

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

Louisiana oil-oil correlation by iso-cyclic, aromatic, and gasoline-range  
hydrocarbons, with an appendix of organic-geochemical rock data from  
selected wells in the Gulf Coast

by

Leigh C. Price<sup>1</sup>

Open-File Report 89-358

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<sup>1</sup>Denver, Colorado



## ABSTRACT

Twenty-three oils from the Caillou Island field, Louisiana, and ten unrelated oils from widely-scattered, North American localities were characterized by gas chromatography. The Caillou Island oils ranged in depth from 2,617-6,060 m (8,398-19,444 ft), in gravity from 0.758-0.889 g/cc (52.8-27.6° API), had widely variable physical characteristics ranging from black oil to straw yellow condensate-like oil, and exhibited no correlation of physical properties versus depth. Oils were compared by measuring relative peak heights of selected aromatic and saturated hydrocarbons (HC's) in the n-C<sub>8</sub> to n-C<sub>21</sub> range. (The n-paraffins had been removed from the saturated HC's by molecular sieve.) The measured relative peak heights were summed over carbon-number intervals of 2 to 7.5, normalized by percentage to each other, and plotted. In spite of this relatively unsophisticated manual technique, the relatively inefficient gas-chromatographic column (1.8 m x 2 mm packed column 3 percent GC SE-30 on 100-200 mesh Gas Chrom Q) which was employed, and the highly variable physical characteristics of the Caillou Island oils, these oils, by the resultant plots, obviously belonged to one family, and therefore, presumably, had a common source. With one exception (Lake Barre field, 3.2 km (2 mi) north of Caillou Island), the other ten oils, by these plots, exhibited no correlation to the Caillou Island oils, or to each other. These results were confirmed by C<sub>4</sub>-C<sub>7</sub> HC analyses.

Although biomarker-classed C<sub>13</sub>-C<sub>21</sub> isoprenoid HC's were used in some of these plots, in other plots, "generic" iso-cyclic saturated, and aromatic HC's were also used, HC's which are not considered to be biomarker-classed HC's. These "generic" HC's, present in oils in concentrations second only to the n-paraffins and in concentrations much higher than conventional iso-cyclic biomarkers, may, because of their higher concentrations, give a broader-based sampling and characterization of oils than do such biomarkers.

## INTRODUCTION

The present study was undertaken: 1) to examine the possibility if the oils in a series of vertically "stacked" reservoirs in a single field were genetically related and as such, had a common history of origin, migration, and accumulation, and 2) to determine if the common HC's found in crude oils could be used in oil-oil correlations. The oils of the Caillou Island field, southern Louisiana (Fig. 1) were chosen for this study as: 1) Texaco made 23 oils in the field available, 2) a large vertical interval of stacked oil reservoirs exists at Caillou Island (1,219 to beyond 6,705 m; 4,000 to beyond 22,000 ft), and 3) the geology of the area is well known.

## GEOLOGY

The following discussion is largely taken from Frey and Grimes (1970). The Caillou Island oil field, southern offshore Louisiana (Fig. 1), is part of the Bay Marchand-Timbalier Bay-Caillou Island salt complex (Fig. 2), the largest salt feature in the onshore southern Louisiana-offshore Louisiana region. This salt ridge extends east-west along the southern Louisiana coastline of Lafourche and Terrebonne Parishes and is more than 47.3 km (28 mi) long and up to 20.3 km (12 mi) wide. The salt ridge may be part of an even larger east-west trending salt feature, as gravity and subsurface data suggest that the ridge continues eastward to the Grand Isle 16 and 18 domes and westward to the Lake Pelto dome for an overall length of over 96.6 km (60 mi).



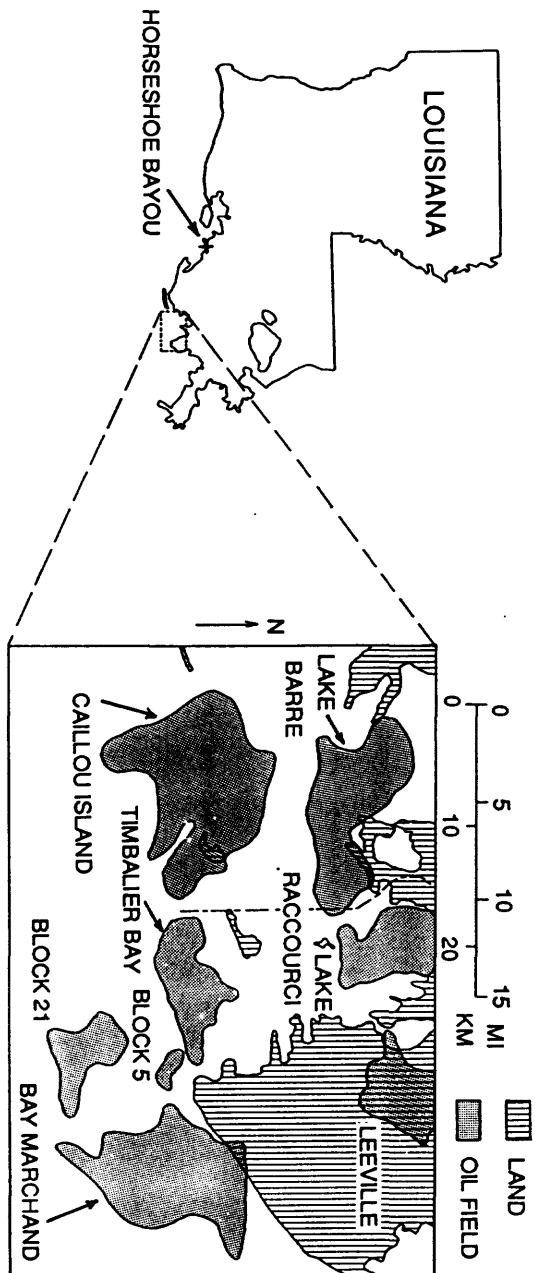


Figure 1. Index map showing location of Caillou Island and adjacent oil fields. Location of Horseshoe Bayou oil field is shown by cross on map of Louisiana. Boundary line delineates Terrebonne and Lafourche parishes.



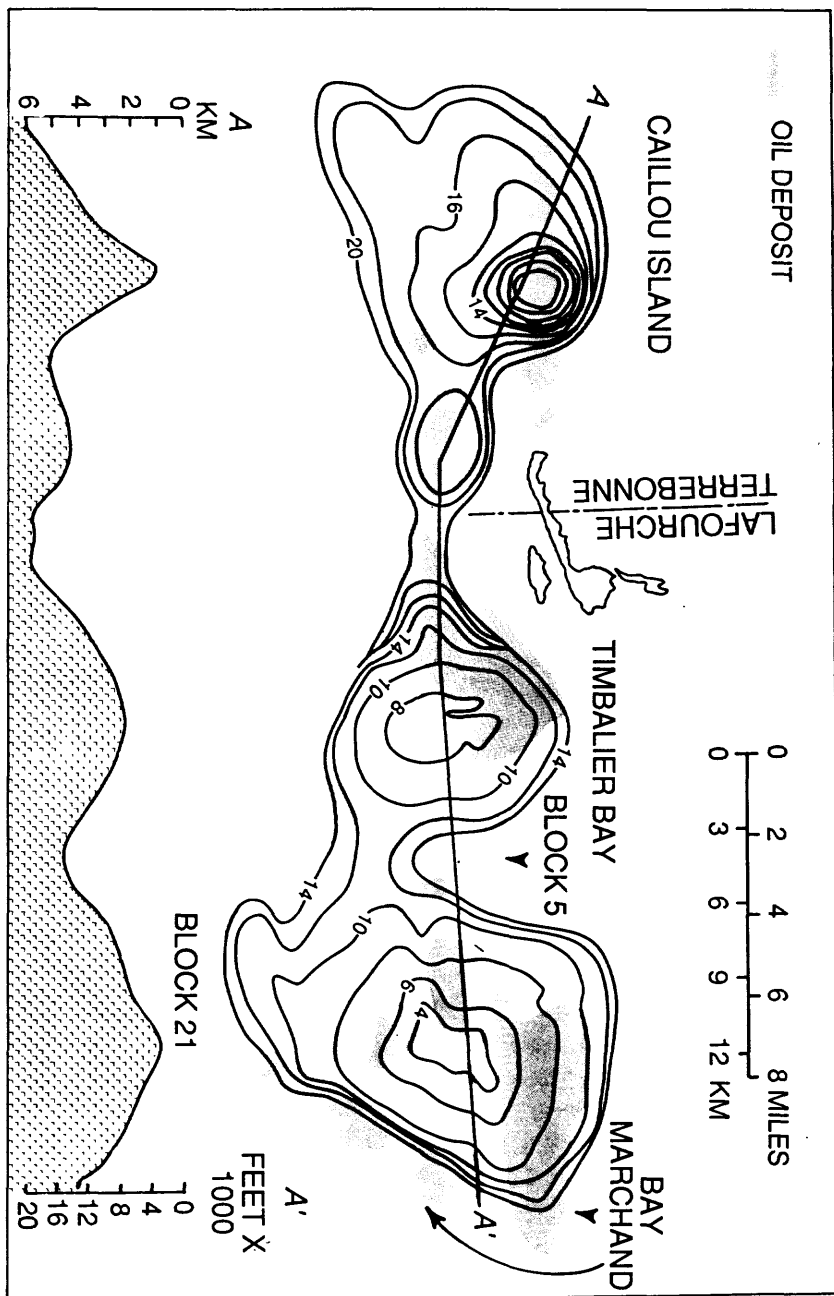


Figure 2. Structure map on top of and cross section through the Caillou Island to Bay Marchand salt ridge. After Frey and Grimes (1970).



In this area of southern Louisiana, a thick sequence of Miocene and younger sediments have been deposited over another thick sequence of older Cenozoic and Mesozoic rocks. Three general lithologic facies are present in the Miocene and younger sediments of this area: 1) A massive-sandstone facies, 50-75 percent sandstone with interbedded thin shales, was deposited in a nearshore, inner-neritic, continental environment with minor marine transgressions. 2) An interbedded facies of alternating sandstone (10-50 percent) and marine shale, was deposited across a shelf at neritic depth. 3) A massive-shale facies of dark gray, marine shales with less than 10 percent sandstone was deposited at outer-neritic to bathyl depths. The electric log of the Placid Oil Company 2857-1 well, which was drilled on the west flank of the Caillou Island field, shows the Pleistocene to Pliocene, massive-sandstone facies extending to about 2,591 m (8,500 ft), and the Miocene interbedded facies extending to about 5,181 m (17,000 ft) with a probable projection to beyond 6,096 m (20,000 ft).

Generally, with increase in depth, or within one time stratigraphic unit in going from north to south, the lithologic facies grade from the massive-sandstone, through the interbedded sandstone-shale, to the massive-shale facies. The latter two facies contain most of the hydrocarbon (HC) reserves of the area, although HC deposits in the sandstones of the massive-shale facies tend to be of smaller relative volume and abnormally pressured. Ninety percent of the HC reserves of the Bay Marchand-Timbalier Bay-Caillou Island complex are contained in interbedded upper Miocene sandstones, and to a lesser extent in the massive-shale, facies. Nine percent of the HC reserves are found in Pliocene sands, one percent are found in Pleistocene sands, both of which are principally the massive-sand facies.

The regional structure of this area of the Gulf Coast is monoclinal with a south dip that generally increases with depth. Dips are about 0.57 percent (30 ft/mi) in the massive-sand facies, 5.68 percent (300 ft/mi) in the interbedded facies, and 15.5 percent (800 ft/mi) or greater in the massive-shale facies. These generalized dips are greatly disrupted by local salt features, and/or normal faults. The structure of Bay Marchand-Timbalier Bay-Caillou Island area, is controlled by diapiric salt (and related diapiric shale) of huge proportions (Fig. 2). At a depth of 6,096 m (20,000 ft), the salt complex comprises an area in excess of 225 km<sup>2</sup> (140 mi<sup>2</sup>), and contains about 322 km<sup>3</sup> (200 mi<sup>3</sup>) of salt. A projection of the ridge downward to its Late Triassic to Early Jurassic source would result in a volume of salt in this complex of staggering proportions. As the cross section of figure 2 demonstrates, individual domes on top of the salt ridge have achieved the size of mountains, with vertical reliefs of up to 5,181-5,486 m (17,000-18,000 ft). The upwelling of this salt and diapiric shale has controlled the resulting complex structure of the area. Many different oil-trap types are present in the salt-ridge complex, including supradomal closure, salt and shale truncation (both resulting from sandstones abutting against diapiric rock), stratigraphic sandstone pinchout to shale, fault traps, and unconformity traps which resulted from the cyclic growth of the salt domes. As is common throughout the Gulf Coast, greater reserves occur on the downside of fault blocks, where the sands are better developed.

Due to the complex structure of this area, many separate oil reservoirs exist in the trend. Frey and Grimes (1970) noted that at Bay Marchand over 125 separate reservoirs are present, ranging in depth from 365.7 to 4,877 m (1,200 to 16,000 ft). Furthermore, the Caillou Island field has some of the deepest, if not the deepest oil production in the world. Frey and Grimes (1970) noted



that favorable sandstone development at great depth is found on the north side of the salt ridge at Caillou Island, and that the depth of eventual oil production there appears to be limited only by technologic and economic considerations.

## SAMPLES

Twenty-three oils from various producing sandstones at different depths at Caillou Island were supplied by Texaco Inc., as well as oils from the Horseshoe Bayou, and Lake Barre oil fields, drill-chip cuttings from deep wells in all three fields, and information on the oils, the fields and the wells. The physical characteristics of the Caillou Island oils varied widely, and these oils certainly did not appear to be genetically related from that standpoint. Oil gravities varied from 0.768 to 0.889 g/cc (52.8-27.6° API; table 1) and oil colors varied from light, condensate-like, straw-yellow oils to moderately viscous, black oils.

## METHODS

API gravities of the whole crude oil were measured in house. Two or three ml of each oil was taken to constant weight on a nitrogen evaporator. Constant weight was defined as a weight within 5 percent of the previous weight after a timed 5 minute blowdown at 25°C. This constant weight was taken as the C<sub>15</sub><sup>+</sup> fraction, which made up between 11.6 to 19.7 weight percent of the Caillou Island oils (Table 1). After removing and weighing the asphaltenes from the C<sub>15</sub><sup>+</sup> fraction, this fraction was separated, by silica-gel chromatography into saturated HC's, aromatic HC's, and resins (Table 1). Gas chromatography was carried out on the C<sub>15</sub><sup>+</sup> saturated and aromatic HC's.

Silica-gel chromatography was also carried out on all the whole Caillou Island oils (C<sub>15</sub>- compounds not removed by evaporation) and on 10 unrelated oils from widely-separated geographic localities (Table 2). The n-paraffins were removed from the saturated HC fractions by molecular sieves, and gas chromatography was performed on the remaining (whole) saturated-, and aromatic-HC fractions. With the only basis of choice being that compounds be present in all the oils under study, specific compounds in the saturated-, and aromatic-HC fractions were chosen for comparison between the different oils. The relative concentrations of these compounds were determined manually by drawing valley to valley tangents and peak bisectrices on the peaks of interest of each chromatogram and measuring peak heights. After measuring peak heights of individual compounds, certain compounds were chosen for a group, and their peak heights were summed and normalized to each other, in percentages. Plots were then made of the percent of each compound (on the vertical scale) in such a group, versus the compound on the horizontal scale. The shapes of the resulting normalized-percentage, compound-distribution plots for the Caillou Island oils and for the ten geographically-separated oils were then compared with each other.

This work was carried out in 1977-1979 using an inefficient gas chromatographic column (1.8 m x 2 mm packed column, 3 percent GC SE-30 on 100-200 mesh Gas Chrom Q). Slight variance in column temperature, programming conditions, injection-port temperature, or carrier-gas flow rates caused measurable to significant changes in relative peak heights for the same sample in multiple runs. In spite of close monitoring, variance in gas-chromatographic



conditions likely led to some analytical error. Certainly, present-day, computerized gas chromatographs with automatic samplers, efficient columns, and electronic integration of well-resolved individual peaks, would give better results than those of this study. Computerization would have permitted many more cross correlations to have been examined, than were examined. The results of this study, although not optimized to the level possible, were noteworthy; thus the reader is asked to bear with some the obviously outdated gas chromatograms displayed in this paper.

Gasoline-range ( $C_4$ - $C_7$ ) HC analyses were also carried out on the Caillou Island oils and on 11 other oils from widely-separated geographic localities both by Geochem Laboratories, Houston, Texas and in house at the Denver Federal Center.

## RESULTS

### Oil Composition

Figures 3A and 3B respectively show plots of oil gravity and weight percent  $C_{15-}$  compounds in the oils, versus depth, for the Caillou Island oils analyzed in this study. It may be suggested that the data in figure 3A have a moderate trend (shown by the dashed line) of decreasing specific (increasing API) gravity from 2,438-5,791 m (8,000-19,000 ft); however, other interpretations of the data are also possible (solid lines). For example, it appears that from 2,438 to 4,115 m (8,000 to 13,500 ft), an invariant trend of oil gravity versus depth exists for heavier oils, and from 4,419 to 5,852 m (14,500 to 19,200 ft), with the exception of one sample, another invariant trend of oil gravity, versus depth, exists, for lighter oils. From 5,852 m (19,200 ft) to total depth, a strong trend of oils becoming heavier with depth exists. With the exception of the 5,727-5,738 m (18,790-18,828 ft) sample, the percentage of  $C_{15-}$  material exhibits two invariant and parallel trends (shown by the dashed lines) versus depth, one centered around 82 percent and one centered around 88 percent (Fig. 3B). Thus, the Caillou Island oils show no correlation of decreasing oil gravity or of increasing percentage of  $C_{15-}$  compounds, with reservoir depth.

Different chemical parameters of the Caillou Island oils are plotted versus oil gravity in figure 4. As would be expected, the oils exhibit a moderate correlation of becoming lighter with increase in their content of  $C_{15-}$  material (Fig. 4A). With the exception of the 5,727-5,738 m (18,790-18,828 ft) sample, these oils plot as two very tight and parallel trends of increasing lightness with increase in  $C_{15-}$  material. Whether these two tight trends are mere coincidence or result from genetic, migration, accumulation, or post-accumulation phenomena are unknown. Considering the lack of scatter on the two lines, mere coincidence would seem unlikely. The two parallel lines of figure 4A are quite similar to the two parallel, invariant, lines of figure 3B, and therefore may be a result of the same process(es).

The weight percent of resins plus asphaltenes in the  $C_{15+}$  oil fractions exhibits no clear correlation with oil gravity between 0.904 to 0.802 specific ( $25^\circ$  to  $45^\circ$  API) gravity (Fig. 4B), but does exhibit a strong correlation of decreasing percentages with increasing oil lightness, for oils lighter than 0.802 specific ( $45^\circ$  API) gravity. A broad, but definite, trend of the oils becoming lighter with an increase in the  $C_{15+}$  saturated to  $C_{15+}$  aromatic HC ratio is present in figure 4C. A good correlation of increasing percentages of



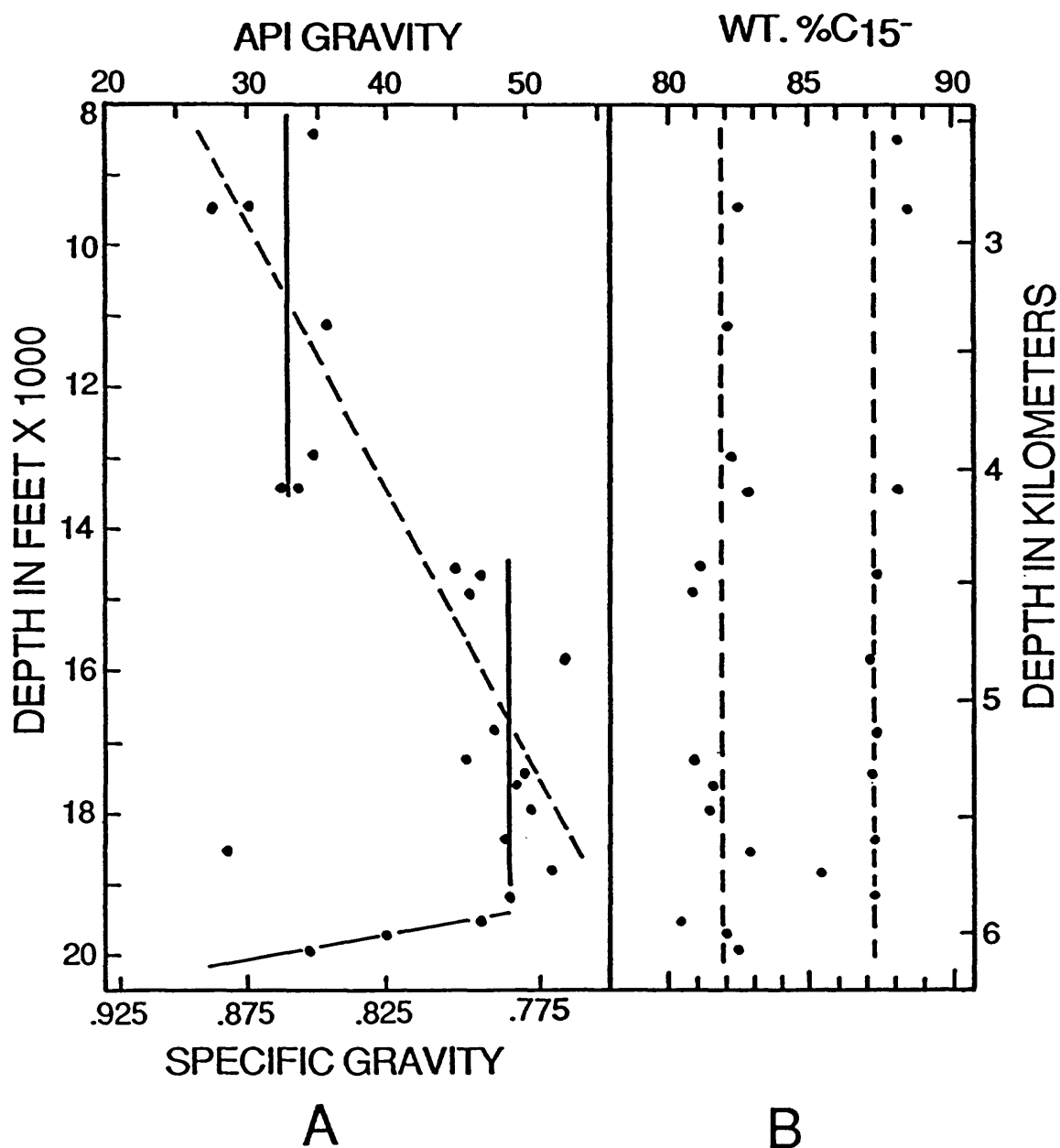


Figure 3. Plots of oil gravity (A) and weight percent of C<sub>15</sub>- material (B) for Caillou Island oils, versus depth. Dashed and solid lines are explained in text. Data from Table 1.



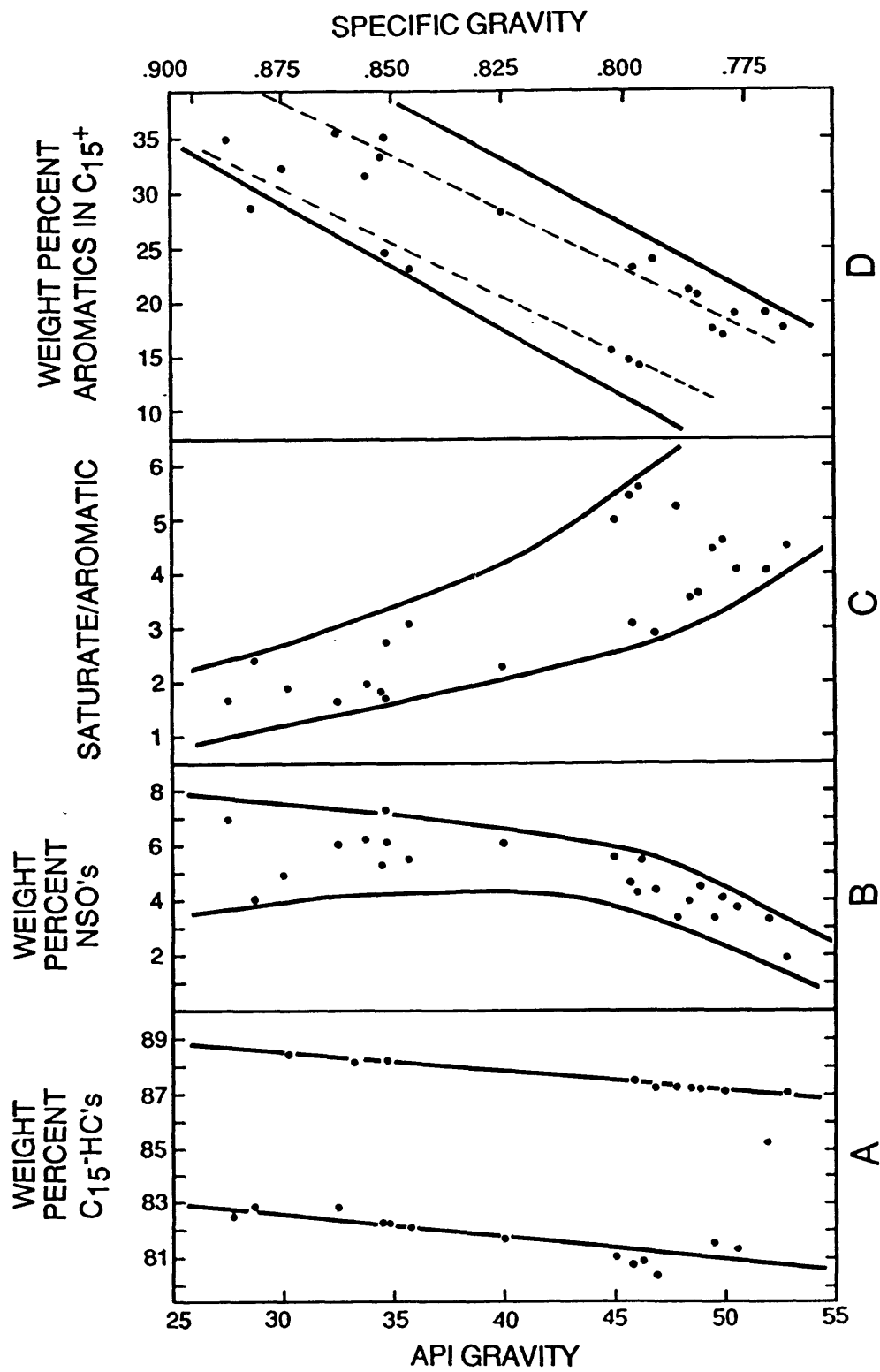


Figure 4. Plots, versus oil gravity, of weight percent  $C_{15}^{+}HC's$  (A), weight percent resins and asphaltenes (NSO's) in  $C_{15}^{+}$  fraction (B),  $C_{15}^{+}$  saturated HC to aromatic HC ratio (C), and weight percent aromatic HC's in  $C_{15}^{+}$  fraction (D) for the Caillou Island oils. Solid and dashed lines are explained in text. Data from table 1.



C<sub>15</sub><sup>+</sup> aromatic HC's with the oils becoming heavier is present in figure 4D. One may also call for two moderately-tight and parallel trends (as shown by the light dashed lines) of the oils becoming heavier with increase in the percentage of the aromatic HC's in the C<sub>15</sub><sup>+</sup> material. These trends would be analogous to the two parallel trends in the data sets of figures 3B and 4A.

The C<sub>15</sub><sup>-</sup> fraction makes up the bulk of the Caillou Island oils (80 to 88 percent, table 1. The chemistry and physical characteristics of the C<sub>15</sub><sup>-</sup> fraction were not examined in this study; and because the C<sub>15</sub><sup>-</sup> fraction makes up most of the oils, conclusions concerning correlations of different parameters of oil chemistry with oil gravity, or with each other, would be tenuous. With this in mind, we may tentatively conclude that in the Caillou Island oils, if the trends in the C<sub>15</sub><sup>-</sup> material of the oils parallel those observed in the C<sub>15</sub><sup>+</sup> material, then increasing oil lightness has some relationship to, or is controlled by, decreasing percentages of aromatic HC's.

## COMPOUND OIL TYPING

### Saturated HC's

Figure 5 gives the original gas chromatograms of the iso-cyclic HC's which were used to construct the normalized-percentage, compound-distribution plots shown below. The numbered peaks in figure 5A lie around n-C<sub>9</sub>; the numbered peaks in figure 5B approximately lie in the n-C<sub>9</sub> to n-C<sub>12</sub> range; and the numbered peaks in figure 5C approximately lie in the n-C<sub>12</sub> to n-C<sub>19</sub> range and are all isoprenoid HC's, with the exception of the I-12 peak which may or may not be the C<sub>12</sub> isoprenoid HC. The peaks in figures 5A and 5B are unidentified iso- and cyclo-alkanes, and were chosen for measurement because, on the basis of retention time, they were present in all the Caillou Island oils and in all the ten geographically-separated oils (Table 2).

Figure 5D is a present-day gas chromatogram of an unsieved, whole, saturated HC fraction from one of the Caillou Island oils. This chromatogram, and the two subsequent chromatograms (Figures 5E and 5F), were not used in the construction of the normalized-percentage, compound-distribution plots. These three chromatograms have been shown to aid the reader in identifying the peaks which were used in the construction of the subsequent compound-distribution plots. Figures 5E and 5F are gas chromatograms of the sieved, whole, saturated-HC fraction of the same Caillou Island oil sample. In figure 5E, the C<sub>12</sub> to C<sub>21</sub> isoprenoids, and the more prominent numbered peaks of figures 5A and 5B, have been labeled.

Figure 5F is an expansion of the 5 to 20 minute interval of the chromatogram of figure 5E, and peaks 1-9, 12 and 13; and 15-17, 19-22, 24, 30, and 31 from figures 5A and 5B respectively have been tentatively labeled in figure 5F. Many of the numbered peaks of figures 5A and 5B are actually multiple peaks in figure 5F. Thus peak 6 (figure 5A) is actually comprised of two peaks in figure 5F, and peak 9 (figure 5A) is comprised of a major peak and four lesser peaks in figure 5F. Other cases of multiple peaks have been so labeled in figure 5F.

Peak distributions, heights, and retention times in the chromatograms from the two different analytical conditions are quite different for the same samples. Therefore, the overall appearances of the chromatograms run under the two gas-chromatographic conditions are quite different for the same samples.



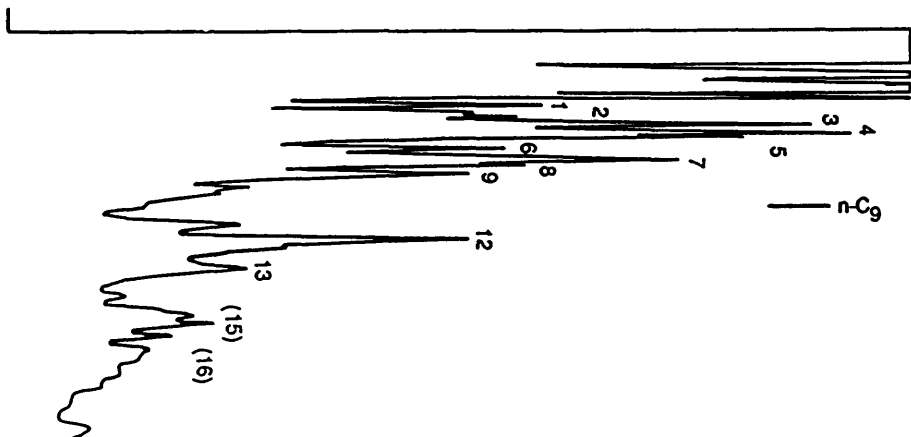


Figure 5A.

Original gas chromatogram of the iso-cyclic saturated HC fraction of the 5,468-5,478 m (17,942-17,974 ft) Caillou Island oil sample showing peaks 1-9, 12 and 13 which were used in compound-distribution plots. Approximate elution time of  $n-C_9$  is also given. Peaks 15 and 16 from figure 5B shown in parenthesis.



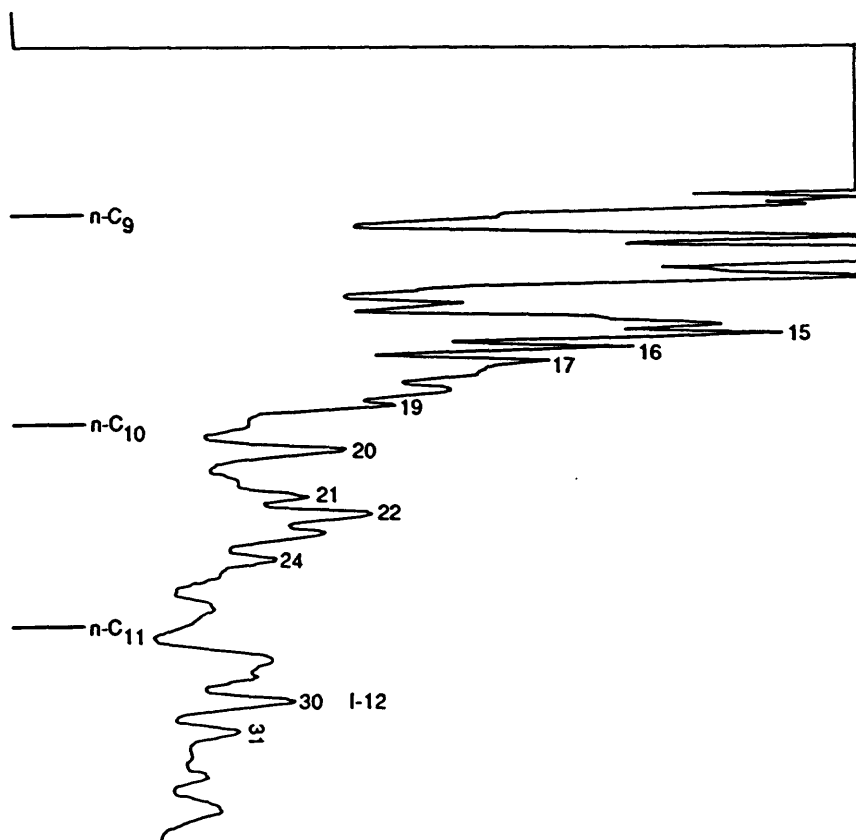


Figure 5B.

Original gas chromatogram of the iso-cyclic saturated HC fraction of the 5,468-5,478 m (17,942-17,974 ft) Caillou Island oil sample showing peaks 15-17, 19-22, 24, 30 and 31 which were used in compound-distribution plots. Approximate elution times of  $n-C_9$  to  $n-C_{11}$  are also given.



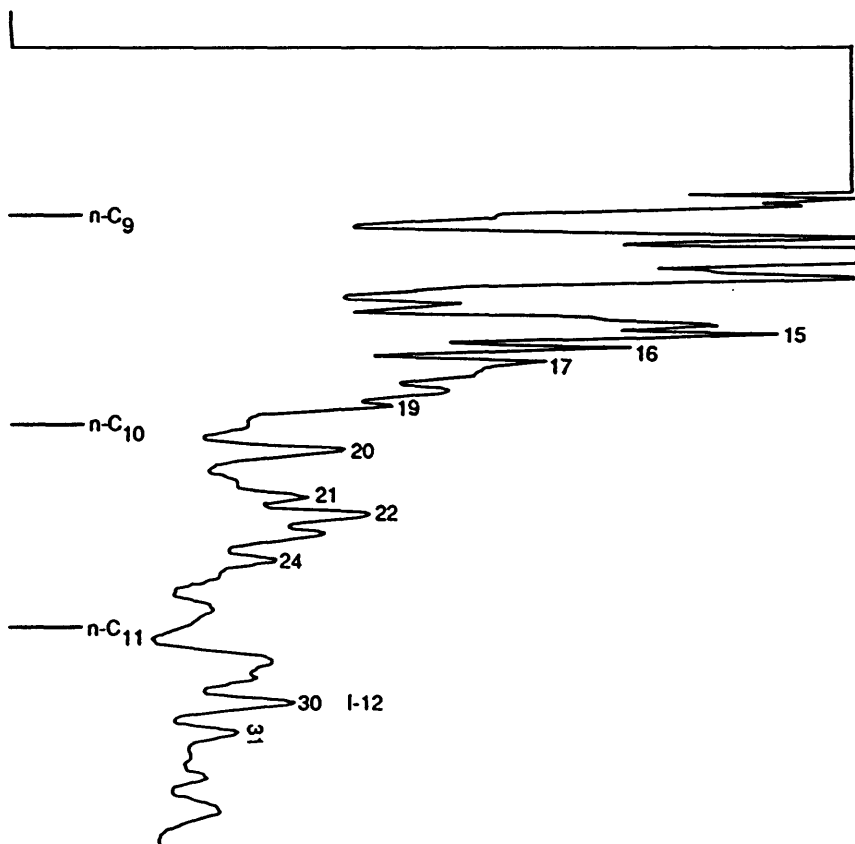


Figure 5C.

Original gas chromatogram of the iso-cyclic saturated HC fraction of the 5,595-5,606 m (18,358-18,394 ft) Caillou island oil sample showing the C<sub>12</sub> (I-12) through C<sub>21</sub> (I-21) isoprenoid HC's which were used in compound-distribution plots. Approximate elution times of n-C<sub>12</sub> to n-C<sub>19</sub> are also given.



