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THE WEST FALMOUTH OIL SPILL

Data Available in November, 1971

II. Chemistry

by

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TECHNICAL REPORT

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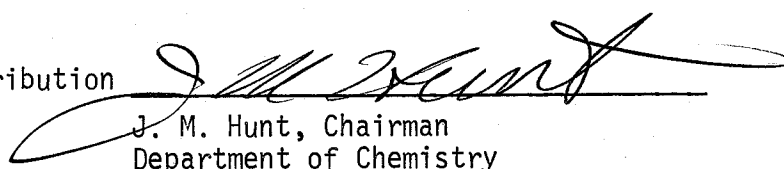

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INTRODUCTION

A spill of 650,000 to 700,000 liters of #2 fuel oil in Buzzards Bay, Mass., USA, on September 16, 1969, has severely polluted the coastal waters, the marshes, the offshore sediments and the shellfish resources of Falmouth and of Bourne, Mass. In preliminary publications and reports (Blumer et al. 1970, b,c,d, 1971a) we have discussed the chemical and biological data available during the first few months after the accident. The present report documents the continuation of our analytical effort; we include analyses of stations that had not previously been covered and present the data that were available by October, 1971.

Three distinct, though partly overlapping, series of events followed the spill. First, within the first few hours or days after the accident, there was a very heavy kill of those organisms which came into contact with the oil. It extended over all phyla and over benthic and intertidal organisms. Next, within weeks or months after the spill, the oil pollution spread to areas that had not been immediately affected; and the kill extended, though in some cases more slowly than the spread of the oil, to outlying areas. Oil entered the marine food web and made the shellfish resources of our area unacceptable to human nutrition. The oil showed an unexpected persistence in the sediments and in marine life, especially in view of its relatively low boiling range and of earlier assertions that fuel oil pollution was transitory in nature and without long-term consequences. For considerable time after the spill, the oil pollution of the sediments prevented the resettlement by the original fauna. Now, degradation of the oil has become evident. Biochemical and physical

processes lead to a gradual reduction of the oil content of the polluted sediments. Concurrent with the degradation, there has been a gradual reduction in the immediate toxicity of the oil in the sediments. This has permitted resettlement of the polluted region first by the most resistant opportunists and later by a more varied and more normal fauna. However, oil-derived hydrocarbons have remained at all stations during the entire two year span for which data are now available, and it appears that the life span of pollution, even by a low boiling fuel oil must be measured in terms of many years.

The eventual aim of this study is the documentation of the effects, the persistence and the eventual disappearance of pollutant hydrocarbons from a relatively small spill in a limited and previously clean coastal area. Of necessity, most of our analytical effort in the past was aimed at a survey of the extent of the oiling of the sediments and of some of the commercially important animals. As the degradation proceeds, we expect to devote a greater effort to a more detailed chemical analysis of the hydrocarbons remaining in the environment in order to define and understand the modes of degradation and to correlate chemical analyses with biological data. Parallel investigations on the weathering of different oils under other ecological and climatic circumstances are under way here and should, in combination with the West Falmouth study, give a more realistic assessment of the environmental hazard and persistence of crude oil than has been available until now.

METHODS

The methods used were essentially the same as those described in our previous reports. An effort was made to carry out all gas chromatograms on the same Apiezon L column in order to facilitate comparison between chromatograms. However, that column failed by mid-1971 and was replaced by a similar column. The resulting improvement in resolution is noted in the most recent chromatograms (e.g. Station 31, August 1971).

The aromatic hydrocarbon fraction of some sediment extracts was isolated by column chromatography. About 30-45 mg of total hydrocarbons that were recovered as described by Blumer et al., 1970 b,c,d, were separated on a 1 ml column of silica gel, deactivated with 5% water. Pentane was used as the eluent in fractions of 0.7, 0.5, 1, 2 and 2 ml, followed by 4 ml pentane with 10% benzene. Fraction 1, corresponding to the column dead-volume, was devoid of sample; fraction 2 contained saturated hydrocarbons; the aromatics were eluted in fractions 4 and 5. The mixed saturated-aromatic fraction 3 was rechromatographed on a column of the same dimensions with pentane (0.7, 0.5, 0.5, 0.5 ml) elution. Fractions 2 and 3 contained additional saturates while fraction 4 contained aromatics. The combined aromatics were subjected to mass spectral analysis (CEC-DuPont 21 - 104 mass spectrometer, magnetic scan, 1600 V accelerator voltage, beam current 40 ua, 8 V ionization potential).

In the low voltage mass spectra of the aromatic fraction, all peaks belonging to the benzene, naphthalene, tetrahydronaphthalin- and diphenyl-series were normalized to a total peak intensity of 1000. The plots

(Fig. 4) give the relative peak distributions within the aromatic-series, without resolving the individual isomers and without correction for different mass spectral sensitivities between and within series. The plots are comparable and can be interpreted in terms of relative concentrations and of changes in relative composition but not in terms of exact amounts.

THE DISTINCTION BETWEEN INDIGENOUS AND POLLUTANT HYDROCARBONS

The identification and quantitative determination of hydrocarbon pollutants is more difficult than that of purely synthetic chemical pollutants. There, eg. in the case of chlorinated hydrocarbon pesticides, pure chemicals can be isolated for which no natural background exists; therefore, the analytical measurement defines directly the pollution level.

This is not the case with hydrocarbons. All organisms and all recent geological samples contain hydrocarbons of biochemical origin. These have to be determined and an allowance has to be made for their presence in the identification of hydrocarbon pollutants. Failure to detect this natural hydrocarbon background in environmental samples usually suggests the use of samples or of methods which are inadequate for the detection of hydrocarbon pollutants at low concentration levels.

Fortunately, sufficient structural and compositional differences exist between biologically and pollution-derived hydrocarbons to permit the qualitative distinction and their detection in each other's presence.

The exact quantitative determination of petroleum pollution in environmental samples is further complicated by the compositional complexity of crude oil. In analytical separations of petroleum hydrocarbons, losses of low or high boilers are almost unavoidable and the separation of the more polar petroleum fraction from those biochemicals with which it overlaps in polarity is difficult. Fortunately, in the case of the #2 fuel oil spilled in Buzzards Bay these difficulties are minimized; the narrow structural and boiling point range permits an easy separation of the oil from the lipids and a recovery without substantial losses of high and low boilers.

The identification of the fuel oil contamination in the samples from West Falmouth is based on several simultaneous observations:

1. Hydrocarbon Concentration in the Sediments

Biologically derived hydrocarbons occur in all recent sediments in amounts which depend on the type of source material, the total organic content and the degree of preservation, among other factors. Because of the variability of the indigenous hydrocarbon concentrations, weights of hydrocarbon extracts are indicative of pollution only if they exceed significantly, in a particular area, the range of the normal environmental background.

The natural hydrocarbon background level in the sediments at Buzzards Bay can be estimated in two ways. Table I lists analyses of samples taken before the arrival of the pollution, outside of the polluted area or within the polluted area in a core at a depth where gas chromatography shows the absence of fuel oil hydrocarbons. The average hydrocarbon content of these samples is 7.1 mg/100 g dry sediment.

In many of the polluted samples analyzed in the course of this study, especially during the present year, gas chromatograms demonstrate the presence of pollutants at concentrations comparable to, or below that of the indigenous sedimentary hydrocarbons. In these cases, the total measured hydrocarbon content is but slightly higher than the hydrocarbon background level. An inspection of the data of Table II for the first part of 1971 suggests that the offshore stations, with the exception of the heavily polluted river stations and Stations 31 and 10, contain indigenous and pollutant hydrocarbons averaging about 5 mg/100 g sediment. Thus, the average hydrocarbon background in Buzzards Bay appears to lie close to 5-7 mg/100 g sediment and it seems to exceed rarely 10 mg/100 g dry sediment.

Because of the variability of the indigenous hydrocarbon content, hydrocarbon weights in the sediments at West Falmouth, if considered alone, are indicative of pollution only if they exceed 10 mg/100 g dry sediment, such as at the river stations, at the offshore Station 31, and in some samples, at Station 10.

In spite of these limitations, hydrocarbon weights, even at low levels, are important if used in conjunction with gas chromatography for the study of trends in the relative concentration of biologically and pollution derived hydrocarbons.

In terms of their environmental role and toxicity, the indigenous and the pollutant hydrocarbons must be considered separately. The indigenous hydrocarbons are normal components of a stable environment; few, if

100 ppm

any, are toxic, and recent research has suggested that some may have well defined biochemical roles. Most of the hydrocarbon pollutants in fossil fuels are foreign to the marine environment and numerous components are toxic to living organisms.

A polluted sediment contains indigenous and generally harmless hydrocarbons in addition to the generally harmful hydrocarbon pollutants. The toxicity of the fossil fuel component is largely independent of the presence and of the concentration of the indigenous hydrocarbons; the petroleum hydrocarbons retain their potential for adverse biological effect, even if they are present at levels below the natural hydrocarbon background. Thus, whether the pollutants are present at higher or lower concentrations than the indigenous hydrocarbons is principally irrelevant in consideration of the toxicity.

2. Boiling Point Distribution

The fuel oil spilled at West Falmouth has a boiling range of 170° - 370° C. The normal paraffins range from about n-decane to n-docosane with a maximum in the C_{14} - C_{15} region. A large number of isomeric and homologous hydrocarbons are present whose boiling points overlap; in the gas chromatograms, which are graphic expressions of the boiling point distribution, this results in a broad, unresolved background over which are superimposed the resolved or partly resolved peaks of the normal and iso-alkanes and of some other homologous series.

A similar boiling point distribution and predominance of complex homologous series from about C_{10} - C_{22} is observed in the polluted sediments and organisms in Buzzards Bay, but it is absent at greater distances

from the site of the spill.

Our identification of the fuel oil pollution in this area is based on several criteria, which are discussed in this section of the report. Among others, one of these criteria is the boiling point distribution of the sedimentary hydrocarbons within the fuel oil boiling range. In informal discussions it has been suggested to us that the existence of a hydrocarbon "envelope" (Figure 7) in the fuel oil boiling range might be a normal feature of the sedimentary hydrocarbons, rather than being associated with residues of fuel oil from this spill. This, then, would make doubtful the ability to recognize the fuel oil pollution in this area.

It would be of the greatest importance to petroleum geochemists to find in unpolluted recent sediments hydrocarbons which have all the characteristics of #2 fuel oil, including the restriction to the particular boiling range. In spite of world wide analyses of recent sediments, such evidence does not exist. Thus, there is no support for the suggestion that a boiling point envelope in the fuel oil boiling range is a normal feature of sedimentary hydrocarbons. We wish to summarize the additional evidence that leads us to reject this assumption, specifically for the Buzzards Bay sediments, but also for other recent marine sediments.

- 1) Hydrocarbons showing the 170 - 370⁰ boiling envelope are found within Buzzards Bay only within the area affected by the 1969 spill. This feature is absent in control samples collected during this investigation, as well as in earlier analyses from this area (Clark and Blumer, 1967).

- 2) The magnitude of the envelope decreases radially outward from the focal point of the heaviest pollution.

3). At one and the same station, the magnitude of this envelope decreases in time as weathering reduces the pollution level.

4). In the core taken at the heavily polluted Station 31, the 170 - 370°C boiling envelope occurs only in the uppermost three inches of sediment. Hydrocarbons are present below this level but show the boiling point distribution common to unpolluted recent sediments (Stevens et al., 1956).

5). Similarly, cores from the intertidal region of Wild Harbor River (Blumer et al., 1970d) show the envelope in the uppermost, but not in the lower section. The only exception comes from the coarse sand in the bottom section of core #2, which contains undegraded oil, whose major and minor components correlate with those present in the spilled oil.

6). The literature contains numerous analyses of hydrocarbons from recent marine sediments and from marine plants and animals. None show an exclusive hydrocarbon envelope in the 170 - 370°C boiling range.

7). The biochemical processes, which are responsible for the formation of the hydrocarbons contained in recent unpolluted sediments, are specific, aimed nonrandom processes. They generate a simple assemblage of products. In all cases where hydrocarbons of marine organisms or of recent (unpolluted) sediments have been studied by medium resolution gas chromatography (columns of about 3000 theoretical plates), the hydrocarbons in the range to at least C₂₂ have been resolved into individual compounds, no continuous unresolved background was found, especially not in the exact 170 - 370° boiling range. Above C₂₂ a more complex hydrocarbon mixture,

not fully resolved by medium resolution GC may be present, simply because of the rapidly increasing number of possible isomers; however, this has not been demonstrated conclusively for conditions that excluded sample contamination and the formation of artifacts.

8). On the other hand, the diagenetic processes involved in petroleum formation at depth randomize the sedimentary organic matter through inter- and intra-molecular scrambling and produce a hydrocarbon mixture of enormous complexity, which cannot be resolved completely by present medium or high resolution gas chromatography.

9). The medium resolution gas chromatograms of the sediment extracts from the affected areas in Buzzards Bay show the presence in the fuel oil boiling range of an incompletely resolved hydrocarbon mixture, containing among other components, extended series of homologous and isomeric branched, alicyclic and aromatic hydrocarbons. Thus, the hydrocarbon composition in these Buzzards Bay sediments, within this boiling range, is unlike that of recent unpolluted organisms or sediments; on the other hand, it corresponds in complexity to the hydrocarbon composition of all crude oils, formed from organic matter at depth.

3. Hydrocarbon Type Distribution

The hydrocarbons in living organisms are relatively simple and few in number; one or a few components may exceed all others by orders of magnitude. In general, normal and iso-alkanes and alkenes predominate, cyclo-alkanes, cycloalkenes and especially aromatics are in the minority.

If present, aromatic hydrocarbons occur in small amounts and are limited to a small number of unsubstituted rings or to compounds with a low degree of substitution.

Extensive analyses exist of the hydrocarbons in benthic and planktonic plants and animals of the Western North Atlantic (Blumer, 1967; Blumer and Thomas, 1965a,b; Blumer et al., 1963, 1964, 1969, 1970a; Clark and Blumer, 1967; Youngblood et al., 1971).

In contrast, crude oil and oil products are extremely complex mixtures, containing many homologous series with most adjacent members occurring at approximately the same concentrations. Olefinic hydrocarbons are absent in crude oil and in straight run distillates but they may be present in cracked products. Large amounts of varied substituted branched, cyclic and aromatic hydrocarbons exists, often with mixed structures.

Thus, a large number of potential parameters exists for the distinction between the indigenous hydrocarbons of recent sediments and the fossil fuels. Usually, the extent of the analytical effort rather than the number of inherent differences limits the analytical differentiation. A few of the parameters which distinguish the fuel oil from the indigenous hydrocarbons in the sediments of Buzzards Bay will be discussed:

a. Isoprenoid Alkanes: In recent marine organisms pristane predominates within the isoprenoid alkanes; phytane and farnesane may be present at lower concentrations, but the homologues below farnesane and from C_{16} - C_{18} have never been detected. In crude oil, on the other hand, an unbroken series extending to the C_{21} isoprenoid occurs; the ratios between individual members are variable and are characteristic for different crude oils. Correspondingly, the oil spilled at West Falmouth and the residual oil in the sediments contain the isoprenoid alkanes from C_{13} to at least C_{20} (the

C₂₁ homologue is not separated from n-nonadecane on our Apiezon L columns). The similarity in the relative abundance of the isoprenoid alkanes permits the correlation of the oil in the sediments with the spilled oil and confirms the identity of the oil remaining at the different stations for a long period after the spill.

b. Olefins: Attempts to hydrogenate the hydrocarbons recovered from the sediments with high hydrocarbon content lead to no observable changes in the gas chromatograms in the region below C₂₀. This demonstrates the absence of major olefinic contributors in these samples. In biogenic material, on the other hand, olefins would almost certainly be present in that range. Many chromatograms from the less polluted stations show, immediately above n-eicosane, one or several large components. That these exceed in amount the adjacent compounds by a large margin immediately suggests their biochemical derivation. That they are of an olefinic nature, as hydrogenation demonstrates, supports this.

c. Aromatic Hydrocarbons: Mass spectral analysis of the aromatic fraction from sediment extracts at low ionization potential shows the presence in fuel oil, in the polluted sediments and in contaminated shellfish, of continuous homologous series of substituted aromatics. Thus, we have identified in these samples benzenes substituted with 4 to 13 carbons, naph-

thalenes substituted with 0 - 9 carbons and diphenyls with 0 - 7 carbon atoms. These homologous series of substituted aromatics are common to crude oils and are not present in living organisms or in recent sediments. Again, this ties the hydrocarbons in the sediments at West Falmouth to the spilled oil.

4. Biologically and Pollution-Derived Hydrocarbons in a Core at Station 31:

Analyses of consecutive sections from a core taken at Station 31 in September 1971, two years after the spill, demonstrate particularly well the differences between pollutants and indigenous hydrocarbons and the persistence of their distinguishing features (Table III and Fig.5).

Chromatogram 'a' represents the uppermost inch of the core and agrees with the chromatograms from grab samples taken at the same station on and before September, 1971. The chromatogram shows the presence of partially degraded fuel oil; its boiling range still corresponds to that of the original oil. Within this boiling range, almost the entire straight chain hydrocarbon content has been depleted, presumably by biochemical processes. The large unresolved boiling point envelope is due to the presence of the many overlapping homologues and isomers, especially within the cyclic and aromatic hydrocarbons, which are characteristic of fossil fuels. Superimposed over this background are partially or fully resolved peaks; the most prominent ones are those of pristane, of phytane and of the homologous C₁₈ isoprenoid, in order of decreasing amounts.

The secondary rise of the chromatographic envelope at carbon numbers above C₂₅ in this and other highly polluted samples appears due, almost entirely, to column bleed. This is evident from chromatograms from the same

station run with relatively larger aliquots and at lesser recorder sensitivity. Thus, no such rise is evident in the chromatograms from Station 31 through August, 1971 (Figure 14).

Because of the rapid decrease in hydrocarbon content with depth, increasingly large aliquots of the total extracts of the deeper samples were chromatographed and a higher gas chromatographic recorder sensitivity was used; this explains the higher background, due to column bleed, in Figure 5 b, c and especially in d (Table III).

Chromatograms from the deeper section of the core (Figure 5c and d) show a picture that is typical for the indigenous hydrocarbons of recent marine sediments. The amounts of normal paraffins increase from n-heptadecane, whose presence is barely perceptible, to, and probably beyond, the analytical limit of the columns used here. Odd carbon-number paraffins predominate strongly; thus the C_{25} and C_{27} alkanes exceed the adjacent even carbon number homologues by a factor of five to six. (The conventional carbon preference index over the C_{20} to C_{32} range was not calculated because of the apparent mixed composition of some peaks). This odd carbon number predominance in the higher boiling paraffin range is characteristic of young marine sediments (Stevens et al., 1956), including those of Buzzards Bay (Clark and Blumer, 1967) and of plant waxes (reviewed by Clark, 1966); in crude oil it is found rarely and is much less pronounced. Chromatograms of the polluted sediments from West Falmouth within the first months after the spill show that no odd carbon predominance was present in the spilled fuel oil.

The paraffin concentration in the deeper section of the core increases steeply above C_{21} ; the boiling range of the fuel oil on the other hand lies below that. Numerous minor components are present, notably the principal low boiling peak just before n-heptadecane, possibly one of the $n-C_{17}$ olefins which are common in marine plants.

Below three inches depth this core apparently contains no, or only small amounts of fuel oil derived hydrocarbons. The principal arguments are:

1. The high odd carbon predominance which extends here throughout the entire boiling range of the sedimentary hydrocarbons. In the fuel oil, odd and even carbon number paraffins occur at comparable concentrations.
2. In this lower core section, hydrocarbons boiling above the fuel oil range predominate.
3. Pristane, the principal resolved component of the partly degraded fuel oil is a minor component of the lower core sections, if present at all.
4. The lower core sections, in contrast to the uppermost part, show no unresolved envelope in the boiling range of the fuel oil.
5. Within the fuel oil boiling range, the minor hydrocarbon peaks ("fingerprints") correlate poorly between the contaminated top and to the two bottom sections of the core.

The core sections from 1 - 3 inches (Figure 5b) shows mixed hydrocarbon derivation from recent biochemical sources and from fuel oil. It is intermediate also in terms of its hydrocarbon content (Table III). Again, the

principal arguments are:

1. Below C_{21} no strong odd carbon predominance is found and already $n-C_{22}$ is more abundant relative to the adjacent homologues than in the lower core sections. The presence of biologically derived hydrocarbons, on the other hand, is evident from the high odd carbon predominance above C_{22} .

2. Hydrocarbons within the fuel oil boiling range are more abundant here than in the lower core sections; also, they exceed in quantity the higher boiling biologically derived hydrocarbons.

3. Phytane from oil is a major component together with the adjacent C_{19} and C_{18} isoprenoids; as in the fuel oil, the pristane/phytane ratio is close to unity. In unpolluted sediments, pristane predominates.

4. This core section shows the unresolved hydrocarbon envelope which is characteristic of the fuel oil.

5. The correlation of the minor hydrocarbon peaks with those in the top section of the core and in the fuel oil is excellent.

The analyses show that fuel oil at Station 31 has penetrated the sediments only to approximately 3 inches. This suggests little if any sediment reworking by physical or biological agents. Greater penetration was found in the marshes. There, oil derived from the 1969 spill penetrated at least 5 feet below the surface (Blumer et al., 1970c). The greater penetration of the marsh sediments relative to those offshore is due to their greater permeability and to the fluctuations of the water table with tidal and weather cycles.

As in the marshes, bacterial degradation at Station 31 is slower below than at the surface. In view of the known slow rate of hydrocarbon degradation under anaerobic conditions, this is not unexpected.

The presence of less degraded oil just below the sediment surface has biological implications. In spite of the increasing degradation and gradual detoxification of the oil at the sediment surface, a reservoir of less degraded oil exists just below it. Even when the repopulation of the sediment surface becomes possible, burrowing organisms will still encounter a fresher oil at moderate depth.

Our routine offshore samples are collected with a grab which penetrates 4-6 inches of sediment. To obtain reproducible samples we retain only the uppermost inch of sediment for analysis. The agreement between the analyses of the uppermost core section and the grab samples at Station 31 demonstrates that remixing of the sediment does not occur during our routine sampling.

THE ENVIRONMENTAL ALTERATION OF SPILLED OIL ("WEATHERING")

Crude Oil or oil products spilled in nature are altered by evaporation, by dissolution and by bacterial and chemical attack. The gross effects of these four types of processes on the chemical composition of spilled oil can be predicted (Blumer et al., 1970d; Ehrhardt and Blumer, 1972). Conversely, the compositional changes in a spilled oil over an extended period of time can be interpreted in terms of the rates and of the processes that are active in the oil degradation. Thus, observations on spilled oil

samples can yield significant data on the environmental fate of oil; these would be difficult to gather in laboratory experiments.

The investigation at West Falmouth, now extends over more than two years. It provides the longest existing continuous series of observations on persistence and degradation of an oil under environmental conditions in a controlled area that had not been subjected to previous heavy oil pollution. Some of our analytical data will now be discussed in the light of the processes which affect the amounts and the composition of the oil in the polluted area:

1. Quantitative Changes in the Oil Content of the Sediments

The fuel oil in the bottom sediments at Station 31 still exceeds the indigenous hydrocarbon content by more than an order of magnitude, two years after the spill. Because of their high contamination level, these samples are well suited to a study of the quantitative trend in the pollution level.

The analyses (Fig. 1a and Table II) show, after an initial rise between September and October 1969, a stable oil content at Station 31 through December 1969. By March 1970, the oil content at that location had increased more than tenfold and, in spite of gradual degradation since then, it has remained above the 1969 level for two years. The rise in the oil content of the sediments at Station 31 during winter 1969/70 has been interpreted as the result of a heavy influx of undegraded oil from the same spill, most likely from the marshes and their aquifers.

After this event, the oil content at Station 31 decreased, rapidly at first and then more slowly. A cautious extrapolation of the trend at that station suggests that the fuel oil may remain above the detection level for at least another two years, and probably longer.

The quantitative hydrocarbon data alone do not permit deductions on the nature of the processes which are responsible for the depletion of the oil. However, the gas chromatograms (Blumer et al., 1970d) show that the rapid decrease in oil content of the sediments at Station 31 between March and May 1970, is not paralleled by similarly rapid changes in the chemical composition of the oil, which would result from dissolution or bacterial degradation. This suggests that the depletion of the oil in this initial stage is due primarily to release of unaltered oil in particulate form into the water column. Correspondingly, oil films were observed in the vicinity of this station for a considerable time after the spill (Blumer et al. 1969, that report contains an analysis of an oil film from Station 31; Blumer et al. 1970d).

The sediments of Buzzards Bay have a moderate total organic content (Clark and Blumer, 1967 quote a value of 1.1% for a sample taken outside the presently polluted area). Such sediments do not have a particularly great retentive capacity for hydrocarbons. Therefore, it is likely that the very heavy loading with fuel oil observed in March, 1970 (1.2% on dry weight basis) represents a supersaturation of the sediment with oil. At lower pollution levels, the oil can be expected to be retained more strongly by the organic and inorganic matrix of the sediment and depletion would then

result principally from the slower processes of dissolution and gradual biodegradation.

In Wild Harbor River, as at Station 31, the oil content exceeds considerably the level of the indigenous hydrocarbons. The scatter of the analytical data (Table II) is greater than at Station 31, probably because of the greater sediment inhomogeneity. Therefore, average data for River Stations II, IV and V were calculated (Fig.16), they show a similar trend of slowly decreasing oil content as offshore. Again, cautious extrapolation suggests that the oil will remain detectable for at least another two years. It is not clear, whether the apparent rise in oil content at Station IV, from September/October 1969 to December, 1969/April 1970 represents a redistribution of oil within the Wild Harbor River area or statistical scatter.

2. The Degradation of the Straight and Branched Chain Paraffins

Laboratory studies have shown that the degradation of normal paraffins by bacterial concentrates proceeds more rapidly than that of the corresponding branched isomers. Our field observations confirm this. In contrast to laboratory experiments which often show more rapid degradation, but which are difficult to interpret in terms of environmental events, our observations at West Falmouth provide a realistic time scale of the environmental persistence of different hydrocarbon types.

The ratio of n-heptadecane to pristane is a sensitive indicator of the incipient stages of bacterial degradation, at least as long as the multi-branched hydrocarbons (e.g. pristane) are not attacked (Blumer et al., 1970c).

This ratio ($n\text{-C}_{17}/P$) remained nearly constant at Station 31 during the first three months after the spill. (Fig.2). In contrast, at the less heavily polluted Stations 7 and 20, this ratio decreased more rapidly, during the same period. This suggests that - at least in the marine samples - noticeable bacterial attack is delayed in areas where heavy oiling has taken place. By December 1969, a decrease of $n\text{-C}_{17}/P$ is noticed at Station 31 and the gas chromatograms show the decrease of all n -paraffin peaks relative to the adjacent branched chain compounds.

By March 1970, concurrent with the considerable increase in oil content at Station 31, $n\text{-C}_{17}/P$ reverted to its initial value. There are several observations that suggest very strongly that this rise in oil content and the reversal in the extent of biodegradation is the result of repollution with the same fuel oil. No biological processes are known that would produce this specific hydrocarbon mixture. No new large spill was observed in this area during winter, 1969/1970. The chromatograms before and after this event show exact agreement in boiling range, boiling point distribution, and in the distribution of the major and minor components ("fingerprints"). In addition, a reversal in the trend of the $n\text{-C}_{17}/P$ values was observed during that winter and early spring at stations more distant from shore (e.g. Stations 7 and 20). In combination, these data point to a general seaward movement of the oil from the 1969 spill during the first winter. We note that undegraded fuel oil was still present at some locations in the marshes at and below the surface by February 1970 (in April 1970, River Station V had a $n\text{-C}_{17}/P$ of 1.65). Thus, the marshes and their aquifers may represent a source for the oil influx to Station 31 in early 1970.

After this event, as after the initial pollution, the heptadecane to pristane ratio at Station 31 did not decrease drastically for several months. The more rapid loss of the straight chain paraffins at less polluted stations and the occurrence of a lag time at the heavily oiled Station 31 suggest possibly an induction phenomenon rather than one due to climatic conditions.

In spite of the rapid decrease in n-paraffin concentration during Spring and Summer 1970, small amounts of straight chain hydrocarbons have remained in the sediments during the entire two years for which observations are available now.

No such delay in the bacterial attack on the straight chain hydrocarbons is noted in the marshes. This may reflect the greater permeability, better aeration and the higher redox potential of the marsh sediments relative to the offshore sediments. As in the absolute hydrocarbon concentrations, a greater scatter is noted between successive measurements of the n-C₁₇/P ratio in marsh samples than offshore; again, this reflects the greater inhomogeneity of the marsh sediments.

The branched chain hydrocarbons are also attacked, though at a slower rate than their straight chain homologues. A comparison of analyses from Sediment Station 31 (e.g., December 1969 and August 1971) shows a marked decrease of the amplitude of the pristane and phytane peaks relative to the unresolved background envelope.

3. The Pristane-Phytane Ratio

Bacterial degradation and physical processes, such as evaporation and dissolution change the ratios between hydrocarbons of different structural

series, e.g. the heptadecane-pristane ratio. However, bacterial and chemical degradation exhibit little selectivity between closely adjacent members of the same or of related homologous series, (Blumer *et al.*, 1970d). For this reason, we have suggested that ratios between adjacent members of homologous series or between certain selected adjacent isomers are relatively constant and should be of diagnostic value in the identification of a spilled oil, long after its release to the environment.

The data now available confirm this. In the sediments of Station 31 (Fig. 2a), the pristane/phytane ratio has remained remarkably constant over a two year period. The average value of 1.17 ± 0.09 is very different from that encountered in unpolluted recent sediments, which contain little, if any phytane (Snyder and Blumer, 1965). No systematic trend is evident from the data and the scatter may be caused more by errors in the measurement of the peak heights, which involves a large background correction, than by actual differences in the ratios. A more accurate determination of this ratio should be possible if it is measured in chromatograms of iso-alkane concentrates. Greater variations in the pristane/phytane ratios are observed in special situations, e.g. where evaporation of the oil plays a considerable role (Ehrhardt and Blumer, 1972). There, the difference in boiling points may be sufficient to lead to a more rapid loss of the lower boiling pristane, compared to phytane.

Different crude oils often differ drastically in the ratios between adjacent isomers or homologues. This, in combination with the environmental persistence of certain isomer ratios, suggests applications in oil source identification. Many such ratios are available and the present

data suggest that spill identification should be possible over extended time spans.

4. Changes in the Boiling Point Distribution

It has often been stated that a spilled oil loses its low boiling components rapidly through evaporation and dissolution. Our present experience does not confirm this for the West Falmouth oil spill. The boiling point distribution of the oil in the sediments at the offshore Station 31 and in the marshes (River Stations II, IV and V) remains remarkably similar to that of the spilled oil, and after two years still extends as low as the boiling points of n-tridecane and n-dodecane. The retention of the low boiling hydrocarbons appears not to be strongly dependent on the pollution level. Even at intermediate (7, 10, 30) and distant stations (20, 37) with intermediate and low oil content, hydrocarbons in the C_{13} to C_{14} range are still present.

The boiling point envelope of an oil should decrease more rapidly at lower than at higher molecular weights if evaporation or dissolution occur during the weathering of an oil. Correspondingly, the gas chromatographic envelope should recede toward higher carbon numbers as the oil ages. Graphically this can be displayed by plotting against time the position, in terms of equivalent n-paraffin carbon numbers, at which the unresolved chromatographic envelope under the n-alkane peak reaches a certain value, e.g. 10% of its maximum. This $C_n^{10\%}$ value is given in Fig. 3 for Station 31 and River Station IV; the very moderate slope of the curve is an expression of the stability of the boiling point distribution of the fuel oil hydrocarbons at these stations.

The volatility and solubility of hydrocarbons depend strongly on their molecular weight. Therefore, the evaporative and solubility losses in spilled oil decrease sharply with increasing molecular weight, and spilled oil stabilizes gradually in its boiling point distribution. From our data it appears now that the boiling point at which stabilization occurs and the rate at which oil is stabilized is determined primarily by two factors: the environmental temperature and the substrate at the site of the oil. Thus, oil which is incorporated into the bottom sediments soon after a spill loses little of its low boiling hydrocarbon content through evaporation or dissolution; these losses can be expected to be even less at lower water temperatures than those of Buzzards Bay. Crude oil lumps from the open ocean ("tar balls") stabilize at a slightly higher level, at least in their outside layers. A $C_n^{10\%}$ of 16 - 17 is commonly encountered here. Also, the stabilization of stranded oil ("beach tar") leads to greater volatility losses in a warmer than a cooler climate.

Stranded crude oil on Martha's Vineyard Island, Massachusetts U.S.A. has now been under our observation for 16 months (Ehrhardt and Blumer, unpublished data). Relatively rapid initial aging moved $C_n^{10\%}$ to 16 - 17 during the first six months. After that, evaporative losses have become less and the resulting beach tar has now stabilized near a $C_n^{10\%}$ of 18. In the warmer climate of Bermuda, more rapid evaporation occurs (Blumer and Jones, unpublished data). These data suggest that earlier assumptions of a rapid evaporation of spilled oil at sea may have been erroneous.

5. Changes in the Aromatic Hydrocarbon Distribution

The oil in the sediments at West Falmouth is altered principally through biodegradation and dissolution. Gas chromatograms and chemical analyses taken at different times after the spill permit us to assess the relative contribution of these processes. Bacterial degradation exhibits little selectivity between adjacent members of homologous series over a fairly wide boiling range, while dissolution depletes strongly the lower boiling homologues. If we use these criteria, the gas chromatograms of West Falmouth sediments suggest that the straight and branched hydrocarbons are depleted principally through biochemical attack. This is not so in the case of the aromatic hydrocarbons, especially the lower boiling ones. The mass spectra of the aromatic concentrates from March 1970 and April 1971, at Station 31 (Fig. 4) show an overall increase of the benzenes and of the tetrahydronaphthalenes at the expense of the naphthalenes. Within the benzenes the homologues substituted with four and six alkyl carbons have decreased relative to those containing seven to thirteen alkyl carbons. This is attributed to the greater water solubility of the less substituted benzenes.

A similar and more pronounced change has occurred within the naphthalenes where the parent hydrocarbon and the homologues with 1-3 alkyl carbons have been strongly depleted in relative concentration, while the contribution of the C₄ - C₉ alkyl substituted naphthalenes has increased, relatively speaking. Again, the greater solubility of the less substituted naphthalenes explains this change.

Similar but less pronounced changes in the molecular weight distribution are observed within the tetrahydronaphthalenes and the diphenyls. The lower members of both homologous series are depleted, though less completely than in the naphthalene series. Again, this is in keeping with the greater water solubility of the lower homologues. The changes in the relative composition of the saturate and of the aromatic fraction at Station 31 between March 1970 and April 1971, are also evident from the gas chromatograms (Fig. 6). In March 1970, the normal paraffins from C₁₂ to C₂₃ dominated the saturated fraction and many well defined peaks in the aromatic fraction were superimposed over a large unresolved background. We have not yet established the identity of the individual aromatic peaks but comparison with other chromatograms of fuel oils suggests the presence of alkylated naphthalenes. By April 1971, the normal paraffins in the saturated fraction have sharply decreased, though the individual members from n-C₁₄ to n-C₂₃ are still recognizable. Phytane, pristane and the C₁₈ isoprenoid now predominate over a large unresolved background. A remarkable change has taken place in the chromatograms of the aromatic fraction. The well defined individual peaks have disappeared almost entirely; the one outstanding peak which had not been present in the March 1970 sample is probably associated with a biochemically derived polyolefin which co-chromatographs with the aromatic fraction on silica gel.

The changes observed in the gas chromatograms are in agreement with the results of the mass spectra analysis. The biodegradation of the saturates and the dissolution of the less substituted aromatics has led to a residual oil in which the simpler individual hydrocarbons and the simple homologous series are depleted. The remaining mixture is richer than the

original oil in the complex and chromatographically overlapping series of isomers and higher homologues that are so characteristic of the higher boiling branched and saturated fraction of crude oil.

It should be noted that the low voltage mass spectra do not reflect the true complexity of the aromatic fraction since they do not resolve between the great number of isomers. Thus, the 13 isomeric dimethylnaphthalins or the 18 dimethyltetralins are each represented by a single peak. These, and the much larger number of more highly substituted aromatics have slightly different boiling points and are not, or only partly resolved by gas chromatography; therefore, they contribute to the complex unresolved background of the chromatograms.

On the whole, without regard to changes in the hydrocarbon distributions within homologous series, the saturated and the aromatic hydrocarbons at Station 31 appear to be depleted at approximately the same rate. The aromatic content of the residual oil in the sediments changed only little between March 1970 and April 1971, from 31% to 28%. At other locations, for instance where intense water-wash occurs, a more rapid depletion of the more soluble aromatics is possible. Thus, the hydrocarbons recovered from a coarse, sandy layer at the bottom of a core in Wild Harbor River (Core 2, Blumer et al., 1970d) exhibit an unusually low background, relative to the straight chain hydrocarbons. Bacterial degradation is not advanced, as is evident from the high heptadecane/pristane ratio (1.4) but the ratio of n-pentadecane to the background at the same elution position is more than twice as high as at any other station. This suggests intense water washing in the aquifers of the marsh, resulting in the depletion of the more soluble aromatics.

DISCUSSION OF THE CHROMATOGRAMS

The present report compiles all chromatograms of sediment samples from West Falmouth that had been analyzed by the end of November 1971, including those reported by Blumer et al., (1970d). Use has been made of these chromatograms already in the discussion above; many additional interpretations will have to await the completion of our sampling and analytical program. The following discussion is therefore limited to some additional findings that appear important at the present time.

Station 31

Throughout the span of this investigation this has been the most heavily polluted location. The large additional influx of oil to this station during the first winter after the accident raised the oil content of the sediments to 1.2% on a dry weight basis. In spite of the degradation of the oil through biochemical processes and through dissolution, oil remains at levels which still exceed those during the first few months after the accident. Cautious extrapolation suggests that the oil level will remain above the detection limit for at least another two years and possibly longer.

In spite of the initially rapid degradation of the normal alkanes, these hydrocarbons are still present in lesser amounts. The depletion of the saturates and of the aromatics appears to proceed at roughly the same rate and the aromatic content has remained close to 30% between March 1970, and April 1971. The relative changes in the type distribution of the aromatic hydrocarbons at this location have been discussed above.

River Stations II, IV and V

The analyses of the sediments at these stations have been discussed above. The fuel oil content at these stations is still well above the indigenous hydrocarbon background. The average oil content is given in Figure 1 and has already been discussed above.

The gas chromatograms of the samples from Wild Harbor River show excellent agreement in terms of boiling point distribution, in the ratios of adjacent homologue and isomer pairs and in the "fingerprint" pattern. Extended correlation is possible within the same station, between the different river stations and between these and the offshore stations (see the chromatograms for River Station V and Station 31, August 1971). This correlation is maintained throughout the full two years for which analyses are available now. It is remarkable that after two years it is still possible to establish the approximate boiling range of the spilled oil, and to correlate the "fingerprint" of the oil between different stations and with the accidentally spilled oil.

