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IN SAN FRANCISCO BAY, CALIFORNIA

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By

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ABSTRACT

*In an ongoing study of sources of organic input to San Francisco Bay, the 1988 spill of more than 400,000 gallons of a San Joaquin Valley crude oil from a shoreline refinery operated by Shell Oil Company has been investigated. The aim of the work was to find geochemical parameters that could be used to differentiate this oil from the chronic petrogenic background in the local Bay sediments and thus identify this oil's impingement on the sediments. The Shell crude oil has a partially degraded character and therefore lacks several categories of compounds, such as *n*-alkanes and isoprenoid hydrocarbons, that might have aided the differentiation. In addition, the sediments, which receive input from anthropogenic petroleum contamination, pyrogenic sources, and urban drainage, contain many of the same chromatographically resolvable constituents as the oil. Therefore, comparisons of relative amounts of selected constituents were found to be best suited for the differentiation. Ratios of compounds from the hopane and sterane biomarker suites, and polycyclic aromatic hydrocarbons (PAH's) and their alkyl derivatives were utilized to identify Shell oil contamination in the local North Bay sediments. Co-occurring organic constituents in the sediments were also investigated for input sources.*

INTRODUCTION

Much research has been devoted to distinguishing sources of hydrocarbons in recent marine and estuarine sediments. Goals of this source discrimination have been varied; they include (1) elucidation of the origins of complex hydrocarbon mixtures and assessment of the magnitude of source contributions (e.g. Prah and Carpenter, 1984, Columbo and others, 1989); (2) evaluation of depositional environments, past and present environmental conditions, depositional processes, and the historical record of types of input (e.g. Wade and Quinn, 1979, Venkatesan and others, 1980, Pruell and Quinn, 1985, and Brassell and Eglinton, 1986); (3) determination of the existence and extent of anthropogenic pollution (e.g. Spies and others, 1985, Shiaris and Jambard-Sweet, 1986); (4) determination of the existence, extent, and fate of petrogenic impingement both from natural sources (e.g. Rowland and Maxwell, 1984, Killops and Howell, 1988) and from spillage (Gundlach and others, 1983, Boehm and others, 1987); and (5) investigation of sediment transport and transport mechanisms (Albaiges and others, 1984, Hostettler and others, 1989). This study is part of an on-going investigation of sources of organic constituents, mainly hydrocarbons, including biomarkers and other biogenic lipids, in surficial sediments of San Francisco Bay. The

work focuses on an area in the North Bay (Fig. 1) where crude oil from a shoreline refinery had spilled into the Bay.

On April 22-23, 1988, nearly 400,000 gallons of a San Joaquin Valley crude oil were accidentally released from the Martinez Refinery and Manufacturing Complex of Shell Oil Company into Peyton Slough (Fig. 1). From there the oil infiltrated surrounding marshes and flowed into Suisun Bay and the Carquinez Straits, where wind and tidal currents aided its dispersal. Spill containment and clean-up measures were instigated on April 23. Samples for our study were collected shortly thereafter on April 29 from an intertidal area impacted by the spill (Martinez) and from a neighboring bay (Southampton) that was by-passed by the spill and just outside the spill domain. A sample of unreleased crude oil from the ruptured tank and a composite crude oil sample from the clean-up efforts were also collected. Our study investigates possible methods for distinguishing the spilled oil from the chronic petrogenic background that is present throughout the Bay (Hostettler and others, 1989). It also addresses possible sources of co-occurring organic substituents in these sediments.

EXPERIMENTAL

Sample collection. Six different sites were investigated, and seven sediment samples were collected. Five samples came from four intertidal sites within the spill-impacted area near Martinez (SF-15,16,17,18 and 21) and two came from intertidal sites outside of the spill area near Southampton (SF-19 and -20). Sediments obviously coated with large amounts of spilled oil were not collected because assessment of the magnitude of the contamination was not the purpose of this study. Two oils were collected in aluminum cans; one sample (SF-23) came from the ruptured tank (non-dispersed) and the other sample (SF-24) from a composite of oil from the clean-up procedures. The oil is a very viscous, asphaltic crude oil from the San Joaquin Valley, California.

Figure 1 shows the sample locations. In general, the Martinez sediments contained more sand and the Southampton sediments more mud. One Southampton sample (SF-19) had an oil-like sheen on its surface. Because this sample came from outside the spill-impacted area, the source of the sheen could not be the spilled oil. The method of sediment collection included spooning damp surficial sediment into pre-cleaned aluminum cans (samples SF-15,16,19,20), a pushcore (SF-17, 0-7 cm, and SF-18, 7-14 cm), and a boxcore, top sediment (SF-21). All samples were immediately transported to the laboratory where they were frozen and freeze-dried (sediments) or refrigerated (oils) until analyzed.

Extraction and fractionation. Sediment samples (approximately 100 g) and the crude oils (approximately 50 mg) were analyzed as previously described by Hostettler and others, 1989, focusing on the unbound organic constituents. Six fractions were collected after liquid chromatography on silica and alumina. The six fractions and their dominant constituents were: (1) hexane (aliphatic hydrocarbons including hopane and sterane biomarkers); (2) 20% benzene in hexane (aromatics including polycyclic

aromatic hydrocarbons, PAH's); (3) 40% benzene in hexane; (4) 60% benzene in hexane (*n*-aldehydes); (5) 100% benzene (long-chain acyclic methyl ketones); and (6) methanol (polar, possible N,S,O-containing molecules, none of which were positively identified).

Gas chromatography and mass spectrometry. Procedures for gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) have been described previously (Hostettler and others, 1989). Ratios of various compounds (Tables 1-3) were calculated using peak areas or peak heights. Odd-even-predominance (OEP) values were calculated by the method of Scalan and Smith (1970), and a factor using terrigenous alkane concentrations normalized to Total Organic Carbon (TOC), ΣC_{25-31} , was calculated as in Prahl and Carpenter (1984). Among the aliphatic sesquiterpenoids (molecular weight 204), the identification of (+)-longifolene was done by comparison and co-injection with a known standard. A probable epimer, (-)-longifolene, the dominant sesquiterpene in our samples, which gives an identical mass spectrum, but for which no standard was available, was tentatively identified (Simoneit, personal communication, 1990).

RESULTS

Spilled oil. The oil from the Shell refinery (hereafter called Shell oil) is a very viscous, asphaltic crude oil from the San Joaquin Valley, California. The free sulfur content is apparently low, based on the observation that activated copper powder did not discolor in the presence of a solution of the oil in dichloromethane; no quantitative measurements of sulfur were made.

Hexane extracts. Gas chromatographic analysis of the hexane fraction of the Shell oil indicates that this fraction is dominated by an Unresolved Complex Mixture (UCM) of branched and cyclic alkanes, seen as "humps" in the chromatograms (Fig. 2). Few distinctly resolved components are present. An aliphatic UCM is a common constituent of petroleum (Kennicutt and others, 1987). The sediments also contain UCM in varying amounts. The source of the UCM in the sediments cannot be unambiguously ascertained because it could come from several sources; it is considered indicative of petroleum contamination or biodegradation (Brassell and Eglinton, 1980). In our samples the petroleum contamination could be either from the spilled oil or from a chronic background of petrogenic input; we could not differentiate the relative magnitude of the contributors to the sediment hexane UCM.

Some components or systems of components in the Shell oil can be identified by mass spectra, specific-ion profiles in the GC/MS chromatograms or Selected Ion Monitoring (SIM); these components include the biomarkers and other cyclic aliphatic hydrocarbons discussed below. However, the oil lacks many groups of compounds that are prominent in the sediments. The Shell oil contains no *n*-alkanes or isoprenoid hydrocarbons; this is a characteristic common to some San Joaquin Basin crude oils which have a highly asphaltic nature and show evidence of moderate biodegradation

(Curiale and others, 1985; Kruge, 1986).

