PORT VALDEZ SEDIMENT CORING PROGRAM
FINAL 2004 MONITORING REPORT

Prepared for:

PRINCE WILLIAM SOUND
RCAC
Regional Citizens' Advisory Council

Prepared by:

KINNETIC
LABORATORIES
INCORPORATED

In Association With:

**Florida Institute of Technology &
TDI Brooks International, Inc.**

January 2006

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FINAL 2004 MONITORING REPORT

Prepared for:

**Prince William Sound
Regional Citizens' Advisory Council
339 Hazelet Avenue
Valdez, AK 99686**

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ABSTRACT

Sediment cores were collected from eight locations in the vicinity of the Alyeska Marine Terminal (AMT), Port Valdez, and surrounding waters in order to construct a history of any hydrocarbon contamination that may have occurred due to the ballast water treatment plant (BWTP) discharge, AMT operations and associated tanker traffic, and other anthropogenic sources. Sediment ages and sedimentation rates were determined using the man-made radionuclides Cesium[137] in tandem with excess Lead[210]. Detailed polycyclic aromatic and saturate hydrocarbon analyses were also performed on each core for source identification, weathering, and for correlation with historic events that have occurred in Port Valdez over the last 50 to 100 years. Sedimentation rates were found to be fairly high throughout the study area, ranging from a low 0.2 to 0.4 centimeters/year (cm/yr) offshore of Gold Creek to a high of approximately 1.5 cm/yr offshore of Lowe River. Accumulations of relatively high levels of weathered polycyclic aromatic and saturated hydrocarbons were found in the vicinity of the AMT that were sourced to Alaska North Slope crude and the BWTP discharge. Clear evidence was also seen in the vicinity of the AMT of construction activities, of hydrocarbon contamination from the 1964 Great Alaskan Earthquake, and of a submarine sediment slide that had occurred in the vicinity of the AMT, most likely during the 1964 Earthquake. Other Port Valdez sites indicated low level 'background' hydrocarbon concentrations throughout the historic record with no evidence of anthropogenic inputs. Sediment from Galena Bay exhibited a very different hydrocarbon pattern from that seen in Port Valdez, with a strong un-weathered petrogenic signature which would indicate coal or other source rock, a high prevalence of biogenic sources, and no evidence of hydrocarbon accumulations from anthropogenic sources.

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EXECUTIVE SUMMARY

This report presents results of sediment chemistry monitoring in the vicinity of the Alyeska Marine Terminal (AMT), Port Valdez, and surrounding waters. The Prince William Sound Regional Citizens' Advisory Council (RCAC) is interested in the long-term input of hydrocarbons from the operation of the AMT and other anthropogenic (human-induced) sources of hydrocarbon input into Port Valdez and surrounding waters. This study was designed to examine these long-term inputs by obtaining sediment cores from the area and measuring hydrocarbon accumulations as a function of time as determined by radiological sediment dating techniques.

To better define the extent of historic hydrocarbon inputs into Port Valdez and surrounding waters, a sediment coring program was conducted by RCAC in 2004. The basic objective of this program was to collect sediment cores and determine sedimentation rates and hydrocarbon concentrations at select locations in the Port Valdez area. Sediment ages and sedimentation rates were determined using the man-made radionuclides Cesium^{137} in tandem with excess Lead^{210}. By using two different radioisotopes, sedimentation rates could be verified by independent methods. Detailed hydrocarbon analyses were also performed on each core for source identification, weathering, and correlation with historic events that have occurred in Port Valdez over the last 50 to 100 years. This program was conducted by Kinnetic Laboratories, Inc. in association with the Florida Institute of Technology and TDI-Brooks International Inc.

The sediment core sampling effort was performed during June 2004. The research vessel M/V *Auklet* was utilized for all sampling efforts. To address the goals and objectives of the program, replicate cores were collected from seven locations in Port Valdez and from one at a presumed "clean" reference site in Galena Bay. The seven locations in Port Valdez included: three sites in the immediate vicinity of the ballast water treatment plant (BWTP) discharge, one site offshore of the AMT, one site offshore of the City of Valdez, one site offshore of Gold Creek, and another offshore of Lowe River. The AMT sites near the BWTP included one site that was located as close to the BWTP diffuser as possible, with additional stations located up- and down-coast along the same depth contour and in the prevailing current direction from the diffuser. Sediment cores were obtained with either a gravity or box corer.

Sediment cores were analyzed for radionuclides to determine sedimentation rates, a suite of hydrocarbon parameters, total organic carbon, aluminum, and by visual descriptive and photographic documentation. The following is a brief summary of key findings.

- Sedimentation accumulation rates in Port Valdez were found to range from a high of approximately 1.5 cm/yr at Lowe to a low of 0.2 to 0.4 cm/yr at Gold. These rates were found to be consistent with past studies in the area that found higher rates near the head of Port Valdez, which is closer to the major sediment input from the Lowe River, with lower rates extending to the west down the longitudinal axis of the Port.

- Hydrocarbon concentrations at the four deep water sites in Port Valdez (AMT-East, Gold, Lowe, and Valdez) exhibited the typical "background" signature of hydrocarbons with low -level accumulations of petrogenic, pyrogenic, and biogenic hydrocarbons.

- Hydrocarbon accumulations at the three inshore AMT sites (AMT-D33, AMT-West, and BWTP) that were located along the same depth contour as the BWTP discharge showed clear accumulations of relatively high levels of weathered polycyclic aromatic and saturated hydrocarbons. The source of these hydrocarbons was determined to be Alaska North Slope crude

which began to accumulate following the construction of the AMT and startup of the BWTP. The highest levels were found to exceed the NOAA's Effect Range –Low (ERL) level in three samples at the location nearest to the BWTP discharge. Hydrocarbon profiles at BWTP showed very low level concentrations prior to the BWTP startup, followed by a steady increase that was found to correspond with increased oil flow through the pipeline and discharges from the BWTP. Hydrocarbon concentrations at BWTP were found to have declined in recent years corresponding to the decreases in pipeline output, tanker traffic, and discharges from the BWTP.

- Evidence suggested in both the sediment geochronology and the hydrocarbon analyses that a submarine sediment slump may have occurred in the vicinity of the AMT that dated from the 1960s and most likely occurred during the 1964 Great Alaskan Earthquake. There appeared to be lost layer of sediment at one of the inshore AMT sites (AMT-D33); a corresponding accumulation of sediment at a deeper offshore site (AMT-East) located directly offshore substantiated the slide. Geophysical investigations that were conducted during 2005 by the United States Geological Survey in Port Valdez have also documented evidence of submarine slides in Port Valdez.

- Based on the historic evidence of submarine slides that occurred in Port Valdez and the steep bathymetry in the vicinity of the AMT, a future earthquake could generate a slide that would remobilize hydrocarbon-contaminated sediments. However, given that the contamination is localized both in space and time (sediment depth), the hydrocarbons are highly degraded, and the hydrocarbon contamination is bound up with the sediments, it is probable that there would not be a large risk to the marine environment should this occur.

- Evidence of the 1964 Earthquake was also seen at another AMT site (AMT-West), where hydrocarbon accumulations were seen in one layer of the core that dated from around the time of the earthquake. This petroleum contamination was found to closely match tar ball samples that have been documented in Prince William Sound and are believed to have been released during the 1964 Earthquake. It has been documented that the 1964 Earthquake and the resulting tsunami heavily damaged port facilities in Valdez which resulted in releases of fuel oil, paving tars, and other petroleum products into the marine environment.

- Evidence was also seen at two of the AMT sites (AMT-West and BWTP) of coarser-grained sediment and sharp bits of stone that had been deposited approximately 25-30 years ago. It is believed that this layer is probably related to AMT construction activities (pile driving, blasting, etc.) that occurred during that time period.

- The sedimentation rate in Galena Bay was found to be in the range of 0.35 to 0.46 cm/yr, with good agreement found between the two dating techniques. The sediments in Galena Bay were found to have higher total organic carbon (TOC) and water content and were also found to have very different hydrocarbon characteristics from the background sediments in Port Valdez. Galena showed a strong un-weathered petrogenic signature which would indicate coal or other source rock; a high Carbon Preference Index (CPI) and high perylene concentrations from biogenic sources; and no evidence of hydrocarbon accumulations from anthropogenic sources.

1.0   INTRODUCTION

The Prince William Sound Regional Citizens' Advisory Council (RCAC) is an independent organization that was formed in 1989 in response to the T/V *Exxon Valdez* oil spill (EVOS). The RCAC was later certified under the Federal Oil Pollution Act of 1990. Operating under a contract with Alyeska Pipeline Service Company, the RCAC acts to minimize the environmental impacts associated with the terminal and the oil transportation tanker fleet. The RCAC's mission includes the performance of research designed to help understand and evaluate environmental impacts associated with oil transportation, including baseline research conducted prior to another spill event.

The RCAC is interested in the long-term input of hydrocarbons from the operation of the Alyeska Marine Terminal (AMT) and other anthropogenic sources of hydrocarbon input into Port Valdez and surrounding waters. Oil transportation and associated activities have had notable effects on the marine environment in the study area of Port Valdez and Prince William Sound (PWS). The latter area of course has received much attention since the March 1989 grounding of the T/V *Exxon Valdez*, but in actuality, contamination input into the area has a much longer history. For example, petroleum contamination was observed in the old Valdez town site sediments and attributed to petroleum product spillage during the Great Alaskan Earthquake of 1964 (Chesler et al., 1976). With construction of the Trans-Alaska Pipeline and the AMT in Port Valdez, hydrocarbon inputs into this area have continued.

Hydrocarbon inputs associated with the AMT include large documented spills such as the EVOS in PWS, the 1994 T/V *Eastern Lion* spill in Port Valdez, the 1997 Ballast Water Treatment Plant (BWTP) spill in Port Valdez, smaller spills and oil sheens associated with tanker loading operations, and long-term chronic input from the BWTP effluent discharge. Discharge from the BWTP outfall is treated ballast water from inbound tankers that still contain residual oil remaining after the treatment process. Chronic inputs of petroleum hydrocarbons to the marine environment such as that from the BWTP, defined as long-term, continuous release of low concentrations of hydrocarbons, have been found to be statistically more of a problem than oil spills (National Research Council, 1985).

Other sources of petroleum hydrocarbon in the area include long-term contamination from both point and non-point source inputs from the City of Valdez, inputs from the municipal small boat harbor in Valdez, natural background concentrations of petroleum hydrocarbons from source rock such as coal, biogenic inputs from terrestrial sources, and boating activity and spills within Port Valdez. For example, the 1964 earthquake and the resultant tsunamis caused the introduction of fuel oil and asphalt derived from California source oils into Port Valdez and subsequently into PWS (Kvenvolden et al., 1995). These authors noted that residues of these California-sourced products have been found throughout the northern and western parts of PWS, typically in the form of tar balls found on beaches at the high tide line.

Environmental baseline studies including hydrocarbon investigations were first conducted in Port Valdez in 1971, prior to the construction and operation of the AMT (e.g., Hood et al., 1973; Kinney, 1973). Sediment, tissue, and water samples collected in Port Valdez prior to the operation of the terminal showed little evidence of petroleum contamination (Kinney, 1973). Port Valdez appeared to be a typical coastal marine environment with low levels of hydrocarbons which were generally biogenic in nature. Further environmental studies were conducted during 1976 through 1978 which included the time period of prior to and following the startup of operations at the BWTP (Colonell, 1980). During the first few years of the BWTP operation, petroleum hydrocarbons associated with the BWTP effluent

(light aromatic hydrocarbons) were detected in water samples collected near the discharge although none were initially seen in the sediments or tissues (Shaw et al., 1980). Sediment samples collected in 1980-82 indicated that petroleum had started to accumulate within a few hundred meters of the discharge (Shaw et al., 1985). Mussels (*Mytilus edulis*, now called *Mytilus trossulus*) and clams (*Macoma balthica*) collected in the vicinity of the discharge also showed elevated concentrations of petroleum hydrocarbons (Shaw et al., 1986).

Continuing refinements in hydrocarbon analytical techniques has resulted in the use of different methods being utilized during similar sediment studies carried out since about 1987, making comparison with historical data difficult. Studies conducted by PWS RCAC in Port Valdez since 1993 have included these analytical refinements, and the use of polycyclic aromatic hydrocarbon (PAH) fingerprinting techniques have clearly indicated that the source of sediment contamination in the vicinity of the BWTP diffuser is the effluent from the BWTP (KLI, 1996 and 2003; Payne et al., 1998 and 2003). The results of the sediment coring program presented in this report also utilized these refinements in analytical technique and were able to accurately examine both the concentration and composition of hydrocarbons that have occurred through time in Port Valdez.

Numerous studies have also been conducted by Alyeska as part of their National Pollutant Discharge Elimination System (NPDES) permit monitoring for the BWTP since its startup. These studies have included intense sediment chemistry and benthic biological sampling all around the BWTP discharge and have clearly shown a buildup of hydrocarbons in the sediments in the vicinity of discharge with high concentrations also seen in the prevailing upcoast and downcoast current direction (e.g. Blanchard et al., 2002 and 2003; Feder and Shaw, 1986 and 1988; Feder et al., 2001; Shaw, 1988; Shaw and Hameedi, 1988; Shaw et al., 1985 and 2000).

In order to determine chronological changes in petroleum hydrocarbon contamination, age-dating of sediments and sediment accumulation rates are needed. The primary source of sediments in Port Valdez is the Lowe River with lesser inputs coming from Mineral Creek, Valdez Glacier Stream, and Shoup Glacier Stream (Sharma and Burbank, 1973). Historic data indicate that the sedimentation rates in Port Valdez vary widely. Higher sedimentation rates were found near the head of the fjord on the eastern end, with rates decreasing along the longitudinal axis of Port Valdez (Klein, 1983; Naidu and Klein; 1988, and Sharma and Burbank, 1973). The lowest rates were found on the western end of the fjord. By examining varves (sedimentary layers) in sediment cores and being able to discern the 1964 Earthquake event, Sharma and Burbank (1973) determined sedimentation rates to be as high as 13.5 centimeters/year (cm/yr) at the head of the Port, decreasing to 1.9 cm/yr at a distance of 6 kilometers (km) from the mouth of the Lowe River, with a mean linear rate of 1.7 cm/yr for the entire Port. Klein (1983) measured sediment accumulation rates in three cores from the western part of Port Valdez and the Valdez Arm based on excess Lead^{210} (Pb^{210}) and found them to range from 0.11 to 0.52 cm/yr. Assuming a deposition rate of about 0.5 to 2.0 cm/yr in the proposed study area in Port Valdez, a core length of 25 to 100 cm is needed to span a 50-yr time period.

In PWS itself, sediment deposition rates appear to be somewhat lower than those in the Port. Offshore sedimentary basins were studied to a limited extent by the U.S. Geological Survey (USGS) as possible sinks for hydrocarbon contamination following the EVOS (Bothner et al., 1990; Carlson and Reimnitz, 1990; Rapp et al., 1990; and Reimnitz and Carlson, 1990). Results of these studies indicate that the offshore sedimentation rates in PWS range from 0.3 to 0.4 cm/yr. Bothner et al. (1990) dated two cores in PWS using Pb^{210} and plutonium isotopes and calculated a depositional rate of 0.32 and 0.30 cm/yr in the vicinities of Montague Strait and Snug Harbor, respectively. Assuming a constant sediment deposition at these rates, a 30-cm core in PWS would enable background hydrocarbon levels to be

determined over a time span of approximately 100 years. Bothner et al. (1990) also found that bioturbation (sediment mixing caused by the burrowing and movement of organisms) was present in both cores from depths of 0 to 11 cm. This bioturbation implies that sediments and hydrocarbons have the potential to be mixed uniformly in at least the upper 10 cm of sediments.

To better define the extent of anthropogenic and other historic hydrocarbon inputs into Port Valdez and surrounding waters, a sediment coring program was conducted by RCAC in 2004. The basic objective of this program was to collect sediment cores and determine sedimentation rates and hydrocarbon concentrations at select locations in Port Valdez. Sediment ages and sedimentation rates were determined using the man-made radionuclide Cesium^{137} (^{137}Cs, first introduced to Earth by bomb testing during the early 1950s; half-life = 30 year [yr]) in tandem with excess Lead^{210} (^{210}Pb, a naturally occurring decay product of Uranium^{238} [^{238}U]; half-life ^{210}Pb = 22.3 yr). By using two different radioisotopes, sedimentation rates could be verified by independent methods. Detailed hydrocarbon analyses were also performed on each core for source identification, weathering, and correlation with historic events that have occurred in Port Valdez over the last 50 to 100 years.

This program was conducted by Kinnetic Laboratories, Inc. (KLI), in association with the Florida Institute of Technology (FIT), TDI-Brooks International Inc. (TDI-Brooks), and its affiliated laboratory B&B Laboratories, Inc. (BBL), for RCAC and was in response to the *Request for Proposals (RFP) for Sediment Coring – Port Valdez*, RFP Number 961-04-01. We would also like to acknowledge Dave Janka, owner and Captain of the M/V *Auklet* that was utilized for the sampling efforts. The purpose of this report is to present the results of that program.

2.0   APPROACH

2.1   Goals and Objectives

As was provided in the RFP and proposal which served as the program study plan for the program, the general goals and objectives for the Sediment Coring - Port Valdez Program were to:

- Collect sediment cores within the mixing zone around the discharge pipe and within Port Valdez and from a reference site in Eastern PWS.

- Conduct chemical analyses on select sediment horizons within the cores to detect the presence and concentration of hydrocarbons from the AMT or other sources.

- Conduct radio-isotope dating of the sediments to determine the rate of sedimentation in the Port and to date trends in hydrocarbon input into the sediment column. These two datasets would show if there have been changes over time of hydrocarbon deposition into the sediments in the Port and if any time periods of increased hydrocarbon accumulation could be correlated to changes in operations at the AMT.

- Gain information regarding the sediment stability in the Port and assess the potential risk for earthquake induced, re-introduction of hydrocarbons buried beneath the seabed back into the water column and possibly into the food chain in the Port.

2.2   Study Design

The study was designed to address all of the general goals and objectives listed above and included the following specific scope of work:

- Replicate sediment cores were collected at six locations in Port Valdez. One core was collected from a presumed "clean" reference site in Galena Bay. Undisturbed sediment cores were collected with sufficient length to allow analysis of sediments deposited prior to the 1964 Earthquake if possible.

- Radio-isotope analysis was performed using the radionuclides ^{210}Pb and ^{137}Cs on the cores in order to date deposition of sediment horizons and determine sedimentation rates in key areas of the Port.

- Chemical analyses including advanced forensic techniques were performed on select sediment horizons to detect the presence and source of hydrocarbons and in the sediments.

- The relative abundance of aluminosilicates and organic matter were determined in selected sediments as a tool for normalizing hydrocarbon concentrations and for helping to identify any anomalies in the distribution of radionuclides.

- Major historical events that reflected impacts to the sediment deposition and/or periods of sediment redistribution or erosion such as the 1964 earthquake were identified where possible in the sediment column.

- An assessment was conducted, based on the data from this study, to determine the potential for any buried hydrocarbons in the sediment column to be reintroduced into the water column and food chain due to a seismic event.

Our goal in designing the program was to not only provide RCAC with the study requested, but to provide the best scientific study possible with the funds that had been allocated. To maximize the amount of useful data collected and analyzed for the program, oversampling was utilized in the field, and a two-tier approach was utilized in the laboratory. Field methodology involved oversampling at discrete intervals over the entire core length for both geochronology and hydrocarbon analyses. This oversampling approach allowed the study to focus on specific intervals of interest that arose during the first tier of chemistry analyses. In the laboratory, the first tier of analysis involved preliminary dating of each core and hydrocarbon analyses from the surface, mid-depth, and near-bottom of each core. These data were then examined with respect to hydrocarbon concentrations and when certain events (e.g., 1964 Earthquake and AMT startup) might have occurred based on the preliminary sedimentation rates. Additional hydrocarbon samples were then selected for analysis based on these results with emphasis placed on specific time intervals and cores that warranted further investigation. At the same time that the second tier of hydrocarbon analyses was being performed, the core dating was refined by running additional sections in each core. Although this tiered approach was somewhat slower than if all of the samples were run at the same time, it ensured that RCAC got the most usable information from the program, since results of the core dating determined which samples were subjected to more detailed hydrocarbon fingerprint analyses.

To address the goals and objectives of the program, replicate cores were collected from seven locations in Port Valdez and from one reference site in Galena Bay that was determined in consultation with RCAC. Initially, six sites were selected in Port Valdez that included three sites in the immediate vicinity of the BWTP discharge: one site offshore of the City of Valdez, one site offshore of Gold Creek, and another offshore of Lowe River (Figure 1). The AMT sites near the BWTP included one site that was located as close to the BWTP diffuser as possible, with additional stations located up- and down-coast along the same bathymetric contour and in the prevailing current direction from the diffuser (Figure 2). Due to difficulties with obtaining good undisturbed representative cores from the eastern-most AMT site, a fourth AMT site was located in deeper water offshore of the AMT.

The first core sampled from each location was used for geochronology and other chemical analyses with the goal of obtaining a reliable record of sediment hydrocarbon accumulation over the past 60-100 years. The second core was utilized for physical characterization and identification of any sediment horizons, annual varves, or other discontinuities that would aid in core dating and interpretation. In addition to these physical measurements, a digital photographic record was collected of each physical characterization core. The geochronology/chemistry core was sub-sectioned into 0.5-2 cm intervals yielding a variable number of samples (20 to >50 samples/core) for age dating and hydrocarbon analyses. In addition to the geochronology measurements using excess ^{210}Pb and ^{137}Cs, select samples from each of the age-dated cores were analyzed for concentrations of individual polycyclic aromatic hydrocarbons (PAH), aliphatic hydrocarbons (AHC), select biomarkers, and other diagnostic and normalizing parameters to aid in source identification.
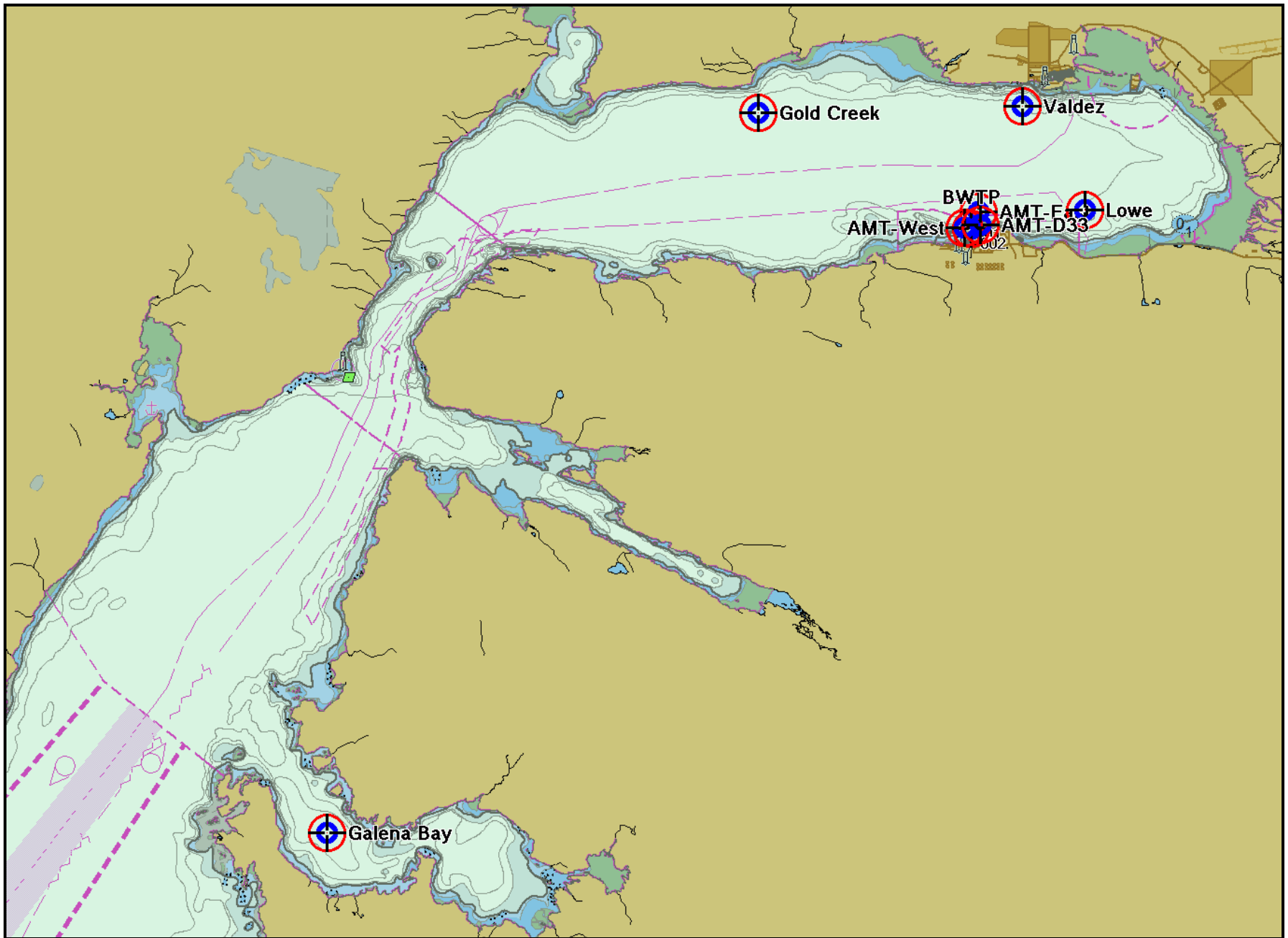
Figure 1. Sediment Coring Locations in Port Valdez and Galena Bay.
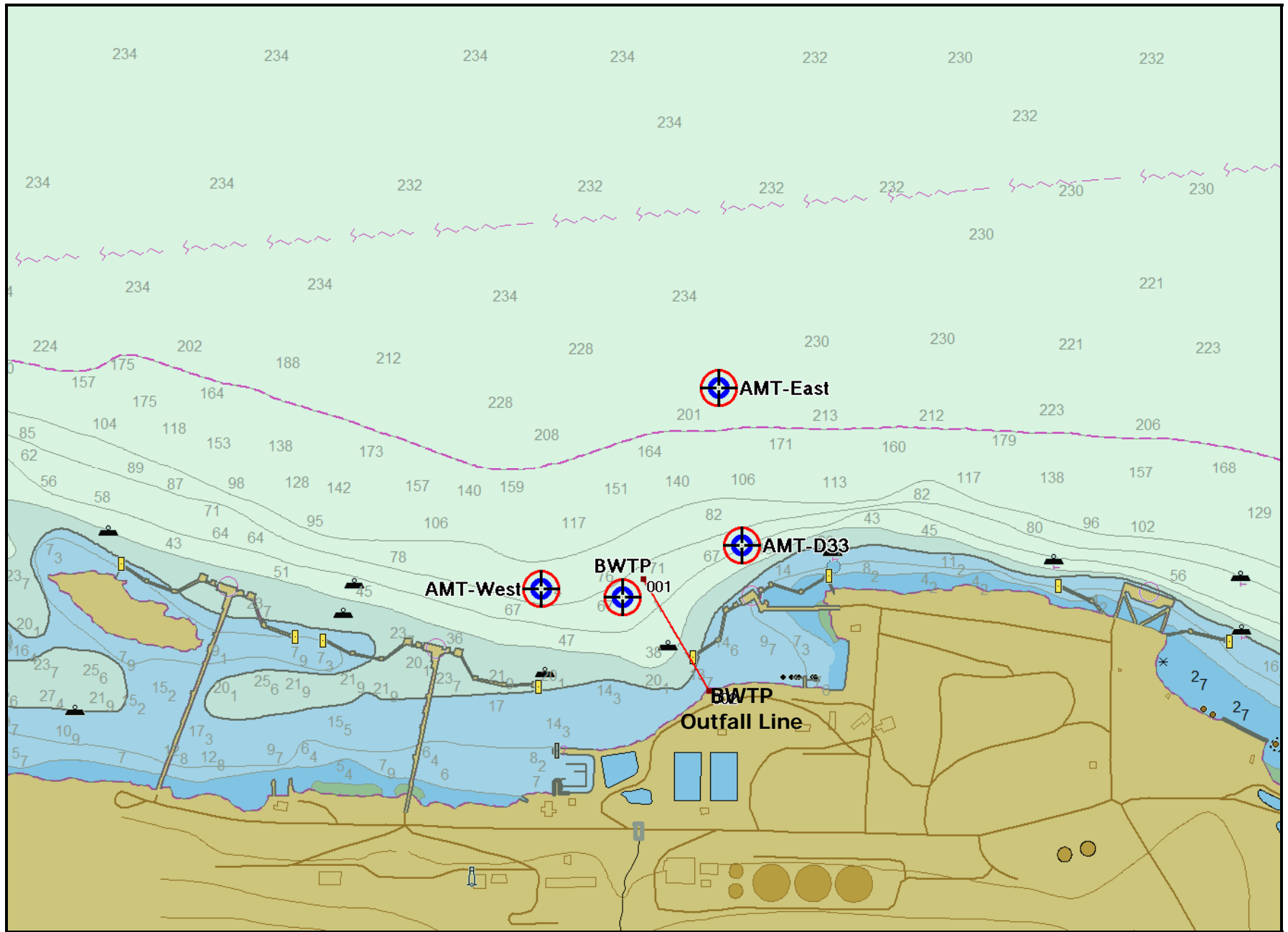
Figure 2. Sediment Coring Locations near the Alyeska Marine Terminal.

