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Geochemical Exploration for Petroleum

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Natural oil seepages observed on the surface of the earth were the first signs that pointed to the possible presence of petroleum accumulations below the surface. The Drake well, located on the basis of such natural seeps and drilled in Pennsylvania in 1859, was the discovery well of the first oil field (*1*). Drilling in the vicinity of these macroseeps has led to the discovery of many other fields.

Summary. Geochemical methods used in exploring for oil and natural gas are based on the premise that hydrocarbons migrate upward from subsurface petroleum accumulations and produce anomalous patterns near the surface. Geochemical exploration techniques are both direct or indirect. Direct techniques require analysis of microquantities of hydrocarbons that occur in the free state in the soil interstices or that are adsorbed on the fine-grained portions of the soil. Indirect geochemical methods are based on the detection, in near-surface soils or in vegetation, of inorganic alteration products that result from upward migration of hydrocarbons.

One important advance in the exploration for oil and gas was the publication, in 1885, of the anticlinal theory, which states that oil and gas tend to accumulate on, or near, the crown of an anticline (*2*). This theory encouraged geologists to search for surface expressions which reflected subsurface structures. Numerous oil and gas fields were found by drilling such surface features, but the most successful discoveries were made when oil or gas seeps were associated with these features.

The introduction of geophysical instruments such as the torsion balance, the gravity meter, and refraction and reflection seismographs to oil and gas exploration in the 1920's led to the discovery of many subsurface structures that contained oil and gas but had no apparent surface expression. Because not all these subsurface structures contain petroleum, a more efficient approach to finding oil and gas would include methods to detect accumulations directly. The most important contribution that direct detection methods can make is in the discovery of stratigraphically trapped gas and oil deposits. An example of such a deposit is the multibillion barrel East Texas oil field that is not associated with structure; it was discovered by chance.

Direct Geochemical Methods

The geochemical methods that are considered to be direct are based on the premise that hydrocarbons migrate upward from subsurface oil and gas accumulations to the earth's surface. Surveys over known oil and gas fields have shown this to be true. The surveys produced recognizable patterns of anomalous quantities of ethane and heavier hydrocarbons that conformed closely to the shapes of the subsurface accumulations. Moreover, anomalies obtained before drilling have also been confirmed by the subsequent discovery of gas or oil fields.

Direct methods use measurements of microquantities of light, saturated hydrocarbons that are present in the interstices of soil (soil air), and both the light hydrocarbons and the heavier aromatic compounds that are adsorbed by the soil.

Soil-air hydrocarbons. The first attempt to relate near-surface hydrocarbons to subsurface deposits was made in Germany in 1929 and reported in 1933 (*3*). The field work consisted of drilling holes to depths of 1 to 2 m, sealing them, and, after 24 to 48 hours, removing a sample of the enclosed air for analysis. The results showed that soil air in holes over a gas deposit contained higher concentrations of methane than did soil air in holes located beyond the edges of the field.

In 1932, Russian investigators began similar investigations. They also collected soil-air samples but from core holes that were usually 2 to 3 m deep. Furthermore, they removed most of the air initially present in the holes before collecting samples for analysis. In addition to methane, the samples contained a "heavy fraction" that presumably included ethane and heavier hydrocarbons (*4*). Considerable success in applying this technique in Russia has been reported (*5*).

Adsorbed soil hydrocarbons. In the United States, investigators entered the field of geochemical exploration in 1936, with the first results published in 1938 (*6*) and 1939 (*7*). Samples of soil, rather than soil air, were used for analysis, and it soon became clear that significantly larger quantities of adsorbed saturated hydrocarbons can be extracted from soil samples than from soil air. Another important advantage of using soil is that sampling can be conducted in all areas including those offshore.

An onshore geochemical survey. One of the early hydrocarbon surveys was conducted in 1946 over the Hastings oil field in Brazoria County, Texas (*8, 9*) (Fig. 1). The productive area, discovered in 1934, covers about 20.2 km^2 and orig-

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inally contained estimated reserves in excess of 500 million barrels (79.5 × 10^6 m^3) of oil. The oil is trapped in the Oligocene Frio Formation at a depth of about 1835 m within a structure of high relief.

The adsorbed ethane and heavier hydrocarbon values, expressed in parts per billion by weight on the dry sample basis (*10*), were obtained from soil samples collected between 2.5 to 3.5 m below the surface (Fig. 1). The hydrocarbon gases were extracted from the soil by heating approximately 100 g of each sample and a 50 percent solution of phosphoric acid to about 95°C in a partial vacuum. The extracted gases were separated and analyzed in a vacuum system by low temperature fractionation and combustion methods (*11*). The analytical technique was simplified in the early 1960's, after the adoption of the hydrogen flame gas chromatograph (*9, 12*).

Variations in hydrocarbon concentration are distinguished by a system of shading (Fig. 1): values ranging from 25 to 49 parts per billion are in the areas of lightest shading, values of 50 to 99 are in the areas of intermediate shading, and values of 100 parts per billion and higher are in the most heavily shaded areas. The halo pattern of anomalous hydrocarbon values at the Hastings field bears a close relation to the outline of the producing area (Fig. 1, dashed line), which suggests that hydrocarbon leakage from subsurface reservoirs occurs principally at oil-water and gas-water contacts (*7, 13*). Although the halo pattern is usually observed over important oil and gas fields, anomalies also develop in which the high hydrocarbon values occur in the near-surface soil directly over productive areas. This type of pattern is often observed over important gas or oil accumulations in stratigraphic traps and hydrocarbon reservoirs that do not have an active water drive.