Stations 6, 7, 9, 10 and 30

All of these stations are located within the outer reaches of Wild Harbor at water depths between 20 and 35 feet. Analyses for Stations 7 and 20 through April and May 1970, were presented in Blumer et al., 1970d. In all samples from these stations fuel oil contamination is still readily apparent from the gas chromatograms. At Station 7, as well as at Station 31, a reversal in the heptadecane to pristane ratio was noted after November 1969; it persisted to April 1970. The increase extends to all normal paraffins throughout their boiling range (compare the ratios between n-alkanes from

C₁₃ - C₁₉ and between adjacent isoprenoid alkanes at Station 7 for November and December 1969 (Blumer et al., 1970d). In view of the relatively high pollution level at these stations it is justified to interpret this as secondary pollution with oil from the 1969 spill, concurrent with the event at Station 31 during the same time interval.

The interpretation of similar events, occurring later, at stations with hydrocarbon levels comparable to the natural background, is more difficult. Two different events are noticed; at Station 7, the heptadecane/pristane ratio reverts, after a long series of low values, to nearly 1:1 in July 1971; all other normal alkanes from C₁₄ to beyond C₂₃ increase similarly. In contrast, at Station 10, in June 1971, heptadecane and nonadecane, but not octadecane and hexadecane, increase very markedly; also, there is a lesser but noticeable increase and predominance of the odd carbon number n-alkanes from C₂₁ to C₂₄. In this latter case, the odd carbon predominance suggests a contribution of recent hydrocarbons from biochemical sources. It is less likely that this is also true for the July 1971 samples at Station 7. There, a recontamination with a less degraded fuel oil is suggested.

These examples show that the interpretation of changes in the hydrocarbon chemistry in polluted sediments has to be made with caution, if the pollution level is at or below the natural hydrocarbon background (as it is at Station 7, in July 1971) and if the hydrocarbons under consideration are also normal products of organisms. Such is not the case and the assignment to pollution can be made with greater certainty if one deals with hydrocarbons that are foreign to organisms, such as the very complex series of branched, cyclic and aromatic hydrocarbons which are the prime constituents

of crude oil.

Stations 5, 20, 35, 36 and 37

This group of stations is more remote from shore than the one just discussed. The water depths here are between 20 and 42 feet. At all of these stations the kill of the benthic fauna was not as immediate as at the stations closer to shore where high concentrations of fresh oil arrived within hours or within a few days after the accident. Station 20 still yielded a normal fauna on September 24, 1969, eight days after the spill, while the gas chromatograms already showed the presence of fuel oil derived hydrocarbons. Three weeks later, gas chromatographic evidence showed the presence of fresher (in terms of biodegradation, measured by the heptadecane/pristane ratio) oil and the biological analysis showed the kill of most ampeliscid amphipods. At Station 37 the normal fauna remained through mid-December, 1969 and the gas chromatogram showed no clear evidence for the presence of fuel oil. By January 1970, there was a precipitous drop in the number of living amphipods and, simultaneously, the gas chromatograms showed the presence of fuel oil derived hydrocarbons. The first gas chromatogram at Station 35 was obtained in October 1969, and showed the presence of fuel oil, that - judging from the low heptadecane/pristane ratio - was more degraded than the oil at the more heavily polluted inshore stations. Here, as in the earliest sample at Station 20, the ampeliscid amphipods survived the arrival of the altered oil. The mass spectral analyses of the oil at Station 31 have shown that the fuel oil loses some of its immediately toxic compounds when the low molecular weight benzenes and naphthalenes are removed by dissolution. At Stations 20 and 35, the fuel oil did not arrive

without some previous alteration. Biochemical alteration is evident at both and exceeds that found at Station 31 in June 1970, already between September 1969 (Station 20), October 1969, (Station 35) and January 1970, (Station 37). Concurrent with the more rapid biochemical alteration there must have been considerable dissolution of the more soluble aromatic hydrocarbons, aided by the transport of the oil from inshore. This is evident from the low amplitude of the background envelope under the normal alkane and isoprenoid peaks, for instance in the sample of September 1969, at Station 20 (compare this to Station 31, September 1969, and March 1970).

Thus, in terms of the toxicity of the oil, the situation encountered is more complex than can be expressed through a qualitative or quantitative observation of the presence of oil. The relative composition of the oil and its changes under the influence of environmental agents affects the toxicity. A reduction in the short term toxicity of the oil occurs slowly in the heavily polluted regions; dissolution of the less substituted benzenes and naphthalenes seems to be principal reason. In the less polluted areas a more rapid loss of the immediate toxicity may occur and we encounter situations, where oil of different degrees of alteration arrives at one location in consecutive waves. This appears to be the case at Station 20 where a degraded oil initially permitted the survival of the amphipods in September 1969, but where the later arrival of a less degraded oil (note the return of the heptadecane to pristane ratio to higher values between October and December 1969) from the same original source caused a severe kill of the benthic organisms.

It should be realized that an oil of wider boiling range may be more persistent, physically and in its toxicity. The fuel oil spilled at West Falmouth is limited in its aromatics essentially to benzenes and naphthalenes and to smaller amounts of other mixed two-ring hydrocarbons and heterocyclics. In whole crude oils and higher boiling distillates, phenanthrenes are present in higher concentrations together with higher ring number aromatics, which are not at all represented in the fuel oil. There, dissolution may not deplete the immediately toxic hydrocarbons as rapidly as here, and long-term poisons (polynuclear aromatics and heterocyclics) are present which are absent from this fuel oil.

A total of over 60 gas chromatographic analyses (not including duplicate runs) are now available from this group of stations. In all samples with the possible exception of two (February 1971, Stations 35 and 36) fuel oil derived hydrocarbons are chromatographically identified for the entire two year period of observation. The pollution level at these stations, in contrast to the stations closer to shore, is similar or less than the natural hydrocarbon background level. Therefore, little trend is evident in the hydrocarbon weights for these stations (Table II).

The gas chromatographic analyses in inshore and marsh samples with high pollution level tie the hydrocarbons in these samples conclusively to each other and to the 1969 West Falmouth oil spill. No new oil spills of comparable or even much smaller size have occurred in this area since the stranding of the "Florida". However, the possibility might exist that minor sources of

pollution, especially near the shipping route Cape Cod Canal, would have gone unobserved. Gas chromatograms should reveal the occurrence of such pollution incidents, if the contribution of the pollutants to the sedimentary hydrocarbons approaches or exceeds the combined background level derived from organisms and the 1969 spill. Thus, additional pollution by a whole crude oil would be evident from a change in the boiling point distribution and from changes in the "fingerprint" pattern of the minor hydrocarbons. No such evidence is found in our chromatograms. Similarly, pollution by a different fuel oil would lead to changes in the boiling point distribution and in the ratios of the major and minor oil components. It is probable that the gas chromatograms from Station 36 document a minor pollution incident which occurred late in 1970 near that station but did not extend to any of the other stations.

The correlation in terms of the boiling point distribution, isomer distribution and fingerprint pattern holds well, regardless of the degree of biodegradation of the oil, both within the heavily polluted samples and between them and most lightly polluted ones. Thus, the gas chromatograms agree very well between Station 31, January 1971 (158 mg hydrocarbons/100 g dry sediment), and Station 20, April 1971 (5 mg hydrocarbons/100 g sediment). At Station 36 this correlation holds through September 1970 but is lost in November 1970. Through September 1970, the oil in the sediments at this station exhibits the boiling point distribution, the pristane/phytane ratio and the fingerprint pattern of the 1969 spill. By November, the boiling point distribution is shifted towards the lower carbon numbers, the pristane/phytane ratio is more

than twice as high as in September, other major hydrocarbons are present (a large peak eluting between C_{14} and C_{15}) and the fingerprint pattern no longer correlates with that in the inshore samples. Our data from Station 31 show that the pristane/phytane ratio is conservative for at least two years, in spite of the gradual degradation of the oil. This ratio could be raised through the contribution to the sediments of biochemically derived pristane; however, the samples at Station 36 do not show the addition of the other biochemically produced alkanes or alkenes which are associated with organisms. In fact, the common biologically produced olefin eluting just beyond C_{20} is present in lesser relative concentration in November 1970 than in the other samples from this station. In combination, the observed changes in the hydrocarbon distribution suggest strongly that contamination of the sediments in Station 36 has taken place with small amounts of another low boiling fuel (kerosene) of unknown origin sometime between September and November 1970. Without access to the spilled oil or to a wider range of other samples showing the same contamination, it is not possible to state whether this new contaminant was initially low in n-paraffins, as some oils are, or whether it had been altered strongly between the time of release to the environment and the discovery at Station 36.

Samples taken at the same station in August 1970 again show an increased pristane peak relative to that of phytane. This pristane/phytane ratio is intermediate between that at Station 31 and that at Station 36 in November 1970 and the correlation with the "Florida" oil in terms of boiling point

distribution and fingerprint pattern is better; this may reflect a mixed origin of the pollution, from the "Florida" accident and the minor event of November 1970, or a biochemical contribution of the pristane or even a third minor spill at this site. Continued monitoring at this station should shed more light on the origin and fate of this contamination.

General Discussion and Conclusions

The present findings confirm and extend those reported two and eight months after the West Falmouth oil spill. Specifically, the conclusions of our report of September 1970 (Blumer, et al., 1970 d) still stand; they are reproduced in Appendix I, since the original report will no longer be reprinted.

An independent group of investigators at this laboratory has studied the incorporation of this oil into the salt marsh ecosystem, quantitatively and qualitatively (Burns and Teal, 1971). Again, our earlier findings were confirmed.

The investigation at West Falmouth now extends over more than two years. It provides the longest continuous series of observations on the extent, persistence, effect and fate of oil pollution in a controlled area that had not been subjected to previous heavy oil pollution. Also, it is at the present time the only such study that combines sensitive and objective analytical methods with a detailed survey of the smaller but more susceptible components of the intertidal and benthic fauna. It is not surprising that our findings differ from, and are more severe than, those of previous investigations that were limited to the gross, visual observation of the degree of oiling and to

the study of the larger, less sensitive and transitory components of the fauna, especially of fishes and of large intertidal organisms.

1) Analytical Methods and Their Interpretation

In contrast to synthetic chemical pollutants, hydrocarbons are not foreign to the marine environment. However, the hydrocarbons in fossil fuels differ in composition and toxicity from the indigenous hydrocarbons of living organisms. The analytical distinction between indigenous hydrocarbons and hydrocarbon pollutants is possible and the methods chosen for this investigation possess adequate specificity and sensitivity for this purpose. Further refinement of these techniques is possible, e.g. by more detailed analytical separations, followed by mass spectrometric analysis, but our experience shows that even simple gas chromatographic techniques permit the detection of fossil fuels in polluted shellfish (Blumer et al., 1970a, b), in marsh organisms (idem; Burns and Teal, 1971) and in the surface and subsurface strata of marine and intertidal sediments (Blumer et al., 1970b; present report).

The potential for the identification of pollutants in the presence of indigenous hydrocarbons and other natural lipids, which gas chromatography provides can only be realized if use is made of the full sensitivity of this method. This requires caution and the avoidance of contamination during sampling and workup and the preliminary separation of the hydrocarbon fraction from other components of the sediment which would interfere with their determination. Some recent investigations of the effect and fate of spilled oil have now made use of newer analytical methods.

However, in some cases gas chromatography was applied directly to entire extracts of sediments or of animal tissues, without the previous removal of non-hydrocarbon components, such as elemental sulfur and lipids. Such a procedure fouls the gas chromatograph, leads to deterioration of the column and is inaccurate and insensitive.

2) Persistence of the Pollution

Hydrocarbon analyses are available now for the Buzzards Bay sediments adjacent to the shores of West Falmouth, Mass. for the period from September 1969, to November 1971. At all stations where fuel oil pollution was detected during this period, regardless of the pollution level, it remains detectable, with the possible exception of the February 1971 samples at Stations 35 and 36. On the other hand, control stations outside this area show the absence of those chromatographic features which we identify with the oil pollution.

In the most heavily affected areas (River Station IV, Station 31) the fuel oil still exceeds the indigenous hydrocarbon content by a considerable margin. Cautious extrapolation of the falling hydrocarbon levels suggests that oil will be detectable in the surface sediments at these stations for a total period exceeding four years.

Below the immediate surface the oil is even more stable. Between 2.5 and 7.5 cm depth at Station 31, the oil degradation lags behind that at the immediate surface by 14 months, 24 months after the spill. This is in agreement with accepted facts of hydrocarbon geochemistry and suggests extremely long persistence of oil that penetrates the sediment or

is buried below the immediate surface, for instance by sediment redistribution or by dredging. Such buried oil may be degraded only if the sediment is reworked by mechanical or biological agents. This implies also, that burying organisms may encounter a pool of less degraded - and therefore more toxic - oil even after resettlement of the immediate surface becomes possible.

Compared to laboratory experiments, the oil degradation at West Falmouth proceeds slowly. The degradation of the straight chain hydrocarbons becomes noticeable soon after the spill in the less heavily polluted areas, but in highly polluted marine sediments, a lag time of several months may precede the more rapid depletion of these compounds. In spite of the preferential removal of the straight chain hydrocarbons, they persist at low concentrations levels. This agrees with previous knowledge on the persistence of biologically derived normal paraffins in recent sediments.

The great differences between the degradation rates in the laboratory and in the field urge caution in extrapolating from the former to the latter. Too many parameters, that are not usually controlled in the laboratory, affect the persistence of oil in the environment. Oil is distributed between all components of the entire ecosystem and may have vastly different half lives depending on such factors as the availability of water, of oxygen and of suitable microorganisms. The persistence after two years of even a fraction of the easily attacked normal paraffins throws some doubt on the expected effectiveness of bacterial seeding as a means of reducing environmental oil residues in polluted sediments.

The degradation of the branched and cyclic hydrocarbons proceeds even more slowly than that of the normal paraffins. Even after two years, isoprenoid and cyclic saturated and aromatic hydrocarbons are still very much in evidence in the sediments and in the organisms of Buzzards Bay and its marshes.

"Degradation" of the aromatics seems to proceed mostly through dissolution rather than through bacterial utilization. The more soluble lower molecular weight and less substituted aromatics of the fuel oil disappear gradually, while the more substituted and higher boiling aromatic hydrocarbons persist.

The preferential bacterial degradation of some saturates and the dissolution of some aromatics preserves the overall saturate/aromatic ratio of the fuel oil remaining in the sediment, but not the individual hydrocarbon distribution.

Evaporation, if it has contributed at all, plays a minor role in the weathering of the oil at West Falmouth. The boiling point distribution of the oil in the sediments two years after the spill is still close to that of the fuel oil and hydrocarbons as low as C_{12} have been preserved in the sediments and organisms. In view of this, statements suggesting the rapid evaporation of the lower boiling petroleum hydrocarbons in the environment should be re-examined. According to some authors, spilled oil was assumed to evaporate rapidly (Canevari, 1971). Oil taken up by organisms and sediments cannot evaporate, and our experience at West Falmouth shows the extended retention of almost the entire boiling range of even a low boiling oil.

The environmental ageing does not severely alter the ratios between adjacent members of homologous series (e.g. the pristane/phytane ratio). The conservative nature of such isomer ratios, which may differ characteristically between different oils, provides the basis for oil correlation and oil "fingerprinting" or "tagging" for very extended periods after a spill. Correspondingly, repollution of an affected area by a new spill can be recognized from the analysis of such isomer and homologue ratios.

3) Biological Damage and Recovery

The events following the 1969 West Falmouth oil spill can be grouped into three distinct, though partly overlapping phases: the immediate kill within the heavily oiled area, the spread and the persistence of the damage to more distant areas with delayed mortality in the outermost regions, and the recovery extending gradually inward from the less to the more heavily polluted regions.

The heavy immediate kill caused by the fuel oil at West Falmouth confirms the findings of other investigators on the effects of fuel oil spills in other oceanic regions.

The spread of the pollution to areas not immediately affected by the spill is documented here. A similar spread of the pollution was observed after the blowout off Santa Barbara; there, the spread was attributed to oil transport on the surface of suspended mineral matter. It is likely that similar events follow whenever oil is introduced into sea water containing suspended sediments. All recent sediments contain some organic matter, this is more hydrophobic than the mineral matter and it has a con-

siderable adsorptive capacity for petroleum. Other processes may have contributed to the spread of the pollution; release of oil from heavily oiled inshore and offshore sediments either in droplet form or in solution has been observed here, directly or indirectly.

The toxicity of the #2 fuel oil is associated to a large extent with the aromatic hydrocarbons of low ring number and low degree of substitution. This is also the most water soluble component of the fuel oil, a factor which may have contributed to the extent of the immediate kill in the heavily oiled area. On the other hand, redistribution of the oil to outlying areas results in partial depletion of these most soluble hydrocarbons. Thus, the oil which appeared several months after the spill at more distant stations was less immediately toxic than the fresh oil spilled inshore.

At some remote stations (e.g. Station 35) the pollution remained a single event, occurring a considerable time after the spill and caused by an oil that had been depleted in aromatics during the transport. There, the analytical identification of an altered fuel oil is possible even though the biota have not been measurably affected.

At intermediate stations (e.g. Station 20) the pollution appears to have arrived in two or more waves; first as an oil depleted in aromatics, not causing a severe kill and later as a fresher, but still redistributed, oil with higher aromatic content and leading to a severe biological effect.

A gradual recovery and repopulation is now being observed at many of the stations affected by the 1969 spill. Surprisingly, the detoxification

of the superficial layer of the bottom sediments appears due mainly to the gradual dissolution of the lower molecular weight and less substituted aromatic hydrocarbons. At this time it is an open question, whether the concurrent biodegradation of the normal, iso- and cycloalkanes contributes significantly to the detoxification of the sediment. Again, this throws doubt on the effectiveness of cleanup attempts involving bacterial seeding.

It is environmentally significant that the lower boiling hydrocarbons are removed from the sediments by dissolution rather than by bacterial degradation. This implies that a polluted sediment can supply these toxic hydrocarbons to the water column, unaltered and for a long time after a spill.

Comparisons between the recovery documented here and that expected under other circumstances should consider the limitations of our investigation and the particular features of the oil and the environment involved at West Falmouth. Especially, the following points should be considered:

1). Discussed here is only the recovery of the benthic fauna living at or just below the sediment-water interface.

2). The oil degradation within the sediment is slow compared to that at the surface. Considerably greater sediment penetration has been found at Santa Barbara than here. Under such circumstances oil may have a persistence that is long even on a geological time scale.

3). The amount of oil spilled and the extent of the polluted area at West Falmouth is relatively small. Here, juvenile organisms can be recruited from the surrounding unpolluted regions at a rate and in numbers which might not be available in the much larger area that has been affected by a

catastrophic spill.

4). At this point, we document principally the resettlement and the growth of animals recruited as juveniles from outside of the polluted area. It cannot be ruled out, though this is very difficult to confirm, that animals may remain affected in their metabolism, reproductive potential and genetic makeup. These factors are rarely considered in laboratory toxicity tests, which usually are of short duration. Yet, as our experience demonstrates, the environmental oil may persist during the entire life span of an organism, or even during many successive generations.

5). The fuel oil spilled at West Falmouth contained little tricyclic aromatics and none of the four or higher membered polycyclic aromatics which are common in higher fuel oils and whole crude oils. These hydrocarbons, including the phenanthrenes, possess both short and long term toxicity. They are less soluble and therefore more persistent than the benzenes and naphthalenes. Thus, a higher boiling fuel oil or a whole crude oil would retain its toxicity considerably longer than the fuel oil spilled at West Falmouth. Conversely, the recovery rate measured here, even within the observational limits, should be expected to be greater than in areas affected by larger spills and/or by less refined fuels.

6). Oil remains in the sediments after repopulation becomes possible. It is a foreign component of a normal marine sediment and may give rise to unanticipated hazards. Thus, hydrocarbon pollutants in sediments may concentrate other unpolar pollutants, e.g. pesticides, and make them available to organisms in places and in concentrations that would not be typical of an otherwise unpolluted area.

7). Hydrocarbons remain in the sediments even after resettlement becomes possible. They become accessible to the marine food chain and may be incorporated into fisheries products. In that sense, the area has not recovered, even if it supports life again, but it remains a source of petroleum derived hydrocarbons for higher organisms and ultimately for the human diet. There, petroleum hydrocarbons are a foreign component whose intentional addition to food would not be permitted under existing laws. Ironically, no uniform regulations exist and no modern analytical techniques have been standardized, to judge the acceptability of oil polluted sea food for human nutrition.

4) Present Findings and Earlier Knowledge

The recent concern about the environmental and public health implications of oil pollution was triggered by the stranding of the "Torrey Canyon" in 1967. Long before that time, basic information existed on the composition of petroleum, on the toxicity of some of its components and on the persistence of hydrocarbons in the environment. Much of this knowledge was acquired through efforts within or sponsored by the oil industry. This body of knowledge is accepted by scientists and was never considered controversial, even if it implicated some components of petroleum as a human health hazard. (Eckardt, 1967).

Thus, the toxicity of crude oil and crude oil fractions for man and most other organisms has long been recognized and has been attributed both to short-term and to more slowly acting but more persistent poisons. The

uptake through the diet, of hydrocarbons, by lower and higher animals, and the stability of the hydrocarbons in animal lipids is similarly well established. Finally, the preservation of hydrocarbons in anoxic marine sediments is one of the keys to the current thought on petroleum formation.

These background data suggest the hazards and persistence of oil pollution qualitatively. Our results do not contradict these established background data, but they define more rigidly the magnitude of the problem and the time scale of the hydrocarbon persistence.

We believe that the extensive past experience regarding the toxicity and persistence of hydrocarbons has been neglected in environmental considerations. Together with modern analytical techniques it can help us to arrive at a realistic assessment of the hazard of oil pollution.

5) Are the Effects and the Persistence of the West Falmouth Oil Spill Unique?

The questions whether other oil spills have had or would have similar effects and a similar persistence is often raised. We have discussed this in a recent article (Blumer et al., 1971) from which we quote:

"Some scientists are convinced that the effects at West Falmouth are a special case and have little applicability to spills of whole, unrefined crude oils. They contend that #2 fuel oil is more toxic than petroleum and that therefore it has effects that would not be comparable to those of whole petroleum. We cannot agree with this view. Fuel oil is a typical oil-refining product. It is frequently shipped by sea, especially along coastal routes, and it is spilled in accidents like those which occurred at West Falmouth and off Baja California following the grounding of the

"Tampica Maru" in 1957, (North, 1964).

More importantly, fuel oil is a part of petroleum, and as such it is contained within the whole petroleum. Surely, hydrocarbons that are toxic when they are in fuel oil must also be toxic when they are contained in petroleum. Therefore, the effects observed in West Falmouth are typical both for that fuel oil and the whole crude oil. In terms of chemical composition, crude oils span a range of molecular weights and structures. Many light crude oils have a composition not too dissimilar from that of fuel oil and their toxicity and effects on the environment are similar. Other heavier crude oils, while still containing the fuel oil components, contain higher proportions of the long-lasting poisons that are much more persistent and that includes, for instance, some compounds that are potent carcinogens (cancer-producing agents) in experimental animals. Such heavy crude oils can be expected to be more persistent than fuel oil, and they will have longer lasting long term effects. Even weathered crude oils may still contain these long-term poisons, and in many cases some of the moderately low-boiling, immediately toxic compounds. In our view, these findings differ from those of other investigators principally for two reasons: Our study is based on objective measurements and is not primarily concerned with the mobile, adult marine species -- the fish whose migratory history is largely unknown -- or the highly resistant intertidal forms of life. We are studying quantitatively the effects of the spill on the sessile (bottom) animals that cannot escape the spill or the polluted sediment and that are thus exposed to chronic pollution. Since all classes of bottom animals are severely affected by the oil, we believe that the

effects on free-swimming animals should be just as drastic. The difficulty of measuring the total impact of oil on the marine life has led many to doubt the ecological seriousness of oil pollution. Our findings, extending far beyond the period when the visual evidence of the oil has disappeared, are based on objective chemical analyses and quantitative biological measurements, rather than on subjective visual observations. They indict oil as a pollutant with severe biological effects.

It is unfortunate that oil pollution research has been dominated so strongly by subjective, visual observations. Clearly, oil is a chemical that has severe biological effects, and therefore oil pollution research, to be fully meaningful, must combine chemical with biological studies. Those few investigators who are using objective chemical techniques find patterns in the environmental damage by oil that are similar to those demonstrated by the West Falmouth oil spill. Thus, R. A. Kolpack reported that oil from the blowout at Santa Barbara was carried to the sea bottom by clay minerals and that within four months after the accident the entire bottom of the Santa Barbara basin was covered with oil from the spill (Kolpack, 1970). Clearly, this is one of the most significant observations in the aftermath of that accident. A concurrent and complimentary biological study would have appreciably enhanced our understanding of the ecological damage caused by the Santa Barbara oil spill.

G. S. Sidhu and co-workers, applying analytic methods similar to those used by us, showed that the mullet, an edible finfish, takes up petroleum hydrocarbons from waters containing low levels of oil pollution from refinery outflows. In their chemical structures the hydrocarbons isolated

by the investigators are similar to those found in the polluted shellfish of West Falmouth. The compounds differ markedly from those hydrocarbons present as natural components in all living organisms, yet closely approximate the hydrocarbons in fossil fuels (Sidhu et al., 1970).

Numerous results of crude-oil toxicity tests, alone or in the presence of dispersants, have been published in the literature. However, in almost all cases such tests were performed on relatively hardy and resistant species that can be kept in the laboratory, and on adult animals, for short time periods under unnatural conditions or in the absence of food. At best, such tests may establish only the relative degree of the toxicity of various oils. We are convinced that the exposure of more sensitive animals, especially young ones, to oil pollution over many months would demonstrate a much greater susceptibility to the damaging effects of the oil. Such effects have been demonstrated in the studies of the West Falmouth oil spill. These studies represent a meaningful field test in open waters.

Thus, we believe that the general toxic potential and the persistence of the West Falmouth oil are typical of most oils and oil products both at the sea bottom and in the water column."

Acknowledgements

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Appendix

The West Falmouth Oil Spill - Eight Months After the Accident, Conclusions

(From Blumer et al., 1970d, p. 22-26).

The present findings confirm and extend those reported two months after the accident in West Falmouth. Chemical analysis is well suited for the distinction between the natural hydrocarbons in the environment and the pollution derived from the fuel oil. The presence of the fuel oil in sediments and organisms can still be demonstrated conclusively eight months after the accident. Alteration and degradation, though slow, is now recognizable; it is primarily the result of dissolution and bacterial degradation. However, the "ageing" or "weathering" of the spilled oil has not yet resulted in detoxification. Specifically, we arrive at the following conclusions:

Persistence and Spread of the Pollution

Oil from the accident has been incorporated into the sediments of the tidal rivers and marshes and into the offshore sediments, down to 42 feet, the greatest water depth in the sea.

The fuel oil is still present in inshore and offshore sediments, eight months after the accident.

The pollution has been spreading on the sea bottom and now covers at least 5,000 acres offshore and 500 acres of marshes and tidal rivers. This is a much larger area than that affected immediately after the accident.

Bacterial degradation of the oil is slow; degradation is still negligible in the most heavily polluted areas and the more rapid degradation in outlying, less affected areas has been reversed by the influx of less degraded oil from the more polluted regions. Thus, secondary pollution from heavily affected areas continues for a long time after the accident.

The kill of bottom plants and animals has reduced the stability of marshland and sea bottom; increased erosion results and may be responsible for the spread of the pollution along the sea bottom.

Bacterial degradation first attacks the least toxic hydrocarbons. The hydrocarbons remaining in the sediments are now more toxic on an equal weight basis than immediately after the spill.

Oil has penetrated the marshes to at least 1-2 feet depth; after deposition, bacterial degradation within the marsh sediment is still negligible eight months after the accident.

Biological Effects of the Pollution

Where oil can be detected in the sediments there has been a kill of animals; in the most polluted areas the kill has been almost total. Control stations outside the area contain normal, healthy bottom faunas.

The kill associated with the presence of oil is detected down to the maximum water depth in the area.

The Ampeliscid amphipods are highly sensitive to small concentrations of oil and serve as an excellent biological indicator of this type of pollution.

A massive, immediate kill occurred offshore during the first few days after the accident. Affected were a wide range of fish, shellfish, worms, crabs and other crustaceans and invertebrates. Bottom living fishes and lobsters were killed and washed up on the beaches. Trawls in 10 feet of water showed 95% of the animals dead and many still dying. The bottom sediments contained many dead clams, crustaceans and snails.

Fish, crabs, shellfish and invertebrates were killed in the tidal Wild Harbor River; and in the most heavily polluted locations of the river almost no animals have survived.

The affected areas have not been repopulated, nine months after the accident.

Mussels that survived last year's spill as juveniles have developed almost no eggs and sperms.

Effect on Commercial Shellfish Values

Oil from the spill was incorporated into oysters, scallops, softshell clams and quahaugs. As a result, the area had to be closed to the taking of shellfish.

The 1970 crop of shellfish is as heavily contaminated as was last year's crop. Closure will have to be maintained at least through this second year and it has now been extended to areas more distant from the spill than last year.

Oysters that were removed from the polluted area and that were maintained in clean water for as long as 6 months retained the oil without

change in composition or quantity. Thus, once contaminated, shellfish cannot cleanse themselves of oil pollution.

The tidal Wild Harbor River, a productive shellfish area of about 22 acres, contains an estimated 4 tons of the fuel oil. This amount has destroyed the shellfish harvest for two years. The severe biological damage to the area and the slow rate of biodegradation of the oil suggest that the productivity will be ruined for a longer time.

The presence or absence of an "oily smell" is no clue for the presence of oil pollution in fish or shellfish. Only a small fraction of petroleum has a pronounced odor; this may be lost while the more harmful long-term poisons are retained. Boiling or frying may remove the odor, but will not eliminate the toxicity.

Shellfish areas in North Falmouth and Bourne which were not closed last fall had to be closed now on the basis of analysis that showed the presence of hydrocarbons derived from the West Falmouth oil spill. In view of the persistence of the oil in shellfish, closure may have to be maintained for a prolonged time.

TABLE I

Indigenous Hydrocarbons in Unpolluted Sediments from Buzzards Bay

Sample	Hydrocarbon Content mg/100 g Dry Sediment	Notes
Station 37, Nov. '69	4.0	Sampled before the arrival of the pollution
Station 90, June '71	2.6	Station south of polluted area (Fig. 1), 30' water depth
Station 90, July '71	11	
Station 90, Aug. '71	13	
Rhodes II	2.1	Station south of polluted area
Rhodes IV	9.4	
Station 31, Core, Sept. '71, Section C	7.4	Core samples taken below the polluted top 3 inches. See this report.
Station 31, Core, Sept. '71, Section D	6.9	

TABLE II

HYDROCARBON CONTENT OF BUZZARDS BAY SEDIMENTS

in mg hydrocarbons/100 g dry sediment

Year	Month	Station numbers, off-shore											River Stations			
		5	6	7	9	10	20	30	31	35	36	37	90	II	IV	V
1969	Sep.			6.9			3.9		55					59	45	
	Oct.			19			4.4		110	4.6					55	
	Nov.			14	24	15	2.4		110	5.3	2.0	4.0				
	Dec.			12			25	4.5		110	6.0			76	150	180
1970	Jan.										6.2	4.4				
	Feb.											3.8	51	120	15	
	Mar.								1240			3.5				
	Apr.			4.8		28	6.2		450	4.2	2.1	5.9			140	190
	May			6.5		25	3.5		210	4.9	2.5	7.0	52	40	77	
	Jun.			4.5		18	2.4		400	5.3	2.9	6.7	44	23	78	
	Jul.			7.4		14	2.5		240	6.4	4.3	5.7	75	150	40	
	Aug.					9.2			120		2.9	4.1				
	Sep.			2.6	5.9	9.4	4.9		210	7.9	6.1	4.2				
	Oct.												63	81	56	
1971	Nov.			4.3		9.8	3.1		300	11	6.8	8.5	22	18	45	
	Dec.			5.0	11	8.0	3.4		190				45	35	55	
	Jan.		4.9						160	5.4	4.0	5.0				
	Feb.			5.4	6.7	9.4	3.4	3.2		3.3	3.1	7.3				
	Mar.								200				39	34	29	
	Apr.	1.8	6.6	3.5	7.7	5.6	5.2		200				37	86		
	May															
	Jun.			4.5	5.6	8.8	3.6		230	4.4	4.2	4.6	2.6	15	19	40
	Jul.	3.3		1.1		4.6	2.3				6.0		11	34	27	16
	Aug.	3.7	15	1.3	6.1	5.4	2.0		130	3.5	14	5.6	13	14	40	32
Sep.			3.0		8.4	5.4		130	4.5	3.9	4.6					
Oct.													15	34	19	

All data rounded to two significant figures

TABLE III

Core, Station 31, Silver Beach Harbor, September 1971 (Fig. 5 a-d).

Section	Depth below Sediment Surface	Hydrocarbons mg/100 g dry wt.	Relative Sensitivity of recorder
a	0 - 1"	117	1
b	1" - 3"	56	2
c	3" - 8"	7.4	2
d	8" - 13"	6.9	8

Legends

- Figure 1 - Oil content in the sediments at Station 31 (Fig. 1a) and in Wild Harbor River, average at Station II, IV and V (Fig. 1b).
- Figure 2a - Pristane to phytane ratio at Station 31.
- Figures 2b and 2c - Normal heptadecane to pristane ratio at Station 31 and at Wild Harbor River Station IV.
- Figure 3 - The loss of the low boiling hydrocarbons in the sediments at Station 31, in Wild Harbor River (Station IV) and in tar on a beach at Bermuda. $C_n^{10\%}$ refers to the position in the chromatogram, in terms of equivalent normal paraffin carbon numbers, at which the unresolved boiling envelope below the normal alkane peaks reaches 10% of its maximum amplitude.
- Figure 4 - Distribution of homologous benzenes, naphthalenes, tetrahydronaphthalenes and diphenyls at Station 31, March 1970 and April 1971.
- Figure 5 - Gas chromatograms from sections of a core taken at Station 31 in September 1971. See Table III for depth, hydrocarbon content and relative attenuation of the recorder.
- Figure 6 - Gas chromatograms of the saturated and aromatic hydrocarbon fraction at Station 31, March 1970 and April 1971, with and without the addition of normal alkane standards with 14, 16, 18, 20 and 22 carbons. See Methods (this report) for description of the fractionation.
- Figure 7 - Explanatory gas chromatogram. The high background in the $C_{12}-C_{23}$ range ("envelope") is due to the incomplete resolution of the large number of homologous and isomeric branched and cyclic hydrocarbons in the fuel oil.

Figures 8 - 18 - Gas chromatograms of extracts from sediments, offshore samples; station numbers and date of collection indicated on chromatograms. For locations, see Part I of this report.

Figure 19 - Gas chromatograms of extracts from uncontaminated Buzzards Bay sediments.

Figures 20-22 - Gas chromatograms of extracts from River Stations

*SILVER BEACH HARBOR
STATION 31*

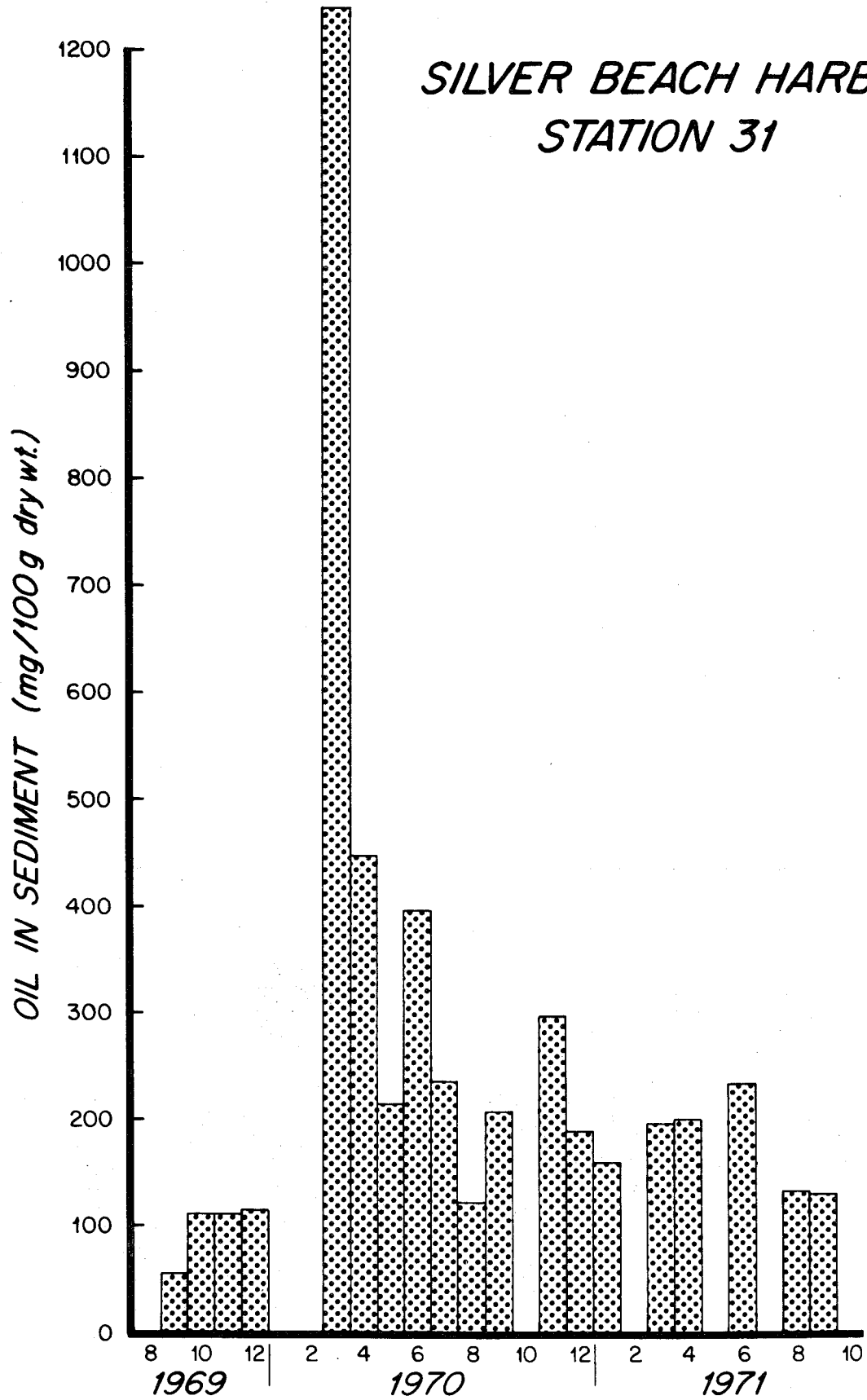


Figure 1a.

