

Exxon Valdez Oil Spill
State/Federal Natural Resource Damage Assessment Final Report

Petroleum Hydrocarbons in Near-Surface Seawater of Prince William Sound, Alaska, following
the *Exxon Valdez* Oil Spill I: Chemical Sampling and Analysis

Air/Water Study Number 3
Final Report

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Study History: Air/Water #3 (Geographic and Temporal Distribution of Dissolved and Particulate Petroleum Hydrocarbons in the Water Column) was first funded in 1989. In 1991 the study was renamed Subtidal Study Number 3 (Bio-availability and Transport of Hydrocarbons) but the objectives remained the same. The project was funded for closeout and renamed again in 1992 to Subtidal Study Number 3A to reflect the coordination with a related project (ST #3B). Two final reports will result from this project, hydrocarbons in caged mussels and hydrocarbons in the water. Two *Exxon Valdez* Oil Spill Symposium Proceedings papers resulting from this work are: Petroleum Hydrocarbons in Caged Mussels Deployed in Prince William Sound, Alaska after the *Exxon Valdez* Oil Spill, and Chemical Sampling and Analysis of Petroleum Hydrocarbons in Near-surface Seawater of Prince William Sound, Alaska after the *Exxon Valdez* Oil Spill.

Abstract: We sampled 32 locations during each of three sampling periods between 31 March through 8 May 1989 in Prince William Sound, Alaska, for hydrocarbons in seawater at depths of 1-m and 5-m following the grounding of the T/V *Exxon Valdez* on 24 March 1989. Samples were analyzed for 22 alkane and 43 polynuclear aromatic hydrocarbon (PAH) analytes.

Results indicate that PAHs derived from *Exxon Valdez* crude oil contaminated seawater to depths of at least 5 m, and at concentrations ranging to 6.24 ± 0.63 $\mu\text{g/l}$, at nine contiguously located stations in the general region encompassing northwest Montague Strait - northern Knight Island - Smith Island, 1 to 2 weeks following grounding of the vessel. The highest PAH concentrations were near heavily oiled beaches that continued to contaminate adjacent seawater for at least 5 weeks at concentrations ranging up to 1.59 $\mu\text{g/l}$.

These results show that *Exxon Valdez* crude oil PAHs were available to subsurface marine fauna the first few weeks following grounding of the T/V *Exxon Valdez*, especially in near-shore, near-surface waters that are biologically productive. Measured PAH concentrations, however, were well below those acutely toxic to marine fauna.

Keywords: Alkanes, *Exxon Valdez*, hydrocarbons, oil spill, PAH, seawater

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EXECUTIVE SUMMARY

We sampled 32 locations in Prince William Sound (PWS), Alaska, for petroleum hydrocarbons in seawater at depths of 1-m and 5-m following the grounding of the T/V *Exxon Valdez* on 24 March 1989 to evaluate the extent of seawater contamination resulting from the spilled crude oil. Most of the sampling locations were visited during each of three sampling periods between 31 March through 8 May 1989. Seawater samples were collected in triplicate at each location and depth, and were immediately extracted into dichloromethane. A total of 501 samples were collected; of these, 243 were analyzed for 22 alkane and 43 polynuclear aromatic hydrocarbon (PAH) analytes. All replicate samples from the first sampling period were analyzed, but only one sample from each depth from the second and third sampling periods was analyzed for reasons of economy.

Results indicate that PAHs derived from *Exxon Valdez* crude oil contaminated seawater to depths of at least 5 m, and at concentrations ranging to 6.24 ± 0.63 $\mu\text{g/l}$, at nine contiguously located stations in the general region encompassing northwest Montague Strait - northern Knight Island - Smith Island, 1 to 2 weeks following grounding of the vessel. Results for the alkane hydrocarbons indicate the probable presence of dissolved PAHs at some locations, and dispersed oil droplets in addition at others. The highest PAH concentrations were near heavily oiled beaches; these beaches were apparently a reservoir of spilled *Exxon Valdez* oil (EVO) that continued to contaminate adjacent seawater for at least 5 weeks following grounding of the T/V *Exxon Valdez*. However, seawater PAH concentrations declined substantially by 5 weeks, probably due to (1) dilution resulting from the flushing action of ocean currents through the Sound, and (2) microbial decomposition. By five weeks following grounding, PAH concentrations attributable to EVO persisted at only two of the nine sampling stations where contamination was evident 1 to 2 weeks following grounding, at concentrations ranging up to 1.59 $\mu\text{g/l}$.

These results show that *Exxon Valdez* crude oil PAHs were available to subsurface marine fauna the first few weeks following grounding of the T/V *Exxon Valdez*, especially in near-shore, near-surface waters that are particularly productive areas biologically. Measured PAH concentrations, however, were well below levels that are acutely toxic to marine fauna.

INTRODUCTION

The *Exxon Valdez* oil spill (EVOS) of 24 March 1989 in PWS, Alaska, is the largest and most thoroughly studied accidental oil spill in U.S. history. At least 260,000 barrels (41,400 m³) of Prudhoe Bay crude oil were released into the Sound by the spill, which subsequently contaminated the Alaska coastline and adjacent marine waters to distances more than 1,100 km from the spill origin at Bligh reef. This spill is scientifically significant because PWS was nearly pristine prior to this spill (Karinen et al. 1993), so confounding petroleum hydrocarbons from sources other than this oil spill were generally absent. Consequently, the chemical fate and biological effects of oil from this spill should be unambiguous.

Weather conditions after this oil spill were particularly favorable for transport of petroleum hydrocarbons to the subsurface seawater column, thus providing a unique opportunity to investigate hydrocarbon contamination of seawater from a large, cold-water oil spill. Ambient seawater and air temperatures in the neighborhood of 4°C after the spill decreased evaporation and increased solubilities of petroleum hydrocarbons compared with spills at warmer temperature. A storm occurred in the Sound after 3 days of calm weather that immediately followed the spill, so the spilled oil initially formed a continuous slick on the sea-surface, and then was thoroughly mixed with sub-surface seawater by wave action during the storm. Combined, these conditions should promote the solution of slightly soluble petroleum hydrocarbons into seawater. As a result, concentrations of these hydrocarbons below the oil slick should be among the highest observable due to a large-scale accidental oil spill.

We sampled seawater along and adjacent to the path followed by the spilled oil inside PWS for 5 weeks beginning 1 week after the grounding of the T/V *Exxon Valdez*, to determine concentrations of petroleum hydrocarbons that dissolved or dispersed into the seawater column. Our general objectives were to characterize and document petroleum hydrocarbon concentrations at depths of 1-m and 5-m at the sampled locations and times. We collected 501 seawater samples at 32 sampling locations, and analyzed 243 of these for 22 alkane and 43 PAH analytes.

OBJECTIVES

The original objectives of this study were stated in the State/Federal Natural Resource Damage Assessment Plan for the EVOS of August 1989 (p. 42), as follows:

- A. Document water column hydrocarbon concentrations at a range of depths, locations, and times.
- B. Quantify injury to water resources.

- C. Relate water injury to biological injury.
- D. Evaluate trends in ambient water quality through measurements of hydrocarbons in a biological indicator (*Mytilus*) as a surrogate for chemical measurements.
- E. Identify potential alternative methods and strategies for restoration of lost use, populations, or habitat where injury is identified.

This document addresses objectives A and B above. The remaining objectives will be addressed in companion documents.

METHODS

Sampling Stations

A total of 32 stations were sampled along or adjacent to the oil path inside PWS at least once during three sampling periods. The first sampling period began 31 March 1989, the third period ended 8 May 1989, and each period lasted 3 to 6 days.

Physical data recorded at each station included location (geographic latitude and longitude), sampling time, and temperature and salinity at sampling depths. Latitude and longitude were determined from the sampling vessel's Loran system and by taking bearings from radar images. The temperature of the sampled seawater was measured by a digital thermometer; the salinity was measured with a refractometer, comparing the sample to a known standard. These data are presented in Tables I-1 through I-3 in Appendix I for each of the three sampling periods, arranged according to the sequence that the stations were sampled. The location of the sampling stations are also depicted in Figure 1, where the sampling station numbers correspond with those of Tables I-1 through I-3. In addition, Figure 1 depicts the path of prevailing ocean currents (Galt et al. 1991), and of the spilled *Exxon Valdez* crude oil, through PWS.

Sample Collection

At each sampling station and time, triplicate seawater samples were collected at both 1-m and 5-m depths. Seawater samples were collected by pumping seawater through a stainless steel tube into a 2-liter vacuum flask with a peristaltic suction pump. Separate stainless steel tubes were cut to length for 1-m and for 5-m sampling depths. These tubes were arched at one end so that they could be passed through a rubber stopper fitted to the vacuum flask on the deck of the boat used for sampling. The side arm of the flask was connected to the peristaltic pump with silicone pump tubing. The seawater sample contacted only stainless steel or glass during collection, and was not exposed to hydrocarbon vapors.

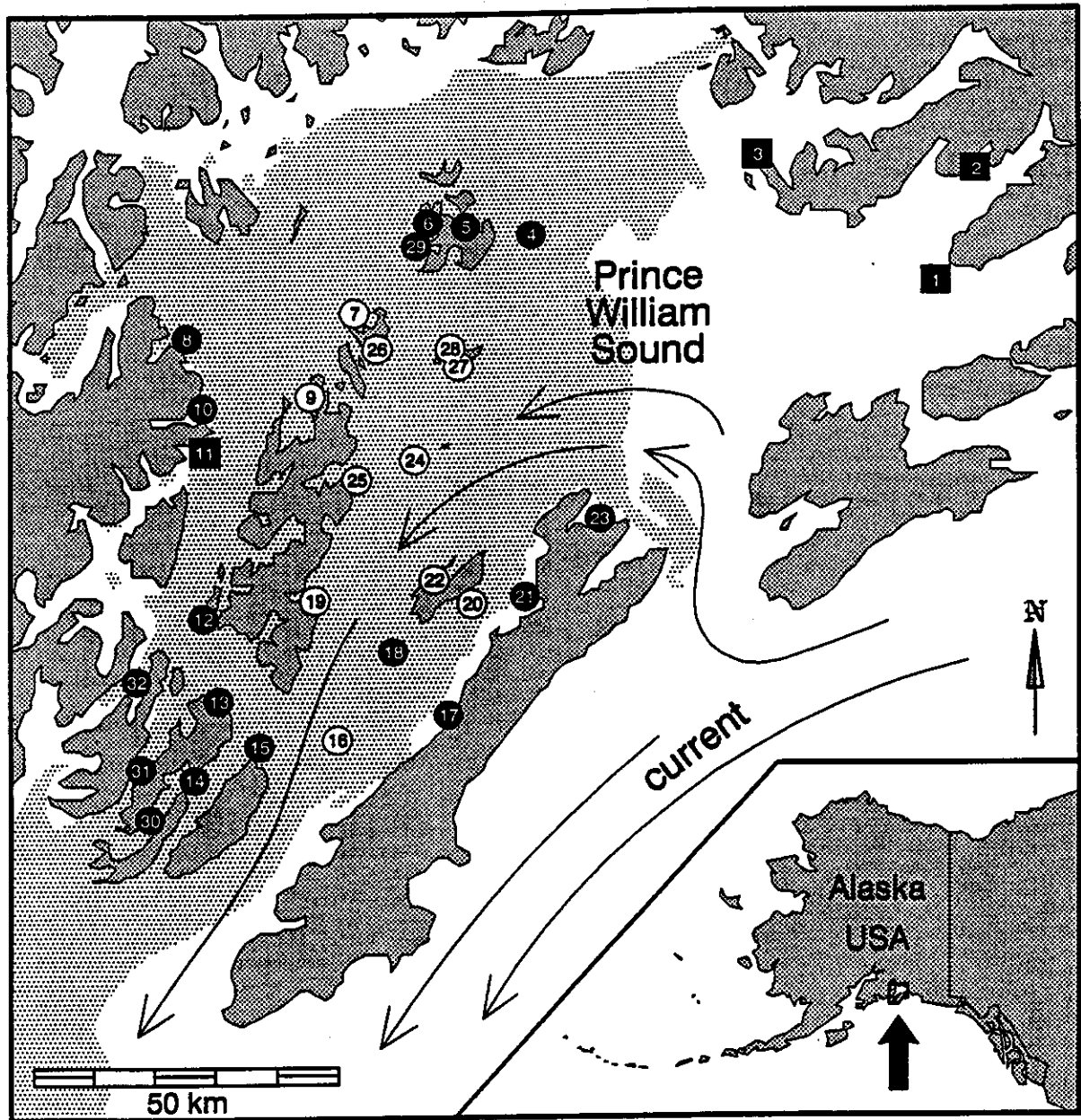


Figure 1.--Station locations in PWS, Alaska, where sub-surface seawater hydrocarbons were measured after the EVOS of 24 March 1989. Station numbers within symbols correspond to the station numbers of Tables I-1, 2, and 3 in Appendix I. Arrows indicate the direction of prevailing oceanic currents through the Sound (Galt et al. 1991). Shaded area indicates the path of surface oil through the Sound. ○ = Stations where PAHs from the spilled oil were definitely detected. ■ = Control stations. ● = Other stations sampled.

The end of the stainless steel tube that penetrated the sea surface was protected from surface oil contamination by a 10-cm length of tygon¹ tubing which had been heat sealed on one end to form a cover for the end of the steel tube entering the water. The tube cover had an internal diameter such that the tubing had to be soaked in hot water to allow it to be fitted over the steel tube end. The tube cover was blown off the end of the steel tube with compressed air from a scuba tank after the covered end was lowered to the sampling depth. The scuba tank was connected to the above-surface end of the steel tube with laboratory vacuum-line tubing. Twine was tied to the tygon tube cover prior to submersion to allow recovery of the cover after it was blown off. Tube covers were used only once and were discarded after recovery.

After a tube was in place at sampling depth, the tube, the vacuum flask, and the peristaltic pump were connected and about 1.5 l of seawater was collected. This seawater was used to rinse a 1-l glass graduated cylinder and three 1-l teflon separatory funnels three times each. The rinses and excess seawater were discarded. Another 1.5 l of seawater was pumped from the sampling depth, and 900 ml of this seawater was measured with the graduated cylinder and transferred to a teflon separatory funnel.

Sample Extraction

Each 900-ml seawater aliquot was extracted within 1 minute of collection by shaking with 50 ml dichloromethane for 1 minute, and allowing 1 minute for separation. The dichloromethane was drained into either 25-ml liquid scintillation vials with teflon-lined lids, or 120-ml glass jars with teflon-lined lids. Both types of containers had been rinsed previously with dichloromethane. The 900-ml seawater aliquot was extracted again with 25 ml dichloromethane for 1 minute and allowed to separate for 1 minute. This extract was combined with the previous extract. Excess seawater in the flask was discarded. Two additional 900-ml seawater aliquots from the sampling depth were similarly pumped and extracted.

After extractions were completed, the separatory funnels, graduated cylinder, and filter flask were each rinsed three times with dichloromethane, and the sampling tube was quickly pulled vertically out of the water so that seawater inside drained as the end of the tube left the sea surface. The tube was cleaned with dichloromethane prior to use at the next sampling station. Glassware preparation, sample collection, and extraction were similar at the second sampling depth at each station.

Sample Storage

Extracts of seawater samples were stored in sealed, teflon-lined jars inside a locked container at ambient temperature (ca 5°C) for up to 5 days, until the end of the sampling cruise.

¹Reference to trade name does not indicate endorsement by the National Marine Fisheries Service, NOAA.

On return to port, the samples were frozen to -20°C and transferred to the Auke Bay Laboratory for storage at -20°C .

Preparation of Extracts for Hydrocarbon Analysis

The seawater sample extracts were prepared and analyzed by procedures presented in detail by Larsen et al. (1992). Briefly, each sample was spiked with $500\ \mu\text{l}$ hexane solution containing six deuterated surrogate aromatic hydrocarbon standards (listed in Table II-1, Appendix II), then dehydrated by filtration through 50 g anhydrous sodium sulfate. The sample jar(s) and filtration apparatus were successively rinsed with 3-4 aliquots of 2 ml dichloromethane, followed by a 5-ml dichloromethane rinse of the filtration apparatus only, with all the rinses added to the extract. The combined dichloromethane extracts and rinses were reduced in volume over steam to ca 2 ml, and the dichloromethane solvent was replaced with hexane by addition of 1.5 ml hexane and boiling over steam to a final volume of ca 1 ml. The hexane solution was spiked with $50\ \mu\text{l}$ hexane containing $42\ \text{ng}/\mu\text{l}$ dodecylcyclohexane (DCH), and with $25\ \mu\text{l}$ hexane containing $80\ \text{ng}/\mu\text{l}$ hexamethylbenzene (HMB) as internal standards for alkane and aromatic hydrocarbon analyses, respectively, and then transferred to a 2-ml glass bottle with a PTFE-lined screwcap for storage at -20°C until gas chromatographic analysis.

PAH Analysis

1. Instrumental Method

PAHs in samples and in standards were separated and analyzed with a Hewlett-Packard 5890 series II gas chromatograph equipped with a 5970B mass selective detector (MSD). The injection volume was $2\ \mu\text{l}$ into a splitless injection port at 300°C . The initial oven temperature was 60°C , increasing at 10°C per minute immediately following injection to a final temperature of 300°C which was maintained for 25 minutes. The chromatographic column was a 25-m fused-silica capillary (0.20 mm inside diameter) coated with a $0.33\text{-}\mu\text{m}$ -thick film of 5% phenyl methyl silicone. The inlet pressure of the helium carrier gas was maintained at 70 kPa.

The chromatographic column eluted into the 70-kV electron impact MSD through a 300°C transfer line. The ionizer temperature and pressure were 240°C and 10^{-5} torr, respectively. The MSD was operated in the selected ion monitoring (SIM) mode, and the specific ions and retention time windows of the SIM Table were chosen to detect all the calibrated aromatic hydrocarbons, the surrogate standards, and the 200 most prominent peaks found on the total ion chromatogram of an aliquot of crude oil from the hold of the T/V *Exxon Valdez* analyzed as a sample, with the MSD operating in the scan mode. The MSD was tuned with mass 69, 102, and 512 fragments of perfluorotributylamine prior to each batch of samples analyzed.

2. PAH Identification

A. Calibrated PAHs

Calibrated PAHs were identified on the basis of retention time and ratio of two mass fragment ions characteristic of each hydrocarbon. Calibrated PAHs are listed in Table II-2, Appendix II, and include dibenzothiophene and the aromatic hydrocarbons in Standard Reference Material (SRM) 1491 supplied by the National Institute of Standards and Technology (NIST). Also listed in Table II-2 are standardized abbreviations for these PAHs the mass of the quantification ion, the mass of the confirmation ion, and the mean ratio of these two ions in the calibration standards. Chromatographic peaks were identified as a calibrated aromatic hydrocarbon if both ions were co-detected at retention times within ± 0.15 minutes of the mean retention time of the hydrocarbon in the calibration standards, and if the ratio of the confirmation ion to the quantification ion was within $\pm 30\%$ of the expected ratio.

B. Uncalibrated PAHs

Uncalibrated aromatic hydrocarbons include the carbon methyl-substituted isomers of naphthalene, fluorene, dibenzothiophene, phenanthrene, fluoranthene, and chrysene together with standardized abbreviations listed in Table II-3, Appendix II. Uncalibrated aromatic hydrocarbons were identified by the presence, within a relatively wide retention time window, of a single mass fragment ion that is characteristic of the alkyl-carbon number of uncalibrated aromatic hydrocarbon sought. Table II-3 lists the mass of the fragment ions used for both identification and measurement, and the retention time windows used. The retention time windows for uncalibrated aromatic hydrocarbons were much wider than those for calibrated aromatic hydrocarbons. Mass fragments of uncalibrated aromatic hydrocarbons that eluted outside the windows listed in Table II-3 would not have been detected.

3. PAH Measurement

A. Calibrated PAHs

Concentrations of calibrated PAHs in the dichloromethane extracts were estimated by a method using a multiple internal standard employing a 5-point calibration curve for each calibrated aromatic hydrocarbon. The deuterated surrogate standards that were initially spiked into each sample were treated as internal standards, where each surrogate compound was associated with one or more calibrated PAHs (see Tables II-2 and II-3, Appendix II). A calibration curve for each calibrated PAH and batch of samples analyzed was based on five different hexane dilutions of dibenzothiophene and NIST SRM 1491, where 1 ml of each dilution contained the same amount of deuterated surrogate standard as was spiked into the samples. Each calibration curve was derived from linear regression of the ratio of MSD/SIM quantification ion response of the calibrated PAH and the associated deuterated surrogate standard as the ordinate, and the ratio of the amount of calibrated PAH and the amount of deuterated surrogate in 1 ml of each of five calibration standards as the abscissa. The highest calibration standard was 25

times more concentrated than the lowest standard, and PAH concentrations in the lowest standard was less than 3 times higher than those that would have resulted from samples containing PAHs at the method detection limits (see below).

The amount of a calibrated PAH in the dichloromethane extract of a water sample was calculated as the product of the inverse of the slope of the calibration curve regression line, the ratio of MSD/SIM quantification ion response of the calibrated PAH and the associated deuterated surrogate standard for the sample extract, and the amount of the deuterated surrogate standard associated with the PAH. The concentration of a calibrated PAH in the original water sample was calculated as the ratio of the amount of the hydrocarbon in the dichloromethane extract and the original sample volume of seawater (900 ml). This procedure compensated for losses of calibrated PAHs during sample preparation.

B. Uncalibrated PAHs

Concentrations of uncalibrated PAHs in the seawater samples were determined by using calibration curves and procedures for the most similar calibrated PAH. The MSD/SIM response of the quantification ion of each uncalibrated PAH identified, bearing the same number of methyl substituents and derived from the same unsubstituted PAH, were summed; this sum was used in place of the most similar calibrated PAH response in the procedure described above for calculating concentrations of calibrated PAHs. For example, the fluorene calibration curve and procedure were used for all the methyl-substituted fluorenes identified, but the 1-methylphenanthrene calibration curve and procedure were used for all the methyl-substituted phenanthrenes.

4. Detection Limits

MDLs were estimated for each calibrated PAH analyte following the procedure described in Appendix B, 40 CFR Part 136. The estimated detection limit concentrations for each calibrated PAH analyte are listed in Table III-1, Appendix III.

MDLs for uncalibrated PAHs were not experimentally determined. Consequently, detection limits for these analytes are arbitrarily assumed as the MDL of the most closely related calibrated PAH analyte.

5. Quality Assurance

A. String Structure and Quality Control Samples

Samples were analyzed in batches consisting of 12 samples, which together with 5 calibration curve standards and 5 quality control samples arranged in a specific sequence, were denoted as strings. Replicated samples were always analyzed in different strings. The five quality control samples included two mid-level calibration standards, two reference samples, and a method blank. One mid-level calibration standard, one reference sample, and the method blank

were analyzed in the middle of each string, and the remaining two quality control samples were analyzed at the end of each string. The mid-level calibration standards were analyzed to verify instrument stability during analysis of the string; results are summarized in Table IV-2, Appendix IV. The reference samples were prepared as hexane dilutions of NIST SRM 1491 and dibenzothiophene that were spiked into 75 ml dichloromethane, and then processed and analyzed as a sample to determine accuracy and precision within and among strings. The PAH amounts used to prepare the reference samples are equivalent to PAH concentrations of about 1 µg/l seawater. The method blank was usually prepared as a 75 ml aliquot of the dichloromethane used for sample processing that was processed and analyzed as a sample to determine contamination. However, the remaining dichloromethane that was used to extract the seawater samples of the first sampling period was used to prepare method blanks for five of the strings. The dichloromethane used for the first sampling period extractions was of uncertain purity, but was used because of its timely availability. Absence of PAH contaminants in the dichloromethane used during succeeding sampling periods was verified before use.