An offshore geochemical survey. The results of a survey of an area located in the Gulf of Mexico about 160 km southeast of New Orleans, Louisiana, and completed in 1974 are shown in Fig. 2 (*14*). Sediment samples were collected 1.8 m below the sea bottom from 256 stations that were located 800 m apart along north-south profiles 1600 m apart (*15*). The water depth ranges from 97 m at the northwest corner of the survey to 567 m at the southeast corner. The hydrocarbons were removed from the fine-grained portions of the sediment samples by acid extraction and analyzed by a hydrogen flame chromatograph.

A halo-type ethane and heavier hydrocarbon anomaly in the eastern part of the area sampled is shown by a heavy dashed line (Fig. 2). The anomaly was considered of high merit and graded "A" before the lease sale that included the area surveyed. A well located within the anomaly was drilled in 1975 and gas and oil zones were encountered. The dotted outline indicates the area within which additional productive wells were drilled and represents the approximate limits of the producing area. The estimated reserves of the field, named Cognac, are in excess of 50 million barrels (8 × 10^6 m^3) of oil.

Aromatic hydrocarbons. Crude oils usually contain appreciable amounts of aromatic compounds including naphthalenes (two ring) and phenanthrenes (three ring). These substances fluoresce when dilute solutions of the oils that contain them are exposed to ultraviolet light. In spite of their high molecular weights, the aromatics often occur in near-surface soils and sediments over and around oil fields. When organic solvent extracts of these near-surface samples are exposed to ultraviolet light,

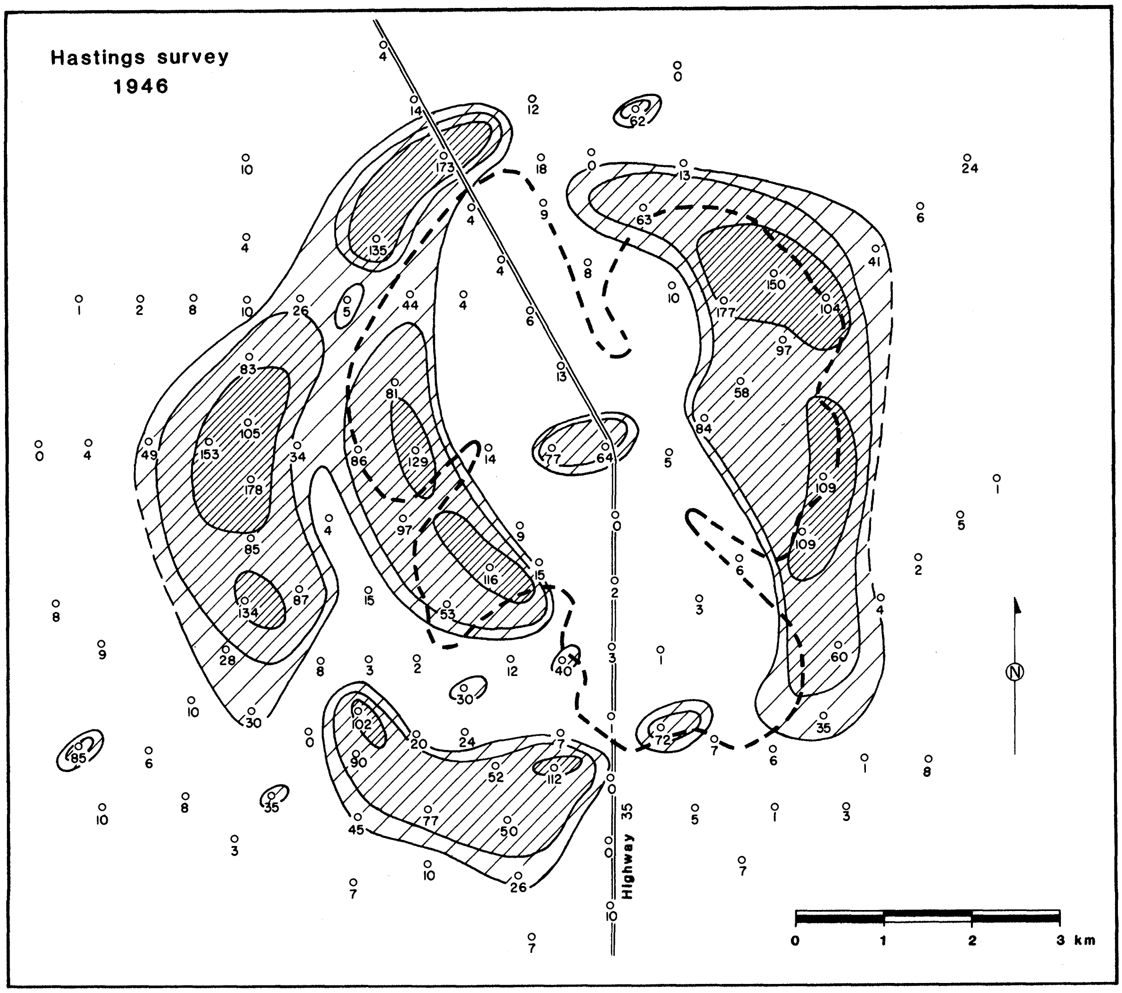


Fig. 1. Adsorbed ethane and heavier hydrocarbon values from soil samples taken at depths of 2.5 m to 3.5 m at the Hastings field. Values are in parts per billion by weight; anomalous values (in shaded areas) produced a halo pattern that conforms closely to the outline (dashed line) of Hastings oil field in Brazoria County, Texas. [Adapted from (*8*)]

fluorograms are obtained that resemble those of crude oils.