3.0 MATERIALS AND METHODS

3.1 Field Collection Methods

Sediment core sampling was performed with a borosilicate-lined gravity corer at locations where relatively high sedimentation rates (> 0.3 cm/yr) were expected. A Gray-O'Hara box corer was used at sites where low sedimentation rates were expected to minimize disturbance of the depositional layers. When the box core was utilized, sub-cores were taken by hand using a 3.5-inch internal diameter (ID) borosilicate core liner. After a successful core was obtained, the sediment core and liner were removed, capped, and stored in a vertical position to minimize disturbance of the underlying sediment until processing could be performed.

In the field, the gravity and box corer were decontaminated between each replicate or each failed core which brought up any sediment. Decontamination procedures that were used between replicates included the removal of residual sediment by rinsing with seawater, followed by rinsing with high-purity de-ionized water to remove traces of seawater. The gear was then rinsed with high-purity acetone, to remove residual water, and high-purity hexane, to remove hydrocarbons. The gear was allowed to briefly air dry before redeployment. Potential hexane contamination of the samples from this rinsing procedure was not of concern as hexane is not a target analyte for this program. Care was taken during the rinsing procedure to contact all interior surfaces of the corer including the cutter, catcher, and core liner that would come into contact with the sediment. Between stations, an additional step of thoroughly washing the corer and utensils with Alconox® and rinsing with seawater was employed prior to the decontamination procedure. Solvents and de-ionized water were dispensed from Teflon® squirt bottles. All solvent wastes were collected and returned to land for proper disposal.

Processing of all cores took place at RCAC's office in Valdez. Upon return to Valdez and within 24 hours after collection, each core was extruded vertically in 0.5- to 2-cm thick intervals. The outer rim of sediment (1-2 millimeters [mm] thick) was carefully scraped away with a Teflon spatula and discarded. This process removed the sediment that had smeared upward during sampling so that it was not introduced into the sample to be processed for age-dating. In the top 10 cm of the core, subsectioning was carried out in 0.5- to 1-cm thick layers for radionuclide analysis and in 2-cm thick layers for hydrocarbon analysis. From 10 cm to the bottom of the core, 2-cm thick layers were sampled. Sediment collected from each layer for radionuclide analysis was placed in a separate, tared and labeled polycarbonate snap-cap vial with a layer of Parafilm in place under the cap. The vials were packed in sealed plastic containers for shipment to the laboratory. Sediment collected for the analysis of PAH/AHC were placed in either 60-milliliter (mL) or a 125-mL pre-cleaned and certified glass jars equipped with a Teflon®-lined lid and immediately frozen, remaining frozen during shipment to the analytical laboratory. Sediment jars were filled with some minimal headspace remaining to allow expansion of the sample during freezing.

All field operations for the program were conducted in accordance with KLI's Vessel Safety Plan. This includes, for example, the use of personal flotation devices (PFDs) when in the skiff or when working with equipment over the side such as the gravity or box corer, use of hard hats when working during lifting operations with a crane or boom, vessel safety briefings, etc.

3.2 Sample Documentation and Chain of Custody Procedures

Sample documentation was initiated in the field with the use of pre-printed Core Effort Logs and Core Sampling Logs. Documentation continued during core processing with a Core Profile Log with sample information, Sample Identification/Chain of Custody Forms (COCs), and pre-printed sample labels. The field leader was responsible for review and approval of all field documentation.

The Core Sampling Logs were used to record information collected at each sampling site. This information included survey and station designation, date, time, navigation coodinates, water depth, length of core, observations of sediment characteristics, and any field measurements and other observations. Core Profile Logs contained sampling processing date and time, station identification, sample identification, core measurements and observations, and names of personnel performing the measurements.

Sediment Core Effort Logs were used to record each drop of the corer, including station designation, date, time, and depth of drop, navigational information, and success or failure of each attempt. This type of information is generally intended for KLI's use and can be used to describe bottom type in specific areas, help determine sampling locations, and provide estimates of time needed to successfully sample in a given area as well as allowing the evaluation of equipment performance. For example, due to the irregular bathymetry and rocky bottom near the BWTP, multiple attempts were often necessary to get a successful core at the AMT sites.

Pre-printed labels included project identification, analysis type, date of collection, and a pre-assigned sample identification number. Station designations were not included on the sample labels so that analytical laboratory personnel were unaware of sampling locations.

Sample identification and integrity was ensured by a rigidly-enforced chain of custody program. COCs provide specific information concerning the identification, handling, and shipment of samples. Pertinent information from the sample label was transferred onto the COC, along with other information as required. The original of each COC was packed with the samples in coolers for shipment to the laboratories. The Field Leader retained a copy of each form for the field records and for tracking purposes should a shipment become lost or delayed. Upon receipt of the samples at the analytical laboratory, the Laboratory Sample Custodian signed the samples in by checking all sample labels against the COC information and noting any discrepancies as well as sample condition (e.g., containers damaged during shipment). Internal sample tracking procedures at the laboratory were initiated immediately upon receipt of samples as determined by the laboratories' standard operating procedures.

3.3 Navigation

Navigation and station location included the use of nautical and topographic charts, radar, and a differential global positioning system (DGPS). Since the selective availability has been discontinued for the GPS system, navigational coordinates now obtained using this system are even more accurate than those available in the past. A DGPS equipped with the differential wide area augmentation system (WAAS) capability was utilized to further increase the precision of navigation information particularly with respect to the location of the BWTP discharge. Station locations (longitude and latitude) were recorded on the appropriate log forms during sampling activities. Coordinates were verified and plotted with a computer based National Oceanic and Atmospheric Administration (NOAA) nautical charting and mapping system. Tidal information for the nearest NOAA tidal reference station was obtained from

a field computer using Tide1 Rise and Fall® tide prediction software (Micronautics, Inc., 2004) in order to correct all depth information to the mean lower low water (MLLW) level datum.

3.4   Analytical Methods

3.4.1   Radionuclides

Laboratory Procedures

Upon return to the laboratory at FIT, the tared vials containing sediment were freeze dried and then reweighed to determine water content. For radiometric measurements, ~10 grams (g) of homogenized, freeze-dried and powdered sediment were sealed in a flat-bottom polystyrene vial. After ~3 weeks, the time required to achieve secular equilibrium between ^{226}Radium (^{226}Ra) and ^{222}Radon (^{222}Rn), the activities of various radionuclides were determined using a well-type, intrinsic germanium (WiGe) detector constructed by Princeton Gamma Tech. The activities of ^{210}Pb and ^{137}Cs were monitored at 46.5 kiloelectron volt (keV) and 661.6 keV, respectively, and the activity of ^{226}Ra was determined via the daughter nuclides, ^{214}Pb at 295.2 keV and 351.9 keV, and ^{214}Bismuth (^{214}Bi) at 609.3keV. Each sample was counted for two to three days to obtain optimal counting statistics (coefficient of variance <10 percent [%]). The geometric effect, detector efficiency and counting accuracy were determined using U.S. National Institute for Standards and Technology (NIST) standard reference material (SRM) 4350B (river sediment), NIST SRM 4354 (freshwater lake sediment), and SRMs RGU-1 and RGTh-1 from the International Atomic Energy Agency.

Data Analysis and Modeling

Sediment accumulation rates and sediment ages were determined using the following: (1) the slope of the line for natural logarithm (ln) excess ^{210}Pb (where excess ^{210}Pb = total ^{210}Pb – ^{226}Ra) versus sediment depth, and (2) two different models for excess ^{210}Pb, the constant initial concentration (CIC) model and the constant rate of supply (CRS) model. In the most straightforward approach, sedimentation rates (S) were determined using equation 1:

$$S = (- \lambda)/(\text{slope ln excess } ^{210}\text{Pb/sediment depth}) \qquad (1)$$

where λ (ln 2/half life) is the decay constant of ^{210}Pb (0.693/22.3 yr = 0.031/yr). Sedimentation rates determined using the excess ^{210}Pb data were checked using the time markers determined from the activity of ^{137}Cs by plotting the activity of ^{137}Cs versus age determined from the excess ^{210}Pb data. Use of ^{137}Cs to help validate results from data for excess ^{210}Pb are based on the fact that no ^{137}Cs was present on Earth prior to atmospheric testing of nuclear weapons in the early 1950s. Therefore, the occurrence of ^{137}Cs in a sediment layer is used to state that any layer containing ^{137}Cs was deposited since 1950. In some cases, a spike in the activity of ^{137}Cs corresponds to peak atmospheric testing of nuclear weapons in 1963 (Robbins and Edgington, 1975). However, the problems of sediment mixing and slumping impact the vertical distributions for both ^{137}Cs and excess ^{210}Pb.

The CIC or CRS models also were used to determine sediment accumulation rates. The CIC model assumes a constant initial concentration of excess ^{210}Pb and constant sedimentation rates over time (Koide et al., 1973; Krishnaswami et al., 1971; Robbins and Edgington, 1975). If this assumption is valid, excess ^{210}Pb activity (A in disintegrations per minute per gram [dpm/g]) at a certain depth can be initially described by the basic radioactive decay law as follows:

$$A = A_o e^{-\lambda t} \tag{2}$$

where A_o is the excess ^{210}Pb activity at the sediment-water interface, λ is the decay constant of ^{210}Pb and t is time.

The cumulative dry mass (M_c) in grams/centimeter squared (g/cm^2) is obtained by the following equation:

$$M_c = \sum_{i=1}^{n} \rho_i d_i \tag{3}$$

$$\rho_i = \rho_s (1-\phi) \tag{4}$$

where M_c is the cumulative dry mass (g/cm^2), ρ_i represents the dry density (grams/centimeter cubed [g/cm^3]) at i_{th} depth of core sediment as shown in Eq 4, where ρ_s is the average density of sediment and ϕ is porosity at sediment depth, and d_i is the thickness of the i_{th} depth interval (cm). The average density of Port Valdez sediment was assumed to be 2.65 g/cm^3 (Klein and Hurlburt, 1977). After substituting t $= M_c/S$ where S is the sediment accumulation rate (g/cm^2/ yr), Eq 2 can be rewritten as follows:

$$\ln A = \ln A_o - (\lambda/S)M_c \tag{5}$$

The sediment accumulation rate (S) for each core can be calculated from the slope of the best-fit linear equation between cumulative dry mass and excess ^{210}Pb activity from Eq 5. The age at a certain depth is estimated by dividing cumulative dry mass by the mean sediment accumulation rate.

The CRS model assumes a constant supply of excess ^{210}Pb, but variable inputs of dry sediment (Appleby and Oldfield, 1978; Hermanson, 1990). If these assumptions are satisfied, then the integrated inventory (I) of excess ^{210}Pb beneath sediment of age t is

$$I = I_{Total} e^{-\lambda t} \tag{6}$$

where I_{Total} is the total inventory of excess ^{210}Pb in the sediment column (dpm/cm^2), λ is the decay constant of ^{210}Pb and t is time. The total inventory of excess ^{210}Pb can be calculated from the following:

$$I_{Total} = \sum_{i=1}^{n} A_i M_i \tag{7}$$

where A_i is the activity of excess ^{210}Pb at depth i and M_i is the dry mass (g/cm^2) at the thickness of the i_{th} depth interval. The sediment age (t) at the i_{th} depth interval is

$$t = \frac{1}{\lambda} \ln\left(\frac{I_{Total}}{I} \right) \tag{8}$$

Age dating of sediment with potentially high levels of organic matter or variable amounts of aluminosilicates can be complicated by potential contributions of authigenic ^{226}Ra and sedimentary processes that include physical and biological mixing of bottom sediment, erosion and lateral deposition by storms or earthquakes, and variable sedimentation rates over time.

3.4.2 Total Aluminum and Total Organic Carbon

To determine concentrations of total Aluminum (Al) in sediments, ~40 milligrams (mg) of dry sediment were dissolved in Teflon beakers using concentrated, high-purity hydrofluoric, nitric, and perchloric acids ($HF-HNO_3-HClO_4$) as described in Trefry and Metz (1984). Samples of the certified reference materials (CRM) MESS-3, a marine sediment prepared by the National Research Council (NRC) of Canada also were processed to test for analytical accuracy. Sediment samples, CRMs, and procedural and reagent blanks were analyzed by flame atomic absorption spectrometry (FAAS) using an acetylene-nitrous oxide flame. The method detection limit was 0.1% and all samples contained >6% Al. All analytical techniques followed manufacturers' specifications and laboratory SOPs that follow EPA methods described for Series 7000 (EPA, 1991).

For total organic carbon (TOC), a 0.5 to 1 gram portion of the freeze-dried sediment was placed in a 10-mL Pyrex beaker. Then, 1 mL of distilled deionized water (DDW) and 2 mL of concentrated hydrochloric acid (HCl) were added to remove any inorganic carbon present. The sediment was dried at 60°C and re-weighed to determine the increase in weight due to the formation of hydrated calcium chloride ($CaCl_2 \cdot 2H_2O$) as a result of adding HCl. Then, approximately 200 to 400 mg of pre-treated sediment were weighed into ceramic boats and combusted at 900°Celcius (C) in a Shimadzu TOC-5050A carbon system with SSM-5000A solid sampling module following the manufacturer's instructions. The TOC content of the sediment samples was determined using a four-point calibration curve with pure sucrose as the standard. The TOC concentrations were corrected to account for the increase in sediment mass following the addition of HCl. The calibration curve was checked every 10 samples by analyzing CRM MESS-3.

3.4.3 Hydrocarbons

The analytical strategy for the hydrocarbon analyses in this program is summarized in Table 1 and described in detail in this section. The analytical approach included the use of compound-specific measurements for organic parameters such as PAH, AHC, and select biomarkers to assess hydrocarbon concentrations in sediments. As noted above, TOC and Al determinations were made in sediments to aid in interpretation and for use in normalizing hydrocarbon concentrations.

All hydrocarbon analytical procedures were fully documented in the laboratory's Standard Operating Procedures (SOPs), as listed in Table 2. Each SOP:

- fully describes the methods to be used for analysis,
- is up-to-date, and
- supplies evidence that it meets the quality control standards stated for the project in the Quality Assurance Project Plan (QAPP).

Table 1.   Analytical Strategy for Hydrocarbon Analyses in Sediments.

Parameter	Description	Method
Polycyclic aromatic hydrocarbons (PAH)	2 to 6-ring polycyclic aromatic hydrocarbon compounds; includes homologous series of aromatic hydrocarbons consisting of unsubstituted (parent) compounds, such as naphthalene, and substituted compounds, which are similar structures with alkyl side chains that replace hydrogen ions, such as C_1-naphthalene, and selected biomarkers	Gas chromatograph/ mass spectrometry (GC/MS) in the selected ion monitoring (SIM) mode
Aliphatic hydrocarbons (AHC)	Fully saturated normal alkanes (paraffins) and branched alkanes, n-C_{10} to n-C_{34}; includes the isoprenoid compounds pristane and phytane that are often the most abundant isoprenoids in petroleum hydrocarbons	Gas chromatography with flame ionization detection (GC/FID)
Unresolved complex mixture (UCM)	A mixture of hydrocarbons of undefined structure that are not separated by gas chromatographic techniques; represented by the total resolved plus unresolved area minus the total area of all peaks that have been integrated; a characteristic of some fresh oils and most weathered oils	Gas chromatography with flame ionization detection (GC/FID)

Individual hydrocarbon analytes are provided in Table 3, which also includes individual method detection limit (MDL) for each compound. Analytes include PAH, AHC (normal alkanes, pristane, and phytane), select biomarkers (hopanes and oleanane), and the unresolved complex mixture (UCM). Samples were analyzed as described in the SOPs using essentially the same methods that have been used for the RCAC Long-Term Monitoring Program (LTEMP), the Minerals Management Service (MMS) Arctic Nearshore Impact Monitoring in Development Area (ANIMIDA) and Beaufort Sea Monitoring Programs (BSMP), NOAA Mussel Watch and National Status and Trends Programs, and other nationally recognized programs.

Table 2.   Hydrocarbon Analytical Standard Operating Procedures for the Project.

SOP No.	Standard Operating Procedure
1003	Extraction of Soils and Sediments for Aliphatic, Aromatic and Chlorinated Hydrocarbons
1005	Determination of Total Organic and Inorganic Carbon in Soils and Sediments
1006	Aromatic Hydrocarbon Determination by Selected Ion Monitoring - Gas Chromatography/ Mass Spectrometry
1009	Sample Receiving, Storage, and Tracking
1012	Preparation of Tissue, Water, Soils, and Sediment for Extraction
1013	Determination of Total Petroleum Hydrocarbon in Extracts of Tissue and Sediment
1016	Aliphatic Hydrocarbon Determination by Gas Chromatography/Flame Ionization Detection
1018	Data Management Plan

Table 3.   List of Target Hydrocarbon Analytes and Method Detection Limits.

PAH Compounds (ng/dry g)		PAH Compounds (ng/dry g)		AHC Compounds (mg/dry g)	
Decalin	0.17	Dibenzothiophene	0.15	$n\text{-}C_{10}$	0.011
C1-Decalins	0.35	C1-Dibenzothiophenes	0.31	$n\text{-}C_{11}$	0.012
C2-Decalins	0.35	C2-Dibenzothiophenes	0.31	$n\text{-}C_{12}$	0.008
C3-Decalins	0.35	C3-Dibenzothiophenes	0.31	$n\text{-}C_{13}$	0.013
C4-Decalins	0.35	Fluoranthene	0.21	$n\text{-}C_{14}$	0.014
Naphthalene	0.17	Pyrene	0.19	$n\text{-}C_{15}$	0.017
C1-Naphthalenes	0.33	C1-Fluoranthenes/Pyrenes	0.39	$n\text{-}C_{16}$	0.013
C2-Naphthalenes	0.35	C2-Fluoranthenes/Pyrenes	0.39	$n\text{-}C_{17}$	0.011
C3-Naphthalenes	0.35	C3-Fluoranthenes/Pyrenes	0.39	Pristane	0.012
C4-Naphthalenes	0.35	Naphthobenzothiophene	0.20	$n\text{-}C_{18}$	0.013
Benzothiophene	0.17	C1-Naphthobenzothiophenes	0.41	Phytane	0.012
C1-Benzothiophenes	0.35	C2-Naphthobenzothiophenes	0.41	$n\text{-}C_{19}$	0.011
C2-Benzothiophenes	0.35	C3-Naphthobenzothiophenes	0.41	$n\text{-}C_{20}$	0.014
C3-Benzothiophenes	0.35	Benz(a)anthracene	0.13	$n\text{-}C_{21}$	0.014
Biphenyl	0.14	Chrysene	0.17	$n\text{-}C_{22}$	0.013
Acenaphthylene	0.19	C1-Chrysenes	0.35	$n\text{-}C_{23}$	0.013
Acenaphthene	0.13	C2-Chrysenes	0.35	$n\text{-}C_{24}$	0.011
Dibenzofuran	0.20	C3-Chrysenes	0.35	$n\text{-}C_{25}$	0.014
Fluorene	0.19	C4-Chrysenes	0.35	$n\text{-}C_{26}$	0.012
C1-Fluorenes	0.39	Benzo(b)fluoranthene	0.29	$n\text{-}C_{27}$	0.012
C2-Fluorenes	0.39	Benzo(k)fluoranthene	0.23	$n\text{-}C_{28}$	0.012
C3-Fluorenes	0.39	Benzo(e)pyrene	0.31	$n\text{-}C_{29}$	0.011
Carbazole	0.33	Benzo(a)pyrene	0.22	$n\text{-}C_{30}$	0.012
Anthracene	0.19	Perylene	1.38	$n\text{-}C_{31}$	0.013
Phenanthrene	0.14	Indeno(1,2,3-c,d)pyrene	0.28	$n\text{-}C_{32}$	0.012
C1-Phenanthrene/Anthracenes	0.29	Dibenzo(a,h)anthracene	0.15	$n\text{-}C_{33}$	0.010
C2-Phenanthrene/Anthracenes	0.29	C1-Dibenzo(a,h)anthracenes	0.31	$n\text{-}C_{34}$	0.012
C3-Phenanthrene/Anthracenes	0.29	C2-Dibenzo(a,h)anthracenes	0.31		
C4-Phenanthrene/Anthracenes	0.29	C3-Dibenzo(a,h)anthracenes	0.31		
		Benzo(g,h,i)perylene	0.14		
Individual Alkylated Isomers & Hopanes					
2-Methylnaphthalene	0.20	C29-Hopane	1.11		
1-Methylnaphthalene	0.13	18a-Oleanane	1.11		
2,6-Dimethylnaphthalene	0.20	C30-Hopane	1.11		
1,6,7-Trimethylnaphthalene	0.10				
1-Methylphenanthrene	0.20				

A brief description of the hydrocarbon analytical procedures that were used for this program are provided in the following subsections.

Sediment Extraction for Aliphatic, Aromatic, and Total Petroleum Hydrocarbons

This SOP provided an accurate and precise method for extraction, isolation, and concentration of selected organic compounds from soil and sediment samples. It achieved analyte recoveries equivalent to those from Soxhlet extraction, using less solvent and taking significantly less time. Final extracts were used in the quantitative determination of PAH, AHC, and TPH by chromatographic procedures. This procedure was also used to extract soil and sediment samples for gravimetric determination of extractable organic material (EOM).

An automated extraction apparatus (Dionex ASE200 Accelerated Solvent Extractor) was used to extract various organics from 1 to 15 g (usually 10 g if adequate material was present) of pre-dried sample. The extractions were performed using 100% dichloromethane inside stainless-steel extraction cells held at elevated temperature and solvent pressure. The extracted compounds dissolved in the hot solvent were collected in 60-mL glass vials. Extracts were concentrated to a volume of 1-3 mL, using an evaporative solvent reduction apparatus (Zymark TurboVap II or water bath), and if necessary, processed through a clean-up column in order to minimize matrix interference. Extracts were then concentrated to a final volume of 1 mL and submitted for determination of hydrocarbon analytes.

Aromatic Hydrocarbon Determination by Selected Ion Monitoring

PAH and their alkylated homologues were determined using a gas chromatograph/mass spectrometry (GS/MS) technique in the selected ion monitoring (SIM) mode. The gas chromatograph was temperature-programmed and operated in splitless mode. The capillary column was a Agilent Technologies HP-5MS (60 m long by 0.25 mm ID and 0.25 micrometer [μm] film thickness). Carrier flow was by electronic pressure control. The autosampler was capable of making 1 to 5 microliter (μL) injections. The mass spectrometer was capable of scanning from 35 to 500 atomic mass units (AMU) every second or less, utilizing 70 volts electron energy in electron impact ionization mode. The data acquisition system allowed continuous acquisition and storage of all data during analysis and was capable of displaying ion abundance versus time or scan number.

Calibration solutions were prepared at five concentrations ranging from 0.02 to 1 μg/mL by diluting a commercially available solution containing the analytes of interest (typically NIST SRM 2260). For each analyte of interest, a relative response factor (RRF) was determined for each calibration level. The 5 response factors were then averaged to produce a mean RRF for each analyte.

An analytical set consists of standards, samples, and quality control samples. Each extraction batch was analyzed as an analytical set including samples and some or all of the following quality control samples: method-blank, duplicate, matrix-spike, matrix-spike duplicate, and/or blank spike, blank spike duplicate, and SRM.

Aliphatic Hydrocarbon Determination by Gas Chromatography/Flame Ionization

This quantitative method was for the determination of AHC in extracts of sediment. Quantitation was performed by high resolution, capillary gas chromatography with flame ionization detection (GC/FID). Normal alkanes with 10 to 34 carbons (C_{10} to C_{34}), and the isoprenoids pristane and phytane were

determined with this procedure. The gas chromatograph was temperature-programmed and operated in split mode. The capillary column was a Restek Scientific RTX-1 (30 m long by 0.25 mm ID and 0.25 μm film thickness). Carrier flow was regulated by electronic pressure control. The autosampler was capable of making 1 to 5 ml injections. Dual columns and FIDs were used. The data acquisition system was by HP Chemstation software, capable of acquiring and processing GC data.