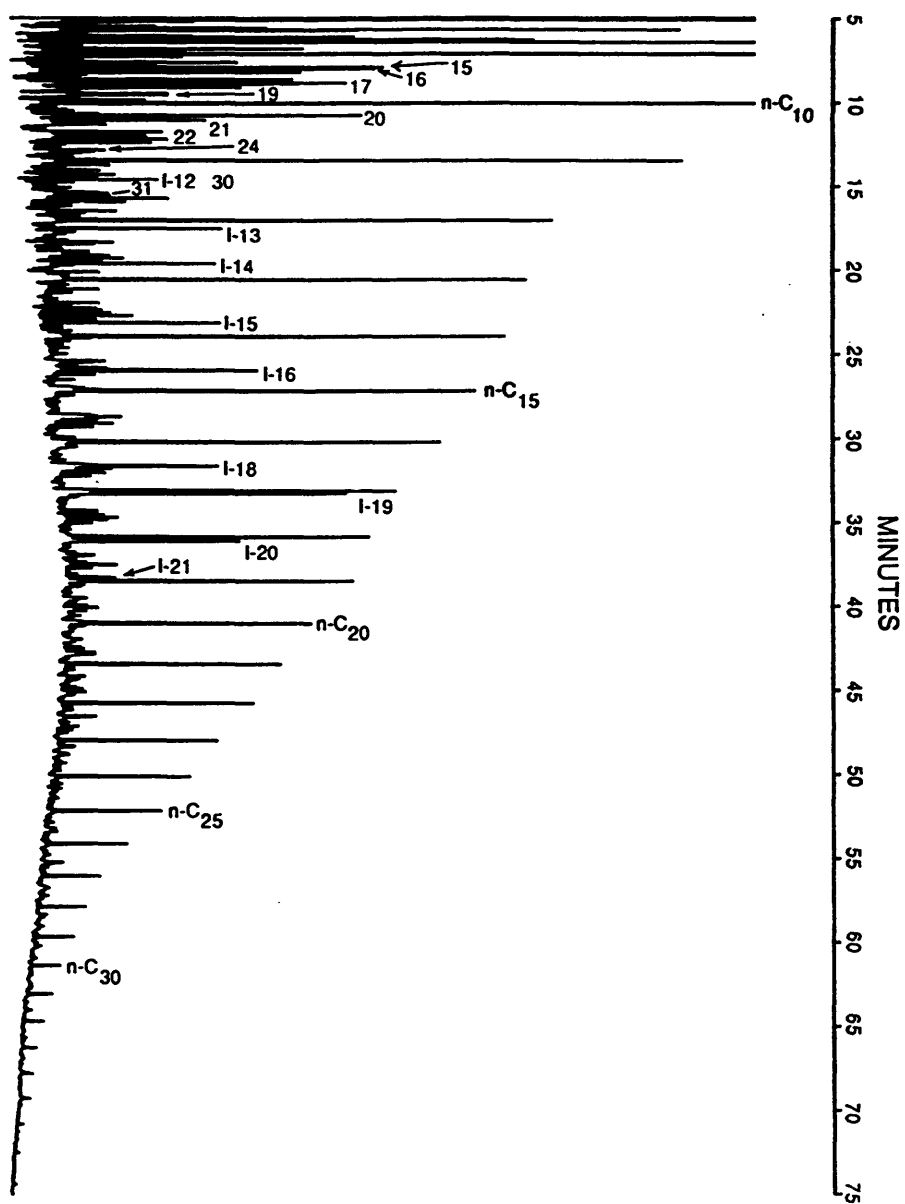


Figure 5D.

Gas chromatogram of whole saturated HC fraction of the 6,079-6,084 m (19,944-19,960 ft) Caillou Island oil sample showing the n-paraffins ( $n\text{-C}_{10}$ ,  $n\text{-C}_{15}$ ,  $n\text{-C}_{20}$ ,  $n\text{-C}_{25}$ , and  $n\text{-C}_{30}$  are labeled), the  $\text{C}_{12}\text{-C}_{21}$  isoprenoid HC's (I-12 to I-21), and other iso-cyclic saturated HC's (peak numbers 15-31, from figure 5B). Column conditions were 0.3 mm x 30 m fused silica with DB-1, initial temperature was  $50^{\circ}\text{C}$  for 2 minutes, programming rate was  $4^{\circ}\text{C}/\text{minute}$  to  $320^{\circ}\text{C}$  with an upper temperature limit of 8 minutes, column gas flow rate 25 cc/minute hydrogen, injection port  $340^{\circ}\text{C}$ , and detector temperature (FID)  $350^{\circ}\text{C}$ .



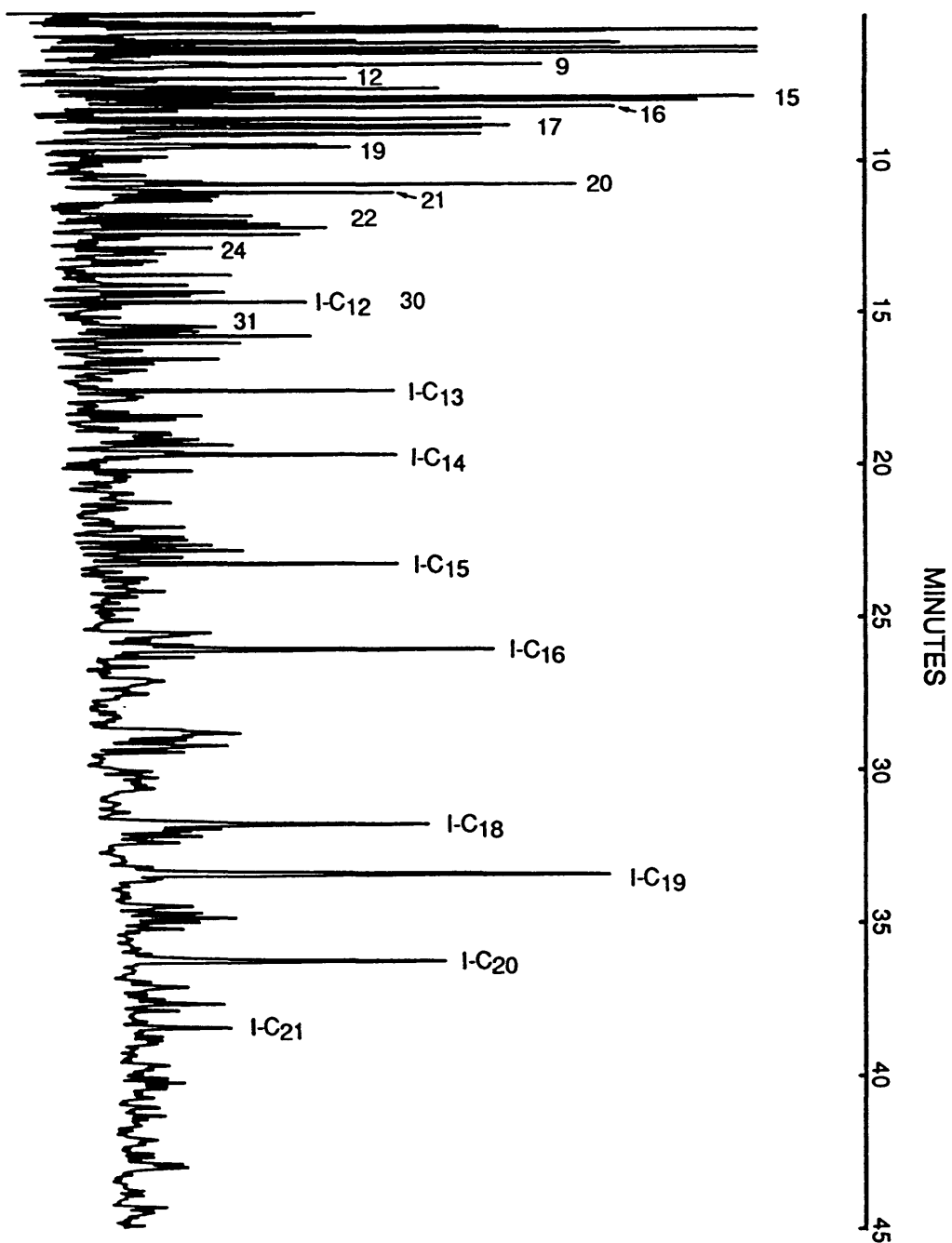


Figure 5E. Gas chromatogram of the iso-cyclic saturated HC fraction of the 6,079-6,084 m (19,944-19,960 ft) Caillou Island oil sample showing the C<sub>12</sub> to C<sub>21</sub> isoprenoid HC's (I-12 to I-21) and other iso-cyclic saturated HC's (peak numbers 9-31, from figures 5A and 5B). Column conditions as in Figure 5D caption.



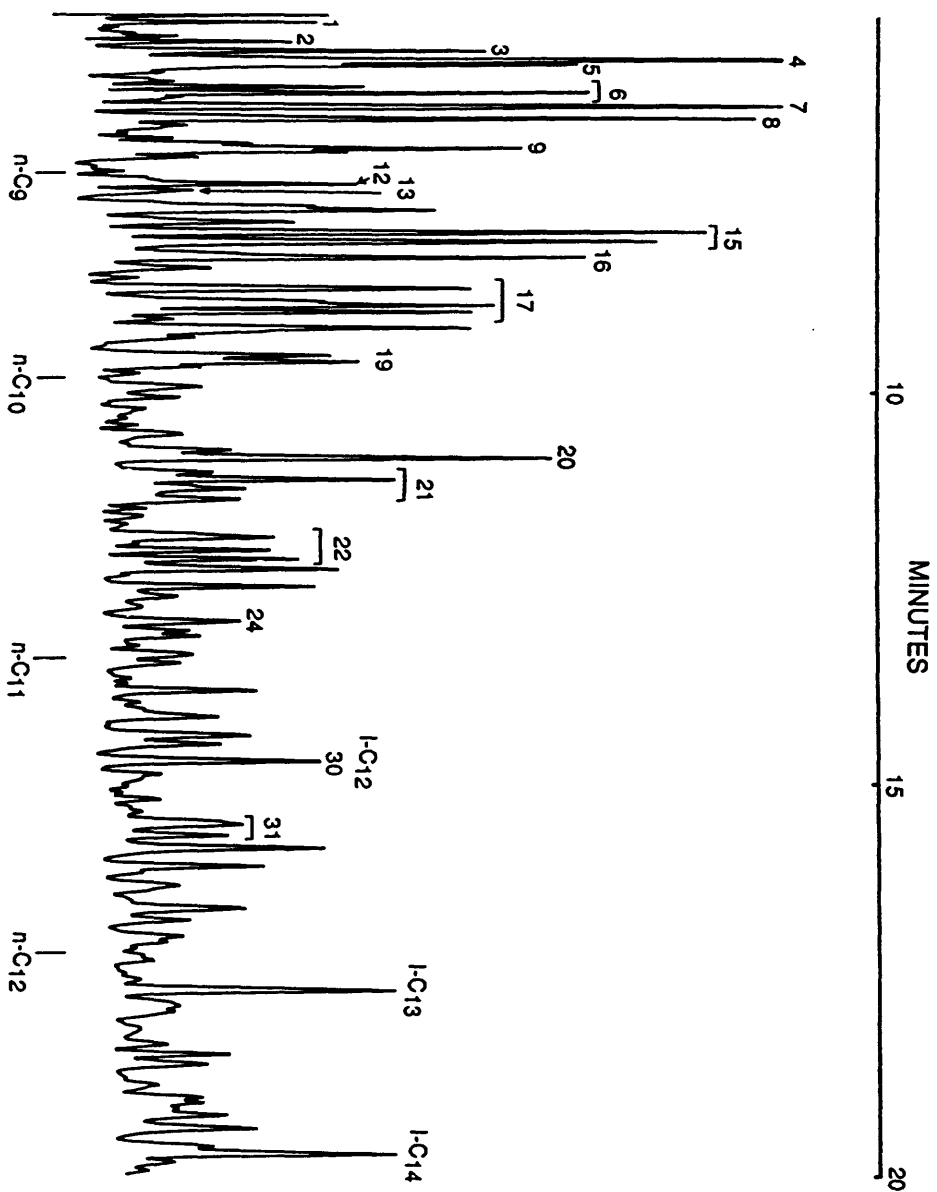


Figure 5F. Gas chromatogram of the iso-cyclic saturated HC fraction of the lower molecular weight portion of the iso-cyclic saturated HC fraction from the 6,079-6,084 m (19,944-19,960 ft) Caillou Island oil sample showing peak numbers 1-31 of figures 5A and 5B. The approximate elution times of n-C<sub>9</sub> to n-C<sub>12</sub> are also shown. Evaporation of the lightest HC's occurred in this sample during its preparation for gas chromatography. Column conditions as in figure 5D caption.



For example, in figure 5E, I-C<sub>19</sub> is the highest peak. By contrast, in Figure 5C, and in all the other original gas chromatograms of the Caillou Island oil samples (including the 6,079-6,084 m sample), I-C<sub>16</sub> was the largest peak (by peak height).

This comparison of the older and newer gas chromatograms underscores several points made above and also reveals several other points. As stated: 1) The gas chromatographic conditions originally employed are obviously antiquated. 2) Peak-area integration is much preferable to peak-height measurement with this oil-oil correlation technique. 3) Much better results would have been obtained in this study had present-day, computerized, gas chromatography been employed. Other points revealed by comparison of the older and newer gas chromatograms are: 1) The correlation of the peaks between the older and newer gas chromatograms are sometimes tenuous, because of the disparate appearance between the two chromatograms. 2) Many of the peaks in the older chromatograms are actually composed of well-separated, multiple, larger peaks, and or multiple smaller peaks, in the newer chromatograms.

C<sub>16</sub> to C<sub>21</sub> isoprenoid HC distributions for the Caillou Island oils are plotted in figures 6 to 8. The oils of figures 6 and 7 have the same C<sub>16</sub> to C<sub>21</sub> isoprenoid HC distributions, and thus belong to a single compositional subfamily. These oils were plotted in two different figures as an aid to the reader. However, the oils in figures 6 and 7 exhibit no relationship with each other regarding oil gravity or percentage of C<sub>15</sub>- material. The oils of figure 8 plot as a second compositional subfamily and are characterized by the fact that: 1) they contain larger normalized percentages of the C<sub>16</sub> isoprenoid HC (37 to 49 percent) compared to the oils of figures 6 and 7 (26 to 33 percent), and 2) the oils all have 0.798 g/cc specific gravities or less (API gravities of 45.0° or greater), but exhibit no correlation to the amount of C<sub>15</sub>- material (81.4 to 87.5 percent). If the C<sub>16</sub> isoprenoid HC is excluded from consideration, and only the C<sub>18</sub> to C<sub>21</sub> isoprenoid HC's are plotted, then a much tighter distribution of a single compositional family of oils results (not shown). This fact suggests that considering normalized-percentage, compound-distribution plots over wider carbon-number ranges results in an increase in scatter for a single family of oils, compared to the results obtained for more limited carbon-number ranges.

In figure 9, the boundaries from the two Caillou Island oil subfamilies from figures 6 to 8 have been superimposed on each other. In figure 10, the stippled area represents the area enclosed by the two subfamilies of figure 9, and this stippled area has been superimposed on a compound-distribution plot of the C<sub>16</sub> to C<sub>21</sub> isoprenoid HC's for the 10 geographically separated oils (Table 2). With the exception of the Lake Barre oil, none of the oils falls within the stippled area of the Caillou Island oils, although the oil from the Horseshoe Bayou field is close. Another difference exhibited by the C<sub>16</sub>-C<sub>21</sub> isoprenoid HC plots for the 10 random oils, is the distinct non-parallel nature of their plots, which is in sharp contrast to the very parallel nature of the Caillou Island oil plots.

The isoprenoid HC's are considered biomarker-classed compounds, and isoprenoid HC distributions have previously been used to classify oils into genetic families. For example, Clayton and Swetland (1980) used the C<sub>15</sub> to C<sub>20</sub> isoprenoid HC's to classify different oils in the Denver basin into genetically-related families. The tight distribution of the C<sub>16</sub> to C<sub>21</sub> isoprenoid HC plots of the Caillou Island oils, therefore, suggests that all these oils belong to a



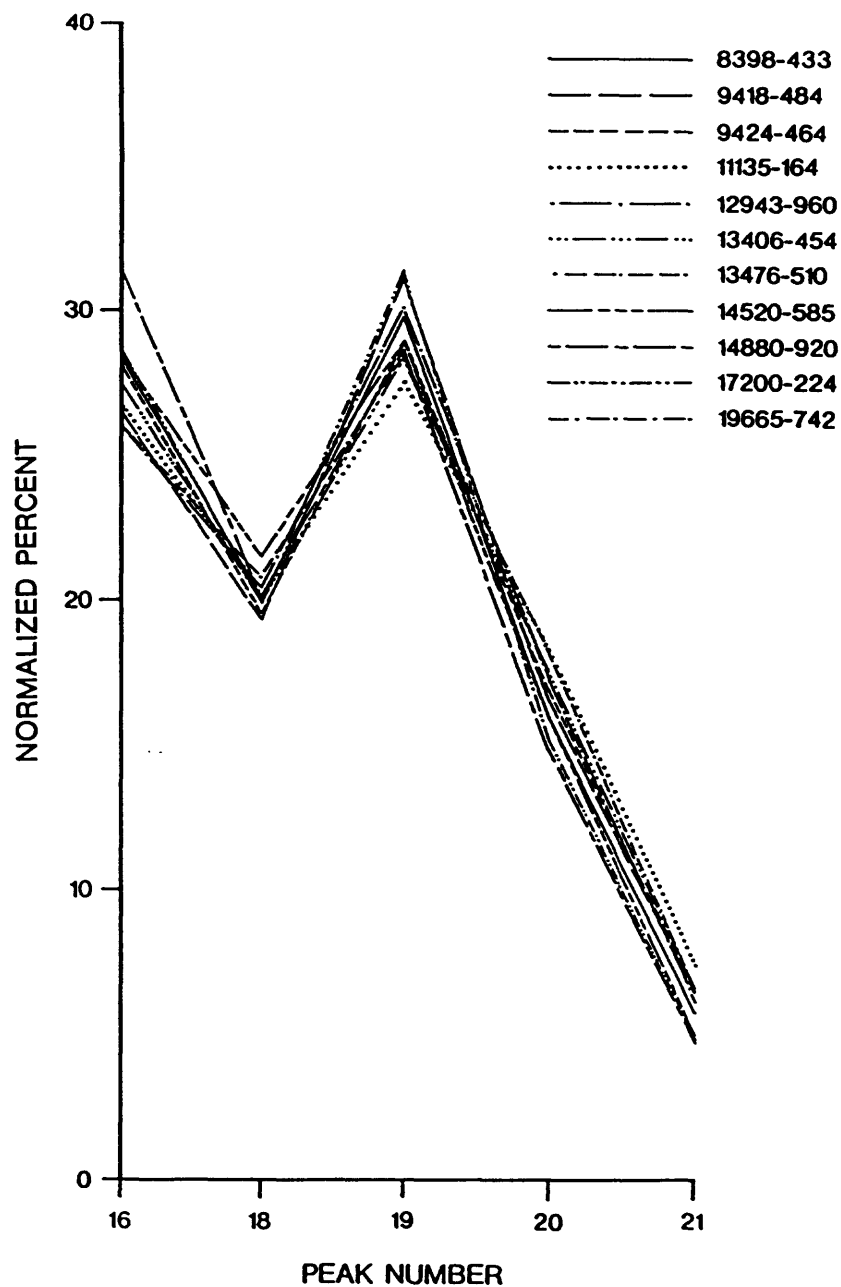


Figure 6. Normalized-percentage, compound-distribution plots for the  $C_{16}$ - $C_{21}$  isoprenoid HC's of 11 Caillou Island oils. Oil sample depths in this, and all subsequent, compound-distribution plots, are given in feet and not meters.



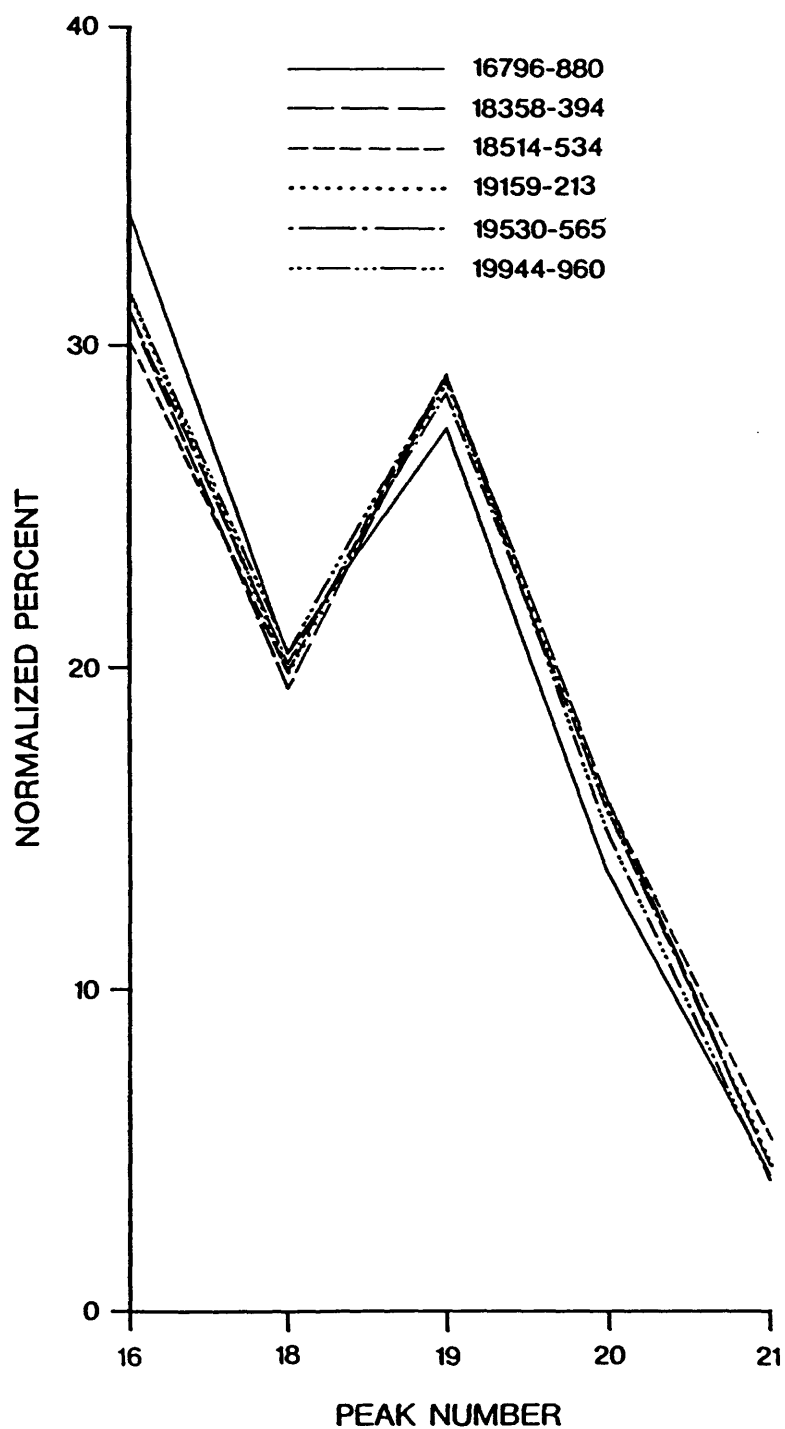


Figure 7. Normalized-percentage, compound-distribution plots for the  $C_{16}$  to  $C_{21}$  isoprenoid HC's of 6 Caillou Island oils.



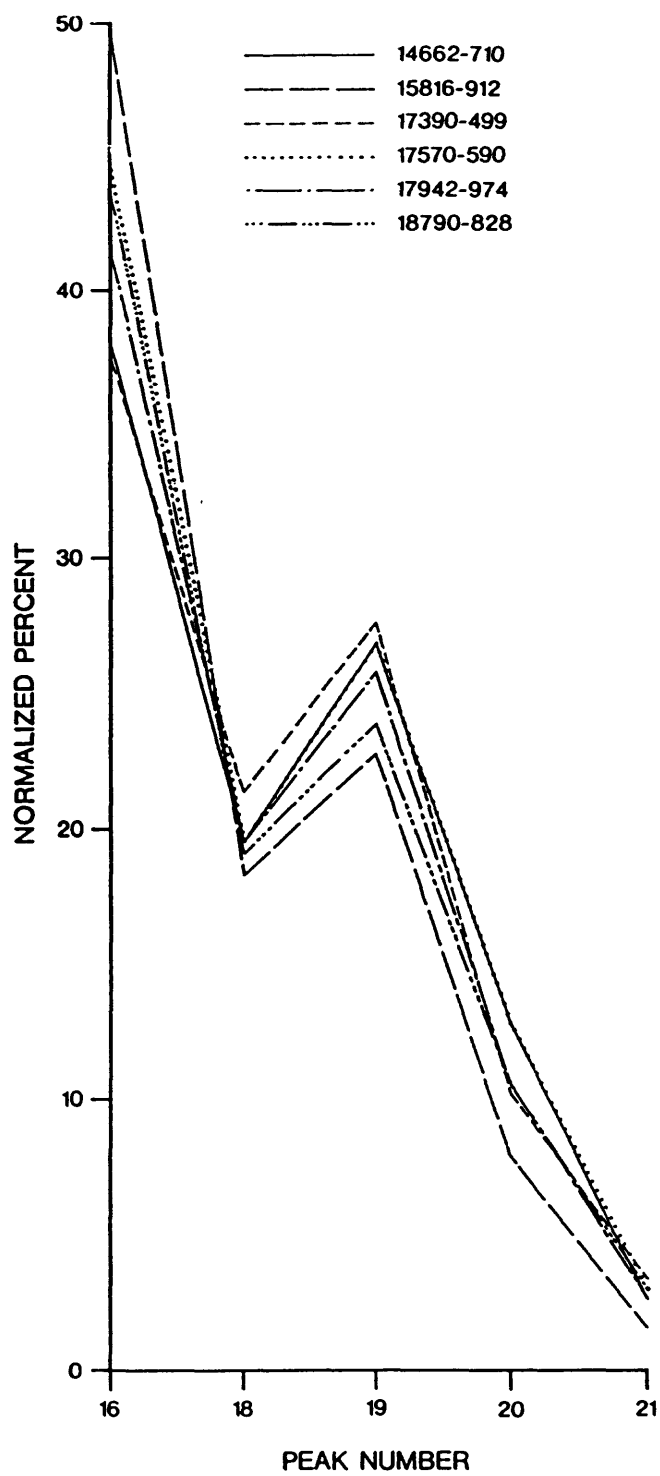


Figure 8. Normalized-percentage, compound-distribution plots for the  $C_{16}$  to  $C_{21}$  isoprenoid HC's of 6 Caillou Island oils.



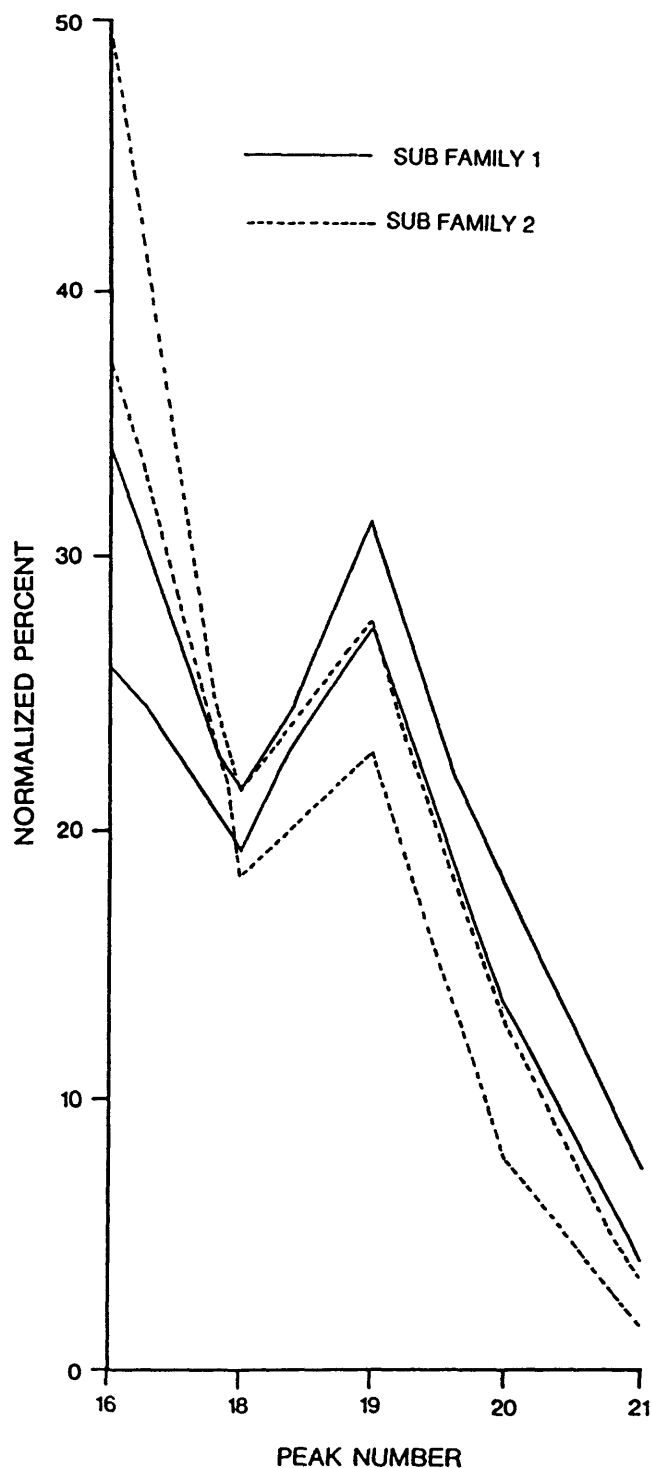


Figure 9. Area overlay of the normalized-percentage, compound-distribution plots for the  $C_{16}$  to  $C_{21}$  isoprenoid HC's of the Caillou Island oil subfamilies. Subfamily one is from the plots of figures 6 and 7, subfamily two is from the plots of figure 8.



single genetic family. This implies that these oils have been generated from the same source rock, or sequence of source rocks, and have had a similar, or the same, histories of primary migration, accumulation, and post-accumulation processes. These conclusions are supported by the lack of correlation exhibited by the  $C_{16}$  to  $C_{21}$  isoprenoid HC plots of the geographically-separated (and, therefore, presumably genetically-unrelated) oils of figure 10.

The  $C_{16}$  to  $C_{21}$  isoprenoid HC distribution plot of the Lake Barre oil is an exception to these conclusions. When the 10 random oils were chosen for analysis, the Lake Barre and Horseshoe Bayou oils were chosen blindly with no knowledge of their geographic locations. In the normalized-percentage, compound-distribution plots of all the different compound sets used in this study, the plots for the Lake Barre oil always fell within the Caillou Island oil family overlay. At first this was thought to indicate a flaw in the method, that an apparently unrelated oil would show such consistent strong genetic matches to the assumed Caillou Island oil family. However, after the locations of the Horseshoe Bayou and Lake Barre oil fields were identified (Fig. 1), it became apparent that the consistent genetic match of the Lake Barre oil with the Caillou Island oils was instead due to their proximity (Fig. 1). Thus, the consistent genetic match of the Lake Barre oil with the Caillou Island oils strongly suggests that the oils of both fields are of one genetic family, which is reservoired in (at least) two separate structures. On this basis, it would not be surprising if the oils of the Timbalier Bay, Bay Marchand, and other surrounding fields, also belonged to this genetic family.

The Horseshoe Bayou oil, on the basis of the  $C_{16}$  to  $C_{21}$  isoprenoids HC's exhibited a near genetic match to the Caillou Island oil family, in spite of being geographically distant from Caillou Island (Fig. 1). However, the compound-distribution plots of the Horseshoe Bayou oil, for the other compound sets examined, exhibited significant differences to those for the Caillou Island oil family. Thus, the Horseshoe Bayou oil appeared to belong to a different genetic family than the Caillou Island oils. This point demonstrated the need for multiple compound sets with this technique of oil-oil correlation.

$C_{12}$ - $C_{16}$  isoprenoid HC distribution plots were also constructed for the Caillou island oils, and two subfamilies resulted (Fig. 11); although overall, by this plot, all the oils again apparently belonged to one genetically-related family. Inclusion of the  $C_{16}$  isoprenoid HC in the plots significantly expanded the area occupied by the Caillou Island oil family (Fig. 11). Compound-distribution plots for these same oils, using only the  $C_{12}$ - $C_{15}$  isoprenoid HC's gave significantly tighter plots (not shown), which again demonstrated that this oil correlation technique is more effective over limited carbon-number ranges. The  $C_{12}$ - $C_{16}$  isoprenoid HC distribution plots of the 10 random oils (with the Caillou Island oil family overlay) are given in figure 12. Again the lack of parallel nature is obvious for the isoprenoid HC distribution plots of the 10 random, unrelated oils, compared to the very parallel nature of the same plots for the 23 genetically-related Caillou Island oils. The Lake Barre oil again exhibits a genetic link to the Caillou Island oils, as its  $C_{12}$ - $C_{16}$  isoprenoid HC distribution plot falls within the area overlay for the Caillou Island oils. Two other oils, by figure 12, also exhibit a genetic match to the Caillou Island oils. These oils, Prudhoe Bay and Red Fork, both are geographically distant from (Table 2), and not possibly genetically related to, the Caillou Island oils. These two false genetic matches again demonstrate the need for using multiple compound-distribution plots with this method of oil correlation.



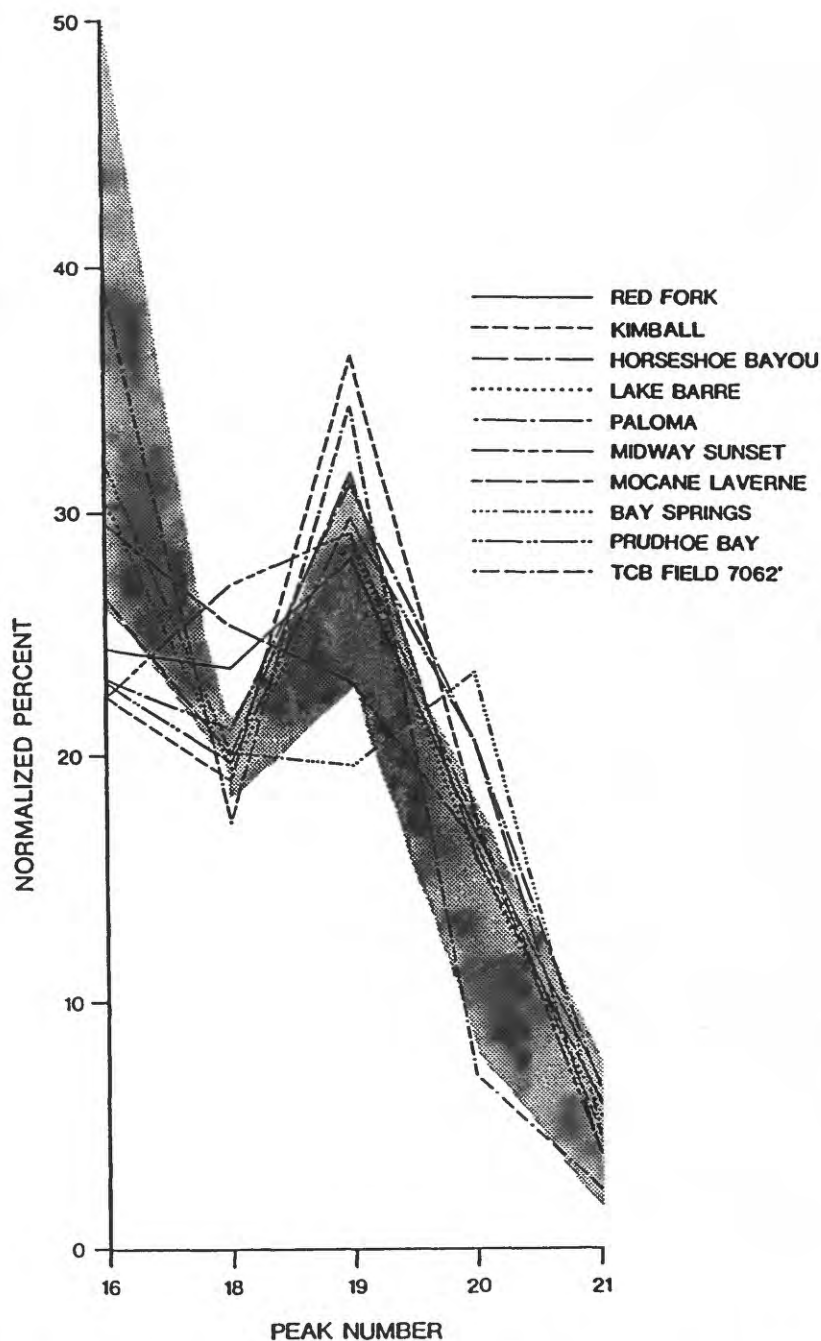


Figure 10. Normalized-percentage, compound-distribution plots for the  $C_{16}$ - $C_{21}$  isoprenoid HC's of the 10 random oils geographically separated from Caillou Island. The area overlay for these same plots for the Caillou Island oil family (from Fig. 9) is shown by the stippled pattern.



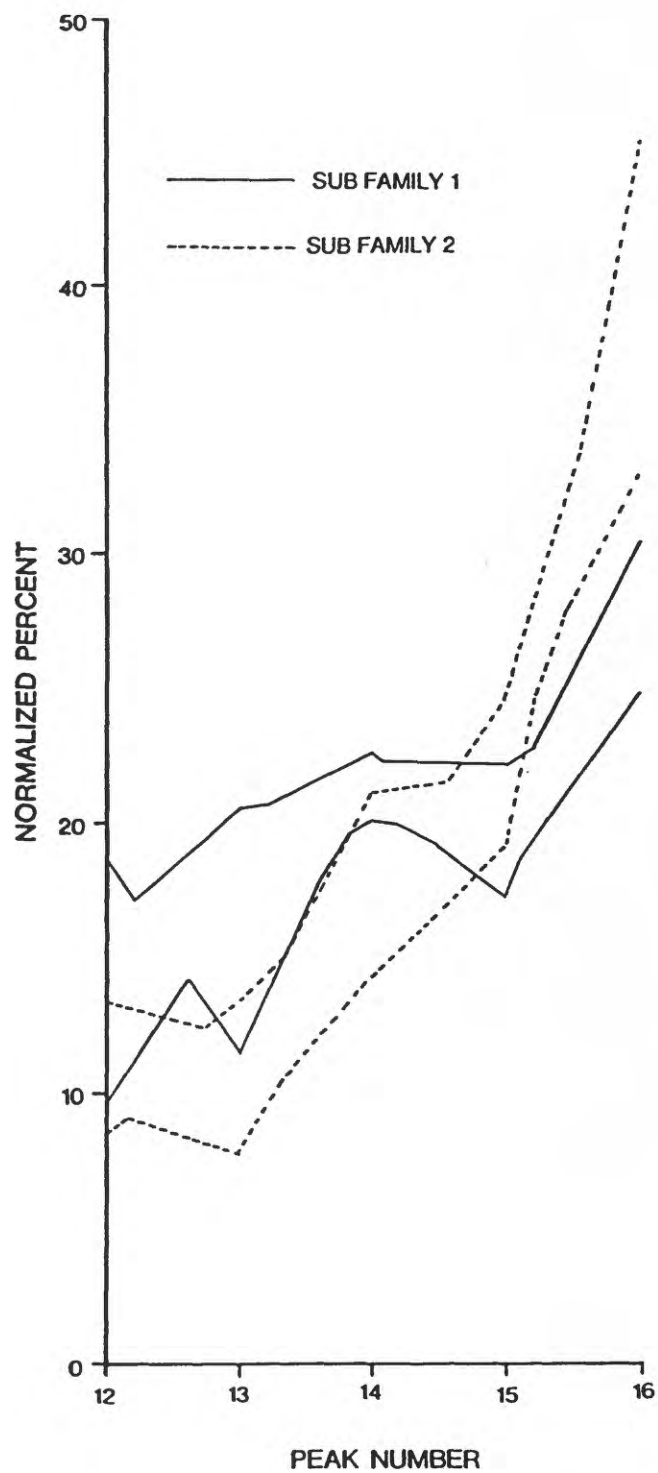


Figure 11. Area overlay of the normalized-percentage, compound-distribution plots for the  $C_{12}$  to  $C_{16}$  isoprenoid HC's of the Caillou Island oil subfamilies.