Fluorograms of two samples of crude oil and one of a sediment are shown in Fig. 3 (*16*). Dilute solutions of the oils in spectroscopically pure hexane and a hexane extract of the sediment sample were exposed to ultraviolet light with a wavelength of 265 nm (*17*). The first oil, with a gravity of 35.9° API (American Petroleum Institute standard) produced two emission peaks at 320 and 365 nm. The second oil, 29.2° API, produced a shoulder at 320 nm and a distinct peak at 365 nm. The fluorogram of the sediment sample shows a slight shoulder at 320 nm and a distinct peak at 365 nm. The sediment sample was taken near a fault located on the north side of the Hondo oil field in the Santa Barbara Channel, offshore of California. The field is producing heavy oil ranging from 14° to 26° API gravity, a fact that supports the observation that the ratio of the 365 nm peak height to the 320 nm peak height is related to the gravity of oil; the higher the ratio, the lower the API gravity.

Problems, Solutions, and Applications to Exploration

The data from early hydrocarbon surveys revealed three recurring problems associated with the adsorbed hydrocarbon technique. One was related to lithological properties of the sample medium, another was caused by soil acidity in certain areas, and the third problem resulted from the presence of biogenic methane in most near-surface soils.

Lithology. Sands have low affinities toward hydrocarbons whereas clays are generally highly adsorptive. A process to remove sand from soils and sediments was adopted in 1970 after experiments showed that most of the hydrocarbons present in the sample are so tightly bound to the fine-grained fraction (particle size, <63 μm) of the soil that the samples could be subjected to wet sieving and filtration procedures (*14, 18*).

When the sand removal process was used on samples from areas of high sand content, anomalies of much greater contrast than had been obtained previously resulted. In areas where the sand content was less than about 25 percent, no significant benefits were observed at first and, therefore, the process was not used on samples from such areas.

Soil acidity. Well-defined, near-surface adsorbed hydrocarbon anomalies

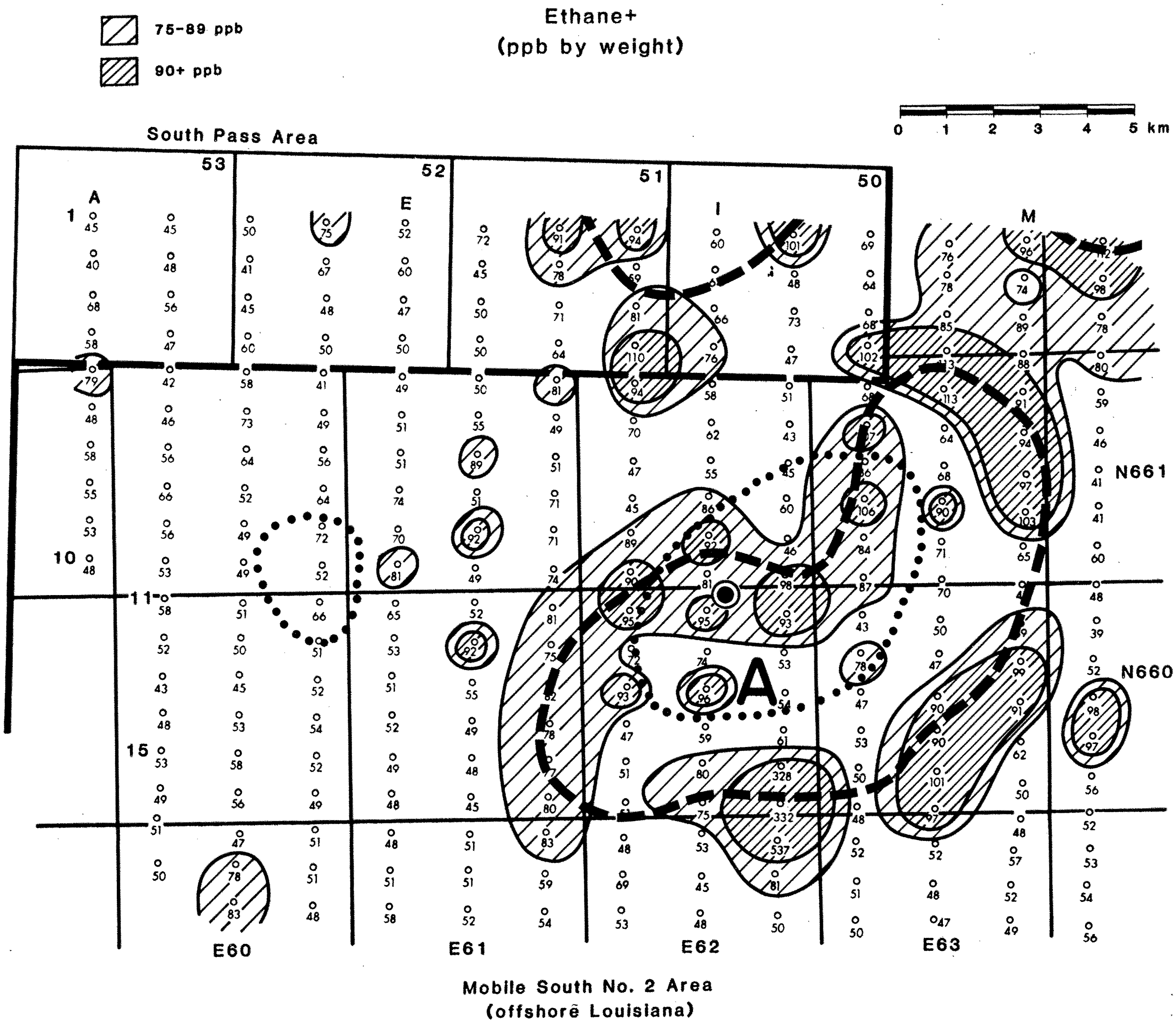


Fig. 2. Ethane⁺ (sum of ethane through pentane values) map of a survey conducted in the Gulf of Mexico. The heavy dashed line outlines an anomaly of high merit (A) in the eastern part of the survey that reflects an area considered prospective. A well (large solid circle) located within the anomaly, was drilled after the survey was completed and became the discovery well of the Cognac field (*14*). Mobile South No. 2 Area has been renamed Mississippi Canyon Area.

