DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

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COMPARISON OF *EXXON VALDEZ* OIL WITH EXTRACTABLE MATERIAL FROM DEEP-WATER BOTTOM SEDIMENT IN PRINCE WILLIAM SOUND AND THE GULF OF ALASKA

John B. Rapp, Frances D. Hostettler, and Keith A. Kvenvolden
U.S. Geological Survey, Menlo Park, CA

INTRODUCTION

On March 24, 1989, the oil tanker *Exxon Valdez* collided with Bligh Reef in Prince William Sound and released about 11 million gallons of Alaska North Slope crude oil into the environment. Currents and wind spread the oil through the western parts of the sound and southwestward along the coast of the Gulf of Alaska (Kenai Peninsula, Kodiak Island, and beyond). Pollution of the beaches and wildlife was soon observed. The objective of our study, conducted 1 1/2 months after the spill, was to determine if oil had been incorporated into the bottom sediment at sampling locations where water depths ranged from 95 to 755 meters.

Many factors contribute to the fact that oil can sink from the surface of the water and be incorporated into the bottom sediment. Low-molecular-weight compounds may be volatilized on exposure to air, other low-molecular-weight compounds may be leached into the water (e.g., polycyclic aromatic hydrocarbons), and particulate matter may be incorporated into the oil. All these factors would tend to increase the density of the oil, which would sink as it became heavier than the water. Once on the bottom, the oil may be incorporated into the sediment by bioturbation or by burial with fresh sediment. The rates at which these factors act depend on several variables, including the characteristics of the oil (high vs. low gravity, aromatic rich vs. aliphatic rich, etc.) and environmental conditions (wind, currents and temperature).

Levels of oil pollution range from levels visible to the naked eye, such as a thick layer of oil on a beach, to levels of parts per billion and parts per trillion, detectable only with sophisticated analytical equipment. To the question "Is this sample polluted with oil?" must be added the phrase "and, if so, at what concentration level". If a pollutant is not normally present in the sample matrix, the procedure would be to isolate the pollutant from the sample, measure its concentration, and state that the sample was polluted at that concentration level. If a pollutant is normally present in the sample matrix, the interpretation is more complex. The background level (range of concentrations) must first be determined. In order for a sample to be called "polluted", the concentration of the pollutant must exceed this background range. The level of pollution is then defined as the difference between the concentration of the pollutant in the sample and that in the background. Oil is an extremely complex mixture of organic compounds, and many of its constituents occur naturally in unpolluted sedimentary systems. Because of this complexity, it is useful to compare gas chromatograms and mass fragmentograms of oil fractions (e.g. aliphatic and aromatic fractions) with the corresponding sample fractions in order to find differences between the patterns of the oil constituents and those of the background sample constituents. The greater the difference between the patterns, the easier it is to determine if a sample is polluted.

METHODS

Heavy Hydrocarbons

Sampling: Samples were obtained by box corer between May 11 and May 14, 1989, from the M/V *Farnella*. Fifteen sites were sampled for hydrocarbon analyses: 12 from within Prince William Sound (Figure 1A) and 3 from the Gulf of Alaska between the sound and Kodiak Island (Figure 1B). The top 8 cm of sediment were subsampled from box cores except station 6A, where an additional sample was taken from 18 to 22 cm. All samples analyzed for hydrocarbons were obtained from sites where the water was deeper than 100 m except station 18A, where the water depth was 95 m. Table 1 contains the sample numbers and the corresponding water depths at the stations. The letter after the station number indicates which of the multiple box cores was sampled. Hereafter, the sample number is referred to only by the station number except station 6, for which the sampling interval is appended (e.g., 6: 18 to 22 cm). Sediments were sampled with an acetone-rinsed stainless-steel cylinder, placed into glass jars (previously heated to 450 °C.) with solvent-rinsed aluminum-foil-lined lids, and immediately frozen. Before storage, portions of the samples were observed with visible light and with ultraviolet light (long wave at 365 nm and short wave at 254 nm).

Initially we were concerned that oil floating on the water might contaminate the sampling equipment as it was deployed. The concern did not materialize because no oil was seen on the water surface at any of the sampling sites.

Laboratory Preparation: Samples were kept frozen from the time of sampling until they were freeze dried. The freeze-dried sediment was ground until it passed through a 32 mesh screen. Samples weighing 100 g were extracted three times with dichloromethane (DCM) on a wrist-action shaker (200 ml DCM for 2 hours, 100 ml for 2 hours, and 100 ml for 15 minutes). The extracts were concentrated to <5 ml on a rotary evaporator and passed through activated copper to remove elemental sulfur. The resultant sulfur-free extract (SFE) was analyzed by gas chromatography and an aliquot was weighed.

Eight samples (2, 4, 7, 9, 12, 15 and 17) were fractionated by liquid-solid chromatography. The solvent of the SFE was exchanged with hexane on a rotary evaporator, and the SFE was applied to a column of 5-g and 2.5-g activated silica gel (Davidson Nos. 923 and 62, respectively) and 2.5-g deactivated (5% water) alumina. The column was eluted with hexane, 20, 40, 60% benzene in hexane, benzene, and methanol to produce 6 fractions. The hexane fraction contained normal alkanes, isoprenoids, and polycyclic biomarkers. The 20% benzene in hexane contained polycyclic aromatic hydrocarbons (PAH's). All fractions were analyzed by gas chromatography (GC). The hexane and 20% benzene in hexane fractions were analyzed by gas chromatography/mass spectrometry (GC/MS).

Analysis: Gas chromatography was performed on a gas chromatograph with flame ionization detector and a 30-m x 0.3-mm DB-1 bonded-phase fused-silica capillary column. The temperature program used was: initial temperature 90 °C for 3 min followed by a ramp of 4 °C/min to 310 °C, and a final hold for 20 min. Injection port and detector temperatures were 300 °C, and column-inlet pressure was 10 psi helium, splitless injection. GC/MS used a 30-m x 0.3-mm SE-54 bonded-phase fused-silica capillary column with splitless injection. Two temperature programs were used: 1) initial temperature 60 °C, fast ramp to 90 °C, 6 °C/min to 300 °C then hold for 10 min; and 2) initial temperature 150 °C, fast ramp to 200 °C, 1 °C/min to 300 °C. Hydrocarbon biomarkers in the hexane fraction were analyzed using selected ion

monitoring (SIM), monitoring mass to charge ratio (m/z) 191 for terpanes and triterpanes and 217 for steranes and diasteranes. Biomarker identifications were made as in previous studies (Kvenvolden and others, 1985). Selected ratios were calculated (see Table 3) using peak heights. Organic carbon was determined on the freeze-dried, 32 mesh samples by wet combustion following the procedure of Bush (1970).

Gaseous Hydrocarbons

In addition to analysis for heavy hydrocarbons, six samples from two sites (9 and 10) were analyzed for gaseous hydrocarbons. Procedures for gas analyses were adapted from Kvenvolden and Redden (1980). Samples were collected by gravity coring, and 10-cm-long segments of each core were placed in metal cans, prepared with septa-covered ports. To each can was added enough degassed water to establish a 100-cc headspace when the can was sealed. The headspace was purged with helium through the septa, and the can was stored in a freezer. For gas extraction, the samples were thawed, and the cans were shaken vigorously for ten minutes. Gases diffused into the headspace, a portion of which was analyzed by gas chromatography. Concentrations of the hydrocarbon gases were determined by integration. The chromatograph was calibrated with standard mixtures of gases. Results for hydrocarbon gases are reported in parts per million (ppm) of the gas mixture and in microliters/liter (µl/l) of wet sediment; air and CO_2 are reported as percentages of gas mixture. Partition coefficients, based on averages from other studies, were used to correct for differences in hydrocarbon gas solubilities: C_1 (methane) is 0.8; C_2 (ethane) is 0.7; and $C_{2:1}$ (ethene) is 0.6 . Results and a brief discussion are given in Appendix 3.

RESULTS AND DISCUSSION

Samples were collected by box corers in order to preserve the surface ooze which represents the most recent accumulation of sediment. The thin, brownish soupy layer of ooze was seen in most box cores, but no oil was visible. When viewed under long-wave (365 nm) and short-wave (254 nm) ultraviolet light, none of the samples showed fluorescence. Oils contain many organic compounds that fluoresce under ultraviolet light (e.g., polyaromatic hydrocarbons (PAHs)). Observation under ultraviolet light is a much more sensitive test for most crude oils than observation with visible light. None of the samples appeared to be polluted at these two levels of sensitivity.

The concentrations of organic carbon in the freeze-dried samples are given in Table 1. The organic carbon content of the samples is low, ranging from 0.27% in sample 15 to 1.1% in samples 4 and 12. These levels give no indication of pollution, although organic carbon is the least sensitive pollution parameter measured.

Sulfur-Free Extract (SFE): Figure 2A is the gas chromatogram of the sulfur-free extract of the *Exxon Valdez* oil. It is essentially identical to figure 2B, the gas chromatogram of the hexane fraction of the *Exxon Valdez* oil. This similarity results because the oil is mainly aliphatic and contains mostly normal alkanes. The low-molecular-weight alkanes have the highest concentrations. The concentrations then decrease with increased molecular weight. The decrease is generally uniform with an individual alkane concentration being intermediate between the concentrations of the alkanes of adjacent carbon numbers. This chromatographic pattern is a signature for the oil. If the sediments were polluted with this oil, this pattern would be superimposed on the natural background pattern.