In contrast to the oil, the gas chromatograms of the sediments both from inside and outside the spill area show, as the dominant aliphatic hydrocarbon system, the high molecular weight *n*-alkanes with the odd-even predominance (OEP) characteristic of terrigenous plant wax sources (Eglinton and Hamilton, 1967). OEP values are given in Table 1. Lower molecular weight *n*-alkanes and the isoprenoid hydrocarbons, pristane and phytane, characteristic of marine, algal, or non-biodegraded petrogenic sources, are generally present in only minimal amounts relative to the higher molecular weight *n*-alkanes. The low-range *n*-alkanes do appear in small but discernible amounts relative to the high-range *n*-alkanes at sites outside of the spill area, SF-19 and SF-20 (Southampton). At SF-21 pristane and phytane dominate the low range alkanes. The low amounts of lower molecular weight alkanes relative to higher molecular weight alkanes may be due to the susceptibility of the former to preferential degradation (Brassell and others, 1983); similar observations were made in the South Bay study (Hostettler and others, 1989). The lack of *n*-alkanes and isoprenoids in the Shell oil obviously precludes their use in discerning spill oil characteristics within the sediments.

Another prominent feature of the hexane fraction of the sediments and not the oil is a group of several sesquiterpenes, molecular weight 204 atomic mass units (amu), with one strongly dominant member, tentatively identified as (-)-longifolene. These compounds appear in varying amounts relative to the *n*-alkanes in all the sediments. At site SF-15 (-)-longifolene appears in highest concentration, approximately equivalent to *n*-C₂₉. This compound was also the dominant member of the sesquiterpene series in sediment samples from the earlier South Bay study (Hostettler and others, 1989) and is assumed to have a terrigenous higher plant source.

Cyclic aliphatic hydrocarbons, including biomarkers, are the final prominent substituents of the hexane fractions. The Shell oil and the sediments contain most of the same constituents. The GC/MS SIM of ions with mass-to-charge (*m/z*) ratio 191 (Figs. 3 and 4) and 177 (Fig. 3) indicates the presence of tricyclic and pentacyclic triterpanes; *m/z* 177 also indicates the presence of 25-demethylated triterpanes. SIM of *m/z* 217 (Fig. 5) shows that steranes are present, and *m/z* 253 (not shown) indicates the presence of monoaromatic steranes. The suite of *m/z* 191 tricyclic terpanes contains C₂₀-C₂₉ with C₂₃ as the dominant member; the distribution of the compounds is very similar in all samples, oil and sediments. Among the pentacyclics, the $\alpha\beta$ -hopane series is the major series with C₂₇-C₃₅ present. The C₂₉ and C₃₀ homologs (norhopane and hopane) are the dominant members. The presence of a C₂₈ homolog, 28,30-bisnorhopane, is also noted. This compound is considered a strong marker for Miocene oils from the Monterey Formation, which includes the San Joaquin Basin (Curiale and others, 1985), but it is also present in the Bay sediment extract fractions, both from this study and the earlier work (Hostettler and others, 1989). In all cases 28,30-bisnorhopane appears as a peak smaller than the peaks from the norhopane and hopane homologs. Also present in the Shell oil and all Bay samples from both studies is a low to moderate amount of oleanane, considered a marker for terrigenous input (Philp, 1985); this compound is only rarely found in Monterey Formation oils (Curiale

and others, 1985). No hopenes or compounds in the $17\beta(H),21\beta(H)$ -hopane series, reflecting immature biogenic or microbial input, are seen in the Bay sediments or in the Shell oil. The mass fragmentograms of m/z 177 (25-demethylated triterpanes, Fig. 3) and m/z 253 (monoaromatic steranes, not shown) closely resemble those reported by Curiale and others (1985) from naphthenic, non-paraffinic San Joaquin Basin oils. The distribution of components in the m/z 177 and 253 systems is similar for the Bay sediments, both impacted and non-impacted, and for the spill oil, thus limiting the use of these compounds for identifying the spilled oil in the sediments. No unique biomarker compounds in any of the SIM fragmentograms are found that clearly differentiate the Shell oil from the Bay sediments.

Three traditional maturity indicators (Mackenzie, 1984) from the biomarker chromatograms are considered: $\alpha\beta$ -C₃₁ S/(S+R) hopane ratios in both sediment extracts and oil show equilibrium or full maturity values (0.6 in all samples). T_m/T_s ratios, which here might have maturity and/or source implications (Seifert and Moldawen, 1978), have a narrow range of 1.2-1.9 with no observably different trends between spill oil and sediments. The $\alpha\alpha\alpha$ -C₂₉ S/(S+R) sterane ratios (0.5 at equilibrium) show a significant range, 0.28 to 0.46. The two highest values, 0.45 and 0.46, are observed in the Shell oil, and the lowest values in the subsurface pushcore sample, SF-18. Otherwise most of the values cluster at an intermediate level with no useful differentiation. Neither oil nor sediment exhibit any clear difference in abundances of C₂₉ $\alpha\alpha\alpha$ - vs. $\alpha\beta\beta$ -steranes, a comparison which has been used to differentiate between Monterey Formation oils (Curiale and others, 1985). These maturity indicators, therefore, could not be used to identify spilled oil in the sediments.

Variations in the relative amounts of selected constituents within the samples fractions, however, did show some differences between the oil and the sediments. Other studies have utilized ratios similar to the following to describe differences between hydrocarbon assemblages (e.g., Kruege, 1986, and Killops and Howell, 1988). First, in the m/z 191 fragmentograms the relative abundances of the tricyclic hydrocarbons vary with respect to the pentacyclic hydrocarbons. This variation is reflected in the ratio comparing the major member of each group, C₂₃ for the tricyclics and C₃₀ for the pentacyclics (Table 1). The Shell oils (SF-23 and -24) have significantly more of the tricyclics, and the sediments (SF-15 through -21) have more of the pentacyclics, as shown by the oil ratios, 2.3 and 2.5, versus sediment ratios, 0.23 to 0.89. Within the sediments the highest ratios are at sites SF-15, 17 and 21. Second, the proportions of $\alpha\beta$ -C₂₉ and -C₃₀ vary from spill oil to sediments, with norhopane higher in the spill oil (norhopane/hopane ratios of 2.0) and hopane higher in the sediments (norhopane/hopane ratios from 0.70 to 1.1, with the highest values at sites SF-15 and 17). Third, in the m/z 217 fragmentograms the major difference is the dominance of either the $\beta\alpha$ -C₂₇ diasterane epimers (as in the Shell oil) or the $\alpha\alpha\alpha$ -C₂₉ sterane epimers (as in the unimpacted Bay sediments). San Joaquin Basin oils commonly show relatively lower abundance of the C₂₉ steranes (Curiale and others, 1985). However, Monterey Formation oils in general have low diasterane content relative to other steranes (Curiale and others, 1985), so the fact that the Shell oil is dominated by diasteranes is possibly due to moderate biodegradation (Requejo and Halpern, 1989).

Ratios comparing these two compound classes (the C_{27} - $\beta\alpha$ diasterane pair to the regular C_{29} - $\alpha\alpha\alpha$ sterane pair) have values of 5.2 and 4.7 for the Shell oil and 0.64-2.3 for the Bay sediments; samples SF-15, 17 and 21 have the most intermediate values. Lastly, further examination of the m/z 217 fragmentogram of the Shell oil in the lower range shows the presence of two resolved lower molecular weight tetracyclics, molecular weight 288 amu and a probable methyl homolog at 302 amu; the first is tentatively identified by full-scan GC/MS as $5\alpha(H)$ -pregnane by comparison with literature spectra (Philp, 1985). The pregnane is present in all samples, but a ratio of it to the regular C_{29} - $\alpha\alpha\alpha$ steranes again shows a useful differentiation. The Shell oils have the highest values, and samples SF-16, 18 and 20 the lowest. Samples SF-15, 17, 19 and 21 have intermediate values. Except for SF-19, this trend is consistent with that shown in the above mentioned ratios. Sediment samples where extracts consistently have higher values of these ratios, SF-15, 17 and 21, are suggested to be impacted to varying degrees by the spilled oil.

Other parameters utilizing data from the hexane fractions were calculated for the sediment samples. All sediments show a dominance in the high molecular weight n -alkanes of the odd-carbon-number members, measured by OEP and indicating terrigenous input (Table 1). Terrigenous character is also shown by the parameters ΣC_{25-31} and SIM 57/191 (Tables 1 and 2). In these three parameters the two Southampton samples, SF-19 and 20 give the lowest values, indicating the lowest relative terrigenous character.