B. Calibration Curve Linearity and Surrogate Standard Recoveries

Calibration curve linearity, expressed as the square of the correlation coefficient of regression (r^2), was greater than 0.99 for more than 95% of the PAH calibration curves. Recoveries of the deuterated surrogate standards, that were added to each sample, were estimated by comparing the ratio of deuterated surrogate response and the HMB internal standard of a sample with the mean of the same ratio derived from the calibration standards of the sample string (1 ml of each calibration standard contained the same amounts of these standards as was added to each sample, and each sample was concentrated to about 1 ml for instrumental analysis). PAHs that were associated with deuterated surrogate standard recoveries of less than 40% or more than 150%, were treated as missing, affecting 2.1% of the PAH data.

C. Analytical Precision and Accuracy

The accuracy and precision of the analytical procedure were evaluated on the basis of the results of the two reference samples analyzed with each string; these results are summarized in Table IV-1, Appendix IV. Mean accuracy, determined as the ratio of the mean amount of calibrated PAH found in the reference samples of the 21 strings analyzed for this study and the amount added, ranged from 88.8% to 107.3%. Corresponding coefficients of variation (CV's, i.e., the ratio of the standard deviation and the mean of the calibrated PAHs found in the reference samples) ranged from 2.7% to 17.2% (median, 7.4%).

D. Contaminants in Method Blanks

Calibrated PAHs above respective MDLs were detected six times in the analysis of 25 calibrated PAHs in each of the 21 method blanks. Four of these were due to naphthalene in the method blanks prepared from the remaining dichloromethane that was used to extract seawater samples during the first sampling period (naphthalene was not determined in 1 of these 5 method blanks due to unacceptable surrogate standard recovery). The mean concentration of naphthalene

in the dichloromethane used during the first sampling period was equivalent to 137 ± 19 ng/l seawater (95% confidence interval). Both 1- and 2-methylnaphthalene were also consistently measured in this dichloromethane at 18.0 ± 3.6 and 22.2 ± 3.2 ng/l, respectively, which were just below the MDLs of these PAHs.

Uncalibrated PAHs above estimated MDLs were detected 31 times in the analysis of 18 uncalibrated PAHs in each of the 21 method blanks.

Alkane Hydrocarbon Analysis

1. Instrumental Method

Alkanes in samples and in standards were separated and analyzed with a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector (FID). The injection volume was 1 μ l into a splitless injection port at 300°C. The initial oven temperature of 60°C was maintained for 1 minute, then increased at 6°C per minute to a final temperature of 300°C which was maintained for 26 minutes. The chromatographic column was a 25-m fused silica capillary (0.20 mm inside diameter) coated with a 0.33- μ m-thick film of 5% phenyl methyl silicone. The helium carrier gas was 0.80 ml per minute, and the column effluent was combined with 34 ml per minute nitrogen make-up gas before entering the FID. The FID was operated with hydrogen and air flowing at 33 and 410 ml per minute, respectively.

2. Alkane Hydrocarbon Identification

Alkane hydrocarbons were identified on the basis of their retention times. Any peak detected above the integrator threshold within $\pm 0.25\%$ of the mean retention time of an alkane in the calibration standards was identified and quantified as that alkane. The calibration standards were prepared at our Laboratory, and contain the normal alkanes from decane through triacontane (i.e., C-10 through C-30)², 2,6,10,14-tetramethylpentadecane (pristane), and 2,6,10,14-tetramethylhexadecane (phytane). However, pentadecane and phytane co-eluted in the gas chromatograph with two of the deuterated surrogate standards that were added initially for quantifying PAHs, precluding analysis for these two alkanes.

3. Alkane Hydrocarbon Measurement

Concentrations of alkanes in the dichloromethane extracts were estimated with the internal standard method employing a 5-point calibration curve for each calibrated alkane hydrocarbon. The DCH that was spiked into each sample just prior to instrumental analysis was the internal standard. A calibration curve for each alkane and batch of samples analyzed was based on five different hexane dilutions of the alkane calibration standard, where 1 ml of each dilution contained the same amount of DCH as was spiked into each sample. Each calibration curve was derived

²See Table IV-2, Appendix IV for key to standardized abbreviations.

from linear regression of the ratio of response of the calibrated alkane and DCH as the ordinate, and the ratio of the amount of calibrated alkane and the amount of DCH in 1 ml of each of five calibration standards as the abscissa. The highest calibration standard was 50 times more concentrated than the lowest, and was equivalent to a concentration of alkane in seawater of about 50 µg/l.

4. Detection Limits

MDLs were not estimated for the alkanes.

5. Quality Assurance

A. String Structure and Quality Control Samples

Samples were analyzed in strings comprising 12 samples, 5 calibration curve standards, and 6 quality control samples arranged in a specific sequence. Replicated samples were always analyzed in different strings. The six quality control samples included two mid-level calibration standards, two reference samples, a method blank, and a NIST-supplied alkane standard. One mid-level calibration standard, one reference sample, and the method blank were analyzed in the middle of each string, and the remaining three quality control samples were analyzed at the end of each string. The mid-level calibration standards were analyzed to verify instrument stability during analysis of the string; the results are summarized in Table IV-4, Appendix IV. The reference samples were prepared as hexane dilutions of a composite alkane standard prepared in our Laboratory, spiked into 75 ml dichloromethane, and then processed and analyzed as a sample to determine precision within and among strings. The alkane amounts used to prepare the reference samples were equivalent to alkane concentrations of about 10 µg/l seawater. The method blank was usually prepared as a 75-ml aliquot of the dichloromethane used for sample processing that was processed and analyzed as a sample to determine contamination. However, the remaining dichloromethane that was used to extract the seawater samples of the first sampling cruise was used to prepare method blanks for five of the strings. One ml of a NIST-supplied alkane standard labelled QA-CH-2 was spiked with DCH and analyzed at the end of each string to evaluate the accuracy of the analytical process for the alkanes contained in this standard.

B. Calibration Curve Linearity

Calibration curve linearity, expressed as the square of the correlation coefficient of regression (r^2), was greater than 0.99 for more than 95% of the alkane calibration curves. Alkane recoveries were not determined.

C. Analytical Precision and Accuracy

The precision of the analytical procedure was evaluated on the basis of the results of the two reference samples analyzed with each string; these results are summarized in Table IV-3, Appendix IV. Mean CV's of alkanes in the reference samples ranged from 3.6% to 24.0%

(median, 8.1%). The accuracy of the analytical procedure was evaluated on the basis of the results for the NIST QA-CH-2 samples; these results are summarized in Table IV-5, Appendix IV. Mean accuracy, determined as the ratio of the mean amount of alkane found in the QA-CH-2 samples of the 21 strings analyzed for this study and the amount present, ranged from 86.2% to 103.8%. Corresponding CV's ranged from 5.0% to 16.0% (median, 6.7%).

D. Contaminants in Method Blanks

Alkanes were detected 23 times at equivalent seawater concentrations greater than 100 ng/l in the analysis of 21 alkanes in each of the 21 method blanks. Eleven of these were due to decane, undecane, and dodecane inconsistently detected in the method blanks prepared from the remaining dichloromethane that was used to extract seawater samples during the first sampling period.

Data Analysis

Sample PAH correlation with *Exxon Valdez* crude oil PAHs

The similarity of relative PAH concentrations (1) measured in seawater and (2) measured in EVO was determined with the product-moment correlation coefficient. Each of 19 selected PAH concentrations in a sample, or in EVO, were considered as components of a vector for that sample, or for EVO. The correlation coefficient was calculated as the inner product of these two vectors. Mean sample PAH concentrations were used when available. Vector components were reduced by the number of these 19 selected PAHs that were below the MDL in the sample considered. The significance of these correlation coefficients was evaluated with Student's *t*-test, where *t* is calculated as:

$$t = r\sqrt{(n-2) / (1-r^2)}$$

and compared with critical values of *t* with *n*-2 degrees of freedom; *r* is the calculated correlation coefficient. PAH distributions in a sample were considered significantly correlated with PAH distributions in EVO if the calculated *t* exceeded the critical value of *t* at the Type I probability level of 0.05 or less, with at least 9 of the 19 selected PAHs detected above MDLs in the sample.

The 19 PAHs were selected on the basis of three criteria: (1) presence in EVO at readily detectable relative concentration, (2) absence of extraneous contamination sources (this excludes naphthalene), and (3) linear independence. This latter criterion precluded using both 1-methylphenanthrene and C-1 phenanthrenes, for instance, because these are not linearly independent. Where there was a choice between calibrated and uncalibrated PAHs, uncalibrated PAHs were selected for inclusion. The following 19 PAHs were used: 1-methylnaphthalene, 2-methylnaphthalene, C-2 naphthalenes, C-3 naphthalenes, C-4 naphthalenes, biphenyl, fluorene, C-1 fluorenes, C-2 fluorenes, C-3 fluorenes, dibenzothiophene, C-1 dibenzothiophenes, C-2 dibenzothiophenes, C-3 dibenzothiophenes, phenanthrene, C-1 phenanthrenes, C-2 phenanthrenes, C-3 phenanthrenes, and C-4 phenanthrenes.

EVO-PAHs

Total PAHs attributable to EVO were estimated in samples where PAHs were highly significantly ($P < 0.01$) correlated with corresponding PAHs in EVO. This estimate was the sum of measured PAHs used to calculate the correlation coefficient; plus an amount of naphthalene proportional with measured amounts of 1- and 2-methylnaphthalene, consistent with this same proportion in EVO. In every case, the naphthalene calculated in this manner as attributable to EVO was less than the measured amount of naphthalene in the sample.

Aromatic hydrocarbon enrichment factor (AHEF)

We calculated an AHEF as an indicator of dissolved EVO-PAHs. This AHEF was calculated for samples containing EVO-PAH as the ratio of measured EVO-PAH concentration, and a mean predicted EVO-PAH concentration based on the alkane measurements for the sample. The mean predicted EVO-PAH concentration for a sample was calculated in three steps. First, the ratio of EVO-PAH and n-nonadecane (C-19) in crude oil was multiplied by the measured concentration of n-nonadecane in the sample, yielding a predicted EVO-PAH concentration for the sample based on n-nonadecane. Second, this calculation was repeated for each larger n-alkane through n-heptacosane (C-27), yielding a total of nine predicted EVO-PAH concentrations for the sample, based on the nine n-alkanes from n-nonadecane through n-heptacosane. Finally, the mean predicted EVO-PAH was calculated as the mean of the three lowest predicted EVO-PAH concentrations calculated for the sample. Alkanes in the range C-19 through C-27 were used because they were probably the least abundant in PWS seawater (Karinen et al. 1993) due to natural sources, they were abundant in EVO, and they are both non-volatile and insoluble in seawater, so they may serve as marker compounds for particulate EVO. A mean of the three lowest predicted EVO-PAH concentrations was calculated to minimize bias due to the possible presence of these n-alkanes from natural sources.

Error Propagation

The variance of EVO-PAH concentrations based on triplicate analyses was calculated as the sum of the variances of the PAHs used to calculate the EVO-PAH of each triplicate.

RESULTS

The concentrations of the calibrated PAHs, the uncalibrated PAHs, and the alkanes determined for this study are tabulated in Appendix III, in Tables III-1, III-2, and III-3, respectively, for samples collected during the first sampling period. Tables III-4 through III-9, Appendix III, contain these results for the second and third sampling periods. Also listed in Tables III-1 through III-3 are results of analysis of 1 μ l of crude oil from the hold of the T/V *Exxon Valdez*. Following is a summary and interpretation of the results in these Tables.

Sampling Stations where PAHs were Consistent with EVO

PAHs consistent with EVO were clearly present in seawater during the first sampling period at the contiguously located stations listed in Table 1. The 11 stations listed in Table 1 satisfied the following criteria: (1) at least 9 of the 19 selected PAHs were detected at one of the depths sampled the first sampling period, and (2) these PAHs were significantly correlated with corresponding PAHs in EVO ($P < 0.05$). PAHs were detected in these samples according to their relative concentration in EVO; i.e., in samples where only nine of the selected PAHs were detected, these generally corresponded with the nine highest relative PAH concentrations in EVO (Table III-1, Appendix III). Every station where more than 10 selected PAHs were detected during the first sampling period is included in Table 1, indicating that whenever numerous PAHs were detected, they were significantly correlated with corresponding PAHs in EVO (and usually strongly correlated, with $P < 0.001$).

The 11 stations listed in Table 1 constituted less than 40% of the stations sampled, yet they accounted for more than 85% of the calibrated PAHs detected during the first sampling period (naphthalene excluded). Also, PAHs that were not present at readily detectable relative concentrations in EVO (see Table III-1, Appendix III), were not detected in samples from any of the stations listed in Table 1. In particular, unsubstituted PAHs with four or five aromatic rings, which are characteristic of combustion products, were not detected in any of the samples of this study. PAHs consistent with EVO were identified at fewer of the sampling stations after the first sampling period. During the second sampling period, PAHs in samples were strongly correlated ($P < 0.001$) with PAHs in EVO at 5 of the 11 initially identified stations; however, PAHs were not determined in another 5 of these stations (Table 1). During the third sampling period, PAHs in samples were strongly correlated at only 2 of the 11 initially identified stations, with PAHs not determined at only 1 of the remaining stations (Table 1). Note that PAHs consistent with EVO were never identified at any station during the second or third sampling periods that were not also identified during the first sampling period. In addition, a greater number of selected PAHs were usually detected during the first sampling period than during subsequent sampling periods at all stations and depths.

The stations listed in Table 1 were contiguously located (Fig. 1). The locations of these samples included northern and eastern Knight Island, Eleanor Island, Smith Island, Green Island, and northern and western Montague Strait. The beaches of these islands were the first to be contaminated by the spilled oil.

Concentrations of PAHs Attributed to EVO

During the first sampling period, the highest summed concentrations of PAHs attributed to EVO-PAH were adjacent to beaches that were heavily contaminated by the spilled oil. Concentrations of EVO-PAH at these stations ranged from 1.26 ± 0.40 $\mu\text{g/l}$ seawater (mean \pm 95% confidence interval, $n = 3$ here and following, except where noted) to 6.24 ± 0.63 $\mu\text{g/l}$ (Table 2). Concentrations of EVO-PAH were somewhat lower at stations listed in Table 1 that were not adjacent to heavily contaminated beaches, ranging from 0.91 ± 1.81 $\mu\text{g/l}$ ($n = 2$) to 2.23

Table 1.--PWS, Alaska, seawater sampling stations and depths where measured PAHs were significantly correlated with EVO-PAHs, following the grounding of the T/V *Exxon Valdez* on Bligh reef, 24 March 1989. Listed for each of three sampling periods is the correlation coefficient, r , of (n) selected PAHs in EVO with corresponding PAHs detected above MDLs at the station and depth, and the Type I error probability, P (n-2 degrees of freedom). N/A = not available, samples not analyzed. Hyphens indicate fewer than nine selected PAH analytes detected (see Methods section). NS = not significant.

Sampling station	Depth (m)	First sampling 3/31/89-4/4/89		Second sampling 4/12/89-4/15/89		Third sampling 5/2/89-5/8/89	
		r	(n) P	r	(n) P	r	(n) P
Adjacent to heavily oiled beaches:							
Northwest Bay	1	0.869	(18) <0.001	0.859	(16) <0.001	0.926	(15) ^a <0.001
	5	0.904	(18) <0.001	0.637	(10) <0.05	-	(8) -
Herring Bay	1	0.907	(14) <0.001	0.919	(18) <0.001	0.947	(13) <0.001
	5	0.926	(16) <0.001	0.782	(9) <0.05	-	(3) -
Snug Harbor	1	0.882	(14) <0.001	0.948	(17) <0.001	-0.125	(12) NS
	5	-	(6) -	0.982	(13) <0.001	-	(1) -
Bay of Isles	1	0.864	(12) <0.001	N/A		-	(3) -
	5	0.725	(15) <0.01	N/A		-	(1) -
S.E. Eleanor Is.	1	0.960	(18) <0.001	0.959	(16) <0.001	0.580	(15) <0.05
	5	0.965	(17) <0.001	0.808	(14) <0.001	0.294	(10) NS
N. Smith Island	1	0.926	(17) <0.001	0.932	(13) <0.001	-	(7) -
	5	0.921	(12) <0.001	0.576	(11) ^a NS	-	(7) -
Other stations:							
S. Montague Str.	1	-	(7) -	N/A		N/A	
	5	0.939	(9) <0.001	N/A		N/A	
S. Green Island	1	-	(2) -	N/A		-	(4) -
	5	0.686	(10) <0.05	N/A		-	(1) -
N. Green Island	1	-	(2) -	N/A		-	(1) -
	5	0.622	(15) <0.05	N/A		-	(4) -
N. Montague Str.	1	0.938	(13) <0.001	N/A		-	(5) -
	5	0.910	(15) <0.001	N/A		-	(1) -
S. Smith Island	1	0.926	(18) <0.001	-	(7) -	-	(7) -
	5	0.934	(14) <0.001	-	(8) -	0.660	(11) <0.05

^aC1F not included in calculation of r ; concentration of C1F in this sample was anomalously high.

Table 2.--Total PAHs attributed to EVO at 1-m and 5-m depths in PWS, Alaska, following the grounding of the T/V *Exxon Valdez* on Bligh reef 24 March 1989. PAHs were attributed to EVO if they were highly correlated ($P < 0.01$) with PAHs in EVO (see Table 1). Listed below are the sum of the seawater PAHs concentrations attributed to EVO, calculated according to the method described in the text (see Methods section), together with the sampling station, depth, and sampling period. These concentrations ($\mu\text{g/l}$ seawater) are means of triplicate samples $\pm 95\%$ confidence intervals for stations sampled during the first sampling period; otherwise, they are based on single samples. N/A = not available, samples not analyzed. Hyphens indicate PAHs not sufficiently correlated with EVO.

Sampling station	Depth (m)	First sampling period ($\mu\text{g/l}$)	Second sampling period ($\mu\text{g/l}$)	Third sampling period ($\mu\text{g/l}$)
Adjacent to heavily oiled beaches:				
Northwest Bay	1	4.72 \pm 1.18	2.18	1.59 ^a
	5	3.06 \pm 0.59	1.29	-
Herring Bay	1	2.86 \pm 2.77 ^b	4.00	0.92
	5	2.46 \pm 0.50	0.83	-
Snug Harbor	1	6.24 \pm 0.63	2.41	-
	5	-	1.03	-
Bay of Isles	1	1.31 \pm 0.34	N/A	-
	5	1.58 \pm 2.65 ^b	N/A	-
S.E. Eleanor Is.	1	3.08 \pm 0.66	1.60	-
	5	2.80 \pm 0.67	1.64	-
N. Smith Island	1	2.51 \pm 0.56	1.48	-
	5	1.26 \pm 0.40	-	-
Other stations:				
S. Montague Str.	1	0.96 \pm 0.22	N/A	N/A
	5	0.91 \pm 1.81 ^b	N/A	N/A
N. Montague Str.	1	1.11 \pm 0.34	N/A	-
	5	1.10 \pm 0.49	N/A	-
S. Smith Island	1	2.23 \pm 0.62	-	-
	5	1.12 \pm 0.32	-	-

^aCIF not included in calculation of r ; concentration of CIF in this sample was anomalously high.

^bBased on duplicate samples; third sample not analyzed.

$\pm 0.62 \mu\text{g/l}$. Mean concentrations of EVO-PAH were usually somewhat higher at the 1-m depth than at the 5-m depth, but often not significantly.

Concentrations of EVO-PAH generally declined after the first sampling period. These concentrations were usually lower by a factor of about 2 from the first to the second sampling periods (Table 2). By the third sampling period, PAHs could be attributed to EVO only at the 1-m depth at two stations that were adjacent to heavily contaminated beaches, at concentrations of 0.92 and 1.59 $\mu\text{g/l}$ (Table 2).

PAHs at Control Stations

Four stations, Olsen Bay, Gravina Point, Snug Corner Cove, and Granite Bay, were outside the path of the spilled oil (Fig. 1), so they may be considered control stations to evaluate hydrocarbon concentrations from sources not related to the oil spill. Except for naphthalene and C-2 naphthalenes, PAHs, especially calibrated PAHs, were rarely detected at control stations during the first sampling period. Naphthalene and C-2 naphthalenes were consistently detected at all four stations and at both sampling depths. Naphthalene concentrations were elevated, ranging from $0.323 \pm 0.077 \mu\text{g/l}$ (Granite Bay, 1 m) to $0.778 \pm 0.637 \mu\text{g/l}$ (Gravina Point, 5 m), while C-2 naphthalenes were lower, ranging from $0.034 \pm 0.034 \mu\text{g/l}$ (Granite Bay, 1 m) to $0.215 \pm 0.814 \mu\text{g/l}$ (Gravina Point, 1 m). Only one other calibrated PAH was detected at one of these stations at low concentration; $0.050 \pm 0.054 \mu\text{g}$ dimethylnaphthalene/l seawater at Gravina Point, 5 m. Other uncalibrated PAHs were detected sporadically at low concentration at these control stations; the detection frequency ranged from 0 (Snug Corner Cove, 5 m) to 9 (Gravina Point, 5 m). At these stations, PAHs were never significantly correlated with corresponding PAHs of EVO ($P > 0.3$).

Calibrated PAHs were detected more frequently at control stations during the second and third cruises. Both 1- and 2-methylnaphthalene were detected at least at one depth at all the control stations except Gravina Point, which was not sampled during the second or third sampling periods. Concentrations of these PAHs ranged up to $0.076 \mu\text{g/l}$. Also, biphenyl was detected at Olsen Bay and at Snug Corner Cove at concentrations ranging up to $0.055 \mu\text{g/l}$. Otherwise, the distribution, detection frequency, and concentrations of detected PAHs at these station were similar to those of the first sampling period, with one notable difference; nine of the selected PAHs were detected at Olsen Bay, 5-m depth, during the third sampling cruise, and these were significantly correlated with corresponding PAHs in EVO ($P < 0.05$).

The distribution, detection frequency, and concentrations of detected PAHs at the remaining stations of this study not listed in Table 1, were usually not appreciably different than those at control stations. At these stations, too few PAHs were detected to reliably identify sources, and detected PAHs were generally at low concentrations. However, naphthalene was consistently detected at all stations and at both depths, at concentrations usually well above the MDL. The C-2 naphthalenes were almost always detected, except during the third sampling period, although at concentrations that were often quite low.

Aromatic Hydrocarbon Enrichment Factors (AHEF)

The AHEF calculated for the stations listed in Table 1 indicated the presence of both particulate oil and dissolved PAHs at these stations. The AHEF values calculated for these stations during the first sampling period ranged from 0.70 to 6.07 (Table 3). The AHEF values near 1 suggest that PAHs may be associated with particulate oil, while values substantially greater than 1 indicate predominantly dissolved PAHs. AHEF values were substantially greater than 1 at Northwest Bay, Herring Bay, and Snug Harbor, ranging from 3.90 to 6.07 at these stations during the first sampling period, while AHEF values were generally closer to 1 at the remaining stations listed in Table 1 (Table 3). AHEF values tended to remain well above 1 at all stations considered in Table 1 during the second sampling period, ranging from 1.59 to 4.90. The two AHEF values calculated for the third sampling period were 1.84 and 0.42 at 1-m depth, Northwest Bay and Herring Bay respectively.

Alkanes

Relative alkane concentrations changed substantially from the first to the third sampling periods at stations where oil contamination was negligible. We calculated mean alkane concentrations for 6 of these stations sampled during the first and third sampling periods (Figs. 2 and 3, respectively): Eshamy Bay, Granite Bay, Main Bay, Olsen Bay, Port Chalmers, and Snug Corner Cove. These six stations were outside the path of the spilled oil through the Sound, and were sampled during both periods. During the first sampling period, the normal alkanes C-19, C-21, and C-25 through C-34 were prominent at these stations (Fig. 2), while the remaining normal alkanes and pristane were detected only sporadically at low concentrations. However, at the third sampling period, mean concentrations of the normal alkanes C-19, C-21, and C-25 through C-34 decreased by factors of about 2 compared with the first sampling period, while mean concentrations of the remaining alkanes increased substantially, especially C-10, C-11, and pristane (Fig. 3).

