REPORT ON THE COMPOSITION OF OIL FROM THE REGION OF NEW HYDROCARBON UPWELLING IN THE SANTA BARBARA CHANNEL

by

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Preface

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Background

On the morning of 4 June 1973, workers on Atlantic Richfield Company's Platform Holly in the Santa Barbara Channel reported to the U.S. Coast Guard the presence of a sizable oil slick emanating from a submarine source approximately one mile ESE of the platform. Along with the oil, workers also reported that large quantities of gas were issuing forth.

Although this region of the Santa Barbara Channel is widely known to contain numerous areas of natural hydrocarbon seepage, the new oil and gas upwelling was occurring at a location that, over the past five years or more, was normally free of seepage. Because of its potential polluting effects and its unknown cause, this new region of hydrocarbon upwelling became the subject of considerable attention and scrutiny. Among those investigating the new seepage were the California Division of State Lands, the California Department of Fish and Game, the U.S. Coast Guard, Clean Seas, Inc. (an oil industry cooperative for oil spill cleanup), and Atlantic Richfield Oil Company.

Scope of the Report

During the past four years, I have participated in a number of studies dealing with various aspects of natural oil seepage.* Of principal interest has been the physicochemical behavior of oil from the nearshore seeps in the vicinity of Coal Oil Point. Having this background data, I immediately became interested in comparing the composition of oil from

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* A bibliography of some of these studies is presented at the end of this report.

this new upwelling with that from the previously existing seeps at and around Coal Oil Point, and with produced oils from various formations in the same general vicinity.

This report, therefore, deals with certain chemical analyses of the oils in question. More specifically, these analyses are gas chromatography (gc), and trace concentrations of nickel (Ni) and vanadium (V) as determinted by atomic absorption spectrophotometry. The oils analyzed during this effort are listed in Table 1.

The geographical setting of the oil seepage areas is shown in Figure 1. This figure, taken from a recent study by Fischer and Stevenson (1973), shows the location of the new upwelling * in relation to hydrocarbon seeps that were documented during the period 1946 to 1947 by geologists from Signal Oil Company. As mentioned previously, this region has been generally free of hydrocarbon seepage for the past five years or so.

Preliminary Efforts

Because of the widespread interest in this new hydrocarbon seep, efforts were made to determine, as quickly as possible, how this oil compared with oil from the previously existing nearshore seeps. Two samples of the oil were therefore obtained on 6 June 1973. The first sample, amounting to less than 1 cm^3, was collected on 4 June by U.S. Coast Guard personnel (Group Santa Barbara). The second sample was collected the following day by Clean Seas, Inc., and contained substantially more oil than the first (100 cm^3 or more). Both samples were collected from the ocean surface immediately above the area of upwelling.

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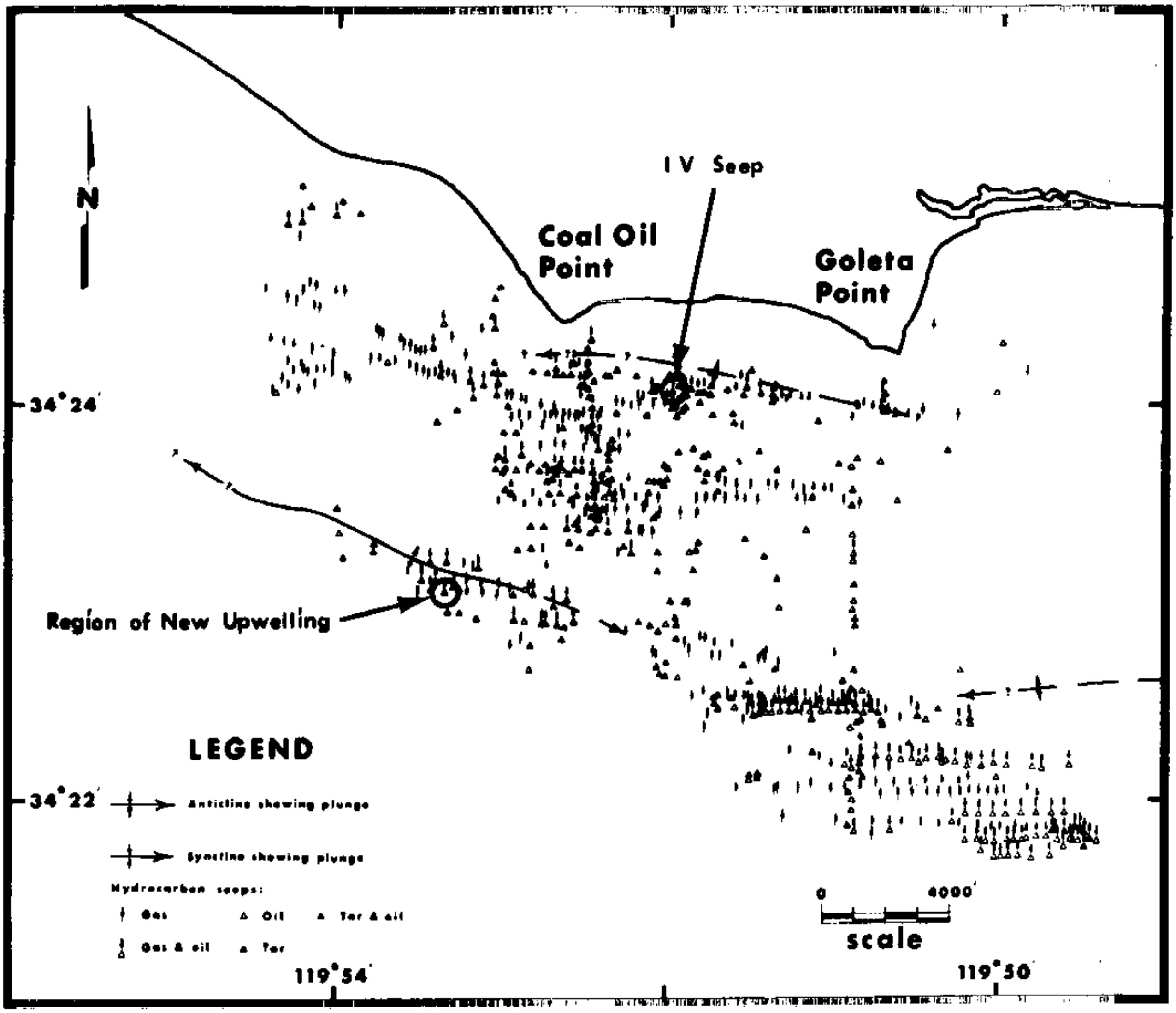
* As determined by information provided by Clean Seas, Inc.