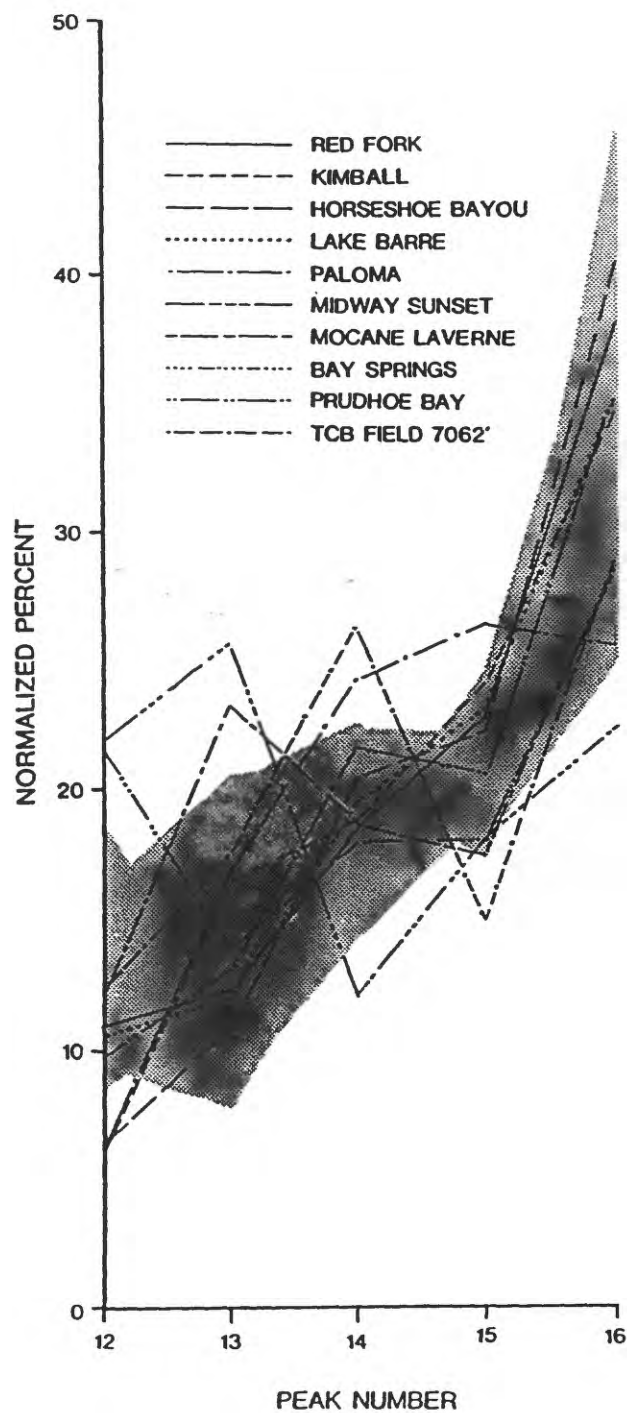


Figure 12. Normalized-percentage, compound-distribution plots for the  $C_{12}$  to  $C_{16}$  isoprenoid HC's of the 10 random oils geographically separated from Caillou Island. The area overlay for these same plots for the Caillou Island oil family (from Fig. 11) is shown by the stippled pattern.



Normalized-percentage, compound-distribution plots for the entire range of  $C_{12}$  to  $C_{21}$  isoprenoids are given for the Caillou Island oils which plot as two subfamilies (Figs. 13 and 14). Figure 15 gives the area overlays for the two subfamilies of the 23 Caillou Island oils. The  $C_{12}$ - $C_{21}$  isoprenoid HC distribution plots of the 10 random oils, with the area overlay of the Caillou Island oil family, are given in figure 16. In figure 16, six of the ten random oils fall within the area overlay of the Caillou Island oils and thus, by this plot, would appear to be genetically related to the Caillou Island oils. Furthermore, the other four random oils (Paloma, Mocane-Laverne, Bay Springs, and Horseshoe Bayou) give  $C_{12}$ - $C_{21}$  isoprenoid HC distribution plots which fall just slightly outside the area overlay of the Caillou Island oils. These poor results are because, as the carbon-number range of the compound set chosen for analysis increases, the discriminatory powers of this method decrease, and can disappear entirely. In this case, a carbon-number range of 10 was examined, and the method failed. This limitation was previously highlighted in the  $C_{16}$ - $C_{21}$  isoprenoid HC distribution plots (Figs. 6-9), a carbon-number range of 6. In that case, by decreasing the carbon-number range to 4, and plotting only the  $C_{18}$ - $C_{21}$  isoprenoid HC's, the 23 Caillou Island oils gave much tighter plots, compared to the plots for the  $C_{16}$ - $C_{21}$  isoprenoid HC's (Fig. 9). This oil correlation technique is most effective when carbon-number ranges of two or less are employed, as demonstrated below.

It is believed that limited carbon-number ranges (2 optimum, 4 maximum) are needed for this method, because of generation-migration processes. It is probable that with advancing generation stages, the percentages of lower-molecular-weight HC's increase, compared to the percentages in oils which were generated earlier from the same source rock, or sequence of source rocks. Therefore, varying percentages of lower-molecular-weight HC's can be expected in a given family of oils, depending on the generation stage of the particular oil. Also, post-accumulation, secondary migration by gas solution (which is apparently pervasive in the Gulf Coast province, Thompson and Kennicutt, 1988) would alter original carbon-number distributions. The result of all this is that large carbon-number ranges of any compound set examined will reflect these differences and lead to a decrease, or total loss, of the discriminatory ability of this method.

Figures 17 and 18 give normalized-percentage, compound-distribution plots for iso- and cyclo- alkanes with peak numbers 1-13 from Figure 5A. These peaks elute roughly around  $n-C_9$ . Figure 19 gives the area overlay for the compound-distribution plots of figures 17 and 18. Figure 20 gives the compound-distribution plots for the 10 random oils (Table 2) with the area overlay for the Caillou Island oil family (Fig. 19) superimposed. The compound-distribution plots of the numbered peaks of figure 5A for the 23 Caillou Island oils (Figs. 17 and 18) have very tight, parallel trends, trends which strongly resemble those in the compound-distribution plots for the  $C_{12}$ - $C_{16}$  (Fig. 11) and  $C_{16}$ - $C_{21}$  (Figs. 6-9) isoprenoid HC's for the same 23 oils. On the other hand, the compound-distribution plots for the same saturated HC's of the 10 random oils exhibit a high degree of variance and decreased parallelism. Only the compound-distribution plot of the Lake Barre oil falls within the area overlay of the Caillou Island oil family. Thus, the compound-distribution plots in figures 17-19 also strongly suggest that the 23 Caillou Island oils belong to one genetically-related family. However, the HC's plotted in figures 17-19 are not biomarker-classed HC's; they are "generic" HC's, apparently found in abundance in most, or all "normal" oils. These facts suggest that



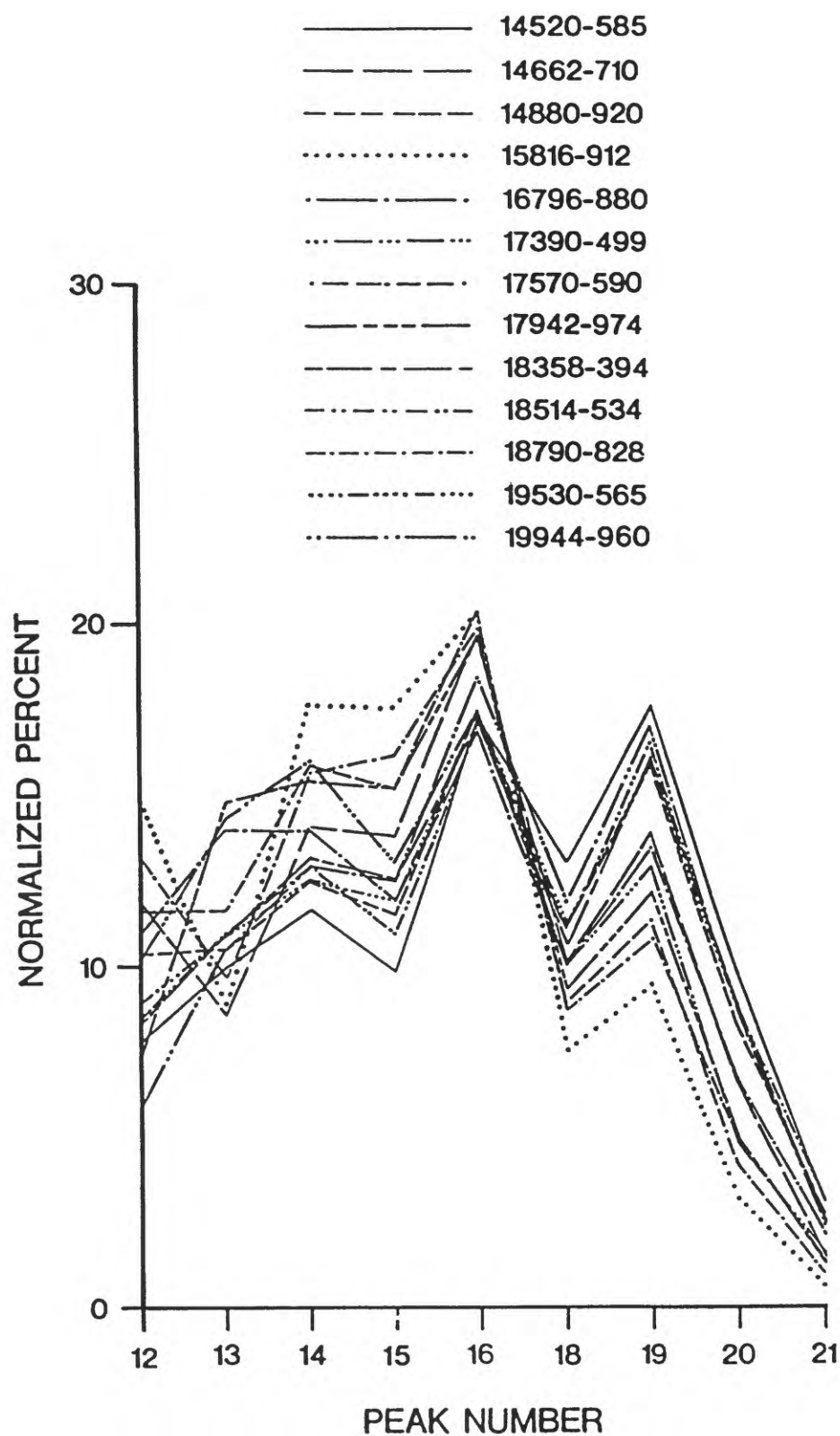


Figure 13. Normalized-percentage, compound-distribution plots for the  $C_{12}$  to  $C_{21}$  isoprenoid HC's of 13 Caillou Island oils.



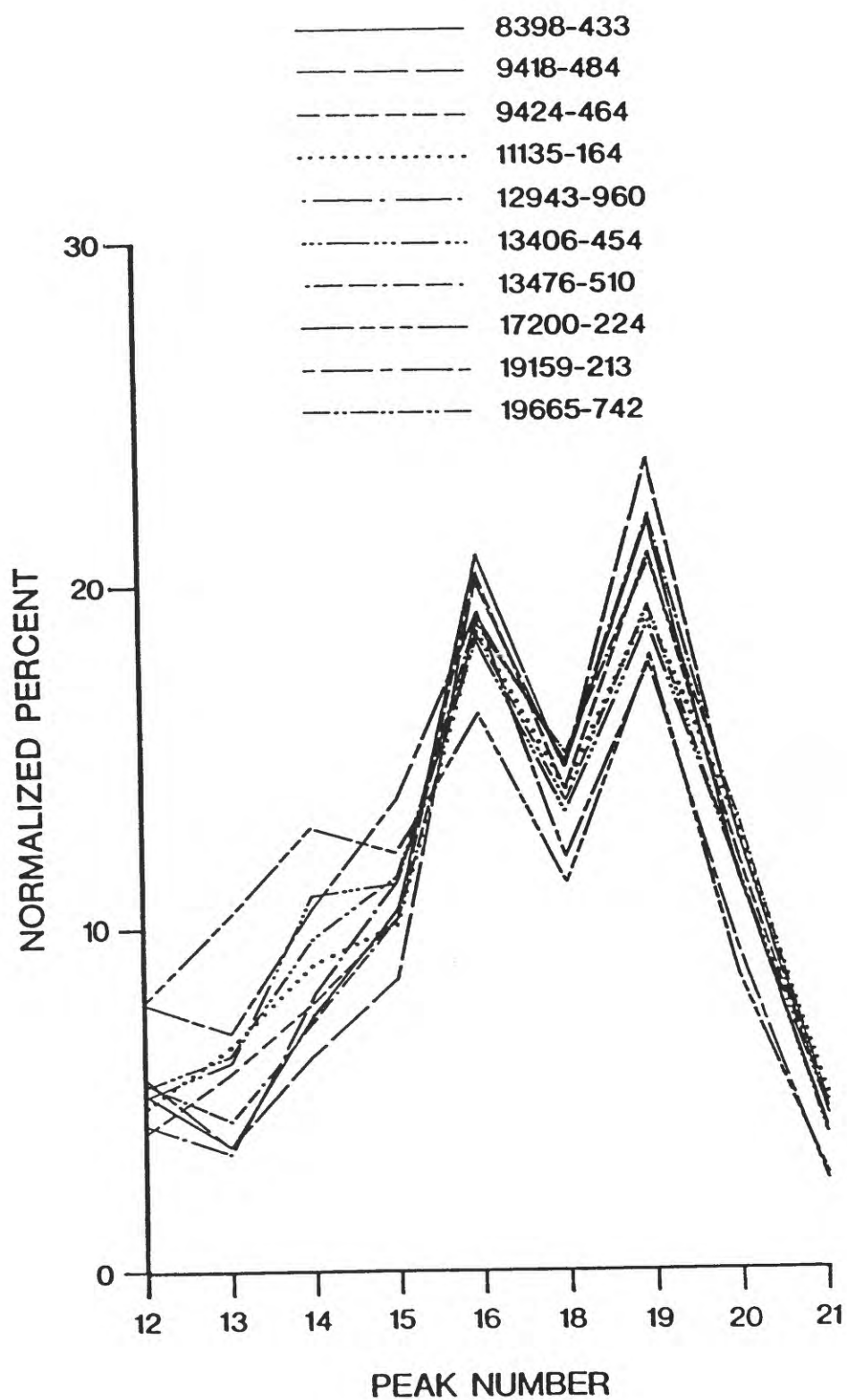


Figure 14. Normalized-percentage, compound-distribution plots for the  $C_{12}$  to  $C_{21}$  isoprenoid HC's of 10 Caillou Island oils.



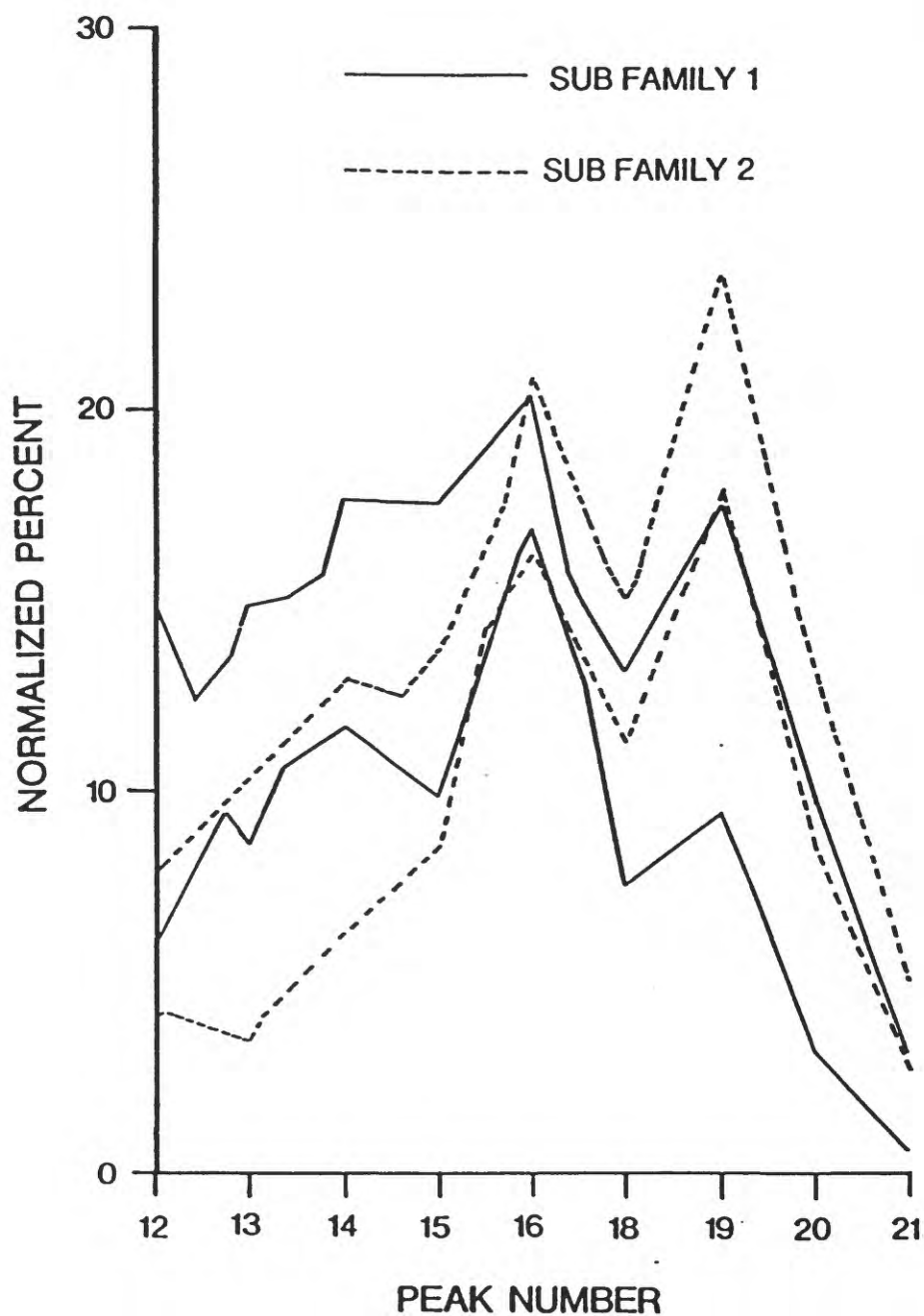


Figure 15. Area overlay of the normalized-percentage, compound-distribution plots for the  $C_{12}$  to  $C_{21}$  isoprenoid HC's of the Caillou Island oil subfamilies. Subfamily one is from the plots of figure 13; subfamily two is from the plots of figure 14.



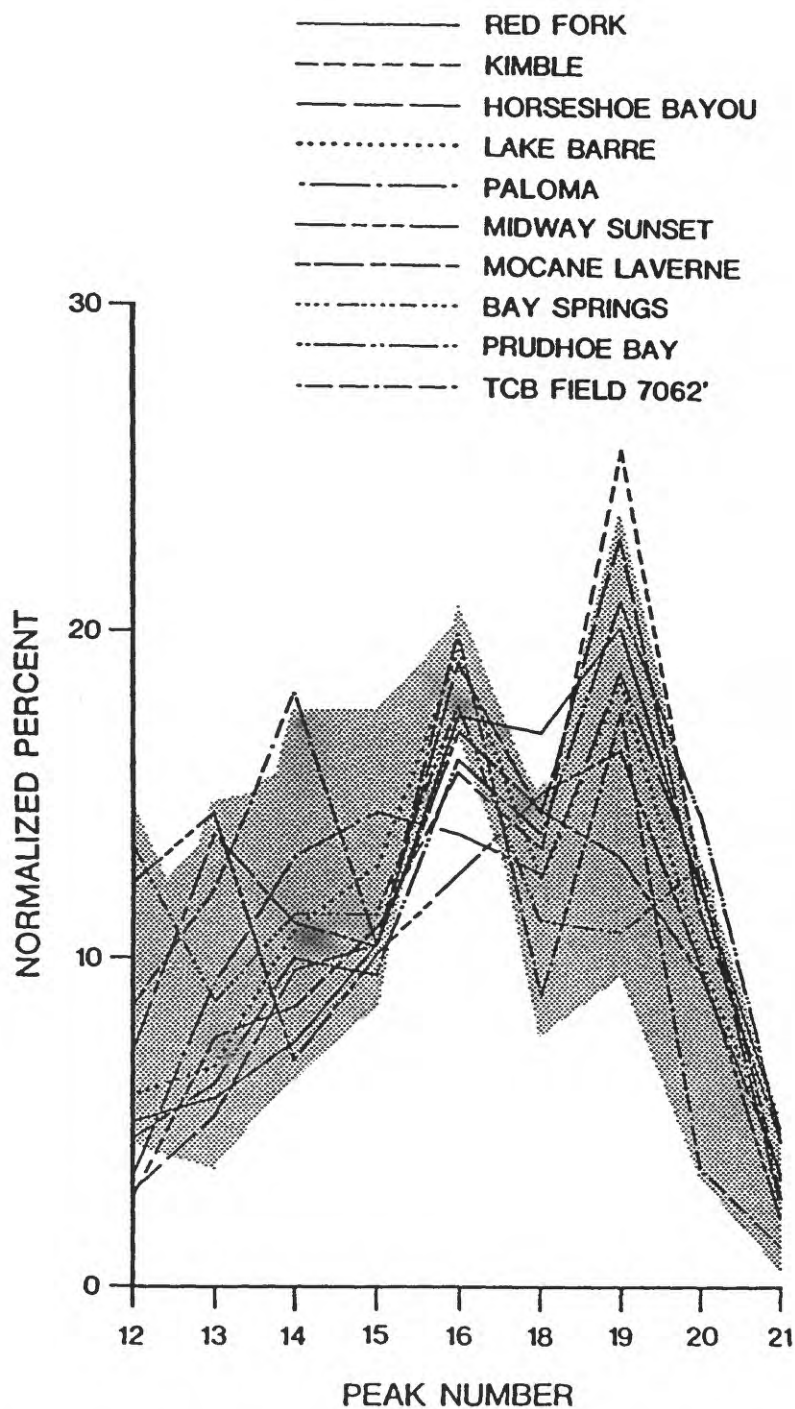


Figure 16. Normalized-percentage, compound-distribution plots for the  $C_{12}$  to  $C_{21}$  isoprenoid HC's of the 10 random oils geographically separated from Caillou Island. The area overlay for these same plots for the Caillou Island oil family (from Fig. 15) is shown by the stippled pattern.



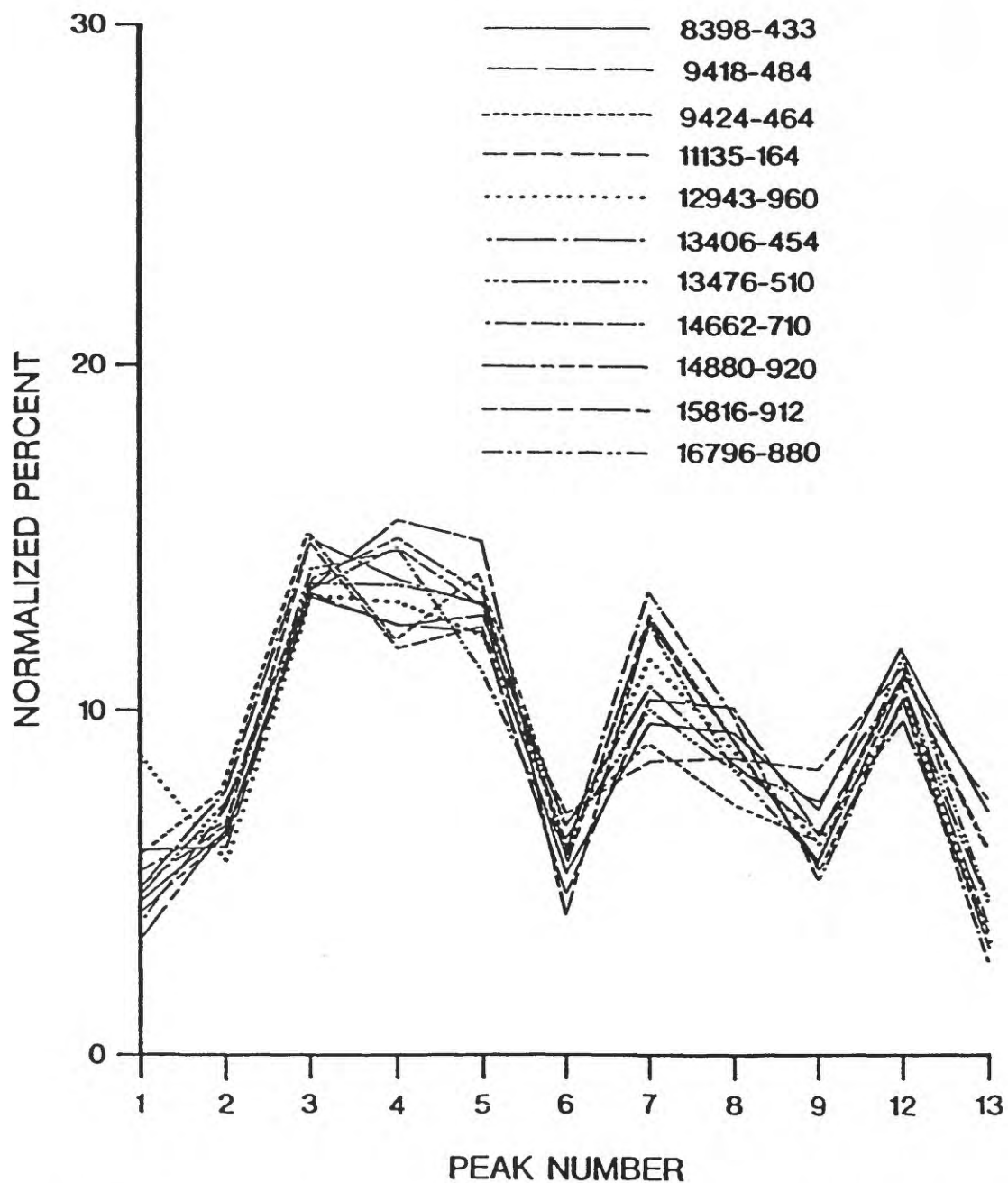


Figure 17. Normalized-percentage, compound-distribution plots for the iso-cyclic alkanes (peaks 1-9, 12, and 13 from Fig. 5A) of 11 Caillou Island oils.



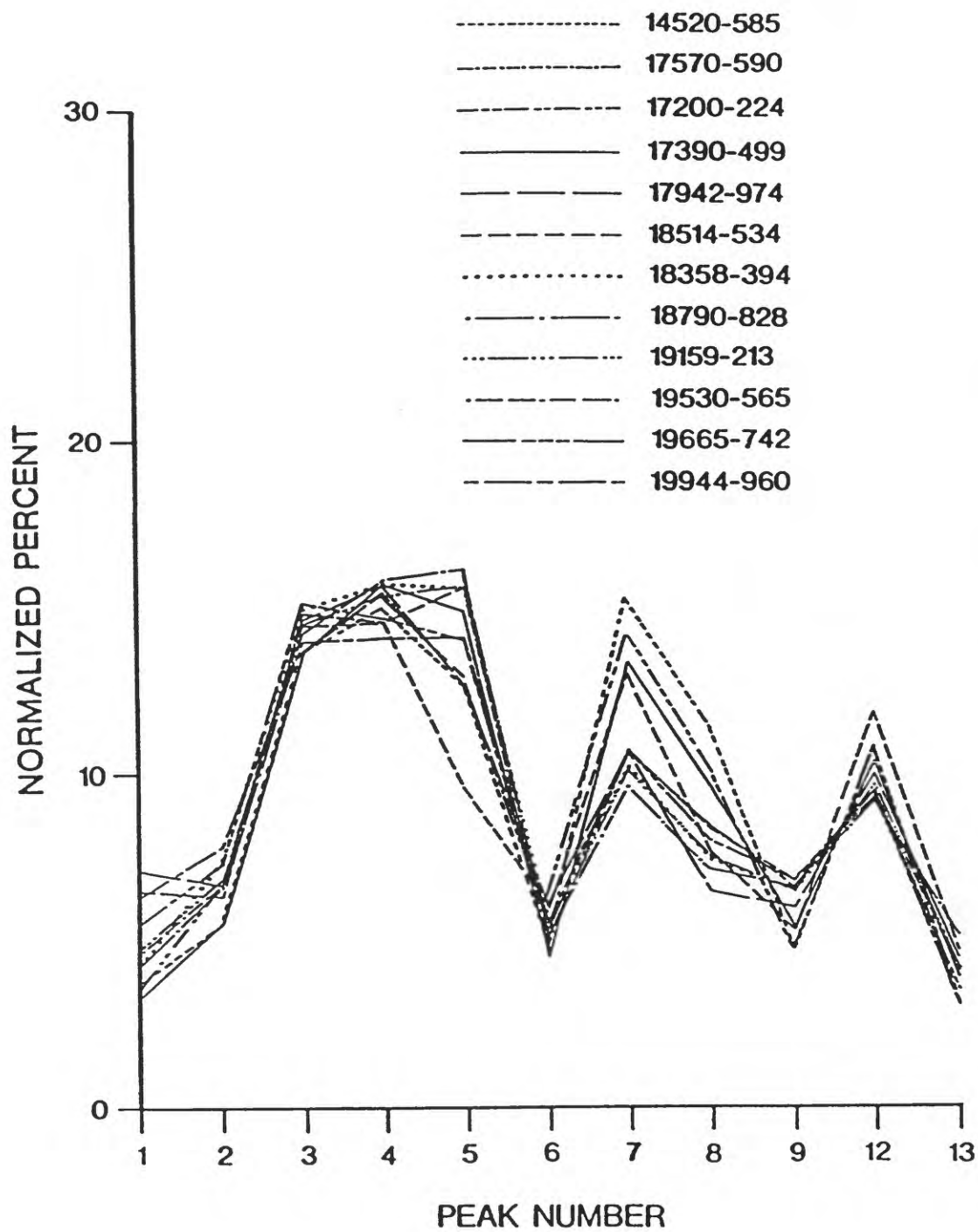


Figure 18. Normalized-percentage, compound-distribution plots for the iso-cyclic alkanes (peaks 1-9, 12, and 13 from Fig. 5A) of 12 Caillou Island oils.



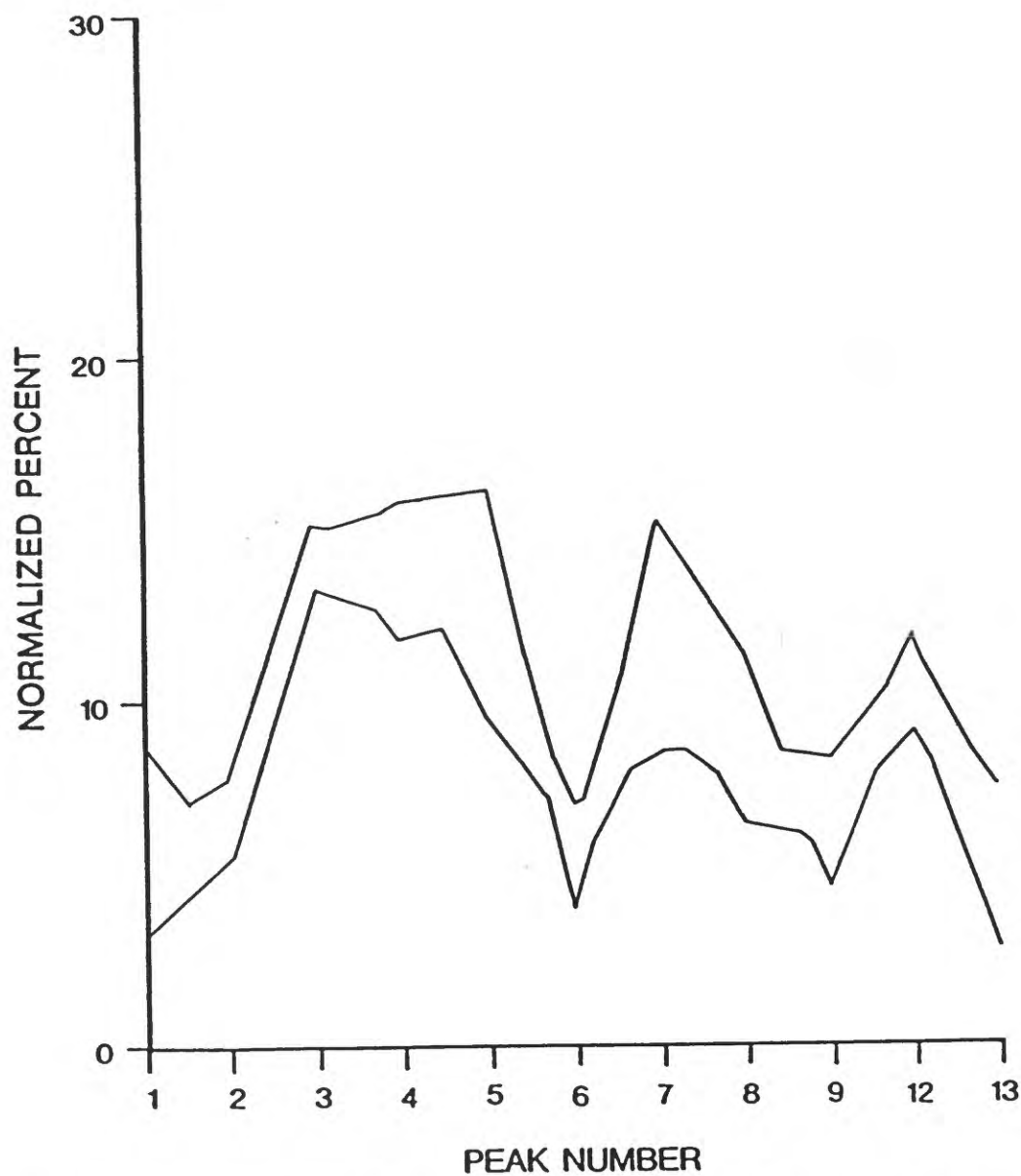


Figure 19. Area overlay of the normalized-percentage, compound-distribution plots for the iso-cyclic alkanes (peaks 1-9, 12, and 13 from Fig. 5A) of the Caillou Island oil subfamily from figures 17 and 18.



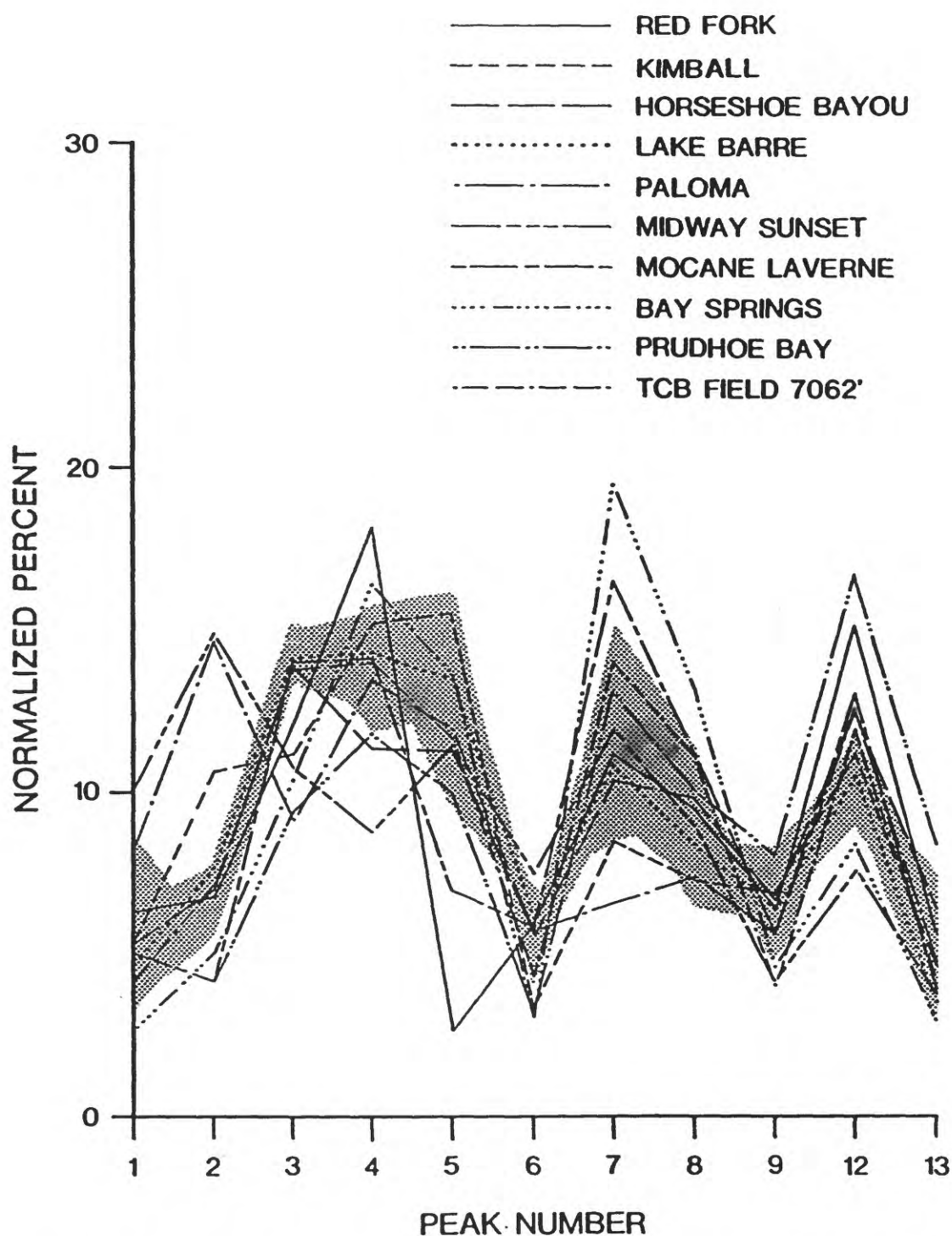


Figure 20. Normalized-percentage, compound-distribution plots for the iso-cyclic alkanes (peaks 1-9, 12, and 13 from figure 5A) from the 10 random oils geographically separated from Caillou Island. The area overlay for the same plots for the Caillou Island oil family (Fig. 19) is shown by the stippled pattern.



