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A Critical Overview of and Proposed Working  
Model for Hydrocarbon Microseepage

By

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## CONTENTS

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	Page
Abstract .....	1
Introduction.....	2
Migration Mechanism.....	5
Bacterial Influence.....	12
Bacteria.....	12
Chimneys.....	19
Biogenic Methane.....	27
Halos.....	29
DGD Methods - Pros and Cons.....	36
Soil - Air HCS.....	36
Soil-Sorbed HCS.....	36
Soil-Occluded HCS.....	39
Microbiologic Surveys.....	42
Integrative-Absorption.....	46
Discussion.....	53
HC Microseepage Fluxes.....	53
Optimum use of DGD.....	57
Hypotheses.....	62
Correcting the Record.....	64
Conclusions.....	67
Acknowledgment.....	72
References.....	73

## ILLUSTRATIONS

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	Page
Figure 1. Solubility of a whole crude oil in methane for different isotherms as a function of pressure with water present.....	9
2. Gas chromatograms of crude-oil solute samples showing distinct qualitative changes as a function of the pressure and temperature at which the system was equilibrated.....	10
3. Soil-sorbed HC concentrations for the Krasnodar region, Soviet Union.....	17
4. Example of a paraffin-dirt bed associated with HC microseepage in Sabine County, Texas.....	18
5. Radioactivity in various shales overlying the Westrose oil field, Alberta Canada.....	20
6. Soil-carbonate traverse across an oil field.....	24
7. Explanation of surface geochemical halos by caprock plugging.....	31
8. HC gas logging examples for a new field wildcat discovery well near Rosenberg, Fort Bend County, Texas, and for a dry hole in neighboring Harris County, Texas.....	32
9. Soli's (1957) explanation for soil-air and soil-sorbed HC anomalies.....	33

# CONTENTS--continued

	Page
10. Soil-sorbed ethane traverses run at different times (May and September, 1937) over the Hastings oil field, Brazoria County, Texas.....	35
11. Ethane soil-air survey of the Hilbig oil field, Bastrop County, Texas.....	37
12. Volatile organic compounds found in various environments.....	51
13. Solubility of water in methane as a function of pressure and temperature.....	55
14. Geology and results of a soil-gas survey over the Ryckman Creek field, Wyoming.....	60
Table 1. ....	53

# A Critical Overview of and Proposed Working Model for Hydrocarbon Microseepage

by Leigh C. Price

## ABSTRACT

Since the concept of surface geochemical exploration (SGE) for oil and gas was first proposed by Sokolov and Laubmeyer over 50 years ago, the major Western effort has been the merchandising of various methods. Except for Soviet efforts, little research has been conducted on the causes, mechanism, consequences, and correct utilization of SGE or hydrocarbon (HC) microseepage. No area of science may achieve its full practical (commercial) application until the basic principles of that scientific area have been fully delineated. Such delineation has certainly not occurred with HC microseepage. Answers are needed to: (1) the HC microseepage transport mechanism, (2) the cause of the celebrated "halo" anomaly, (3) the degree and nature of the interaction of microseeping HCS with their environment, (4) the characteristics and causes of "chimneys" over HC deposits, and (5) the optimum method for the detection and measurement of HC microseepage.

Although minimal fundamental research has been carried out on HC microseepage, the existing data, when combined with established principles in petroleum geology and geochemistry, are sufficient to construct a realistic working hypothesis for HC microseepage. The only transport mechanism in agreement with observed data is the vertical migration of microbubbles of natural gas through microfracture systems over HC deposits. The role of aerobic and anaerobic bacteria in the sediments at all levels above HC deposits, but especially in surface soils, has been unrecognized in the published literature. Various bacteria, by attacking vertically migrating (including microseeping) HCS, utilize free or complexed oxygen and produce  $\text{CO}_2$  (and  $\text{S}^{2-}$  by sulfate reduction). Thus, the pH and eH of the leaking HC environment is dramatically changed, as consequently are the stability fields of the different mineral species in that environment. Such changes result in the precipitation (or solution and mobilization) of different mineral species and elements, such that the rock column above a leaking HC deposit becomes measurably different than laterally equivalent rocks. In other words a "chimney" is created. "Halo" anomalies are due to near-surface oxidation of microseeping (or other vertically migrating) HCS by aerobic bacteria and other microbes.

SGE is controversial. Some investigators deny the existence of HC microseepage. Others maintain that even if it does exist, it cannot outline surface traces of HC deposits. Published data clearly establish the existence of HC microseepage and the fact that it does outline distinct surface traces of HC deposits. The Soviets have had marked success using SGE. Published examples exist of fields discovered solely or largely on the basis of SGE, and probably a much greater number of unpublished examples exist. There is no question that SGE has been a viable exploration tool. The question is whether SGE techniques can meaningfully contribute to the future search for HCS in stratigraphic and (or) low-relief traps.

Direct geochemical detection techniques have not taken advantage of the revolution in analytical chemistry over the last 25 years. Conventional soil-air and soil-survey techniques require deep sampling (at least 6 ft, 2 m). The resulting need for truck-mounted augers drastically decreases field mobility and increases field time and expenses. Moreover, the analytical methods for these techniques are tedious and expensive. In my opinion, the optimum methods for the detection of  $C_2$ - $C_5$  microseeping HCS have not yet been devised. However, whatever method is used, its optimum employment will depend on full cognizance of the seasonal (climatological) and geographic variance of the microbiologic filter through which microseeping HCS must pass.

## INTRODUCTION

Surface and near surface geochemical exploration (SGE) for hydrocarbon (HC) deposits can be broken into two broad categories: direct geochemical detection (DGD) techniques and indirect geochemical detection (IGD) techniques. (The abbreviations SGE, HC, DGD, and IGD will be used throughout this paper). DGD techniques are based on the (substantiated) assumption that  $C_1$  to  $C_5$  HCS migrate to the Earth's surface from thermogenic HC deposits to form anomalously high measurable surface concentrations of  $C_1$  to  $C_5$  HCS. However, methane is not uniquely indicative of thermogenic HC deposits (Horvitz, 1939, 1954, p. 1206-1207; Kartsev and others, 1959; Sokolov and others, 1959, 1971; Davis, 1967, p. 203; Bernard, 1981; and Philp and Crisp, 1982, p. 3) and has only limited applicability as an indicator of HC deposits. On the other hand,  $C_2$ - $C_5$  HCS are uniquely indicative of thermogenic HC deposits (Sokolov and others, 1971; Davis, 1976, p. 203; Horvitz, 1980, p. 243; Bernard, 1981; and Philp and Crisp, 1982, p. 3) and anomalous surface concentrations of  $C_2$ - $C_5$  HCS are considered excellent exploration tools. In this paper HC microseepage is defined as the migration of principally the  $C_1$  to  $C_5$  HCS from HC deposits to the Earth's surface to form HC (and other) anomalies. (As discussed below,  $C_6$ + HCS also migrate to the Earth's surface by physical forces other than those responsible for HC microseepage, and these  $C_6$ + HCS also form anomalies.) A DGD method is any technique which measures either a relative or absolute concentration of  $C_2$ - $C_5$  HCS, or a microbial response thereof, in the surface or near surface environment. Such methods include analyses for  $C_2$ - $C_5$  HCS either sorbed onto or occluded in soils, soil-air analyses, microbiologic analyses, and integrative absorption. These techniques are discussed below.

IGD methods can be divided into two classes: 1) those related to or caused by vertically migrating HCS, and 2) those unrelated to vertically migrating HCS, but thought to be possibly diagnostic of HC deposits. IGD methods of the first class are based on the premise that vertically migrating HCS from HC deposits somehow change the physical characteristics of surface and near surface soils above the deposits (or even of the entire sediment column above a HC pool). The reasons for and mechanisms of these changes invariably are never specified nor understood. Techniques which measure such changes are termed IGD methods for two reasons: 1) Such changes may be caused by factors other than HC microseepage from thermogenic HC deposits (discussed below). 2) When due to microseepage from HC deposits, such changes are a secondary, or indirect, result of HC microseepage. Kartsev and others (1959, p. 43) Davidson (1967), Debnam (1969, p. 4), and Duchscherer (1981A, p. 203) all listed different IGD methods of the first class, which include:

radiometric analyses, re-dox potential, bitumen analyses (luminescence or fluorescence), soil "salt" (mainly carbonates) analyses, trace metal or trace element analyses, geobotanical analyses, soil mineralogy (lithological), hydrochemical, and magnetic analyses. Many of these techniques can result from HC microseepage, and are discussed below. An IGD method characteristic of the second class is helium surveying.

Surface geochemical exploration for petroleum is controversial. As McCrossan and others (1972, p. 4) noted,

"Surface geochemical prospecting for petroleum has had a long and checkered history going back almost 40 years. Much of the work done in this field has been of a rather superficial nature without proper regard for the many variables involved. Consequently, many misleading conclusions have been based on overly simplified assumptions, resulting in periods of interest followed by periods of disillusionment. Very little of the published work is sufficiently broad in scope or comprehensive enough to have clearly settled the issue one way or the other. Much that has been written on this subject has been published in the trade journals and is either poorly documented or not documented at all-----."

Philp and Crisp (1982, p. 25) have noted,

"The literature on geochemical prospecting is frequently contradictory and confused. There is a lack of vigour in many descriptions, much pertinent data from the major oil companies have not been published and some data (usually the most optimistic) are provided by companies offering geochemical prospecting services."

After an exhaustive literature review on the subject, I could not agree more with these statements. Since the inception of SGE, due to the initial efforts of Laubmeyer (1933) and Sokolov (1936), with few exceptions, the Western emphasis has been (and continues to be) placed on the merchandising of insufficiently documented and researched SGE methods. Unfortunately, there has been little fundamental research into the causes, mechanism(s), consequences, and optimum utilization of SGE. Although a voluminous literature exists on SGE, for its size this literature is remarkably uninformative and at times offers more contradiction than fact. SGE is an area where speculation and unsubstantiated claims far outweigh hard data - a condition best summed by S. L. Clemens (1883, p. 174), a.k.a. - Mark Twain, "There is something fascinating about science. One gets such wholesale returns of conjecture out of such a trifling investment in fact." The definitive literature on the subject of SGE is largely from the intense Soviet effort in this area and from Western microbiologists. The established Western trend of assertions of the exploration proficiency of various SGE methods unsubstantiated by published rigorous scientific research continues to the present. The poor Western record in this area is somewhat understandable. The Soviet efforts have been government centralized and controlled, with the result of full scientific disclosure. On the other hand, Western commercial SGE ventures, if successful, certainly would gain nothing by full disclosure of their method. Nonetheless, articles in both scientific and trade journals which largely serve to advertise various SGE methods with little or no meaningful scientific documentation are suggestive of "95 percent sure" stock

or commodity market trading techniques. It would be most surprising if an inexpensive, simple, easily employed, and accurate method, which finally fulfilled the early promises of SGE, was offered as a service for general use. It is more likely that a true "breakthrough" in this field would not be widely publicized, but rather would be employed by its developer as the effective exploration tool it would be.

Different investigators have offered reasons why SGE has not been accepted to the degree that it should be (Davidson, 1963, p. 98-100, 1967; Debnam, 1969, p. 1; Hunt, 1979, p. 428; Duchscherer, 1981B, p. 312; Dennison, 1983, p. 161-162; and Kuzmin, 1983, p. 1089). There is probably some validity to many of these reasons. However, no area of science will achieve its full practical (commercial) application until the basic principles and controlling parameters of that scientific area are delineated. Such delineation certainly has not occurred with SGE methods based on HC microseepage. Explanations are needed to: (1) the microseepage migration mechanism, (2) the celebrated "halo" anomaly, (3) the degree and consequences of the interaction of microseeping (and other vertically migrating) HCS with their environment, (4) the characteristics and causes of "chimneys", and (5) how, or even if, microseeping HCS create indirect anomalies (soil salt, iodine etc.). Further, it is quite likely that optimum methods to detect and measure HC microseepage have not yet been developed.

Although this paper is not intended as a review of the field, at times it probably approaches that status. Reviews have been given by Kartsev and others (1959, by far the most definitive work), Debnam (1969, p. 1-6), Boyle and Garret (1970, p. 63-65), McCrossan and others (1972, p. 4-8), Siegel (1974), Hunt (1979, p. 425-433, somewhat negatively oriented), and Philp and Crisp (1982, the most recent comprehensive review). The models of this paper have been developed on the basis of what reliable data exist in the literature, established principles from related fields, and extrapolations based on my best scientific judgement when necessary. Little consideration has been given to undocumented published and (or) verbal claims or opinions. No new data or research are presented in this paper. Some of this paper's points may appear redundant or obvious to some investigators. However, significant misconceptions, erroneous assumptions, and faulty reasoning characterize much of the published literature on this topic, even current publications. A purpose of this paper is to address these errors in print even if some points may appear obvious to some investigators. Minimal fundamental research has been carried out on HC microseepage in the last 50 years; however, enough basic data exist which can be combined with established geologic/geochemical principles to construct a realistic working model for HC microseepage on which future rigorous and proper scientific Western research can be based. Such is the principal purpose of this paper. Perhaps the publication of new data from such research will reveal that many of the concepts of this paper are invalid and will have to be rejected. If so, this paper will have served its purpose. In any case, I believe that the models developed in this paper are much closer to reality than other published models and (or) speculative hypotheses concerning HC microseepage or the vertical migration of HCS to the Earth's surface in general.

## MIGRATION MECHANISM

Mac Elvain (1963, p. 133) stated that knowledge of the actual mechanism by which  $C_1$  to  $C_5$  HCS migrate to the Earth's surface is unimportant. Instead he contended that it's much more important to recognize that such migration happens in the first place. In my opinion, this attitude is partially incorrect. Knowledge of the HC microseepage mechanisms(?) would allow better utilization of SGE methods and give them more credibility. The principal migration mechanisms proposed to explain HC microseepage are: (1) diffusion (Rosaire, 1940; Kartsev and others, 1959; Baijal, 1962; Siegel, 1974, p. 231; Donovan and Dalziel, 1977; Duchscherer, 1980, 1981A,B, 1983; and Dennison, 1983), (2) effusion (Rosaire, 1940; Kartsev and others, 1959; Baijal, 1962; Donovan and Dalziel, 1977; Dennison, 1983; and Duchscherer, 1981B, 1983), (3) vertical transport of HCS by deep basinal waters (Pirson, 1960, 1963; Donovan and Dalziel, 1977; Davidson, 1981; and Duchscherer, 1981B, 1983), and (4) "permeation" (Horvitz, 1950, p. 939; Baijal, 1962, p. 8-10, a mechanism unexplained by those authors).

The American Geological Institute (1976, p. 120) defines diffusion as, "The spreading out of molecules, atoms, or ions into a vacuum, a fluid, or a porous medium, in a direction tending to equalize concentrations in all parts of a system." Hunt (1979, p. 425-428) gave an elucidating discussion of the improbability of diffusion controlling HC microseepage. (Also see Mac Elvain, 1969). Hunt (1979) pointed out that appreciable vertical diffusion distances through shales of near zero permeability can be achieved only over hundreds of millions of years, times far too long for relevance to HC microseepage. Hunt (1979, p. 428) concluded, and I could not agree more, "Clearly vertical diffusion from petroleum accumulations buried at depths such as 1,700 m (5,600 ft) is not the mechanism causing surface geochemical anomalies." Jones and Drozd (1983), on the basis of their studies, also rejected diffusion as a possible migration mechanism for HC microseepage. The strongest arguments against diffusion are: 1) Because it is a spherically dispersive process with no enhanced vertical component, it cannot possibly account for the sharp surface outlines of HC deposits. 2) Accounting for "halo" anomalies (discussed below) by diffusion is impossible. 3) As Hunt (1979) established, diffusion is far too slow to account for the rapid anomaly developments and (or) disappearances caused by changes in reservoir pressure (discussed below). 4) If diffusion were the migration mechanism responsible for HC microseepage, surface anomalies would involve much greater concentrations of  $C_6$ + HCS than they do. Rosaire (1940) recognized the dispersive nature of diffusion and attempted to reconcile the serious contradiction of the observed data with diffusion by an improbable scenario (discussed below) of vertically migrating gases evaporating ground water and triggering lateral ground water flow to cause a halo anomaly. Some investigators, including Dennison (1983), have called for an "enhanced vertical component" of diffusion. This is simply not possible, for as noted, diffusion is spherically dispersive. Further, as Mac Elvain (1969, p. 18) noted, "---- pure diffusion-mechanics control of a methane concentration in a sedimentary column would expand and dilute the gas two feet laterally for each foot of vertical ascent." Diffusion is the process, however, which is largely responsible for establishing the "background" levels of surface HC concentrations in sedimentary basins, not to be confused with the HCS which microseep from HC deposits and cause the anomalies against the background measurements.



Effusion is a term directly contradictory to HC microseepage. The American Geological Institute (1976, p. 139) defines effusion as, "The act or process of effusing or pouring out----." In a geologic sense, effusion refers to unrestrained flow, or ejection of fluids, especially volcanic fluids (lava) and thus contradicts the concept of losses of small amounts of HCS (microseepage). In such usage, effusion would refer to intermittent or continuous monophasic flow of crude oil or natural gas along faults or fractures according to Darcy's Law combined with the principles of two (or more) phase fluid flow, in other words macroseepage of crude oil and (or) natural gas. Microseepage by effusion would result in surface-anomaly HC concentrations orders of magnitude higher than they are and significant concentrations of  $C_6+$  HCS.

Different investigators contend that HC microseepage anomalies are due, at least partly, to vertical movement of deep-basinal compaction waters, or meteoric-recharge waters, through HC deposits to the Earth's surface (Pirson, 1960, 1963, 1964, 1969; Donovan and Dalziel, 1977; Roberts, 1980; and Davidson, 1982, 1984). Such waters are believed to carry HCS and dissolved mineral species which results in formation of different anomalies. Pirson (1960, 1963, 1964B, 1969) and Roberts (1980, 1981) have constructed elaborate "forced draft" or "deep water discharge" theories, wherein primary petroleum migration and accumulation is achieved by HC traps "filtering out" junk molecules or solubilized oil from water allowing the water to pass through the HC deposit to the Earth's surface. Based on past and ongoing personal studies on the origin, migration, and accumulation of crude oil, the accumulation scenarios of Pirson (1960, 1963, 1964B, and 1969) and Roberts (1980 and 1981) are most improbable. Evidence of significant flow of deep-basinal compaction waters up major fault zones does exist from different petroleum basins (Price, 1976, p. 229-239; Roberts, 1981; and Jones, 1981, 1984), as well as a few examples of flow of deep-basinal compaction waters up major faults cutting HC deposits. However, there is no published evidence of significant vertical flow of compaction (or meteoric-recharge) waters through HC deposits in traps of slight to moderate structural complexity and especially through stratigraphic traps. Further, the principles of two-phase fluid flow and Darcy's Law dictate that such vertical water flow through the oil-charged porosity of a HC deposit is impossible. (See Chapman (1982) for a fuller discussion of the point.) The creation of HC microseepage (or other) anomalies from vertical flow of deep-basin compaction or meteoric-recharge waters through HC deposits to the Earth's surface is not possible. Darcy's Law dictates that significant fluid flow vertically through shales, a direction of effective zero permeability, is not possible. There is no evidence of such flow, and there would be if it were occurring. Such flow would result in much higher surface HC concentrations than those that are observed and would also result in significant concentrations of  $C_6+$  HCS. There is no question that significant flow of deep-basin compaction waters occurs up faults and fractures in sedimentary basins, and as discussed below, HCS in aqueous solution in these waters do create surface anomalies. However, such anomalies are not from HC microseepage and are not necessarily an indication of, or related to, a HC deposit.

Data from Nature provide evidence of and put rigid restraints on the HC microseepage migration mechanism. The speed with which surface HC anomalies appear or disappear (a matter of weeks to months) from reservoir pressure changes thousands of feet deep testifies to rapid vertical movement of HC gases. For example, Hunt (1979, p. 431) cited a Soviet study where a few months after underground gas storage, the gas content of a water sand located 300 m (984 ft) above the storage reservoir increased ten times over its initial value. The concentration of HC-oxidizing bacteria also increased significantly in this sand. Heroy (1980, p. 8) noted that a repressurization of the Hilbig oil field, Bastrop County, Texas, during secondary recovery attempts, caused a surface HC anomaly over the field to increase in intensity. The study of Coleman and others (1977) also provided evidence of the speed of HC microseepage.

Sokolov and others (1971) provided other data which point to the migration mechanism. The Soviets, in their strong commitment to SGE, routinely carry out coring programs to depths of 6 to 20 m (19.7 to 65.6 ft) as well as exploration/research coring programs to 500 m (1,640 ft) or deeper. Quantitative analyses of soil-air and soil-sorbed HCS are carried out along the entire length of the core in these programs ("HC gas logging"). Microseeping HCS at the Earth's surface have no or only negligible amounts of  $C_6+$  HCS (Sokolov, 1970; Sokolov and others, 1971; and Philp and Crisp (1982, p. 3). However, Sokolov and others (1971) noted that in the deeper coring programs, a chromatographic effect is noticed over oil deposits, with a progressive increase in the appearance and concentration of higher molecular weight HCS with increase in depth. (See fig. 8 this paper). Kartsev and others (1959, p. 315) noted a similar feature: below the Earth's surface, with decreasing distance above oil deposits, increasing populations of bacterial species which consume only higher molecular weight HCS are observed. Horvitz (1939) and Rosaire (1940) describe similar cases down successful exploration wells.

Other evidence of the HC microseepage migration mechanism is in the sharp surface boundaries of apical or halo anomalies formed directly over HC deposits. Reports of slight lateral offsets of HC anomalies, even in cases of strong lateral ground-water flow in shallow sands, are unusual, and most investigators contend that ground-water flow does not laterally displace HC anomalies (Mac Elvain, 1963; Siegel, 1974; Horvitz, 1980; and Jones and Drozd, 1983). Thus, a strong vertical (gravitational) component must be present in the migration mechanism. Such a component can only be supplied by the buoyancy differences from monophasic HC movement through water. However, the lack of significant concentrations of  $C_6+$  HCS in HC microseepage surface anomalies dictates that a gas phase must be migrating as opposed to a crude-oil phase. The speed with which HC anomalies appear and disappear in response to reservoir pressure changes and the very low HC concentrations in these anomalies further dictate that "bulk" gas flow (effusion) cannot be occurring. Instead, a colloidal size or microbubble of HC gas must be migrating.

Mac Elvain (1969), in a well documented, elegant, and simple presentation, first proposed the formation of HC microseepage anomalies from the vertical ascent of ultra-small (colloidal size) gas bubbles. Their small size allows frictional ("clinging") effects to be overcome by Brownian motion. As Mac Elvain (1969, p. 25) noted,

"In this manner, colloidal-size gas bubbles are readily displaced upward by the surrounding water at rates up to several millimeters per second regardless of any sedimentary particles that may intrude in the way of their upward zig-zag Brownian path. Such exceedingly small bubbles can quickly ascend hundreds and even thousands of feet in a manner not available to large gas bubbles or to individual gas molecules. Large bubbles contain too large a surface area to be able to demonstrate kinetic or Brownian oscillation while individual molecules of dissolved gas possess insufficient difference of density for gravitational displacement even though they are jostled mightily by the Brownian effect."

The vertical ascent of colloidal gas bubbles to form HC-microseepage anomalies also explains the "chromatographic effect" of higher and higher concentrations of higher and higher molecular weight HCS with decreasing distance to HC deposits observed by Horvitz (1939), Rosaire (1940), Kartsev and others (1959), and Sokolov and others (1971) and the fact that HC microseeps are composed dominantly of the  $C_1$  to  $C_4$  HCS. Crude oil-methane solubility data of Price and others (1983) establish that HC gas can dissolve and transport significant amounts of higher molecular weight HCS. However, as temperature and especially pressure decrease, both the amount (fig. 1) and the molecular weight (fig. 2) of the HCS carried in the gas phase significantly decrease. Microbubbles of HC gas migrating vertically from an oil deposit will carry dissolved higher molecular weight ( $C_6+$ ) HCS. As such bubbles ascend the sediment column above the oil deposit, they encounter lower pressures and temperatures. This causes  $C_6+$  HCS to progressively exsolve from the gas phase and be left behind in the sediment column over the oil deposit in precisely the observed pattern - i.e., increasing concentrations of higher molecular weight HCS with decreasing distance from the HC deposit. A direct result of this migration mechanism is that surface anomalies from true HC microseepage in onshore sedimentary basins cannot possibly involve significant concentrations of  $C_6+$  HCS. Such HCS exsolve from vertically-migrating HC-gas microbubbles long before these bubbles reach the Earth's surface. To test this hypothesis, a natural gas atmosphere was established in a closed container over hexane at 22 to 25°C and one atmosphere. After the system had equilibrated, the hexane concentration in the natural gas atmosphere was measured by gas chromatography. Within the limits of the analysis, this concentration was no different than that due only to hexane partial pressure. The latter was determined by measuring the hexane concentration in the atmosphere over hexane in another vessel containing only hexane and air without natural gas under the same conditions. The results of this experiment support earlier investigations and confirm that microseepage by migration of HC-gas microbubbles can involve only insignificant amounts of  $C_6+$  HCS at the Earth's surface. Onshore surface anomalies involving  $C_6+$  HCS are due to other migration mechanisms (effusion/macroseepage, diffusion, or vertical water transport). However, because of the high pressures generated by significant sea-water columns, offshore HC microseepage anomalies should involve  $C_6+$  HCS.