Alkane concentrations were generally elevated during the first sampling period at stations identified as contaminated by EVO in Tables 2 and 3, especially at the stations where the AHEF was relatively low. At stations and depths listed in Table 3 where the AHEF was greater than 2, mean concentrations of all alkanes except C-19 were consistently higher than corresponding alkanes at stations where EVO contamination was negligible (cf. Figs. 2 and 5). At stations and depths where the AHEF was less than 2, mean alkane concentrations were usually higher still, especially the normal alkanes from C-19 through C-26 (cf. Figs. 4 and 5). Note that at both contaminated and uncontaminated stations during the first sampling period, a local relative minimum normal alkane concentration occurs at C-22 or C-23.

By the third sampling period, alkane concentrations at uncontaminated stations are generally similar to concentrations at stations where contamination by EVO had been detected (Table III-9, Appendix III).

Table 3.--AHEF of EVO-PAHs at 1-m and 5-m depths in PWS, Alaska, following the grounding of the T/V *Exxon Valdez* on Bligh reef, 24 March 1989. The AHEF is the ratio of measured EVO-PAHs and expected EVO-PAHs, based on measurements of n-alkanes from nonadecane through heptacosane in samples and EVO (see Methods section in text for calculation of the AHEF). The AHEF is listed below for each station and sampling period where EVO-PAHs were determined (Table 2). N/A = not available, samples not analyzed. Hyphens indicate EVO-PAHs not determined.

Sampling station	Depth (m)	First sampling period	Second sampling period	Third sampling period
Northwest Bay	1	4.42	3.91	1.84
	5	3.90	2.53	-
Herring Bay	1	4.19	3.74	0.42
	5	4.84	1.59	-
Snug Harbor	1	6.07	4.90	-
	5	-	2.08	-
Bay of Isles	1	1.32	N/A	-
	5	3.37	-	-
S.E. Eleanor Is.	1	0.86	3.75	-
	5	1.14	3.74	-
N. Smith Island	1	1.25	4.78	-
	5	2.48	-	-
S. Montague Str.	1	1.41	N/A	N/A
	5	1.33	N/A	N/A
N. Montague Str.	1	0.70	N/A	-
	5	1.12	N/A	-
S. Smith Island	1	0.76	-	-
	5	0.87	-	-

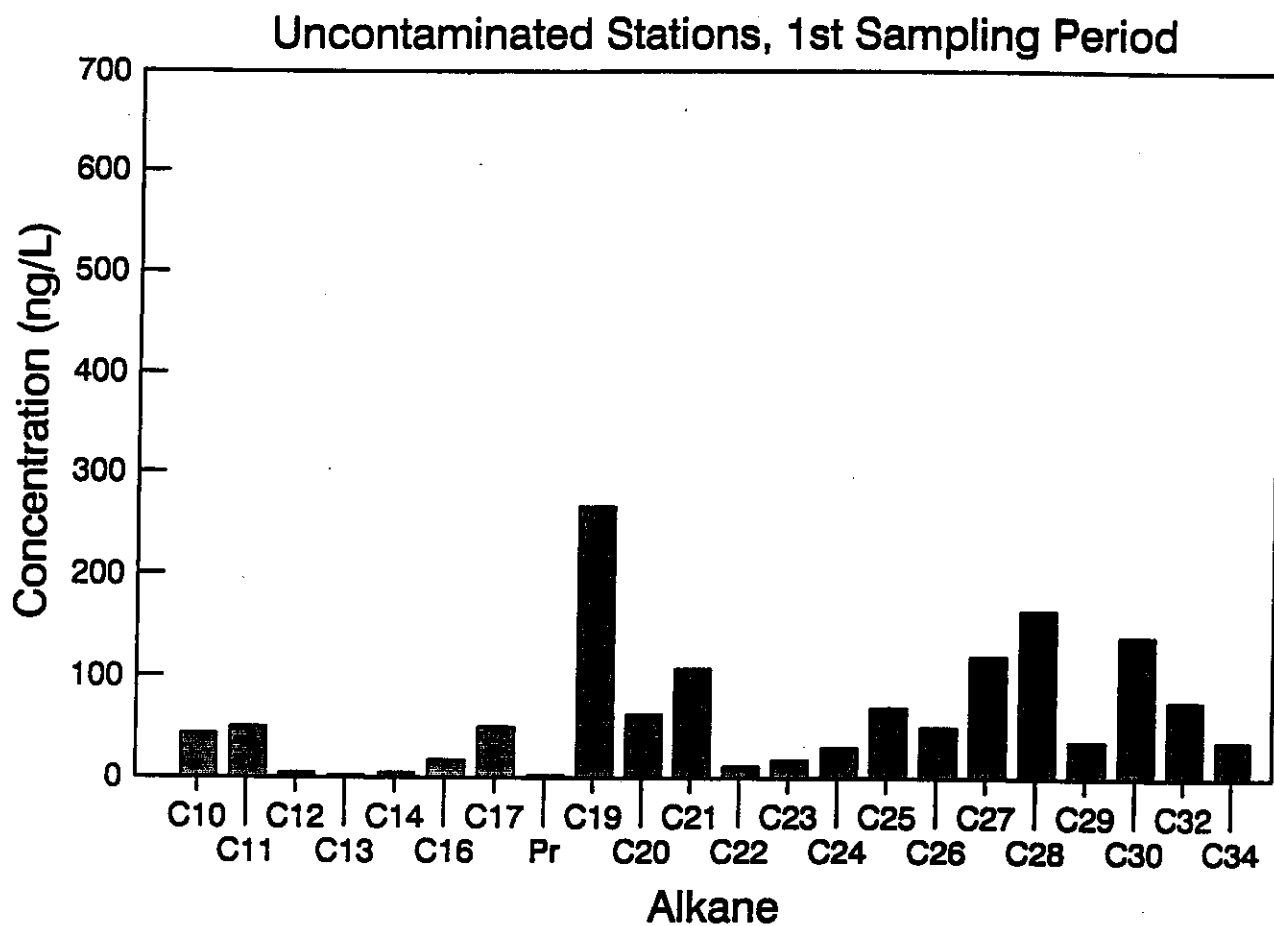


Figure 2.--Mean alkane concentrations for 6 stations where oil contamination was negligible during the first sampling period. Each mean alkane concentration is based on samples from Eshamy Bay, Granite Bay, Main Bay, Olsen Bay, Port Chalmers, and Snug Corner Cove (n = 36) taken during the first sampling period. Concentrations are ng alkane/L seawater. Pr = pristane. Data are from Table III-3, Appendix III.

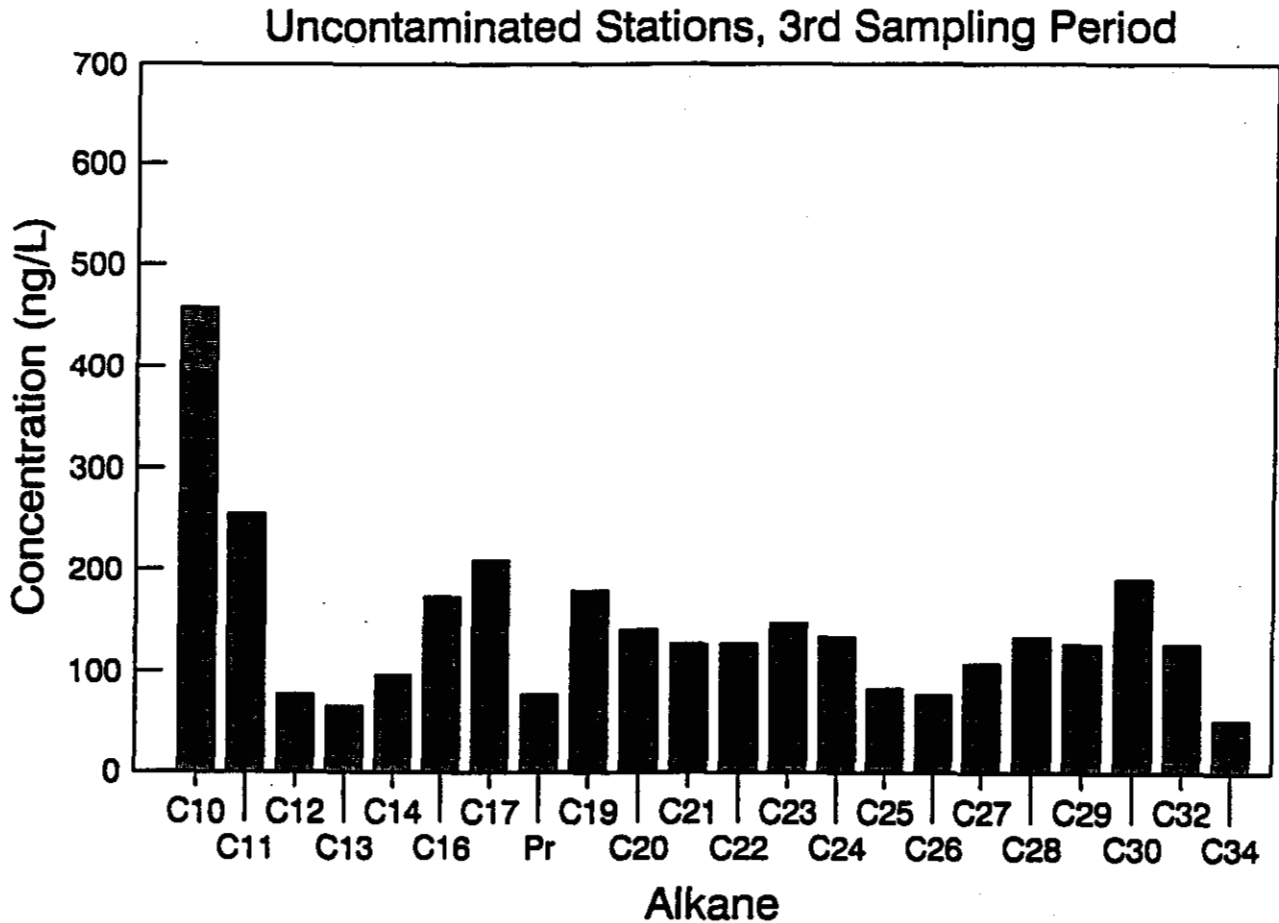


Figure 3.--Mean alkane concentrations for 6 stations where oil contamination was negligible during the third sampling period. Each mean alkane concentration is based on samples from Eshamy Bay, Granite Bay, Main Bay, Olsen Bay, Port Chalmers, and Snug Corner Cove (n = 12) taken during the first sampling period. Concentrations are ng alkane/L seawater. Pr = pristane. Data are from Table III-9, Appendix III.

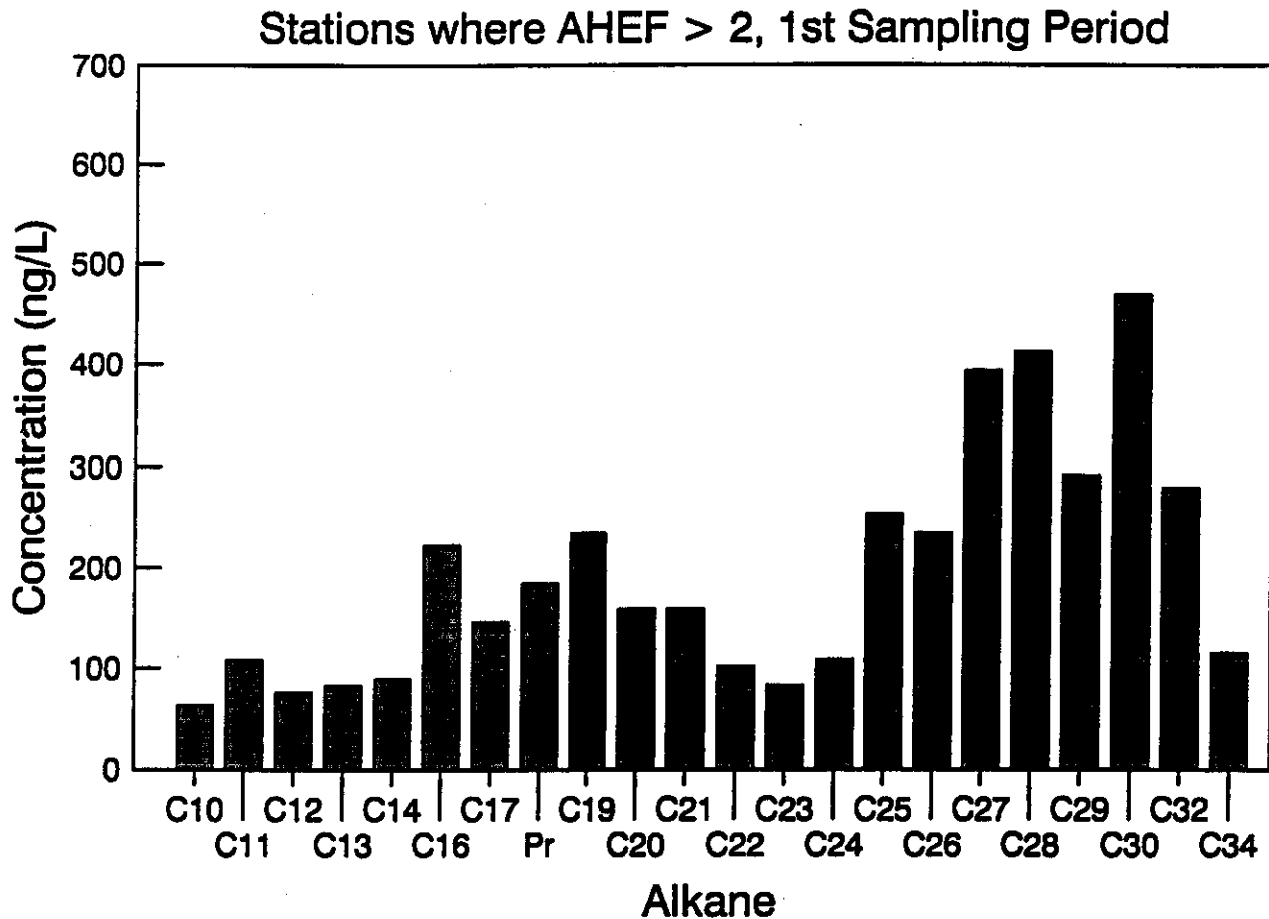


Figure 4.--Mean alkane concentrations for first sampling period stations and depths listed in Table 3 where the AHEF is greater than 2. Each mean alkane concentration is based on samples from Bay of Isles (5-m), Herring Bay, North Smith Island (5-m), Northwest Bay, and Snug Harbor (1-m) (n = 19) taken during the first sampling period. Concentration units are ng alkane/L seawater. Pr = pristane. Data are from Table III-3, Appendix III.

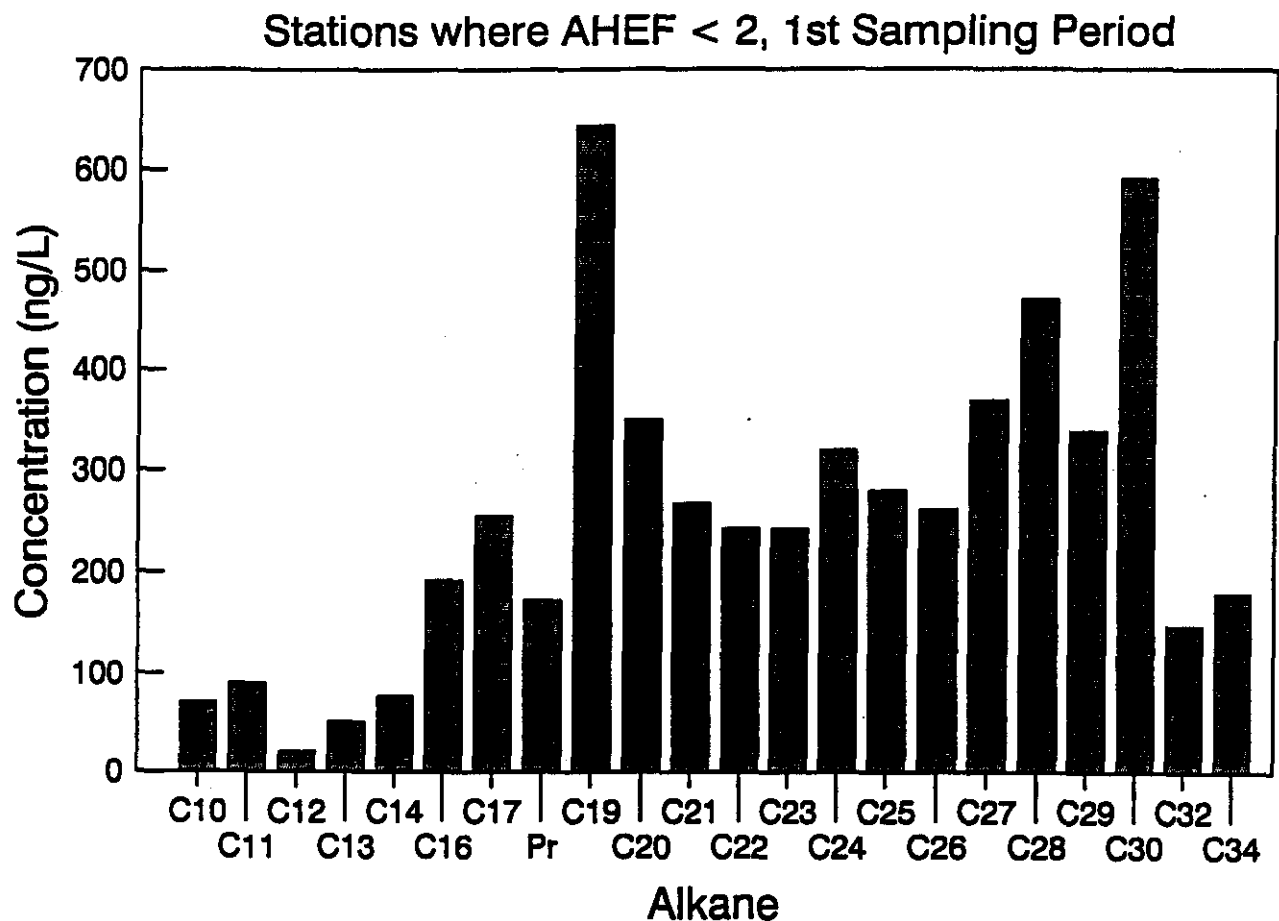


Figure 5.--Mean alkane concentrations for first sampling period stations and depths listed in Table 3 where the AHEF is less than 2. Each mean alkane concentration is based on samples from Bay of Isles (1-m), North Montague Strait, North Smith Island (1-m), Southeast Eleanor Island, South Montague Strait, and South Smith Island (n = 29), taken during the first sampling period. Concentration units are ng alkane/L seawater. Pr = pristane. Data are from Table III-3, Appendix III.

DISCUSSION

1. PAHs at the stations listed in Table 1 were from EVO

Crude oil spilled from the hold of the T/V *Exxon Valdez* was the proximate source of the elevated PAH concentrations found in seawater at the stations listed in Table 1. This conclusion derives from the close association of samples containing elevated PAH concentrations with areas directly impacted by the spilled oil, the strong correlation of relative PAH concentrations in these samples and in the spilled oil, the general absence of these PAHs in samples from areas marginal or distant from the path of the spilled oil, and the absence of a plausible alternative explanation of these observed results. Extraneous contamination of these samples with crude oil in the field (e.g., by initial contact of the sampling apparatus with the oil slick) was unlikely because stations where low concentrations of seawater PAHs were expected (and found) were commingled with stations where higher PAH concentrations were expected (and found) in the sampling sequence of stations sampled. This indicates that PAHs sampled at contaminated stations did not also contaminate samples collected from otherwise uncontaminated stations. Analysis of method blanks and the extraction solvent used during the first sampling period obviate laboratory contamination or the solvent as significant PAH sources. During the first sampling period when we measured the highest PAH concentrations in collected samples, we observed almost no other vessel traffic in most of the areas contaminated by the spilled oil, making refined petroleum products associated with marine transportation an unlikely source. Finally, combustion sources may be eliminated as significant because unsubstituted 4-to-5-ring aromatic hydrocarbons, characteristic of combustion sources, were not detected, and the quality control results associated with analysis of these samples indicated these compound would have been detected if present at concentrations that would indicate combustion sources as significant.

Diesel oil associated with the vessels we used to collect samples may also be explicitly eliminated as a substantial source of the seawater hydrocarbons detected. Suites of hydrocarbons characteristic of diesel oil were consistently absent at control stations and at stations near the periphery of the path followed by the spill through PWS. During the first sampling period, we deliberately alternated our sampling sequence between heavily and lightly (or un-oiled) stations (compare Fig. 1 and the sampling sequence given in Appendix Table I-1), to assess possible "carry-over" effects among stations or hydrocarbon contaminants introduced by the sampling vessel. Our results show that these effects are negligible: hydrocarbon suites characteristic of petroleum products are consistently present at the stations near Knight and Green islands, and are consistently absent at the peripheral stations. The stations near Knight island where the highest PAHs were found in seawater corresponded exactly with stations the most grossly oiled stations during the first sampling period, where the seasurface was often covered by a continuous oil slick. The association of detected PAHs characteristic of petroleum with the most heavily oiled stations, together with the consistent absence of these hydrocarbon suites at stations more distant from the spill path, corroborates the spilled oil as the source of these hydrocarbons, and obviates the sampling vessel as a substantial alternative source.

We conclude, therefore, that all of our results are consistent with the identification of EVO as the source of the elevated PAHs detected (although additional sources of naphthalene were indicated), and there is no evidence for an alternative source.

2. Accuracy and precision

The PAH concentrations we measured in seawater from the stations listed in Table 1 may be underestimated. The quality control data acquired during analysis of these samples indicated that our estimates of elevated PAH concentrations in the dichloromethane extracts were accurate to within $\pm 20\%$, at high levels of frequency and of statistical confidence, based on comparison with NIST-certified PAH standards. We did not, however, evaluate the overall extraction efficiency of PAHs from seawater into dichloromethane. Given the relatively small extraction volumes and short extraction times, it is quite possible that less than 99% of PAH compounds present in EVO-contaminated seawater were extracted. However, based on our previous experience using similar methods, we believe that at least 80% of these PAHs were extracted. Other causes of underestimation are probably not significant because the samples were extracted soon after collection and were stored frozen in the dark, and dichloromethane solutions of PAHs are stable indefinitely under these conditions. No causes of overestimation were evident.

The concentrations of PAHs measured herein are consistent with similar measurements of seawater PAH concentrations following other cold-water oil spills. For example, Law (1978) found that a similar suite of PAHs as were measured in the present study ranged up to 1.7 $\mu\text{g/l}$ and 1.1 $\mu\text{g/l}$ at 1-m and 5-m depths, respectively, below the oil slick that resulted from the *Ekofisk* blow-out in April, 1977, in the North Sea; and work quoted therein indicates PAH concentrations ranged up to 8.1 $\mu\text{g/l}$ at sampling stations nearer the source of the oil.

As expected, the generally decreasing detection frequency and concentrations of EVO-PAHs with time indicate the operation of well-known mechanisms of PAH dilution and decomposition. The prevailing ocean current that continuously flushes the Sound may account for the dilution and removal of the high initial PAH concentrations observed, as may microbial decomposition (Ballerini et al. 1982).