Benzene fraction--20%. The major feature of the chromatogram of the 20B fraction of the Shell oil is again a UCM; an aromatic UCM is present in all the samples. However, the modality of the UCM differs in the different samples. Figure 6 shows that three modes appear, indicated in order of retention time by 1, 2, and 3. The Shell oil has a strong mode 1, weak 2 and 3, whereas the unimpacted sediment, e.g. at Southampton, has no mode 1, a dominant mode 2, and a moderate mode 3. The figure indicates that SF-17 clearly has the spill oil mode 1, along with approximately equivalent mode 2 and moderate mode 3; SF-18 and -19 have no clear mode 1, only modes 2 and 3. On chromatograms of sites not shown, only SF-15 has a low level of mode 1 (Table 3).

Other than UCM, the 20B fraction contains mainly PAH's. San Joaquin Basin oils frequently contain aromatic thiophenes and their alkylated derivatives (Curiale and others, 1985); the persistence of these compounds in the environment has been used in other studies to evaluate oil contamination (Berthou and others, 1987). However, the aromatic thiophenes were not seen at the levels of detection in this study. The aromatic characteristics of the Shell oil include a dominance of C_1 to C_3 alkylated PAH's, especially phenanthrenes and naphthalenes. The relative abundances of the alkylated PAH isomers compared to the parent PAH's differs between the Shell oil and the sediments. Oils, in general, have more of the alkylated PAH's than the non-alkylated parents. Several studies (Radke and others, 1982, Prahl and Carpenter, 1983, and Killips and Howell, 1988) have used ratios of alkylated to non-alkylated parent PAH's as parameters to indicate maturity or petrogenic character. To help differentiate

oil-impacted sediments from non-impacted sediments (Table 3), we utilize the methyl phenanthrene ratio MP/P (Prahl and Carpenter, 1983) which has been reported to range from 0.5-1.0 for sediments dominated by combustion PAH's and 2-6 for petroleum or sediments dominated by petroleum, and a dimethyl phenanthrene ratio DMP/P (Killops and Howell, 1988) in which the oil range is somewhat higher. Samples SF-19 and 20 have the lowest values for these ratios in the sample set. The spill oil has the highest values. Only SF-17 has values clearly in the oil range.

A clear visual differentiation can be seen on the chromatograms between the patterns of the methyl phenanthrenes in the spill oil and the sediments (Fig. 7 and Table 3). The distribution of the four isomers (3MP, 2MP, 9MP and 1MP in order of elution) in the Shell oil is such that 9MP is the most abundant and 1MP is the least, significantly lower than the other three isomers; in non-impacted sediment extracts all four isomers produce similar peak heights or have the 3MP/2MP doublet higher than the 9MP/1MP. Only in sample SF-17 is the pattern of the methylphenanthrene isomers clearly the same as that of the Shell oil.

The Shell oil and the sediments also contain a prominent suite of tri-aromatic steranes, monitored by the major ion at m/z 231 and commonly found in oils. The distribution of tri-aromatic steranes is very similar to that reported by Killops and Howell (1988) and Mackenzie and others (1981). Like the mono-aromatic sterane fragmentograms (m/z 253) from the hexane extracts, all the sediment and the oil samples contain a similar distribution of the m/z 231 tri-aromatics; thus this aspect is not useful for differentiation. However, because the tri-aromatics are so prominent in the chromatograms of the oils, along with the prominence of the above-mentioned methylated phenanthrenes, a ratio of the major constituent of the tri-aromatic sterane suite and the major constituent of the dimethylphenanthrene suite (m/z 206) serves as a useful source parameter. This ratio indicates two different ranges--high values for non-impacted sediments and low values for the Shell oil samples and probably-impacted sediments. Only SF-21 has an anomalously high value.

In addition, the sediment 20B extracts show a variety of source signatures different from the Shell oil. Chromatograms of samples SF-19 (Fig. 6) and 20 (not shown), taken from Southampton Bay which is outside of the spill-impacted area, are dominated by compounds widely attributed to combustion sources spread by aeolian transport (Laflamme and Hites, 1978) or urban drainage/street run-off (Gschwend and Hites, 1981), namely, fluoranthene and pyrene and lesser amounts of phenanthrene, chrysene and other non-alkylated PAH's. Alkylated homologs are in very low concentration relative to the parent PAH's. This signature was also prominent in the sediments reported in the earlier study of South Bay (Hostettler and others, 1989). Recent petrogenic input, here from anthropogenic sources, which would be expected to show significantly higher amounts of alkylated homologs relative to the parents, is a relatively minor contributor to this fraction in the Southampton Bay samples. Site SF-19 shows evidence of contamination input at slightly higher levels than the other sites, indicated by the higher TOC and EOM (Table 1), the noted surface sheen on collection, and the low OEP₂₉.

The core at SF-17/18 shows a different set of source signatures and, therefore, a different distribution of constituents from sample SF-19 (Fig. 6). Both segments of the core's 20B fraction contain the compound 2,6-di-*t*-butylbenzoquinone, with the top segment SF-17 containing a significantly higher amount than the bottom segment; none of the other samples contain this compound. SF-18, the deeper segment in the core, is dominated by a group of di- and tri-aromatic tetracyclics tentatively identified as some of the same compounds reported by Laflamme and Hites (1979) in recent Amazon River and Cariaco Trench sediments, and suggested to be diagenetically derived from triterpenoid precursors and widespread in sediments. SF-18 also contains the prominent suite of tri-aromatic steranes. SF-18 is the only sample where the compound *p,p'*-DDE, a stable metabolite of DDT, is clearly identified, but the fact that this is the only sub-surface sample examined in this study may be an indication of its wider presence at slightly sub-surficial levels in the study area. The suite of probable combustion-related compounds in this sample is very low in relative abundance; however, the alkyl homologs are even lower, giving quite small MP/P and DMP/P ratios.

The top of the core, SF-17, has characteristics significantly different from the bottom; many parameters show Shell oil character. After the benzoquinone, the dominant compounds are the tri-aromatic steranes, which dominate the oil chromatograms. The di- and tri-aromatic tetracyclics seen in the bottom part of the core are in much lower relative concentrations than in the upper part. Alkylated PAH's are significantly more prominent than non-alkylated PAH's (MP/P and DMP/P values are the highest in the sediment set, closest to the spill oil values), and the combustion suite is very minor. SF-17 contains the most clearly defined Shell oil UCM.

Samples from the other sediment sites contain mixtures of all of these various source signatures.

Benzene fraction--60%. The Shell oil contains no resolved components in this fraction, only a broad, featureless UCM; thus there is nothing in the 60B fraction that is useful for differentiating the Shell oil from the sediment extracts. However, all of the sediment samples contain a suite of *n*-aldehydes, similar to that noted in the previous study (Hostettler and others, 1989); these compounds were shown to be of terrigenous origin. The distribution of *n*-aldehydes in this study is somewhat different, however (Fig. 8). As before, the series ranges from C₁₀ to C₃₄ with C₂₂ and higher even-carbon-numbered homologs appearing in notably greater abundance. In addition to the group of *n*-aldehydes with a C_{max} around C₃₀, however, there is a second suite with C₂₂ as its most abundant member. The two modes vary in relative importance with the C₂₂ mode being strongest at Southampton sites and C₃₀ at Martinez sites. There is ongoing discussion in geochemical literature as to the possibility of a precursor/product relationship between *n*-aldehydes and *n*-alkanes (see Hostettler and others, 1989, and references therein). In our study the *n*-alkanes in the hexane fractions (Fig. 2), however, show only a single C_{max} at C₂₉ in all the sediments. Because there is no *n*-alkane maximum corresponding to the aldehyde C₂₂, a precursor/product relationship in this system is not obvious. It is possible that different primary higher

plant terrigenous input is responsible for the two different aldehyde systems.

Benzene fraction--100%. As above, the Shell oil has no resolved peaks in this fraction. However, resolved components do appear in the sediment samples--a homologous series of long-chain acyclic methyl ketones accompanied by the C₁₈ isoprenoidal methyl ketone (Fig. 8). The *n*-alkan-2-ones range from C₂₃ to C₃₅, show a strong odd-carbon dominance, and have one or two apparent modes, with maxima at C₂₅ and/or C₂₉. The long-chain and isoprenoid methyl ketone series has been reported in various geologic settings, e.g. peat (Lehtonen and Ketola, 1990), shale (Saban and others, 1979) and marine sediment (Ikan and others, 1973). Its source has been suggested to be microbial oxidation of the terrestrially derived *n*-alkanes and isoprenoids, although conflicting evidence has been reported (Cranwell, 1981). Because the Shell oil has no methyl ketones, this fraction is also not useful for tracking the oil spill.