TABLE 1. OILS ANALYZED FOR THIS REPORT

	Name	Description	Analyses Performed
1.	IV Seep	Natural seepage oils collected from the ocean floor one-half mile offshore from Isla Vista	gc, Ni, V
2.	New Seep (4 June)	Oil collected by the U.S. Coast Guard from the ocean surface above the area of new hydrocarbon upwelling	gc
3.	New Seep (5 June)	Same as 2. above. Sample collected by Clean Seas, Inc.	gc, Ni, V
4.	New Seep (27 June)	Same as 2. above. Sample collected by Atlantic Richfield Oil Co.	gc, Ni, V
5.	Sisquoc	Produced oil from the Sisquoc formation, Santa Barbara Channel	gc, Ni, V
6.	Monterey	Produced oil from the Monterey formation, Santa Barbara Channel	gc, Ni, V
7.	Vaqueros	Produced oil from the Vaqueros formation, Santa Barbara Channel	gc, Ni, V



<u>Figure 1</u>

Location of the area of new hydrocarbon upwelling, and the Isla Vista (IV) natural oil seep, in relation to natural hydrocarbon seeps reported during the period 1946 to 1947. After Fischer and Stevenson (1973).

Gas chromatography analysis using our standardized procedure (Sivadier and Mikolaj, 1973) showed the samples to be identical. Because of insufficient sample size, no additional work was done with the 4 June sample. The 5 June sample, however, was further analyzed for trace concentrations of Ni and V using an atomic absorption procedure developed by Delaney (1972).

Results of these preliminary analyses were communicated to the U.S. Coast Guard on 8 June 1973. The major findings were:

1. The oil from the area of new hydrocarbon upwelling was significantly different in its composition from oil originating at the nearshore natural seeps off Isla Vista and Coal Oil Point.
2. The two major differences were
   a. Oil from the new seep had a much higher concentration of nickel.
   b. Oil from the new seep contained noticeable amounts of normal paraffins out to carbon number 30, and possibly beyond.

Subsequent to these preliminary findings, discussions with other individuals and groups who were also studying the problem raised some questions concerning the accuracy of the findings listed above. In view of the fact that the instruments used in our analyses had been on standby for several months, and the operators were somewhat "rusty", it appeared desirable to repeat the analyses under less hectic conditions. Also, the significant differences (at least apparent) in composition invited further analyses to compare the new seep oil with various produced oils from the Santa Barbara Channel.