The gas chromatograms of the SFE of the 16 sediment samples are shown in appendix 1. The chromatograms are normalized so that the largest peak is at full scale. This method of display is useful in that it attempts to compensate for several concentration problems such as variations in carbon content and grain size between samples (e.g., if an environment contains organic material with clayey sediment and sandy sediment, an extract of the clay would generally have a higher concentration than an extract of the sand, but their chromatograms, when normalized as above, would look essentially the same). There appear to be two major systems in the SFE extracts of these sediments. One system contains a cluster of high-molecular-weight compounds, whereas the other system contains a few discrete low-molecular-weight compounds. Most of the major compounds in both systems, after fractionation on the silica/alumina column, appeared in the methanol fraction, indicating they are polar compounds. This result would be expected in biological samples. The oil pattern is not apparent in any of these samples. There seems to be a homologous series of compounds in the medium-molecular-weight range of some of the samples, but the trend for the series in this range is for a constant to an increasing concentration with increasing molecular weight, which is opposite to the trend for the oil.

The concentrations of the sulfur-free extracts (SFE) are given in Table 1. The average value was 40 μg/g dry sediment with a standard deviation of 15. Sample 4 contains the highest concentration (78 μg/g). This high concentration is not the result of oil pollution because the gas chromatogram of the SFE shows no oil pattern.

The concentration of total hydrocarbons in the samples (Table 2, Total HC) ranges from 3.3 to 11.1 μg/g dry sediment, which is in the range found by Venkatesan and Kaplan (1982) in sediment of the Gulf of Alaska and the Kodiak Shelf.

Hexane Fraction: The normal alkanes and the isoprenoid hydrocarbons, pristane and phytane, were identified in the gas chromatograms of the hexane fraction. Figure 2B is the gas chromatogram of the hexane fraction of the *Exxon Valdez* oil. As stated before, the oil pattern shows that concentrations of low-molecular-weight alkanes are highest, and concentrations decrease with increasing molecular weight. The gas chromatograms of the hexane fractions of the eight sample extracts are shown in Figure 3. More than one source pattern can be observed in the various samples. Terrigenous input is characterized by odd-number-carbon predominance in the high-molecular-weight *n*-alkanes (n-C_{25}, n-C_{27}, n-C_{29}, n-C_{31}), the highest peak in this area usually being n-C_{27} or n-C_{29}. In these samples it is n-C_{27}. All the sample chromatograms contain this characteristic terrestrial input pattern. The chromatograms of samples 4, 10, 12 and 15 are dominated by this pattern. Another group of compounds that form a pattern in the chromatograms is n-C_{15}, n-C_{17}, and pristane. This pattern is probably due to marine input with pristane and n-C_{17} from marine plankton and some pristane possibly from benthic organisms (Venkatesan and Kaplan, 1982). This pattern, with pristane forming a local maximum, is evident in all the samples and dominates in samples 2 and 17. A third pattern containing n-C_{13}, n-C_{14} and n-C_{15} dominates in samples 7 and 9. This pattern might be due to oil, but the pattern is unlike that of the *Exxon Valdez* oil. The discrepancy at the low-molecular-weight end ($< n$-C_{14}) might be explained by the laboratory procedure in which evaporation of the sample to near dryness in order to exchange solvents preferentially removes the low-molecular-weight compounds. There is also a discrepancy between the oil and the sediments for compounds $>n$-C_{14}; the concentrations of adjacent *n*-alkanes decrease with increasing molecular weight much more rapidly in the sample extracts than in the oil.

The concentration of the hexane fraction (Table 2, aliphatics) from the eight samples ranges from 2.1 to 7.0 μg/g dry sediment, within the range found by Shaw and Baker (1978)

in sediment of Port Valdez before completion of the trans-Alaska pipeline. The ratio of aliphatics to sulfur free extract (H/SFE in Table 2) shows an anomalously high value for sample 15 (24%) compared to the rest of the samples (5.6% to 9.4%). The ratio attempts to compensate for variables, such as organic carbon content and grain size of different samples that affect organic-matter concentrations. The high ratio for sample 15 indicates that the sample is richer in aliphatics compared to the SFE than the other samples and may be an indication of some kind of pollution.

Biomarkers (terpanes and steranes): Mass fragmentograms at mass-to-charge ratio (m/z) 191 (terpanes) and m/z 217 (steranes) are given in Figures 4 and 5. Geochemical parameters of these biomarkers and one aromatic biomarker are listed in Table 3. The following ratios were calculated:

C_{23}-tricyclic/αβ-hopane--Describes the relative proportions of the major member of the two suites of terpanes in the sample set.

Tm/Ts--This is a ratio of 17α(H)-22,29,30-trisnorhopane to 18α(H)-22,29,30-trisnorneohopane. It has been used as a maturity parameter (Seifert and Moldowan, 1978), and as a source parameter if the hydrocarbons have similar maturities.

αβ-hopane (C_{30}/C_{29})--This ratio has been used for source correlations (Palacas and others, 1984).

Diploptene/αβ-hopane--Describes the magnitude of the diploptene dominance over αβ-hopane in the sample set.

C_{31}-αβ-homohopane (S/(S+R))--This is a maturity indicator (Ensminger and others, 1974). With increasing maturity the biologic configuration of 22R is equilibrated to a 60:40 mixture of 22S and 22R epimers, giving an equilibrium ratio of 0.6 (Mackenzie, 1984).

C_{29}-ααα-cholestane (S/(S+R))--This is a maturity indicator (Mackenzie and others, 1980) which reaches 0.5 at equilibrium.

MPR 9--This is a ratio of the 9-methylphenanthrene homolog to phenanthrene, one of several methylphenanthrene indices introduced by Radke and others (1982) as maturity parameters.

The m/z 191 fragmentogram of the *Exxon Valdez* oil (Fig. 4) shows two clearly delineated families of terpanes, the tricyclics and tetracyclics (C_{20}-C_{29}, peaks 1-10) and the pentacyclics (C_{27}-C_{33}, peaks 11-25). Of particular interest in the tricyclic region is the dominance of C_{23} and the triplet consisting of a C_{24} tetracyclic and two probable epimers of the C_{26} tricyclic. This triplet with the three peaks of about equal heights is characteristic of North Slope crude oil in general (Kvenvolden and others, 1985) and of the *Exxon Valdez* oil. Of interest in the pentacyclic (also called triterpane) region is the dominance of αβ-hopane (peak 18) and the dominance of the S over the R epimer of C_{31} (peak 21), which gives a ratio of 0.6, the value for full maturity. No compounds are present in the oil which indicate recent biogenic contributions or geologic immaturity. The ratio of the peak heights of the dominant tricyclic (C_{23}, peak 5) and the dominant pentacyclic (αβ-C_{30}-hopane, peak 18) gives an indication of the relative proportions of the two suites of compounds in the oil and at each site (Table 3).

The remainder of the m/z 191 fragmentograms in Fig. 4 are of the eight fractionated sediment samples. The most notable feature of the sediment fragmentograms is that the majority of them are dominated by diploptene (peak 22). This is a compound of very recent input to

the sediment that has been widely reported to be present in coastal sediments from Washington (Prahl and Carpenter, 1984) to Alaska (Venkatesan and Kaplan, 1982). Its source has been attributed to vascular plants or microorganisms (Prahl and Carpenter, 1984) or bacteria or algae (Venkatesan and Kaplan, 1982), especially of a marine origin (Venkatesan, 1988). In our samples the appearance of diploptene coincides with that of the structurally related 22,29,30-trisnorhop-17(21)-ene (peak 12). In full-scan runs (not shown), samples rich in diploptene also contain tentatively identified cholestenes and fernenes. These unsaturated sterenes and terpenes are further indication of recent input to the sediments from biogenic sources. All of the sediment contains significant amounts of diploptene, but the ratio of diploptene to the αβ-hopane is lowest at sites 9 and 15.

The next dominant series in the m/z 191 fragmentograms is the tricyclics. If the sediment has been significantly contaminated by *Exxon Valdez* oil, the relative proportion of the tricyclics found in the sediment samples would have to approach that seen in the oil. As can be seen on the sediment fragmentograms and in Table 3, the relative amount of tricyclics with respect to the pentacyclics is considerably less than that in the oil. The pattern of components is, however, quite similar, with the possible exception of the triplet (Fig 4, "peak" 8). Here, the components are the same but their relative proportions vary somewhat. The presence of the tricyclics, even in these low amounts, could be considered to represent a background level of oil in the sediment throughout the region. Other authors (Shaw and others, 1985; Venkatesan and Kaplan, 1982) have reported low but measurable levels of petroleum-related chemicals in sediment in this general area since the opening of the trans-Alaska pipeline and the subsequent heavy tanker traffic in the Gulf of Alaska. The highest values for the ratio of tricyclics to pentacyclics, after the value for the *Exxon Valdez* oil, are found at sites 4 (Snug Harbor), 9 (deep hole, west of Naked Island) and 15 (south of Knight Island).