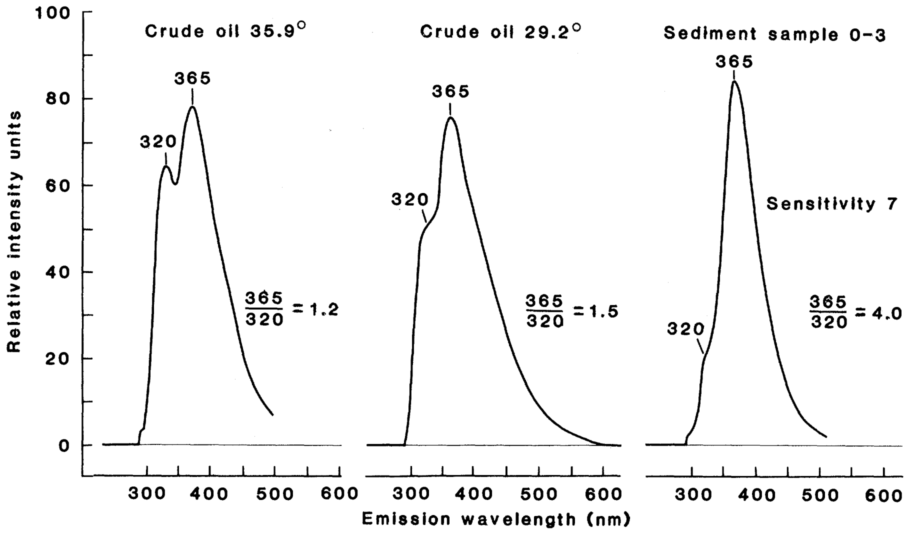
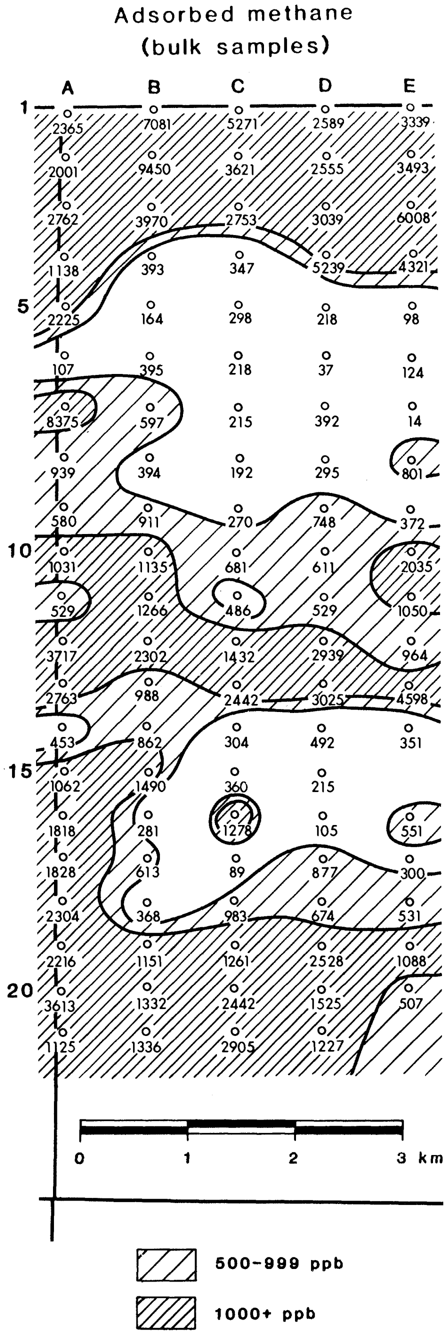


Fig. 3 (above). Fluorograms show that the sediment sample (0–3) taken near the Hondo oil field in the Santa Barbara Channel contains the same aromatic hydrocarbon compounds that are present in crude oils. Ratios of 365 nm peak heights to those of 320 nm are related to the gravity of oil; the higher the ratio, the lower the API gravity. The Hondo field produces oil ranging from 14° to 26° API gravity (*16*). Fig. 4 (right). Adsorbed methane values obtained by acid extraction of hydrocarbons from bulk samples followed by chromatographic analysis. Samples were taken from depths of approximately 4 m in marshy Lake Pagie area, Terrebonne Parish, Louisiana. High methane values suggest biogenic source.



are usually found to be associated with recently discovered oil or gas fields (*9*). Occasionally, however, an anomaly was not observed in such cases, and it was found that the soils in these areas are acidic, sometimes having a *p*H as low as 3. Apparently, the acidic nature of the soils prevented the hydrocarbons from being adsorbed.

Experiments were conducted in which samples of about 300 cm^3 of the acid soil were sealed immediately after collection in 1-liter glass jars containing 500 cm^3 of distilled water. After vigorous shaking, samples of the headspace gas were withdrawn from the jars and analyzed by hydrogen flame chromatography. Anomalous amounts of hydrocarbons in the methane through pentane range were found in the headspace of soil samples taken over and adjacent to oil and gas fields, supporting the indication that acid soils bind light hydrocarbons poorly. The headspace hydrocarbons are classified as "interstitial," and their concentrations are expressed as 10^{-6} cm^3 hydrocarbon per cubic centimeter of soil. This technique belongs in the same group as those in the soil-air category. It is of interest to note that aromatic hydrocarbons are not affected by soil acidity.