3. Geographic distribution of PAHs derived from EVO

The contiguous location of the stations listed in Table 1, and the similarity of 1-m and 5-m PAH concentrations during the first sampling period, indicate a large mass of contaminated seawater in the region of northwest Montague Strait - northern Knight Island - Smith Island. This contaminated water mass may have resulted from the storm that occurred 3 to 5 days following the tanker grounding. This storm may have generated persistent, small droplets of the spilled crude oil in the seawater column, that were being flushed out of the Sound during the first sampling period. This would account for several results: the geographic contiguity of the stations, including the open-water stations in Montague Strait, where elevated PAHs were measured; the AHEF's of the open-water stations (near 1), which were consistent with PAHs associated with particulate oil; the similarity of PAH concentrations found at 1-m and 5-m depths,

indicating nearly homogenous mixing of dispersed oil to a depth of at least 5 m; and the general absence of EVO-PAHs at the open-water sites by the second sampling period.

4. Beach reservoirs of stranded oil

Heavily oiled beaches apparently were a reservoir of spilled EVO that continued to contaminate adjacent seawater after the first sampling period. Stations where elevated seawater EVO-PAHs were detected during the second and third sampling periods were also contaminated during the first sampling period, were among the first beaches to be heavily oiled by the spill, and were enclosed within bays. These conditions may result in the stable association of relatively unweathered oil with these beaches. PAHs in this oil may re-enter adjacent seawater as oil-coated particulates mixed with seawater by wave action during subsequent storms, or as PAHs that dissolve into seawater from beached oil or re-floated surface slicks. Assuming that AHEF values substantially greater than unity indicate PAH enrichment in seawater, the high AHEF's associated with the elevated PAH concentrations measured at these stations indicate that dissolution of PAHs was an important process at these stations.

The validity of the assumption that higher AHEF values indicate seawater PAH enrichment may be assessed in part by calculating AHEFs for weathered whole oil during the period of this study. The PAH composition of mousse oil collected from the seasurface at Snug Harbor, Bay of Isles, and off northern Smith Island 11 days following the spill were reported by Sale et al. (1995). Calculation of AHEFs as defined herein for these samples results in values that range from 0.59 to 0.87. These values lower than unity indicate that losses of PAH from the crude oil itself are more rapid than are losses of normal alkanes due to, say, microbial decomposition, at least for the first 11 days following the spill. It was during this same period that we observed the highest AHEF values of our study. We therefore conclude these higher AHEF values are not due whole, particulate oil dispersed into the seawater column that has preferentially lost normal alkane compared with PAH due to *e.g.* microbial decomposition.

5. Uncalibrated PAHs were subject to greater interference than calibrated PAHs

The uncalibrated PAHs measured in this study were subject to substantially higher levels of interference than the calibrated PAHs, due to differences in measurement criteria. The criteria used to detect the uncalibrated PAHs were less selective than were those used for the calibrated PAHs; uncalibrated PAHs were detected by a single fragment ion within a wide range of retention times, whereas calibrated PAHs were detected by two fragment ions within a narrow range of retention times. Effects of the selectivity differences between uncalibrated and calibrated PAHs may be seen in the larger variances in replicate samples for uncalibrated PAHs (Tables in Appendix III), and in their increased detection frequencies in method blanks. Thus, the MDLs assumed for the uncalibrated PAHs that are calculated from the calibrated PAHs were probably underestimates. Although these interferences may lead to ambiguous results near detection limits, analysis of the uncalibrated PAHs provide a characteristic fingerprint of relative PAHs at elevated concentrations, because they are numerous, and are present at higher relative concentrations than are homologous unsubstituted PAHs in crude oils.

6. Unknown naphthalene contamination source

Additional sources of naphthalene apart from EVO were evident in all samples, suggesting sampling contamination sources for naphthalene only. This conclusion derives from the ubiquity of naphthalene at a minimum apparent concentration of about $0.4 \mu\text{g/l}$ during the first sampling period; a similar pattern of naphthalene detection persisted at lower minimum concentrations during the second and third sampling periods. Although some of this naphthalene was due to contamination levels equivalent to about $0.13 \mu\text{g/l}$ in the dichloromethane used during the first sampling period, the remainder indicates additional unknown contamination sources.

7. Confounding sources of alkanes in seawater were evident during the period of this study

Determination of alkanes derived from EVO was obscured by temporally variable alkanes from diverse natural sources. The relatively high C-19 and C-21 alkanes found at stations where contamination was negligible probably derive from marine phytoplankton, while the C-25 through C-34 alkanes are characteristic of terrestrial plant waxes; indeed, these alkanes were frequently detected in mussels sampled in the Sound prior to this oil spill (Karinen et al. 1993). The general increase of alkane concentrations, including pristane, from the first to the third sampling periods, coincides with the spring phytoplankton bloom that is characteristic of Alaskan coastal marine waters, which is probably the source of these increased alkane concentrations. In particular, Karinen et al. (1993) noted a dramatic spring increase of pristane concentrations of mussels in the Sound during 1977 through 1980, which they speculated may be associated with detrital material derived from marine copepods. Pristane associated in this manner would have been extracted and detected using the methods of this study, and our observation of increased pristane concentrations in seawater during the third sampling period compared with the first is consistent with a planktonic or detrital source.

The relatively high concentrations and the temporal variability of the alkanes interfere with determination of the form of EVO detected in seawater. The presence of normal alkanes from C-19 through C-27 from biological sources may bias interpretation of the AHEF, because predicted EVO-PAHs were calculated on the assumption that all of the alkanes at the three lowest concentrations within this interval came from EVO. Although we constructed our AHEF index to take advantage of the general relative minimum of alkanes between C-19 and C-27, the presence of additional alkanes from sources other than EVO will tend to bias interpretation of these AHEF's in favor of particulate oil. As a result, dissolved EVO-PAHs are probably more widespread than indicated in Table 3.

Relation to biological effects

Although readily detectable, these concentrations of EVO-PAHs were well below levels that are acutely toxic to marine fauna (Brodersen et al. 1977; Rice et al. 1979). On the other hand, these data demonstrate that PAHs from *Exxon Valdez* crude oil were available to subsurface marine fauna the first few weeks following the oil spill, especially in near-shore, near-surface waters that are particularly productive areas biologically.

CONCLUSIONS

1. PAHs derived from *Exxon Valdez* crude oil contaminated seawater to depths of at least 5 m, and at concentrations ranging to $6.24 \pm 0.63 \mu\text{g/l}$, in the general region encompassing northwest Montague Strait - northern Knight Island - Smith Island, 1 to 2 weeks following grounding of the vessel. The highest PAH concentrations were found near heavily oiled beaches.
2. Heavily oiled beaches were apparently a reservoir of spilled EVO that continued to contaminate adjacent seawater for at least 5 weeks after grounding of the T/V *Exxon Valdez*.
3. Seawater PAH concentrations declined substantially by 5 weeks following grounding of the T/V *Exxon Valdez*.
4. PAHs from *Exxon Valdez* crude oil were available to subsurface marine fauna the first few weeks after grounding of the T/V *Exxon Valdez*, especially in near-shore, near-surface waters that are particularly productive areas biologically. Measured PAH concentrations, however, were well below levels that are acutely toxic to marine fauna.

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APPENDIX I

Table I-1.--Description of stations sampled for hydrocarbons in seawater in PWS, Alaska, 7 to 11 days following the grounding of the T/V *Exxon Valdez*. Station latitude, longitude, sampling date, sampling time (ADT = Alaska daylight time), depth, seawater temperature, and seawater salinity are listed below for each station sampled. Station numbers correspond with those of Figure 1, and are listed below in the chronological order sampled.

Sampling site	Date	Station	Sequence	Depth (m)	N Latitude	W Longitude	Salinity (‰)	Temp. (°C)	ADT
Gravina Point	03/31/89	1	1	1	60°36'31"	146°18'11"	31.8	4.4	22:58
				5			31.2	3.8	23:41
Olsen Bay	04/01/89	2	2	1	60°43'41"	146°13'45"	30.7	3.7	08:13
				5			30.7	3.3	06:58
Snug Corner Cove	04/01/89	3	3	1	60°44'42"	146°41'41"	32.1	5.1	11:45
				5			32.6	5.6	12:24
E. Naked Island	04/01/89	4	4	1	60°39'22"	147°13'34"	32.0	6.6	16:59
				5			32.5	6.0	15:47
McPhearson Bay	04/01/89	5	5	1	60°40'06"	147°22'53"	31.4	4.7	18:20
				5			31.4	4.1	18:57
Cabin Bay	04/01/89	6	6	1	60°39'52"	147°26'50"	31.0	4.4	20:31
				5			31.5	4.1	21:24
NW Bay, Eleanor Is.	04/01/89	7	7	1	60°33'27"	147°35'20"	31.2	4.3	23:29
				5			31.2	3.9	12:20
Main Bay	04/02/89	8	8	1	60°32'59"	148°04'21"	31.8	5.1	09:10
				5			31.2	4.8	07:55
Herring Bay	04/02/89	9	9	1	60°29'07"	147°43'30"	31.7	4.7	11:15
				5			30.8	4.8	11:45
Eshamy Bay	04/02/89	10	10	1	60°27'54"	147°57'59"	31.3	4.4	14:15
				5			31.5	4.7	13:52
Granite Bay	04/02/89	11	11	1	60°24'53"	147°57'23"	32.2	4.8	17:08
				5			31.2	6.9	16:51
Squire Island	04/02/89	12	12	1	60°13'56"	147°57'11"	30.4	4.3	19:53
				5			30.5	4.3	19:35
Shelter Bay	04/02/89	13	13	1	60°07'38"	147°55'01"	31.2	3.2	21:50
				5			31.2	3.3	21:26
Sawmill Bay	04/03/89	14	14	1	60°03'20"	148°00'54"	31.6	3.5	00:17
				5			31.5	3.4	23:47
Sleepy Bay	04/03/89	15	15	1	60°05'00"	147°50'38"	31.7	3.2	02:12
				5			31.9	3.3	01:47
S. Montague Strait	04/03/89	16	16	1	60°04'35"	147°40'48"	31.1	4.0	08:30
				5			31.5	3.9	08:06
S. Montague Island	04/03/89	17	17	1	60°06'07"	147°26'13"	32.8	5.3	10:05
				5			32.3	4.5	09:40
Mid Montague Strait	04/03/89	18	18	1	60°10'22"	147°33'10"	31.9	5.1	11:33
				5			32.2	5.2	11:13
Snug Harbor	04/03/89	19	19	1	60°14'25"	147°43'12"	31.2	5.9	13:57
				5			31.4	5.4	13:34
S. Green Island	04/03/89	20	20	1	60°14'59"	147°23'24"	32.1	5.0	16:45
				5			30.8	5.3	16:01
Port Chalmers	04/03/89	21	21	1	60°15'24"	147°13'30"	31.9	5.1	18:20
				5			32.1	4.9	17:51
N. Green Island	04/03/89	22	22	1	60°15'52"	147°26'12"	31.8	4.3	20:30
				5			31.9	4.4	20:15
Rocky Bay	04/04/89	23	23	1	60°20'19"	147°06'30"	30.7	4.5	00:25
				5			31.5	4.5	00:01
N. Montague Strait	04/04/89	24	24	1	60°23'52"	147°30'08"	31.6	4.6	08:48
				5			31.5	4.3	08:24
Bay of Isles	04/04/89	25	25	1	60°23'14"	147°37'44"	30.9	4.8	10:41
				5			31.6	4.3	10:10
SE Eleanor Island	04/04/89	26	26	1	60°32'24"	147°35'41"	31.7	4.8	13:05
				5			31.8	4.5	12:18
S. Smith Island	04/04/89	27	27	1	60°31'20"	147°20'14"	31.5	4.9	14:47
				5			31.2	4.7	14:35
N. Smith Island	04/04/89	28	28	1	60°31'18"	147°24'06"	31.8	4.4	16:28
				5			31.7	4.5	16:03

Table I-2.--Description of stations sampled for hydrocarbons in seawater in PWS, Alaska, 19 to 22 days following the grounding of the T/V *Exxon Valdez*. Station latitude, longitude, sampling date, sampling time (ADT = Alaska daylight time), depth, seawater temperature, and seawater salinity are listed below for each station sampled. Station numbers correspond with those of Figure 1, and are listed below in the chronological order sampled.

Sampling site	Date	Station	Sequence	Depth (m)	N Latitude	W Longitude	Salinity (‰)	Temp. (°C)	ADT
Gravina Point	04/12/89	1	1	1	60°36'31"	146°18'11"	32.0	4.4	09:30
				5					
Olsen Bay	04/12/89	2	2	1	60°43'41"	146°13'45"	30.2	5.2	11:50
				5					
Snug Corner Cove	04/12/89	3	3	1	60°44'42"	146°41'41"	31.8	4.8	14:04
				5					
E. Naked Island	04/12/89	4	4	1	60°39'22"	147°13'34"	32.6	5.6	16:20
				5					
McPhearson Bay	04/12/89	5	5	1	60°39'43"	147°22'53"	32.0	4.9	17:29
				5					
Cabin Bay	04/12/89	6	6	1	60°39'52"	147°26'50"	31.8	5.1	18:53
				5					
Outside Bay	04/12/89	29	7	1	60°40'22"	147°34'52"	31.9	5.1	20:35
				5					
Eshamy Bay	04/13/89	10	8	1	60°27'54"	147°57'59"	29.4	4.4	07:00
				5					
Main Bay	04/13/89	8	9	1	60°32'59"	148°01'07"	30.6	4.7	08:50
				5					
NW Bay, Eleanor Island	04/13/89	7	10	1	60°33'27"	147°35'20"	31.3	4.3	10:35
				5					
Herring Bay	04/13/89	9	11	1	60°29'07"	147°43'30"	31.7	5.5	11:53
				5					
Granite Bay	04/13/89	11	12	1	60°36'31"	146°13'45"	31.7	5.7	13:24
				5					
Squire Island	04/13/89	12	13	1	60°13'56"	147°57'11"	31.1	5.5	14:30
				5					
Sawmill Bay	04/14/89	14	14	1	60°02'16"	147°58'14"	32.0	5.3	15:23
				5					
S. Elrington Pass	04/14/89	30	15	1	59°59'21"	148°06'46"	31.6	5.3	16:29
				5					
Prince of Wales Pass	04/14/89	31	16	1	60°03'02"	148°06'47"	32.0	5.5	17:38
				5					
W. Bainbridge Island	04/14/89	32	17	1	60°09'15"	148°07'15"	31.4	5.9	19:04
				5					
Shelter Bay	04/14/89	13	18	1	60°07'38"	147°55'01"	31.2	5.0	20:13
				5					
Sleepy Bay	04/14/89	15	19	1	60°05'00"	147°50'64"	31.4	4.2	21:30
				5					
S. Montague Strait	04/15/89	16	20	1	60°04'35"	147°40'48"	31.9	4.9	07:28
				5					
S. Montague Island	04/15/89	17	21	1	60°06'07"	147°26'13"	31.3	4.6	08:46
				5					
Mid Montague Strait	04/15/89	18	22	1	60°10'22"	147°33'10"	31.8	4.8	09:44
				5					
Snug Harbor	04/15/89	19	23	1	60°14'25"	147°43'12"	31.4	5.1	10:50
				5					
S. Green Island	04/15/89	20	24	1	60°14'59"	147°23'24"	31.8	5.1	12:19
				5					
Port Chalmers	04/15/89	21	25	1	60°15'24"	147°13'30"	31.2	5.8	13:10
				5					
N. Green Island	04/15/89	22	26	1	60°15'52"	147°24'25"	32.9	5.8	14:18
				5					
N. Montague Strait	04/15/89	24	27	1	60°23'52"	147°30'08"	32.4	5.8	15:19
				5					
SE Eleanor Island	04/15/89	26	28	1	60°32'24"	147°35'41"	31.6	6.1	16:33
				5					
N. Smith Island	04/15/89	28	29	1	60°31'18"	147°24'06"	31.6	5.6	17:28
				5					
S. Smith Island	04/15/89	27	30	1	60°31'20"	147°20'14"	32.0	5.9	18:19
				5					

Table I-3.--Description of stations sampled for hydrocarbons in seawater in PWS, Alaska, 39 to 45 days following the grounding of the T/V Exxon Valdez. Station latitude, longitude, sampling date, sampling time (ADT = Alaska daylight time), depth, seawater temperature, and seawater salinity are listed below for each station sampled. Station numbers correspond with those of Figure 1, and are listed below in the chronological order sampled.

Sampling site	Date	Station	Sequence	Depth (m)	N Latitude	W Longitude	Salinity (‰)	Temp. (°C)	ADT
Snug Corner Cove	05/02/89	3	1	1	60°44'42"	146°41'41"	30.6	8.0	14:05
				5					
Cabin Bay	05/03/89	6	2	1	60°39'52"	147°28'06"	31.0	7.5	05:57
				5					
Outside Bay	05/03/89	29	3	1	60°38'36"	147°28'42"	31.3	6.8	07:55
				5					
McPhearson Bay	05/03/89	5	4	1	60°39'43"	147°22'53"	31.6	5.9	13:01
				5					
E. Naked Island	05/03/89	4	5	1	60°39'22"	147°13'34"	31.0	6.4	14:35
				5					
Rocky Bay	05/03/89	23	6	1	60°20'19"	147°06'05"	32.0	6.0	18:18
				5					
Olsen Bay	05/05/89	2	7	1	60°43'41"	146°13'45"	23.7	7.7	13:12
				5					
S. Smith Island	05/05/89	27	8	1	60°31'07"	147°21'20"	31.4	4.8	18:53
				5					
N. Smith Island	05/05/89	28	9	1	60°31'42"	147°22'30"	32.8	4.8	20:00
				5					
SE Eleanor Island	05/05/89	26	10	1	60°32'07"	147°34'03"	30.4	7.0	21:42
				5					
NW Eleanor Island	05/06/89	7	11	1	60°33'06"	147°37'06"	29.7	6.0	06:41
				5					
Herring Bay	05/06/89	9	12	1	60°29'07"	147°43'30"	28.9	6.0	09:39
				5					
Main Bay	05/06/89	8	13	1	60°32'59"	148°01'07"	24.9	6.8	11:55
				5					
Eshamy Bay	05/06/89	10	14	1	60°27'54"	147°57'57"	28.9	6.5	14:42
				5					
Granite Bay	05/06/89	11	15	1	60°24'53"	147°57'23"	26.2	6.2	16:04
				5					
Squire Island	05/06/89	12	16	1	60°13'56"	147°57'10"	30.2	6.2	18:18
				5					
W. Bainbridge Is.	05/06/89	32	17	1	60°08'36"	148°05'36"	28.3	6.0	19:58
				5					
Shelter Bay	05/06/89	13	18	1	60°07'38"	147°55'01"	28.5	5.2	07:14
				5					
Prince of Wales Pass	05/07/89	31	19	1	60°05'00"	148°05'15"	30.5	5.2	09:31
				5					
S. Elrington Pass	05/07/89	30	20	1	59°59'21"	148°06'46"	30.8	5.2	11:32
				5					
Sawmill Bay	05/07/89	14	21	1	60°03'43"	147°58'40"	30.6	5.8	13:00
				5					
Snug Harbor	05/07/89	19	23	1	60°14'24"	147°42'55"	30.8	6.5	19:00
				5					
Mid Montague Strait	05/08/89	18	24	1	60°10'22"	147°33'10"	31.2	6.0	09:03
				5					
S. Green Island	05/08/89	20	25	1	60°14'59"	147°23'24"	31.2	6.2	10:31
				5					
Port Chalmers	05/08/89	21	26	1	60°15'24"	147°13'30"	27.0	6.6	11:54
				5					
N. Green Island	05/08/89	22	27	1	60°16'15"	147°28'00"	30.3	7.2	15:58
				5					
Bay of Isles	05/08/89	25	28	1	60°23'14"	147°37'44"	31.0	7.2	17:57
				5					
N. Montague Strait	05/08/89	24	29	1	60°23'52"	147°30'08"	30.6	7.8	19:15
				5					

APPENDIX II

Table II-1.--Deuterated surrogate aromatic hydrocarbon standards used for determination of PAHs in seawater samples collected from PWS, Alaska, following the grounding of the T/V *Exxon Valdez*. The deuterated surrogate aromatic hydrocarbon standards, each identified by a number in the left-hand column, are listed below, together with the quantification ion mass and the concentration in hexane of each of the standards in the sample spiking solution. A 500- μ l aliquot of this solution was spiked into each environmental or quality control sample analyzed for PAHs. The identification numbers in the left-hand column were used to relate the calibrated PAH analytes listed in Table II-2, following, with the deuterated standards listed here.

ID number	Name	Mass of quantification ion	Concentration in spike solution (ng/ml)
1	Naphthalene - d ₈	136	2.50
2	Acenaphthene - d ₁₀	164	2.50
3	Phenanthrene - d ₁₀	188	2.00
4	Chrysene - d ₁₂	240	2.00
5	Benzo[a]pyrene - d ₁₂	264	2.50
6	Perylene - d ₁₂	264	2.50

Table II-2.--Calibrated PAHs determined in seawater samples collected from PWS, Alaska, following the grounding of the T/V *Exxon Valdez*. The calibrated aromatic hydrocarbons, and standardized abbreviations for them, are listed below, together with the identification number of the associated surrogate standard (see Table II-1 preceding), quantification ion mass, confirmation ion mass, and the mean ratio of these two ions in the calibration standards, of which the latter three are used for identification.

PAH	Abbreviation	Quantification ion mass	Confirmation ion mass	Expected ion ratio	ID number of surrogate standard used
Naphthalene	Naph	128	127	15	1
2-Methylnaphthalene	Menap2	142	141	88	1
1-Methylnaphthalene	Menap1	142	141	88	1
2,6 Dimethylnaphthalene	Dimeth	156	141	67	2
2,3,5 Trimethylnaphthalene	Trimeth	170	155	90	2
Biphenyl	Biphenyl	154	152	28	1
Acenaphthylene	Acenthy	152	153	13	2
Acenaphthene	Acenthe	154	153	99	2
Fluorene	Fluorene	166	165	92	2
Dibenzothiophene	Dithio	184	152	15	3
Phenanthrene	Phenanth	178	176	19	3
Anthracene	Anthra	178	176	18	3
1-Methylphenanthrene	Mephen1	192	191	57	3
Fluoranthene	Fluorant	202	101	15	3
Pyrene	Pyrene	202	101	19	3
Chrysene	Chrysene	228	226	25	4
Benz-a-anthracene	Benanth	228	226	28	4
Benzo-b-fluoranthene	Benzobfl	252	253	22	5
Benzo-k-fluoranthene	Benzokfl	252	253	22	5
Benzo-e-pyrene	Benepy	252	253	23	5
Benzo-a-pyrene	Benapy	252	253	24	5
Perylene	Perylene	252	253	25	6
Indeno-1,2,3 cd-pyrene	Indeno	276	277	24	5
Dibenzo-a,h-anthracene	Dibenz	278	279	22	5
Benzo-g,h,i-perylene	Benzop	276	277	23	5

Table II-3.--Uncalibrated PAHs determined in seawater samples collected from PWS, Alaska, following the grounding of the T/V *Exxon Valdez*. The uncalibrated aromatic hydrocarbons, and standardized abbreviations for them, are listed below, together with the quantification ion mass and retention time windows used for identification.