The last series of importance in the m/z 191 fragmentograms is the αβ-triterpanes (hopanes). Only minor amounts of the ββ- or βα-hopanes (moretanes) are observed. The ββ-hopanes are immature compounds whose source is biological material, whereas βα- and αβ-epimers (especially the latter) indicate the same sources but significant aging or maturation. The limit of maturity for these compounds is indicated when the 22S and 22R epimers of the αβ-homohopanes (C_{31} and higher homologs) reach their equilibrium value of 0.6 (Mackenzie, 1984). In none of our sediment samples has the epimerization at C_{22} reached the equilibrium value (see Table 3 and Fig. 4), indicating that no sediment sample contains a substantial amount of a fully mature oil. However, at least one source (Shaw and others, 1985) suggests that just the appearance of the αβ-hopanes is evidence of oil impingement, although all of the samples he reported had S/S+R values at equilibrium. The ratios signaling the highest maturity are at sites 9, 15, and 17 (Table 3). The Tm/Ts ratio for the *Exxon Valdez* oil is lower than for any of the sediment samples, as would be expected because of the maturity of the oil. If a mature oil were mixed with an immature sediment, the Tm/Ts ratio of the sediment would decrease. The sample with the lowest ratio is from site 15. The $\alpha\beta C_{30}/\alpha\beta C_{29}$ ratio shows very little variation within the sediment samples, but the sample with the value closest to that of the oil is from site 15.

One other compound of interest that is seen in the extracts from all the sediment samples is oleanane (peak 17 in Fig. 4). This compound has been reported in oils that have terrigenous sources. Kvenvolden and others (1989) have reported oleanane in oil seeps and petroliferous-smelling mud along the coast of Washington. This compound is not seen in either the *Exxon Valdez* oil or typical North Slope crude oils (Kvenvolden and others, 1985).

The m/z 217 fragmentograms (Fig. 5) also show different characteristics for the oil and the sediment. The oil fragmentogram gives the signature of fully mature components--the diacholestanes and other epimers dominate the less mature ααα-cholestanes, and the 20R and 20S epimers of the latter are at their equilibrium value (S/[S+R]=0.5). The three ααα-cholestane homologs are at approximately equal concentrations, judging from peak heights. Most of the sediment samples have a significantly less mature signature: the ααα-cholestanes dominate, and their R epimer is the more abundant. The C_{29} homolog is at higher concentration than the C_{27} and C_{28} in most samples. Only the fragmentogram from site 15 has a pattern similar in some respects to that of the oil; its S/[S+R] value is the highest of the sediment; it contains more of the mature constituents. The sample is, however, dominated by the C_{29} ααα-cholestane. Site 4 has a moderately high ratio (Table 3).

Aromatic Fraction: The concentration of the aromatic fraction in the samples ranges from 1.2 to 4.4 μg/g dry sediment (Table 2, aromatics). The ratio of aromatics to sulfur-free extract (20B/SFE in Table 2) also shows, as did the ratio of aliphatics to sulfur-free extract, an anomalously high value for sample 15 (13%) compared to the other samples (4.4% to 10.2%). The high ratio for sample 15 indicates that the sample is richer in aromatics compared to the SFE than the other samples even though its concentration is still not particularly high. These anomalies suggest that this sample is polluted, but other evidence from the aromatic fraction does not fully support this suggestion.

Figure 6 shows a full-scan GC/MS run of the aromatic fraction from the oil. This fraction contains the PAH constituents. The two other chromatograms in the figure are from sediment sites 4 and 15 which show the range of aromatics seen in the full sample set. The relative amount of aromatic hydrocarbons to aliphatic hydrocarbons is low throughout the sample set, especially in the oil. The aromatic hydrocarbons of the oil are fairly typical of oils in general, namely a suite of low molecular weight PAH's dominated by naphthalene and phenanthrene and their alkylated homologs, mainly C_1 to C_3. The sediment samples contain these same compounds, in varying amounts, but with similar distributions. This observation again suggests that oil-like compounds are present throughout the sample set at a low-level background. The problem is to distinguish the background level from a potential level caused by oil pollution related to the oil spill. One factor that does distinguish between the oil and the sediment is the MPR-9 ratio. The methylated phenanthrene ratio (MPR) is essentially identical among the sediment samples, but differs in the prominence of the 9-isomer in the oil. The MPR-9 ratio is highest for the oil and shows a relatively constant low level for the sediment except for sediment from site 15, which gives an even lower value because it contains more phenanthrene from some other source.

Obviously superimposed on the above-mentioned pattern in the sediment are compounds that are signatures of other sources. At sites 4 (Fig. 6) and 12, and to a lesser extent sites 2, 9, and 11 the dominant compounds are a series of three middle-molecular-weight unknowns that have a base peak on the MS of m/z 155. The spectra of these unknown compounds are given in appendix 2. At site 15 (Fig. 6) the PAH's are dominated by the non-alkylated members, many of which appear only in low abundances at other sites. These compounds may be of pyrogenic origin. The distribution resembles the suite of compounds, usually dominated by pyrene and fluoranthene, that are distributed worldwide in marine sediments, and considered to be spread by eolian transport (LaFlamme and Hites, 1978). Venkatesan and Kaplan (1982) found this same signature in some sediment offshore Alaska. The fractions from the remaining

sites seem to be mixtures of these major suites of compounds.

Extraneous Compounds

Other compounds appear quite prominently in the SFE chromatograms. The high-molecular-weight polar compounds are most probably related to cholesterol from biogenic sources. At site 7 and others, a group of low molecular weight compounds are prominent. The largest peak was found to be 2,6-di-t-butylbenzoquinone, by comparison of its spectra and retention time with that of a known standard. The mass spectrum of this peak is shown in appendix 2. Other compounds possibly related to it are 2,6-di-t-butyl-4-ethylphenol and 2,6-di-t-butyl-4-methyl phenol, tentatively identified and found in varying amounts at this and other sites. No source for this group of aromatics, or the unknowns with the base peak of 155 mentioned above, could be established.

CONCLUSIONS

The observations under visible and ultraviolet light gave no indication of pollution in sediment samples from 15 sites. The organic carbon content of the samples and the gas chromatograms of the sulfur-free extract also give no indication of pollution. The concentrations of the sulfur-free extracts are low except for sample 4, which is higher, but the gas chromatogram of the SFE does not show an oil pattern. The ratios of both aliphatics to SFE and aromatics to SFE are anomalously high for sample 15 (south of Knight Island) and may indicate some pollution. Almost all the biomarker ratios indicate that sample 15 contains the most mature hydrocarbons and thus is the sample most likely to have been tainted with the oil. Indicators from the aromatic fraction, such as methyl phenanthrene ratio-9 and the different source signatures, do not corroborate significant oil contamination, however. Samples 2 and 9 have some biomarker ratios which may indicate some pollution. None of the samples, however, are contaminated above the µg/g (ppm) level. If there is pollution, it is at very low levels, much below the µg/g level.

We recommend that the sites be resampled in order to monitor the hydrocarbon levels. As the oil that remained on the beaches in 1989 has time to oxidize and become partially biodegraded, it will become heavier and more likely to sink in the water column, where it could be incorporated into the sediment at progressively greater water depths.

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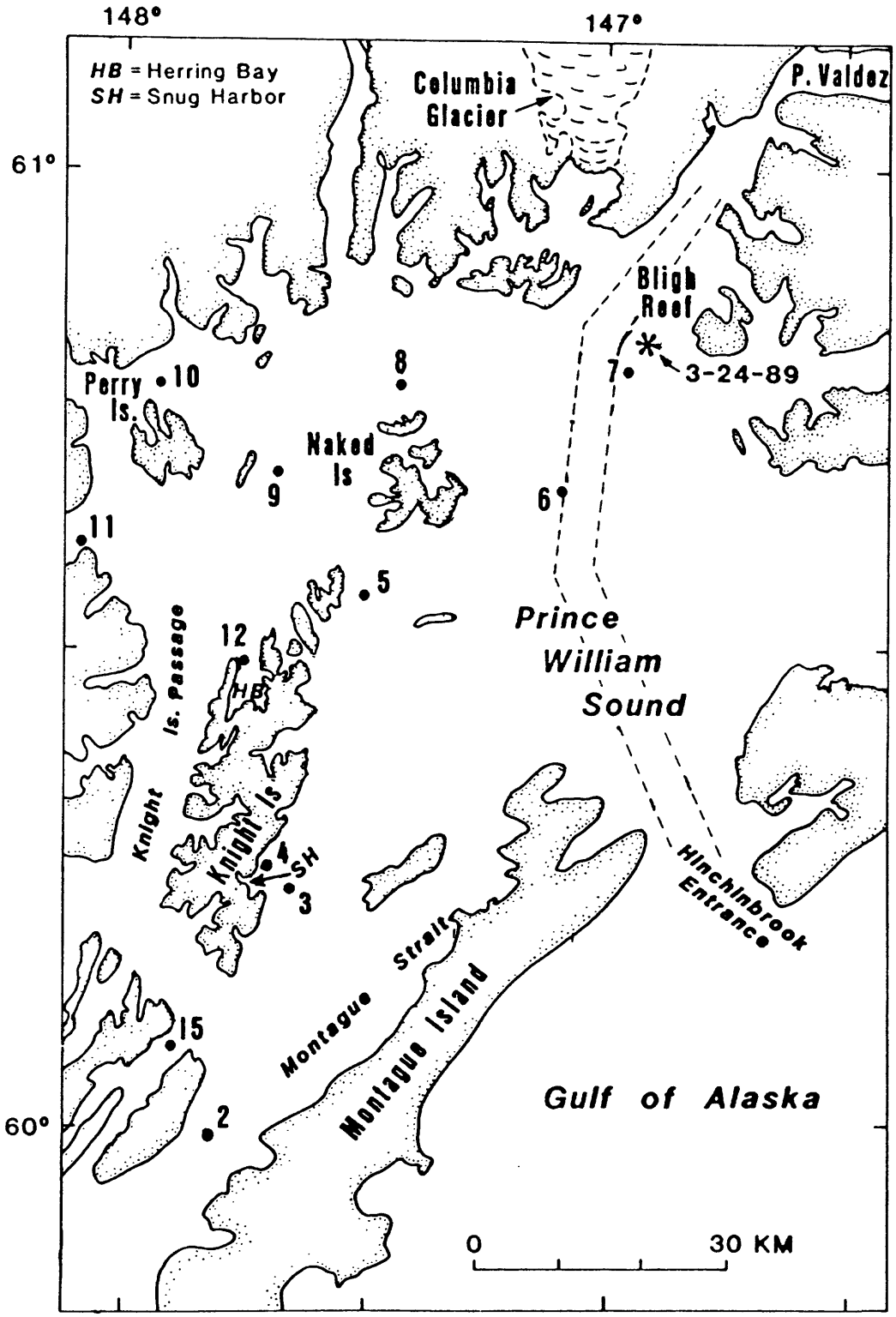


Figure 1A. Map showing location within Prince William Sound of sediment samples taken for hydrocarbon analysis.