**WILD HARBOR RIVER
STATIONS II, IV, V
(average)**

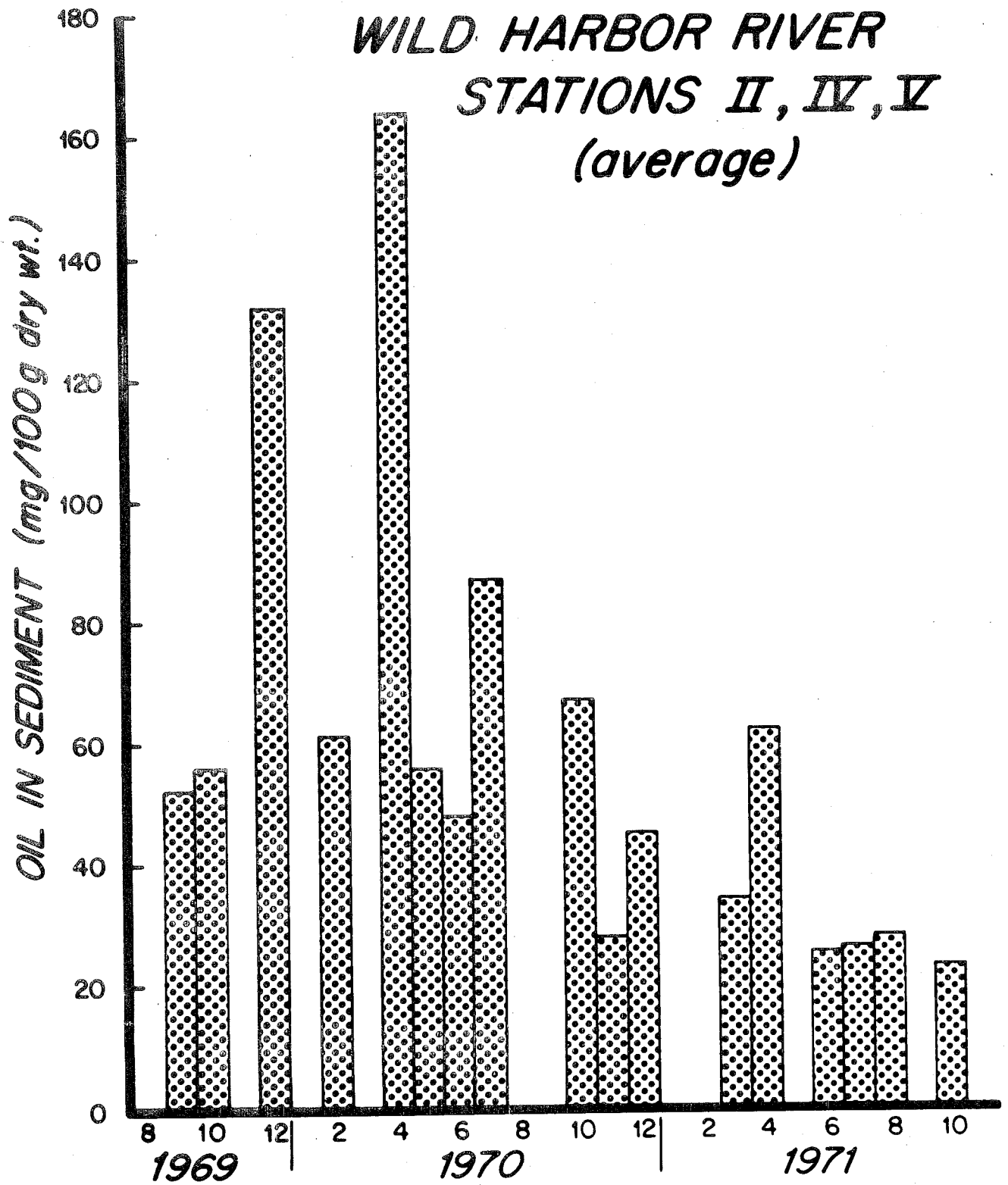


Figure 1b.

**SILVER BEACH HARBOR
STATION 31**

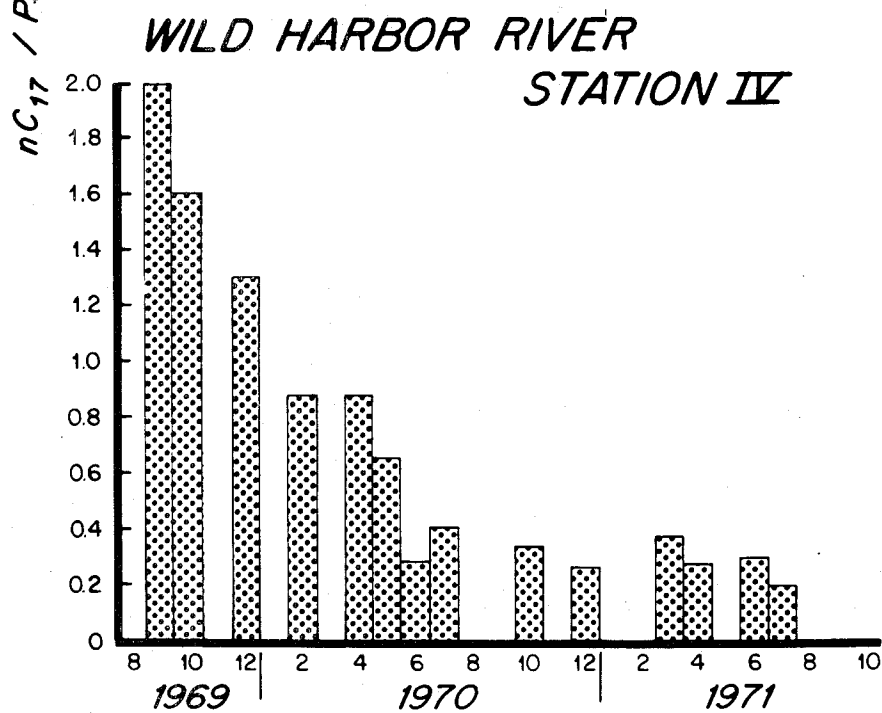
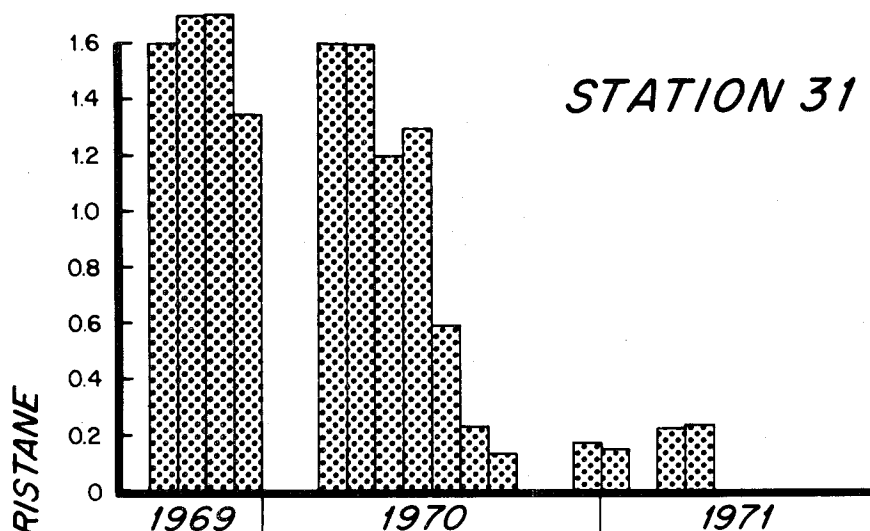
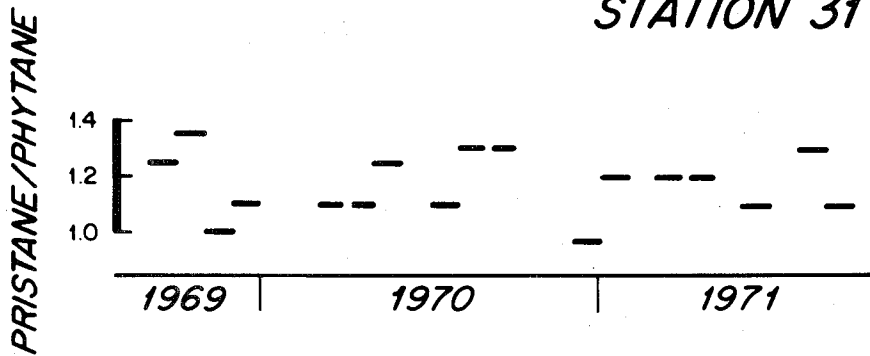


Figure 2a. (top), 2b. (middle), 2c. (bottom)

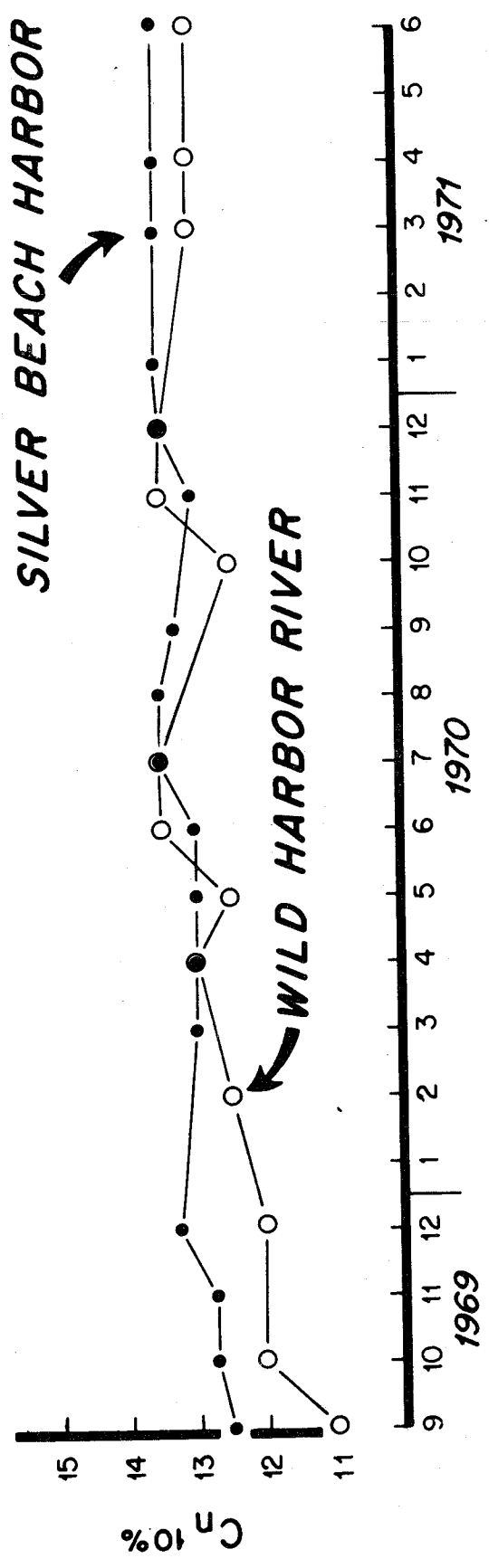


Figure 3.

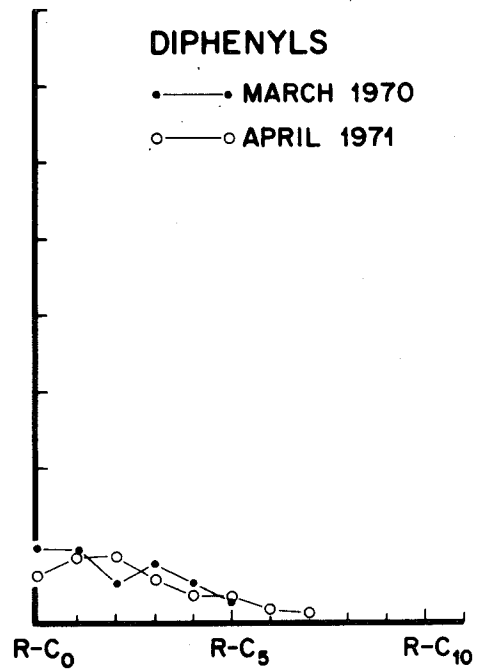
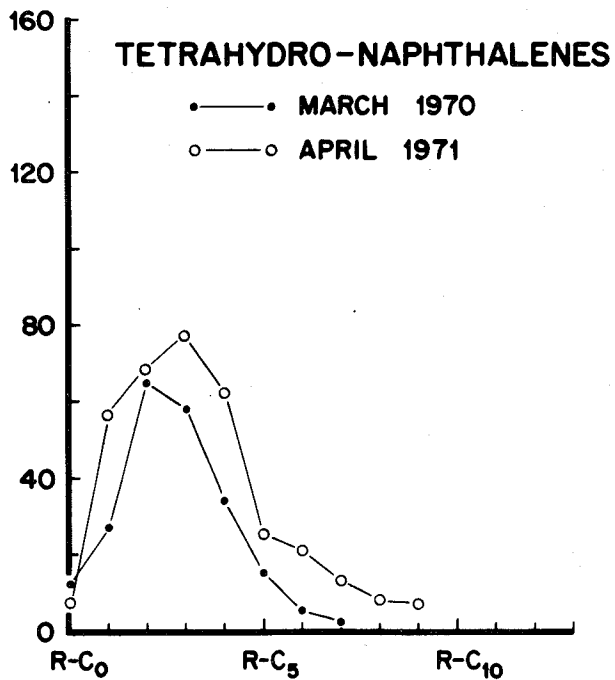
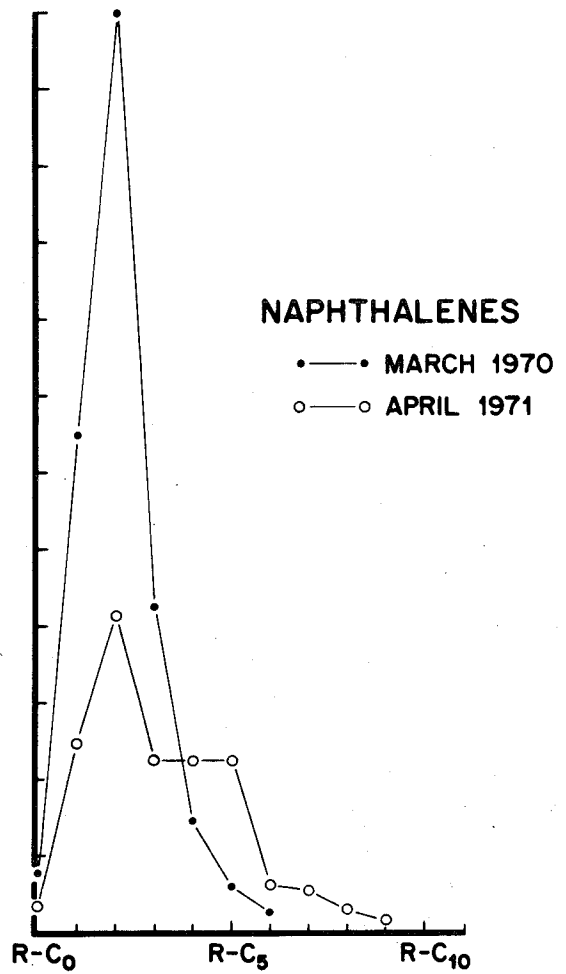
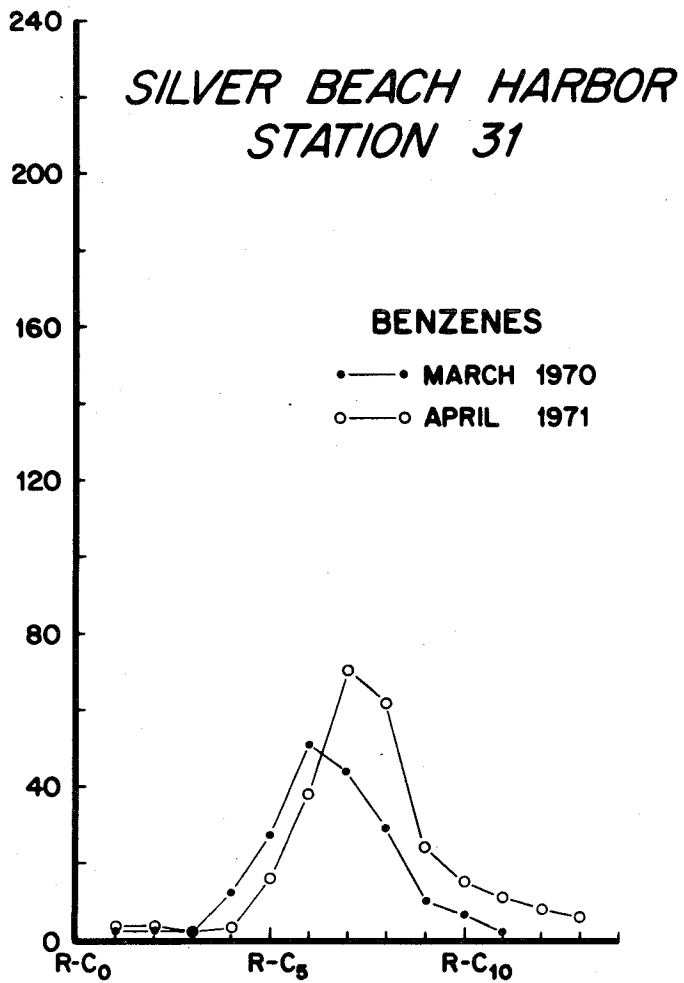


Figure 4.

Gas Chromatograms, Figures 5 - 21

All gas chromatograms were run under comparable conditions. Column changes and other experimental variables affect the elution times. The n-paraffin and isoprenoid series is easily identified in most chromatograms. Biologically derived hydrocarbons, eluting between n-C₂₀ and n-C₂₁ are also recognized, e.g. Station 5, August 1971.

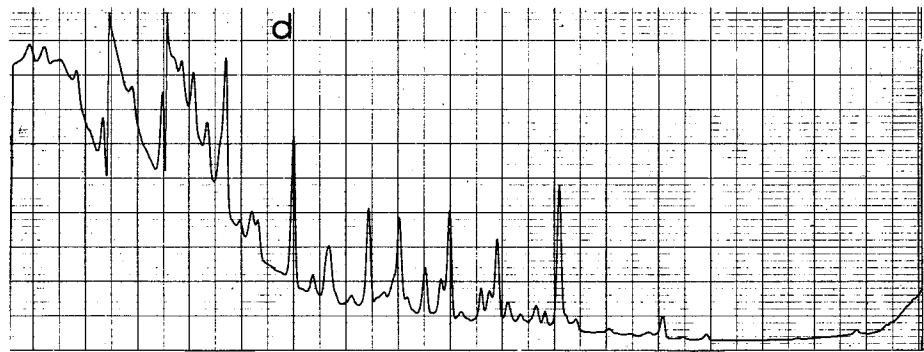
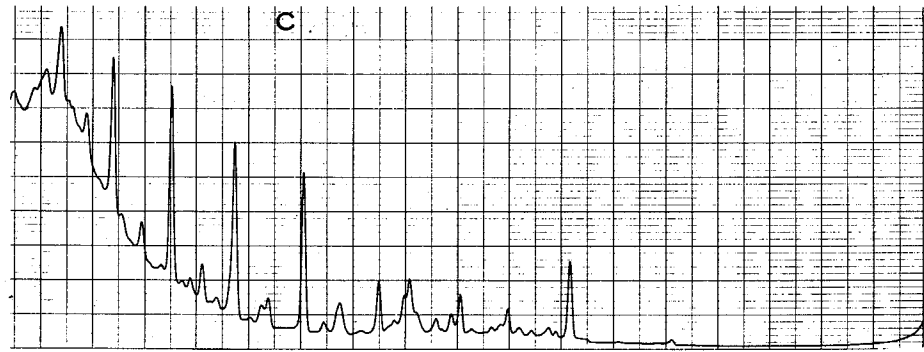
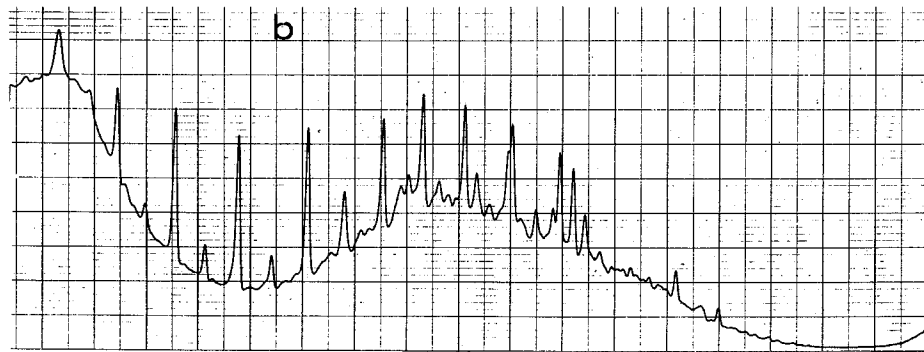
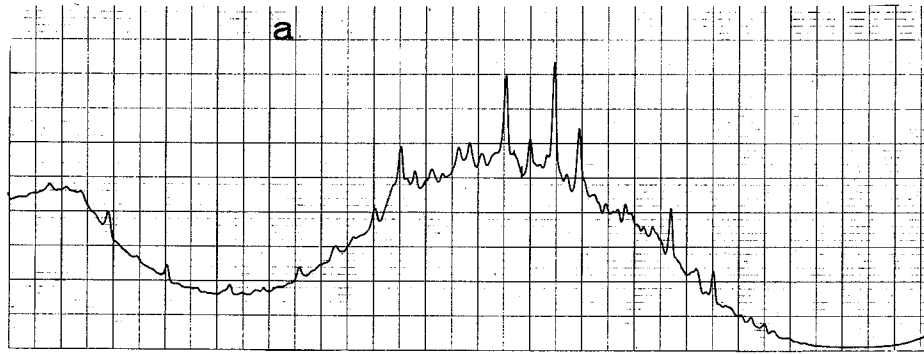


FIGURE 5.

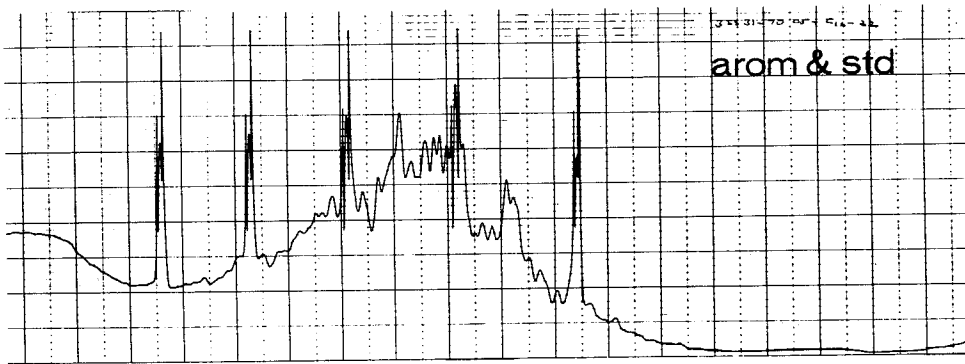
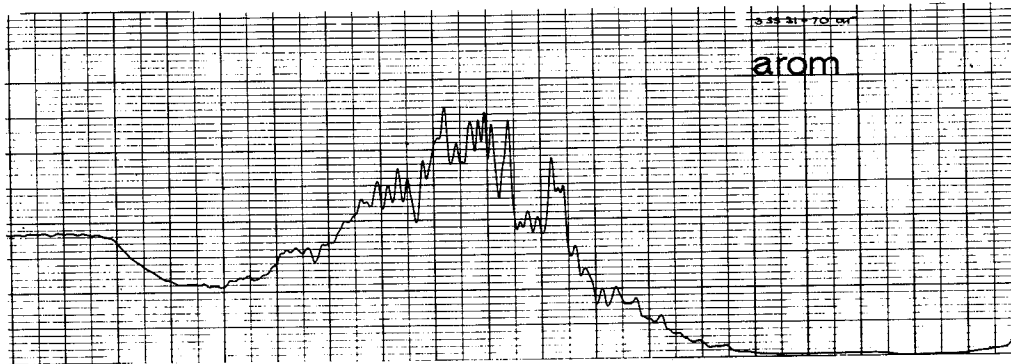
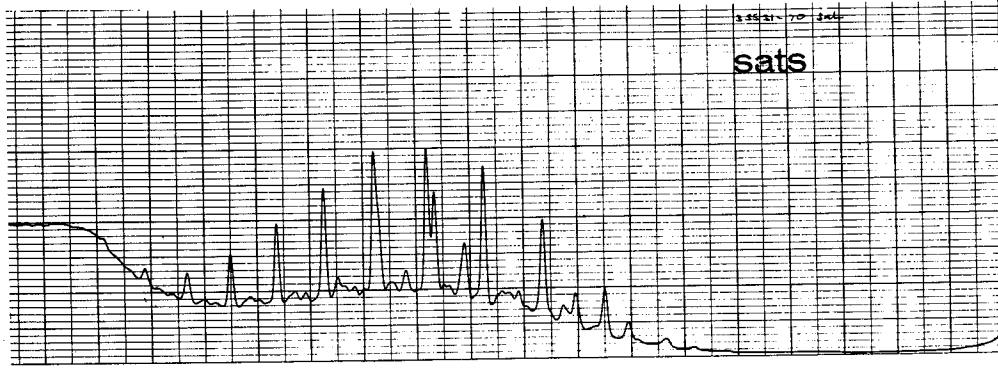


FIGURE 6.
MARCH 1970

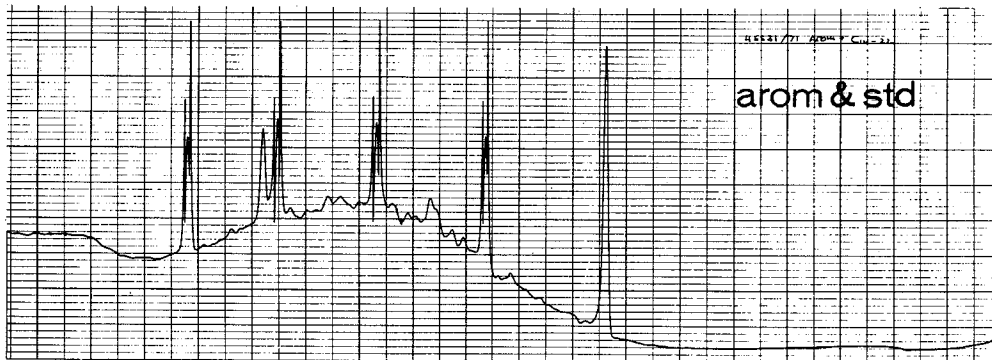
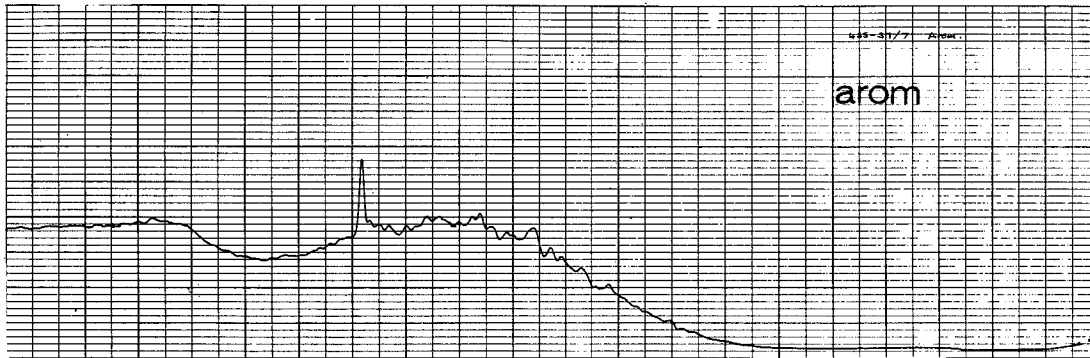
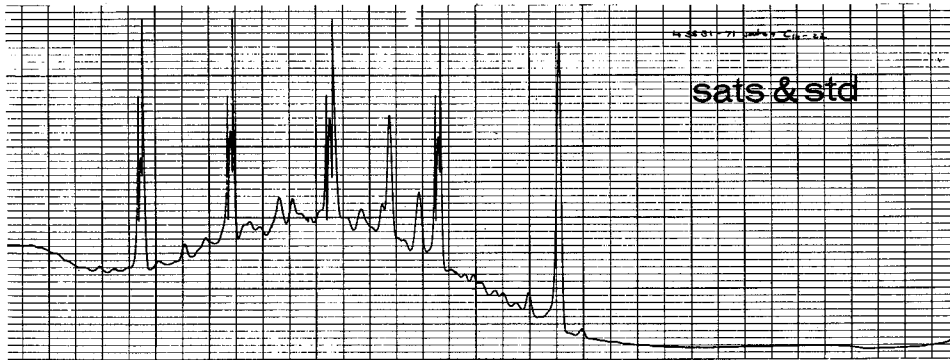
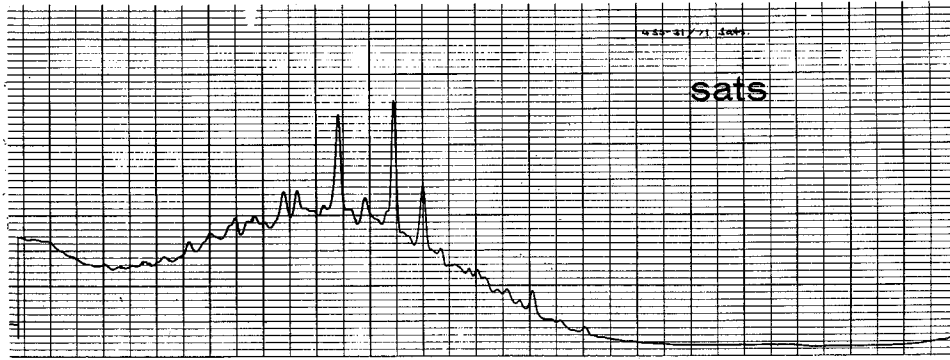


FIGURE 6.
APRIL 1971

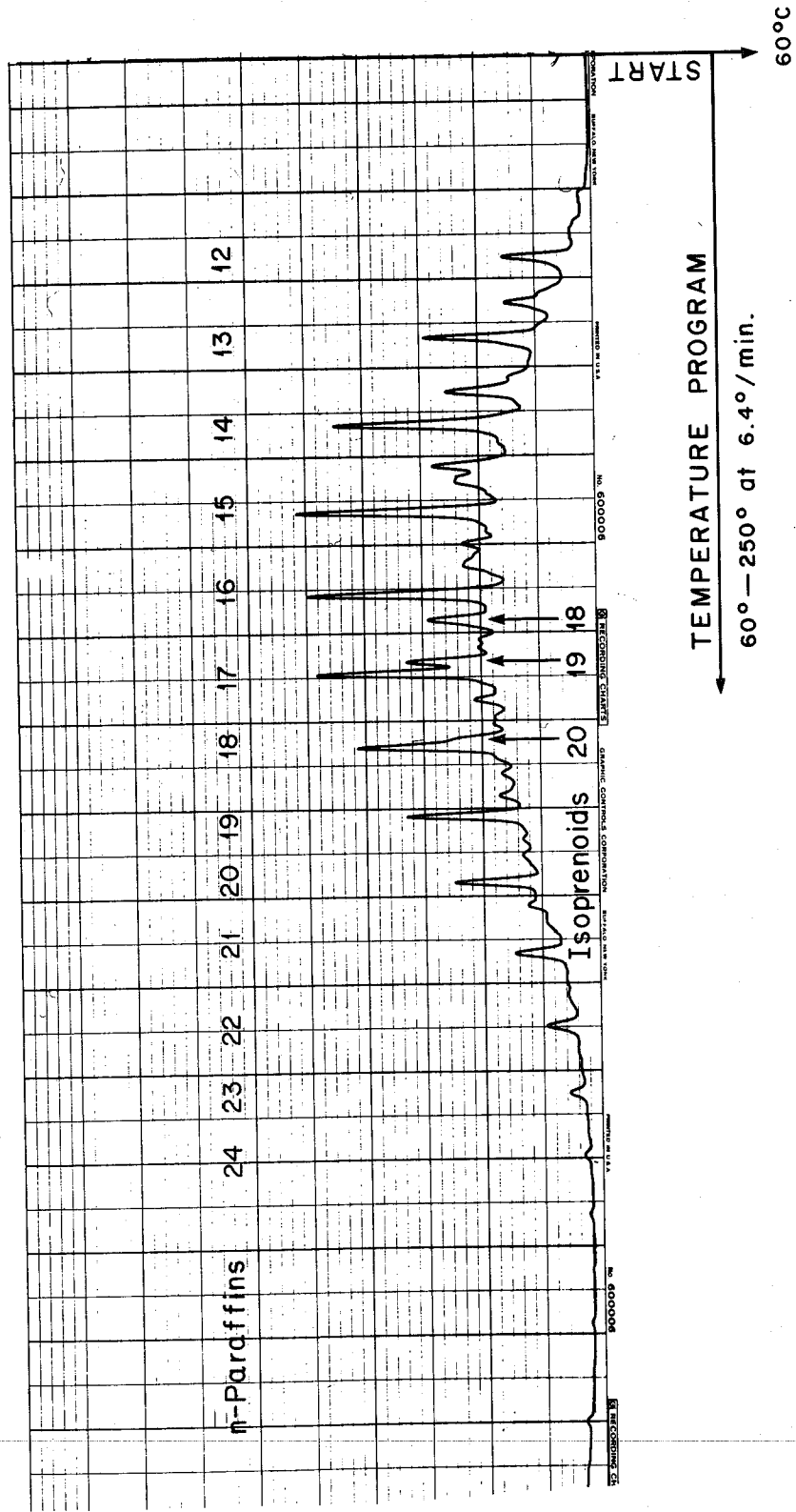


Figure 7.

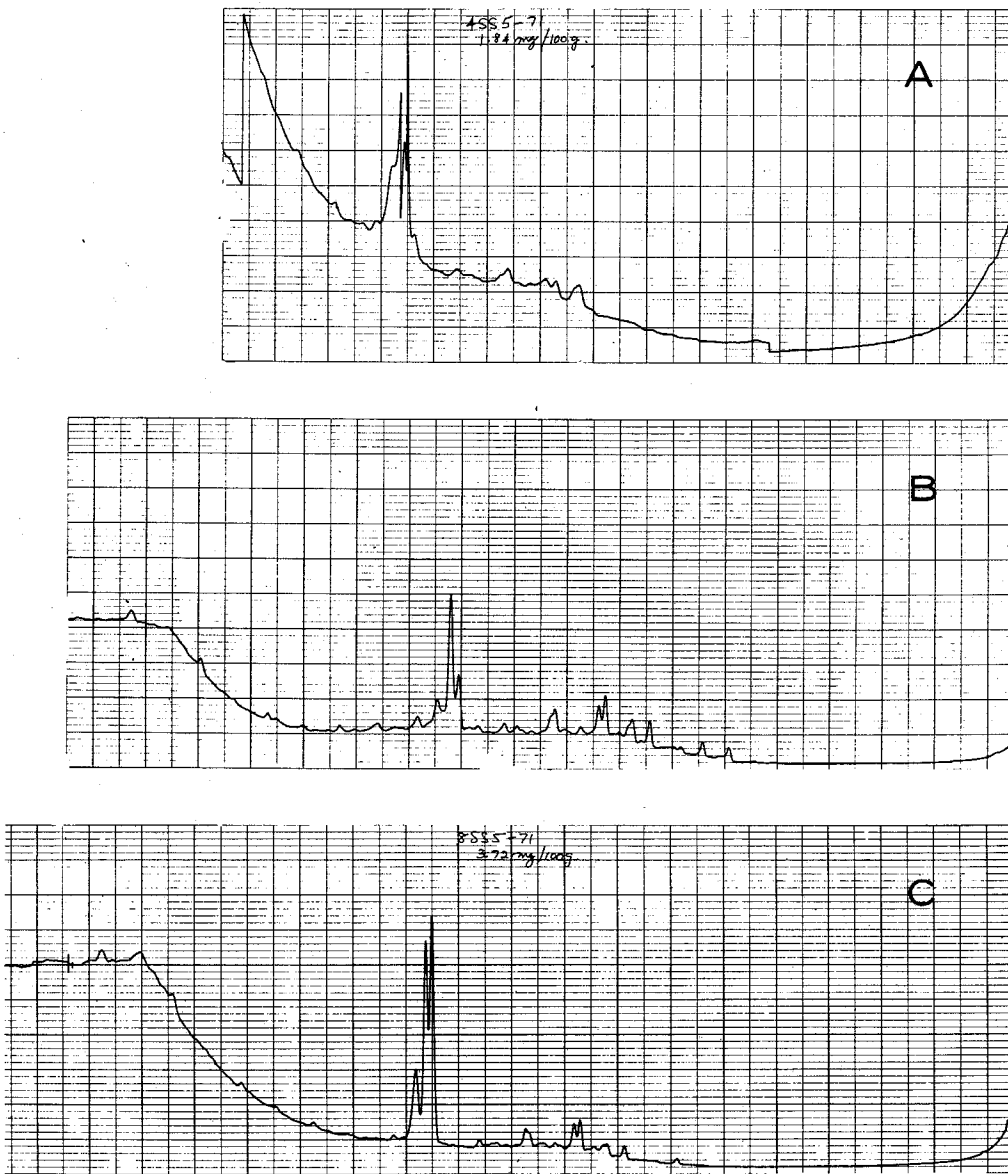


FIGURE 8. STA. 5 APRIL, JULY, AUG. 1971

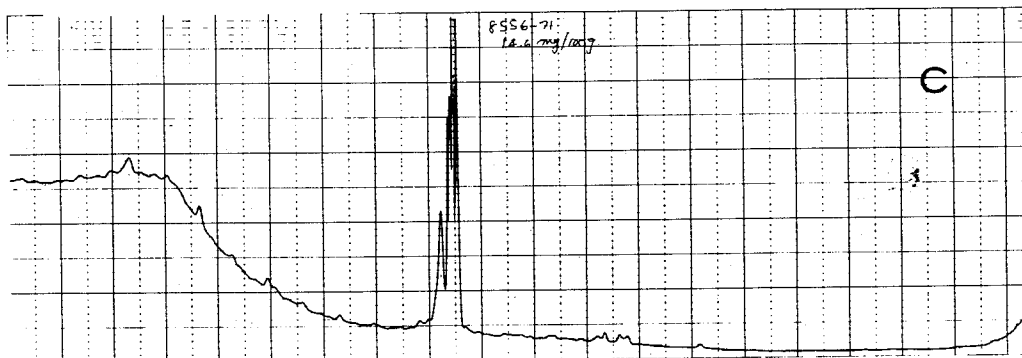
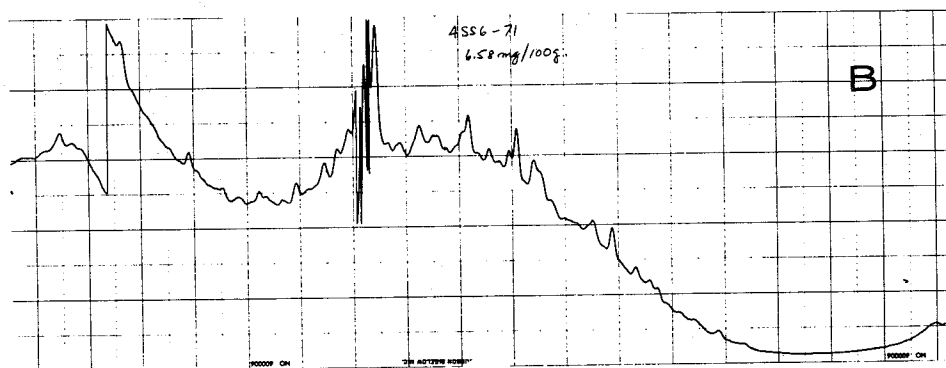
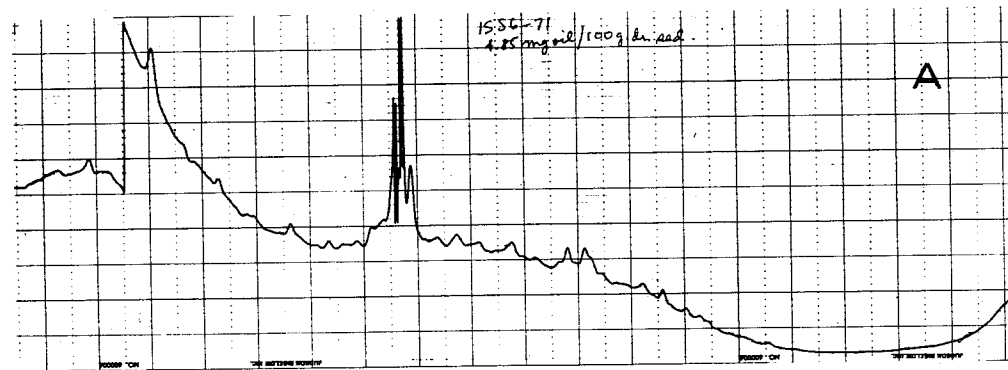