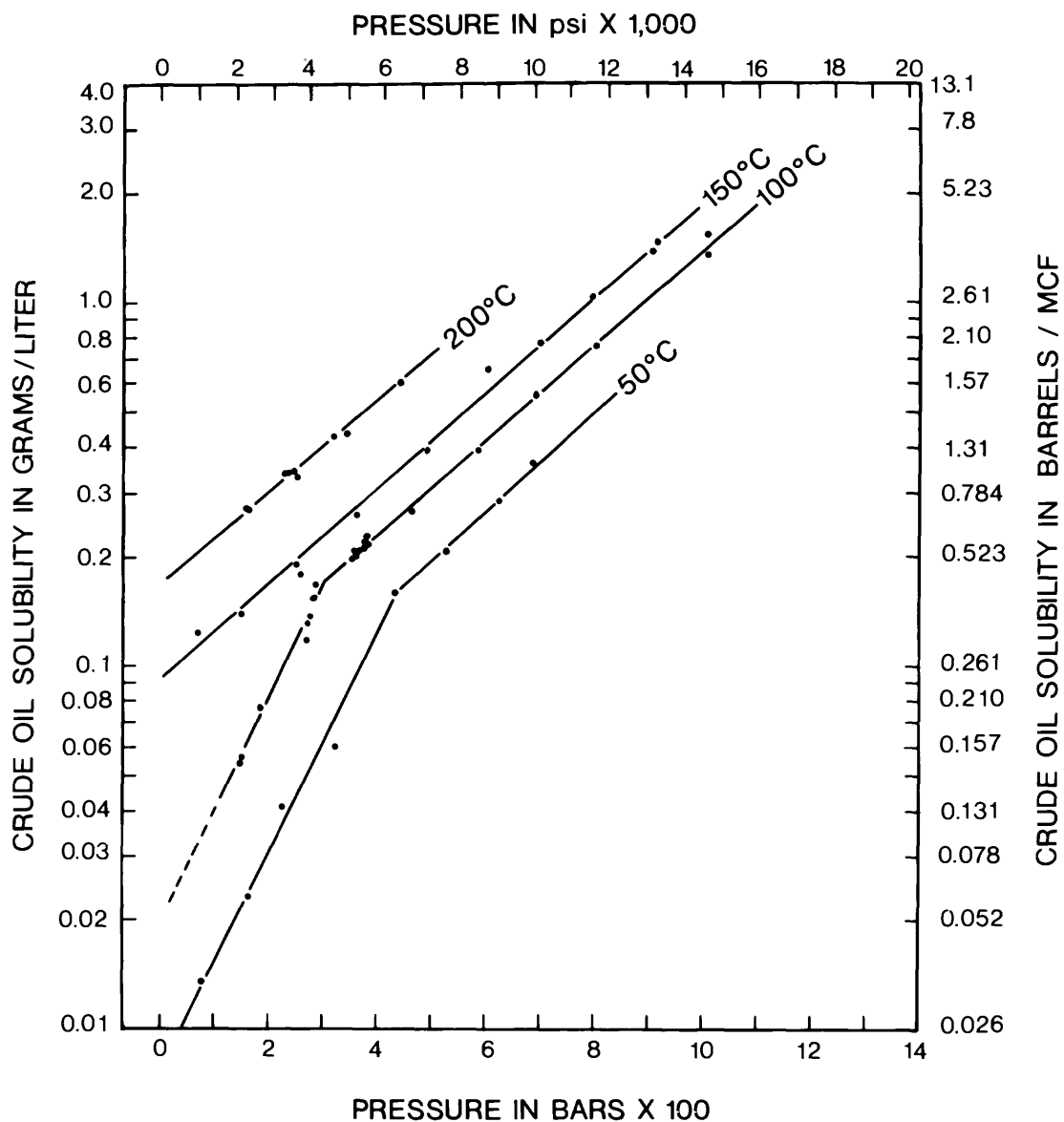


Figure 1. Solubility of a whole crude oil in methane for different isotherms as a function of pressure with water present. Note that with decreases in pressure and temperature, the carrying capacity of methane for  $C_5+$  HCS decreases, especially at lower pressures and temperatures. After Price and others (1983).

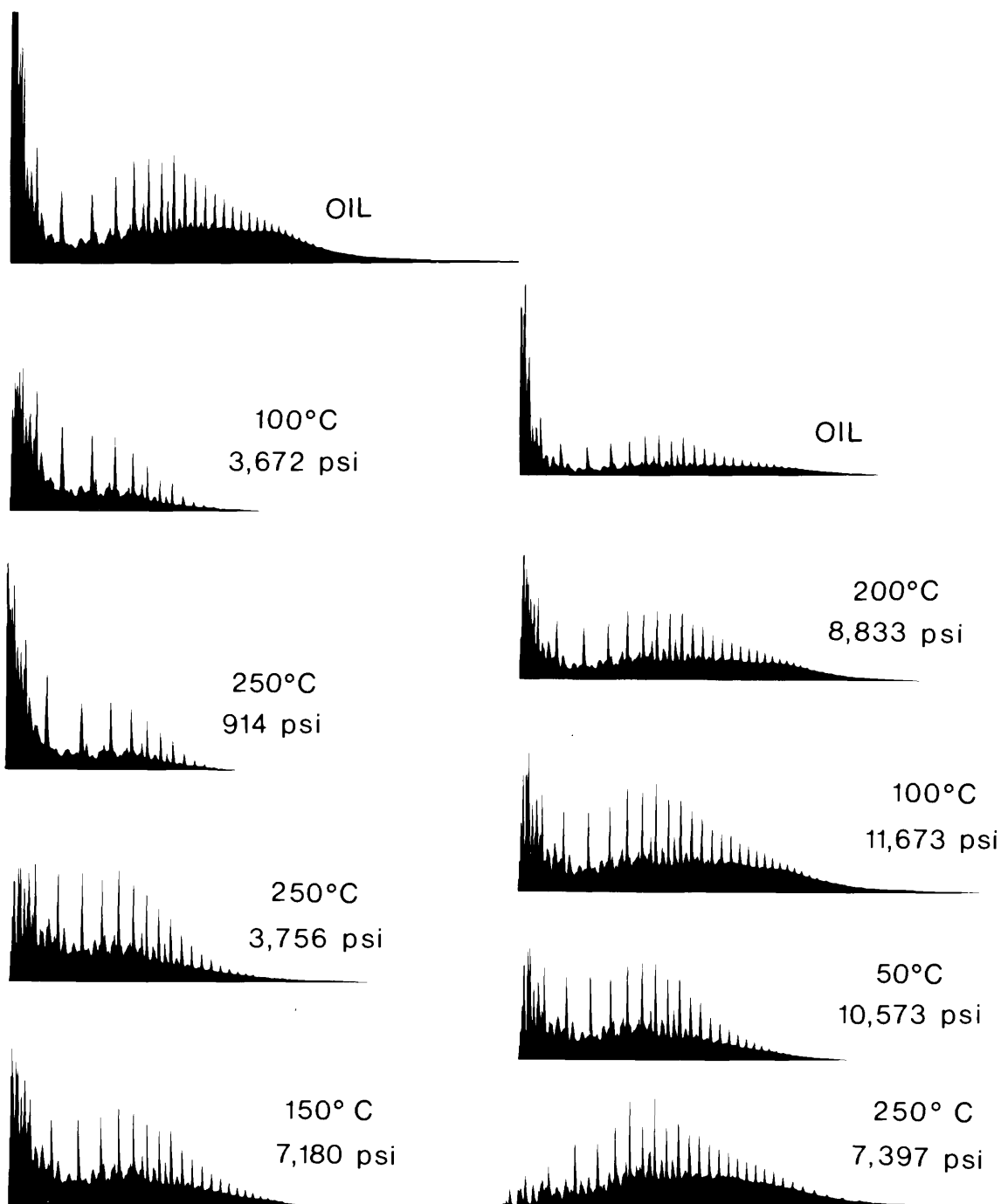


Figure 2. Gas chromatograms of solute samples of crude oil showing distinct qualitative changes as a function of the pressure and temperature conditions at which the system was equilibrated. The arrow over each chromatogram designates the  $C_{15}$  n-paraffin. Note that with decreasing pressure and (or) temperature, the molecular weight of the dissolved oil also decreases. After Price and others (1983).

An unanswered question with any proposed migration mechanism for HC microseepage is the ascent of HC gases through thick shale sections with near zero vertical permeability. All shales do have some degree of lateral permeability. However, in shales which have undergone even moderate lithification and compaction, 10 percent to 90 percent of the shale-pore throats are reduced to sizes too small for the larger complex molecules of petroleum to fit through (Momper (1978, p. B-38). Thus, migration of gas microbubbles through shales appears to be difficult laterally and impossible vertically. Migration of single C<sub>1</sub> to C<sub>5</sub> HC molecules is possible laterally, but not vertically, through a shale.

Some investigators, including Hoffman (1939), Fash (1940, p. 1446-1447, in Rosaire, and others 1940), Horvitz (1950), Davidson (1963), and Duchscherer (1981A) have dismissed the problem of zero vertical shale permeability with the observation that diffusion of noble gases and hydrogen has been documented through the atomic lattice of metals and glass (T'sai and Hogness, 1932; Urry, 1932; Alty, 1933; Burton and others, 1933; Barrer, 1934; Braaten and Clark, 1935; Taylor and Rast, 1938; and Weyl and Pincus, 1938). This allows the conclusion that nothing is truly impermeable and therefore HC gases can vertically pass through shales, which certainly have more permeability, even in the vertical direction, than glass and (or) metal. Duchscherer (1981A, p. 203) has even called for the diffusion of HC gases through the crystal lattices of minerals. There is a flaw in the above reasoning. The molecular diameters of hydrogen and the noble gases used in the above experiments are much smaller than that of the HC gases, and I am not aware of any documentation of HC gases diffusing through metals, glass, mineral lattices, or vertically through shale. The relatively large size of the C<sub>1</sub> to C<sub>5</sub> HC molecules would prevent such diffusion. As Dickey and Hunt (1972, p. 159) noted, "It has been shown repeatedly that hydrocarbons do not diffuse upward from an oil accumulation through shale in measurable amounts."

The very existence of surface HC anomalies and the speed with which these anomalies appear and disappear indicates that whatever the migration mechanism, it must take place through a pervasive microfracture system above HC deposits. Published (Price and others, 1984, p. 113-114, 121) and unpublished research I have carried out suggest that when hot oil moves through cooler sediments along a major secondary migration route or into a trap, the oil will leave a distinct thermal imprint in the overlying (and to some extent underlying) sediments. These thermal imprints can be observed by examining the common inorganic or organic maturation indices. Such thermal imprints have been observed in the Williston, Powder River, Denver, and Anadarko basins. The heat necessary for such imprints would also cause microfracturing in sediments above either major oil deposits or crude oil secondary migration routes. It is also possible (although I have no evidence of this) that all lithified sedimentary rocks have a pervasive microfracture system emplaced in them simply from regional tectonism or "Earth stress."

Meakin (1971, p. 128), discussing the migration mechanism of HC microseepage, noted,

"Unfortunately, research on the migration of HC gases appears to be limited to the USSR -----Stklyanin and others., (1968), in a detailed paper on the conditions, parameters, and means for the ascending migration of natural gas, determined vertical microfractures to be the main avenue of hydrocarbon migration in the Voskresenski petroleum field."

In my opinion, the ascent of microbubbles of natural gas through microfracture systems above HC deposits is the principal migration mechanism responsible for C<sub>1</sub> to C<sub>5</sub> HC microseepage and the resulting surface HC anomalies. It is the only proposed mechanism in agreement with observed data. However, the existence of such microfracture systems clearly has not yet been demonstrated.

#### BACTERIAL INFLUENCE

##### Bacteria

The one element of HC microseepage most overlooked in consideration of the importance of the role it plays is the interaction of bacteria with vertically migrating HCS. This interaction, by this paper, not only accounts for the fundamental basis of most SGE methods, but also explains many of the mysteries of HC microseepage including: the celebrated "halo" anomalies, "disappearing anomalies", chimneys, radiation lows, iron/manganese anomalies, paraffin dirt, and much more. Yet it is the one element which largely has been ignored in Western investigations and thought patterns concerning HC microseepage. Davis (1967, p. 117) expressed a degree of amazement for the disregard given to bacterial processes by Western investigators,

"Microbial activity in soils, and the effect it might have upon hydrocarbon gases or their "oxidized or polymerized products" was not discussed by Rosaire (1939) or his associate, Horvitz (1939). Rosaire did allude to the microbial production of methane in soils and to the biological formation of ethylene, as well. Ethane, propane and butane in soils were particularly significant because they were not known to be produced ordinarily by biological means (Horvitz, 1939; Rosaire 1939).-----In general, workers active in the field of gas surveying including McDermott (1939) and Rosaire and others. (1940) did not discuss microbial activity as a possible factor affecting gas surveys or other geochemical investigations from the standpoint of modifying or destroying the index hydrocarbons."

Kartsev and others (1959, p. 302), discussing the oxidation of microseeping HCS by bacteria, noted,

"The actual magnitude of processes of oxidation of hydrocarbon gases now taking place and their practical significance in oil and gas prospecting were not immediately apparent. It must be noted that even today these phenomena are not adequately studied."

Kartsev and others (1959, p. 306-315) discussed the various forms of bacteria (and related organisms) known to oxidize HCS. All fall under the broad classification of heterotrophic organisms, or those which subsist mainly on preformed organic matter. There are three broad types of bacteria: aerobic, facultative anaerobic, and obligate anaerobic. Aerobic bacteria

depend on the presence of free oxygen for their life processes. Facultative anaerobes can exist either in the presence or absence of oxygen. Obligate anaerobes cannot tolerate even the lowest concentrations of free oxygen. In addition to the many types of aerobic bacteria which oxidize HCS, important anaerobes also exist (denitrifying bacteria and especially sulfate reducing bacteria). All bacteria produce carbon dioxide and organic acids from HC oxidation. In addition, the sulfate reducers produce hydrogen sulphide and the denitrifiers produce free nitrogen and nitrous oxide. As Davis (1956, p. 1444) noted, not only bacteria, but also fungi and actinomycetes readily oxidize HCS in soils. McKenna and Kallio (1965, p. 183) discussing microbes capable of HC oxidation noted,

"Codification of the numerous microbial forms capable of degrading or assimilating hydrocarbons has not been attempted on several grounds. Many reports carry descriptions of new isolates that are, to be kind, meager. Bacteria, yeasts, and fungi possessing the capability are legion, new members of the group are continually being found, and such a list would be relegated to senicide before it appeared in these pages."

Davis (1967, p. 228) discussed the characteristics of actinomycetes, which have traits of both bacteria and fungi. These microbes: 1) heavily populate soils to depths greater than three feet, 2) have remarkable oxidative versatility, 3) can readily adapt to the consumption of HCS, and 4) are spore formers. Many microbes have remarkable adaptive ability.

At the Earth's surface and into the soil layer, the main microbial activity is carried out by aerobic bacteria, fungi, and actinomycetes. However, other bacteria are active over a staggering range of conditions. The basic requirements for bacterial activity are moisture, nutrients, some form of oxygen whether free or reduced, and a food source (Davis, 1967). Zobell (1946, p. 3, 7) noted that a nitrogen source is also required, and that dispersion of HCS (as would be present in a microseepage situation) greatly promotes bacterial activity.

"By dispersing hydrocarbons adsorbed on the surfaces of inert solids, the microbial attack of nearly all kinds of hydrocarbons tested is greatly increased. Certain hydrocarbons which seemed to be invulnerable to microbial attack were quite rapidly decomposed when dispersed throughout the medium on the surfaces of inert solids." (Zobell, 1946, p. 9-10).

Davis (1967, p. 121) noted that although the ordinary view is that soil microbial activity is curtailed in the winter months due to low temperature, Samtsevich (1955) found that soil microbial activity did not slow down at temperatures above 0°C with sufficient soil moisture. Kartsev and others (1959, p. 305) noted, "The metabolism of microorganisms can proceed in a relatively wide range of temperatures between a few degrees below zero and 85-90°C above zero." Oxidation of HCS at the Earth's surface apparently is controlled much more by soil moisture than by soil temperature, as low soil moisture contents can significantly reduce, or even eliminate, soil microbial activity (Soli, 1954, p. 2557; Kartsev and others, 1959, p. 319; and Davis, 1967, p. 121).



Bacterial oxidation of vertically migrating HCS, and bacterial activity in general, is most pronounced at the soil surface layer (Kartsev, 1959, p. 303; Sokolov and others, 1959, p. 620). Zobell (1946, p. 23-25) gave detailed documentation of the universal occurrence of HC-oxidizing bacteria under various surface conditions, including surface soils. "Söhngen (1913) found from 50,000 to 200,000 paraffin-oxidizing bacteria per gram of garden soil and up to 3,000 per ml of ditch water. A marked increase in the abundance of microorganisms in soil treated with paraffin was observed by Jensen (1931)----", (Zobell, 1946, p. 24). Both Zobell (1946) and Davis (1967) have noted that an introduction of HCS into almost any environment invariably leads to pronounced bacterial response. For example, Haas and others (1941) found a bacterial population of 49,000,000 bacteria per ml of crude oil-soaked soil in a Texas crude oil tank battery. Zobell (1946, p. 25) noted,

"There is ample evidence from field and laboratory observations that crude oil is attacked by soil microorganisms. The rapid disappearance of oil from waterways, from soil around refineries, leaking pipe-lines or oil wells, and from polluted beaches is believed to be due largely to the activity of hydrocarbon-oxidizing microorganisms."

Zobell (1946, p. 33) also discussed marked bacterial responses around leaking natural gas lines. Although bacterial activity is most pronounced in surface soils, it can occur at all depths above a leaking HC deposit. Kartsev and others (1959, p. 302-305) have noted that different HC-oxidizing bacteria are found at all depths in the sediment column above HC deposits, and in the edge waters of oil deposits. For example, Telegina and others (1963) found HC-oxidizing bacteria associated with an oil field at a depth of 2,680 m (8,793 ft) and Rybakova (1957) isolated denitrifying and sulfate-reducing bacteria from crude oils at 4,200 m (13,780 ft) in the Apsheron Peninsula.

Crude oil degradation by bacterial attack is an almost universally documented process which has resulted in the loss of huge volumes of crude oil (Davis, 1967; Winters and Williams, 1969; Evans and others, 1971; Bailey and others, 1973; Deroo and others, 1974; Connan and others, 1975; Phillipi, 1977; Tissot and Welte, 1978; Hunt, 1979; and Price, 1980).

As Kartsev and others (1959, p. 305) noted,

"Owing to their small dimensions, microbes easily penetrate the finest cracks, pores, and fissures, and are carried for great distances by dust particles. Because of their small dimensions, microbes have an enormous surface of contact with the surrounding medium. Therefore, encounters of microbes with various molecules occur quite frequently, even when the latter are very highly dispersed in the medium. This permits a number of microorganisms easily to utilize gaseous substances as a source of nourishment."

Thus, bacteria would likely permeate microfracture networks above HC deposits, oxidizing HCS migrating towards the Earth's surface. Some types of bacteria form spores enabling them to "hibernate" at the onset of unfavorable growth conditions. Kartsev and others (1959, p. 308) noted that "spored" and active bacteria are almost ubiquitous in sediments at considerable depths, and also "----- there can be no doubt that the various forms of microorganisms found

in deep-seated sedimentary layers of the earth's crust subsist in these layers for long geological periods." Zobell (1946, p. 4) also noted that bacteria can be recovered from ancient sediments and stimulated to growth. The grand result of all this is a series of environmental niches from the soil layer to HC deposits where different microbial forms, all of which utilize HCS as a food source, may exist.

The effects of microbial oxidation of vertically migrating HCS are staggering in relation to SGE methods. The most obvious result of such oxidation is a decrease in the concentration of: soil-air HCS, HCS dissolved in sediment pore waters, and soil-sorbed HCS, especially in the surface or near surface soil layers where the most intense microbial activity takes place. Kartsev and others (1959, p. 303) appropriately referred to a "biological filter" through which microseeping (or any vertically migrating) HCS must pass to establish a surface anomaly or signal. As those authors noted, quantification of this signal may take any one of three measurement approaches, alone or in any combination: (1) the intensity of bacterial activity for bacteria specific to  $C_2+$  HCS (microbial prospecting), (2) the concentration of soil-air HCS, or (3) the concentration of soil-sorbed HCS. All three analyses simultaneously carried out in Soviet studies have shown that unless HC microseepage is intense, microbial anomalies will not correspond to soil-sorbed or soil-air HC anomalies (Kartsev and others, 1959, p. 334, 338, 340). In other words, in areas where intense bacterial activity can occur, HC microseepage anomalies cannot be established by soil-sorbed or soil-air HC analysis even in areas of significant HC microseepage. Kartsev and others (1959, p. 319), discussing surface microbial activity, noted, "As a result of this, hydrocarbon gases migrating from the depths may be completely oxidized in the presence of a sufficiently developed bacterial filter." Davis (1967, p. 118) noted,

"The utilization of gaseous hydrocarbons in soils is obviously an important factor to consider with respect to soil-gas surveys and this activity becomes all the more important when the concentration of gases being analyzed is in the order of parts per billion or a few parts per million of the interstitial soil gas (Sokolov, 1936; Horvitz, 1939; McDermott, 1939). The question might arise as to why there should be hydrocarbon gases detectable in soils particularly since hydrocarbon-oxidizing microorganisms are so prevalent."

Davis (1967, p. 119) described experiments carried out in glass tubes wherein 50-90 ppm of ethane at low flow rates was passed through soil containing bacteria and actinomycetes and no ethane could be detected in the effluent gas at a sensitivity limit of 5 ppb. Zobell (1946, p. 37) noted,

"Nearly any method of prospecting by chemical assay or "soil analysis" which ignores the effect of bacteria on the hydrocarbon content or other properties of soil can be expected to give anomalous results under certain conditions. Hydrocarbons may be decomposed or altered by microorganisms in the soil almost as fast as the hydrocarbons enter the biosphere from subterranean deposits. The rapidity with which hydrocarbons are decomposed in soil may vary seasonally with the waste content of the soil, its oxygen content, abundance of organic matter, nitrogen content, temperature, growth phase of the organisms and other factors which

influence the abundance, kinds and activity of microorganisms in soil."

Surface bacterial activity thus not only has the capability to obliterate a HC microseepage anomaly as measured by analysis for soil-air or soil-sorbed HCS (Zobell, 1946, p. 37; Kartsev and others, 1959, p. 302, 319; and Davis, 1969, p. 140, 155), but it also can cause seasonal variations in the anomaly intensity as well (Zobell, 1946, p. 37; Kartsev and others, 1959, p. 302; and Davis, 1969, p. 141, 154). Figure 3 shows soil-sorbed HC gas concentration as a function of time for the Krasnodar region in the Soviet Union. In this region, times which correspond to low HC concentrations are times of heavy rains during which maximum microbial activity would take place. During the dry summer months microbial activity decreases and HC concentrations increase.

Surface microbial activity is responsible for paraffin dirt, a waxy-appearing soil associated with gas seepages and thought to be a powerful indicator of HC deposits. As W. E. Pratt in Milner (1925, p. 82) noted, "I feel it to be established that 'paraffin Earth' is found in soils in which aluminum- and iron-bearing clays are present in large proportion in the vicinity of seepages of gas." Also see Barton's (1927) discussion. Although paraffin dirt was most readily recognized in the onshore Gulf Coast province, it also was reported in other areas with tropical to temperate climates including Colombia, Cuba, Roumania, and Burma (Milner, 1925). Davis (1952, 1967) carried out the most definitive published research on paraffin dirt, both in the laboratory and on natural occurrences. In Nature, paraffin dirt is limited to areas of gas micro- or macro-seepages (fig. 4), and has high contents of nitrogen and organic carbon and low contents of lipids and saturated HCS. Radioactive carbon analysis of the organic matter in a paraffin-dirt bed (Davis, 1967, p. 102) showed that only 15 percent of the carbon was "modern" carbon -14; in other words, the carbon of the paraffin-dirt bed was dominantly composed of "old" carbon (>5,700 years) derived from microseeping HCS. Microscopic examination of the organic matter in paraffin dirt revealed heavy concentrations of cell walls of fungi, yeasts, actinomycetes, and bacteria. Davis (1967) was able to manufacture a laboratory paraffin dirt indistinguishable from natural samples by encouraging bacterial growth by passing HC gas through moist soils. He concluded that paraffin dirt was an accumulation of dead bodies and cell walls from microbial activity on microseeping natural gas, a view in total agreement with that of Kartsev and others (1959, p. 215),

"Paraffin dirt" occurs widely in the region of the Gulf Coast. It occurs in the top layer of the soil as yellow-brown, amorphous masses consisting mainly of carbohydrates. (Its composition does not correspond at all to its name.) There is no doubt that this substance is formed from hydrocarbon gases. It is found only where there are gas seeps, and the size of the dirt deposits is directly proportional to the size of the seeps.

Consequently, the simplest hydrocarbon gases may be converted to complex organic substances. This is apparently the result of bacterial activity."

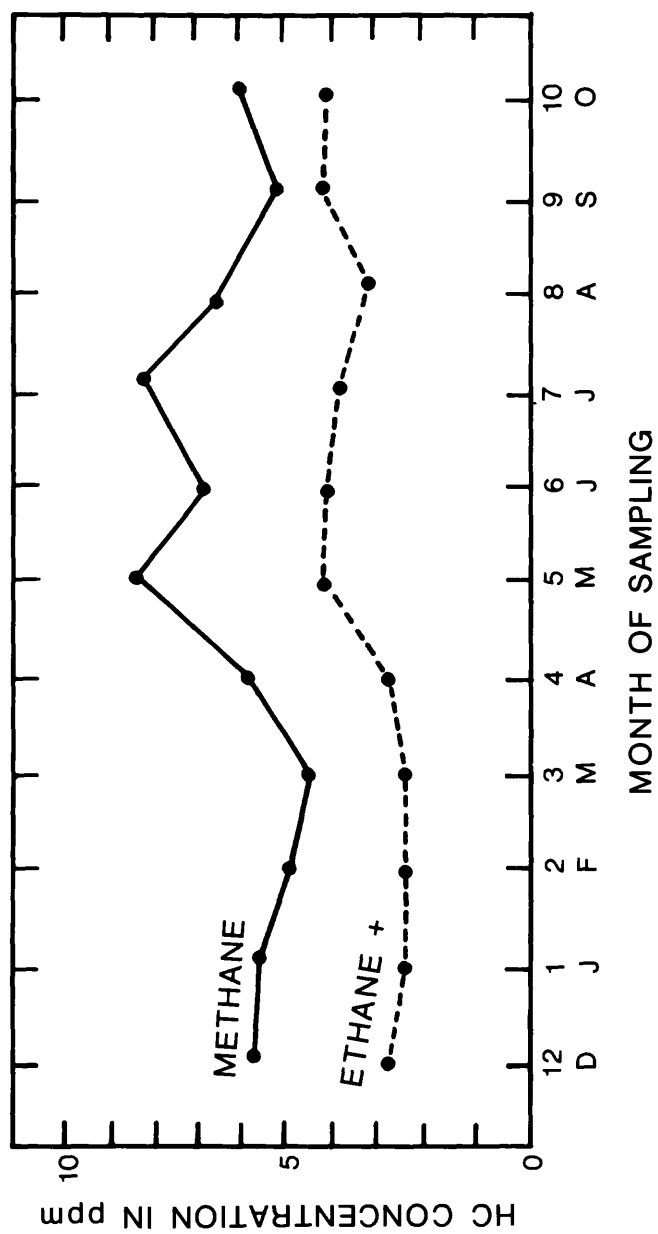


Figure 3. Soil-sorbed HC concentrations for the Krasnodar region, Soviet Union. After Kartsev and others (1959, p. 84).