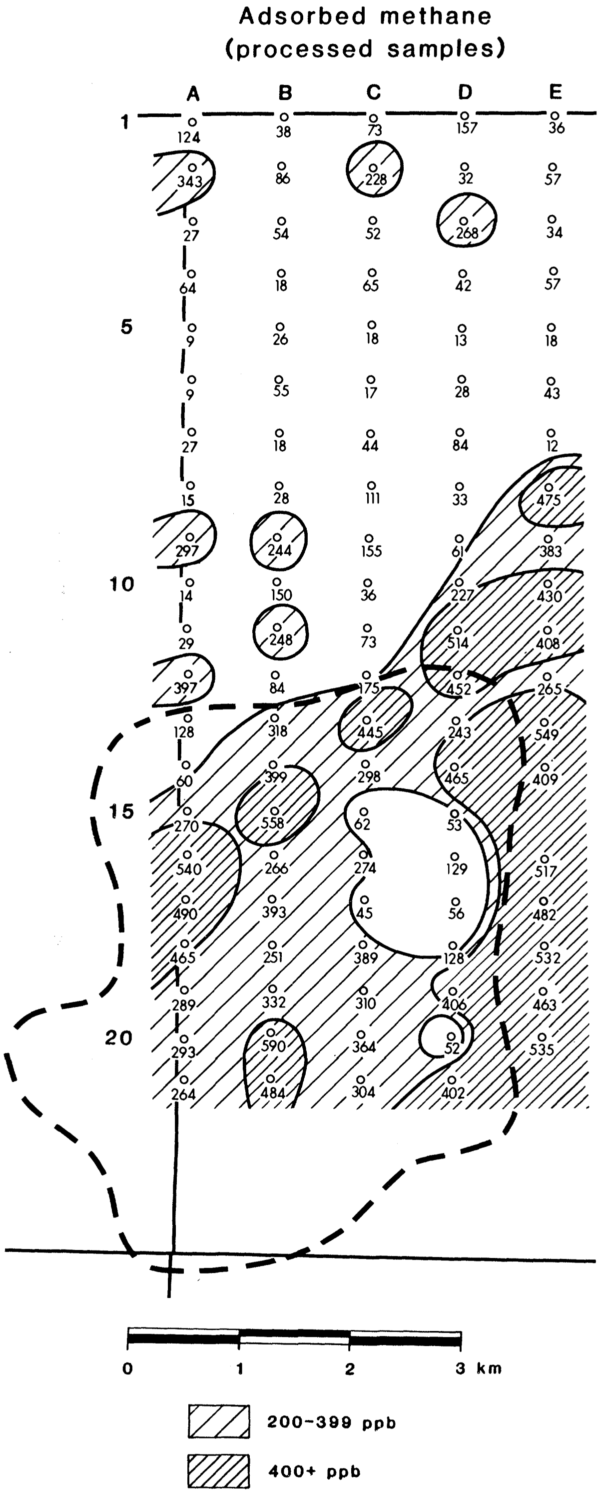
Biogenic methane. Biogenic methane is frequently present in the near-surface as a by-product of bacterial action on organic matter. From the beginning, therefore, methane was separated from the heavier hydrocarbons, and only the heavier fraction that has no known source other than petroleum was considered significant in geochemical exploration (*11*). After the hydrogen flame chromatograph replaced the vacuum analytical technique, biogenic methane in samples from marshy areas created another problem because the chromatographic peaks of methane were often so large that they obscured those of the heavier hydrocarbons.

Removal of biogenic methane from soil. Experimentation indicated that the sand removal process eliminates biogenic methane from soils collected in marshes without affecting the adsorbed thermogenic methane. Chromatograms of the adsorbed hydrocarbons that were removed from the fine-grained portions of the samples by the acid extraction procedure showed clearly the entire suite of saturated hydrocarbons (methane through pentane) and the methane tracked the ethane and heavier hydrocarbons. After noting these results, the practice was adopted of applying the sand removal process to all soil and sediment samples before acid extraction and analysis of adsorbed gases.

A geochemical survey in a marsh. In early 1973, an experimental survey was conducted to determine if, in fact, by applying the sand removal process, a significant methane anomaly could be recognized over a known field that is located under a marsh. In this survey, soil samples were collected at depths of approximately 4 m from 103 stations over and adjacent to such a field (*19*). Adsorbed gases were removed by the acid extraction procedure from both processed and unprocessed (bulk) portions of each sample before analysis for hydrocarbons. The processed portion contained only fine-grained particles smaller than 63 μm but many of the bulk samples contained varying amounts of humic material as well as clay.

The samples were collected every 400 m along north-south lines approximately 800 m apart. The methane values of the bulk samples are shown in Fig. 4. They are expressed in parts per billion by weight and plotted at their respective locations. Values in the lightly shaded areas are in the range from 500 to 999 parts per billion and values of 1000 parts per billion and above are in the heavily shaded areas. The latter areas contain values up to 9450 parts per billion and suggest methane of a biogenic origin.