A calibration curve was established by analyzing each of 5 calibration standards (1.25, 10, 25, 40 and 50 μg/ml), and fitting the data to a straight line using the least square technique. For each analyte of interest, a response factor (RF) was determined for each calibration level. All 5 response factors were then averaged to produce a mean relative response factor for each analyte. If an individual aliphatic hydrocarbon was not in the calibration solutions, a RF was estimated from the average RF of the hydrocarbon eluting immediately before the compound. This is the same factor that was used to calculate the UCM, where the concentration of the total resolved were calculated from the average response factor, the sample size, the dilution factor (if any), the amount of surrogate added, and the resultant peak area using the equation for UCM. Results were reported in ng/g (dry weight) for normal alkanes, pristane, and phytane; UCM were reported in micrograms/gram (μg/g) dry weight.

An analytical set consists of standards, samples, and quality control samples. Each extraction batch was analyzed as an analytical set including samples and some or all of the following quality control samples: method blank, duplicate, matrix spike, matrix spike duplicate, and SRM.

Percent Moisture Determination

Percent moisture (weight/weight basis) was determined in samples by measuring the loss in mass of the sample due to drying at 104 °C to a constant weight. Typically, between one and two g of sample were used for the determination. Wet and dried samples were weighed to the nearest mg.

Total Organic and Inorganic Carbon Determination

Total carbon and TOC were measured independently in oven-dried sediments and soils using a LECO CR-412 Carbon Determinator. Dried sediment was combusted at 1,350°C under an oxygen atmosphere and carbon present in the samples was oxidized to form CO_2 gas. This sample gas then flowed through two scrubber tubes. The first tube contains Drierite ($CaSO_4$) and copper granules to remove water and any chlorine gas, respectively. The second tube contained Anhydrone$^®$ ($Mg(ClO_4)_2$) which removed residual moisture. The sample gas then flowed through a nondispersive infrared (NDIR) detection cell. The NDIR cell measured the mass of carbon dioxide gas present and this mass was converted to a percentage value taking into account the sample weight, and mass curve.

In the NDIR detector cell, infrared energy was emitted from a nichrome wire heated to 850°C. Radiant energy entered the cell through a calcium fluoride window and projects through the cell chamber, which contains carrier or sample gas. Gases absorbed infrared energy as they passed through the cell chamber. As energy exited the cell chamber through a second calcium fluoride window, a precise wavelength filter selectively blocked all wavelengths except that of CO_2 from passing into the detector. The detector responded to the energy changes between the carrier gas and sample gas and ultimately determined the concentration of the carbon contained in the sample.

Prior to analysis, the instrument establishes a baseline. As analysis proceeds, the integrated area under the signal detected was proportional to the amount of CO_2 passing through the NDIR cell. The

computer reads the cell output nine times per second and provides a linearized output. The weight-corrected result was the total weight percent of carbon. The percent TOC was determined by analysis of the dried sediment sample after all inorganic carbon has been removed by acidification with 1.8M (10%) sulfuric acid.

Data Analysis and Reporting

Data analysis results were either acquired by direct connection of the instrument to a computer, or in some cases written in lab notebooks and then entered into a form on the computer. The data were then either transferred to a database automatically as measurements were made, or were entered directly into the database via the use of computer forms. This database was used for all aspects of data storage, error checking, and reporting. Microsoft Excel® was utilized to facilitate data analysis, graphics, reporting, and calculation of summary statistics.

PAH parameters included Total PAH (TPAH) and the fossil fuel pollution index (FFPI; Boehm and Farrington, 1984). Aliphatic hydrocarbon parameters included Total AHC (TAHC), total resolved aliphatic hydrocarbons (TRAHC), total petroleum hydrocarbons (TPH), and the carbon preference index (CPI; Farrington and Tripp, 1977), also known as the odd-even preference index. Ratios such as the CPI are extremely useful for determining potential sources of petroleum in sediments. The UCM was also used as a diagnostic indicator of petroleum contamination and is indicative of petroleum products that have been extensively biodegraded.

While the summed parameters of TPAH and TAHC indicate the total level of hydrocarbon input at a site, they provide no information on the possible sources (i.e., contamination of petrogenic, biogenic, pyrogenic, or diagenic origin). The other parameters including individual PAH and AHC compounds described by Table 4 provide a means of identifying the potential sources of the hydrocarbon inputs.

Data analysis, fingerprinting, and source identification for the hydrocarbon data included narrative descriptions as well as histogram plots of all PAH and AHC data, summary statistics, ratio plots to highlight differences, comparison of summed parameters and ratios.

Table 4.   Hydrocarbon Parameters used in the 2004 Port Valdez Coring Program.

Parameter	Relevance
TPAH	Total PAH as determined by high resolution GC/MS with quantification by selected ion monitoring; defined as the sum of 2 to 5-ring polycyclic aromatic hydrocarbons: Naphthalene + fluorene + dibenzothiophene + phenanthrene + chrysene, and their alkyl homologues + other PAH (excluding perylene); useful for determining TPAH contamination; includes petrogenic, pyrogenic, and diagenic sources
TAHC	Total AHC as defined for the LTEMP quantifies the total n-alkanes (n-C_{10} to n-C_{34}) plus pristane and phytane; represents the total resolved aliphatic hydrocarbons as determined by high resolution gas chromatography with flame ionization detection (GC/FID); includes both petrogenic and biogenic sources
TRAHC	The total resolved aliphatic hydrocarbons, which includes AHC analytes (n-C_{10} through n-C_{34} and pristane and phytane) plus other compounds such as plant waxes and lipids which are not individually identified or reported; includes both petrogenic and biogenic sources
TPH	Total petroleum hydrocarbons is the summation of the total resolved and unresolved aliphatic hydrocarbons
UCM	Petroleum compounds represented by the total resolved plus unresolved area minus the total area of all peaks that have been integrated; a characteristic of some fresh oils and most weathered oils
CPI	The carbon preference index represents the relative amounts of odd and even chain alkanes within a specific boiling range and is defined as follows: $$CPI = 2(C_{27} + C_{29})/(C_{26} + 2C_{28} + C_{30})$$ Odd and even numbered n-alkanes are equally abundant in petroleum but have an odd numbered preference in biological material; a CPI close to 1 is an indication of petroleum and higher values indicate biogenic input (Farrington and Tripp, 1977)
Biomarkers	Three select biomarkers were determined that are often used in hydrocarbon source identification, and included C_{29}-Hopane, C_{30}-Hopane, and 18a-Oleanane

4.0 QUALITY ASSURANCE/QUALITY CONTROL

This program included a comprehensive quality assurance/quality control (QA/QC) program that encompassed all aspects of the project, from initial sample collection through laboratory analysis and data analysis to reporting. The objectives of the QA/QC program were to fully document the field and laboratory data and to maintain data integrity. A brief description of the QA/QC program is provided here, and detailed description is provided in the laboratories individual SOPs and quality assurance program plans and manuals. The QA/QC was designed to allow the data to be assessed by the following parameters:

- Precision
- Accuracy
- Comparability
- Representativeness
- Completeness

These parameters are controlled by adhering to documented methods and procedures and by the analysis of quality control (QC) samples on a routine basis.

4.1 Field Quality Control

Quality control activities in the field included adherence to documented procedures, including those in the proposal and the comprehensive documentation of sample collection and sample identification information.

Sampling procedures used for this program have been documented in the proposal and equipment SOPs. They have also been successfully used on a large number of scientific programs. The use of documented and well-known procedures provided for greater likelihood of obtaining samples uncontaminated by sampling procedures or apparatus. It also helped ensure that data collected over the course of the program are comparable and that the study results are representative of conditions existing at the sampling sites.

Use of extensive field documentation provided a paper trail that existed for each sample and ensured credibility of the data. In addition, sample integrity and identification were ensured by a rigidly-enforced chain of custody program. The chain of custody procedure documented the handling of a sample from the time the sample was collected to the arrival of the sample at the laboratory.

4.2 Laboratory Quality Control

Analytical quality control for this program included adherence to documented procedures, particularly SOPs; calibration of analytical instruments; determination of method detection limits; and use of quality control samples, internal standards, and surrogate solutions.

4.2.1   Adherence to Documented Procedures

The analytical laboratories, FIT and BBL, operate under a quality assurance (QA) program described in their QA management plan and an overall laboratory SOPs. These programs involve the participation of qualified and trained personnel; the use of standard operating procedures for analytical methodology and procedures; a rigorous system of documenting and validating measurements; maintenance and calibration of instruments; and the analysis of QC samples for precision and accuracy tracking.

Documentation in the laboratory included finalizing the original chain of custody forms and generating the internal documents to track samples through the laboratory. The paper trail included the records of various steps of analysis, including calibration and maintenance of equipment, preparation and analyses of samples, and storage conditions (e.g., refrigerator logs).

Hydrocarbon analytical procedures were documented by the SOPs listed in Table 2. Any deviations from the SOPs were documented in the project files. Data affected by such deviations were appropriately qualified as described and have been included in the data appendices of this report. The SOPs are comprehensive and typically provide information concerning proper sample collection, storage, and preservation; required apparatus and materials; analytical procedure; standardization and calibration techniques; quality control samples required; methods of calculating values and assessing data quality; and reporting and performance criteria.

The laboratories followed specific procedures when the data results did not meet acceptable quality criteria, as outlined in the appropriate SOPs. This included the re-analysis of samples, if necessary, due to matrix interferences or other problems. For the hydrocarbon laboratory, all sample results that did not meet QC criteria, if any, were qualified as falling outside QC limits using data qualifiers provided in Table 5. Values that met QC criteria were not typically qualified in the data, but in some cases, a "Y" or "<3xMDL" qualifier may have been used.

Table 5.   Hydrocarbon Qualifiers for Port Valdez Coring Program Data Reporting.

Data Code	Description
B	Analyte reported in blank
D	Sample diluted in order to analyze, therefore surrogate is diluted
I	Interference noted in sample results
J	Quantity below the MDL
U	Not detected (not measured above zero)
NA	Not applicable
M	Matrix interference
X	RPDs for analytes that are <2xMDL
Q	Does not meet QA criteria
Y	Spike levels <50% of the native values are considered invalid
<3xMDL	Values at concentrations greater than MDL but less than three times the MDL and within QC criteria (used for procedural blanks)

4.2.2 Instrument Calibration

Calibration is an integral part of any instrumental analysis. Calibration requirements for each type of analysis used on this program are fully described in the appropriate SOP. Typically, instrument calibration was performed daily and on a per batch basis. For example, for AHC analysis, the gas chromatograph calibration was performed with at least five standards with different concentrations, one of which was near the method detection limit. This initial calibration was verified by the measurement of a calibration standard every six to eight samples.

4.2.3 Determination of Method Detection Limits

The MDLs for the PAH and AHC analyses were determined following the method detailed in the Federal Register 40 CFR Part 136, Appendix B (1988) (refer to Table 3). The MDL is defined as the lowest concentration of analyte that a method can reliably detect. The MDLs were determined by calculating results of seven replicate measurements of one low-level or spiked sample. The results of a Student's t-test at the 99 percent confidence level was multiplied by the standard deviation of the seven replicates to obtain the lowest possible concentration that is quantifiable at this 99 percent confidence limit (i.e., that is not considered an estimate).

MDLs were estimated for analytes not available in the spike solution or in the actual matrix (i.e., biological tissue) by using the closest-related compound. For alkylated homologues such as C_2-naphthalene, MDLs were estimated as twice that of a similar authentic compound. As called for by the procedure, analyte levels greater than 10 times the historical MDL were not used to calculate MDLs; for analytes exhibiting this matrix interference, the MDL was estimated using the closest related compound.

The MDL was adjusted for sample size for each individual sample and each individual analyte for reporting purposes. Analyte concentrations that fell below the calculated MDL but above zero (0) were considered estimates and were qualified with the "J" qualifier. Concentrations equal to zero (0) were not measured and were qualified with the "ND" code for non-detect. The summed parameters of TPAH and TAHC do not include qualifiers.

4.2.4 Internal Quality Control Checks

Internal laboratory QC checks included the use of surrogate solutions and QC samples such as procedural blanks, matrix spike/spike duplicates, laboratory blank spike/spike duplicates, standard reference materials (SRMs), reference oils, and duplicates. Results from these QC samples allow the assessment of quality assurance parameters such as accuracy and precision of the data. A summary of the QC that was conducted by the hydrocarbon laboratory is provided in Table 6.

The key elements to assure laboratory control included evaluations of precision and accuracy. A procedural blank was analyzed with each analytical run. The procedural blank ensured that contaminants were not introduced into the samples as a result of the analysis of the associated samples. The primary measure of accuracy was through the use of samples spiked with known amounts of specified analytes. Acceptance criteria for spike recoveries are listed in Table 6. The primary measure of precision was evaluated by calculating relative percent difference (RPD) between duplicate analyses. The acceptance criteria for duplicate sample RPDs was dependent upon the relationship between analyte levels and limit of detection. Additionally, BBL analyzed an SRM for each batch, as another indicator of accuracy. SRMs were used for assessing the accuracy of a given method (i.e., the closeness of a measurement to the "true" value). For SRMs, certified concentrations of the target analytes are known

to the analyst(s) and are used to provide a check on performance. Performance criteria for both precision and accuracy have been established for the analysis of SRMs along with other QC specifications and are presented in Table 7.

Table 6.   QA Objectives for Precision and Accuracy for PAH, TPH, and AHC Analysis.

Parameter	Analytes	Determined by	Test Frequency	Acceptance Criteria
Accuracy	All	Matrix Spike Blank Spike	5% or 1/batch	Average recovery of all analytes 80 to 120%
Accuracy	All	Procedural Blank	5% or 1/batch	No more than 2 analytes exceed 3x MDL
Accuracy	All	SRM	5% or 1/batch	30% of mean
Precision*	3 X or > LOD	Duplicate	5% or 1/batch	30% average

Table 7.   Key Elements of Laboratory Quality Control for Hydrocarbon Analyses.

Measurement Type	Warning Limit Criteria	Control Limit Criteria	Frequency
INITIAL DEMONSTRATION OF CAPABILITY (PRIOR TO ANALYSIS OF SAMPLES)			
Instrument Calibration	N/A	Correlation coefficient > 0.998 for each analyte See applicable SOPs	Initial, prior to analysis or interspersed
Calibration Relative Standard Deviation (RSD)	N/A	RSD ≤ 15% See applicable SOPs	Each calibration
Instrument Blank	N/A	< MDL	Each calibration
Calculation of Method detection limit	Must be equal to or less than target values (see Table 3)	Must be equal to or less than target values (see Table 3)	Once each year per matrix
Analysis of Accuracy-Based Material	See applicable SOPs	See applicable SOPs	Initial
ON-GOING DEMONSTRATION OF CAPABILITY			
Continuing Calibration Checks using Calibration Standard Solution	N/A	Within ± 25% of true value See applicable SOPs	A minimum of every 10 samples and at the beginning and end of an analytical set
Accuracy (Matrix Spike)	See applicable SOPs	Table 6	One with each matrix and each batch of samples
Accuracy (SRM)	See applicable SOPs	See applicable SOPs	One with each matrix and each batch of samples (if available)
Precision[1,2,3] (RPD)	See applicable SOPs	Table 6	One for every 20 samples
Surrogates	N/A	Recovery specified in the appropriate SOP	Each sample

[1]The use of control charts to monitor precision for analytes of interest follows generally accepted practices. Upper and lower control limits, based on 95% confidence intervals around the mean are evaluated at regular intervals.

[2]Samples to be spiked are chosen at random (or specified by the client); matrix spike solutions contain selected target compounds of interest. The spiked concentration of each target compound in the sample is 10 to 50 times the calculated MDL. In a valid spike, the amount of analyte added is at least as much as was present in the sample originally.

[3]RPD = Relative percent difference between sample and duplicate.

If the laboratory failed to meet accuracy and precision control limit criteria for a given analysis the data for the entire batch of samples was suspect. Calculations and instruments would be checked; the data batch reanalyzed (i.e., re-injected) to confirm the results. If the values were still outside the control limits in the repeat analysis, the laboratory would find and eliminate the source(s) of the problem before continuing with further sample processing.

TOC

The quality assurance/quality control procedure for this program included the analyses of a method blank, SRM, and duplicate per analytical batch of no more than 20 samples. Method blanks were used to determine that sample preparation and analyses were free of contaminants. The duplicate sample was used to determine the precision of the analysis. A SRM is a material for which a mean and confidence interval are certified for carbon. SRMs were used to verify analytical accuracy. All blanks were subject to the identical preparation and analysis steps as samples. SRM samples were not acidified prior to analysis. The QC criterion for blanks specifies that target analytes must be less than 3X the method detection limit. The QC criteria for duplicate samples are 15% RPD for samples with >1.0%TC and 20% RPD for samples with <1.0% TC. The QC criterion for SRMs is ± 5% of the certified value.

AHC and TPH

The quality assurance/quality control procedure for this program included the analyses of a method blank, duplicate, and matrix spike/matrix spike duplicate per analytical batch of no more than 20 samples. Additionally, a laboratory control sample (LCS) was analyzed with each data set. The LCS is a diesel sample that is analyzed with each TPH run and for which controls are established based on performance. Procedural method blanks were used to determine that sample preparation and analyses are free of contaminants. The matrix spike/matrix spike duplicate was used to measure accuracy and precision of the analysis. All QC samples were subject to the identical preparation and analysis steps as samples. The QC criterion for blanks specifies that target analytes not exceed 3X the method detection limits. The QC criteria for spike recoveries are between 40-120%. The QC criterion for RPDs in valid spiked duplicates is ± 30%. The QC criteria for the LCS are between 85 – 115% of the laboratory determined mean.

Surrogate solutions equivalent to 5-10X the MDL were prepared for various hydrocarbon analyses. The appropriate surrogate solution was added to every sample including quality control samples. The data were corrected based on surrogate recovery up to 100%. The QC criteria for surrogate recoveries are between 40-120%.

PAH

The quality assurance/quality control procedure for this program included the analyses of a method blank, laboratory duplicate, matrix spike/matrix spike duplicate and SRM per analytical batch of no more than 20 samples. A standard reference sediment (NIST 1944) and standard reference oil (NIST 1582) were analyzed with this data set. Method blanks were used to determine that sample preparation and analyses were free of contaminants. The duplicate sample was used to determine the precision of the analysis. The matrix spike/matrix spike duplicate was used to measure accuracy and precision of the analysis. A SRM is a material for which a mean and confidence interval are certified for specific analytes. SRMs were selected based on matrix similarities as well as type and level of certified analytes.

All SRMs were traceable to NIST and were used to verify analytical accuracy. All QC samples were subject to the identical preparation and analysis steps as samples. The QC criterion for blanks specifies that no more than 2 target analytes exceed 3X the method detection limits. The QC criteria for spike recoveries are between 40-120%. The QC criterion for RPDs for valid spiked duplicates is ±30%. The QC criterion for RPDs for valid duplicates is ±30%. The QC criterion for the sediment SRM is ±20% the certified mean. The QC criterion for the reference oil SRM is ± 15% the laboratory derived mean.

Surrogate solutions equivalent to 5-10X the MDL were prepared for various hydrocarbon analyses. The appropriate surrogate solution was added to every sample including quality control samples. The data were corrected based on surrogate recovery up to 100%. The QC criteria for surrogate recoveries are between 40-120%, except d12-perylene.

4.2.5   Laboratory Quality Control Results

Detailed descriptions of all QA/QC variances that were noted by the hydrocarbon laboratory are presented in Appendices B and C. No variances were found during the analysis of TOC, TPH, or AHC. For PAH, a number of QC variances were observed during the first batch of samples as a result of high native PAH levels in some of the samples that resulted in high surrogate recoveries and high MS/MSD recoveries in a couple of samples (refer to Appendix B). Chrysene was also detected outside of the specified %RPD QC limit of 20% in one SRM sample. For the second batch of samples, high surrogate recoveries were again noted for two samples due to high native PAH levels. Due to the high PAH levels in these samples, the samples were diluted prior to analysis and annotated with a "D" in the data report. No other PAH variances were noted in the second batch of samples.

5.0 RESULTS AND DISCUSSION

The sediment coring effort was initially scheduled and undertaken in early May 2004; however, due to vessel hydraulic problems, the sampling could not be performed at that time. Sampling was rescheduled and completed during early June 2004. The research vessel *Auklet* was utilized for all sampling efforts. The sampling plan called for the collection of two cores from each of seven locations. Due to the difficulty in obtaining an acceptable core to the east of the BWTP discharge as a result of rocks in the area, the sampling location was moved farther offshore with only one successful core at the target location. This resulted in sampling at eight locations rather the seven originally planned (Figure 1 and Figure 2). At the AMT, an attempt was made to collect cores relatively close to the diffuser outfall and to the east and west along the same bathymetric contour that would represent the dispersed plume from the BWTP discharge.

Sediment cores were obtained with either a 10-cm diameter gravity corer or a Gray O'Hare box corer. At locations where the box core was utilized, two sub-cores were taken from each box core. The determination of which piece of equipment was utilized at each location depended on expected sedimentation rates and sediment type. The box corer is the preferred method for collection for low sedimentation rate areas and for fine unconsolidated sediment, because it disturbs the sediment less; however, the length of the core is limited to less than 35 cm. The gravity corer was used in high sedimentation areas (e.g., offshore Lowe River), and for consolidated sediment where core retention was not a problem. A summary of the sampling information and locations is presented in Table 8.

Table 8.   Sediment Core Sampling Locations and Sampling Information.

Sampling Location	Sample Date	Core Number	Core Length (cm)	Analysis[1] Performed	Water Depth (m)	Latitude (N)	Longitude (W)
AMT-East	6/8/04	Box 1A/1B	29.0	Chem, Geochr, & Desc	233	61° 05.6230'	146° 23.0972'
AMT-West	6/8/04	Box 1A/1B	29.0	Chem, Geochr, & Desc	82.3	61° 05.3990'	146° 23.5045'
AMT-D33	6/8/04	Grav 2	20.5	Chem & Geochr	76.2	61° 05.4468'	146° 23.0428'
BWTP	6/8/04	Grav 2 Grav 3	55.0 37.0	Chem & Geochr Chem & Descr	76.4 74.3	61° 05.3902' 61° 05.3752'	146° 23.3176' 146° 23.3310'
Gold Creek	6/8/04	Box 2A/2B	24.0	Chem, Geochr, & Desc	241	61° 7.040'	146° 29.580'
Galena Bay	6/7/04	Grav 1 Grav 2 Box 1A/1B	97.0 102.5 29.0	Chem & Desc Desc Chem & Geochr	209 207 205	60° 56.797' 60° 56.795' 60° 56.780'	146° 42.284' 146° 42.280' 146° 42.270'
Lowe	6/8/04	Grav 1 Grav 2	80.5 76.0	Chem & Geochr Chem & Desc	192 193	61° 05.6550' 61° 05.6044'	146° 19.9695' 146° 19.9252'
Valdez	6/8/04	Box 1A/1B	26.0	Chem, Geochr, & Desc	195	61° 07.030'	146° 21.800'

[1] Analyses Included: Chem - Hydrocarbons and TOC;   Geochr - Radioisotopes, Al, and TOC
Desc - Sediment descriptions, photographs, and measurements

5.1   Geochronology

Age dating sediments from Port Valdez was difficult due to the tendency for sediments to slide and slump down the steeps slopes of the basin. The 1964 Earthquake further complicated the sediment record in some locations. Nevertheless, the data set for sediment geochronology provides some reliable sedimentation rates and helps identify, in most cases, sediment layers that pre- and post-date development of the AMT in 1977. Distortion in the profiles for radionuclides also points to possible earthquake impacts in some cases.

The overall summary of the geochronology results (Table 9) shows that sedimentation rates range from as low as 0.2 cm/yr at AMT-East to 1.3 cm/yr at Lowe. In addition to the radionuclide data, results also are available (Table 10) for sediment water content and concentrations of TOC and Al. These supporting data help identify any differences in sediment composition among and within sites. A brief, general overview of the results from the seven sites is presented below. Details are provided in subsequent sections on a core-by-core basis.

Table 9.   Summary of Geochronology Results from Sediment Cores.

Core	^{210}Pb sedimentation rate (cm/yr)	^{137}Cs sedimentation rate (cm/yr)	Age at base of core (cm) [core length in cm]	Comments
AMT-West (Box core 1) (n = 8)[1]	0.7	>0.5	Mid-1960s [28 cm]	Mixed layer from 0-7 cm
BWTP (Grav. core 2) (n = 8)	0.6	0.5	Early 1900s [54 cm]	Good results for 0-12 cm; anomalous layer from 12-20 cm
AMT-East (Box core 1) (n = 12)	0.20 (0-15 cm) 0.44 (0-26 cm)	>0.5(?)	1960s at base of 15-cm top layer; maybe 1950s at 26 cm [26 cm]	Possible slump of ~15 cm overlying intact sediment; may be related to 1964 Earthquake
AMT-D33 (Box core 1) (n = 8)	0.2 - 0.5	0.2 - 0.5	1920s [16 cm]	Top of core was lost during sampling. Possible missing layer that may be related to 1964 Earthquake
Lowe (Box core 1) (n = 16)	1.3	>1.5	1950s [72 cm]	-
Gold Creek (Box core 2A) (n = 7)	0.2 (if two layers) 0.5 (one layer)	>0.4 (one layer)	1950s [20 cm]	Mixing, distortion, possibly two separate layers.
Galena Bay (Box core 1) (n = 12)	0.35-0.46	0.46	1950s [22 cm]	^{137}Cs age agrees well with excess ^{210}Pb age

[1] n – number of samples analyzed from core

Table 10. Sediment Core Water Content (ranges) and Concentrations (mean ± standard deviation) of Al, TOC, and ^{226}Ra.