FIGURE 9. STA. 6 JAN., APRIL, AUG. 1971

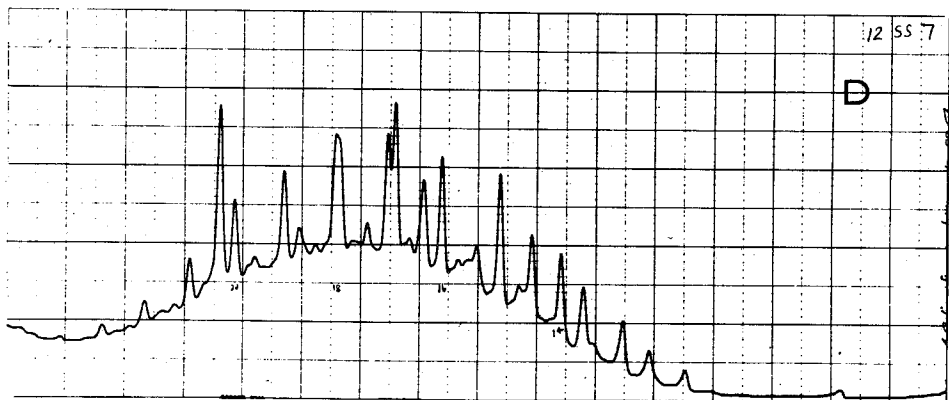
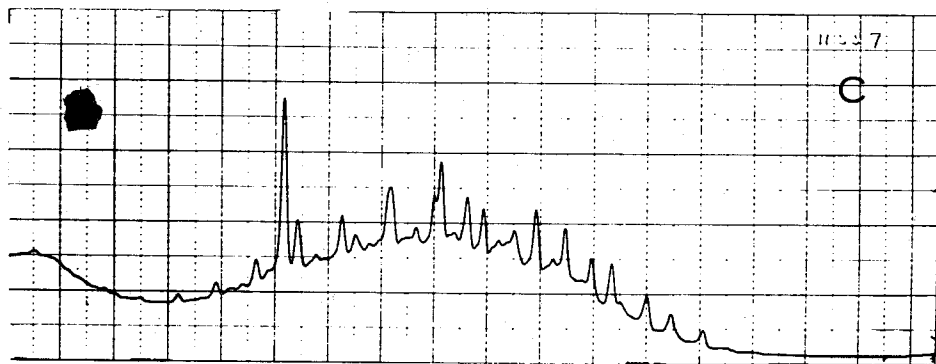
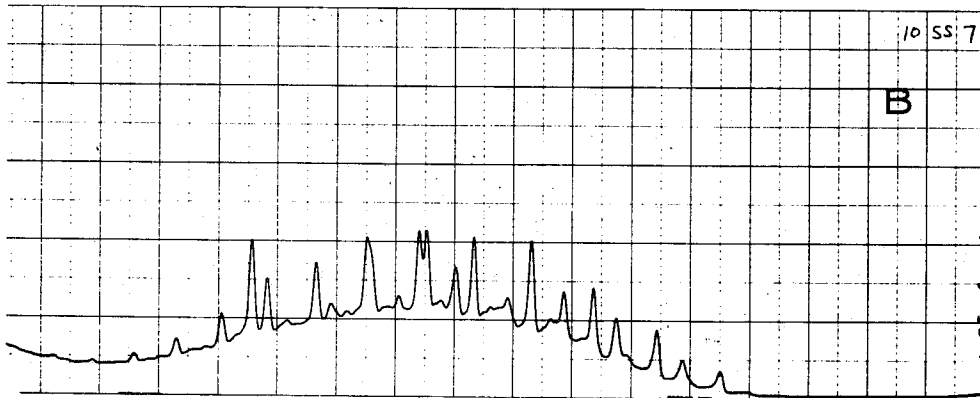
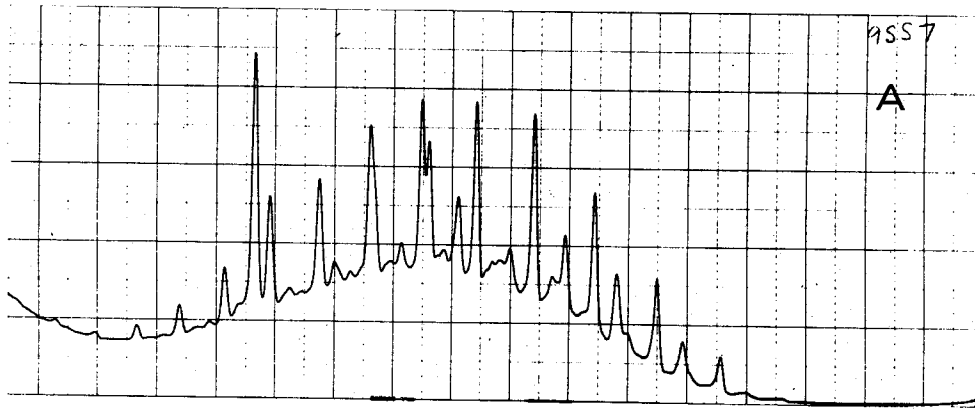


FIGURE 10.
STA. 7
SEPT.-DEC. 1968

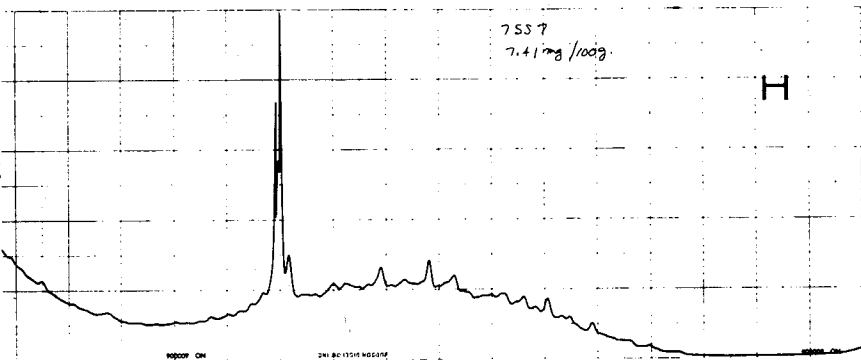
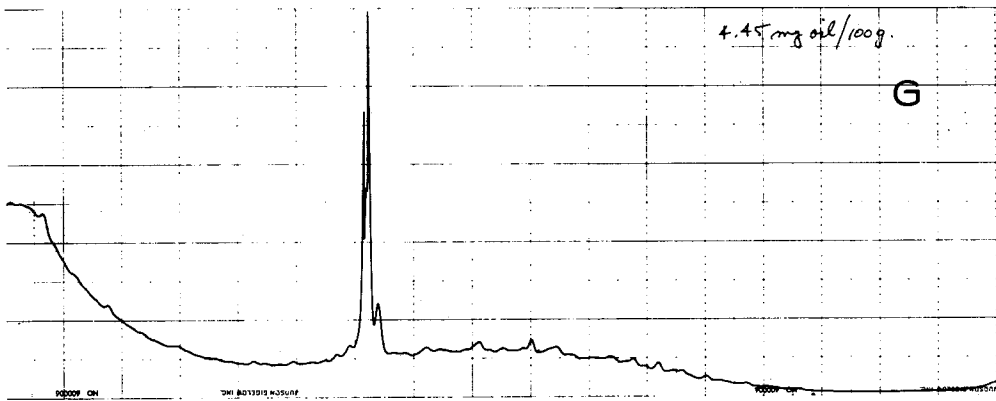
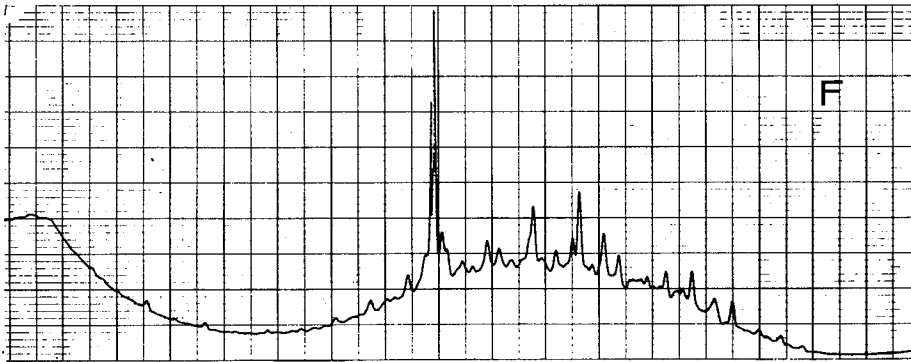
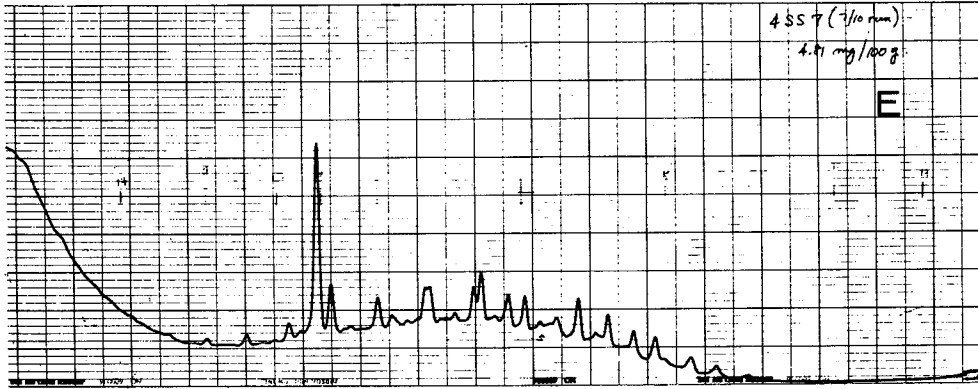


FIGURE 10.
STA. 7
APRIL-JULY 1970

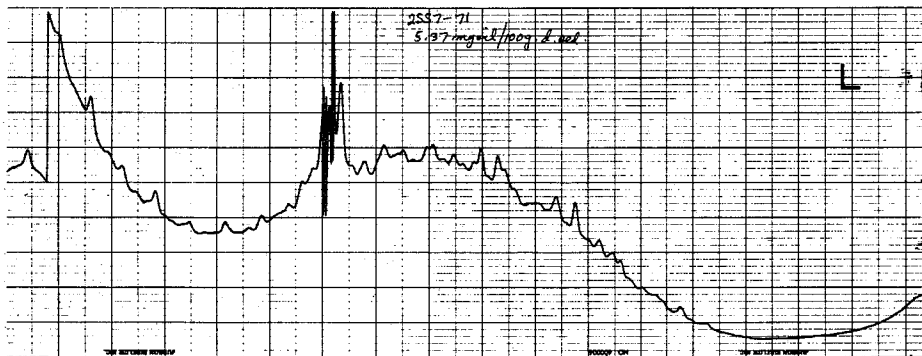
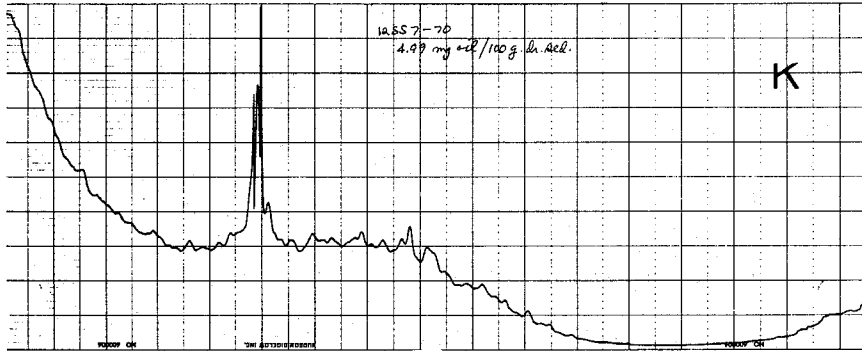
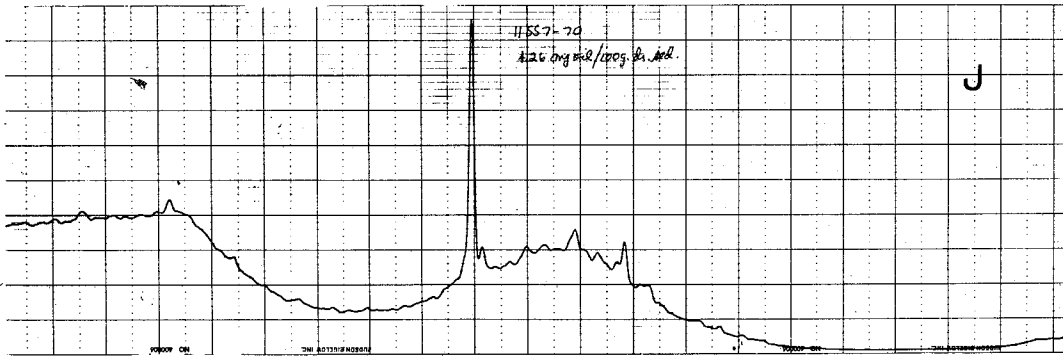
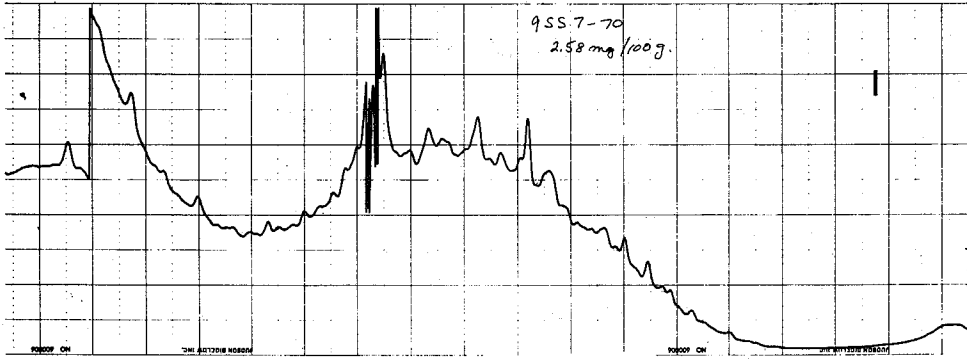


FIGURE 10.
STA. 7
SEPT., NOV., DEC., 1970
FEB. 1971

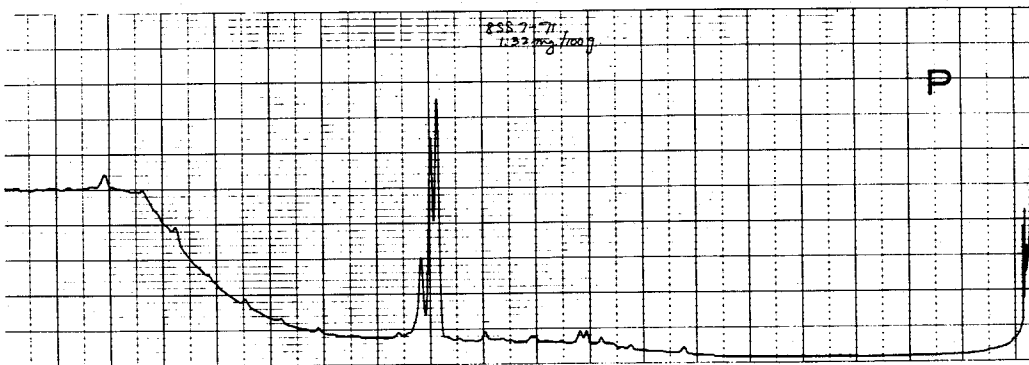
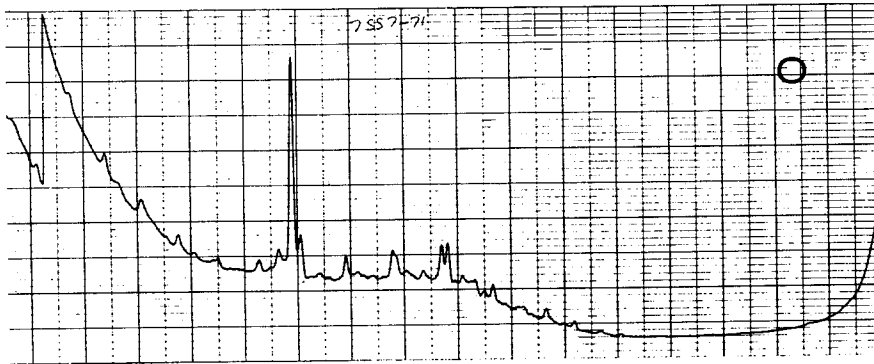
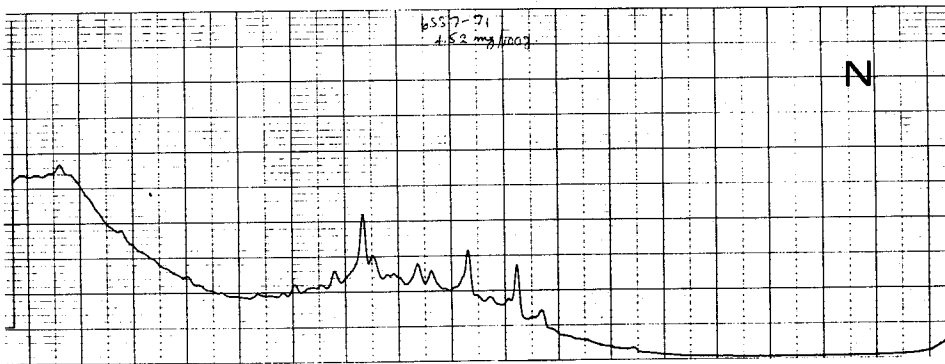
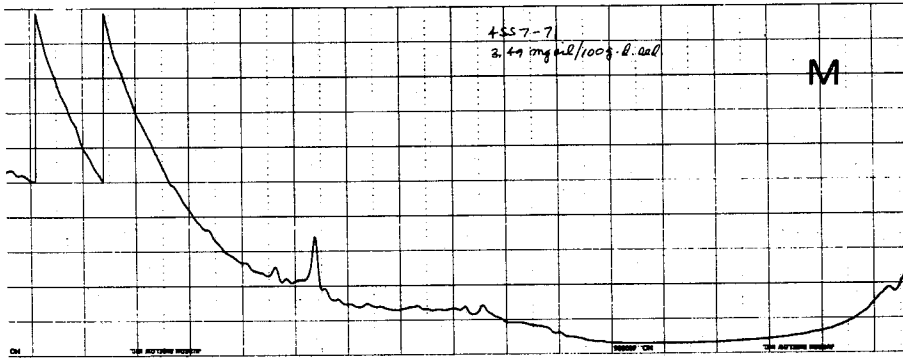


FIGURE 10.
STA. 7
APRIL,
JUNE-AUG. 1971

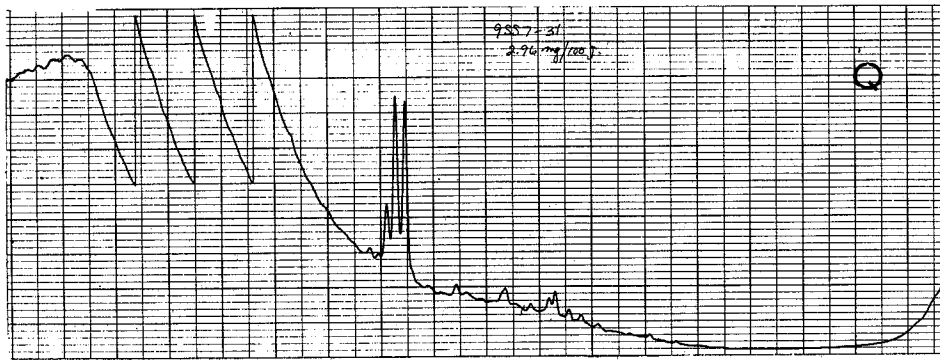


FIGURE 10.
STA. 7
SEPT. 1971

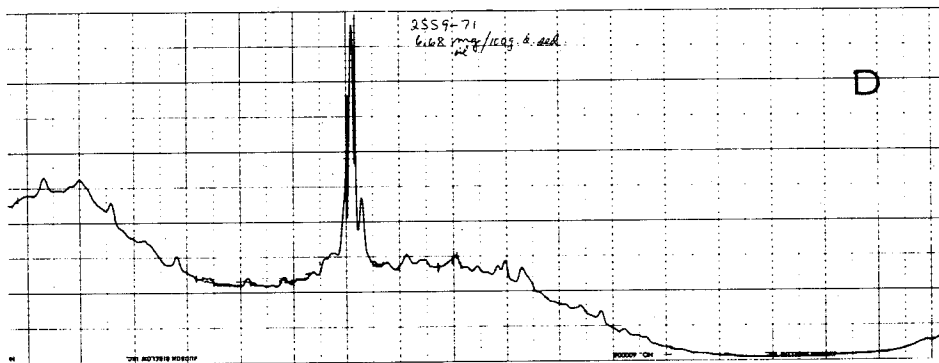
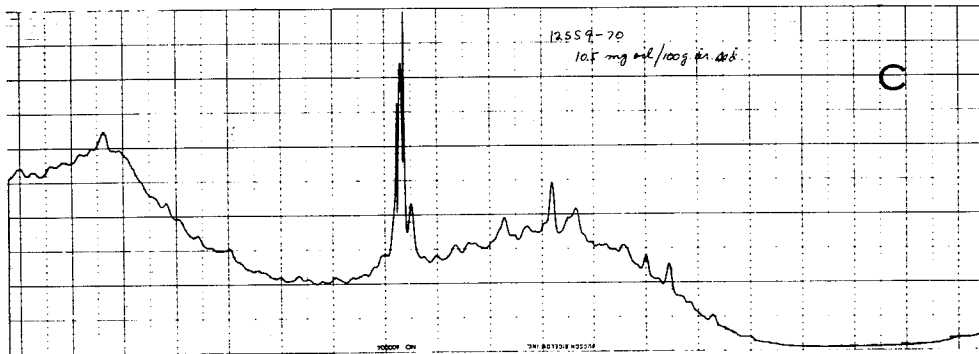
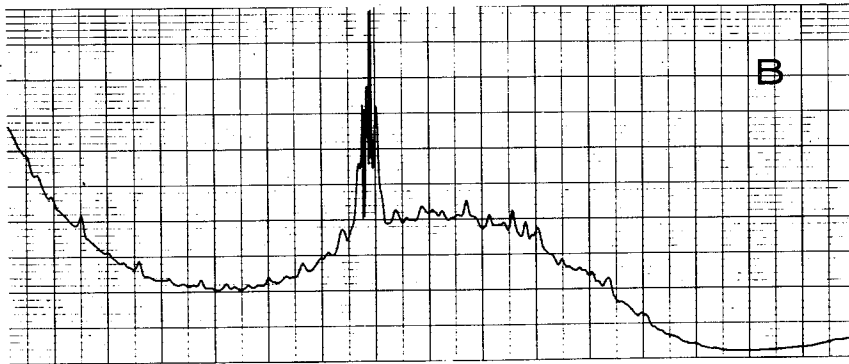
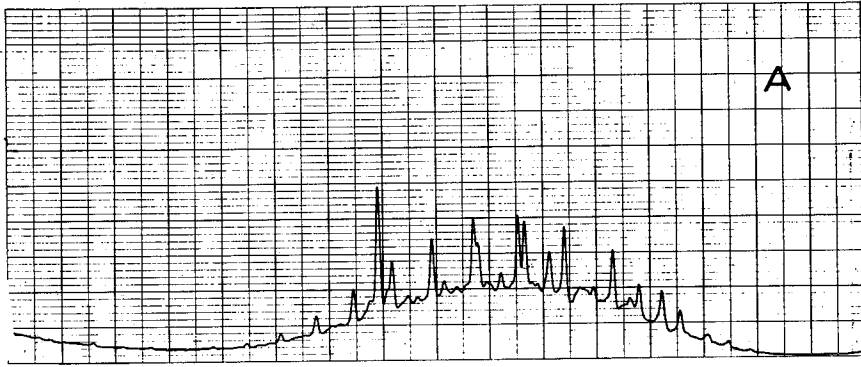


FIGURE 11.
 STA. 9
 NOV. 1969
 SEPT., DEC., 1970
 FEB. 1971

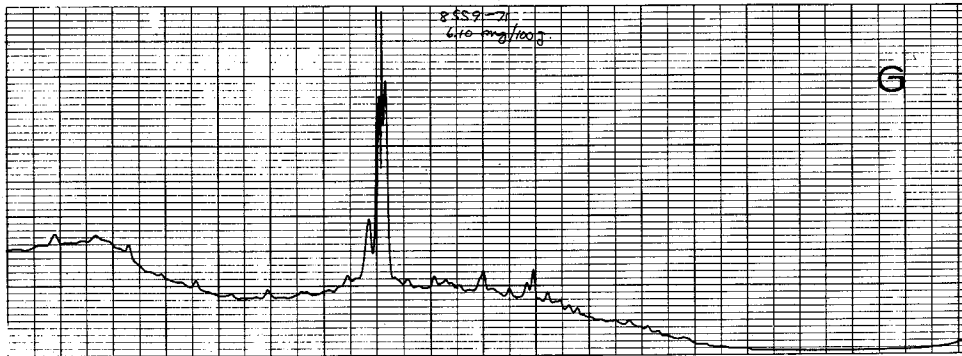
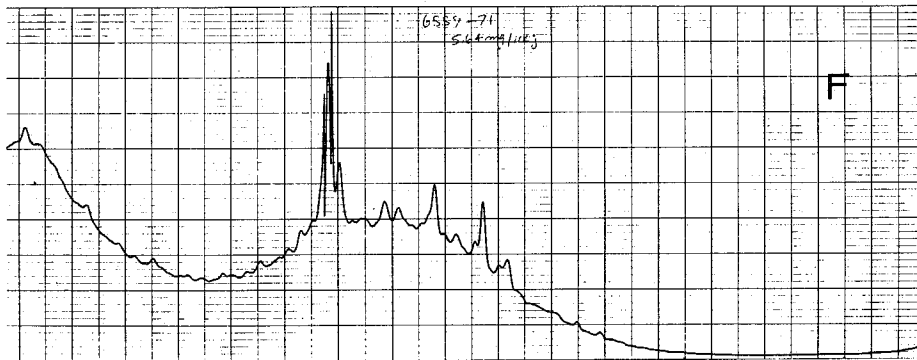
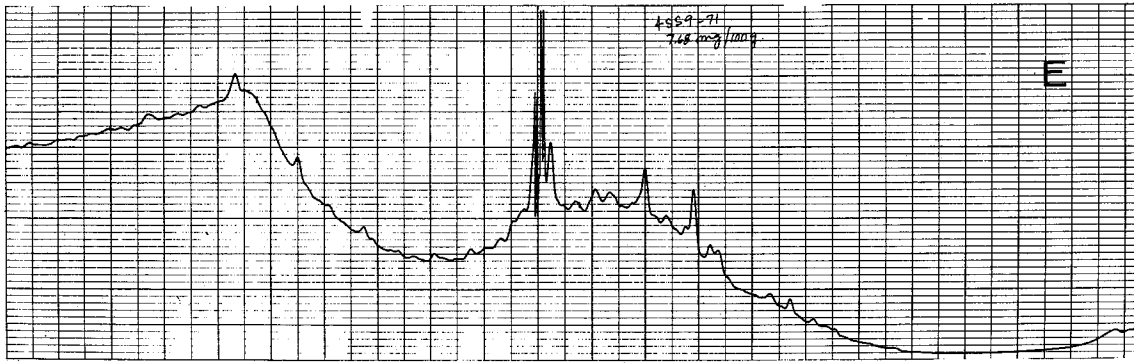


FIGURE 11.
STA. 9
APRIL, JUNE,
AUG., 1971

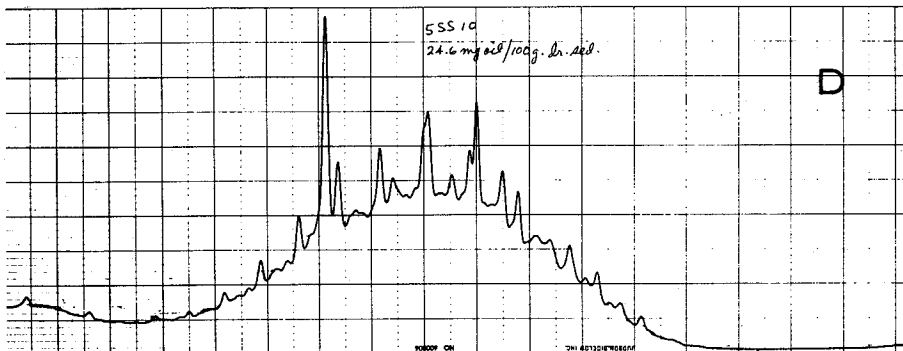
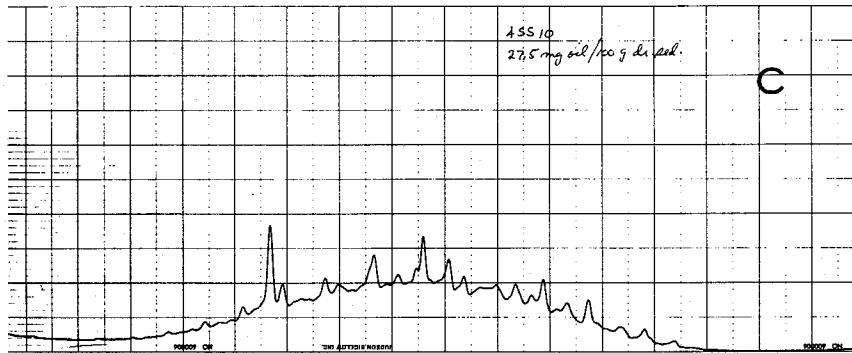
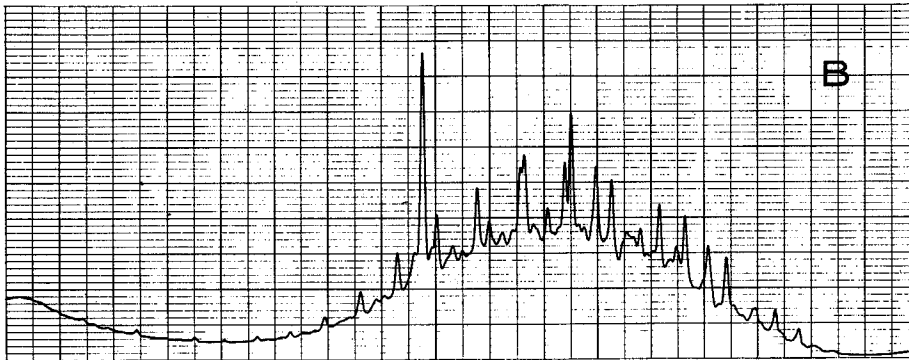
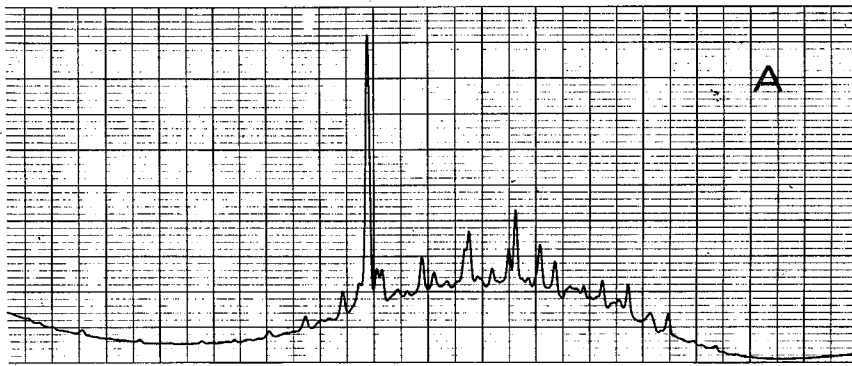


FIGURE 12.
 STA. 10
 NOV., DEC., 1969
 APRIL, MAY 1970

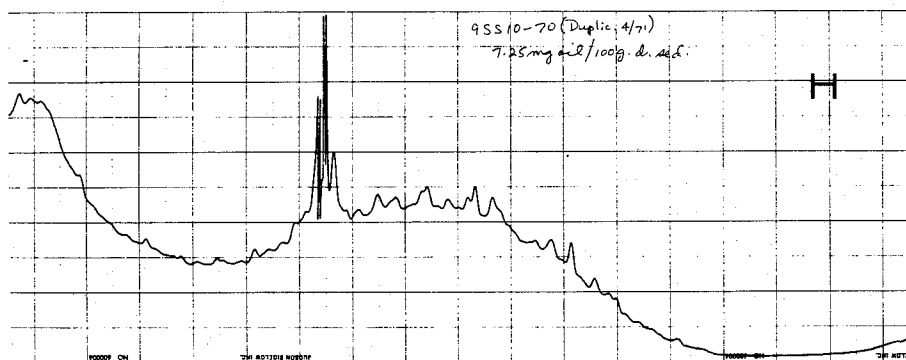
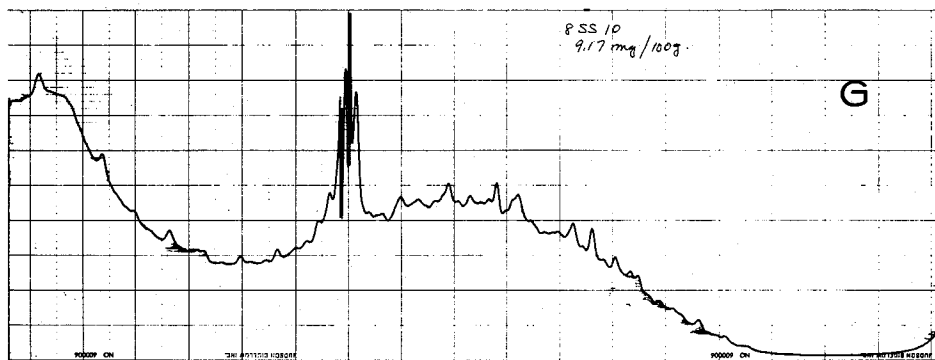
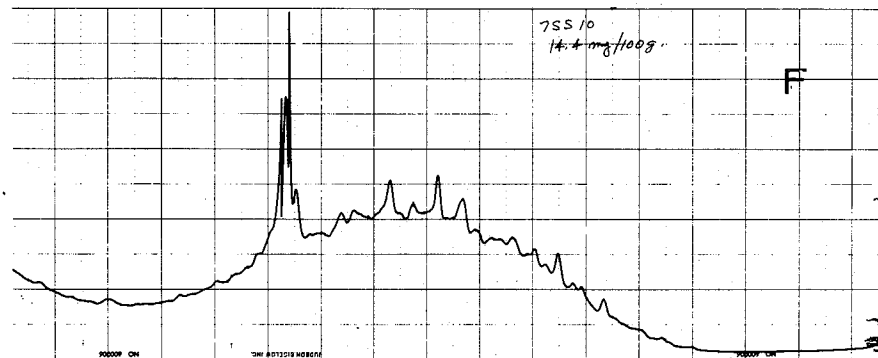
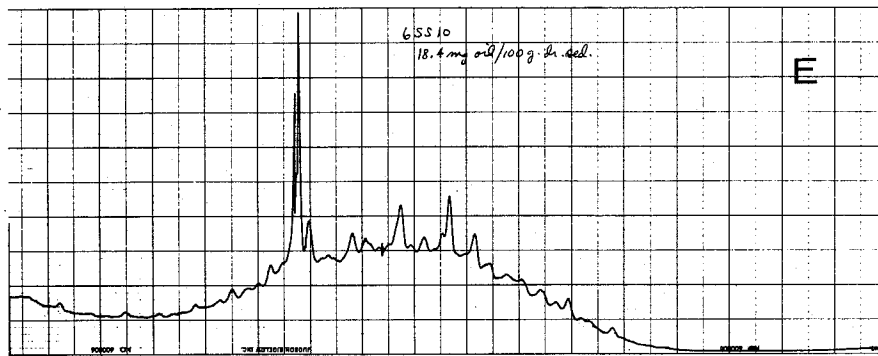


FIGURE 12.
STA. 10
JUNE-SEPT. 1970

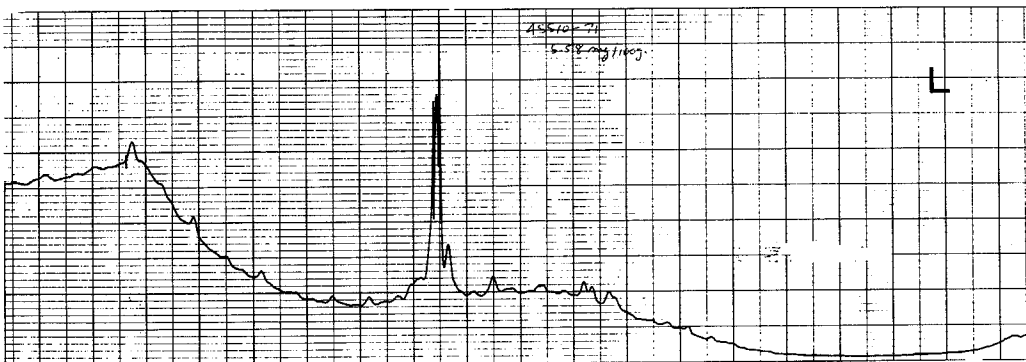
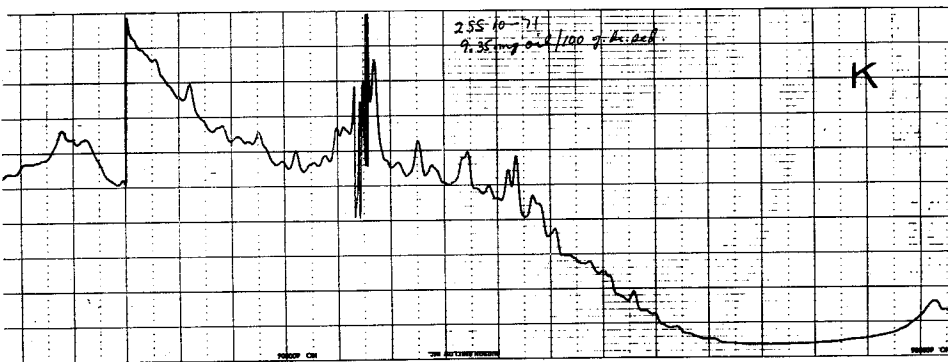
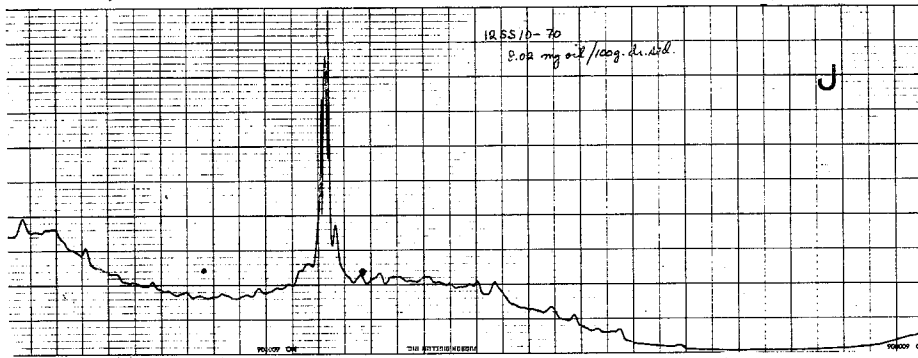
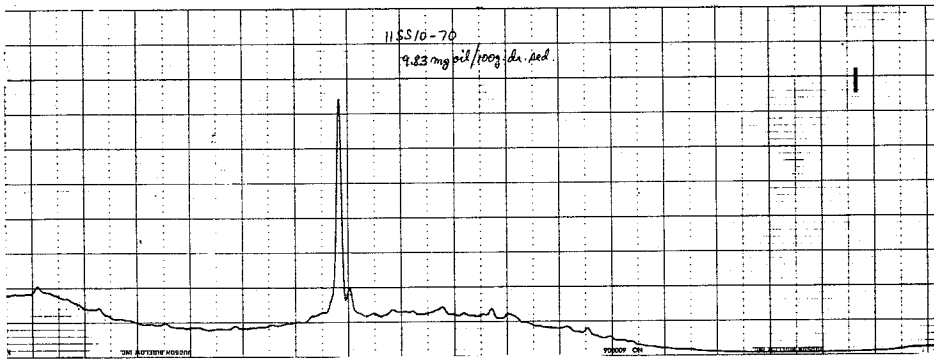