Values for the adsorbed methane that were obtained from the processed samples are shown in Fig. 5. The contrast in the two figures is striking because now a halo-type pattern appears that conforms closely to the producing area (dashed outline). The productive area is known as the Lake Pagie gas-condensate field and is located in Terrebonne Parish, Louisiana, about 105 km southwest of New Orleans. This is a major gas-condensate field with estimated recoverable reserves of more than 28.3 × 10^9 m^3 of gas and 30 million barrels (4.8 × 10^6 m^3) of condensate. The field contains 28 productive sands between 2960 m in the upper Miocene and 5215 m in the Middle Miocene (*20*). The bulk of the reserves are in two sand sections, one topped at a depth of about 4390 m and the other at about 4695 m. The field includes 44 gas-condensate wells and two oil wells (*20*). Twenty-six of the wells are located in the southern part of the area that was sam-



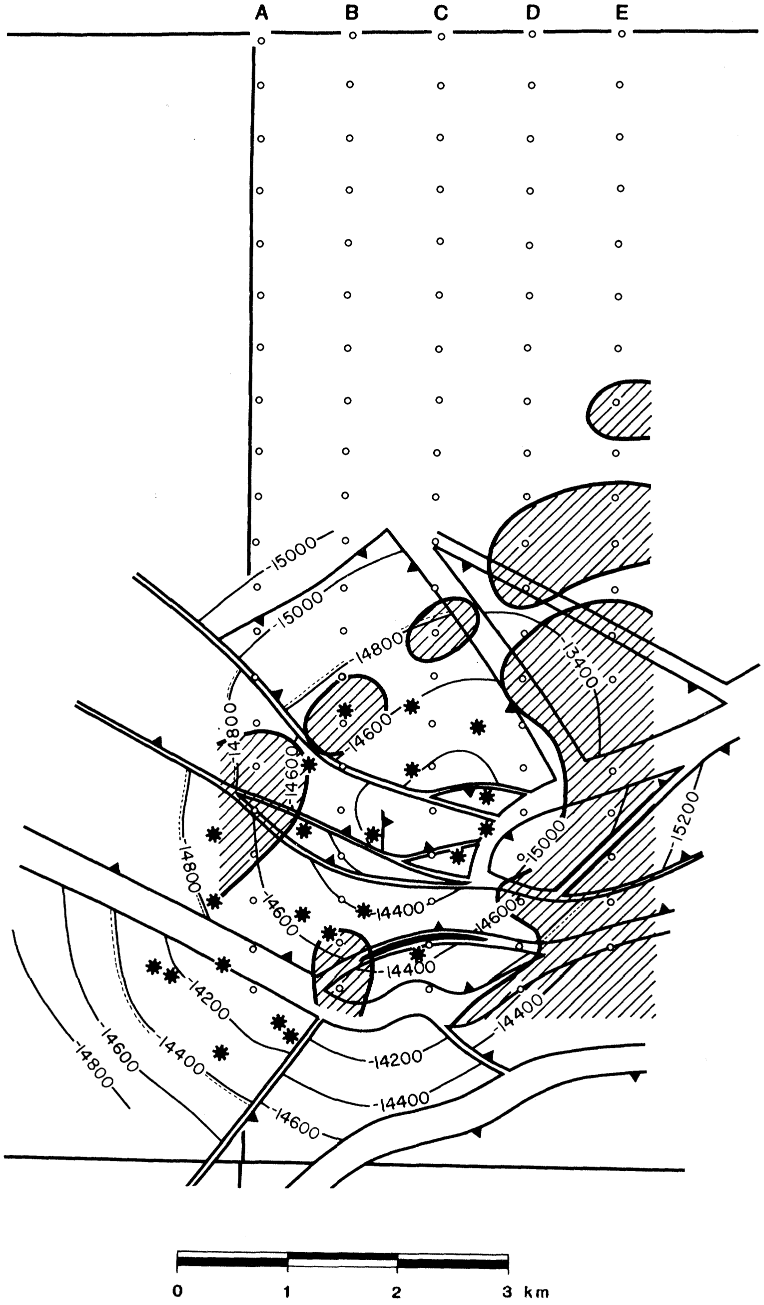


Fig. 5 (left). Adsorbed methane values obtained after subjecting portions of bulk soil samples to the sand removal process before acid extraction of hydrocarbons and chromatographic analysis. The anomaly that resulted correlates well with the productive limits of the Lake Pagie gas-condensate field (dashed line) and is in striking contrast to low methane values in the background area in the northern part of the survey. Comparison with Fig. 4 indicates that biogenic methane, not related to the productive area, was removed. Fig. 6 (right). Subsurface geological structure map of Lake Pagie field including those wells (*) that are producing from two main deep reservoirs. Contours represent depths (in feet) to top of the upper part of these reservoirs (*20*). Shaded areas contain methane values of 400 parts per billion by weight and higher and represent a halo-type anomaly that conforms closely to the productive areas of the deep reservoirs. [Geological data courtesy New Orleans Geological Society] pled and, of these, 23 fall within the methane anomaly produced by the processed samples. The medium values (200 to 399 ppb by weight) over the producing area are believed to result from hydrocarbon leakage at the edges of the many overlapping productive zones and from hydrocarbon migration along some of the faults that are present in the field.

A subsurface geological map of the Lake Pagie field, prepared from information obtained from electrical logs, is shown in Fig. 6. The geological contours represent the depths to the top of the formation identified by *Textularia (W)* 3D; this formation is the upper of the two main producing reservoirs in the field (*20*). Only areas with values of 400 parts per billion and above of methane are superimposed on the geological map in Fig. 6. In addition, only the wells that are producing from the two deep sands are shown in the figure. The high methane concentrations near the north and west edges of the halo-type methane anomaly (shaded areas) conform closely to the gas-water contact (fine dashed lines) at a depth of 4510 m. The eastern band of high concentrations overlies several large faults that bound production in this direction (*20*). The close relation between the methane anomaly and the productive limits of the deep petroleum accumulations is evidence that the methane obtained from processed samples originates in these deep reservoirs.