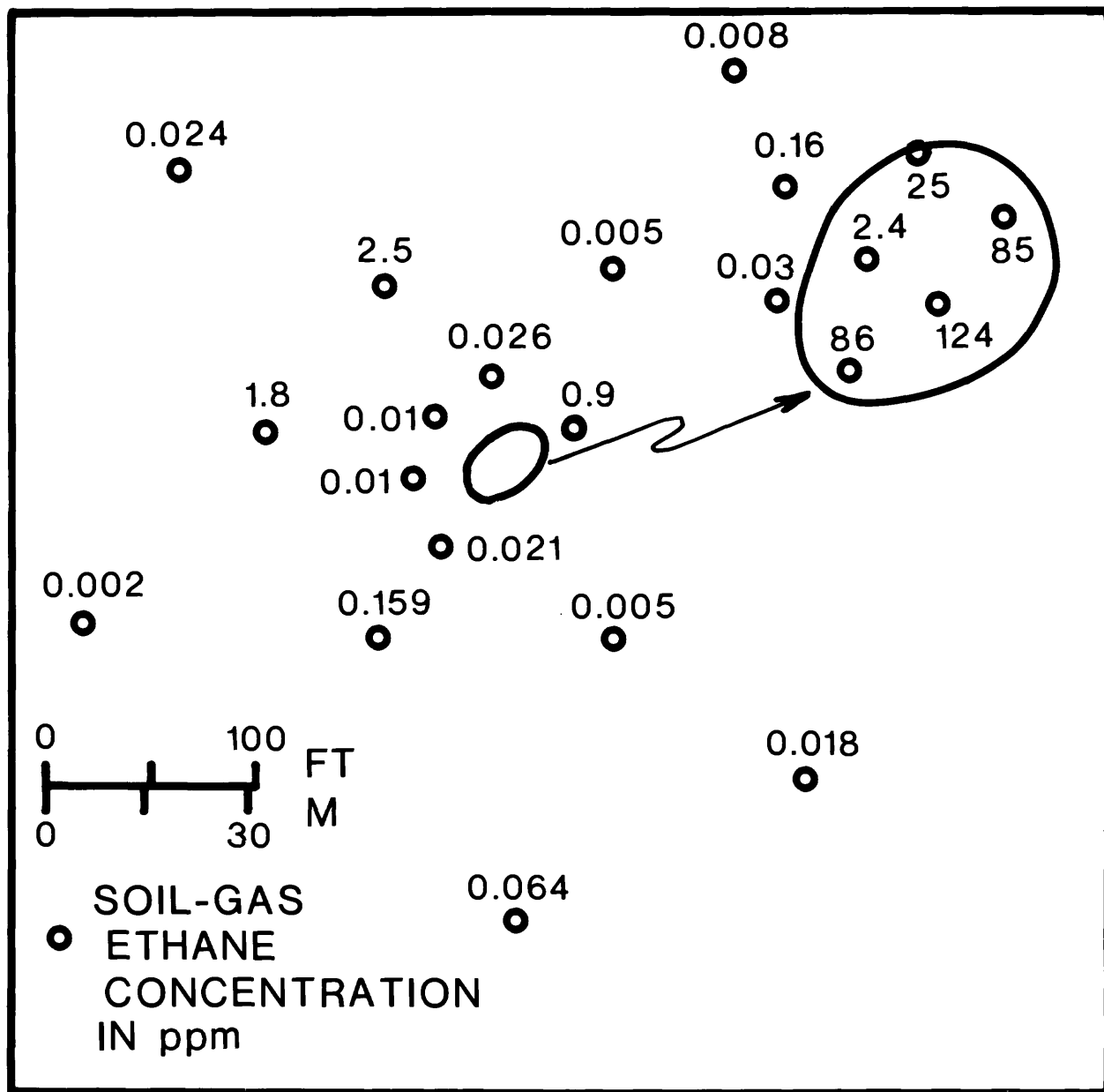


Figure 4. Example of a paraffin dirt bed associated with HC microseepage in Sabine County, Texas. Solid outline shows limits of paraffin dirt bed. Numbers are ethane soil-air concentrations in ppm. Note the association of higher ethane soil-air concentrations with the limits of the paraffin dirt bed. After Davis (1967, p. 102).

Apparently the necessary requirements for the formation of paraffin dirt are an adequate rate of gas microseepage to support an abundant microbial population, and adequate year-around soil moisture. Thus, paraffin dirt could form in any area with a temperate to tropical climate without a defined dry season. The fact that paraffin dirt originates from microbial activity on microseeping HCS has an interesting ramification. Probably because it is so inappropriately named, in the past "paraffin dirt" was sometimes associated with petroleum macroseepage, even though it is an indirect consequence of HC microseepage. Thus, oil exploration on the basis of paraffin dirt is (or was) an IGD technique, a technique responsible for the discovery of vast amounts of oil in the Gulf Coast province alone. Thus, solely on the basis of paraffin dirt, SGE has resulted in the discovery of much more oil than given credit for in the past.

### Chimneys

"Chimneys" are rock columns above HC deposits thought to be modified by vertically migrating HCS, or by some other unknown association due to a HC deposit. Because of these modifications, the rocks above HC deposits are thought to take on different lithological properties compared to surrounding country rocks off structure at equivalent depths. Hence a "chimney" of altered rock is created above a HC deposit. These lithological differences can be gauged by different physical/chemical measurements. Although Pirson (1964C) apparently was the first to use the term "chimney", the concept can be traced further back. Pirson (1960, 1963, 1964A,B,C,D, 1969) developed his hypothesis of chimneys based on radiation lows observed over oil fields (fig. 5) which he sometimes could detect as much as 7,000 ft (2.13 km) above a deposit (Sunniland, Florida, Pirson, 1964C). The effect was also found in surface sediments (Pirson, 1964D). Pirson (1963, 1964C, p. 71) found that gamma-ray log decreases of up to 50 percent (compared to gamma-ray readings in the same shale off the deposit) were best developed over HC deposits in organic-rich black shales (such as the Lower Mississippian-Upper Devonian Woodford Shale and equivalents). Pirson (1969, p. 165) documented the effect in over 30 oil fields in France, Canada, and the United States, and developed an elaborate (and in my opinion incorrect) scenario to explain his observations. This scenario (Pirson, 1969, p. 161-164) is based on assumed geologically-long continued flow of heavily-mineralized deep-basinal compaction waters vertically through (impermeable) sediments to the Earth's surface. Because of temperature and pressure decreases suffered by the upward movement of such waters, minerals were assumed to precipitate in the sediments through which the waters passed. During the earliest stages of such flow, the waters carried "solubilizers" (Baker, 1959) which caused the solution and transport of crude oil to traps where the solubilizers and crude oil were filtered from the waters, resulting in an oil deposit. Eventually the supply of "solubilizers" from deep-basin sediments was used up, which terminated oil migration and accumulation. However, the flow of mineralized waters was postulated to continue, such that mineralization of sediments along the path of the migrating water continued. Pirson (1969) recognized that such water flow would have to be diverted around oil fields. As the sediments above oil fields would no longer be subjected to mineralization, these sediments would eventually become less mineralized than the country rocks off structure at equivalent depths. A consequence of this would be that the sediments over HC deposits would have lower concentrations of the elements causing gamma-ray radiation (Pirson, 1969).

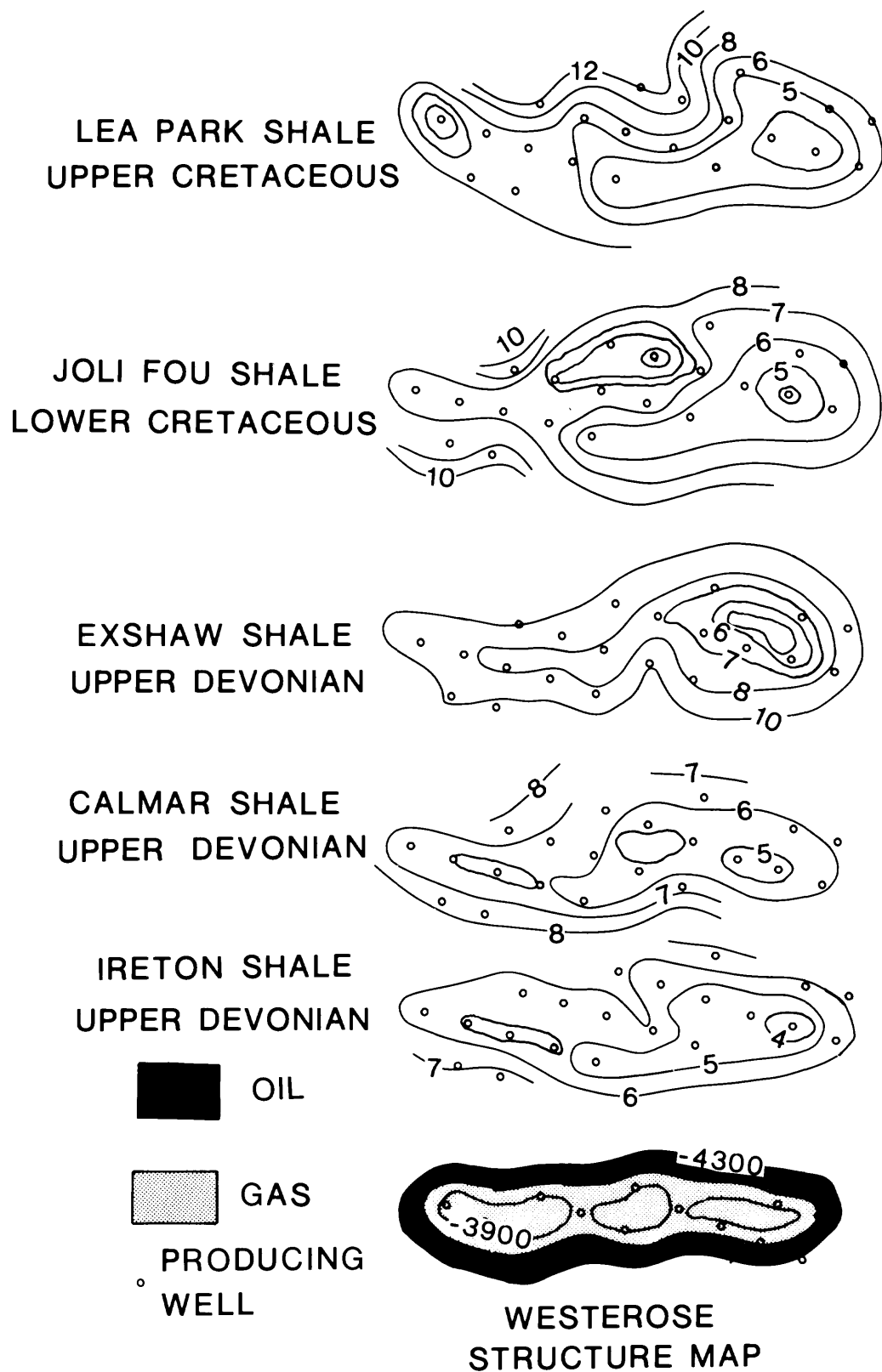


Figure 5. Radioactivity in various shales overlying the Westeros oil field, Alberta Canada, which produces from the Upper Devonian Leduc Formation. Radioactivity measurements as determined from well logs are given in "micro-grams Radium eq./ton units"--after Pirson (1969, p. 176).

Pirson's (1969) theory can be dismissed on four points: (1) The black organic-rich shales which Pirson used (his "optimum significant stratigraphic level" -OSSL) have far above average concentrations of radioactive elements from depositional conditions. Such shales clearly do not become mineralized with radioactive elements during post-depositional burial. (2) Baker's (1959) solubization hypothesis of primary petroleum migration has been shown to be impossible (Price, 1976; and McAuliffe, 1978). (3) The vertical flow of water through impermeable sediments is hydrodynamically impossible. (4) There is no evidence of such vertical water flow, and if it were occurring it would be quite evident. (The documented flow of deep-basinal compaction waters up faults and fractures is not evidence supporting Pirson's (1969) concept.)

Pirson (1969) rejected Alekseyev's (1959) hypothesis that radiation lows over oil fields were due to a leaching of radioactive elements from shales (discussed below). Although I dispute Pirson's (1969) postulated cause of chimneys of radiation lows over HC deposits, I certainly do not dispute his observations that they sometimes exist. Such radiation lows (including surface radiation lows) have also been reported by Lundberg (1952, 1956), Merritt (1952), Alparone (1963), Mac Elvain (1963), Tilloy and Monchaux (1965), Alekseyev and Gottikh (1966), Kilmar (1983), and Curray (1984). Armstrong and Heemstra (1973) provided a literature review of the subject. On the other hand, a straight forward, one-to-one correlation of radiation lows over buried HC deposits can hardly be taken as a given.

Heemstra and others, (1979) in a detailed radiation survey over the Sutherland field, Greenwood County, Kansas, found no correlation between HC production and surface radiometry. They did, however, find a correlation between surface radiometry and topography, with low radiation readings corresponding to bedrock outcrops along ridges and in depressions. High radiation readings were recorded in areas with deep rich topsoil. As discussed below, potassium-40 in clays is responsible for most soil radiation. If the outcropping rocks at Sutherland were carbonates or sandstones, radiation lows over bedrock would be expected. Heemstra and others(1979) encountered other problems in this, and other, radiation surveys they carried out. They found that truck radiation surveys did not correlate to airborne radiation surveys run over the same area. They also found that repetitive truck radiation measurements at the same locality showed large enough diurnal variations to be mistaken for anomalies. Heemstra and others(1979, p. 80) concluded,

"Statements of fact in the literature indicate a relationship exists between petroleum at depth and observable gamma radiation anomalies at the surface and that this relationship can be correlated to light hydrocarbons, gas anomalies at the surface. From studies on the field data made thus far, however, neither of these stated facts can be substantiated. Although the presence of anomalies in the level of natural radiation and hydrocarbon gases at the Earth's surface was measured and observed in this study, their uniqueness to an oil reservoir has not been proven."



Horvitz (1950, p. 939) alluded to the existence of chimneys before Pirson's research, "During the migration of hydrocarbon gases from a petroleum deposit, the formations penetrated are believed to be modified chemically." However, Rosaire (1938) first described and documented chimneys, although he did not actually use the term. Rosaire (1938) noted that in processing geophysical data, a tacit assumption was made that lateral-lithologic variations of stratigraphically-equivalent rocks were minimal. However, he believed that sediments over some oil fields had abnormally-high velocities because these sediments were more highly indurated than off-structure sediments. Rosaire (1938, p. 101) believed that this induration was due to a greater degree of cementation or mineralization in sediments over HC deposits (a direct contradiction to Pirson's (1969) incorrect hypothesis), and noted that induration of sediments over oil fields were apparent to the drillers of the early 1900's, a situation they described as "dome digging". Rosaire (1938) pointed out that developmental drilling of some Gulf Coast oil fields showed that geophysical predictions of the structural relief of these fields were greatly exaggerated, and that the fields were actually in lower relief structures than originally thought (some were in stratigraphic traps). There is no manner of gauging the amount of HCS discovered in low-relief structures and stratigraphic traps because of misinterpretation of geophysical data due to the lateral-lithologic inhomogeneity of equivalent-stratigraphic units (chimneys) created by bacterial oxidation of vertically migrating HCS (discussed below). However, whatever volume of reserves were discovered because of this feature, then like paraffin dirt, an IGD technique would have been responsible for the discovery of a much greater volume of HC reserves than previously realized.

The creation of mineralized chimneys over HC deposits has largely been attributed to HCS being "chemically reduced compounds". By this thinking, as HCS migrate into or through an environment, they "oxidize" to create a reducing environment, which leads to substantial change in the mineralogy of the host sediments (Lundberg, 1952; Donovan, 1974, p. 432; Pirson, 1969, p. 179; Donovan and Dalziel, 1977, p. 1; Heemstra and others, 1979, p. 2; Duchscherer, 1980, p. 194, 1981B; and Sivenas and Beales, 1984). However, this is an erroneous hypothesis. HCS are kinetically stable under all microseepage conditions, and in microbially sterile environments, HCS absolutely will show no tendency to oxidation. However, Nature is not microbially sterile and many microbial forms oxidize HCS in utilizing them as a food source in HC reservoirs, in the sediment columns over reservoirs through which vertically migrating HCS pass, and in soil layers. Microbial HC oxidation consumes either free oxygen ( $O_2$ ) or chemically complexed oxygen ( $SO_4^{2-}$  or  $NO_3^{-2}$  for example). In any case, the redox potential (eH) of the system is significantly affected. A, or the, main product of microbial HC oxidation is  $CO_2$ , which associates with water to form carbonate-biocarbonate species which drastically change the pH of the system. In addition to  $CO_2$ , sulfate-reducing bacteria also produce  $H_2S$ , which also significantly affects the pH of the system. Zobell (1946, p. 12) noted that bacterial activity also produces organic acids. Such pH/eH changes result in totally new mineral-stability fields. Some minerals become unstable and are dissolved and mobilized, and others are precipitated from solution. The rock column in which these acidic species are generated acts as a buffer to neutralize the acidic solutions. Such a neutralization (pH increase) takes place by the

solution of different mineral species. The most apparent mineralogical change from the significant increase in the (neutralized)  $\text{CO}_2$  concentration is precipitation of various carbonates, particularly calcite. Davis (1967, p. 161) made a most relevant point concerning oxidation of crude oil by sulfate-reducing bacteria,

"There is evidence that the activity of sulfate-reducing bacteria in subsurface waters can affect the physical characteristics of the formation (Ashirov and Sazonova, 1962). Lithological examination of certain oil-bearing carbonate reservoirs have revealed that rock in the areas of oil-water contact has been made impermeable due to deposition of calcite (crystalline calcium carbonate). In at least one of these oil accumulations of the Ural-Volga area the pressure of the oil deposit dropped 900 lb./sq. inch relative to the water pressure without water entering the wells, the water being sealed off. Ashirov and Sazonova experimentally showed that sulfate-reducing bacteria in the presence of petroleum can reduce calcium sulfate to sulfide with deposition of calcium carbonate crystals in the cultures. The prismatic crystals formed (particle size, 0.01 mm or less) appear to be similar to the secondary calcite in the reservoir rock. Abd-El-Malek and Rizk (1963) recently reported the development of alkalinity and precipitation of carbonate due to bacterial sulfate reduction in water-logged soils."

The most intense microbial activity takes place in surface soils. Bacterial activity at greater depths in the proposed microfracture chimney above HC deposits clearly would be greatly reduced compared to microbial activity in soil layers. However, as Davis (1967, p. 244) noted, even the lowest levels of microbial activity have a cumulative effect over geologic time. The observations (discussed above) of Kartsev and others (1959, p. 305) concerning the ability of bacteria to "-----penetrate the finest cracks, pores, and fissures-----" has relevance here.

Bacterial oxidation of vertically migrating HCS also causes precipitation of calcite (and other carbonates) in surface and near surface soils, in addition to the calcite precipitation in the sediment column above HC deposits. Kartsev and others (1959, p. 294-295) discussed "soil carbonate-siallite" surveys carried out in Russia. Such surveys are based on enrichments of calcite, silica, and alumina over leaking HC deposits (fig. 6). The high  $\text{CO}_2$  concentrations from microbial HC oxidation of vertically migrating HCS in near surface soils not only causes significant calcite precipitation, but as Kartsev and others (1959, p. 295) noted, the acidic solutions from the high  $\text{CO}_2$  concentrations also alter or decompose clays, from neutralization of these solutions, which results in increased concentrations of silica and alumina. Such clay alteration is most probably responsible for the radiation lows or halos reported over oil fields in surface sediments. Clay decomposition or alteration would liberate potassium from clays, including potassium-40, which as Pirson (1969, p. 164), Heemstra and others (1979) and Kilmar (1983) noted is by far the major contributor to soil radioactivity. In addition, other radioactive elements would be freed and mobilized from clay lattices from neutralization of carbonic acid. The shape of a radioactive anomaly would depend on the degree of mobilization of the

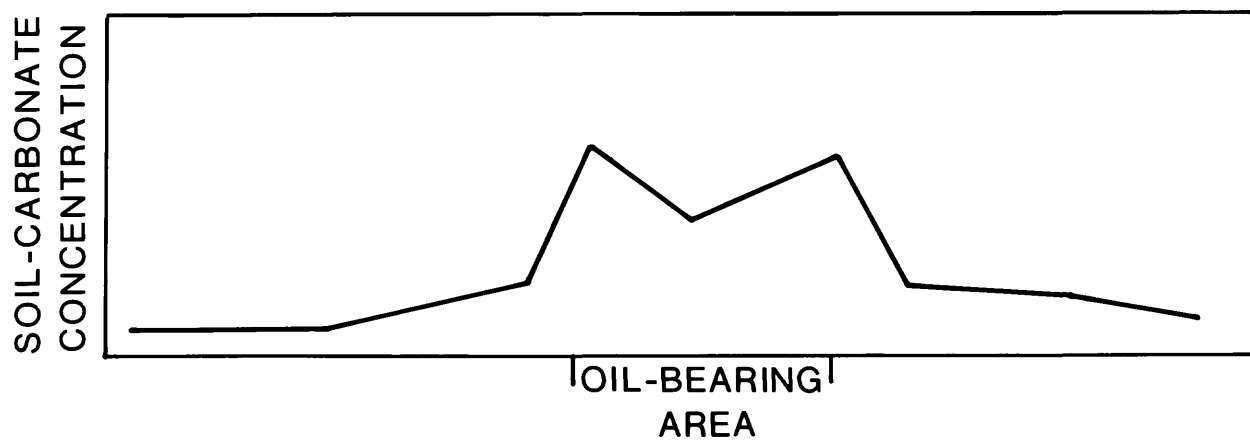


Figure 6. Soil-carbonate traverse across an oil field. After Kartsev and others (1959, p. 295).

radioactive elements. If these elements were transported entirely from the system, a "hole" or low in the normal background readings would result. If the elements were transported to the edges of the vertical projection of the HC deposit to the Earth's surface, where they precipitated from solution, a "halo" or "doughnut" of high values surrounding the low values over the surface projection of the HC deposit would result.

Pirson (1960, p. 95) reported that Lasky (1950) developed an IGD technique based on the "thermal alteration" of surface clay minerals from underlying HC deposits. However, Lasky (1950) gave no details of various SGE techniques he discussed. It is possible that Pirson's (1960) statement was based on personal knowledge of Lasky's clay-alteration technique. Whatever the case, it is also possible that Lasky's (1950) technique was based on changes in surface clays from the carbonic acid resulting from microbial oxidation of vertically migrating HCS.

The SGE techniques of Horvitz (1945, 1950, 1954, 1957, 1965, 1969, 1981) and Duchscherer (1980, 1981A, B, 1983) are based on significant development of "acid soluble soil salts" (mainly calcite) from CO<sub>2</sub> production from microbial oxidation of mainly microseeping HCS. Different investigators have noted a strong correlation between acid-soluble soil salts and "sorbed" HCS (Hoffman, 1939; Horvitz, 1950, 1954, 1972; Colombo, 1959; Debnam, 1969; Poll, 1975; Devine and Sears, 1975, 1977; and Philp and Crisp, 1982). Heating soil samples to liberate "sorbed" HCS, without acid treatment results in determinations of much lower HC concentrations than if the samples are treated with acid and heated (Horvitz, 1950, 1954; Colombo, 1959; and Debnam, 1969). Horvitz (1954, p. 1207-1208), discussing the results of two different soil surveys over the Hastings field, Brazoria County, Texas, one with acid treatment of samples and one with only heat treatment, noted,

"This survey indicates the importance of the acid treatment in the extraction procedure. In an earlier survey (Horvitz, 1939) of the Hastings field conducted in 1937, prior to the introduction of this improvement, values of a much lower magnitude were obtained, and although an anomaly developed a much less distinct pattern resulted. Apparently heating of samples without the acid treatment liberates only the loosely held hydrocarbons."

Horvitz (1950, 1969) passingly referred to HCS occluded rather than sorbed in the soil. From this and other evidence it is clear that the bulk of the HCS that Horvitz measures are not "sorbed" in or on the soil at all, but instead have been incorporated into calcite (and other minerals?) which have been precipitated in soils due to CO<sub>2</sub> buildup from microbial oxidation of microseeping HCS. Such HC occlusions are analogous to the fluid inclusions in ore minerals. A consequence of such HC occlusion is that soil-occluded HC analysis will be less effective in climates not conducive to near surface microbial activity with the resulting calcite precipitation and occlusion of microseeping HCS.

Duchscherer (1981A, p. 208) described his analytical technique as preheating soil samples in an oxygen atmosphere at 500°C to destroy organic matter and desorb loosely bound CO<sub>2</sub>. The samples are then heated in a nitrogen atmosphere to 600°C, which results in a pulse of CO<sub>2</sub> (which Duchscherer has termed "ΔC") being "generated" from the carbonates (mainly calcite?) formed in soil layers above oil deposits. As Duchscherer (1981A) noted, this CO<sub>2</sub> is not due to thermal decomposition of any known carbonate; and although the origin of this CO<sub>2</sub> is unknown, he noted that it is consistently found in soil carbonates above HC deposits and is an excellent indicator of HC deposits. In my opinion, Duchscherer's "ΔC" carbon dioxide may partially result from decrepitation of carbonates due to the thermal expansion of fluid inclusions or CO<sub>2</sub> otherwise occluded in soil carbonates. It is probable that low undetected concentrations of HC gases are also present in Duchscherer's "ΔC" CO<sub>2</sub>. These are the HCS that would be measured by Horvitz.

Geochemical anomalies (including soil-carbonate content, radiation lows, soil-mineral alteration, and occluded CO<sub>2</sub> in soil carbonate) caused by the interaction of abnormal amounts of CO<sub>2</sub> with near surface soils and (or) ground waters are non-specific for thermogenic HC deposits. Abnormal CO<sub>2</sub> concentrations can result from factors other than near surface microbial oxidation of microseeping HCS. Such factors could be geothermal, hydrothermal (ore mineralization), igneous, or metamorphic activity (especially the interaction of any of these with limestones or dolomites), or microseepage from a CO<sub>2</sub> deposit. In petroleum basins it is probable that nearly all such anomalies are caused by HC deposits. However, this would not be true in other geological provinces.

On the other hand, other SGE methods, resulting from calcite precipitation due to abnormal CO<sub>2</sub> concentrations in soils, are specific for HC deposits. For example, because Horvitz measures the concentrations of C<sub>2</sub> to C<sub>5</sub> HCS, his method is specific for thermogenic HC deposits. Donovan (1974) and coworkers (Donovan and Dalziel, 1977; Donovan and others, 1974, 1975, 1979A, 1981; and Henry and Donovan, 1978) studied cementation of near surface rocks (mainly sandstones) by carbonates and the development of magnetite over oil fields (Donovan and Dalziel, 1977; Donovan and others 1979A,B, 1981; Henry and Donovan, 1978; and Dalziel and Donovan, 1984). Donovan and Dalziel (1977) explained the precipitation of such carbonate cements as due to the "oxidation" of "microseeping" HCS resulting in production of CO<sub>2</sub>, which reacts with water to form the carbonate ion, which in turn causes the precipitation of various carbonate minerals. (As discussed, this is not quite the case). Anomalous C<sup>13</sup>/C<sup>12</sup> ratios in carbonate cements were (correctly) attributed to the fact that the carbon in the carbonate ions originated from vertically migrating HCS. (The carbonate cements studied by Donovan and coworkers and crude oil and thermogenic natural gas are depleted in the C<sup>13</sup> isotope, Donovan and Dalziel, 1977). The precipitation of calcite in soils, as noted above, in itself is not specific for HC deposits; however, the anomalous carbon isotope ratios which Donovan and coworkers observed in these cements are specific for HC deposits. Most of Donovan and coworker's investigations were carried out with outcropping sandstones. As Kartsev and others (1959, p. 319) noted, the possibility of microbial activity greatly increases with increase in porosity.