Comparison of Seepage Oils with Produced Oils

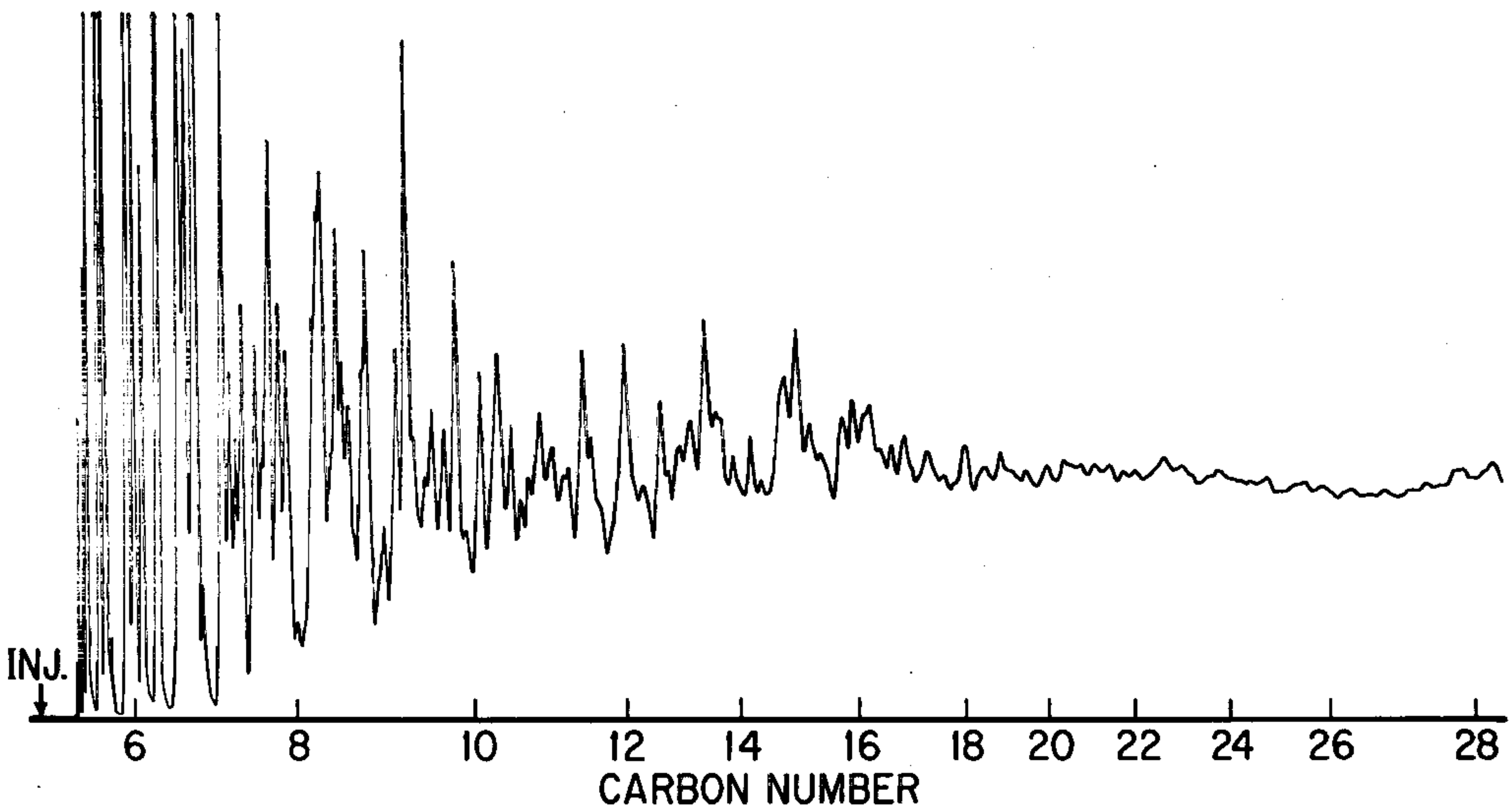
Samples were obtained of oils from four different producing formations in the Santa Barbara Channel. As listed in Table 1, these oils are identified by their source rock. In order of increasing depth and geologic age, these formations are the Sisquoc, Monterey, Rincon, and Vaqueros.

Finally, the remaining oil sample listed in Table 1 was collected from the new seepage area on 27 June for the purpose of determining if the composition of the seep oil was remaining constant.

In preparation for these more thorough and detailed analyses, new gc columns were prepared, and tested for their ability to resolve the n-C_{17}: Pristane and n-C_{18}: Phytane doublets as suggested by Kreider (1971). These tests showed that the new columns were significantly more sensitive than those used in the preliminary analyses. The atomic absorption spectrophotometer was also recalibrated to ensure reliable metal analyses.

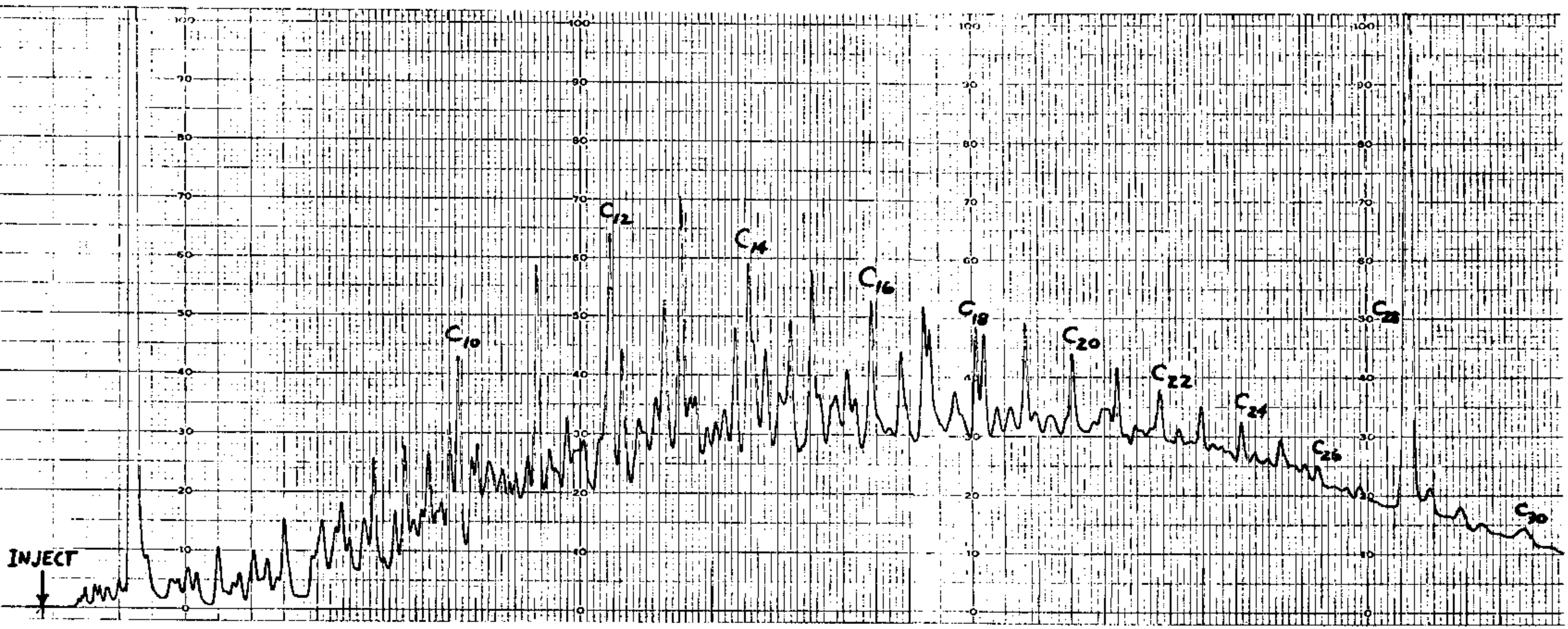
All of the oils were analyzed in their "fresh" state, i.e., no laboratory weathering or distillation was done to remove the more volatile components. Figure 2 shows a chromatogram of the IV seep oil, and Figure 3 shows the oil from the new seep. The difference is striking. As found in the preliminary analysis, the most pronounced difference is the presence of significant amounts of identifiable normal paraffins in oil from the new seep.