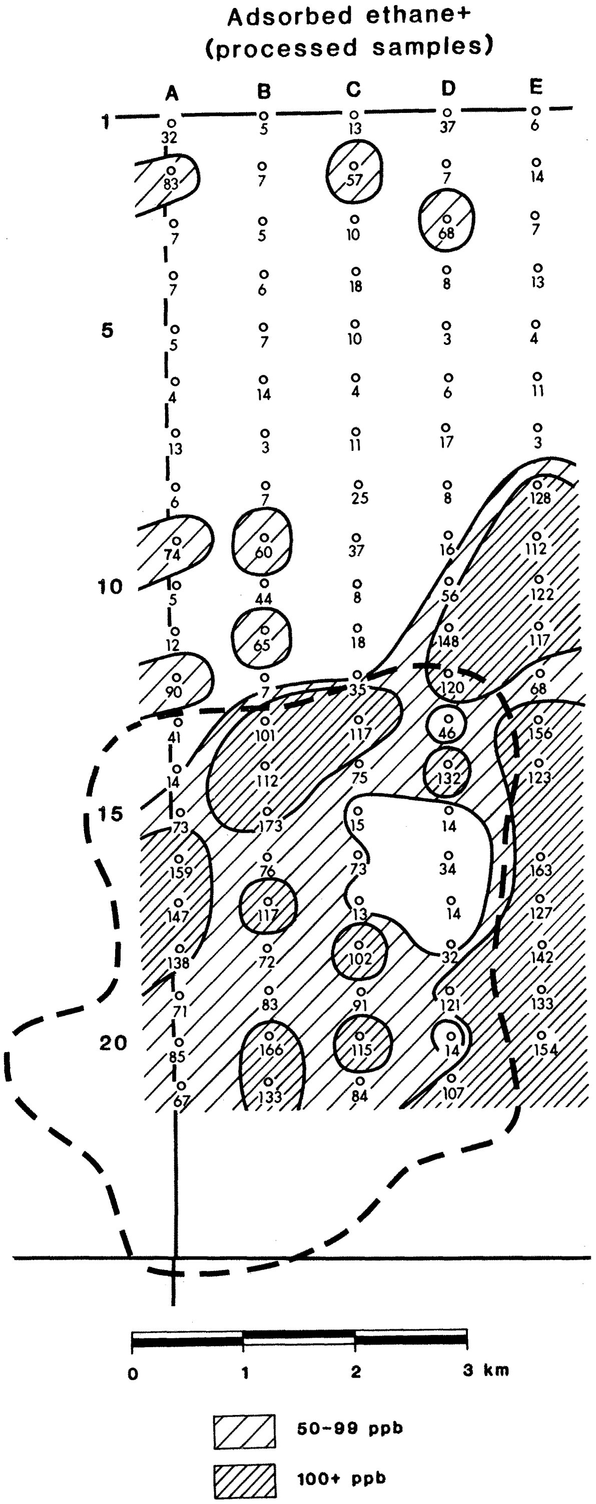


Fig. 7. Ethane$^+$ (ethane through pentane) data obtained from processed samples of Lake Pagie survey. The anomalous pattern is similar to that produced by the methane extracted from processed samples (Fig. 5).

The ethane and heavier hydrocarbon data for the processed samples are shown in Fig. 7. The pattern of anomalous values for this fraction is almost identical to that of the methane of Fig. 5. The excellent correlation between the methane anomaly and that of the ethane and heavier hydrocarbons from the same samples provides additional evidence that the adsorbed methane extracted from the processed samples has a thermogenic source.

Biogenic methane and methane to ethane ratios. The removal of biogenic methane before analysis permits the calculation of methane to ethane ratios that are useful in distinguishing gas from oil reservoirs. Methane to ethane ratios were computed from the unprocessed and processed sample data of the Lake Pagie survey (*21*). Bulk sample ratios range from 15 to 2616 with an average of 227. The methane of the high methane/ethane ratios is clearly biogenic.

The methane/ethane ratios calculated from the processed sample data range from 9 to 57, with an average of 17. The methane/ethane ratios of the data that fall within the Lake Pagie anomaly have an average value of 16. Both averages are indicative of a gas-condensate prone area and are in the range found in subsurface gas-condensate reservoirs. Hydrocarbon anomalies that reflect oil accumulations yield methane/ethane ratios that are usually less than 10. Dry gas deposits are indicated when ratios of 25 or higher are obtained. Other ratios have also been proposed (*22, 23*).

Biogenic methane and carbon isotope ratios. Adsorbed methane extracted from unprocessed (bulk) samples of near-surface soil or sediment yields δ^{13}C values that may occasionally correspond closely to those of methane in subsurface reservoirs (*24, 25*). On the other hand, methane extracted from the fine-grained samples of processed soils and sediment yield C^{13}/C^{12} ratios that are usually the same as those of methane that originates in subsurface reservoirs. In fact, these ratios often produce near-surface patterns that are similar to those of the heavier hydrocarbons themselves (*16*).

Furthermore, since carbon isotope ratios of methane in reservoir gas vary with the contents of the reservoir, carbon isotope ratios determined on adsorbed near-surface methane from processed samples can be used to distinguish gas from oil deposits (*26*).

Indirect Geochemical Methods

As hydrocarbons rise from subsurface petroleum deposits, changes are produced in the chemical composition of overlying formations. Indirect oil and gas exploration techniques have been developed that are dependent on these changes.