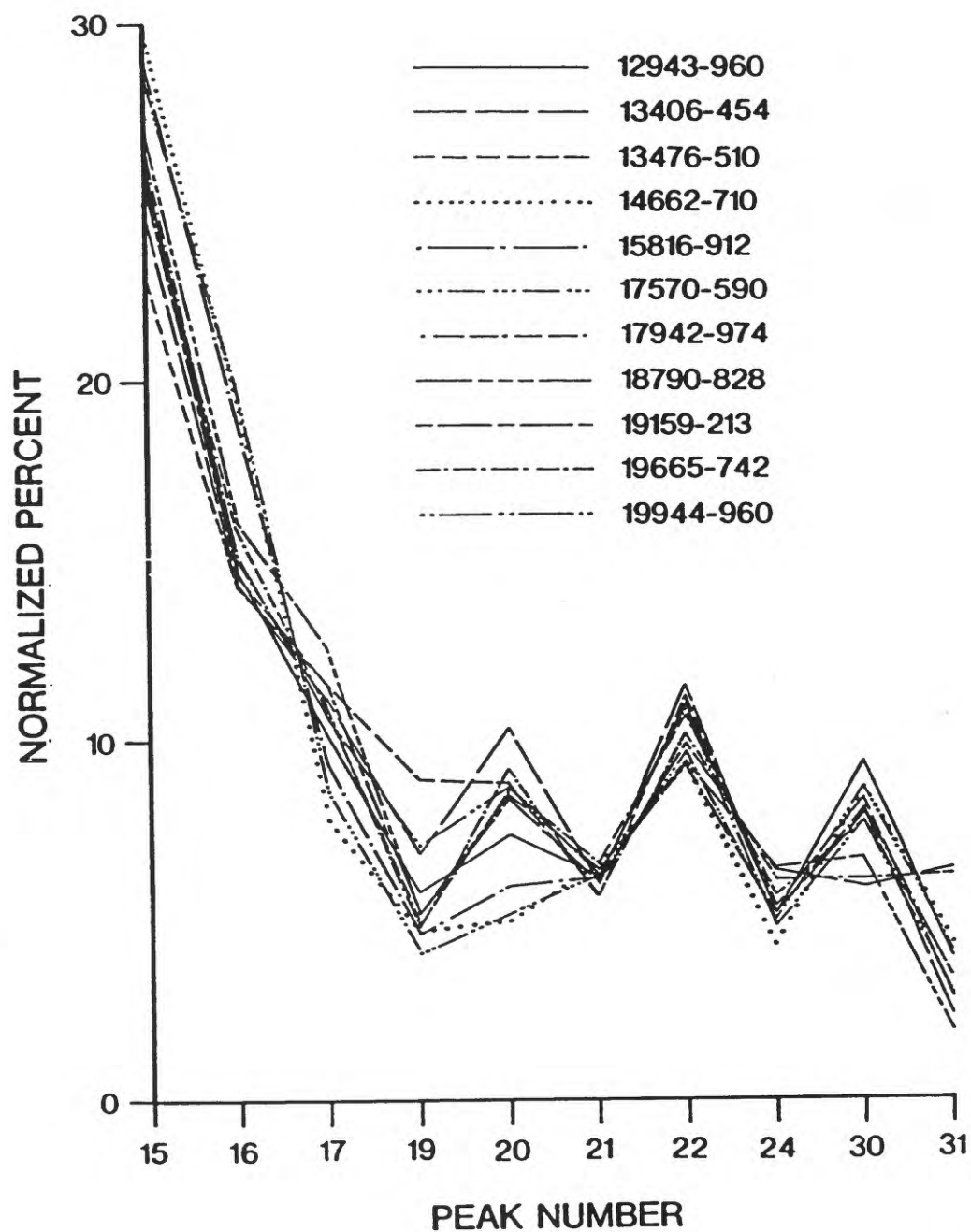


Figure 21. Normalized-percentage, compound-distribution plots for the iso-cyclic alkanes (peaks 15-17, 19-22, 24, 30, and 31 from Fig. 5B) of 11 Caillou Island oils.



normalized-percentage, compound-distribution plots of the common, abundant ("generic") HC's found in oils can be used as an oil-oil correlation tool.

Figures 21 to 23 give normalized-percentage, compound-distribution plots for iso- and cyclo- alkanes with peak numbers 15-31 from figure 5B. These peaks approximately lie in the  $n-C_9$  to  $n-C_{12}$  range. Two subfamilies are evident in figures 21 and 22, subfamilies which are largely due to the greater relative concentrations of peak numbers 30 and 31. By excluding these two peaks from consideration, and considering only peaks 15 to 24 ( $n-C_9$  to  $n-C_{10}$ , for a carbon-number range of only two as opposed to four), much tighter compound-distribution plots result (not shown), and the oils of figures 21 and 22 all plot as one family. Four oils in figure 23 have compound-distribution plots which are significantly different than those of figures 21 and 22, as shown by the subfamily area overlays of figure 24. At least part of the reason for this difference stems from analytical problems. The retention times in the original gas chromatograms for peaks 15 to 31 for the oils of figure 23, were different than those in the chromatograms for the oils of figures 21 and 22. These latter chromatograms were essentially overlays of each other, with respect to peak retention times. Thus, the differences in the compound-distribution plots of the oils in figure 23 may be as much due to errors from manual peak height measurement (compared to electronic peak area integration) as due to actual differences between the oils themselves. Unfortunately, by the time this problem was recognized, the entire gas chromatograph had been replaced.

Figure 25 gives the compound-distribution plots for the iso- and cyclo- alkanes of peak numbers 15 to 31 (Fig. 5B) for the 10 unrelated oils, with the area overlay (Fig. 24) of the 23 Caillou Island oils superimposed. In spite of the relatively poor agreement in the compound-distribution plots for the 23 Caillou Island oils (compared to previous examples) only the compound-distribution plot of the Lake Barre oil falls within the Caillou Island family overlay (Fig. 25). Furthermore, the two factors which reduced the discriminatory powers of this compound set (analytical problems and a carbon-number range of four for the compound set) would be easily correctable, the first by present-day gas chromatographs.

#### Aromatic HC's

Compound-distribution plots were also made up for aromatic HC's. Figure 26 is an original gas chromatogram of the lighter aromatic HC's (toluene to the methylnaphthalenes) from a Caillou Island oil, and figure 27 is an original gas chromatogram of the heavier aromatic HC's (dimethylnaphthalenes to dimethylphenanthrenes) from a Caillou Island oil. The peaks of figure 26 (9, 11, 12, 14-16, 18, 20, 23, and 27) which were used in the construction of the compound-distribution plots below are identified in figure 28 and Table 3, as well as other light aromatic HC's of figure 28. The peaks of figure 27 (4A-6A, 12A, 15A, 17A, 20A, 21A, 24A, 31A, and 38A) which were used in the construction of the compound-distribution plots below are identified in figure 29 and Table 4 as well as other aromatic HC's of figure 29. Compound-distribution plots for the peaks numbered 9-27 in figure 26, reveal that eighteen of the Caillou Island oils plot as a subfamily (Figs. 30 and 31). The 5,643-5,469 m (18,514-18,534 ft) Caillou Island oil has an abnormally high concentration of naphthalene (peak 23, Fig. 26) compared to the other 17 Caillou Island oils. It is not known if this concentration is an artifact of the analytical conditions or if it is a valid characteristic of the oil itself. The five remaining Caillou Island oils



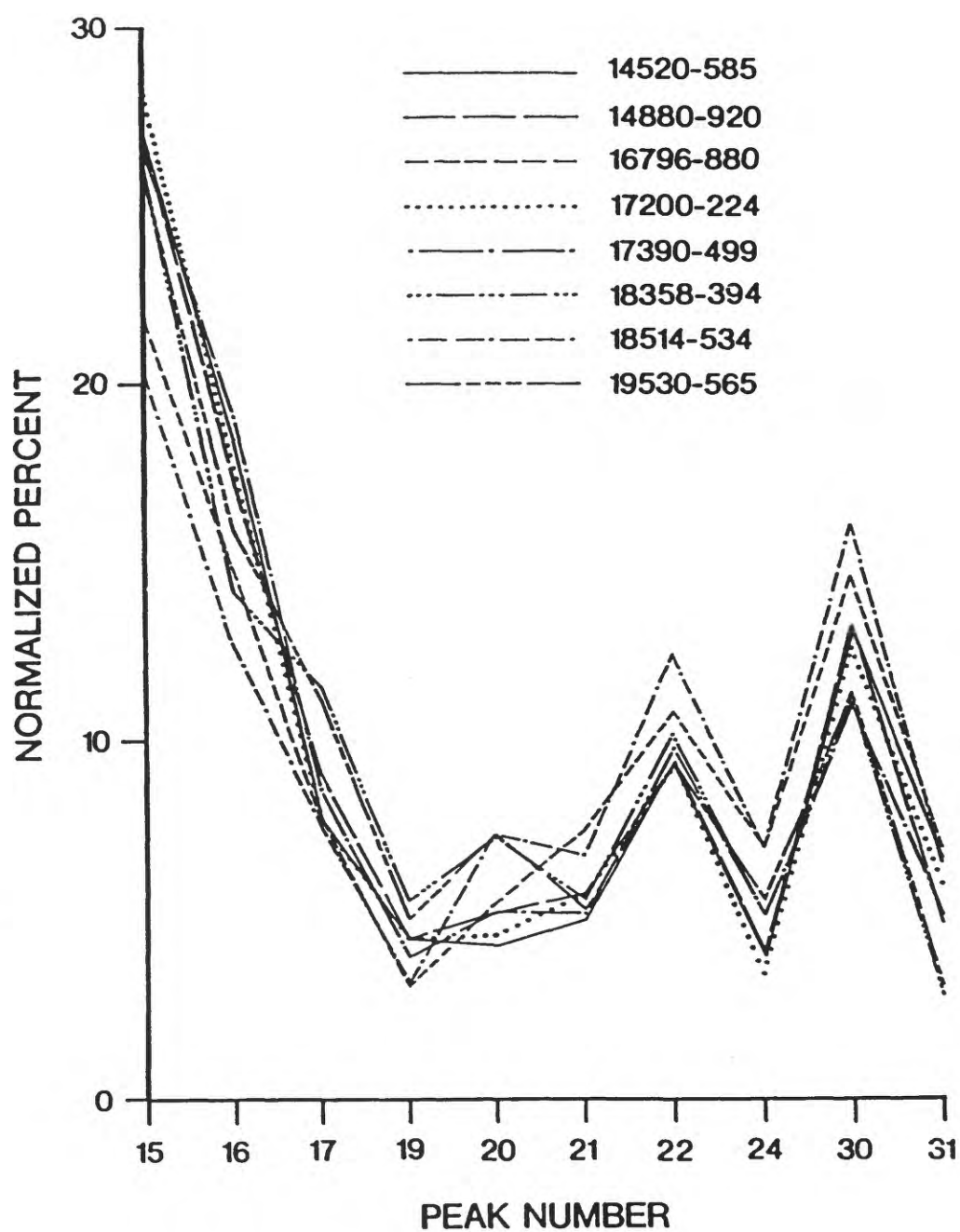


Figure 22. Normalized-percentage, compound-distribution plots for the iso-cyclic alkanes (peaks 15-17, 19-22, 24, 30, and 31 from Fig. 5B) of 8 Caillou Island oils.



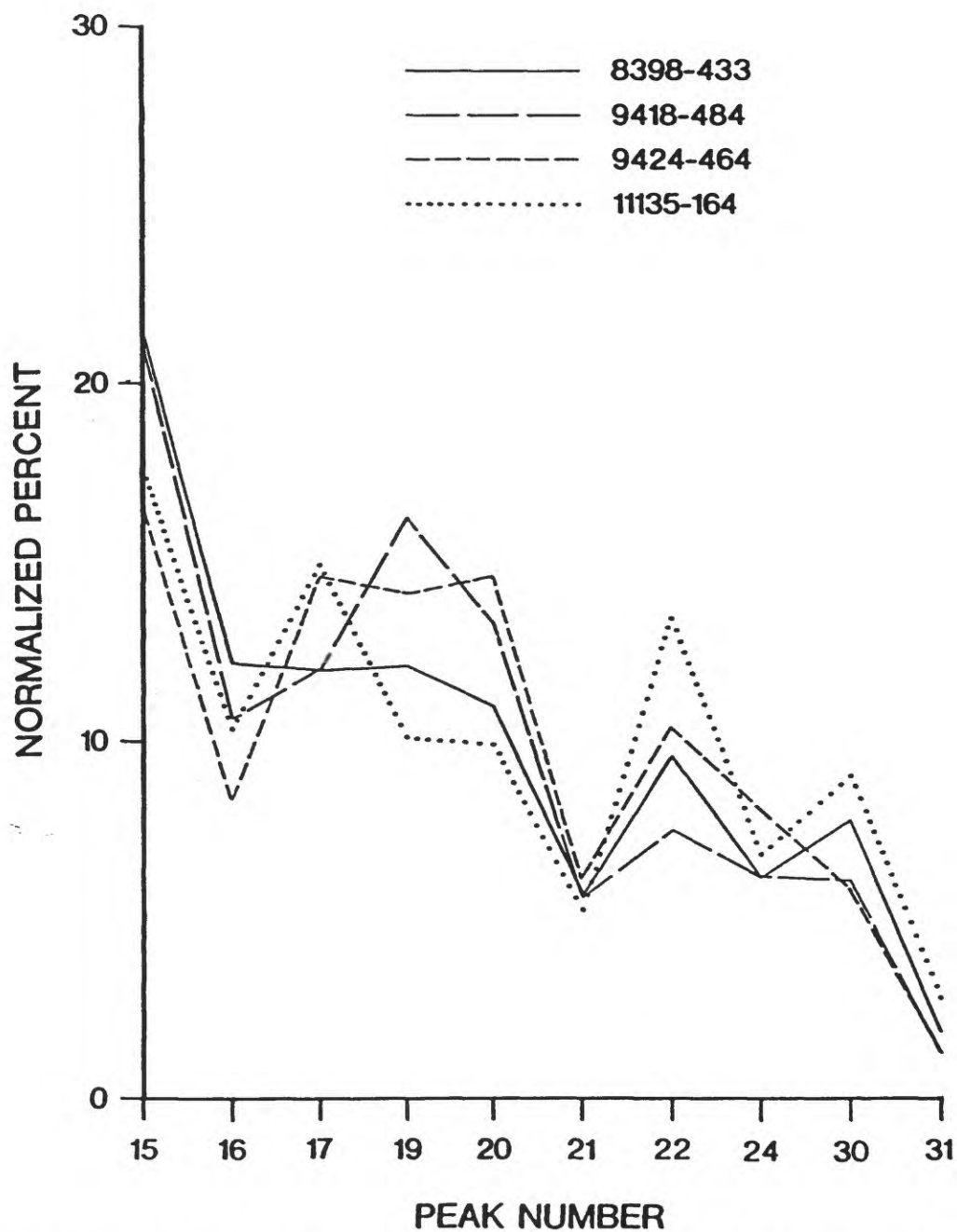


Figure 23. Normalized-percentage, compound-distribution plots for the iso-cyclic alkanes (peaks 15-17, 19-22, 24, 30, and 31 from Fig. 5B) of 4 Caillou Island oils.



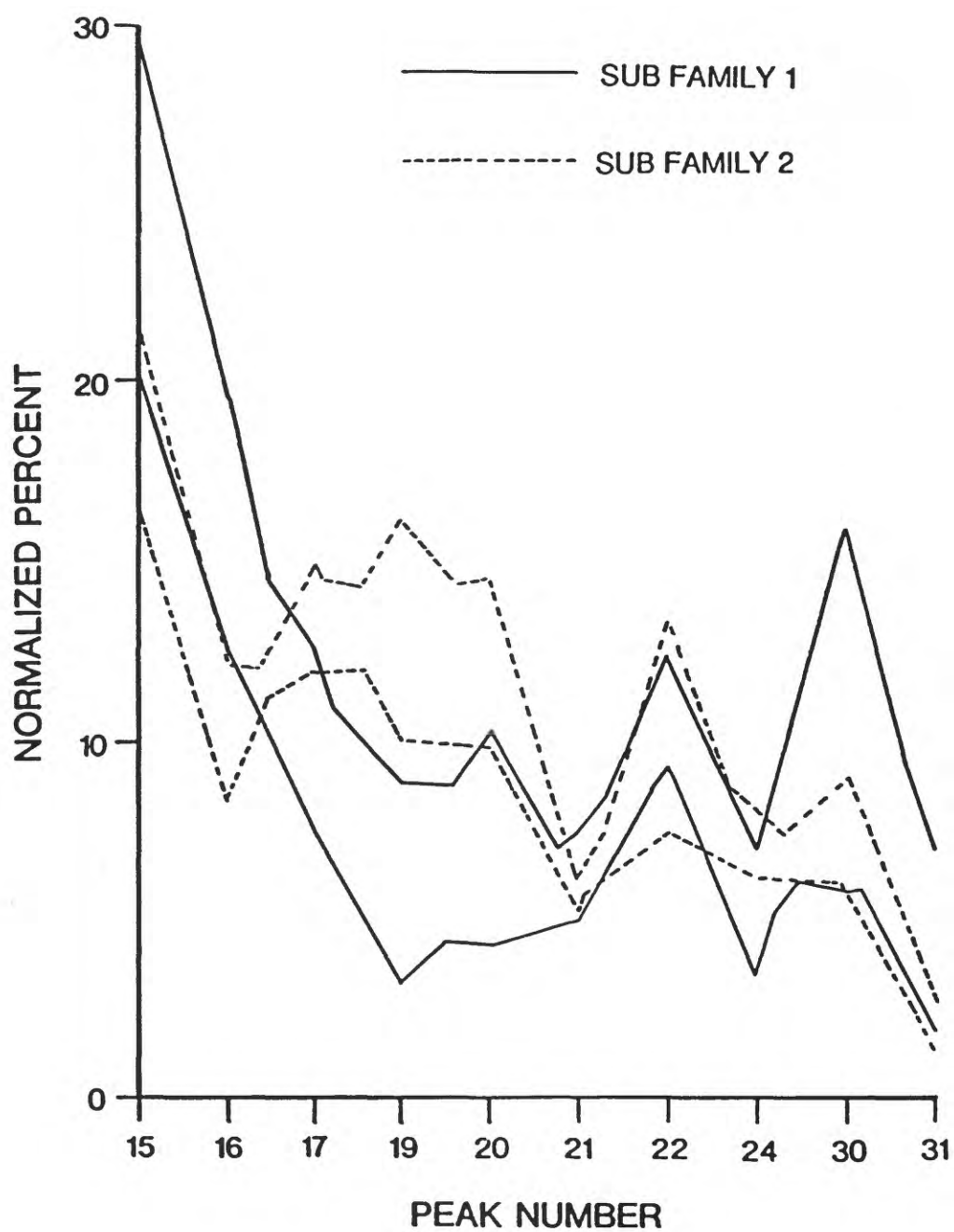


Figure 24. Area overlay of the normalized-percentage, compound-distribution plots for the iso-cyclic alkanes (peaks 15-17, 19-22, 24, 30, and 31 from Fig. 5B) of the Caillou Island oil subfamilies. Subfamily one is from figures 21 and 22; and subfamily two is from figure 23.



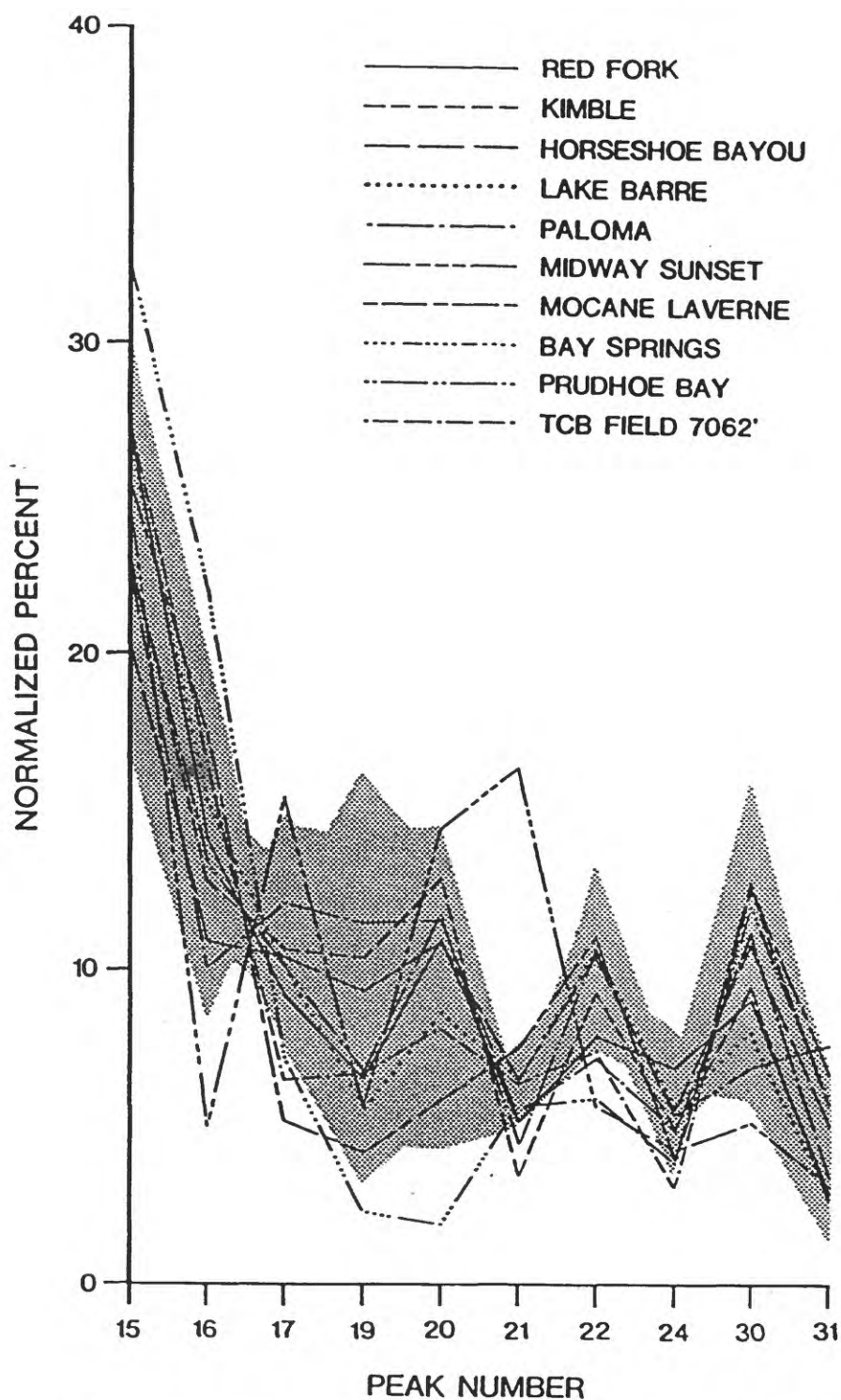


Figure 25. Normalized-percentage, compound-distribution plots for the iso-cyclic alkanes (peaks 15-17, 19-22, 24, 30, and 31 from Fig. 5B) of the 10 random oils geographically separated from Caillou Island. The area overlay for these same plots for the Caillou Island oil family (from Fig. 24) is shown by the stippled pattern.



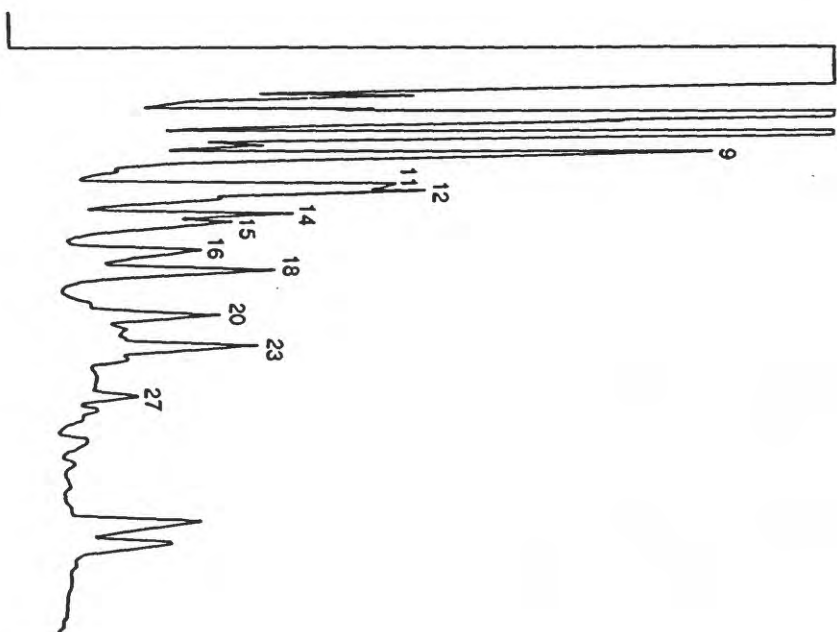


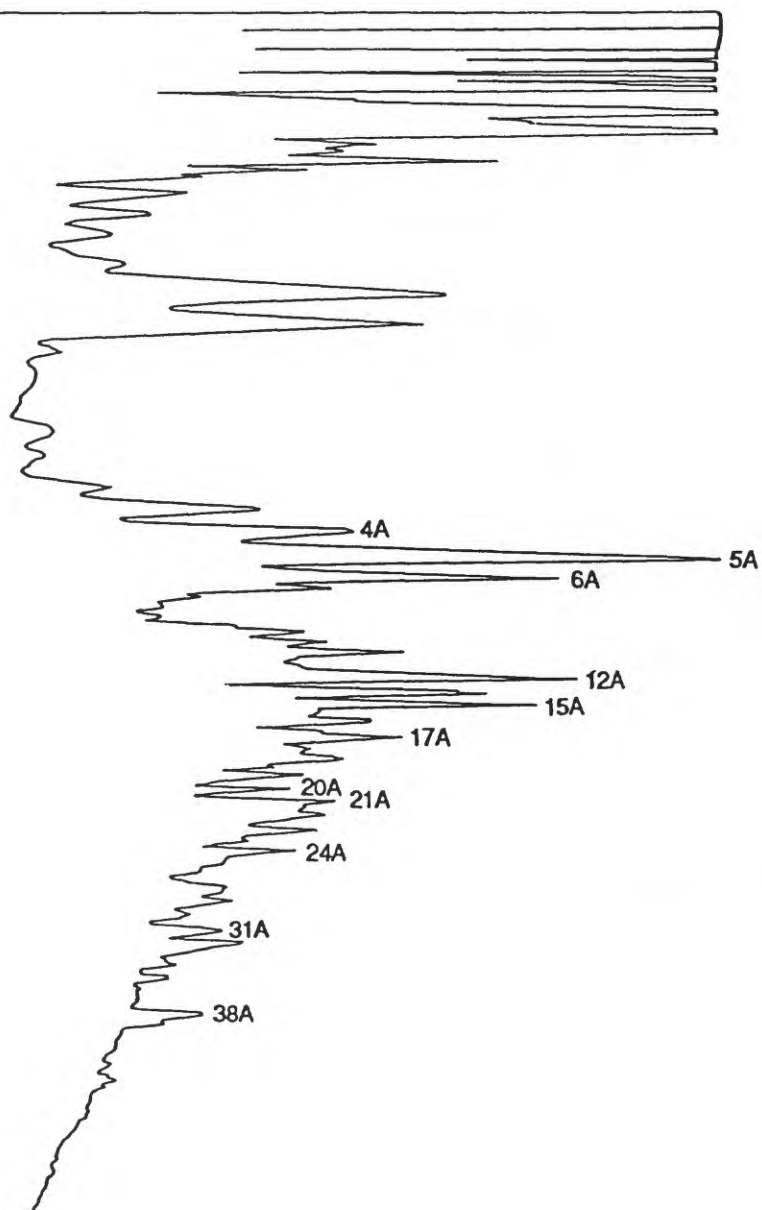
Figure 26.

Original gas chromatogram of the aromatic HC fraction of the 4,469-4,483 m (14,662-14,710 ft) Caillou Island oil sample showing peaks 9, 11, 12, 14-16, 18, 20, 23, and 27 which were used in compound-distribution plots.



Figure 27.

Original gas chromatogram of the aromatic HC fraction of the 5,839-5,856 m (19,159-19,213 ft) Caillou Island oil sample showing peaks 4A-6A, 12A, 15A, 17A, 20A, 21A, 24A, 31A, and 38A which were used in compound-distribution plots.





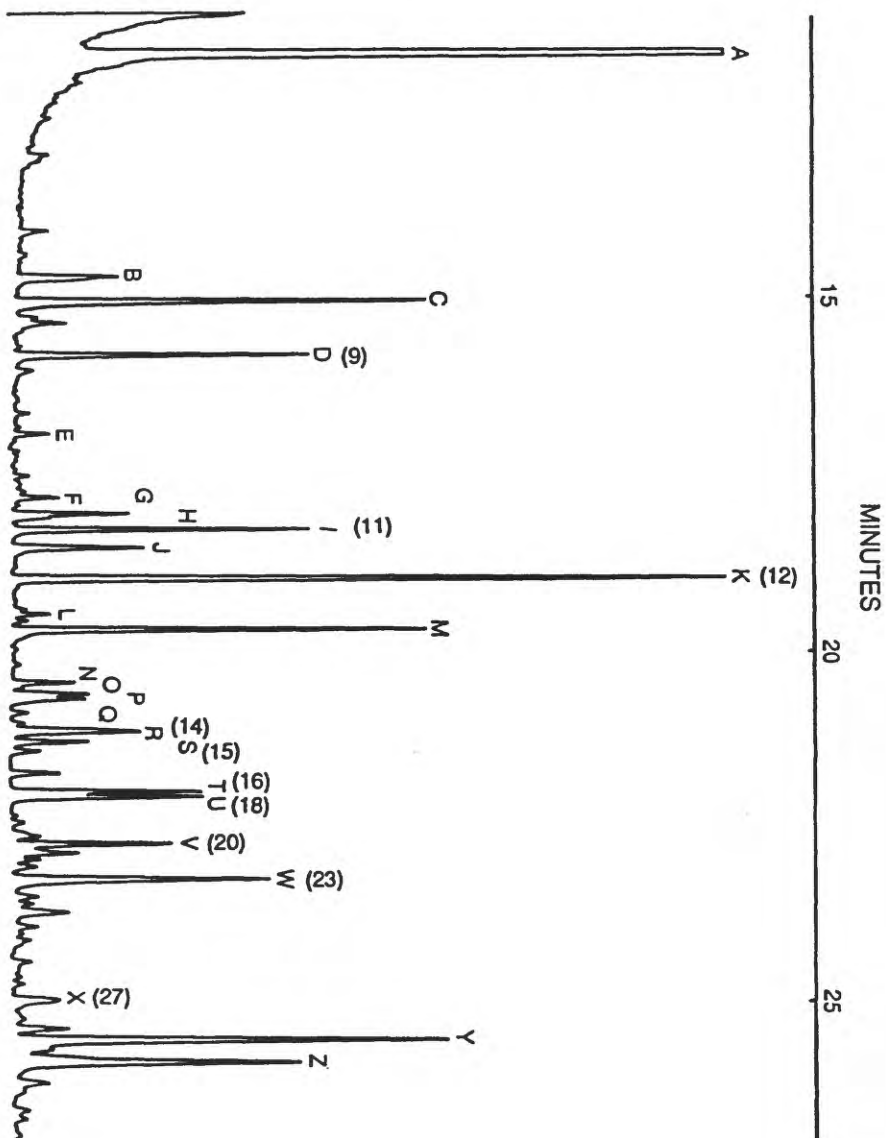
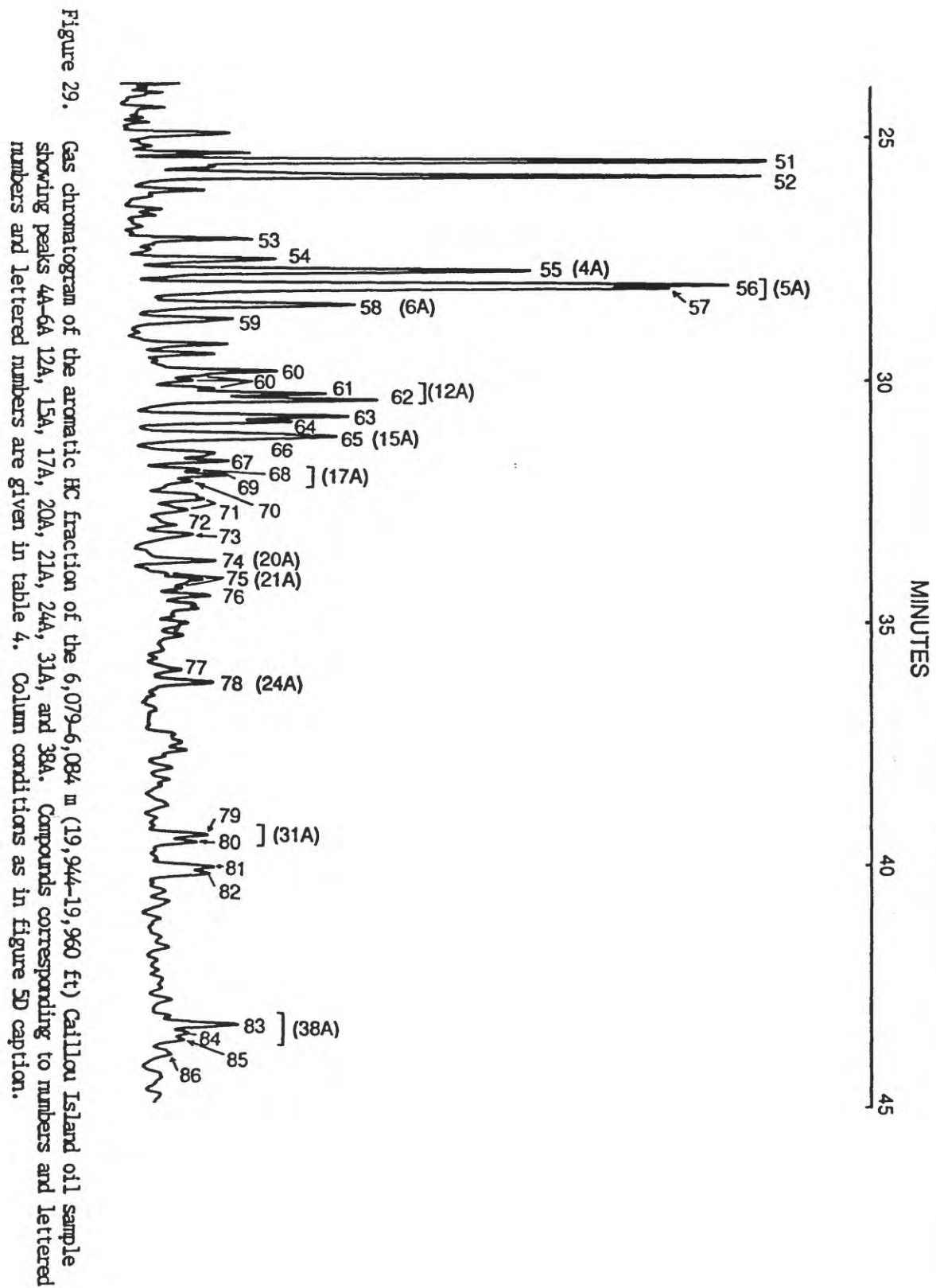


Figure 28.

Gas chromatogram of the aromatic HC fraction of the 6,079-6,084 m (19,944-19,960 ft) Caillou Island oil sample showing peak numbers 9, 11, 12, 14-16, 18, 20, 23, and 27. Column conditions were 0.3 mm x 30 m fused silica with DB-1, initial temperature was 40°C for 10 minutes, programming rate was 10°C/minute to 160°C, and 3°C/minute to 320°C with an upper temperature limit of 30 minutes, injection port 340°C, detector temperature (FID) 350°C, and a column gas flow rate of 25 cc/minute hydrogen. Compound identification was carried out by comparing retention times with known aromatic HC standards and limited mass spectrometry using a Finnigan Mat Ion Trap Detector System. The peaks of figure 16C were subjected to evaporation in preparing this sample for gas chromatography. Compounds corresponding to letters are given in table 3. The results of this and the subsequent gas chromatogram (figure 29) were not used in the construction of the normalized-percentage, compound-distribution plots below.







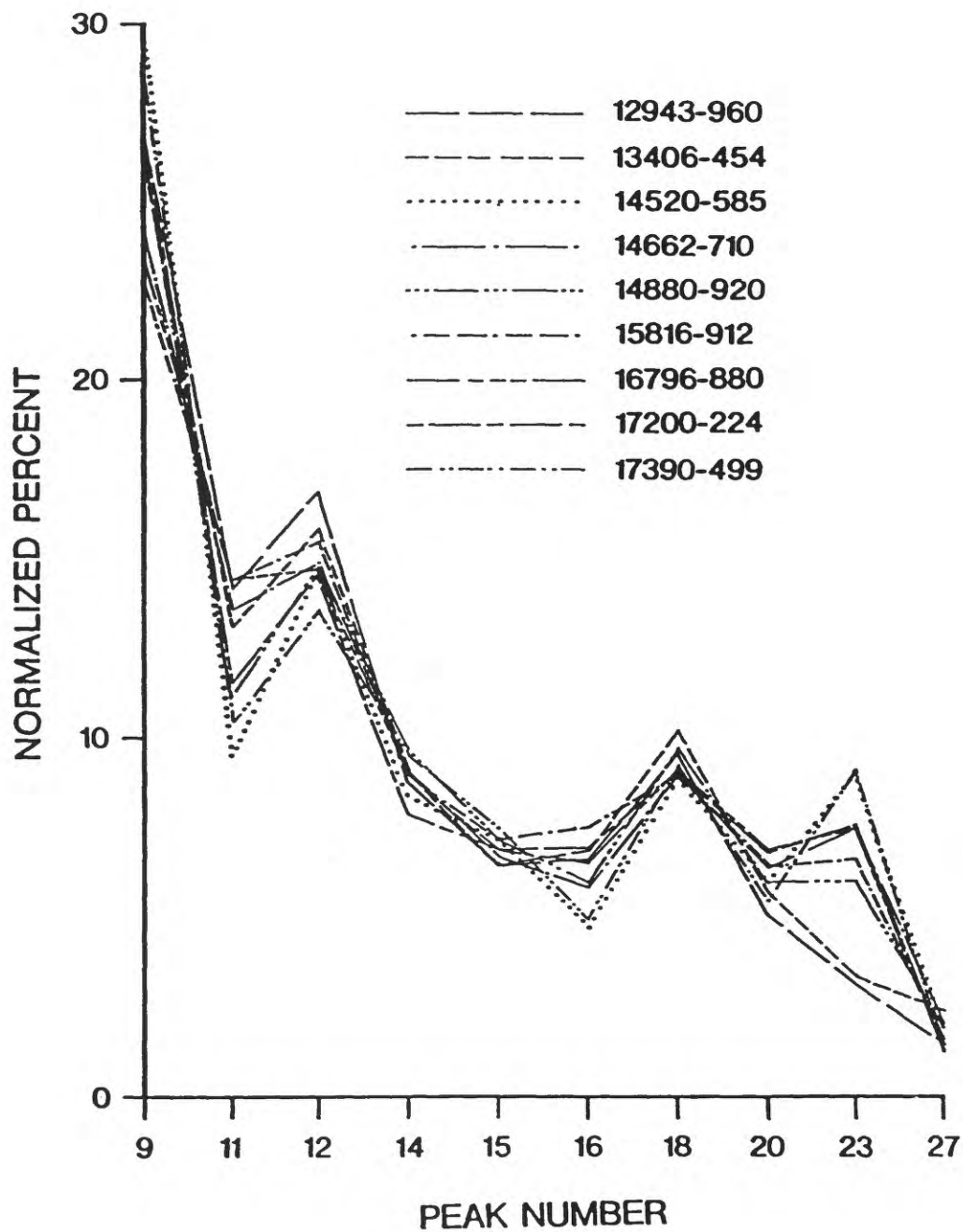


Figure 30. Normalized-percentage, compound-distribution plots for aromatic HC's (peaks 9, 11, 12, 14-16, 18, 20, 23, and 27 from Fig. 26) for 9 Caillou Island oils.