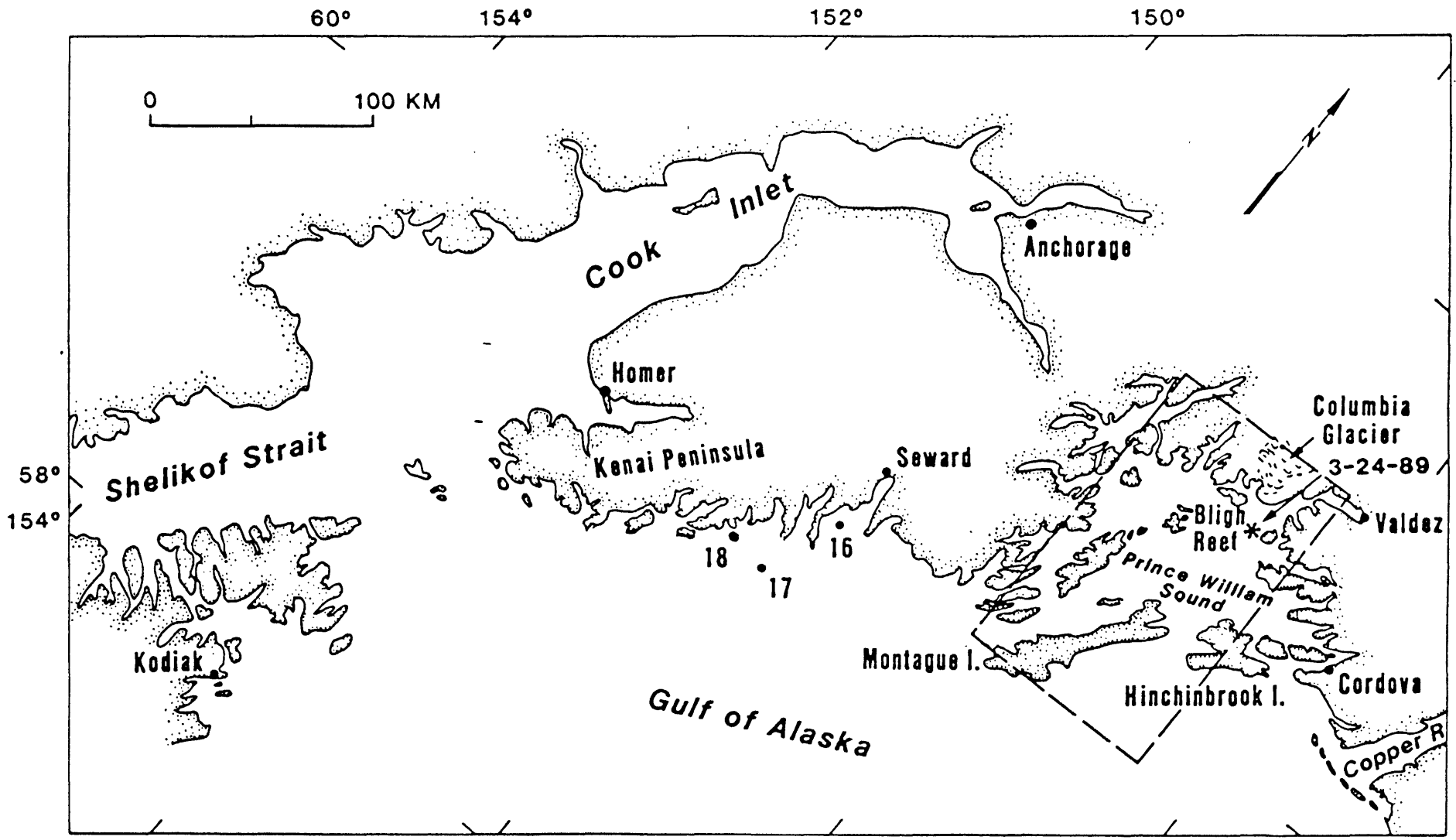


Figure 1B. Map showing location along the Gulf of Alaska coast of sediment samples taken for hydrocarbon analysis.

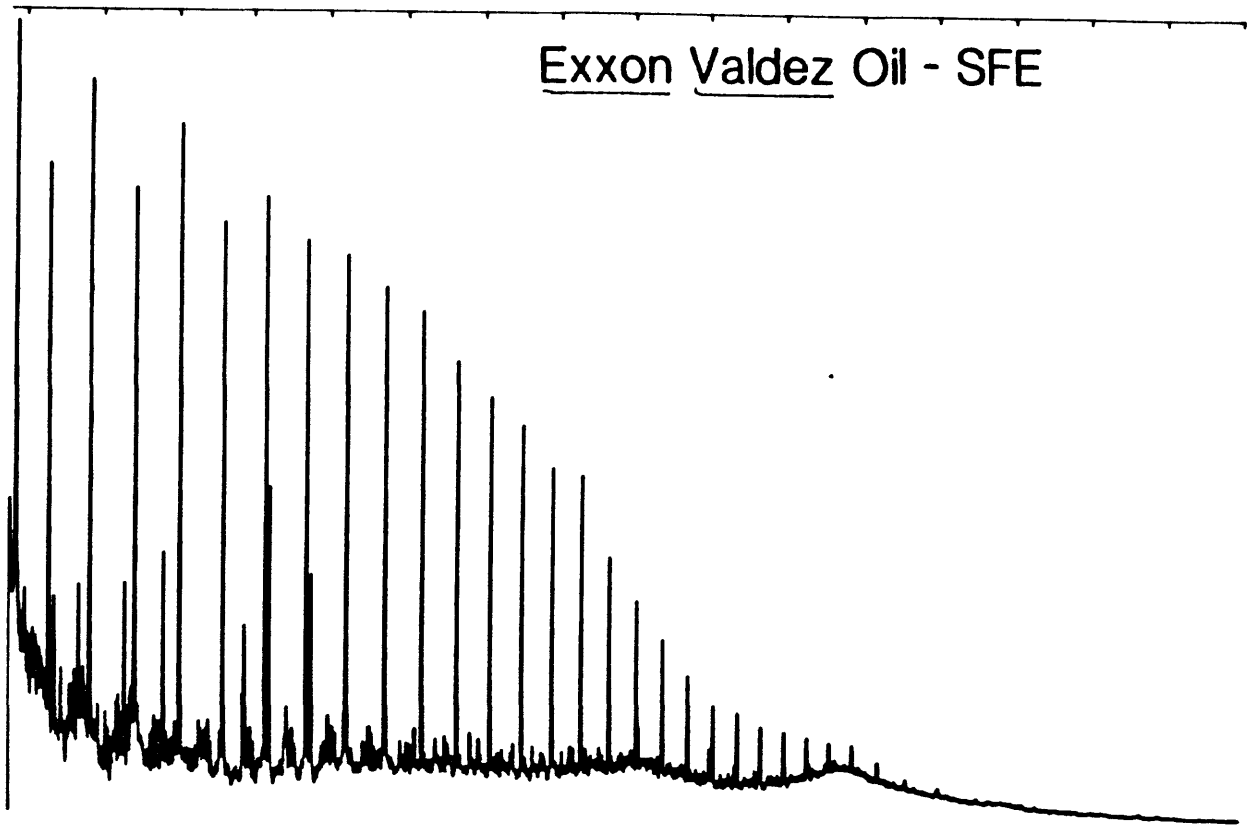


Figure 2A. Gas chromatogram of the sulfur-free extract (SFE) of the *Exxon Valdez* oil.