Donovan and Dalziel (1977, p. 1) explained anomalous distributions of iron and manganese in surface sediments over HC deposits as due to the fact that HCS (and associated  $H_2S$ ) are reduced compounds and, "The passage of hydrocarbons and associated compounds such as hydrogen sulphide through surface rocks causes a reducing environment-----." They proposed that this environment reduced iron and manganese to lower valance states, which resulted in mobilization and removal of the elements, or precipitation of magnetite or maghemite, or coprecipitation of iron and (or) manganese with calcite in carbonate cements over HC deposits. Although  $H_2S$  is generated with petroleum in source rocks, the ubiquitous association of  $H_2S$  or with crude oil is clearly due to sulfate-reducing bacteria oxidizing petroleum HCS after accumulation (Kartsev and others, 1959, p. 36, 310-311; and Davis, 1967, p. 157-194). The creation of the reducing environment called for by Donovan and Dalziel (1977) is clearly from microbial oxidation of vertically migrating HCS which depletes both free ( $O_2$ ) and complexed ( $SO_4^{-2}$ ,  $NO_3^{-2}$ , etc.) forms of oxygen. Magnetic anomalies from such reducing environments would indicate a HC deposit if the anomalies result from microbial oxidation of only microseeping HCS. However, it is probable that such anomalies can also result from microbial oxidation of vertically migrating HCS not directly related to a thermogenic HC deposit. Therefore some of these anomalies may be "false anomalies". Magnetite formation, or other iron-manganese anomalies, form the basis for a number of different electrical-geophysical exploration techniques including, but not limited to, aeromagnetic detection (Donovan and others 1974A,B) and induced polarization (Sternberg and Oehler, 1984).

#### Biogenic Methane

Such methods as carbon isotopic measurement of carbonate cements, aeromagnetic detection, induced polarization, etc. are dependent on the interaction of microbes with vertically migrating HCS, and therefore can indicate a HC deposit. However, such a HC deposit is not necessarily a thermogenic HC deposit, and therefore in a certain sense, can be a type of false anomaly. Rice and Claypool (1981), in a definitive paper, discussed the causes and constraints on the origins of biogenic methane, a byproduct of the attack of organic matter by obligate-anoerobic bacteria during shallow sediment burial and diagenesis. Although most biogenic methane is lost at the sediment-sea water interface during burial, enough is retained and later mobilized such that significant commercial accumulations can result. Such accumulations have been reported worldwide in many different petroleum basins in many different trap types (Rice, 1980; Rice and Claypool, 1981; Gautier, 1981; and Mattavelli and others, 1983), suggesting that biogenic methane accumulations can occur any place in a sedimentary basin in any trap type. The contribution of biogenic methane to the world's natural gas reserves is much greater than generally recognized. Rice and Claypool (1981, p. 23) noted, "Gas of predominantly biogenic origin has made major contributions to the world's reserves (more than 20 percent). We predict that biogenic gas will make an even greater contribution to world energy needs in the future." Rice and Claypool (1981) are probably conservative in their estimate. For example, from analyses of 90 percent of the gas fields in the Po Valley basin, Italy, Mattavelli and others (1983) concluded that 80 percent of the gas in place was biogenic, 10 percent thermogenic, and 10 percent was mixed. Mattavelli and others (1983) documented biogenic gas fields in the basin as

deep as 15,000 ft (4,500 m). Rice and Claypool (1981) estimated Soviet NW Siberian reserves alone at 372 TCF. Clearly, biogenic gas is more widespread and plays a greater energy role than generally recognized.

Biogenic methane is a very "dry" natural gas with  $C_1/C_1-C_5$  ratios always greater than 0.99 (Rice and Claypool, 1981). For example, the biogenic gas deposits of the Po Valley range from 99.40 percent to 99.97 percent  $CH_4$  (Mattavelli and others, 1983, table 1). Further, the bulk of the  $C_2+$  fraction is usually ethane. Deposits of biogenic methane, like all HC deposits, are subject to leakage, which causes problems for certain IGD methods. Rice and Claypool (1981, p. 11) noted, "In the marine-shelf environment, the deposition of discontinuous and relatively impermeable silt and sand enveloped by organic-rich mud and clay provides extremely favorable conditions for both in situ generation and entrapment of biogenic methane." Gautier (1981) described biogenic methane deposits of the northern Great Plains (United States) as occurring in such siltstone "microlenses" with good porosity (30 percent to 40 percent) but poor permeability (3 to 30 md). Because of poor interconnection of the silt lenses, the overall reservoir permeability of such deposits is less than 0.4 md. These (and other) reservoir characteristics make such accumulations next to impossible to recognize by electric log response, and fracture treatment is required for commercial production.

Microseepage from biogenic-gas accumulations results in various anomalies such as magnetic, soil carbonate (including calcite-occluded  $CO_2$ ), and radiation lows. Such anomalies would be identical to anomalies created by microseepage from a thermogenic HC deposit. Drilling such an anomaly would fail to result in a commercial oil discovery. Also, because of the poor reservoir characteristics of some biogenic methane accumulations and the need for fracture treatment for production, even the existence of the biogenic methane might be missed. "Tight" biogenic methane accumulations probably have been responsible for a number of past SGE failures. On the other hand, DGD techniques which measure  $C_2-C_5$  HCS are not subject to such a problem because of the lack of  $C_2-C_5$  HCS in biogenic methane. It is possible that false anomalies caused by biogenic methane are partly responsible for the lower success rate reported by Duchscherer (1981B) for his "first class" anomalies, 38/170 or 22 percent versus 23/39 or 59 percent for Horvitz's (1954) "first class" anomalies.

Stahl and Faber (1981) described an (offshore) Santa Barbara basin geochemical survey where 200 sediment samples were taken over a 400 km<sup>2</sup> (249 mi<sup>2</sup>) area and analyzed for sorbed methane. Isotopic analysis differentiated biogenic methane (being produced temporally) from thermogenic methane leaking from known oil fields. Thermogenic methane "anomalies" had concentrations up to 200 ppb versus biogenic methane concentrations of up to 50,000 ppb, or 250 times greater. (The limited utility of methane, without expensive and difficult isotopic analyses, as an indicator of HC deposits is clearly demonstrated by these data).

SGE techniques have significant potential as exploration tools in the search for oil in stratigraphic traps on the stable shelves of petroleum basins, especially maturely-explored basins. Unfortunately, biogenic methane deposits appear to be abundant in these same areas (Rice and Claypool, 1981;

Gautier, 1981; and Rice, 1984), and most often the deposits are in "tight" reservoirs. Explorationists using SGE methods should always be aware of the possibility of false anomalies caused by biogenic methane deposits on the normally oil-bearing stable shelves of sedimentary basins.

### Halos

Before discussing the cause of halo anomalies found with soil-occluded HC (and other) analyses, the association of the anomaly shapes found with each DGD method will be reviewed, as such associations set the limiting conditions on halo formation. Kartsev and others (1959, p. 101-106, 332-333) and Sokolov (1970) discussed the various anomaly shapes resulting from vertical migration of leaking HCS. Such shapes are: apical (focal), annular (halo), and linear. Apical or focal anomalies are high readings directly over a HC deposit and may be either continuous in the form of one large patch, or discontinuous (spotty) in the form of unconnected patches covering a given area. Halo anomalies, as discussed, have doughnut forms with a ring of high values surrounding the surface trace of a HC deposit and lower central and background values. Halos are either continuous, but apparently more often are discontinuous. Halo and apical anomalies apparently result mainly from HC microseepage. Linear anomalies are found over surface traces of faults, fractures, of faulted-fractured, structurally-intense anticlines. These anomalies involve  $C_6+$  HCS and result from effusion or vertical movement of deep-basinal water carrying significant amounts of dissolved HCS. Once such HCS reach the near surface environment, they would be subject to dispersion through ground waters by diffusion. An anomaly resulting from such a dispersion would be diffuse and difficult to distinguish from an apical anomaly.

As many investigators have noted, halo anomalies are the most common form found with soil-occluded HC analysis (Horvitz, 1950, p. 948-949; 1954, p. 1207; 1957; 1969; 1980, p. 245; 1981; Soli, 1957, p. 134; and Siegel, 1974, p. 235-237). What has not been noted is that the great preponderance of published examples of halos has come from the Gulf Coast, an area of distinctly high soil humidity. The anomaly shape associated with soil-sorbed HC analysis is variable. Kartsev and others (1959, p. 132) stated that soil-sorbed HC anomalies take the same form as soil-air HC anomalies (discontinuous or continuous apical or halo anomalies). Early Western work, carried out before the advent of acid treatment of soils (for soil-occluded HC analysis), reported mainly halo anomalies (Rosaire, 1938, 1940; Horvitz, 1939; McDermott, 1940; Pirson, 1940; and Rosaire and others, 1940), although apical anomalies were reported to a lesser extent (Rosaire, 1938, fig. 6; see fig. 10 this paper). By this paper's model, both apical and halo anomalies could be present with soil-sorbed HC analysis (discussed below). However, in areas of high soil humidity (such as the Gulf Coast where most early Western work was carried out) halos would predominate. Kartsev and others (1959, p. 101-105) reported that discontinuous or continuous apical or halo anomalies are found with soil-air HC analysis although only apical anomalies were observed in the earliest investigations (Laubmeyer, 1933; and Sokolov, 1936). A number of investigators have stated that soil-air HC analysis gives only, or mainly, halo anomalies (Horvitz, 1939, p. 215; 1950, p. 942; Pirson, 1940, p. 1471; 1941, p. 32; 1969; Soli, 1957, p. 134; Baijal, 1962; and Jones and Drozd,



1983, p. 949). By this paper's model, soil-air HC analysis could result in either halo or apical anomalies. Microbiologic prospecting always yields apical anomalies. The rare halo anomalies observed with this method were associated with large faults (Kartsev and others, 1959). As Siegel (1974, p. 239) noted,

"It is noteworthy that several other factors that have been investigated as potential guides in the search for hydrocarbons also present anomalies in halolike forms (radioactivity, electrical conductance, and (or) resistivity, and others), except for microbial density, which presents a full target as an anomaly."

Of all the hypotheses advanced to explain the celebrated halo anomaly found with soil-occluded HC analysis (and other SGE methods), the most popular (fig. 7) is that the sediments (caprock) over the HC deposit have become plugged due to mineralization. This forms an indurated seal, forcing HC microseepage to occur only at the edges of the deposit where such mineralization has not taken place (Rosaire, 1940, p. 1427). Two lines of evidence show that this theory cannot be correct. First, if this were the case, analyses for soil-air and soil-sorbed HCS, and microbiologic surveys would not yield apical anomalies, but would only yield halo anomalies. Such apical anomalies are incontestable evidence that HC microseepage is occurring directly over the HC deposit and not solely on the edges of the deposit. The second line of evidence against the "plugging theory" is in the form of HC-gas logging, wherein HC-gas concentrations are measured as a function of depth down either exploration wells or deep-reconnaissance bore holes such as the Soviets use. In bore holes directly (apically) over HC deposits (fig. 8), HC-gas concentrations continually increase and reach high values just over the HC unit bearing irrespective of the anomaly shape at the Earth's surface (Rosaire, 1940; Horvitz, 1950, p. 959; Sokolov and others, 1959; Stroganov, 1969; Sokolov, 1970, p. 546; and Thompson, 1979, p. 668). In fact, Stroganov (1969) specifically carried out HC-gas logging investigations of surface-halo anomalies and uniformly found high HC concentrations below such anomalies. These observations show that halo-anomaly formation cannot be due to caprock plugging, but instead must be due to a near-surface effect.

In my opinion, Soli (1957) correctly explained the cause of halo anomalies observed with soil-air and soil-sorbed HC analysis. This explanation has largely gone ignored except for a reference by Davis (1967, p. 212-214), and Mac Elvain's (1963A,B) discussion supporting Soli's hypothesis. Soli (1957) hypothesized that intense-bacterial activity in the uppermost-soil layers destroyed most of the vertically-migrating HCS over the center of the surface trace of a HC deposit. As one moved laterally off the center of the deposit, the concentration of vertically-migrating HCS would decrease to values too low to support viable bacterial growth but still higher than the background values (fig. 9). Kartsev (1959, p. 319) noted that a minimal threshold concentration of surface HCS must be exceeded before a viable microbial population can develop, which supports Soli's (1957) hypothesis. Soli's (1957) explanation accounts for halos reported both for

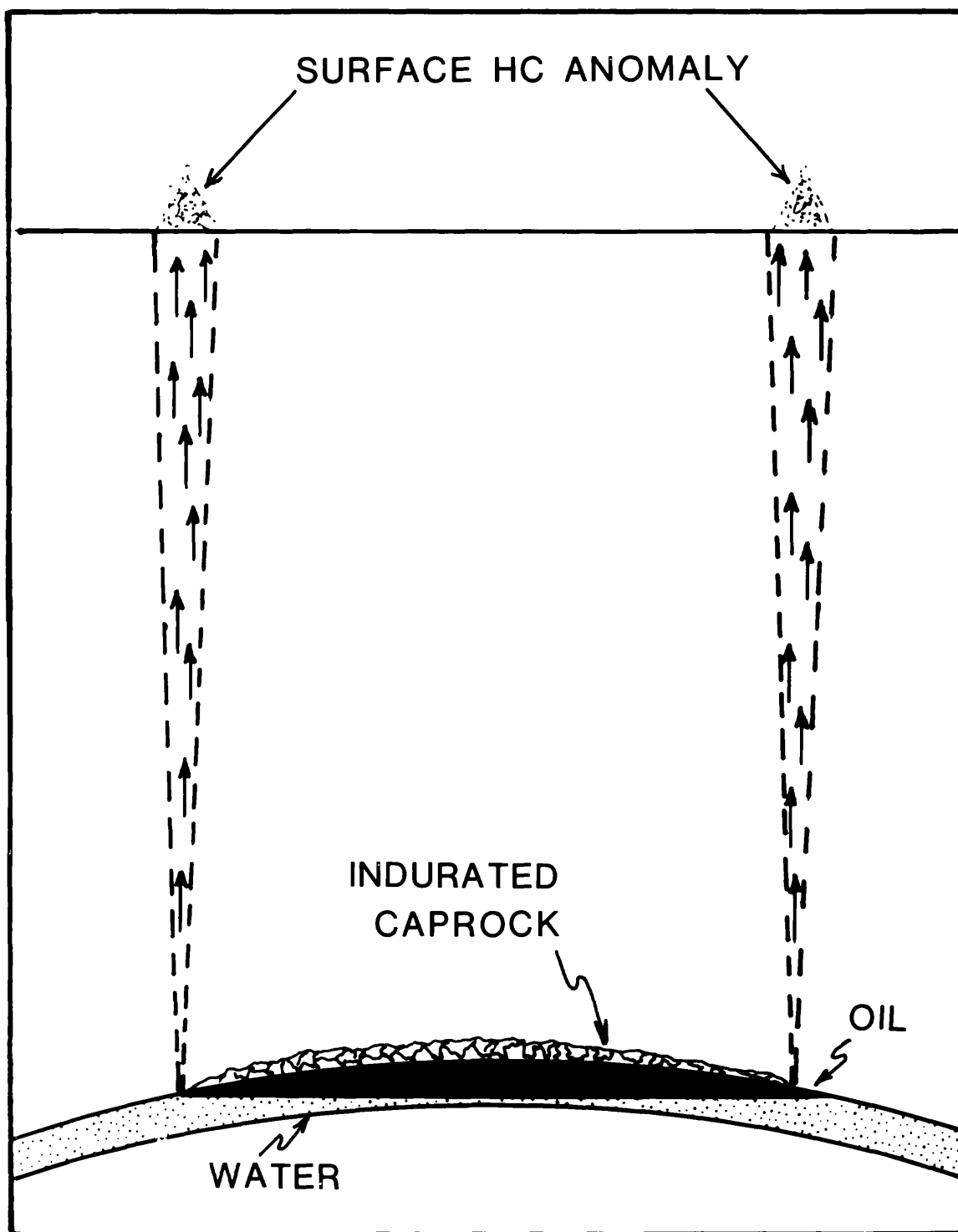


Figure 7. Explanation of surface geochemical halos by caprock plugging.

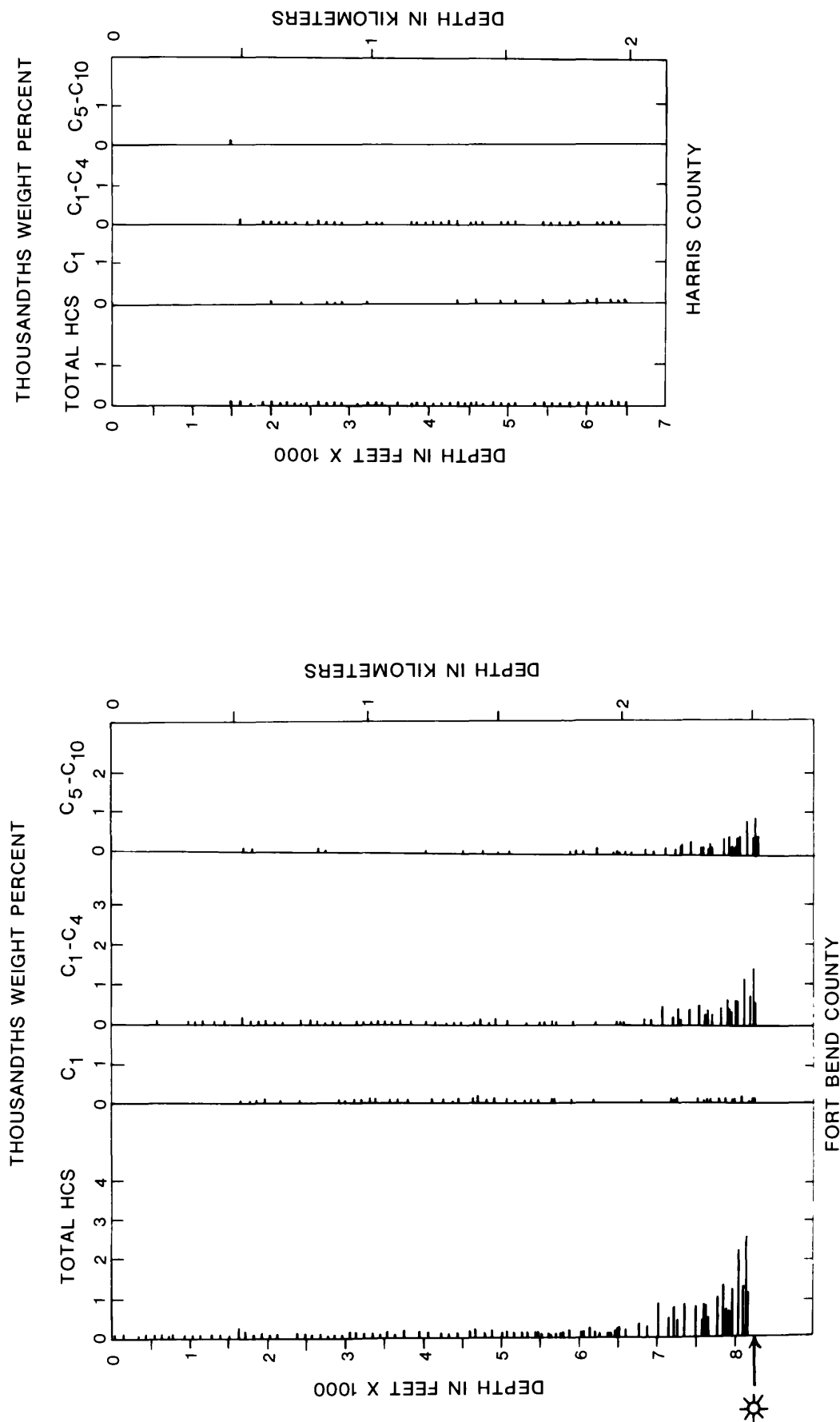


Figure 8. HC gas logging examples for a new field wildcat discovery well near Rosenberg, Fort Bend County, Texas, and for a dry hole in neighboring Harris County, Texas. Note the increase in both total HCS and HC molecular weight as the producing sand (8,246-8,254 ft, 2,513-2,516 km) is approached in the discovery well. After Rosaire (1940).

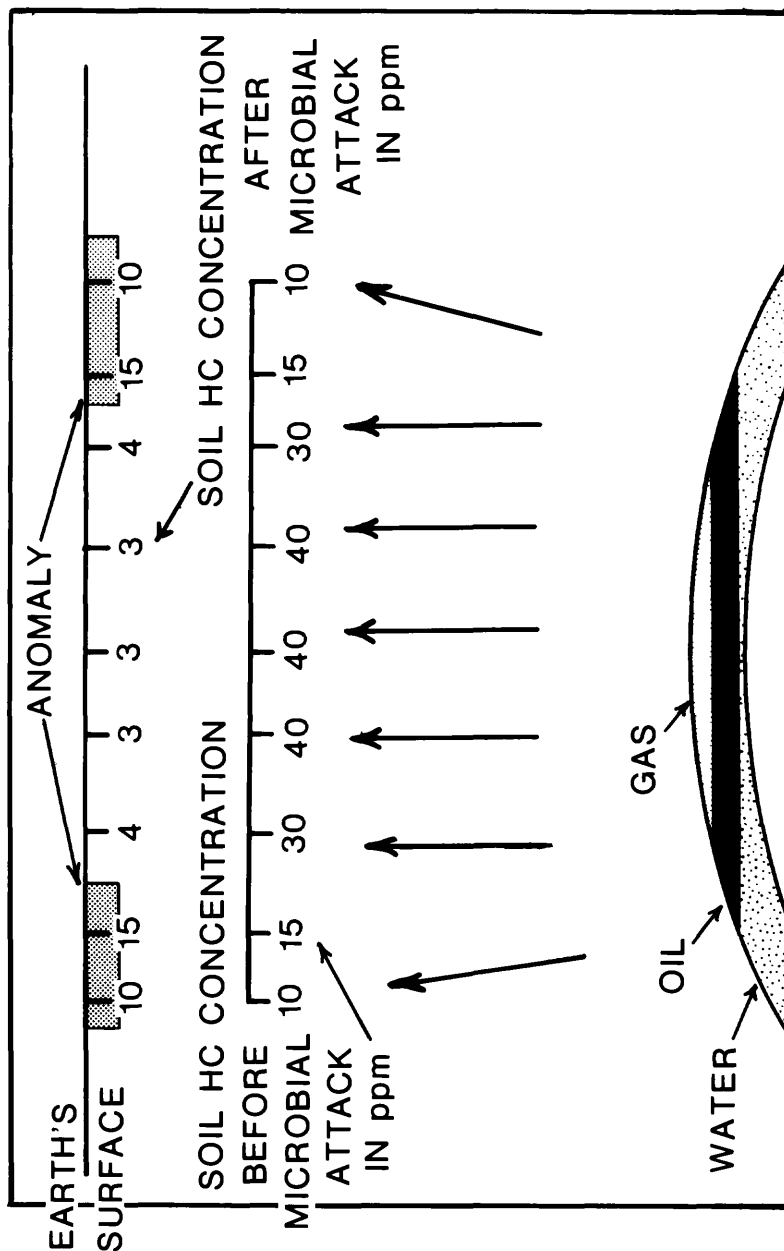


Figure 9. Soli's (1957) explanation for soil-air and soil-sorbed HC anomalies.

soil-sorbed and soil-air HC analysis, but does not fully explain the halos found with soil-occluded HC analysis.

The origins of halos reported for soil-occluded HC analysis, Duchscherer's (1980, 1981A,B, 1983)  $\Delta C$  technique, the soil-carbonate halos of Kartsev and others (1959, fig. 127, fig. 6 this paper), and the "mineralization" halos of McDermott (1940), are all interrelated. In any surface or near-surface environment, only a limited amount of  $Ca^{+2}$  ions are available to precipitate as calcite from the  $CO_2$  concentration buildup from microbial oxidation of vertically migrating HCS. After precipitation of this limited amount of  $Ca^{+2}$  ions, the system will be depleted in  $Ca^{+2}$  ions. The only possibility for further calcite precipitation lies in replenishment of  $Ca^{+2}$  ions to the system. This occurs either by physical transport by ground waters or by diffusion of  $Ca^{+2}$  ions due to the concentration gradient established by the original calcite precipitation. In any case, such  $Ca^{+2}$  ions moving towards the system will encounter elevated concentrations of  $CO_2$ ,  $HCO_3^-$ , etc. and  $CO_3^{+2}$  diffusing away from the apical area of intense microbial activity. Thus, calcite would be precipitated at this ionic meeting at the edges of the apical area before the new  $Ca^{+2}$  ions had a chance to migrate to the center of the apical area, thereby creating the various halo anomalies associated with this precipitated calcite.

Soil-occluded HC analysis should almost always yield halo anomalies by the above model. However, soil-sorbed HC analysis and soil-air HC analysis could yield either halo or apical anomalies depending on the intensity of microbial activity. In fact, because microbial activity can be seasonal, soil-sorbed HC analysis or soil-air HC analysis could at one time of the year yield a halo anomaly and at another time yield an apical anomaly. Also, a strong anomaly at one time of the year could entirely disappear at another time of the year. Philp and Crisp (1982, p. 5-6) described such an instance in soil-air HC surveys they carried out in the Cooper basin, Australia,

"The results of this preliminary study were encouraging, and anomalously high concentrations of  $C_2$  to  $C_4$  hydrocarbons were detected in an area adjacent to a fault previously determined by a seismic survey. The frustrations of this method of prospecting were made abundantly clear one year later, when another survey was performed in the same region and the anomaly could no longer be detected."

Seasonal variation of both anomaly shape and intensity (fig. 10) was also observed by Rosaire (1938) in soil-sorbed ethane surveys run over the Hastings oil field, Brazoria County, Texas, in May and September 1937, where in spite of increased field development, anomaly intensity increased, and anomaly shape changed from halo to apical. By coincidence, Horvitz (1969) reported a disappearing anomaly at Hastings due to reservoir depletion from production. Kartsev (1959, p. 83-86, 120, 302) discussed seasonal fluctuations of both soil-sorbed and soil-air HCS and noted that the concentrations of such HCS vary throughout the year and sometimes vanish entirely. Such seasonal variations and (or) disappearances of soil-sorbed or soil-air HCS is in all probability due to seasonal variation in the intensity of the microbial filter.