Another difference, though not necessarily characteristic, is the absence of volatile components in oil from the new seep. Figure 4 illustrates the effect of progressive stages of evaporation on the composition of IV seep oil. The upper trace corresponds to a 4.5 percent loss in weight, the middle trace to a 10.4 percent loss, and the lower trace to 16.0 percent



<u>Figure 2</u>

Chromatogram of oil from the natural seep at Isla Vista.



<u>Figure 3</u>

Chromatogram of oil from the area of new hydrocarbon upwelling.

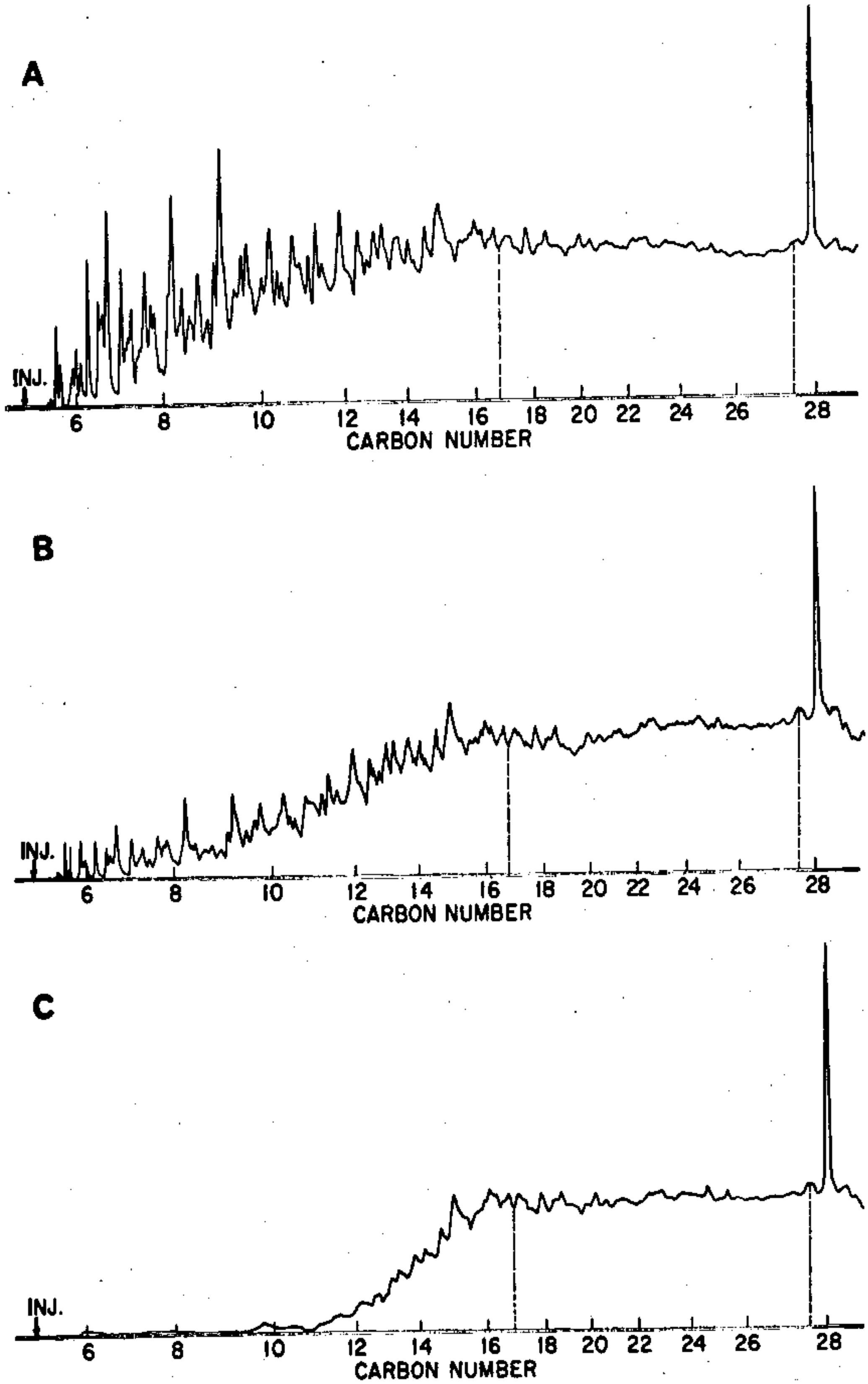


Figure 4

Chromatograms of oil from the IV seep showing progressive stages of evaporation. Sample A has lost 4.5 weight percent, Sample B 10.4 percent, and Sample C 16.0 percent.

loss. All of the other oils analyzed for this report (as well as crude oil analyzed in previous studies) contained measurable amounts of volatile components, i.e., their chromatograms up to n-C_8 - n-C_{10} resembled that shown in Figure 2. Comparison of Figure 3 with Figure 4 would thus indicate that approximately 10 percent of the oil from the new seep was lost by evaporation.