Core	Water Content (% by weight)	TOC (%)	Al (%)	^{226}Ra (dpm/g)
AMT-West (Box core 1)	52 (0-1 cm) to 33 (26-28 cm)	0.31 ± 0.03	8.8 ± 0.5	1.58 ± 0.05
BWTP (Gravity core 2)	56 (0-1 cm) to 33 (52-54	0.38 ± 0.14	9.2 ± 1.0	1.62 ± 0.03
AMT-East (Box core 1)	54 (0-1 cm) to 38 (24-26 cm)	0.33 ± 0.23	8.8 ± 0.7	1.61 ± 0.03
AMT-D33 (Box core 1)	31 (2-3 cm) to 32 (14-16 cm)	0.28 ± 0.04	8.5 ± 0.3	1.62 ± 0.05
Lowe (Box core 1)	53 (0-1 cm) to 33 (70-72 cm)	0.22 ± 0.03	7.0 ± 1.2	1.69 ± 0.07
Gold Creek (Box core 2A)	57 (0-1 cm) to 33 (18-20 cm)	0.23 ± 0.02	9.2 ± 0.6	1.66 ± 0.07
Galena Bay (Box core 1)	72 (0-1 cm) to 55 (24-25 cm)	0.59 ± 0.08	7.8 ± 0.1	1.47 ± 0.07

Overall, the distribution of water content was very similar down-core for sites AMT-West, BWTP, AMT-East, Lowe, and Gold Creek with levels of 52-57% (by weight) in the top layers of sediment, decreasing to 31-33% at depth (Table 10). In contrast, the water content for the site in Galena Bay was significantly higher with a range from 72% in the top layer to 55% at the base of the core. The core from AMT-33 also was distinct with a range of only 31-32% water.

Concentrations of TOC also were relatively uniform with a range of 0.19-0.34% for all samples except sediments from Galena Bay (0.49-0.68%) and the deepest sample from the core at site AMT-East (0.73%). Concentrations of sediment Al for all samples (n = 55) averaged 8.8 ± 0.9% with a range of 6.2-11.2%. Al concentrations for sediments from sites AMT-West, BWTP, AMT-East, Lowe, and Gold Creek were relatively uniform with mean values of ~9% (Table 10). In contrast, Al levels in sediments from Lowe and Galena Bay averaged 7.0 and 7.8%, respectively. The activities of ^{226}Ra averaged 1.61 ± 0.09 dpm/g (n = 71) for all samples. Mean activities for sediments from Galena Bay (1.47 dpm/g) were lower than the average of 1.63 dpm/g for all other sites combined (Table 10).

5.1.1 AMT-West

The data for excess ^{210}Pb support a sedimentation rate of 0.7 cm/yr for the core from site AMT-West based on a linear regression for ln excess ^{210}Pb versus depth with a correlation coefficient (r) of 0.90 (Figure 3). Data for total ^{210}Pb (absolute values, not ln) were plotted in Figure 3 to show the decrease in total ^{210}Pb activity with increasing depth in the sediment core. The mean activity for ^{226}Ra also is shown on Figure 3 as a bar at the center bottom of the figure. The total ^{210}Pb activity will be equal to the activity of ^{226}Ra when all of the excess (unsupported) ^{210}Pb has decayed (i.e., when activity of excess ^{210}Pb is zero).

Results for ^{137}Cs support a sedimentation rate >0.5 cm/yr that is consistent with the ^{210}Pb results. No more definitive rate can be determined using the activity profile for ^{137}Cs because levels of the isotope were detectable throughout the 28-cm long core. The calculate sedimentation rate was based on deposition of 28 cm over more than 54 years (i.e., [(28 cm)/(2004-<1950 yrs)] = >0.5 cm/yr). The bottom layer of the core most likely pre-dates development of the oil port in 1977, but probably not the earthquake in 1964.
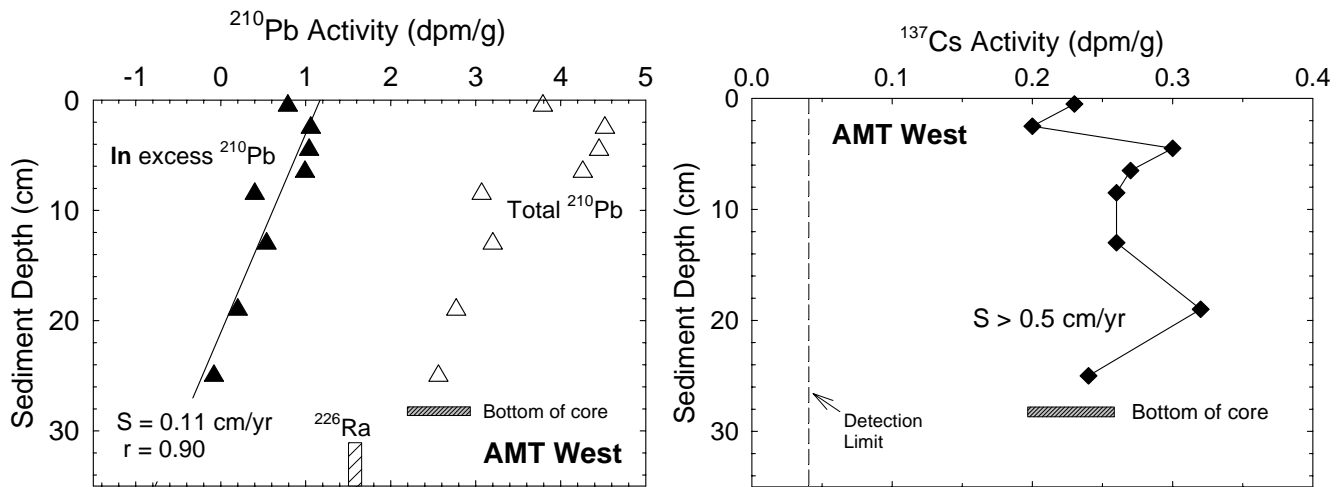

Figure 3.   Vertical Profiles of ln Excess ^{210}Pb, Total ^{210}Pb and Total ^{137}Cs for AMT-West. Box with cross hatching on ^{210}Pb graph shows average activity of ^{226}Ra that is also the activity for supported ^{210}Pb.

The vertical profile for water content shows a non-continuous decrease over the 28-cm core, possibly due to the effects of disruptions in uniform sediment burial due to slumping or mixing (Figure 4). In contrast with the water data, concentrations of TOC and Al were relatively uniform throughout the core.
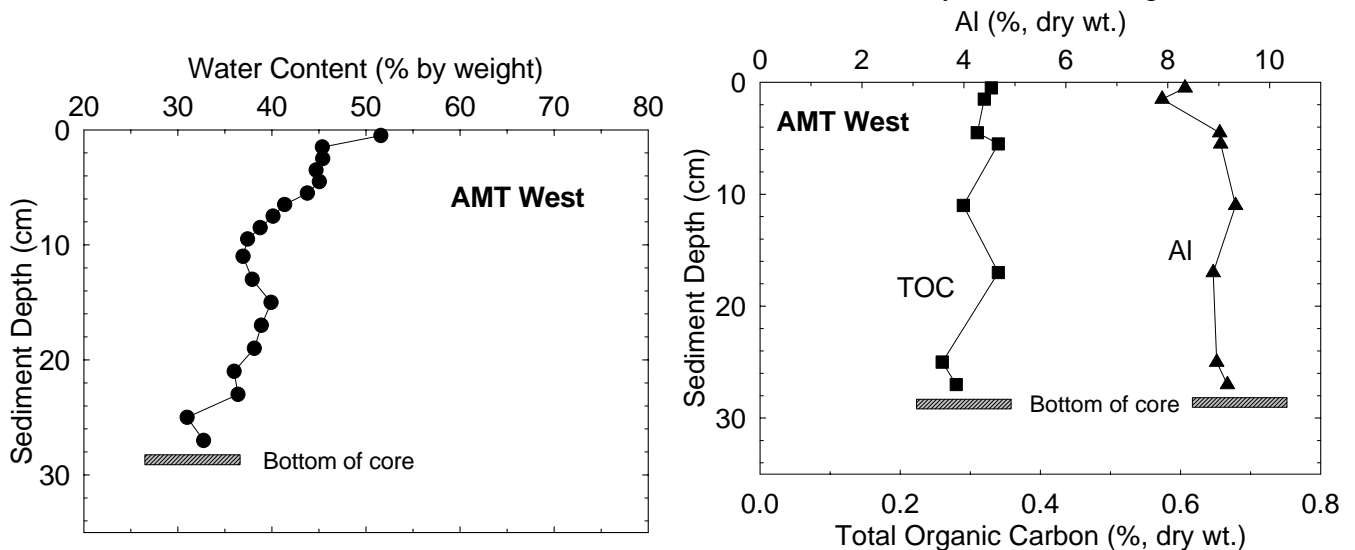

Figure 4.   Vertical Profiles of Water Content and Concentrations of TOC and Al for Site AMT-West.

Results from the CIC model for excess ^{210}Pb (Figure 5) provide dates for each layer. These dates are listed in the Appendix and have an error of ±5 to ±10 years. Thus, the dates used to label vertical profiles for PAH are shown on a decadal basis. When the activities for ^{137}Cs were plotted as a function of age in Figure 5(as determined from the CIC model), the results showed that the core did not extend far enough back in time (older than 1950) to reach a point where no ^{137}Cs was detected.
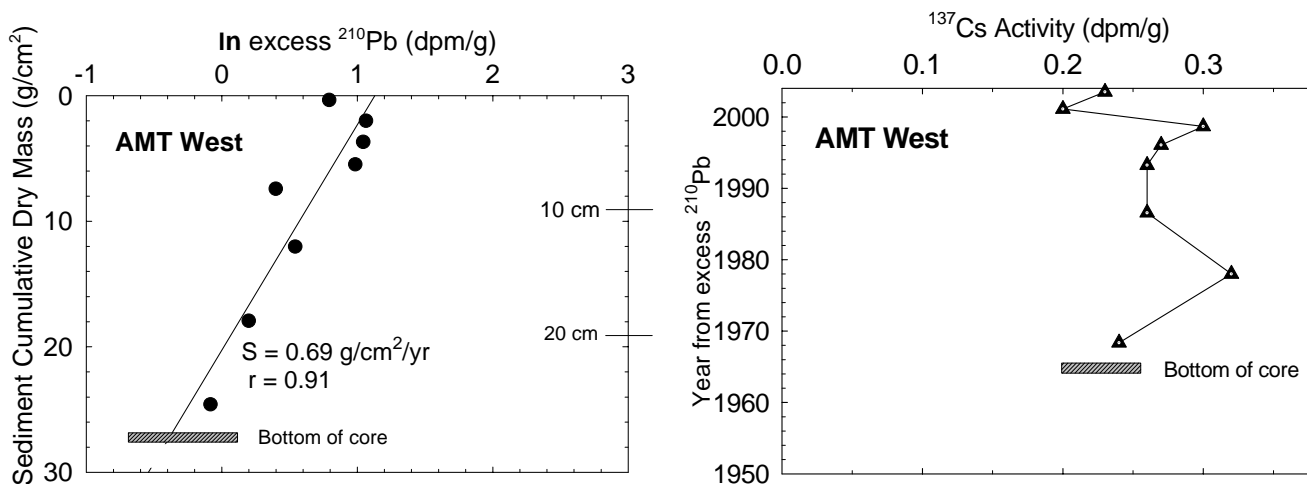

Figure 5. **Profiles Showing ln Excess ^{210}Pb versus Cumulative Dry Mass of Sediment and Activity of ^{137}Cs versus Year from Excess ^{210}Pb Data (CIC model) for Site AMT-West.**

Ages determined by the CIC and CRS models were discordant with discrepancies between the two models yielding older ages using the CRS model (Figure 6). The CIC model was more reliable in this case because the CRS model would date the bottom of the core in the early 1900s and under such conditions, no ^{137}Cs would be observed at the base of the core. Previous investigations have shown such disagreement between models when non-steady state processes in sediment deposition occurred. Such disruptive processes include slumping or rapid inputs of sediment from storms or other events (Hermanson and Christensen, 1991; Appleby, 1993; Kang and Trefry (2003). Thus, the ages that are best applied to each layer in the Appendix were those from the CIC model (Figures 5 and 6).
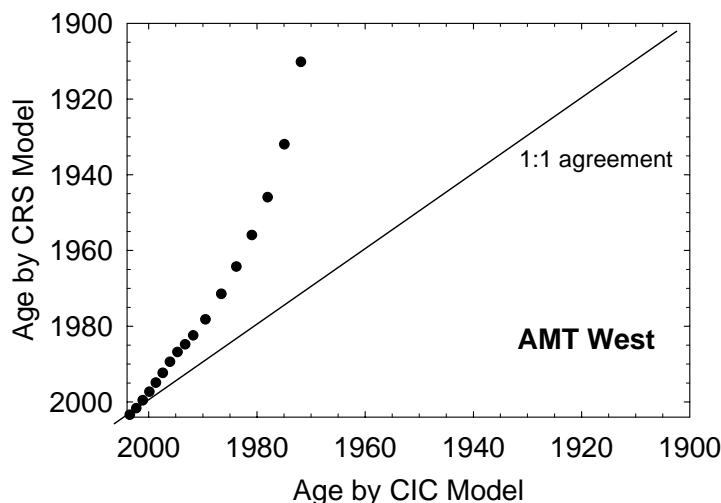

Figure 6. **Comparison of Ages Determined Using the CIC and CRS Models for Site AMT-West.**

5.1.2 BWTP

The vertical profile for ln excess ^{210}Pb for the core from the BWTP site follows a typical exponential decrease for the top 12 cm (Figure 7). Below 12 cm, the activities of excess ^{210}Pb were extremely low or non-detectable. Furthermore, the activities of total ^{210}Pb at depths >12 cm were in good agreement with the mean activity of ^{226}Ra, in support of no detectable amounts of excess (unsupported) ^{210}Pb (Figure 7). This observation for excess ^{210}Pb was consistent with the data for water content that showed an anomalous layer from 12-20 cm (Figure 8). Concentrations of TOC also shifted at ~12 cm; however, no distinct changes in levels of Al were observed (Figure 8).
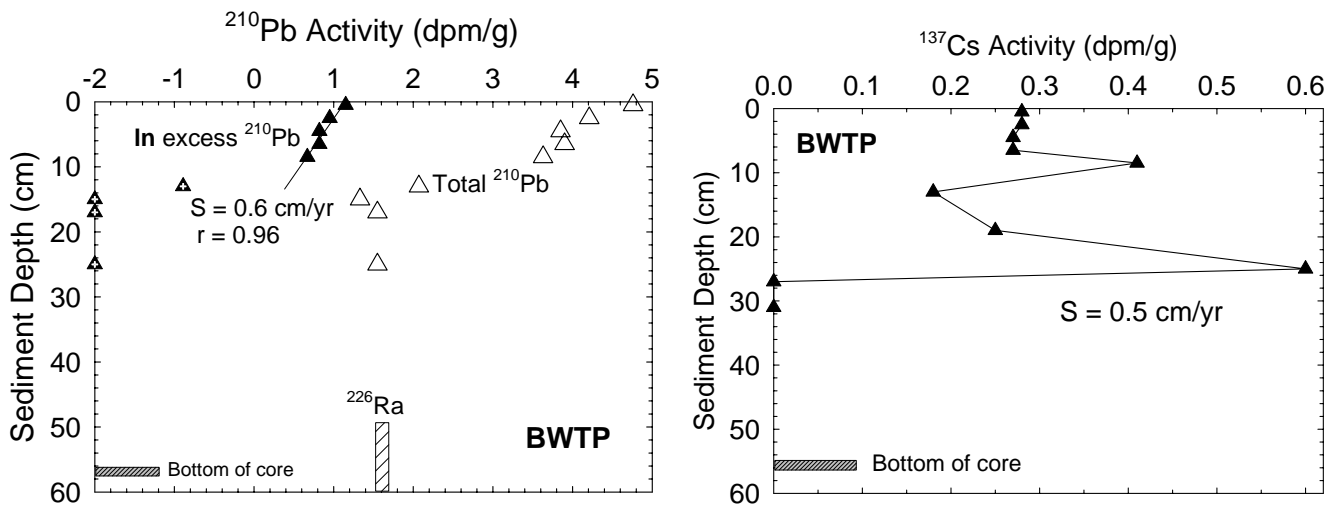

Figure 7. **Vertical Profiles of ln Excess ^{210}Pb, Total ^{210}Pb and Total ^{137}Cs for BWTP.** Box with cross hatching on ^{210}Pb graph shows average activity of ^{226}Ra that is also the activity for supported ^{210}Pb.
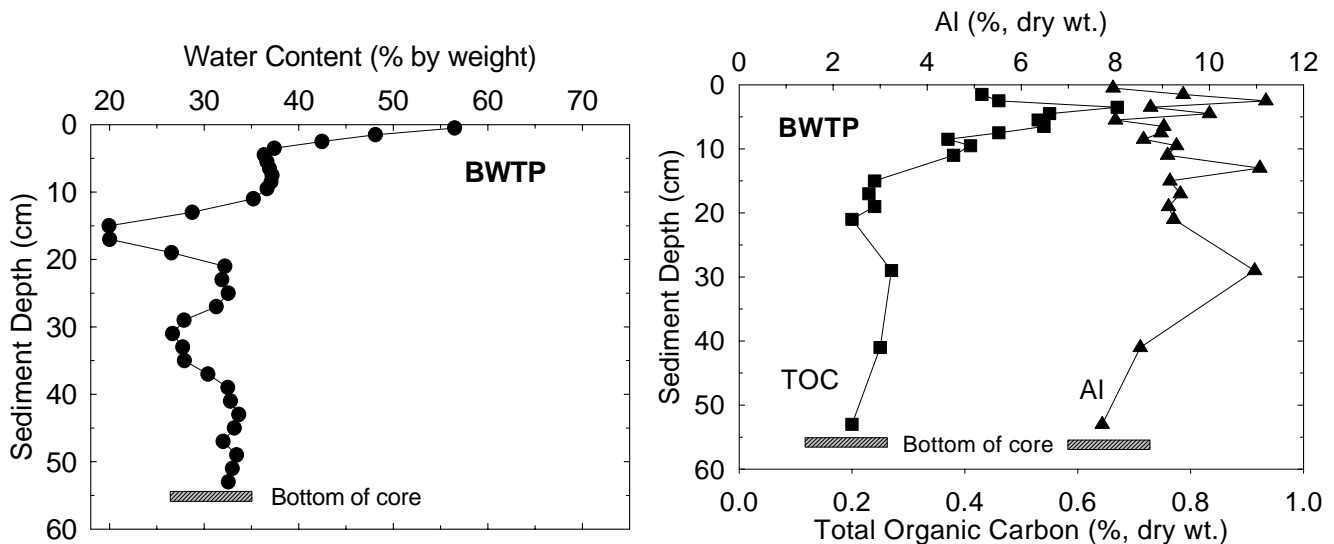

Figure 8. **Vertical Profiles of Water Content and Concentrations of TOC and Al for BWTP.**

Despite the presence of the anomalous layer, the sedimentation rate determined using the excess ^{210}Pb data (from 0-12 cm) was in good agreement with the rate calculated from the profile for ^{137}Cs (Figure 7). The persistence of ^{137}Cs to a deeper depth in the core than the excess ^{210}Pb was an anomaly in the BWTP core; however, we are not able to explain this observation. Nevertheless, when the activities for

[137]Cs were plotted as a function of sediment age as determined using the CIC model (Figure 9), the excess ^{210}Pb and ^{137}Cs gave concordant results that showed an age of ~1950 at a depth of 26 cm in the core (see depth-age data in Appendix A).
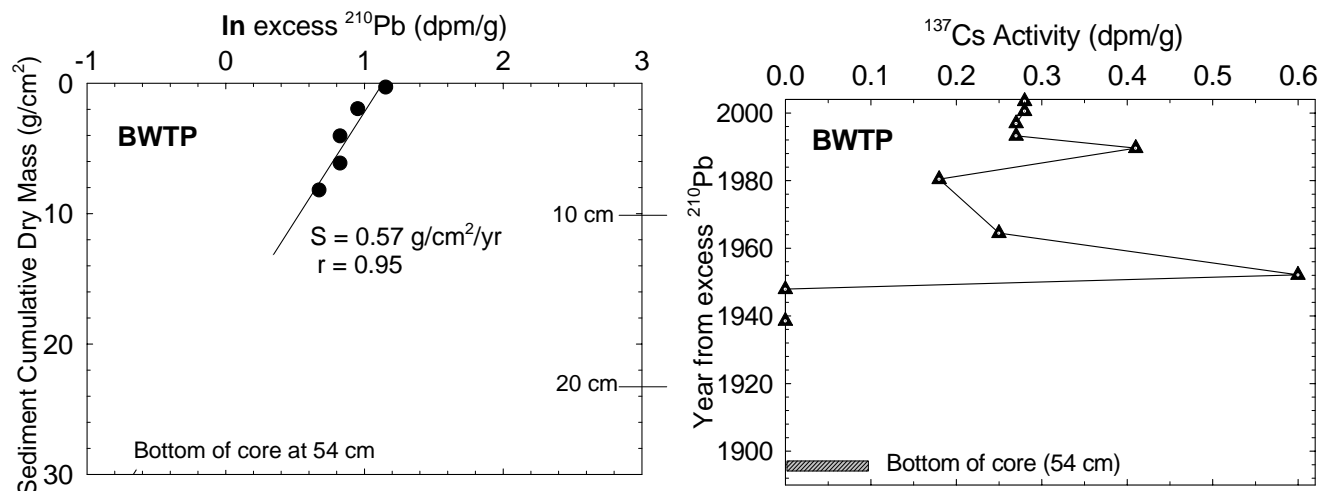

Figure 9. **Vertical Profiles Showing ln Excess [210]Pb Versus Cumulative Dry Mass of Sediment and Activity of [137]Cs Versus Year from Excess [210]Pb Data for BWTP.**

Due to the anomalous layer at 12-20 cm and the absence of excess ^{210}Pb deeper in the core, the CIC and CRS models did not agree in ages. Once again, the CIC model was a better predictor of sedimentation rates because of the high probability of sediment disturbances that distort any constant rate of supply.

5.1.3 AMT-East

The distribution of excess ^{210}Pb in the core from AMT-East was complex (Figure 10) and more than one interpretation was possible for the observed profile. The profile for total ^{210}Pb also showed considerable scatter. If all the excess ^{210}Pb data were used, the sedimentation rate was 0.5 cm/yr with a weak r value of 0.72 (not shown). If only the top 14 cm was used, the sedimentation rate was 0.20 cm/yr with r = 0.97 (Figure 10). Finally, if the 6-13 cm layer was removed, the calculated sedimentation rate was 0.44 cm/yr with r =0.87. The activities of ^{137}Cs were 0.2-0.3 dpm/g throughout the core and support a sedimentation rate >0.5 cm/yr (Figure 8) and suggest that all layers in the core were deposited at the site since 1950. Thus, a sedimentation rate of 0.2 cm/yr, even for just the top 14 cm, would date the 14 cm layer in the 1930s. At this sedimentation rate, no ^{137}Cs should be detectable at 14 cm.

The vertical profiles for water content, TOC, and Al did not clearly support any one of the scenarios described above (Figure 11). For the CIC model, all three trends discussed above for excess ^{210}Pb were used. The best fits to the ^{137}Cs data were found with the complete data set or without the 6-13 cm layer. As a compromise, a sediment accumulation rate of 0.5 g/cm^{2}/yr was used to construct the profile for ^{137}Cs versus age from excess [210]Pb (Figure 12) and for the age-depth results listed in the Appendix. Very poor agreement was determined between the CIC and CRS models with the CRS model again yielding much older dates and slower accumulation rates. Another possible explanation for the observed distribution of radionuclides in the core from site AMT-East is that a layer of sediment slid over the existing layer of sediment, possibly during the 1964 Earthquake. Under these conditions, the upper and lower portions of the core would both contain ^{137}Cs and may have similar sedimentation rates (refer to Figure 10, top panel). However, insufficient evidence is available to support any one possible scenario for sediment accumulation at this site.