FIGURE 12.
STA. 10
NOV., DEC., 1970
FEB., APRIL 1971

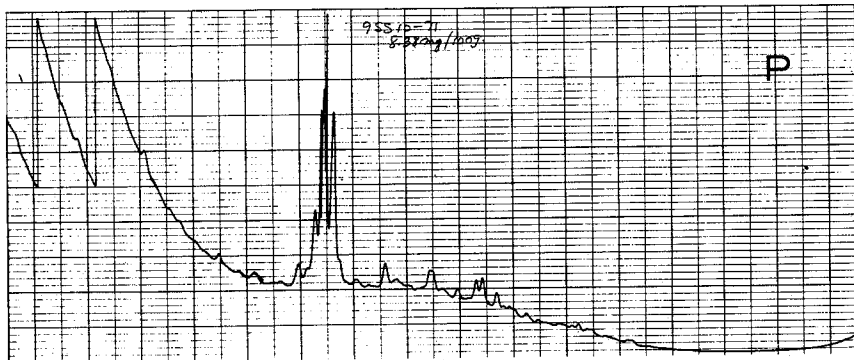
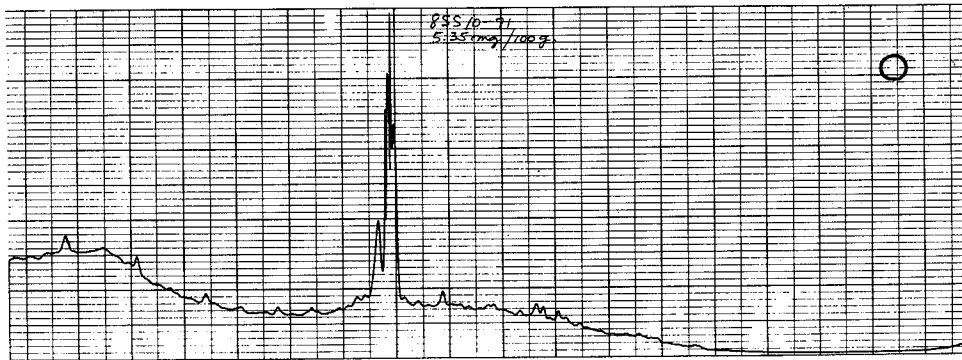
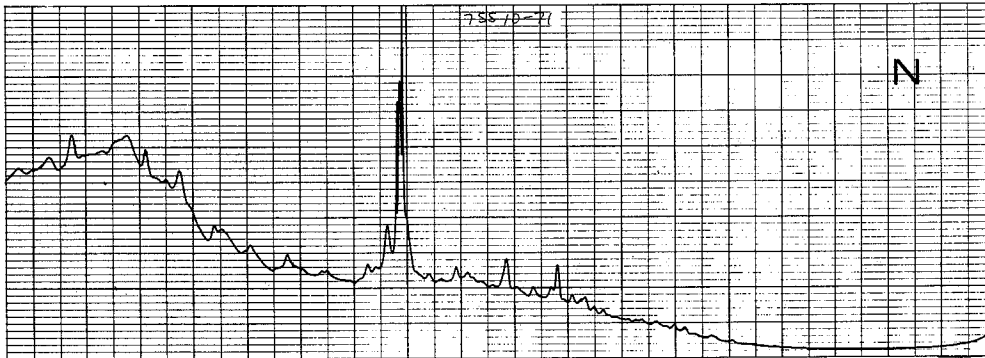
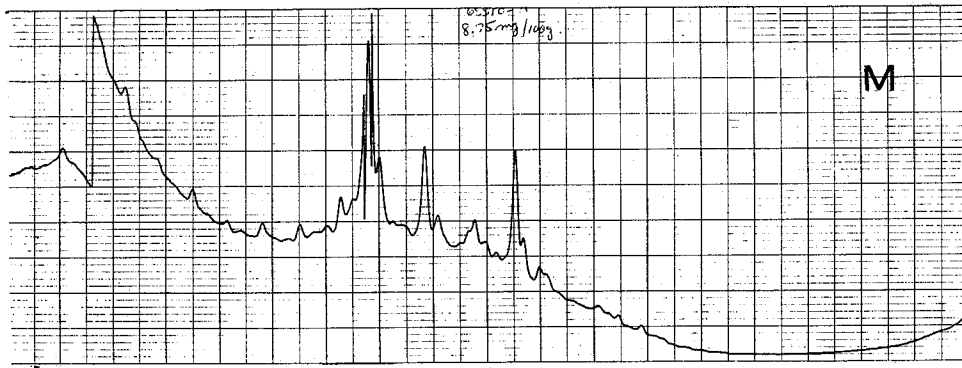


FIGURE 12.
STA. 10
JUNE-SEPT. 1971

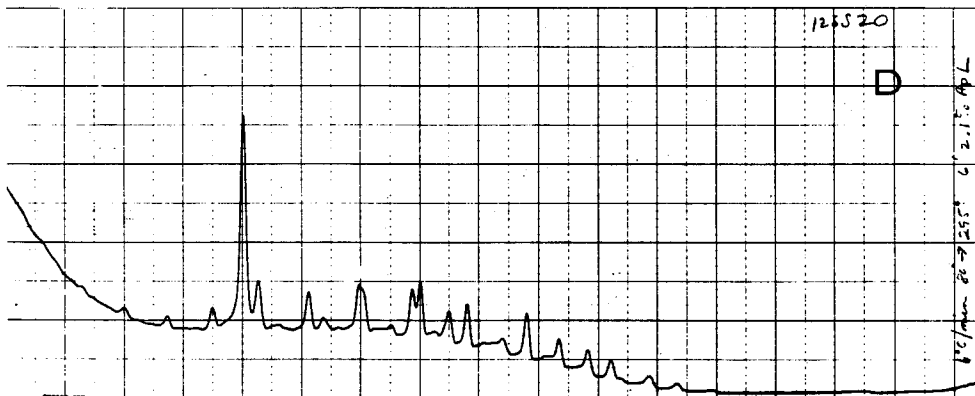
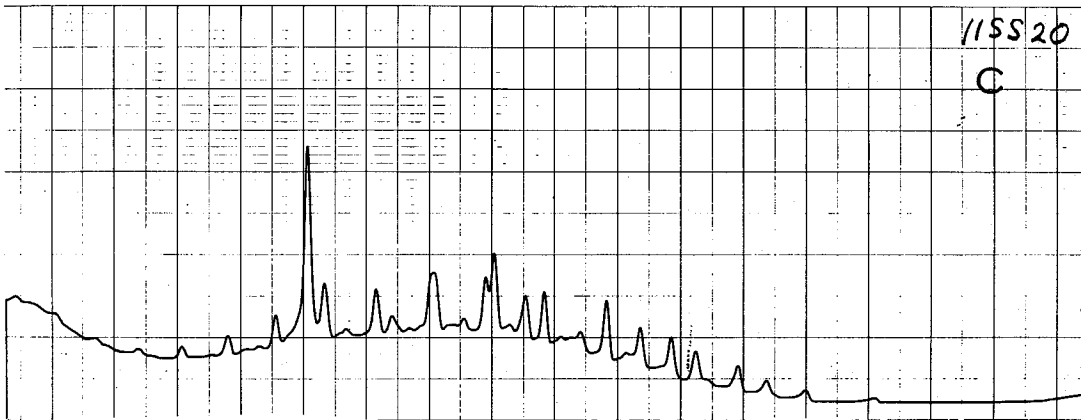
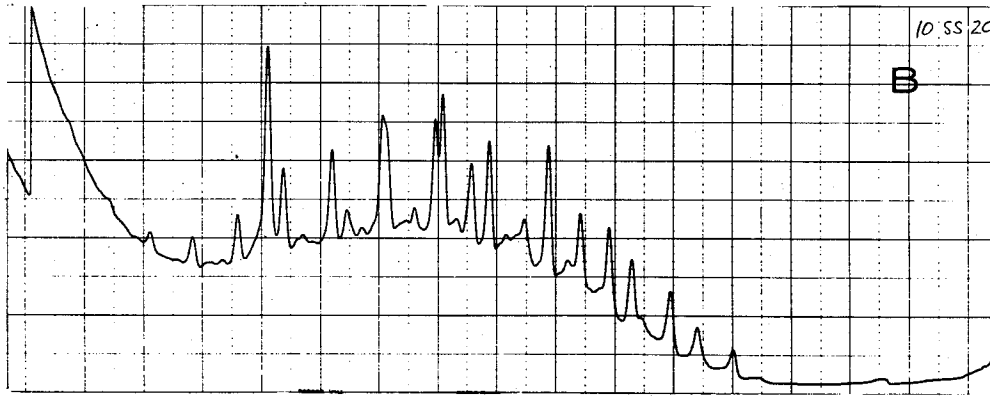
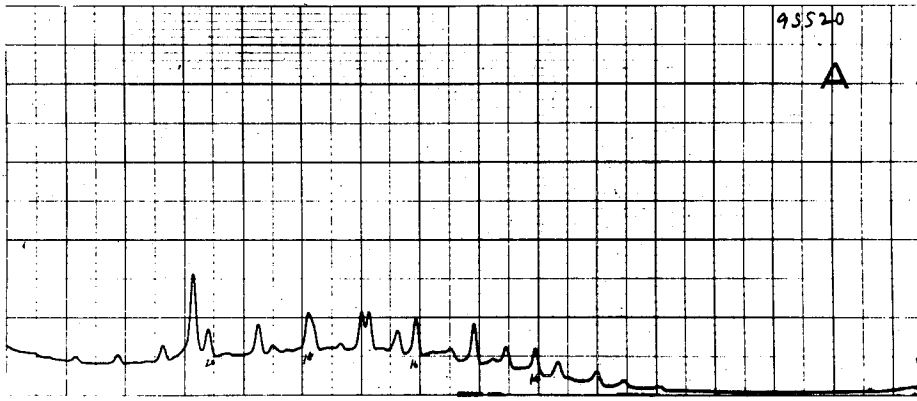


FIGURE 13.
STA. 20
SEPT.-DEC. 1969

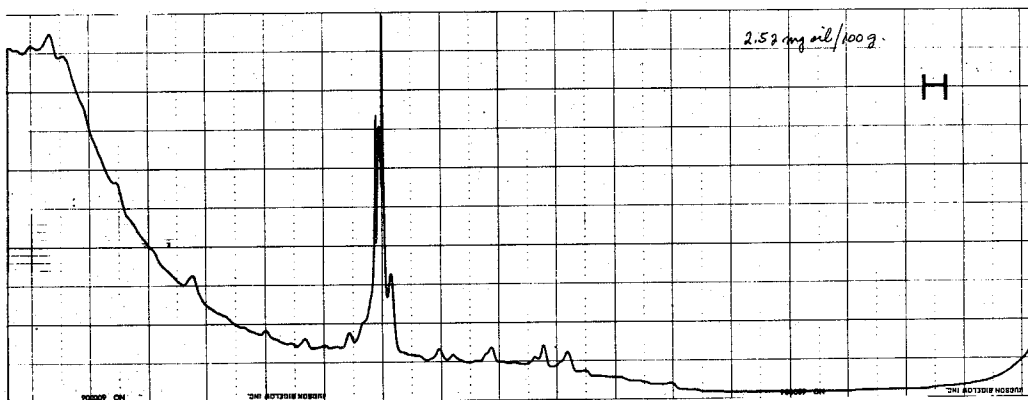
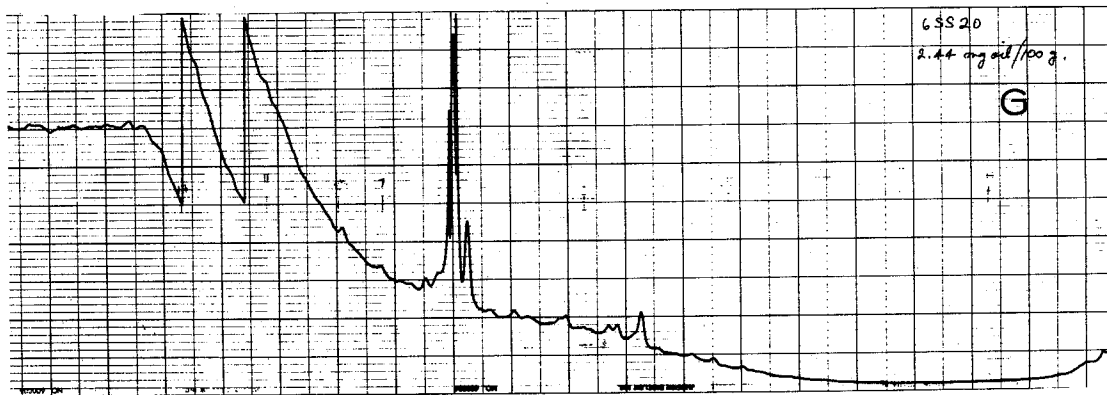
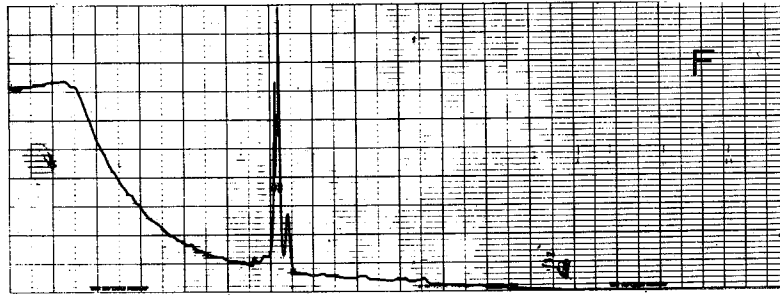
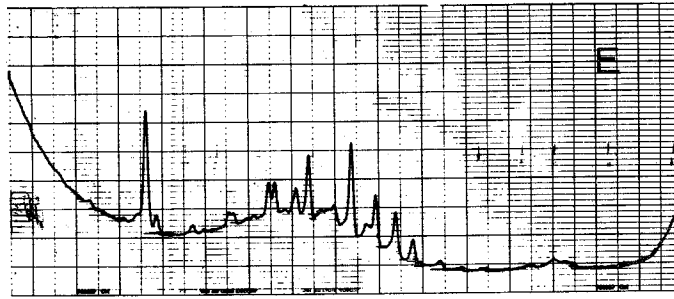


FIGURE 13.
STA. 20
APRIL-JULY 1970

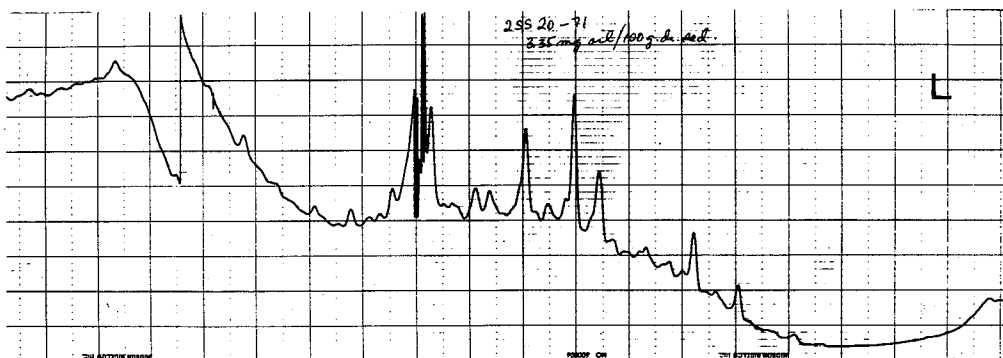
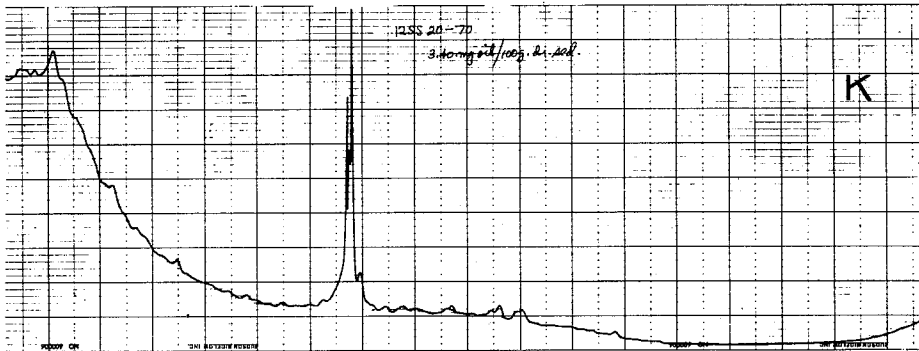
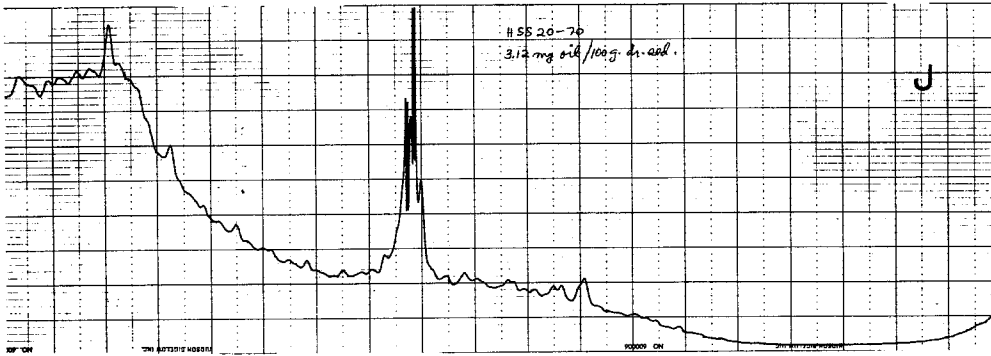
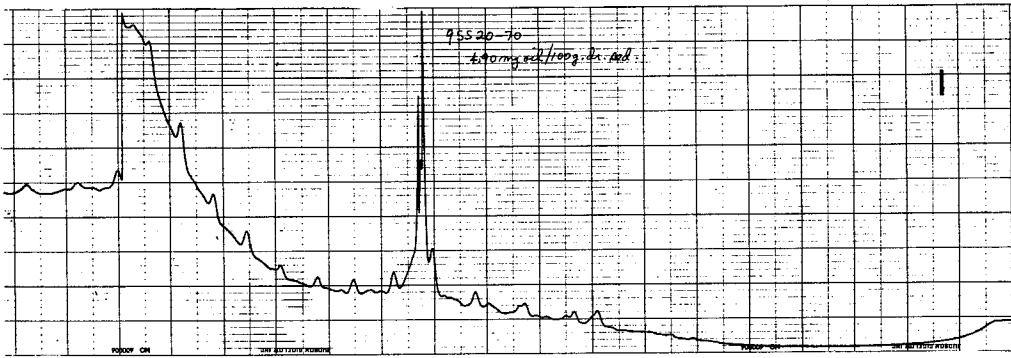


FIGURE 13
 STA 20
 SEPT., NOV., DEC.
 1970
 FEB. 1971

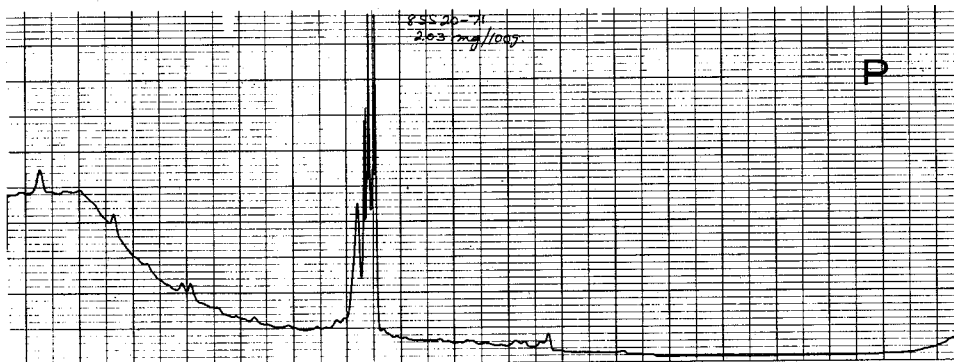
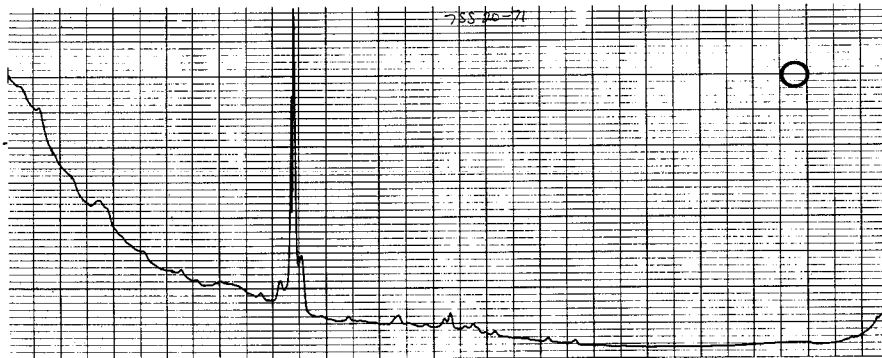
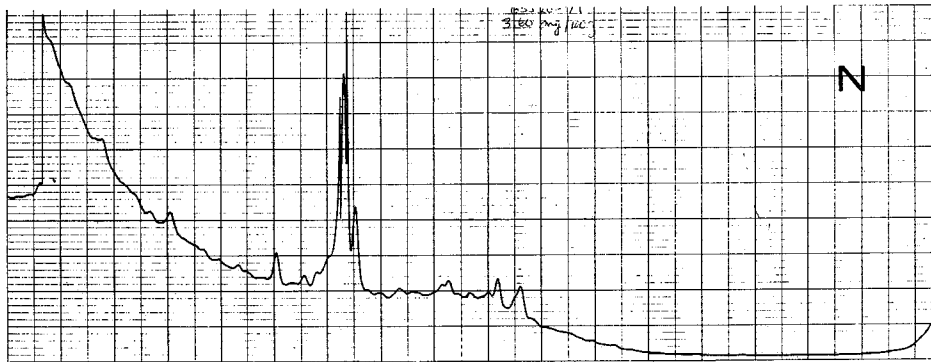
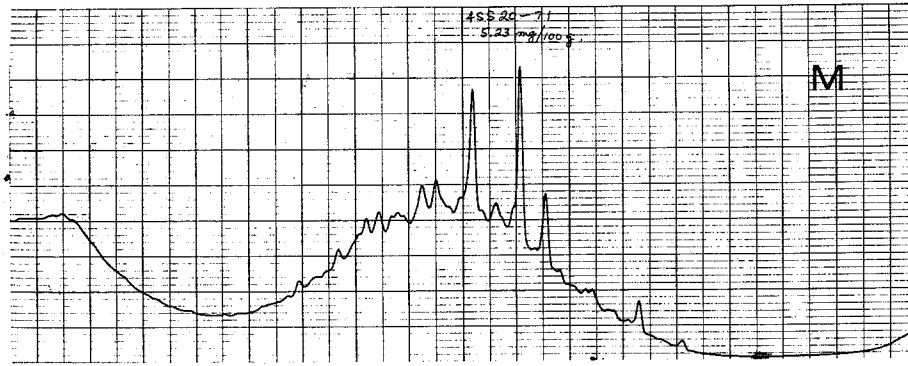


FIGURE 13.
STA. 20
APRIL, JUNE,
AUG. 1971

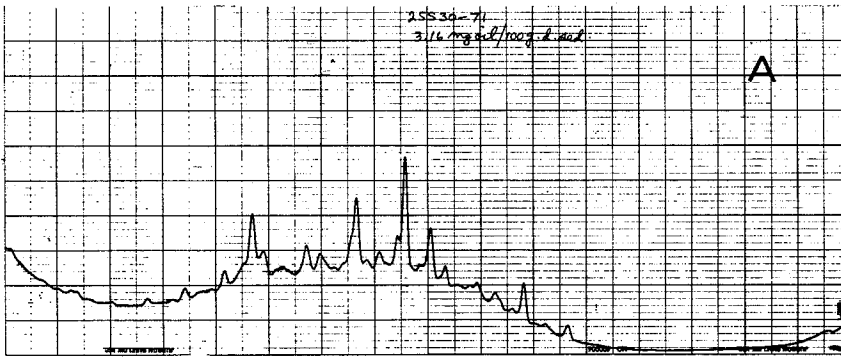


FIGURE 14.

STA. 30
FEB. 1971

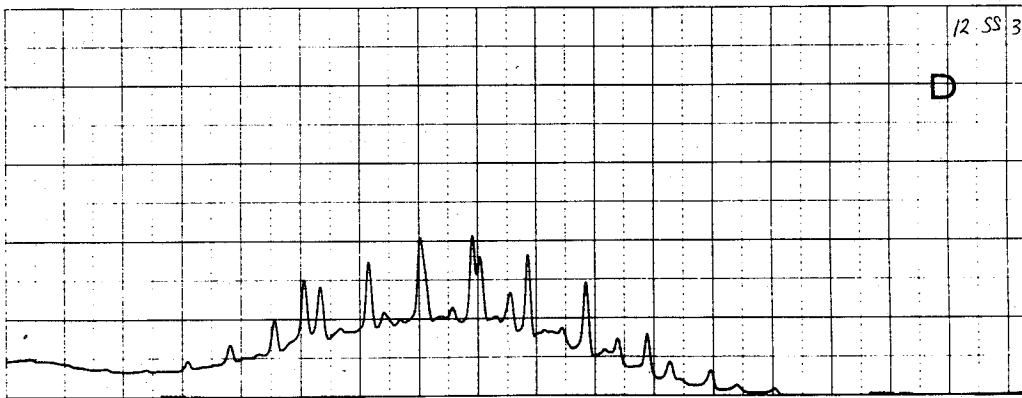
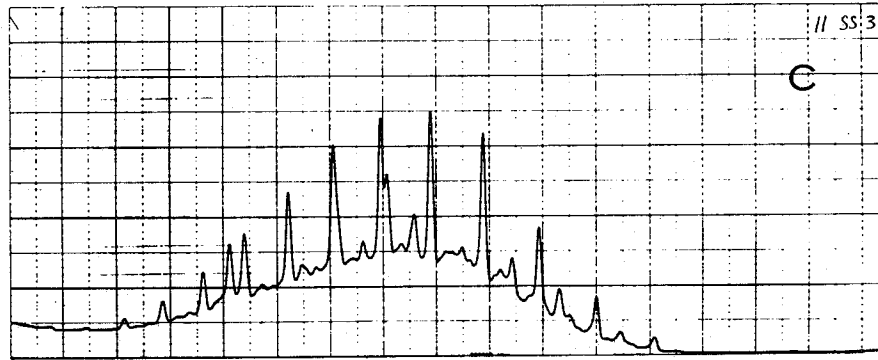
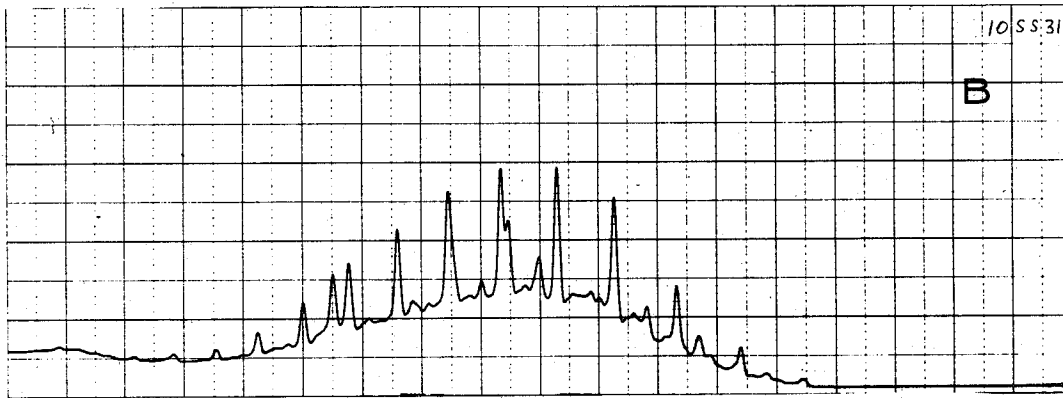
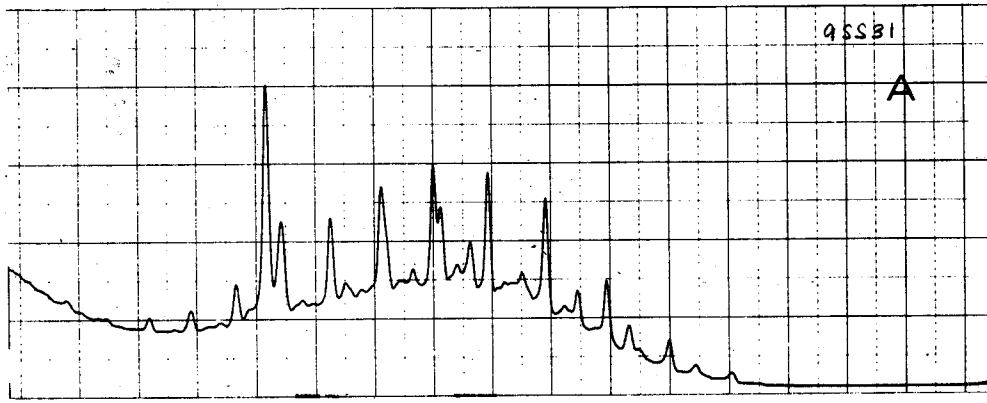


FIGURE 15.
STA. 31
SEPT.-DEC. 1969

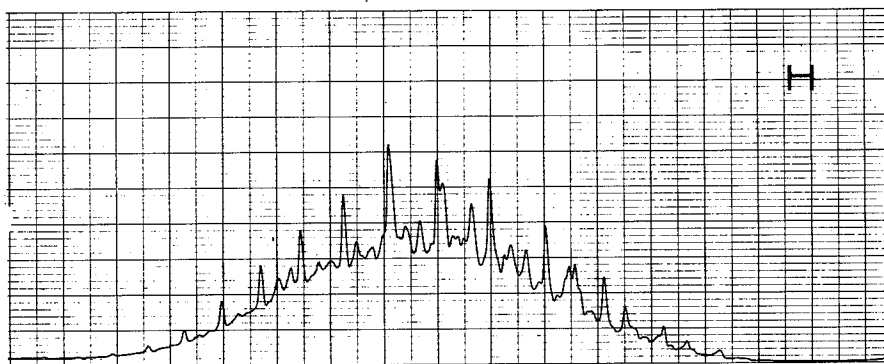
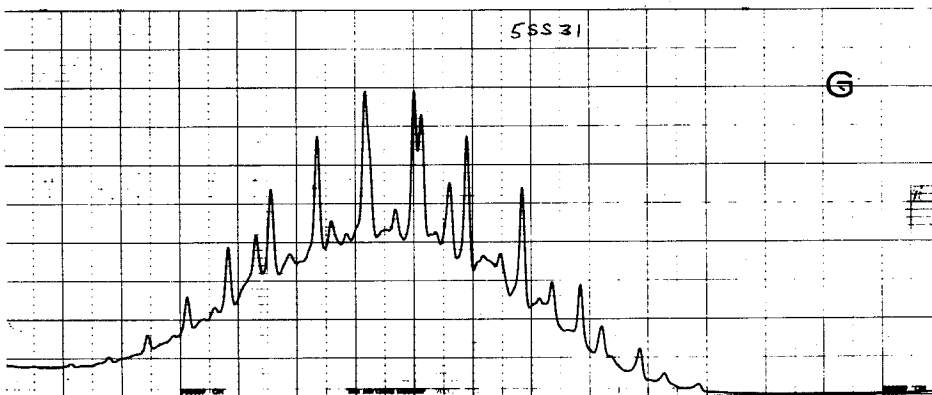
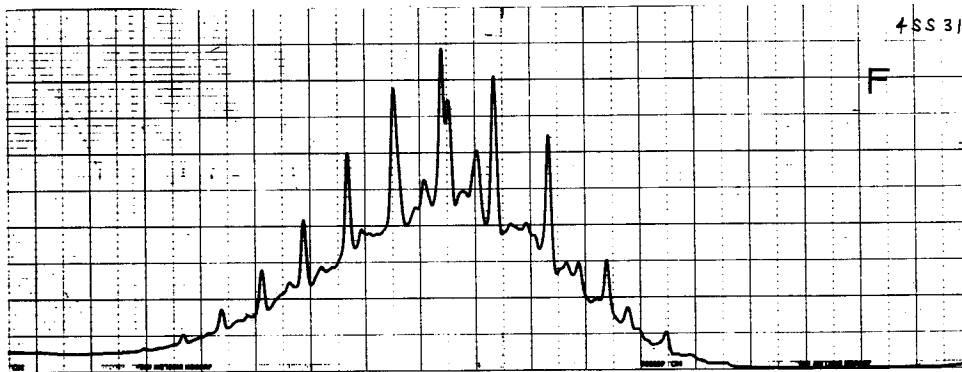
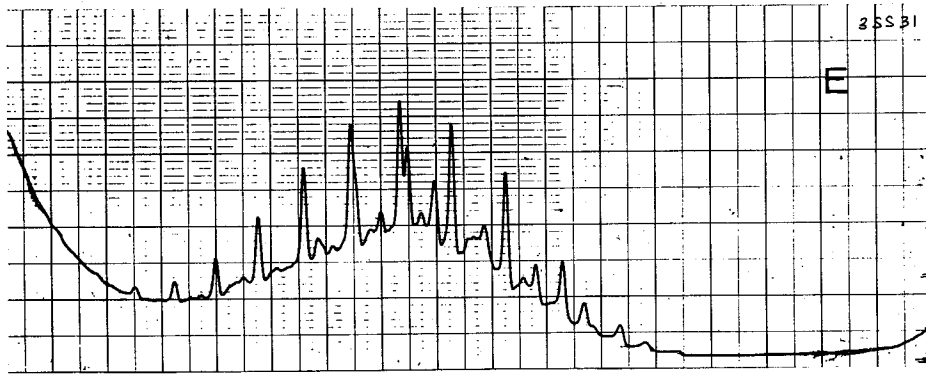


FIGURE 15.
 STA. 31
 MARCH - JUNE 1970

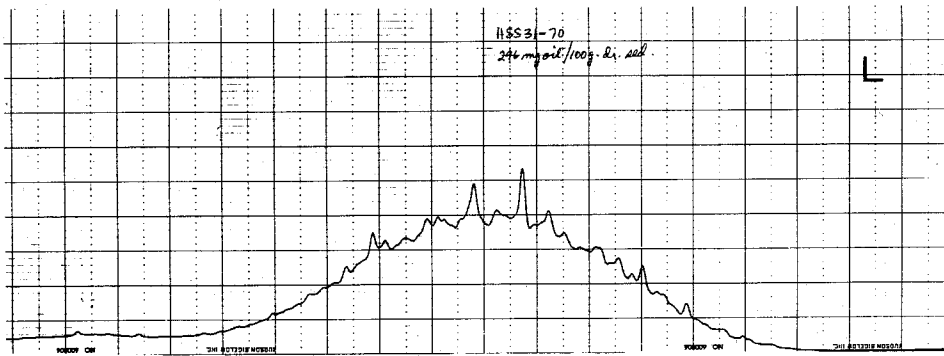
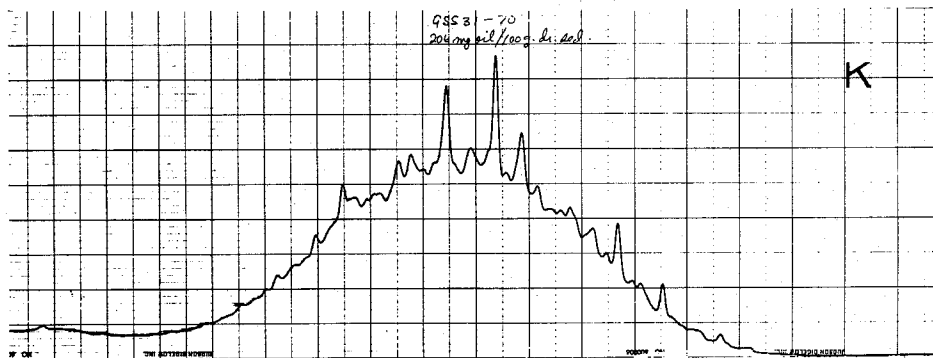
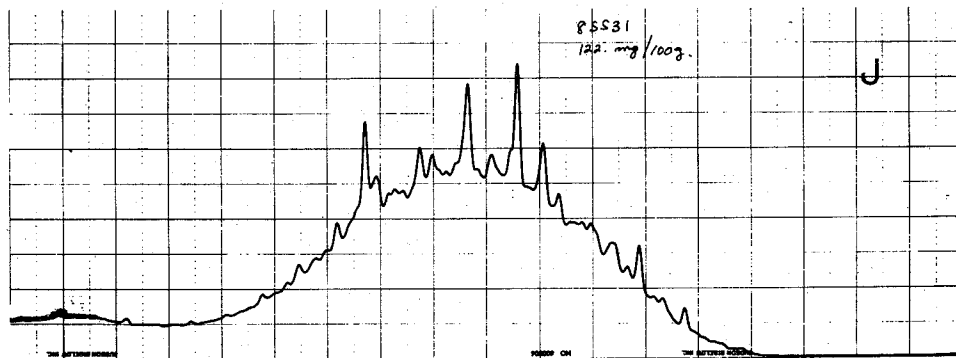
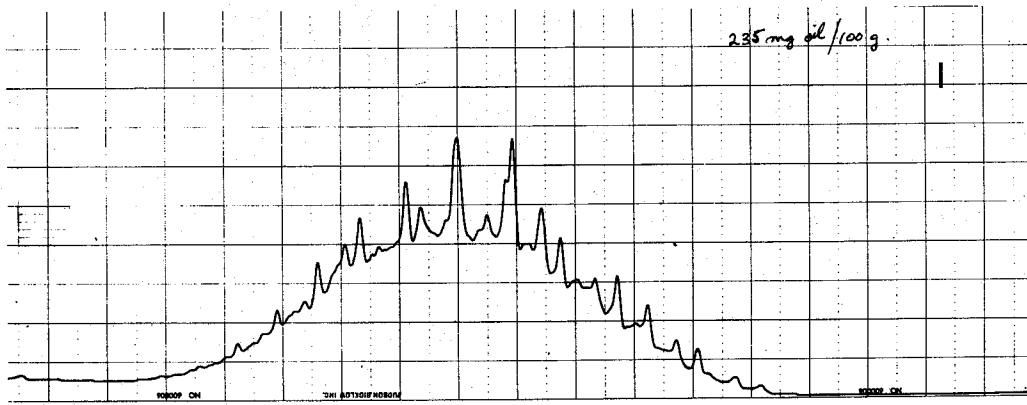