DISCUSSION

Only in sample SF-17 does the geochemical evidence clearly show a strong contribution from the Shell oil. The presence of Shell oil is indicated based on ratios of several molecular parameters. In the biomarker parameters, the two hopane ratios (major tricyclic/major pentacyclic and norhopane/hopane) and the two sterane ratios (C₂₇-diasteranes/C₂₉- $\alpha\alpha\alpha$ steranes and pregnane/C₂₉- $\alpha\alpha\alpha$ steranes), which are source related, have values intermediate between the two extremes of Shell oil and non-impacted sediment. In the PAH fraction, the alkylated phenanthrene ratios clearly are in the Shell oil range; the distribution of methylphenanthrene isomers is the same as that of the Shell oil; the tri-aromatic ratio gives a low value near that of the Shell oil rather than the high values observed in the sediments; and the aromatic UCM modality observed only in the Shell oil is part of the UCM of the PAH fraction of the sediment. SF-17 also has features that come from other sources. For example, its total organic carbon (TOC) content is low, relative to TOC values for other sediments which were not impacted by the oil spill. The high molecular weight *n*-alkane OEP value shows significant terrigenous higher plant wax character, as is true for all the Martinez sites and to a somewhat lesser extent for the Southampton sites. Both the SIM 57/191 ratios and the ΣC_{25-31} parameter, which compare terrigenous to petrogenic input and TOC respectively, have values consistent with a significant terrigenous component.

Two other samples from Martinez sites (SF-15 and 21) have some values that indicate Shell oil impaction but at a lower level than in sample SF-17. Sample SF-15 has lower but still intermediate values for the four biomarker source-related parameters, and in sample SF-21 three of four of these parameters are higher in value than background. The alkylated phenanthrene ratios are apparently not sensitive enough to indicate low levels of oil impaction. The tri-aromatic ratio is clearly nearer the Shell oil range for SF-15. Sample SF-15 shows a low level of the Shell oil aromatic UCM. These results indicate that SF-15 is impacted by the spill oil, but at a lower level than SF-17, and SF-21 may contain very low levels of the oil.

The other four samples, three (SF-16, 18, 19, and 20) indicate no impingement by the Shell oil. These four samples have the lowest values for the four source-related biomarkers parameters, except for one marginally anomalous value for the pregnane parameter at SF-19. The alkylated phenanthrene ratios show the strong dominance of the non-alkylated PAH typical of sediments but not oil. The tri-aromatic ratios are large, quite different from the Shell oil values. Sample SF-18 is a section of a core directly below the oil impacted sample SF-17; therefore it is clear that the Shell oil impact on the sediment was only surficial at the time the samples were collected.

These data indicate that assignment of sources frequently requires a broad spectrum of molecular parameters within a sediment system that is as complex as that found in San Francisco Bay. The results from the four surficial samples in the Martinez area, SF-15, 16, 17 and 21, also indicate that the Shell oil impingement is patchy, even within the area of fairly heavy spill exposure. Similar observations have been made in other studies (e.g., Gundlach and others, 1983, and Owens and others, 1987).

CONCLUSIONS

Several organic geochemical parameters have been found suitable for identification in sediments of the Shell crude oil from the April 22-23, 1988, spill into the Carquinez Straits in north San Francisco Bay. The problem is complicated by the degraded nature of the oil; many of its constituents are not readily resolved by chromatography, and several categories of compounds that might have been used as unique signatories of the oil, such as *n*-alkanes and isoprenoid hydrocarbons, are not present. Also, the sediments already contain essentially all the same chromatographically resolvable constituents as the oil. These compounds come from other sources, primarily a chronic background of petrogenic contamination in the Bay and a pyrogenic and/or urban drainage component. Because of this similarity of constituent types, our study focuses on different relative concentrations of various constituents, utilizing ratios of these compounds. No one chemical constituent or parameter was found that could uniquely determine the presence or absence of the Shell oil; several parameters had to be used in concert for reliability.

Two categories of compounds were most useful for this purpose, the hopane and sterane biomarkers and the PAH's and their alkyl derivatives. The use of selected ratios resulted in the conclusion that one of the investigated sites in the Martinez area was significantly impacted by Shell oil, two contained Shell oil to a lesser extent, and four, including two from an area by-passed by the spill, were not contaminated by the Shell oil. The impact of the oil at the time of collection was surficial only, and the data show that patchiness of oil impingement occurs even within an area of fairly heavy spill oil exposure.

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Table 1. Site information

Sample	Location	TOC ^a	EOM ^b (µg/g)	Fractions, % EOM				OEP ₂₉ ^c	ΣC ₂₅₋₃₁ ^d
				H(%)	B(%)	M(%)	Recovery(%)		
Sediments:									
SF-15	Martinez, near oil	0.58	204	22	32	33	87	8.6	248
SF-16	Martinez, relatively uncontaminated area	0.24	71	20	29	40	89	12.2	304
SF-17	Martinez, push core, near oil, top 7 cm.	0.30	213	31	37	19	87	9.0	420
SF-18	Martinez, push core, bottom 7 cm.	0.52	88	26	37	29	92	12.5	319
SF-19	Southampton, beyond oil spill	1.8	708	15	33	32	80	3.7	119
SF-20	Southampton, beyond oil spill	1.2	395	16	31	29	76	4.3	105
SF-21	Martinez, box core, possibly contaminated	0.38	93	31	31	31	93	10.8	343
Spill Oil:									
SF-23	Shell spill oil, non-dispersed, from ruptured tank			23	33	20	76	nc	0
SF-24	Shell spill oil, from composite clean-up			26	32	19	77	nc	0

^aTOC = Total Organic Carbon

^bEOM = Extractable Organic Material; fractions: H (hexane), B (20,40,60 & 100% benzene) and M (methanol)

^cOEP₂₉ = Defined in text

^dSum of n-alkanes C_{25,27,29,31} normalized to TOC, µg/g OC. See Prahl and Carpenter (1984)

Table 2. Biomarker parameters*

Sample	m/z 191				m/z 217**			SIM m/z $\frac{57}{191}$
	$\frac{T_m}{T_s}$	$\frac{C_{23}tricy}{C_{30}\alpha\beta}$	$\frac{C_{29}\alpha\beta}{C_{30}\alpha\beta}$	$C_{31}\alpha\beta \frac{S}{S+R}$	$\frac{\beta\alpha DC_{27}}{\alpha\alpha\alpha C_{29}}$	$\alpha\alpha\alpha C_{29} \frac{S}{S+R}$	$\frac{pregnane}{\alpha\alpha\alpha C_{29}}$	
Sediments:								
SF-15	1.4	0.62	0.97	0.59	1.9	0.36	0.99	16
SF-16	1.3	0.23	0.71	0.59	1.0	0.41	0.30	21
SF-17	1.6	0.89	1.1	0.58	2.3	0.41	1.3	11
SF-18	1.2	0.28	0.70	0.56	0.72	0.25	0.22	37
SF-19	1.9	0.42	0.66	0.59	0.64	0.42	0.76	3
SF-20	1.5	0.40	0.79	0.59	0.88	0.40	0.48	4
SF-21	1.3	0.62	0.70	0.57	1.3	0.28	0.74	20
Spill Oil:								
SF-23	1.8	2.5	2.0	0.60	5.2	0.45	3.2	0
SF-24	1.7	2.3	2.0	0.61	4.7	0.46	2.8	0

* All ratios defined in text.