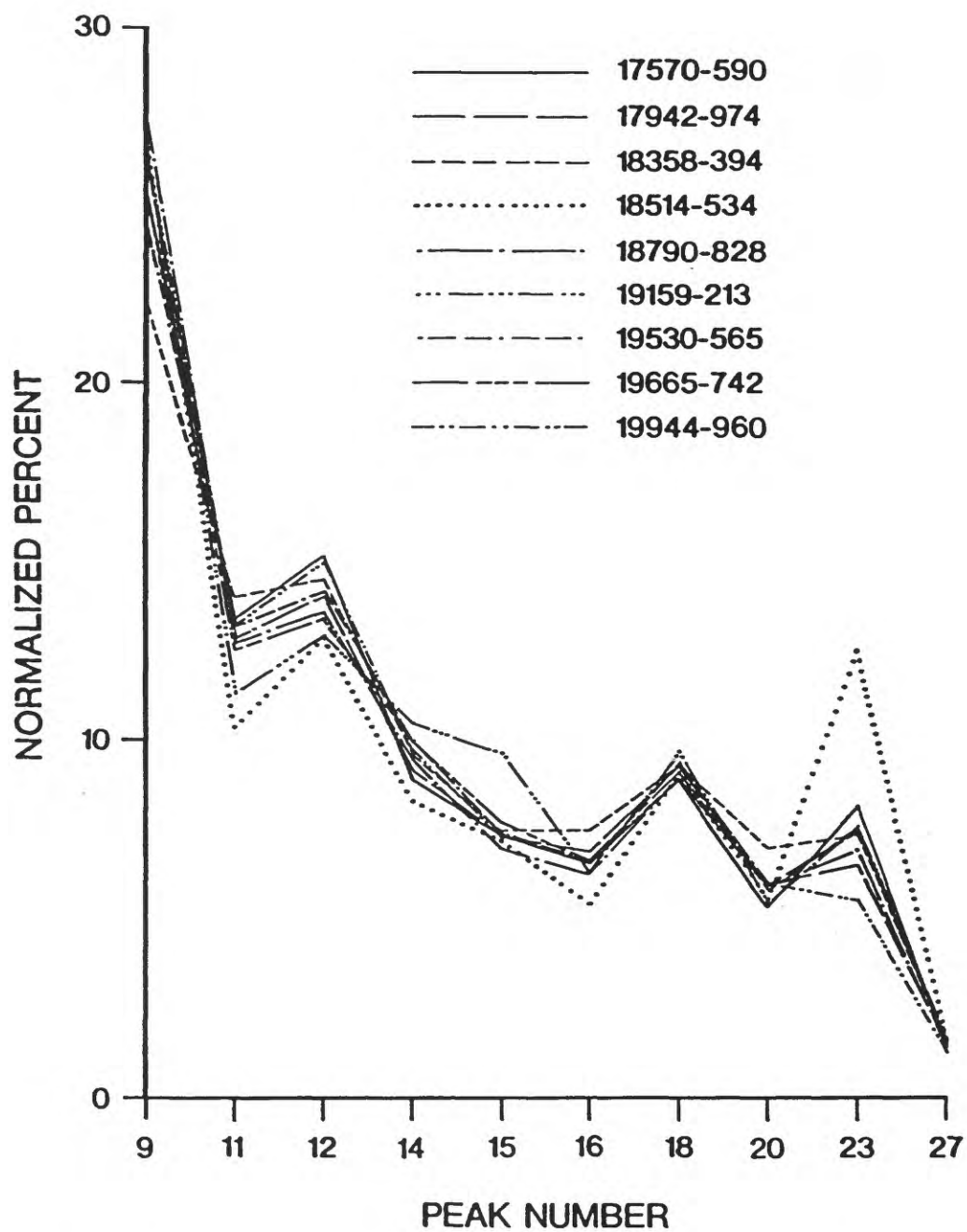


Figure 31. Normalized-percentage, compound-distribution plots for aromatic HC's (peaks 9, 11, 12, 14-16, 18, 20, 23, and 27 from Fig. 26) for 9 Caillou Island oils.



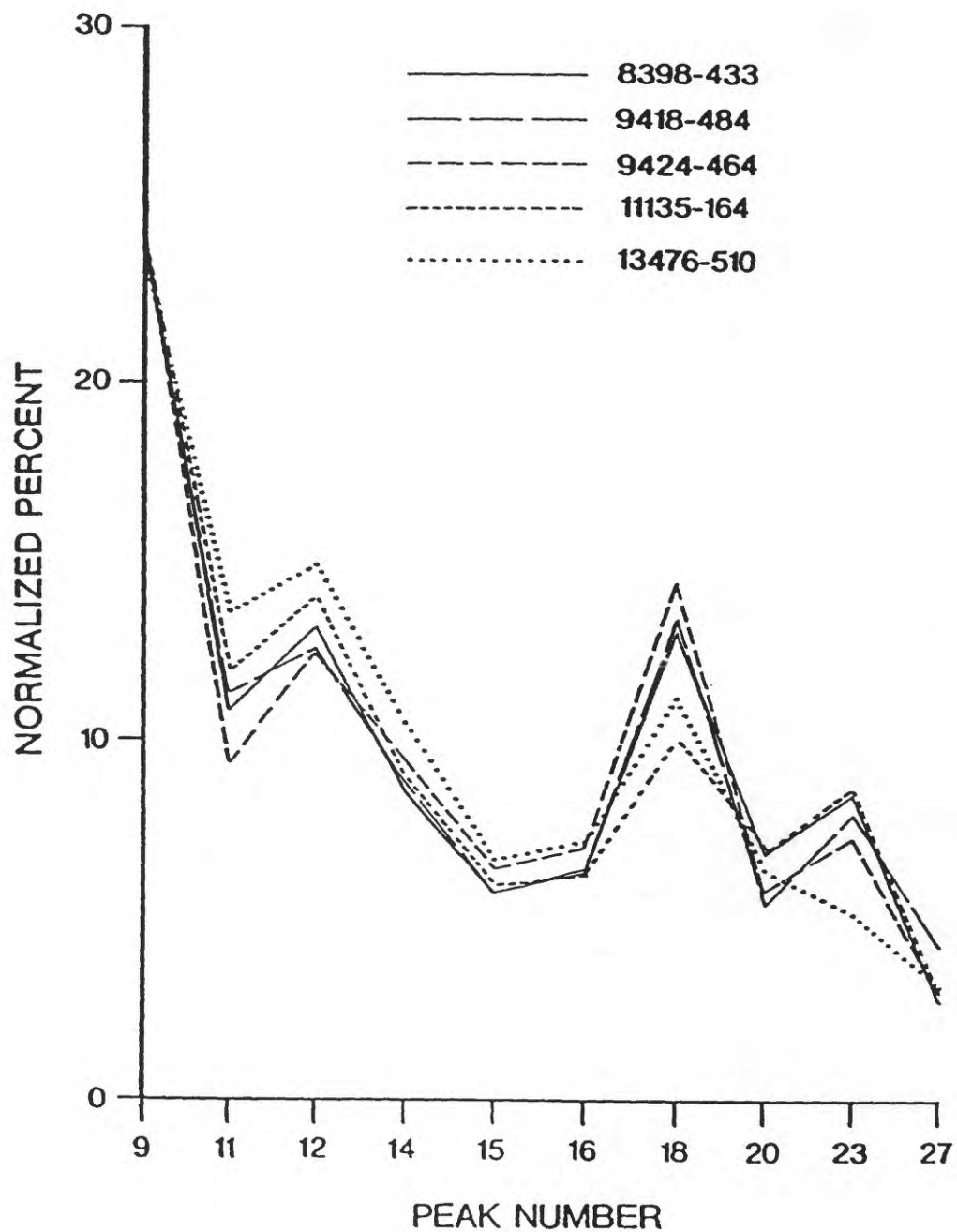


Figure 32. Normalized-percentage, compound-distribution plots for aromatic HC's (peaks 9, 11, 12, 14-16, 18, 20, 23, and 27 from Fig. 26) for 5 Caillou Island oils.



plot as another subfamily (Fig. 32), characterized by relatively high normalized concentrations of 1,2,3,5-tetramethylbenzene (peak 18, Fig. 26). These oils are relatively heavy (27.6-35.7° API, 0.889-0.846 g/cc specific gravity) and are 5 of the 6 shallowest oils. Thus these high concentrations are assumed to be real genetic characteristics, and not analytical artifacts. The area overlays for the compound distribution plots of figures 30 to 32 are given in figure 33. The compound-distribution plots for the aromatic HC's with peak numbers 9-27 (Fig. 26) for the 10 geographically-separated oils are given in figure 34, with the area overlay for the Caillou Island oil family (from Fig. 33) superimposed. The compound-distribution plots for the Lake Barre and Mocane-Laverne oils fall within the area overlay of the Caillou Island oil family. The Mocane-Laverne field is geographically removed from, and obviously not genetically related to, the oils at Caillou Island. No other of the 10 random oils exhibit a match with the area overlay of the Caillou Island oils (Fig. 34), although the oil from the Horseshoe Bayou field is close. Furthermore, as in previous examples, there is a pronounced non-parallel nature in the compound-distribution plots of the 10 random oils of figure 34, compared to the very parallel nature for the same plots of the Caillou Island oils (Figs. 30-33).

Compound-distribution plots for the aromatic HC's of the peaks numbered 4A to 38A in figure 27 for the 23 Caillou Island oils are given in figures 35 to 37. Peak number 4A (2,6- and 2,7- dimethylnaphthalene) in figure 27 has an elution time equivalent to n-C<sub>14</sub>, and peak number 38A (various dimethylphenanthrenes, Table 4) has an elution time between n-C<sub>20</sub> to n-C<sub>21</sub>, for a carbon-number range for this set of compounds of about 7.5. Sixteen of the Caillou Island oils plot as one subfamily (Figs. 35 and 36) and seven of the oils plot as a second subfamily (Fig. 37) characterized by relatively reduced concentrations of peaks 4A and 5A (2,6-, 2,7- and 1,3-, 1,7- dimethylnaphthalenes, respectively). The area overlays for the compound distribution plots of figures 35 to 37 are given in figure 38. The area overlay for the Caillou Island oil family is superimposed over the compound-distribution plots for these same aromatic HC's for the 10 geographically-separated oils in figure 39. The compound-distribution plot of the Lake Barre oil falls within the area overlay of the Caillou Island oil family. None of the compound-distribution plots of the other nine geographically-separated oils falls within the area overlay of the Caillou Island oil family, although the plot for the Mocane-Laverne oil is close. In spite of the fact that this compound set has a carbon-number range of about 7.5, the compound-distribution plots for the Caillou Island oils are quite similar with a well-defined, parallel nature (Figs. 35-38). In contrast, the compound-distribution plots of the ten geographically-separated oils, as in all the previous examples, are distinctly non similar and non parallel.

Compound-distribution plots were constructed (not shown) for peak numbers 4A to 24A of figure 27, by deleting peaks 31A and 38A from consideration. These plots had a carbon-number range of about 4.5, compared to 7.5 for the plots of figures 35-37, as peak 24A (Fig. 27) has a retention time between n-C<sub>17</sub> to n-C<sub>18</sub>. As in previous examples, decreasing the carbon-number range of the compounds under consideration, resulted in much tighter compound-distribution plots with greater discriminatory powers to distinguish genetically related oils.

The peak distribution of the dimethylnaphthalenes (peak numbers 55-60, Fig. 29) is quite similar for many crude oils and rock extracts. Because of this





Figure 33. Area overlays of the normalized-percentage, compound-distribution plots for the aromatic HC's (peaks 9, 11, 12, 14-16, 18, 20, 23, and 27 from Fig. 26) of the Caillou Island oil subfamilies. Subfamily one is from figures 30 and 31; and subfamily two is from figure 32.



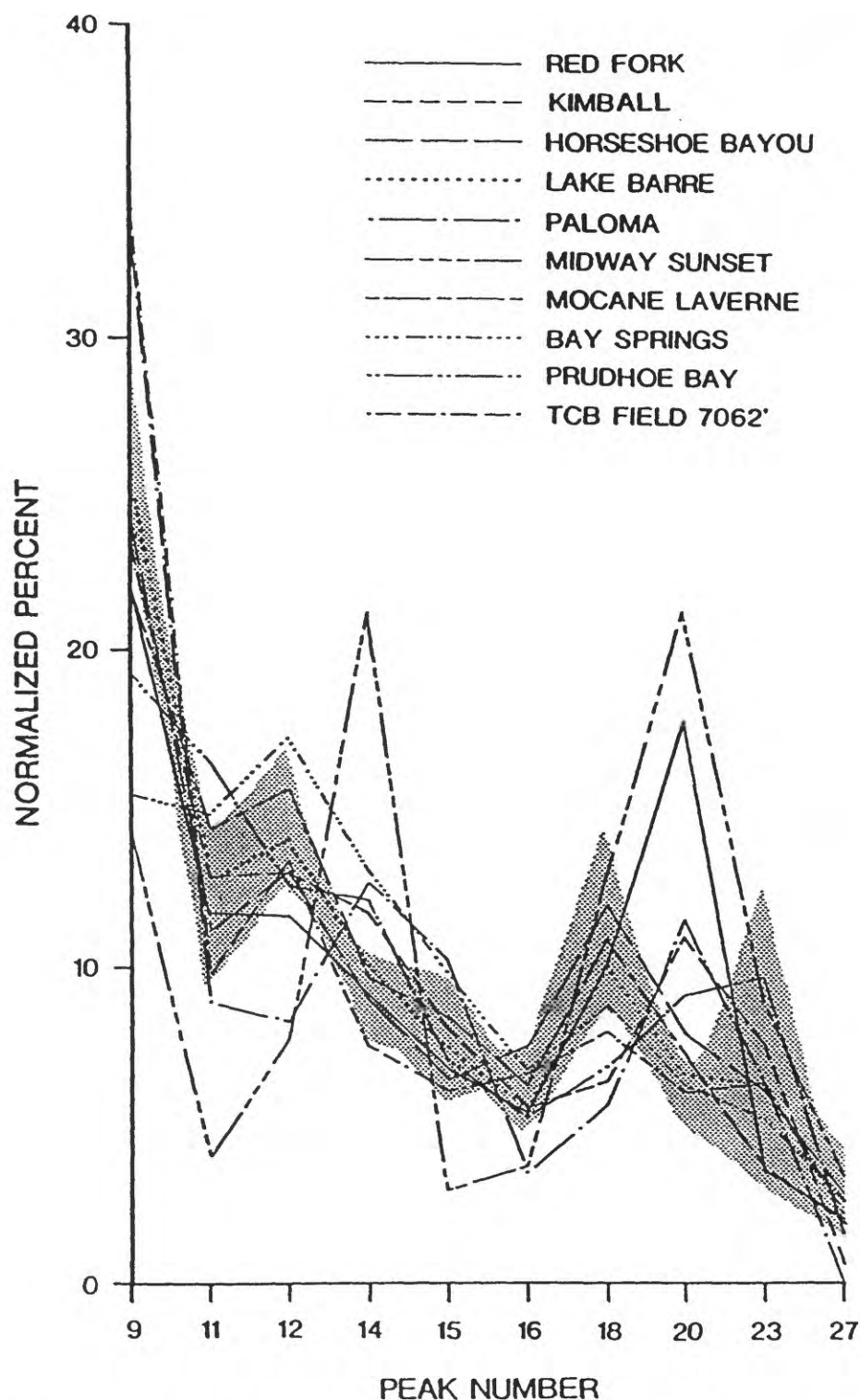


Figure 34. Normalized-percentage, compound-distribution plots for aromatic HC's (peaks 9, 11, 12, 14-16, 18, 20, 23, and 27 from Fig. 26) for the 10 random oils geographically separated from Caillou Island. The area overlay for these same plots for the Caillou Island oil family (Figs. 30-33) is shown by the stippled pattern.



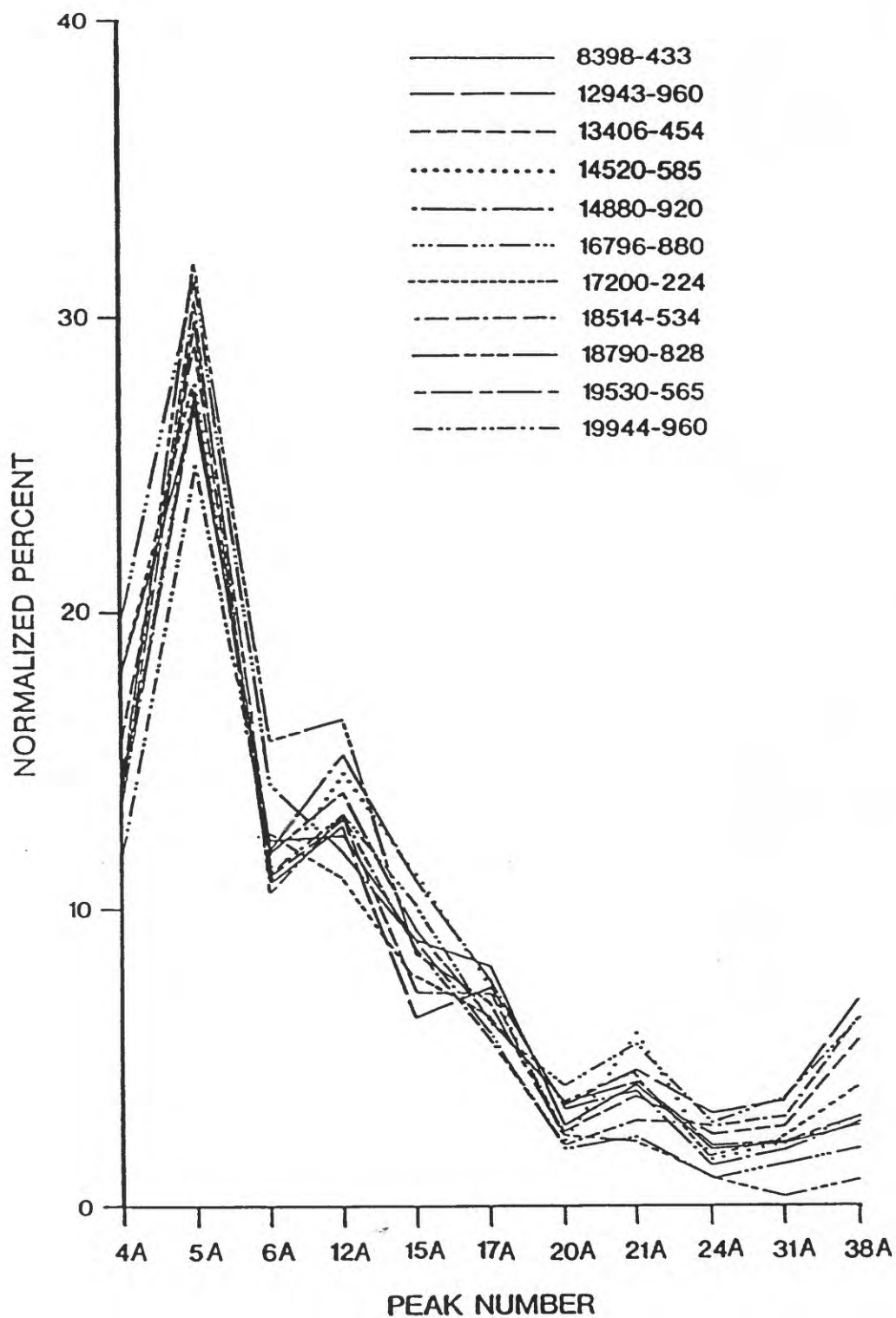


Figure 35. Normalized-percentage, compound-distribution plots for aromatic HC's (peaks 4A-6A, 12A, 15A, 17A, 20A, 21A, 24A, 31A, and 38A from Fig. 27) for 11 Caillou Island oils.



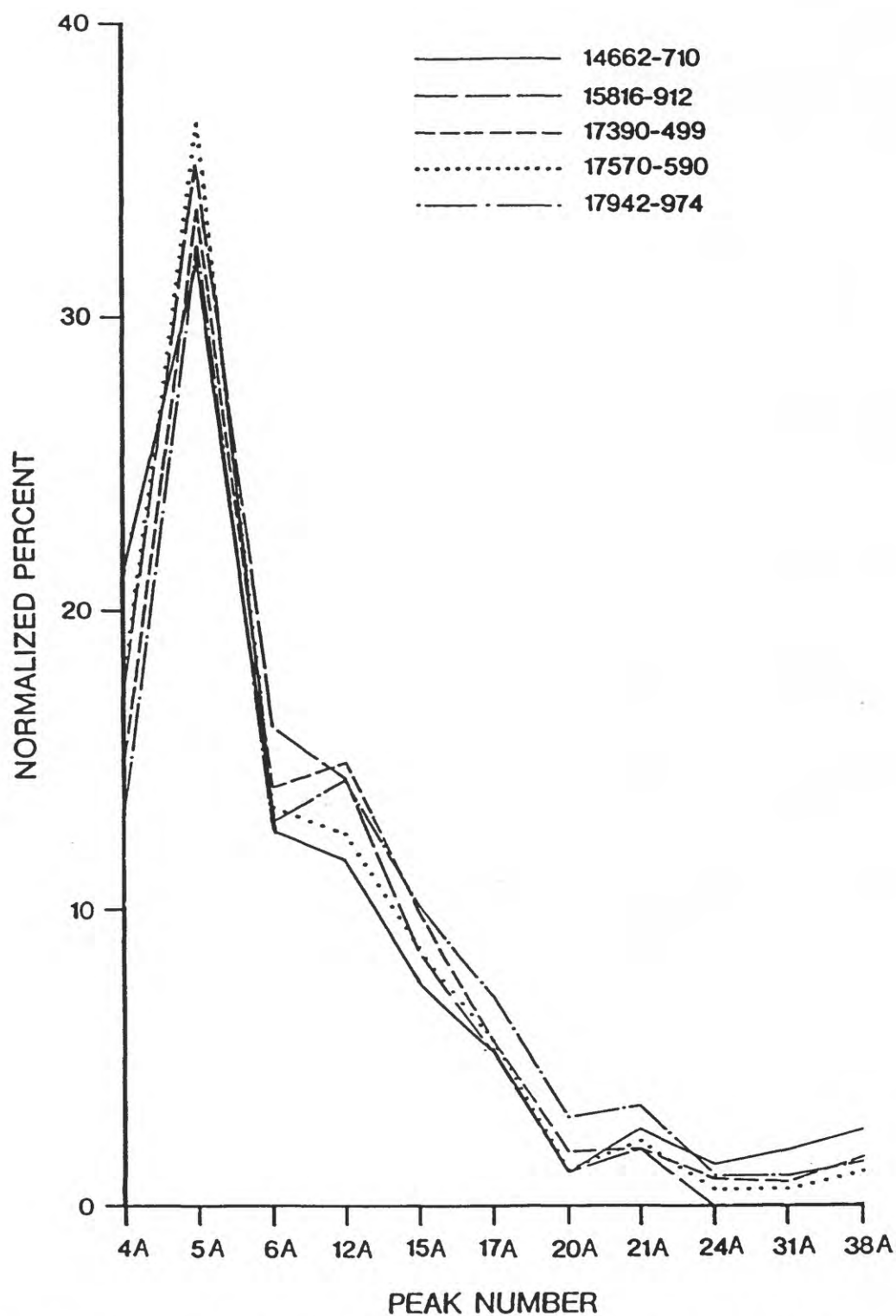


Figure 36. Normalized-percentage, compound-distribution plots for aromatic HC's (peaks 4A-6A, 12A, 15A, 17A, 20A, 21A, 24A, 31A, and 38A from Fig. 27) for 5 Caillou Island oils.



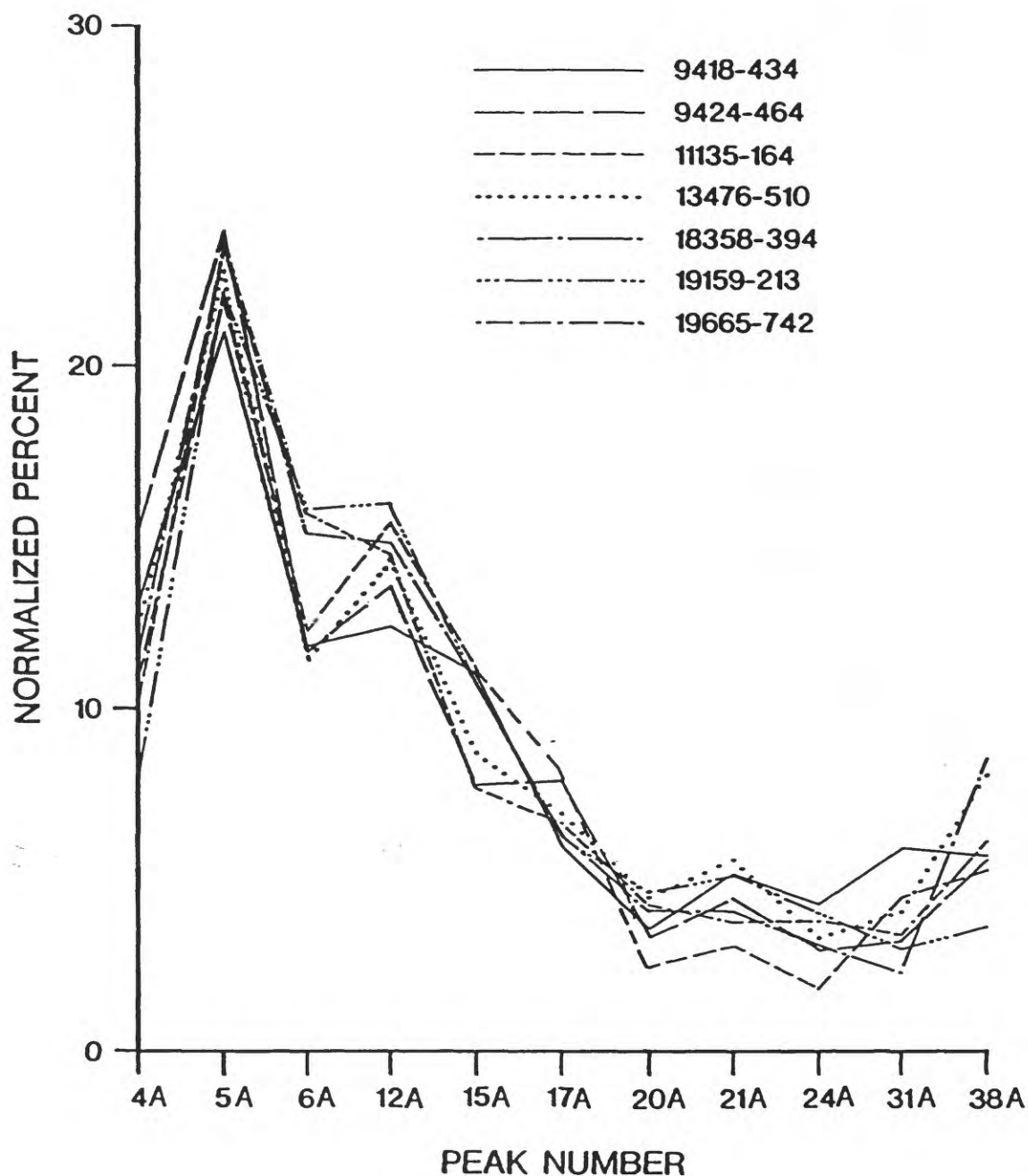


Figure 37. Normalized-percentage, compound-distribution plots for aromatic HC's (peaks 4A-6A, 12A, 15A, 17A, 20A, 21A, 24A, 31A, and 38A from Fig. 27) for 7 Caillou Island oils.



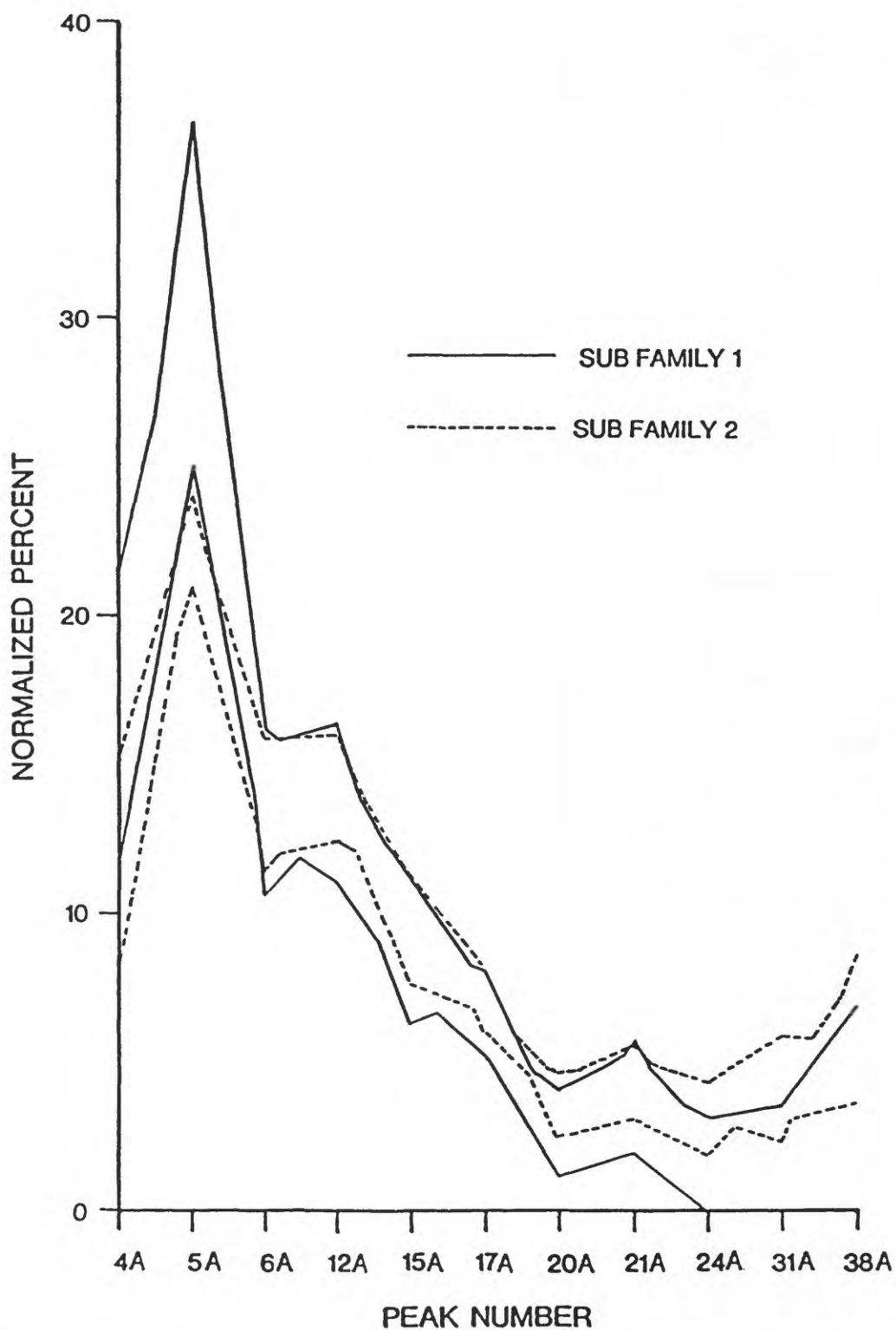


Figure 38. Area overlays of the normalized-percentage, compound-distribution plots for the aromatic HC's (peaks 4A-6A, 12A, 15A, 17A, 20A, 21A, 31A and 38A from Fig. 27) of the Caillou Island oil subfamilies. Subfamily one is from figures 36 and 37; and subfamily two is from figure 38.



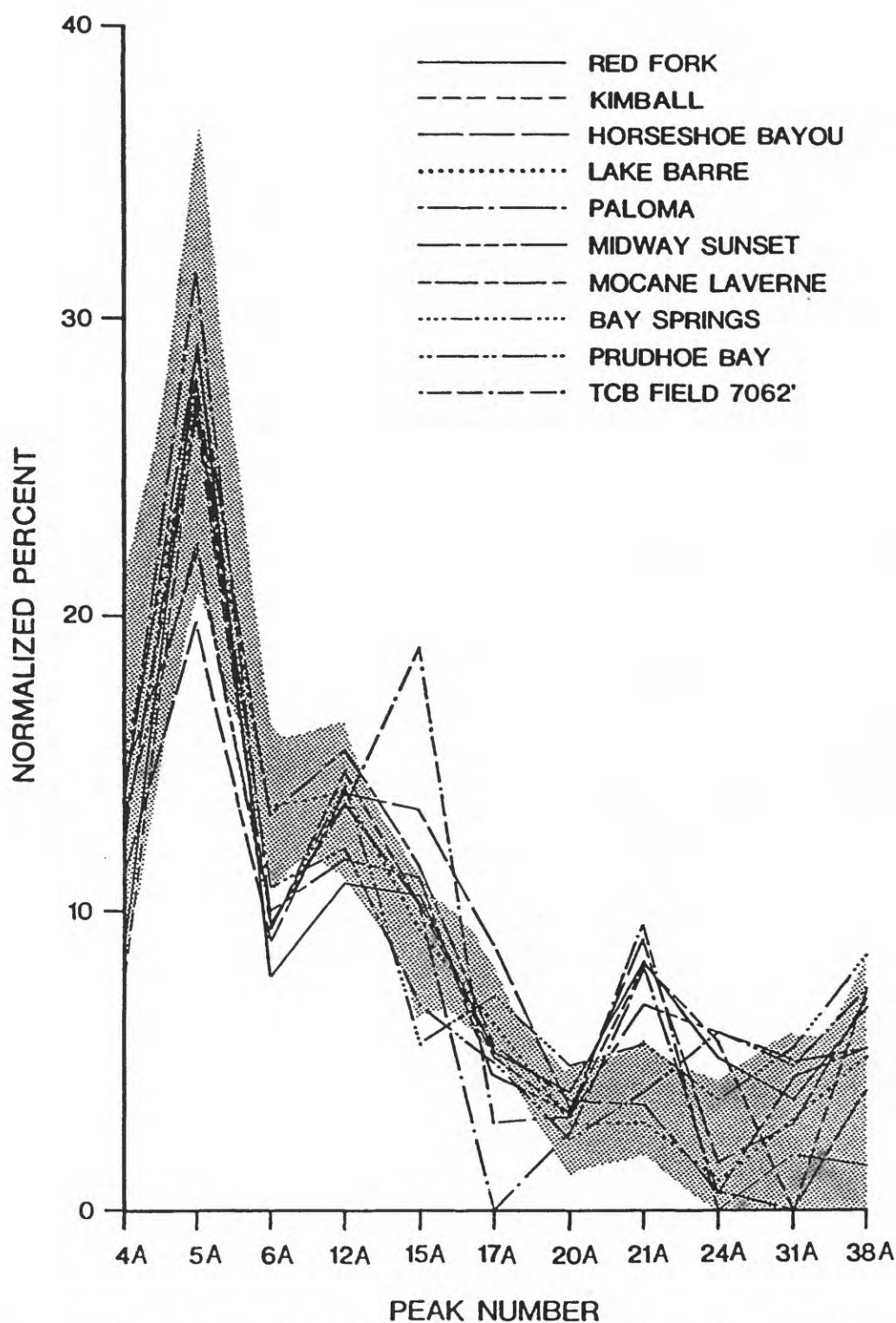


Figure 39. Normalized-percentage, compound-distribution plots for aromatic HC's (peaks 4A-6A, 12A, 15A, 17A, 20A, 21A, 24A, 31A, and 38A from Fig. 27) for the ten random oils geographically separated from Caillou Island. The area overlay for these same plots for the Caillou Island oil family (Figs. 35-38) is shown by the stippled pattern.



# NORMALIZED PERCENTAGE

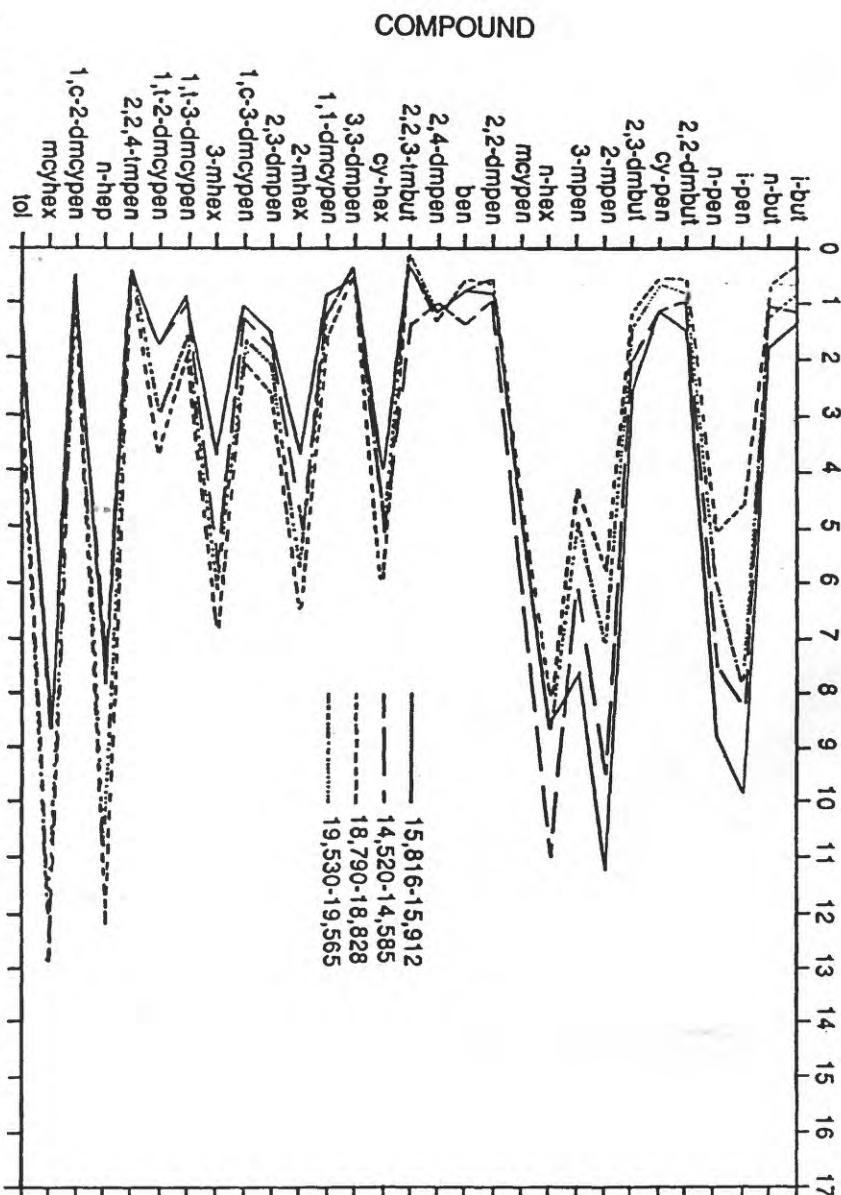


Figure 40.