FIGURE 15.
STA. 31
JULY- SEPT.,
NOV. 1970

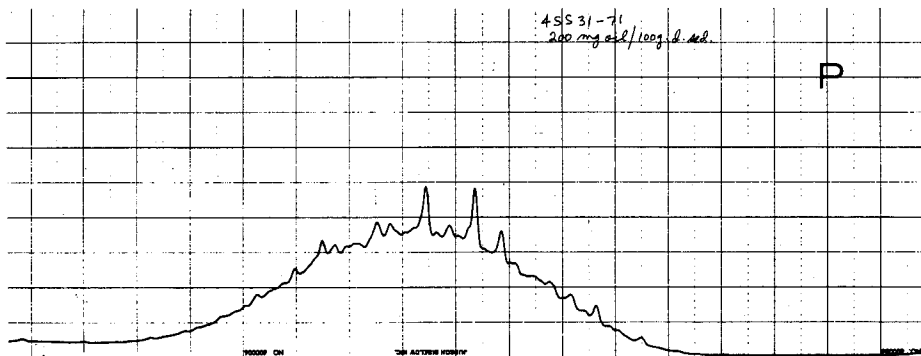
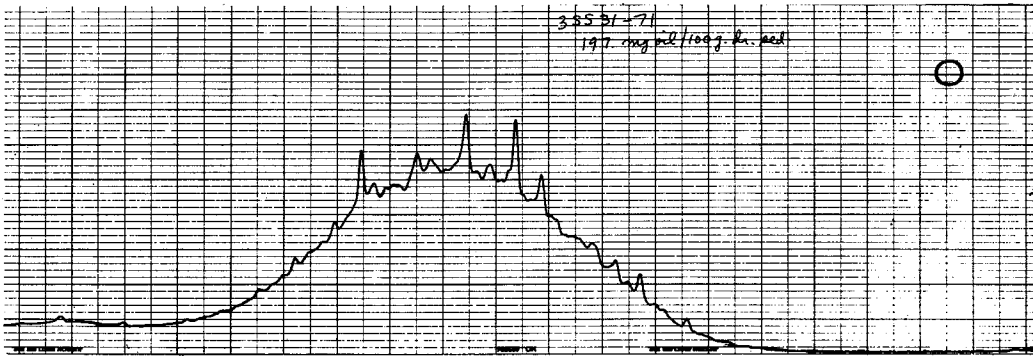
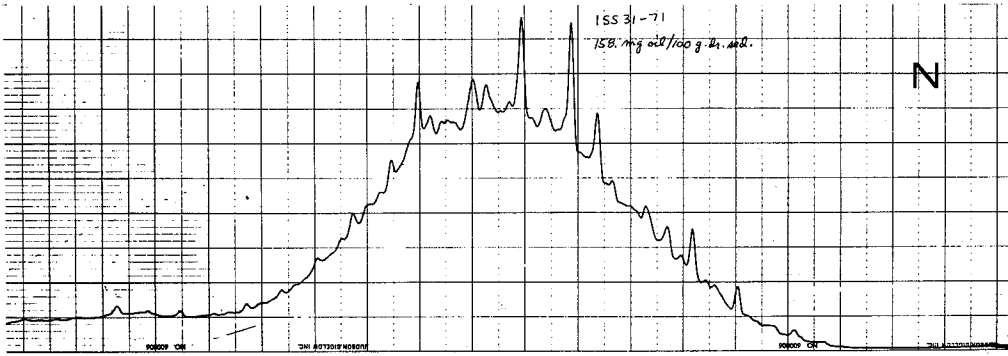
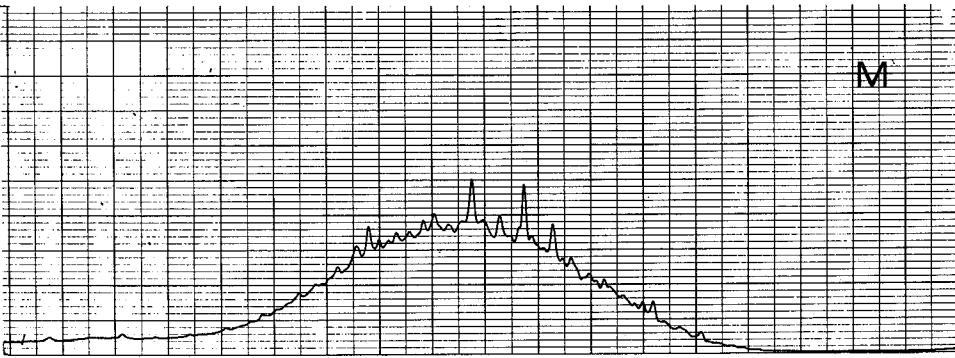


FIGURE 15.
 STA. 31
 DEC. 1970
 JAN. 1971
 MARCH, APRIL 1971

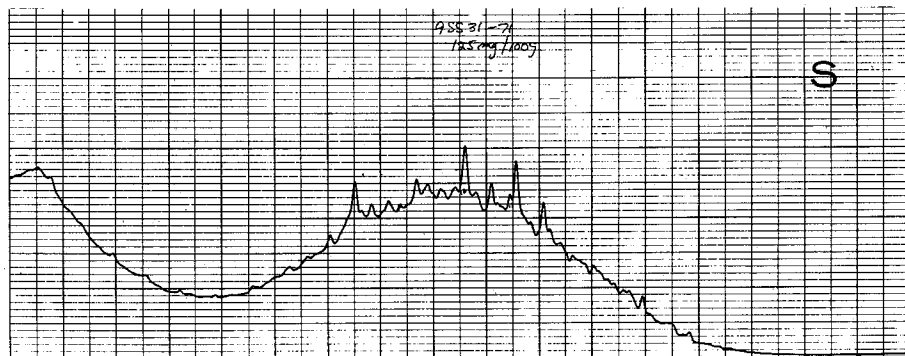
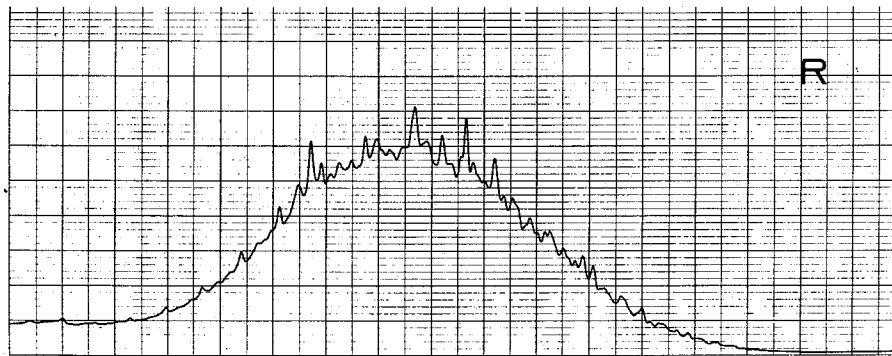
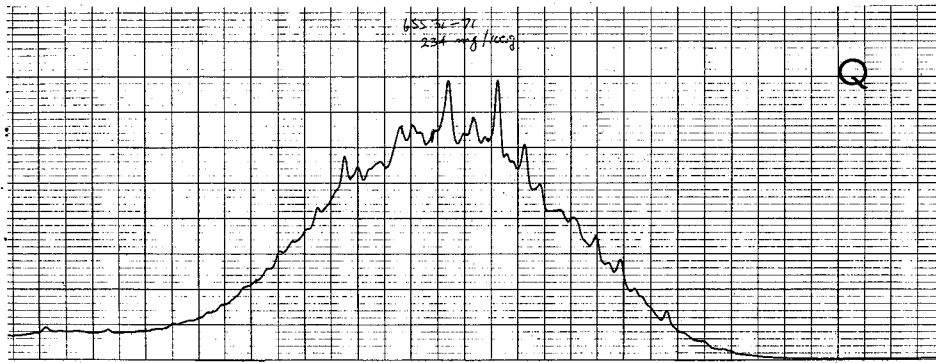


FIGURE 15.
STA. 31
JUNE, AUG.,
SEPT. 1971

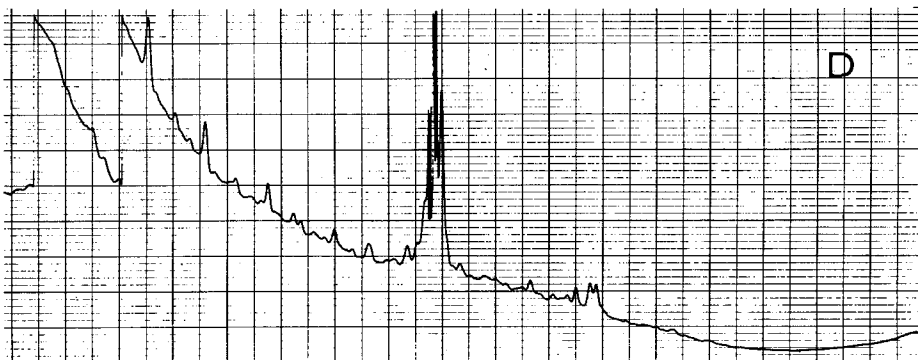
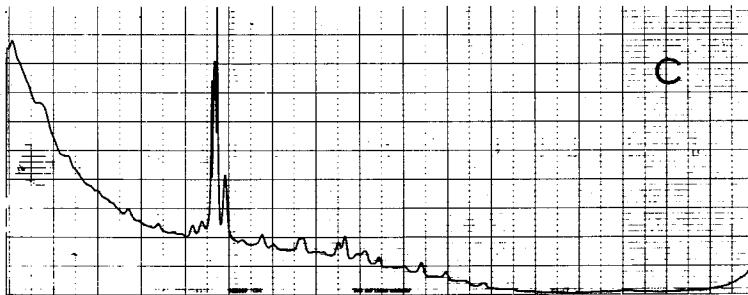
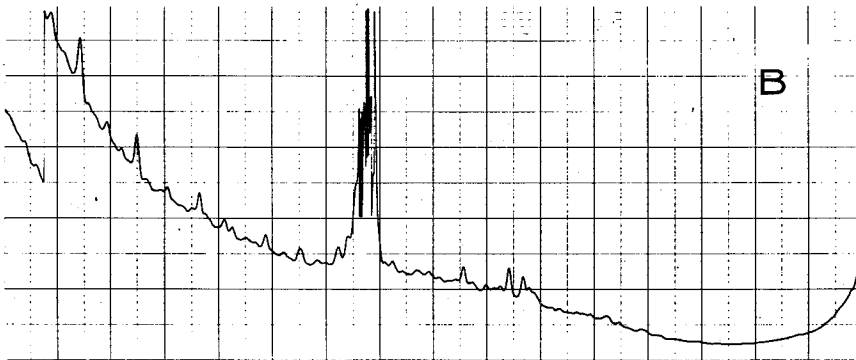
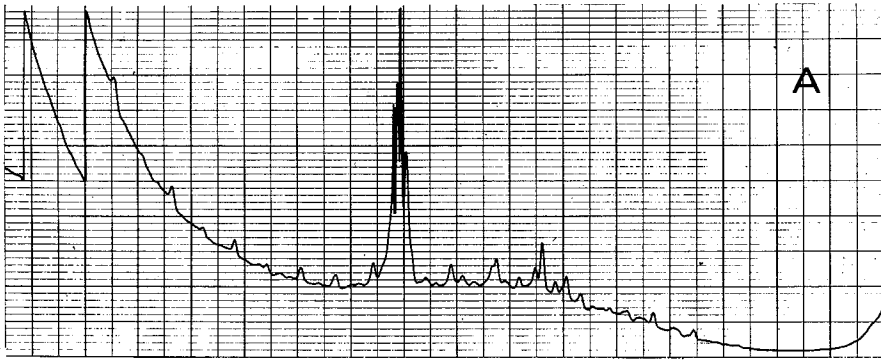


FIGURE 16.
STA. 35
OCT.- DEC. 1969
APRIL 1970

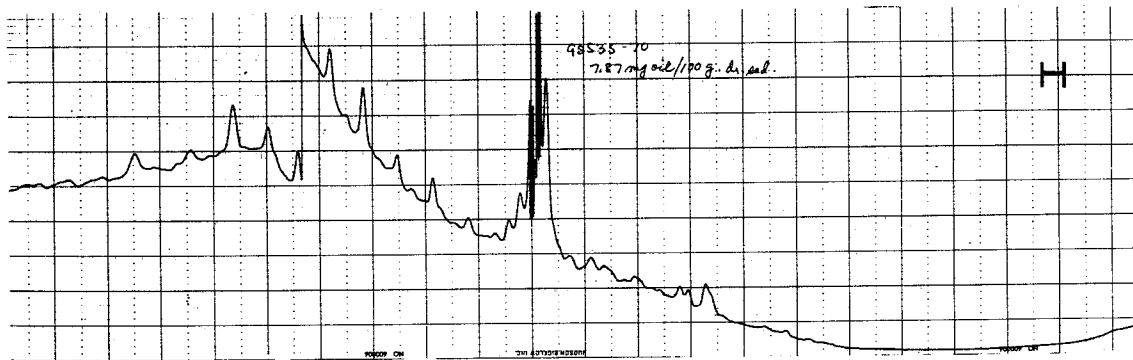
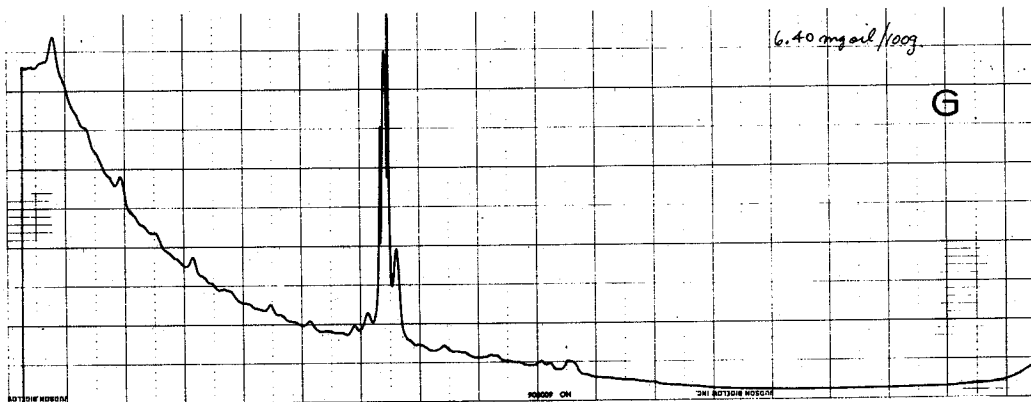
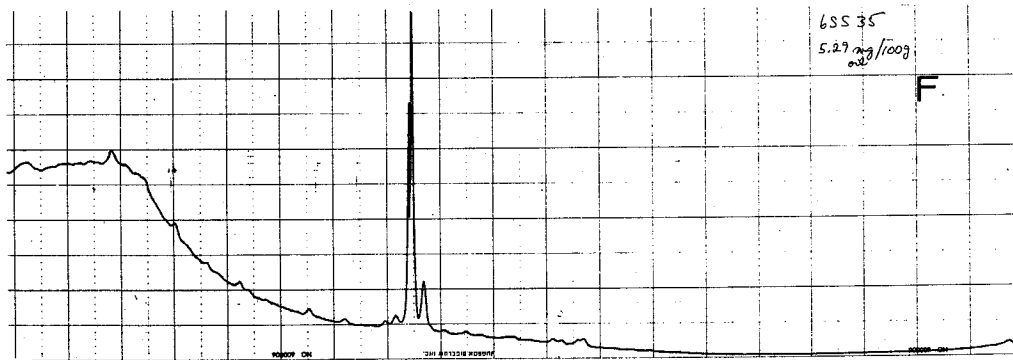
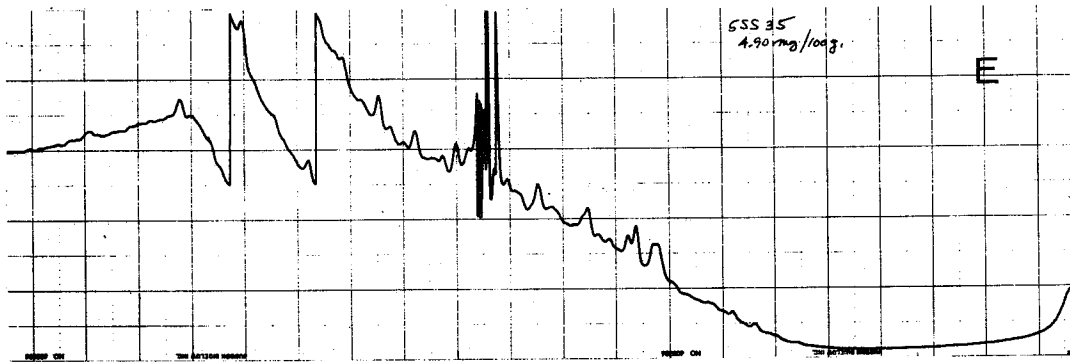


FIGURE 16.
STA. 35
MAY - JULY,
SEPT. 1970

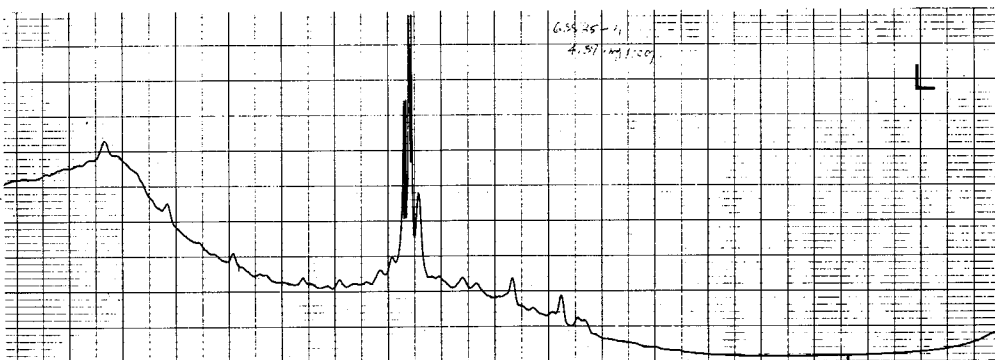
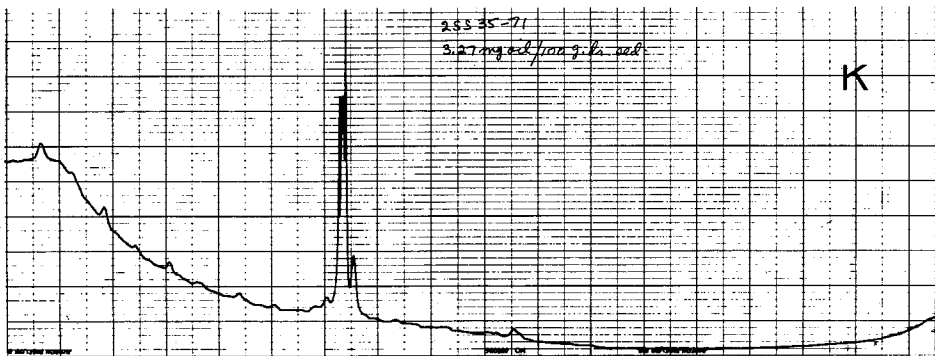
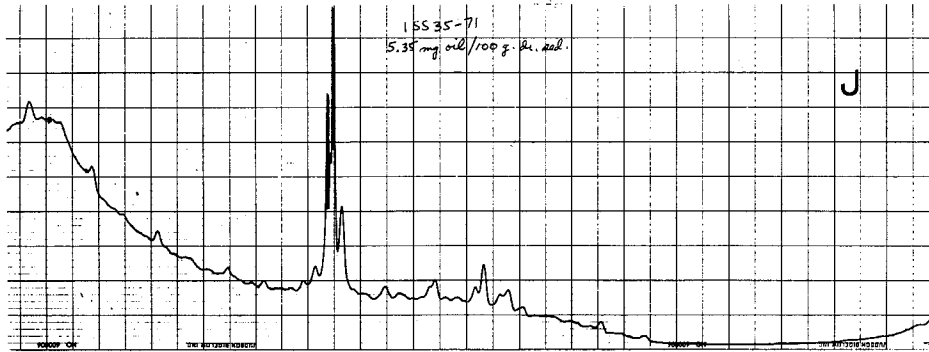
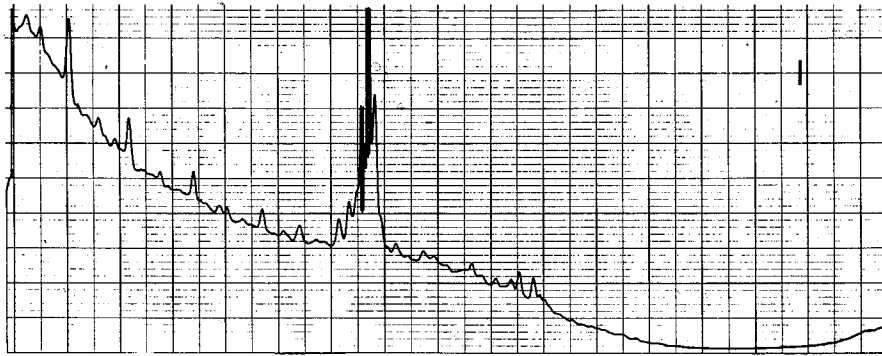


FIGURE 16.
STA. 35
NOV. 1970
JAN., FEB.,
JUNE 1971

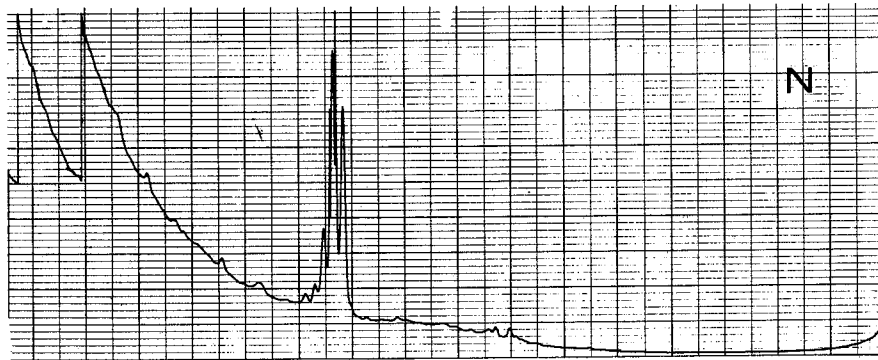
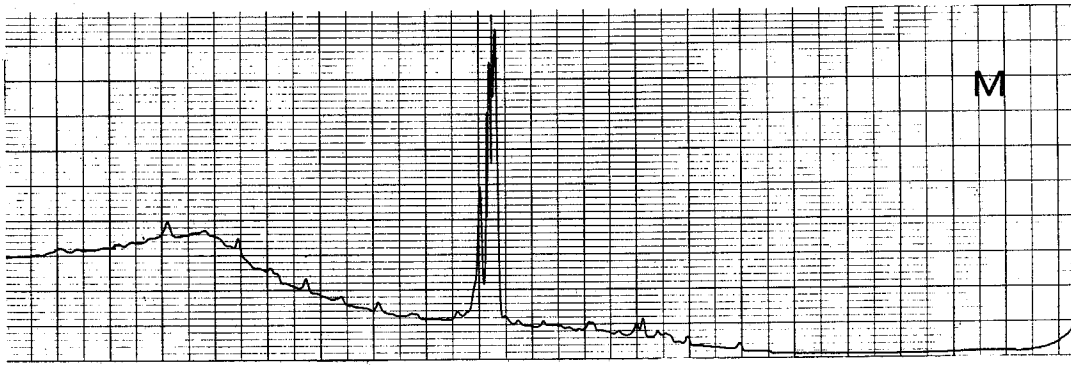


FIGURE 16.
STA. 35
AUG., SEPT. 1971

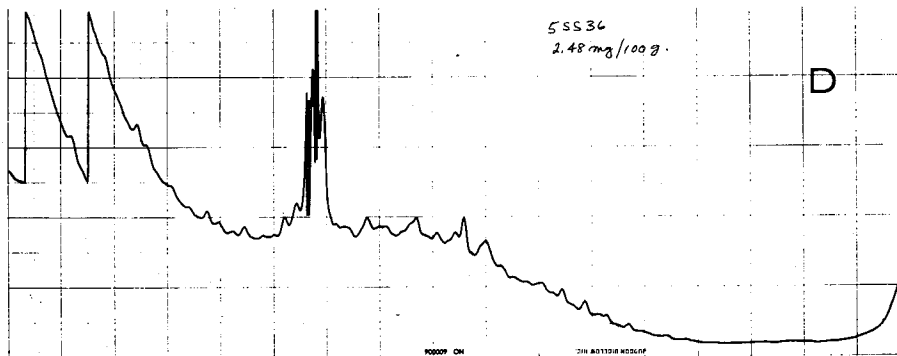
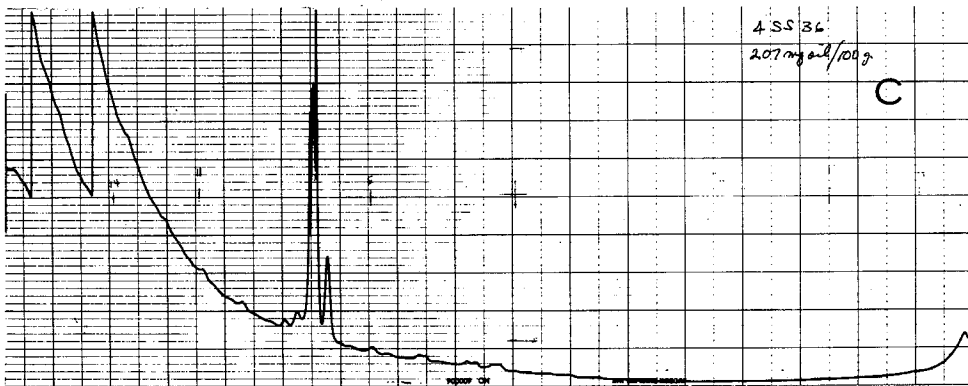
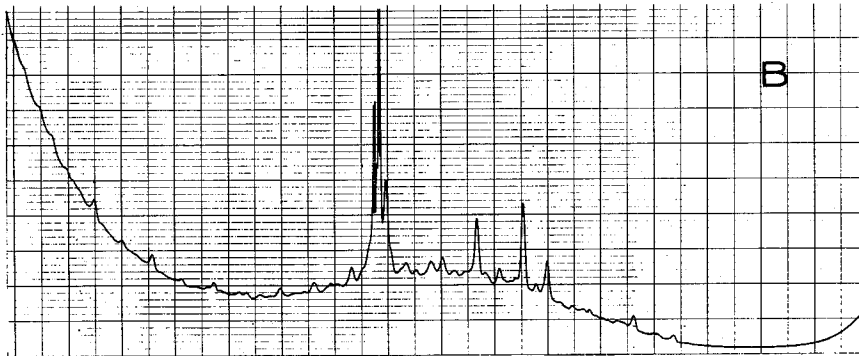
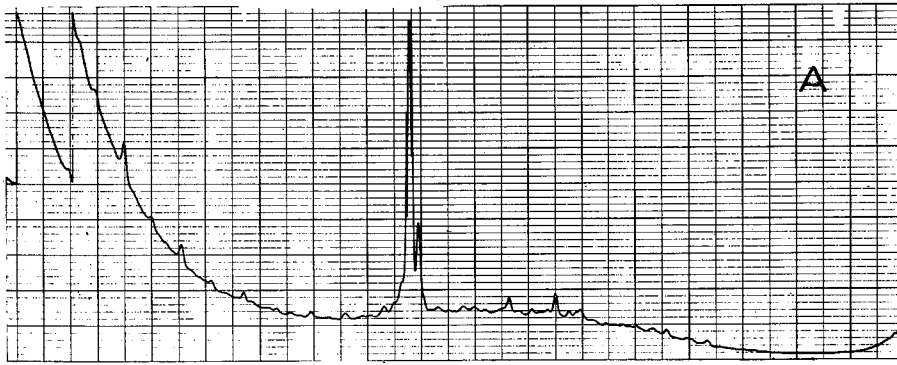


FIGURE 17.
 STA. 36
 NOV. 1969
 JAN.,
 APRIL, MAY 1970

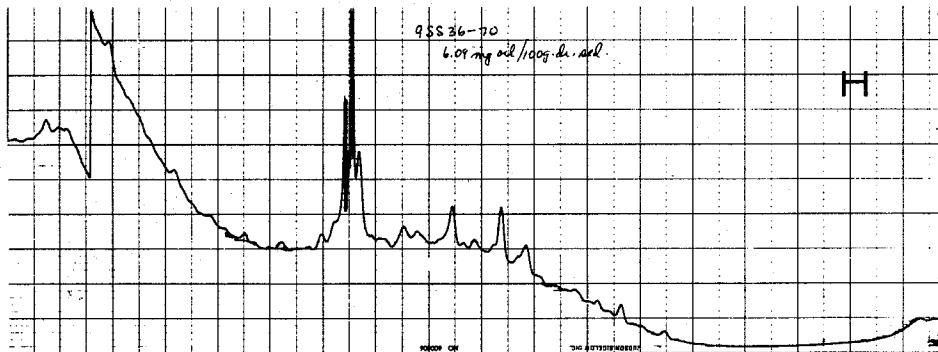
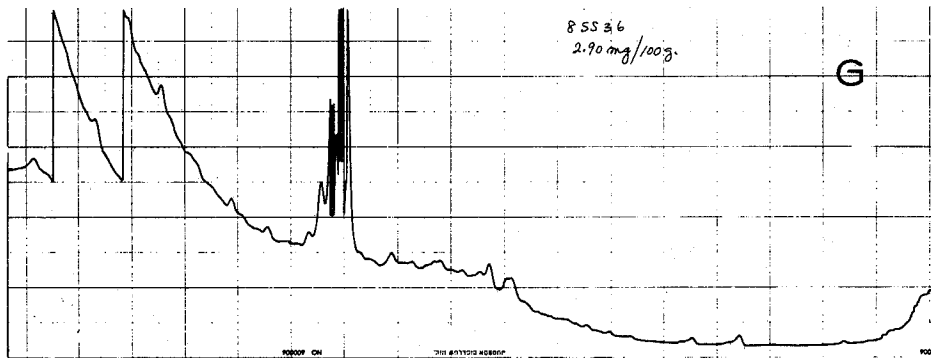
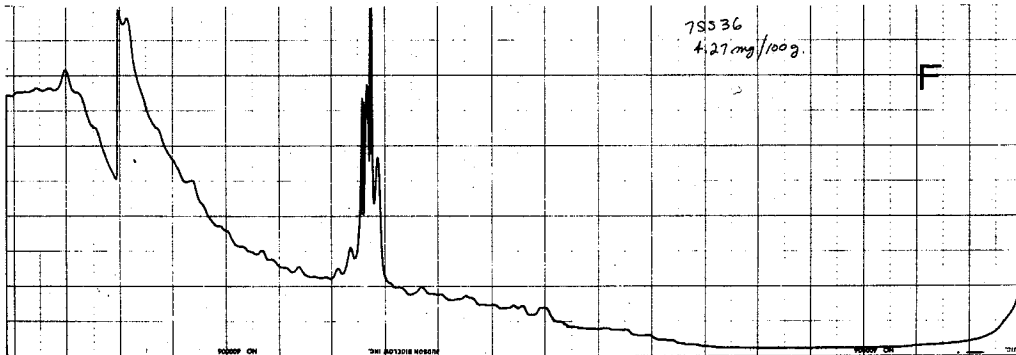
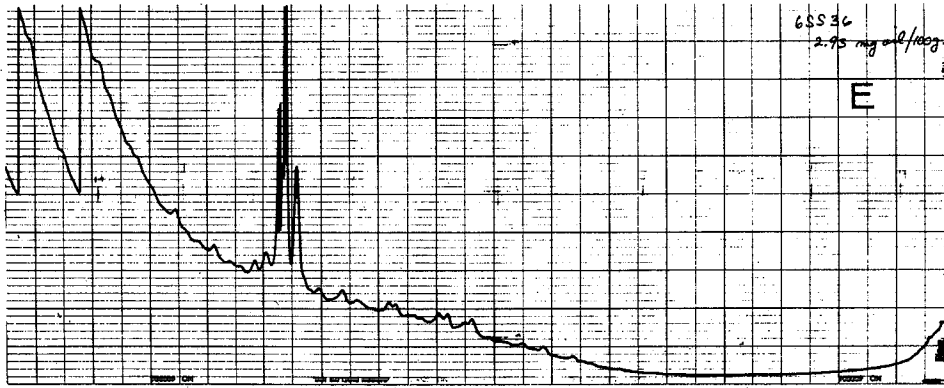


FIGURE 17.
STA. 36
JUNE - SEPT. 1970

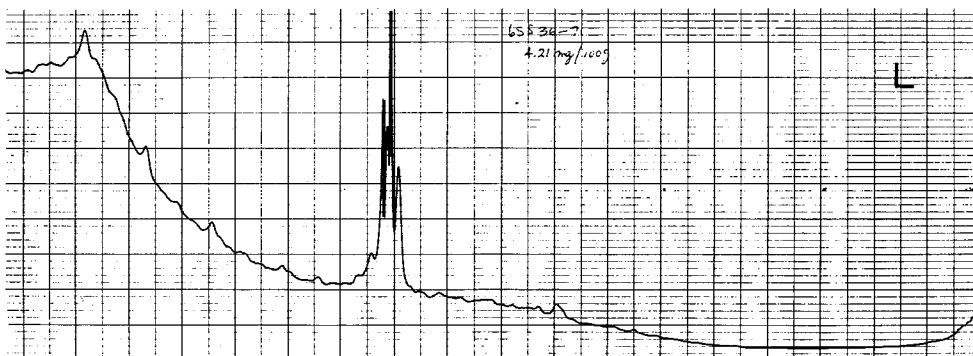
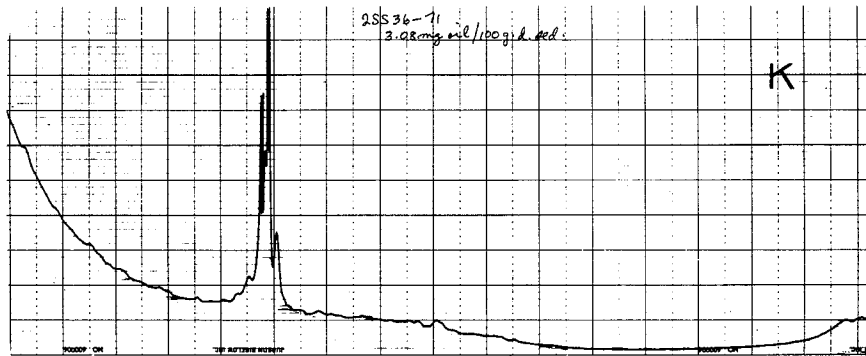
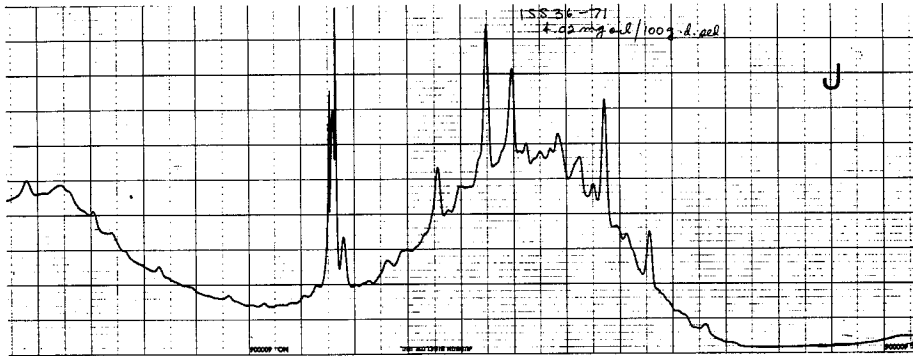
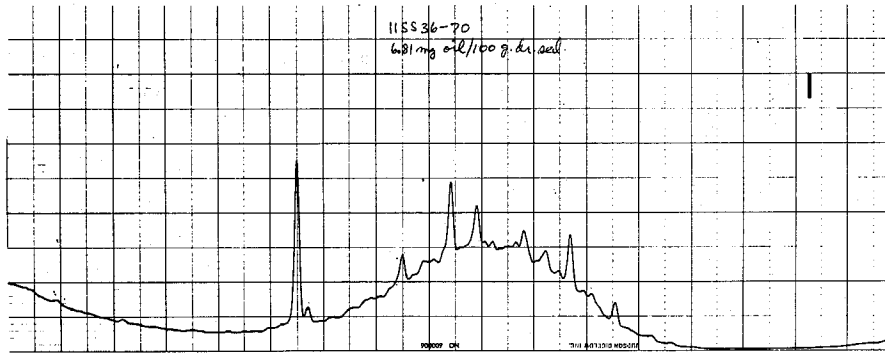


FIGURE 17.