** Both S and R isomers included if not specified

Table 3. Parameters from PAH Fraction

Sample	MP/P*	DMP/P*	Methyl Phenanthrene Isomer Ratios**: 3MP/2MP/9MP/1MP	Triaromatic Ratio: Major: tri-arom/DMP (m/z 231/206)	UCM Modality (#1, Fig. 6) (Rel. Concs.)
Sediments:					
SF-15	0.93	1.3	5/6/6/5.5	0.97	X
SF-16	0.98	2.0	5/6/5.5/5.5	1.8	
SF-17	3.00	7.0	5/5/6/3.5	1.0	XX
SF-18	0.95	1.5	6/4.5/5/4	3.2	
SF-19	0.84	0.74	5/6/4/3.5	5.1	
SF-20	0.64	0.87	5/6/4/3.5	3.8	
SF-21	0.67	0.81	6/5/5/4.5	4.5	
Spill Oil:					
SF-23	4.1	7.6	5/5.5/6/3.5	0.94	XXX
SF-24	4.5	9.3	5.5/5.5/6/3.5	1.3	XXX

* MP/P and DMP/P are alkyl phenanthrene-based ratios. See Prahl and Carpenter (1983) and Killops and Howell (1988)

** Normalized to highest peak as 6

Other terms defined in text

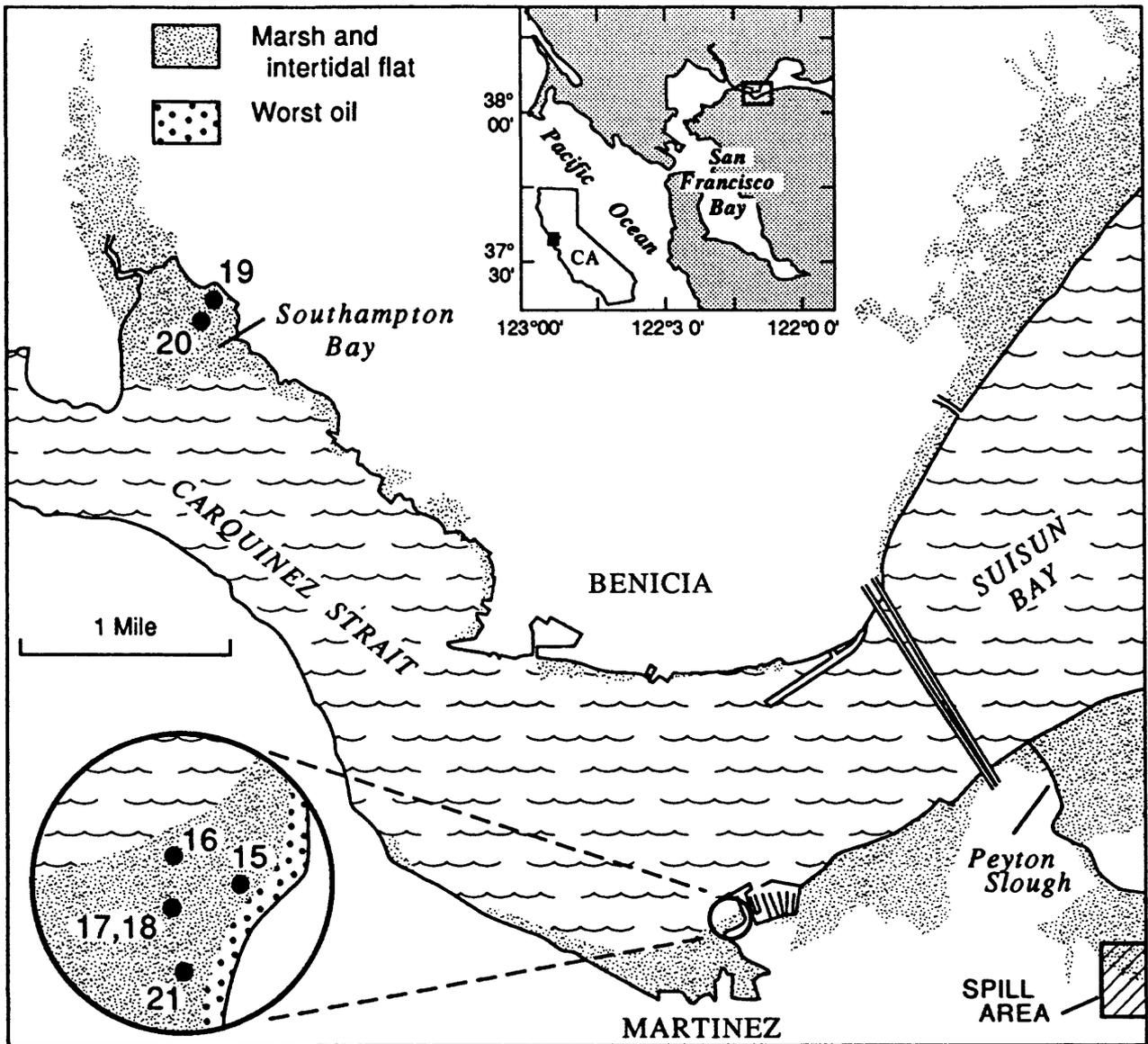


Figure 1. Map of study area

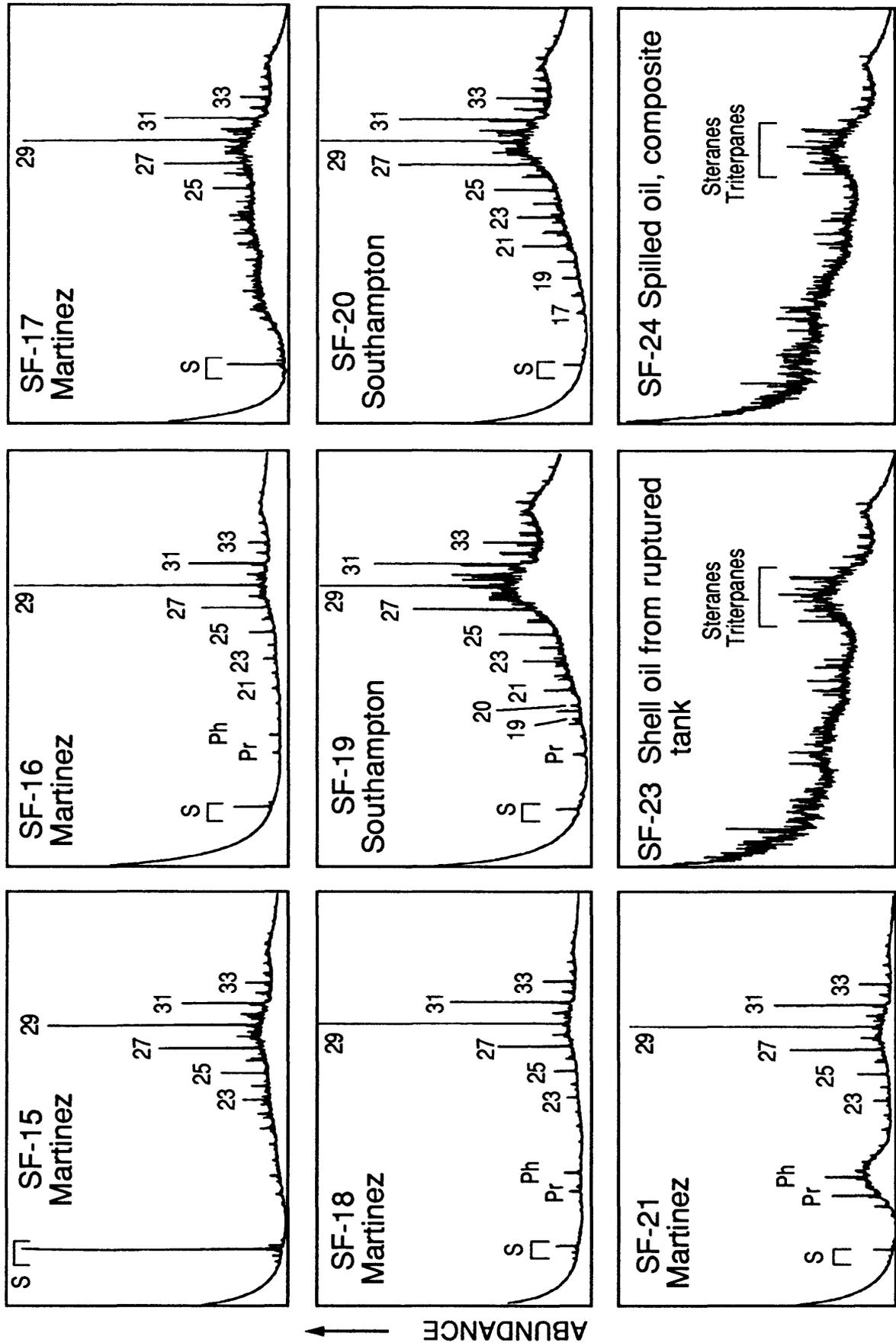


Figure 2. Gas chromatograms of hexane fractions of sediments and spill oil. Carbon numbers of n-alkanes are indicated; Pr, Ph = Pristane, Phytane; S = sesquiterpenes, mol wt. 204