Normalized-percentage, compound-distribution plots for  $C_4$ - $C_7$  HC's for 4 Caillou Island oils. Compound labeling is as follows: i-but is iso-butane; n-but is normal-butane; i-pen is iso-pentane; n-pen is normal-pentane; 2,2-dimbut is 2,2-dimethylbutane; cy-pen is cyclo-pentane; 2,3-dimbut is 2,3-dimethylbutane; 2-mpen is 2-methylpentane; 3-mpen is 3-methylpentane; n-hex is normal-hexane; mcypen is methylcyclopentane; 2,2-dimpen is 2,2-dimethylpentane; ben is benzene; 2,4-dimpen is 2,4-dimethylpentane; 2,2,3-imbut is 2,2,3-trimethylbutane; cy-hex is cyclo-hexane; 3,3-dimpen is 3,3-dimethylpentane; 1,1-dimcypen is 1,1-dimethylcyclopentane; 2-mhex is 2-methylhexane; 2,3-dimpen is 2,3-dimethylpentane; 1,c-3-dimcypen is 1,cis-3-dimethylcyclopentane; 3-mhex is 3-methylhexane; 1,1,3-dimcypen is 1,trans-3-dimethylcyclopentane; 1,1,2-dimcypen is 1,trans-2-dimethylcyclopentane; 2,2,4-impen is 2,2,4-trimethylpentane; n-hep is normal-heptane; 1,c-2-dimcypen is 1,cis-2-dimethylcyclopentane; mcylhex is methylcyclohexane; and tol is toluene. Data from table 5.



similarity, these compounds are not as useful as other compounds for distinguishing between different oil families. Thus, certain generic HC's are more useful than others, with this oil-oil correlation technique.

#### GASOLINE-RANGE HC'S

Gasoline-range ( $C_4$ - $C_7$ ) HC analyses were also carried out on the 23 Caillou Island oils (Table 5) and on 11 geographically-removed oils (Tables 6 and 7) genetically unrelated to the Caillou Island oils. Normalized-percentage, compound-distribution plots for the 29  $C_4$ - $C_7$  HC's analyzed for the 23 Caillou Island oils are shown in figures 40 to 45. For the benefit of the viewer, only 4 oils were put on each plot. The area overlay for the  $C_4$ - $C_7$  HC normalized-percentage, compound-distribution plots for the Caillou Island oil family is given in figure 46, and figure 47 shows the area overlay for the  $C_4$ - $C_7$  HC distribution plots of the Caillou Island oil family superimposed on  $C_4$ - $C_7$  HC distribution plots for three oils from the Mississippi salt basin. The plots for the oils from the Mississippi salt basin exhibit similarity to each other and lay outside of the area overlay for the Caillou Island oil family. Figure 48 gives  $C_4$ - $C_7$  HC distribution plots for three oils from the Anadarko basin with the area overlay for the  $C_4$ - $C_7$  HC distribution plots of the Caillou Island oil family (from Fig. 46). Two of the oils, Logan South and Grand Valley East, show some similarity to each other and are distinctly different than the third oil, Mocane-Laverne. These three oils all fall outside of the area overlay of the Caillou Island oil family. Figure 41 gives  $C_4$ - $C_7$  HC distribution plots for two Upper Texas Gulf Coast oils, and the area overlay for the  $C_4$ - $C_7$  HC distribution plot of the Caillou Island oil family (from Fig. 46). The two Upper Texas Gulf Coast oils appear unrelated to each other by this analysis, and the  $C_4$ - $C_7$  HC distribution plots for these two oils fall outside the area overlay of the Caillou Island oil family. Figure 50 gives a  $C_4$ - $C_7$  HC distribution plot for three oils from the Denver basin. The similarity of the three plots suggests that the oils are genetically related. Clayton and Swetland (1980) based on  $C_4$ - $C_7$  HC, and other, analyses had previously concluded that these, and other, oils in the Denver basin were genetically related. The plots for two of the oils fall outside the area overlay for the Caillou Island oils, but the plot for the third (Singletree field) falls within the Caillou Island overlay. However, the geographic separation between Caillou Island and this oil precludes a possible genetic relationship. This false genetic matchup again underscores the need for multiple analyses in any attempted oil-oil correlation.

Figure 51 gives a ternary plot of n-paraffins, iso-paraffins, and cyclic HC's (aromatic HC's and cyclo-paraffins) for the  $C_4$ - $C_7$  HC's of the 23 Caillou Island oils and for the 11 geographically-removed, random oils. The Caillou Island oils plot in a fairly limited area in the middle of the figure. The two Upper Texas Gulf Coast oils are very close to, or are within, the area occupied by the Caillou Island oils, which again points out the need for multiple analyses with any attempted oil-oil correlation study. The three oils from the Mississippi salt basin lie close together in figure 51 which suggests that these three oils may be genetically related. The same is true for the three oils from the Denver basin. However, by figure 51, the three oils from the Anadarko basin do not appear related to each other, nor do the two oils from the Upper Texas Gulf Coast.

Twelve compounds were arbitrarily chosen from the  $C_4$ - $C_7$  HC analyses of the Caillou Island oils and various summations and ratios were calculated (Table 8A)



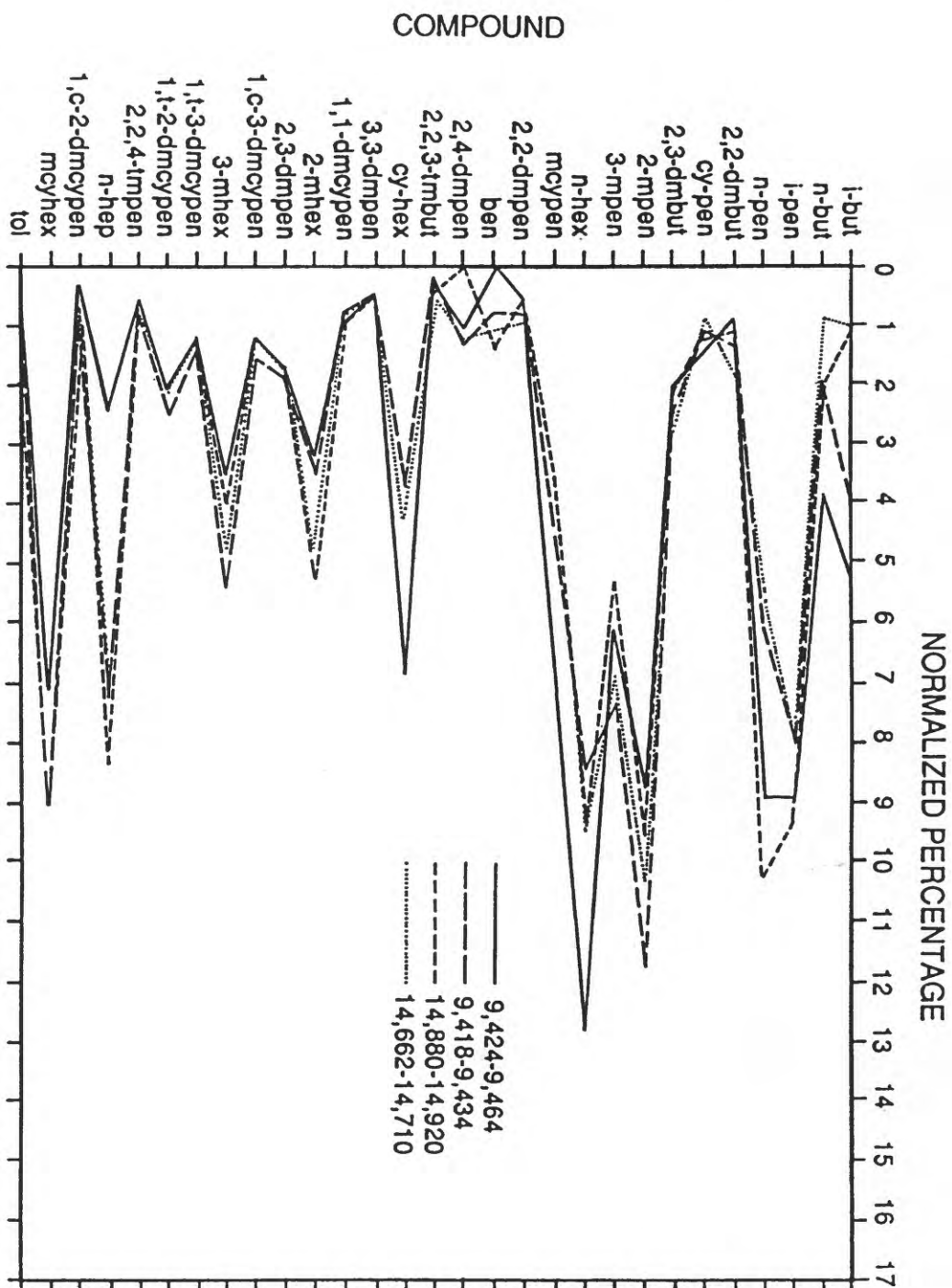


Figure 41. Normalized-percentage, compound-distribution plots of C<sub>4</sub>-C<sub>7</sub> HC's for 4 Caillou Island oils. Compound labeling as in figure 40 caption. Data from Table 5.



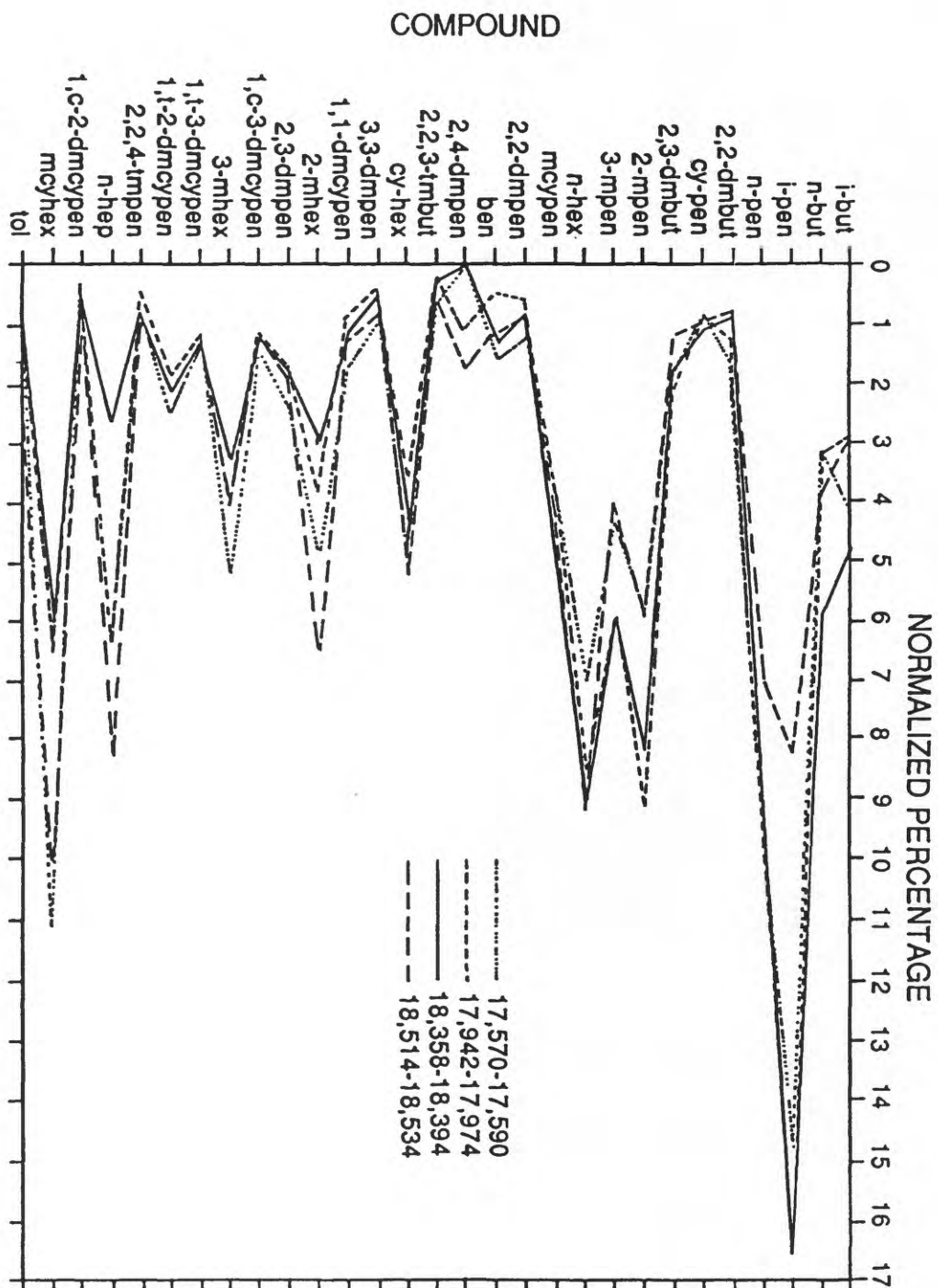


Figure 42. Normalized-percentage, compound-distribution plots of C<sub>4</sub>-C<sub>7</sub> HC's for 4 Caillou Island oils. Compound labeling as in figure 40 caption. Data from Table 5.



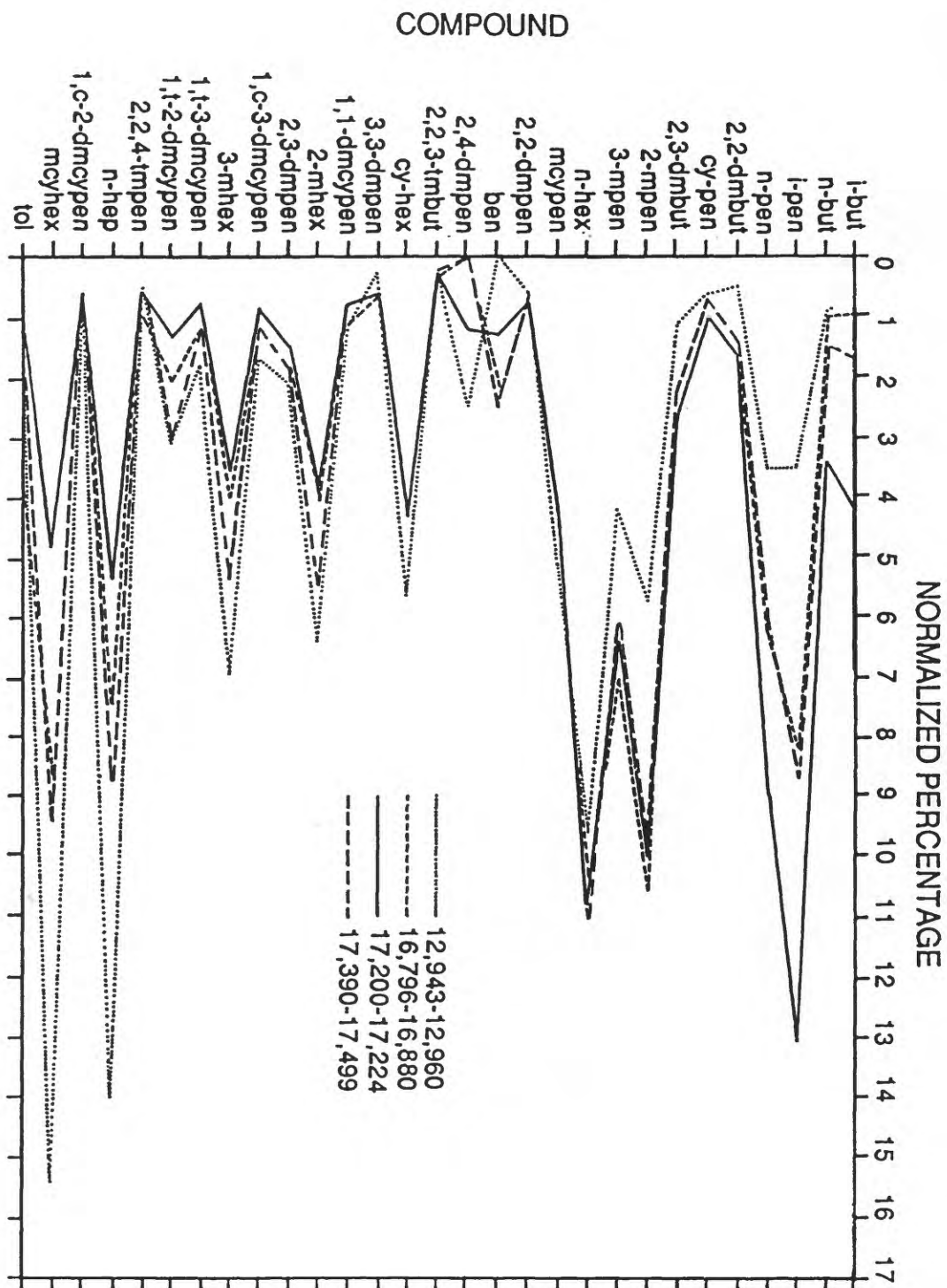


Figure 43.

Normalized-percentage, compound-distribution plots of C<sub>4</sub>-C<sub>7</sub> HC's for 4 Caillou Island oils. Compound labeling as in figure 40 caption. Data from Table 5.



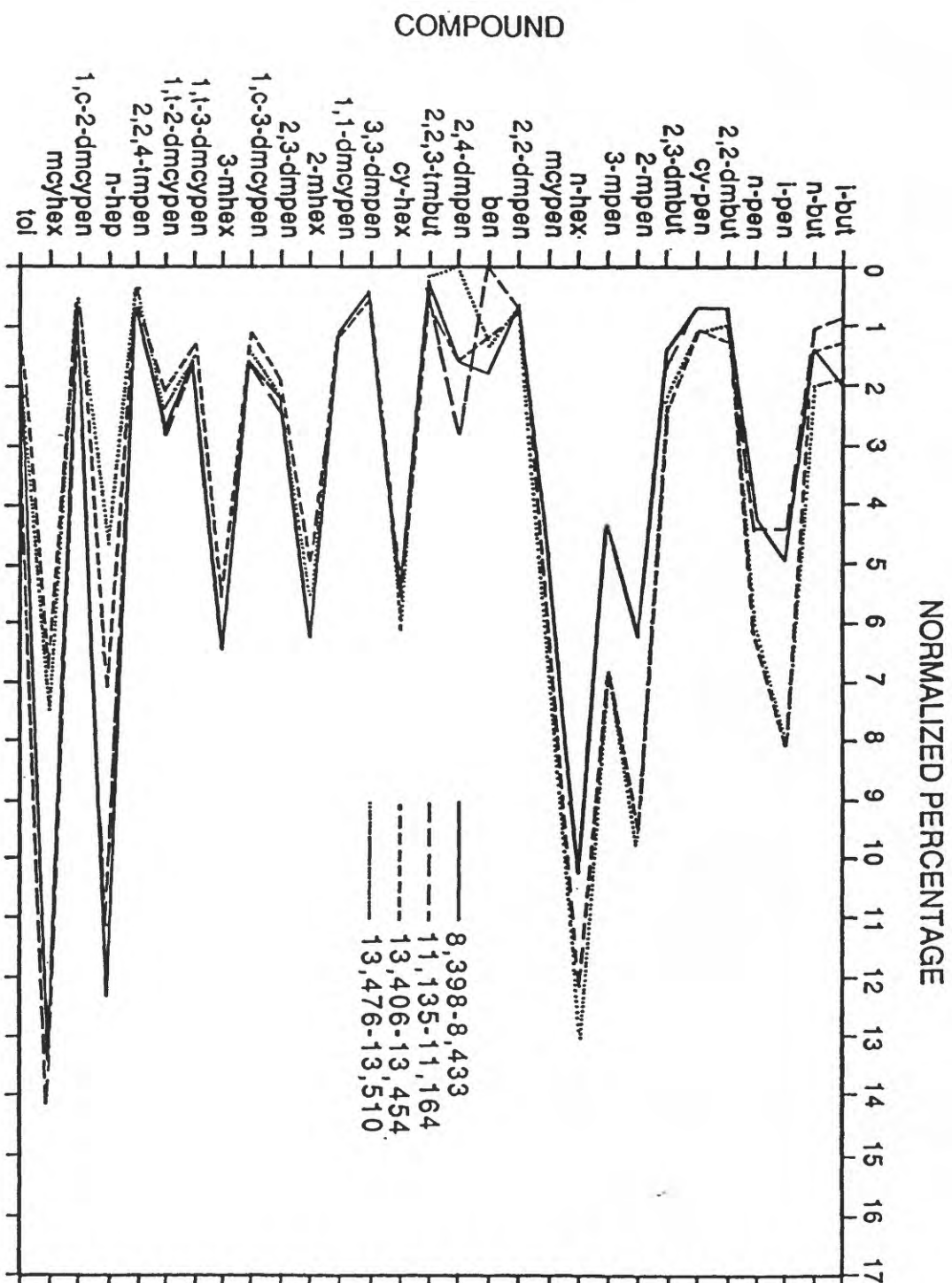
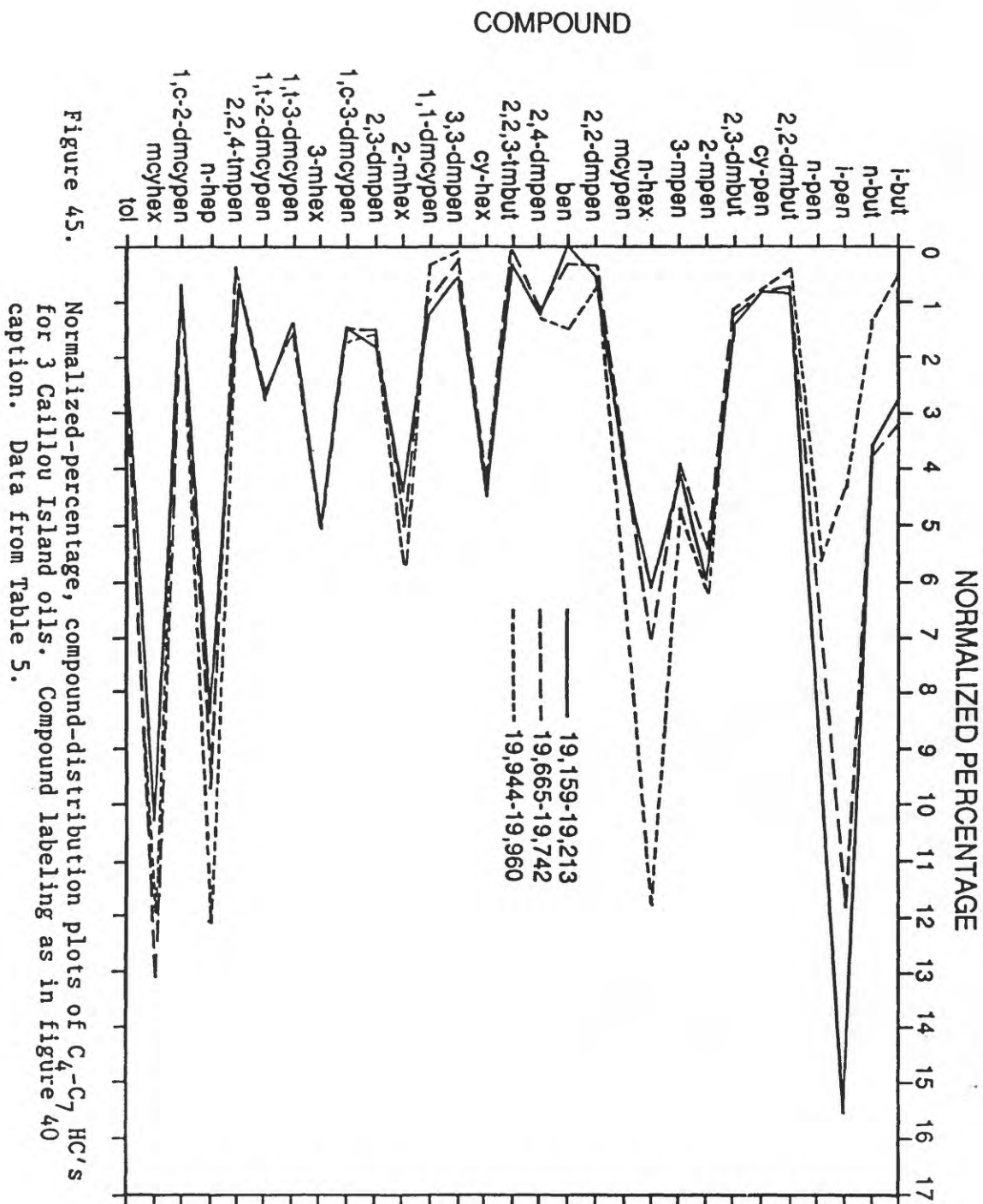


Figure 44.

Normalized-percentage, compound-distribution plots of C<sub>4</sub>-C<sub>7</sub> HC's for 4 Caillou Island oils. Compound labeling as in figure 40 caption. Data from Table 5.







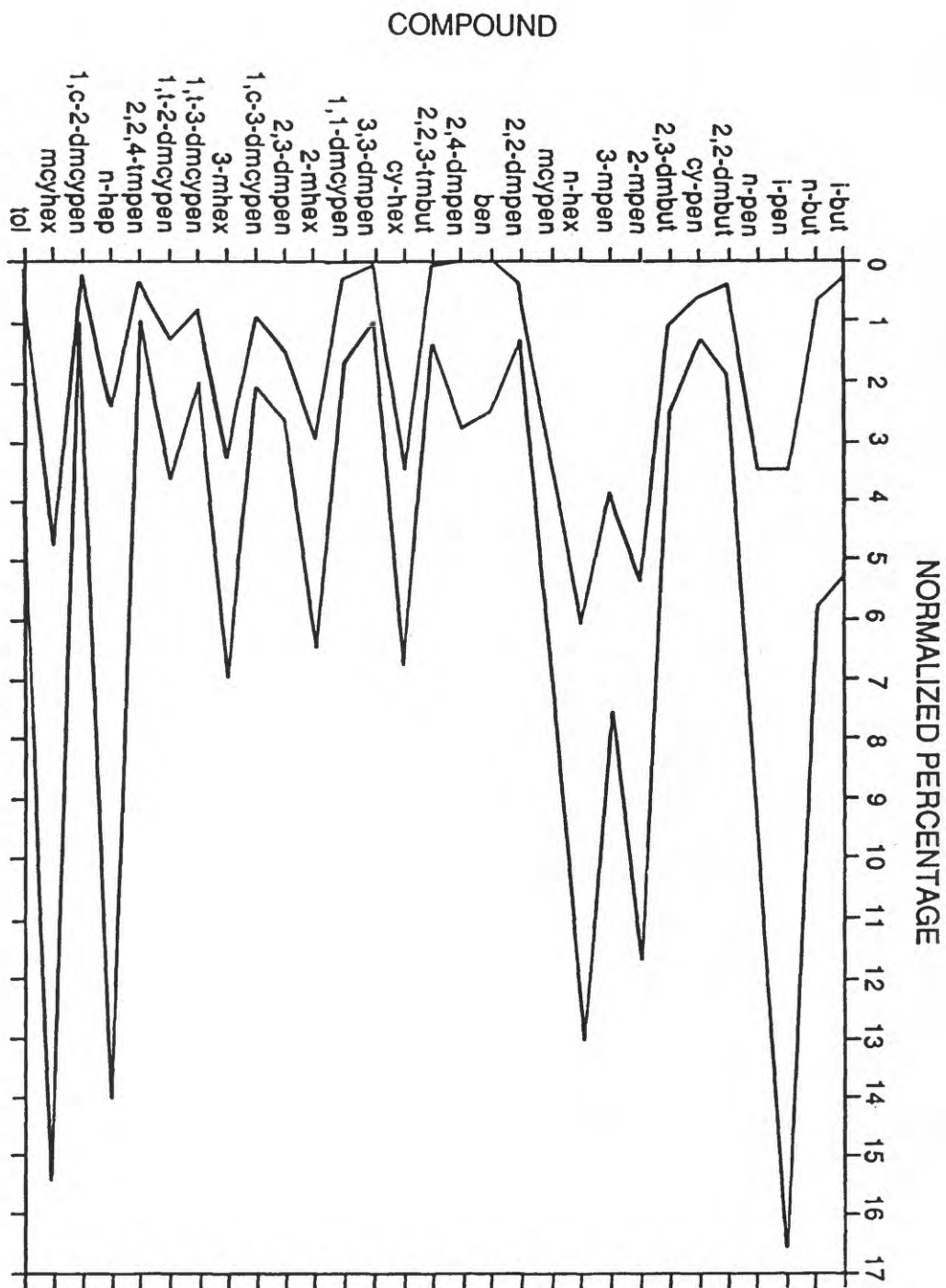


Figure 46. Area overlay of the normalized-percentage, compound-distribution plots for the C<sub>4</sub>-C<sub>7</sub> HC's of the Caillou Island oil family from figures 40 to 46.



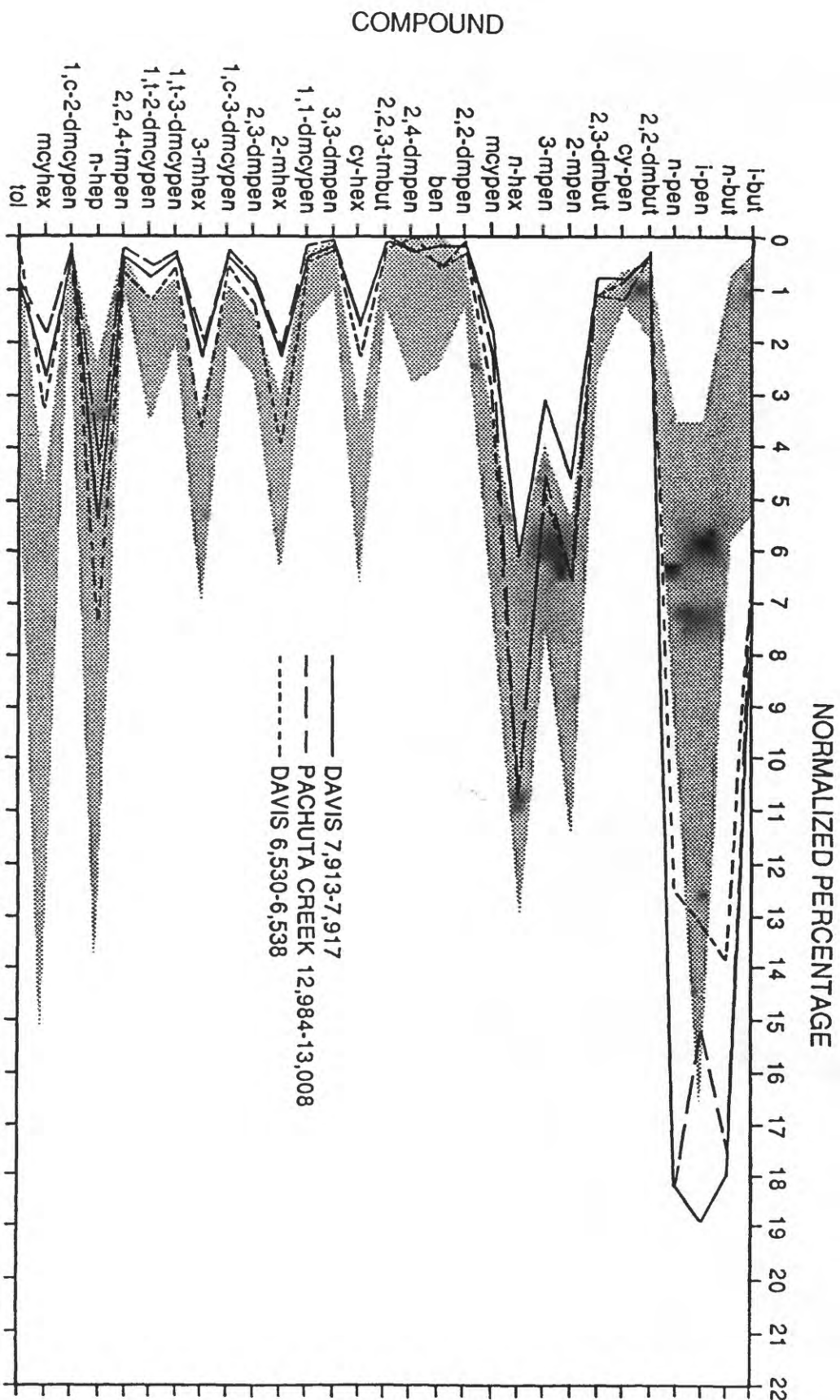
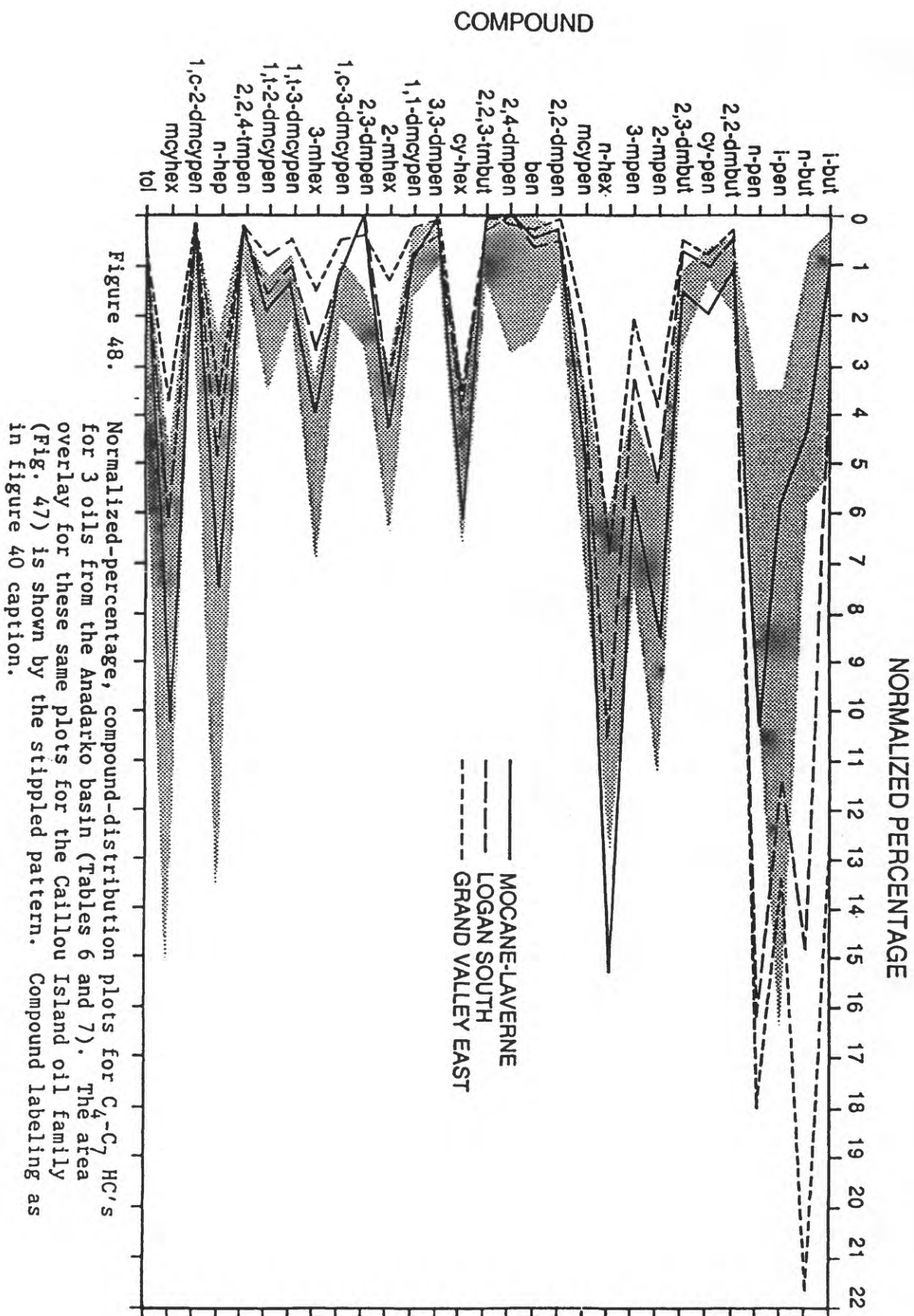


Figure 47.

Normalized-percentage, compound-distribution plots for  $C_4$ - $C_7$  HC's for 3 oils from the Mississippi salt basin (Tables 6 and 7). The area overlay for these same plots for the Caillou Island oil family (Fig. 47) is shown by the stippled pattern. Compound labeling as in figure 40 caption.