STA. 36
NOV. 1970
JAN., FEB.,
JUNE 1971

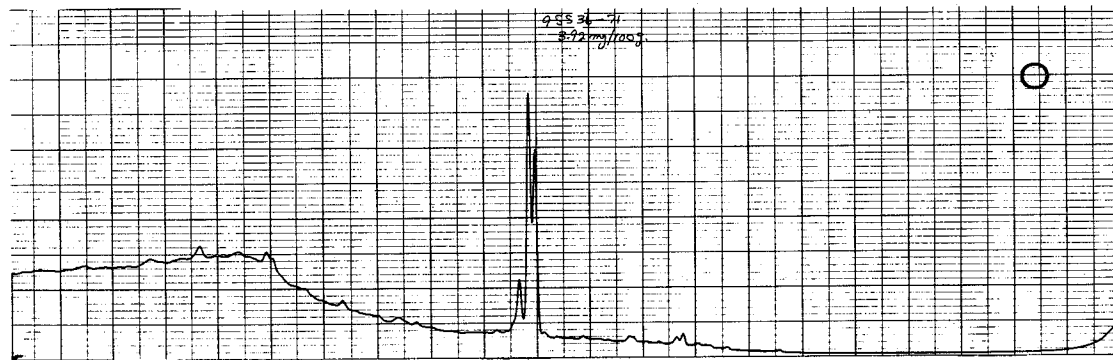
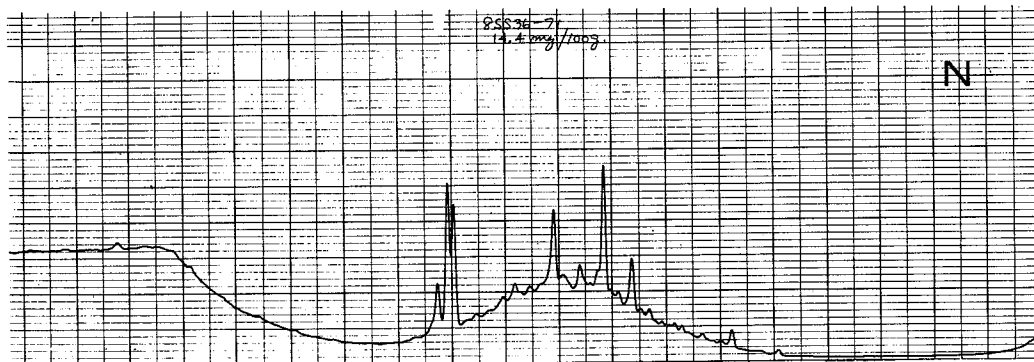
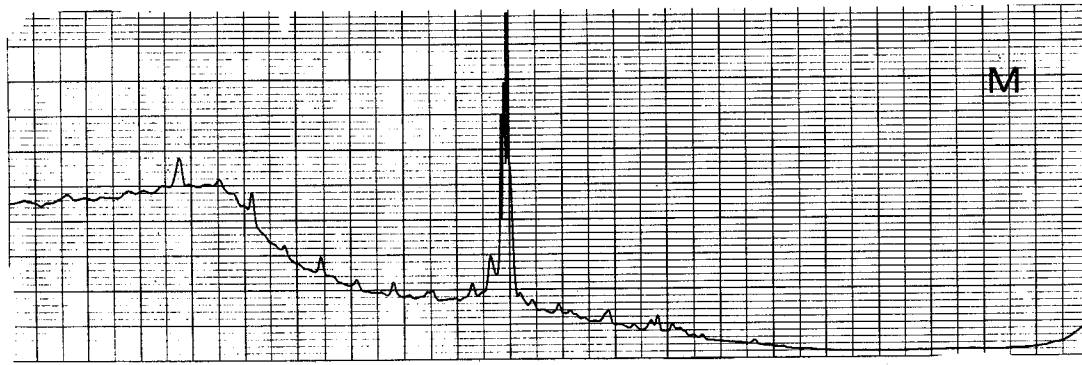


FIGURE 17.
 STA. 36
 JULY - SEPT. 1971

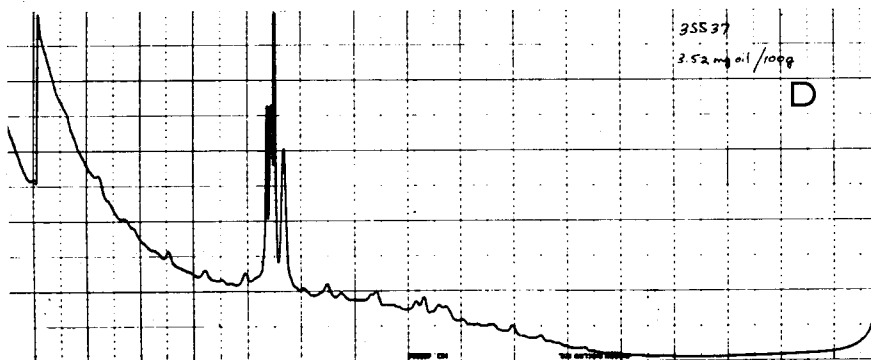
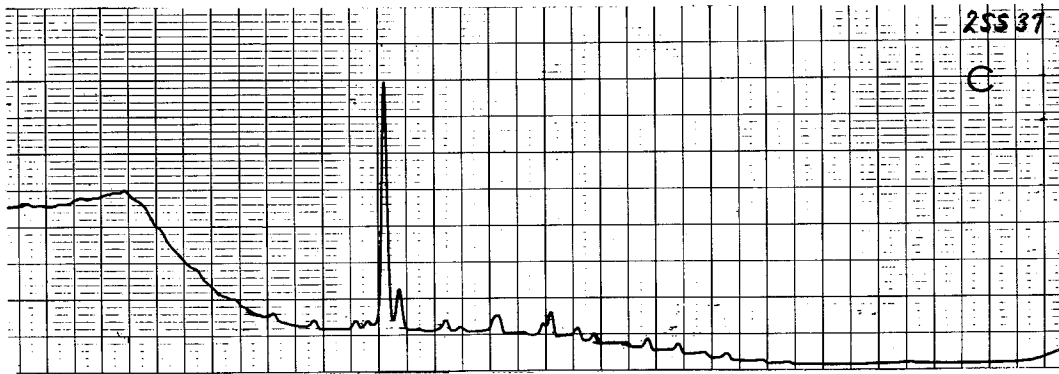
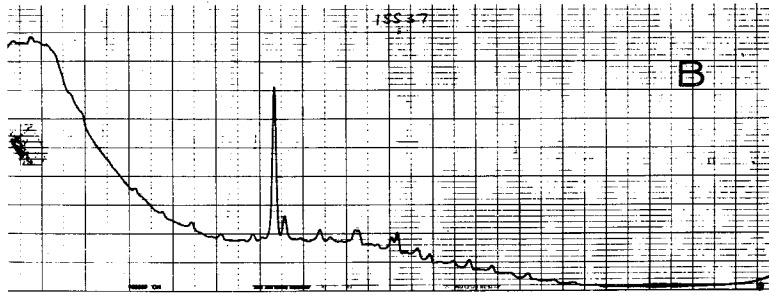
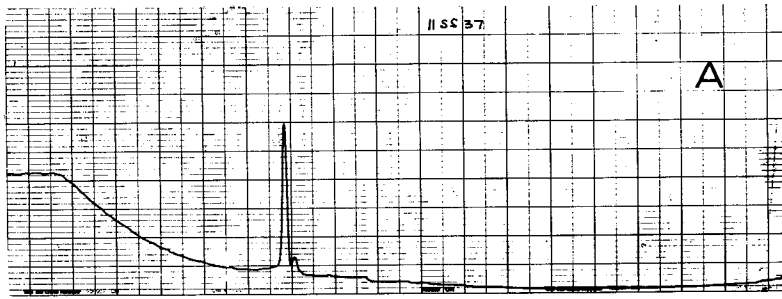


FIGURE 18.
STA 37.
NOV. 1969
JAN.- MARCH 1970

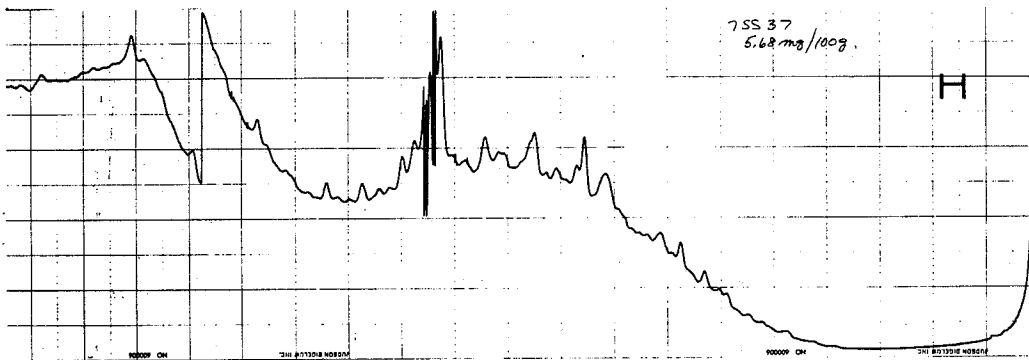
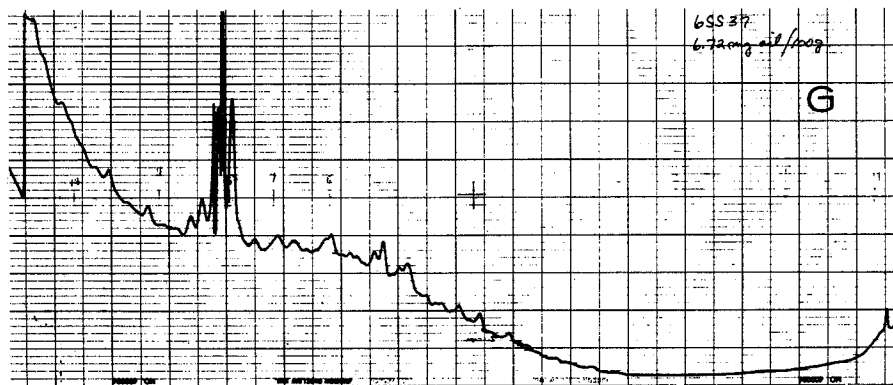
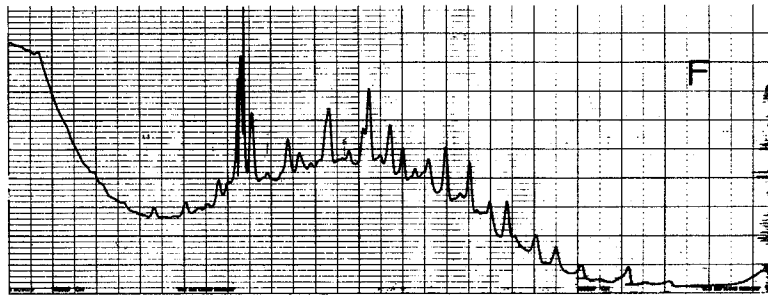
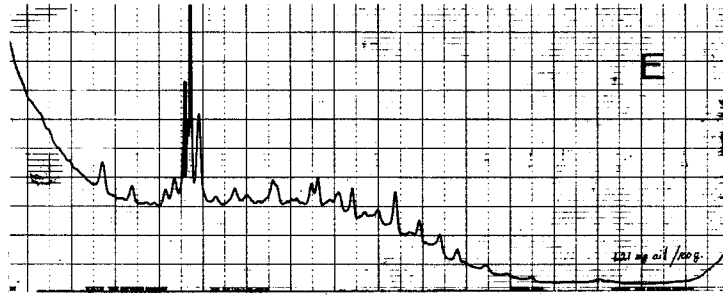


FIGURE 18.
 STA. 37
 APRIL - JULY 1970

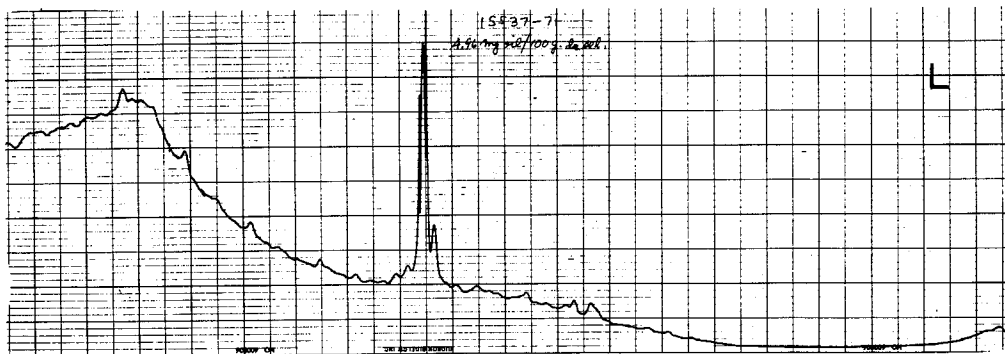
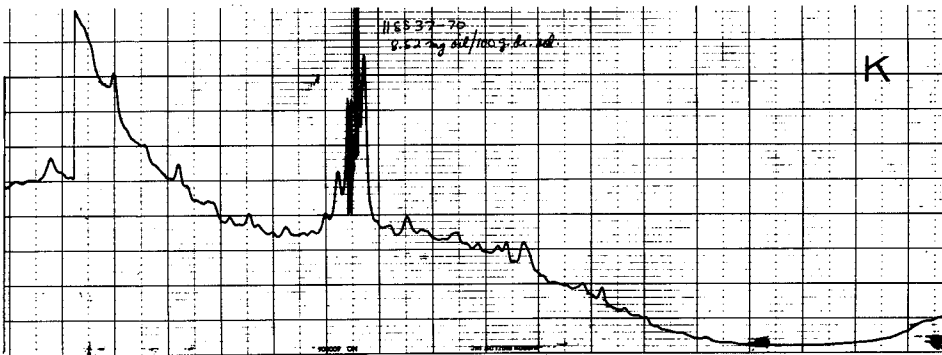
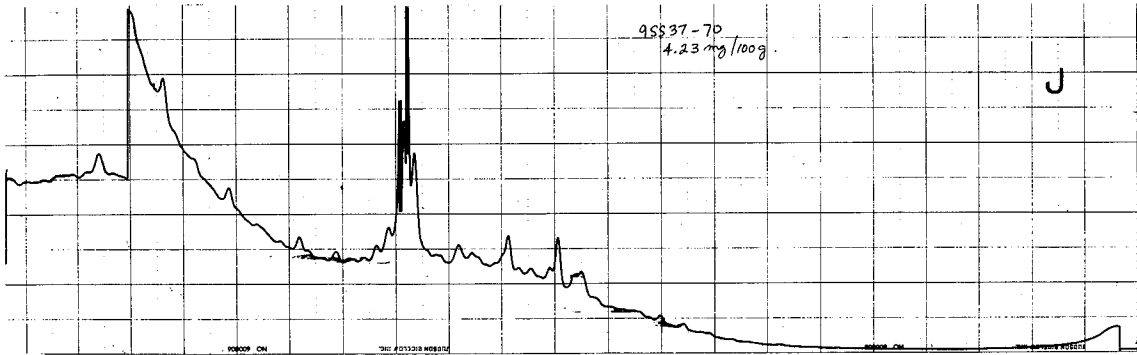
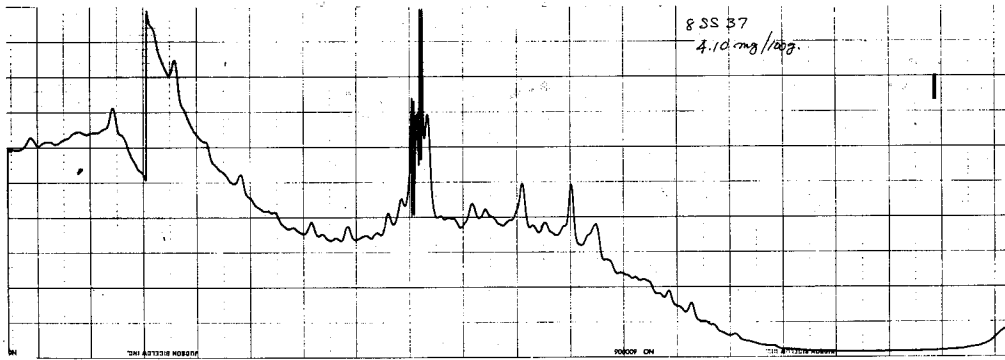


FIGURE 18.

STA. 37
AUG., SEPT.,
NOV. 1970
JAN. 1971

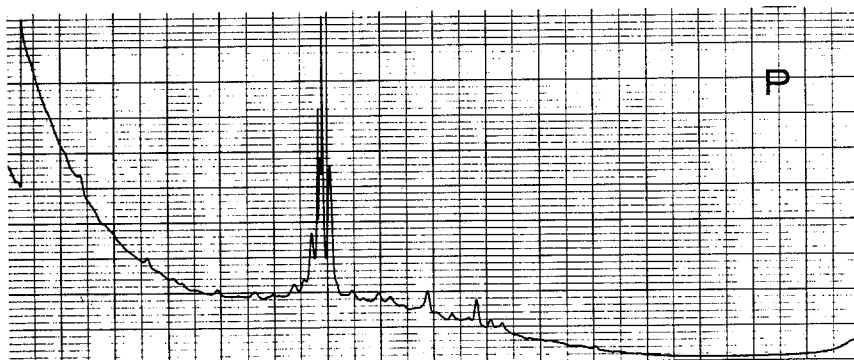
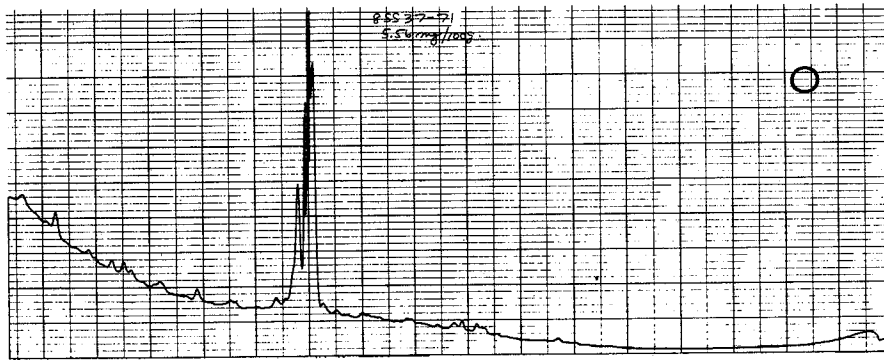
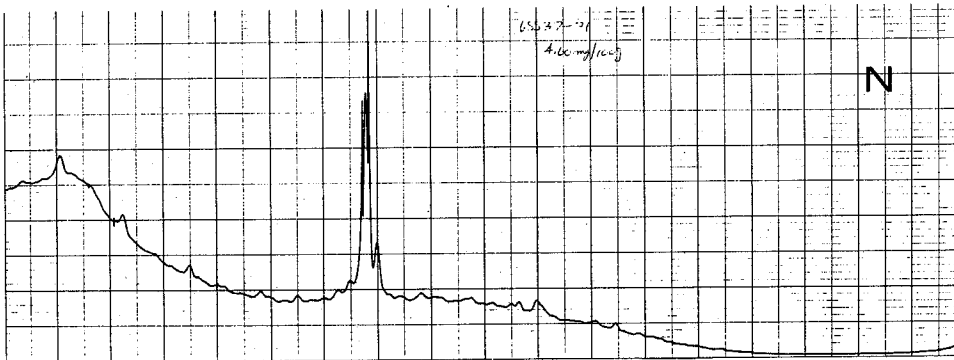
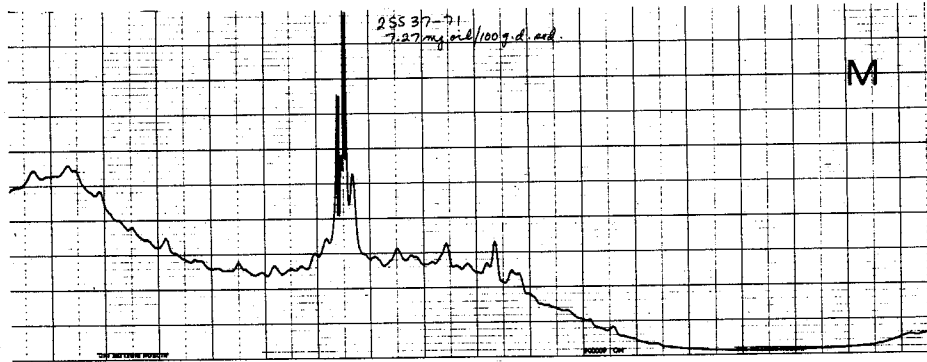


FIGURE 18.
STA. 37
FEB., JUNE,
AUG., SEPT., 1971

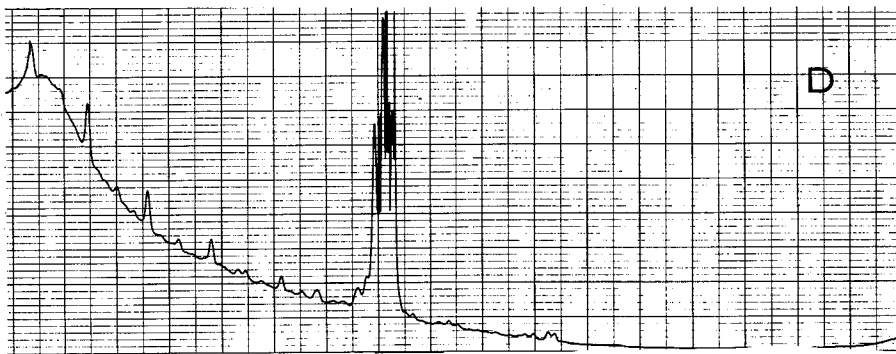
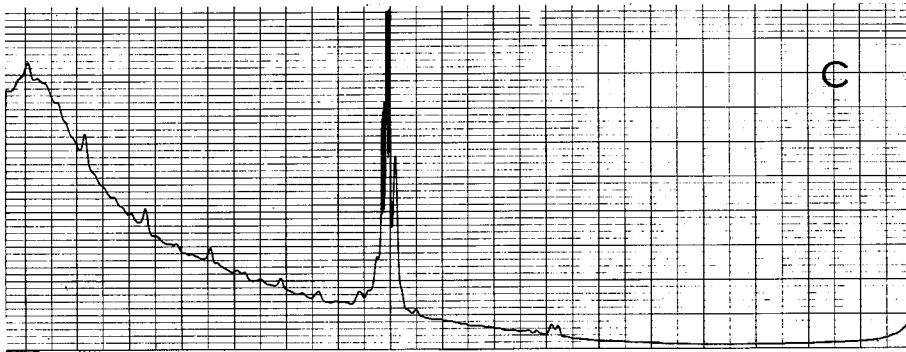
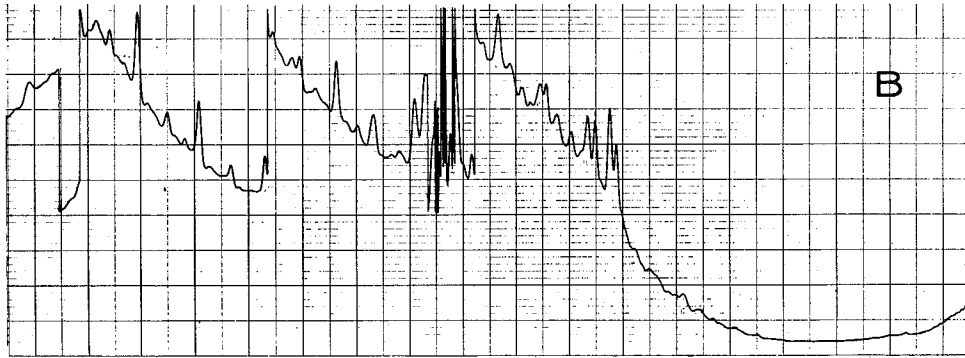
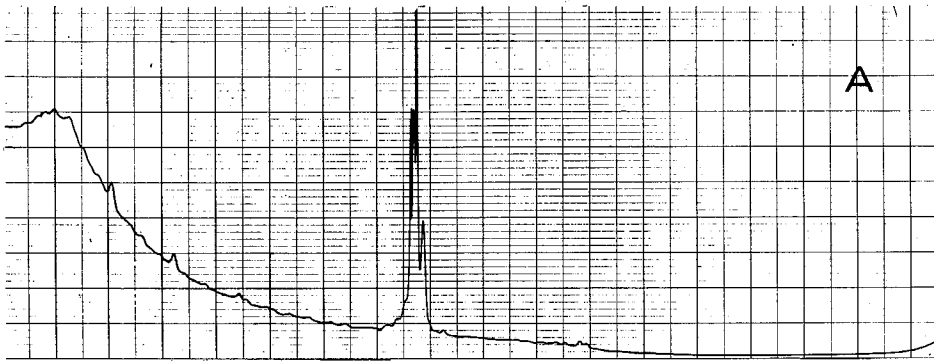


FIGURE 19.
STA. 90
JUNE 1971
(A + B),
JULY,
AUG. 1971

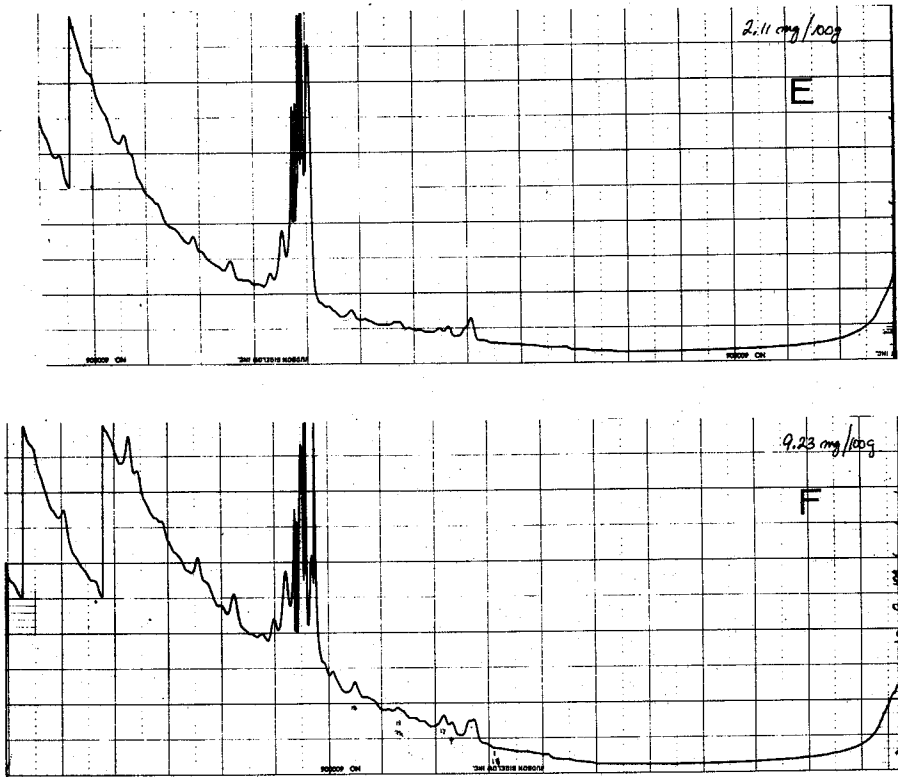


FIGURE 19.

RHODES II,
RHODES IV
1970

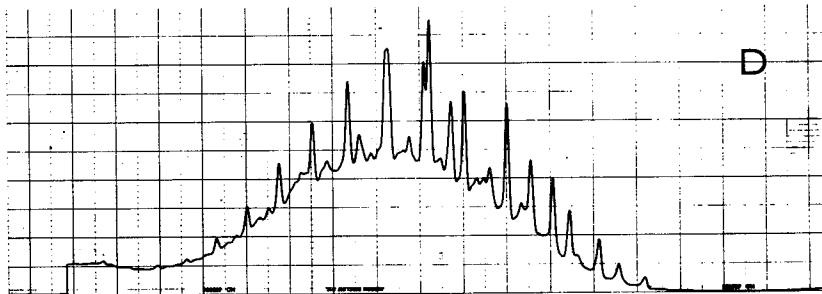
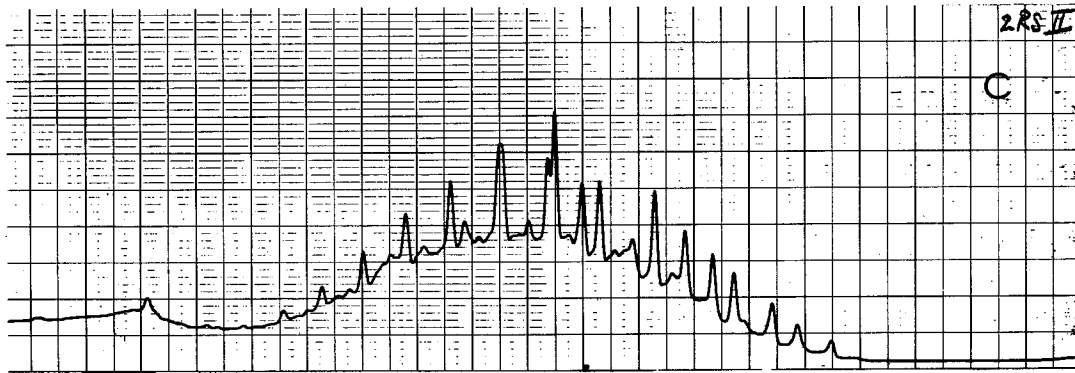
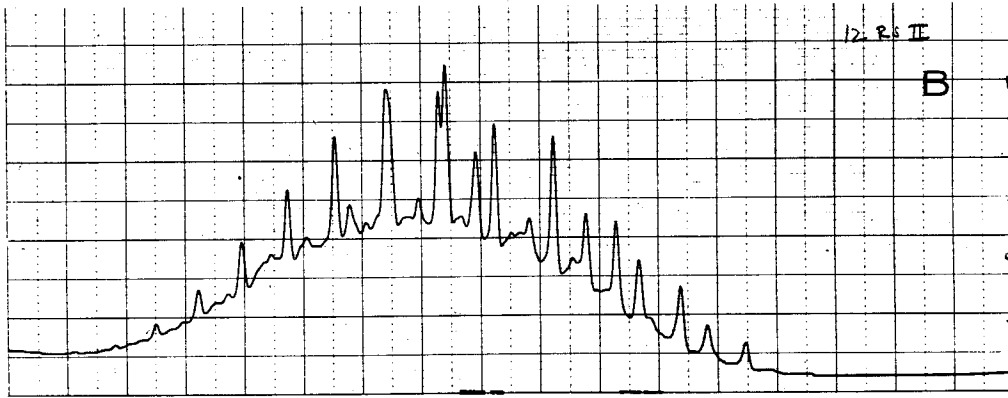
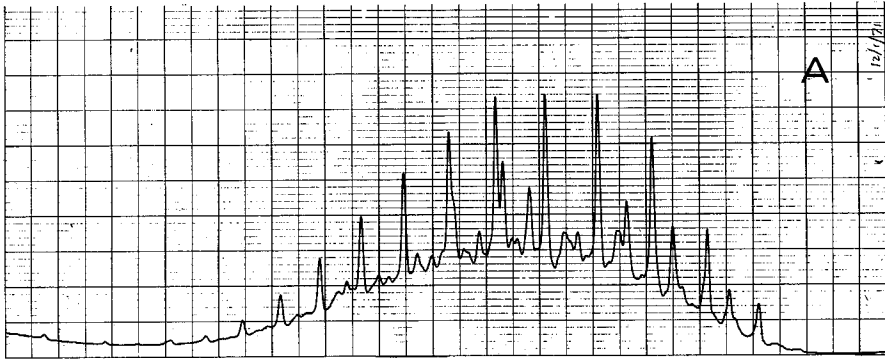


FIGURE 20.
 STA. II
 SEPT., DEC., 1969
 FEB., MAY 1970

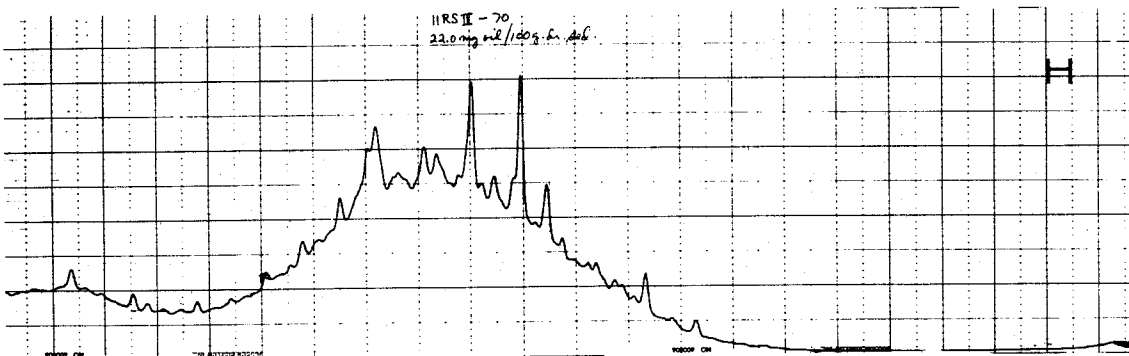
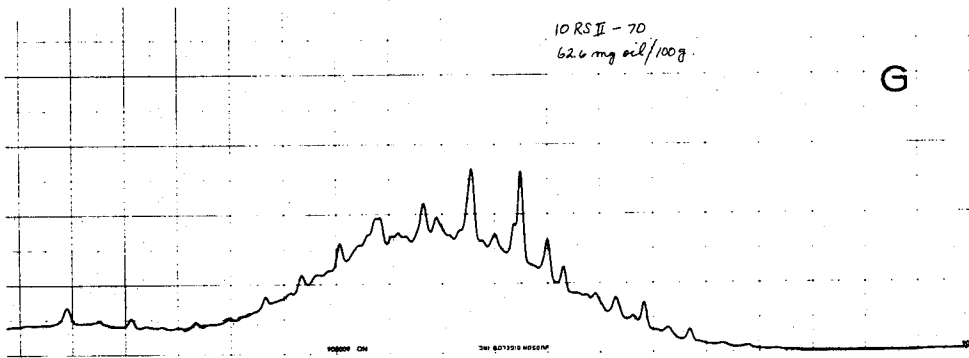
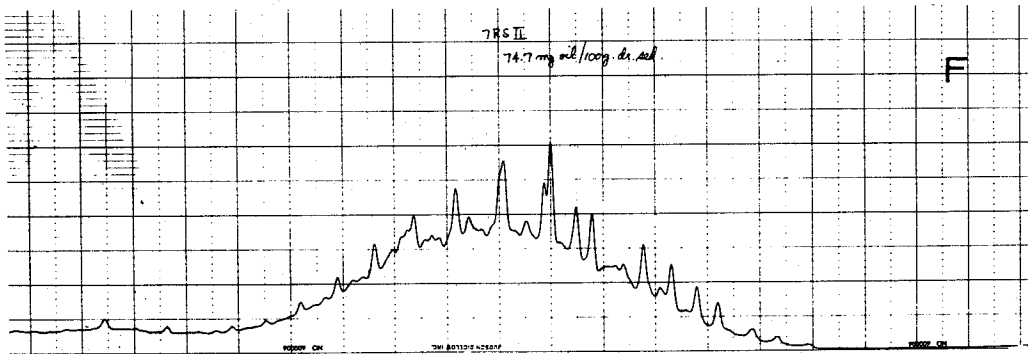
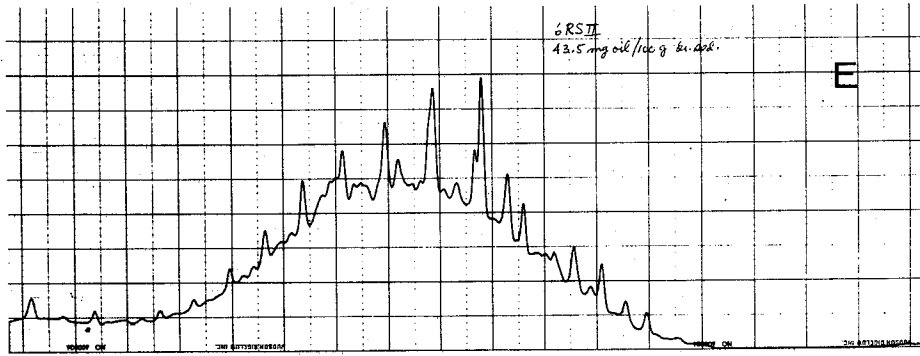


FIGURE 20.
STA. II
JUNE, JULY,
OCT., NOV., 1970

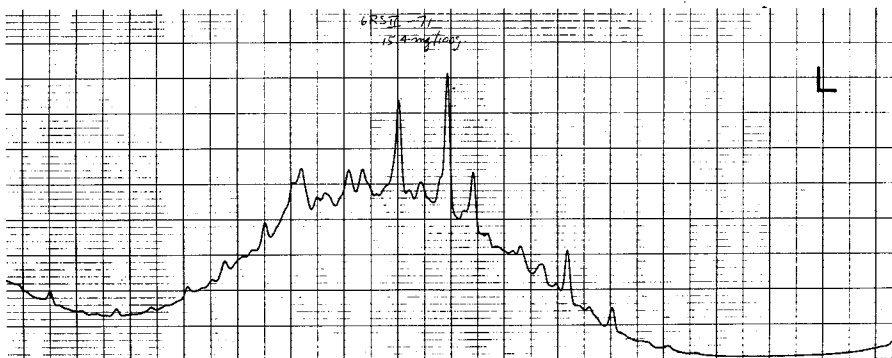
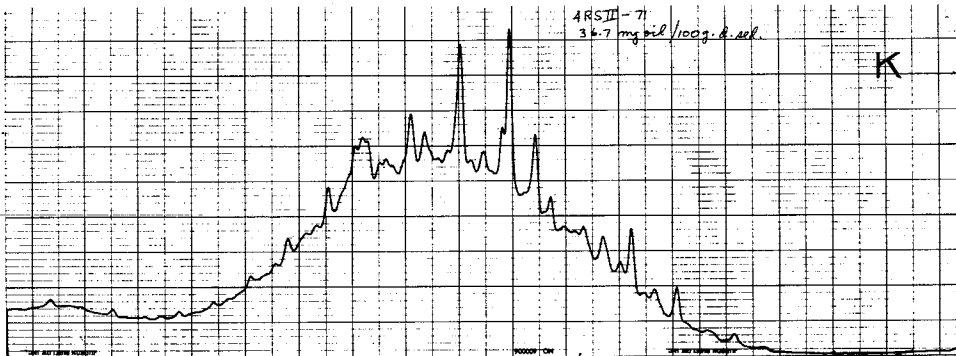
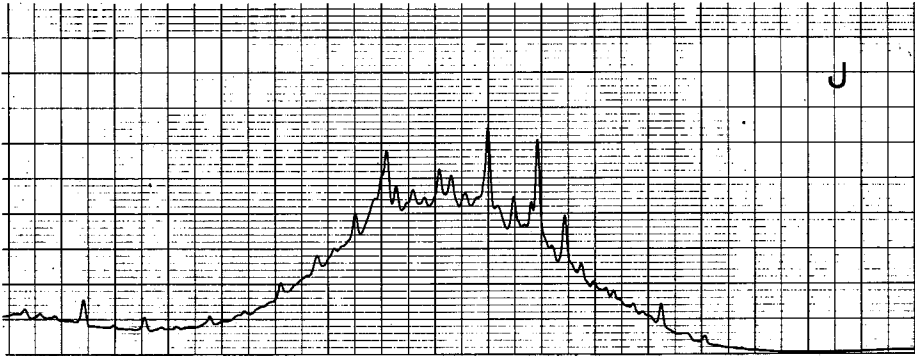
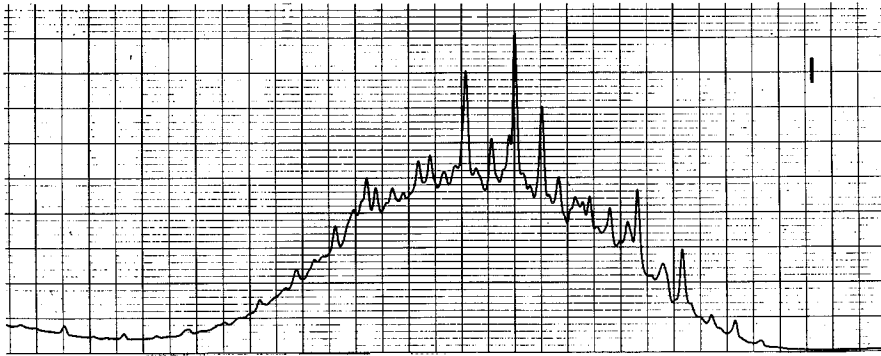