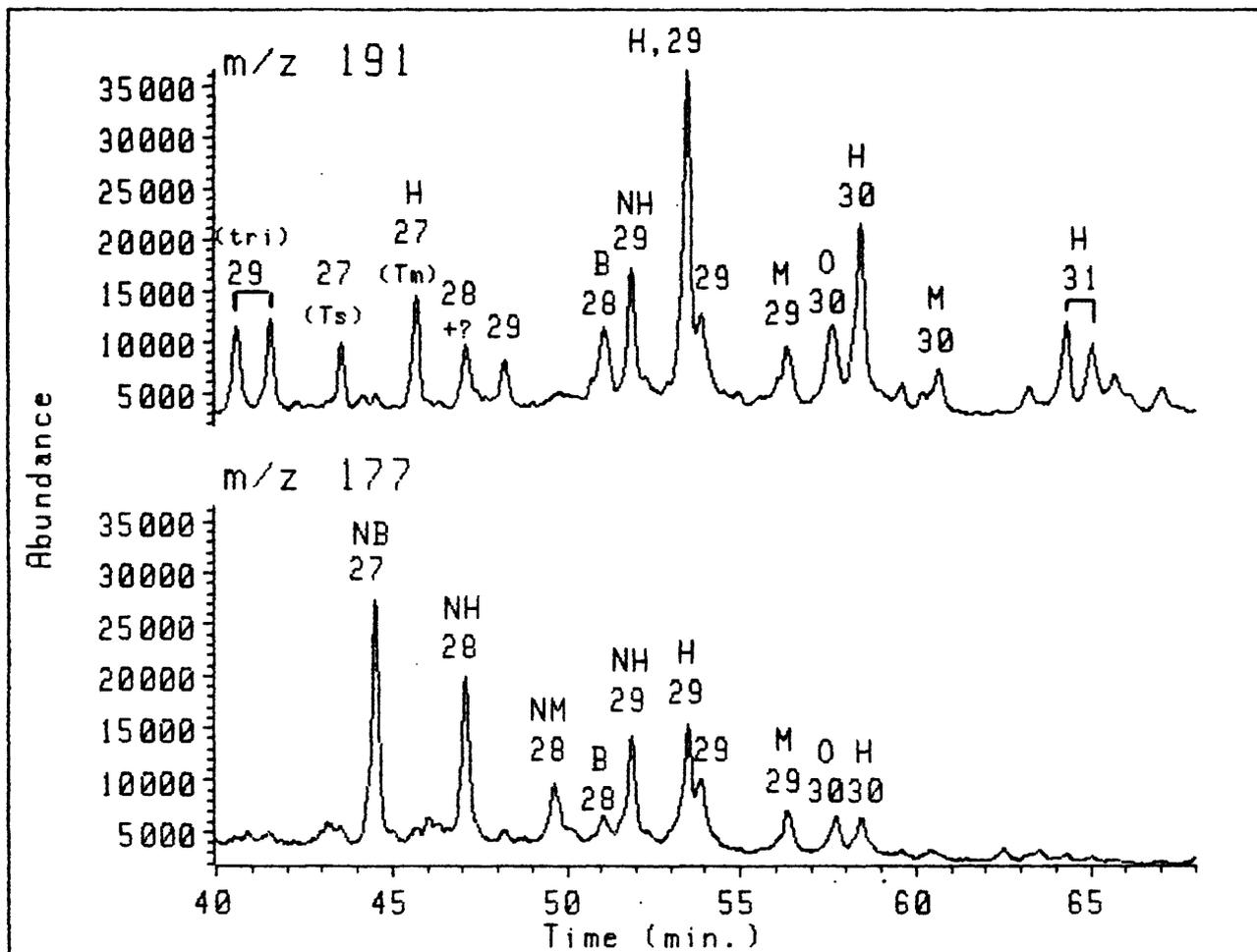


Figure 3. Mass fragmentograms for m/z 191 and 177 of the hexane fraction of the spill oil showing the major pentacyclic triterpanes. Carbon numbers and homologous families are indicated. H = $17\alpha(H),21\beta(H)$ -hopanes; M = $17\beta(H),21\alpha(H)$ -moretanes; B = 28,30-bisnorhopane; N = 25-nor-[triterpane]. Also included are the 22,29,30-trisnorhopanes, $18\alpha(H)$ - [=Ts] and $17\alpha(H)$ - [=Tm], and oleanane (O)

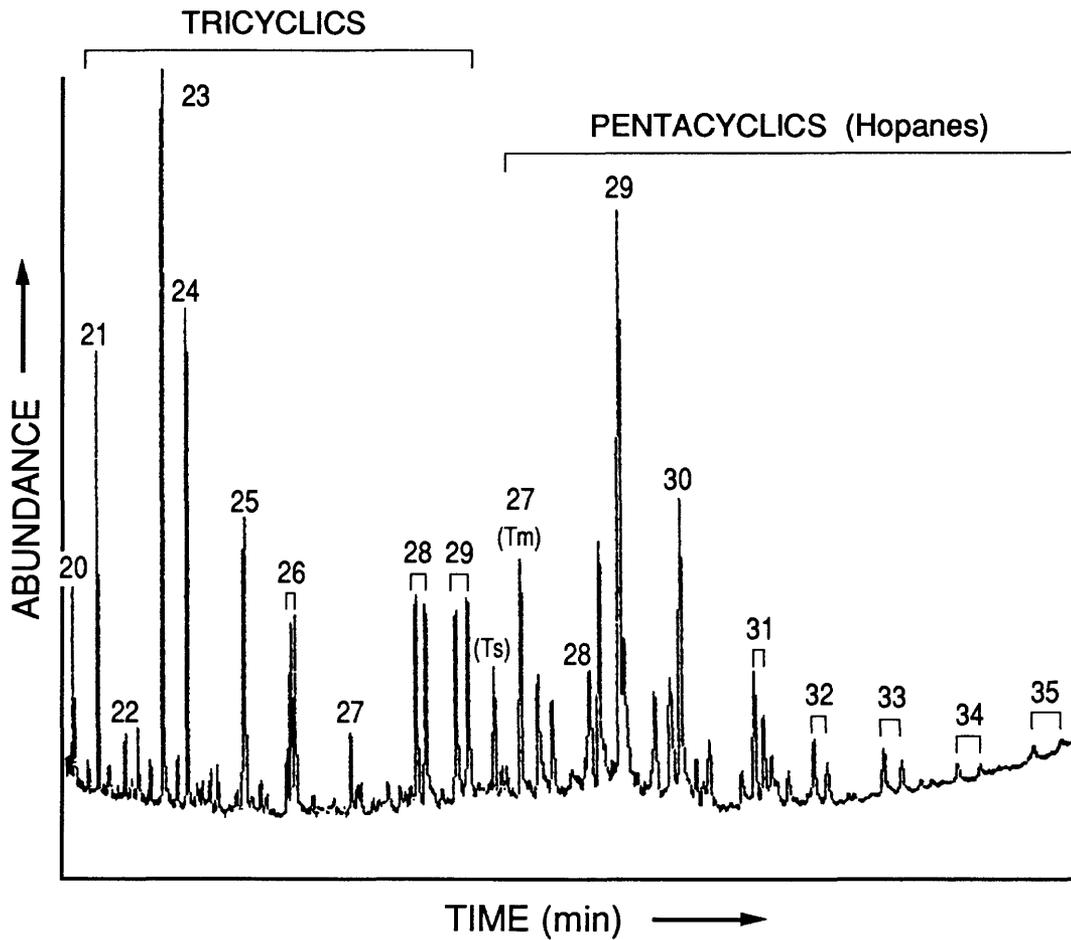


Figure 4. Mass fragmentogram of m/z 191 of the hexane fraction of the spilled oil. The two major suites of terpanes are shown with the carbon number of each member indicated. Brackets indicate R and S epimers; trisnorhopanes (Ts) and (Tm) are also noted