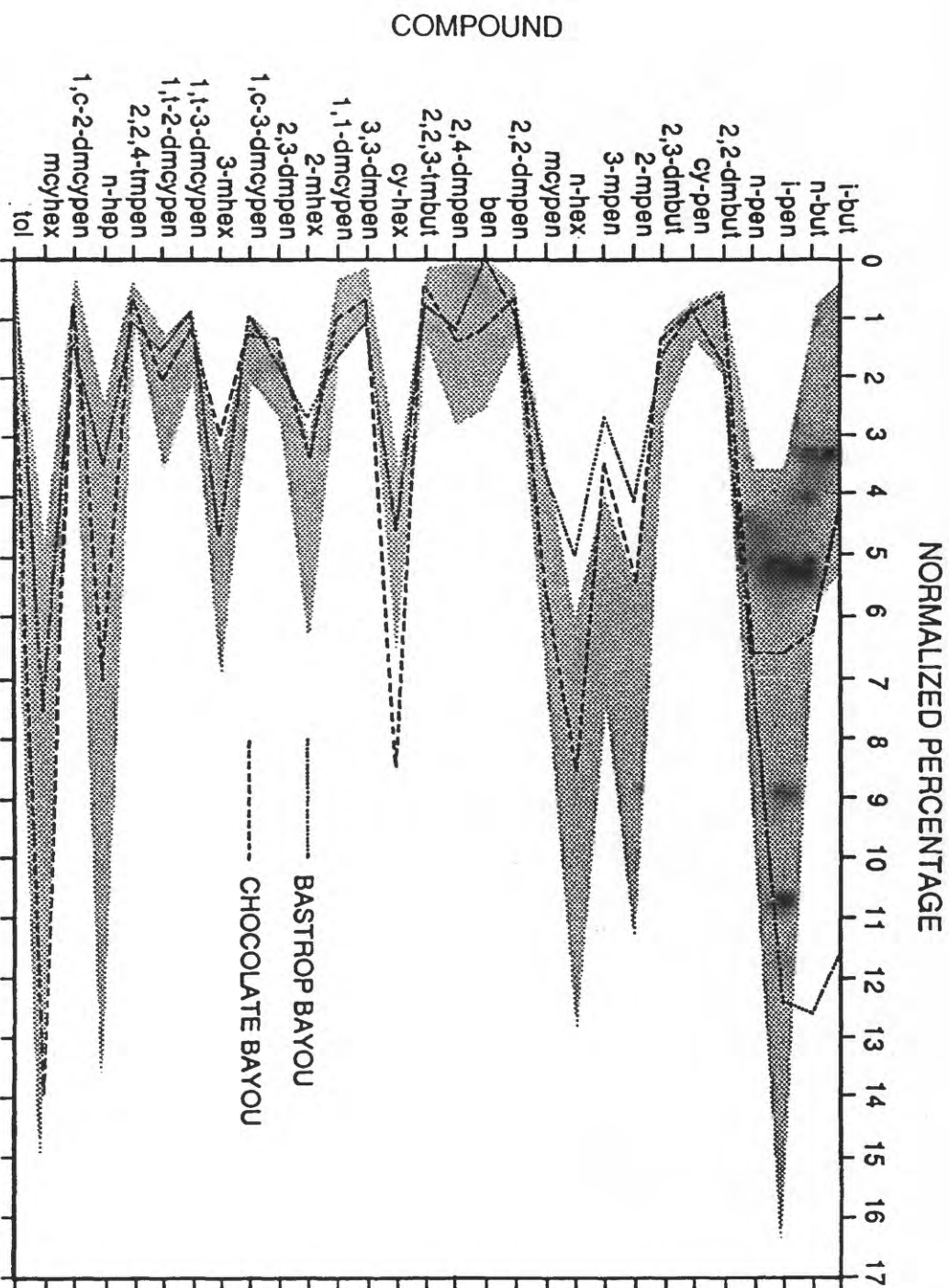


Figure 49. Normalized-percentage, compound-distribution plots for  $C_4$ - $C_7$  HC's for 2 oils from the Upper Texas Gulf Coast (Tables 6 and 7). The area overlay for these same plots for the Caillou Island oil family (Fig. 47) is shown by the stippled pattern. Compound labeling as in figure 40 caption.



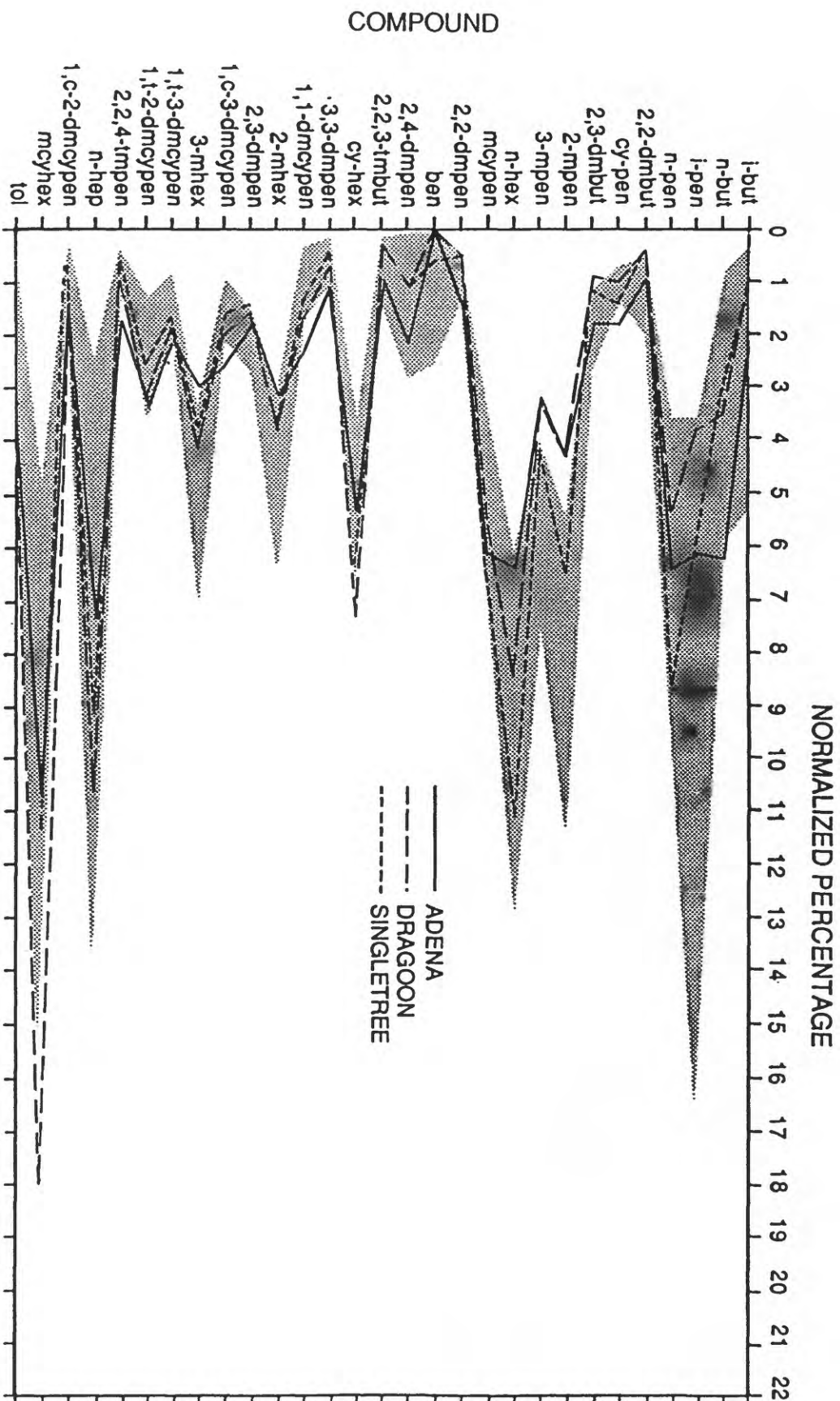


Figure 50.

Normalized-percentage, compound-distribution plots for  $C_4$ - $C_7$  HC's for 3 oils from the Denver basin (Tables 6 and 7). The area overlay for these same plots for the Caillou Island oil family (Fig. 47) is shown by the stippled pattern. Compound labeling as in figure 40 caption.



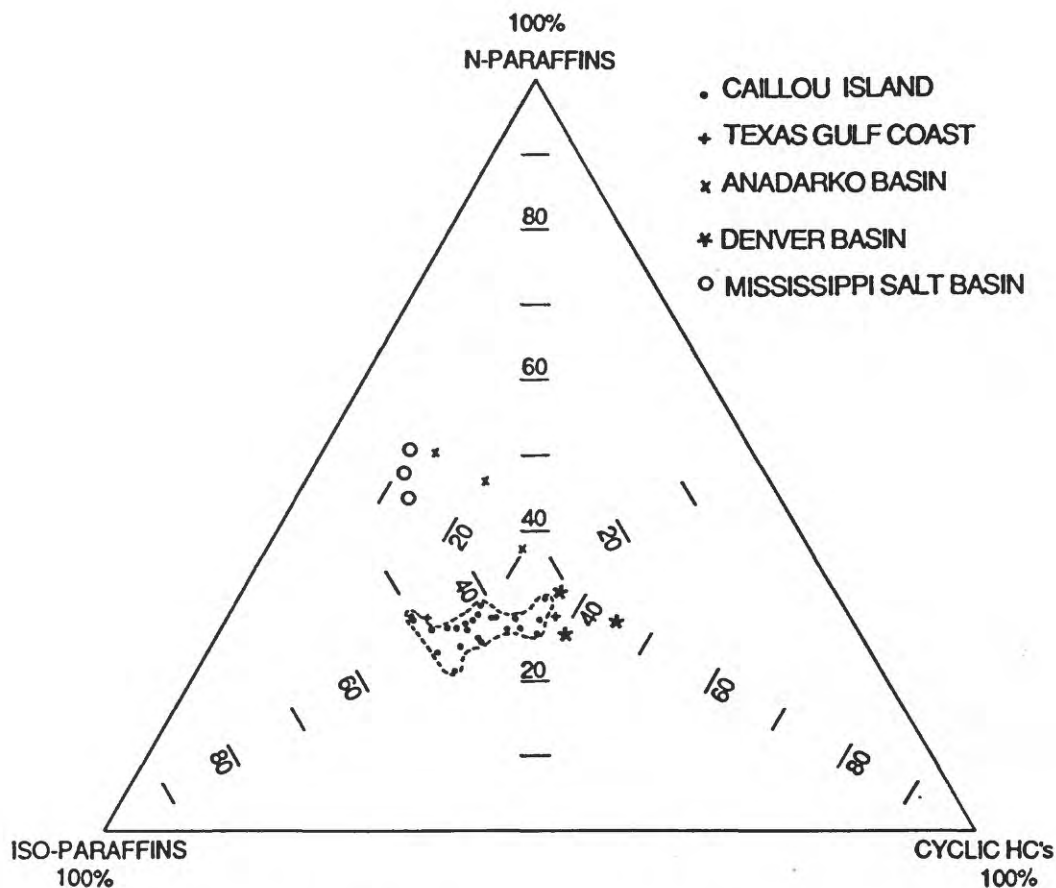


Figure 51. Ternary plot showing percentages of n-paraffins, iso-paraffins, and cyclic HC's (cyclo-paraffins plus aromatic HC's) for the Caillou Island oil family (outlined by dashed line) and for 11 random oils geographically separated from Caillou Island (Tables 5, 6, and 7).



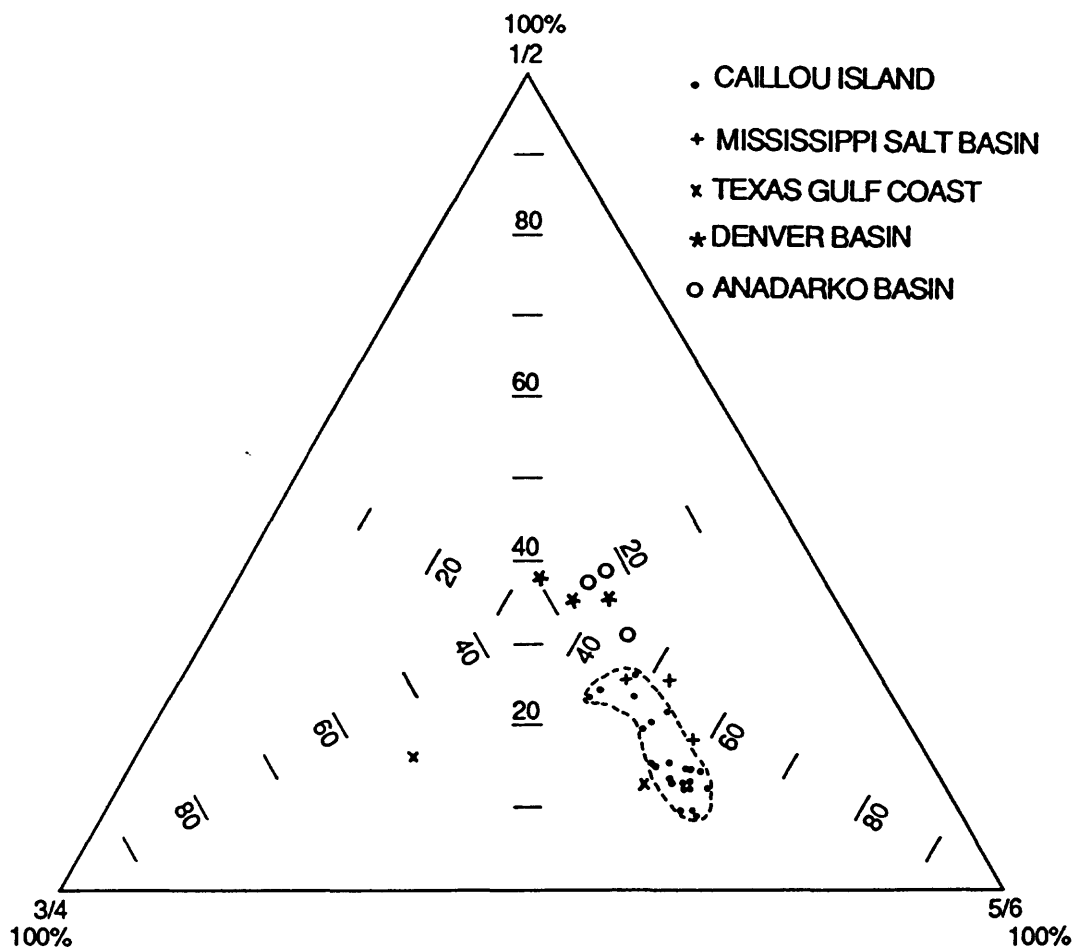


Figure 52. Ternary plot for the ratios of Table 8 for the Caillou Island oil family (outlined by dashed line) and for 11 random oils geographically separated from Caillou Island (Tables 5, 6, and 7).



from the normalized percentages of these compounds (Tables 5 and 7). The numbers from the resulting ratios (1/2, 3/4, 5/6) were summed and normalized with respect to each other (in percent) and plotted (Fig. 52). The same exercise was carried out for the 11 geographically-separated, random oils, the results of which are also plotted in Figure 52. The 23 Caillou Island oils fall in a tight cluster in figure 52, and 10 of the geographically-removed oils fall outside the area of this cluster. One oil from the Mississippi salt basin (Davis field, 2,412-2,413 m, 7,913-7,917 ft) fell within the area occupied by the Caillou Island oils. However, because of geographic separation, this oil is obviously not genetically related to the Caillou Island oil family.

Table 8A

Summations and ratios from C<sub>4</sub>-C<sub>7</sub> HC analysis used to construct figure 53.

1,1-dimethylcyclopentane + 3-methylhexane	1
-----	= -
2-methylhexane + 2,3-dimethylpentane	2
 Cyclopentane + 2,3-dimethylbutane	 3
-----	= -
Methylcyclopentane + 2,2-dimethylpentane	4
 1,trans-3-dimethylcyclopentane + 1,trans-2-dimethylcyclopentane	 5
-----	= -
1,cis-3-dimethylcyclopentane + 1,cis-2-dimethylcyclopentane	6

The data from the gasoline-range HC analyses both confirmed the genetic relationship between the Caillou Island oils and differentiated the geographically-removed oils from the Caillou Island oil family. Furthermore, these data suggested possible genetic relationships between some of the oils geographically removed from Caillou Island. These are not surprising results, as gasoline-range HC analysis has long been established as an effective tool in oil-oil correlation studies. However, like all oil-oil correlation tools, the data from gasoline-range HC analyses must be processed in different ways to avoid the pitfall of false correlations. The results from the gasoline-range HC analyses support the previous conclusion that the Caillou Island oils belong to one genetically-related family, and thus also support the proposal that normalized-percentage, compound-distribution plots, using only the ordinary or "generic" HC's of oil, can be used to establish genetic relationships among oils. This conclusion is further strengthened by the fact that the C<sub>4</sub>-C<sub>7</sub> HC's are "generic" HC's themselves.

In spite of their usefulness as a correlation tool, the compound-distribution plots of the C<sub>4</sub>-C<sub>7</sub> HC's for the Caillou Island oils and for the 11 random oils were, overall, quite similar (Figs. 40-50). All the oils had relatively large concentrations of 2-, and 3-methylpentane; n-hexane; cyclohexane; 2-, and 3-methylhexane; n-heptane; and methylcyclohexane. The amounts of iso-, and n-butane, and iso-, and n-pentane, the lightest C<sub>4</sub>-C<sub>7</sub> HC's, varied but could be quite large. The above compounds: 1) make up a large part of the C<sub>4</sub>-C<sub>7</sub> HC's, 2) largely dictate the shape of the plots in figures 40 to 50 and 3) do not appear to be as discriminatory as other C<sub>4</sub>-C<sub>7</sub> HC's, regarding



delineation of oils into genetically-related families. Furthermore, the  $C_4-C_7$  HC distribution plots for these oils would have even been more similar if the n- and iso-butan-2-yl and pentanes had not been considered in the calculations. These compounds, which are subject to the greatest degree of loss in the  $C_4-C_7$  HC's from post-accumulation processes, sampling errors, and storage problems, introduce the greatest possible degree of error for  $C_4-C_7$  HC analysis. Perhaps focusing on the gasoline-range HC's which are found in oils in lower concentrations, compared to the above-listed HC's, would prove more discriminatory for oil-oil correlation.

The  $C_4-C_7$  HC's listed directly above and certain generic, saturated and aromatic  $C_8+$  HC's appear to consistently occur in different oils in high concentrations. Studies focusing on these  $C_4+$  generic HC's found in high concentrations in oils may offer insights into different processes of oil generation such as the maturation rank(s) at which particular oils originate, kinetic processes in organic metamorphism, migration, fractionation processes, and so on.

## DISCUSSION

### Introduction

The results of this study relate to two principal topics: 1) the utility and advantages of oil characterization by generic HC's, and 2) the implications of a single-family oil characterization of the Caillou Island oils as applied to oil origin, migration, and accumulation at Caillou Island.

### Crude Oil Typing

Many previous studies have carried out oil-oil correlations to classify oils into genetically-related families. The basic premise of most, or all, of these past studies has been that oils which exhibit exact, or very similar, chemical or physical characteristics, whether on a very gross or specific level, are genetically related. Such oils are assumed to have been derived from the same source rock, or sequence of source rocks, to have undergone a similar migration history, and to have been subjected to the same (or a lack of) post-accumulation processes which have altered their physical or chemical characteristics. Conversely, oils which do not have similar characteristics are assumed not to be genetically related and, therefore, not to have had a common history. Many different chemical and physical parameters have been used in past oil-correlation studies, and generally, in these past studies, the sophistication of the method increases as the present time is approached.

An early oil-oil correlation study by Jones and Smith (1965) used the similarities of oil distillation curves (U.S. Bureau of Mines method) to group oils from the Permian basin, west Texas and New Mexico. Koons and others (1974) studied the oils of the lower Cretaceous Tuscaloosa sandstones using paraffin content of the saturated HC's, carbon isotope values of the saturated HC's, sterane distributions, and  $C_4-C_7$  HC analyses. Williams (1974) characterized oils in the Williston basin using carbon isotope ratios, n-paraffin distributions, and optical rotation measurements. Clayton and Swetland (1980) used gas chromatograms of  $C_{15+}$  saturated HC's,  $C_{15}-C_{20}$  isoprenoid distribution plots,  $C_4-C_7$  HC analysis, and carbon and sulfur isotopic ratios to identify oil families, and their potential source rocks, in the Denver basin. Sulfur isotope



ratios have been used by Thode (1981) for oil-oil correlations. Saturated and aromatic HC biomarkers have been used for oil-oil correlations by a great number of different investigators including Tissot and others (1974), Deroo (1976), Claret and others (1977), Rullkötter and Welte (1980), and Welte and others (1982).

A discussion of the relative merit of the various correlation parameters used by different investigators is outside the scope of this work. Most probably isocyclic-biomarker analysis is the most powerful tool available to petroleum organic geochemistry for the correlation and study of oils. This analytical technique offers information on oil maturation rank, the depositional environment of the source rock (and, therefore, OM type in the source rock), and strong correlation abilities. The correlation technique used in this study cannot yield the degree of information which is available from biomarker analysis. However, this present analytical technique does appear to augment biomarker analysis, and it does offer distinct advantages over some other correlation tools, and even has some advantages over biomarker analysis.

The analytical steps for the oil-oil characterization technique of this study are: whole-oil separation chromatography, molecular sieving the n-paraffins from the saturated HC fraction, and computerized gas chromatography. For petroleum organic geochemistry, these are relatively inexpensive and simple analytical methods which do not require a high front end laboratory investment or highly specialized laboratory technicians, especially compared to iso-cyclic biomarker analysis. Discounting the n-paraffins, this analytical technique examines the most abundant compounds of oil in all the different molecular-weight ranges. Thus, a broad-based sampling and characterization of the oil is achieved, compared to some other correlation tools, and especially compared to iso-cyclic biomarkers which are present in oils in much smaller concentrations than the compounds examined in this study. Thus, correlation problems can be avoided which may arise from comingling of small amounts of unrelated oils during secondary migration, or from "leaching" of biomarkers from capping shales or from other rocks along the migration path of an oil.

Some of the aromatic HC's examined in this study have been used by other investigators as oil and/or source-rock maturity indicators (Radke and others, 1982a and b; Radke and Welte, 1983; Radke and others, 1984; Alexander and others, 1985; Alexander and others, 1986; Radke and others, 1986; and Kvalhiem and others, 1987). Furthermore, the possibility has been raised that the concentration distributions of some of these compounds are also influenced or controlled to some extent by source facies (Radke and others, 1984; and Radke and others, 1986). Thus, the possibility arises that such generic HC's might eventually have some use as source-facies, and maturity indicators. As discussed above, examination of the concentration distributions of some generic HC's may offer a tool with which to study the kinetics of HC generation, and perhaps, lead to a better understanding of oil origin and primary migration. Lastly, the examination of high-molecular weight "generic", aromatic HC's may offer a correlation tool for: 1) oils which have been badly degraded by water washing and/or bacterial attack, 2) possibly for tar deposits or heavy oil seeps, or 3) possibly for degraded oil on the ocean's surface, to determine the source of the pollution.



## Origin-Caillou Island Oils

Almost all investigators would no doubt agree that, in spite of the widely differing physical characteristics of the Caillou Island oils, the compound distributions in these (and most likely the Lake Barre and possibly other neighboring) oils dictate that they belong to one genetic family and, therefore, have undergone similar (or the same) histories of origin, migration, and accumulation. However, opinions as to what exactly those histories were and how the data of this study could be used to support different interpretations regarding origin, migration, and accumulation of these oils, would vary widely. This variance of interpretation largely would result from our basic lack of understanding of the processes which control oil origin, migration, and accumulation. The origin of Gulf Coast oils, in spite of a massive published and unpublished research effort, is an enigma that has gone unresolved. I have a preferred interpretation for the origin of oil at Caillou Island, however, reasonable discussion of this preferred interpretation would incorporate much more data and impossibly lengthen this paper. Therefore, a discussion of origin of oil at Caillou Island will be deferred to a future publication.

### SUMMARY AND CONCLUSIONS

1)  $C_{12}$ - $C_{21}$  isoprenoid HC distribution plots for 23 oils from the Caillou Island, and for one oil from the Lake Barre, oil fields, Louisiana were very similar to each other and distinctly different from the same plots for 9 other oils geographically removed from Caillou Island. As the isoprenoid HC's are biomarker-classed compounds, the similarity of the compound-distribution plots suggested that the Caillou Island oils, most probably the Lake Barre oils, and possibly oils from other neighboring fields, were all of the same oil family and genetically related.

2) Normalized-percentage, compound-distribution plots for generic  $n$ - $C_8$  to  $n$ - $C_{12}$  range iso-cyclic and  $n$ - $C_8$  to  $n$ - $C_{21}$  range aromatic HC's, which apparently are found in abundance in most or all oils, gave the same results as the plots for the  $C_{12}$ - $C_{21}$  isoprenoid HC's. As with the isoprenoid HC's, the plots of these generic HC's for the Caillou Island and Lake Barre oils were very similar and parallel to each other, whereas the nine oils geographically removed from Caillou Island gave differing, non-parallel plots.

3) In normalized-percentage, compound-distribution analysis, increasing the the carbon-number range of the compound set examined increases the degree of scatter in the plots for a genetically-related oil set, and decreases the degree of resolution of the method. Carbon-number ranges of 1 to 2 are optimum, and carbon-number ranges above four should be avoided. This effect is possibly due to increasing percentages of lighter HC's being generated from the same source rock, or sequence of source rocks, with increasing maturation rank. Such a generation scenario would result in varying percentages of different carbon-numbers in a given family of oils, dependent on the generation stage of the oil under consideration. It is also likely that migration or post-accumulation processes are also controlling parameters.

4) Gasoline-range ( $C_4$ - $C_7$ ) HC analysis is an established oil-correlation technique.  $C_4$ - $C_7$  HC analysis of the 23 Caillou Island oils and of 11 geographically-separated oils confirmed that the Caillou Island oils were genetically related and of one family, and at the same time were compositionally



distinct from the 11 geographically-separated oils. Furthermore, these analyses suggested possible genetic relations among some of these 11 oils.

5) These  $C_4$ - $C_7$  HC analysis support the conclusion that generic  $C_8+$  iso-cyclic saturated and aromatic HC's can be used in oil-oil correlations, a conclusion further supported by the fact that the  $C_4$ - $C_7$  HC's are generic HC's themselves.

6) As with all oil-correlation techniques, erroneous or false matches can occur with both gasoline-range and normalized-percentage, compound-distribution HC analyses if only one analysis is carried out, or if the data are examined in only a single manner. Therefore, multiple analyses, and/or multiple methods of data processing, are necessary with these, and all, oil-correlation techniques.

7) Certain  $C_4+$  generic HC's appear to consistently occur in high concentrations in most or all "normal" oils. Therefore, study of the concentration distributions of these compounds may offer insights into the different processes which result in the origin, migration, and accumulation of commercial oil deposits.

8) Certain generic HC's in crude oils appear more useful than others for use in oil-oil correlation by normalized-percentage, compound-distribution analysis.

9) Oil correlation by compound-distribution analysis of  $C_8+$  generic HC's in oils offers distinct advantages to some other oil-correlation tools:

- A) For present-day petroleum organic geochemistry, the analytical methods of this technique are some of the simplest and most inexpensive in use. Highly trained specialists, and expensive, sophisticated analytical instruments are not required.
- B) Excluding the n-paraffins, this technique examines the most abundant HC's in oils over all molecular weight ranges and, therefore, achieves a broad-based sampling and characterization of an oil. Furthermore, correlation problems are avoided which may arise either from comingling of small amounts of unrelated oil or from a leaching of compounds from cap rocks or carrier beds during secondary migration.



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Table 1. Results of analyses of 23 Caillou Island oils. Ft is feet, m is meters, WT. %  $C_{15}^-$  HC's is weight percent  $C_{15}^-$  HC's in whole oil. WT. %  $C_{15}^+$  is weight percent  $C_{15}^+$  HC's, resins, and asphaltenes in whole oil. WT. %:  $C_{15}^+$  SAT. HC's,  $C_{15}^+$  ARO. HC's, Resins, and Asphaltenes are respectively weight percent saturated HC's, aromatic HC's, resins, and asphaltenes in the  $C_{15}^+$  fraction of the whole oil.  $C_{15}^+$  SAT fraction of HC's/ $C_{15}^+$  ARO HC's is the ratio of the  $C_{15}^+$  saturated to aromatic HC's.

Sample Depth		Oil Gravity			C <sub>15</sub> <sup>+</sup> Fraction					C <sub>15</sub> <sup>+</sup> SAT.HC's	
in	M	API in °	Specific in g/cc	WT. % C <sub>15</sub> <sup>-</sup>	WT. % C <sub>15</sub> <sup>+</sup>	WT. % C <sub>15</sub> <sup>+</sup> SAT. HC's	WT. % C <sub>15</sub> <sup>+</sup> ARO. HC's	WT. % Resins	WT. % Asphal-tenes	C <sub>15</sub> <sup>+</sup> ARO. HC's	
Ft	M										
8,398-8,438	2,560-2,572	34.7	0.851	88.21	11.79	67.97	24.70	2.90	4.42	2.75	
9,418-9,434	2,870-2,875	30.2	0.875	88.44	11.56	62.12	32.97	3.75	1.16	1.88	
9,424-9,464	2,872-2,884	27.6	0.889	82.45	17.55	58.12	34.95	4.87	2.03	1.66	
11,135-11,164	3,394-3,403	35.7	0.846	82.12	17.88	71.27	23.26	2.77	2.70	3.06	
12,943-12,960	3,945-3,950	34.7	0.851	82.24	17.76	58.66	35.18	4.72	1.44	1.66	
13,476-13,510	4,107-4,118	32.5	0.863	82.83	17.17	58.37	35.61	4.56	1.46	1.63	
13,406-13,454	4,086-4,101	33.8	0.856	88.18	11.82	62.10	31.66	5.34	0.90	1.96	
14,520-14,585	4,425-4,445	45.0	0.802	81.10	18.90	78.71	15.74	1.15	4.41	5.00	
14,662-14,710	4,469-4,483	45.9	0.798	87.47	12.53	72.34	23.38	2.13	2.15	3.09	
14,880-14,920	4,535-4,547	46.2	0.796	80.94	19.06	80.17	14.31	0.59	4.93	5.60	
15,816-15,912	4,820-4,850	52.8	0.768	87.11	12.89	79.57	17.57	0.56	1.38	4.52	
16,796-16,880	5,119-5,145	47.8	0.789	87.32	12.68	81.28	15.38	0.65	2.69	5.28	
17,200-17,224	5,242-5,250	45.7	0.798	80.79	19.21	80.57	14.83	0.72	3.88	5.43	
17,390-17,499	5,300-5,333	49.9	0.780	87.18	12.82	78.87	17.05	1.12	2.96	4.62	
17,570-17,590	5,355-5,361	49.5	0.782	81.57	18.43	79.12	17.70	1.01	2.17	4.47	
17,942-17,974	5,468-5,478	50.6	0.777	81.34	18.66	77.25	19.01	0.92	2.82	4.06	
18,358-18,394	5,595-5,606	48.4	0.786	87.23	12.77	74.91	21.15	0.95	2.99	3.54	
18,514-18,534	5,643-5,649	28.7	0.883	82.85	17.15	67.85	28.12	2.37	1.65	2.41	
18,790-18,828	5,727-5,738	51.9	0.772	85.31	14.69	77.76	19.03	1.00	2.31	4.08	
19,159-19,213	5,839-5,856	48.8	0.785	87.24	12.76	74.75	20.72	0.92	3.61	3.60	
19,530-19,565	5,952-5,963	46.8	0.794	80.34	19.66	71.27	24.38	1.82	2.53	2.92	
19,665-19,742	5,994-6,017	40.0	0.825	81.72	18.28	65.27	28.69	2.60	3.45	2.27	
19,944-19,960	6,079-6,084	34.5	0.852	82.30	17.70	61.24	33.45	3.69	1.62	1.83	



Table 2.--Information on 10 geographically-separated oils which were subjected to normalized-percentage, compound-distribution analysis in this study. NA means not available. Reservoir conditions are given as originally supplied in feet, degrees Fahrenheit, and pounds per square inch (psi), rather than in metric equivalents.

<u>Oil Field</u>	<u>Location/Well</u>	<u>API Gravity</u>	<u>Reservoir</u>	<u>Reservoir Conditions</u>
Prudhoe Bay	North Slope, Alaska	NA	NA	9,505-9,825'
Midway-Sunset	Kern County, California	18°	Pleistocene through Pliocene	~1,750'
Bay Springs	Jasper County, Mississippi, Sec. 27, 2N 10E, well-Shell J. W. Hall-1	47°	Upper Jurassic Cotton Valley Group	14,546-14,558', 262°F
Mocane-Laverne	Harper County, Oklahoma	45.6°	Upper Pennsylvanian Tonkawa Sandstone	5,553-5,562'
Paloma	Kern County, California Sec. 30 31S 26E, well-KCL-B-62-30	29.7°	NA	NA
Horseshoe Bayou	Saint Mary's Parish, Louisiana	34.8°	UL5 sand, segment B	11,836-11,854'
Lake Barre	Lafourche Parish, Louisiana, Unit 18 well #4	NA	8-1 sand, segment E	12,988-13,018', 240°F, 6,000 psi
Kimball	Kimball County, Nebraska 15N 55W	38°	Lower Cretaceous J sandstone	~6,500'
Red Fork	Tulsa County, Oklahoma	34°	Middle Pennsylvanian Oswego Limestone	NA
TCB	Jim Wells and Kleberg Counties, Texas	NA	Oligocene Frio sandstone	7,062'



Table 3

Identification of letter-labeled peaks of figure 16C. Peaks with numbers and letters below are the numbered peaks of figure 16A. Peaks A and K were put offscale, so that the size of the other peaks of figure 16C would be increased.

<u>Letter</u>	<u>Compound</u>
A	toluene
B	ethylbenzene
C	para- and meta-xylene
D (9)	ortho-xylene
E	isopropylbenzene
F	n-propylbenzene
G	meta-ethyltoluene
H	para-ethyltoluene
I (11)	(tentative) unidentified trimethylbenzene
J	ortho-ethyltoluene
K (12)	1,2,4- and 1,3,4- trimethylbenzene
L	isobutylbenzene
M	1,2,3- trimethylbenzene
N	n-butylbenzene
O	meta-diethylbenzene
P	para-diethylbenzene
Q	ortho-diethylbenzene
R (14)	1,3-dimethyl, 4-ethylbenzene
S (15)	(tentative) unidentified dimethylethylbenzene
T (16)	1,2,4,5 tetramethylbenzene
U (18)	1,2,3,5 tetramethylbenzene
V (20)	1,2,3,4 tetramethylbenzene
W (23)	naphthalene
X (27)	(tentative) mass 162, unidentified triethylbenzene?, or diethyldimethylbenzene?, or ethyltetramethylbenzene?
Y	2-methylnaphthalene
Z	1-methylnaphthalene



Table 4

Identification of numbered peaks (51-86) of figure 16D. Peaks 4A-6A, 12A, 15A, 17A, 20A, 21A, 24A, 31A, and 38A from figure 16B are in parenthesis. Compound identification was carried out by mass spectrometry using a Finnigan-Mat Ion Trap Detector System and previous identifications published by Radke et al (1986) and Rowland et al (1986). All unlabeled peaks between peaks 76 and 77 in figure 16D are co-eluting peaks of unidentified pentamethylnaphthalenes and dimethyldibenzofurans. Unlabeled peaks between peaks 78 and 79 in figure 16D are unidentified dimethylfluorenes, trimethyldibenzofurans, and methyldibenzothiophenes. Unlabeled peaks between peaks 82 and 83 in figure 16D are unidentified trimethylfluorenes, tetramethyldibenzofurans, and dimethyldibenzothiophenes. Peaks 79 and 80 in figure 16D (3- , and 2-methylphenanthrenes respectively) are also partially composed of unidentified methyldibenzothiophenes and trimethyldibenzofurans. Peaks 81 and 82 in figure 16D (4- , 9- methylphenanthrene and 1- methylphenanthrene respectively) are also partially composed of unidentified trimethylfluorenes and trimethyldibenzofurans. Peak 51 (2-methylnaphthalene) was put offscale, so that the size of the other peaks of figure 16D would be increased.

Number	Compound
51	2-methylnaphthalene
52	1-methylnaphthalene
53	2-ethylnaphthalene
54	ethylnaphthalene
55 (4A)	2,6-; and 2,7- dimethylnaphthalene
56 (5A)	1,3-; and 1,7- dimethylnaphthalene
57 (6A)	1,6-dimethylnaphthalene
58	1-5-; 1,4-; and 2,3-dimethylnaphthalene
59	1,2-dimethylnaphthalene
60	unidentified dimethylnaphthalene
61 (12A)	1,3,7-trimethylnaphthalene
62	1,3,6-trimethylnaphthalene
63	1,3,5-; and 1,4,6-trimethylnaphthalene
64	2,3,6-trimethylnaphthalene
65 (15A)	1,2,7-; 1,6,7-; and 1,2,6-trimethylnaphthalene
66	unidentified tetramethylnaphthalene
67	1,2,5-trimethylnaphthalene
68	unidentified methyldibenzofuran
69 (17A)	unidentified tetramethylnaphthalene
70	unidentified methyldibenzofuran
71	unidentified methyldibenzofurans and tetramethylnaphthalenes
72	unidentified tetramethylnaphthalene
73	unidentified tetramethylnaphthalene
74 (20A)	unidentified tetramethylnaphthalene
75 (21A)	unidentified tetramethylnaphthalene
76	unidentified penta- and tetramethylnaphthalenes and dimethyldibenzofuran
77	phenanthrene
78 (24A)	unidentified dimethylfluorenes and trimethyldibenzofurans
79 (31A)	3-methylphenanthrene
80	2-methylphenanthrene
81	4- and 9-methylphenanthrenes
82	1-methylphenanthrene
83 (38A)	fluoranthene and 1,3-; 3,9-; 2,10-; and 3,10-dimethylphenanthrenes
84	1,6-; 2,9-; and 2,5-dimethylphenanthrenes
85	1,7-dimethylphenanthrene
86	2,3-; 1,9-; 4,9-; and 4,10-dimethylphenanthrenes



Table 5. Results of gasoline range (C<sub>4</sub>-C<sub>7</sub>) HC analysis of Caillou Island oils in normalized weight percent. N-paraffins, iso-paraffins, and cyclo-paraffins plus aromatics are also given in summed normalized weight percents. FT is feet.