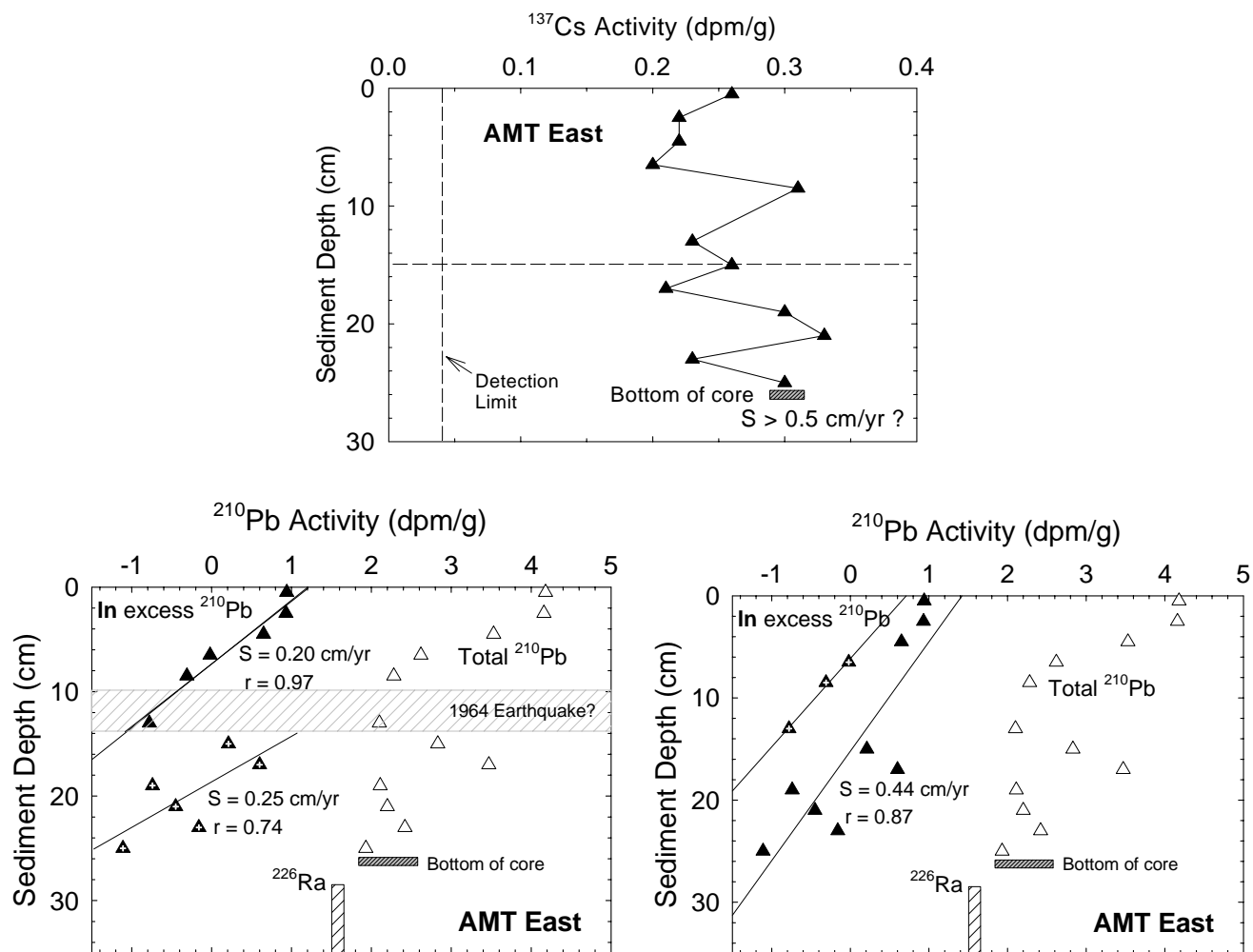**Figure 10. Vertical Profiles of ln Excess ^{210}Pb, Total ^{210}Pb and Total ^{137}Cs for AWT-East.** The horizontal dashed line on the ^{137}Cs plot identifies possible layering effect. Boxes with cross hatching on ^{210}Pb graphs show average activity of ^{226}Ra and supported ^{210}Pb activity.
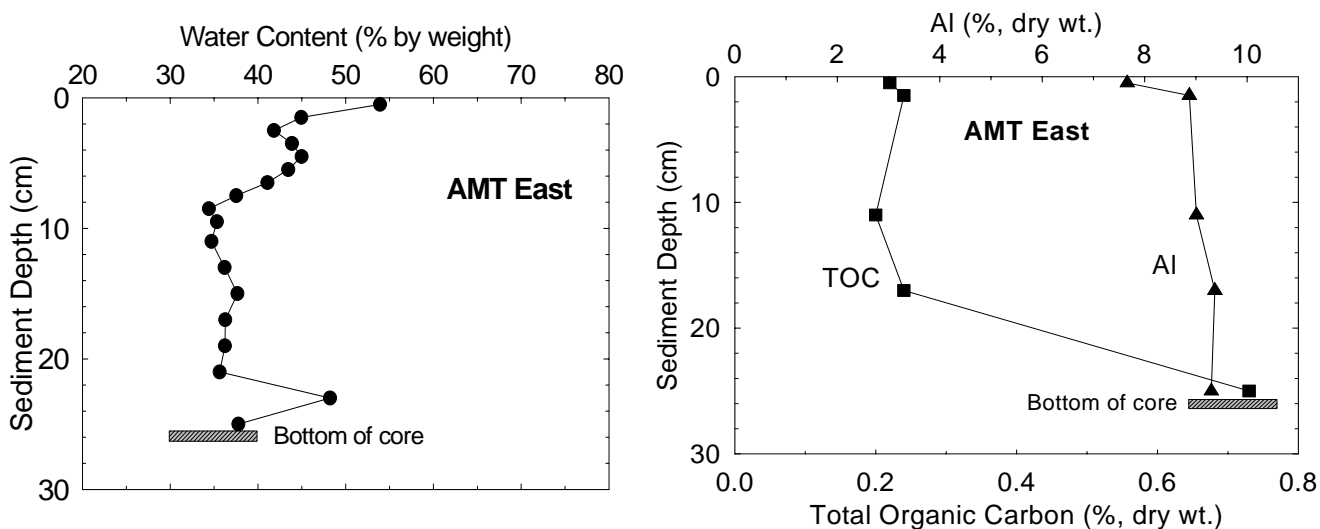

Figure 11. Vertical Profiles of Water Content and Concentrations of TOC and Al for AMT-East.
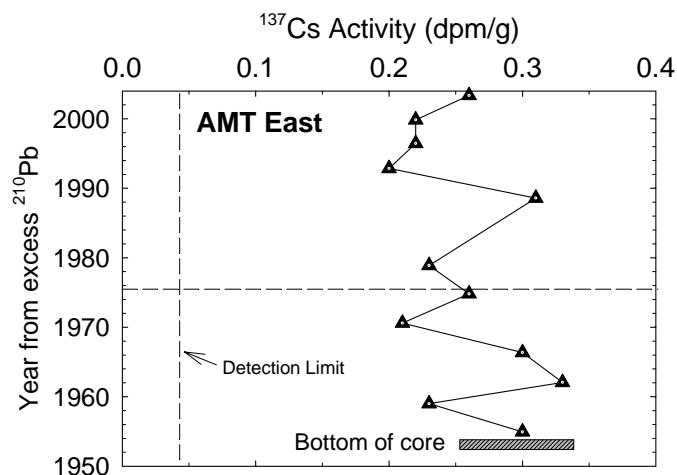
Figure 12. Profile Showing the Activity of ^{137}Cs versus Year from Excess ^{210}Pb for Site AMT-East. The dashed line identifies possible layering effect.

5.1.4 AMT-D33

The vertical profile of ^{137}Cs for sediments from station AMT-D33 showed no detectable activity below 9 cm layer to yield a ^{137}Cs sedimentation rate of 0.18 cm/yr (Figure 13). The profile for excess ^{210}Pb showed low activities of <1 dpm/g throughout the core (Figure 13), possibly the result of a missing top portion of the core. The calculated sedimentation rate based on excess ^{210}Pb was highly dependent on whether the 10-12 cm or 14-16 cm layer was used as the base of core, with rates of 0.19 cm/yr (r = 0.72) using the 10-12 cm section (and not the 14-16 cm section) and 0.50 cm/yr (r = 0.72) using the 14-16 cm section (and not the 10-12 cm section).
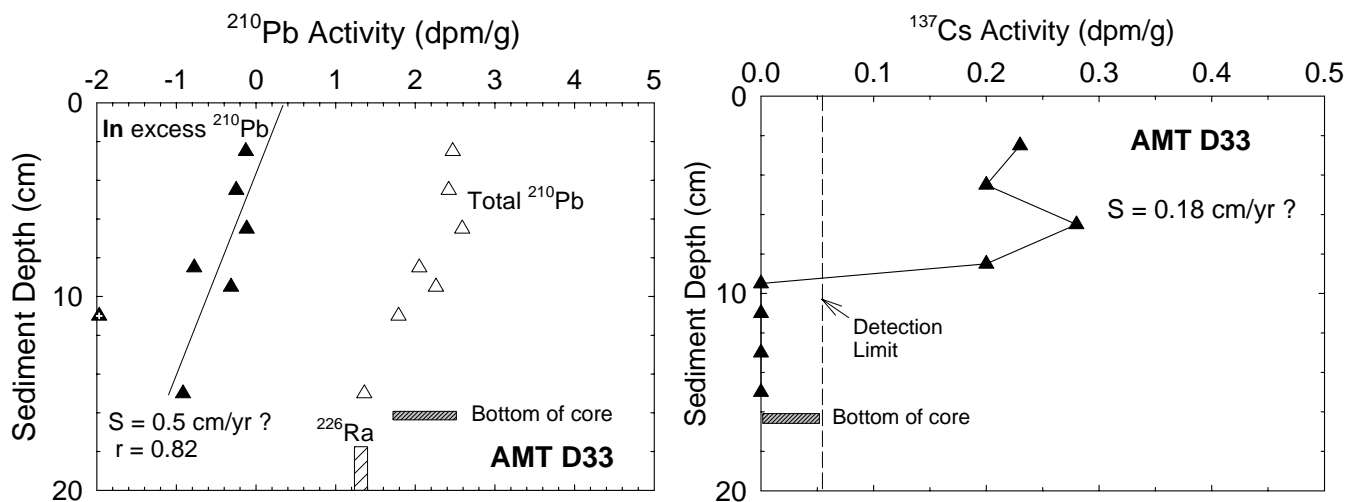
Figure 13. Vertical Profiles of ln Excess ^{210}Pb, Total ^{210}Pb and Total ^{137}Cs for AMT-D33. Box with cross hatching on ^{210}Pb graph shows average activity of ^{226}Ra that is also the activity for supported ^{210}Pb.

Field observations and data for water content support the argument that the top portion of the core was missing due to slumping or was lost during coring operations. A water content of 31% in the upper portion of the core is consistent with sediment depths of 5-10 cm in cores from sites AMT-West, BWTP, AMT-East, and Lowe (Figure 14). Furthermore, the highest activity for excess ^{210}Pb in the core from AMT-D33 of 0.88 dpm/g is more typical of the activity at sediment depths of 7-12 cm at sites AMT-

West, BWTP, AMT-East, and Lowe. For the purposes of this report, the profile for ^{137}Cs versus age from excess ^{210}Pb was constructed with a sediment accumulation rate of 0.37 g/cm^2 (all data) with a starting date of 1978 at 2 cm. This starting data assumes that 8 cm of the core were missing and corrects for the start at 2 cm. The resulting graph (Figure 15) suggests that the 1950 date is relatively clear and that the top of the core analyzed for this study dates at about the 1977 start of the terminal.

Another explanation that supports a higher sedimentation rate is that there were actually two layers missing from the core. Field notes and water content indicate that the top 5-8 cm of sediment was lost from the core. Hydrocarbon analyses discussed later indicate pre-AMT sediments at 14-16 cm in the core with evidence of ANS crude showing up in the 10-12 cm layer. If the excess ^{210}Pb accumulation rate of 0.5 cm/yr is used with this hypothesis, then the top 10-16 years (~1988-2004) of the core was missing followed by approximately 10 cm or 20-25 years (~1964-1988) of accumulation. This would place the 10 cm layer at around the time of the 1964 Earthquake, with sediments below that layer age dating as older that 1950 (based on ^{137}Cs). This discrepancy could be explained by a missing layer at around 10 cm depth in the core although this would not explain the ANS crude seen at 10-12 cm. The preceding discussion re-emphasizes the difficulties of determining sedimentation rates in Port Valdez.
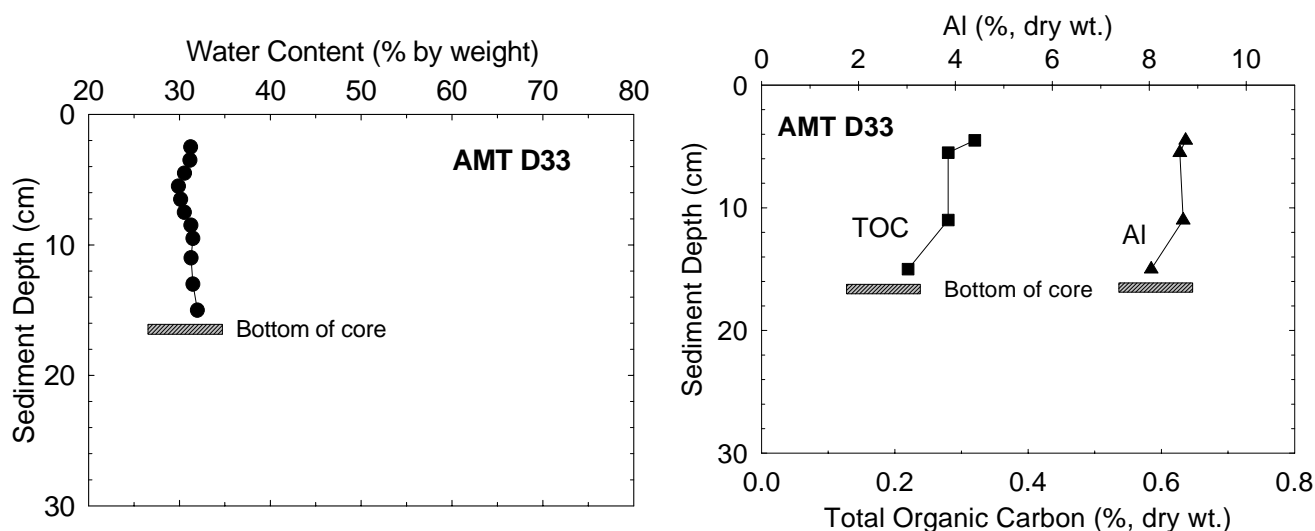

Figure 14.   Vertical Profiles of Water Content and Concentrations of TOC and Al for AMT-D33.
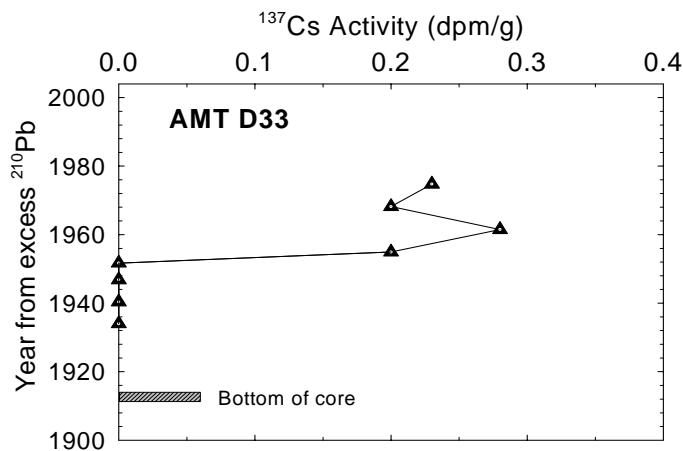

Figure 15.   Vertical Profile Showing the Activity of [137]Cs Versus Year from Excess [210]Pb Data for AMT-D33.

5.1.5 Lowe

The excess ^{210}Pb data for the Lowe site do not follow a well-defined exponential trend (Figure 16). Using all the data, a sedimentation rate of 1.3 cm/yr was calculated. Most adjustments of the data set yielded lower rates. Based on the ^{137}Cs profile, the sedimentation rate was >1.5 cm/yr (Figure 16). Data for water content support that the top of the core was present (Figure 17). Thus, to a best approximation, the profile for ^{137}Cs versus age from excess [210]Pb (Figure 18) suggests that the base of the core dates to the 1950s. At previous sites, for example BWTP (refer to Figure 9), the disappearance of ^{137}Cs was very abrupt. Therefore, the representation of ages in Figure 18 and in the Appendix presents a reasonable time line. Again, the CIC model was preferred relative to the CRS model (Figure 19).

Figure 16. Vertical Profiles of ln Excess ^{210}Pb, Total ^{210}Pb and Total ^{137}Cs for Lowe. Box with cross hatching on ^{210}Pb graph shows average activity of [226]Ra that is also the activity for supported [210]Pb.

Figure 17. Vertical Profiles of Water Content and Concentrations of TOC and Al for Lowe.
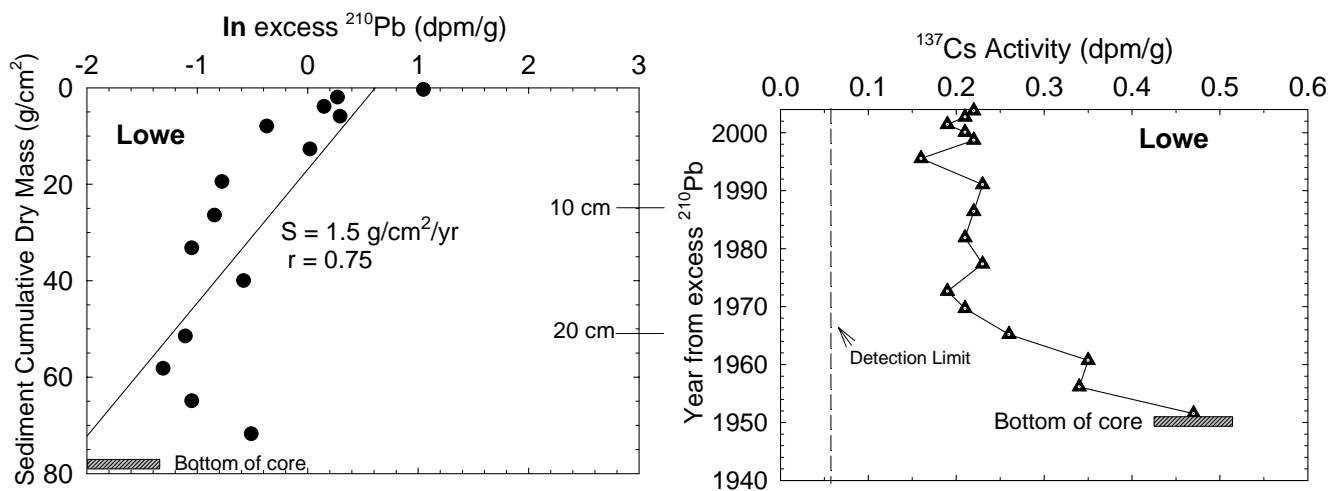
Figure 18. Profiles Showing ln Excess ^{210}Pb versus Cumulative Dry Mass of Sediment and Activity of ^{137}Cs versus Year from Excess ^{210}Pb Data for Lowe.
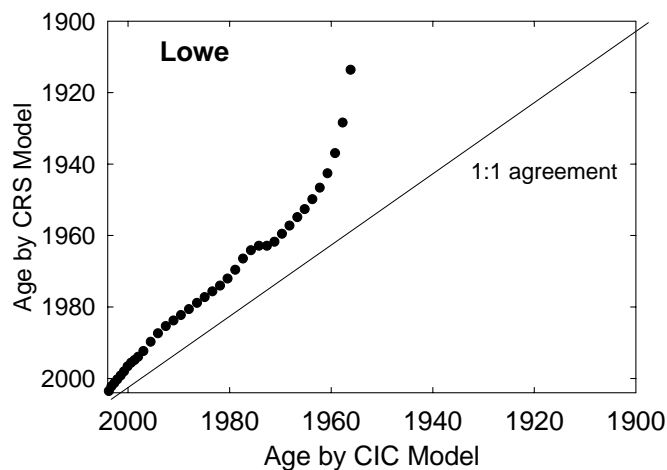
Figure 19. Comparison of Ages Determined Using the CIC and CRS Models for Lowe.

5.1.6 Gold Creek

Results for the core from Gold Creek also appear complex. Once again, the possibility for two distinct surface layers was supported by an abrupt shift in water content in the 7-8 cm layer, followed by a typical surface-layer decrease to the bottom of the core (Figure 20). Similar breaks in continuity were observed in the excess ^{210}Pb and ^{137}Cs profiles (Figure 21). Using the excess ^{210}Pb data for the top 7 cm, the sedimentation rate was 0.15 cm/yr (r = 0.84) and then using the interval of 8-20 cm, the calculated sedimentation rate was 0.21 cm/yr (r = 0.98). If the accumulation rate for the upper 7 cm is 0.15 cm/yr, then the age at 7 cm was in the mid-1950s. This age is consistent with the low, and decreasing, activity of ^{137}Cs at 6-7 cm. Likewise, the 8-20 cm section would have accumulated in ~50 years and thus some ^{137}Cs would still be detectable at the base of the core. If the radionuclide data were taken as a whole for the core, the sedimentation rate from excess ^{210}Pb was ~0.5 cm/yr to yield an age of 40 years at the base of the core. This result was consistent with the ^{137}Cs data.

Figure 20. Vertical Profiles of Water Content and Concentrations of TOC and Al for Gold Creek.
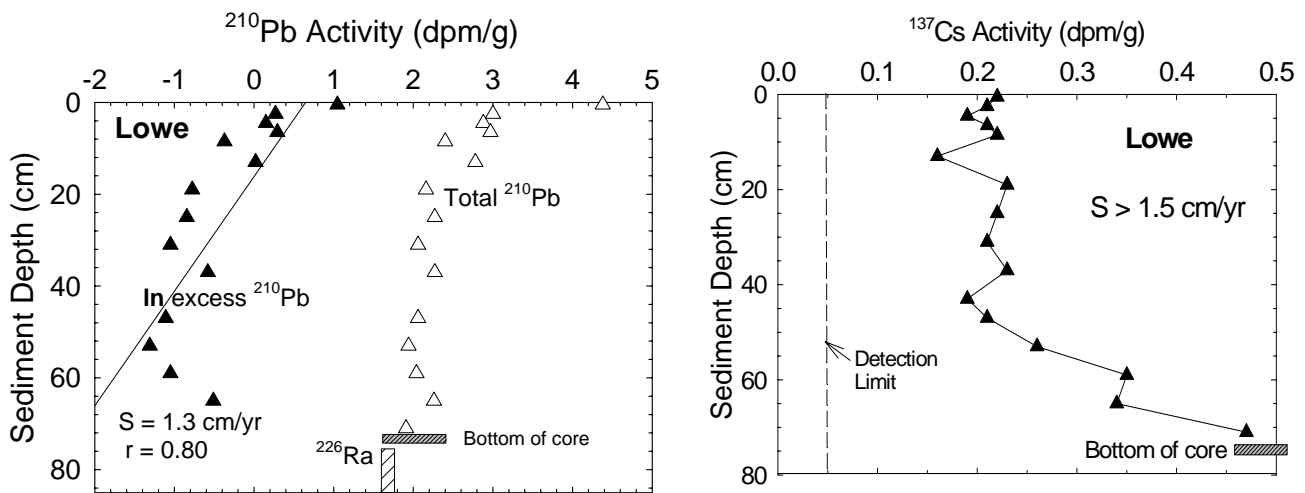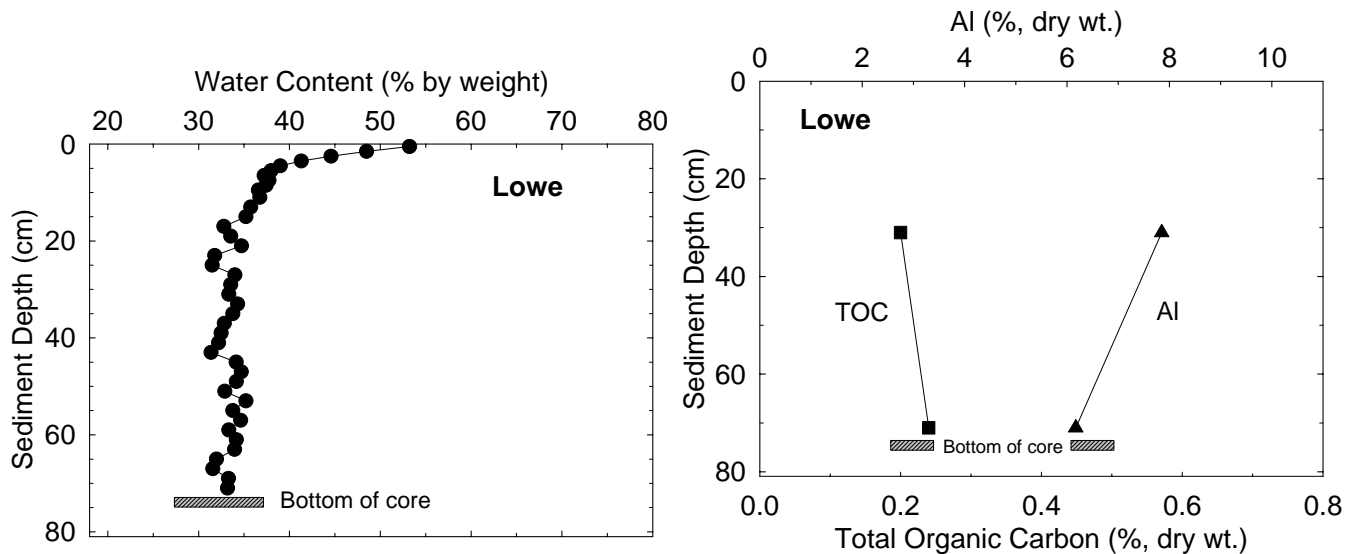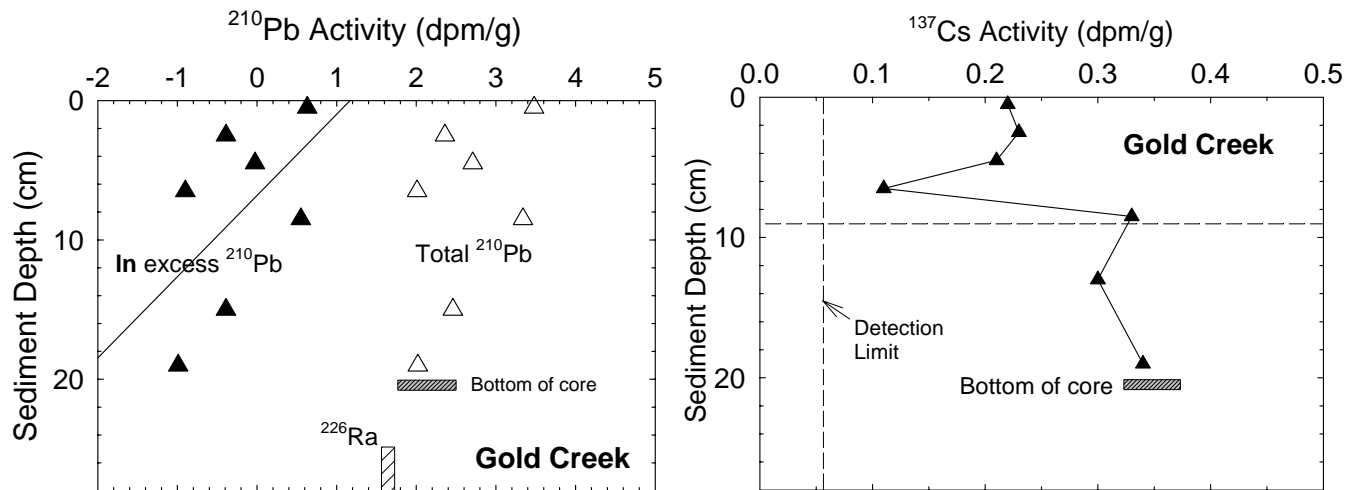

Figure 21. Vertical Profiles of ln Excess ^{210}Pb, Total ^{210}Pb and Total ^{137}Cs for Gold Creek. Box with cross hatching on ^{210}Pb graph shows average activity of ^{226}Ra and supported ^{210}Pb activity. The horizontal dashed line on the ^{137}Cs plot identifies possible layering effect.

