites (selected ones used in this project) should be sampled at the same time for comparison to the impact site data.

- **Add at least two more stations near the LOOP offshore terminal**

Currently, there is only one station very near the center of the ship unloading facility. Depending on wind and current direction at the time of a spill, the one station could easily miss an impact as spilled oil may move in a direction away from any single monitoring station.

- **Retain measurements for the usually measured 10 to 15 primary Polynuclear Aromatic Hydrocarbons, (Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzanthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indenopyrene, Dibenz(a,h)anthracene, Benzo(g,h)perylene, and Total Parent PAH Compounds), sand and clay content, organic matter content, bottom and pore water salinity, and sediment moisture content**

LOOP now has ten years of good data on the PAH compounds. The PAH compounds and the other parameters mentioned are the important parameters associated with an oil spill or likely important covariables, and will provide data that will help interpret sediment PAH levels.

- **Eliminate most other measurements not listed above unless they are needed for evaluating impacts on benthic organisms**

For the purpose of evaluating PAH data needed to determine the impact of an oil spill, most other measurements, including the alkylated PAH compounds, chloride, metals, chemical oxygen demand, Kjeldahl nitrogen, phosphorous, pH, and sulfide, are not essential.

- **Consider adding sampling for measuring the sedimentation rate near the offshore terminal and at stations along the pipeline**

There may be substantial sedimentation occurring in some of these areas which would be important should a spill occur in planning sampling depths for monitoring purposes and considering natural burial rates of petroleum hydrocarbons from a spill that becomes associated with the sediment surface.

- **Consider up to three separate subsamples for each station sampled where subsamples are collected something like 50 meters apart**

This change would allow evaluation of the within-sample variability, increasing the power of the statistical models to detect between-sample differences.

- **In future sampling in open waters and all other locations, use modern differential GPS instrumentation to more precisely locate sampling stations and to facilitate returning to the same sampling location**

This should reduce variability associated with sampling.