Since all the samples obtained at the new seep were collected from the ocean surface, it may be possible that natural weathering phenomena were responsible for the decrease in volatiles. On the other hand, atmospheric evaporation takes a certain amount of time to occur. Samples 2, 3, and 4 in Table 2 were reported to have been collected immediately over the site of upwelling, and in sea and wind conditions that were reasonably calm. Therefore, it may be possible that the absence of volatiles is indeed a characteristic of this seepage oil.

Results of the metal analyses are presented in Table 2. These results also show that the new seepage oil is noticeably different from oil originating at the IV seep (which is characteristic or typical of all the previously existing seeps in the Coal Oil Point area). They also bear out the suspicion that our preliminary finding of an abnormally high nickel concentration was in error. The final row in Table 2 presents the average metal content of the new seep oil under the assumption that the oil samples analyzed had undergone a 10 percent weight loss by atmospheric evaporation.

The question of whether any changes had occurred in the new seep oil during the first three weeks or so of upwelling is resolved in Figure 5. Although the chromatogram of the 5 June sample is not quite as sharp as the 27 June sample, there appears to be little doubt that the two oil samples are identical. This is also borne out by the metal analyses shown in Table 2.

Addressing now the topic of similarity between oil from the new seep and produced oils from various formations in the general vicinity, Table 2

TABLE 2 RESULTS OF TRACE METAL ANALYSES

Oil Sample	Ni(ppm)*	V(ppm)*	Ni/V
IV Seep	115	245	0.47
New Seep (5 June)	59	137	0.43
New Seep (27 June)	61	140	0.43
Sisquoc	44	110	0.40
Monterey	65	158	0.41
Rincon	12	<10	-
Vaqueros	5	<10	-
New Seep (adjusted for 10% weathering loss)	54	125	0.43

* The accuracy of these measurements is estimated to be plus or minus 10 percent.

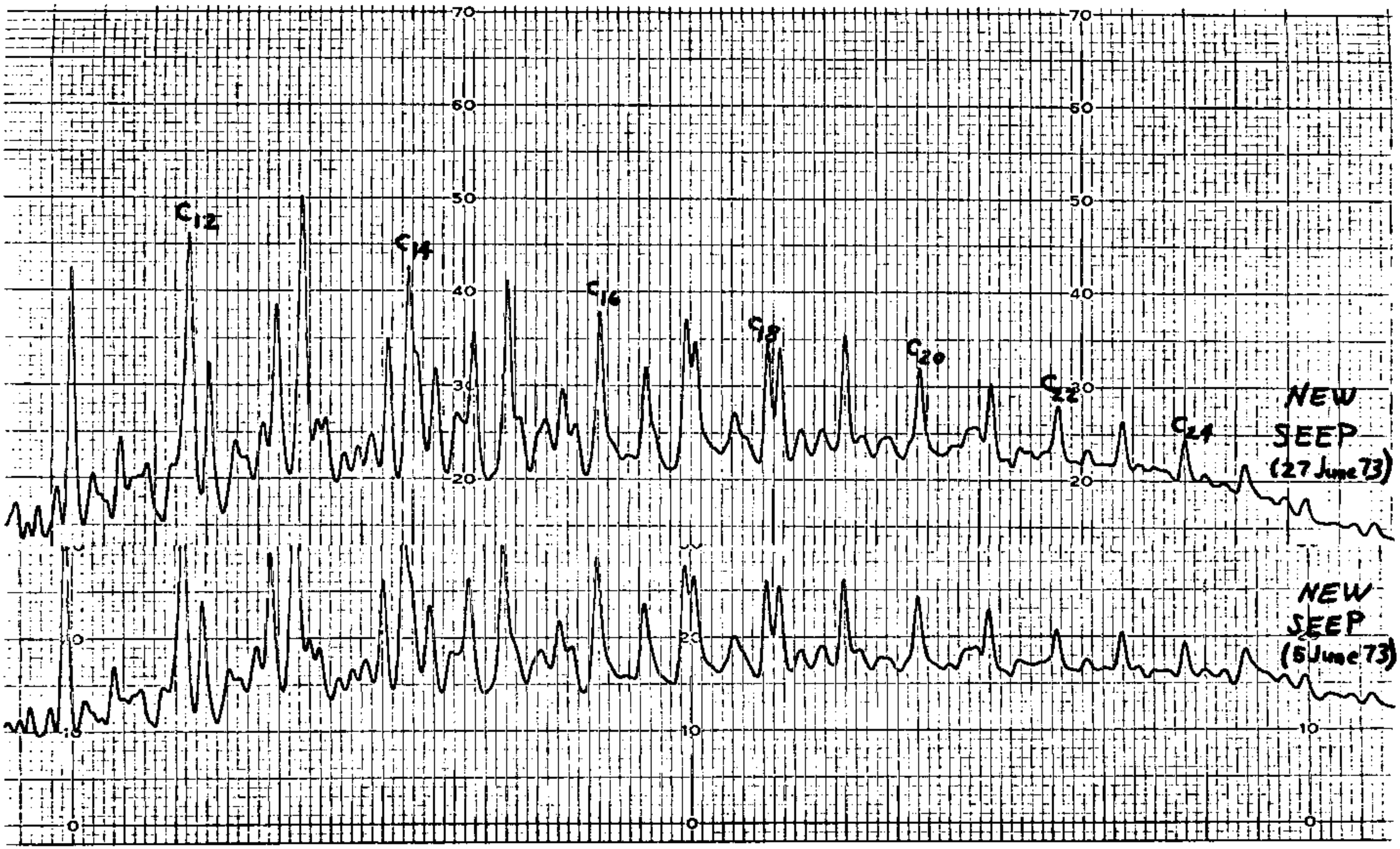


Figure 5

Comparison of chromatograms of oil from the new area of seepage collected on 5 June and 27 June 1973. Note that the upper portion of the C_{11} to C_{15} peaks in the lower trace have been truncated.

shows that the deeper Rincon and Vaqueros formations can be ruled out as potential sources by virtue of their very low concentrations of nickel and vanadium. Oils from the shallower Sisquoc and Monterey formations, however, do show considerable similarity to the new seep oil in their metal content.