5.1.7 Galena Bay

For Galena Bay, the activity of ^{137}Cs approached zero at ~25 cm to yield a sedimentation rate of ~0.5 cm/yr (Figure 22). The profile for excess ^{210}Pb was distorted due to mixing/slumping and supports a range of possible sedimentation rates that range from 0.36-0.45 cm/yr. The water content for the sediment core from Galena Bay was higher than the other cores, suggesting a higher clay content that leads to greater retention of water (Figure 23). When the CIC model was applied to the data, the calculated sediment accumulation rate was 27 g/cm^2/yr (Figure 24). When the ^{137}Cs data were plotted versus age from the excess ^{210}Pb date, the resulting fit was good.
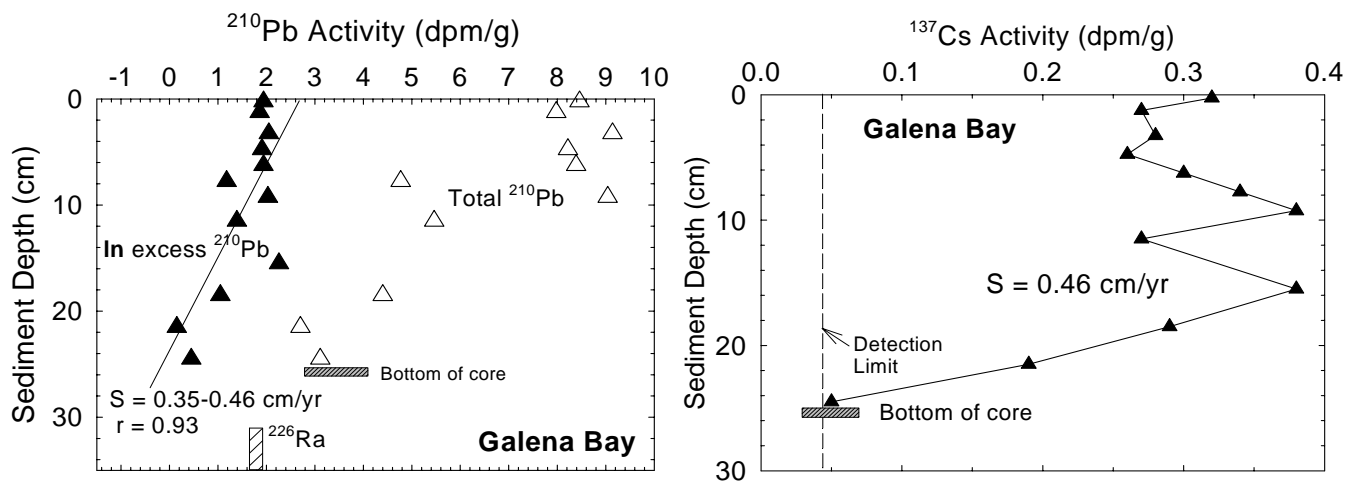
Figure 22.   Vertical Profiles of ln Excess ^{210}Pb, Total ^{210}Pb and Total ^{137}Cs for Galena Bay. Box with hatching on ^{210}Pb graph shows average activity of ^{226}Ra and supported ^{210}Pb activity.
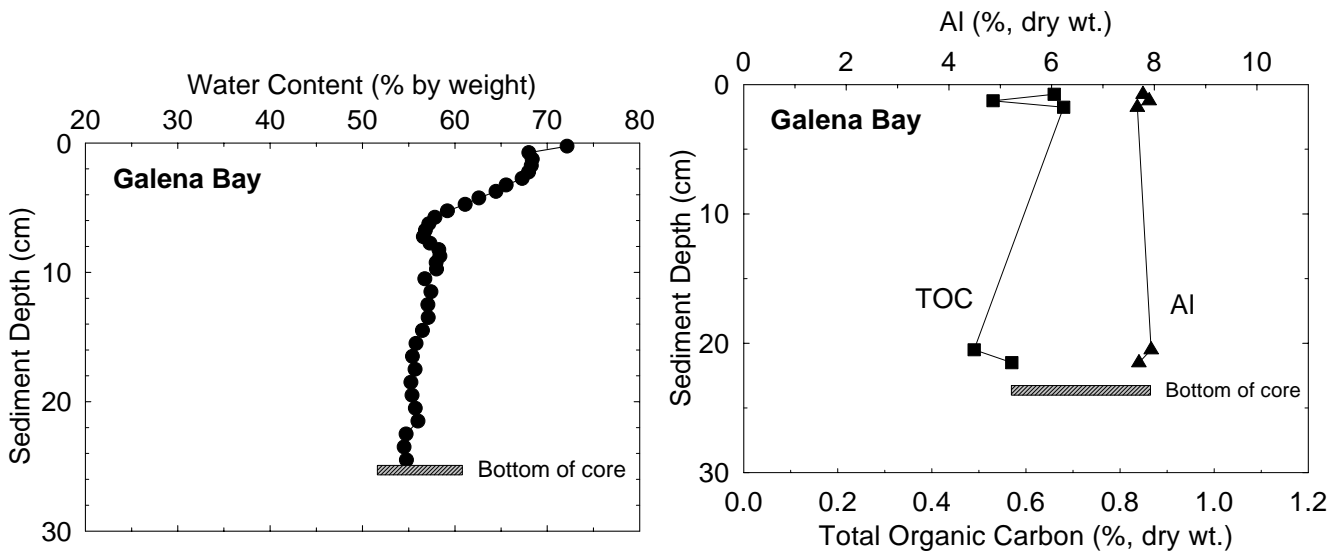
**Figure 23.   Vertical Profiles of Water Content and Concentrations of TOC and Al for Galena.**
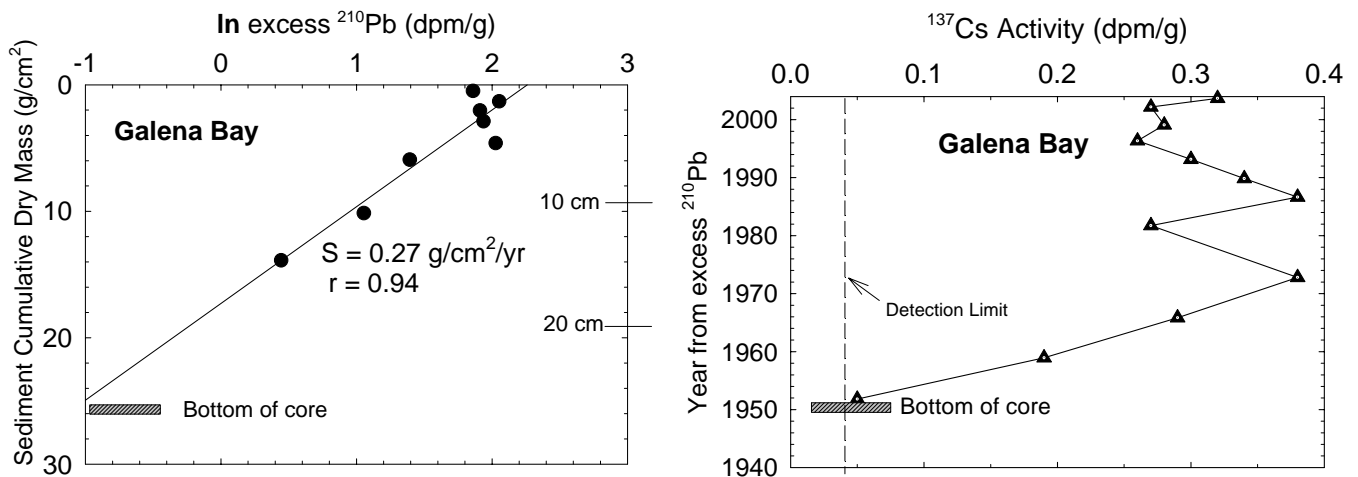
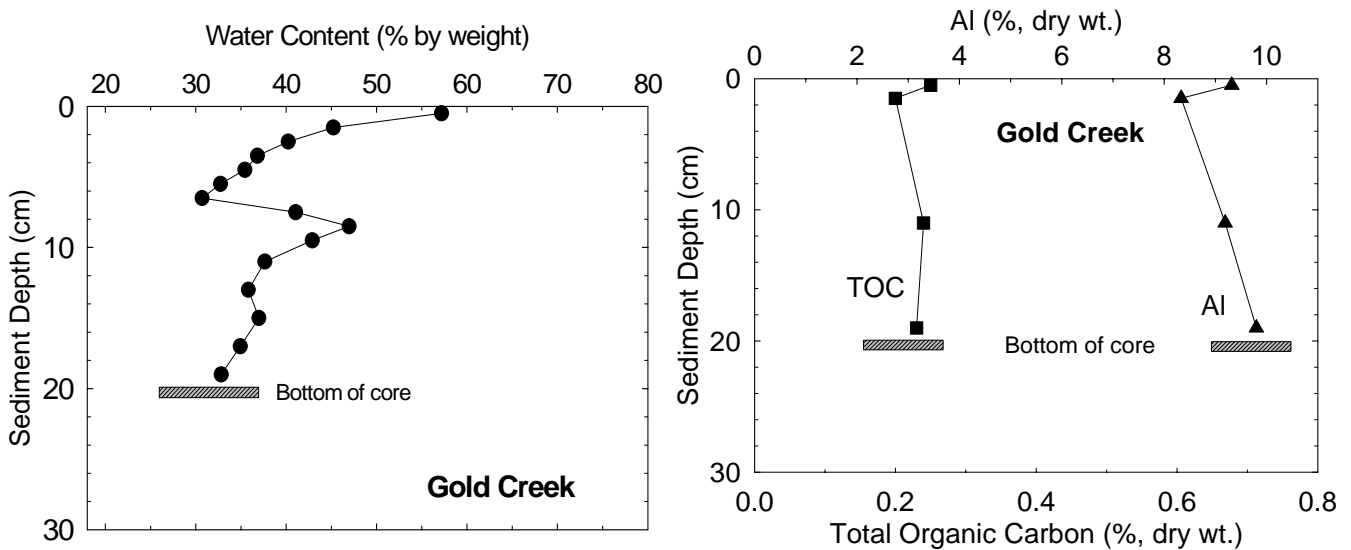**Figure 24.   Vertical Profiles Showing ln Excess ^{210}Pb Versus Cumulative Dry Mass of Sediment and Activity of ^{137}Cs Versus Year from Excess ^{210}Pb Data for Galena Bay.**

5.1.8 Valdez

Radionuclide core dating was not performed on the core from the Valdez site. The study plan and scope of work called for the collection and analysis of cores from seven locations. However, in the field, due to difficulties in obtaining a good core from the AMT-D33, an additional location was added offshore of the AMT, resulting in eight locations. Following the first phase of hydrocarbon analyses and after viewing the preliminary geochronology results, a decision was made in consultation with RCAC to concentrate on the seven locations presented here and to perform only hydrocarbon analyses and physical characterizations on the Valdez site sediment cores.

5.2 Hydrocarbons

All hydrocarbon parameters in this report include analyte values as well as estimated concentrations (i.e., those that were qualified as below the MDL). Therefore, results and discussion presented here are based on data that have not been censored by removing concentrations below the MDL. The reader is referred to the appendices for the full data, including individual analyte values and data qualifiers. The low levels (values below MDL) of some of the analytes, particularly at sites that exhibit "background signature", should be kept in mind while reading this report.

5.2.1 Introduction

Marine sediments are a long-term repository of the residues of petroleum released to the marine environment. Petroleum in the offshore environment can be altered by natural dispersion, evaporation, dissolution, photo-oxidation, and microbial degradation. It tends to adhere to particulates, is deposited in sediments, and is associated with fine-grained material. The presence and composition of petroleum contaminants in sediment are a record of the long-term, chronic accumulation of contaminants thus reflecting the potential for exposure of the resident biota.

Hydrocarbons are an important constituent of petroleum, with PAH and AHC accounting for more than 70 percent of petroleum by weight. While hydrocarbons are ubiquitous in the marine environment, petroleum-derived hydrocarbons can be used to trace petroleum contamination (Brassell et al., 1978; Boehm and Requejo, 1988; Kennicutt and Comet, 1992). Aliphatic hydrocarbons can also be synthesized by planktonic and terrestrial organisms.

Petroleum contains a homologous series of n-alkanes with one to more than 30 carbons with odd and even n-alkanes present in nearly equal amounts, whereas organisms preferentially produce specific suites of normal alkanes with odd numbers of carbons from 15 to 33. Petroleum also contains a complex mixture of branched and cycloalkanes generally not found in organisms, although the latter may be found as degradation products in bacteria. This complex mixture consists of both a resolved and unresolved mixture of compounds, the TRAHC and the UCM, respectively. The TRAHC includes the sum of total resolved aliphatic hydrocarbons which includes the AHC analytes (n-C_{10} through n-C_{34} and pristane and phytane) plus other compounds such as plant waxes and lipids which are not individually identified or reported. The TRAHC value can give additional sourcing information as it may provide a relative measure of biogenic contributions as compared to other sources. The presence and amount of the UCM can be an indicator of petroleum contamination, as it increases over time as petroleum is subject to biodegradation processes.

Petroleum contains monoaromatic and polycyclic aromatic hydrocarbons (PAH), both of which can be toxic to organisms. Monoaromatic hydrocarbons such as benzene, toluene, and xylene are highly

volatile and are quickly lost through evaporative processes. These compounds do not persist in the marine environment for long periods of time and have not been measured in this study. Petroleum contains an extensive suite of PAH, and the amount and composition of the PAH fraction can be effectively used as a tracer of petroleum contamination. PAH are also toxic and serve as an indication of exposure in organisms. In general, PAH are more resistant to microbial breakdown than many aliphatic hydrocarbons and thus tend to persist in the environment longer. Based on consideration of the petroleum chemistry, biological occurrences of hydrocarbons (i.e., interferences), and toxicological effects, AHC and PAH were chosen for this study as the preferred organic tracers of past and present petroleum contamination in Port Valdez.

Polycyclic aromatic hydrocarbons are generally divided into three main sources: biogenic, petrogenic, and pyrogenic. Biogenic PAH are those formed by biological processes or those formed during the early stages of diagenesis. Biogenic PAH that are synthesized by organisms can be easily differentiated from those in petroleum. Most abundant of these is perylene, which is believed to be formed during the bacteriological breakdown of organic matter in marine sediments by a process called early diagenesis (Venkatesan, 1988). Since perylene is not found in petrogenic PAH, it has been excluded from the summation of TPAH in this report.

Petrogenic PAH includes crude oil and its refined products as well as coal and other source rock deposits. Potential sources of petrogenic PAH in Port Valdez area include: Alaska North Slope (ANS) crude and other oil products from the AMT operations, coal residue from natural coal deposits in the area; seep oil or petroleum source rock formations; and other refined petroleum products that have made their way into the marine environment from vessel traffic, City of Valdez, Valdez small boat harbor, or the 1964 Great Alaskan Earthquake. Alaska North Slope crude consists of a mixture of petroleum from the various production fields on the Alaskan North Slope, including Prudhoe Bay, Kuparuk, Endicott, and Lisburne, and exhibits a fingerprint that is quite distinct from that of oil found in other geographic areas. The EVOS of March 1989 consisted of Alaska North Slope crude, which over time has weathered to produce a slightly different fingerprint than that of fresh crude. One method of determining an ANS source is to compare the relative concentrations of the C_2- and C_3-dibenzothiophenes and phenanthrenes; for ANS crude, both of these ratios approximate 1, while the ratio for background sources is closer to 0.2 (Page et al., 1995).

Earlier studies in PWS indicated that petroleum originating from natural seeps in the Gulf of Alaska contributed to the natural hydrocarbons (or "background hydrocarbons") in the study area (Page et al., 1995). The source of this background signature has been the subject of controversy, however, recent work has indicated that natural coal deposits rather than oil seeps may be the predominant source of petrogenic hydrocarbons in the region (Short et al., 1999). An important distinction between these two potential sources is that hydrocarbons in coal residues are much less biologically available than those seen in petroleum. The researchers found that the PAH fingerprints were similar, but biomarker analyses revealed differences between the coal and petroleum seep sources. However, other researchers contend that petroleum seeps and eroding petroleum source rock formations are the predominant source of hydrocarbons in the area. Work performed for the MMS in Cook Inlet and Shelikof Strait indicated that while coal signatures exist in sediments from some areas of Cook Inlet, seep oil is responsible for the predominant background signature (Arthur D. Little, 1998).

Other petroleum products that may have been introduced into the marine environment in Port Valdez include oil products from locations other than Alaska. For example, the Great Alaskan Earthquake of 1964 and the resultant tsunamis caused the introduction of fuel oil and asphalt made from California source oils into Port Valdez, and subsequently into PWS (Kvenvolden et al., 1995). These authors noted

that residues of these California-sourced products have been found throughout the northern and western parts of PWS, typically in the form of tar balls found on beaches at the high tide line.

Petrogenic PAH have a characteristic fingerprint where the parent compounds (i.e., C_0-naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes) are usually at lower concentrations than their alkyl homologues. With weathering, this feature becomes more prominent since the more soluble parent compound (C_0) disappears before the alkyl homologue (C_1), which in turn disappears more quickly than C_2, and so on. This characteristic weathering fingerprint is termed a water-washed profile when the $C_0 < C_1 < C_2 < C_3$ within each PAH group.

Pyrogenic PAH sources include atmospheric fallout and surface runoff from the burning of fossil fuels (diesel, heating oil, gasoline, etc.) and from other pyrogenic sources such as forest fires and camp fires. Creosote, which is used to preserve wood pilings, is usually included in this category also. Pyrogenic PAH are characterized by high molecular weight PAH, greater than C_3-dibenzothiophene, and by high concentrations of the parent compounds compared to their alkyl homologues. A typical pattern for pyrogenic PAH shows decreasing concentration with molecular weight within a group, i.e., $C_0 > C_1 > C_2 > C_3 > C_4$. It has been noted, however, that the PAH in diesel soot has primarily a petrogenic signature (Bence and Burns, 1995).

5.2.2 Polycyclic Aromatic Hydrocarbons

Individual PAH analyte sediment sample data are provided in Appendices B and C. The majority of individual PAH analytes were seen at levels above MDLs for all sediment samples. A summary of hydrocarbon results from the sediment cores is provided in Table 11.

Concentrations of TPAH (less perylene) ranged from a low of 35 parts per billion (ppb or nanograms/gram[ng/g]) to a high of 5,659 ppm (Table 11 and Figure 25), the latter of which exceeds the NOAA Effects Range-Low (ERL) Sediment Guidance level of 4,022 ppb (Long et al. 1995). Three samples were found to exceed the ERL for TPAH. The ERL is based on statistical analyses that NOAA performed on a large number of environmental studies and is defined as the level below which there is a 10% probability that adverse biological effects will occur. Both the high and the low concentrations were observed in the same core obtained at BWTP near AMT's BWTP effluent diffuser. As will be discussed later, concentrations were generally very low in the deeper older sediment from BWTP, with TPAH concentrations increasing substantially in the more recent sediment following the construction of the AMT. The TPAH levels clearly began to increase at approximately 16 cm depth with elevated levels evident from that depth to the surface which would correspond to hydrocarbon inputs from the AMT as supported by the geochronology data.

The PAH fingerprint from the deeper, older pre-AMT sediment was also substantially different from the new post-AMT sediment (Figure 26). The older sediment at BWTP shows low concentrations of PAH with a clear pyrogenic ($C_0 > C_1 > C_2 > C_3 > C_4$) signal in the phenanthrene, fluoranthene, and chrysene series; this is the opposite of the trend seen in crude oil and is probably the result of historic forest fires in the region. The PAH signature in the older sediment also indicated biogenic inputs as seen in the relatively high perylene and petrogenic source rock (shale or coal) inputs as evidenced by the un-weathered low-molecular weight naphthalenes. The pre-AMT signature is in sharp contrast to that seen post-AMT where overall PAH concentrations have substantially increased; a weathered ($C_0 < C_1 < C_2 < C_3 < C_4$) signal is evident in the fluorene, phenanthrene, dibenzothiphene, and fluoranthene series; and contributions from the naphthalenes and perylene have essentially disappeared (Figure 26).

Table 11. Summary of Hydrocarbon Parameters from the Sediment Cores.

| Location	Core No.	Depth (cm)	TPAH (ng/g)	TAHC (ug/g)	TPH (ug/g)	TRAHC (ug/g)	UCM (ug/g)	TOC (%)	EOM (ug/g)	CPI
AMT- D33	Grav 2	0-2	1020	2.86	206	14.1	192	0.58	897	4.8
AMT- D33	Grav 2	4-6	1274	3.83	263	23.9	239	0.57	115	2.2
AMT- D33	Grav 2	10-12	1697	2.47	229	17.5	211	0.52	1055	6.4
AMT- D33	Grav 2	14-16	79	1.26	109	11.0	98	0.44	94	3.4
AMT-East	Box 1	0-2	152	0.70	12	3.6	9	0.44	136	11.0
AMT-East	Box 1	10-12	143	0.67	11	3.7	7	0.38	94	10.0
AMT-East	Box 1	16-18	265	0.93	26	9.1	17	0.43	134	4.8
AMT-East	Box 1	24-26	217	0.72	14	3.3	11	0.69	270	6.0
AMT-West	Box 1	0-2	656	1.79	109	13.9	95	0.56	780	6.3
AMT-West	Box 1	4-6	885	4.00	237	20.5	217	0.62	844	2.5
AMT-West	Box 1	10-12	784	1.92	110	11.8	98	0.52	785	3.5
AMT-West	Box 1	16-18	1486	5.47	371	16.4	355	0.70	1305	1.7
AMT-West	Box 1	24-26	865	2.99	165	17.5	148	0.51	472	3.0
AMT-West	Box 1	26-28	1569	1.46	42	11.0	31	0.47	292	6.1
BWTP	Grav 2	0-2	2691	3.60	950	57.3	892	0.94	4101	1.7
BWTP	Grav 2	2-4	4868	10.64	1894	94.7	1799	1.05	5410	1.2
BWTP	Grav 2	4-6	5659	11.31	1820	85.2	1735	0.97	4570	1.3
BWTP	Grav 2	6-8	4290	5.43	713	48.7	665	0.92	3817	1.4
BWTP	Grav 2	8-10	3394	7.10	927	56.8	870	0.74	2472	1.3
BWTP	Grav 2	10-12	3060	6.22	629	38.3	590	0.75	2101	1.5
BWTP	Grav 2	12-14	1359	4.15	391	29.7	361	0.63	815	2.5
BWTP	Grav 2	14-16	408	1.26	168	10.7	157	0.43	257	3.4
BWTP	Grav 2	16-18	249	1.27	64	7.0	57	0.39	143	10.2
BWTP	Grav 2	18-20	396	1.41	54	9.8	44	0.41	168	8.0
BWTP	Grav 2	20-22	191	1.30	52	11.5	40	0.43	146	8.8
BWTP	Grav 2	28-30	134	1.92	10	8.2	2	0.52	76	12.2
BWTP	Grav 2	40-42	43	1.28	17	6.3	11	0.42	68	10.9
BWTP	Grav 2	52-54	35	1.07	29	6.0	23	0.41	296	12.0
BWTP	Grav 3	0-2	2409	6.38	765	31.0	734	0.85	3107	1.4
BWTP	Grav 3	6-8	2841	8.56	834	42.3	792	0.72	1894	1.9
Galena Bay	Box 1	0-2	705	1.93	29	22.4	7	1.28	380	6.8
Galena Bay	Box 1	20-22	1009	2.97	29	21.3	8	1.10	281	4.9
Galena Bay	Grav 1	60-63	983	4.04	24	16.4	8	1.16	246	5.3
Gold Creek	Box 2	0-2	87	0.80	22	7.4	14	0.41	124	13.5
Gold Creek	Box 2	10-12	159	0.69	14	5.2	9	0.42	116	11.0
Gold Creek	Box 2	18-20	109	0.68	10	4.3	5	0.40	66	12.7
Lowe	Grav 2	0-2	55	0.55	5	3.3	2	0.28	60	9.3
Lowe	Grav 1	30-32	117	0.58	13	8.3	4	0.29	78	4.7
Lowe	Grav 1	70-72	105	0.53	6	3.9	2	0.34	154	10.7
Valdez	Box 1	0-2	268	0.87	14	6.8	7	0.39	156	14.0
Valdez	Box 1	4-6	168	1.25	20	8.5	12	0.42	150	9.4
Valdez	Box 1	10-12	154	0.93	14	3.4	11	0.41	138	7.0
Valdez	Box 1	20-22	141	0.93	11	4.9	6	0.40	104	9.3
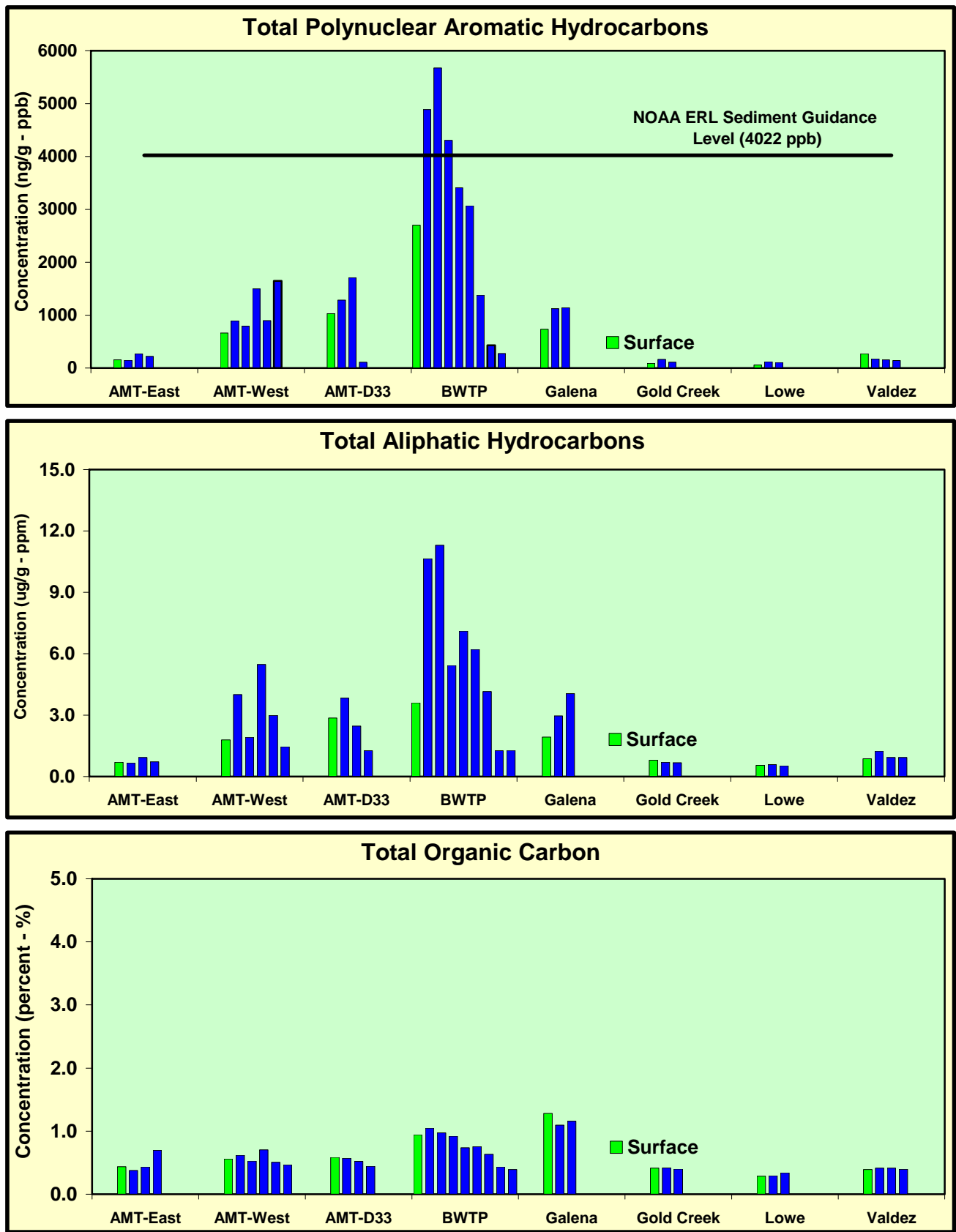
Figure 25. Summary of Sediment TPAH, TAHC, and TOC by Site.
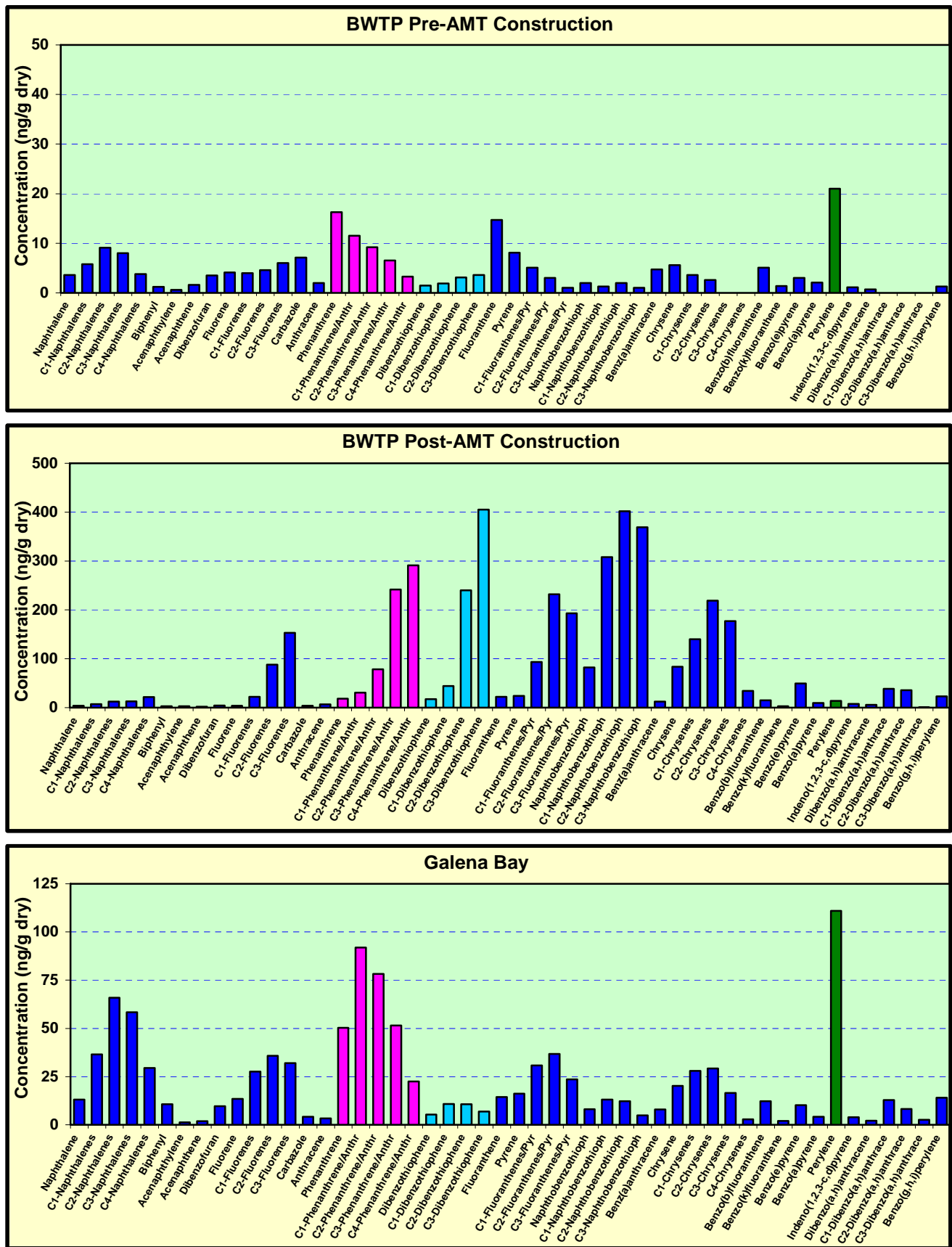
Figure 26.   Sediment Core PAH Histograms from BWTP and Galena Bay, June 2004.