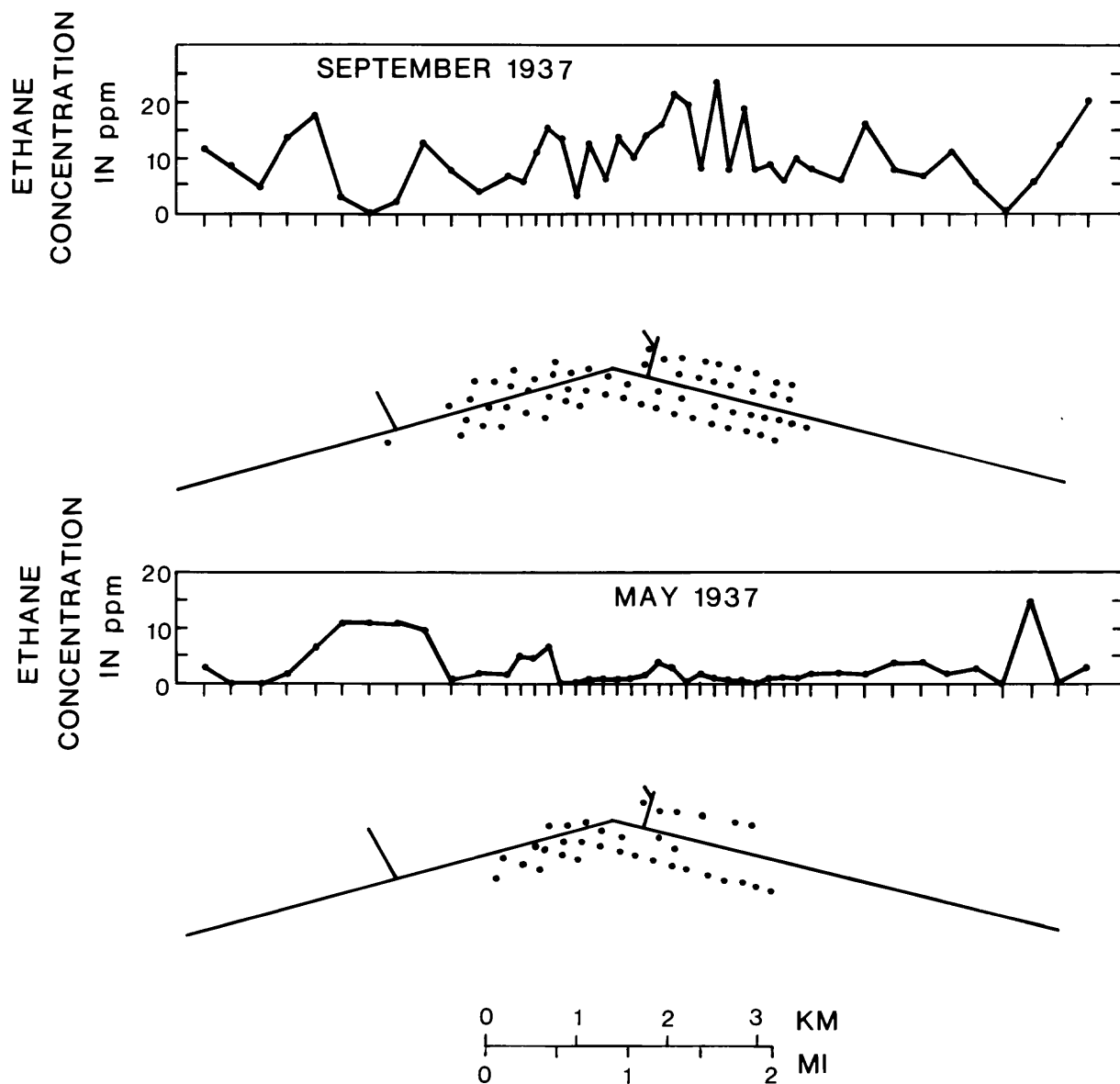


Figure 10. Soil-sorbed ethane traverses run at different times (May and September, 1937) over the Hastings oil field, Brazoria, County, Texas. After Rosaire (1938, p. 109).

## DGD METHODS - PROS AND CONS

Because of the possibility of false anomalies with some SGE methods, only DGD methods which measure  $C_2$ - $C_5$  HC concentrations (unassociated with  $C_6$ + HCS), either relatively or absolutely, are specific for thermogenic HC deposits. Such methods are: soil analysis for occluded and (or) sorbed HCS, soil-air analysis, microbiologic analysis, and integrative absorption.

Depending on the climatological environment, all five methods may show large seasonal variations, and (or) not be applicable at any time in a given area. The first three methods require the drilling of deep bores (at least 6 ft, 1.8 m), which results in long field times and high field expenses. Further, the need for a truck-mounted auger drastically decreases field mobility. For the first four methods, sampling and sample analyses can be time consuming, difficult, and expensive. Other problems also exist individually for all five methods.

### Soil-Air HCS

The low concentrations of  $C_2$ - $C_5$  HCS in soil-air make soil-air sampling and analysis both difficult and open to large errors. Diurnal breathing of soil, and especially climatological variations (wind, rain, heat, cold, snow, barometric pressure, and humidity) which make soil "breathe", put severe limitations on soil-air surveying. Large regional surveys cannot be carried out under equal meteorological or diurnal conditions, and data from different sample localities cannot be directly compared to each other (See Kartsev and others (1959, p. 72-73) for a discussion of soil "breathing"). Intense bacterial activity can obliterate all soil-air HCS. Kartsev and others (1959, p. 85-87) discussed other problems with soil-air analysis. The lack of published results in the Western literature on soil-air analysis suggests that it is not an easily applicable technique. Although Baijal's (1962) research is sometimes referred to as a successful example of soil-air analysis, this is not the case as he incorrectly contoured his data (fig. 11). Kartsev and others (1959, p. 64-106) gave an excellent discussion of soil-air surveying and on page 106 finish with the statement, "In conclusion it should be noted that the gas survey can be perfected much further and is in need of serious investigations of a theoretical character."

### Soil-Sorbed HCS

Soil-sorbed HC analysis is also beset with problems. A detailed discussion of sorption (adsorption, absorption, and chemisorption) is certainly outside the scope of this paper. To this day, sorption is still one of the more or less "black art" areas of physical chemistry. Sorption under controlled laboratory and (or) industrial applications is quite complex. In Nature, where additional variables are present, defining sorption becomes impossible. (Kartsev and others (1959, p. 109-115) discussed sorption in soils. For more rigid physical chemical treatments, see McBain, 1932; Prutton and Maron, 1951, p. 226-239; Bikerman, 1958; Crockford and Knight, 1959, p. 382-392; Barrow, 1961, p. 753-775; Moore, 1962, p. 740-753; and Vold and Vold, 1983, p. 71-114.) The exact mechanism(s) of sorption (and more importantly desorption during analysis) of microseeping HCS has not been defined and

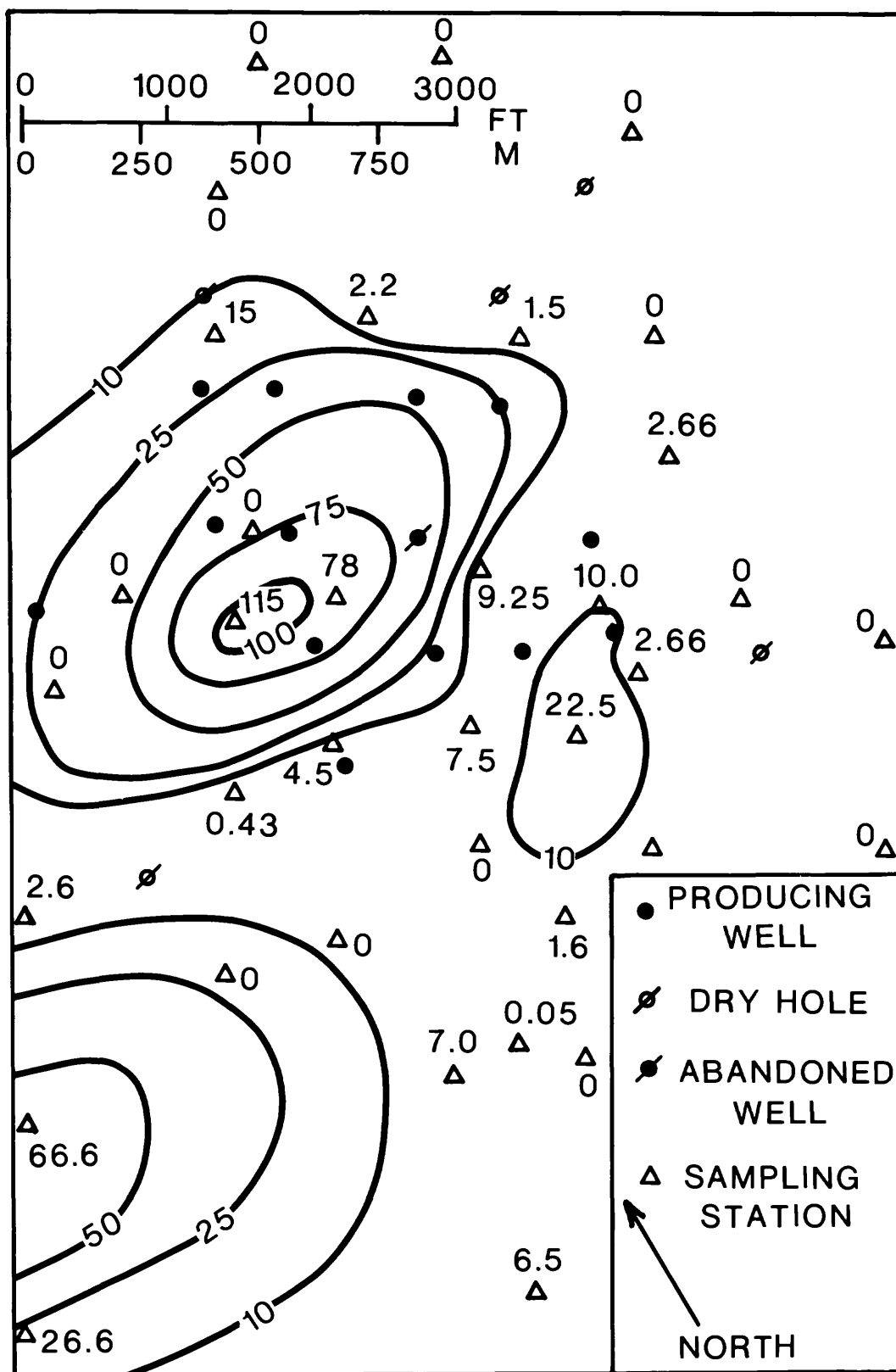


Figure 11. Ethane soil-air survey of the Hilbig oil field, Bastrop County, Texas. Triangles show sampling stations, closed circles are oil-productive wells. After Baijal (1962), with Baijal's (1962) original iso-ethane contours.



probably never will be. Soil is highly complex and its HC sorption capacity can be highly variable over limited lateral distances (Sanderson, 1940; Bronston, 1947; Kartsev and others, 1959, p. 112-114; Sokolov and others, 1971; Horvitz, 1980; and Klusman and Voorhees, 1983). For example, Kartsev and others (1959, p. 114) noted that, "Soil, rich in organic matter, absorbs nearly 50 times as much methane as clay that has no trace of organic matter." Kartsev and others (1959, p. 117-121) also noted that due to inhomogeneity of sorption characteristics in soils, even sample splits from the same core can have much different sorbed-HC concentrations. Devine and Sears (1975) reported poor repeatability for 28 duplicate samples taken one meter (0.30 ft) apart in their study.

Sanderson (1940) discussed factors which could affect HC sorption in soils including the surface, physical shape, and chemical composition of the sorbing particles, as well as the amounts and nature of materials previously sorbed onto the particles, such as  $H_2O$ ,  $CO_2$ , mineral ions (not to mention the various soil gases generated by plant and microbial activity). All these entities will compete for active soil sorption sites with microseeping HCS. It has been stated that variations in soil sorption capacities can be avoided by sieving soil and working only with finer sieve sizes, which purportedly normalizes the soil (Pirson, 1940; and Horvitz, 1980). However, Pirson (1940, p. 1466) noted,

"Measurements, reported to the writer by C. F. Bowden (personel communication), made on samples of clays of the same crystalline composition, but of varying surface chemical nature, indicate that one clay having a surface at least 10 times smaller than another retained twice as much ethane, per equal weight of clay sample, when brought in intimate contact with a sample of air containing a given proportion of ethane. This is in direct contradiction with the expected results and gives ample proof that the mechanism of retention of hydrocarbons by soil depends more on the chemical nature of soils than on their degree of subdivision, grain size, exposed grain surface, and other physical characteristics. From this example, it appears that the particle size plays a secondary role in retaining the gases of leakage in the soil and that correction methods based solely on particle size will yield nondependable results."

Another concern with soil-sorbed HC analysis is the probable microbial attack, in moist samples, of the sorbed HCS after the sample has been taken. This possibility has also been noted by Rosaire and others (1940, p. 1461) and Soli (1957) and could be avoided by freezing samples or by the use of bactericide in the samples after they were taken. Smith and Ellis (1963, p. 1900) found a marked bacterial oxidation of HCS in 200 g soil samples they took in sealed tin cans in their study,

"A series of tests showed a rapid decrease in saturated hydrocarbon gases occurred in some soil samples when stored at 20-35°C. Tests showed this activity was stopped by cooling to 0°C or pasteurizing by heating to more than 60°C."

(This issue would not be present in analysis for soil-occluded HCS, as the HCS are "sealed" in protective carbonates.) The concentrations of lightly sorbed HCS, like soil-air HCS, are most likely highly influenced by factors (diurnal, seasonal, and climatological) which cause soil to breathe. In other words, such surveys may not be reproducible. Sorbed HCS, unlike occluded HCS, are not a signal which has necessarily been integrated over long time periods or even over geologic time, contrary to the claims of some investigators (Rosaire, 1940).

Perhaps the biggest problem with soil-sorbed HC surveys is in quantitative desorption of HCS during analysis. Kartsev and others (1959, p. 122-131) discussed the analytical techniques employed in the Soviet Union for analysis of soil-sorbed HCS. As of 1954 (original publication date of Kartsev and others (1959) in Russia), Soviet investigators were not using acid treatment to liberate occluded HCS. The Soviet analytical techniques are based on thermal or vacuum desorption or combinations of the two. Kartsev and others (1959) discussed the impossibility of assuring that all HCS sorbed in soils have been released during heating (a point previously addressed by Sanderson, 1940, p. 287). Desorption temperatures must be kept below 200°C, as temperatures above 200°C result in the generation of measurable amounts of C<sub>2</sub>+ HC gases from indigenous soil organic matter (unpublished hydrous-pyrolysis data, L. C. Price). As Kartsev and others (1959, p. 122) noted, "Overheating of the rock during gas extraction leads to the formation of new gases, previously not present in the rock. Therefore, it was thought that heating above +100° in order to evolve sorbed hydrocarbon gases was undesirable." Experiments that I have carried out have shown that even if soil samples with sorbed HCS are heated for long times (10-24 hours), such that no more gas is evolved (even under vacuum), the addition of another chemical to the system (dichloromethane), which competes for active sites in the soil, will result in the release of more HC gas. (For an analogous situation with activated charcoal see McBain, 1932, p. 92-95). Quite simply, quantitative desorption of soil-sorbed HCS is not possible using only mild heating (less than 200°C) even under vacuum. All one can do is keep analytical conditions constant, and hope that lithological variation between samples is not so great as to significantly affect the outcome of the survey (an unlikely situation).

#### Soil-Occluded HCS

Many of the problems associated with soil-sorbed HC analysis are removed in analysis for soil-occluded HCS by acid treatment. Acid treatment of soil with complete dissolution of all "acid soluble salts" (hereafter referred to as carbonates) results in quantitative liberation of occluded HCS. In addition, the acid ions would likely compete for active clay sorption sites, perhaps also resulting in quantitative or near quantitative liberation of sorbed HCS. In geographic areas favorable to intense microbial activity (and hence significant soil-carbonate precipitation) the amount of occluded HCS could be much greater than the amount of sorbed HCS. In such cases it may not matter if acid treatment did not quantitatively liberate sorbed HCS. Also, soil-occluded HC surveys do not show the seasonal variation (from the variable intensity of microbial activity) which soil-air and soil-sorbed HC surveys show, as soil carbonates seal and protect occluded HCS from microbial

destruction (L. Horvitz, oral commun., April 17, 1985). However, in cases where the concentration of soil-sorbed HCS was greater than, or near that of the soil-occluded HCS, quantitative desorption of soil-sorbed HCS during occluded HC analysis could become important, and seasonal variations would be possible with soil-occluded HC surveys. Research into the relative amounts of sorbed versus occluded HCS in different geographic-climatological environments would be appropriate.

By far the greatest amount of data on soil-occluded HC surveys have come from the Florida to Texas Gulf Coast. The published anomalies from this area are impressive; however, attempted applications of soil-occluded HC analysis in other geographic areas have demonstrated limitations of the technique. McCrossan and others (1972) carried out an extensive program over 540 mi<sup>2</sup> (1,399 km<sup>2</sup>), taking 4,561 samples of glacial soil at a depth of 5 ft (1.5 m) from the oil-productive Olds-Caroline area of Western Alberta. Analysis for occluded HCS was carried out by acid treatment of the soil samples under vacuum. The authors found no correlation between proven oil production and surface HC anomalies. Subsequent research led them to conclude that most of the measured HCS were syngenetic, originating from carbonate glacial rock fragments eroded from the foothills of the Canadian Rockies to the west. (Before uplift and erosion, the sediments of that area of Western Canada had achieved a high organic-maturation rank, with in situ generation of large amounts of HC gases). The authors concluded that DGD techniques for soil HCS were not applicable in areas of Canada covered by glacial till. Kartsev and others (1959, p. 122, 130) briefly alluded to problems caused by syngenetic gas. It is widely believed that substantial amounts of HC gases are only formed at high maturation ranks. By this belief, syngenetic HC gases would only be a problem where carbonate-bearing rock (including carbonate-bearing shales) of mature organic rank were present in the soil. However, research demonstrates that significant generation of C<sub>1</sub> to C<sub>7</sub> HCS takes place at relatively low maturation ranks (Price, 1985).

Another example of the confusion and (or) errors which can be caused by syngenetic HC gases in carbonate-bearing rock, even of low organic-maturation rank, during soil-occluded HC analysis by acid treatment was given by Heemstra and others (1979). They designed research to test the validity of SGE by drilling exploratory wells based on surface geochemical anomalies. They performed soil-occluded HC analysis ("gas logging") on the cuttings chips from such a well drilled to 2,000 ft (610 m) in Greenwood County, Kansas (See Horvitz (1980, p. 260-262) for a discussion of this technique, which is also discussed above). The rocks in that area of the Anadarko basin are organically immature. The HC gas logging analyses Heemstra and others (1979) carried out showed a high correlation between high concentrations of "absorbed" HC gases with limestones. Heemstra and others (1979) were at a loss to explain this correlation. That correlation was most probably due to acid treatment dissolving organically-immature limestones and freeing low concentrations of syngenetic HC gases, which overwhelmed sorbed/occluded HC gases from microseepage. To avoid the problem of syngenetic gases in analysis for soil-occluded HCS, it may be necessary to run surveys only in reworked, weathered Quaternary soils.

Debnam (1969) ran soil-occluded HC survey traverses across six Canadian oil fields: Gobles, Colchester, and Morpeth in southwestern Ontario; and Innisfail, Pincher Creek, and Joffre Viking in Alberta. Samples were taken from 8 ft (2.4 m) and acid extracted with both 0.05N HCl and 2N HCl. A moderate anomaly (HCS normalized to acid soluble material) was obtained at Gobles, with the 0.05N HCl acid extraction. However, the anomaly disappeared with 2N HCl acid treatment. The Colchester field showed no anomaly. At Innisfail, Debnam (1969, p. 20) called for "-----a pronounced hydrocarbon anomaly, probably of the "halo" type-----." In my opinion no anomaly was evident at Innisfail, from Debnam's (1969) data. Debnam (1969) found no anomaly at Pincher Creek and did not discuss the data for the other two fields most probably because of poor results. Debnam (1969, p. i) concluded,

"Geochemical anomalies appear to be associated with all the fields studied with anomaly intensity roughly proportional to productivity. Each of the "halo" and "solid" types of anomalies can be recognized.

The writer concludes that the geochemical method can be a valuable addition to the usual geological and geophysical exploration methods if used under favourable circumstances."

Debnam's (1969) conclusions are unjustified considering: 1) the anomalies changed as a function of acid strength, 2) the alternate citing of halo or apical anomalies for soil-occluded HC analysis, and 3) the lack of sharp anomalies of either type in most of the data. If anything, Debnam (1969) succeeded in demonstrating the inapplicability of soil-occluded HC analysis in his study areas.

Devine and Sears (1975, 1977) carried out a study in the Cooper basin, Australia centered around the Della gas field in the Strzelecki desert, a region which receives less than 100 mm (4 in.) rain per year. Their study was characterized by difficult analyses and an "extremely noisy range" of low HC concentrations. In the first phase of their study, they took 379 samples from 5 m (16.4 ft) for soil-occluded HC analysis. Of these samples, only 8 had HC concentrations greater than 14 ppb, and only 2 greater than 20 ppb. The authors carried out a more rigorous statistical analysis (not usually the case in SGE methods) that showed soil-occluded HC concentrations at best exhibited a moderately poor correlation with the Della gas field. The correlation of soil-occluded HCS to the field was improved by normalizing HC concentrations to the percentage carbonate ("acid soluble material") for each sample. This resulted in a vague, discontinuous apical anomaly. The low rainfall in the Strzelecki desert makes this an area where near surface microbial activity, and the resulting soil carbonate precipitation, would be expected to be minimal. Thus the disappointing results of the study are expected. This may be a geographic area where analysis for soil-air HCS would be more utilitarian than soil-occluded HC analysis.

The studies of Debnam (1969), McCrossan and others (1972) and Devine and Sears (1975, 1977) document that soil-occluded HC analysis is not universally applicable. The technique appears to be of limited use in true deserts, and situations where noise from syngenetic HCS in soils overwhelms signals generated from HC microseepage. However, when applied in favorable

geographical/climatological conditions, proper use of soil-occluded HC analysis appears to give very favorable results. The technique clearly is superior to soil-air and soil-sorbed HC analyses.

### Microbiologic Surveys

Microbiologic surveys attempt to measure surface and near-surface microbial activity caused specifically by microseeping HCS. The Soviet investigator Mogilevskii (1938, 1940) is clearly the father of this technique. Although the Soviets appear to have had marked success with this method, little Western work has been published, the most authoritative of which is Davis (1967, 1969). Impressive exploration results from microbial surveys have been published. Kartsev and others (1959, p. 333-340) discussed a number of microbial-survey case histories. Mogilevskii (1953) claimed an 80 percent predictive success rate for microbial surveys, but Subbota (1954) maintained not all of these predictions were made on the basis of microbial surveying alone. Sealey (1974A) claimed an 82 percent prediction success, and with "improved techniques" an 85.7 percent prediction success using microbial surveys. However, in the true spirit of Western SGE, Sealey (1974A,B) disclosed absolutely no information on his methods. If 80 percent predictive capabilities for microbial surveys are realities, it is most difficult to understand why the method has not been more extensively employed in Western petroleum exploration.

Kartsev and others (1959, p. 319) discussed the four main types of microbial surveys carried out in the Soviet Union: 1) microbial soil surveys, 2) microbial surveys of cuttings chips from exploration or reconnaissance wells, 3) microbial surveys on core samples ("biologging"), 4) and ground-water microbial surveys. Although as of 1954 microbial ground-water surveying was the most widely utilized method in the Soviet Union, here only microbial-soil surveys are discussed. Contradictions exist in the published literature regarding microbial soil surveying. Mogilevskii (1940) adopted the use of soil surveying for methane-oxidizing bacteria. Western investigators have roundly rejected the use of methane-oxidizing bacteria, because of the non specificity of methane for HC deposits. Mogilevskii attempted to avoid this problem by deep sampling (at least 1.5 m (4.9 ft), and preferably much deeper) to avoid the zone where cellulose-decomposing bacteria (which produce biogenic methane) were active. He also ran concurrent analyses for cellulose-decomposing bacteria, as significant populations of methane-oxidizing bacteria in the absence of cellulose-decomposing bacteria would imply high methane microseepage from HC deposits. However, contradictions even exist concerning the utility of bacteria specific for  $C_2^+$  HCS. Kartsev and others (1959, p. 314) noted,

"However, in the examination en masse of ground samples from known oil-bearing regions, ethane-oxidizing bacteria are found relatively rarely. It may be that these bacteria require special conditions for development. For these reasons ethane-oxidizing bacteria are not now used as indicating organisms in oil-prospecting work."

Thus, as Davis (1969, p. 144) noted, the obvious choice of Soviet investigators carrying out microbial surveying is use of propane-oxidizing bacteria (Mycobacterium rubrum var. propanicum). The Soviet research in this area largely has been carried out by E. N. Bokova and S. I. Kuznetsova. Contrary to the Soviet experience, Davis (1967, 1969) reported no problems in using ethane-oxidizing bacteria (Mycobacterium perrugosum var. ethanicum) in his extensive research on microbial surveying. However, Davis (1969, p. 154) on the basis of his research using ethane-oxidizing bacteria, reached far different conclusions regarding HC microseepage than most other investigators in the field using many different SGE methods dependent on HC microseepage,

"Thus, we have learned that natural gas seepage over oil accumulations is far from invariable, both from an areal and a frequency standpoint. We do not believe that a "blanket emanation" of petroleum gas in soils over petroleum accumulations often exists. In fact, evidence for microseeps suggests that the surface areal diameter of such seeps probably is of the order of 100 ft or less."

Davis also expressed general negative conclusions about SGE in Meakin (1971, p. 128). In light of Davis's conclusions, the Soviet opinion of the utility of ethane-oxidizing bacteria in microbial soil surveying would appear valid. On the other hand, Miller (1976) reported spectacular results for microbial soil surveys using ethane-oxidizing bacteria over producing oil fields (Glenburn, North Dakota; Recluse and Belle Creek, Wyoming; Hyde, Colorado). However, Miller's (1976) results can be explained by a most disturbing conclusion drawn by Davis (1969, p. 153-154),

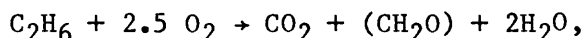
"Our methods for detecting and enumerating hydrocarbon-oxidizing bacteria were developed by using soil samples from oil fields and the samples were taken at depths which ordinarily precluded surface contamination by hydrocarbons. However, gas seepage from oil well boreholes can permeate soils overlying oil fields. The invariability of finding bacteria adapted to the oxidation of ethane over established fields, in contrast to a marked variability in their presence in soils over newly productive areas, strongly suggests that gas seepage often occurs over an oil accumulation only after the oil reservoir is punctured by wells."

Davis's (1969) conclusions in this matter, if correct, would have staggering consequences for SGE, as clearly the best examples of geochemical anomalies through the years have come from surveys over producing fields. There is likely at least some validity to Davis's (1969) point here.