Sample (In FT)	8,398-8,433	9,418-9,434	9,424-9,464	11,135-11,164	12,943-12,960	13,406-13,454	13,476-13,510	14,520-14,585	14,662-14,710	14,880-14,920	15,816-15,912	16,796-16,880
Isobutane	2.0	4.1	5.3	0.9	0.6	1.3	1.9	1.2	1.0	1.1	1.4	0.9
n-Butane	1.4	2.0	3.8	1.1	0.9	1.5	2.0	1.1	0.9	2.2	1.8	1.0
Isopentane	4.9	8.0	8.9	4.4	3.5	7.9	8.0	8.3	8.3	9.3	9.9	8.3
n-Pentane	4.2	6.1	8.9	4.4	3.5	6.2	6.0	7.5	5.6	10.2	8.8	6.4
2, 2-Dimethylbutane	0.7	1.4	0.9	0.8	0.5	1.3	1.0	1.0	1.9	1.1	1.5	1.6
Cyclopentane	0.7	1.1	1.5	0.7	0.6	1.1	1.1	1.1	0.9	1.3	1.2	1.1
2, 3-Dimethylbutane	1.4	2.5	2.0	1.7	1.1	2.4	2.2	2.0	2.8	2.1	2.6	2.6
2-Methylpentane	6.2	11.7	8.8	6.4	5.7	9.6	9.7	9.5	10.3	9.5	11.3	10.6
3-Methylpentane	4.3	7.3	6.1	4.5	4.2	6.8	6.9	6.0	6.8	5.3	7.6	7.0
n-Hexane	10.2	8.4	12.8	10.4	9.6	12.1	13.0	11.0	9.6	0.3	8.6	10.4
Methylcyclopentane	4.7	4.7	7.1	5.1	5.1	5.9	6.9	6.1	4.2	3.6	4.9	4.4
2, 2-Dimethylpentane	0.7	0.8	0.6	0.7	0.6	0.9	0.8	1.0	0.9	0.6	0.8	0.8
Benzene	1.8	0.8	0.0	0.0	0.0	1.2	1.4	1.4	1.2	1.4	0.8	2.2
2, 4-Dimethylpentane	1.6	1.2	1.1	2.8	2.5	1.7	0.0	1.0	1.3	0.0	1.2	0.0
2, 2, 3-Trimeethylbutane	0.3	0.2	0.3	0.3	0.3	0.4	0.2	1.4	0.4	0.4	0.3	0.4
Cyclohexane	5.4	3.7	6.8	5.7	5.6	5.5	6.6	6.1	4.3	3.5	4.0	4.3
3, 3-Dimethylpentane	0.5	0.5	0.4	0.5	0.3	0.6	0.4	0.5	0.6	0.5	0.6	0.7
1, 1-Dimethylcyclopentane	1.1	0.7	1.0	1.2	1.1	1.2	1.2	0.9	1.1	1.3	0.9	1.1
2-Methylhexane	6.2	3.5	3.2	5.7	6.4	5.0	4.9	5.0	4.8	5.0	3.7	4.1
2, 3-Dimethylpentane	2.2	1.9	1.7	2.5	2.1	2.1	2.2	1.8	1.8	1.7	1.5	1.8
1, cis-3-Dimethylcyclopentane	1.6	1.6	1.3	1.6	1.7	1.2	1.4	1.2	1.2	1.2	1.1	1.2
3-Methylhexane	6.4	4.4	3.5	6.2	6.9	5.2	5.1	5.5	4.9	4.0	3.7	4.1
1, trans-3-Dimethylcyclopentane	1.6	1.4	1.3	1.7	1.8	1.3	1.5	1.0	1.1	1.2	0.9	1.2
1, trans-2-Dimethylcyclopentane	2.7	2.5	2.1	2.8	3.1	2.1	2.3	1.7	2.1	2.1	1.8	2.1
2, 2, 4-Trimeethylpentane	0.7	0.7	0.5	0.7	0.6	0.6	0.4	0.4	0.6	0.7	0.6	0.9
n-Heptane	12.3	7.2	2.5	11.1	14.0	7.0	4.6	7.1	8.3	8.3	7.8	7.4
1, cis-2-Dimethylcyclopentane	0.6	0.6	0.3	0.5	0.6	0.4	0.3	0.2	0.5	1.0	0.6	1.1
Methylcyclohexane	13.4	10.0	7.1	14.1	15.4	6.8	7.5	8.7	9.4	10.3	8.4	8.9
Toluene	0.2	1.1	0.3	1.6	1.6	0.5	0.5	0.5	3.2	1.8	1.7	3.4
N-Paraffins	28.1	23.7	28.0	27.0	28.0	26.8	25.6	26.7	24.4	30.0	27.0	25.2
Iso-Paraffins	38.1	49.4	43.3	38.1	35.3	45.8	43.7	44.6	46.4	41.6	46.7	43.8
Cyclo-Paraffins and Aromatics	33.8	27.3	28.8	35.0	36.6	27.2	30.7	28.9	29.2	28.4	26.3	31.0



Table 5. continued.

Sample (in FT)	17,200- 17,224	17,390- 17,499	17,570- 17,590	17,942- 17,974	18,358- 18,394	18,514 18,534	18,790 18,828	19,159 19,213	19,530 19,565	19,665 19,742	19,944 19,960
Isobutane	4.2	1.7	4.2	2.9	4.8	2.9	0.3	2.8	0.9	3.2	0.5
n-Butane	3.4	1.5	3.1	3.2	5.9	4.0	0.7	3.6	1.3	3.8	1.3
Isopentane	13.0	8.7	14.9	16.3	16.6	8.3	4.6	15.5	7.8	11.8	4.3
n-Pentane	9.0	6.2	5.2	10.1	9.5	7.0	5.1	8.6	6.0	6.9	5.6
2, 2-Dimethylbutane	1.7	1.4	1.7	1.3	0.9	0.8	0.6	0.8	0.8	0.7	0.4
Cyclopentane	1.0	0.7	0.8	0.9	1.1	1.0	0.6	0.8	0.7	0.8	0.9
2, 3-Dimethylbutane	2.6	2.2	1.8	2.1	1.8	1.2	1.2	1.4	1.5	1.2	1.1
2-Methylpentane	10.0	9.6	5.8	9.1	8.2	5.9	5.8	6.0	7.1	5.4	6.2
3-Methylpentane	6.4	6.1	4.3	5.9	5.8	4.0	4.3	4.1	4.9	3.9	4.7
n-Hexane	10.8	11.0	7.0	8.5	8.8	9.2	8.1	6.1	8.7	7.0	11.8
Methylcyclopentane	4.3	4.1	3.8	3.9	5.0	4.3	5.1	3.9	4.7	4.2	6.0
2, 2-Dimethylpentane	0.8	0.8	1.2	0.6	0.7	0.8	0.7	0.5	0.6	0.4	0.7
Benzene	1.3	2.5	1.6	0.5	1.3	1.2	0.6	0.0	0.8	0.3	1.5
2, 4-Dimethylpentane	1.2	0.0	0.0	1.1	0.0	1.8	1.4	1.2	1.2	1.1	1.3
2, 2, 3-Trimethylbutane	0.4	0.2	0.7	0.2	0.3	0.5	0.3	0.3	0.1	0.1	0.3
Cyclohexane	4.2	4.3	4.8	3.6	4.3	5.2	6.0	4.3	5.1	4.5	5.5
3, 3-Dimethylpentane	0.6	0.4	1.0	0.4	0.5	0.8	0.5	0.4	0.3	0.3	0.1
1, 1-Dimethylcyclopentane	0.8	0.9	1.7	0.9	1.1	1.2	1.7	1.2	1.2	1.0	0.3
2-Methylhexane	3.8	5.5	4.9	3.8	3.0	5.5	6.5	4.4	5.7	5.0	5.7
2, 3-Dimethylpentane	1.5	1.9	2.4	1.7	1.8	2.0	2.6	1.8	2.1	1.5	1.6
1, cis-3-Dimethylcyclopentane	0.9	1.1	1.5	1.1	1.2	1.1	2.1	1.5	1.7	1.5	1.7
3-Methylhexane	3.5	5.4	5.2	4.0	3.3	5.0	7.0	4.8	6.1	5.2	6.0
1, trans-3-Dimethylcyclopentane	0.8	1.2	1.4	1.1	1.2	1.2	2.0	1.4	1.6	1.5	1.7
1, trans-2-Dimethylcyclopentane	1.3	2.0	2.5	1.9	2.1	2.1	3.7	2.7	3.0	2.6	2.8
2, 2, 4-Trimethylpentane	0.6	0.5	0.8	0.6	0.7	1.0	0.9	0.7	0.6	0.4	0.5
n-Heptane	5.3	8.8	5.9	6.4	2.7	8.3	12.2	8.4	10.9	10.7	12.1
1, cis-2-Dimethylcyclopentane	0.5	0.4	0.3	0.5	0.5	1.0	0.7	0.7	0.5	0.6	0.6
Methylcyclohexane	4.8	9.4	11.1	6.6	6.0	9.9	12.9	10.3	11.7	13.1	11.9
Toluene	1.3	1.4	0.7	0.9	0.6	2.2	1.7	1.7	2.4	1.4	3.0
N-Paraffins	28.5	27.5	21.2	28.2	26.9	28.5	26.1	26.7	26.9	28.4	30.8
Iso-Paraffins	50.3	44.4	48.9	50.0	48.4	40.5	36.7	44.7	39.7	40.2	33.4
Cyclo-Paraffins and Aromatics	21.2	28.0	30.2	21.9	24.4	30.4	37.1	28.5	33.4	31.5	35.9



Table 6.--Information on all geographically-separated oils which had C<sub>4</sub>-C<sub>7</sub> HC analysis performed on them in this study. NA means not available. Reservoir conditions are given as originally supplied in feet, degrees Fahrenheit, and pounds per square inch (psi), rather than in metric equivalents.

Oil Field	Location/Well	API Gravity	Reservoir	Reservoir Conditions	Basin
Davis 6,530-6,538'	Clarke County, Mississippi, A.V. Hamburg 31-16 Well # 1-LT VF62	35°	Cretaceous Washita-Fredericksburg Groups	6,530-6,538', 158°F, 2,871 psi	Mississippi salt basin
Davis 7,913-7,917'	Clarke County, Mississippi, Conoco 32-13 Well #2LT P-52	34°	Lower Cretaceous Paluxy Formation	7,913-7,917', 177°F, 3,750 psi	Mississippi salt basin
Pachuta Creek	Clarke County, Mississippi, Sec. 26 2N 14E, Shell #26-14	31°	Upper Jurassic Smackover Formation	12,984-13,008', 223°F	Mississippi salt basin
Bastrop Bayou	Brazoria County, Texas, Bay Tract-1, Bastrop Bayou Tract-1 #1	31.8°	Bastrop Bay BM-2	6,900', 156°F, 2,000 psi	Upper Texas Gulf Coast
Chocolate Bayou	Brazoria County, Texas, A.M. Vierling #11	41.1°	9,020' Sand	9,040', 161°F, 2,500 psi	Upper Texas Gulf Coast
Logan South	Beaver County, Oklahoma	42°	Upper Pennsylvanian Tonkawa Sandstone	6,006-6,020'	Greater Anadarko
Mokane Laverne	Harper County, Oklahoma	45.6°	Upper Pennsylvanian Tonkawa Sandstone	5,553-5,562'	Greater Anadarko
Grand Valley East	Beaver County, Oklahoma	39.6°	Lower Pennsylvanian Upper Horrovan	6,948-6,987'	Greater Anadarko
Adena	Morgan County, Colorado, Sec 29 2N 57W, Glenn Biddle-1	43°	Lower Cretaceous J Sandstone	~5,600'	Denver
Dragon	Arapahoe County, Colorado, Sec. 15 5S 63W, Champlin 126 Amoco D-1	39°	Lower Cretaceous J Sandstone	7,420-7,450'	Denver
Singletree	Veld County, Colorado, Sec 17 2N 66W, Nels Christensen-2	NA	Upper Cretaceous Sussex (Terry Sandstone Member of Pierre Shale)	NA	Denver



Table 7. Results of gasoline range ( $C_4$ - $C_7$ ) HC analysis of 11 geographically separated oils in normalized weight percent. N-paraffins, iso-paraffins, and cycloparaffins plus aromatics are also given in summed normalized weight percent.

Sample	Davis 6,530- 6,538	Davis 7,913- 7,917	Bastrop Bayou	Choco- late Bayou	Pachuta Creek	South Logan	Grand Valley East	Mokane- Laverne	Dragoon	Adena	Single- tree
Isobutane	6.0	7.1	11.5	4.1	5.4	3.5	12.7	1.1	0.9	2.0	0.9
n-Butane	13.8	18.0	12.6	6.3	17.6	14.8	21.6	4.4	3.5	6.2	3.1
Isopentane	13.1	18.9	12.4	6.6	15.1	11.4	13.4	5.8	3.8	6.1	6.3
n-Pentane	12.5	18.2	7.1	6.6	18.2	16.2	18.0	10.3	5.3	6.4	8.6
2, 2-Dimethylbutane	0.3	0.4	1.8	0.7	0.3	0.4	0.3	1.1	0.4	0.9	0.4
Cyclopentane	0.9	0.8	0.9	0.9	1.2	1.0	0.8	2.0	1.0	1.8	1.4
2, 3-Dimethylbutane	1.1	0.8	1.6	1.3	1.0	0.7	0.5	1.5	0.9	1.8	1.1
2-Methylpentane	6.5	4.6	4.1	5.5	6.6	5.4	3.8	8.5	4.3	4.3	6.5
3-Methylpentane	4.8	3.1	2.7	3.5	4.6	3.3	2.1	5.7	3.2	3.3	4.1
n-Hexane	10.8	6.1	5.0	8.6	10.7	10.6	6.8	15.3	8.4	6.4	11.1
Methylcyclopentane	2.9	1.8	3.6	5.6	2.4	3.8	2.3	5.0	5.6	6.1	6.5
2, 2-Dimethylpentane	0.3	0.2	1.0	0.7	0.1	0.5	0.1	0.3	0.5	1.5	0.5
Benzene	0.6	0.2	0.0	1.2	0.6	0.6	0.3	0.5	0.0	0.0	0.6
2, 4-Dimethylpentane	0.0	0.3	1.2	1.4	0.3	0.0	0.2	0.0	1.1	2.2	1.1
2, 2, 3-Trimethylbutane	0.2	0.1	0.8	0.5	0.1	0.3	0.0	0.1	0.3	0.9	0.3
Cyclohexane	2.3	1.7	4.6	8.5	1.7	4.0	3.5	6.1	7.3	5.3	6.7
3, 3-Dimethylpentane	0.3	0.2	1.1	0.7	0.1	0.3	0.1	0.1	0.7	1.1	0.4
1, 1-Dimethylcyclopentane	0.5	0.4	1.7	1.1	0.2	0.8	0.3	0.9	1.7	2.3	1.3
2-Methylhexane	3.9	2.3	2.7	3.4	2.1	3.4	1.3	4.3	3.8	3.2	3.6
2, 3-Dimethylpentane	1.3	0.9	1.8	1.4	0.8	0.0	0.4	0.0	1.6	1.8	1.4
1, cis-3-Dimethylcyclopentane	0.6	0.4	1.0	1.3	0.3	1.1	0.5	1.2	2.0	2.6	1.6
3-Methylhexane	3.7	2.3	4.7	3.1	2.0	2.8	1.5	4.0	4.1	3.0	3.8
1, trans-3-Dimethylcyclopentane	0.6	0.4	0.9	1.2	0.3	1.0	0.5	1.3	1.9	2.1	1.6
1, trans-2-Dimethylcyclopentane	1.2	0.8	1.6	2.1	0.6	1.6	0.8	2.0	3.2	3.4	2.6
2, 2, 4-Trimethylpentane	0.7	0.4	1.1	0.7	0.3	0.4	0.2	0.3	1.0	1.7	0.6
n-Heptane	7.4	5.4	3.5	7.1	4.3	4.9	3.6	7.5	10.6	7.3	9.1
1, cis-2-Dimethylcyclopentane	0.3	0.4	1.5	0.8	0.2	0.5	0.2	0.3	1.5	2.2	0.7
Methylcyclohexane	3.3	2.7	7.5	13.9	1.9	6.1	3.7	10.2	17.9	10.7	11.3
Toluene	0.3	1.0	0.2	1.2	0.9	0.4	0.6	0.4	3.4	3.2	2.7
N-Paraffins	44.5	47.7	28.2	28.6	50.8	46.5	50.0	37.5	27.8	26.3	31.9
Iso-Paraffins	42.2	41.6	48.5	33.6	38.8	32.4	36.6	32.8	26.6	33.8	31.0
Cyclo-Paraffins and Aromatics	13.5	10.6	23.5	37.8	10.3	20.9	13.5	29.9	45.5	39.7	37.0



## APPENDIX

Tables 8-13 are organic-geochemical data from rocks of 3 well bores in the Gulf Coast. These data do not directly relate to the oil-oil correlation study carried out at Caillou Island. However, these data are referred to in two papers of the Symposium Volume of the Ninth Annual SEPM Gulf Coast Research Conference (Price, 1989a; and Price and Clayton, 1989), a Symposium Volume in which the oil-oil correlation study is also published (Price, 1989b). To avoid another open-file report and to keep all the SEPM data centralized, these tables have been included in this report.



Table 8.--Results of Soxhlet extractions for samples from the Pan American Foerster-1, La Salle County, South Texas Gulf Coast

[T.O.C. wt. % is total organic carbon content in weight percent; CaCO<sub>3</sub> wt. % is carbonate content (expressed as calcite content) in weight %; C<sub>15</sub>+ BIT ppm is the C<sub>15</sub>+ bitumen content in parts per million (rock weight); C<sub>15</sub>+ SAT HC's ppm and C<sub>15</sub>+ ARO HC's ppm are C<sub>15</sub>+ saturated and aromatic hydrocarbons in parts per million (rock weight); C<sub>15</sub>+ TOTAL HC's ppm are the sum of the C<sub>15</sub>+ saturated and aromatic hydrocarbons in parts per million (rock weight); NSO's ppm are the resins and asphaltenes in parts per million (rock weight); C<sub>15</sub>+ BIT, SAT HC's, ARO HC's, TOTAL HC's and NSO's all in mg/g O.C. are respectively the C<sub>15</sub>+ bitumen, saturated hydrocarbons, aromatic hydrocarbons, sum of the saturated and aromatic hydrocarbons, and resins and asphaltenes, all in milligrams per gram of organic carbon; HC's/NSO's is the ratio of the sum of the C<sub>15</sub>+ saturated and aromatic hydrocarbons to resins plus asphaltenes; and SAT/ARO is the ratio of C<sub>15</sub>+ saturated to aromatic hydrocarbons.]

Sample depth in meters	T.O.C. wt. %	CaCO <sub>3</sub> wt. %	C <sub>15</sub> + BIT, ppm	C <sub>15</sub> + SAT HC's ppm	C <sub>15</sub> + ARO HC's ppm	C <sub>15</sub> + TOTAL HC's ppm	NSO's ppm	C <sub>15</sub> + BIT mg/g O.C.	C <sub>15</sub> + TOTAL HC's mg/g O.C.	C <sub>15</sub> + SAT mg/g O.C.	C <sub>15</sub> + ARO mg/g O.C.	NSO's mg/g O.C.	HC's NSO's	SAT ARO
1,756-1,989	0.72	10.3	428	145	57	202	226	59	28.0	20.1	7.92	31.0	0.90	2.54
1,987-2,152	.60	11.8	429	101	57	156	273	72	26.3	16.8	9.50	45.7	.37	1.77
2,152-2,286	.62	9.7	386	83	61	146	242	62	23.2	13.4	9.84	38.8	.60	1.36
2,359-2,469	.55	14.4	437	90	49	139	298	80	25.3	16.4	8.91	54.7	.47	1.84
2,469-2,670	.49	20.2	430	132	62	194	236	88	39.5	26.9	12.6	48.5	.82	2.13
2,640-2,749	.56	19.7	350	92	38	130	220	63	23.2	16.4	6.79	39.8	.59	2.42
2,749-2,957	.37	13.7	354	126	39	165	189	96	44.5	34.0	10.5	51.5	.87	3.23
2,957-3,078	.50	20.8	408	114	53	167	241	82	33.4	22.8	10.6	48.6	.70	2.15
3,078-3,200	.59	29.4	397	171	45	216	181	67	36.6	29.0	7.63	30.4	1.19	3.80
3,383-3,444	.30	78.7	148	89	18	107	41	49	35.7	29.7	6.00	13.3	2.61	4.94
3,444-3,688	.37	78.3	126	65	14	79	47	34	21.4	17.6	3.78	12.6	1.68	4.64
3,688-3,871	.46	78.4	126	79	9	88	38	27	19.1	17.1	1.98	8.15	2.34	8.64
3,932-4,115	.68	78.0	172	na	na	na	na	25	na	na	na	na	na	na
4,115-4,298	.38	79.1	176	72	20	92	84	46	24.3	19.0	5.26	21.7	1.10	3.60
4,298-4,481	.25	90.1	163	69	10	79	84	65	31.6	27.6	4.00	33.4	.94	6.90
4,481-4,602	.26	89.9	192	67	5	72	120	74	27.8	25.8	1.90	46.2	.60	13.40
4,602-4,724	.24	88.6	193	108	6	114	78	80.4	47.7	45.2	2.50	32.7	1.46	19.1
4,724-4,846	.24	83.3	252	112	6	118	134	105	49.2	46.7	2.50	55.8	.88	18.7
4,846-5,151	.42	39.3	556	238	42	280	276	132	67.0	56.7	10.0	65.0	1.01	5.67
5,151-5,334	.48	16.2	828	483	62	545	283	172	114	101	12.9	58.1	1.92	7.79
5,334-5,456	.48	10.1	740	424	52	476	264	154	99.1	88.3	10.8	54.9	1.80	8.15
5,456-5,578	.41	47.8	442	229	42	271	171	118	66.1	55.9	10.2	51.9	1.58	5.45
5,578-5,761	1.51	23.3	467	127	36	165	302	31	10.8	8.4	2.38	20.2	.55	3.53
5,761-5,882	.85	15.1	304	95	37	192	172	36	15.6	11.2	4.35	20.9	.77	2.57
5,882-6,066	.41	65.0	186	62	9	71	115	45	17.3	15.1	2.20	27.7	.62	6.89
6,066-6,188	.39	80.5	200	77	21	98	102	51	25.1	19.7	5.38	25.9	.96	3.67
6,188-6,309	.93	64.3	302	105	21	126	176	33	13.6	11.3	2.26	19.4	.72	5.00
6,309-6,492	.54	75.0	259	93	18	111	148	48	20.5	17.2	3.33	27.5	.75	5.17
6,492-6,614	.60	66.5	138	62	8	70	68	23	11.6	10.3	1.33	11.4	1.03	7.75



Table 9. Mean  $R_o$  values for samples from the Pan American Foerster-1, LaSalle County, South Texas Gulf Coast

Depth in km	$R_o$	Standard Deviation
2359-2469	0.77	0.17
2749-2957	0.88	0.14
2804-2859	1.07	0.16
2957-3078	1.21	0.23
3078-3200	1.11	0.16
3140-3383	0.97	0.24
4602-4724	2.53	0.82
4968-5151	3.20	0.54
5151-5334	3.33	0.38
5334-5456	3.78	0.45
5456-5578	3.80	0.52
5761-5883	4.16	0.66



Table 10. Results of ROCK EVAL pyrolysis for composite samples of the Pan American Foerster-1, La Salle County, South Texas Gulf Coast

[T.O.C. is total organic carbon content in weight %; S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub> ppm are parts per million (by rock weight) of the S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub> pyrolysis peaks respectively; S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub> mg/g O.C. are the S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub> pyrolysis peaks normalized to organic carbon (mg/g O.C.); T.R. is the transformation ratio (also called P.I. or production index and equal to S<sub>1</sub>/S<sub>1</sub>/S<sub>2</sub>); T<sub>max</sub> is the temperature in °C at the maximum of the S<sub>2</sub> pyrolysis peak; and C<sub>15</sub><sup>+</sup> HC's/S<sub>1</sub> is the ratio of total C<sub>15</sub><sup>+</sup> HC's as determined by Soxhlet extraction (Table 8) to the S<sub>1</sub> pyrolysis peak where both values are in mg/g O.C.]

Sample depth in meters	T.O.C. ppm	S <sub>1</sub> ppm	S <sub>2</sub> ppm	S <sub>3</sub> ppm	S <sub>1</sub> mg/g O.C.	S <sub>2</sub> mg/g O.C.	S <sub>3</sub> mg/g O.C.	T <sub>max</sub>	%C <sub>15</sub> <sup>+</sup> HC's	S <sub>1</sub>
1,756-1,987	0.72	45	150	400	6.25	20.8	55.6	.231	7.69	4.48
1,987-2,152	.60	56	350	220	9.33	58.3	36.7	.138	11.8	2.79
2,152-2,286	.62	78	360	220	12.6	58.1	35.5	.178	9.7	1.82
2,359-2,469	.55	110	240	230	20.0	43.6	41.8	.314	14.4	1.25
2,469-2,640	.49	62	280	200	12.6	57.1	40.8	.181	20.2	3.18
2,640-2,749	.56	50	210	220	8.93	37.5	39.2	.192	19.7	2.58
2,749-2,957	.37	61	160	200	16.5	43.2	54.0	.276	13.7	2.73
2,957-3,078	.50	85	130	220	17.0	26.0	44.0	.395	20.8	2.00
3,078-3,200	.59	80	100	290	13.6	16.9	49.2	.445	29.4	2.72
3,383-3,444	.30	74	10	370	24.6	3.33	123	.881	78.7	1.46
3,444-3,688	.37	30	50	490	8.11	13.5	132	.375	77.5	2.59
3,688-3,871	.46	73	400	1,110	15.9	87.0	241	.154	78.4	NA
3,932-4,115	.68	97	360	1,320	14.3	52.9	194	.212	78.0	NA
4,115-4,298	.38	50	80	730	13.2	21.0	192	.385	79.1	1.82
4,298-4,481	.25	45	20	720	18.0	8.0	288	.692	90.1	1.78
4,481-4,602	.26	43	20	710	16.5	7.69	273	.682	89.9	1.55
4,602-4,724	.24	75	10	540	31.2	4.47	225	.882	88.6	NA
4,724-4,846	.24	52	280	720	21.7	117	300	.157	83.3	2.26
4,968-5,151	.42	121	520	670	28.8	124	159	.189	433	2.33
5,151-5,334	.48	143	280	320	29.8	58.3	66.7	.338	427	3.83
5,456-5,578	.41	186	120	275	45.4	29.3	55	.608	433	1.23
5,761-5,882	1.51	138	1,000	1,390	9.12	66.2	92.0	.121	23.3	1.21
5,944-6,066	.85	9	720	430	1.06	84.7	50.6	.012	15.1	15.1
6,066-6,188	.41	26	70	820	3.06	17.1	96.5	.152	65.0	5.56
6,188-6,309	.39	46	10	540	11.8	2.56	138	.821	80.5	2.12
6,370-6,492	.93	103	470	1,160	11.1	50.5	125	.180	64.3	1.26
6,492-6,614	.54	90	190	520	16.7	35.2	96.3	.322	75.0	1.26
6,614-6,704	.60	59	230	970	9.83	38.3	162	.204	66.5	3.46



Table 11.--Results of ROCK EVAL pyrolysis for picked shale (and picked limestone) samples of the Pan American Foerster-1, La Salle County, South Texas, Gulf Coast

[T.O.C. is total organic carbon content in weight percent; S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub> ppm are parts per million (by rock weight) of the S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub> pyrolysis peaks respectively; S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, and S<sub>1</sub> + S<sub>2</sub> mg/g O.C., are the S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>, and sum of the S<sub>1</sub> and S<sub>2</sub> pyrolysis peaks normalized to organic carbon (mg/g O.C.); T.R. is the transformation ratio (also called P.I. or production index and equal to S<sub>1</sub>/S<sub>1</sub> + S<sub>2</sub>); and T<sub>max</sub> °C is the temperature in °C at the maximum of the S<sub>2</sub> pyrolysis peak.]

Sample depth in meters	T.O.C.	S <sub>1</sub> ppm	S <sub>2</sub> ppm	S <sub>3</sub> ppm	S <sub>1</sub> mg/g O.C.	S <sub>2</sub> mg/g O.C.	S <sub>3</sub> mg/g O.C.	T.R.	T <sub>max</sub> °C	Comments	S <sub>1</sub> + S <sub>2</sub> mg/g O.C.
Shales											
1,756-1,810	0.64	40	310	320	6.25	48.4	50.0	.114	431		54.6
1,987-2,042	.59	20	350	230	3.40	59.3	39.0	.054	434		62.7
2,152-2,207	.62	30	650	240	4.84	105	38.7	.044	436		110
2,414-2,469	.52	40	410	310	7.69	53.3	40.3	.126	436		60.1
2,469-2,505	.60	40	540	240	6.67	90.0	40.0	.069	435		90.7
2,640-2,694	.60	30	590	230	5.00	98.3	38.3	.048	435		103
2,804-2,859	.50	50	340	200	10.0	68.0	40.0	.128	441		78
2,896-2,957	.48	50	310	260	10.4	64.6	54.2	.139	440		75
2,957-3,018	.50	50	240	210	10.0	48.0	42.0	.094	445		58
3,078-3,139	.65	60	320	320	9.23	49.2	49.2	.158	445		58.4
3,200-3,261	.52	70	320	210	13.5	61.5	40.4	.180	462		75
3,322-3,383	3.95	1,330	3,870	480	33.7	42.0	12.2	.445	475		75.7
3,383-3,444	.57	100	550	210	17.5	96.5	36.8	.152	438		114
3,444-3,688	.52	120	470	210	23.1	90.4	40.4	.203	433		114
3,688-3,749	.55	100	510	320	18.2	92.7	58.2	.164	434		111
3,932-3,993	.67	130	650	340	19.4	97.0	50.7	.167	411		116
4,115-4,176	.50	130	490	350	26.0	98.0	70.0	.208	435		124
4,176-4,236	1.10	280	900	360	25.4	82.0	32.7	.236	329		107
4,542-4,602	.53	140	560	390	26.4	106	73.6	.200	434		132
4,664-4,724	.62	190	680	500	30.6	110	80.6	.218	429		140
4,785-4,846	.55	150	590	300	27.3	107	54.5	.203	432		134
5,028-5,090	.24	70	220	180	29.2	91.7	75.0	.241	432		121
5,090-5,151	.42	100	270	220	23.8	64.3	52.4	.270	337		88.1
5,212-5,273	.40	160	500	210	40.0	125	52.5	.242	356		165
5,273-5,334	.49	130	300	160	26.5	61.2	32.6	.302	335		86.7
5,334-5,395	.59	110	230	150	18.6	38.9	25.4	.324	336	Dark grey shale	57.5
5,334-5,395	.49	120	250	200	24.5	51.0	40.8	.324	341	Medium dark grey shale	74.5
5,395-5,456	.43	100	290	180	23.2	67.4	41.9	.256	342	Light grey shale	90.6
5,395-5,456	.52	110	270	150	21.2	51.9	28.8	.290	342	Grey shale	73.1
5,456-5,517	.41	120	290	200	29.3	70.7	48.8	.293	352		80.0
5,517-5,578	.49	110	220	210	22.4	44.8	42.8	.333	339		65.2
5,578-5,639	.45	130	250	230	28.9	55.6	51.1	.342	330	Grey shale	84.5
5,578-5,639	.20	40	60	160	20.0	30.0	80.0	.400	319	Sandstone	50.0
5,578-5,639	.93	200	310	360	21.5	33.3	38.7	.392	324	Dark grey shale	54.8
5,761-5,822	.38	50	150	230	13.2	39.5	60.5	.250	341		52.7
5,822-5,882	.90	140	290	310	15.6	32.2	34.4	.326	333		47.8
6,127-6,188	.53	110	230	350	20.6	43.4	66.0	.323	327		64.0
6,370-6,431	.33	50	80	280	15.2	24.2	84.8	.385	342		39.4
6,431-6,492	.35	50	50	180	14.3	14.3	51.4	.667	313		28.6
6,492-6,553	.70	120	110	250	17.1	15.7	35.7	.552	340		32.8
6,553-6,614	.56	40	40	200	7.14	7.14	35.7	.667	288		14.3
6,614-6,704	.75	30	30	150	4.00	4.00	37.5	.667	312		8.00
Limestones											
3,261-3,322	0.09	10	20	250	11.1	22.2	277	.333	435		33.3
3,383-3,444	.07	10	40	180	14.3	57.1	257	.200	455		71.4
3,444-3,688	.13	20	20	150	15.4	15.4	115	.500	368		30.8
3,810-3,871	.08	20	30	180	25.0	37.5	225	.400	416		62.5
3,993-4,115	.11	30	20	180	27.3	18.2	163	.600	305		45.5
4,236-4,298	.08	20	20	240	25.0	25.0	300	.500	305		50.0
4,298-4,481	.10	20	20	260	20.0	20.0	260	.500	334		40.0
4,481-4,542	.11	20	10	250	18.2	9.10	227	.666	278		27.3
4,602-4,664	.09	20	20	300	22.2	22.2	333	.500	423		44.4
4,724-4,785	.10	30	30	220	30.0	30.0	220	.500	392		60.0
4,968-5,028	.07	20	30	150	28.6	42.8	214	.400	387		71.4
5,151-5,212	.16	60	170	190	37.5	106	118	.261	352		143.5
5,456-5,517	.08	20	20	120	25.0	25.0	150	.500	359		50.0
5,578-5,639	.16	50	80	220	31.2	50.0	137	.385	324		81.2
6,188-6,309	.11	20	40	190	18.2	36.4	172	.666	348		54.6
6,614-6,704	.30	40	40	220	13.3	13.3	73.3	.500	288		26.6



Table 12. Results of ROCK EVAL analysis for cuttings chips samples from the Texaco Inc. State Lease 4666-1 well bore Terrebonne Parish, Louisiana, in the Caillou Island oil field. FT is feet, M is meters. T.O.C. is total organic carbon.  $S_1$ ,  $S_2$ ,  $S_3$  and  $S_1+S_2$  ppm; and  $S_1, S_2, S_3$  mg/gO.C. are respectively those ROCK EVAL pyrolysis peaks in parts per million (by rock weight) or normalized to organic carbon (milligrams per gram).  $T_{max}$  is the temperature in  $^{\circ}\text{C}$  at the maximum of the  $S_2$  pyrolysis peak. T.R. is the transformation ratio, also called the production index (P.I.) and equal to  $S_1/S_1+S_2$ .

SAMPLE DEPTH		T.O.C.	$S_1$	$S_2$	$S_3$	$S_1+S_2$	$S_1$	$S_2$	$S_3$	$T_{max}$	T.R.
in	M										
FT	M		ppm	ppm	ppm	ppm	mg/gO.C.	mg/gO.C.	mg/gO.C.		
8,176	2,492	.37	130	260	580	390	35.1	64.9	157	328	.351
8,476	2,583	.28	100	120	720	220	35.7	42.9	257	307	.454
8,776	2,675	.40	130	260	780	390	32.5	65.0	195	366	.333
9,096	2,772	.30	100	160	860	260	33.3	53.3	286	365	.385
9,376	2,858	.26	70	130	940	200	26.9	50.0	361	331	.350
9,696	2,955	.31	50	180	1,030	230	16.1	58.1	332	374	.217
9,976	3,041	.34	110	200	1,160	310	32.3	58.8	341	367	.355
11,296	3,443	.34	90	180	820	270	26.5	52.9	270	374	.333
11,676	3,559	.38	90	210	1,170	300	23.7	55.3	308	374	.300
12,576	3,833	.45	100	270	680	370	22.2	60.0	151	415	.270
12,976	3,955	.40	50	230	530	280	12.5	57.5	132	409	.179
13,896	4,235	.31	120	120	1,370	240	38.7	38.7	442	420	.500
14,396	4,388	.30	30	190	600	220	10.0	63.3	200	418	.136
14,896	4,540	.36	40	310	870	350	11.1	86.1	242	420	.114
15,296	4,662	.39	50	330	970	380	12.8	84.6	249	421	.131
15,696	4,784	.44	60	430	740	490	13.6	97.7	168	421	.122
15,976	4,869	.35	60	330	770	390	17.1	94.2	220	423	.154
16,496	5,028	.51	100	540	990	640	19.6	106.0	194	424	.156
16,876	5,144	.52	70	500	840	570	13.5	96.2	162	422	.123
17,337	5,284	.45	120	440	540	560	26.7	97.8	120	424	.214
17,667	5,385	.44	110	370	900	480	25.0	84.1	204	430	.229
18,440	5,620	.43	90	370	370	470	20.9	86.0	86.0	423	.195
18,830	5,739	.41	100	320	780	420	24.4	78.0	190	431	.238
19,130	5,831	.36	70	250	970	320	19.4	69.4	269	433	.218
19,540	5,956	.44	120	420	800	540	27.3	95.4	182	430	.223
19,870	6,056	.55	120	470	660	590	21.8	85.4	120	433	.203
20,230	6,166	.47	130	430	670	560	27.7	91.5	143	433	.232
20,410	6,221	.44	120	380	640	500	27.3	86.4	145	433	.240



Table 13. Results of ROCK EVAL and  $R_o$  analyses of cuttings chips samples from the Marathon J. Burton-LeBlanc et al-1 wellbore southern East Baton Rouge Parish, Louisiana. The cuttings from this well were heavily contaminated with organic-based drilling fluid, so the ground powder of each sample was exhaustively Soxhlet extracted to remove non-indigenous organic compounds. Hence, no data are available for the  $S_1$  pyrolysis peak or the transformation ratio ( $S_1/S_1+S_2$ ). FT is feet. T.O.C. is total organic carbon.  $S_2$  and  $S_3$  ppm, and  $S_2$  and  $S_3$  mg/g O.C. are respectively those ROCK EVAL pyrolysis peaks in parts per million (by rock weight) or normalized to organic carbon (milligrams per gram).  $T_{max}$  is the temperature in  $^{\circ}C$  at the maximum of the  $S_2$  pyrolysis peak.  $R_o$  is vitrinite reflectance with standard deviation (Std. Dev.), and number of readings (n).

Sample Depth in FT	T.O.C.	$S_2$ ppm	$S_3$ ppm	$S_2$ mg/g O.C.	$S_3$ mg/g O.C.	$T_{max}$	$R_o$		
							$R_o$	Std. Dev.	n
3,990-4,080	41.37	47,320	37,180	114	89	429	0.29	0.04	51
4,440-4,470	0.76	370	3,290	48	432	414	0.34	0.04	51
4,890-4,980	0.48	200	1,440	41	300	413	0.31	0.03	45
5,400-5,470	0.73	380	1,800	52	246	413	0.36	0.05	46
5,790-5,820	0.68	220	1,300	32	191	413	0.29	0.03	21
6,240-6,270	0.14	40	510	28	364	400			
6,690-6,710	0.42	160	1,730	38	411	415			
7,200-7,230	0.16	70	920	43	575	414	0.35	0.05	47
7,650-7,710	0.28	140	780	50	278	408			
7,890-7,920	0.25	80	590	32	236	411	0.35	0.05	41
8,640-8,670	0.25	90	380	36	152	420			
9,090-9,150	0.71	350	790	49	111	423	0.40	0.04	57
9,570-9,600	0.83	510	700	61	84	422			
10,020-10,050	1.33	890	1,230	66	92	428	0.45	0.06	55
10,470-10,500	1.56	1,670	780	107	50	427			
10,920-10,950	1.68	1,740	620	103	36	432	0.47	0.06	51
11,370-11,400	1.62	1,600	760	98	46	435			
11,700-11,730	1.46	1,320	650	90	44	436	0.45	0.05	55
14,400-14,430	1.02	820	790	80	77	439	0.56	0.06	8
14,610-14,640	1.20	910	810	75	67	443	0.60	0.10	55
14,940-14,970	1.15	1,150	590	100	51	441	0.55	0.08	55
15,330-15,360	1.04	720	830	69	79	439	0.59	0.09	51
15,720-15,750	1.03	830	560	80	54	442			
15,780-15,810	1.10	830	820	75	74	444	0.79	0.09	55
16,020-16,050	1.36	760	360	55	26	447	0.79	0.10	39
16,050-16,080	1.40	970	450	69	32	445			
16,920-16,950	2.06	3,440	450	166	21	437			
16,950-17,070	1.75	4,320	660	246	37	402	1.07	0.08	25
17,280-17,340	1.11	980	610	88	54	419			
18,720-18,810	0.79	400	310	50	39	405	1.10	0.21	15
19,140-19,200	0.76	1,000	520	131	68	408			
19,230-19,290	1.22	2,640	820	216	67	418	1.38	0.19	27
20,340-20,370	0.84	590	390	70	46	404	2.04	0.31	65
20,670-20,730	0.81	430	360	53	44	400			
20,850-20,910	0.71	510	320	71	45	399			
21,000-21,030	0.83	310	370	37	44	399	2.12	0.34	55
21,360-21,420	0.72	300	380	41	52	425	1.45	0.25	35
21,570-21,630	0.82	630	390	76	47	405	1.61	0.23	51
21,750-21,780	1.17	1,290	370	110	31	374	2.22	0.27	65