Name	Abbreviation	Quantification ion mass	Retention time window (min.)
C2 - Naphthalenes	C2naph	156	11.0 - 14.5
C3 - Naphthalenes	C3naph	170	12.5 - 16.5
C4 - Naphthalenes	C4naph	184	14.0 - 18.5
C1 - Fluorenes	C1fluor	180	15.0 - 18.0
C2 - Fluorenes	C2fluor	194	16.5 - 20.0
C3 - Fluorenes	C3fluor	208	18.0 - 21.5
C1 - Dibenzothiophenes	C1dithio	198	17.0 - 21.0
C2 - Dibenzothiophenes	C2dithio	212	18.0 - 23.0
C3 - Dibenzothiophenes	C3dithio	226	19.5 - 26.0
C1 - Phenanthrenes/Anthracenes	C1phenan	192	17.5 - 20.5
C2 - Phenanthrenes/Anthracenes	C2phenan	206	19.0 - 22.5
C3 - Phenanthrenes/Anthracenes	C3phenan	220	20.0 - 23.5
C4 - Phenanthrenes/Anthracenes	C4phenan	234	21.0 - 25.0
C1 - Fluoranthenes/Pyrenes	C1fluora	216	20.0 - 28.0
C1 - Chrysenes	C1chrys	242	24.5 - 27.5
C2 - Chrysenes	C2chrys	256	26.0 - 29.0
C3 - Chrysenes	C3chrys	270	27.0 - 31.0
C4 - Chrysenes	C4chrys	284	28.0 - 33.0

APPENDIX III

Table III-1--Concentrations (ng/l) of calibrated PAHs (see Table II-2, Appendix II for key to standardized abbreviations) found at 1-m and 5-m depths in seawater in PWS, Alaska, 7 to 11 days following the grounding of the T/V *Exxon Valdez*. Sample stations are those listed in Table I-1, Appendix I, and are presented below in the chronological order sampled. Results of triplicate determinations are followed by 95% confidence intervals in parentheses; results of duplicate determinations are separated by commas; and results of single determinations are presented alone. Also presented in the topmost row are results (ng) of analysis of 1 μ l unweathered crude oil spilled from the hold of the T/V *Exxon Valdez* determined by methods of this study, and in the bottom-most row are experimentally determined MDLs for these calibrated PAHs in seawater analyzed by methods of this study. The density of the crude oil was assumed to be 0.8882 g/ml, as reported by Clark et al. (1977).

Sequence	Sample site*	Depth (m)	Naph	Menap2	Menap1
<i>Exxon Valdez</i> crude 1 μ L			671	1170	907
1	GRAVB	1	745 (516-975)	-	-
		5	778 (141-1415)	-	-
2	OLSEN	1	537 (401-673)	-	-
		5	665 (277-1053)	-	-
3	SNUGC	1	709 (153-1264)	-	-
		5	614 (140-1087)	-	-
4	ECNAKEI	1	687 (295-1077)	-	-
		5	570 (433-707)	-	34.9 ^b
5	MCPHERS	1	563 (278-848)	-	42.3 ^b
		5	851 (-7.02-1780)	-	43.6 ^b
6	CABIB	1	752 (224-1280)	103 (81.6-124)	89.6 ^b (74.9-104)
		5	722	93.0 ^b	83.6 ^b
7	NWBAY	1	1280 (677-1874)	773 (272-1270)	675 (221-1130)
		5	968 (669-1266)	424 (378-471)	363 (310-417)
8	MAINB	1	340	-	-
		5	412 (253-573)	-	43.5 ^b , 34.6 ^b
9	HERRB	1	530, 681	305, 503	281, 462
		5	506 (327-686)	308 (120-497)	286 (123-448)
10	ESHAB	1	337 (325-349)	-	76.9 ^b
		5	321 (295-346)	-	-
11	GRANB	1	323 (245-401)	-	63.2 ^b
		5	330 (289-371)	-	-
12	SQUII	1	326 (168-485)	-	62.1 ^b
		5	356 (238-475)	-	1220
13	SHELB	1	354 (320-388)	40.9 ^b	63.0 ^b (-27.5-154)
		5	346 (305-387)	-	-
14	SAWMB	1	350 (268-433)	-	150
		5	324 (299-349)	-	-
15	SLEEB	1	375 (280-471)	57.9 ^b (42.8-73.1)	78.9 ^b (-11.8-170)
		5	368 (277-460)	45.5 ^b , 40.3 ^b	35.7 ^b (23.5-47.9)
16	SMONTS	1	476 (423-530)	147 (129-166)	158 (46.0-270)
		5	472, 405	123, 101	127, 91.8 ^b
17	SMONTI	1	362 (262-463)	-	-
		5	361 (315-408)	-	-
18	MMONTS	1	334 (244-424)	-	-
		5	348 (279-418)	-	31.7 ^b
19	SNUGH	1	976 (869-1082)	1010 (798-1210)	911 (732-1090)
		5	474 (457-492)	120 (101-140)	105 (98.9-112)
20	SGREEI	1	467 (447-488)	-	55.1 ^b
		5	543 (421-664)	-	47.8 ^b
21	PCHAL	1	459 (348-569)	-	32.5 ^b
		5	341 (-317-1000)	-	-
22	NGREEI	1	782 (354-1209)	-	47.4 ^b (-4.93-99.7)
		5	2280 (-2170-6740)	52.3 ^b , 47.4 ^b	51.7 ^b (16.0-87.4)
23	ROCKB	1	1620 (-1330-4570)	-	-
		5	865 (104-1620)	-	-
24	NMONTS	1	772 (626-918)	105 (60.7-149)	99.6 (75.4-124)
		5	929 (317-1540)	81.4 ^b (66.0-96.80)	74.3 ^b (67.3-81.3)
25	BOISL	1	708 (490-926)	153 (96.4-210)	152 (15.6-288)
		5	698, 1220	102, 119	103, 124
26	SELEAI	1	770 (468-1070)	207 (182-234)	208 (150-265)
		5	714 (427-1000)	197 (162-233)	182 (177-186)
27	SSMITI	1	629 (352-906)	160 (132-188)	146 (133-158)
		5	991 (-202-2180)	99.0 (87.9-111)	97.2 (74.5-120)
28	NSMITI	1	814 (304-1320)	241 (191-293)	234 (157-311)
		5	745 (315-1170)	127 (108-148)	121 (99.6-142)
MDL			33.5	37.4	28.7

Table III-1.--Continued.

Sequence	Sample site ^a	Depth (m)	Dimeth	Trimeth	Biphenyl
<i>Exxon Valdez crude</i> 1 μ L			722	346	186
1	GRAVB	1	-	-	-
		5	49.7 ^b (-4.03-103)	-	-
2	OLSEN	1	-	-	-
		5	-	-	-
3	SNUGC	1	29.4 ^b	-	-
		5	-	-	-
4	ECNAKEI	1	51.9 ^b (-6.74-111)	-	-
		5	-	-	-
5	MCPHERS	1	-	-	-
		5	34.8 ^b , 30.3 ^b	-	-
6	CABIB	1	47.1 ^b (27.3-67.0)	-	-
		5	58.9 ^b , 48.5 ^b	-	-
7	NWBAY	1	234 (135-334)	81.1 ^b (41.2-121)	129 (56.1-201)
		5	161 (154-168)	53.2 ^b (43.0-63.5)	69.2 ^b (62.0-76.4)
8	MAINB	1	-	-	-
		5	-	-	-
9	HERRB	1	118, 165	54.2 ^b	70.6 ^b , 92.4
		5	114 (62.6-166)	50.0 ^b (32.2-67.8)	64.8 ^b (26.5-103)
10	ESHAB	1	-	-	-
		5	-	-	-
11	GRANB	1	-	-	-
		5	-	-	-
12	SQUII	1	-	-	-
		5	-	-	-
13	SHELB	1	29.3 ^b	-	-
		5	38.9 ^b (20.9-56.8)	-	-
14	SAWMB	1	-	-	-
		5	29.5 ^b	-	-
15	SLEEB	1	44.0 ^b (10.5-77.5)	-	-
		5	32.6 ^b , 41.0 ^b	-	-
16	SMONTS	1	64.2 ^b (38.5-89.8)	27.5 ^b	31.3 ^b , 32.7 ^b
		5	73.5, 78.2	26.2 ^b , 27.4 ^b	-
17	SMONTI	1	31.0 ^b	-	-
		5	35.4 ^b	-	-
18	MMONTS	1	29.7 ^b	-	-
		5	36.7 ^b	-	-
19	SNUGH	1	355 (248-462)	138 (110-166)	198 (131-265)
		5	40.4 ^b (26.0-54.8)	-	-
20	SGREEI	1	43.6 ^b	-	-
		5	38.0 ^b	-	-
21	PCHAL	1	31.1 ^b	-	-
		5	35.0 ^b , 36.4 ^b	-	-
22	NGREEI	1	-	-	-
		5	83.1 ^b , 35.7 ^b	-	-
23	ROCKB	1	-	-	-
		5	-	-	-
24	NMONTS	1	51.1 ^b (33.3-68.9)	29.5 ^b , 26.1 ^b	-
		5	48.5 ^b (19.0-78.0)	-	-
25	BOISL	1	58.3 ^b (49.2-67.4)	31.1 ^b , 32.8	-
		5	48.0 ^b , 51.2 ^b	-	-
26	SELEAI	1	112 (101-122)	69.2 ^b , 57.0 ^b	43.1 ^b (38.1-48.2)
		5	112 (78.5-145)	55.7 ^b , 68.1 ^b	47.8 ^b (30.8-64.8)
27	SSMITI	1	101 (66.4-136)	51.4 ^b	40.3 ^b (20.5-60.0)
		5	52.9 ^b (24.4-81.3)	-	-
28	NSMITI	1	106 (83.8-129)	44.7 ^b , 56.3 ^b	47.2 ^b (34.2-60.2)
		5	60.5 ^b (41.4-79.6)	28.5 ^b , 27.7 ^b	32.5 ^b
MDL			28.7	25.7	29.7

Table III-1 --Continued

Sequence	Sample site ^a	Depth (m)	Fluorene	Dithio	Phenanth	Mephenl
Exxon Valdez crude 1 μ L			82.3	185	250	171
1	GRAVB	1	-	-	-	-
		5	-	-	-	-
2	OLSEN	1	-	-	-	-
		5	-	-	-	-
3	SNUGC	1	-	-	-	-
		5	-	-	-	-
4	ECNAKEI	1	-	-	-	-
		5	-	-	-	-
5	MCPHERS	1	-	-	-	-
		5	-	-	41.9 ^b	-
6	CABIB	1	-	-	-	-
		5	-	-	-	-
7	NWBAY	1	45.6 ^b (12.0-79.3)	69.8 ^b (37.0-103)	83.6 ^b (53.8-113)	60.8 ^b , 70.1 ^b
		5	-	37.9 ^b (31.8-43.9)	53.3 ^b (48.8-57.9)	57.9 ^b
8	MAINB	1	-	-	-	-
		5	-	-	-	-
9	HERRB	1	35.3 ^b , 50.4 ^b	59.2 ^b , 78.3	77.7, 82.5	-
		5	31.4 ^b (26.5-36.3)	-	70.5 ^b (52.5-88.5)	47.7 ^b , 51.8 ^b
10	ESHAB	1	-	-	-	-
		5	-	-	-	-
11	GRANB	1	-	-	-	-
		5	-	-	-	-
12	SQUII	1	-	-	-	-
		5	-	-	-	-
13	SHELB	1	-	-	-	-
		5	-	-	-	-
14	SAWMB	1	-	-	-	-
		5	-	-	-	-
15	SLEEB	1	-	-	-	-
		5	-	-	-	-
16	SMONTS	1	-	-	33.5 ^b , 30.6 ^b	32.9 ^b
		5	-	-	-	-
17	SMONTI	1	-	-	-	-
		5	-	-	-	-
18	MMONTS	1	-	-	-	-
		5	-	-	-	-
19	SNUGH	1	87.0 ^b (57.0-117)	128 (107-151)	149 (97.5-201)	75.6 (-8.53-160)
		5	-	-	-	-
20	SGREEI	1	-	-	-	-
		5	-	-	-	-
21	PCHAL	1	-	-	-	-
		5	-	-	-	-
22	NGREEI	1	-	-	-	-
		5	-	-	-	-
23	ROCKB	1	-	-	-	-
		5	-	-	-	-
24	NMONTS	1	-	26.6 ^b , 28.3 ^b	38.0 ^b , 34.6 ^b	45.9 ^b , 45.3 ^b
		5	-	-	30.4 ^b , 39.4 ^b	-
25	BOISL	1	-	-	32.7 ^b , 61.4 ^b	27.0 ^b
		5	-	-	-	-
26	SELEAI	1	-	50.0 ^b (46.3-53.6)	74.7 (42.8-107)	71.8 (32.9-111)
		5	30.4 ^b	45.6 ^b (40.1-51.1)	65.6 ^b (46.5-84.6)	72.9 (-6.74-152)
27	SSMITI	1	-	41.1 ^b (31.5-50.6)	54.1 ^b (51.1-57.2)	63.6 (-1.09-128)
		5	-	-	30.6 ^b	29.3 ^b
28	NSMITI	1	-	37.8 ^b (33.6-42.0)	51.8 ^b (35.5-68.1)	-
		5	-	-	47.0 ^b	-
MDL			29.3	26.1	29.8	26.8

^aSee Table III-10 for key to sampling site abbreviations.^bConcentrations above MDL, but below lowest calibration standard.

Table III-2.--Concentrations (ng/l) of uncalibrated PAHs (see Table II-3, Appendix II for key to standardized abbreviations) found at 1-m and 5-m depths in seawater in PWS, Alaska, 7 to 11 days following the grounding of the T/V *Exxon Valdez*. Sample stations are those listed in Table I-1, Appendix I, and are presented below in the chronological order sampled. Results of triplicate determinations are followed by 95% confidence intervals in parentheses; results of duplicate determinations are separated by commas; and results of single determinations are presented alone. Also presented in the topmost row are results (ng) of analysis of 1 μ l unweathered crude oil spilled from the hold of the T/V *Exxon Valdez* determined by methods of this study, and in the bottom-most row are experimentally determined MDLs for the most similar calibrated PAHs in seawater analyzed by methods of this study. The density of the crude oil was assumed to be 0.8882 g/ml, as reported by Clark et al. (1977).

Sequence	Sampling site ^a	Depth (m)	C2naph	C3naph	C4naph
<i>Exxon Valdez</i> crude 1 μ L			3110	2220	831
1	GRAVB	1	593, 28.6	30.9	-
		5	87.8 (2.76-173)	-	70.5
2	OLSEN	1	248	-	39.5
		5	57.5 (-3.31-118)	-	29.3
3	SNUGC	1	425	-	-
		5	74.8, 29.0	31.6	-
4	ECNAKEI	1	247.7 (-347-842)	-	-
		5	99.3	-	-
5	MCPHERS	1	767, 62.8	-	-
		5	106 (27.3-185)	36.4	137
6	CABIB	1	283 (65.4-500)	103 (64.3-141)	54.4
		5	223, 194	97.3, 63.5	-
7	NWBAY	1	1210 (417-2000)	511 (266-756)	134 (114-154)
		5	737 (565-908)	331 (253-409)	83.8, 197
8	MAINB	1	38.7, 756	31.5	-
		5	57.4, 36.0	-	40.9
9	HERRB	1	888, 601	388, 349	149, 91.1
		5	577 (324-830)	315 (224-407)	88.3 (-17.2-194)
10	ESHAB	1	65.9 (-33.0-165)	-	42.1, 72.8
		5	125, 28.2	-	47.8
11	GRANB	1	31.5, 48.4	-	69.6
		5	99.7	-	129
12	SQUH	1	27.6, 80.5	-	51.0
		5	27.7, 57.9	-	-
13	SHELB	1	105 (66.4-143)	33.5, 41.3	-
		5	135 (-215-485)	27.2	40.8
14	SAWMB	1	75.1 (33.7-117)	45.5	31.6
		5	129 (-188-447)	39.7	62.6
15	SLEEB	1	173 (77.5-268)	84.9 (48.0-122)	27.0
		5	185 (120-489)	62.8, 78.2	-
16	SMONTS	1	281 (155-407)	149 (132-166)	29.1, 35.4
		5	244, 256	123, 161	51.1
17	SMONTI	1	58.5	-	-
		5	102 (-152-354)	-	-
18	MMONTS	1	31.2, 64.6	-	68.2
		5	40.5, 177	-	-
19	SNUGH	1	1730 (1260-2190)	828 (712-943)	124 (62.9-185)
		5	181.1 (167-195)	90.2 (78.3-102)	-
20	SGREEI	1	55.6 (18.3-92.9)	33.5	-
		5	94.3 (29.1-160)	46.8 (28.2-65.4)	30.8
21	PCHAL	1	27.6, 31.1	-	-
		5	76.4	28.3	-
22	NGREEI	1	65.5 (3.34-128)	27.0	-
		5	1790 (-5047-8620)	66.2 (7.39-125)	109
23	ROCKB	1	965, 352	-	-
		5	100 (-111-311)	-	-
24	NMONTS	1	262 (79.9-444)	121 (2.31-240)	76.0
		5	257 (-203-533)	98.6 (6.52-191)	51.2, 90.2
25	BOISL	1	320 (260-381)	137 (103-171)	57.1 (-8.64-123)
		5	416, 213	113, 113	26.9, 156
26	SELEAI	1	542 (492-592)	368 (295-441)	195 (104-289)
		5	538 (314-761)	325 (199-451)	151 (-21.5-324)
27	SSMITI	1	532 (32.0-1030)	242 (184-300)	96.3 (-26.6-219)
		5	289 (35.6-541)	121 (88.1-155)	58.4, 90.8
28	NSMITI	1	528 (328-728)	272 (118-425)	157 (24.7-339)
		5	308 (151-465)	150 (138-163)	126
MDL			27.4	25.7	25.7

Table III-2.--Continued.

Sequence	Sampling site ^a	Depth (m)	C1fluor	C2fluor	C3fluor
<i>Exxon Valdez crude 1 µL</i>			181	118	34.4
1	GRAVB	1	87.8	160	160 (-282-602)
		5	134	50.5, 105	58.0 (-1.97-118)
2	OLSEN	1	106	29.8	53.3
		5	34.9, 118	-	62.7, 39.1
3	SNUGC	1	-	32.7, 76.0	83.6
		5	78.1	-	65.2
4	ECNAKEI	1	-	46.1, 46.7	94.3
		5	-	38.4	117
5	MCPHERS	1	-	-	99.3
		5	317, 33.2	77.2	40.0
6	CABIB	1	35.9	51.9	42.6
		5	-	-	-
7	NWBAY	1	71.4 (10.2-133)	32.6, 108	91.3
		5	25.6, 178	168	109
8	MAINB	1	102	101	113
		5	58.7	80.5	55.8
9	HERRB	1	57.0, 60.2	29.8	39.0
		5	54.5 (-2.34-111)	48.7, 197	44.5, 85.3
10	ESHAB	1	142, 198	-	43.5
		5	64.0	97.2	46.5, 85.6
11	GRANB	1	151	-	42.4
		5	178	125	81.6, 42.9
12	SQUII	1	139, 46.0	-	37.1
		5	103	67.3	85.2
13	SHELB	1	48.9 (1.64-96.2)	-	32.1
		5	226	88.3	138
14	SAWMB	1	54.4, 105	-	-
		5	99.6	184	108, 54.7
15	SLEEB	1	69.1, 33.3	-	29.7
		5	-	-	174, 47.0
16	SMONTS	1	33.2	-	41.9
		5	-	46.0	33.1
17	SMONTI	1	-	-	-
		5	-	-	177
18	MMONTS	1	115, 34.8	-	-
		5	53.0	144	31.5, 170
19	SNUGH	1	93.3, 84.6	51.6	43.6
		5	79.8	-	33.1, 62.6
20	SGREEI	1	-	-	-
		5	58.0, 90.0	-	67.2, 52.9
21	PCHAL	1	-	-	-
		5	-	39.7	73.1, 57.8
22	NGREEI	1	32.6	-	-
		5	71.1, 402	142	98.3 (-96.0-293)
23	ROCKB	1	48.1, 129	223	56.2, 57.1
		5	50.9, 44.9	-	35.3, 72.4
24	NMONTS	1	38.2	73.2	53.3
		5	50.0, 91.7	93.0	34.3, 69.3
25	BOISL	1	91.5, 116	50.4, 179	55.3
		5	44.5, 249	245	34.5, 97.1
26	SELEAI	1	140 (9.01-272)	117 (90.8-144)	78.9 (-19.2-177)
		5	87.5 (-122-296)	98.8 (-128-326)	104 (-59.3-267)
27	SSMITI	1	39.0, 59.0	40.4, 92.0	35.6, 108
		5	51.9 (-0.15-104)	-	43.8, 58.1
28	NSMITI	1	163 (73.8-400)	44.7 (20.0-69.4)	61.8
		5	163, 30.0	132	98.8, 80.8
MDL			29.3	29.3	29.3

Table III-2.--Continued.

Sequence	Sampling site ^a	Depth (m)	C1dithio	C2dithio	C3dithio
<i>Exxon Valdez crude</i> 1 μ L					
1	GRAVB	1	339	482	370
		5	29.9	28.3	99.4
2	OLSEN	1	43.9, 47.0	30.8	136, 30.8
		5	-	-	51.7
3	SNUGC	1	27.7	-	34.2
		5	-	-	-
4	ECNAKEI	1	28.0	-	-
		5	-	-	35.5
5	MCPHERS	1	27.0	-	44.3
		5	105	49.0	40.9
6	CABIB	1	35.2	-	41.1
		5	-	-	-
7	NWBAY	1	78.7 (26.8-130)	46.1, 71.8	87.7
		5	60.9 (5.78-116)	32.0, 51.9	92.5, 48.4
8	MAINB	1	33.6	-	83.6
		5	-	-	-
9	HERRB	1	71.7 52.6	42.6, 29.8	-
		5	53.0 (38.2-67.9)	43.2, 37.6	26.2
10	ESHAB	1	34.9	-	39.5, 53.2
		5	-	-	-
11	GRANB	1	52.5	-	33.5
		5	64.5	28.6	67.0
12	SQUII	1	31.4	-	-
		5	-	-	-
13	SHELB	1	-	-	-
		5	-	-	-
14	SAWMB	1	-	-	-
		5	39.0	-	-
15	SLEEB	1	36.3	-	-
		5	-	-	-
16	SMONTS	1	36.9	-	-
		5	37.0, 42.2	29.8, 27.5	-
17	SMONTI	1	-	-	-
		5	-	-	-
18	MMONTS	1	40.8	-	-
		5	-	-	-
19	SNUGH	1	99.9 (70.4-129)	47.2 (4.67-89.8)	-
		5	-	-	41.5
20	SGREEI	1	-	-	-
		5	26.6, 34.5	-	59.5, 26.8
21	PCHAL	1	-	-	-
		5	-	-	27.4
22	NGREEI	1	-	-	-
		5	34.3, 155	116.2	101, 1500
23	ROCKB	1	48.9	30.4	745, 41.7
		5	-	-	80.2
24	NMONTS	1	45.5 (19.6-71.4)	38.6 (-3.6-80.8)	78.8, 28.2
		5	36.8 (15.8-57.8)	31.5, 50.3	124
25	BOISL	1	40.7 (19.7-61.6)	31.4	33.6
		5	72.6	35.4	118, 53.8
26	SELEAI	1	112 (41.7-183)	92.1 (30.6-154)	104.5 (64.2-145)
		5	90.0 (20.1-160)	89.1 (55.7-122)	64.9 (2.19-128)
27	SSMITI	1	82.0 (66.7-97.2)	86.2 (28.4-144)	81.6 (-74.9-238)
		5	40.1 (11.0-69.3)	18.8, 40.0	50.7, 44.6
28	NSMITI	1	84.5	60.1 (10.1-110)	57.5 (33.2-81.8)
		5	58.1	35.0	44.8, 28.4
MDL			26.1	26.1	26.1

Table III-2.--Continued.