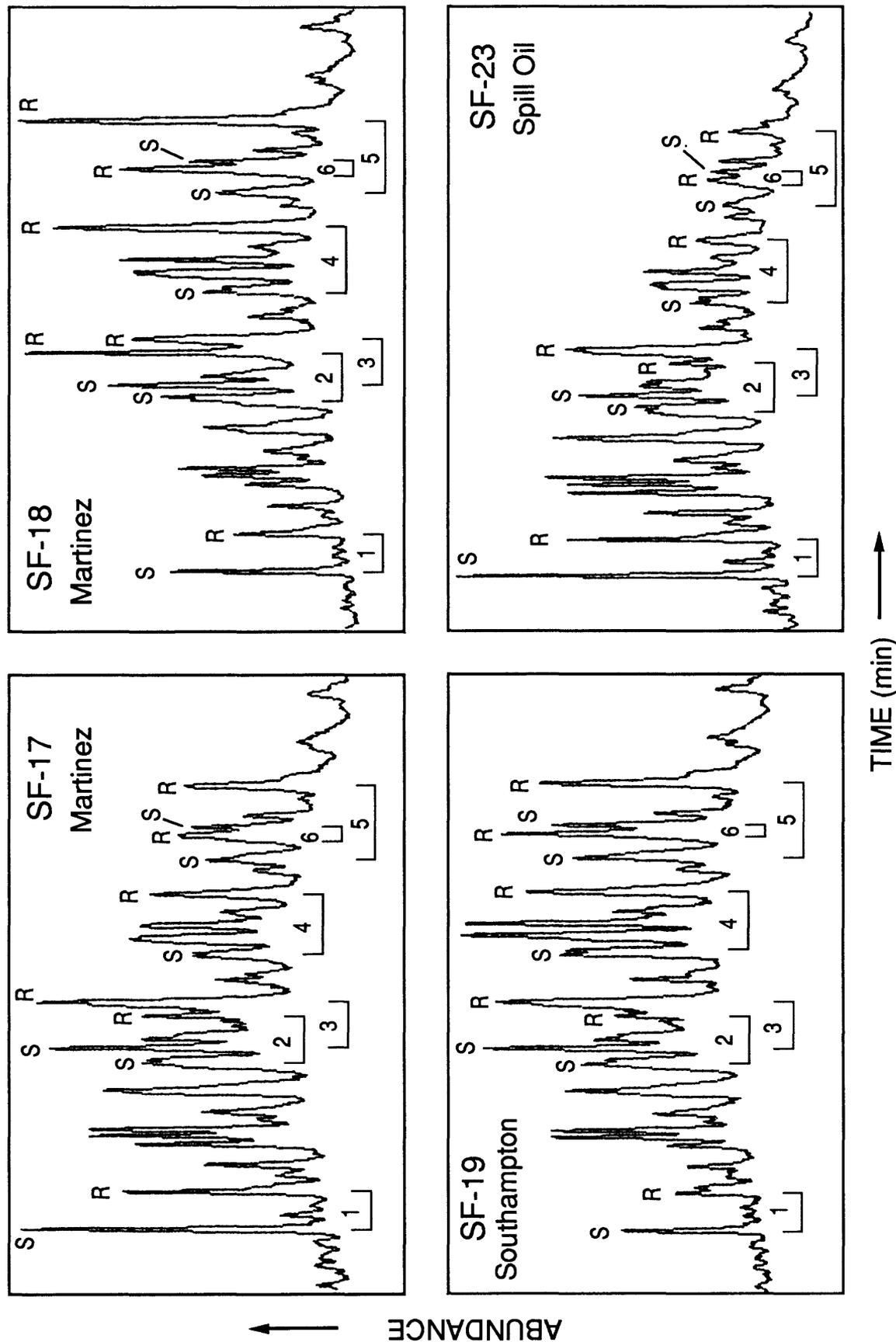
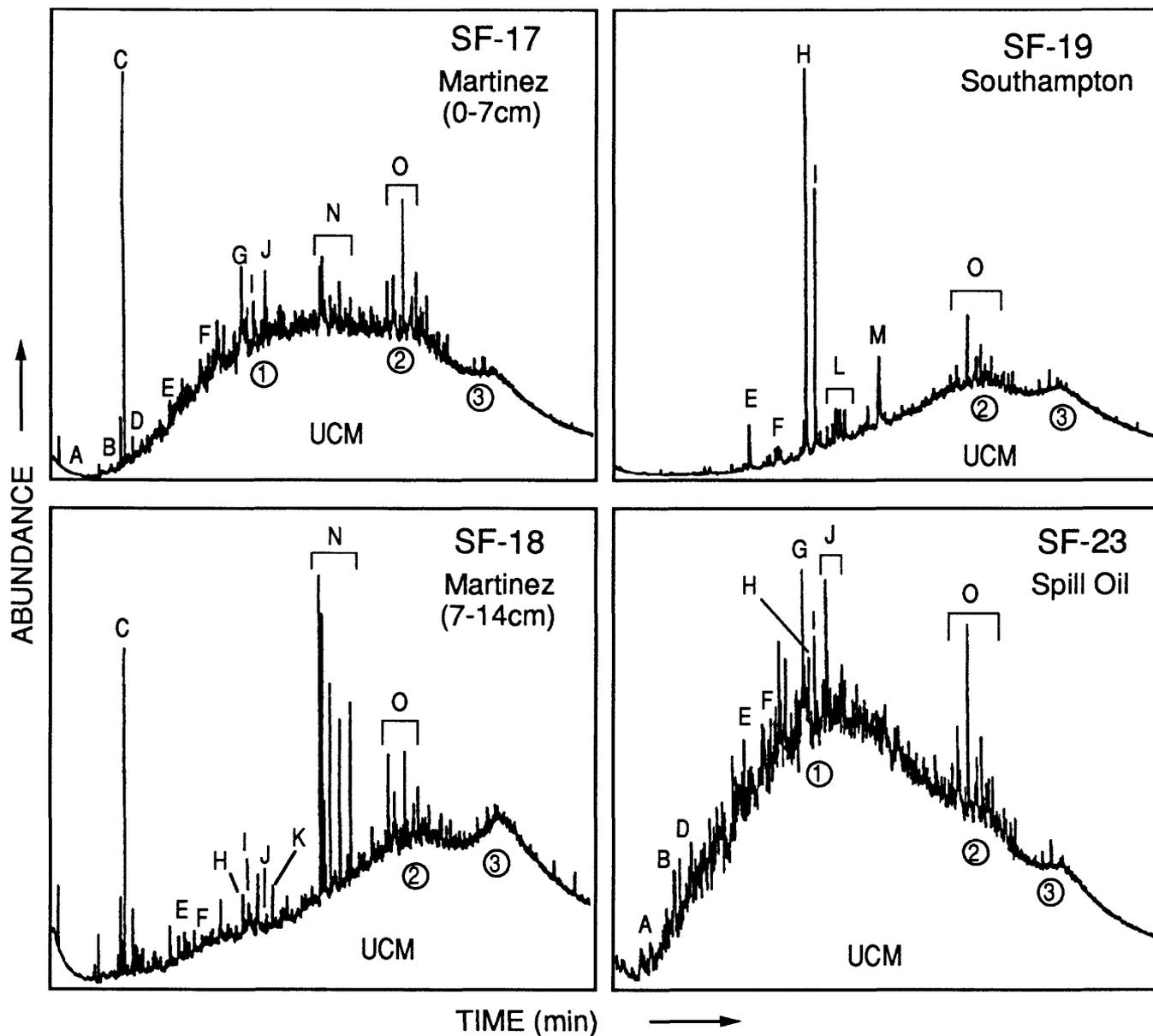


Figure 5. Mass fragmentogram of m/z 217 of representative sediment and oil hexane fractions. Key: 1 = $\beta\alpha D27$; 2 = $\alpha\alpha 27$; 3 = $\beta\alpha D29$; 4 = $\alpha\alpha 28$; 5 = $\alpha\alpha 29$; 6 = $\alpha\beta 29$, where $\beta\alpha D = 13\beta(H)$, $17\alpha(H)$ -diasteranes and $\alpha\alpha$ and $\alpha\beta = 5(H)$, $14(H)$, $17(H)$ -steranes, with carbon numbers given and R and S epimers at C-20 indicated



A = C₁ Naphthalenes (142)
 B = C₂ Naphthalenes (156)
 C = Cc1c(C)c(O)c(O)c1 2,6-di-t-butyl-benzoquinone (177)
 D = C₃ Naphthalenes (170)
 E = Phenanthrene (178)
 F = C₁ Phenanthrenes (192)
 G = C₂ Phenanthrenes (206)
 H = Fluoranthene (202)
 I = Pyrene (202)