FIGURE 20.
STA. II
DEC. 1970
MARCH, APRIL,
JUNE, 1971

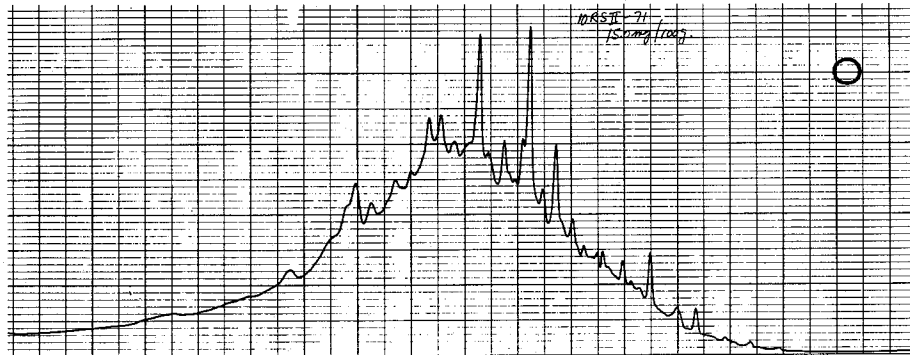
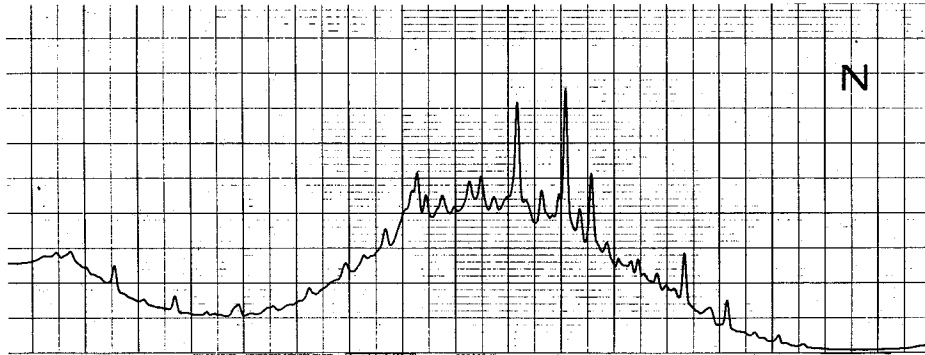
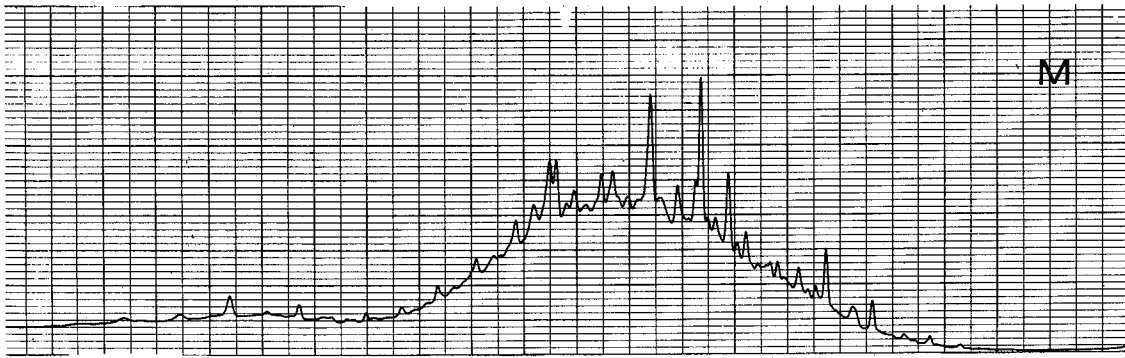


FIGURE 20.
STA. II
JULY, AUG.,
OCT. 1971

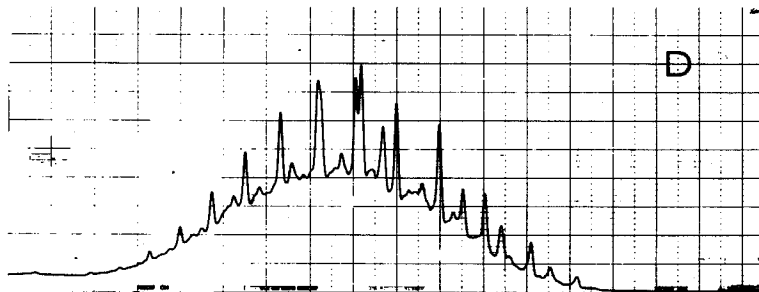
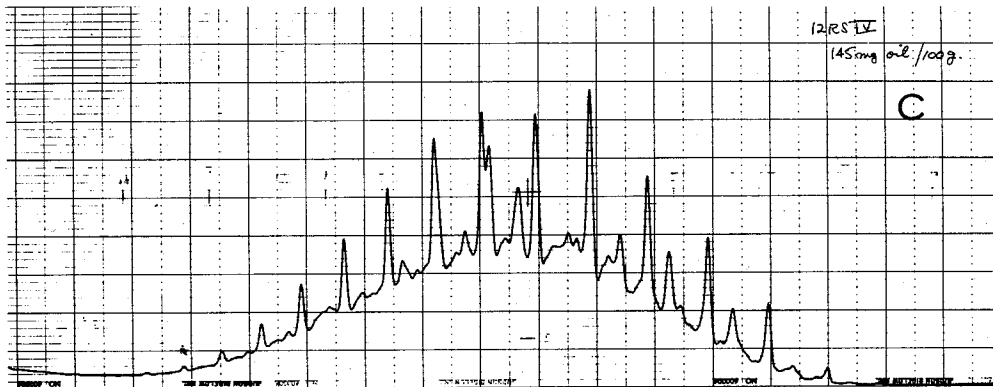
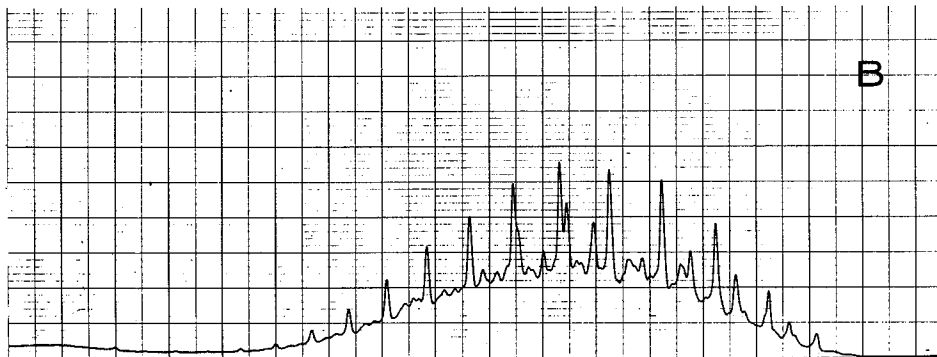
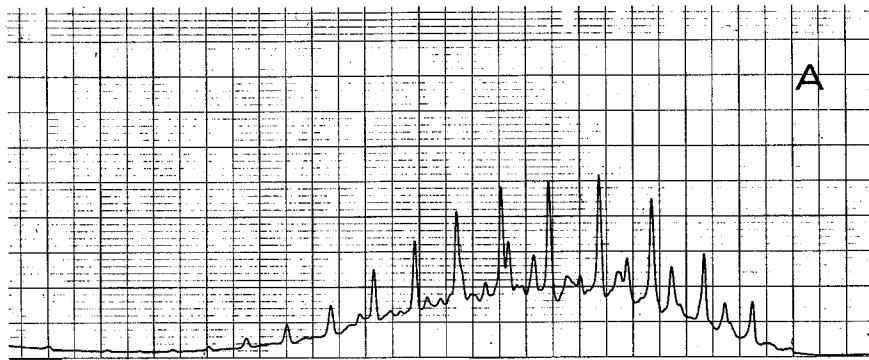


FIGURE 21.
 STA. IV
 SEPT., OCT.,
 DEC. 1969
 FEB. 1970

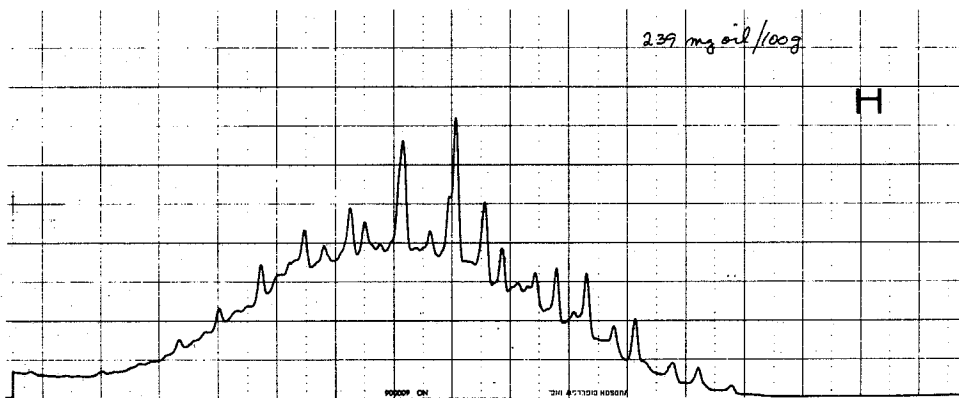
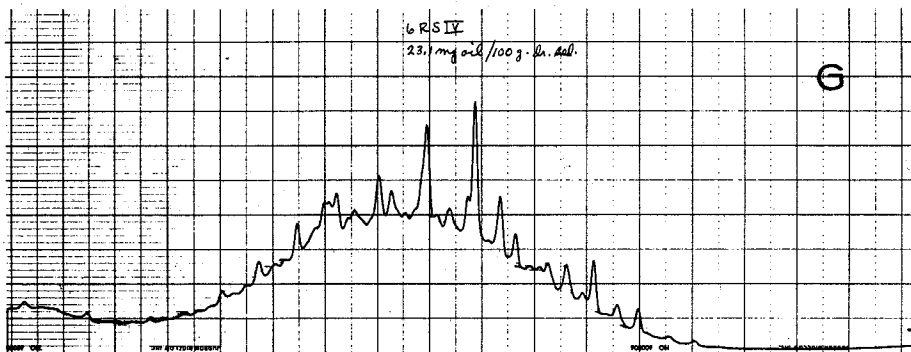
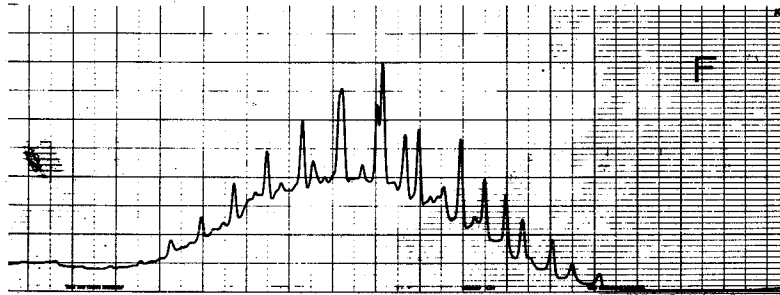
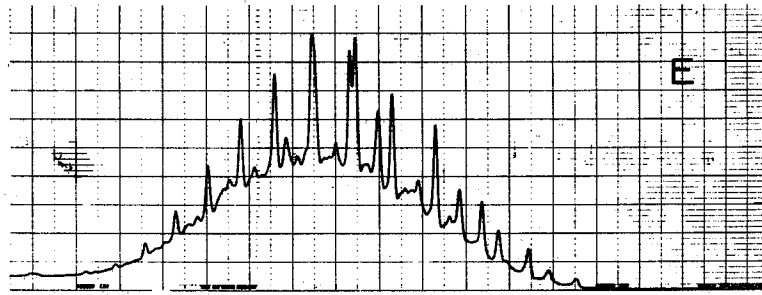


FIGURE 21.
 STA. IV
 APRIL-JULY 1970

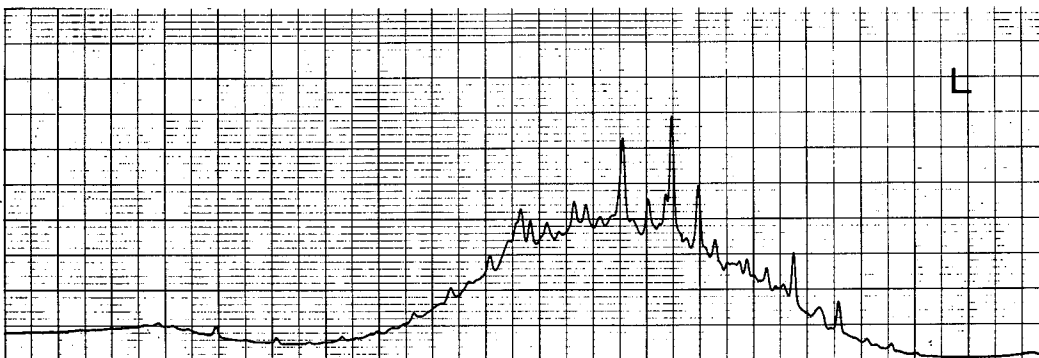
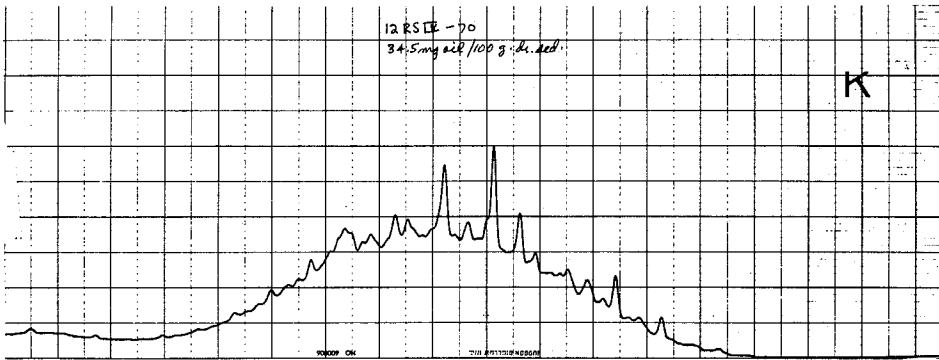
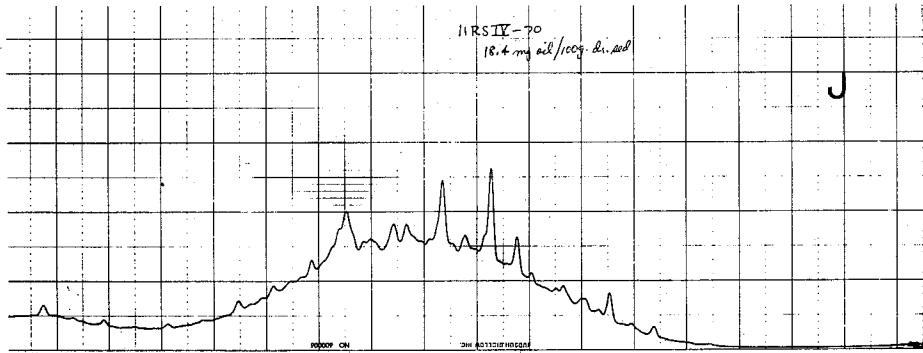
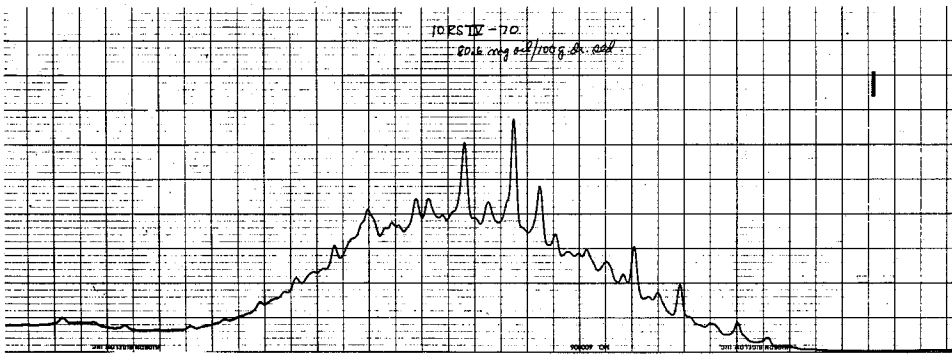


FIGURE 21.
STA. IV
OCT.-DEC. 1970
FEB. 1971

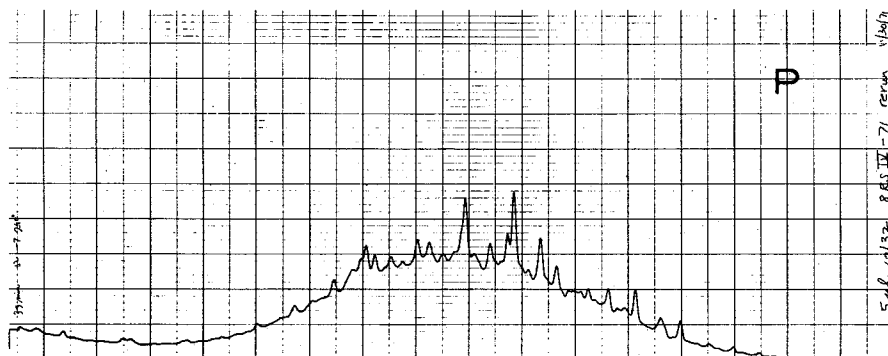
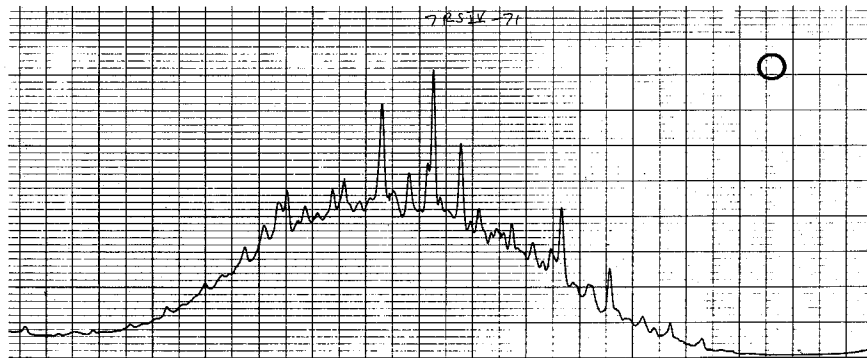
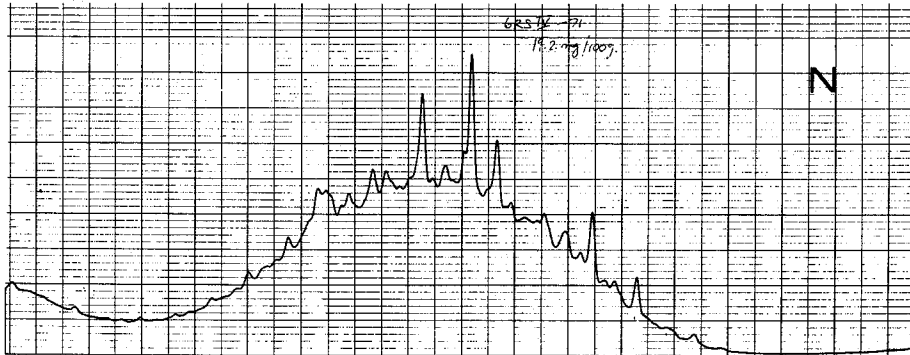
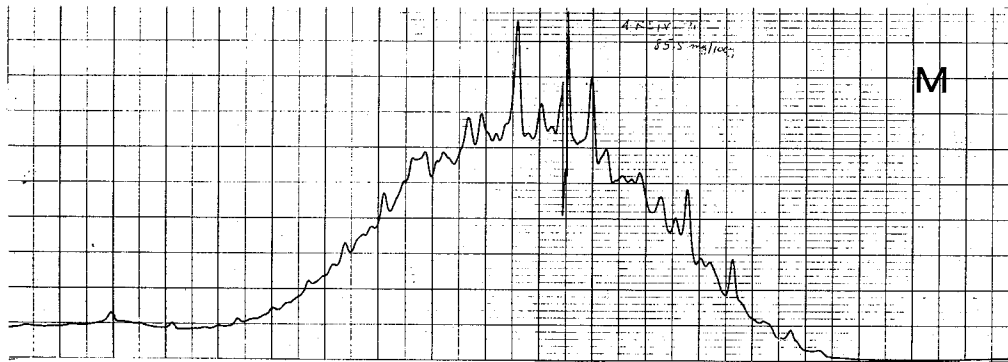


FIGURE 21.
STA. IV
MARCH,
JUNE - AUG. 1971

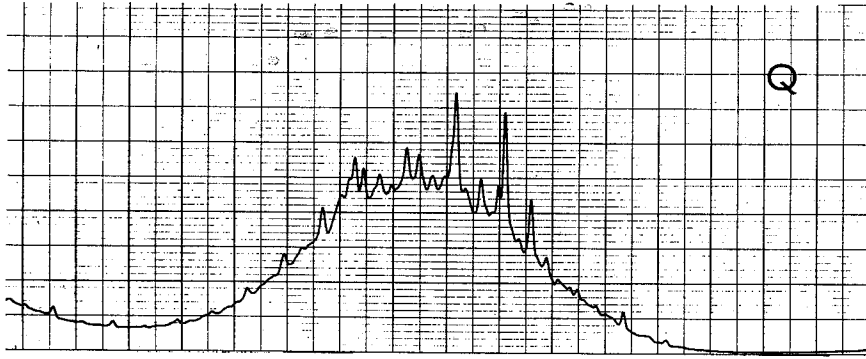


FIGURE 21.
STA. IV.
OCT. 1971

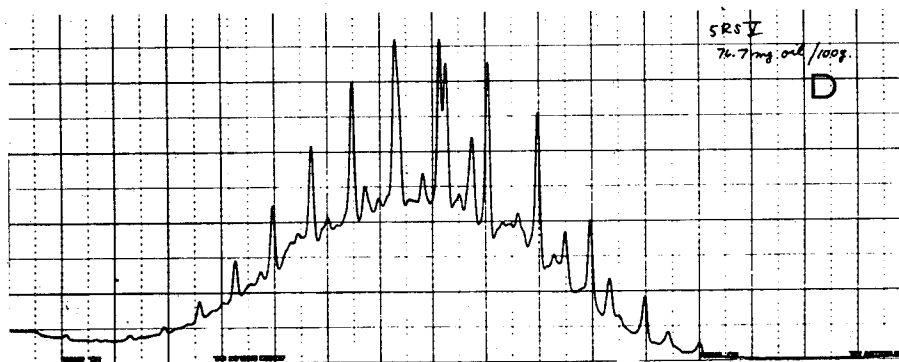
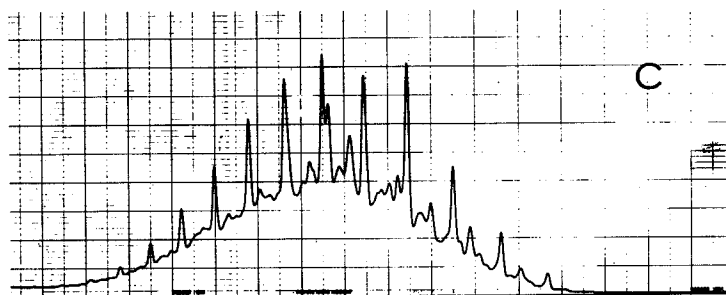
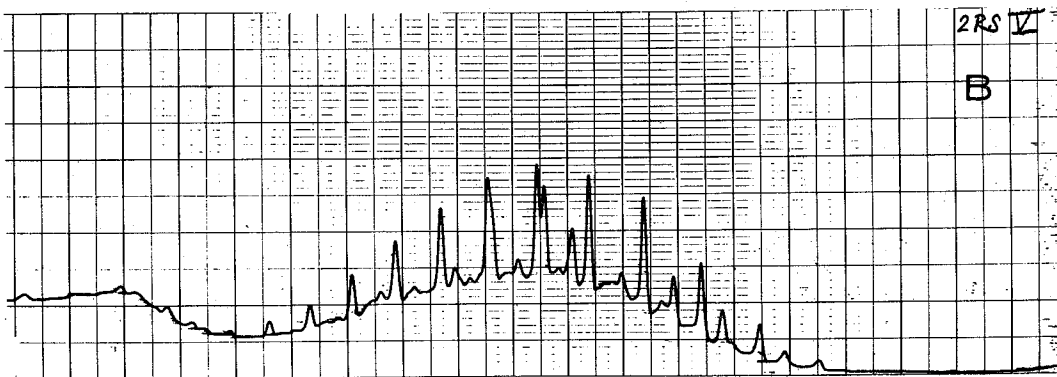
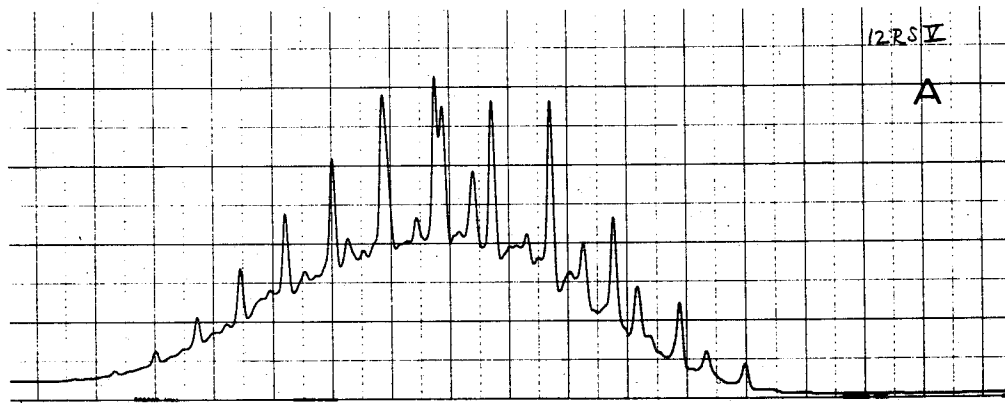


FIGURE 22.

STA. V
DEC. 1969
FEB. 1970
APRIL, MAY 1970

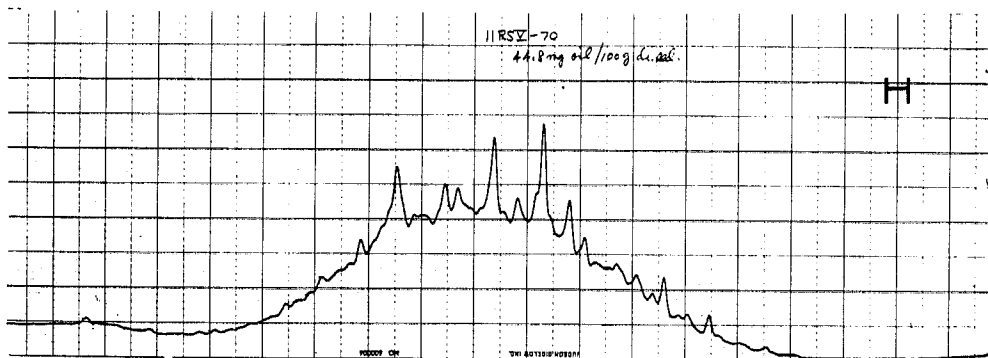
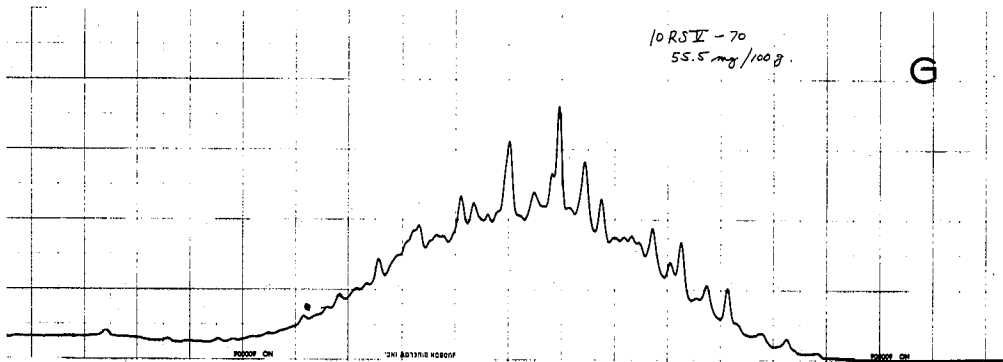
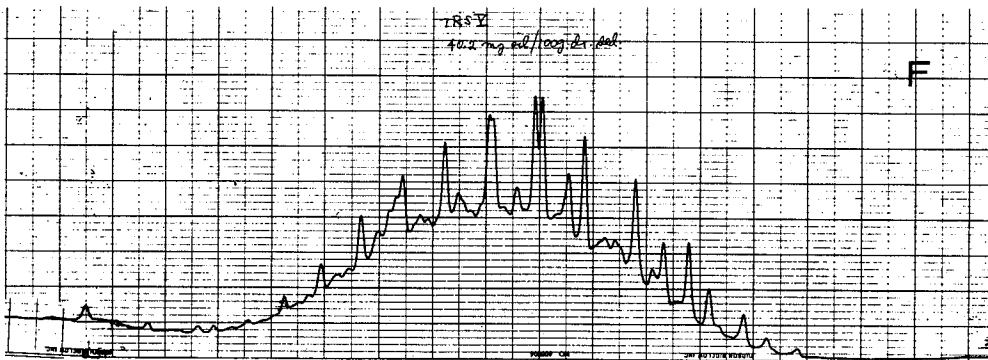
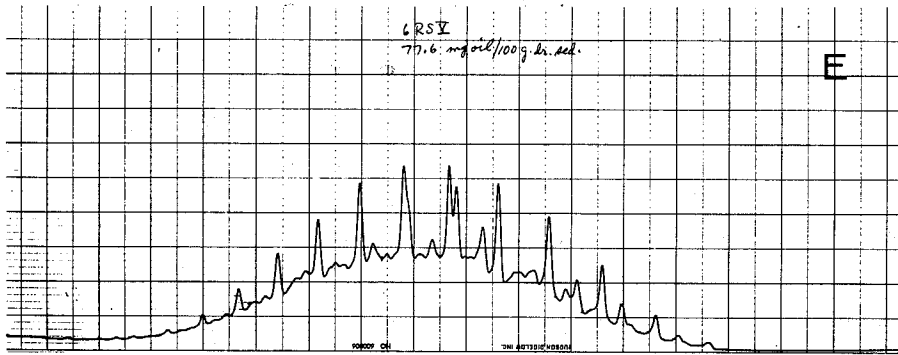


FIGURE 22.
STA. V
JUNE, JULY,
OCT., NOV. 1970

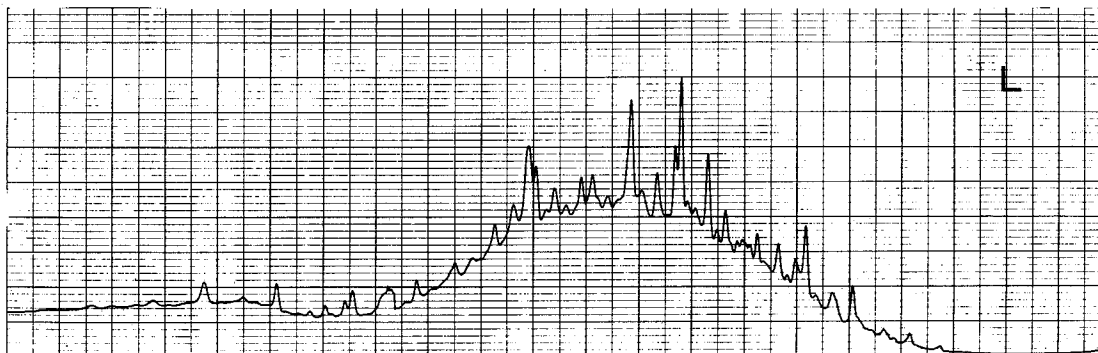
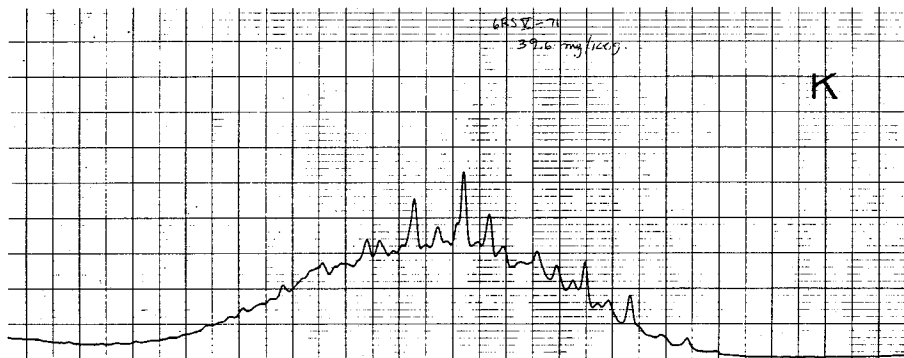
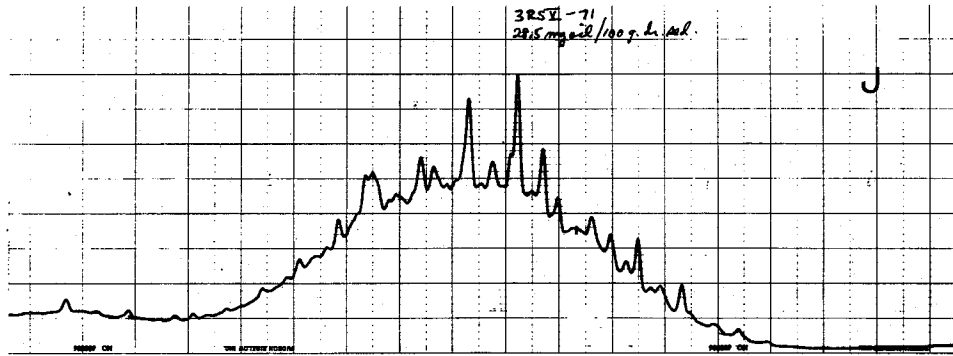
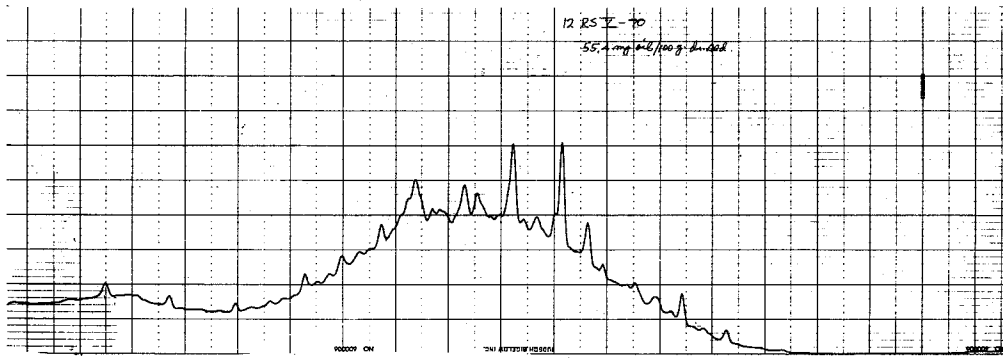


FIGURE 22
STA. V
DEC. 1970
MARCH, 1971,
JUNE, JULY 1971

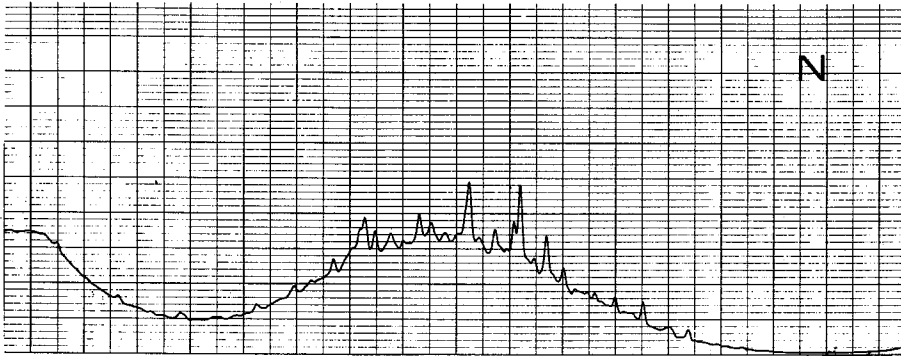
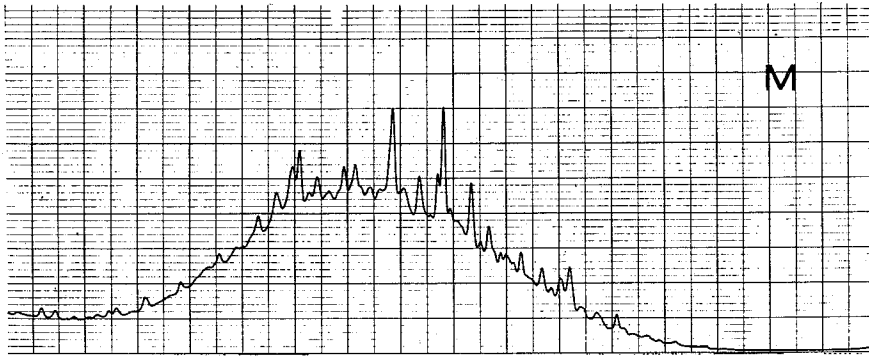


FIGURE 22.
STA. V
AUG., OCT. 1971

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THE WEST FALMOUTH OIL SPILL. Data Available in November, 1971. II. Chemistry. by M. Blumer and J. Sass. 57 pages, 3 tables and 22 figures. April 1972. Contract N00014-66-C0241: NR 083-004, Environmental Protection Administration 18050 EBN, and the National Science Foundation GA-19472.

A spill of 650,000 to 700,000 liters of #2 fuel oil on September 16, 1969 has contaminated the coastal areas of Buzzards Bay, Massachusetts. Our continuing chemical study is aimed at a documentation of the effects, the persistence and the eventual disappearance of the pollutant hydrocarbons in this area. The present report summarizes the chemical data which were available in November 1971.

1. Oil Pollution

2. Shellfish

3. Sediments

I. Blumer, M.

II. Sass, J.

III. N00014-66-C0241; NR 083-004

IV. Environmental Protection Administration

V. NSF GA-19472

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WHOI-72-19

THE WEST FALMOUTH OIL SPILL. Data Available in November, 1971. II. Chemistry. by M. Blumer and J. Sass. 57 pages, 3 tables and 22 figures. April 1972. Contract N00014-66-C0241: NR 083-004, Environmental Protection Administration 18050 EBN, and the National Science Foundation GA-19472.

A spill of 650,000 to 700,000 liters of #2 fuel oil on September 16, 1969 has contaminated the coastal areas of Buzzards Bay, Massachusetts. Our continuing chemical study is aimed at a documentation of the effects, the persistence and the eventual disappearance of the pollutant hydrocarbons in this area. The present report summarizes the chemical data which were available in November 1971.

1. Oil Pollution

2. Shellfish

3. Sediments

I. Blumer, M.

II. Sass, J.

III. N00014-66-C0241; NR 083-004

IV. Environmental Protection Administration

V. NSF GA-19472

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