Sequence	Sample site ^a	Depth (m)	C1phenan	C2phenan	C3phenan	C4phenan
<i>Exxon Valdez crude 1 μL</i>						
1	GRAVB	1	668	749	480	99.5
		5	62.7	129	266 (-335-867)	-
2	OLSEN	1	35.9, 36.7	94.9, 38.5	110 (75.2-146)	75.4
		5	27.0	-	-	-
3	SNUGC	1	-	-	87.5	-
		5	-	-	-	-
4	ECNAKEI	1	-	-	52.6, 33.0	-
		5	-	-	46.4	-
5	MCPHERS	1	-	27.6	-	-
		5	52.9	-	-	-
6	CABIB	1	35.1, 36.2	58.0	41.0	-
		5	42.1	-	-	-
7	NWBAY	1	114 (78.7-150)	70.9, 128.7	86.0	51.4
		5	102 (75.4-129)	74.6 (-46.8-196)	32.8, 212	118
8	MAINB	1	-	103	106	-
		5	-	38.2	-	-
9	HERRB	1	90.4, 90.5	39.2, 27.9	-	-
		5	90.0 (81.1-98.9)	61.5 (9.08-114)	32.2	-
10	ESHAB	1	-	-	-	-
		5	-	58.5	-	-
11	GRANB	1	-	-	-	-
		5	31.6	53.1	123	-
12	SQUII	1	-	-	-	-
		5	-	49.1	-	-
13	SHELB	1	-	-	-	-
		5	-	40.4, 139.3	-	-
14	SAWMB	1	-	64.1	-	-
		5	-	147, 33.1	63.4	-
15	SLEEB	1	37.6, 27.8	-	-	-
		5	-	146	-	-
16	SMONTS	1	38.8 (-2.41-79.9)	-	-	-
		5	53.6, 37.5	46.4	-	-
17	SMONTI	1	-	-	-	-
		5	-	200	-	-
18	MMONTS	1	-	-	-	-
		5	-	185	-	-
19	SNUGH	1	162 (125-198)	56.1 (8.71-104)	30.5	-
		5	-	-	-	-
20	SGREEI	1	-	-	-	-
		5	39.0 (23.4-54.6)	27.7, 42.4	134	-
21	PCHAL	1	-	-	-	-
		5	-	-	-	-
22	NGREEI	1	-	-	-	-
		5	37.1, 298	554, 37.0	312, 107	68.2, 1630
23	ROCKB	1	61.9	118	-	516
		5	-	29.7	71.6	35.0
24	NMONTS	1	72.8 (24.3-121)	63.9 (-9.45-137)	74.8	56.9
		5	89.2	54.2 (-11.5-120)	167	47.4
25	BOISL	1	49.5, 56.8	44.0	-	-
		5	50.8, 65.0	47.4, 81.3	-	85.5
26	SELEAI	1	161 (104-217)	142 (11.1-272)	215 (-373-803)	39.2, 6.5
		5	161 (91.7-231)	179 (118-240)	174 (-263-611)	55.5
27	SSMITI	1	132 (98.5-166)	130 (-3.48-263)	92.0 (4.82-179)	81.0
		5	59.3 (39.3-79.3)	67.7 (13.3-122)	31.3	67.2
28	NSMITI	1	82.2 (30.4-134)	73.3 (27.5-119)	123 (-240-486)	-
		5	49.3 (2.16-96.4)	103, 64.0	-	-
MDL			26.8	26.8	26.8	26.8

^aSee Table III-10 for key to sampling site abbreviations.

Table III-3.--Concentrations (ng/l) of alkanes (see Table IV-3, Appendix IV for key to standardized abbreviations) found at 1-m and 5-m depths in seawater in PWS, Alaska, 7 to 11 days following the grounding of the T/V *Exxon Valdez*. Sample stations are those listed in Table I-1, Appendix I, and are presented below in the chronological order sampled. Results of triplicate determinations are followed by 95% confidence intervals in parentheses; results of duplicate determinations are separated by commas; and results of single determinations are presented alone. Also presented in the topmost row are results (ng) of analysis of 1 μ l unweathered crude oil spilled from the hold of the T/V *Exxon Valdez* determined by the methods of this study. The density of the crude oil was assumed to be 0.8882 g/ml, as reported by Clark et al. (1977).

Sequence	Sample site	Depth (m)	C-10	C-11	C-12	C-13
<i>Exxon Valdez</i> crude 1 μ L			4230	3510	3460	3713
1	GRAVB	1	101	119	-	-
		5	71.1	105 (-66.0-275)	42.8	-
2	OLSEN	1	-	-	-	-
		5	148, 69.0	61.2, 95.1	-	-
3	SNUGC	1	-	61.5 (35.1-87.4)	-	-
		5	125, 206	181 (128-234)	37.8	63.0
4	ECNAKEI	1	47.1	78.2 (39.8-117)	14.8	11.4
		5	160	90.9, 131	-	-
5	MCPHERS	1	-	-	-	-
		5	119 (-28.3-266)	104, 41.1	42.4	-
6	CABIB	1	35.7	155, 45.6	170, 38.7	-
		5	225, 173	65.0, 105	39.1	16.1, 44.8
7	NWBAY	1	90.4	124 (2.04-246)	148 (97.3-198)	148 (0.56-296)
		5	333, 120	213 (59.2-366)	217 (79.1-354)	242, 289
8	MAINB	1	63.2	-	-	-
		5	151, 42.8	109 (46.8-171)	44.3	38.1
9	HERRB	1	-	74.5, 24.6	34.7	79.1, 14.7
		5	-	36.9, 96.1	76.7, 36.3	74.0, 21.8
10	ESHAB	1	-	-	-	-
		5	84.0	28.5, 108	-	-
11	GRANB	1	46.3	-	-	-
		5	-	140	60.4	-
12	SQUII	1	47.7	-	-	38.9
		5	56.7	74.4, 89.0	92.4	-
13	SHELB	1	-	-	-	-
		5	-	92.6	97.6	72.6
14	SAWMB	1	-	-	-	-
		5	64.2	114	78.7	-
15	SLEEB	1	-	19.3	19.6	17.4
		5	97.0	-	126	-
16	SMONTS	1	-	21.4, 51.7	27.2	27.9
		5	132, 111	64.9	-	68.3
17	SMONTI	1	-	67.5, 37.9	-	-
		5	82.2	-	163	-
18	MMONTS	1	-	28.3	-	-
		5	-	-	-	-
19	SNUGH	1	159	79.6, 83.5	154	141, 201
		5	107, 96.2	74.1	96.8	110
20	SGREEI	1	73.0	109, 36.8	124	-
		5	299, 78.2	170	40.0	36.0
21	PCHAL	1	256	29.4, 180	-	-
		5	193, 194	205, 64.7	29.4	-
22	NGREEI	1	204	157, 113	-	-
		5	361 (126-597)	199 (88.5-310)	-	22.9
23	ROCKB	1	119	126, 92.6	14.6	-
		5	184, 77.8	83.1, 119	-	-
24	NMONTS	1	-	163, 138	-	-
		5	121 (-27.3-270)	118, 180	35.7	49.9
25	BOISL	1	111, 66.6	62.4 (22.3-102)	-	65.2, 112
		5	63.6, 188	111, 167	65.6	50.2
26	SELEAI	1	160, 155	94.9 (-35.9-226)	53.4	121 (31.4-211)
		5	175	274, 121	94.7	70.5, 84.3
27	SSMITI	1	-	115 (35.2-194)	100 (38.7-161)	109, 119
		5	179 (-102-460)	193, 167	88.7	71.2
28	NSMITI	1	135, 190	116 (-25.0-256)	69.1	123 (16.7-229)
		5	311	144 (43.7-243)	51.9	38.9

Table III-3--Continued.

Sequence	Sample site ^a	Depth (m)	C-14	C-16	C-17	Pristane
<i>Exxon Valdez Crude 1 μL</i>			3450	2850	2540	2130
1	GRAVB	1	-	268 (-511-1048)	66.8, 147	-
		5	41.9	113 (-77.3-303)	67.9, 57.1	42.0
2	OLSEN	1	-	-	-	-
		5	-	144	129 (-39.8-298)	-
3	SNUGC	1	-	145	46.0	-
		5	39.7	-	90.1 (-66.6-247)	28.3
4	ECNAKEI	1	22.6	66.2	72.7, 69.5	19.1
		5	50.0, 32.6	-	74.2 (27.2-121)	24.4
5	MCPHERS	1	-	111	37.6	-
		5	46.9, 43.0	28.1, 117	104, 109	54.8
6	CABIB	1	104, 30.8	114 (30.4-199)	89.7 (24.5-155)	84.3, 44.6
		5	60.1, 60.7	149, 65.9	105 (90.1-120)	63.7, 58.8
7	NWBAY	1	156 (122-191)	302 (164-440)	165 (62.7-267)	615 (-859-2090)
		5	215, 340	282 (-191-755)	203 (31.1-375)	102, 285
8	MAINB	1	-	190, 81.9	40.7, 61.4	-
		5	42.2, 36.5	125	39.7, 66.0	35.4
9	HERRB	1	71.9, 38.1	132, 217	104, 78.9	96.0, 98.1
		5	120, 42.2	233 (-208-675)	203, 235	271, 166
10	ESHAB	1	-	-	179 (-90.8-449)	-
		5	-	-	40.7	22.5
11	GRANB	1	-	31.6	288, 47.5	-
		5	87.4	27.5	68.9	38.9
12	SQUII	1	61.0, 38.7	65.1, 34.9	136 (-72.5-345)	35.4
		5	98.6	50.0, 197	52.2	485
13	SHELB	1	43.8	-	48.6, 152	-
		5	66.2	32.8	49.3	35.4
14	SAWMB	1	-	24.8	114 (-51.1-280)	-
		5	50.1	-	-	-
15	SLEEB	1	48.4	77.4 (15.3-140)	89.0 (-36.0-214)	45.0
		5	105	77.5	57.4, 60.1	-
16	SMONTS	1	61.2	93.2 (55.0-131)	108 (32.4-183)	69.5, 70.4
		5	89.4	167, 91.3	138, 111	110
17	SMONTI	1	-	29.6	61.3	-
		5	235	-	-	-
18	MMONTS	1	-	31.1	55.6, 49.9	-
		5	30.1	-	104, 35.9	-
19	SNUGH	1	170, 239	453, 338	297, 249	340, 197
		5	88.9	49.2	61.2, 126	27.9
20	SGREEI	1	22.5	65.0 (12.0-118)	81.7 (33.9-129)	50.6, 52.2
		5	43.0	49.6	138 (6.78-270)	54.0
21	PCHAL	1	25.8	30.9	35.5	-
		5	32.2	29.1	61.3	-
22	NGREEI	1	28.3	329	43.7, 49.5	-
		5	41.7	82.4	144, 565	258
23	ROCKB	1	15.3	77.2	130	85.0, 403
		5	-	-	108, 91.6	-
24	NMONTS	1	44.7, 41.1	136, 189	159 (121-198)	133 (98.0-167)
		5	45.6	101 (45.0-158)	155 (-15.7-326)	117 (-4.35-238)
25	BOISL	1	93.9 (59.7-128)	108 (8.54-207)	211 (-29.7-451)	83.4, 182
		5	41.0	145, 178	103, 145	82.3
26	SELEAI	1	170 (50.1-289)	359 (25.7-693)	524 (59.4-988)	406 (-210-1020)
		5	111, 141	310 (-62.5-682)	325 (134-516)	234, 342
27	SSMITI	1	116 (68.8-164)	332 (232-433)	324 (232-417)	267 (205-330)
		5	82.1, 69.9	160 (55.1-266)	176 (55.8-297)	122, 158
28	NSMITI	1	158 (62.7-254)	243 (61.5-424)	429 (-27.2-885)	302 (-186-790)
		5	47.7	115 (6.85-224)	101 (76.0-127)	76.5

Table III-3--Continued.

Sequence	Sample site ^a	Depth (m)	Exxon Valdez crude μL			
			C-19	C-20	C-21	C-22
1	GRAVB	1	2280	1990	1890	1900
		5	871	139 (-149-426)	3010 (-3390-9410)	52.5 (2.01-103)
2	OLSEN	1	152 (-99.1-403)	49.1, 53.4	1052 (838-1270)	37.4, 45.4
		5	96.4, 446	-	153 (60.2-246)	-
3	SNUGC	1	418 (-554-1390)	32.8, 228	119 (-10.3-248)	37.7
		5	198	18.3	230 (145-315)	-
4	ECNAKEI	1	372 (-674-1420)	86.1 (-99.7-272)	333 (-91.8-758)	32.9, 18.4
		5	134 (-33.8-301)	28.3	593 (-109-1300)	37.6
5	MCPHERS	1	200, 179	586, 34.1	770 (-483-2020)	1701, 51.4
		5	86.6	31.8	165 (-37.9-368)	73.8, 31.2
6	CABIB	1	174 (-6.58-355)	124, 95.3	230 (-176-635)	48.2, 91.5
		5	137 (9.82-264)	76.5 (66.1-87.0)	209 (5.12-412)	77.8 (46.5-109)
7	NWBAY	1	149 (-1.38-299)	99.5 (37.8-161)	149 (52.5-246)	69.1, 79.2
		5	330 (-266-925)	219 (-82.6-522)	206 (94.3-318)	105 (74.4-135)
8	MAINB	1	245, 452	228, 221	236 (109-364)	133, 163
		5	154, 193	-	162 (16.0-309)	-
9	HERRB	1	102, 73.2	25.7, 45.0	236 (54.4-419)	16.3, 39.5
		5	164, 131	182, 105	116, 109	108
10	ESHAB	1	256 (203-309)	263 (-35.9-562)	198, 268	192, 191
		5	1004 (-1103-3110)	286 (-297-868)	68.2	67.4
11	GRANB	1	93.8	16.4	-	-
		5	1689, 90.9	458	-	-
12	SQUII	1	289, 252	212	108	125
		5	584 (-783-1950)	77.4, 350	71.8	185, 25.0
13	SHELB	1	38.3, 329	-	-	-
		5	293 (-443-1030)	170	-	-
14	SAWMB	1	193, 122	-	-	-
		5	604 (-487-1700)	158 (-50.3-367)	-	-
15	SLEEB	1	52.4, 150	-	-	-
		5	308 (-425-1040)	105 (-77.3-287)	70.1 (48.0-92.3)	104 (76.9-131)
16	SMONTS	1	187 (-26.6-401)	272	244	104
		5	228 (-149-605)	110 (-2.04-221)	95.1 (30.8-159)	119 (62.1-176)
17	SMONTI	1	247, 199	157, 130	161, 104	122, 101
		5	180	33.3	33.8	56.9
18	MMONTS	1	215 (24.9-406)	-	-	-
		5	310 (-134-754)	35.3	32.9	33.4
19	SNUGH	1	187 (-47.3-422)	25.1	34.0	26.2
		5	379, 231	294, 291	312, 169	412, 129
20	SGREEI	1	249 (-378-876)	183, 146	101	58.1
		5	161 (34.3-287)	64.3 (39.0-89.5)	68.5 (51.9-85.0)	65.9 (44.2-87.5)
21	PCHAL	1	431 (-160-1020)	208 (35.0-380)	286	78.1, 236
		5	148, 41.2	20.4	-	22.1
22	NGREEI	1	190 (-53.7-435)	97.5	95.4	48.9
		5	155, 180	32.9, 94.3	61.1 (27.7-94.5)	58.8, 33.3
23	ROCKB	1	968 (-2170-4110)	250, 2691	290, 3897	1241
		5	363, 878	218	1556	141
24	NMONTS	1	393, 252	25.4	230, 78.7	32.3
		5	336 (-25.5-697)	239 (0.260-478)	259 (46.6-471)	229 (102-356)
25	BOISL	1	346 (-405-1100)	203 (-114-519)	146 (106-187)	135 (45.5-224)
		5	691 (-471-1850)	301 (-132-735)	139 (51.1-228)	135 (59.9-210)
26	SELEAI	1	217, 318	98.3	317	114
		5	1443 (-31.8-2920)	881 (-322-2080)	537 (-362-1440)	465 (-285-1220)
27	SSMITI	1	801 (-507-2110)	437 (98.6-775)	379 (245-512)	343 (245-441)
		5	521 (337-704)	454 (161-746)	410 (357-463)	451 (130-773)
28	NSMITI	1	369 (87.7-650)	226 (85.9-366)	279 (-198-757)	163 (102-224)
		5	1358 (-345-3060)	494 (-340-1330)	280 (27.1-532)	262 (45.5-479)
		5	236 (-197-670)	141, 98.5	132, 107	102, 92.8

Table III-3--Continued.

Sequence	Sample site'	Depth (m)	C-23	C-24	C-25	C-26
Exxon Valdez crude 1 μ L			1630	1450	1190	1130
1	GRAVB	1	294 (-176-765)	107 (58.8-154)	269, 502	410 (-631-1450)
		5	42.6, 139	47.8, 52.2	630 (-1440-2700)	137 (-76.6-350)
2	OLSEN	1	-	71.2	-	48.4, 183
		5	83.2	57.5	67.8	132, 166
3	SNUGC	1	50.8	189	46.9	223
		5	85.2, 33.6	64.4, 27.9	115, 144	90.7, 184
4	ECNAKEI	1	102, 52.0	66.3	305, 83.9	476, 148
		5	1774, 100	1406, 56.7	3071, 83.9	1150, 95.7
5	MCPHERS	1	63.4, 39.2	90.6, 49.2	145, 64.8	319, 62.4
		5	47.9, 111	69.2, 121	110, 128	89.8, 181
6	CABIB	1	81.1 (50.4-112)	176, 66.6	110 (-0.687-221)	122 (-67.6-311)
		5	53.2, 71.1	82.5, 87.3	88.5, 113	88.3, 120
7	NWBAY	1	133 (91.9-174)	156 (-112-424)	191 (-28.7-411)	196 (-149-542)
		5	111, 164	139, 169	454 (-636-1540)	120, 1197
8	MAINB	1	-	51.9	184, 137	79.2
		5	18.8, 61.7	28.8, 49.5	184 (-332-700)	74.4, 191
9	HERRB	1	95.0, 81.3	100, 84.2	90.6, 70.5	58.2, 55.2
		5	120, 25.3	74.6, 82.9	221 (-423-865)	104, 67.0
10	ESHAB	1	106	216	46.9	24.9, 187
		5	-	165, 75.1	28.2, 285	64.7
11	GRANB	1	-	-	-	118
		5	138	28.0	610, 47.9	33.4
12	SQUII	1	124, 30.7	85.4, 37.2	33.9, 102	41.3, 88.1
		5	-	-	578	-
13	SHELB	1	29.7	56.5	26.4	-
		5	-	34.9	869	-
14	SAWMB	1	-	-	40.8	63.3
		5	-	-	355	-
15	SLEEB	1	122 (2.33-242)	125 (81.9-169)	87.3 (55.8-119)	88.6 (31.5-146)
		5	81.8	105, 74.2	77.4, 102	-
16	SMONTS	1	169 (-50.3-388)	234 (28.1-439)	142 (-55.7-341)	106, 150
		5	141, 89.4	198, 97.9	347, 110	496
17	SMONTI	1	105	51.5	52.1	27.3
		5	-	-	-	-
18	MMONTS	1	33.9	57.3	50.4	39.1, 483
		5	26.9	32.6	134	274
19	SNUGH	1	215, 104	223, 147	180, 215	84.1, 647
		5	-	44.4	77.2	28.7
20	SGREEI	1	74.1 (52.9-95.2)	156 (31.1-280)	128 (-4.70-261)	227 (-418-872)
		5	277	203	105, 172	110, 65.4
21	PCHAL	1	19.8	102, 18.9	53.1, 46.3	78.6, 3.44
		5	58.8	95.2	217	126
22	NGREEI	1	46.2, 33.3	61.0, 39.5	45.2, 37.8	77 (-34.0-188)
		5	1143	1159 (-3390-5710)	5909	537, 2465
23	ROCKB	1	211	220	787	4453
		5	48.9	76.9	39.6	381, 61.9
24	NMONTS	1	196 (127-266)	242 (176-308)	277 (-102-656)	199 (118-280)
		5	126 (73.8-178)	168 (14.2-322)	141 (-49.6-332)	90.8 (78.3-103)
25	BOISL	1	146 (55.8-236)	207 (65.3-348)	96.6 (61.8-131)	114 (93.3-135)
		5	172	319	554, 408	1341
26	SELEAI	1	465 (-391-1320)	624 (-535-1780)	505 (-686-1700)	526 (-527-1580)
		5	306 (199-413)	342 (234-450)	464 (-365-1290)	252 (116-388)
27	SSMITI	1	461 (-111-1030)	581 (-198-1360)	524 (-348-1400)	466 (107-824)
		5	155 (121-189)	183 (164-202)	181 (70.4-292)	384 (-707-1470)
28	NSMITI	1	280 (45.9-515)	441 (135-746)	291 (-21.6-604)	277 (191-364)
		5	130, 75.1	147, 145	268 (-447-984)	171, 70.3

Table III-3--Continued.

Sequence	Sample site'	Depth (m)	C-27	C-28	C-29	C-30
Exxon Valdez crude 1 μ L			1050	731	723	471
1	GRAVB	1	490 (-557-1540)	1079, 806	710, 1009	1262, 2188
		5	249 (87.5-411)	336 (-51.7-724)	175, 1272	283, 1702
2	OLSEN	1	155, 443	273, 281	-	204 (-29.6-438)
		5	220, 168	263	156	266
3	SNUGC	1	443	601, 43.7	-	349, 125
		5	79.1, 433	144	273	753
4	ECNAKEI	1	203, 140	1067, 213	343 (-272-959)	391 (-199-981)
		5	1716, 88.9	405	53.7, 353	40.7, 324
5	MCPHERS	1	698, 115	1710, 93.5	181	1646, 389
		5	253, 194	529 (-593-1650)	141, 69.0	51.1, 187
6	CABIB	1	236, 114	123	569, 37.4	513 (-1000-2030)
		5	153, 358	291 (-463-1050)	214, 171	397, 48.0
7	NWBAY	1	233 (-137-603)	75.9, 514	631, 156	410 (-764-1580)
		5	194, 1760	127, 2065	84.5, 1212	77.6, 1300
8	MAINB	1	252, 218	1290	96.8	374 (-367-1120)
		5	246, 440	263	284	376
9	HERRB	1	102, 77.9	218, 56.5	281, 68.9	452, 106
		5	291, 137	327, 72.8	568, 209	332, 332
10	ESHAB	1	58.2	371 (-240-981)	41.5	-
		5	85.7, 145	-	24.6	85.8
11	GRANB	1	-	558	-	520, 216
		5	552, 57.4	616, 105	47.8	46.6
12	SQUII	1	63.8, 209	172, 747	63.4, 315	282 (112-452)
		5	-	134	65.3, 225	102, 251
13	SHELB	1	40.9	169	42.2	195
		5	371, 40.4	403, 67.9	173, 115	489, 153
14	SAWMB	1	120, 108	276, 299	163, 324	286, 619
		5	201	371	318 (-373-1010)	529 (-597-1660)
15	SLEEB	1	283 (-325-890)	575 (-667-1820)	268 (-216-752)	936 (-1440-3310)
		5	105, 69.8	86.6	143, 117	205, 369
16	SMONTS	1	72.4, 87.5	118, 270	86.9, 114	221 (107-336)
		5	756	970	922	863
17	SMONTI	1	42.2	178	68.6	182, 96.7
		5	-	-	-	58.8
18	MMONTS	1	39.2, 1010	157, 656	79.4	136, 387
		5	490	363	601	302
19	SNUGH	1	363, 604	829, 797	1069, 472	2333, 300
		5	41.9	125 (-15.5-266)	161, 143	276 (113-439)
20	SGREEI	1	367 (-267-1000)	312, 578	295 (-243-833)	350 (-8.16-708)
		5	325, 85.7	69.6	87.7	79.9
21	PCHAL	1	204, 87.7	175, 212	110, 40.2	46.0
		5	139	162	205, 147	215, 223
22	NGREEI	1	354 (-460-1170)	122, 1479	113, 60.2	742 (-1750-3240)
		5	401, 17578	610, 14386	6055	-
23	ROCKB	1	653, 6087	7363	9499	4177, 163
		5	304, 115	371, 182	215	264
24	NMONTS	1	312 (-320-944)	421 (-693-1530)	367 (-540-1270)	822 (-1640-3290)
		5	374, 110	603, 74.9	68.3	106
25	BOISL	1	143 (-37.9-325)	558, 337	174, 243	268 (131-405)
		5	2068, 391	1524, 550	818	1730
26	SELEAI	1	753 (-632-2140)	998 (-180-2180)	698 (-1020-2420)	1331 (-1900-4560)
		5	202 (40.4-364)	246 (64.6-427)	177 (-14.8-369)	524
27	SSMITI	1	767 (226-1310)	753 (-56.7-1560)	737 (57.0-1420)	1089 (-278-2460)
		5	1266, 195	1457, 198	820, 212	1815, 442
28	NSMITI	1	483 (-43.9-1010)	644 (-194-1480)	484, 844	780 (-566-2130)
		5	274 (-230-777)	272 (-185-729)	55.5	285

Table III-3--Continued.