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ANS is indicated by the ratio of the C_2- and C_3-dibenzothiophenes to phenanthrenes (most values ~1). Previous work in the area by numerous investigators has shown the natural background PAH signature in the PWS region to have a ratio of ~ 0.2 for C_2- and C_3-dibenzothiophenes to phenanthrenes, while ANS rations have a value near 1.0. This difference clearly indicates that the PAH in the subtidal sediments seen at this location are not from natural background sources but are more likely due to the discharges from the BWTP and/or tanker operations. The fact that the chrysenes are present would indicate ANS crude rather than ANS diesel fuel as the source of the hydrocarbon input. From the clear ANS signature and the station's close proximity to the BWTP diffuser, it would appear that the hydrocarbon source is from the BWTP discharge itself rather than other potential inputs from the AMT.

A vertical profile of TPAH in the BWTP core is presented in Figure 27, where the geochronology of the core is based on a sedimentation rate of 0.5 cm/yr. The output of the Alyeska pipeline is plotted on a relative scale as a surrogate for the BWTP discharge which clearly indicate that TPAH concentrations increase after the AMT startup and then begin to decrease after North Slope oil production peaks and then begins to decline. There appears to be lag between the pipeline peak (1988) and the peak in hydrocarbon concentrations (~1994). This lag and could be more related to operational changes that occurred at AMT in the 1990s rather than to pipeline output. The pre-AMT sediments have much lower TPAH levels with high accumulations in the top 14 cm of sediment. A small increase in TPAH was also seen at around the time of the 1964 Earthquake which did not appear to be related to hydrocarbon inputs into Port Valdez, but appeared to be related to a large peak in perylene in that particular sample.

Concentrations of PAH in the sediment at AMT-West and AMT-D33 were also found to be elevated as a result of the AMT operations and/or the ballast water discharge with TPAH levels ranging from 656 to 1,569 ppb in the six samples analyzed at AMT-West. The highest concentration was seen at the bottom of the AMT-West core (Table 11 and Figure 25). The ^{210}Pb dating indicated a sedimentation rate of 0.7 cm/yr which would date the bottom hydrocarbon sample at AMT-West in the mid-1960's, pre-AMT, which would not account for the high hydrocarbon levels seen at this level. Possible explanations for this discrepancy are that the bottom layer in the core had accumulations of hydrocarbons that were not related to the AMT, the sediment had been disturbed during AMT construction activities, or that the actual sedimentation rate was >0.7 cm/yr. To determine the reason for this apparent discrepancy, the PAH signature was examined and compared to the typical ANS crude PAH distribution. The PAH signature from the deepest sample (PVC04HYD019) at AMT-West was dominated by 3-, 4- and 5-ring PAH with large peaks in fluoranthene and pyrene (refer to Appendix B) which is characteristic of either a combustion related pyrogenic source or creosote that has been shown to have a similar PAH distribution (Page et al. 1995). The next deepest sample (PVC04HYD018) from AMT-West appeared to be mixture of sources including weathered ANS, pyrogenic inputs, and the natural background petrogenic and biogenic signature. It is believed that the source of the large pyrogenic signal in these cores was the result of the 1964 Earthquake as discussed later in the biomarker section.

The TPAH at AMT-D33 ranged from a low of 79 ppb at the bottom (14-16 cm) of the core to 1,697 ppb in the upper portion of the core, indicating that the bottom of the core pre-dated AMT while the three upper samples were post-AMT with elevated TPAH levels. Geochronology at AMT-D33 confirmed that the bottom sample in the core was pre-1950, whereas 2 cm higher in the core the hydrocarbon analyses indicated that sample was post-AMT. A possible explanation for this is that there is a missing layer in the core that may have been the result of slumping during the 1964 Earthquake that caused a subsurface sediment slide into the deeper offshore area. Both AMT-West and AMT-D33 were located in 75-80 m water depth along the same bathymetric contour as BWTP and the outfall diffuser and in a region where the onshore-offshore bottom gradients were relatively steep. Offshore of the AMT and Port Valdez the ocean bottom is generally relatively flat with water depths of 200-240 m.
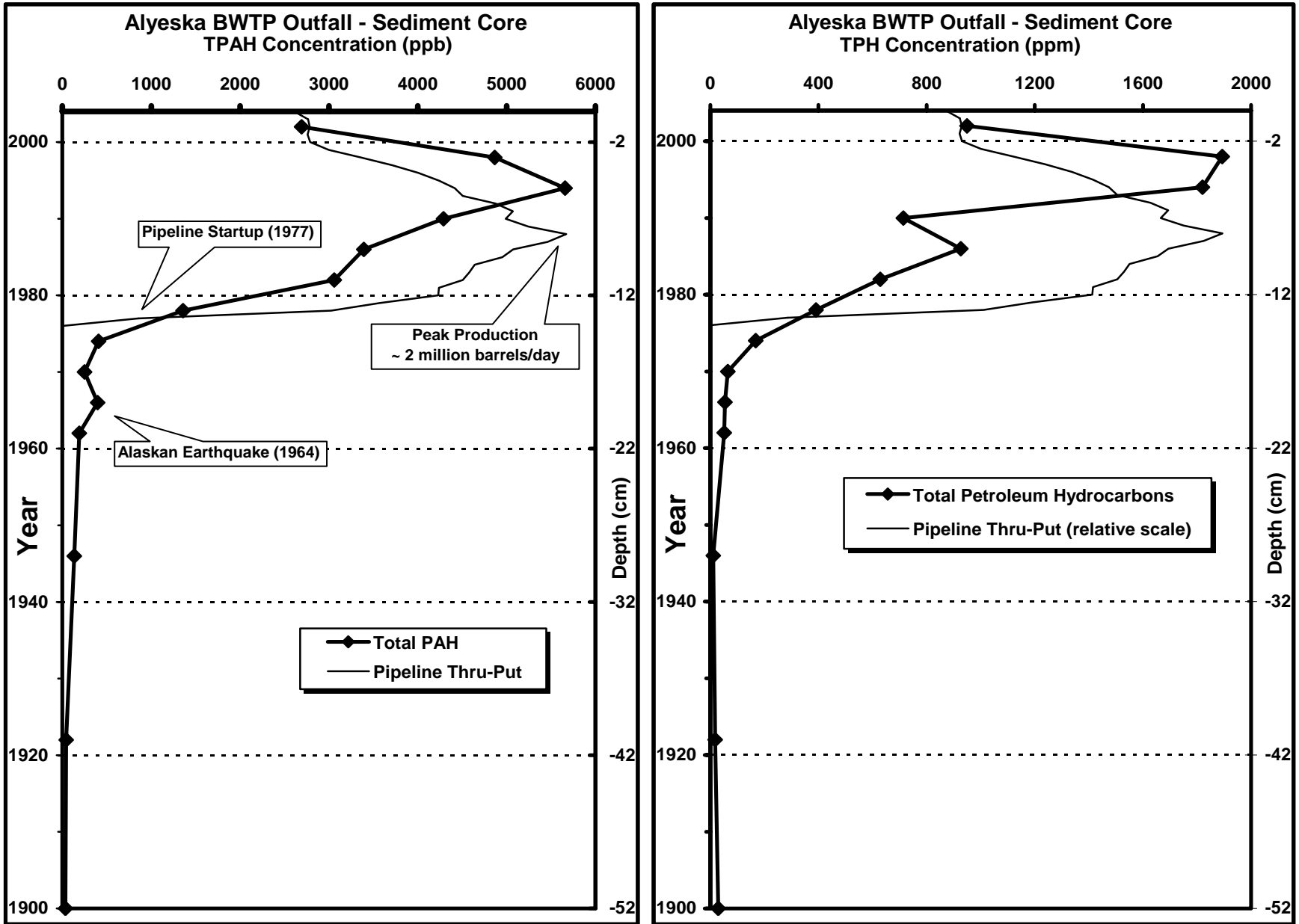
Figure 27.   Sediment Core TPAH and TPH Profiles from the Alyeska BWTP Discharge Area.

The PAH signature in the upper sediments at AMT-West and AMT-D33 were similar to that seen at BWTP, with clear ANS crude input that had been heavily weathered, although concentrations were somewhat less than those seen at BWTP (refer to Appendices B and C). Another characteristic of these three sites is that the PAH in the recent sediments have a heavily-weathered signature. The average ratio of C_2-chrysene to C_2-phenanthrene can be used as an indication of the degree of weathering. With weathering, this ratio increases since the alkyl phenanthrenes are degraded more quickly than the alkyl chrysenes. This ratio was found to be around 0.2 for EVOS crude oil just after the spill in 1989 and had increased to 0.5 in 1991 in PWS beach sediment (Bence and Burns, 1995). At BWTP, AMT-West, and AMT-D33, the mean C_2-chrysene/C_2-phenanthrene ratio in the recent post-AMT sediments were found to be generally >2.0. This ratio indicates that with an ANS crude source, the oil had weathered substantially, which is consistent with past data from this area. If the source had been diesel fuel, this ratio would have been very small since the high molecular weight chrysenes are not found in diesel fuel.

The fourth AMT site where cores were obtained was AMT-East, located in much deeper (233 m) water offshore of AMT-D33 which was itself on a steep slope in 76 m of water. Concentrations of TPAH at AMT-East ranged from 143 to 265 ppb in the four samples analyzed with slightly higher concentrations at the deeper sediment depths. The geochronology from this site was found to be complicated as a result of complex distribution of radionuclides. One explanation is that a layer of sediment was deposited over the existing layer of sediment at this site during the 1964 Earthquake. This theory is actually supported by the hydrocarbon and geochronology data from AMT-East where there appears to be a missing layer of sediment. One possible explanation is that a subsurface sediment slide occurred during the 1964 Earthquake, resulting in sediment from the shallower inshore AMT-D33 site being transported to deeper water offshore and being deposited as a sediment plume at AMT-East. The PAH fingerprint from AMT-East appears to be a typical background signature made up of primarily low-level petrogenic PAH that are bound to petrogenic source rock with lesser contributions from pyrogenic PAH sources. Biogenic inputs also appeared to be small as evidenced by the low levels of perylene.

TPAH concentrations were found to be low and representative of background conditions at the Gold Creek, Lowe, and Valdez sites where TPAH concentrations were generally less than 200 ppb (Table 11 and Figure 25). The surface sample at Valdez was found to be slightly higher at 268 ppb relative to the three deeper samples that ranged from 141 to 168 ppb, but this increase was not evident in other hydrocarbon parameters and was not attributed to anthropogenic hydrocarbon contamination. The PAH fingerprints from these three locations also suggests a background-type signature primarily made up of petrogenic PAH with low levels that are bound to petrogenic source rock with lesser contributions from pyrogenic PAH sources (refer to Appendices B and C).

Galena Bay TPAH concentrations were found to be substantially elevated relative to Gold Creek, Lowe, and Valdez with TPAH ranging from 705 to 1,009 ppm (Table 11 and Figure 25). No observable difference was seen between the surface (0-2 cm) sediment at Galena Bay and the deeper (60-63 cm) sediment that dated from approximately the late 1800's (refer to Table 9), which would suggest that the PAH at this location are naturally-occurring and not of anthropogenic origin. The histogram from Galena Bay shows a strong un-weathered petrogenic signature which would indicate coal or other source rock inputs (Figure 26). The naphthalene series which is low in molecular weight and the PAH series that typically weathers most quickly was found to be un-weathered, indicating that the hydrocarbons are bound to the sediment and not prone to weathering and are therefore not biologically available to the marine environment. The alkyl-phenanthrenes were found to be much higher than the alkyl-dibenzothiophenes which is characteristic of the background PAH signature for the PWS region. Biogenic inputs were also indicated in the PAH signature from Galena Bay as seen by the relatively high

perylene concentrations. One reason for the higher background signal compared to the other sites is the high TOC and clay content seen at this site.

5.2.3   Saturated Hydrocarbons

The analysis of saturated hydrocarbons included the n-alkanes (n-C_{10} through n-C_{34}) plus pristane and phytane, where the summation is defined as TAHC; TRAHC that included TAHC analytes plus other compounds such as plant waxes and lipids which are not individually identified or reported; the UCM; and TPH which is the summation of all resolved and unresolved components. Concentrations of individual aliphatic hydrocarbons by station and sample are presented in Appendices B and C. A summary of saturated hydrocarbon parameters is presented by station and sample in Table 11. TRAHC concentrations ranged from 6.0 to 94.7 parts per million (ppm) or micrograms/gram (ug/g) at BWTP (Table 11 and Figure 28). In general, locations and samples that showed hydrocarbon inputs in the PAH analyses from the AMT ballast water discharge and other tanker operations also exhibited elevated levels of TAHC, TRAHC, UCM, and TPH.

At the BWTP site, TAHC levels ranged from 1.07 ppm (ug/g dry weight) in the deeper pre-AMT sediments to 11.31 ppm in the shallow post-AMT construction sediments (Table 11 and Figure 28). Likewise, the UCM which is an indication of hydrocarbon weathering ranged from 2 near the bottom of the sediment core to 1,799 ppm near the surface of the core. This same trend was also reflected in the TPH concentrations that ranged from 10 to 1,894 ppm with a accumulation of TPH clearly starting to occur at around the time the AMT started operations (Figure 27). The AHC histograms at BWTP showed a very marked and dramatic difference between the pre- and post-AMT sediments (Figure 29). The pre-AMT sediments had much lower AHC concentrations overall with a clear odd-to-even preference in the higher molecular weight alkanes, as seen in the high CPIs that ranged from 8.0 to 12.2 (Table 11). This type of AHC signature is a clear indication of biogenic inputs that are typical of naturally-occurring plant waxes from terrestrial sources. The post-AMT sediments indicated a much higher predominance of higher molecular weight aliphatic hydrocarbons as compared to the lower weight compounds, which would indicate a weathered source, and the odd alkanes were slightly higher but still similar in concentration to the even alkanes. The CPIs in the post-AMT sediments ranged from 1.2 to 2.5, which is an indication that petrogenic hydrocarbons are the primary source with smaller amounts of biogenic inputs.

Concentrations of AHC at the two other inshore AMT sites, AMT-West and AMT-D33, also showed a clear indication, particularly in the upper sediments, of petroleum contamination in the saturate hydrocarbon fraction, with levels approximately 50% of those seen at BWTP (Figure 28). TAHC levels at AMT-West ranged from 1.46 to 5.47 ppm, and those at AMT-D33 ranged from 1.26 to 3.83 ppm (Table 11). Concentrations of TRAHC, UCM, and TPH were also elevated at these two locations relative to the other four sites in Port Valdez. The TRAHC ranged from 11.0 to 20.5 ppm at AMT-West and from 11.0 to 23.9 ppm at AMT-D33. The relatively high UCM at these two sites indicated ongoing petroleum weathering processes and ranged from 31 to 355 ppm for both sites combined whereas the UCM at the other five sites (AMT-East, Galena, Gold Creek, Lowe, and Valdez) were all found to be <22 ppm (Table 11 and Figure 28). A very similar pattern can be seen in TPH concentrations, with BWTP having the highest concentrations followed by AMT-West and AMT-D33, and only trace levels of TPH at the other five locations. The CPI values at AMT-West and AMT-D33 were slightly higher than those seen at BWTP as a result of lower inputs of petrogenic hydrocarbons compared to that at BWTP, but these values were still less the CPI values seen at the other five locations. Likewise, the AHC signature from AMT-West and AMT-D33 exhibited a signal that was predominantly petrogenic in origin with lesser amounts of biogenic terrestrial plant wax material (refer to Appendix B and C).
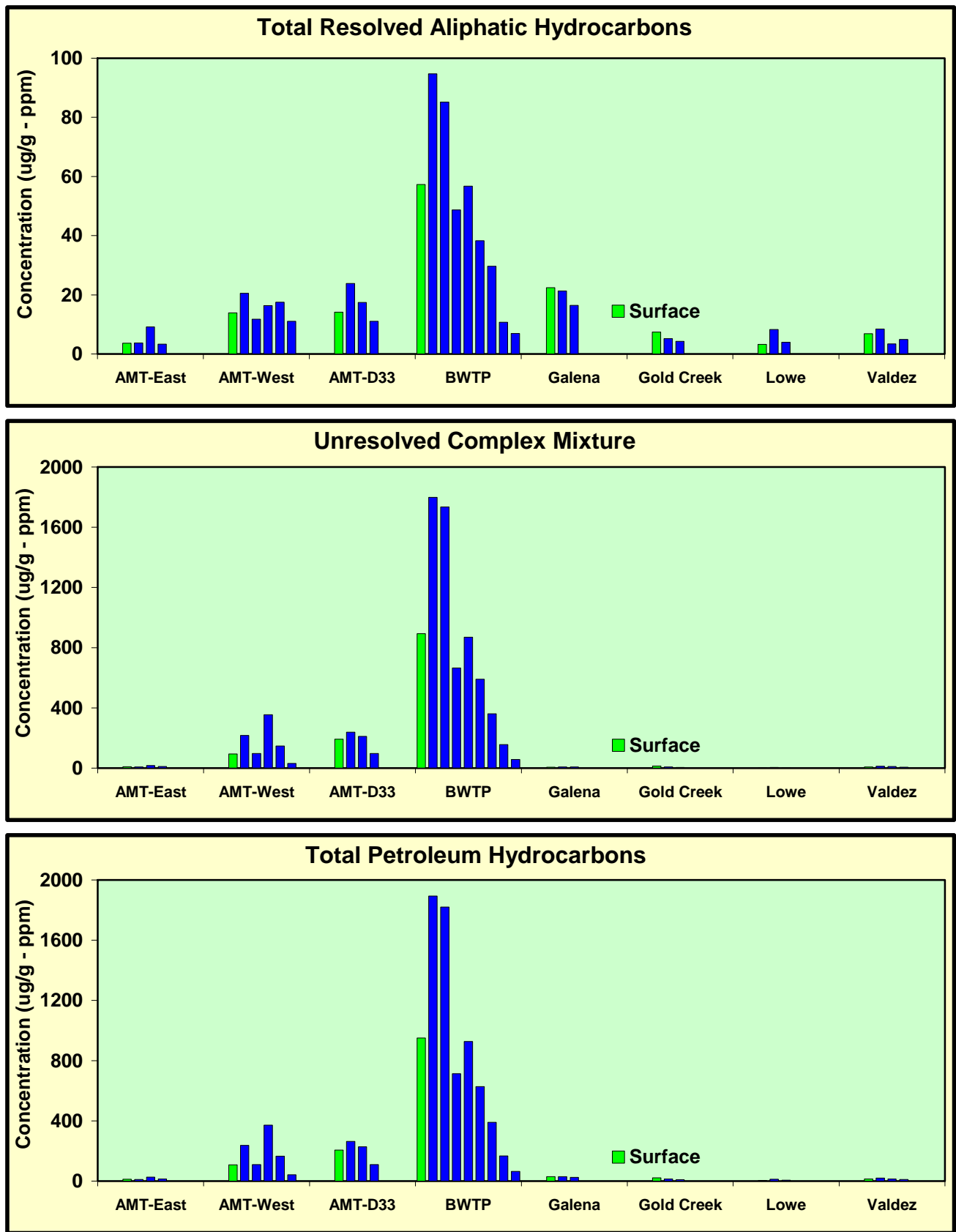
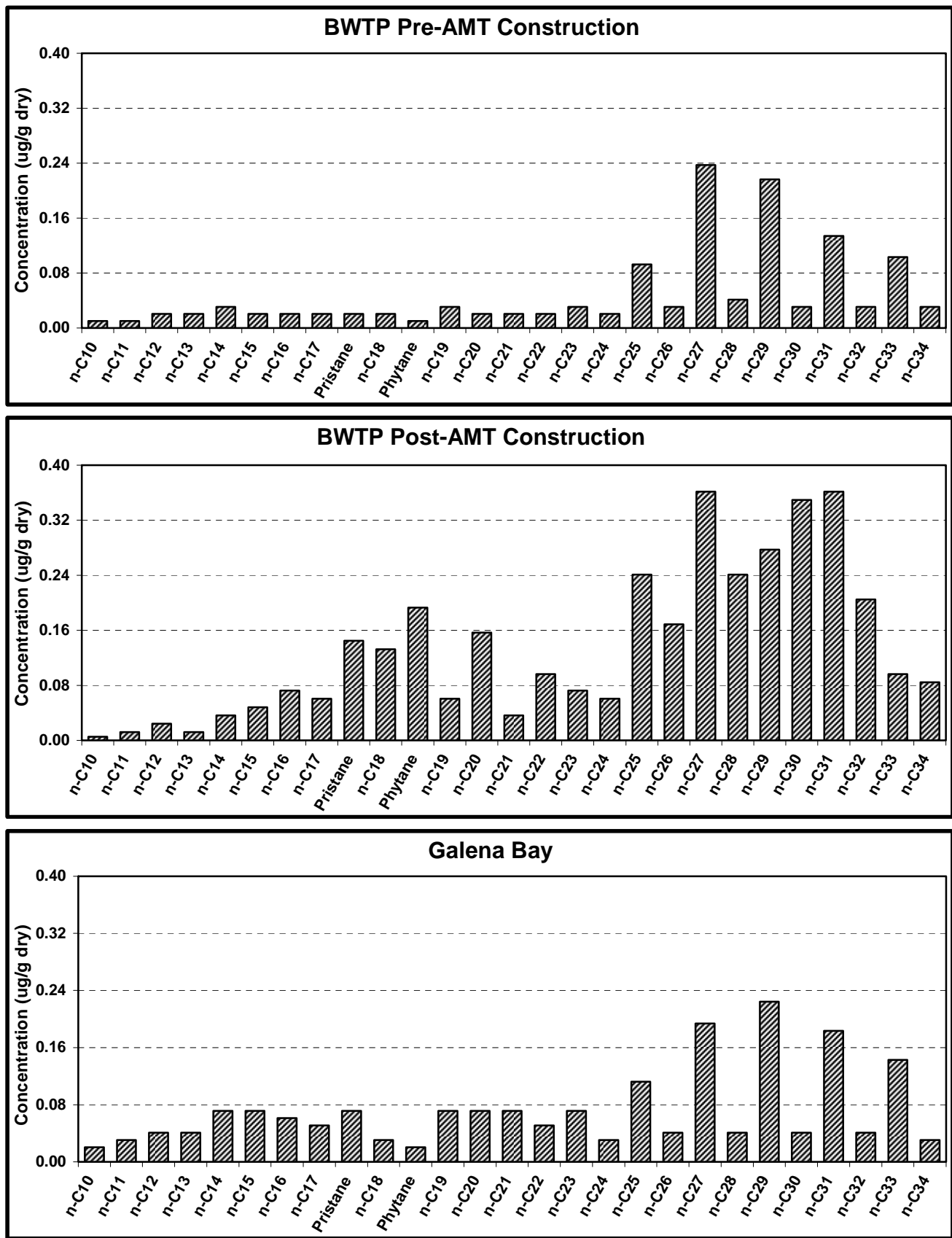**Figure 28.   Summary of Sediment TRAHC, UCM, and TPH by Station.**

Figure 29.   Sediment Core AHC histograms from BWTP and Galena Bay, June 2004.