One indirect method is based on the conversion of ferric to ferrous iron by the migrating hydrocarbons (*27*). Since ferrous iron is essential to plant growth, it is assimilated by vegetation. That this occurs is shown by the presence of anomalously high concentrations of ferrous iron in pine needles and sagebrush leaves over the Bell Creek oil field in Montana (*28*). An aeromagnetic survey over the same area also showed an anomaly that is thought by some to be related to the reduction of hematite to magnetite by hydrocarbons migrating upward.

Another indirect technique is based on the decomposition of carbonates at temperatures in the range from 500° to 600°C. Anomalies produced by the resulting carbon dioxide are reported to be of the halo-type and are believed to be related to subsurface petroleum deposits (*29*). Additional indirect techniques have been proposed (*30*).

Conclusions

Direct methods of geochemical exploration involve the measurement in near-surface soils of microquantities of the light, straight-chain and the heavier, aromatic hydrocarbons that characterize subsurface oil and gas deposits. In general, the highest concentrations of hydrocarbons found in the near-surface are firmly bound to fine-grained soil and sediment particles. However, hydrocarbons are also found that are loosely bound and some are present in the free state within the soil interstices.

The value of the direct methods is enhanced when biogenic methane that is indigenous to near-surface soils and sediments is eliminated before analysis. This is accomplished by sieving and filtering procedures that remove sands and other coarse-grained materials as well as the biogenic methane. Hydrocarbons are extracted from the resulting fine-grained material that yield methane/ethane ratios and carbon-isotope ratios that fall within the same ranges as those of reservoir gases. These ratios are useful in predicting if the near-surface gases originate in gas or oil accumulations. The inclusion of aromatic hydrocarbon data in geochemical studies improves the accuracy with which these predictions can be made.

Indirect geochemical methods measure inorganic alteration products in near-surface soils that result from upward migration of hydrocarbons. These methods are most useful in conducting reconnaissance surveys.

When geochemical methods are integrated with geological, geophysical, and other valid exploration techniques, the chance of finding gas and oil is substantially increased. However, in the event a well-defined hydrocarbon anomaly is not supported by structural data, the possibility should be considered that the anomaly is reflecting an oil or gas accumulation that is hidden in a stratigraphic trap.

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10. The data are expressed on the dry sample basis, but the samples were not dried before analysis. A separate portion of each sample was used to determine the moisture content that is needed to calculate the hydrocarbon values on the dry sample basis.
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15. Unlike land surveys, where samples should be taken 1.8 to 3.7 m below the earth's surface, or deeper, depending on the area to be evaluated, experimentation with offshore sediments indicated that satisfactory data could be obtained from samples taken immediately below the water-sediment interface. However, in practice, offshore samples are usually taken from depths of 1.8 m or more below the bottom of the sea to avoid problems caused by shifting of sediments by water currents and storms.
16. L. Horvitz, paper presented at the AAPG/UNITAR Exploration for Heavy Crude Oil and Bitumen Research Conference, Santa Maria, Calif., 29 October to 2 November 1984.
17. The following procedure is used in the author's laboratory to determine relative amounts of aromatic compounds in soils and sediments: 10 cm^3 of spectroscopically pure hexane is added to 1 g of fine-grained soil or sediment that has been dried at 40°C. The mixture is allowed to stand at ambient temperature for 15 minutes with intermittent shaking. The clear liquid above the sediment is then poured into a quartz cuvette, and the cuvette is introduced into a fluorescence spectrophotometer (Perkin-Elmer model 204). The solution is exposed to ultraviolet light at 265 nm and fluorescence emission intensity as a function of wavelength is recorded on chart paper for the range of wavelengths from 300 nm to about 600 nm. Emissions at 320 and 365 nm are expressed in peak height units after sensitivity and attenuation factors are taken into account. For other fluorescence techniques see: O. E. Campbell, *World Petroleum,* March 1946; J. M. Brooks *et al.*, in Proceedings of the 15th Offshore Technology Conference, Houston, Texas, 2–5 May 1983, OTC 4624, pp. 393–400; C. F. Hebert, in *Unconventional Methods in Exploration for Petroleum and Natural Gas,* M. J. Davidson and B. M. Gottlieb, Eds. (Southern Methodist Univ. Press, Dallas, 1983), vol. 3, pp. 40–58.
18. The process for removing coarse-grained material from soils and sediments involves stirring 300 to 1000 g of the bulk sample in a blender with distilled water for about 5 minutes. By wet sieving, the coarse material is removed and the fraction that passes through a 63-μm sieve is used for analysis. The distilled water that collects with the fine-grained fraction is removed by filtration. During the blending operation, loosely bound hydrocarbons (LBH) may be released. Although the quantities are usually negligible, occasionally they are anomalous and provide supplementary data that is useful in interpreting the results of a geochemical survey. Therefore, a sample of the headspace gas is removed from the blender before the sieving operation and analyzed for its hydrocarbon content. The LBH values are expressed in 10^{-7} cm^3 hydrocarbon per gram of soil or sediment.
19. The samples were taken by LaTerre Production Company (now a subsidiary of Tenneco Oil Company) and sent to L.H.'s laboratory for analysis without disclosing the locations of the samples or the area from which they were taken. After the analytical data were submitted to LaTerre, a station location map showing the Lake Pagie field was received.
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30. The three volumes of *Unconventional Methods in Exploration for Petroleum and Natural Gas,* published by Southern Methodist Univ. Press, Dallas, in 1969, 1981, and 1983, respectively, contain papers presented at three symposia sponsored by the Institute for the Study of Earth and Man.
31. I thank Tenneco Oil Company and Union Oil Company for permission to publish the geochemical data obtained in the Lake Pagie area. I also express my appreciation to E. P. Horvitz and S. A. Horvitz for assistance in the preparation of this article.