Sequence	Sample site ^a	Depth (m)	C-32	C-34
<i>Exxon Valdez Crude</i> 1 μ L				
		N/A	N/A	
1	GRAVB	1	1629, 1506	-
		5	908	718
2	OLSEN	1	-	-
		5	572	-
3	SNUGC	1	-	-
		5	693	857
4	ECNAKEI	1	493 (431-554)	204
		5	760	-
5	MCPHERS	1	375	-
		5	48.1, 57.4	-
6	CABIB	1	433	-
		5	776, 74.4	-
7	NWBAY	1	417	-
		5	37.1, 1049	857
8	MAINB	1	248	-
		5	986	-
9	HERRB	1	415, 67.6	186
		5	877, 309	429, 75.1
10	ESHAB	1	-	-
		5	116	-
11	GRANB	1	-	-
		5	-	-
12	SQUII	1	74.7, 117	-
		5	94.1	-
13	SHELB	1	-	-
		5	168	-
14	SAWMB	1	108, 413	-
		5	245	-
15	SLEEB	1	173, 337	-
		5	156	-
16	SMONTS	1	91.7	-
		5	148	-
17	SMONTI	1	91.4	-
		5	-	-
18	MMONTS	1	106	-
		5	-	-
19	SNUGH	1	882	-
		5	203	157
20	SGREEI	1	92.2	-
		5	70.1	-
21	PCHAL	1	81.4	-
		5	226	583
22	NGREEI	1	286, 48.5	-
		5	3146	1239, 20280
23	ROCKB	1	1241	987
		5	390	755
24	NMONTS	1	174, 84.8	1152
		5	280	1039
25	BOISL	1	-	-
		5	921	750
26	SELEAI	1	72.6, 574	127, 658
		5	115	108
27	SSMITI	1	690 (-1070-2450)	1003
		5	846	749
28	NSMITI	1	-	121, 260
		5	388	-

^aSee Table III-10 for key to sampling site abbreviations.

Table III-4.--Concentrations (ng/l) of calibrated PAHs (see Table II-2, Appendix II for key to standardized abbreviations) at 1-m and 5-m depths in seawater in PWS, Alaska, 19 to 22 days following the grounding of the T/V *Exxon Valdez*. Sample stations are those listed in Table I-1, Appendix I, and are presented below in the chronological order sampled.

Sequence	Sampling site ^a	Depth (m)	Naph	Menap2	Menap1	Dimeth	Trimeth	Biphenyl	Fluorene	Dithio	Phenanth	Menphen1
30	SSMITI	1	589	79.3 ^b	48.9 ^b	-	-	-	-	-	-	-
		5	2270 ^c	235	129	-	-	-	-	-	-	-
2	OLSEN	1	618	46.6 ^b	-	-	-	55.1 ^b	-	-	-	-
		5	557	62.8 ^b	32.9 ^b	-	-	-	-	-	-	-
3	SNUGC	1	549	69.1 ^b	36.3 ^b	-	-	41.3 ^b	-	-	-	-
		5	487	65.4 ^b	35.4 ^b	-	-	31.5 ^b	-	-	-	-
12	GRANB	1	554	75.6 ^b	39.8 ^b	-	-	-	-	-	-	-
		5	97.1	-	-	-	-	-	-	-	-	-
10	NWBAY	1	1150	307	235	90.8	41.9 ^b	124	-	33.3 ^b	56.7 ^b	-
		5	2000 ^c	269	181	55.1 ^b	-	79.9 ^b	-	-	32.9 ^b	28.2 ^b
29	NSMITI	1	811	170	132	65.7 ^b	37.3 ^b	54.2 ^b	-	29.5 ^b	60.8 ^b	-
		5	2850 ^c	358	221	67.3 ^b	33.0 ^b	69.5 ^b	-	-	40.8 ^b	-
28	SELEAI	1	420	149	123	71.0 ^b	40.7 ^b	68.8 ^b	-	34.4 ^b	60.4 ^b	-
		5	1380	209	153	63.8 ^b	34.3 ^b	96.3	-	-	46.1 ^b	42.1 ^b
8	ESHAB	1	495	54.0 ^b	36.4 ^b	-	-	33.2 ^b	-	-	-	-
		5	874	108	60.3 ^b	-	-	32.3 ^b	-	-	-	-
23	SNUGH	1	307	252	210	117	59.9 ^b	58.1 ^b	31.2 ^b	46.3 ^b	75.9 ^b	31.7 ^b
		5	119	111	86.9 ^b	53.1 ^b	28.1 ^b	-	-	-	38.5 ^b	-
6	CABIB	1	423	88.5 ^b	58.4 ^b	-	-	-	-	-	-	-
		5	2180 ^c	256	154	36.7 ^b	-	-	-	-	-	-
11	HERRB	1	1990 ^c	453	357	164	84.7	229	57.9 ^b	84.3 ^b	131	54.4 ^b
		5	661	132	87.8 ^b	37.0 ^b	-	73.1 ^b	-	-	-	-
MDL			33.5	37.4	28.7	28.7	25.7	29.1	29.3	26.1	29.8	26.8

^aSee Table III-10 for key to sampling site abbreviations.

^bConcentrations above MDL, but below lowest calibration standard.

^cConcentrations above highest calibration standards.

Table III-5 --Concentrations (ng/l) of uncalibrated PAHs (see Table II-3, Appendix II) for key to standardized abbreviations) found at 1-m and 5-m depths in seawater in PWS, Alaska, 19 to 22 days following the grounding of the T/V Exxon Valdez. Sample stations are those listed in Table I-1, Appendix I, and are presented below in the chronological order sampled.

Sequence	Sampling site ^a	Depth (m)	C2naph	C3naph	C4naph	C1fluor	C2fluor	C3fluor	C1dithio	C2dithio	C3dithio	C1phenan	C2phenan	C3phenan	C4phenan	
30	SSMITI	1	80.9	55.9	-	94.9	46.9	-	-	-	-	-	46.7	-	-	
		5	111	64.7	-	275	61.7	32.4	-	-	-	-	-	38.9	-	-
2	OLSEN	1	97.5	66.2	-	48.6	-	-	-	-	29.6	-	-	-	-	-
		5	47.9	26.3	-	48.7	-	-	-	-	-	-	-	-	-	-
3	SNUGC	1	61.0	-	-	46.3	45.9	-	-	-	-	-	-	-	-	-
		5	63.7	-	-	51.0	-	-	-	-	-	-	-	27.8	-	-
12	GRANB	1	55.8	41.9	-	56.4	-	-	-	-	-	-	-	27.5	-	-
		5	52.1	31.5	-	-	-	-	-	-	-	-	-	-	-	-
29	NSMITI	1	306	208	71.4	81.0	-	-	32.4	-	-	67.7	51.3	120	-	
		5	305	197	51.8	1160	232	-	38.4	-	-	59.7	31.1	-	-	-
28	SELEAI	1	340	232	91.7	87.7	38.8	30.6	40.9	30.9	-	90.5	60.9	27.4	-	
		5	305	209	39.9	126	117	-	33.7	26.2	-	72.9	55.5	32.5	-	
8	ESHAB	1	60.5	45.3	-	59.9	91.9	-	-	-	-	-	-	-	-	
		5	70.5	41.7	-	80.6	-	-	-	-	-	-	-	30.0	-	
23	SNUGH	1	542	339	138	155	67.8	33.8	54.2	41.0	-	110	77.5	30.9	-	
		5	232	153	60.8	32.8	32.5	34.9	30.5	29.6	-	62.2	59.3	42.3	-	
6	CABIB	1	110	64.7	-	41.1	-	-	-	-	-	-	-	-	-	
		5	161	77.5	-	112	-	-	-	-	-	-	-	-	-	
10	NWBAY	1	423	251	103	129	55.9	43.2	37.2	28.5	-	75.1	58.1	43.1	-	
		5	254	150	62.0	138	-	-	-	-	-	50.0	39.6	-	-	
11	HERRB	1	777	495	190	194	115	62.1	95.3	72.3	33.2	192	133	65.9	-	
		5	176	106	43.9	69.4	-	-	-	-	-	42.5	32.5	-	-	
MDL			27.4	25.7	25.7	29.3	29.3	29.3	26.1	26.1	26.1	26.8	26.8	26.8	26.8	

^aSee Table III-10 for key to sampling site abbreviations.

Table III-6-- Concentrations (ng/l) of alkanes (see Table IV-3, Appendix IV for key to standardized abbreviations) found at 1-m and 5-m depths in seawater in PWS, Alaska, 19 to 22 days following the grounding of the T/V *Exxon Valdez*. Sample stations are those listed in Table I-1, Appendix I, and are presented below in the chronological order sampled.

Sequence	Sampling site ^a	Depth (m)	Concentration (ng/l)										
			C-10	C-11	C-12	C-13	C-14	C-16	C-17	Pristane	C-19	C-20	C-21
30	SSMITI	1	100	198	67.5	17.4	18.7	11.1	64.4	33.1	25.2	27.3	50.2
		5	-	309	127	16.2	20.6	15.4	160	26.1	37.3	49.1	85.3
2	OLSEN	1	-	72.7	96.2	-	38.9	261	53.1	-	61.8	51.4	83.0
		5	-	142	67.8	18.1	15.7	128	39.0	-	23.5	25.0	62.6
3	SNUGC	1	-	167	77.5	26.9	18.7	895	33.0	14.7	-	13.2	43.2
		5	-	169	76.3	27.7	15.2	371	35.6	15.6	16.6	21.4	61.3
12	GRANB	1	-	113	60.8	26.1	16.7	180	46.9	23.5	29.1	32.1	63.9
		5	-	60.3	45.2	28.5	29.2	4.08	27.9	17.0	19.0	24.9	59.8
29	NSMITI	1	160	211	56.6	7.24	25.6	480	50.3	23.0	48.5	51.9	72.8
		5	294	376	138	3.07	26.1	413	526	88.7	193	26.4	67.4
28	SELEAI	1	67.4	71.2	39.5	8.02	35.6	399	68.0	32.7	64.1	65.0	93.4
		5	125	160	73.1	4.63	22.8	397	77.7	-	54.4	65.7	94.8
8	ESHAB	1	111	169	64.9	13.4	19.0	306	39.3	-	21.6	42.7	66.0
		5	107	156	85.2	18.7	19.1	10.7	62.0	23.7	25.4	32.3	70.7
23	SNUGH	1	55.8	68.3	47.5	2.13	34.2	7.04	100	38.5	76.3	74.2	97.1
		5	46.6	54.8	64.1	21.4	54.4	286	50.7	41.4	69.1	75.4	107
6	CABIB	1	81.4	117	75.1	22.8	30.5	526	30.6	-	22.8	33.2	73.6
		5	133	207	112	11.8	26.2	448	69.5	-	23.7	22.4	59.7
10	NWBAY	1	-	197	87.2	24.1	33.6	19.5	88.1	52.1	73.9	73.5	110
		5	131	189	96.4	13.3	45.5	1.27	105	-	64.3	67.0	104
11	HERRB	1	162	249	105	-	48.8	35.4	169	75.2	170	172	200
		5	82.5	94.7	57.6	13.3	50.4	2.45	91.3	38.6	82.9	84.3	114

Table III-6.-- Continued.

Sequence	Sampling site ^a	Depth (m)											
			C-22	C-23	C-24	C-25	C-26	C-27	C-28	C-29	C-30	C-32	C-34
30	SSMITI	1	74.4	69.4	67.5	34.6	41.0	31.1	26.7	25.6	352	-	-
		5	87.3	93.2	98.1	73.2	99.2	41.1	54.4	64.8	324	73.5	-
2	OLSEN	1	231	325	320	267	158	164	153	142	181	236	-
		5	105	111	89.3	54.7	73.6	80.3	160	339	595	492	172
3	SNUGC	1	86.3	86.9	65.4	30.0	31.4	16.3	25.2	30.1	245	-	-
		5	142	196	222	174	169	180	329	756	1685	1125	361
12	GRANB	1	102	92.1	73.4	36.8	44.8	-	27.4	19.5	143	-	-
		5	94.3	95.1	93.3	55.9	40.1	25.1	50.8	85.1	437	116	-
29	NSMITI	1	110	96.1	69.8	29.0	33.2	26.5	28.3	28.9	144	-	-
		5	103	105	110	39.2	55.0	44.7	39.0	48.7	250	61.3	-
28	SELEAI	1	133	119	85.9	43.5	43.3	51.5	30.6	27.8	100	33.6	-
		5	129	112	102	51.8	70.5	57.5	50.8	60.6	93.8	60.3	-
8	ESHAB	1	109	105	69.8	26.2	26.4	41.9	29.9	35.1	135	37.9	-
		5	99.1	100	79.5	48.0	64.7	50.2	50.4	75.7	370	47.0	-
23=	SNUGH	1	142	129	110	49.6	93.3	46.9	40.8	34.5	36.3	35.5	-
		5	153	133	121	58.2	99.1	47.3	50.0	53.9	86.1	57.9	-
6	CABIB	1	137	114	65.7	27.7	33.8	34.1	33.1	37.0	71.4	-	-
		5	98.6	95.9	88.6	32.5	50.0	47.4	71.0	104	158	111	68.5
10	NWBAY	1	131	133	98.5	93.5	108	136	79.2	47.2	97.9	-	-
		5	145	147	137	65.3	71.5	65.8	69.3	82.8	77.8	82.6	-
11	HERRB	1	225	198	144	100	97.8	111	60.9	58.3	71.3	42.0	-
		5	158	147	112	48.8	66.3	45.7	58.7	90.0	202	231	157

^aSee Table III-10 for key to sampling site abbreviations.

Table III-7.--Concentrations (ng/l) of calibrated PAHs (see Table II-2, Appendix II for key to standardized abbreviations) found at 1-m and 5-m depths in seawater in PWS, Alaska, 39 to 45 days following the grounding of the T/V *Exxon Valdez*. Sample stations are those listed in Table I-1, Appendix I, and are presented below in the chronological order sampled.

Sequence	Sampling site ^a	Depth (m)	Concentrations (ng/l)									
			Naph	Menap2	Menap1	Dimeth	Trimeth	Biphenyl	Fluorene	Dithio	Phenanth	Menphen1
1	SNUGC	1	110	-	-	-	-	-	-	-	-	-
		5	813	79.0 ^b	45.1 ^b	-	-	-	-	-	-	-
2	CABIB	1	151	-	-	-	-	-	-	-	-	-
		5	109	-	-	-	-	-	-	-	-	-
3	OUTSI	1	241	43.4 ^b	-	-	-	-	-	-	-	-
		5	380	51.2 ^b	-	-	-	-	-	-	-	-
4	MCPHERS	1	390	-	-	-	-	-	-	-	-	-
		5	50.3 ^b	-	-	-	-	-	-	-	-	-
5	ECNAKEI	1	333	42.8 ^b	-	-	-	-	-	-	-	-
		5	327	43.9 ^b	-	-	-	-	-	-	-	-
6	ROCKB	1	219	-	-	-	-	-	-	-	-	-
		5	876	88.9 ^b	50.7 ^b	-	-	-	-	-	-	-
7	OLSEN	1	508	54.1 ^b	36.1 ^b	-	-	-	-	-	-	-
		5	260	40.3 ^b	29.4 ^b	-	-	-	-	-	-	-
8	SSMITI	1	204	-	-	-	-	-	-	-	-	-
		5	300	46.4 ^b	29.8 ^b	-	-	-	-	-	-	-
9	NSMITI	1	143	-	-	-	-	-	-	-	-	-
		5	427	40.7 ^b	28.7 ^b	-	-	-	-	-	-	-
10	SELEAI	1	208	41.1 ^b	42.3 ^b	32.8 ^b	28.1 ^b	-	-	30.1 ^b	48.0 ^b	-
		5	423	46.7 ^b	32.5 ^b	-	-	-	-	-	-	-
11	NWBAY	1	833	119	136	52.8 ^b	32.8 ^b	-	-	48.3 ^b	65.3 ^b	27.9 ^b
		5	1275	122	82.1 ^b	-	-	-	-	-	-	-
12	HERRB	1	462	64.5 ^b	76.2 ^b	40.0 ^b	-	-	-	31.3 ^b	41.3 ^b	-
		5	51.8 ^b	-	-	-	-	-	-	-	-	-
13	MAINB	1	74.6 ^b	-	-	-	-	-	-	-	-	-
		5	210	-	-	-	-	-	-	-	-	-
14	ESHAB	1	1220	109	69.9 ^b	-	-	-	-	-	-	-
		5	48.0 ^b	-	-	-	-	-	-	-	-	-
15	GRANB	1	161	-	-	-	-	-	-	-	-	-
		5	706	62.8 ^b	44.7 ^b	-	-	-	-	-	-	-
16	SQUIB	1	173	-	-	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-	-	-	-
17	BAINP	1	82.2 ^b	-	-	-	-	-	-	-	-	-
		5	800	53.9 ^b	40.6 ^b	-	-	-	-	-	-	-
18	SHELB	1	36.6 ^b	-	-	-	-	-	-	-	-	-
		5	401	40.6 ^b	-	-	-	-	-	-	-	-
19	PWALEP	1	1400	102	69.6 ^b	-	-	-	-	-	-	-
		5	1150	84.0	49.5 ^b	-	-	-	-	-	-	-
20	ELRIP	1	743	84.1	48.9 ^b	-	-	-	-	-	-	-
		5	536	44.5 ^b	34.1 ^b	-	-	-	-	-	-	-
21	SAWMB	1	425	49.9 ^b	29.8 ^b	-	-	-	-	-	-	-
		5	37.9	-	-	-	-	-	-	-	-	-
23	SNUGH	1	711	85.0	59.5 ^b	-	-	-	-	-	-	-
		5	106	-	-	-	-	-	-	-	-	-
24	MMONTS	1	68.4	-	-	-	-	-	-	-	-	-
		5	364	-	32.4 ^b	-	-	-	-	-	-	-
25	SGREEI	1	960	95.5	54.1 ^b	-	-	-	-	-	-	-
		5	247	-	-	-	-	-	-	-	-	-
26	PCHAL	1	406	48.7 ^b	-	-	-	-	-	-	-	-
		5	268	-	-	-	-	-	-	-	-	-
27	NGREEI	1	134	-	-	-	-	-	-	-	-	-
		5	482	55.2 ^b	31.1 ^b	-	-	-	-	-	-	-
28	BOISL	1	187	-	-	-	-	-	-	-	-	-
		5	36.0	-	-	-	-	-	-	-	-	-
29	NMONTS	1	437	47.8 ^b	31.1 ^b	-	-	-	-	-	-	-
		5	162	-	-	-	-	-	-	-	-	-
MDL			33.5	37.4	28.7	28.7	25.7	29.1	29.3	26.1	29.8	26.8

^aSee Table III-10 for key to sampling site abbreviations.

^bConcentrations above lowest MDL, but below lowest calibration standard.

Table III-8.--Concentrations (ng/l) of uncalibrated PAHs (see Table II-3, Appendix II for key to standardized abbreviations) found at 1-m and 5-m depths in seawater in PWS, Alaska, 39 to 45 days following the grounding of the T/V *Exxon Valdez*. Sample stations are those listed in Table I-1, Appendix I, and are presented below in the chronological order sampled.

Sequence	Sampling site ^a	Depth (m)	C2naph	C3naph	C4naph	C1fluor	C2fluor	C3fluor
7	OLSEN	1	55.7	-	-	71.0	-	-
		5	90.8	133	112	50.6	36.8	-
1	SNUGC	1	31.4	-	-	-	-	-
		5	30.5	-	-	53.9	-	-
5	ECNAKEI	1	-	-	-	66.2	-	-
		5	29.8	-	-	33.5	-	-
4	MCPHERS	1	-	-	-	39.5	74.6	-
		5	-	-	-	-	-	-
2	CABIB	1	-	-	-	-	-	-
		5	-	45.4	36.3	34.3	-	-
11	NWBAY	1	264	186	106	104	45.9	-
		5	112	53.0	-	380	-	-
13	MAINB	1	-	-	-	45.6	-	-
		5	-	-	-	86.4	-	-
12	HERRB	1	197	136	46.0	56.9	38.2	49.6
		5	37.1	-	-	32.4	-	68.0
14	ESHAB	1	44.4	-	-	158	-	-
		5	-	-	-	-	-	-
15	GRANB	1	-	-	-	29.5	-	-
		5	-	-	-	259	-	-
16	SQUIB	1	-	-	-	-	-	-
		5	-	-	-	-	-	-
18	SHELB	1	39.2	-	-	79.8	-	-
		5	39.0	31.3	-	75.4	-	-
21	SAWMB	1	33.3	-	-	284	-	-
		5	29.3	-	-	-	30.2	-
24	MMONTS	1	-	-	-	-	-	-
		5	-	-	-	62.8	39.4	-
23	SNUGH	1	75.9	34.7	30.1	237	35.0	-
		5	35.4	-	-	-	-	-
25	SGREEI	1	35.9	-	-	87.2	-	-
		5	-	-	-	61.3	-	-
26	PCHAL	1	30.0	-	-	110	-	-
		5	-	-	35.7	120	-	-
27	NGREEI	1	-	-	-	117	-	-
		5	30.5	-	-	37.0	-	-
6	ROCKB	1	-	-	-	35.1	-	-
		5	38.8	-	-	77.5	-	-
29	NMONTS	1	50.1	32.5	-	104	-	-
		5	-	-	-	56.9	-	-
28	BOISL	1	48.8	26.2	-	83.0	-	-
		5	-	-	-	31.8	-	-
10	SELEAI	1	172	140	117	176	59.8	41.9
		5	82.9	79.4	31.2	53.7	33.3	-
8	SSMITI	1	47.6	69.3	63.8	83.8	-	-
		5	58.9	59.9	59.0	-	44.4	-
9	NSMITI	1	48.0	53.0	57.8	52.9	34.0	-
		5	48.3	51.3	40.4	73.1	-	-
3	OUTSI	1	-	-	-	-	-	-
		5	-	-	-	40.3	-	-
20	ELRIP	1	48.8	27.0	-	117	-	-
		5	38.8	-	-	110	-	-
19	PWALEP	1	32.9	-	-	103	39.4	-
		5	33.4	-	-	196	-	-
17	BAINP	1	29.9	-	-	-	-	-
		5	28.8	-	-	69.7	-	-
MDL			27.4	25.7	25.7	29.3	29.3	29.3

Table III-8.--Continued.