As a more detailed means for comparison, Figure 6 shows the central portion (C_{11} to C_{27}) of chromatograms for each of the three oils, i.e., Sisquoc, New Seep, and Monterey. Inspection of Figure 6 shows all of the oils to have the same features in general, but to differ, each from the other(s) in some of their detail. The general similarity is illustrated in Figure 7 where the ratio of n-paraffin peak height to C_{20} is plotted against the carbon number. In this plot it should be noted that peak heights were not corrected for possible drifts in baseline due to column bleed. While this effect is believed to be small, there nevertheless is some uncertainty in the results for the higher carbon numbers.

On the other hand, it can be observed from Figure 6 that the structure between C_{11} and C_{12}, and between C_{13} and C_{14} is noticeably different for each of the three oils. Similarly, the new seep oil resembles Monterey in the region C_{12} to C_{13}, while both differ from the Sisquoc. Conversely, in the region C_{15} to C_{16}, the new seep oil resembles Sisquoc and both of these are different from Monterey.

Another point of comparison is provided by examining the structure of the doublets at n-C_{17} and n-C_{18}. These doublets are produced by the presence in the oil of isoprenoid hydrocarbons, pristane and phytane. Recent studies on the origin, migration, and accumulation of oil and gas (Colombo, 1971) have shown that the relative amounts of these isoprenoids bear a definite relationship to the age of the host rock in which the oil is found.

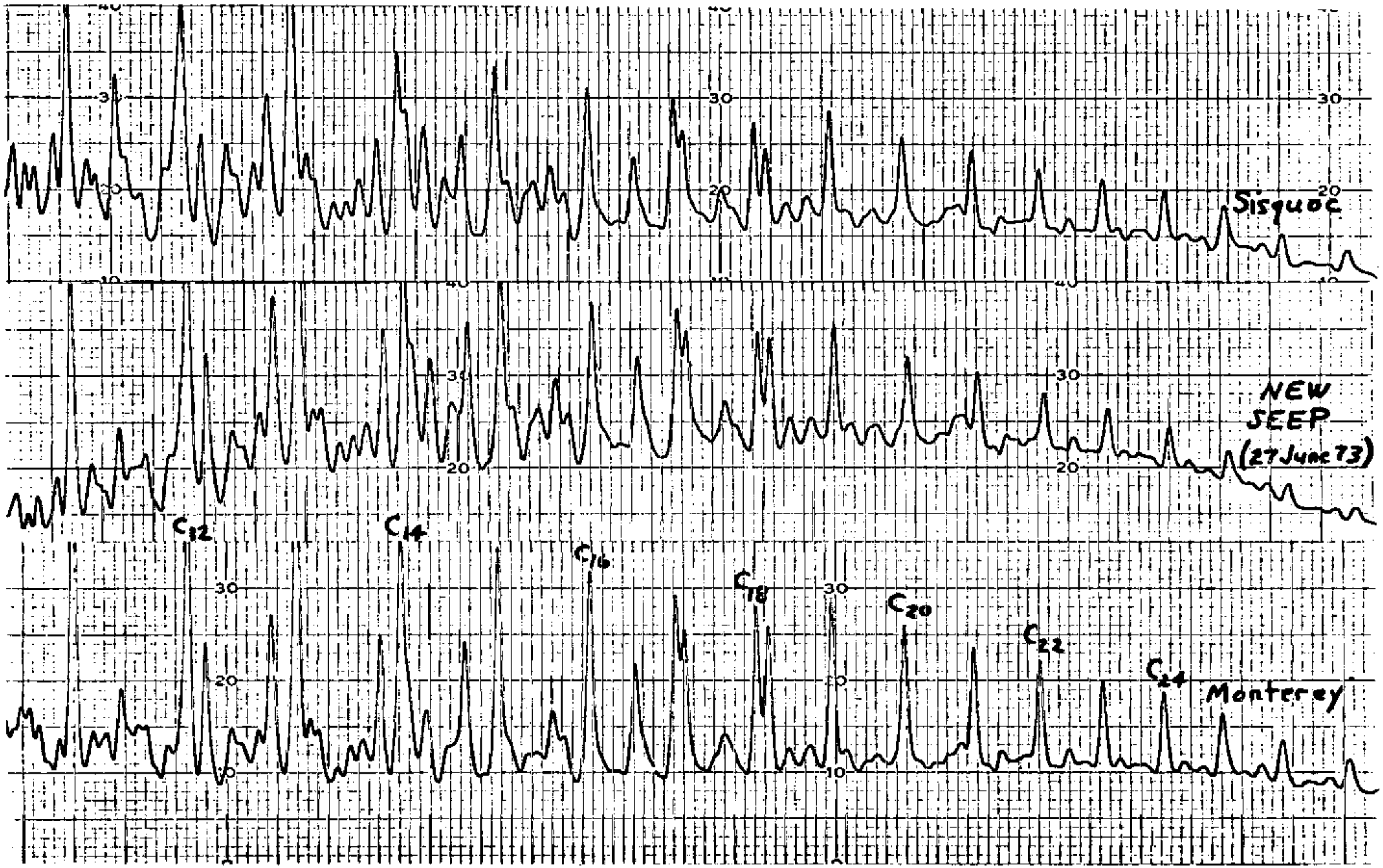


Figure 6

Comparison of chromatograms of oil from the new area of seepage with produced oils from the Sisquoc and Monterey formations in the Santa Barbara Channel. Note that the upper portion of some of the peaks between C_{11} to C_{15} have been truncated.