There is no uniform agreement on the correct sampling depth for microbial soil surveys. Strawinski (1955) recommended a depth of 0.61 m (2 ft). Kartsev and others (1959) recommended minimum depths of 2 to 3 m (6.6 to 9.8 ft). Most of the surveys they discuss apparently were carried out over the 2 to 4 m (6.6 to 13.2 ft) range, although some were carried out as deep as 15 to 30 m (49.2 to 98.4 ft). Völz and Schwartz (1958, 1962) called for a depth of 1.5 to 2.5 m (4.9 to 8.2 ft). Davis (1967) advised depths of at least 1 to 1.5 ft (0.30 to 0.46 m), although he believed depths greater than 3 ft (0.92 m) are better. Apparently he carried out much of his research out at depths

of 1 to 15 ft (0.30 to 4.6 m). Miller (1976) advised sampling depths of 2 to 3 ft (0.61 to 0.92 m). It is likely that sampling depth is one of the critical controlling parameters of microbial soil surveying, and different sampling depths in different studies could lead to divergent results and conclusions. The most intense microbial activity clearly takes place in the uppermost soil layers, and it is here that one would suppose the largest bacterial populations would develop in response to microseeping HCS. It would seem that intense bacterial activity at depths in excess of 2 m (6.6 ft) would be limited by atmospheric exchange with the soil-air to replenish the necessary oxygen.

In addition to the apparent ill-defined nature of microbial soil surveying, serious sampling and analytical problems also exist. Three analytical techniques have been generally utilized: manometric (gas-uptake), visual, and microscopic. With the first two analytical techniques, a given amount of nutrient solution is added to a fixed amount of soil in a suitable small reaction vessel, resulting in a slurry. As Davis (1969, p. 148) noted, in a closed system bacterial activity results in a decrease in system gas pressure as more gas is utilized than produced. For example, with ethane, Davis (1969) wrote the reaction as:



where  $(\text{CH}_2\text{O})$  is bacterial cell substance. Such a decrease in system gas pressure, which is directly related to the intensity of bacterial activity, can be monitored with a manometer attached to the reaction vessel. For example, over a given time interval, a significant population of ethane oxidizers in a sample will result in a much greater pressure decrease in a system where ethane is the food source, than in the same system with a small original population of ethane oxidizers. The visual analytical technique involves an estimate of the volume of a distinctive bacterial film which forms in a reaction vessel from bacterial activity on a given food source. This volume is calculated by multiplication of the estimated film thickness by the estimated area of the vessel that the film covers. As of 1954, this was the analytical technique exclusively employed by the Soviets (Kartsev and others, 1959). The microscopic (or plating) analytical technique consists of spreading small amounts of soil as thinly as possible on mineral agar plates and allowing bacterial colonies to form in an air and ethane (or other HC) atmosphere. After a sufficient time, the colonies are microscopically examined and classified. Davis (1967, p. 234-245) discussed other unsatisfactory analytical techniques he attempted, and other less widely employed analytical techniques.

Common problems to all three analytical methods are: sampling, laboratory adaption to food sources by different microbes, and incubation times. Incubation times for measurable reactions apparently run 15 to 30 days, thus preventing quick analyses. As Davis (1967, p. 220-221) noted, sampling presents the biggest problem, as soil within the same sample can vary considerably in texture and moisture content; and indigenous HC oxidizers are not uniformly distributed throughout soil, but exist as isolated colonies. Attempts to evenly disperse such colonies by homogenization by drying the soil followed by grinding or sieving results in a promotion of actinomycetes, which

can flourish under dry conditions. During the subsequent incubation period, actinomycetes then adapt to the HC gas food source, thus negating the manometric analysis. Reproducibility in sample analysis is also of prime concern, as Davis (1967, p. 221) stated,

"Actually, the preferred method of treating soil to be assayed for ethane-oxidizing bacteria involves a minimum of handling and analysis as soon after collection as possible. Lack of reproducibility in the assay of a given sample can be compensated by averaging the results of replicate analyses of the soil sample."

In large areal surveys, significant time is spent in the field before the samples are returned to a laboratory for preparation and incubation. Thus, samples taken at the first part of the survey will likely suffer a pronounced decrease in bacterial activity, compared to samples taken at the end of the survey. Such samples from the same survey would not be directly comparable.

Davis (1967, p. 227) raised a very serious question concerning microbial adaption to  $C_2-C_5$  HC consumption during laboratory incubation. The whole purpose of microbial-soil surveying is to measure microbial populations which specifically utilize  $C_2-C_5$  HCS (from microseepage) or have adapted to the use of  $C_2-C_5$  HCS in the field. (For example, Strawinski and Tortorovich (1955) described a case wherein methane-oxidizing bacteria from a HC microseep had adapted to the utilization of ethane, propane, and butane; however, the same bacteria laterally off the seep could only utilize methane). But, as Davis (1967, p. 227) noted,

"Microorganisms exist, however, which can adapt rapidly by means of their versatile enzymic systems to utilize a large variety of compounds. These organisms will therefore utilize ethane in the laboratory without having previously been associated with it in the field."

Davis (1967) noted that actinomycetes and molds are so adaptive in the laboratory; however, because they are morphologically distinct, they can be easily identified under the microscope. Such adaptive capability renders manometric (gas-uptake) analytical results untrustworthy, especially considering the long required incubation times, and also requires microscopic examination of the incubated samples by personnel trained in microbiology. This significantly increases analysis time and expense.

There are obviously major problems in microbial soil surveying. Microbial oxidation of microseeping HCS clearly plays a pivotal role in all DGD methods (and SGE in general), yet no easily employed, inexpensive, and trustworthy method is available to measure anomalous surface microbial activity due to HC microseepage. Davis (1967, 1969) clearly raised disturbing questions concerning microbial soil surveying and SGE in general. Perhaps these questions are in reality meaningless, as they could be due to Davis's exclusive employment of ethane-oxidizing bacteria in all his investigations, a tool the Soviets clearly found unsatisfactory. Davis's (1967, p. 207; 1969, p. 144) cursory dismissal of the contradiction between his and the Soviet results as due to the "possible" lack of pure ethane in the Soviet Union is



unsatisfactory and uncharacteristic of the rigorous approach that the Soviets have taken regarding SGE.

### Integrative Absorption

Integrative absorption is the use of absorbents (charcoal, silica gel, etc.) or any other "collectors," in shallow (1 to 2 ft, 0.3 to 0.6 m) surface holes to measure the relative flux of microseeping HCS over areas of interest. The technique has not been widely used in the past. Pirson (1946) was the first to report its use, but Horvitz (1950, p. 942-943) gave a more complete description of Pirson's (1946) technique. Pirson buried sorbent tubes in 5 cm (2 in.) diameter holes, 0.6 m (2 ft) deep for 24 hours. The tubes were removed and desorbed in the laboratory, and the amount of desorbed ethane was "quantitatively" measured. Pirson (1946, p. 312) reported precisions of  $\pm 10$  percent for low leakage areas and  $\pm 100$  percent in high leakage areas, and also reported mixed (mainly negative?) success. Pirson (1946) found it necessary to apply a number of different "correction factors" at each sample locality including topographic, ground-water flow, climatic, seasonal atmospheric, soil nature (particularly soil permeability), and lastly "deep geologic effects." Pirson (1946, p. 320) concluded that the results of nine years of research did not suggest that the "emanometric" technique showed promise of being any more effective than other SGE techniques in use at the time.

Points concerning Pirson's (1946) investigations warrant comment, as his approach as well as the pre-1950 lack of sophisticated analytical techniques for HC gas analysis (pre gas chromatography) negated some of the advantages of integrative absorption. The need for so many "correction factors" introduces an unwelcome degree of subjectivity into the method. This in turn results in a high degree of uncertainty being introduced into the data of such surveys. The pre-1950 analytical techniques make it very possible that Pirson (1946) was not always measuring microseeping HC gases but instead indigenous surface HC and non-HC gases (discussed below). Pirson assumed unrealistically high HC gas microseepage rates (discussed below). As such, he left his "emanometers" buried for only 24 hours which defeats the principal advantage of this technique, compared to soil-air and soil-sorbed HC surveys, which is an "integrative" time period long enough to overcome diurnal, climatological, barometric, or even seasonal effects.

Kartsev and others (1959, p. 65, 75-82) discussed the technique of drawing soil air through sorbent tubes to concentrate HC gases, which greatly increased the signal generated by soil-air HCS. However, this method is not equivalent to integrative absorption. As Kartsev and others (1959, p. 82) noted, "In practical use this method has encountered a number of difficulties of a procedural character and has not as yet been used as extensively as it deserves." Heemstra and others (1979) described a rudimentary technique similar to integrative absorption they carried out at the Sutherland field Greenwood County, Kansas. A soil-air sample was taken from a 10 cm (4 in.) hole and analyzed for  $C_1$  to  $C_4$  HCS using a field gas chromatograph. A large soft-drink container (Dixie cup?) was inverted and sealed in the hole by dirt. After 24 hours, personnel returned to the sample sites and withdrew air samples from the inverted cups by inserting syringe needles through the cup

tops (inverted bottoms). These samples were also analyzed for  $C_1$  to  $C_4$  HCS by gas chromatography, and the difference between the two analyses was taken as the HC flux at each site for 24 hours. Understandably, a number of problems were encountered with this technique. The cups adsorbed HCS, were made soft and pliable by water and heat, and were crushed by livestock in the area. In addition, "heavier hydrocarbons", which caused analytical problems, were present in the soil-air samples. The "cup" survey which Heemstra and others (1979) carried out showed an inverse (negative) correlation to the results of an occluded-HC soil survey taken from 2.7 m (9 ft) holes over the same area, but did show correlation with an "aerial HC survey" run by Geophysical Systems Corp., Dallas (reference Thompson (1981) for description of this method).

PETREX personnel (Hickey and others, 1983A,B; and Klusman and Voorhees, 1983) reported an integrative-absorption technique combining pyrolysis with mass-spectrometry (MS). Ferro-magnetic wires, whose ends are coated with activated carbon bonded to the wire by inorganic cement, are placed in holes 6 to 10 in. (15.2 to 25.4 cm) deep and covered by aluminum cans which are then covered by 2 to 4 in. (5 to 10 cm) of dirt. The assembly is left in the ground for at least a week, during which time vertically migrating HCS are sorbed by the charcoal. After retrieval from the field, the wire is heated to the curie point of the metal. This causes desorption of the sorbed HCS which are analyzed using mass-spectrometry and a multivariant computerized statistical package, "ARTHUR". Published examples of use of this technique are limited to areas of petroleum production, or possible petroleum production, associated with faulting or fracturing (Hickey and others, 1983B, p. 1342) where upward migration of HCS by effusion or, more likely, transport by deep-basinal compaction waters is occurring.

As Klusman and Voorhees (1983) noted, there are major advantages to using integrative-absorption techniques to measure microseeping HCS. By negating the need for deep (2 m to 600 m, 6.6 to 1,969 ft) bore holes, the number of samples which can be taken per unit time is dramatically increased, even considering that two field trips are necessary with integrative-absorption techniques. For example, Klusman and Voorhees (1983) discussed a study which they carried out in the Green River basin at the Patrick Draw oil field which duplicated an earlier study carried out by Richers and others (1982). Whereas the Richers and others (1982) survey required 120 field-man-days and power equipment for augering, Klusman and Voorhees (1983) carried out the same survey in 6 field-man-days with hand tools. Decreasing field time by a factor of 20 clearly greatly decreases field expenses. The use of hand tools with integrative-absorption techniques, instead of truck-mounted power augers, greatly increases field mobility, allowing more detailed surveys to be carried out. Another major advantage with integrative-absorption techniques, compared to soil-air and soil-sorbed HC surveys, lies in the integrative aspect. Barometric, climatological, diurnal and even seasonal variations in microseepage HC concentrations can be negated by leaving the collectors buried for sufficient time. Depending on the analytical method used, integrative-absorption analyses can be much quicker and cheaper than soil-air or soil-occluded or soil-sorbed HC analyses.

Although integrative absorption has the potential to be a major breakthrough in DGD, there are problems with the technique. The principal problem with the technique arises from its strongest attribute, the ability to carry out surveys at soil depths of 6 to 24 in. (15 to 60 cm). Unfortunately this is also the realm of most intense microbial and plant activity. As Kartsev and others (1959, p. 315) noted, "The zone with the greatest bacterial population and variety of morphological and physiological groups of bacteria is the soil zone." Kartsev (1959, p. 65) discussed early (1945) Soviet research which revealed that nitrous oxide ( $N_2O$ ), from soil microbial processes, was the main component of upper layer soil gas,

"At that time the first experimental work on gas surveying by accumulation of hydrocarbons on silica-gel was done. E. K. Gerling and B. M. Nakashidze then proved conclusively that the incombustible component of the heavy fraction consists of nitrous oxide and often constitutes 80-95 percent of the entire gas. Since nitrous oxide is mainly formed in the uppermost soil layer, it was decided to resort to the gas survey only for combustible gases."

(This early Soviet research also demonstrated that the thermogenic HC component of soil gas is usually less than 1 percent, most of which is methane). Davis (1967, p. 126) discussing this Soviet research, critically noted,

"Nitrous oxide which has the same molecular weight as propane can be a problem in soil-gas analysis. It is practically impossible to remove it prior to analysis. In mass-spectral analysis nitrous oxide is ionized to nitric oxide (NO) which has the same molecular weight as ethane."

Nitrous oxide will be taken up by absorbents, and although not a problem in gas chromatographic (GC) analysis using flame ionization detection,  $N_2O$  could possibly lead to errors in mass-spectrometric analysis, as Davis (1967) noted. Besides  $N_2O$ , other products of microbial and plant life processes are quite capable of interfering with integrative absorption. Kartsev and others (1959, p. 73-75) in discussing early Soviet work noted,

"Investigations with the TG-5A apparatus showed that the methane fraction contains, besides methane, carbon monoxide and volatile organic substances of complex composition.-----The heavy hydrocarbon fraction also consists of certain complex volatile organic substances which are absorbed by activated charcoal. Volatile organic compounds contained in the soil may be evolved by plants and in the bacterial decomposition of the remains of organic matter.

N. G. Kholodnyi ascertained that various organs of plants liberate complex volatile organic compounds into the atmosphere and that these (phytogenic) substances are a constant component of the atmosphere at the earth's surface wherever there is plant cover; the odors of flowers, barks, and leaves are due to phytogenic substances in the atmosphere. Further investigations by N. G. Kholodnyi led to the conclusion that gaseous organic substances contained in the soil air are formed in part under the influence of microorganisms in dead

organic remains and in part in the tissues of living plants and animals for which the soil is the natural habitat. The author considers that the gaseous organic substances may consist of methane and volatile esters, alcohols, and acids.

Special investigations conducted in 1946-1948 by M. I. Subbota showed that volatile organic substances are liberated not only by the soil, but also by plant roots. It is of interest to note that the liberation of volatile organic substances proceeds at different intensities in different seasons. The maximum quantity of emanation is observed during the period of vigorous growth of the plants and, after that, during the time of their flowering. The unique seasonal character of the liberation of organic substances is well known to specialists who study ester-bearing plants.

It is evident from this that soil gas contains a great variety of combustible gases formed within the soil layer itself: methane, volatile organic substances, carbon monoxide, and others. In order to avoid these soil gases, it is necessary to go to greater depths below the soil or to construct apparatus that will determine hydrocarbon gases not by the products of combustion, but directly. For correct interpretation of the results of gas surveying, it is necessary to employ heavy hydrocarbons and methane for the most part."

Zobell (1946, p. 33, 41) also noted that plants and bacteria produce unsaturated gaseous hydrocarbons in the upper soil layers.

Little Western research has been carried out on the indigenous organic compounds existing in the upper soil layers, as such compounds pose no problem for soil-air, soil-occluded, or soil-sorbed HC analyses whose samples are from depths where microbial and plant activity is greatly reduced. Therefore, the possible interference of indigenous organic compounds with those methods is minimal. However, the possible degree of interference of such compounds with integrative-absorption techniques is high. Because of the integrative aspect of the technique, even small concentrations of these compounds could be summed up over time to give possibly large interfering or misleading signals. An example of such confusing signals was given by Pirson (1946), who observed that his integrative-absorption technique led to "artificial anomalies" which were often of a greater magnitude than the significant measurements, and which in turn led to a number of dry holes being drilled. Pirson (1946) found that topographic highs resulted in low fluxes of HC microseepage whereas higher than normal fluxes were associated with areas where the water table was closer than normal to the Earth's surface, such as parallel to (dry or running) stream beds or "ground-water mounds". Such areas of high moisture content are optimum for both plant and microbial life and the associated organic compounds which they produce. Although Pirson (1946) believed he was measuring only ethane, due to the pre-1950 rudimentary organic analytical techniques, it is quite likely that he was measuring minor amounts of thermogenic HC gases overshadowed by larger concentrations of plant and (or) microbially produced volatile organics. I am not aware of a sorbent which effectively takes up ethane; activated charcoal does not (David Osborne, Exploration Research Laboratories, Salt Lake City, oral commun.).

Another example of the confusion which can be caused by plant and (or) microbially produced organics is the exchange between Smith and Ellis (1963) and Horvitz (1972). Smith and Ellis (1963) contended that data they presented (fig. 12) showed that saturated  $C_2$ - $C_5$  HC gases could be produced by plants, and thus analysis of soils for  $C_2$ - $C_5$  HCS was not necessarily specific for thermogenic HC deposits. Horvitz (1972) effectively replied to and negated the points made by Smith and Ellis (1963) in regards to occluded-HC soil analysis. However, the compounds which Smith and Ellis (1963) discussed could be a significant problem for integrative-absorption techniques. Heemstra and others (1979, p. 53) discussed soil-air analytical problems with their "cup integration" in surface holes, problems which were not encountered in their analysis of soils for occluded HCS. These problems were likely due to organic compounds indigenous to the soil they worked with.

Volatile organic compounds (as well as  $CO_2$  and  $N_2O$ ) generated by plants and (or) microbes also could "poison" collectors by taking up active sorbent sites and reducing sorbent capacity to take up microseeping thermogenic HCS. This would depend on the surface area of the collector, the time of burial, and the relative intensity of plant and (or) microbial activity. Another possible problem is bacterial attack of sorbed HCS in moist collectors after they are taken from the ground.

Klusman and Voorhees (1983, p. 2) believe that computerized pyrolysis-mass spectrometric analysis is superior to gas-chromatography (GC) as an analytical tool for integrative absorption,

"Gas chromatography has some inherent disadvantages as a highly automated system. The ability to separate hydrocarbons changes with column characteristics resulting in possible changes in retention times as well as relative peak positions. This makes the system difficult to computerize. Separation of hydrocarbons heavier than about  $C_6$  usually requires a long analysis time and the need of an additional analytical device, such as a mass spectrometer or ft-infrared spectrometer."

I am in disagreement with Klusman and Voorhees (1983). Perhaps for the apparent application of their technique (identification of HC anomalies caused by either effusion of  $C_6$  + HCS, or migration of  $C_6$ + HC-bearing deep-basin waters up faults and fractures,  $C_6$ + HC analysis is important. However, the  $C_1$  to  $C_5$  HCS make up all or most of microseeping HCS, and GC analysis of  $C_1$  to  $C_5$  HCS can be accomplished in 2 to 4 minutes. (GC analysis of HCS up  $C_{18}$  can be carried out in at most 15 minutes with oven-temperature programming.) As the  $C_6$ + HCS are not usually present in significant concentrations with true HC microseepage, analysis for  $C_6$ + HCS is clearly unnecessary in most cases. I have carried out hundreds of analyses using gas-solid GC columns and have observed no change in peak retention time for  $C_1$  to  $C_5$  HCS which would cause problems for bench computers. Hundreds of analyses carried out using gas-liquid GC have not resulted in the problems cited by Klusman and Voorhees, 1983 (David Osborne, Exploration Research Labs, Salt Lake City, oral commun.). Horvitz (1969, p. 207) incorporated gas chromatography into his occluded-HC soil analysis method after investigating mass spectrometry, as well as several other methods, and finding them unsuitable for his needs.

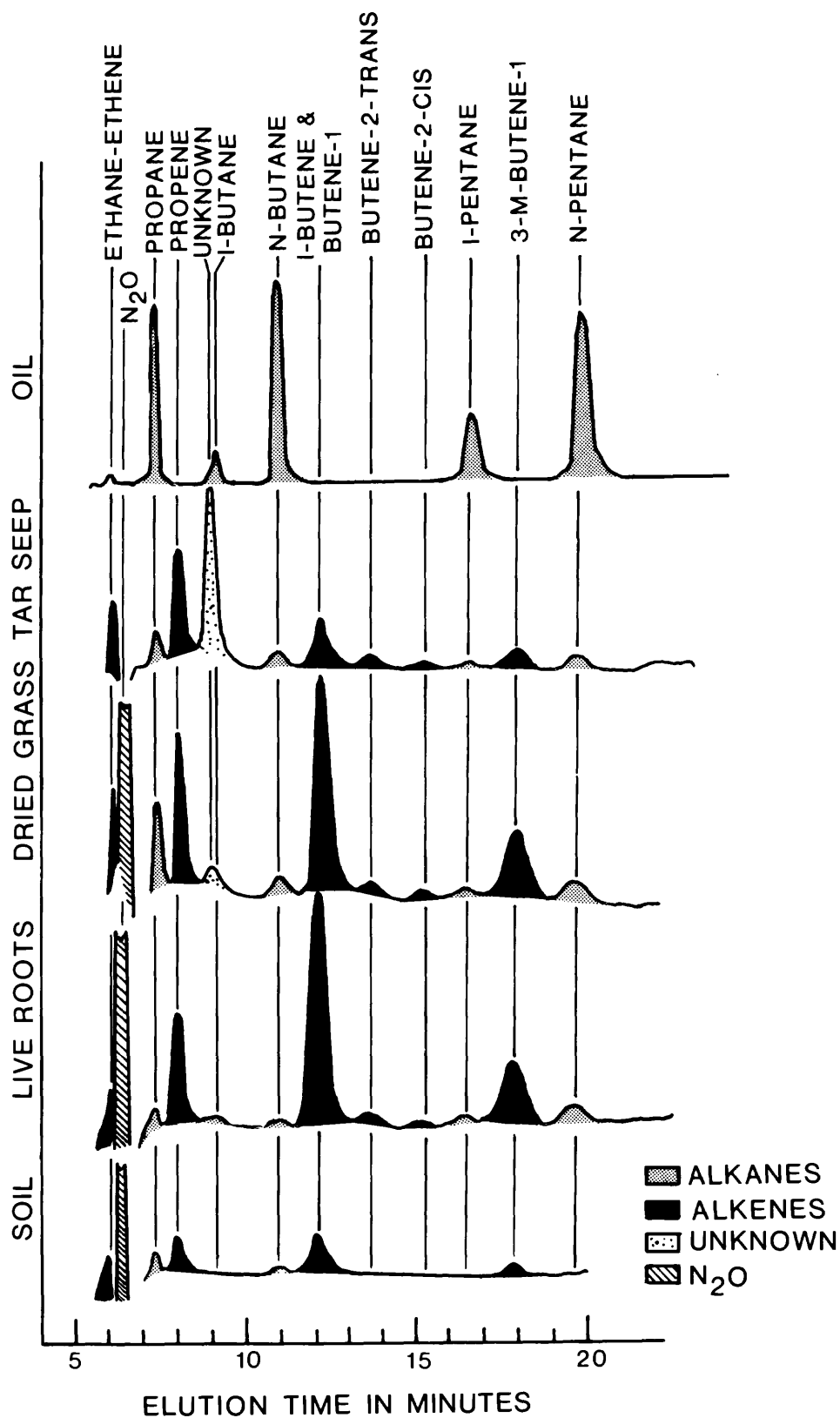


Figure 12. Volatile organic compounds found in various environments or sources. Note the high component of nitrous oxide in roots, grass and soil, as well as the fact that bacterial attack of a tar seep has resulted in a number of volatile organic compounds usually not found in crude oil. The manufacture of such compounds would be expected also in surface microbial oxidation of microseeping HCS. After Smith and Ellis (1963).

Davis (1969, p. 154) discussing soil-gas analysis by gas-chromatographic, as opposed to mass-spectrometric, methods stated,

"Gas-chromatographic methods are the most recent and the best methods of soil-gas analysis, because the gases are readily identified and quantitatively measured. The methods are relatively simple, sensitive and inexpensive."

GC analysis offers distinct advantages over pyrolysis-MS analysis, the two most important of which are: 1) analysis cost, and 2) the possibility for multiple analyses with gas chromatography as opposed to a "one shot" pyrolysis-MS analysis. The latter advantage allows both a check on accuracy/reproducibility as well as coinjection of a spike of a known internal standard of  $C_1$ - $C_5$  HCS with the unknown for positive identification of sample peaks in the unknown. This is not possible with pyrolysis-MS analysis, and the distinct possibility of confusing mass-spectral ions from organic (and inorganic, Davis, 1967, p. 126) compounds indigenous to soils, makes positive compound identification a first priority in integrative-absorption techniques. Certainly Horvitz's (1972) resolution of the questions raised by Smith and Ellis (1963) would not have been possible using only mass spectrometric analysis. Analysis cost per sample for computerized mass-spectrometry with multivariant statistical analysis is much greater than that of GC analysis using a desk-top computer. There is little advantage in slashing field costs with integrative-absorption techniques only to burden the method with unnecessarily high analytical costs.

There are, no doubt, a host of other yet unrecognized problems and disadvantages with integrative absorption in general. Given past experience in SGE, such problems will surface if the technique is more widely employed. Nonetheless, integrative absorption offers the potential to be a major breakthrough in DGD. This status will be achieved only after the necessary background research has been completed. Like all DGD methods, the interaction of integrative absorption with the seasonal development and subsequent decline of the microbial filter must always be kept in mind, and the fact that historically, the uppermost soil layer has been the most difficult niche in which to carry out DGD. As Sokolov and others (1959, p. 670) noted,

"For most methods, and especially for gas methods, the layers at the very surface are unfavorable for the detection of anomalies, owing to intensive gas exchange between these layers and the atmosphere, and to the intensive biochemical processes occurring in them."

## DISCUSSION

### HC-Microseepage Fluxes

Different investigators have called for very high microseepage HC rates (fluxes) when considered over geologic time. Other investigators have subscribed to HC microseepage mechanisms, which a-priori involve very high HC fluxes. Rosaire (1938, p. 110) called for an oil "microseepage" rate at the Hastings field of 10,000 barrels (bbls) per day. On the basis of both his "geodynamic" and "emanometric" methods, (Pirson, 1941, 1946) has given different estimates of HC fluxes. For example, Pirson (1941) called for an ethane flux of  $23 \text{ mm}^3/24 \text{ hours/ft}^2$  (or  $8,000 \text{ ft}^3/\text{year/mi}^2$ ) at the Music Mountain gas field in northern Pennsylvania. Duchscherer (1981B, p. 320) called for fluxes of, "----several hundred cubic feet of gas being lost to the atmosphere per square yard of surface area per year." When projected over geologic time, such fluxes result in the loss of staggering amounts of HCS (Table 1).