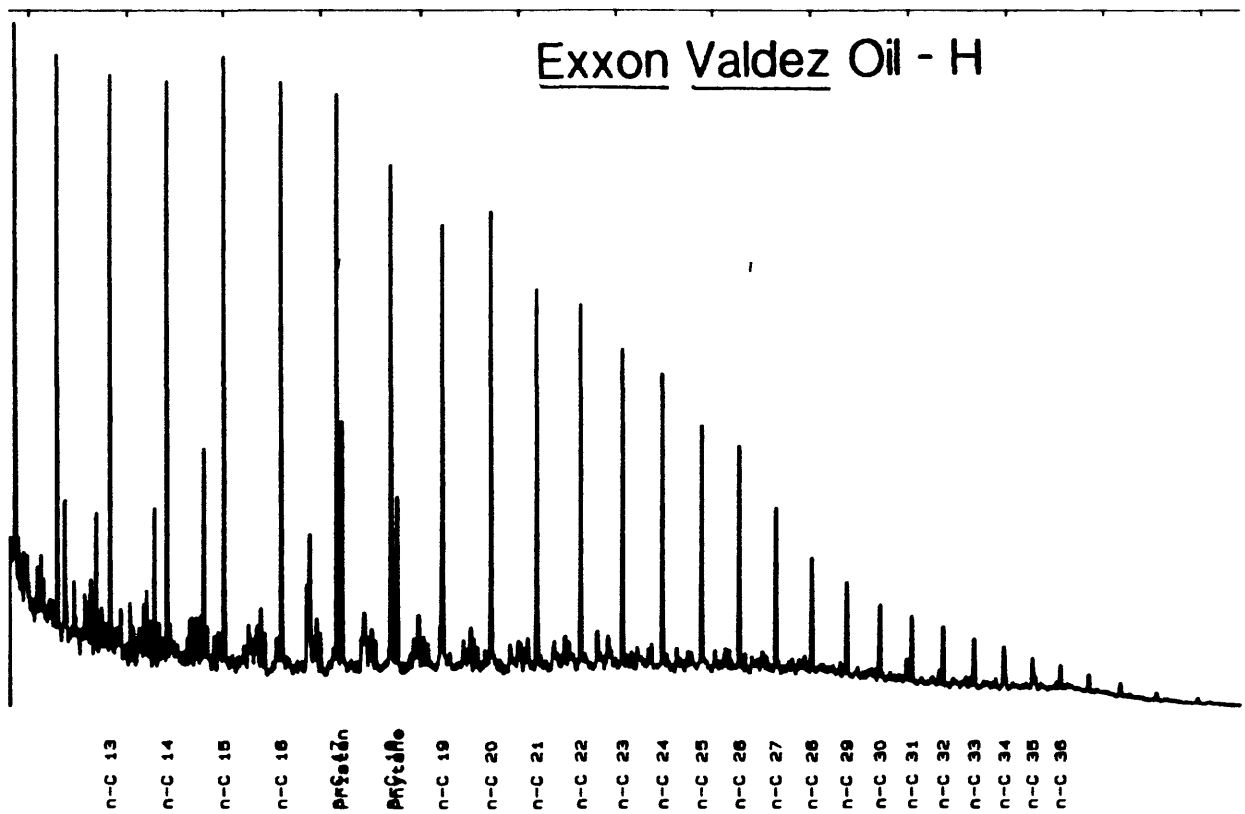


Figure 2B. Gas chromatogram of the hexane fraction of the *Exxon Valdez* oil.

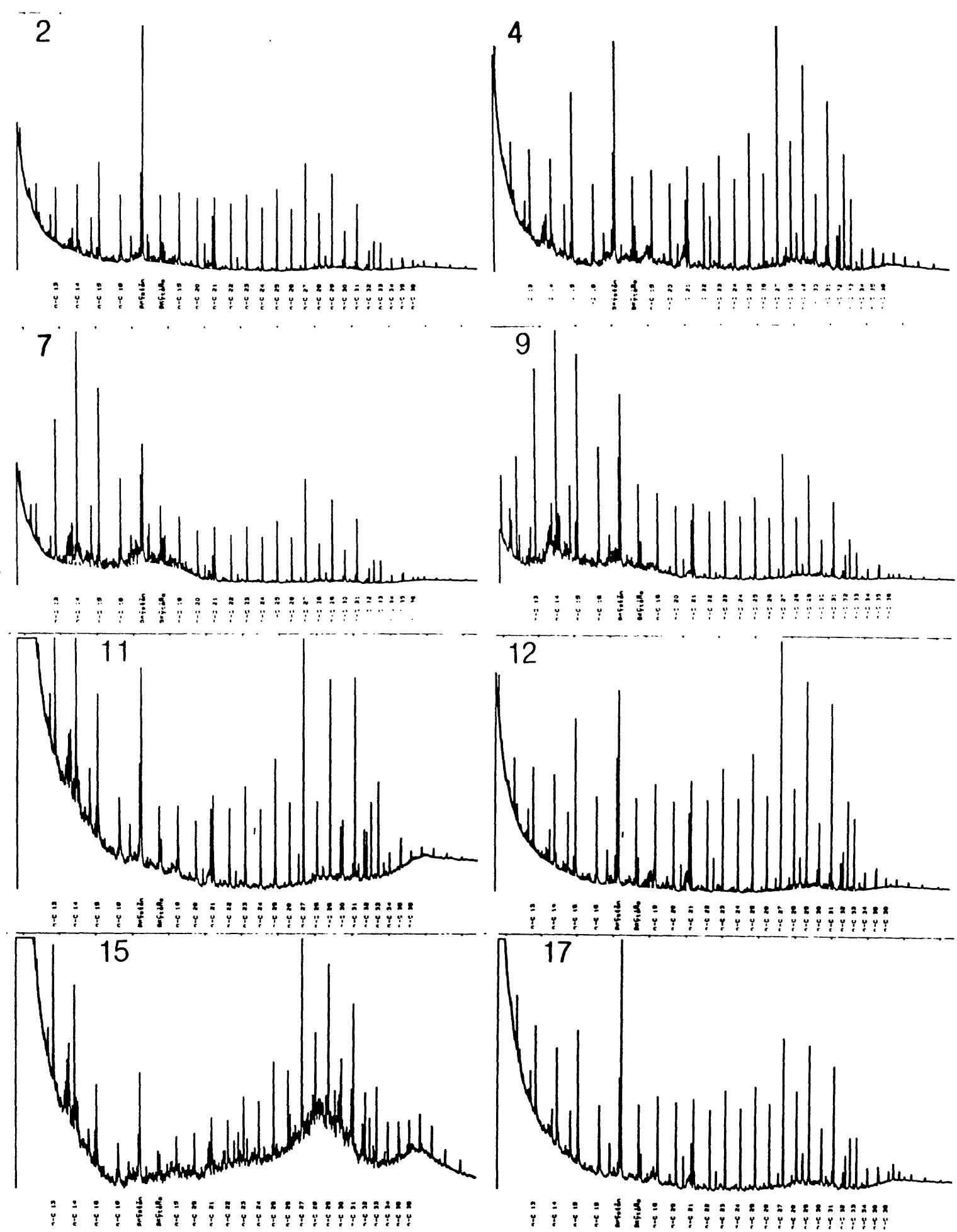


Figure 3. Gas chromatograms of the hexane fractions of eight sediment samples.

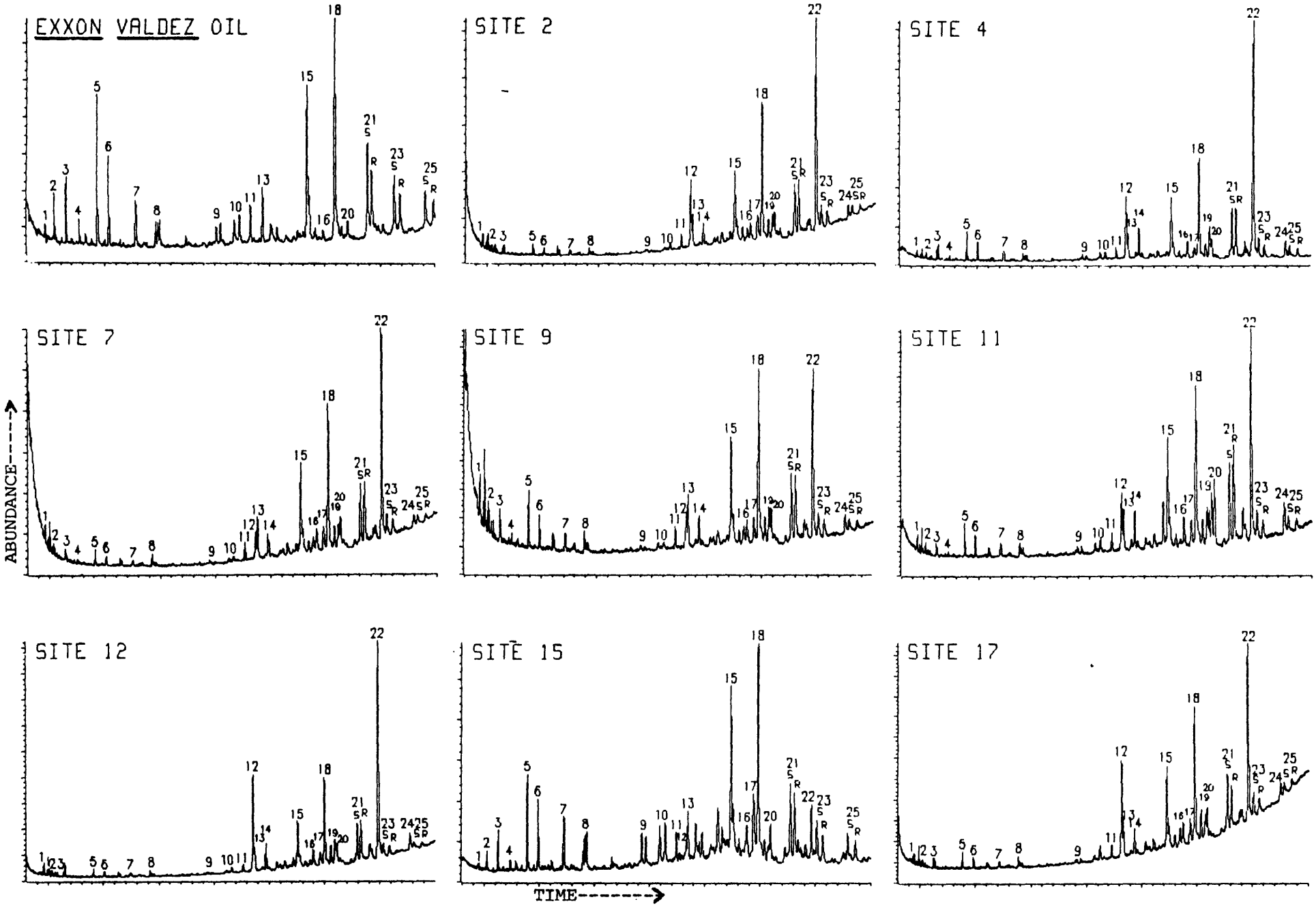


Figure 4. Mass fragmentograms (m/z 191) showing the distribution of terpanes (tricyclics 1-10; pentacyclics or triterpanes 13-25 in *Exxon Valdez* oil and eight sediment samples from Prince William Sound, Alaska. Identifications are given in table 4.