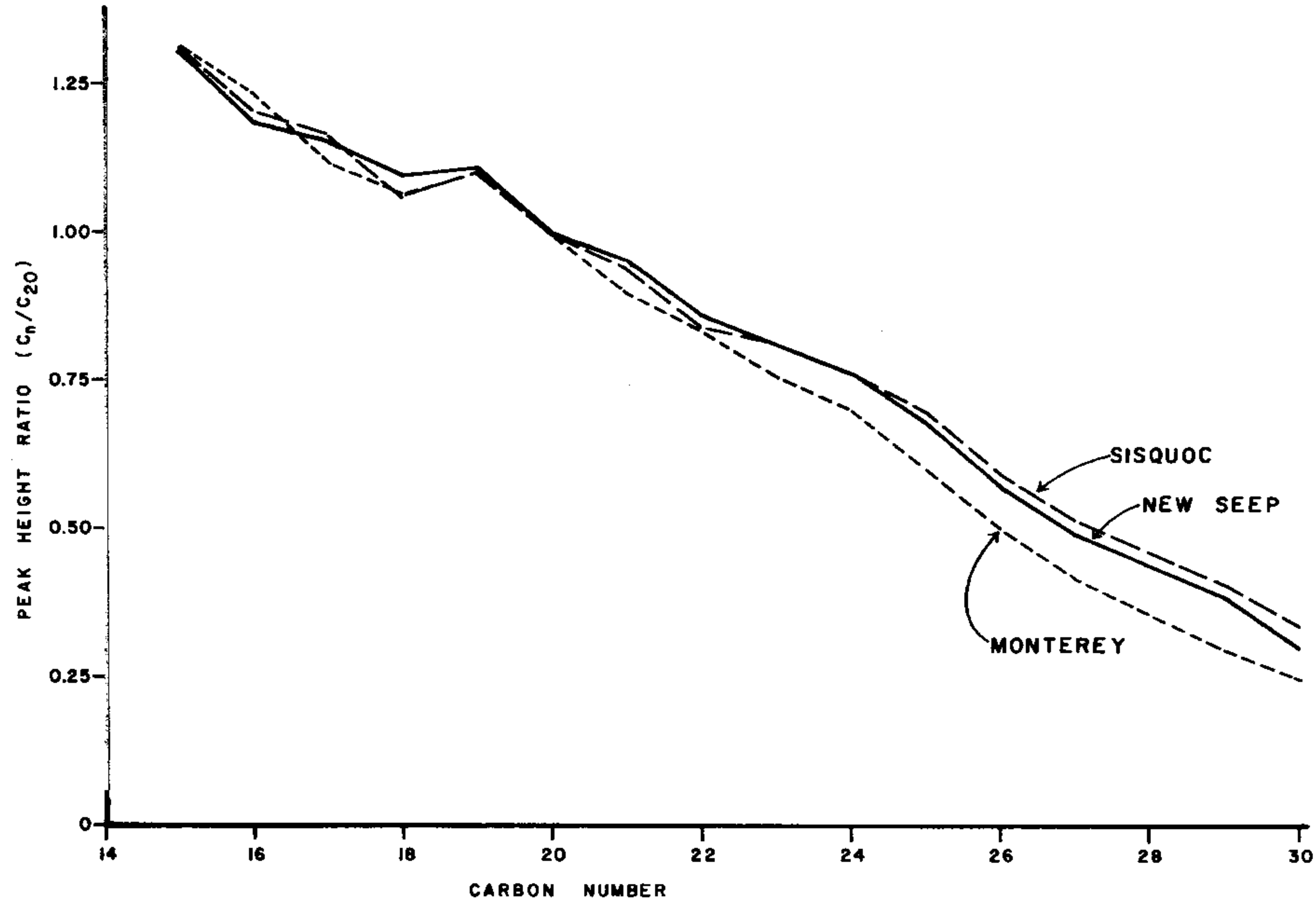


Figure 7

Comparison of n-paraffin profiles of oil from the new area of seepage with produced oils from the Sisquoc and Monterey formations in the Santa Barbara Channel. Note that peak heights have been normalized with respect to carbon number 20.

In Figure 8, the structure of these doublets, as determined from normalized chromatograms, is shown in bar graph form for the Monterey and Sisquoc oils and for the new seep oil. The characteristic features are the relative heights of the n-paraffin and isoprenoid peaks, and the minimum between them. It should be pointed out that these features are a very strong function of the experimental conditions of analysis, and therefore should not be interpreted on an absolute basis. Nevertheless, since each of the oils was analyzed at the same time under identical conditions, and the features shown in Figure 8 were reproducible to within ± 2 percent, the differences among oil samples indicate that each originates from a different geological formation.