Concentrations of saturated hydrocarbons at the other four Port Valdez locations (AMT-East, Gold Creek, Lowe, and Valdez) were very similar in terms of both overall low levels and individual analyte distribution. The TAHC levels at these stations ranged from to 0.67 to 0.93 ppm at AMT-East, from 0.69 to 0.80 ppm at Gold Creek, from 0.53 to 0.58 ppm at Lowe, and from 0.87 to 1.25 ppm at Valdez (Table 11 and Figure 25). TRAHC levels were also very similar at these four sites with concentrations ranging from a low of 3.3 ppm at both AMT-East and Lowe to a high of 9.1 ppm at AMT-East (Table 11 and Figure 28). The UCM at these four sites were all <18 ppm indicating essentially little evidence of weathered hydrocarbons (Table 11 and Figure 28). The resulting TPH concentrations were also low at these sites with concentrations ranging from 5 to 26 ppm (Table 11 and Figure 28). The sediments at these four sites show a clear odd-to-even preference in the higher molecular weight alkanes as seen in the high CPIs that ranged from 4.7 to 14.0 (Table 11). This type of AHC signature is similar to that seen in the pre-AMT sediments at BWTP and is a clear indication of biogenic inputs that are typical of naturally-occurring plant waxes from terrestrial sources (refer to Appendices B and C for individual sample histograms).

The saturate hydrocarbon distribution at Galena Bay was found to be somewhat different than the background type sediments in Port Valdez, and probably reflects the different source material as evidenced by the higher clay and TOC content previously described. The TAHC levels in Galena Bay were found to be much higher than the background sediments in Port Valdez and similar in concentration to those seen at AMT-West and AMT-D33 that had been heavily influenced by the AMT, with concentrations ranging from 1.93 to 4.04 ppm (Table 11 and Figure 25). Elevated levels relative to the Port Valdez background sediments were also seen in TRAHC with concentrations ranging from 16.4 to 22.4 ppm. The UCM at Galena Bay, however, was found to be very low, with concentrations <9 ppm for all samples indicating essentially no weathered hydrocarbons (Table 11 and Figure 28). As expected, the TPH levels were also low with all concentrations <30 ppm. The AHC distribution at Galena Bay clearly indicates an odd-to-even preference in the higher molecular weight alkanes which is reflected in the relatively high CPIs for this site as a result of biogenic inputs (Figure 28 and Figure 29). Based on the location of Galena Bay, the sediments in the Bay probably come from a number of sources including terrestrial runoff from streams, inputs from PWS, and glacial inputs from the Port Valdez area, whereas the Port Valdez sediments primarily come from glacial inputs with lesser amounts from terrestrial sources.

5.2.4   Total Organic Carbon and Extractable Organic Material

The analyses of TOC and EOM were also conducted on each hydrocarbon sample in addition to the TOC analyses that were performed as part of the geochronology measurements. With the exception of Galena Bay, which was found to have relatively high TOC concentrations, background sediments in Port Valdez fell ranged from 0.28 to 0.69 % TOC content (Table 11 and Figure 25). The TOC content in the Galena Bay sediments were approximately twice as high, ranging from 1.10 to 1.28 %. The TOC content at BWTP was also found to be relatively high as a result of hydrocarbon accumulations in the recent sediments with levels ranging from 0.63 to 1.05 %. The TOC content at AMT-West and AMT-D33, the two other sites that exhibited hydrocarbon contamination also had slightly elevated TOC levels (Table 11). The relationship of hydrocarbon concentrations as a function of TOC can clearly be seen in Figure 30, where TPAH less perylene versus TOC are plotted as a scatter plot. The regression of TPAH versus TOC (excluding Galena Bay) was found to have a strong linear relationship (regression coefficient, $R^2 = 0.81$), with sediments from the three post-AMT construction sites exhibiting higher TPAH and TOC.
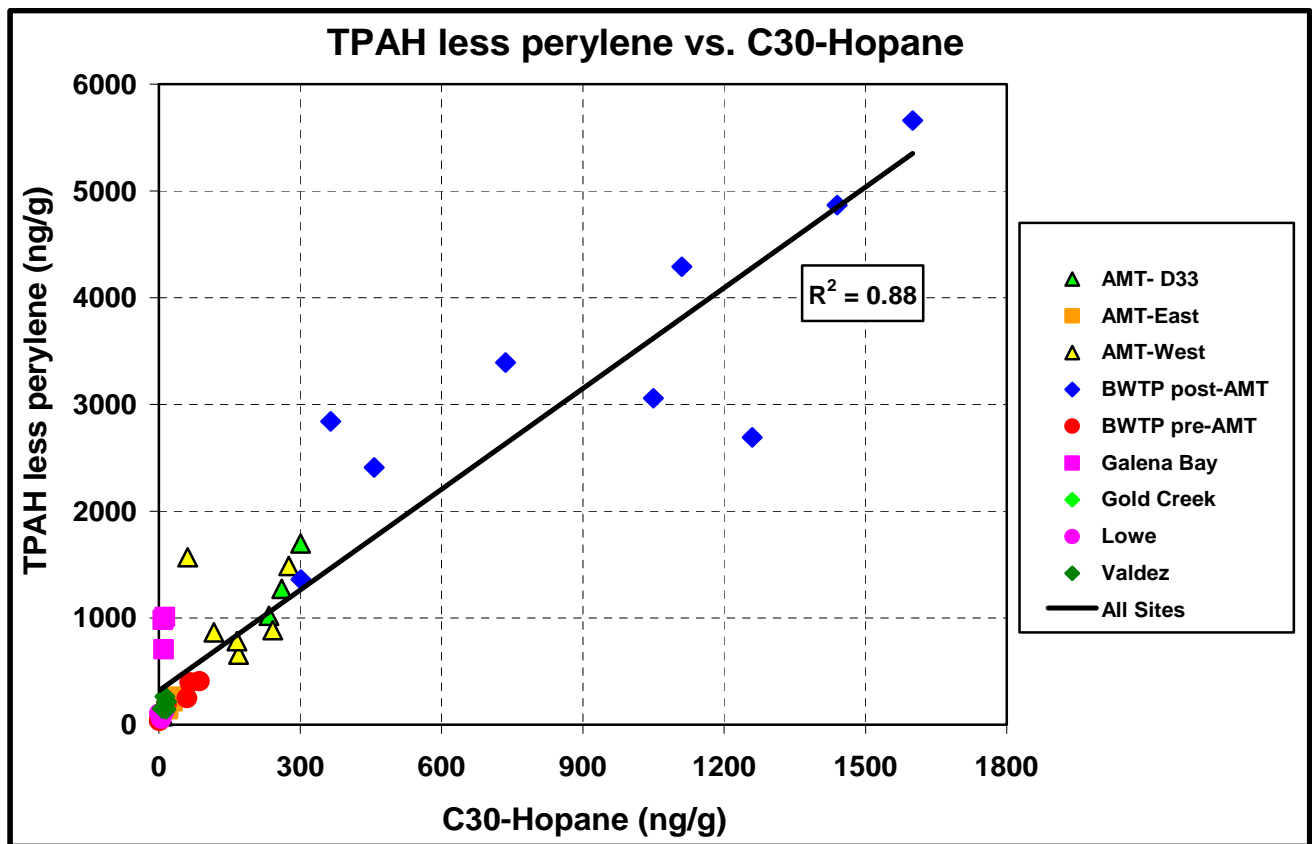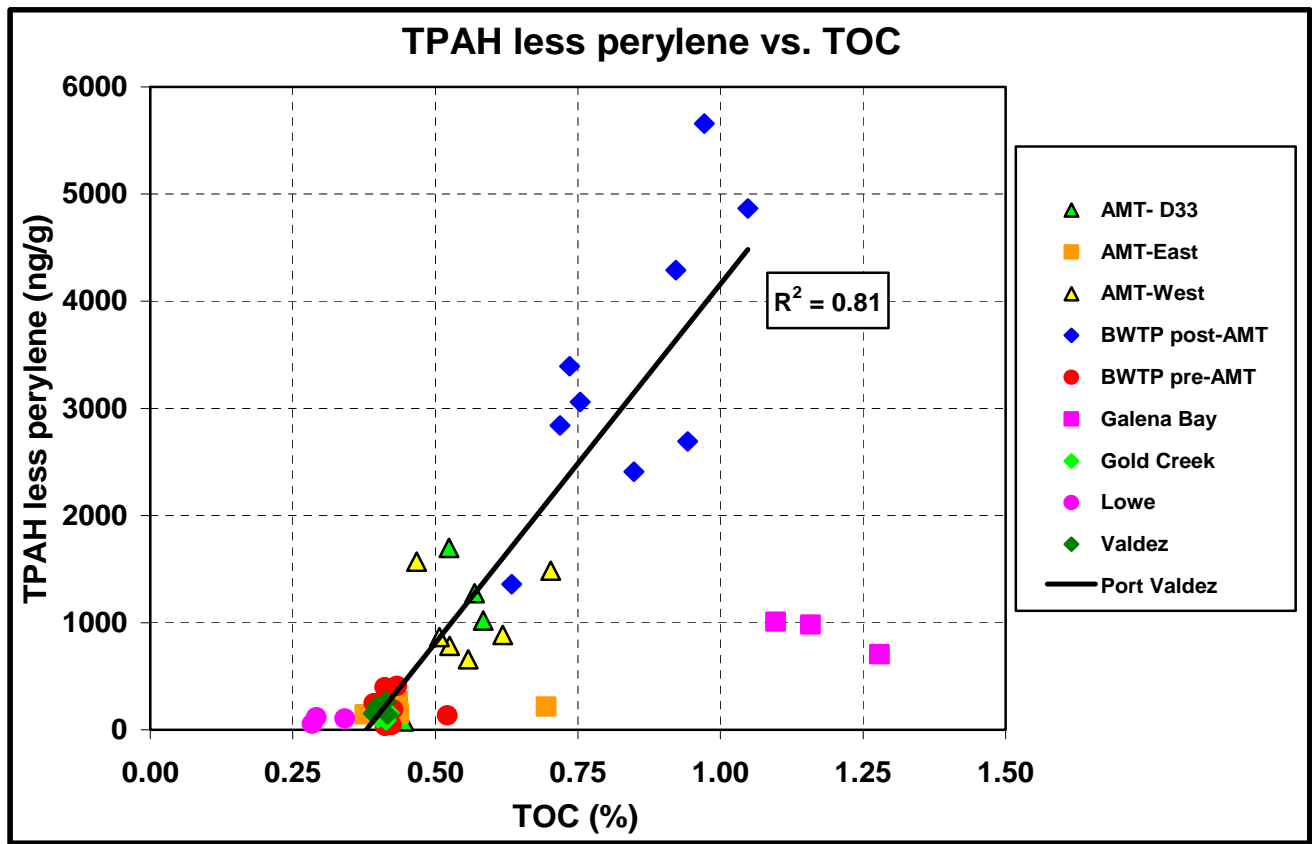
Figure 30.   Scatter Plot of TPAH less perylene versus TOC and C₃₀-Hopane.

The EOM in the background and pre-AMT sediments in Port Valdez ranged from a low of 60 ppm to high of around 300 ppm (Table 11). The Galena Bay sediments were found to be slightly higher ranging from 246 to 380 ppm. This is in contrast to the post-construction sediments at AMT that have accumulations of hydrocarbons where the EOM ranged from 115 to 1055 ppm at AMT-D33, from 472 to 1305 ppm at AMT-West, and from 257 to 5410 ppm at BWTP.

5.2.5 Biomarkers

The analysis of biomarkers is very useful in the identification of the source of oil residues since they are essentially molecular fossils that are present in oil that reflect characteristics of the source rock. Each sediment sample was analyzed for three select biomarkers, C_{29}-Hopane, 18a-Oleanane, and C_{30}-Hopane. The biomarker 18a-Oleanane was found to be absent in the vast majority of samples including those in the post-AMT sediments since it has been shown not to be a component in ANS crude and EVOS residues (Bence et al. 1996). Oleanane, however, was found in the three samples from Galena Bay, at trace levels in one sediment sample from BWTP that dated from the time of 1964 Earthquake, and in two samples from the bottom of the core at AMT-West that also dated from the mid-1960s prior to the AMT startup (refer to Appendices B and C).

The presence of oleanane near the AMT indicates the presence of a non-North Slope petroleum product that dated from around the time of the 1964 Earthquake that probably resulted from the release of petroleum into the marine environment during the earthquake. Kvenvolden et al. (1993 and 1996) analyzed tar balls on beaches in Prince William Sound after the EVOS and found a number that contained a suite of 25-norhopanes plus 18a-Oleanane. Based on the biomarker ratios, and carbon isotope analyses, they sourced the tar balls as oils originating in California that had come from the Monterey Formation. Prior to the startup of the AMT, petroleum products in Alaska were shipped to Alaska by barge from California with both Valdez and Whittier serving as ports of entry. Valdez had large storages of both fuel oil and asphalt that were known to have been damaged during the tsunami from Great Alaska Earthquake of 1964 that resulted in releases into Port Valdez.

The PAH signature from the deepest sample (PVC04HYD019) at AMT-West was dominated by 3-, 4- and 5-ring PAH with large peaks in fluoranthene and pyrene (refer to Appendix B) which is characteristic of either a combustion related pyrogenic source or creosote that has been shown to have a similar PAH distribution (Page et al. 1995). The other sample (PVC04HYD018) from AMT-West, that indicated the presence of oleanane, appeared to be mixture of sources including weathered ANS, pyrogenic inputs, and the natural background petrogenic and biogenic signature. The BWTP sample that was found to have trace levels of oleanane was the typical background PAH signature that showed a combination of low level inputs from petrogenic, pyrogenic, and biogenic sources.

The detection of the oleanane biomarker in Galena Bay further confirms a different background source in these sediments compared to the background sediments in Port Valdez, since oleanane produced by terrestrial flowering plants is associated with source rock from the post-Cretaceous/Tertiary time period. Since this biomarker was found in all three sediment samples from Galena Bay, with the oldest dating back into the late 1800's, it is thought that the source may be from eroded source rock that deposited into the bay rather than the result of a petroleum release as seen in the AMT sediments.

Concentrations of the triterpane biomarkers C_{29}-Hopane and C_{30}-Hopane were found in most samples with ratios of C_{30}/C_{29}-Hopane in the range of 1.2 to 1.8. It has been found that a characteristic of crude oils including ANS crude is a triterpane pattern that is dominated by the C_{30}-hopane component. The fact that these hopanes are dominant in most samples further confirms a product heavier than diesel,

since triterpanes are typically removed during the distillation process. The relationship of hydrocarbon concentrations as a function of C_{30}-Hopane can clearly be seen in Figure 30, where concentrations of TPAH versus C_{30}-Hopane are plotted as a scatter plot. The regression of TPAH versus C_{30}-Hopane was found to have a strong linear relationship (regression coefficient, $R^2 = 0.88$), with sediments from Galena Bay falling outside of the regression with lower levels of hopane compared to TPAH levels.

5.2.6 Core Descriptions

In addition to the core that was obtained for geochronology and chemistry analyses, a second core was obtained at each site to provide a photographic record and to obtain physical descriptions of the sedimentary record. In the case of the gravity core, a second core was obtained from the site, whereas with the box core, the second core was obtained as a subsample from within the box core sample. With the exception of AMT-D33, descriptive cores were obtained at each site. The photographic record for each site is presented in Figure 31.

It was originally anticipated that the descriptive cores would provide information that would aid in the geochronology measurements through identification of annual varves, sediment horizons, and other discontinuities in the sedimentary record. However, with few exceptions noted, the physical descriptions of the cores and photographic record were not very revealing. The sediment in all of the cores consisted of a fine, sticky, grey silt/clay that adhered to sampling implements and made slicing of the core difficult. Although the chemistry analyses indicated that Galena Bay had higher TOC content, this was not noticed in the physical description. However, it was noted that the Galena Bay cores were softer than the other cores which may be explained by the higher water content that was measured. Some dark banding and patches of black anoxic ("rotten egg smell") sediment was observed in a number of cores, in particular the core from Lowe, however these bands did not appear to be related to annual events and were probably the result of increased organic material.

A couple of other notable items were observed in two cores adjacent to the AMT. Some oil sheen was observed coming off of the upper 2 cm of the BWTP core. Also, a very noticeable petroleum smell was observed down to approximately 8 cm depth in the same core. A layer of shell hash, fine gravel, and sharp pieces of stone was also observed at 12-15 cm depth at BWTP. Based on the geochronology, this layer is probably associated with the AMT construction rather than the 1964 Earthquake which would have been somewhat deeper in the core. A discontinuity of coarser sediment was also observed at AMT-West at 15 cm depth in the core which would correspond to the same AMT construction time period. Since AMT construction would have included pile driving, blasting, and other intrusive activities, it is assumed that this layer of coarser sediment was deposited during construction and resulted from a combination of these physical disturbances.
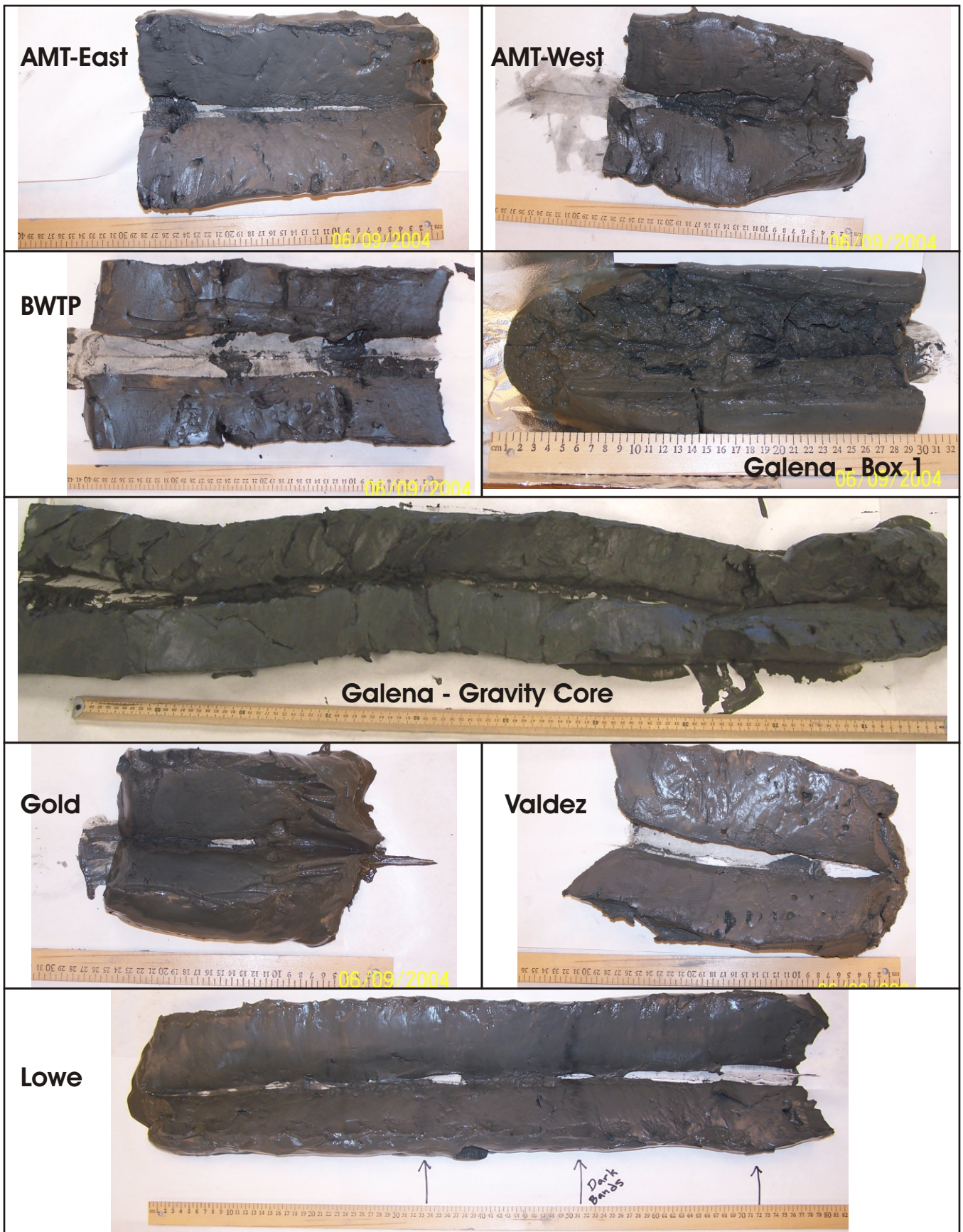
Figure 31. Photographic Record of Descriptive Sediment Cores, June 2004.

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6.0   SUMMARY

The field sampling for the Port Valdez Sediment Coring Program was conducted in June 2004. Cores were successfully obtained from a total of eight sites that included seven in Port Valdez, and one a presumed "clean" location in Galena Bay. The Port Valdez sites included four adjacent to the AMT and three offshore locations near Gold Creek, Valdez, and Lowe River. Sediment cores were analyzed for radionuclides to determine sedimentation rates, a suite of hydrocarbon parameters, TOC, Al, and visual descriptive and photographic documentation. The following is a brief summary of key findings.

- Sedimentation accumulation rates in Port Valdez were found to range from a high of approximately 1.5 cm/yr at Lowe to a low of 0.2 to 0.4 cm/yr at Gold. These rates were found to be consistent with past studies in the area that found higher rates near the head of Port Valdez, which is closer to the major sediment input from the Lowe River, with lower rates extending to the west down the longitudinal axis of the Port.

- Hydrocarbon concentrations at the four deep water sites in Port Valdez (AMT-East, Gold, Lowe, and Valdez) exhibited the typical "background" signature of hydrocarbons with low-level accumulations of petrogenic, pyrogenic, and biogenic hydrocarbons.

- Hydrocarbon accumulations at the three inshore AMT sites (AMT-D33, AMT-West, and BWTP) that were located along the same depth contour as the BWTP discharge showed clear accumulations of relatively high levels of weathered polycyclic aromatic and saturated hydrocarbons. The source of these hydrocarbons was determined to be Alaska North Slope crude which began to accumulate following the construction of the AMT and startup of the BWTP. The highest levels were found to exceed the NOAA's Effect Range –Low (ERL) level in three samples at the location nearest to the BWTP discharge. Hydrocarbon profiles at BWTP showed very low level concentrations prior to the BWTP startup, followed by a steady increase that was found to correspond with increased oil flow through the pipeline and discharges from the BWTP. Hydrocarbon concentrations at BWTP were found to have declined in recent years corresponding to the changes in BWTP operations and to decreases in pipeline output, tanker traffic, and discharges from the BWTP.

- Evidence suggested in both the sediment geochronology and the hydrocarbon analyses that a submarine sediment slump may have occurred in the vicinity of the AMT that dated from the 1960s and most likely occurred during the 1964 Great Alaskan Earthquake. There appeared to be a lost layer of sediment at one of the inshore AMT sites (AMT-D33); a corresponding accumulation of sediment at a deeper offshore site (AMT-East) located directly offshore substantiated the slide. Geophysical investigations that were conducted during 2005 by the United States Geological Survey in Port Valdez have also documented evidence of submarine slides in Port Valdez.

- Based on the historic evidence of submarine slides that occurred in Port Valdez and the steep bathymetry in the vicinity of the AMT, a future earthquake could generate a slide that would remobilize hydrocarbon-contaminated sediments located in the vicinity of the BWTP discharge. However, given that the contamination has been show to be localized both in space and time (sediment depth), the hydrocarbons are highly degraded and weathered, and the hydrocarbon contamination is bound up with the sediments, it is probable that there would not be a large risk to the marine environment should this occur.

- Evidence of the 1964 Great Alaskan Earthquake was also seen at another AMT site (AMT-West), where hydrocarbon accumulations were seen in one layer of the core that dated from around the time of the earthquake. This petroleum signature was found to closely match tar ball samples that have been documented in Prince William Sound and are believed to have been released during the 1964 Earthquake. It has been documented that the 1964 Earthquake and the resulting tsunami heavily damaged port facilities in Valdez which resulted in releases of fuel oil, paving tars, and other petroleum products into the marine environment.

- Evidence was also seen at two of the AMT sites (AMT-West and BWTP) of coarser-grained sediment and sharp bits of stone that had been deposited approximately 25-30 years ago. It is believed that this layer is probably related to AMT construction activities (pile driving, blasting, etc.) that occurred during that time period.

- The sedimentation rate in Galena Bay was found to be in the range of 0.35 to 0.46 cm/yr, with good agreement found between the two dating techniques. The sediments in Galena Bay were found to have higher TOC and water content and were also found to have very different hydrocarbon characteristics from the background sediments in Port Valdez. Galena showed a strong un-weathered petrogenic signature which would indicate coal or other source rock; a high CPI and high perylene concentrations from biogenic sources; and no evidence of hydrocarbon accumulations from anthropogenic sources.

7.0   RECOMMENDATIONS

Our recommendations for the program should future sediment core sampling be undertaken within Port Valdez are briefly outlined below:

- The program should attempt to fill in data gaps and focus on the area in the vicinity of the AMT where sediment hydrocarbon contamination was documented since sources of anthropogenic inputs were not found at other locations in Port Valdez. In order to focus on specific locations at the AMT, recent USGS geotechnical data from 2005 should be utilized to identify the areas of sediment deposition and historic submarine slides in selecting sampling locations.

- Additional sampling in Port Valdez should be considered at one of the historic sites studied by Naidu and Klein (Klein, 1983; and Naidu and Klein, 1988) to demonstrate the distinct difference and better sedimentary record at these more distant and deeper sites (e.g., 61° 6.35' N and 146° 32.5' W). The purpose of this sampling would be to help minimize concern for the degree of sediment mixing and distortion found in our study area.

- Increase core penetration depth in order to get to a sediment depth of zero excess ^{210}Pb and zero ^{137}Cs activity. Both box and gravity corers were utilized for this program. Although the box corer yielded a less disturbed core, the sediment cores were only 25-30 cm in length which limited geochronological interpretations. It is recommended that any future sampling efforts utilize a gravity or piston type corer to achieve greater sediment penetration depths.

- In addition to the geochronology and detailed hydrocarbon analyses, future sampling should consider additional analyses (e.g., x-ray, carbon isotope stratigraphy, and metals) on select samples to aid in the sediment interpretations.

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