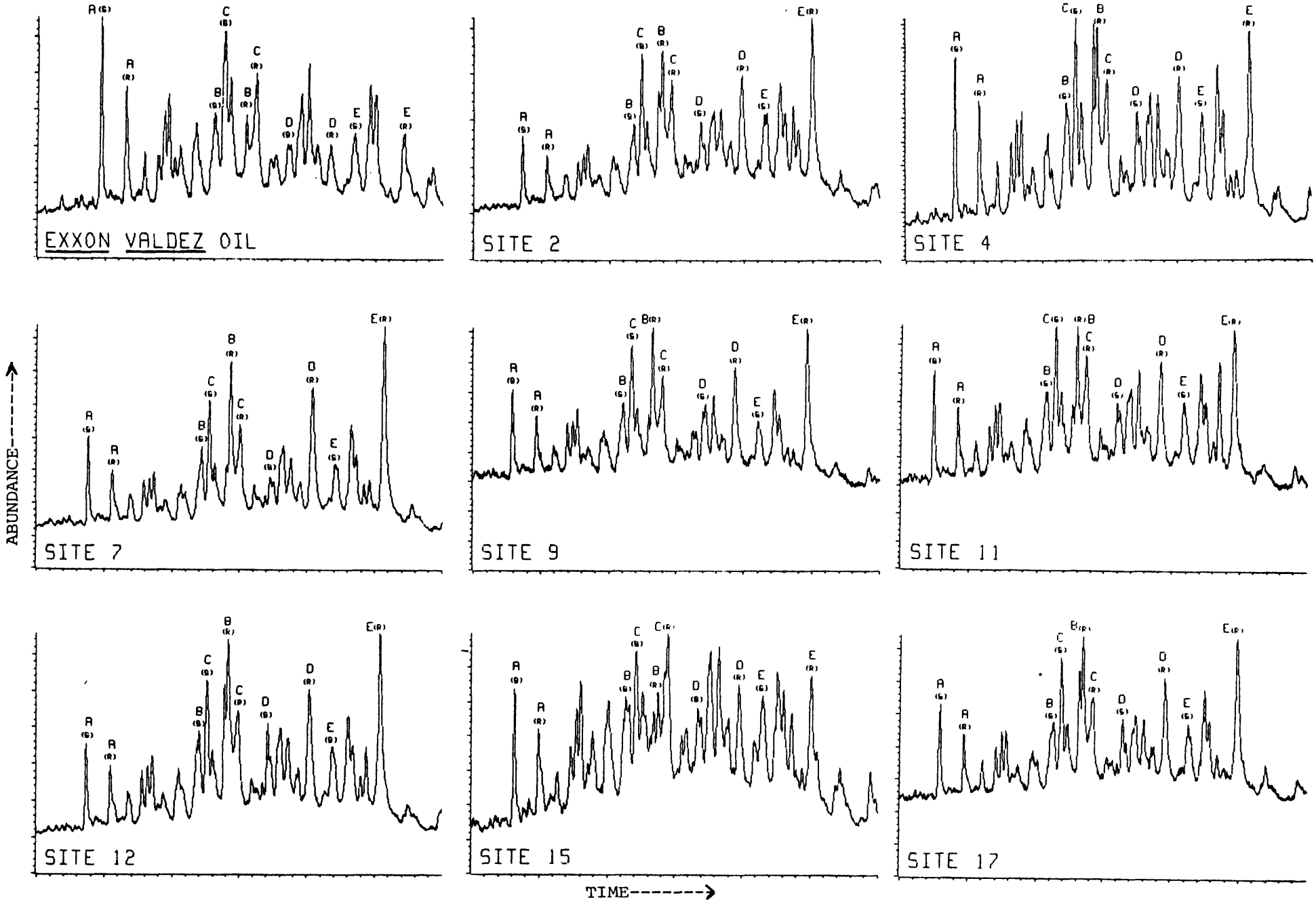


Figure 5. Mass fragmentograms (m/z 217) showing the distribution of steranes in *Exxon Valdez* oil and eight sediment samples from Prince William Sound, Alaska. Identifications are given in table 4.

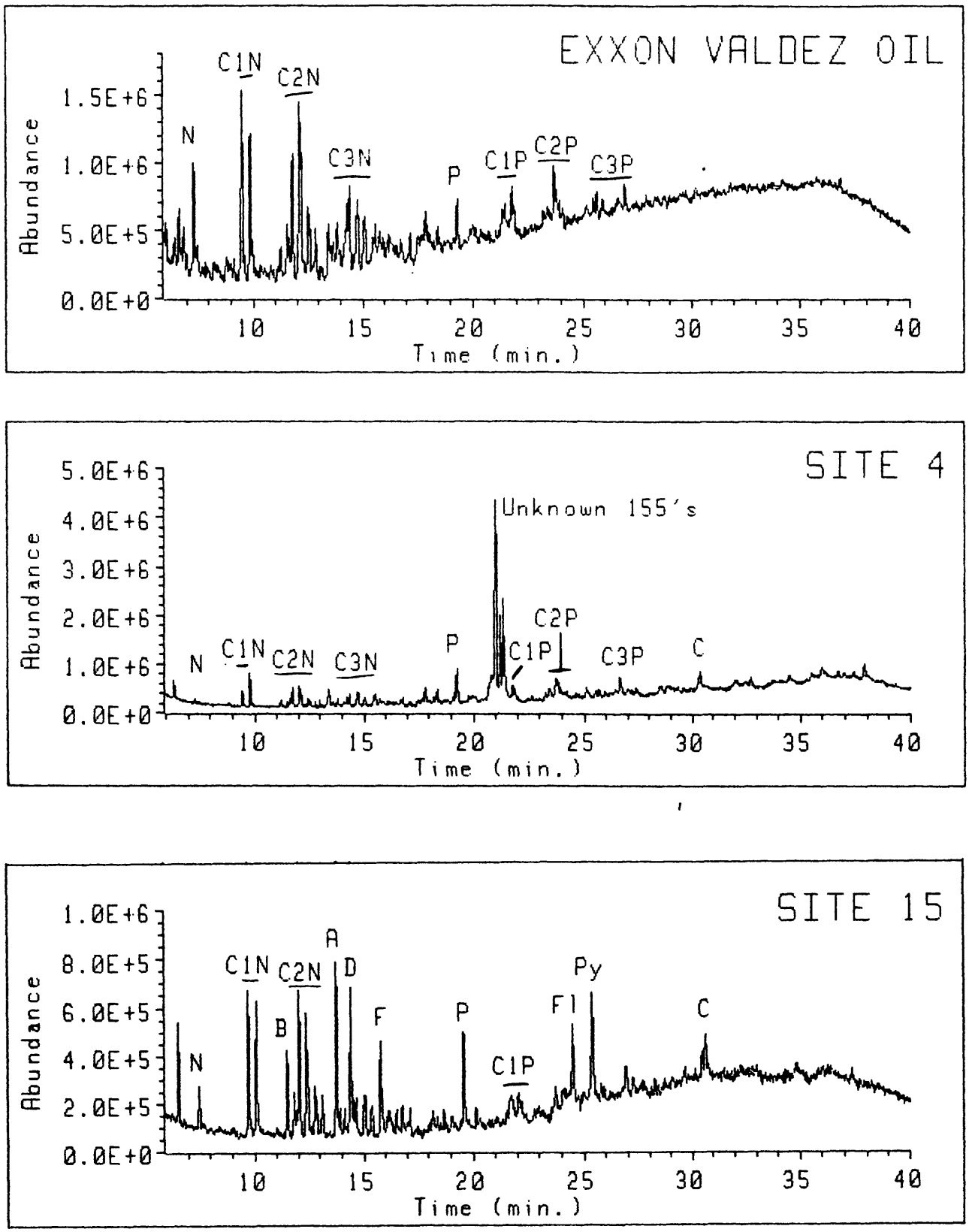


Figure 6. Aromatic hydrocarbons. GC/MS chromatograms of the aromatic fraction of the *Exxon Valdez* oil and selected sediment samples. Identifications are: N (naphthalene), B (biphenyl), A (acenaphthene), D (dibenzofuran), F (fluorene), P (phenanthrene), Fl (fluoranthene), Py (pyrene), C (chrysene), and C1, C2, etc. (number of alkyl substituents on any of the preceding parent PAH's).