Summary

Analysis by gas chromatography, and measurement of trace concentrations of nickel and vanadium by atomic absorption spectrophotometry were performed on oil from the area of new hydrocarbon upwelling in the Santa Barbara Channel. Results of these determinations were then compared to similar analyses made on oil from previously existing natural seeps near Coal Oil Point, and from produced oils originating in the Sisquoc, Monterey, Rincon, and Vaqueros formations of the Santa Barbara Channel.

The major findings from these comparative analyses are summarized below:

1. The chemical composition of oil from the new area of hydrocarbon upwelling is significantly different from oil originating at the nearshore natural seeps in the vicinity of Coal Oil Point.
   a) Compared to oil from the Coal Oil Point region, the new seep oil contains approximately one-half the concentration of nickel and vanadium.

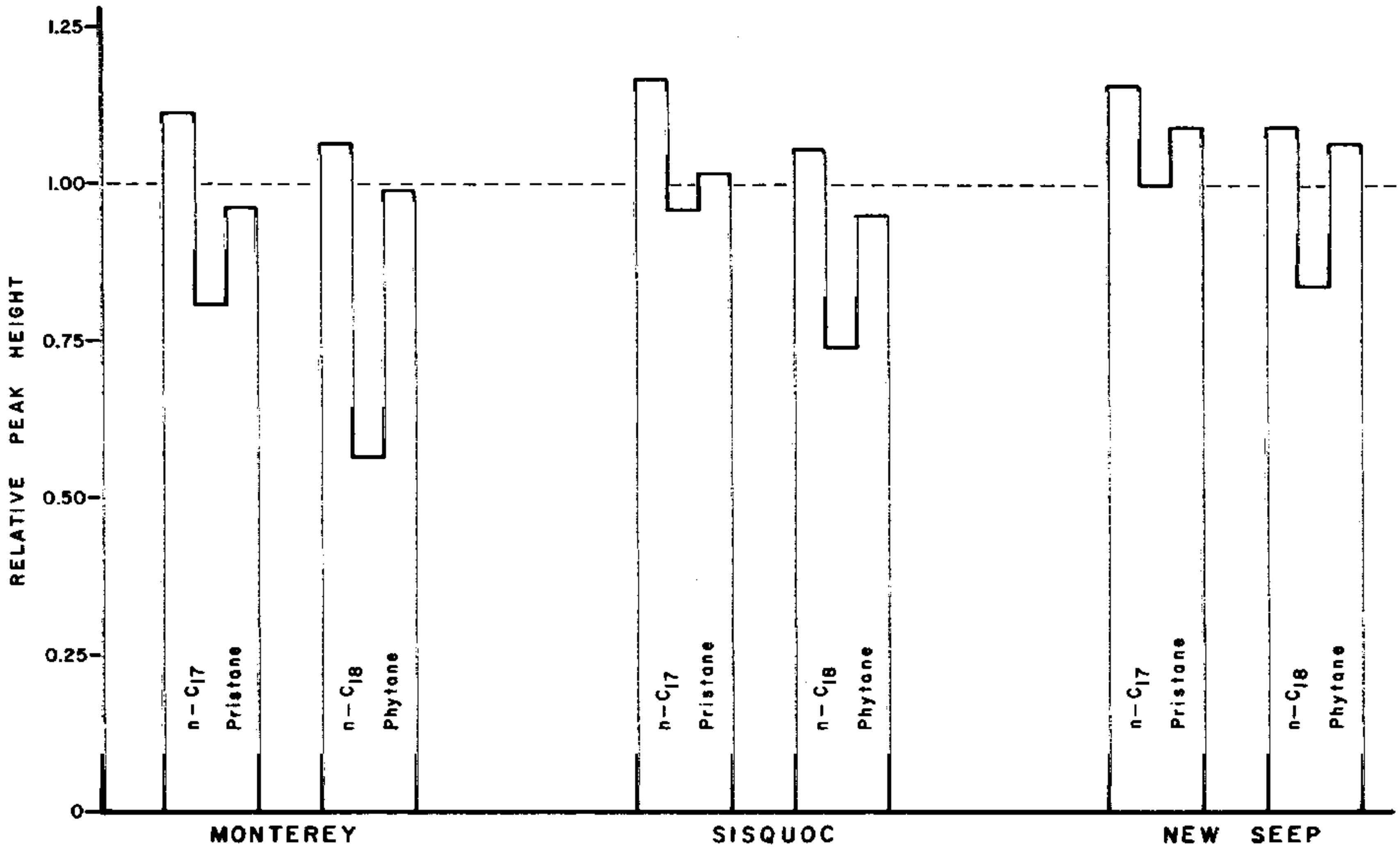


Figure 8

Schematic comparison of $n\text{-}C_{17}$/Pristane and $n\text{-}C_{18}$/Phytane doublets in chromatograms of oil from the new area of seepage with produced oils from the Sisquoc and Monterey formations in the Santa Barbara Channel. Peak heights shown are normalized with respect to carbon number 20.

b) Coal Oil Point seepage oil is highly naphthenic in its base, while oil from the new seep contains significant amounts of normal paraffins out to carbon number 30 and beyond.

2. Oil from the new area of seepage is significantly different from produced oils originating in the Rincon and Vaqueros formations of the Santa Barbara Channel.

3. Oil from the new seepage area is generally similar to oils produced from the Sisquoc and Monterey formations of the Santa Barbara Channel, both in its concentration of nickel and vanadium, and in its gc fingerprint. However, detailed inspection and comparison of the chromatograms made during this study indicate that neither of the production oils analyzed were identical to oil from the new area of seepage.

4. The site of the new hydrocarbon upwelling is located in the middle of an area where, during the period 1946 to 1947, previous oil and gas seeps of natural origin have been reported.

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