Table 1.

Source	Flux	Amount lost in one million years
Rosaire (1938)	10,000 bbls/day of oil	3.65 trillion bbls of oil
Pirson (1941)	$23 \text{ mm}^3/24 \text{ hrs/ft}^2$ of ethane	1.6 trillion $\text{ft}^3$ of gas
Duchscherer (1981B)	$300 \text{ ft}^3/\text{year/yd}^2$ of HC gas	17.90 quadrillion $\text{ft}^3$ of gas

Assumptions: Pirson (1941)-Compositionally, ethane represents only 10 volume percent of the gas in the pool. Field size is  $20 \text{ mi}^2$ .  
Duchscherer (1981B) - Field size is  $20 \text{ mi}^2$ . "Several" equals three.

If one assumes a lower Miocene oil emplacement at Hastings, 84 trillion bbls of oil would have been lost there due to microseepage since accumulation. A mid-Pennsylvanian gas emplacement at Music Mountain, would have resulted in a loss of 480 trillion  $\text{ft}^3$  of gas from that pool. Clearly the "microseepage" rates of Table 1 are geologically untenable. Even fluxes millions of times less are untenable, in my opinion. Two assumptions are possible with regard to the "reservoir" of HCS supporting HC microseepage. It may be assumed that HC generation, primary and secondary migration, and accumulation are processes which constantly occur in sedimentary basins, and hence the HC pool is constantly being replenished. Or it may be assumed that these processes occur only during short periods of geologic time. Substantial research that I have carried out on the subject has led me to conclude that the latter scenario is usually the case.

A detailed discussion of the origin and evolution (through geologic time) of petroleum basins, HC origin and migration, and accumulation of commercial HC deposits is certainly outside the scope of and relevancy to this paper. Thus, I will give only a brief and undocumented review of what I believe is the usual scenario based on unpublished research.



HC generation and primary migration are heat-driven processes resulting from either (or both) increasing burial or an increasing geothermal gradient. The cessation of burial or a decreasing geothermal gradient causes termination of both HC generation and migration. Also, a steeply decreasing geothermal gradient, coupled with or due to basinal uplift and erosion, results in a marked cooling (and contraction) of a sedimentary basin and its pore waters. Such pore-water cooling results in two events: (1) the precipitation of a substantial amount of silica-alumina minerals (mainly clays), and other minerals, in sediment pores, and (2) the creation of less than hydrostatic fluid-pressure gradients in most sediments of the basin (this is especially prevalent in sediments on the stable shelves of such basins). The precipitation of clays in the porosity of coarse-grained sediments in such basins greatly restricts (but does not totally halt) basinal fluid flow from either meteoric water recharge or deep-basin compaction. This mineral precipitation also effectively helps to seal off HC deposits throughout the basin, especially in stratigraphic and low-relief traps on the stable shelves of sedimentary basins. Without such a sealing and disruption of fluid flow, commercial HC pools would (geologically) quickly be destroyed by water washing and diffusion (see calculations in Price, 1980, p. 21-26). Petroleum basins, which have had such large decreases in geothermal gradients, may be termed "dead" basins. This contrasts them from "live" basins (such as the coastal and offshore portions of the Gulf Coast basin as well as some California coastal basins), where processes leading to the accumulation of commercial HC deposits are still proceeding. Most interior cratonic American petroleum basins have fluid-pressure gradients less than hydrostatic, especially sediments (and HC deposits) on the stable shelves of these basins. (See Dicky and Cox (1977) and Magara (1981) for examples and discussion). Such basins have had substantial decreases from their maximal geothermal gradients. Therefore, I do not believe that the HC deposits of these basins can be "constantly replenished" to account for the very high HC microseepage fluxes proposed by different investigators.

Mills and Wells (1919) first proposed gas-induced evaporation of ground water, a concept amplified by Nisle (1941). Other investigators (including Tripp, 1945; Donovan and Dalziel, 1977; and Duchscherer, 1981B, p. 320) have also called upon the mechanism to explain different observed features including: halos of any kind, radiometric anomalies, "soil salt" anomalies, and anomalous oxygen and (or) carbon-isotopic compositions of soil carbonates. According to Mills and Wells (1919), natural gas vertically diffusing through the sediment water column by molecular solution exsolves near the Earth's surface (due to pressure decrease) and forms a free-gas phase. Because it is undersaturated with respect to water, this free gas phase takes ground water into solution, thereby evaporating ground water, which causes precipitation of soil salts, isotopic fractionations, etc.

Gas-induced ground-water evaporation, in my opinion, is most unlikely for three reasons: (1) As discussed, diffusion of HC gas vertically through impermeable sediments is not possible. (2) The amounts of gas required are unrealistically large. (3) HC microseepage probably results in exactly opposite features as those proposed to occur with gas-induced ground-water evaporation. As to the second point, the solubility of water in an HC gas phase, especially at temperatures below 100°C, is limited at best (fig. 13).

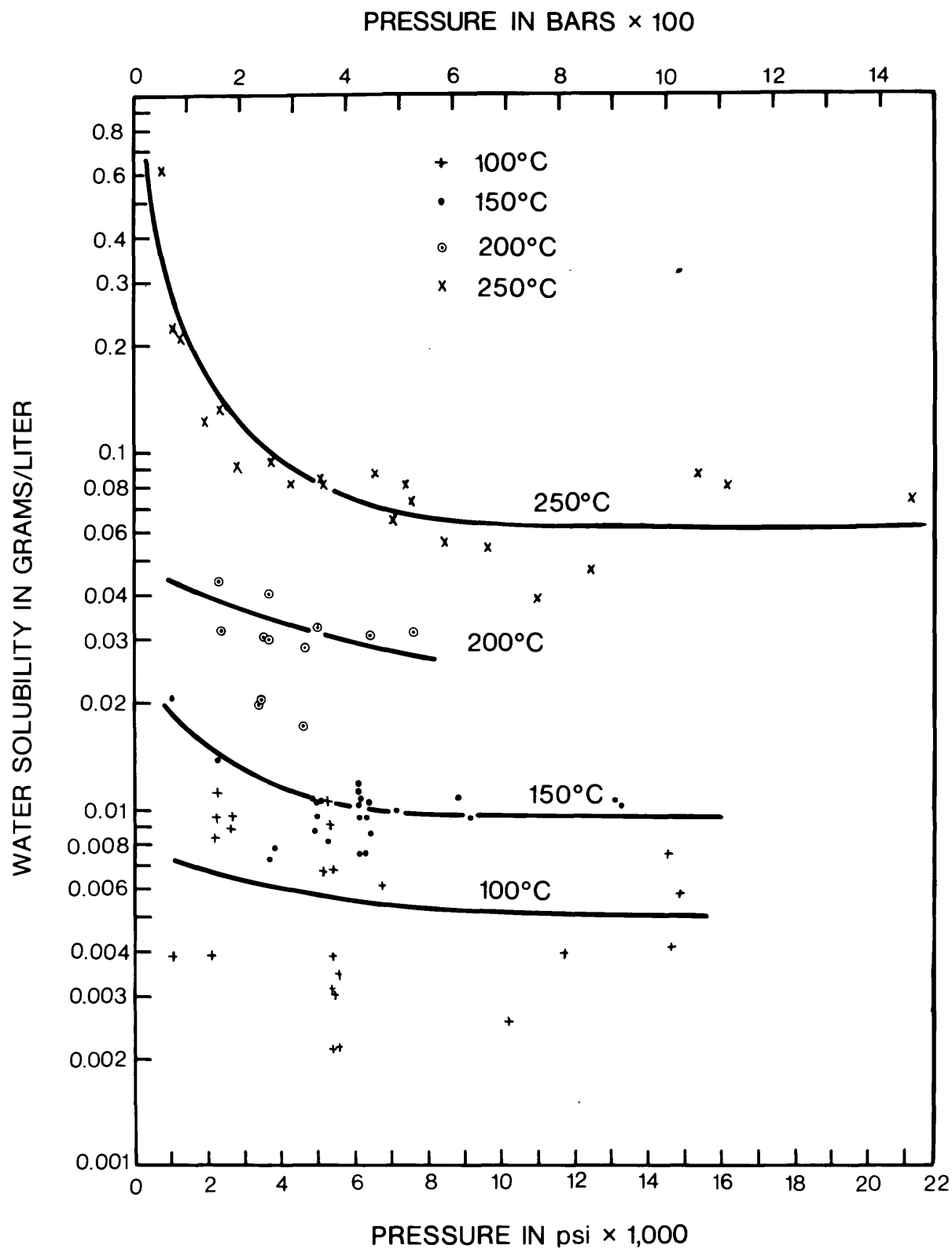


Figure 13. Solubility of water in methane gas as a function of pressure and temperature. After Price and others (1983).

"Mineral salts" are present in ground waters from the ppm to the 0.5 percent level, depending on the species. In cases of low concentrations of trace "salts" or metals, almost all the ground water would have to be "evaporated" to cause precipitation of the mineral species. Mass balance calculations can be carried out to show that unrealistically large gas volumes would be required for precipitation of the reported amounts of various soil salts. The fact that most of the microseeping HC gas will be destroyed by bacterial oxidation makes the amount of gas required even larger and more unrealistic. As proposed in this paper, the principal HC microseepage mechanism is the vertical migration of microbubbles of natural gas. Thus, by the data of figure 13, such a migration mechanism would transport deep-basinal water by such gas bubbles to the Earth's surface where the water would exsolve from the gas phase due to pressure and temperature decline. This is the exact opposite result of the hypothesis of gas-induced ground-water evaporation. Whether or not this entrained water could in turn take up other elements or salts which form surface anomalies (such as iodine--Kartsev and others, 1959, p. 293; Gallagher, 1984) is another matter not addressed here.

HC gas microseepage rates, by this paper's model, are probably millions and perhaps even hundreds of millions of times smaller than the fluxes called for by some investigators. Effusion rates are another matter; however, effusion results in a more rapid (compared to HC microseepage) destruction of oil pools. The change in sediment lithology over some oil pools in Southern Oklahoma has been attributed to HC microseepage by some investigators (including Seager, 1938, in discussion section of Rosaire, 1938, p. 120; Donovan and Dalziel, 1977; and Duchscherer, 1981A). The Southern Oklahoma portions of the Anadarko-Ardmore basins have some of the most pronounced structural intensity of petroleum basins worldwide, rivaling and (or) surpassing that of the Ploiesti district of Romania, and the Los Angeles-Ventura basins. The intense faulting and macrofracturing of Southern Oklahoma make it probable that the various distinct anomalies observed over many of the fields there are not due to HC microseepage but have been caused by effusion. These fields have been occasionally cited as models for HC microseepage. However, the anomalies developed over these fields are much stronger and more intensely evolved than normal. These fields do serve as a model, but a model wherein the effects of effusion overwhelm those of HC microseepage. The structural intensity and magnitude of anomaly development over these fields make it remarkable that any oil is left in the fields at all, much less the large reserves they do have.

Kartsev and others, (1959, p. 67) and Sokolov and others, (1959, p. 669) both discussed cementation of fractures above oil deposits. Sokolov and others, (1959) noted that such fractures in Paleozoic rocks are more heavily cemented than fractures in Tertiary rocks in regions of similar structural intensity. Baijal (1962) stated that fractures above oil pools become mineralized and closed with time. These observations, and the above discussion on chimneys and lithologic reservoir alteration by bacteria, suggest that leaking HC deposits may "heal" themselves over geologic time from mineral precipitation resulting from bacterial oxidation of leaking HCS. However, conjecture on the behavior of these systems over geologic time is highly speculative, especially considering that so little is known about even their temporal behavior.

Use of DGD and other SGE methods in "live" petroleum basins may result in false anomalies, which would not be encountered in "dead" petroleum basins. There is a general, but undocumented, belief among petroleum organic geochemists that most of the HCS that migrate from source rocks never form commercial deposits. Instead, especially in structured basins, these HCS are lost to seepage (and presumably microseepage) as well as to other factors. If this belief is true, then such HC effusions and microseepages would create false surface anomalies not necessarily caused by a commercial HC deposit. It is relevant that the majority of published (and possibly unpublished) Western research on SGE has been carried out in the onshore coastal Gulf Coast, a "live" petroleum basin.

#### Optimum Use of DGD

From its inception, the immediate attempted Western application of SGE has been as a front-line exploration tool. Few would argue with the conclusion that, at least in the West, SGE techniques have not yet achieved major success as primary exploration tools. Limited data are occasionally quoted to suggest that SGE might be more effective as a tool to check prospects generated by other exploration methods rather than as a primary exploration tool. For example, Kuzmin (1983) noted that while 58 percent of the anomalies he worked with were proven productive on drilling, 79 percent of the prospects condemned by SGE were dry holes on drilling. However, such percentages for negative predictions are, in reality, unimpressive. If one assumes a new field wildcat success ratio of 1 in 9 to 1 in 11 for the last 50 years, by simply condemning all prospects and not drilling any wells at all, one could achieve a negative predictive success ratio of 89 percent to 91 percent. Thus, negative predictions for wildcat wells based on SGE would have to be in the range of 95 percent to 99 percent correct to be an effective "negative" exploration tool.

Perhaps the most powerful utilization of SGE would have been (and still would be) as a tool to determine field boundaries after new field discoveries or for extensions of older producing fields. The graveyard of dry and abandoned wells which surround established fields, testify to the tremendous waste of developmental drilling. It is probable that had SGE methods proven themselves as tools for developmental drilling and for extensions of older producing fields, then the possible contribution that SGE methods, when correctly employed, could make to rank petroleum exploration would have been more obvious. This in turn might have led to the investment of the basic research needed to fully delineate the controlling parameters for the full and proper use of HC microseepage and other SGE methods.

Different investigators have noted that HC "microseepage" is most intense along fault and fracture zones, and that DGD methods should be based on the identification of such fault zones (Weisman, 1979; Jones, 1982; Richers and others, 1982; Jones and Drozd, 1983; Hickey et al, 1983B; Klusman and Voorhees, 1983). "In general, the best application of the surface prospecting technique is in areas with tectonic activity.", (Weisman, 1979, p. 388). Hickey and others (1983B, p. 1342) noted,

The application of integrative gas geochemistry combined with mass spectrometry and the use of pattern recognition procedures, has enabled rapid characterization of microseepage of gases along faults and fractures. This has been accomplished by incorporating the activated carbon/Curie point wire collector in gas geochemical surveys of faulted and fractured structures which serve as conduits to the subsurface-----. From these interpretations, an exploration model which utilizes fault leakage as a parameter will be discussed."

Jones (1982, p. 245), discussing HC microseepage, noted,

"-----the upward migration of reservoired light hydrocarbons into near-surface soils represents a viable mechanism, allowing surface geochemical exploration techniques to be utilized for regional hydrocarbon evaluations.

Geochemical investigations indicate that seep magnitudes depend on tectonic activity to aid migration along the fault and fracture avenues which appear to provide the major migration pathways."

There is no question that surface "microseepage" HC concentrations are greatest over surface traces of faults and fractures. Sokolov and others (1959, p. 672), commenting on the experience of the Soviets, noted,

"Many points where high hydrocarbon concentrations were observed were related to zones of disjunctive disturbances. In some cases it was possible thus to trace disturbance lines in solid rocks capped by drift. The shape of the gas anomalies was often determined by the disjunctive disturbances."

However, finding a fault zone is not equivalent to finding commercial HCS. If anything, a fault zone would be more likely to yield false anomalies, as even if a pool of commercial HCS were fault associated, the pool could be laterally displaced (sometimes greatly) from the fault zone. Fault zones, in all probability, also yield anomalies not caused by or associated with commercial HC deposits. The vertical movement of deep-basin waters up faults is well documented, even in "dead" petroleum basins (Price, 1976, p. 229-230; Roberts, 1981; Jones, 1981, 1984). Such waters are enriched in dissolved HCS compared to surface waters because of increased aqueous solubility of HCS at elevated burial temperatures (Buckley and others, 1958; Price, 1976, 1979, 1981A,B; Price and others, 1981). Deep-basin waters moving up fault zones undergo temperature decrease, causing the exsolution of both oil and gas from these waters. The exsolved globules of gas and oil continue to migrate with the waters vertically up the fault zone, but now also as a consequence of buoyancy. The end result is an enrichment of HCS, compared to normal low background values, along the surface traces of fault zones. This enrichment would appear as an HC anomaly but would be caused solely by HCS dissolved in deep subsurface waters and not by a commercial HC deposit.

The migration mechanism(s) responsible for fault-associated HC anomalies obviously differ from the migration mechanism, as advocated in this paper, responsible for HC microseepage over unfaulted HC deposits. (Fault anomalies could also be caused by intermittent monophasic gas and (or) oil migration from buoyancy (effusion), and by diffusion through and up the waters of the fault plane, besides by vertical transport of deep-basinal waters). Therefore, anomaly signal characteristics over fault zones would be different than signal characteristics of anomalies created by HC microseepage from unfaulted HC deposits. The latter signal is dominantly composed of  $C_1$ - $C_5$  HCS with no or low concentrations of  $C_6$ + HCS (Sokolov, 1970; Sokolov and others, 1971; and Philp and Crisp, 1982, p. 3). However, "fault anomalies", because of the upward transport of  $C_6$ + HCS, can have significant  $C_6$ + HC concentrations, "Studies conducted in the Denver-Julesburg basin of Colorado, Green River basin of Wyoming, the hingeline of Utah, and the Las Animas arch of Colorado all produced fault-related samples where higher ( $< C_7$ ) molecular weight components were encountered.", (Hickey and others, 1983B, p. 1342).

The intensity and characteristics of fault-related anomalies depend on many parameters, such that it will not always be possible to distinguish between faults associated with possible commercial HC production and "non-productive faults." Discounting effusion, signal intensity of fault anomalies depend on the volume of water transported up a fault and the original solution capacity of the water for HCS. Water volume depends on hydraulic potential and fault transmissivity. Solution capacity depends on the original pressure, salinity, gas content, and especially temperature of the water (Price, 1976, 1979, 1981A; and Price and others, 1981). A vertically transmissive fault tapping high-temperature deep-basin compaction waters which have a high hydraulic potential would generate a much stronger signal or anomaly than a "tighter" fault linked with an HC pool at much shallower depths and with formation waters of lower hydraulic potential and lower HC solution capabilities. Based on my experience with aqueous HC solubility (Price, 1976, 1979, 1981A; and Price and others, 1981), HCS dissolved in fault-borne waters and originating from a HC pool, either close to or removed from a fault, would not necessarily always yield a "fingerprint" characteristic of a HC pool. Also, a HC pool removed from a fault by some distance could generate a false anomaly at the surface trace of such a fault. An example would be active water washing of an oil pool by meteoric-water recharge (Price, 1980), with the waters transported some distance from the HC pool and up a fault. Hunt (1979, p. 430) pointed out that Eastern European organic geochemists at the Third International Geochemical Conference, "----- concluded that areas with complicated tectonics involving faulting and thrusting give unfavorable results in surface prospecting because fault zones are preferential migration paths." Such an example was given (fig. 14) in a soil-gas survey across the Ryckman Creek field, Wyoming, by Jones and Drozd (1983). The "anomaly" over the Ryckman Creek field is not well developed compared to adjacent false anomalies caused by faulting. As Jones and Drozd (1983, p. 947) noted, "The hydrocarbon seeps occur directly over the subcrop of the thrust faults, and thus gases would appear to migrate along the thrust plane and then vertically through the Tertiary section-----."

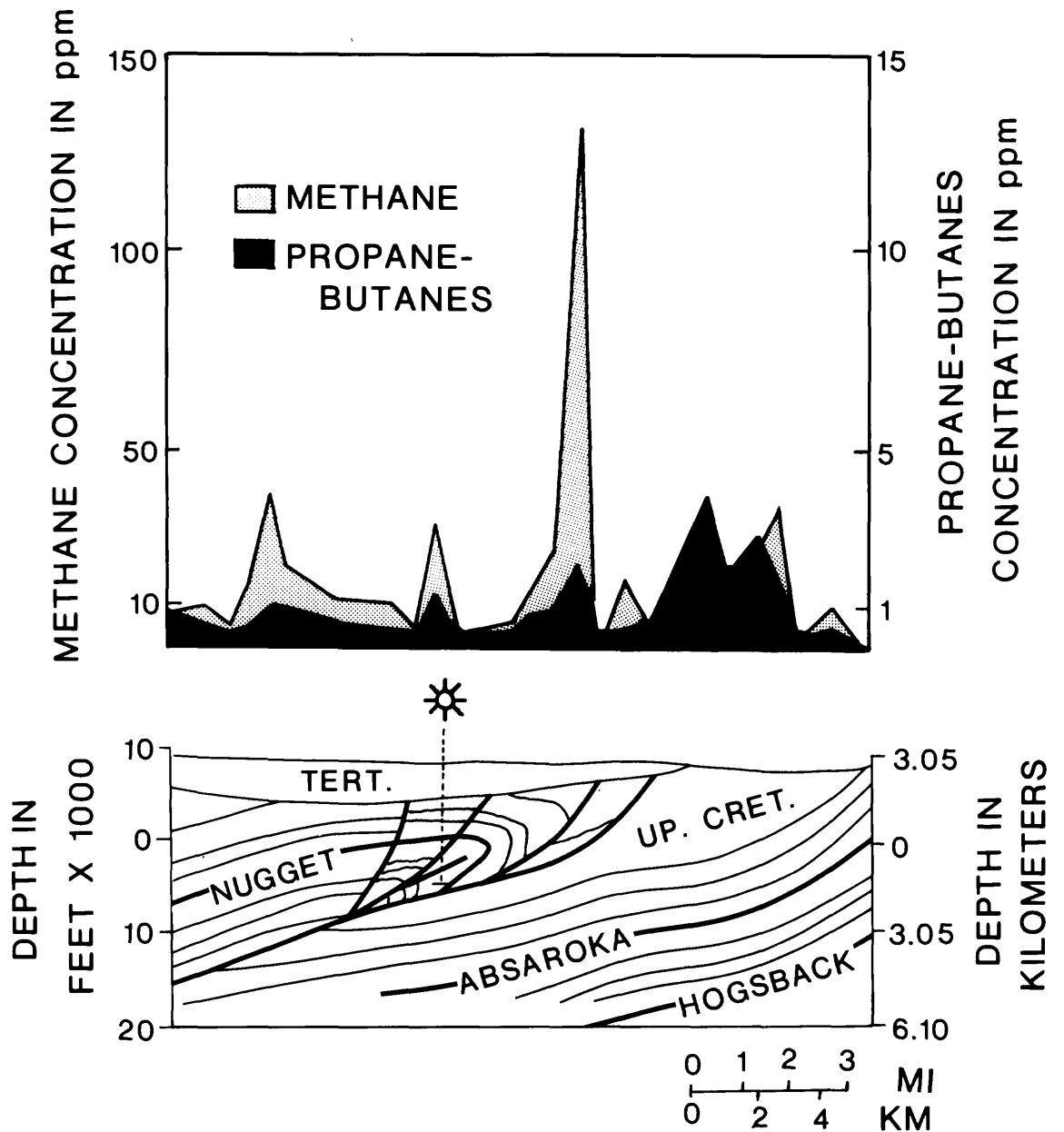


Figure 14. Geology and results of a soil-gas survey over the Ryckman Creek field, Wyoming. Note that the "anomaly" over the field is less intense than adjacent false anomalies. Nugget, Absaroka, and Hogsback refer to those thrust faults, respectively. After Jones and Drozd (1983, p. 950).

Contrary to the opinions of some investigators, DGD methods are not best suited to tectonically disturbed areas; in fact, this is the one area for which they are most ill suited. Fault zones do give much stronger HC anomalies than those produced by microseepage HC deposits in unfaulted, flat-lying sediments of the stable shelves of sedimentary basins (Sokolov, 1970, p. 545). However, if such strong signals over faults are not necessarily caused by commercial HC deposits, then such signals lose much of their relevance to petroleum exploration. We are not in the business of discovering and producing faults. Seismic methods have proven reliable at locating these features. As Jones and Drozd (1983, p. 932) noted,

"Geochemical prospecting must be used with caution, and only in conjunction with geologic and geophysical tools, because the location and shape of many geochemical anomalies are governed more by the local tectonic structure of the region than by the position and shape of the actual deposit."

Fedynsky and others (1975) also noted that faults can shift HC anomalies laterally from the HC deposits causing them.

If SGE is to make a significant contribution to oil exploration in America, it is to be in the search for oil pools in stratigraphic and low-relief traps on the stable shelves of maturely-explored onshore American petroleum basins. Hamm (1969, p. 13) noted,

"The industry has not yet developed a finding tool with high resolving power for the discovery of stratigraphic-trap fields. The principal finding methods being used today are subsurface geology based upon information from outcrops, wells, and various types of geophysical data. The batting average on stratigraphic-trap drilling is quite low. It is here that unconventional methods of oil exploration may make a major contribution."

The need for an effective exploration method for stratigraphic traps has also been noted by a myriad of other investigators (including Davidson, 1963, p. 98; Jones and Drozd, 1983, p. 933; and Kuzmin, 1983, p. 1094). Acknowledging this need and the possible contribution which SGE methods could make almost borders on redundancy; however, the record here is not encouraging. Kartsev and others (1959, p. 106), discussing DGD on the stable shelves of petroleum basins, noted,

"Sometimes a large oil formation is in no way indicated by gas survey results. This has been known to occur with formations characterized by undisturbed tectonics and the virtual absence of faults. This is most often observed in the case of platform formations."

(The Soviet use of "platform" is equivalent to the stable-shelf area of flat-lying sediments in a basin past the hingeline of the basin). Sokolov and others (1959, p. 574) noted,



"In the platform regions of the USSR the effectivity of gas surveying with sampling from several depths was not high, though in individual, more disturbed districts anomalies were obtained at the sites of oil and gas fields (Ukhta, etc.)----- . On the Russian platform in most cases no hydrocarbon gas anomalies were detected at all in the surface layers above oil deposits in Paleozoic sediments, this evidently being due to the low intensity of vertical gas migration from the deposits."

Sokolov and others (1971) and Hunt (1981) also noted that DGD methods are weakest in areas of flat-lying sediments. Of all the examples of DGD anomalies published in Western trade and scientific journals, few are over stratigraphic traps.

An area where DGD may make a significant contribution to oil exploration (besides developmental drilling and field extension) is as the primary exploration tool for stratigraphic HC accumulations. This contribution has not yet been made, and the record is not encouraging. However, it may be made possible by the development and proper use of an inexpensive and simple integrative-absorption technique, which can be used by the small independents, who mainly explore this niche of onshore sedimentary basins.