Sequence	Sampling site ^a	Depth (m)	C1dithio	C2dithio	C3dithio	C1phenan	C2phenan	C3phenan	C4phenan
7	OLSEN	1	-	-	-	-	-	83.3	-
		5	-	-	-	48.6	38.3	-	-
1	SNUGC	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
5	ECNAKEI	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
4	MCPHERS	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
2	CABIB	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	79.1	-
11	NWBAY	1	91.5	63.6	40.3	115	83.1	42.9	-
		5	-	-	-	36.0	27.3	-	-
13	MAINB	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	70.5	-
12	HERRB	1	32.5	27.1	-	63.8	45.3	-	-
		5	-	-	-	-	-	-	-
14	ESHAB	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	38.7	-
15	GRANB	1	-	-	-	-	-	45.5	-
		5	-	-	-	-	-	-	-
16	SQUIB	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
18	SHELB	1	-	-	-	31.7	29.9	-	-
		5	-	-	-	28.0	-	-	-
21	SAWMB	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
24	MMONTS	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
23	SNUGH	1	44.8	47.3	42.9	48.6	36.3	-	-
		5	-	-	-	-	-	-	-
25	SGREEI	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
26	PCHAL	1	-	-	-	-	-	-	-
		5	31.1	-	-	-	-	-	-
27	NGREEI	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
6	ROCKB	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	45.9	-
29	NMONTS	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
28	BOISL	1	-	-	-	-	27.2	-	-
		5	-	-	-	-	-	-	-
10	SELEAI	1	70.4	61.2	31.6	88.1	52.4	-	-
		5	-	-	-	35.1	32.4	135	-
8	SSMITI	1	27.3	-	-	43.8	27.3	-	-
		5	27.0	28.2	-	47.8	41.3	36.0	-
9	NSMITI	1	-	-	-	40.6	36.2	-	-
		5	-	-	-	36.0	-	-	-
3	OUTSI	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
20	ELRIP	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
19	PWALEP	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
17	BAINP	1	-	-	-	-	-	-	-
		5	-	-	-	-	-	-	-
MDL			26.1	26.1	26.1	26.8	26.8	26.8	26.8

^aSee Table III-10 for key to sampling site abbreviations.

Table III-9.--Concentrations (ng/l) of alkanes (see Table IV-3, Appendix IV for key to standardized abbreviations) found at 1-m and 5-m depths in seawater in PWS, Alaska, 39 to 45 days following the grounding of the T/V *Exxon Valdez*. Sample stations are those listed in Table I-1, Appendix I, and are presented below in the chronological order sampled.

Sequence	Sampling site*	Depth (m)	C-10	C-11	C-12	C-13	C-14	C-16	C-17	Pristane	C-19	C-20	C-21
7	OLSEN	1	531	324	131	75.2	39.8	67.6	222	121	233	91.6	97.0
		5	426	333	99.4	84.2	97.7	605	686	527	535	452	347
1	SNUGC	1	928	251	86.5	47.6	29.3	31.7	70.0	43.4	47.5	46.0	97.3
		5	1307	509	114	37.4	38.7	27.0	198	-	49.5	73.5	210
5	ECNAKEI	1	651	383	122	45.5	33.2	43.3	232	138	78.3	63.0	87.8
		5	736	358	139	61.7	32.5	43.4	129	89.6	70.1	68.1	104
4	MCPHERS	1	653	322	86.0	47.6	29.2	50.1	152	116	58.2	50.9	84.8
		5	638	334	96.1	29.5	-	40.5	137	68.7	58.9	42.6	93.1
2	CABIB	1	809	297	107	34.9	35.9	27.9	82.7	48.7	56.2	-	77.4
		5	599	223	85.1	48.2	28.5	180	344	283	229	172	192
11	NWBAY	1	1112	558	155	82.0	82.5	81.6	452	-	526	81.5	156
		5	2170	1210	221	81.8	104	254	822	-	225	175	155
13	MAINB	1	320	160	61.1	153	569	849	241	135	343	147	50.4
		5	385	229	74.9	54.2	68.1	91.5	319	-	80.0	59.5	116
12	HERRB	1	603	364	86.4	89.5	131	157	166	98.3	620	1134	2867
		5	326	218	83.2	58.1	61.0	59.8	129	80.7	53.3	42.4	78.3
14	ESHAB	1	531	336	82.7	55.4	62.7	77.6	121	-	50.6	40.3	54.7
		5	276	157	66.7	47.4	48.8	92.6	85.2	50.1	113	74.4	105
15	GRANB	1	114	100	41.0	58.1	75.7	110	142	73.3	81.3	65.9	99.0
		5	216	270	85.4	45.7	53.1	51.9	118	-	139	41.9	63.7
16	SQUIB	1	124	123	50.6	51.2	45.3	67.6	86.0	40.3	60.9	57.7	83.5
		5	57.3	89.0	27.3	41.6	44.8	41.5	86.6	68.8	69.8	33.5	47.8
18	SHELB	1	98.4	92.1	28.7	33.7	34.4	57.3	206	113	95.7	97.8	127
		5	106	112	50.6	62.3	42.7	48.9	257	-	436	201	84.0
21	SAWMB	1	280	152	-	105	79.9	87.0	519	-	128	37.5	37.7
		5	231	107	29.2	68.9	52.8	87.2	112	58.7	71.3	65.4	168
24	MMONTS	1	233	94.1	42.6	44.8	47.6	54.5	86.7	50.3	55.9	35.6	67.6
		5	283	202	56.2	50.6	49.0	35.6	139	62.5	66.6	41.4	65.5
23	SNUGH	1	364	408	124	53.3	39.3	41.4	85.3	-	417	496	152
		5	209	119	53.0	32.1	26.0	36.5	55.2	48.0	84.6	50.3	136
25	SGREEI	1	434	254	71.2	39.7	39.4	41.1	215	-	35.6	38.5	75.4
		5	265	113	69.0	59.6	34.6	49.2	141	-	42.0	-	31.9
26	PCHAL	1	196	159	48.4	34.1	50.6	42.9	287	-	109	72.1	120
		5	303	295	70.9	48.7	38.9	42.5	56.5	-	443	541	158
27	NGREEI	1	195	70.4	44.9	-	32.5	-	270	-	193	-	107
		5	315	200	53.0	52.5	49.8	65.5	108	53.8	56.6	39.8	175
6	ROCKB	1	431	339	81.6	29.7	32.2	34.4	235	97.3	121	91.4	187
		5	424	263	96.8	41.9	36.5	31.6	238	-	91.6	83.4	118
29	NMONTS	1	204	132	42.2	44.3	42.5	68.6	259	-	160	60.5	125
		5	153	109	76.5	-	52.5	64.8	154	-	499	385	297
28	BOISL	1	153	140	50.5	52.3	45.4	36.0	39.5	-	43.6	31.0	67.7
		5	125	66.9	-	43.6	34.4	51.6	87.8	49.6	102	-	33.8
10	SELEAI	1	252	127	66.3	113	202	187	282	165	1196	551	156
		5	487	242	91.7	113	139	215	237	162	155	163	149
8	SSMITI	1	481	230	105	196	510	641	416	282	766	458	191
		5	584	261	121	110	201	402	343	287	278	204	173
9	NSMITI	1	483	228	100	114	218	2677	290	221	208	155	207
		5	652	273	103	117	160	358	369	263	250	166	137
3	OUTSI	1	688	392	132	53.7	66.0	33.9	137	79.7	70.1	75.5	220
		5	811	333	121	57.7	47.8	20.7	128	-	41.5	50.4	101
20	ELRIP	1	255	279	89.1	84.8	52.9	165	505	-	68.0	51.7	163
		5	193	186	61.5	56.9	43.0	35.8	61.7	-	47.2	42.6	82.4
19	PWALEP	1	419	364	103	62.2	49.6	58.6	61.2	-	78.7	55.8	83.2
		5	247	195	-	120	91.0	92.9	387	-	111	43.4	138
17	BAJNP	1	70.2	65.0	42.5	55.5	48.2	52.7	76.7	54.4	74.0	48.9	135
		5	234	229	68.4	111	73.4	88.4	210	88.4	77.6	64.1	118

Table III-9.-- Continued.

Sequence	Sampling site ^a	Depth (m)	C-22	C-23	C-24	C-25	C-26	C-27	C-28	C-29	C-30	C-32	C-34
7	OLSEN	1	58.7	72.0	122	160	169	171	142	150	593	594	317
		5	304	254	134	82.8	100	122	146	173	228	208	208
1	SNUGC	1	133	107	83.1	55.8	34.2	68.0	37.1	68.4	67.1	-	-
		5	298	507	585	99.3	32.9	36.5	43.9	47.6	131	151	-
5	ECNAKEI	1	130	127	83.1	91.6	62.1	102	54.0	80.6	54.7	-	-
		5	123	107	62.9	60.6	54.7	98.8	45.3	69.3	-	-	-
4	MCPHERS	1	126	130	74.4	89.0	83.4	89.9	49.6	62.2	48.9	-	-
		5	128	197	100	54.5	-	43.9	37.7	115	67.1	-	-
2	CABIB	1	131	151	180	214	239	220	145	174	167	-	-
		5	164	142	132	153	26.1	68.0	-	80.1	-	-	-
11	NWBAY	1	141	162	301	168	232	136	186	164	133	75.6	54.8
		5	132	114	110	65.8	63.7	83.0	62.7	109	125	-	-
13	MAINB	1	84.2	74.5	79.9	82.6	65.2	98.6	94.8	92.2	64.7	-	-
		5	84.7	73.2	57.0	49.0	67.9	97.1	74.5	97.9	83.4	-	-
12	HERRB	1	4084	4999	4251	5102	127	130	105	186	177	150	-
		5	90.0	81.7	67.0	68.8	91.3	103	158	165	193	124	88.5
14	ESHAB	1	75.6	90.6	92.4	59.8	65.2	55.9	70.9	67.1	90.6	52.6	-
		5	115	112	85.5	92.2	185	272	261	286	226	-	-
15	GRANB	1	50.3	44.5	56.8	98.0	66.5	74.5	130	212	283	360	91.0
		5	66.6	80.9	120	54.1	49.7	57.6	172	121	163	96.1	-
16	SQUIB	1	47.6	44.4	46.2	55.7	65.2	84.3	92.1	134	162	223	-
		5	49.0	45.3	32.3	40.4	39.0	38.2	98.6	102	127	147	-
18	SHELB	1	102	88.7	90.2	111	107	105	57.8	85.9	92.4	-	-
		5	58.8	51.2	53.8	96.3	113	241	179	248	119	134	-
21	SAWMB	1	53.2	52.4	73.1	36.1	45.6	43.9	66.2	80.7	127	70.6	-
		5	373	371	286	269	259	266	477	569	816	663	244
24	MMONTS	1	100	149	73.3	50.7	33.3	41.8	66.6	87.0	140	134	-
		5	87.6	102	79.4	32.3	-	42.2	113	151	221	171	72.0
23	SNUGH	1	167	175	184	185	145	-	1554	670	420	80.0	-
		5	180	158	99.2	103	68.4	80.9	101	99.0	277	239	-
25	SGREEI	1	84.3	73.8	63.7	62.6	73.1	122	271	625	972	891	306
		5	47.5	33.8	35.5	-	-	-	-	51.4	76.4	-	-
26	PCHAL	1	91.1	126	70.2	40.7	28.3	39.4	111	126	156	94.0	-
		5	173	208	167	178	112	261	368	141	254	-	-
27	NGREEI	1	239	289	292	267	253	226	214	174	190	95.8	-
		5	185	167	49.9	41.3	47.0	44.6	81.3	68.1	122	64.1	-
6	ROCKB	1	279	227	81.6	74.3	59.2	56.4	66.4	70.6	92.7	-	-
		5	129	116	78.2	84.3	47.0	86.5	50.2	65.0	-	-	-
29	NMONTS	1	131	149	152	151	154	124	213	161	196	114	-
		5	348	378	175	194	140	100	53.6	59.4	215	-	-
28	BOISL	1	114	182	285	169	174	141	171	192	304	166	101
		5	48.6	80.6	180	152	88.5	28.5	87.9	149	353	263	-
10	SELEAI	1	109	62.3	63.8	57.3	124	213	329	257	246	175	256
		5	74.8	66.2	90.7	138	241	330	432	619	716	732	404
8	SSMITI	1	113	117	159	266	225	325	464	369	306	255	197
		5	104	84.6	87.8	120	213	382	251	249	239	269	214
9	NSMITI	1	181	227	96.1	210	403	466	606	687	683	667	466
		5	78.5	68.1	80.0	132	178	232	235	306	331	449	255
3	OUTSI	1	317	270	88.4	83.9	73.8	86.1	89.5	111	172	96.5	-
		5	134	204	164	186	94.4	144	55.7	90.1	-	-	-
20	ELRIP	1	157	157	66.1	57.2	49.4	55.4	73.1	80.2	93.4	117	-
		5	115	131	115	42.9	36.9	36.9	61.1	80.8	135	86.3	-
19	PWALEP	1	106	105	89.3	49.9	40.9	40.4	73.6	50.4	83.2	55.1	-
		5	295	270	319	146	100	67.2	141	180	282	203	146
17	BAINP	1	50.1	37.9	33.6	38.0	40.0	73.1	48.1	84.4	309	274	-
		5	120	127	122	71.8	137	237	658	1396	2345	2025	844

^aSee Table III-10 for key to sample site abbreviations.

Table III-10.--Key to sampling site abbreviations.

Sampling site	Abbreviation
Gravina Point	GRAVB
Olsen Bay	OLSEN
Snug Corner Cove	SNUGC
East Naked Island	ECNAKEI
McPhearson Bay	MCPHERS
Cabin Bay	CABIB
Northwest Bay, Eleanor Island	NWBAY
Main Bay	MAINB
Herring Bay	HERRB
Eshamy Bay	ESHAB
Granite Bay	GRANB
Squire Island	SQUII
Shelter Bay	SHELB
Sawmill Bay	SAWMB
Sleepy Bay	SLEEB
South Montague Strait	SMONTS
South Montague Island	SMONTI
Mid Montague Strait	MMONTS
Snug Harbor	SNUGH
South Green Island	SGREEI
Port Chalmers	PCHAL
North Green Island	NGREEI
Rocky Bay	ROCKB
North Montague Strait	NMONTS
Bay of Isles	BOISL
Southeast Eleanor Island	SELEAI
South Smith Island	SSMITI
North Smith Island	NSMITI

APPENDIX IV

Table IV-1.--Summary of calibrated PAH concentrations measured in reference samples. Two reference samples were processed and analyzed with each batch of 12 seawater samples from PWS. Listed below for each calibrated PAH is (1) the mean measured concentration, calculated from all the reference samples analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as the ratio of (2) and (1); (4) the nominal PAH concentrations present in each reference sample, as determined by the National Institute of Standards and Technology (NIST) (except for dibenzothiophene); (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4); and (6) the number, n, of reference samples included for these calculations. A total of 21 batches were analyzed; n may be less than twice this number due to unacceptable recovery of associated deuterated surrogate standards (see Methods section). Except for dibenzothiophene, which was purchased commercially, the PAHs in these reference samples were derived from Standard Reference Material 1491, supplied by NIST. The concentrations are reported as ng PAH/l seawater.

PAH	Mean (1)	Std Dev (2)	CV (3)	Amount Spiked (4)	Percent Accuracy (5)	n (6)
Naphthalene	1180	33.1	0.0281	1140	103	40
2-Methylnaphthalene	1320	57.6	0.0435	1300	102	40
1-Methylnaphthalene	1390	54.9	0.0394	1370	101	40
2,6-Dimethylnaphthalene	1220	50.4	0.0415	1190	102	42
2,3,5-Trimethylnaphthalene	1110	66.9	0.0603	1090	102	42
Biphenyl	1190	63.4	0.0533	1160	103	42
Acenaphthylene	1150	74.4	0.0647	1150	99.8	42
Acenaphthene	1230	33.1	0.0269	1200	102	42
Fluorene	1230	82.1	0.0666	1200	103	42
Dibenzothiophene	800	59.0	0.0738	900	88.8	36
Phenanthrene	1190	67.4	0.0564	1160	103	42
1-Methylphenanthrene	1220	93.5	0.0768	1160	105	42
Anthracene	1260	139	0.111	1290	97.2	42
Fluoranthene	1010	90.7	0.0897	978	103	42
Pyrene	999	104	0.104	975	102	42
Benz-a-anthracene	548	76.9	0.140	594	92.3	40
Chrysene	1240	130	0.105	1160	107	40
Benzo-b-fluoranthene	932	161	0.173	869	107	38

Table IV-2.--Summary of calibrated PAH concentrations measured in calibration stability samples. A mid-level calibration standard was analyzed in the middle and near the end of each batch of 12 seawater samples from PWS to verify the stability of the calibration curve determined initially for the batch. Listed below for each calibrated PAH is (1) the mean measured concentration, calculated from all the verification standards analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as the ratio of (2) and (1); (4) the nominal concentration of the standard; (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4); and (6) the number, n, of verification standards included for these calculations. A total of 21 batches were analyzed; n may be less than twice this number due to unacceptable recovery of associated deuterated surrogate standards (see Methods section). Concentrations are reported as ng PAH/l seawater.

PAH	Mean (1)	Std Dev (2)	CV (3)	Amount Spiked (4)	Percent Accuracy (5)	n (6)
Naphthalene	347	3.61	0.0104	345	101	42
2-Methylnaphthalene	379	11.3	0.0299	395	96.1	42
1-Methylnaphthalene	402	10.8	0.0269	415	96.8	42
2,6-Dimethylnaphthalene	340	12.0	0.0353	360	94.5	42
2,3,5-Trimethylnaphthalene	303	16.4	0.0542	330	91.9	42
Biphenyl	344	12.9	0.0375	350	98.1	42
Acenaphthylene	323	18.3	0.0566	348	92.9	42
Acenaphthene	359	7.99	0.0223	364	98.6	42
Fluorene	331	21.6	0.0653	364	91.0	42
Dibenzothiophene	376	12.4	0.0328	400	94.1	42
Phenanthrene	343	7.21	0.0210	351	97.7	42
1-Methylphenanthrene	308	15.4	0.0501	350	87.9	42
Anthracene	372	23.0	0.0618	391	95.0	42
Fluoranthene	253	17.6	0.0698	296	85.5	42
Pyrene	251	19.9	0.0793	295	85.1	42
Benz-a-anthracene	171	19.2	0.112	180	95.3	40
Chrysene	337	35.7	0.106	352	95.9	40
Benzo-b-fluoranthene	230	22.9	0.0997	263	87.6	41

Table IV-3.--Summary of alkane concentrations measured in reference samples. Two reference samples were processed and analyzed with each batch (except for the first 6 batches) of 12 seawater samples from PWS. Listed below for each alkane (and the standardized abbreviation) is (1) the mean measured concentration, calculated from all the reference samples analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as the ratio of (2) and (1); (4) the nominal alkane concentrations present in each reference sample; (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4); and (6) the number, n, of reference samples included for these calculations. A total of 21 batches were analyzed; n is less than twice this number because reference samples were not included with the first six batches analyzed, and because of documented processing errors. These reference samples were prepared from commercially purchased alkanes. The concentrations are reported below are calculated as ng alkane/l seawater.

Alkane	Abbreviation	Mean (1)	Std Dev (2)	CV (3)	Amount Spiked (4)	Percent Accuracy (5)	n (6)
n-Decane	C-10	11200	985	0.0883	12800	87.5	29
n-Undecane	C-11	11100	1010	0.0907	12100	91.7	29
n-Dodecane	C-12	12100	993	0.0824	12900	93.5	29
n-Tridecane	C-13	12600	1020	0.0809	13300	94.7	29
n-Tetradecane	C-14	12200	934	0.0766	12300	99.5	30
n-Hexadecane	C-16	12800	881	0.0686	13200	97.4	30
n-Heptadecane	C-17	13800	491	0.0356	14500	95.5	30
Pristane		14000	926	0.0662	13600	103	30
n-Octadecane	C-18	15800	943	0.0598	15400	102	24
n-Nonadecane	C-19	13700	3300	0.240	13500	102	30
n-Eicosane	C-20	12100	549	0.0453	12000	100	30
n-Heneicosane	C-21	11400	694	0.0607	11800	97.2	30
n-Docosane	C-22	13000	794	0.0613	13400	96.9	30
n-Tricosane	C-23	11600	724	0.0626	12000	96.6	30
n-Tetracosane	C-24	12000	821	0.0685	12500	96.2	30
n-Pentacosane	C-25	11400	830	0.0727	11800	97.0	30
n-Hexacosane	C-26	11400	1060	0.0929	11700	98.0	30
n-Heptacosane	C-27	5230	1080	0.206	4930	106	30

Table IV-4.--Summary of alkane concentrations measured in calibration stability samples. A mid-level calibration standard was analyzed in the middle and near the end of each batch of 12 seawater samples from PWS to verify the stability of the calibration curve determined initially for the batch. Listed below, for each alkane (and the standardized abbreviation) is (1) the mean measured concentration, calculated from all the verification standards analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as the ratio of (2) and (1); (4) the nominal concentration of the standard; and (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4). A total of 42 verification standards in the 21 batches analyzed were included for these calculations. Concentrations are reported as ng alkane/l seawater.

Alkane	Abbreviation	Mean (1)	Std Dev (2)	CV (3)	Amount Spiked (4)	Percent Accuracy (5)
n-Decane	C-10	12500	782	0.0627	12700	98.0
n-Undecane	C-11	12100	745	0.0617	12100	99.6
n-Dodecane	C-12	13000	709	0.0546	12900	101
n-Tridecane	C-13	13500	592	0.0438	13300	102
n-Tetradecane	C-14	13000	428	0.0329	12700	102
n-Pentadecane	C-15	12200	297	0.0243	12000	102
n-Hexadecane	C-16	13400	230	0.0171	13200	102
n-Heptadecane	C-17	14200	302	0.0212	14500	98.3
Pristane		14500	465	0.0321	13600	108
n-Octadecane	C-18	15700	210	0.0134	15400	102
n-Nonadecane	C-19	13700	244	0.0178	13500	102
n-Eicosane	C-20	12300	300	0.0245	12100	101
n-Heneicosane	C-21	11900	389	0.0327	11800	101
n-Docosasne	C-22	13500	558	0.0413	13400	101
n-Tricosane	C-23	12100	603	0.0500	12000	101
n-Tetracosine	C-24	12500	722	0.0576	12500	101
n-Pentacosane	C-25	11800	757	0.0642	11800	101
n-Hexacosane	C-26	11700	826	0.0703	11700	100

Table IV-5.--Summary of alkane concentrations measured in alkane accuracy evaluation standards. One accuracy evaluation standard analyzed at the end of each batch of 12 seawater samples from PWS to verify the accuracy of alkane determinations. Listed below for each alkane (and the standardized abbreviation) is (1) the mean measured concentration, calculated from all the verification standards analyzed; (2) the standard deviation associated with (1); (3) the coefficient of variation (CV), calculated as the ratio of (2) and (1); (4) the nominal concentration of the standard, as determined by the National Institute of Standards and Technology (NIST); and (5) the percent accuracy, calculated as 100 times the ratio of (1) and (4). A total of 42 verification standards in the 21 batches analyzed were included for these calculations. The alkanes in this standard were derived from an alkane standard supplied by NIST labelled QA-CH-2. Concentrations are reported as ng alkane/l seawater.

Alkane	Abbreviation	Mean (1)	Std Dev (2)	CV (3)	Amount Spiked (4)	Percent Accuracy (5)
n-Decane	C-10	8770	805	0.0925	9300	93.5
n-Undecane	C-11	9120	789	0.0865	10580	86.2
n-Dodecane	C-12	8890	717	0.0865	9300	95.6
n-Tridecane	C-13	8400	627	0.0746	8700	96.6
n-Tetradecane	C-14	8410	581	0.0691	8630	97.4
n-Pentadecane	C-15	8250	530	0.0642	8480	97.2
n-Hexadecane	C-16	7220	432	0.0599	7400	97.5
n-Heptadecane	C-17	6550	384	0.0587	6830	95.8
Pristane		4500	301	0.0668	4340	104
n-Octadecane	C-18	6320	333	0.0527	6410	98.5
Phytane		490	24.8	0.0506	450	109
n-Nonadecane	C-19	5370	274	0.0509	5480	98.0
n-Eicosane	C-20	5210	260	0.0500	5270	98.8
n-Docosane	C-22	4170	229	0.0550	4280	97.3
n-Tetracosane	C-24	3060	210	0.0686	3210	95.3
n-Hexacosane	C-26	2220	195	0.0880	2360	93.9
n-Octacosane	C-28	1500	167	0.112	1600	92.9
n-Triacontane	C-30	1050	169	0.160	1160	90.9