Table 1. Water depths at sample sites and concentrations of organic carbon and sulfur-free extract (SFE)

Sample Number*	Water Depth (m)	Organic Carbon(%)	SFE (μg/g)
2A	246	0.72	37
3A	267	0.78	47
4A	125	1.10	78
5A	213	0.80	35
6A(0-8cm)	400	0.46	35
6A(18-22cm)	400	**	22
7C	394	0.59	44
8B	480	0.64	42
9A	755	0.80	58
10C	338	0.77	43
11	400	0.56	28
12B	205	1.10	56
15A	240	0.27	29
16B	277	0.66	38
17B	115	0.44	22
18A	95	0.58	23

* All samples analysed are from the sediment surface except for site 6A where a surface sample (0-8 cm) and a subsurface sample (18-22 cm) were taken. The letter following the site number indicates which of multiple box cores was sampled.

** Not determined

Table 2. Hydrocarbon Concentrations and Ratios to SFE

Sample Number	Aliphatics (H) µg/g	Aromatics (20B) µg/g	H/SFE	20B/SFE	Total HC (H+20B) µg/g
2	3.0	3.5	8.0%	9.4%	6.5
4	6.7	4.4	8.6%	5.6%	11.1
7	3.0	4.3	6.8%	9.8%	7.3
9	4.0	4.5	6.8%	7.7%	8.5
11	2.1	1.2	7.3%	4.4%	3.3
12	3.1	3.0	5.6%	5.3%	6.1
15	7.0	3.8	24%	13%	10.8
17	2.1	2.2	9.4%	10.2%	4.3

Table 3. Organic geochemical parameters from *Exxon Valdez* oil and sediments from Prince William Sound *

Site	m/z 191					m/z 217	
	$\frac{C_{23}\text{tricy}}{C_{30}\alpha\beta}$	$\frac{Tm}{Ts}$	$\frac{C_{30}\alpha\beta}{C_{29}\alpha\beta}$	$\frac{\text{Diploptene}}{C_{30}\alpha\beta}$	$C_{31}\alpha\beta\frac{S}{S+R}$	$C_{29}\alpha\alpha\alpha\frac{S}{S+R}$	MPR 9
Exxon Valdez oil	.71	1.4	1.4	0	.60	.46	.84
Site 2	.09	2.0	1.9	1.6	.49	.25	n.c.
Site 4	.30	1.9	1.7	2.4	.50	.34	.36
Site 7	.12	2.0	1.6	1.5	.50	.18	.40
Site 9	.33	2.3	1.6	1.0	.52	.24	.42
Site 11	.21	2.0	1.5	1.3	.45	.31	.40
Site 12	.09	2.0	1.9	2.5	.50	.24	.38
Site 15	.59	1.7	1.3	.25	.53	.43	.15
Site 17	.13	2.5	1.7	1.3	.56	.27	.40

* All ratios defined in text.
n.c. = not calculated

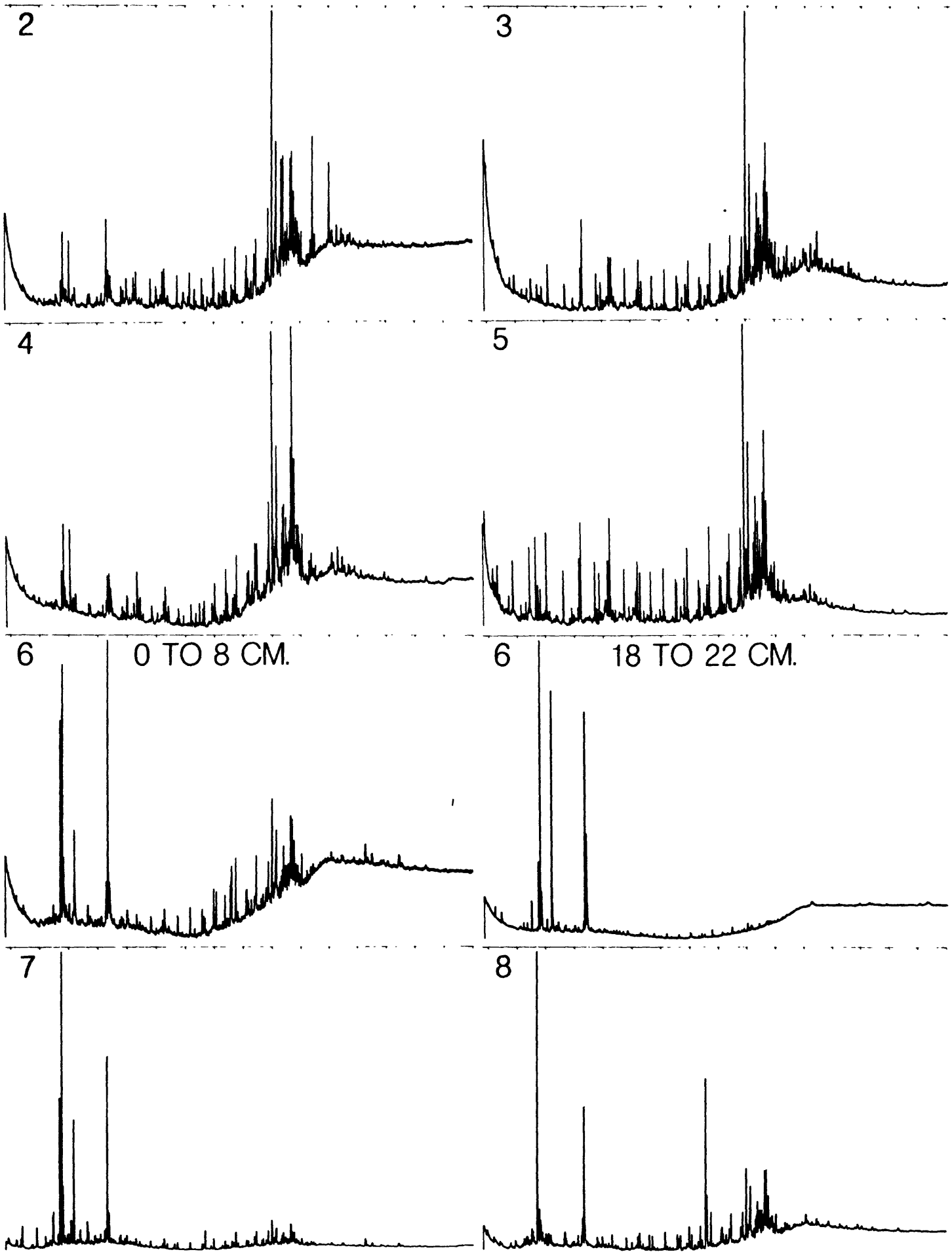
Table 4. Identification of terpanes and steranes