### Hypotheses

Several hypotheses may be advanced on the basis of the HC-microseepage model advocated in this paper. If surface and near-surface bacterial activity is the dominant controlling parameter of the surface concentration of microseeping HCS, then the concentration of soil-air and soil-sorbed HCS should be inversely proportional to microbial activity. Evidence supporting or contradicting this premise can only come from microbiologic, soil-gas and (or) soil-sorbed HC surveys simultaneously run over the same area. Kartsev and others (1959, p. 333-340), after noting that the Soviets frequently carry out such surveys, discussed examples. The results of a soil-gas/microbiologic survey carried out in the Northern Caucasus region, led Kartsev and others (1959, p. 334) to conclude, "It should be noted that the greatest microconcentrations of gases are found in areas where hydrocarbon microflora is absent." (Also see Kartsev and others, 1959, figure 148 with accompanying discussion). Kartsev and others (1959, p. 340) also noted,

"When the influx of hydrocarbon gases is intense, complete or partial superposition of gas maxima on the microbiological ones is observed. With a feeble gas source, on the contrary, the zones of microbiological and gas anomalies may fail to coincide within the boundaries of a given gas field. Therefore, for correct interpretation of geochemical anomalies it is necessary to take into account not only the microbiological and gas indices separately, but also the specific way they are related in space. Only on the basis of these data can the actual output of hydrocarbon gases at any given depth be determined; this includes not only freely evolved gases, but also those absorbed by the bacterial filter."

An obvious converse corollary to the first premise is that microseepage-HC areas, which have weak or no microbiologic activity, would be expected to have significant concentrations of soil-sorbed or soil-air HCS.

A second premise, by this paper's model, is that the shape, intensity, and generation of occluded-HC soil anomalies is dependent on the presence of significant surface microbial activity. Occluded HCS clearly depend on the precipitation of calcite for occlusion, and such precipitation in turn clearly depends on the generation of high  $\text{CO}_2$  concentrations from microbial oxidation of microseeping HCS. Further, with one exception, the shape of occluded-HC anomalies should always be continuous or discontinuous halos and not apical anomalies, as discussed above. The one exception would be microseepage from small HC deposits, whose anomalies could appear as focal anomalies due to either sampling density (sample sites too far apart to distinguish fine details) or insufficient amounts of microbially generated  $\text{CO}_2$  to overcome a greater incoming flux of  $\text{Ca}^{+2}$  ions. Horvitz (1954, p. 1207; 1980, p. 247) noted that small HC deposits sometimes yield apical and not halo anomalies with occluded-HC soil surveys. Another consequence of the second premise is that occluded-HC anomalies (and other associated carbonate based anomalies) will be absent or weak in areas where surface microbial development is prevented. For example, such anomalies will be absent in true deserts where year-round lack of adequate soil moisture and very deep water tables would preclude near-surface microbial development. The data of Devine and Sears (1975, 1977) from the Strzelecki desert, Australia (discussed above) support this hypothesis. Although occluded-HC soil surveys are not expected to be effective in deserts, integrative-absorption surveys should be especially effective in such regions. Other factors besides low-soil moisture can also prevent soil bacterial activity, and therefore occluded-HC soil analysis may also be inapplicable in areas other than deserts. For example, the absence of sufficient mineral nutrients also limits surface bacterial activity (Davis, 1967, p. 119-121) and apparently soil "poisons" can restrict or prevent soil microbial activity. Kartsev and others (1959, p. 334) discussed a case wherein areas within a well developed microbial anomaly from HC-microseepage were devoid of microbial life. These areas, "----- corresponded to surface outcroppings of pyritized clays having an acid reaction which is unfavorable for bacterial activity."

Bacterial oxidation of vertically migrating HCS is clearly the major unacknowledged controlling parameter of SGE. However, it is likely that there are other unrecognized parameters which play lesser, yet significant roles. For example, Horvitz (1939, p. 217) noted that a sorbed-HC soil survey at the Ramsey field, Payne County, Oklahoma, conducted in the winter over snow-covered ground, yielded much higher HC concentrations than a later replicate survey conducted in the summer. Horvitz (1939) attributed the higher HC concentrations to the snow cover producing a seal, which reduced the escape of soil HCS to the atmosphere. Kartsev and others (1959, p. 121) also discussed the increase in soil-sorbed HC gas concentrations from plugging of surface capillaries by water or ice. (Conceivably, a rain storm could temporarily block soil porosity and also cause a brief concentration increase in soil-air and soil-sorbed HCS.) Part of Horvitz's (1939) winter HC concentration increase also would be expected to be due to a decrease in microbial activity

from low winter air temperatures, although the data of Samtsevich (1955), as discussed by Davis (1967, p. 121), seemingly contradict this hypothesis.

### Correcting the Record

Dickey and Hunt (1972), Hunt (1979, 1981), and Neglia (1979) have taken negative positions with respect to SGE. Neglia (1979, p. 594) stated, "The basic concept of geochemical prospecting--the assumption that a superficial halo of dispersion of hydrocarbons must be present above every oil and gas accumulation--is not true." Unfortunately, Neglia (1979) gave no data or discussion supporting his conclusion. Dickey and Hunt (1972) concluded that it was unlikely SGE would ever prove useful for two reasons. The first was that "many surveys" by major oil company research laboratories had shown that no HC diffusion aureole exists radially outward from effusive macroseeps. This is similar to a logic employed by many proponents of SGE, which is that if macroseeps exist, then a-priori, microseeps must exist. For example McDermott (1940, p. 860) noted, "In view of the prevalence of visible oil and gas seeps, that is leakage from buried accumulations, it is only reasonable to expect a much greater occurrence of microscopic leakage." Debnam (1969, p. 1) made a similar statement. By this paper's model, such logic simply is not correct. If macroseeps and microseeps originate by two different and independent migration mechanisms, the existence of one does not a-priori guarantee the existence of the other. The second reason preventing a possible significant contribution by SGE, as given by Dickey and Hunt (1972), was their valid contention that vertical diffusion of HCS is not possible through impermeable shales, nor can diffusion possibly explain the shape of halo, or any other, anomalies. However, just because HC microseepage does not occur by diffusion does not mean that it does not occur at all. Dickey and Hunt's (1972) point here has no bearing on the possible existence or nonexistence of HC microseepage.

Concerning the Soviet effort, Dickey and Hunt (1972, p. 158) noted, "Surface geochemical methods have been used extensively in Russia with the same discouraging results as in the United States." This statement simply does not agree with the published literature. The Soviets have made a major commitment over the last 50 years to surface and near-surface geochemical prospecting, approaching the topic much more scientifically than the Western effort. Consequently the Soviets have published the bear's share of the meaningful research on HC microseepage. Kartsev and others (1959, p. 65), discussing the early Soviet commitment, noted, "In 1940 the specialized office Neftegazos'emka (Oil-gas survey) was organized for prospecting work; the scientific director was V. A. Sokolov. Every year Neftegazos'emka sent 25-30 production and research parties to various parts of the Soviet Union." Thompson (1981, p. 240-241), discussing the magnitude of the more recent Soviet commitment, noted,

"While predominantly employed conventional methods of exploration continue to offer less than promising results in the United States, Soviet research institutes have spent years attempting to develop and refine geochemical techniques for locating oil and gas reservoirs. In fact, more research effort in this area has probably been expended in the Soviet Union than any other nation.

It has been reported (Sweet, 1966) that in the 1950s the Soviets maintained as many as three hundred geochemical crews in the field at one time. The reason for this intensive Soviet investigation is clear--success in developing direct and indirect detection methods could effect huge economic impact in exploration after Davidson (1967)."

Soviet technology in many fields clearly lags behind Western, and especially American, technology. Yet the Soviets now produce more crude oil than any other nation on Earth, and probably would produce even more if it were not for their lag in production technology. I find it too coincidental that the Soviets, who have made such concentrated efforts in SGE, have achieved such exploration successes in spite of a general overall lagging technology.

Sokolov and others (1959, p. 674) noted, "Reviewing the data on gas surveying predictions we get the following results. Under favorable geological conditions the proportion of correct predictions is rather high--about 70 percent." Discussing the success of SGE, Kartsev and others (1959, p. 65) noted,

"With the aid of the gas survey, several oil formations were independently discovered. Several tens of formations were discovered by a combination of prospecting methods, among which the gas survey was not the least important. The great majority of gas anomalies have not yet been tested by drilling. Gas surveying became firmly established in the general complex of oil prospecting work."

Kartsev and others (1959, p. 333-340) described a number of fields discovered on the basis of SGE (microbiologic, soil-air, and soil analysis). Sokolov and others (1979, p. 539) also discuss a number of case histories,

"According to the data of A. Ya. Krems, L. A. Anischenko and others, surface gas anomalies in the Komi region led to the discovery of the Kush-Koy, Djebol, Njamed, Nibel, Voy-Voj and other new petroleum and gas fields. The success of gas surveys on the platform structures of the Komi region is about 90 per cent.

During a survey of seismic shot-holes in 1957 at the mouth of the Pechora river near Naryan-Mar, a marked heavy hydrocarbon (C<sub>2</sub>-C<sub>5</sub>) gas anomaly was discovered. This information was the basis for carrying out oil and gas exploration work in the Zapolyarye area of the European part of the USSR. Later, oil and gas pools in Permian carbonate and terrigenous sediments were discovered there in a zone called the Yuryahinsko-Kumzhinskii swell. This is one of the more recent rich oil-bearing provinces of the USSR.

In the middle Volga region, according to the data of M. I. Zeidelson and others, the efficiency of surface gas surveys was about 70-80 per cent. Some nineteen fields were discovered, including Muchanovo, Kajemjakino and others."

Kuzmin (1983) discussed results of other Soviet geochemical surveys where of 45 anomalies, 26 resulted in commercial pools for a 65 percent success ratio. Dickey and Hunt's (1972) appraisal of "discouraging Soviet results" is erroneous.

Hunt (1979, p. 425-433), in some detail, strongly condemns SGE. His discussion and rejection of diffusion as the migration mechanism for HC microseepage is valid. Hunt (1979, p. 433) concluded that such migration had to occur via "erratic pathways" (presumably faults and fractures), and that because of such migration routes, "Surface geochemical prospecting cannot outline oil or gas accumulations at depth except in rare cases." This statement and that of Neglia (1979, p. 594) simply do not agree with the published record, which clearly demonstrates that in many cases SGE distinctly outlines surface boundaries of known fields--Horvitz (1939, fig. 2, Hastings, Friendswood; 1945, figs. 1, 2, Heidelberg; 1954, fig. 1, Hastings, Manvel; 1957, figs. 1, 2, large area with 11 fields at junction of Wharton, Matagorda, and Jackson Counties Texas, fig. 3, Bonney, figs. 5, 6, Little Beaver; 1965, figs. 1, 2, unnamed gas field, figs. 4-6, North League City; 1969, figs. 4-6, Pierce Junction, figs. 7, 8, Kemah, 1980, fig. 6, Flomation-Jay-Blackjack Creek; 1981, figs. 1-3, Francitas, figs. 4-8, Cognac, offshore field), McDermott (1940, figs. 2, 3, Cedar Lake, fig. 7, Coles Levee, Canal, Ten Section), Ransone (1947, fig. 2, Hardy; 1969, fig. 2, Sixto), Kartsev and others (1959, numerous examples), and Duchscherer (1981B, fig. 4, Hanson, fig. 6, New Cypress, fig. 8, Midland; 1982, fig. 6, Ten Section, fig. 8, Sleepy Hollow, fig. 10, Conley). Rosaire (1940, p. 1459, in Rosaire and others, 1940) pointed out that halo patterns were also present at Ezzell, Eureka, Welsh, Turkey Creek, Reynolds and Sugarland in the Gulf Coast; Coalinga, Northeast Coalinga, Greeley, Rio Bravo, Huntington Beach, Rosecrans, Dominguez, Montebello, and Signal Hill in California; Goldsmith and Bennet in the Permian basin; Ramsey, Stroud, Sac, and Fox in Oklahoma; and Hebron in Pennsylvania. Weisman (1979, p. 371), discussing the efforts of Horvitz Laboratories, noted,

"Horvitz has examined tens of thousands of near-surface sediment samples from both onshore and offshore areas for the saturated hydrocarbons through pentane. Recognizable hydrocarbon distribution patterns were observed over known fields. Similar patterns were found in areas which has been examined but not yet tested for hydrocarbon production. Follow-up studies indicate a high percentage of anomalies in originally unexplored areas subsequently were found to be associated with petroleum accumulations."

Jones and Drozd (1983, p. 940), discussing the results of an extensive Gulf Oil Company soil-air analyses research program, noted, "----- show that both structural and stratigraphic traps produce positive or direct surface anomalies-----." Johnson (1963, p. 98, then Exploration Research Director for Sinclair Research) noted, "----- many soil-hydrocarbon maps are in the literature and indicate definite relationship between surface accumulation of hydrocarbons and oil fields."

Clearly some detractors of SGE have overstated their case, which is understandable considering the general lack of Western rigorous scientific development of the topic. However, there is no doubt that HC microseepage occurs. Nor is there any doubt that it can result in different anomalies that, either alone or in combination, distinctly outline the surface traces of HC deposits. Nor is there any doubt that SGE can be, and has been, a powerful petroleum exploration tool. The Soviets appear to have had marked success using SGE techniques. A number of literature examples exist of American oil fields discovered solely on the basis of SGE--Stormont (1939, East Mathis); Horvitz (1945, figs. 1, 2, Heidelberg field definition after wildcat discovery); Ransone (1947, Hardy; 1958, Sojourner; 1969, Sixto); Horvitz (1965, figs. 1, 2, unnamed gas field; figs. 4-6, North League City); and Denison (1983, p. 162, Stoney Point). Horvitz (1954) reported that of 109 anomalies revealed by geochemical surveys 39 had been drilled with 23 new fields discovered. Duschscherer (1982) reported 39 new field discoveries based on the drilling of 171 geochemical anomalies. Thus, it is probable that a significant number of "geochemical confirmations" exist that will never be published. A large but unknown amount of oil has been discovered because of paraffin dirt and lithologic enhancement of low-relief structures in geophysical surveys (Rosaire, 1938). As these are both IGD methods resulting from HC microseepage, much more oil has been discovered by IGD methods than previously realized by both detractors and proponents of SGE. The real question confronting SGE is if it can be used as a viable exploration tool for oil fields in stratigraphic and low-relief traps on the stable shelves of maturely-explored American petroleum basins. In my opinion, the answer to this question is no, if we continue to use 50-year-old procedures and if the controlling parameters of HC microseepage continue to go unresearched.

#### CONCLUSIONS

1. In this paper: (A) HC microseepage refers to the migration of the  $C_1$  to  $C_5$  HCS from HC deposits to the Earth's surface. (B) Direct geochemical detection (DGD) is defined as any surface geochemical exploration (SGE) method based on the measurement of concentrations of  $C_2$  to  $C_5$  HCS or measurement of the bacterial response from such HCS. Such methods are soil-air, soil-occluded or soil-sorbed HC analyses, microbiologic analysis, and integrative absorption. (C) Methane is not considered to be a unique indicator of thermogenic HC deposits.
2. In this paper indirect geochemical detection (IGD) is defined as any method based on the measurement of a physical parameter which is an indirect result of and caused by the vertical migration of HCS (including HC microseepage) from HC deposits. Such methods are radiometric, redox, bitumen analysis, soil salt, trace metal or element, geobotanical, soil mineralogy, hydrochemical, and magnetic. Other IGD methods are methods unrelated to vertically migrating HCS, such as helium surveying.
3. Diffusion, effusion, and vertical water movement through HC deposits and (or) impermeable sediments cannot be the migration mechanism responsible for HC microseepage. That mechanism is hypothesized as the vertical ascent of colloidal-size microbubbles of HC gases through microfracture systems over HC deposits. However, diffusion of HCS through sediments

and microfracture systems, slowly over geologic time, is partly responsible for background surface HC concentrations in petroleum-bearing sedimentary basins. Effusion, which in a geologic context is the continuous or intermittent monophasic flow of oil and (or) gas up fault and (or) fracture systems, is responsible for macroseepage. The vertical transport of deep-basin waters, carrying dissolved HCS up faults and fractures is responsible (at times in conjunction with effusion) for HC anomalies, which involve  $C_6+$  HCS, observed at the surface traces of such fault and fracture systems in sedimentary basins.

4. The vertical ascent of colloidal-size bubbles of natural gas (carrying dissolved  $C_6+$  HCS) through microfracture systems over HC deposits is the only proposed HC microseepage migration mechanism in agreement with observed data: (A) the speed with which HC surface anomalies appear or disappear in response to reservoir pressure changes; (B) the chromatographic effect of increasing amounts of  $C_6+$  HCS with decreasing distance from HC deposits; (C) the fact that  $C_1$  to  $C_5$  (mainly  $C_1$  to  $C_3$ ) HCS predominantly compose microseeping HCS at the Earth's surface; and (D) the strong gravitational component reflected by the sharp surface boundaries of anomalies above HC deposits.

The existence of microfracture systems above HC deposits, as proposed in this paper, clearly has not yet been demonstrated.

5. Bacterial interaction with vertically migrating HCS (including microseeping HCS) is the most important controlling parameter in SGE. This interaction has largely been disregarded in the past.
6. Although the maximum microbial activity occurs in surface soils, a significant number of bacteria oxidize HCS over a staggering range of conditions, including all sediment depths from a HC deposit to the Earth's surface.
7. Surface bacterial activity can totally obliterate a HC anomaly caused by microseeping HCS, as measured by soil-air or soil-sorbed HC analyses, or integrative absorption. Such activity can also cause large seasonal variations in such anomalies.
8. Paraffin dirt is the result of surface bacterial utilization of microseeping HCS, and is therefore an IGD method which has been responsible for the discovery of large amounts of crude oil in the Gulf Coast region.
9. HCS are kinetically stable under all microseepage conditions and do not create reducing environments. Such environments are clearly due to microbiologic oxidation of vertically migrating HCS (including microseeping HCS).

10. "Chimneys" are rock columns above leaking HC deposits having different physical characteristics than stratigraphically equivalent rocks off the HC deposit. By this paper's model, chimneys are created by the interaction of various bacteria with vertically migrating HCS (including microseeping HCS). Significant amounts of  $\text{CO}_2$ , and to a lesser extent  $\text{H}_2\text{S}$  and organic acids, are produced by this interaction. These reactive chemical species significantly change the eH and pH of the environments in which the bacteria are active and also change mineral stability fields in rock columns above HC deposits. These changes result in the solution and mobilization of some mineral species and the precipitation of other species.
11. A number of such mineralogic changes have been observed in rock columns above HC deposits: (A) Radioactivity decreases have been documented in shales and soils above HC deposits compared to background values. These decreases, by this paper's model, are due to acidic solutions created by bacterial oxidation of vertically migrating HCS which cause clay breakdown (as these solutions are neutralized) and leach potassium 40 from clays during clay breakdown and (or) other radioactive elements from organic-rich black shales. (B) The induration of sediments documented above HC deposits, is believed due to carbonate precipitation from the microbially produced  $\text{CO}_2$  and from silica cementation due to clay breakdown to silica and alumina from neutralization of the acidic solutions caused by high  $\text{CO}_2$  concentrations. (C) Changes in iron/manganese-bearing mineral species from eH/pH alterations have been documented and are also believed due to bacterial oxidation of vertically-migrating HCS. The resulting iron/manganese mineralogic modifications result in anomalous magnetic and (or) electric potential measurements compared to unaltered country rocks.
12. By this paper's model, intense apical microbial activity over leaking HC deposits in the near-surface environment creates anomalous concentrations of  $\text{CO}_2$  and other carbonate species, which diffuse radially outward to meet inward diffusing  $\text{Ca}^{+2}$  ions. This ionic meeting results in a halo precipitation of carbonate surrounding the apical area of highest microbial activity, which in turn roughly outlines the surface trace of the HC deposit.  $\text{CO}_2$  and HCS are occluded in the calcite during its precipitation. This proposed scenario results in the halo anomalies observed for: (A) Duchscherer's  $\Delta\text{C}$  technique (at least partly so), (B) analysis for soil-occluded  $\text{C}_2\text{-C}_5$  HCS (Horvitz), and (C) soil- $\text{CaCO}_3$  ("soil salt") surveys.
13. By this paper's model (apparently borne out by observation from Nature): (A) Soil-air and soil-sorbed HC anomalies can be either apical or halos with halos predominating in humid climates. (B) Soil-occluded HC anomalies should always be halos. (C) Microbial anomalies should always be apical.



14. Intense apical microbial oxidation of microseeping HCS results in the halo anomalies sometimes found with soil-air and soil-sorbed HC analyses. By this paper's model (and in accordance with Soli's (1957) hypothesis), the higher HC concentrations of the ring portion of the halo anomaly represent microseeping HC concentrations too low to sustain intense microbial activity.
15. Conclusive evidence from Nature demonstrate that caprock "plugging" above HC deposits is not responsible for halo anomalies due to sealing of the apical area of the deposit by cementation. This evidence is in the form of HC-gas-logging surveys run over fields with halo anomalies, and the fact that soil-air and soil-sorbed HC surveys sometimes give apical anomalies, and almost universally, microbial surveys give apical anomalies.
16. Geochemical anomalies caused by abnormal CO<sub>2</sub> concentrations in near surface soils and (or) ground waters are non-specific for thermogenic HC deposits, as such anomalies can be caused by factors other than microbial oxidation of microseeping HCS. Such anomalies are soil-carbonate contents, radiation lows, soil mineral alteration, and occluded CO<sub>2</sub> in soil carbonates.
17. HC microseepage or leakage from biogenic methane deposits, including "tight" and (or) noncommercial biogenic methane deposits, can create many of the same geochemical anomalies created by HC microseepage from thermogenic HC deposits (including magnetic and carbon isotopic anomalies). Therefore, only DGD methods which measure C<sub>2</sub>-C<sub>5</sub> HCS can be considered specific for thermogenic HC deposits. "False anomalies" from microseeping biogenic methane deposits likely have been responsible for many geochemical failures, especially on the stable shelves of sedimentary basins.
18. DGD surveys specific for thermogenic HC deposits (soil analyses for (occluded?) or sorbed HCS, soil-air analysis, microbial analysis, and integrative absorption) all can show large seasonal variations in certain geographic-climatological environments. In different geographic-climatological-environments, different DGD methods may never be applicable.

The first four methods require deep (at least 6 ft, 1.8 m) surface boreholes, which results in long field times, high field expenses, and low field mobility. Sampling for these methods can be difficult and (or) expensive; and sample preparation and analysis can be time consuming, difficult, and (or) expensive.

19. Soil-air analysis is difficult because of very low concentrations of C<sub>2</sub>-C<sub>5</sub> HCS in soil air. Because of soil breathing (caused by a number of different factors) the method for the most part is not reproducible and data from large regional surveys are not comparable.

20. Analysis for (soil-sorbed HCS is undependable because of: (A) inhomogeneous sorption characteristics of soils over short lateral distances (which results in poor sample reproducibility), (3) concentration changes caused by seasonal, diurnal, or climatological factors, (C) but especially because of non-quantitative desorption of soil-sorbed HCS during thermal/vacuum analyses.
21. Analysis for soil-occluded HCS by acid treatment of soils is clearly superior to soil-air and soil-sorbed HC analyses, although problems also exist with this technique: (A) The ratio of sorbed to occluded HCS could affect the analysis. (B) The method is not applicable in certain cases. Examples are: 1) true deserts where a lack of soil moisture prevents significant soil microbial activity, and 2) areas where the soil contains unweathered carbonate bearing rock fragments with significant contents of syngenetic HC gases.
22. The proper use of microbial soil surveying is apparently yet ill defined, and problems exist despite very impressive prediction rates by some investigators. An analytical technique has not been developed that is quick, easily employed, trustworthy, and inexpensive. Serious contradictions exist between different studies. Considering the pivotal role which microbial oxidation of microseeping HCS (and vertically migrating HCS in general) plays in DGD methods (and SGE methods in general), resolution of these contradictions and problems would be appropriate.
23. Integrative absorption is the use of absorbents (activated charcoal, silica gel, etc.), or other "collectors", in shallow (1-2 ft, 0.3 to 0.6 m) surface holes to measure the flux of microseeping HCS over a given area. Major advantages exist with integrative-absorption compared to other DGD methods: (A) greatly decreased field time and field expenses, (B) greatly increased field mobility, (C) the negation of barometric, climatological, diurnal, and even seasonal variations by leaving collectors buried for sufficient time periods, and (D) significant possible decreases in sample-analysis expense and difficulty by gas-chromatographic analysis of the  $C_1$  to  $C_5$  HCS. Although the technique has the potential to be a major breakthrough in DGD, it also has drawbacks and limitations: (A) Early attempts at integrative-absorption were failures because of incorrect utilization of the technique, and insufficient analytical capabilities for microconcentrations of HC gases. (B) The sparse application of the method has not yet revealed all its shortcomings. (C) The principal limitation of integrative-absorption is its application in the upper soil zone, which is the realm of the most intense plant and microbial activity. This activity produces, or has the potential to produce, different organic and inorganic compounds, which can lead to significant analytical problems and (or) errors. (D) Methane and ethane, the most abundant microseepage HC gases, are not retained by most absorbents.

24. DGD methods, contrary to previous expressed opinions, are ill suited as exploration tools in tectonically disturbed areas because of the possibility of false anomalies over surface traces of faults and fractures from: (A) the discharge of deep basinal waters carrying dissolved HCS up faults, and (B) displacement of anomalies away from the surface trace of a field by faulting associated with the field.
25. In my opinion, the present optimum use of DGD methods is in field definition after a wildcat discovery and in extension of older producing fields.
26. The area of greatest possible contribution of DGD methods to petroleum exploration is in the search for fields in stratigraphic and low-relief traps, invisible to seismic surveying, in flat-lying sediments on the stable shelves of petroleum basins. However, this is an area where the previous record of DGD has not been encouraging.
27. The high HC microseepage rates called for by some investigators are geologically untenable.
28. The creation of surface anomalies by gas-induced ground-water evaporation is unlikely: (A) The amounts of required gas are unrealistically large. (B) A HC microseepage mechanism based on diffusion is not possible. (C) The HC microseepage mechanism favored in this paper produces the exact opposite results of gas-induced ground-water evaporation.
29. It is possible, but undocumented, that some microseeping and (or) effusing HC deposits "seal" themselves due to mineral precipitation in macrofractures and microfractures from bacterial oxidation of vertically migrating HCS.
30. Ongoing primary and (or) secondary migration in "live" petroleum basins (coastal Gulf Coast) may create false surface anomalies. However, this is an undocumented hypothesis.
31. HC microseepage does exist and can create surface anomalies which outline HC pools and therefore can be used as a viable exploration tool.
32. A myriad of proposals for definitive research on HC microseepage and SGE methods could be made. However, the most important step that could possibly be taken at this point are high-quality translations of the post-1960 definitive Soviet publications, emphasizing books and long journal review articles. The effort put into the Kartsev and others (1959) translation is to be highly applauded.

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