KEY

J = C₃ Phenanthrenes (220)
 K = p,p'-DDE (318)
 L = C₁ Pyrene/Fluoranthene (216)
 M = Chrysene (228)
 N = Di- and tri-aromatic tetracyclics (292,274 and others) as seen in Laflamme and Hites (1979); 5 major peaks
 O = Triaromatic steranes (231) as seen in Mackenzie *et al.* (1981)
 UCM = Unresolved Complex Mixture, 3 maxima: ①, ②, ③

Figure. 6. Gas chromatograms of representative sediment and spill oil 20B fractions (PAH-containing). Major constituents noted in Key with m/z of major ion(s) useful in identification by GC/MS

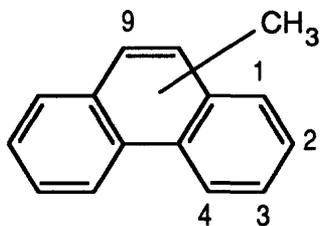
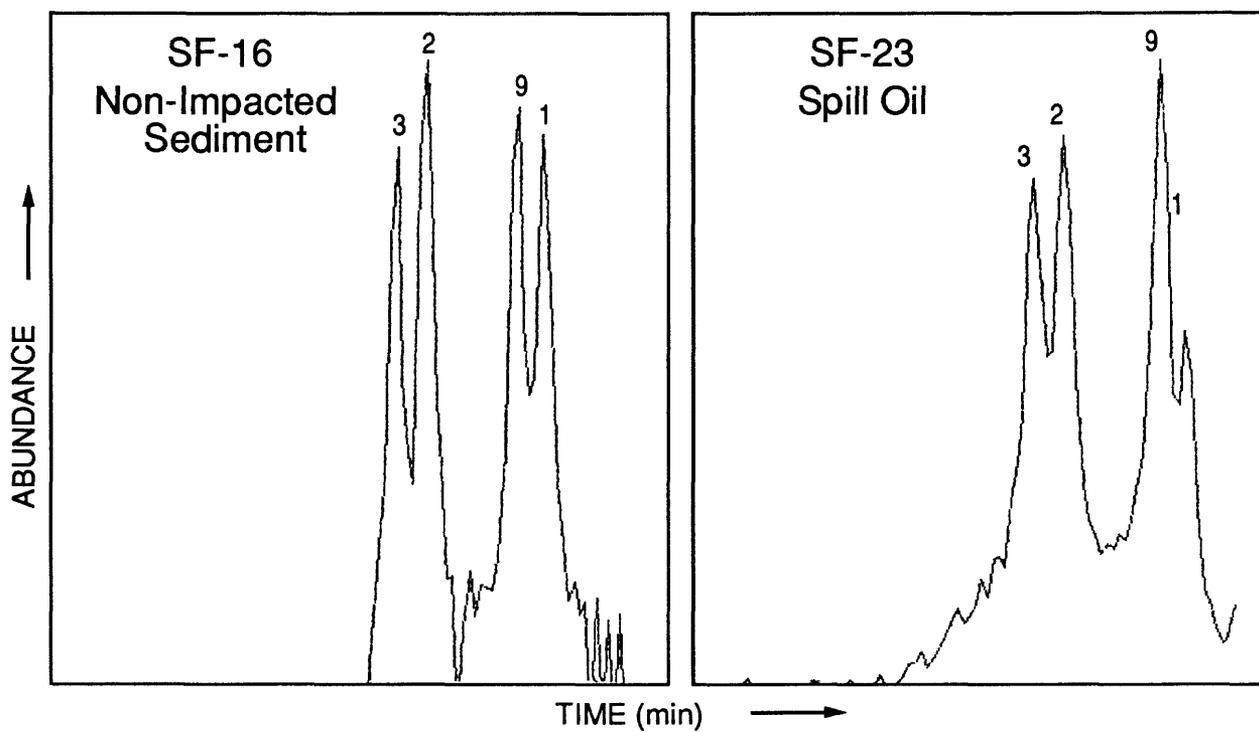


Figure 7. Mass fragmentograms (m/z 192) showing the methyl phenanthrene isomer distribution patterns in sediment and spill oil. See Table 3 for ratios at all the sampling sites

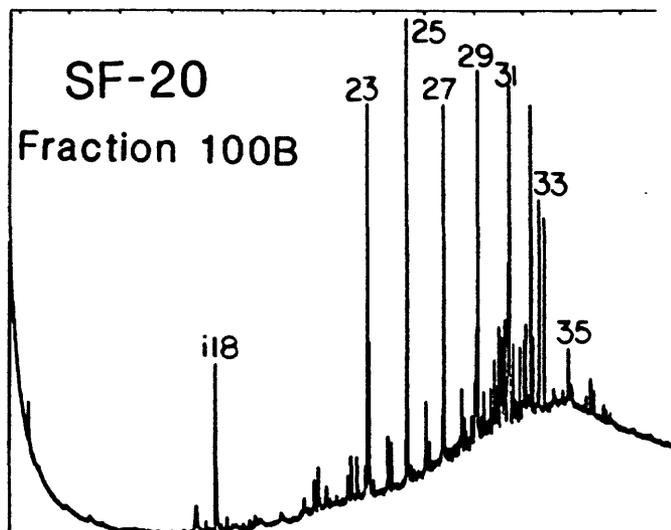
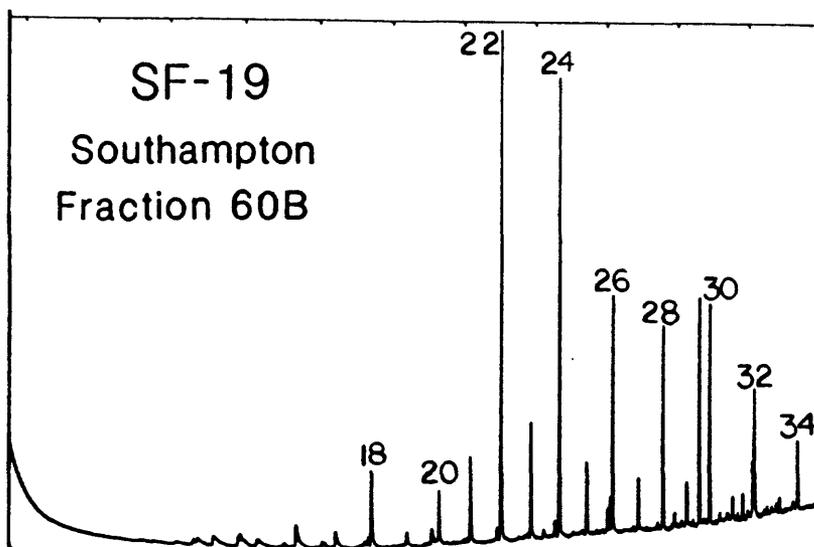
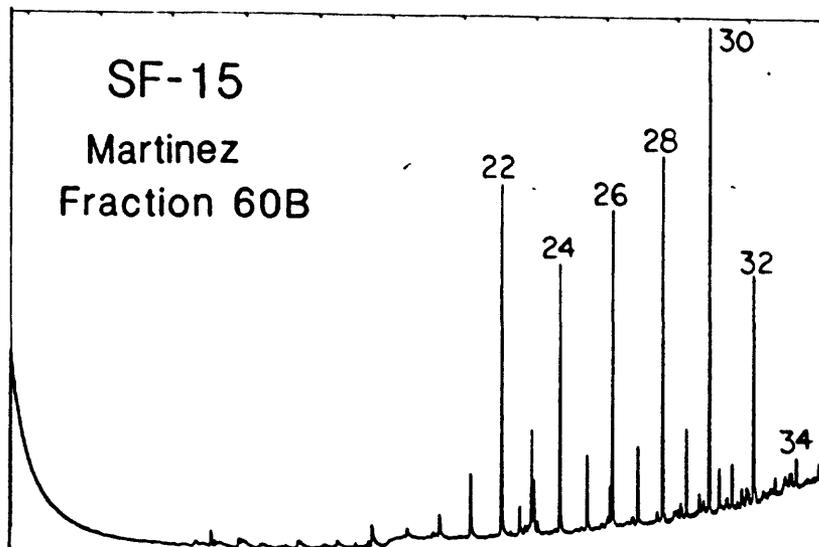


Figure 8. Gas chromatograms of representative fraction 60B (contains mainly n-aldehydes) and 100B (methyl ketones). Carbon numbers are indicated; i = isoprenoid