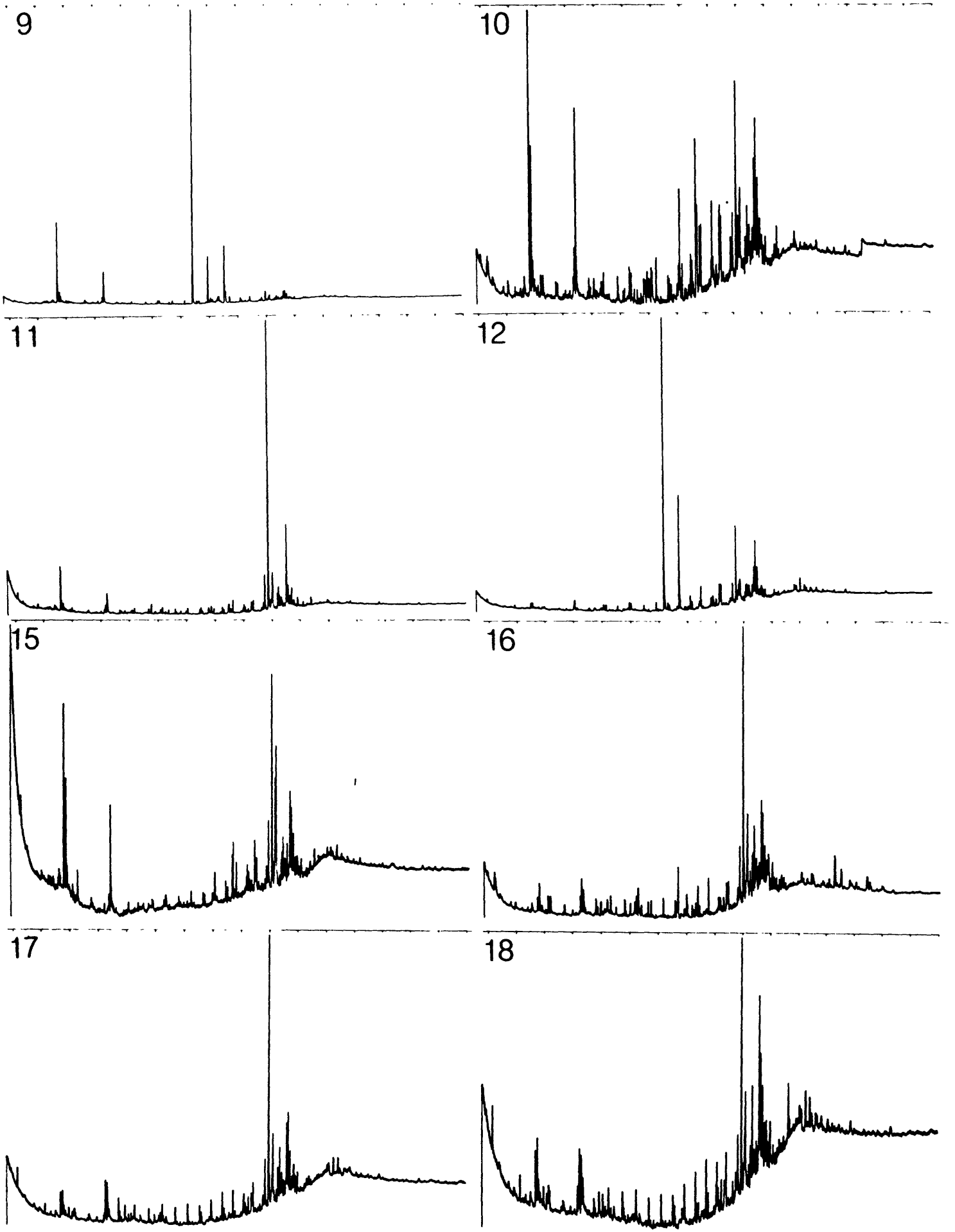
Peak	Compound	
TERPANES and TRITERPANES (m/z 191)		
1	C_{19} tricyclic terpane	C_{19}
2	C_{20} tricyclic terpane	C_{20}
3	C_{21} tricyclic terpane	C_{21}
4	C_{22} tricyclic terpane	C_{22}
5	C_{23} tricyclic terpane	C_{23}
6	C_{24} tricyclic terpane	C_{24}
7	C_{25} tricyclic terpane	C_{25}
8	Triplet: C_{24} tetracyclic terpane	C_{24}
	C_{26} tricyclic terpane (?S)	C_{26}
	C_{26} tricyclic terpane (?R)	C_{26}
9	C_{28} tricyclic terpanes (?S and R)	C_{28}
10	C_{29} tricyclic terpanes (?S and R)	C_{29}
11	18α(H)-22,29,30-trisnorneohopane (Ts)	C_{27}
12	22,29,30-trisnorhop-17(21)-ene	C_{27}
13	17α(H)-22,29,30-trisnorhopane (Tm)	C_{27}
14	17β(H)-22,29,30-trisnorhopane	C_{27}
15	17α(H),21β(H)-30-norhopane	C_{29}
16	17β(H),21α(H)-30-normoretane	C_{29}
17	18α and/or β(H)-oleanane	C_{30}
18	17α(H),21β(H)-hopane	C_{30}
19	17β(H),21β(H)-norhopane	C_{29}
20	17β(H),21α(H)-moretane	C_{30}
21	17α(H),21β(H)-homohopane(22 S and R)	C_{31}
22	17β(H),21β(H)-hop-22(29)-ene (diploptene)	C_{30}
23	17α(H),21β(H)-bishomohopane(22 S and R)	C_{32}
24	17β(H),21β(H)-homohopane	C_{31}
25	17α(H),21β(H)-trishomohopane(22 S and R)	C_{33}
STERANES and DIASTERANES (m/z 217)		
A(S)	13β(H),17α(H)-diacholestane(20S)	C_{27}
A(R)	13β(H),17α(H)-diacholestane(20R)	C_{27}
B(S)	5α(H),14α(H),17α(H)-cholestane(20S)	C_{27}
C(S)	24-ethyl-13β(H),17α(H)-diacholestane(20S)	C_{29}
B(R)	5α(H),14α(H),17α(H)-cholestane(20R)	C_{27}
C(R)	24-ethyl-13β(H).14α(H)-diacholestane(20R)	C_{29}
D(S)	24-methyl-5α(H),14α(H),17α(H)-cholestane(20S)	C_{28}
D(R)	24-methyl-5α(H),14α(H),17α(H)-cholestane(20R)	C_{28}
E(S)	24-ethyl-5α(H),14α(H),17α(H)-cholestane(20S)	C_{29}
E(R)	24-ethyl-5α(H),14α(H),17α(H)-cholestane(20R)	C_{29}

APPENDIX 1

Gas Chromatograms of the Sulfur-Free Extracts

of the 18 Analyzed Samples

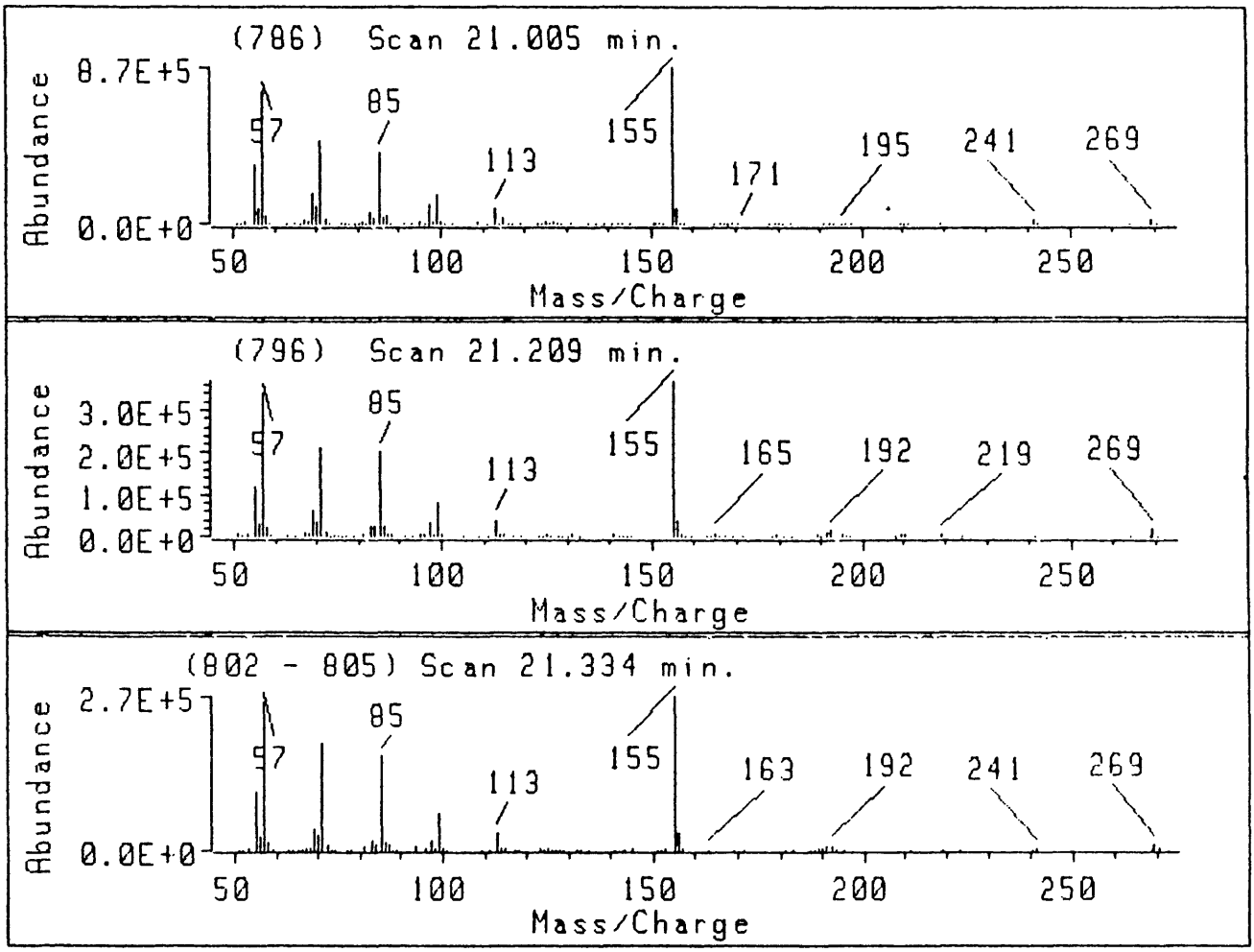

2
3
4
5
6
0 TO 8 CM.
6
18 TO 22 CM.
7
8


9
10
11
12
15
16
17
18

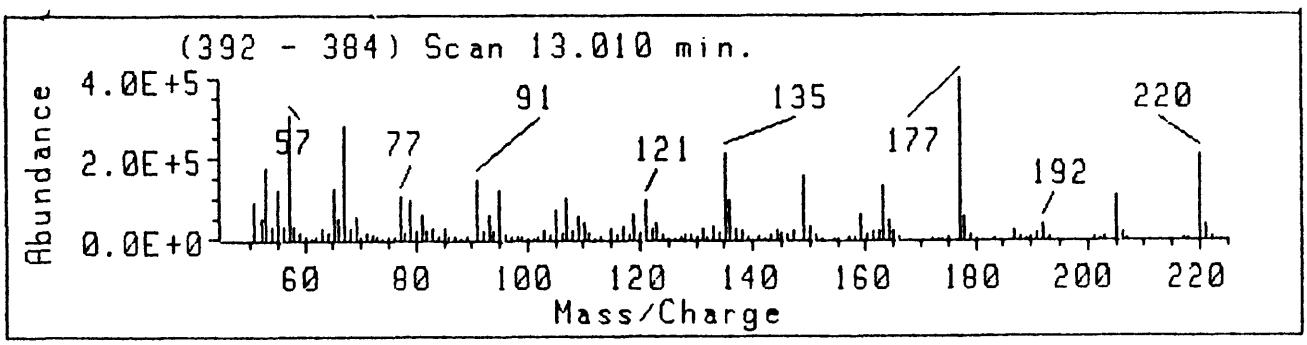
APPENDIX 2

1. Mass Spectra of unknowns with base peak m/z 155 from site 4.

2. Mass spectrum of 2,6-di-t-butylbenzoquinone found at several sites.



1. Mass spectra of Unknowns with base peak 155 from Site 4.



2. Mass spectrum of 2,6-di-t-butylbenzoquinone found at several sites.